POLITECHNIKA
GDAŃSKA
WYDZIAŁ CHEMICZNY

Imię i nazwisko autora rozprawy: mgr inż. Michał Gągol
Dyscyplina naukowa: Technologia Chemiczna

ROZPRAWA DOKTORSKA

Tytuł rozprawy w języku polskim: **Zjawisko kawitacji hydrodynamicznej oraz akustycznej w połączeniu z zaawansowanymi procesami utleniania, jako skuteczne metody oczyszczania ścieków z produkcji asfaltów**

Tytuł rozprawy w języku angielskim: **Hydrodynamic and acoustic cavitation phenomena in combination with advanced oxidation processes as an effective methods of wastewater treatment from production of bitumens**

Promotor *podpis*	Promotor pomocniczy *Podpis*
prof. dr hab. inż. Józef Tadeusz Haponiuk, prof. zw. PG	dr hab. inż. Grzegorz Boczkaj, prof. nadzw. PG

Gdańsk, rok 2018

Składam serdeczne podziękowania

Panu ***profesorowi Józefowi Haponiukowi***
za zaufanie i szansę na realizację studiów doktorskich
oraz za życzliwość i nieocenioną pomoc

Panu ***profesorowi Grzegorzowi Boczkajowi***
za wskazanie interesującego tematu rozprawy, nieustanną motywację,
przekazaną wiedzę i pomoc przy realizowaniu badań

kolegom i koleżanką z Katedry Technologii Polimerów oraz
Katedry Inżynierii Chemicznej i Procesowej
za uśmiech i miłą atmosferę w pracy

szczególne podziękowania kieruje również do moich Bliskich:
Doroty, mamy Elżbiety, taty Jerzego i brata Pawła
za ciągłą motywację, otuchę i wyrozumiałość

Badania zawarte w pracy doktorskiej zostały sfinansowane
przez Ministerstwo Nauki i Szkolnictwa Wyższego,
projekt „IUVENTUS PLUS" nr. 0040/IP2/2015/73

Za pomoc w realizacji badań podziękowania składam
Grupie Lotos S.A. w szczególności
Lotos Asfalt Sp. z o. O

oraz Bandelin electronic GmbH & Co. KG
za wypożyczenie reaktora kawitacji akustycznej

Spis treści przewodnika po publikacjach

ZAŁĄCZNIKI:

- Publikacje wraz z oświadczeniami współautorów o wkładzie merytorycznym i udziale autorskim:

1) **M. Gągol**, A. Przyjazny, G. Boczkaj, Wastewater treatment by means of advanced oxidation processes based on cavitation – A review, Chem. Eng. J. 338 (2018) 599-627.
2) G. Boczkaj, **M. Gągol**, M. Klein, A. Przyjazny, Effective method of treatment of effluents from production of bitumens under basic pH conditions using hydrodynamic cavitation aided by external oxidants, Ultrason. Sonochem. 40 (2018) 969–979.
3) **M. Gągol**, A. Przyjazny, G. Boczkaj, Highly effective degradation of selected groups of organic compounds by cavitation based AOPs under basic pH conditions, Ultrason. Sonochem. 45 (2018) 257–266.
4) **M. Gągol**, A. Przyjazny, G. Boczkaj, Effective method of treatment of industrial effluents under basic pH conditions using acoustic cavitation – a comprehensive comparison with hydrodynamic cavitation processes, Chem. Eng. Process. 128 (2018) 103-113.

Wykaz skrótów i akronimów

Skrót/Akronim	Termin anglojęzyczny	Termin polskojęzyczny
AC (KA)	*Acoustic Cavitation*	Kawitacja akustyczna
AOPs	*Advanced Oxidation Processes*	Zaawansowane procesy utleniania
BTEX-N	*Benzene/ Toluene / Etylbenzene / Xylene and Naphtalene*	benzen/ toluene / etylobenzen/ ksylen i naftalen
BOD_5 (BZT_5)	*Biological Oxygen Demand*	Biologiczne zapotrzebowanie na tlen
COD (ChZT)	*Chemical Oxygen Demand*	Chemiczne zapotrzebowanie na tlen
FPD	*Flame Photometric Detector*	Detektor płomieniowo-fotometryczny
GC	*Gas Chromatography*	Chromatografia gazowa
HC (KH)	*Hydrodynamic Cavitation*	Kawitacja hydrodynamiczna
MS	*Mass Spectrometry*	Spektrometria mas
O-VOCs (O-LZO)	*Oxygen – Volatile Organic Compounds*	Tlenowe – lotne związki organiczne
PAHs (WWA)	*Polycyclic Aromatic Hydrocarbons*	Wielopierścieniowe węglowodory aromatyczne
pH	Hydrogen ion activity	Aktywność jonów wodorowych
r_{ox}	*The mole ratio of the amount of oxidant added to COD of the effluent*	Stosunek molowy ilości wprowadzanego utleniacza do CHZT ścieku
TOC (OWO)	*Total Organic Carbon*	Ogólny węgiel organiczny
USD	*United States Dollar*	Dolar amerykański
UV-C	*Ultraviolet Irradiation (200 – 280 nm)*	Promieniowanie ultrafioletowe (200 – 280 nm)

Streszczenie pracy w języku polskim

W pracy doktorskiej przedstawiono wyniki badań nad zastosowaniem kawitacji hydrodynamicznej oraz akustycznej, wspomaganych zewnętrznymi odczynnikami utleniającymi (ozonem; nadtlenkiem wodoru; oraz ich mieszaniną – tzw. odczynnikiem peroxone) do obniżenia ładunku zanieczyszczeń ścieków rzeczywistych z produkcji asfaltów. Przeprowadzono szczegółową analizę zmian zawartości lotnych związków organicznych tlenu i siarki oraz porównano efektywność obniżania sumarycznych wskaźników zanieczyszczenia: CHZT i BZT$_5$. Wykazano, że najskuteczniejszy proces oczyszczania ścieków z produkcji asfaltów oraz ścieków modelowych obejmuje kawitację hydrodynamiczną wspomaganą odczynnikiem peroxone. Uzyskano wysoką efektywność utleniania fenolu i jego pochodnych charakteryzujących się wysoką biotoksycznością. Analiza ekonomiczna procesów oczyszczania wskazała, że kawitacja hydrodynamiczna wspomagana AOPs może stanowić efektywną metodę wstępnego, chemicznego oczyszczania ścieków z produkcji asfaltów, stosowaną przed etapem oczyszczania biologicznego.

Streszczenie pracy w języku angielskim

The dissertation presents the results of research on the application of hydrodynamic cavitation and acoustic cavitation aided by external oxidation reagents (ozone; hydrogen peroxide; and their mixture - Peroxone) to reduce the load of pollutants present in real effluents from production of bitumens. A detailed analysis of changes in the content of volatile organic oxygen and sulfur compounds was carried out and the efficiencies of reducing the total pollution ratio: COD and BOD$_5$ were compared. It has been shown that the most effective treatment process of wastewater from the production of bitumens and of model wastewater include hydrodynamic cavitation aided by peroxone. High efficiency of oxidation of phenol and its derivatives having high biotoxicity was obtained. The analysis of economics of the treatment processes revealed that hydrodynamic cavitation process combined with AOPs can be an effective method of preliminary chemical treatment of wastewater from production of bitumens, used prior to the biological treatment stage.

1. Wprowadzenie

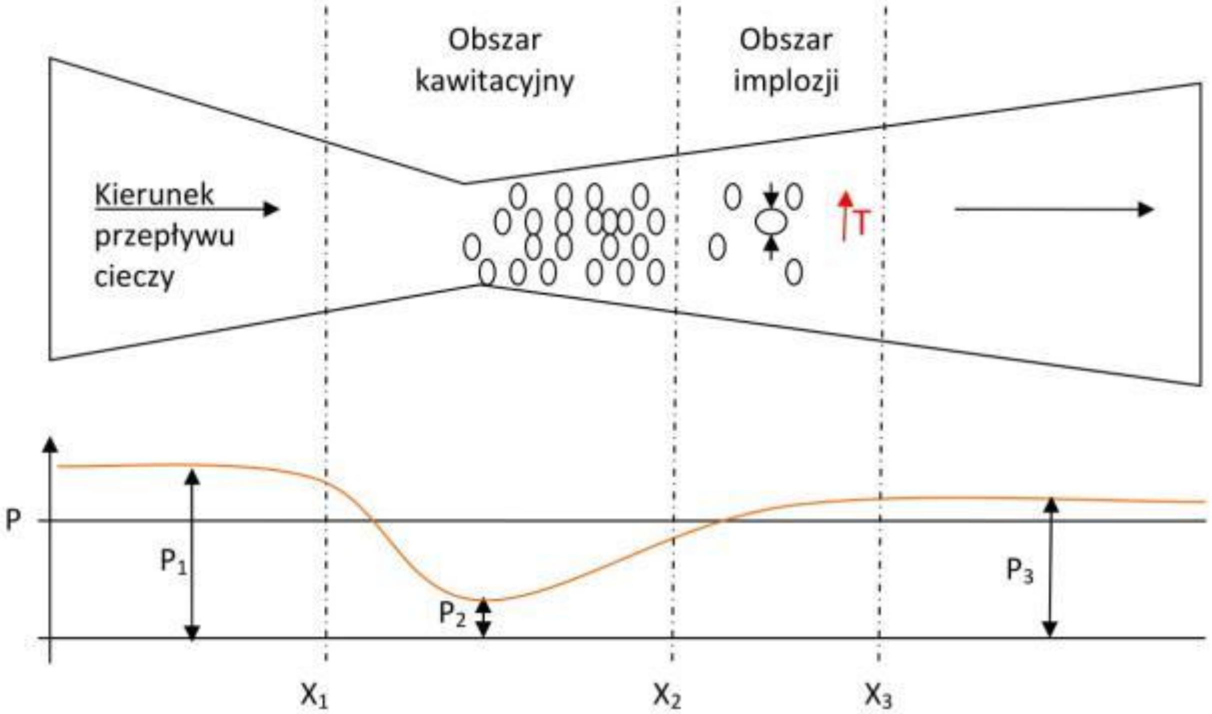
Kawitacja to gwałtowne przejście fizyczne ze stanu ciekłego do stanu gazowego na skutek zmniejszenia ciśnienia statycznego w układzie, co skutkuje pojawieniem się w cieczy, tzw. pęcherzy kawitacyjnych o ogromnej sile implozji (zjawisko powstawania pęcherzy kawitacyjnych w strumieniu przepływającej cieczy przedstawiono na Rysunku 1). Głównymi czynnikami wpływającymi na ich powstawanie są: temperatura, ciśnienie statyczne płynu oraz ciśnienie dynamiczne, związane z liniową prędkością przepływu płynu. Wraz ze spadkiem lokalnego ciśnienia statycznego w strudze przepływającej cieczy, spada również jej temperatura wrzenia, co powoduje wzmożone parowanie i pojawianie się pęcherzy gazowych. Podczas ponownego wzrostu ciśnienia, pęcherze „zapadają się" (implodują), generując przy tym falę uderzeniową o ogromnej sile destrukcyjnej. W czasie nanosekundowej implozji, temperatura wewnątrz zapadającego się pęcherzyka może osiągnąć nawet 4700 °C, a ciśnienie około 1000 MPa [1-3]. Efekt ten jest wykorzystywany w technologiach oczyszczania ścieków, ponieważ proces może prowadzić do efektywnej degradacji zanieczyszczeń. Umożliwia również rozpad cząsteczek wody do wielu indywiduów chemicznych, w tym indywiduów rodnikowych o wysokim potencjale utleniającym m.in. $HO\cdot$, $HO^{2-}\cdot$, nadtlenku wodoru (H_2O_2), które reagują z większością zanieczyszczeń organicznych [4].

Obecnie, zjawisko kawitacji stosuje się w wielu branżach technologicznych, m.in. przy [5]:

- wytwarzaniu emulsji;
- oczyszczaniu różnego rodzaju powierzchni;
- pompach tłoczących lepkie płyny;
- zabiegach kosmetycznych, sonicznych szczoteczkach do zębów;
- procesach wspomagających oczyszczanie ścieków.

Ze względu na warunki powstawania i rozwoju pęcherzyków kawitacyjnych, kawitację podzielono na [5]:

- kawitację hydrodynamiczną;
- parową;
- gazową;
- wibracyjną tzw. kawitację akustyczną.



Rysunek 1. Zjawisko powstawania pęcherzy kawitacyjnych w strumieniu cieczy przepływającej przez zwężkę Venturiego
P_1 / P_3 – ciśnienie statyczne na wejściu/wyjściu do przewężenia, P_2 – ciśnienie statyczne w przewężeniu, P – prężność pary nasyconej płynu

W technologii oczyszczania ścieków wykorzystuje się głównie kawitację hydrodynamiczną oraz akustyczną. W przypadku kawitacji hydrodynamicznej, pęcherzyki gazowe generowane są poprzez specjalne konstrukcje reaktorów bądź układów przepływowych, wymuszających przepływ cieczy pod obniżonym ciśnieniem. Polega to na wywołaniu lokalnego spadku ciśnienia statycznego cieczy poniżej wartości krytycznej, poprzez miejscowy wzrost prędkości przepływu lub zmianę warunków przepływu np. zakrzywienie linii przepływu, oderwania strumienia cieczy od opływanego ciała czy też przewężeń kanałowych. Kawitacja akustyczna do tego celu wykorzystuje falę akustyczną, która pojawia się w cieczy na skutek jej drgań, bądź też drgań jej otoczenia. Drgania wywołuje się przy pomocy ultradźwięków, które rozrywają ciecz lub wprawiają w drgania ciała stałe w niej zanurzone.

Zjawisko kawitacji, stosowane do oczyszczania fazy wodnej, znalazło szerokie zastosowanie m.in. przy wspomaganiu procesu biologicznego i fizyko-fotochemicznego usuwania zanieczyszczeń organicznych [6]. Zjawisko kawitacji umożliwia bardziej efektywne generowanie rodników hydroksylowych, odpowiedzialnych za utleniania większości zanieczyszczeń oraz odpowiada za wytworzenie w oczyszczanym medium lokalnych tzw. „gorących miejsc” (*ang. hot spots*), w których implodujące pęcherzyki gazowe powodują nagłe skoki ciśnienia i temperatury. Umożliwia to zajście dodatkowej dysocjacji zanieczyszczeń na drodze pirolitycznej [7]. Dodatkowo, zanieczyszczenia organiczne posiadające tendencję do przechodzenia w stan gazowy mogą przenikać do tworzących się pęcherzy kawitacyjnych, które implodując z ogromną energią jeszcze bardziej efektywnie będą wspomagać proces utleniania [8].

Wygenerowana siła implozji pęcherzyków kawitacyjnych często wykorzystywana jest również do rozbijania struktur mikroorganizmów i bakterii zawartych w ścieku. Rozbicie struktur mikroorganizmów umożliwia m. in. bardziej efektywne osuszanie biomasy oraz produkcję biogazu [9], co znacząco poprawia pracę oczyszczalni ścieków.

Proces kawitacji wspomaga przede wszystkim generowanie na drodze chemicznej wysokoreaktywnych rodników hydroksylowych, umożliwiających utlenianie szerokiej gamy zanieczyszczeń organicznych, takich jak np.: kwasy karboksylowe [10-11], pestycydy [12-13], alkohole [14-15], rozpuszczalniki chloroorganiczne [16] czy też produkty pochodzenia farmaceutycznego [17-19]. Dzieje się tak, kiedy do oczyszczanego medium wprowadzi się dodatkowy utleniacz chemiczny będący w stanie wygenerować rodnik hydroksylowy. Pęcherzyki kawitacyjne zagęszczają ilość rodników w danym miejscu przyczyniając się dodatkowo do homogenizacji całego układu, a tym samym poprawy efektywności procesu utleniania [20].

Zastosowanie kawitacji hydrodynamicznej oraz akustycznej w procesie oczyszczania ścieków gwarantuje znaczny wzrost efektywności utleniania zanieczyszczeń, o czym świadczą liczne doniesienia literaturowe [21]. Wciąż próbuje się jednak poznać wszystkie ścieżki degradacji zanieczyszczeń i ograniczyć koszty związane z tworzeniem i działaniem instalacji technologicznej. Problem stanowi również optymalizacja procesu pod kątem osiągnięcia wysokiego stopnia utleniania, ze względu na dużą ilość parametrów mających wpływ na przebieg procesu m. in.: pH, temperatura, stężenia reagentów, ciśnienie tłoczenia, stężenie i rodzaj zanieczyszczeń czy też czas reakcji.

2. Przegląd metod wytwarzania kawitacji do degradacji zanieczyszczeń w środowisku wodnym (Publikacja nr 1)

Miarą intensywności zjawiska kawitacji jest tzw. liczba kawitacyjna, która wyrażona jest poprzez następującą równość matematyczną:

$$L_k = \frac{P_2 - P_v}{\frac{1}{2}\rho V_o^2} \ (1),$$

gdzie P_2 to ciśnienie na odcinku o przepływie niezaburzonym za elementem wywołującym kawitację; P_v to prężność pary cieczy; v_o i ρ to liniowa prędkość przepływu i gęstości przepływającej cieczy.

Pęcherzyki gazowe pojawiają się w układzie reakcyjnym, kiedy wartość liczby kawitacyjnej osiąga wartość w przedziale 0-1 [12, 22-25]. Liczba kawitacyjna zależy przede wszystkim od:

- ciśnienia na wejściu do elementu konstrukcyjnego wywołującego wzrost energii kinetycznej przepływającego medium (zwiększenie liniowej prędkości przepływu);
- właściwości fizykochemicznych tłoczonego medium oraz początkowego promienia pęcherza gazowego inicjującego proces kawitacji;
- wymiarów geometrycznych konstrukcji odpowiedzialnej za wywołanie zjawiska kawitacji, a w szczególności, stosunku średnic przewężenia do średnicy części odprowadzającej;
- procentowego odsetku przestrzeni otwartej w przewężeniu (w stosunku do powierzchni zamkniętej), przez którą tłoczy się ciecz.

Odpowiednia konstrukcja przewężenia ma wpływ na zmianę warunków ciśnieniowych podczas przepływu oczyszczanego medium. Umożliwia to uzyskanie optymalnego rozkładu ciśnień przed i za elementem konstrukcyjnym odpowiedzialnych za uzyskanie aktywnej objętości chmury kawitacyjnej, w której dochodzi do utleniania zanieczyszczenia. Jeśli konstrukcja umożliwia spadek i utrzymanie ciśnienia tłoczenia cieczy w okolicy punktu krytycznego, opisującego prężność pary tłoczonego medium, wówczas możliwe jest wytworzenie chmury pęcherzy kawitacyjnych. Po przejściu cieczy przez strefę kawitacyjną następuję gwałtowny wzrost ciśnienia, co prowadzi do implozji pęcherzy, powodującej lokalny przyrost ciśnienia i temperatury. Wpływa to pozytywnie na zwiększenie efektywności degradacji zanieczyszczeń.

Na podstawie wyników badań dostępnych w literaturze, stwierdzono, że reaktory kawitacji akustycznej, spośród dostępnych reaktorów kawitacyjnych, gwarantują największy stopień utlenienia zanieczyszczeń organicznych znajdujących się w fazie wodnej w stosunkowo krótkim czasie (0,5 – 2 h). Najczęściej stosowane moce wzbudzenia przy utlenianiu zanieczyszczeń organicznych mieszczą się w przedziale od 40 do nawet 750 W przy częstotliwości wzbudzenia 20-520 kHz, co gwarantuje utlenienie zanieczyszczeń organicznych na poziomie 30-60% [1, 4, 22, 25-35]. Jednakże, ze względu na bardzo wysokie koszta zużycia energii w tego typu procesach, (koszt oczyszczania zwiększa się niemal 3-krotnie, w porównaniu do procesu kawitacji hydrodynamicznej) procesy tego typu znajdują zastosowanie najczęściej w oczyszczaniu ścieków w skali laboratoryjnej (oczyszczanie roztworów do 500 mL) [33]. Przy oczyszczaniu znacznie większych ilości ścieków najlepszym rozwiązaniem pozostaje zjawisko kawitacji hydrodynamicznej wywołane za pomocą kryzy lub zwężki. Oczyszczane objętości ścieków osiągają nawet 150 L, gwarantując efektywność utlenienia zanieczyszczeń organicznych na poziomie 10-37% [36]. Najczęściej, czas potrzebny do osiągnięcia efektywności powyżej 20% wynosi ponad 3 h ciągłego prowadzenia procesu [8, 28, 30]. Oznacza to wielokrotną cyrkulację oczyszczanego strumienia przez element kawitacyjny. Należy zaznaczyć, że obecnie zjawisko kawitacji stosowane do oczyszczania ścieków z zanieczyszczeń organicznych wspomaga się dodatkowymi zaawansowanymi metodami utleniania takimi jak: proces Fentona [12], naświetlanie ścieku lampami UV [37] czy też dodatkiem silnych utleniaczy, m.in. nadtlenku wodoru albo ozonu [22]. Umożliwia to przeprowadzenie utlenienia zanieczyszczeń na bardzo wysokim poziomie efektywności 70-100% w znacznie krótszym czasie (1 – 2 h) [38].

3. Przegląd metod oczyszczania ścieków za pomocą zaawansowanych procesów utleniania opartych na zjawisku kawitacji (Publikacja nr 1)

Jedną z najbardziej efektywnych metod utleniania zanieczyszczeń, znajdujących się w medium wodnym, jest metoda hybrydowa. Łączy ona zjawisko kawitacji z zaawansowanymi procesami utleniania (AOP – ang. *Advanced Oxidation Process*).

W procesach AOPs stosuje się bardzo reaktywne rodniki hydroksylowe o wysokim potencjale utleniającym. Teoretycznie, rodniki hydroksylowe można otrzymać na drodze ponad dwudziestu różnych procesów chemicznych. W praktyce istnieją trzy podstawowe drogi, które najczęściej stosowane są w procesach utleniania [39]:

- chemiczna;
- fotochemiczna;
- fotokatalityczna.

Droga chemiczna polega głównie na wygenerowaniu reaktywnych rodników hydroksylowych w wyniku przeprowadzenia reakcji chemicznej. Mogą one być generowane przy użyciu utleniaczy takich jak: nadtlenek wodoru, ozon lub ich mieszaniny tj. peroxone. Ze względu na wysoki potencjał utleniający, wynoszący 2,8 V, rodniki są w stanie utlenić większość zanieczyszczeń organicznych i nieorganicznych znajdujących się w oczyszczanym medium [40-41]. Inne odczynniki służące do otrzymywania rodników hydroksylowych na drodze chemicznej to: odczynnik Fentona oraz mieszanina ozonu z anionem wodorotlenkowym, anion nadsiarczanowy i mononadsiarczanowy.

Drogi fotochemicznego i fotokatalitycznego utleniania charakteryzuje ścisłe podobieństwo mechanizmów utleniania. Wykorzystuje się w nich procesy tworzenia wolnych rodników przy użyciu promieniowania UV, silnych utleniaczy chemicznych (procesy fotochemiczne) oraz dodatkowo tlenków metali przejściowych o właściwościach półprzewodnikowych (procesy fotokatalityczne) np. tlenek tytanu, żelaza, cynku.

Najczęściej zjawisko kawitacji wspomagane procesami AOPs stosuje się w początkowym etapie oczyszczania ścieków, przed metodami biologicznymi, co pozwala zwiększyć efektywność i ekonomiczność procesu. Metody hybrydowe wydają się być najlepszą alternatywą stosowaną do oczyszczania ścieków przemysłowych zawierających skomplikowany ładunek zanieczyszczeń. Jednak, ze względu na wysoką cenę instalacji technologicznej oraz wciąż słabo poznane mechanizmy reakcji chemicznych i fizycznych (zachodzących ze względu na obecność wysokoreaktywnych rodników hydroksylowych) jak i trudność z ustabilizowaniem procesu generowania pęcherzyków kawitacyjnych, procesy te nie są popularne w skali przemysłowej.

Ponadto, przebieg procesów zależy w dużej mierze od mniej ważnych parametrów procesowych z punktu widzenia innych metod utleniania, takich, jak np: czas przebywania zanieczyszczeń w reaktorze, prędkość przepływu, ciśnienie tłoczenia czy też charakteru zanieczyszczeń i właściwości fizykochemiczne oczyszczanego medium, co w znaczący sposób utrudnia optymalizację.

Przedmiotem badań przeglądowych było zebranie dokładnych informacji na temat obecnie stosowanych instalacji kawitacyjnych (AOPs) do utleniania szerokiej grupy zanieczyszczeń organicznych występujących w medium wodnym, oraz porównanie efektywności i ekonomiczności poszczególnych procesów. Scharakteryzowano również, wszystkie istotne parametry procesowe mające wpływ na efektywność procesu oczyszczania w warunkach kawitacji.

Wykazano, że zaawansowane metody utleniania oraz zjawisko kawitacji coraz częściej wykorzystywane są do utleniania szerokiej gamy związków organicznych zawartych w ściekach przemysłowych. Charakteryzują się przy tym wysokim stopniem degradacji oraz znaczącym obniżeniem poziomu biotoksyczności ścieku. Zastosowanie tych metod do oczyszczania jednych z najbardziej biotoksycznych ścieków, ścieków z przemysłu chemicznego, może znacząco poprawić efektywność ich oczyszczania. Połączenie wysokoreaktywnych rodników hydroksylowych z dużą siłą implozji umożliwia rozbicie i utlenienie większości zanieczyszczeń organicznych, nieusuwalnych przy stosowaniu innych tradycyjnych metod oczyszczania.

Kawitacja hydrodynamiczna i akustyczna wspomagana zaawansowanymi metodami utleniania m.in.: O_3, H_2O_2, UV i procesem Fentona, może być alternatywą dla obecnie stosowanych metod. Wykazano całkowite utlenienie szerokiej gamy zanieczyszczeń organicznych, w tym trudno degradowalnych związków organicznych należących do grupy: farmaceutyków, barwników organicznych, insektycydów oraz fenolu i jego pochodnych.

Analiza ekonomiczna wykazała, że obecnie ze względu na niski koszt konstrukcji reaktorów oraz niskie zużycie energii elektrycznej w porównaniu do kawitacji akustycznej, jedynie kawitacja hydrodynamiczna może zostać przystosowana do pracy w instalacjach przemysłowych.

Szczegółową analizę wyników przeglądu literaturowego dotyczącego obecnie stosowanych metod kawitacyjnych w połączeniu z zawansowanymi metodami utleniania do degradacji zanieczyszczeń organicznych występujących w medium wodnym, ich efektywności i ekonomiczności opublikowano w czasopiśmie *Chemical Engineering Journal* [21] (załącznik 1).

4. Podsumowanie artykułu przeglądowego

Ścieki poprodukcyjne ze względu na bogaty ładunek zanieczyszczeń stanowią dziś poważne obciążenie środowiskowe. Wymagają znacznego nakładu finansowego, w celu ich oczyszczenia do stanu, umożliwiającego swobodne odprowadzenie ich z zakładu produkcyjnego do środowiska. Obecność wysokotoksycznych związków organicznych oraz nieorganicznych wymusza konieczność stosowania zaawansowanych technologii oczyszczania, gwarantujących wysoki stopień degradacji zanieczyszczeń.

Na podstawie wykonanego przeglądu literatury stwierdzono, że zaawansowane procesy utleniania oraz zjawisko kawitacji coraz częściej wykorzystywane są do degradacji szerokiej gamy związków organicznych zawartych w ściekach przemysłowych. Połączenie wysokoreaktywnych rodników hydroksylowych z dużą siłą implozji umożliwia utlenienie większości zanieczyszczeń organicznych, nieusuwalnych przy stosowaniu innych tradycyjnych metod oczyszczania.

Zastosowanie metody hybrydowej (tj. połączenia zjawiska kawitacji z AOPs) w początkowym etapie oczyszczania ścieków poprodukcyjnych, przed metodami biologicznymi, wydaje się być w pełni uzasadnione. Jednak, problem stanowić może dokładna kontrola reakcji chemicznych przebiegających na drodze nieselektywnej w wyniku obecności w układzie rodników hydroksylowych. Trudno również dobrać odpowiednie warunki procesowe, wymagające chociażby odpowiedniego pH czy też stężenia poszczególnych składników reakcyjnych. Dodatkowo, wysoki koszt instalacji technologicznej często stanowi największe ograniczenie do zastosowania tego typu metod w wielu przedsiębiorstwach.

Dane dostępne w literaturze pokazują, że sam proces kawitacji hydrodynamicznej i akustycznej umożliwia osiągnięcie co najmniej 10% skuteczności utleniania różnego rodzaju zanieczyszczeń występujących w medium wodnym. Związki, które łatwo ulegają degradacji (ponad 50% utlenienie) w warunkach kawitacyjnych to przede wszystkim: aldehydy, ketony i zw. chlorowcopochodne. Dla tych związków, wydłużenie czasu trwania procesu oczyszczania powinno pozwolić na prawie całkowitą degradację zanieczyszczeń. Związki trudno degradowalne w warunkach kawitacyjnych (skuteczność utleniania w zakresie od 10 do 50%) obejmują: farmaceutyki, barwniki organiczne, fenol i jego pochodne nitrowe, insektycydy oraz alkohole. W tym przypadku czas potrzebny do utlenienia zanieczyszczeń może być zbyt długi, a proces nieopłacalny. W takich przypadkach do głosu dochodzą procesy hybrydowe.

Metody oczyszczania medium wodnego w warunkach kawitacji wspomaganej dodatkiem zewnętrznych utleniaczy, takimi jak ozon, nadtlenek wodoru lub nadsiarczany zapewniają wysoką skuteczność degradacji. Procesy hybrydowe powodują znaczny wzrost efektywności oczyszczania. Efektywność utleniania zanieczyszczeń trudno degradowalnych często wzrasta z poziomu 10 - 20%, w przypadku zastosowania wyłącznie procesu kawitacji, do ponad 60% dla metod hybrydowych. Wpływa to również na zmniejszenie kosztów i czasu trwania procesu oczyszczania, a tym samym na jego ekonomiczność.

5. Cel oraz zakres badań

Celem głównym pracy było zbadanie możliwości zastosowania kawitacji hydrodynamicznej wspomaganej procesami AOPs do oczyszczania ścieków rzeczywistych z produkcji asfaltów, charakteryzujących się złożonym składem oraz wysokim ładunkiem zanieczyszczeń. Zbadanie czy kawitacja może być stosowana na wstępnym etapie oczyszczania ścieków rafineryjnych, przed etapem biologicznym.

Cel główny pracy osiągnięto poprzez realizację celów szczegółowych:

- przygotowanie pogłębionego przeglądu literaturowego na temat reaktorów kawitacyjnych, umożliwiającego zaprojektowanie i zbudowanie reaktora kawitacji hydrodynamicznej;
- zbadanie wpływu poszczególnych parametrów procesowych na efektywność degradacji wybranych grup związków chemicznych;
- zbadanie możliwości zwiększania efektywności degradacji zanieczyszczeń poprzez zastosowanie procesów hybrydowych (tj. połączenia degradacji w warunkach kawitacji z zastosowaniem utleniaczy zewnętrznych) oraz zbadanie synergizmu tych procesów;
- porównanie efektywności degradacji w warunkach kawitacji oraz procesów hybrydowych dla kawitacji hydrodynamicznej i kawitacji akustycznej.

Ściek rzeczywisty z produkcji asfaltów stanowi duże obciążenie dla działania rafineryjnej oczyszczalni ścieków ze względu na zawartość związków tlenoorganicznych, toksycznych dla mikroorganizmów wchodzących w skład osadu czynnego, stosowanego na etapie oczyszczania biologicznego. Badaniami objęto ścieki modelowe oraz ścieki rzeczywiste z produkcji asfaltów dostarczone przez Lotos Asfalt Sp. z o. o. (Grupa LOTOS S.A.). Ściek modelowy przygotowano w oparciu o parametry fizykochemiczne i skład ścieków rzeczywistych, w celu dokładnego poznania mechanizmów utleniania wybranych grup zanieczyszczeń organicznych bez wpływu skomplikowanej matrycy ścieków rzeczywistych.

6. Zastosowanie kawitacji hydrodynamicznej wspomaganej dodatkowymi utleniaczami jako skutecznej metody oczyszczania ścieków z produkcji asfaltów o zasadowym pH (Publikacja nr 2)

Produkcja i stosowanie asfaltów naftowych stanowi duże wyzwanie w zakresie ochrony środowiska. Problem dotyczy zarówno zjawiska generowania podczas procesu produkcyjnego lotnych związków organicznych oraz WWA, jak również powstawania ścieków po-oksydacyjnych. Gazy odlotowe powstające podczas produkcji (oksydacji) asfaltów są oczyszczane z zastosowaniem skruberów zraszanych olejem płuczkowym albo wodnym roztworem ługu sodowego. Pozostałe zanieczyszczenia gazowe są utylizowane termicznie, natomiast do oczyszczenia pozostaje absorbat stanowiący tzw. ścieki po-oksydacyjne. Obecność w ścieku po-oksydacyjnym wysokotoksycznych związków organicznych oraz nieorganicznych wymusza konieczność stosowania zaawansowanych technologii oczyszczania, gwarantujących wysoki stopień utleniania. W przypadku działu asfaltów stanowiącego część rafinerii ropy naftowej, ścieki po-oksydacyjne są kierowane do zakładowej oczyszczalni ścieków. Jednak ich specyficzny skład stanowi utrudnienie dla ich oczyszczania biologicznego. Ścieki po-oksydacyjne charakteryzują się wysoką zawartością związków organicznych, w tym związków zawierających w swej strukturze atomy tlenu (ketony, aldehydy, etery, alkohole), azotu (głównie pochodne pirydyny oraz aminy alifatyczne i aromatyczne), a także siarki. Do oczyszczania tego rodzaju ścieków wymagane jest zastosowanie oczyszczania chemicznego, korzystnie z wykorzystaniem AOPs.

Przedmiotem prezentowanych badań było sprawdzenie efektywności oczyszczania ścieków z produkcji asfaltów przy zastosowaniu układu reakcyjnego do kawitacji hydrodynamicznej (zaprojektowanego na podstawie danych zgromadzonych dzięki przedstawionemu w pracy przeglądowi literaturowemu – (projekt: mgr inż. Michał Gągol i dr hab. inż. Grzegorz Boczkaj; wykonanie: Pan Bogusław Świątoniowski) w połączeniu z nadtlenkiem wodoru, ozonem oraz odczynnikiem peroxone.

Wykazano, że kawitacja hydrodynamiczna stosowana jako samodzielny proces wstępnego oczyszczania ścieków z produkcji asfaltów, bądź też wspomagana dodatkowymi procesami utleniania, może stanowić doskonałą metodę obniżania ładunku zanieczyszczeń ścieków z procesów chemicznych. Najefektywniejszy proces utleniania uzyskano przy liczbie kawitacyjnej 0.14. Kolejne badane procesy kawitacyjne prowadzono w warunkach zapewniających uzyskanie właśnie takiej wartości liczby kawitacyjnej. Przeprowadzone badania wykazały, że proces kawitacji hydrodynamicznej wspomagany ozonowaniem oraz odczynnikiem peroxone przy stosunku molowym O_3/H_2O_2 równym 1:6,7 stanowi efektywną metodę wstępnego oczyszczania ścieków z produkcji asfaltów. Peroxone to utleniacz stanowiący połączenie nadtlenku wodoru oraz ozonu wprowadzanych jednocześnie do środowiska reakcji. W badaniach objętych pracą doktorską, nadtlenek wodoru oraz ozon wprowadzane były jako osobne strumienia, aczkolwiek w tym samym miejscu zwężki Venturiego stosowanego reaktora (ozon wprowadzano jako strumień w powietrzu bezpośrednio z generatora, a nadtlenek wodoru jako 30-to procentowy roztwór wodny – tzw. perhydrol - za pomocą pompy). Istotnym elementem nowości naukowej przeprowadzonych badań, jest fakt, że odczynnik peroxone do tej pory nie był używany w połączeniu z zjawiskiem kawitacji do utleniania zanieczyszczeń organicznych zawartych w roztworze wodnym. Proces kawitacji hydrodynamicznej wspomagany ozonowaniem i peroxone-m zapewnił obniżenie wskaźników sumarycznego zanieczyszczenia ścieku, kolejno: ChZT o 40% i 59% oraz BZT_5 o 50% i 65%. Badania wykazały wysoki synergizm procesu kawitacji hydrodynamicznej + peroxone, który wyniósł 1,77, a dla kawitacji hydrodynamicznej w połączeniu z ozonowaniem 1,20. Synergizm procesów wyrażony jest poprzez stosunek wartości obniżenia wskaźnika ChZT ścieku (wyrażonego w mgO_2/L) procesu łączonego do sumy efektywności procesów realizowanych indywidualnie.

W przypadku odczynnika peroxone istotne znaczenie na efektywność procesu ma stosunek molowy O_3/H_2O_2. Badania wykazały, że dwukrotnie niższa zawartość H_2O_2 w mieszaninie - stosunek O_3/H_2O_2 wynoszący 1:2,9, skutkuje istotnym obniżeniem efektywności w stosunku do zmiany wskaźnika ChZT ścieku – zmiana ChZT o 25%, synergizm procesu równy 0,5. Roztwory nadtlenku wodoru są stabilne w warunkach kwaśnych i obojętnych. Warunki alkaliczne (pH 10,5) sprzyjają szybkiemu rozkładowi nadtlenku wodoru z utworzeniem wody oraz anionu perhydroksylowego (HOO^-):

$$H_2O_2 + HO^- \overset{pH>7}{\Longleftrightarrow} HOO^- + H_2O \quad (2)$$

Aniony perhydroksylowe charakteryzują się niższym potencjałem utleniającym niż rodniki hydroksylowe. Dlatego też, dotychczas nie stosowano nadtlenku wodoru przy oczyszczaniu roztworów wodnych o zasadowym pH. Jednak, w warunkach kawitacyjnych oraz obecności rozpuszczonego ozonu, nadtlenek wodoru rozkładany jest głównie do rodników hydroksylowych (reakcja 3) odpowiedzialnych za reakcje utleniania zanieczyszczeń organicznych. Umożliwia to zwiększenie efektywności utleniania zanieczyszczeń oraz uzyskanie wysokiego obniżenia wskaźnika ChZT i BZT_5 ścieku.

$$2O_3 + H_2O_2 \xrightarrow{kawitacja} 2HO^{\cdot} + 3O_2 \ (3)$$

Powstałe rodniki hydroksylowe charakteryzują wysokie stałe szybkości reakcji względem różnego rodzaju zanieczyszczeń organicznych (stałe szybkości od 10^8 do 10^{11} M^{-1}, s^{-1}), przez co są one zużywane natychmiastowo w reakcjach z obecnymi w ścieku związkami organicznymi. Utleniają zawarte w ścieku zanieczyszczenia prowadząc, w końcowym etapie do powstania wody i CO_2 (reakcja 4- na przykładzie utleniania metanolu)

$$CH_3OH + HO^{\cdot} \rightarrow C^{\cdot}H_2OH \xrightarrow{HO^{\cdot}/O_2} CH_2O \xrightarrow{HO^{\cdot}/O_2} HCOOH \xrightarrow{HO^{\cdot}/O_2} CO_2 + H_2O(4)$$

Kiedy do układu reakcyjnego wprowadza się niedomiar nadtlenku wodoru – poniżej optymalnego dla peroxone-u stosunku molowego względem ozonu, powstaje zbyt mało rodników hydroksylowych, które nie są w stanie efektywnie utlenić występujących w ścieku zanieczyszczeń. Dlatego też, zaobserwowano znaczący spadek efektywności obniżania wskaźników ChZT i BZT_5 ścieku przy stosunku molowy O_3/H_2O_2 równym 1:2,9. Dodatkowo, przy źle dobranym stosunku utleniaczy rodniki hydroksylowe zużywane są w reakcjach niepożądanych min.: przez aniony perhydroksylowe (które, zgodnie z reakcją 2 będą generowane z nadmiarowego nadtlenku wodoru), prowadząc do powstania wody i tlenu (reakcja 5).

$$HOO^- + HO^{\cdot} \xrightarrow{pH>7\ (kawitacja)} H_2O + O_2 \ (5)$$

Dlatego też, dla kolejnych badanych procesów kawitacyjnych z peroxone-m, stosowano dawkę utleniaczy umożliwiającą osiągnięcie stosunku molowego O_3/H_2O_2 1:6,7 (r_{ox} = 1,5). Wskaźnik r_{ox} wyraża stosunek ilości wprowadzanego utleniacza (w przeliczeniu na liczbę moli HO·) do wartości wskaźnika CHZT ścieku (w przeliczeniu na liczbę moli O_2). Umożliwiło to zapewnienie optymalnego stężenia w roztworze składników mieszaniny peroxone oraz maksymalnej efektywności utleniania zanieczyszczeń organicznych wyrażonych poprzez wskaźniki sumarycznego zanieczyszczenia: ChZT i BZT_5.

Pozostałe procesy (KH + H_2O_2 - dla tego procesu nie odnotowano synergizmu) oraz samej kawitacji hydrodynamicznej gwarantują obniżenie ChZT kolejno o 20 i 13 %, a obniżenie BZT_5 o 49 i 18%.

Dodatkowo, w procesie KH + O_3 oraz KH + peroxone udało się utlenić wszystkie badane związki tlenoorganiczne występujące w ścieku przy jednoczesnym odbarwieniu ścieku i zmniejszeniu jego drażliwości zapachowej. Szczególnie istotnym wnioskiem z tej części pracy jest bardzo efektywna degradacja związków aromatycznych – fenolu i jego pochodnych, charakteryzujących się wysoką biotoksycznością. Efektywne utlenienie fenolu i jego pochodnych podczas procesu oczyszczania wstępnego może ochronić osad czynny i umożliwiać efektywną biodegradację pozostałych zanieczyszczeń.

W przypadku badanego rodzaju ścieków, utlenienie związków tlenoorganicznych przed etapem biologicznym jest korzystne z punktu widzenia kondycji osadu czynnego przystosowanego, w przypadku rafineryjnych oczyszczalni ścieków, do zanieczyszczeń węglowodorowych. Zastosowanie zjawiska kawitacji hydrodynamicznej wspomaganej zewnętrznymi utleniaczami nie wymaga zastosowania złożonej aparatury i opiera się na konwersji energii elektrycznej na ciśnienie tłoczenia medium i wykorzystaniu prostych elementów wywołujących kawitację (tj. przewężenie kanałowe), co czyni procesy z tej grupy stosunkowo bezobsługowymi i łatwymi do kontroli procesowej.

Szczegółowe wyniki badań dotyczące efektywności oczyszczania ścieków z produkcji asfaltów przy zastosowaniu kawitacji hydrodynamicznej w połączeniu z zawansowanymi metodami utleniania (ozonem, nadtlenkiem wodoru oraz peroxone-m) opublikowano w czasopiśmie *Ultrasonics - Sonochemistry* [42] (załącznik 2).

7. Wysoko efektywna degradacja wybranych związków organicznych w warunkach kawitacyjnych wspomaganych zaawansowanymi procesami utleniania przy zasadowym pH (Publikacja nr 3)

Przedmiotem badań było sprawdzenie efektywności utleniania w warunkach kawitacji hydrodynamicznej oraz kawitacji akustycznej 15 modelowych zanieczyszczeń organicznych (2-etylotiofen, dibutylosulfid, ditertbutylosulfid, nitrobenzen, 2-nitrofenol, 2-nitrotoluen, benzen, etylobenzen, toluen, o-ksylen, fenol, 4-etylofenol, m-krezol, o-krezol, naftalen) zawartych w przygotowanym, na podstawie znanej charakterystyki ścieku rzeczywistego, ścieku modelowym.

Bardzo złożony skład ścieków asfaltowych utrudnił analizę efektywności badanych metod w odniesieniu do poszczególnych grup zanieczyszczeń. Dlatego też, przeprowadzono badania dla ścieku modelowego, charakteryzującego się kontrolowanym składem. Zbadano efektywność procesów kawitacji hydrodynamicznej i akustycznej stosowanych samodzielnie oraz wspomaganych dodatkowymi utleniaczami (nadtlenkiem wodoru, ozonem oraz peroxone-m). Przedstawiono również szczegółowe porównanie tych dwóch metod kawitacyjnych.

Kawitacja akustyczna to zjawisko fizyczne, które do rozpoczęcia procesu generowania pęcherzyków gazowych w objętości oczyszczanego medium wodnego wykorzystuje energię ultradźwięków [32-33, 38, 43]. Ultradźwięki są źródłem energii, która umożliwia zapoczątkowanie procesu wzrostu pęcherzyka, a następnie jego implozję, której towarzyszy lokalny wzrost ciśnienia i temperatury roztworu. Takie warunki promują reakcje tworzenia reaktywnych rodników hydroksylowych (•OH), które odpowiadają za reakcje utleniania zanieczyszczeń znajdujących się w oczyszczanym medium [1, 27, 44-45]. Dodatkowo, generowanie fali akustycznej w roztworze powoduje powstawanie lokalnych ruchów turbulentnych oraz mikro-cyrkulacji płynu, tzw. „strumieni akustycznych”, które dodatkowo wspomagają procesy fizyko-chemiczne zachodzące w roztworze ograniczając znacząco opory przenoszenia masy [33]. Tego typu zjawiska przyczyniają się do wzrostu efektywności generowania rodników hydroksylowych oraz transportu cząsteczek cieczy i zanieczyszczeń w niej występujących w okolice implodujących pęcherzyków, co powoduje wysoki stopień utlenienia zanieczyszczeń organicznych [46-49].

Wykazano, że zjawisko kawitacji hydrodynamicznej jak i kawitacji akustycznej w połączeniu z nadtlenkiem wodoru, ozonem oraz peroxone-m gwarantuje wysoką efektywność utleniania zanieczyszczeń organicznych występujących w zasadowym ścieku modelowym. Najbardziej efektywny proces odnotowano dla kawitacji hydrodynamicznej oraz akustycznej połączonych z peroxone-m (100 % utlenienia wszystkich badanych zanieczyszczeń modelowych w czasie pierwszych 60 minut procesu). Wynika to przede wszystkim z efektywnego generowania rodników hydroksylowych w warunkach kawitacyjnych w obecności nadtlenku wodoru oraz ozonu przy zasadowym pH oczyszczanego roztworu oraz odpowiedniej dawki utleniaczy.

Dla kolejnego badanego procesu, kawitacji hydrodynamicznej oraz akustycznej połączonych z ozonowaniem, odnotowano 100 % utlenienie badanych zanieczyszczeń modelowych po około 180 minutach trwania procesów oczyszczania. Zjawisko kawitacji umożliwia ograniczenie oporów wymiany masy za sprawą tworzących się w objętości roztworu stref mikro-cyrkulacji i turbulencji płynu. Konsekwencją tego zjawiska jest zwiększenie stężenia rozpuszczonego ozonu w objętości oczyszczanego ścieku. To z kolei, przekłada się na zwiększenie liczby rodników hydroksylowych i bardziej efektywny proces degradacji.

Istotnym wnioskiem z tej pracy jest możliwość efektywnego stosowania nadtlenku wodoru w zasadowym pH w warunkach kawitacji. Wiadomo, że nadtlenek wodoru w zasadowym pH ulega rozkładowi do mniej reaktywnych form rodnikowych, niż rodniki hydroksylowe. Zastosowanie warunków kawitacji umożliwia jego efektywną konwersję do rodników hydroksylowych, co przekłada się na wysoką efektywność utleniania. Dla kawitacji hydrodynamicznej oraz akustycznej połączonych z nadtlenkiem wodoru odnotowano ponad 90 % utlenienie wszystkich badanych zanieczyszczeń modelowych w czasie 180 minut, za wyjątkiem 2-nitrofenolu (66,9 % - KA + H_2O_2; 62,9 % - KH + H_2O_2). Wykazano, że stałe szybkości degradacji nitrowych pochodnych benzenu oraz fenolu i jego pochodnych są najniższe w porównaniu do badanych zanieczyszczeń organicznych. Wynika to głównie z licznych produktów przejściowych powstających podczas ich utleniania (m.in. p, o, m - krezoli) oraz powstających zanieczyszczeń wtórnych generowanych za sprawą wolnych grup chemicznych m.in. grupy azotanowej NO_3^-.

W przypadku zastosowania wyłącznie procesu kawitacji hydrodynamicznej oraz akustycznej przy utlenianiu zanieczyszczeń modelowych odnotowano ponad 90 % utlenienie związków z grupy BTEX+N oraz siarkoorganicznych w czasie 180 minut trwania procesów oczyszczania.

Dla poszczególnych związków modelowych kawitacja hydrodynamiczna wykazuje wyższą o około 5-10 % efektywność degradacji w porównaniu do kawitacji akustycznej. Wynika to z większej intensywności zjawiska kawitacji w przewężeniu kanałowym zwężki, niż w obszarze pracy wzbudników sonicznych. Kawitacja hydrodynamiczna oraz akustyczna stosowane samodzielnie, bez dodatku utleniaczy zewnętrznych, nie są efektywnymi metodami utleniania związków zawierających ugrupowania nitrowe oraz fenolu i jego pochodnych. Szczególnie fenol i jego pochodne stanowią zagrożenie dla środowiska naturalnego ze względu na wysoką biotoksyczność. Dlatego, zawartość tych związków powinna być ściśle kontrolowana na każdym etapie oczyszczania roztworów wodnych pochodzenia przemysłowego.

Z punktu widzenia ekonomiki poszczególnych procesów kawitacyjnych oraz AOPs wykazano, że najbardziej ekonomicznymi procesami utleniania zanieczyszczeń organicznych są procesy hybrydowe, łączące zjawisko kawitacji z dodatkowymi procesami AOPs. Wynika to przede wszystkim z niemal 3-krotnego skrócenia czasu prowadzenia procesu niezbędnego do osiągnięcia zamierzonej efektywności utlenienia. Na podstawie analizy kosztów prowadzenia procesu oczyszczania ścieku zawierającego zanieczyszczenia z grupy BTEX-N wykazano, że najbardziej ekonomicznym procesem jest proces kawitacji hydrodynamicznej oraz akustycznej w połączeniu z ozonowaniem, w porównaniu do pozostałych badanych procesów AOPs (koszt prowadzenia procesu oczyszczania wynosi kolejno 0.14 i 0.10 PLN L^{-1}). Jednakże, w porównaniu do procesów kawitacyjnych występujących w połączeniu z peroxone-m, wymaga on 2-krotnie dłuższego czasu prowadzenia procesu oczyszczania.

Szczegółowe wyniki badań dotyczące efektywności oczyszczania ścieku modelowego zawierającego 15 związków organicznych przy zastosowaniu kawitacji hydrodynamicznej oraz akustycznej w połączeniu z zaawansowanymi metodami utleniania (ozonem, nadtlenkiem wodoru oraz peroxone-m) opublikowano w czasopiśmie Ultrasonics - Sonochemistry [50] (załącznik 3).

8. Efektywna metoda oczyszczania ścieków przemysłowych o zasadowym pH w warunkach kawitacji akustycznej – kompleksowe porównanie z procesami dotyczącymi kawitacji hydrodynamicznej (Publikacja nr 4)

Celem badań, prezentowanych w tej pracy, było sprawdzenie możliwości zastosowania oraz ocena efektywności procesu kawitacji akustycznej, wspomaganej dodatkowo procesem ozonowania, nadtlenkiem wodoru, peroxone-m oraz światłem UV do wstępnego oczyszczaniu ścieków z produkcji asfaltów. Jest to jedna z pierwszych prac, w której prezentowane są wyniki badań dotyczące wykorzystania reaktora kawitacji akustycznej do utleniania zanieczyszczeń zawartych w ścieku rzeczywistym. W pracy, przedstawiono również szczegółowe porównanie procesów kawitacji akustycznej z AOPs z procesami kawitacji hydrodynamicznej prezentowanymi w poprzedniej pracy badawczej.

Wykazano, że kawitacja akustyczna stosowana jako samodzielny proces wstępnego oczyszczania ścieków z produkcji asfaltów, bądź też wspomagana dodatkowymi procesami utleniania może stanowić efektywną metodę obniżania ładunku zanieczyszczeń ścieku z produkcji asfaltów. Najbardziej efektywnym procesem, spośród badanych procesów kawitacji akustycznej, jest proces wspomagany odczynnikiem peroxone (zapewniający obniżenie wskaźnika ChZT ścieku o 46 % i BZT_5 o 55 %; synergizm procesu 1,5). Kiedy proces kawitacyjny wspomagano dodatkowo naświetlaniem światłem UV-C otrzymano wzrost efektywności obniżenia wskaźnika ChZT ścieku średnio o 5% i BZT_5 o 10% dla poszczególnych procesów kawitacyjnych (w tym również dla procesów kawitacji hydrodynamicznej). Promieniowanie UV-C poprawia skuteczność utleniania związków organicznych zawierających podwójne wiązania C = C, takich jak np. fenol i jego pochodne [51], barwniki naftolowe [52], a także chlorowane pochodne etylenu [53]. Wykazano, że podczas pierwszych trzech godzin trwania procesu oczyszczania ścieku w warunkach kawitacyjnych rodniki hydroksylowe są zużywane głównie do utleniania prostych związków organicznych, takich jak alkohole. Związki trudnodegradowalne wymagają znacznie dłuższego czasu oczyszczania i ulegają utlenieniu do prostszych związków organicznych dopiero po 3 godzinach trwania procesu kawitacyjnego. Proste związki organiczne często zawierają podwójne wiązania C = C, co pozwala na ich skuteczną degradację za pomocą energii promieniowania UV-C. Uzyskane wyniki badań wskazują na możliwość zastosowania sekwencyjnego procesu oczyszczania ścieków. Pierwszy etap mógłby obejmować sam proces kawitacji, a następnie foto-utlenienie zanieczyszczeń organicznych za pomocą UV-C. Takie podejście pozwoliłoby zwiększyć ekonomiczność procesu.

Warto zaznaczyć, że wyniki badań efektywności utleniania zanieczyszczeń organicznych uzyskane w procesie kawitacji hydrodynamicznej i akustycznej w połączeniu z peroxonem są najlepsze spośród dotychczas opublikowanych w literaturze wyników badań oczyszczania ścieków przemysłowych o zasadowym pH [54]. Szczególnie, że badane w ramach niniejszej pracy ścieki stanowią rzeczywiste ścieki przemysłowe o bardzo złożonym składzie. Pozostałe procesy (sama KA / KA + O_3 / KA + H_2O_2 gwarantują obniżenie ChZT kolejno o 10, 20 i 40 % oraz BZT_5 o 11, 20 oraz 40 %. Dodatkowo, odnotowano wysoki synergizm dla procesu kawitacji akustycznej w połączeniu z nadtlenkiem wodoru 1,79 i brak synergizmu w procesie wspomaganym ozonowaniem.

W przypadku porównania procesu kawitacji akustycznej z procesem kawitacji hydrodynamicznej, dla takich samych warunków procesowych, odnotowano nieco wyższe efektywności utlenienia zanieczyszczeń organicznych dla procesu kawitacji hydrodynamicznej (efektywność obniżenia wskaźnika ChZT i BZT_5, kolejno dla procesów: KH: 13%,15%; KH+ H_2O_2: 20%, 49%; KH+ O_3: 39,7%, 40,1%; KH + peroxone: 59% i 65%). W przypadku badanych procesów kawitacyjnych największą różnicę zaobserwowano w przypadku zjawiska kawitacji wspomaganego ozonowaniem (obniżenie wskaźnika ChZT i BZT_5 dla procesu KA + O_3, kolejno 19,5% i 19,6% oraz KH + O_3 39,7% i 40,1%). Wynika to głównie z nadciśnienia w strefie wprowadzania utleniacza do zwężki Venturiego, co zwiększa rozpuszczalność ozonu w fazie ciekłej. W przypadku zastosowania nadtlenku wodoru jako dodatkowego odczynnika utleniającego, okazało się, że to kawitacja akustyczna zapewnia większą wydajność utleniania w porównaniu z kawitacją hydrodynamiczną,. Korzystny wpływ ultradźwięków na cząsteczki H_2O_2 pozwala zwiększyć wydajność generowania rodników hydroksylowych w warunkach alkalicznych, gdzie większość nadtlenku rozkładałaby się na mniej aktywne indywidua chemiczne. Największy synergizm spośród procesów kawitacji hydrodynamicznej odnotowano dla procesu z peroxone-m (synergizm = 1,77), a w przypadku kawitacji akustycznej z nadtlenkiem wodoru (synergizm = 1,79).

Ponadto, procesy KA i KH w połączeniu z peroxone-m umożliwiają całkowitą degradację wszystkich badanych zanieczyszczeń organicznych przy jednoczesnym odbarwieniu ścieku i zmniejszeniu jego nieprzyjemnego zapachu.

Szczególnie istotnym wnioskiem z tej części pracy, podobnie jak w przypadku badań nad kawitacja hydrodynamiczną, jest bardzo efektywna degradacja związków aromatycznych – fenolu i jego pochodnych dla procesu kawitacji akustycznej + AOPs.

Badania tej pracy wykazały również generowanie wielu wtórnych zanieczyszczeń z grupy O-LZO (w trakcie trwania procesu oczyszczania), których szczegółowa kontrola procesowa umożliwia adekwatną ocenę badanych procesów utleniania. Najważniejsze wtórne zanieczyszczenia obejmują furfural (samodzielne procesy KH i KA oraz procesy kawitacyjne połączone z nadtlenkiem wodoru) i 2-metylocykloheksanon (samodzielny proces KA oraz proces KA połączony z AOPs, z wyjątkiem odczynnika peroxone). Ich stężenie podczas procesów oczyszczania metodami AOPs powinno być szczególnie kontrolowane ze względu na ich wysoką toksyczność w stosunku do osadu czynnego. Wykazano również, że zjawisko kawitacji w połączeniu z AOPs jest skuteczną metodą utleniania organicznych związków siarki. Prawie 100% utlenienie związków siarki uzyskano po mniej niż 30 minutach oczyszczania zarówno w przypadku zjawiska kawitacji hydrodynamicznej, jak i kawitacji akustycznej.

Szczegółowe wyniki badań dotyczące efektywności oczyszczania ścieku rzeczywistego w warunkach kawitacji akustycznej w połączeniu z zawansowanymi metodami utleniania (ozonem, nadtlenkiem wodoru oraz peroxone-m) oraz ich porównanie z wynikami dla procesu kawitacji hydrodynamicznej opublikowano w czasopiśmie Chemical Engineering and Processing: Process Intensification [55] (załącznik 4).

9. Podsumowanie artykułów badawczych

Głównym celem badań realizowanych w ramach pracy doktorskiej było zbadanie możliwości zastosowania kawitacji hydrodynamicznej oraz akustycznej wspomaganych procesami AOPs do oczyszczania ścieków rzeczywistych z produkcji asfaltów. Przeprowadzone badania wykazały, że:

- najefektywniejszy proces degradacji zanieczyszczeń organicznych w warunkach kawitacji hydrodynamicznej dla zaprojektowanego układu reakcyjnego uzyskuje się w przypadku zastosowania objętościowego natężenia przepływu i ciśnienia tłoczenia ścieku przez przewężenie umożliwiających osiągnięcie liczby kawitacyjnej 0,14;
- w warunkach kawitacji najefektywniej degradowane są związki siarko-organiczne oraz związki z grupy BTEX-N;
- sam proces kawitacji nie jest bardzo efektywnym procesem utleniania fenolu i jego pochodnych oraz związków azoto-organicznych;
- w procesie kawitacji hydrodynamicznej połączonej z utleniaczem peroxone przy molowym stosunku ilości wprowadzonego utleniacza (w przeliczeniu na mole HO·) do wartości chemicznego zapotrzebowania tlenu (ChZT) (w przeliczeniu na mole O_2) - $r_{ox} = 1,5$ (stosunek molowy ozonu do nadtlenku wodoru 1:6,7) uzyskuje się najbardziej efektywny proces obniżania sumarycznych wskaźników zanieczyszczenia ścieku (CHZT 59%, BZT_5 65%);
- kawitacja hydrodynamiczna połączona z peroxone-m umożliwia całkowite utlenienie badanych zanieczyszczeń organicznych w czasie 60 minut trwania procesu oczyszczania przy jednoczesnym odbarwieniu ścieku i zmniejszeniu jego drażliwości zapachowej;
- kawitacja hydrodynamiczna oraz akustyczna połączona z peroxone-m charakteryzuje stosunkowo wysoki wskaźnik synergizmu wynoszący, kolejno 1,77 i 1,79;
- zjawisko kawitacji połączone z AOPs umożliwia efektywne utlenianie fenolu i jego pochodnych, które charakteryzują się wysoką biotoksycznością w stosunku do osadu czynnego stosowanego na etapie biologicznego oczyszczania ścieków rafineryjnych;
- podczas prowadzenia procesu oczyszczania ścieków z produkcji asfaltów w warunkach kawitacji + AOPs dochodzi do generowania zanieczyszczeń wtórnych,

obejmujących furfural (samodzielny proces kawitacji hydrodynamicznej i akustycznej oraz procesy kawitacyjne połączone z nadtlenkiem wodoru) i 2-metylocykloheksanon (samodzielny proces kawitacja akustyczna oraz proces KA połączony z AOPs, z wyjątkiem odczynnika peroxone);

- kawitacja hydrodynamiczna w porównaniu do kawitacji akustycznej w połączeniu z zaawansowanymi procesami utleniania umożliwia osiągnięcie wyższych (o 5-10%) efektywności utleniania zanieczyszczeń organicznych dla poszczególnych procesów z wyjątkiem procesu wspomaganego nadtlenkiem wodoru;
- z ekonomicznego punktu widzenia kawitacja hydrodynamiczna jest lepszym rozwiązaniem w przypadku zastosowań przemysłowych w porównaniu do kawitacji akustycznej, głównie ze względu na koszt wzbudników sonicznych rosnący wraz ze wzrostem skali instalacji;
- ocena efektywności AOPs wyłącznie na podstawie zmian ChZT i BZT_5 jako parametrach kontroli procesowej oczyszczania ścieków bez szczególnej kontroli efektywności degradacji poszczególnych grup związków chemicznych, w tym kontroli powstawania ubocznych produktów utleniania, może prowadzić do fałszywych wniosków na temat efektywności i przydatności badanych procesów oczyszczania. W przypadku ścieków rzeczywistych z produkcji asfaltów, w ścieku występują m.in. węglowodory alifatyczne i cykliczne (w formie rozpuszczonej w fazie wodnej), nie podatne na utlenianie na drodze AOPs. Ich obecność w ściekach ma wpływ na mierzone ChZT i BZT_5, jednak ta część ChZT i BZT_5 jest „stała" – nie możliwa do obniżenia w przypadku procesów AOPs, stąd sumaryczna efektywność mierzona tymi wskaźnikami jest istotnie zaniżona, w porównaniu do poszczególnych grup związków chemicznych. Jednocześnie, obecność węglowodorów alifatycznych i cyklicznych nie stanowi problemu technologicznego z punktu widzenia kolejnego – biologicznego oczyszczania ścieków za pomocą osadu czynnego przystosowanego do degradacji zanieczyszczeń węglowodorowych. Natomiast, efektywna degradacja związków tlenoorganicznych jest wysoce pożądana – co zapewniają opisane w niniejszej pracy procesy oczyszczania w warunkach kawitacji w połączeniu z AOPs - przed etapem oczyszczania biologicznego.

Zatem, kawitacja hydrodynamiczna w połączeniu z odczynnikiem peroxone stanowi efektywną metodę chemicznego oczyszczania ścieków z produkcji asfaltów, która może być zastosowana przed etapem biologicznego oczyszczania ścieków.

10. BIBLIOGRAFIA

[1] Y.L. Song, J.T. Li, Degradation of C.I. Direct Black 168 from aqueous solution by fly ash/H2O2 combining ultrasound, Ultrason. Sonochem. 16 (2009) 440–444.

[2] K.S. Suslick, Sonochemistry, Science 247 (1990) 1439–1445.

[3] C.D. Wu, Z.L. Zhang, Y. Wu, L. Wang, L.J. Chen, Effects of operating parameters and additives on degradation of phenol in water by the combination of H2O2 and hydrodynamic cavitation, Desalin. Water Treat. 53 (2015) 462–468.

[4] M.A. Beckett, I. Hua, Elucidation of the 1,4-dioxane decomposition pathway at discrete ultrasonic frequencies, Environ. Sci. Technol. 34 (2000) 3944–3953.

[5] P. R. Gogate, A.B. Pandit, A review and assessment of hydrodynamic cavitation as a technology for the future, Ultrason. Sonochem. 12 (2005) 21–27.

[6] A.G. Chakinala, P.R. Gogate, A.E. Burgess, D.H. Bremner, Treatment of industrial wastewater effluents using hydrodynamic cavitation and the advanced Fenton process, Ultrason. Sonochem. 15 (2008) 49–54.

[7] A.J. Barik, P.R. Gogate, Degradation of 4-chloro 2-aminophenol using a novel combined process based on hydrodynamic cavitation, UV photolysis and ozone, Ultrason. Sonochem. 30 (2016) 70–78.

[8] S. Raut-Jadhav, D. Saini, S. Sonawane, A. Pandit, Effect of process intensifying parameters on the hydrodynamic cavitation based degradation of commercial pesticide (methomyl) in the aqueous solution, Ultrason. Sonochem. 28 (2016) 283–293.

[9] M.V. Bagal, P.R. Gogate, Wastewater treatment using hybrid treatment schemes based on cavitation and Fenton chemistry: a review, Ultrason. Sonochem. 21 (2014) 1–14.

[10] D.H. Bremner, S. Carlo, A.G. Chakinala, G. Cravotto, Mineralisation of 2,4-dichlorophenoxyacetic acid by acoustic or hydrodynamic cavitation in conjunction with the advanced Fenton process, Ultrason. Sonochem. 15 (2008) 416–419.

[11] I. Grcic, M. Obradovic, D. Vujevic, N. Koprivanac, Sono-Fenton oxidation of formic acid/formate ions in an aqueous solution: from an experimental design to the mechanistic modeling, Chem. Eng. J. 164 (2010) 196–207.

[12] S. Raut-Jadhav, V. Kumar Saharan, D. Pinjari, S. Sonawane, D. Saini, A. Pandit, Synergetic effect of combination of AOP's (hydrodynamic cavitation and H2O2) on the degradation of neonicotinoid class of insecticide, J. Hazard. Mater. 261 (2013) 139–147.

[13] P.R. Gogate, P.N. Patil, Combined treatment technology based on synergism between hydrodynamic cavitation and advanced oxidation processes, Ultrason. Sonochem. 25 (2015) 60–69.

[14] D. Drijvers, H. van Langenhove, L. Nguyen, T. Kim, L. Bray, Sonolysis of an aqueous mixture of trichloroethylene and chlorobenzene, Ultrason. Sonochem. 6 (1999) 115–121.

[15] A.A. Pradhan, P.R. Gogate, Degradation of p-nitrophenol using acoustic cavitation and Fenton chemistry, J. Hazard. Mater. 173 (2010) 517–522.

[16] Z. XiaoBin, Z. JiaKai, Q. LiMin, Z. XueJun, Calculation and verification of dynamical cavitation model for quasi-steady cavitating flow, Int. J. Mass Transfer. 86 (2015) 294–301.

[17] N. Tran, P. Drogui, L. Nguyen, S.K. Brar, Optimization of sono-electrochemical oxidation of ibuprofen in wastewater, J. Environ. Chem. Eng. 3 (2015) 2637–2646.

[18] M. Zupanc, T. Kosjek, M. Petkovšek, M. Dular, B. Kompare, B. Širok, Z. Blazeka, E. Heath, Removal of pharmaceuticals from wastewater by biological processes, hydrodynamic cavitation and UV treatment, Ultrason. Sonochem. 20 (2013) 1104–1112.

[19] M. Zupanc, T. Kosjek, M. Petkovšek, M. Dular, B. Kompare, B. Širok, M. Strazˇar, E. Heath, Shear-induced hydrodynamic cavitation as a tool for pharmaceutical micropollutants removal from urban wastewater, Ultrason. Sonochem. 21 (2014) 1213–1221.

[20] K.P. Mishra, P.R. Gogate, Intensification of degradation of Rhodamine B using hydrodynamic cavitation in the presence of additives, Sep. Purif. Technol. 75 (2010) 385–391.

[21] **M. Gągol**, A. Przyjazny, G. Boczkaj, Wastewater treatment by means of advanced oxidation processes based on cavitation – A review, Chem. Eng. J. 338 (2018) 599-627.

[22] C. D. Wu, Z. L. Zhang, Y. Wu, L. Wang, L. J. Chen, Effects of operating parameters and additives on degradation of phenol in water by the combination of H2O2 and hydrodynamic cavitation, Desalin. Water Treat., 53 (2015) 462-468.

[23] V. S. Moholkar, P. Senthilkumar, A. B. Pandit, Hydrodynamic cavitation for sonochemical effects, Ultrason. Sonochem., 6 (1999) 53-65.

[24] M. P. Badve, M. N. Bhagat, A. B. Pandit, Microbial disinfection of seawater using hydrodynamic cavitation, Sep. Purif. Technol., 151 (2015) 31-38.

[25] M. Petkovšek, M. Mlakar, M. Levstek, M. Strazar, B. Širok, M. Dular, A novel rotation generator of hydrodynamic cavitation for waste-activated sludge disintegration, Ultrason. Sonochem., 26 (2015) 408-414.

[26] M. Petkovšek, M. Zupanc, M. Dular, T. Kosjek, E. Heath, B. Kompare, B. Širok, Rotation generator of hydrodynamic cavitation for water treatment, Sep. Purif. Technol., 118 (2013, 415-423.

[27] K. K. Jyoti, A. B. Pandit, Water disinfection by acoustic and hydrodynamic cavitation, Biochem. Eng. J., 7 (2001) 201-212.

[28] S. M. Ashrafizadeh, H. Ghassemi, Experimental and numerical investigation on the performance of small-sized cavitating venturis, Flow Meas. Instrum., 42 (2015) 6-15.

[29] S. J. Doktycz, K. S. Suslick, Interparticle collisions driven by ultrasound, Sonochemistry, Sci. 247 (1990) 1067-1069.

[30] P. R. Gogate, Cavitation: an auxiliary technique in wastewater treatment schemes, Adv. Env. Res., 6 (2002) 335-358.

[31] P. R. Gogate, Cavitational reactors for process intensification of chemical processing applications: a critical review, Chem. Eng. Process., 47 (2008) 515-527.

[32] A. K. Shriwas, P R. Gogate, Ultrasonic degradation of methyl Parathion in aqueous solutions: intensification using additives and scale up aspects, Sep. Purif. Technol., 79 (2011) 1-7.

[33] S. Asgharzadehahmadi, A. A. A. Raman, R. Parthasarathy, B. Sajjadi, Sonochemical reactors: Review on features, advantages and limitations, Renew. Sustain. Energy. Rev., 63 (2016) 302-314.

[34] P. N Patil, S. D. Bote, P. R. Gogate, Degradation of imidacloprid using combined advanced oxidation processes based on hydrodynamic cavitation, Ultrason. Sonochem., 21 (2014) 1770-1777.

[35] M. Zupanc, T. Kosjek, M. Petkovšek, M. Dular, B. Kompare, B. Širok, M. Strazar, E. Heath, Shearinduced hydrodynamic cavitation as a tool for pharmaceutical micropollutants removal from urban wastewater, Ultrason. Sonochem., 21 (2014) 1213-1221.

[36] M. T. Angaji, R. Ghiaee, Decontamination of unsymmetrical dimethylhydrazine waste water by hydrodynamic cavitation-induced advanced Fenton process, Ultrason. Sonochem., 23 (2015) 257-265.

[37] Grcic I., Obradovic M., Vujevic D., Koprivanac N., Sono-Fenton oxidation of formic acid/formate ions in an aqueous solution: from an experimental design to the mechanistic modeling, Chem. Eng. J., 164 (2010) 196-207.

[38] M. Gągol, G. Boczkaj, Przegląd metod wytwarzania kawitacji do degradacji zanieczyszczeń organicznych w środowisku wodnym, Aparatura Badawcza i Dydaktyczna 22 (2017) 62-71.

[39] J. Nawrocki, Zaawansowane procesy utleniania w oczyszczaniu wody, Ochr. Sr. 74 (1999) 32–36.

[40] L. J. Xu, W. Chu, N. Graham, Sonophotolytic degradation of phthalate acid esters in water and wastewater: influence of compound properties and degradation mechanisms." Journal of hazardous materials 288 (2015): 43-50.

[41] E. Gonze, L. Fourel, Y. Gonthier, P. Boldo, A. Bernis, Wastewater pretreatment with ultrasonic irradiation to reduce toxicity, Chem. Eng. J. 73 (1999) 93–100.

[42] G. Boczkaj, **M. Gągol**, M. Klein, A. Przyjazny, Effective method of treatment of effluents from production of bitumens under basic pH conditions using hydrodynamic cavitation aided by external oxidants, Ultrason. Sonochem. 40 (2018) 969–979.

[43] N. Mahamuni, G. A. Yusuf, Advanced oxidation processes (AOPs) involving ultrasound for waste water treatment: a review with emphasis on cost estimation, Ultrason. Sonochem. 17 (2010) 990-1003.

[44] B. Neppoliana, H. Junga, H. Choi, J. H. Leea, J. W.Kang, Sonolytic degradation of methyl tert-butyl ether: the role of coupled Fenton process and persulphate ion, Water Res. 36 (2002) 4699-4708.

[45] A.G. Chakinala, D.H. Bremner, P.R. Gogate, K.C. Namkung, A.E. Burgess, Multivariate analysis of phenol mineralisation by combined hydrodynamic cavitation and heterogeneous advanced Fenton processing, Appl. Catal. B: Env- iron. 78 (2008) 11-18.

[46] D. Liu, E. Vorobiev, R. Savoire, J. L. Lanoisellé, Comparative study of ultrasound-assisted and conventional stirred dead-end microfiltration of grape pomace extracts, Ultrason. Sonochem. 20 (2013) 708-714.

[47] I. Worapun, K. Pianthong, P. Thaiyasuit, Optimization of biodiesel production from crude palm oil using ultrasonic irradiation assistance and response surface methodology, J. Chem. Technol. Biotechnol. 87 (2012) 189-197.

[48] A. S. Badday, A. Z. Abdullah, K. T. Lee, M. S. Khayoon, Intensification of biodiesel production via ultrasonic-assisted process: a critical review on fundamentals and recent development, Renew. Sustain. Energy. Rev. 16 (2012) 4574-4587.

[49] I. Lee, J.Han, The effects of waste-activated sludge pretreatment using hydrodynamic cavitation for methane production, Ultrason. Sonochem. 20 (2013) 1450-1455.

[50] **M. Gągol**, A. Przyjazny, G. Boczkaj, Highly effective degradation of selected groups of organic compounds by cavitation based AOPs under basic pH conditions, Ultrason. Sonochem. 45 (2018) 257–266.

[51] D. R. Reddy, G. K. Dinesh, S. Anandan, T. Sivasankar, Sonophotocatalytic treatment of Naphthol Blue Black dye and real textile wastewater using synthesized Fe doped TiO_2, Chem. Eng. Process. 99 (2016) 10-18.

[52] R. Kidak, N.H. Ince, Catalysis of advanced oxidation reactions by ultrasound: A case study with phenol, , J. Hazard. Mater. 146 (2007) 630-635.

[53] A. Hirvonen, T. Tuhkanen, P. Kalliokoski, Formation of chlorinated acetic acids during UV/H2O-oxidation of ground water contaminated with chlorinated ethylenes, Chemosphere 32 (1996) 1091-1102.

[54] P. Ramteke, P. R. Gogate, Treatment of toluene, benzene, naphthalene and xylene (BTNXs) containing wastewater using improved biological oxidation with pretreatment using Fenton/ultrasound based processes, J. Ind. Eng. Chem. 28 (2015) 247-260.

[55] **M. Gągol**, A. Przyjazny, G. Boczkaj, Effective method of treatment of industrial effluents under basic pH conditions using acoustic cavitation – a comprehensive comparison with hydrodynamic cavitation processes, Chem. Eng. Process. 128 (2018) 103-113.

11. WYKAZ DOROBKU NAUKOWEGO

Publikacje z listy filadelfijskiej:

[1] **M. Gągol**, G. Boczkaj, J. Haponiuk, K. Formela, Investigation of volatile low molecular weight compounds formed during continuous reclaiming of ground tire rubber, Polym. Degrad. Stab.119 (2015) 113-120; IF: 3,386, Q1.

[2] K. Formela, **M. Gągol**, J. Haponiuk, Chromatografia gazowa jako skuteczne narzędzie kontroli procesu wytłaczania, Przem. Chem. 94 (2015) 1286-1290; IF: 0,385, Q4.

[3] G. Boczkaj, **M. Gągol**, M. Klein, A. Przyjazny, Effective method of treatment of effluents from production of bitumens under basic pH conditions using hydrodynamic cavitation aided by external oxidants, Ultrason. Sonochem. 40 (2018) 969–979; IF: 4,218, Q1.

[4] **M. Gągol**, A. Przyjazny, G. Boczkaj, Wastewater treatment by means of advanced oxidation processes based on cavitation – A review, Chem. Eng. J. 338 (2018) 599-627; IF: 6,216, Q1

[5] **M. Gągol**, A. Przyjazny, G. Boczkaj, Highly effective degradation of selected groups of organic compounds by cavitation based AOPs under basic pH conditions, Ultrason. Sonochem. 45 (2018) 257–266; IF: 4,218, Q1.

[6] **M. Gągol**, A. Przyjazny, G. Boczkaj, Effective method of treatment of industrial effluents under basic pH conditions using acoustic cavitation – a comprehensive comparison with hydrodynamic cavitation processes, Chem. Eng. Process. 128 (2018) 103-113; IF: 2,234, Q2.

Pozostałe publikacje:

[1] P. Kosmela, **M. Gągol**, K Formela, K. Węsierska, Ł. Piszczyk, Ekologiczne pianki poliuretanowe otrzymane z surowców odnawianych, Modyfikacja polimerów stan i perspektywy i roku 2015/ ed. Ryszard Steller i Danuta Żuchowska Wrocław: TEMPO s.c. 2015, s.93-97.

[2] **M. Gągol**, P. Kosmela, Ł. Piszczyk, J. Haponiuk, K. Formela K.: Kontrola jakości materiałów polimerowych wytwarzanych metodą wytłaczania: stan obecny i perspektywy

rozwoju// Modyfikacja polimerów stan i perspektywy w roku 2015/ ed. Ryszard Steller i Danuta Żuchowska Wrocław: TEMPO s.c., 2015, s.298-301.

[3] **M. Gągol**, G. Boczkaj, Przegląd metod wytwarzania kawitacji do degradacji zanieczyszczeń organicznych w środowisku wodnym, Aparatura Badawcza i Dydaktyczna, 1 (2017) 62-71.

[4] G. Boczkaj, A. Fernandes, **M. Gągol**, Studies on treatment of bitumen effluents by means of Advanced Oxidation Processes (AOPs) in basic pH conditions, W : Frontiers in Wastewater Treatment and Modelling: FICWTM 2017/ ed. Giorgio Mannina Palermo: Springer, 2017, s.510-515.

Postery konferencyjne:

[1] **M. Gągol**, J. Haponiuk, Ł. Piszczyk, G. Boczkaj, K. Formela, On-line/in-line Measurments during Extrusion of Polymer Blends and Composites, Third International Conference on Polymer Procesng and Characterization (ICPPC 2014), Indie, 2014.

[2] P. Kosmela, **M. Gągol**, K Formela, K. Węsierska, Ł. Piszczyk, Ekologiczne pianki poliuretanowe otrzymane z surowców odnawianych, Modyfikacja polimerów stan i perspektywy i roku 2015, Kudowa-Zdrój, Polska 2015.

[3] **M. Gągol**, P. Kosmela, Ł. Piszczyk, J. Haponiuk, K. Formela K.: Kontrola jakości materiałów polimerowych wytwarzanych metodą wytłaczania: stan obecny i perspektywy rozwoju// Modyfikacja polimerów stan i perspektywy w roku 2015 Kudowa-Zdrój, Polska 2015.

[4] G. Boczkaj, A. Fernandes, **M. Gągol**, Studies on treatment of bitumen effluents by means of Advanced Oxidation Processes (AOPs) in basic pH conditions, Frontiers International Conference on Wastewater Treatment (FICWTM), Palermo, Włochy, 2017.

Podsumowanie:

Suma IF: 20,657

Suma pkt. MNISW: 225

Załącznik 1

Publikacja nr 1:

M. Gągol, A. Przyjazny, G. Boczkaj, Wastewater treatment by means of advanced oxidation processes based on cavitation – A review, Chem. Eng. J. 338 (2018) 599-627.

Chemical Engineering Journal 338 (2018) 599–627

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Review

Wastewater treatment by means of advanced oxidation processes based on cavitation – A review

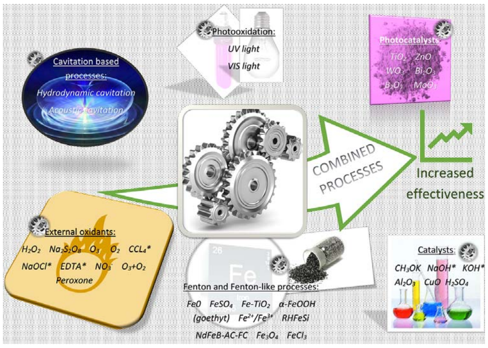
Michał Gągol[a], Andrzej Przyjazny[b], Grzegorz Boczkaj[a,*]

[a] Gdańsk University of Technology, Faculty of Chemistry, Department of Chemical and Process Engineering, Gdansk, Poland
[b] Kettering University, 1700 University Avenue, Department of Chemistry & Biochemistry, Flint, MI 48504, USA

HIGHLIGHTS

- Application of hydrodynamic and acoustic cavitation to oxidation of organic pollutants.
- Design of cavitation devices for effluent treatment.
- Comparison of efficiency of oxidation of organic pollutants in the cavitation processes.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Hydrodynamic cavitation
Acoustic cavitation
Sonocavitation
Wastewater treatment
AOP
Pollutant degradation

ABSTRACT

Hydrodynamic and acoustic cavitation combined with advanced oxidation processes (AOPs), including, among others, the Fenton process, is a promising alternative to the technologies of wastewater treatment technologies in use today. The present review discusses processes based on cavitation combined with AOPs and evaluates their effectiveness in oxidation of organic contaminants. Complete degradation of, among others, *p*-nitrotoluene, *p*-aminophenol, 1,4-dioxane, alachlor, chloroform, trichloroethylene, sodium pentachlorophenate and carbon tetrachloride was achieved by using hydrodynamic cavitation or acoustic cavitation alone. Cavitation is also an effective method of disinfection of water. Complete oxidation of hardly degradable organic contaminants, including pharmaceuticals, organic dyes, insecticides, phenol and its derivatives was observed when using hybrid processes: hydrodynamic or acoustic cavitation combined with the Fenton process, ozonation, hydrogen peroxide, UV irradiation, catalysts and persulfates. The review also discusses the cavitational reactors used in the wastewater treatment and the effect of process parameters (including pH, temperature, concentration and kind of contaminants) on the effectiveness of oxidation. The oxidation effectiveness for individual treatment methods is compared and their advantages and limitations discussed. The analysis of economics of the treatment processes performed to evaluate the possibility of scaling up reveals that the only economical processes should be based on hydrodynamic cavitation (mainly due to low cost of reactors and low consumption of electrical energy compared with ultrasonic reactors).

---

[*] Corresponding author at: Gdansk University of Technology, Faculty of Chemistry, Department of Chemical and Process Engineering, 80-233 Gdansk, G. Narutowicza St. 11/12, Poland.
E-mail address: grzegorz.boczkaj@pg.edu.pl (G. Boczkaj).

https://doi.org/10.1016/j.cej.2018.01.049
Received 5 September 2017; Received in revised form 28 November 2017; Accepted 8 January 2018

1. Introduction

Treatment of industrial effluents has long been a challenge for modern technologies combining high effectiveness of degradation of pollutants with low costs of the process. At the same time, new technological developments should incorporate the concept of green chemistry [1]. It is thus an interesting area of research dealing with the development of effective technologies for degradation of specific chemical compounds or selected groups of pollutants. The developed procedures are validated by using real effluents for which they are intended.

Advanced oxidation processes (AOP) have been of substantial interest for many years [2–4]. They combine high effectiveness of pollutant removal through oxidation reactions with highly efficient generation of hydroxyl radicals, often aided by catalytic and photocatalytic processes.

A recent trend in treatment of industrial effluents involves the use of advanced oxidation processes combined with cavitation (Fig. 1). This paper attempts to summarize and evaluate these processes in relation to existing AOPs and to indicate trends in research on the application of cavitation to treatment of industrial effluents.

2. Cavitation phenomenon and types of cavitation

Cavitation is the rapid transition from the liquid to the gaseous state as a result of lowering the pressure which is accompanied by the formation in the liquid of so-called cavitation bubbles having a tremendous force of implosion (the formation of cavitation bubbles in a stream of flowing liquid is shown in Fig. 2). The main parameters affecting their formation are: temperature, static pressure of a fluid and dynamic pressure associated with the linear velocity of a fluid. A decrease in a local static pressure in a stream of flowing liquid results in a drop of its boiling point which causes increased evaporation and the appearance of gas bubbles. During a subsequent increase in pressure the bubbles implode generating an intense shock wave with a great destructive force. A nanosecond long implosion the temperature inside the collapsing bubble can reach as much as 4726.8 °C, and the pressure around 9869 atm [5–7]. This effect is often employed in effluent treatment technologies because it enhances the process of removal of pollutants. It enables decomposition of water molecules into a variety of species with a high oxidation potential, including HO€·, $\mathrm{HO2}^{-\cdot}$ and H_2O_2, which react with the majority of organic pollutants [8].

Cavitation is presently used in a number of technologies, such as [9]:

- production of emulsions,
- cleaning various surfaces,
- highly efficient heating devices,
- pumps for viscous fluids,
- cosmetic treatments, acoustic toothbrushes,
- or in processes aiding effluent treatment.

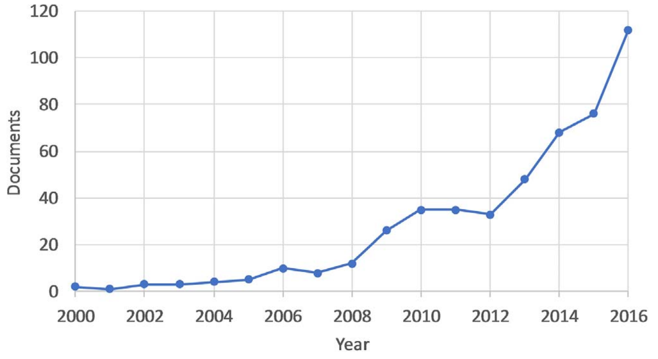


Fig. 1. Documents about cavitation combined with AOPs in wastewater treatment from 2000 to 2016 (based on *Scopus.com* base files available on 04.09.2017).

Cavitation is classified with respect to conditions of formation and development of cavitation bubbles into [9]:

- hydrodynamic cavitation,
- vaporous cavitation,
- gaseous cavitation,
- and vibrational cavitation, so-called acoustic cavitation.

Treatment of effluents makes use mostly of hydrodynamic and acoustic cavitation. In hydrodynamic cavitation, gas bubbles are generated by special design of reactors or flow systems forcing a liquid to flow under reduced pressure. This involves the creation of a local drop in static pressure of a liquid below the critical value by a local increase in flow rate or change in external conditions, such as flow line curvature, detachment of liquid stream from the side of the container or channel constrictions. Acoustic cavitation uses an acoustic wave which appears in a liquid as a result of its vibrations or vibrations of the surroundings. The vibrations are generated by ultrasounds which break apart the liquid or cause vibrations of the solid bodies immersed in it.

3. Hydrodynamic cavitation in degradation processes of organic contaminants in aqueous phase

Hydrodynamic cavitation has found a widespread use in treatment of the aqueous phase, for example to aid biological and physico-chemical removal of organic pollutants [10]. Cavitation enables more efficient generation of hydroxyl radicals responsible for oxidation of the majority of contaminants. It also creates in the medium being treated local hot spots in which imploding gas bubbles causes sudden spikes in pressure and temperature. This allows further dissociation of contaminants by pyrolysis [11]. In addition, volatile organic pollutants can penetrate into the cavities being formed which, imploding with a high energy will aid the oxidation process even more effectively [12].

The collapse energy of cavitation bubbles is often used to destroy the structures of microorganisms and bacteria present in effluents. The destruction of structures of microorganisms allows, among others, more effective drying of biomass and production of biogas [3], which improves the operation of wastewater treatment plants.

In a physical-photochemical approach, cavitation initiates the process of oxidation of contaminants on the surface of photochemical catalysts, improving the electron transfer process by creating electron hole pairs [13]. Cavitation also enhances chemical generation of highly reactive hydroxyl radicals, thus enabling oxidation of a variety of organic pollutants, such as carboxylic acids [14,15], pesticides [16,17],

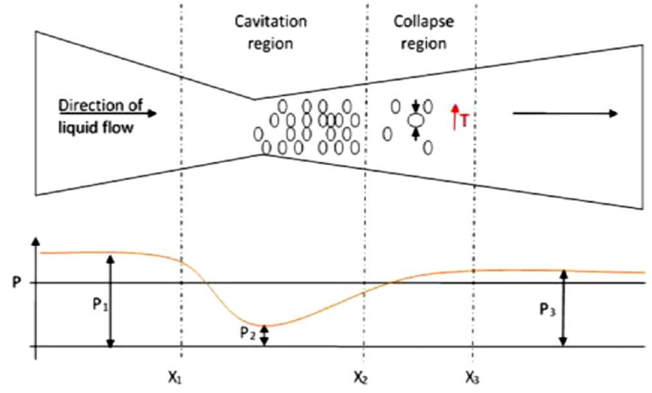


Fig. 2. Scheme of formation of gas bubbles in Venturi tube by hydrodynamic cavitation. P_1/P_3 static pressure before/after throat, P_2 – static pressure in throat, P – vapor pressure of liquid.

Table 1
Degradation of different organic compounds in sono/hydrodynamic cavitation processes.

Compounds	Process conditions	Major mechanism*	Degradation products	Ref
Toluene, Benzene, Naphthalene, Xylene	Sono-cavitation 22 kHz, 120 W, H_2O_2 (1–2 gL^{-1}) Fe^{2+} (0.5–3 gL^{-1})	RP	–	[122]
Chlorobenzene, Trichloroethylene	Sono-cavitation 520 kHz, 14 W, H_2O_2 (1–2 gL^{-1}) Fe^{2+} (0.5–3 gL^{-1}	RP + RR	Styrene, dichlorobenzene	[18]
Chlorobenzene	Sono-cavitation 800 kHz, 1.5 kW,	RP + RR	Intermediate products: 4-chlorophenol, acetylene, hydroquinone,	[131]
Ibuprofen	Sono-cavitation 3.5 A 30 W	RR	Carbon dioxide, water	[21]
Clofibric acid, Ibuprofen, Naproxen, Ketoprofen, Diclofenac	Hydrodynamic cavitation + H_2O_2 (3.4 gL^{-1})	RR	–	[22]
2,4-dinitrophenol	Hydrodynamic cavitation + extra oxidants Orifice plate: thickness 1 mm, diameter 25 mm, one hole (diameter 2 mm), T = 35 °C; p = 3.95 atm; pH = 4	RP + RR	Intermediate products: benzoquinone, hydroquinone, nitrates, nitrites, formic, oxalic and acetic acids	[29]
Chloroform	Sono-cavitation 200 kHz	RP	–	[132]
Phenol	Sono-cavitation 487 kHz, 30 W, Air 0.05 mM	RR	Intermediate products: *p*-, *o*-benzoquinone, hydroquinone, organic acids	[133]

* RP – pyrolysis in cavity interior; RR – radical attack in solution.

alcohols [18,19], chlorinated solvents [20] or pharmaceuticals [21–23]. This happens when a chemical oxidant capable of generation of the hydroxyl radical characterized by a high oxidation potential is introduced to the medium being treated. Cavitation bubbles concentrate the radicals at the site and also homogenize the system thus improving the effectiveness of reduction [24].

Application of hydrodynamic cavitation in effluent treatment ensures a substantial increase in the efficiency of oxidation of contaminants, as demonstrated by a number of literature reports (Tables 1 and 2). However, research continues on the elucidation of all the paths of degradation reactions of pollutants and on the reduction of costs associated with operation of the equipment. Another problem is optimization of the process to maximize the degree of oxidation due to a large number of parameters affecting cavitation, including pH, temperature, reagent concentration, inlet pressure, kind and concentration of contaminants, and time of reaction.

3.1. *Effectiveness of removal of chemical and microbiological pollutants by hydrodynamic cavitation*

Hydrodynamic cavitation used as a single process of oxidation or disintegration of a contaminant due to homogenization and the force of implosion of air bubbles is most commonly used to disrupt bacterial cultures and persistent organic compounds, such as pesticides. In the case of bacteria, it was demonstrated that the degree of disruption of bacteria *Escherichia coli* present in tap water can exceed 90% in less than 15 min by using a cavitation reactor with a properly selected pressure of the flowing medium (98.69 atm) [25]. Similarly, the disruption of cultures of pathogenic bacteria *Microcystis aeruginosa* occurring in surface waters using hydrodynamic cavitation alone can achieve their reduction by up to 94% [26]. When disrupting microbiological pollutants, expressed as soluble chemical oxygen demand (SCOD), it was demonstrated that industrial effluents subjected to cavitation had SCOD increased from 45 mgL^{-1} to poziomu 601 mgL^{-1}. In addition, the production of biogas from the activated sludge collected after pretreatment by hydrodynamic cavitation increased by 12.7%, which further demonstrates the effectiveness of cavitation in disruption of cultures of microorganisms [27].

Hydrodynamic cavitation was found to be effective for degradation of organic compounds characterized by high biotoxicity and low biodegradability, such as pesticides and their derivatives. The degree of oxidation is not as large as in the case of microorganisms but in combination with advanced oxidation processes it can reach 100%. The insecticide triazophos can serve as an example. Triazophos occurring in sewage was found to be resistant to degradation by conventional treatment methods. The use of hydrodynamic cavitation resulted in oxidation of about 50% of triazophos. The addition of the Fenton reagent resulted in an increase in oxidation yield to 80%. The best result was obtained by combining cavitation with ozonation when almost 100% of the insecticide was degraded [17]. Similar results were obtained for degradation of neonicotinoid pesticides [16].

The results of investigations demonstrating a large synergism between cavitation and AOPs during degradation of organic pollutants in water were also described in papers on treatment of industrial effluents containing contaminants expressed as total organic carbon (TOC). Combination of cavitation with the Fenton reagent added to the medium being treated resulted in a substantial reduction of biotoxicity of the effluent and lowering of the pollutant load by 80% [10] and by 60% for the effluents characterized by very high biotoxicity [28].

In the case of practically nondegradable compounds, such as 2,4-dinitrophenol it was demonstrated that homogenization and the force of implosion of cavitation bubbles combined with a high oxidation potential of hydroxyl radicals resulted in a reduction of content of this type of compounds to a level of 1% [29].

3.2. *Cavitation aided by advanced oxidation processes*

According to literature reports, one of the most effective methods of removal of contaminants from aqueous media is a hybrid method combining hydrodynamic cavitation with advanced oxidation processes (AOPs). The main combinations of cavitation with advanced oxidation processes used for the treatment of aqueous media are shown in Fig. 3. Individual sections listing the components of hybrid processes also mention unique designs in each of the regions, which are compiled based on the references compared in Tables 2 and 3.

AOP processes make use of very reactive hydroxyl radicals with a high oxidation potential. In theory, hydroxyl radicals can be obtained via over twenty different chemical processes. In practice, there are two main processes that are commonly used [30]:

- generation of hydroxyl radicals through chemical reactions,
- photochemical generation of hydroxyl radicals.

The chemical method involves generation of reactive hydroxyl radicals by way of a chemical reaction. They can be generated using oxidants such as hydrogen peroxide and ozone or their combination, so-

Table 2
Comparison of different studies using hydrodynamic cavitation processes.

Process	Type of WW	Conditions	Efficiency	Comments/additional information	Ref
HC/OR	Model wastewater: *Microcystis aeruginosa* (30 µg L^{-1} chlorophyll *a*)	T: 20 °C pH: no information t: 8 min HC: orifice plate (p = 0.59 atm, v = 1980 Lh^{-1}, L_k = 0.43) OR: O_3 1.9 × 10^{-3} $gmin^{-1}$	HC/OR: 100% OR: 35% HC: 20%	Regardless of suction or extrusion, some hydrodynamic cavitation occurs with the 5, 10 and 12 mm orifices, but turbulent flow and cycle number are higher with 12 mm orifice so greater removal of algae is seen with this orifice	[112]
HC/OR + UV	Model wastewater: Polyacrylamide 0.2% solution	T: 32 °C pH: no information t: 3 hHC: slit Venturi tube (p = 2.96 atm, L_k = 0.21) OR: O_3 400 mgh^{-1}, H_2O_2 0.2% solution UV: 254 nm, 8 W	HC: 35.4% UV: 40.1% OR: O_3 50% HC/OR: O_3 60%; H_2O_2 83% HC/OR + UV: H_2O_2 97.3%	Degradation is favored under UV irradiation and not significantly dependent on the power of UV light.	[109]
HC/Fenton	Model wastewater: Rhodamine B 5 mgL^{-1}	T: 25 °C pH: 3 t: 2 hHC: orifice plate (p = 5.72 atm, v = 80 $Lmin^{-1}$ L_k = 0.27) Fenton (generation of reagents during the cavitation process): H_2O_2 0.28 mgL^{-1}, Fe^{2+} 9.0 mgL^{-1}	HC: 10% HC/Fenton: 71%	Geometrical characteristics of the orifice plates such as hole's depth, diameter and number showed a significant effect on the advanced Fenton process, induced by HC	[47]
HC	Model wastewater: KI 1% solution	T: 36 °C pH: no information t: 20 minHC: orifice plate (p = 2.04 atm, v = 5.5 $Lsec^{-1}$ L_k = 0.20)	Iodine liberated in 15 passes at 30 psi discharge pressure 5.0 × 10^{-6} gmL^{-1}	It can be found that iodine liberated per unit energy input (cavitational yield) for hydrodynamic cavitation is 3 times higher than acoustic cavitation	[53]
HC/OR	Interesterification of waste cooking oil: Linoleic acid 73.4% Oleic acid 18.3% Palmitic acid 6.7% Stearic acid 1.6%	T: no information pH: < 7 t: 60 minHC: slit Venturi tube (p = 2.96 atm, L_k = 0.60)OR: oil to methyl acetate molar ratio 1:12, catalyst concentration (1% by weight of the charged oil)	HC/OR: 89%	The energy efficient approach based on the use of hydrodynamic cavitation as compared to the conventional method and ultrasound assisted synthesis has been confirmed	[74]
HC	Model wastewater: KI 2000 ppm	T: 25 °C pH: no information t: 15 minHC: the stator–rotor assembly (204 indentations – 12 mm in diameter and 20 mm deep; L_k = 0.40, 3000 RPM)	HC: iodine liberation 50 ppm	It has been established that the speed of rotation plays an important role on fluid flow, giving rise to the pressure changes and mass transfer of fluid flow in the reactor	[56]
HC/OR	Model wastewater: Imidacloprid 25 mgL^{-1}	T: 32 °C pH: 2.7 t: 45 min HC: circular Venturi tube (p = 14.8 atm, v = 610 Lh^{-1} L_k = 0.067) OR: imidacloprid: H_2O_2 (molar ratio 1:40)	HC: 11.4% OR: 11.2% HC/OR: 100%	Combination of hydrodynamic cavitation with H_2O_2 process lead to a substantial synergetic effect conferring synergetic coefficient of 22.79	[16]
HC/Fenton	Industrial wastewater: TOC 6 gL^{-1} COD 17 gL^{-1}	T: 35 °C pH: 10.7 t: 5 hHC: orifice plate (p = 0.1 atm, v = 0.25 Lh^{-1} L_k = no information) OR: H_2O_2 1900 ppm,the zero valent iron pieces (80 g; 50 pieces of 1 cm × 2 cm, L-shaped having thickness of 0.10 cm)	HC/Fenton: 70% TOC (t = 2,5h)85% COD (t = 2,5h)	The iron content in the solution increased with longer treatment time due to continuous leaching of iron during the flow and with higher operating pressure and a maximum value of about 250 mg/L of iron in solution was observed such treatment contained less than 10 mg/L iron	[10]
HC		T: 31.3 °C pH: 7.84	HC: 99.9% inactivation	Depending on the available budget and time requirements, diverse setup configurations can be applied	[25]

(*continued on next page*)

Table 2 (*continued*)

Process	Type of WW	Conditions	Efficiency	Comments/additional information	Ref
	Water: Inactivation of *E. coli* in water 37.3 $CFUmL^{-1}$	t: 15 minHC: cavitating jet apparatus (p = 98.7 atm, L_k = 0.14)			
RGHC	Waste-activated sludge disintegration: SCOD 45 gL^{-1}	T: 40 °C pH: no information t: number of passes through RGHC system – 20RGHC: rotation generator (2850 RPM, v = 400 $Lmin^{-1}$)	HC: increase SCOD from initial 45 mg/L up to 602 mg/L by only 20 passes through RGHC, the biogas production increased for 12.7% in case of disintegrating WAS with RGHC	Comparison between the analysis of hydrodynamic and biological results leads to conclusion that cavitation aggressiveness has more important role than cavitation extent by WAS disintegration	[27]
HC/Fenton	Model wastewater: 2,4-dichlorophenoxyacetic acid 0,235 gL^{-1}	T: 18 °C pH: 2.5 t: 90 minHC: orifice plate (p = 102.07 atm, v = 5.2 $Lmin^{-1}$, L_k = no information) Fenton: H_2O_2 1,9 gL^{-1},the zero valent iron pieces (150 g, 2 × 1 cm)	Fenton: 10% TOC HC/Fenton: 70% TOC (t = 20 min)	After 20 min of treatment the residual TOC is reduced to 30% and this probably represents the remaining highly recalcitrant small organic molecules	[14]
HC/Fenton	Industrial wastewater (25 times dilution with fresh water): TOC 14 gL^{-1} COD 42 gL^{-1}	T: 20 °C pH: 1.7 t: 150 minHC: orifice plate (p = 0.1 atm, L_k = no information) Fenton: H_2O_2 1,9 gL^{-1},the zero valent iron pieces (150 g, 100 pieces of 1 cm × 2 × 0.2 cm)	HC/Fenton: 60% TOC	Presence of copper windings on iron pieces did not result in beneficial effects possibly attributed to the blockage of the iron surface for generation of hydroxyl radicals	[28]
HC/Fenton	Model wastewater: Triazophos 20 ppm	T: 22 °C pH: 3 t: 90 minHC: orifice plate (p = 4.93 atm, L_k = 0.29) Fenton: Triazophos: $FeSO_4$:H_2O_2 1:4:4 (molar ratio) OR: O_3 1,92 gh^{-1}	HC: 50% (t = 30 min) HC/Fenton: 83% (t = 30 min), 83% TOC (t = 90 min)HC/OR: 89% (t = 30 min),96% TOC (t = 90 min) OR: 70%	It has been established that the degradation of triazophos depends not only on flow rate of ozone but also on the location of injection of ozone (better results when ozone was injected directly in the solution tank)	[17]
HC/OR	Model wastewater:dye pollutants viz. orange acid-II (OA-II) and brilliant green (BG) 20 mgL^{-1}	T: 20 °C pH: 3 t: 120 minHC: orifice plate (p = 4.93 atm, L_k = no information) OR: H_2O_2 95,2 mgL^{-1}, sodium hypochlorite 1250 mgL^{-1}, sodium persulfate 535 mgL^{-1}	HC: 27% TOC HC/OR: H_2O_2 55% (OA-II), 80% (BG), 73% TOC; $Na_2S_2O_8$ 100% (OA-II, t = 60 min) NaOCL 75% (OA-II, t = 30 min)	Brilliant green is comparatively easier to treat as compared to the orange acid dye which can be explained on the basis of the structure of the dye including the chromophore group	[135]
HC/Fenton	Model wastewater: Dimethylhydrazine 5 mgL^{-1}	T: 25 °C pH: 3 t: 120 minHC: orifice plate (p = 2.96 atm, v = 120 $Lmin^{-1}$, L_k = 0.46) Fenton: H_2O_2 0,25 mgL^{-1}, the zero valent iron pieces (100 pieces of 15 × 60 × 1 mm)	HC: 37% HC/iron: 71% HC/Fenton: 98.6%	Formic acid and acetic acid, as well as nitromethane, were identified as oxidation by-products	[48]
HC/Fenton + OR	Model wastewater: 2,4-dinitrophenol (DNP) 20 ppm	T: 35 °C pH: 4 t: 60 minHC: orifice plate (p = 3.95 atm, L_k = no information) OR: DNP:H_2O_2 1:5 (molar ratio), Fenton: H_2O_2:$FeSO_4$ (0.1:0.6 gL^{-1}), H_2O_2:Fe (0.3:0.6 gL^{-1})	HC: 12,3%HC/OR: H_2O_2 21,3% HC/Fenton: H_2O_2/$FeSO_4$ 100%, H_2O_2/Fe 54%	The cavitational yield obtained using hydrodynamic cavitation is 1.25 × 10^{-6} mgJ^{-1}, which is higher as compared to acoustic cavitation	[29]
HC/Fenton + OR	Model wastewater: Imidacloprid 20 ppm	T: 34 °C pH: 3 t: 120 minHC: slit Venturi tube (p = 3.95 atm, L_k = 0.34, v = 1250 Lh^{-1}) OR: H_2O_2 80 gL^{-1}, $FeSO_4$:$Na_2S_2O_8$ 1:4 (molar	HC: 12.85% HC/Fenton: H_2O_2:$FeSO_4$ 100% (t = 60 min), H_2O_2: Fe^0 100% (t = 60 min) HC/OR: H_2O_2 100%, $FeSO_4$:$Na_2S_2O_8$ 99%	Extent of degradation observed in case of slit Venturi was higher than that obtained for orifice plate	[71]

(*continued on next page*)

Table 2 (*continued*)

Process	Type of WW	Conditions	Efficiency	Comments/additional information	Ref
		ratio) Fenton: H_2O_2:$FeSO_4$ 2:2 (molar ratio), H_2O_2:Fe^0 2:1 (molar ratio)			
HC/OR	Model wastewater:Reactive orange 4 (RO-4) 40 ppm	T: 23 °C pH: 2 t: 120 minHC: circular Venturi tube ($p = 4.93$ atm, $L_k = 0.15$, $v = 410\,Lh^{-1}$) OR: RO-4: H_2O_2 1:30 (molar ratio), O_3 3 gh^{-1}	HC: 14.67% HC/OR: H_2O_2 31.90%, O_3 76.25% OR: H_2O_2 4.65%, O_3 21%	The combination of HC with ozone proves to be the most energy efficient method for the degradation of RO-4 as compared to HC alone and the hybrid process of HC and H_2O_2	[81]
EFM-HC	Waste activated sludge COD 10.5 gL^{-1}	T: 37 °C pH: 7.2 t: 180 minHC: crisscross pipe ($p = 4.93$ atm, L_k = no information, $v = 30\,Lmin^{-1}$) EFM: an electric field of 80 V, graphite electrodes ($\Phi 20 \times 750$; anode and cathode)	HC: 33.5% EFM: 9.6% EFM-HC: 47%	Electric field has a great potential for efficient disintegration of WAS for as an additional option in a combination treatment	[46]
HC/OR	Wastewater from wood finishing industry COD 38 gL^{-1}	T: 20 °C pH: 6.18 t: 20 min HC: the stator–rotor assembly (204 indentations – 12 mm in diameter and 20 mm deep, 2200 RPM ($p = 4.44$ atm, $L_k = 0.27$, $v = 5\,Lh^{-1}$) OR: H_2O_2 5 g/L	HC/OR: 46%	Increase in the residence time of the wastewater inside the cavitating device increases the rate of degradation up to an optimum value, beyond which any further increase in the residence time decreases the degradation due to a reduction in the cavitational activity	[49]
HC/Fenton + OR	Model wastewater: Dichlorvos (DCV) 20 ppm	T: 31 °C pH: 3 t: 60 minHC: orifice plate ($p = 4.93$ atm, L_k = no information) OR: DCV:H_2O_2 1:0.8 (molar ratio), CCl_4 3 mgL^{-1} Fenton: $FeSO_4$:H_2O_2 3:1 (molar ratio)	HC: 16% HC/Fenton: 91.5% HC/OR: H_2O_2 17%, CCl_4 26.8%	Addition of CCl_4 increases the extent of degradation by a greater magnitude as compared to hydrogen peroxide, which can be attributed to the formation of more stable oxidizing species like HOCl and Cl_2	[50]
HC/Fenton + OR	Model wastewater: Methyl parathion 20 ppm	T: 39 °C pH: 3 t: 120 minHC: orifice plate ($p = 3.95$ atm, L_k = no information) OR: H_2O_2 0.2 gL^{-1} CCl_4 5.0 gL^{-1} Fenton: H_2O_2:$FeSO_4$ 0.2/0.8 gL^{-1}	HC: 44% HC/Fenton: 90% HC/OR: CCl_4 83%, H_2O_2 99.8%	Radical scavenger: *tert*-butanol and $NaHCO_3$	[85]
HC/OR	Model wastewater: *Microcystis aeruginosa* 3×10^9 $CFUL^{-1}$	T: 25 °C pH: 8.3–8.9 t: 10 minHC: orifice valves ($p = 3.95$ atm, L_k = no information, $v = 360\text{–}840\,Lh^{-1}$) OR: O_2 0.5 $Lmin^{-1}$	HC/OR: 88.1%	HC was shown to increase the zeta potential of algal cells, resulting in cell aggregation	[26]
HC/OR + UV	Suspended activated sludge (after biological treatment):clofibric acid (CLA), ibuprofen (IB), naproxen (NP), ketoprofen (KP), diclofenac (DF), carbamazepine (CBZ) 1 μgL^{-1}	T: no information pH: 2–3 t: 60 minHC: symmetrical Venturi pipe ($p = 5.92$ atm, L_k = no information) OR: 20 mL 20% H_2O_2 UV: 254 nm, 6 W	OR: DF 28%, NP 38%, CBZ 4%, KP 11%, IB 8%, CLA 5% HC/OR: DF 77%, NP 86%, CBZ 72%, KP 52%, IB 48%, CLA 45% HC/OR + UV: DF 99.9%, NP 99.9%, CBZ 89%, KP 29%, IB 19%, CLA 23%	For ibuprofen, naproxen, ketoprofen and diclofenac the highest contribution to overall removal was attributed to biological treatment, for clofibric acid UV treatment was the most efficient, while for carbamazepine hydrodynamic cavitation/hydrogen peroxide process and UV treatment were equally efficient	[22]
HC/OR	Urban wastewater: ibuprofen (IB), naproxen (NP), ketoprofen (KP), diclofenac (DF), carbamazepine (CBZ) 1 μgL^{-1}	T: 50 °C pH: no information t: 15 min HC: two facing rotors – 12/11 grooves and teeth with an 8° inclination, 7 mm deep, 10 mm	HC: DF 45%, NP 44%, CBZ 24%, KP 24%, IB 28%, CLA 15% HC/OR: DF 82%, NP 83%, CBZ 72%, KP 66%, IB 60%, CLA 48%	The aggressiveness of hydrodynamic cavitation, which is related to the design of the cavitating device, influences the amount of free radicals formed and consequently the removal efficiency	[23]

(*continued on next page*)

Table 2 (*continued*)

Process	Type of WW	Conditions	Efficiency	Comments/additional information	Ref
		wide (p = 0.99 atm, L_k = no information) OR: H_2O_2 340 mgL^{-1}			
HC	Waste-activated sludge: COD 10 gL^{-1}	T: 150 °C pH: 12 t: 15 minHC: orifice plate (p = 6.91 atm, L_k = 2.79)	HC: 53.47% (temperature 20%; NaOH 13.9%, HC 22.67%)	HC was found to be an effective physical technique with relatively low power consumption and ease of scaling-up	[65]
HC/OR	Model wastewater: $K_4Fe(CN)_6$ (CA) 20 ppm	T: 30 °C pH: 2 t: 120 minHC: Venturi tube (p = 5.92 atm, L_k = no information, v = 461 Lh^{-1}) OR: CA: H_2O_2 1:5 (molar ratio)	HC: 44.02% HC/OR: 51.29%	Cavitational yield: $1.88{\cdot}10^{-10}$ gmol J^{-1} (HC), $6.96{\cdot}10^{-12}$ gmol J^{-1} (US)	[136]
HC	Model wastewater: Alachlor 50 mgL^{-1}	T: 40 °C pH: 5.9 t: 100 minHC: a cylindrical swirling cavitation chamber (p = 5.92 atm, L_k = no information, v = 3600 Lh^{-1})	HC: 99%	It found that many degradation products formed during the process, and some of them were qualitatively identified by GC–MS	[139]
HC	Water disinfection: 7000 $CFUmL^{-1}$	T: no information pH: no information t: 120 minHC: the cavitating valve – ball type (p = 3.4 atm, L_k = no information)	HC: 45%	Hydrodynamic cavitation appears to be an attrd physical disinfection technique, which can be effectively used to disinfect water for bathing as well as drinking purposes on a large scale	[55]
HC/Fenton + OR	Model wastewater: Rhodamine B 10 ppm	T: 40 °C pH: 2.5 t: 45 minHC: Venturi tube (p = 4.84 atm, L_k = 0.091, v = 400 Lh^{-1}) Fenton: H_2O_2:$FeSO_4$ 5:1 (molar ratio) OR: H_2O_2 200 mgL^{-1}, CCl_4 1 gL^{-1}	HC: 60% (t = 120 min) HC/Fenton: 99.9% HC/OR: H_2O_2 99.9%, CCl_4 82% (t = 120 min)	HC/CCl_4 – mechanism is based on the generation of chlorine radicals due to the degradation of chloroalkanes under cavitating conditions	[24]
HC/Fenton + OR	Model wastewater:Methomyl (MET) 25 ppm	T: 20 °C pH: 2.5 t: 60 minHC: circular Venturi tube (p = 2.96 atm, L_k = 0.18, v = 375 $Lmin^{-1}$) Fenton: H_2O_2:$FeSO_4$ 20:1 (molar ratio) OR: MET:H_2O_2 1:30 (molar ratio), O_3 2 gh^{-1}	HC: 13.9% HC/OR: O_3 71%, H_2O_2 97.25% HC/Fenton: 99.37% (t = 30 min) OR: H_2O_2 2.86%	Highest rate of mineralization was observed using HC + Ozone process as compared to other hybrid processes *i.e.* 70.79% of TOC reduction with first order mineralization constant of 20 × 10^{-3} min^{-1}	[12]
HC/OR	Microbial disinfection of seawater: 10^7 $CFUmL^{-1}$	T: 60 °C pH: 10 t: 15 min (50 passes)HC: slit Venturi tube (p = 2.96 atm, L_k = 0.1) OR: sodium hypochlorite 5 ppm	HC: 100% (8.5% disinfection per pass)HC/OR: 100% (13% disinfection per pass)	The combination of chlorination along with the hydrodynamic cavitation also increases the rate of disinfection compared to that of conventional chlorination. Quantity of chlorine required reduces when it is used in combination with hydrodynamic cavitation which can reduce the amount of disinfection byproducts formed during the conventional chlorination process	[38]
HC/OR	Model wastewater: ibuprofen, ketoprofen, carbamazepine diclofenac 1 μgL^{-1}	T: 60 °C pH: no information t: 15 min HC: two opposite rotors – 12/11 grooves and teeth with an 8°/0° inclination, distance 0.8 mm (p = 0.99 atm, L_k = 0.35, v = 3 $Lmin^{-1}$) OR: H_2O_2 10 mL/L solution	HC: 16% HC/OR: 82%	Temperature (possibly only the extent of cavitation) and the amount of hydrogen peroxide are important for removal process, while unexpectedly the removal does not increase with prolonged time of exposure to cavitation	[39]
HC	Model wastewater: tetrachloride, chloroform 0.05 mML^{-1}	T: 25 °C pH: 3 t: 200 minHC: orifice plate (p = 1.91 atm, L_k = no information, v = 640 Lh^{-1})	HC: 55%	The upstream pressure and the initial concentration of chlorocarbons have substantial effects on the degradation of chlorocarbons. The rate of conductivity does not increase linearly with upstream pressure, but an optimal pressure does exist	[89]

(*continued on next page*)

Table 2 (*continued*)

Process	Type of WW	Conditions	Efficiency	Comments/additional information	Ref
HC/Fenton	Model wastewater: Phenol 2.5 mML^{-1}	T: 35 °C pH: 2.5 t: 120 minHC: orifice plate and blade (p = 0.1 atm, L_k = no information, v = 8.65×10^{-5} Ls^{-1}) Fenton: H_2O_2 2000 mgL^{-1}, the zero valent iron pieces (80 g, 50 pieces of 1 × 2 × 0.1 cm)	HC/Fenton: 60%	The efficacy of the treatment scheme is enhanced by high operating pressures, an increase in the oxidant dosage and a lowering of the pollutant concentration	[61]
HC/OR	Real wastewater from bitumen production (identyf. compounds in ppm):1-propanal (38.8)2-pentanone (16.8)1-hexanol (3.0)1-heptanol (2.1)phenol (13.4)m-cresol (8.2)	T: 40 °C pH: 10.5 t: 360 minHC: Venturi tube (p = 7.9 atm, L_k = 0.14, v = 520 Lh^{-1}) OR: H_2O_2 72 mLL^{-1}, O_3 9.41 gh^{-1}	HC: 1-propanal (86.8%); 2-pentanone (75.9%); 1-hexanol (20.6%); 1-heptanol (17.0%); phenol (12.8%); m-cresol (30.7%) HC/H_2O_2: 1-propanal (99.7%); 2-pentanone (91.6%); 1-hexanol (58.9%); 1-heptanol (31.2%); phenol (100%); m-cresol (100%) HC/O_3: 1-propanal (100%); 2-pentanone (99.9%); 1-hexanol (100%); 1-heptanol (97.0%); phenol (100%); m-cresol (100%)	By-product identified by GC analysis: *furfural*	[144]

*HC – hydrodynamic cavitation; OR – oxidizing reagent; RGHC – rotation generator of hydrodynamic cavitation; EFM-HC – electric field-assisted modified hydrodynamic cavitation.

called peroxone. Due to their high oxidation potential, equal to 2.8 V, the radicals can oxidize practically every organic and inorganic contaminant occurring in a medium being treated [31]. Other reagents used for the chemical generation of hydroxyl radicals include the Fenton reagent and a mixture of ozone with the hydroxide anion, persulfate and monopersulfate.

The Fenton reagent, first developed in 1894, is characterized by nonselective oxidation properties. Accordingly, it has first been used for effluent treatment in the 1960s. In such a case, pollutants react with free radicals in an uncontrolled way which forces a larger number of reactions and hence improves the effectiveness of oxidation process (up to 90% of pollutants can be removed). The Fenton reagent is a mixture of hydrogen peroxide with divalent iron cation. The iron cation (Fe^{2+}) initiates the reduction reaction of hydrogen peroxide resulting in the formation of hydroxide ions and reactive hydroxyl radicals [31].

Most often, hydrodynamic cavitation aided by AOPs is used in the initial stage of effluent treatment, prior to biological methods, which improves the effectiveness and reduces the cost of the process. The hybrid methods seem to be the best solution to treatment of industrial effluents containing a complex load of pollutants. However, due to high cost of the equipment, incompletely elucidated mechanisms of physical and chemical processes taking place in the presence of highly reactive hydroxyl radicals, and the problems with stability of generation of cavitation bubbles, these processes require further research. In addition, they are affected by a number of less important process parameters, such as residence time of pollutants in the reactor, flow rate, inlet pressure or the nature of contaminants, which makes optimization more difficult.

3.2.1. *Sequential and simultaneous oxidation during hydrodynamic cavitation combined with addition of external oxidants*

Sequential oxidation in hydrodynamic cavitation aided by external oxidants involves a multistep oxidation process. In simultaneous oxidation, instead of a multistep degradation there is just one main process of degradation of a pollutant resulting in its complete removal.

The choice of single- or multistep oxidation of a contaminant depends primarily on its physical and chemical properties, such as bond energies, volatility or hydrophilicity [32]. Several types of oxidation reactions can occur during degradation of a pollutant by both hydrodynamic and acoustic cavitation. The most important of these are degradation of a pollutant via pyrolytic decomposition and pyrolytic decomposition of water yielding chemical species with a high redox potential which subsequently react with pollutant molecules.

Degradation via pyrolytic decomposition of pollutants usually takes place inside a collapsing cavitation bubble. Due to a rapid increase in pressure and temperature in the bubble or in the liquid phase, when a pollutant molecule is near the collapsing bubble, some chemical bonds break and the molecule is converted to a less chemically aggressive form. Degradation inside the gaseous bubble takes place mostly for the pollutants having a vapor pressure similar to water vapor pressure. Pollutants of this kind are capable of penetration into the inside of the cavitation bubbles. The energy concentrated inside the bubbles allows decomposition of the majority of pollutants having strong covalent bonds, mostly due to high pressure and temperature in the order of 9869 atm and 4726.8 °C, respectively, generated during implosion of individual bubbles [5–7]. This kind of degradation usually promotes a single-step conversion to a less toxic form.

The second type of pyrolytic degradation occurs in the liquid phase and involves mainly pollutants having a low volatility, often due to a high molecular weight. The energy of collapsing bubbles causes pyrolytic decomposition of water molecules resulting in formation of reactive hydrogen ($H^{\cdot}$) and hydroxyl ($OH^{\cdot}$) radicals [33]. The radicals formed react with pollutant molecules in their vicinity in single- or multistep chemical reactions [34]. This allows a conversion of the pollutant to a simple inorganic compound or an organic compound having a significantly lower toxicity. This path of degradation of

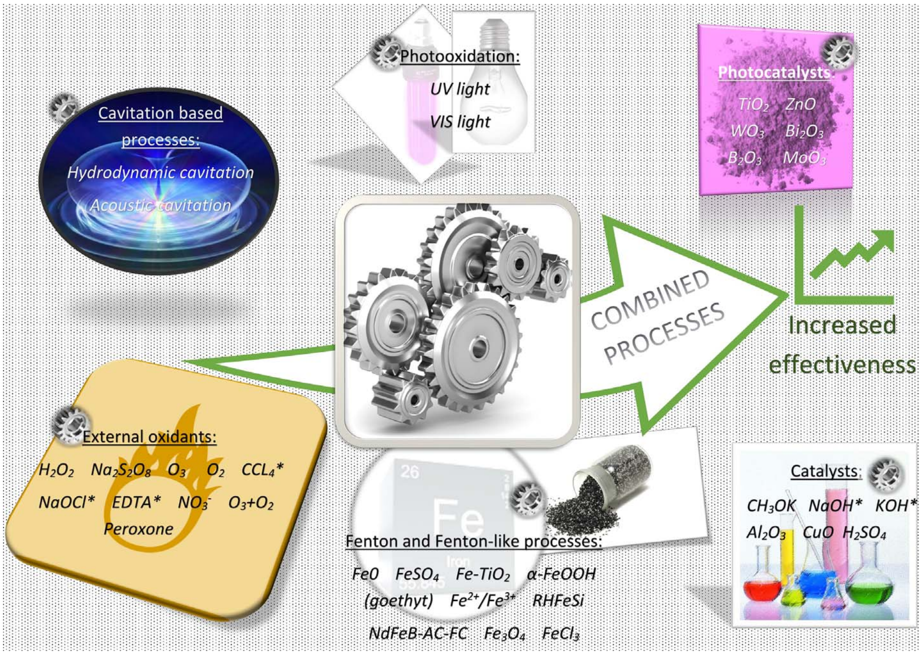


Fig. 3. Cavitation in combination with AOPs in wastewater treatment processes. EDTA – was found to break down O—O bond of oxygen and produce H_2O_2 in a Fe/EDTA system [94]; NaOCl – commonly known as bleaching agent, is frequently used as a disinfectant for treating drinking water [135]; CCl_4 – as a hydrophobic organic compound, is prone to enter the cavitation bubbles and undergoes degradation by pyrolytic cleavage to produce large amount of Cl radicals [85,123,137]; NaOH and KOH – used as alkaline catalysts in combined process with hydrodynamic cavitation for methane production [65].

pollutants usually occurs in several steps, especially for pollutants with strong covalent bonds.

The kind and nature of the reaction are affected not only by volatility, boiling point and strength of covalent bonds of a pollutant but also by its hydrophilicity which determines the location of a pollutant in the reaction mixture [35]. Hydrophilicity is a strong affinity of a molecule to polar solvents. Pollutants containing in their structure hydrophilic groups, such as phenol or chlorophenol, will undergo degradation reactions both in the bulk of effluent being treated and in the liquid-bubble interfacial region, where the gaseous bubbles collapse. In this case degradation occurs mostly via pyrolytic decomposition of water and reactions with the generated hydroxyl radicals. On the other hand, for hydrophobic pollutants, such as benzene, the only possible reaction site is the inside of the cavitation bubble where it is degraded pyrotically. Owing to conditions prevailing inside cavitation bubbles this method ensures the most rapid and effective decomposition compared to degradation of hydrophilic pollutants in the liquid phase by reactive hydroxyl radicals. Consequently, volatile hydrophobic pollutants entering the inside of gaseous bubbles will be degraded more efficiently than nonvolatile hydrophilic pollutants dissolved in the bulk of the effluent when using hydrodynamic or acoustic cavitation.

The three reaction zones in the cavitation process are shown in Fig. 4.

The main mechanisms of degradation of various types of organic pollutants in hydrodynamic/acoustic cavitation processes are compiled in Table 1.

3.2.2. Equipment used to generate cavitation and comparison of their effectiveness for degradation of effluent pollutants

The cavitational yield determining the efficiency of degradation of chemical pollutants in the case of hydrodynamic cavitation depends on four main parameters [36]:

- inlet pressure into the system,
- physicochemical properties of liquid and initial radius of the nuclei initiating the cavitation process,
- diameter of the constriction used for the generation of cavities, and especially the ratio of diameters of throat and recovery sections,
- percentage free area offered for the flow.

Geometry of the device used to initiate cavitation affects not only the number of cavitation events but also their effectiveness related to the pressure and temperature generated during the collapse of individual cavitation bubbles. Proper design of the throat influences pressure conditions during the flow of a medium being treated, which allows obtaining the optimum distribution of pressure before and after the element responsible for the generation of an appropriate active volume of the cavitation cloud in which decomposition of a pollutant takes place.

In hydrodynamic cavitation used for removal of chemical pollutants from wastewater, constrictions placed in appropriate positions of the installation through which the medium being treated is pumped are used for the inception of the gaseous bubbles. The role of the constriction is to increase kinetic energy of the flowing liquid at the expense of pressure drop under appropriate temperature conditions. If the design allows pressure drop and maintaining it near the critical point, a cloud of cavitation bubbles can be generated. After the liquid passes through the cavitation zone, a rapid increase in pressure takes place resulting in the collapse of the bubbles and local increases in pressure and temperature. This improves the effectiveness of removal of pollutants.

When designing new cavitation installations, special attention is paid to ensure an appropriate pressure drop during transition through the constriction. The geometry is optimized, including diameter of the inlet and outlet of the constriction, the angle at which the initial pressure is restored and flow conditions of a liquid, such as the extent of generation of eddies and turbulence. The most common constrictions are various types of Venturi tubes [12], throttle valves [37] and orifices [38] with a proper diameter of the channels through which the medium is pumped. An increasing use of cavitation reactors in which the pressure drop of a liquid below its vapor pressure is accomplished by mechanical rotors has been observed [27,39]. Selection of a proper design allows generation of the bubbles with an efficiency close to that of acoustic cavitation. Acoustic cavitation enables the most efficient removal of pollutants; however, its operational cost is high due to high consumption of energy by ultrasound generators. Consequently, the designs of constricted channels of similar cavitation characterisitics are sought which would allow cost reduction of the treatment and a wider application of hydrodynamic cavitation for the removal of chemical pollutants [37].

Table 3
Comparison of different studies using ultrasound processes.

Process	Type of WW	Conditions	Efficiency	Comments/additional information	Ref
US US/UV	Model wastewater: MMP 0.01 M DMP 0.01 M DEP 0.01 M DBP 0.01 M	T: 28 ± 2 °C pH: 7.5 t: 90 min US: 400 kHz UV: 1.03 x 10^{-5} Ls^{-1}	(US) US/UV:DMP (25%) 95%; t = 90 minMMP (28%) 75%; t = 90 minDBP (4.38%; t = 90 min) 98%; t = 40 minDEP (9.3%) 98%; t = 90 min	Radical scavenger: *tert*-butanol (100 mM)	[31]
US/EO	Model wastewater: Ibuprofen 10–100 μgL^{-1}	T: 5–40 °C pH: 6.6 t: 30–180 min US: 520 kHz, 20 W EO: 3.6–35.7 $mAcm^{-2}$ (4.09 A)	US/EO:IBU (20 μgL^{-1}) 87.5%; t = 110 minIBU (100 μgL^{-1}) 83.6%; t = 110 min	The total treatment cost was estimated to 3.93 $$m^{-3}$	[21]
US/Fenton	Real wastewater: Toluene, Naphthalene, Xylene, Benzene 3–3.5 gL^{-1}	T: 24 °C pH: 7 t: 40 min US: 22 kHz, 120 W Fenton: Fe^{2+} 2.0 gL^{-1} ($FeSO_4 \times 7\ H_2O$) and H_2O_2 1.0 gL^{-1}	US/Fenton: Toluene 75.5% Naphthalene 71.6% Xylene 76.3% Benzene 81.4%	The biodegradability index value increased from 0.17 to 0.39 in 40 min	[122]
US/EO	Water: Diclofenac 5–50 μgL^{-1}	T: 22 °C pH: 4 t: 20 min US: 850 kHz, 120 W EO: 94 WL^{-1}, 7.2 V	US/EO:Diclofenac 96.8% (50 μgL^{-1}; t = 5 min)	With increasing pH the degradation of Diclofenac decreases (at pH 4 a DCF degradation of 96.8% within 5 min could be reached, whereas at pH 9.9 only 85.1%)	[134]
US/Fenton	Water: 2,4-dichlorophenoxyacetic acid 0.235 gL^{-1}	T: 22 °C pH: 3 t: 60 min US: 20 kHz, 45 W Fenton: Fe^0 (powder) 0.6 gL^{-1} and H_2O_2 1.9 gL^{-1}	US/Fenton: TOC 57%	The use of zero-valent iron and H_2O_2 in conjunction with acoustic cavitation is a very effective means of destroying high concentrations of 2,4-D	[14]
US/OR	Real wastewater:dye orange acid-II (OA-II) dye brilliant green (BG) 20 mgL^{-1}	T: 20 °C pH: 3 t: 120 min US: 20 kHz, 80 W OR: H_2O_2 0.10 gL^{-1} NaOCl 1.25 gL^{-1} $Na_2S_2O_8$ 1.61 gL^{-1}	US: BG 68% OA-II 49,5% US/OR: H_2O_2 77% (OA-II); 78% (BG) NaOCl 72% (OA-II); 81% (BG) $Na_2S_2O_8$ 70% (OA-II); 82% (BG)	For all the oxidants, an optimum loading was found to be dependent on the dye and oxidant used	[135]
US	Water: Bacterial 6980 $CFUmL^{-1}$	T: 35 °C pH: 7 t: 20 min US: 22 kHz, 240 W	US: 85% disinfection	The physical methods of water disinfection are still quite expensive compared to the chemical disinfection methods	[55]
US/OR	Model wastewater: $K_4Fe(CN)_6$ 20 ppm	T: 30 °C pH: 2 t: 80 min US: 22 kHz, 750 W OR: $K_4Fe(CN)_6$:H_2O_2 1:5 (mol:mol)	US: $K_4Fe(CN)_6$ 54.17% US/OR: $K_4Fe(CN)_6$ 61.22%	The moles of potassium ferrocyanide degraded per unit energy using hydrodynamic cavitation is order of magnitude higher than using acoustic cavitation	[136]
US/Fenton + OR	Model wastewater: alachlor 20 ppm	T: 28 °C pH: 3 t: 60 min US: 400 kHz, 80 W OR: H_2O_2 0,2 gL^{-1} CCL_4 3 gL^{-1}	US: 3.5% US/OR: H_2O_2 8.6% CCL_4 32.2% $FeSO_4$:H_2O_2 100% Fe:H_2O_2 96.4%	Radical scavenger: n-butanol; sodium bicarbonate	[123]

(*continued on next page*)

Table 3 (*continued*)

Process	Type of WW	Conditions	Efficiency	Comments/additional information	Ref
		Fenton: $FeSO_4$:H_2O_2 (mol:mol) 1:1 Fe:H_2O_2 (mol:mol) 1:3,5			
US	Model wastewater: Trichloroethylene 3,24 mML^{-1} Chlorobenzene 3,44 mML^{-1}	T: 29 °C pH: 7 t: 120 min US: 520 kHz, 14 W	US: Trichloroethylene 100% (t = 90 min)Chlorobenzene 50% (t = 120 min)	The influence of TCE on the physical and chemical factors determining the sonolysis rate of CB proves that volatile organic compounds can strongly affect each other's sonolysis	[18]
US/Fenton + OR	Containing wastewater Dichlorvos (DCV) 20 ppm	T: 25 °C pH: 3 t: 120 min US: 20 kHz, 270 W OR: DCV:H_2O_2 (mol:mol) 0.75:1 CCl_4 2gL^{-1} Fenton: $FeSO_4$:H_2O_2 (mol:mol) 3:1	US: 51.8% US/OR: H_2O_2 62.5%% CCL_4 76.2% $FeSO_4$:H_2O_2 100%	The extent of degradation increased with an increase in the power density due to enhanced cavitational activity	[137]
US	Model wastewater: Pentachlorophenate 0.1 mML^{-1}	T: 20 °C pH: 7 t: 120 min US: 500 kHz, 65 W	US: 100%	The energy consumption for total pollutant mineralization is very high	[32]
US/Fenton + OR	Model wastewater: methyl Parathion 20 ppm	T: 30 °C pH: 2.5 t: 60 min US: 20 kHz, 270 W OR: H_2O_2:mP (mol:mol) 10:1 CCl_4:mP (mol:mol) 25:1 TiO_2:mP (mol:mol) 1:1 Fenton: $FeSO_4$:H_2O_2 (mol:mol) 3:1	US: 51.8% US/OR: H_2O_2 97.4%% CCL_4 26% $FeSO_4$:H_2O_2 95.5% TiO_2 32.5%	There is a strong memory effect of ultrasound in the presence of H_2O_2 which makes stand alone samples of mP to degrade over time after an initial acoustication treatment is given to the samples	[59]
US/Fenton	Model wastewater: Formic acid 250 mgL^{-1}	T: 29 °C pH: 3 t: 30 min US: 20 kHz, 200 W Fenton: Fe^{2+}/H_2O_2 3.75:80 mML^{-1} $Fe^{2+}/S_2O_8{}^{2-}$ (mol:mol) 1:30	US/OR: $Fe^{2+}/S_2O_8{}^{2-}$ 94% (t = 5 min) Fe^{2+}/H_2O_2 60%	First-order reaction kinetics	[15]
US/Fenton + OR	Model wastewater: Methyl *tert*-butyl ether 2.5 mgL^{-1}	T: 20 °C pH: 5.8 t: 300 min US: 20 kHz, 200 W Fenton: Fe^{2+}/H_2O_2 1.08:500 mML^{-1} OR: $S_2O_8{}^{2-}$ 10 mML^{-1}	US: 60% US/Fenton:94% (t = 120 min)100% (t = 150 min) US/ $S_2O_8{}^{2-}$: 98%	Several intermediates were identified by GC analysis, out of which *tert*-butyl formate and acetone were major intermediates	[60]
US/Fenton + OR	Model wastewater: *p*-nitrophenol 5 gL^{-1}	T: 28 °C pH: 3.7 t: 90 min US: 25 kHz, 1000 W Fenton: Fe^{2+}/H_2O_2 1/5 gL^{-1} OR: H_2O_2 5 gL^{-1}	US: 48.3% US/Fenton: 66.4% US/ H_2O_2: 59%	The results suggest that an optimum loading of hydrogen peroxide exists and it is critical to establish this optimum concentration as any unutilized hydrogen peroxide can add to effluent COD	[19]
US/OR + UV	Model wastewater: Naphthol Blue Black dye 1 gL^{-1}	T: no information pH: 2 t: 60 min	Model wastewater:US/UV: 3% (pH 6.8), 41% (pH 2)	The combined sonolysis and photolysis process (3% color removal) was more beneficial than individual sonolysis (2% color removal) and photolysis (1% color removal) from the experimental results of NBB dye	[13]

(*continued on next page*)

Table 3 (*continued*)

Process	Type of WW	Conditions	Efficiency	Comments/additional information	Ref
	Real textile wastewater: TOC 423 mgL^{-1}	US: 37 kHz, 200 W OR: H_2O_2 44,1 mmolL^{-1} Fe 3 gL^{-1} TiO_2 4 gL^{-1} UV: UV-C, 256 nm, 4 W	US/UV/ H_2O_2: 94%US/UV/ Fe: 55% (pH 6.8) US/UV/ TiO_2 58% (pH 6.8) US/UV/ Fe:TiO_2 1:7 (mol:mol) 73% (pH 6.8) Real textile wastewater:US/UV/ Fe: 80% TOC (pH 8) US/UV/ TiO_2 85% TOC (pH 8) US/UV/ Fe:TiO_2 1:7 (mol:mol) 91% (pH 8)		
US/OR	Model wastewater: 2,4-dichlorophenol 100mgL^{-1}	T: 20 °C pH: 6.5 t: 180 min US: 20 kHz, 385 W OR: Fe 25 gL^{-1} EDTA 0.32 mM	US: 10% US/Fe: 20% Fe: 80%US/Fe/EDTA: 100% (t = 60 min)	No significant differences in the degradation of DCP was found at different initial DCP concentrations ranged from 50 to 150 mgL^{-1}	[94]
US/Fenton	Model wastewater: azo dye Acid black 1 0.081 mML^{-1}	T: 40 °C pH: 3 t: 30 min US: 40 kHz, 50 WL^{-1} Fenton: Fe^{2+} 0,025 mML^{-1} H_2O_2 8 mML^{-1}	US/Fenton: 98,83% (t = 30 min)90% (t = 10 min)	The effect of various inorganic anions on the degradation of AB1 is in the following decreasing order: $SO_3^{2-} > CH_3COO^- > Cl^- > CO_3^{2-} > HCO_3^- > SO_4^{2-} > NO_3^-$,	[95]
US	Model wastewater: Chloroform, carbon tetra-chloride 0.05 mML^{-1}	T: 25 °C pH: 3 t: 60 min US: 850 kHz, 40 W	US: 100%	Organic products from the degradation of carbon tetrachloride and chloroform have demonstrated the formation and recombination of free radicals, *e.g.*, CCl_4,C_2Cl_4, and C_2Cl_6 are produced from the degradation of $CHCl_3$	[89]
US	Aqueous solution 1,4-Dioxane 1 mML^{-1}	T: 25 °C pH: 7.5 t: 120 min US: 358 kHz, 128 W	US: 95%	Ethylene glycol diformate, methoxyacetic acid, formaldehyde, glycolic acid, and formic acid were found to be the major intermediates of 1,4-dioxane degradation	[8]
US/UV + OR	Model wastewater: Nonylphenol 0.01 mML^{-1}	T: 29 °C pH: 6.6 t: 90 min US: 400 kHz UV: 253.7 nm, Intensity 3.44×10^{-6} L^{-1}s^{-1} OR: NO_3^{-1} 10 mgL^{-1}	US: 78% UV: 68%US/UV: 98% (t = 60 min) US/UV/NO_3^{-1}: 100%	Radical scavenger: HCO_3^-	[138]
US/Fenton + UV	Model wastewater: Phenol 200 mgL^{-1}	T: no information pH: 3 t: 600 min US: 34 kHz 120 W Fenton: H_2O_2 700 mgL^{-1} Fe^{2+} 20 mgL^{-1} UV: 420 nm, 250 W	US/Fenton/UV: 93% US/Fenton: 72% Fenton: 61.9%	The sono-photo-Fenton process shows 93% phenol degradation and 84.6% COD reduction under optimum conditions	[99]
US/Fenton + NaCl	Model wastewater: reactive brilliant red 10 mgL^{-1}	T: 25 °C pH: 5,5 t: 240 min US: 20 kHz 150 W Fenton: H_2O_2 20 µmolL^{-1} Fe^{2+} 5 µmolL^{-1} NaCL 1.5 molL^{-1}	US: 21% US/NaCl: 69% US/Fenton: 77% US/Fe^{2+}: 55% H_2O_2: 3%	It was found that the degradation of reactive brilliant red K-BP in aqueous solution follows pseudo-first-order reaction kinetics	[100]

(*continued on next page*)

Table 3 (*continued*)

Process	Type of WW	Conditions	Efficiency	Comments/additional information	Ref
US/OR	Model wastewater:nitrobenzene (NB) 100 μML^{-1}	T: 25 °C pH: 2.4 t: 120 min US: 500 kHz 48.3 W OR: O_3 10 mlmin^{-1}	US/O_3: NB 87% O_3: NB 73%	Several intermediates were identified by GC analysis, out of which *4-nitrophenol, 3-nitrophenol and 4-nitrocatechol* were major intermediates	[113]
US/OR	Model wastewater:Azobenzene (AB) and Methyl Orange (MO) 10 μML^{-1}	T: 15 °C pH: 6.5 t: 300 min US: 500 kHz 50 W OR: O_3 5 mlmin^{-1}	US: AB and MO 20% (t = 150 min) US/O_3: AB and MO 80% (t = 25 min) O_3: AB and MO 25% (t = 25 min)	Nitrobenzene and benzoquinone, two rather persistent byproducts of sonolysis, are rapidly and completely mineralized by the combined oxidation treatment	[115]
US/OR	Model wastewater: Pentachlorophenol 20 μML^{-1}	T: 30 °C pH: 7.3 t: 250 min US: 20 kHz 1340 WL^{-1} OR: O_3 3 Lmin^{-1}	US/OR: 100% (t = 200 min)	Octachlorodibenzodioxin (OCDD), a known product of PCP combustion, was not detected	[116]
US/OR	Model wastewater: Methyl *tert*-Butyl Ether 0,5 mML^{-1}	T: 20 °C pH: 6.8 t: 60 min US: 205 kHz 200 WL^{-1} OR: O_3 0.3 mML^{-1}	US: 92%US/OR: 100% (t = 30 min)	Several intermediates were identified by GC analysis, out of which *tert-Butyl formate, tert-butyl alcohol, methyl acetate* were major intermediates	[117]
US/OR	Model wastewater: *p*-nitrotoluene 100 mgL^{-1}	T: 50 °C pH: 10 t: 30 min US: 20 kHz 400 W OR: O_3 3.8 gh^{-1}	US/OR: 100% (t = 15 min)	Of the total organic carbon (TOC) reduction, 8, 68, and 85% were observed with US, O_3, and a combination of US and O_3 after reaction for 90 min	[119]
US/OR	Model wastewater: *p*-Aminophenol 16 gL^{-1}	T: 50 °C pH: 11 t: 60 min US: 20 kHz 400 W OR: O_3 5.3 gh^{-1}	US: 100% (t = 90 min)US: 95% (t = 60 min)US/OR: 100% (t = 30 min)	Several intermediates were identified by GC analysis, out of which *acetic acid, but-2-enedioic acid, phenol, 4-iminocyclohexa-2,5-dien-1-one* were major intermediates	[120]
US	Model wastewater: aqueous KI solution 1%	T: 36 °C pH: no information t: 20 min US: 20 kHz 600 W	US: 35%	The Energy efficiency: 35.3×10^{-9} gmJ^{-1}	[53]
US	Model wastewater: Sodium pentachlorophenate 0,1 mML^{-1}	T: 20 °C pH: 7.5 t: 120 min US: 500 kHz 65 W	US: 100%	After an acoustication period longer than 2 h (which corresponds to a dissipated energy of 1.6 GJ m^{-3}), toxicity became low enough to be harmless for the bacteria	[32]

---

[*] US – ultrasound process; EO – electrochemical oxidation; OR – oxidizing reagent.

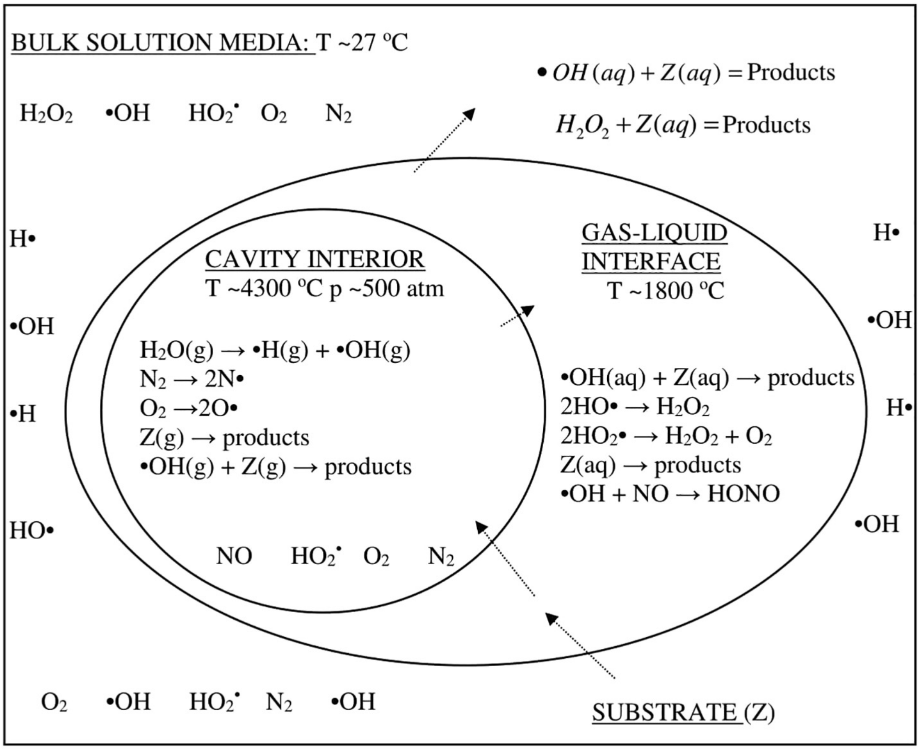


Fig. 4. Three reaction zones in the cavitation process [96].

3.3. Venturi tubes

By applying the Bernoulli equation to determine the behavior of a liquid flowing through a constriction (Fig. 5), the following equation can be derived:

$$\frac{\nu_1^2}{2} + gh_1 + \frac{p_1}{\rho} = \frac{\nu_2^2}{2} + gh_2 + \frac{p_2}{\rho} + g\sum h_{i,str} \tag{1}$$

ν is the fluid flow speed at a point on a streamline, p is the pressure at the chosen point, ρ is the density of the fluid, g is the acceleration due to gravity, and h is the elevation of the point above a reference plane, accounting for potential energy.

The equation describes the energy of a fluid as the sum of kinetic, potential and static pressure (p_1 and p_2) energies, respectively, in the analyzed cross sections while $\sum_{i,str}^{h}$ is the energy lost by the stream due to resistance to flow which is converted to thermal energy during the passage of the fluid through the constriction. If the elevation of the pipe on both sides of the constriction is the same, then the potential energy term can be neglected and Eq. (1) can be simplified to the following form (Eq. (2)), which explains the increase in fluid flow speed in the constriction with the simultaneous decrease in pressure.

$$\frac{\nu_1^2}{2} + \frac{p_1}{\rho} = \frac{(\uparrow)\,\nu_2^2}{2}{}_2 + \frac{(\downarrow)\,p_2}{\rho} + g\sum h_{i,str} \tag{2}$$

A negative nature of this effect is used to reduce the degree of pollution of various effluents in installations making use of hydrodynamic cavitation. When the liquid speed in the constriction increases, the pressure in the constriction is greatly reduced and the liquid can evaporate generating destructive cavitation bubbles even at a low temperature. In many cases, this can damage the equipment; however, proper design and geometry of the constriction allow to control the process, which makes it a useful tool for degradation of chemical and microbiological water pollution.

3.3.1. Types and effect of geometry of Venturi tube on effectiveness of degradation

A classical Venturi tube is a choking element consisting of a convergent inlet called a confusor, a cylindrical throat, and a divergent section called a diffuser (Fig. 6).

Geometry of a Venturi tube has a significant effect on the inception of cavitation when used for the removal of organic pollutants. When designing the tube, special attention is paid to, among others, the

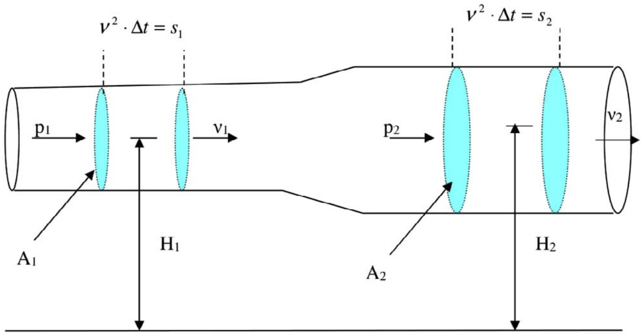


Fig. 5. Schematic flow of fluid through the constriction described via the law of Bernoulli. p_1/p_2 –pressure in/after throat; ν_1/ν_2 – flow rate of liquid in/after throat; A_1/A_2 – cross section of throat/pipe; H_1/H_2 – height of the pipe in/after throat (calculated to the measurement point).

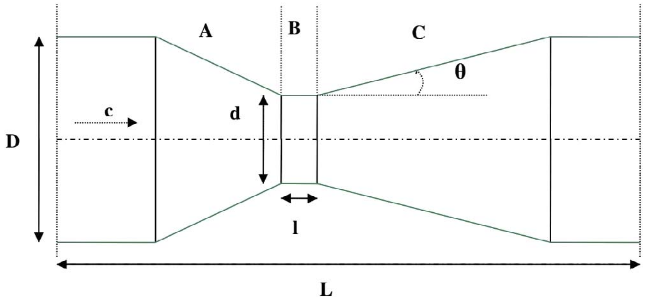


Fig. 6. Scheme of Venturi tube. A – convergent section; B – throat; C – divergent section; D – diameter; d – diameter of throat; L – length; l – length of throat; θ – half angle of divergent section, c – flow direction.

diameter and length of the throat or the angle of the divergent section which is responsible for the initial pressure recovery by the pumped medium. Inception of cavitation takes place when geometry of the Venturi tube allows obtaining the ratio of outlet to inlet pressure at a level of 0.8 (liquid critical pressure factor) [36,40–45]. Below this level the linear speed of a liquid is constant and independent of outlet pressure (pressure in the diffuser). This is called cavitating turbulent flow. The gaseous bubbles are formed in the throat of the Venturi tube and they collapse in the diffuser. These conditions provide the highest efficiency of generation of hydroxyl radicals. With an increase of pressure in the diffuser the direction of collapse of the cavities shifts towards the throat. The implosion space becomes more limited. With a further increase of pressure in the diffuser and thus after exceeding the critical pressure factor of 0.8, cavitation is stopped. The optimum ratio of diameter to length of the throat and the angle of the divergent ensuring high efficiency of cavitation in oxidizing organic pollutants are 1:1 and 7° respectively [36,40–45].

3.4. Orifice plates

Orifice plates are the next devices used to restrict flow of a pumped medium in order to initiate cavitation. In contrast with Venturi tubes, orifice plates constitute an obstacle blocking the flow of a liquid being pumped. The liquid in a certain segment of a pipe can only flow through orifices drilled in a plate which have an appropriate surface area of openings. In laboratory studies, the area of openings is typically 40–60 mm^2 with a total surface area of the plate ranging from 300 to 500 mm^2 [29,46,47]. An appropriate number and arrangement of orifices in the plate ensure an increase in kinetic energy of the pumped medium at the expense of pressure drop and hence a proper cavitational yield. An example of an orifice plate used for inception of hydrodynamic cavitation is shown in Fig. 7.

Compared with acoustic cavitation, the inception of gaseous bubble formation using an orifice plate or a Venturi tube is associated with the problem of low efficiency of pressure recovery behind the constriction. In the case of hydrodynamic cavitation, the pressure loss across the constriction can reach 73% [36]. In order to obtain a high cavitational yield, the pressure should rapidly return to its initial value which results in a higher energy of collapse of gaseous bubbles. To maintain the acceptable cavitational yield when using an orifice plate, two approaches are possible. The first one relies on an increase in inlet pressure of the treated medium, which entails the use of expensive high-pressure pumps and constructions capable of withstanding high pressures. The second, simpler, approach involves designing the free area of an orifice plate in such a way as to reduce pressure losses and thus to improve the efficiency of recovery of the inlet pressure behind the constriction resulting in an increase in the number of cavitational events and higher degree of removal of organic pollutants.

3.4.1. Types and effect of orifice plate geometry on effectiveness of degradation

Appropriate geometry of the orifice plate ensures obtaining a good pressure profile which includes the pressure drop of the pumped medium below the water vapor pressure (thus enabling the inception of cavitation bubbles) and the pressure increase to the initial state which takes place behind the constriction (affecting the cavitational yield). Creation of the optimum pressure profile through the geometry of an orifice plate results in a high cavitational yield and thus a high degree of removal of organic pollutants [29,46,48–50].

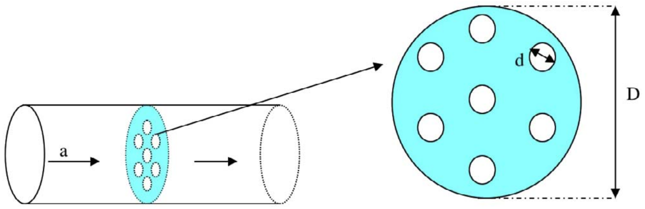


Fig. 7. Scheme of orifice plate. a – flow direction; D – diameter of orifice plate; d – circular hole diameter.

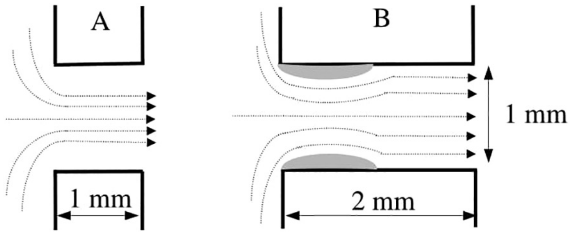


Fig. 8. Schematics for the assumed flow region in the orifice plates type (A) (*separated flow*) and (B) (*reattachment flow* after vena contracta) [47].

A comprehensive investigation of the effect of orifice plate geometry on cavitational yield was carried out by Ghayal et al. [51] and Parsa and Zonouzian [47]. In both papers the effect of number of holes in a plate, their diameter as well as the thickness of the plate and the total flow area on the effectiveness of decolorization of Rhodamine B [47] and transesterification of triglycerides [51]. Parsa demonstrated that the thicker the plate the higher the inlet pressure (and higher pressure drop) and the lower the flow rate. This effect can be attributed to the change in flow pattern of the medium. The flow pattern for a thinner plate is separated flow (Fig. 8a) while for a thicker plate the flow pattern is reattached flow (Fig. 8b).

An increase in plate thickness results in a higher inlet pressure (from 5.72 to 6.42 atm) for the orifice plate B due to the higher frictional pressure drop. This leads to a lowered flow rate and an increase in the cavitation number (from 0.27 to 0.31). The friction causes substantial pressure losses inside the gaseous bubbles, thus reducing the force of their collapse and efficiency of decomposition of Rhodamine B (drop in extent of decolorization from 71.1% to 64.8%). With an increase in hole diameter of the plate (orifice plate C: 16 holes with a 2 mm diameter; orifice plate D: 64 holes with a 1 mm diameter) at the same total cross-sectional area (50.2 mm^2), the authors as well as Sivakumar [52] observed an increase in the extent of decolorization of Rhodamine B, caused by the greater force of collapse of gaseous bubbles due to an increase in their critical radius. In addition, an increase in total cross-sectional area of the plate brings about a decrease in the extent of decolorization of Rhodamine B due to lower inlet pressure, higher cavitation number and a lower energy of collapse of the gaseous bubbles.

Ghayal et al. [53] investigated three additional parameters of an orifice plate: α, β and γ on the efficiency of transesterification of triglycerides. The geometrical parameter α corresponded to the ratio of total perimeter of holes to the total flow area of the plate. It was demonstrated that an increase in α resulted in an increased conversion of triglycerides (from 77% for the orifice plate with $\alpha = 0.4$ to 94% for $\alpha = 1.33$). The parameter α is closely related to the number of holes in the plate and their diameter. A comparison of conversions for the plates with the same flow area revealed that the plate with a greater number of holes and a smaller hole diameter (larger value of α) yields a higher degree of conversion. This is due to a larger number of the cavity generating spots. In reactions whose efficiency is affected by the mass transfer resistance, a greater value of α can limit the resistance. Similar results of investigations were reported by Kumar [53].

The next parameter β is defined as the ratio of hole diameter to the pipe diameter. The plate with the smallest hole diameter was found to provide maximum conversion of triglycerides. This can be attributed to a larger number of cavities and hence of the cavitational events limiting mass transfer resistance and improving emulsification.

The last investigated parameter γ is defined as the ratio of the total flow area of the orifice plate to the cross-sectional area of the pipe. An increase in γ was found to improve the degree of conversion of triglycerides. For the plates having the same γ value and thus similar flow

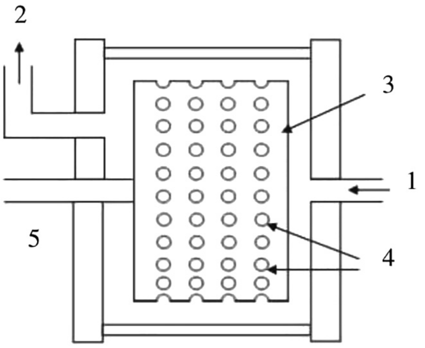


Fig. 9. Schematic of the cavitating device (stator and rotor assembly) [49]. 1 –inlet; 2 – outlet; 3 – rotor; 4 – indentations; 5 – gear shaft.

rates, the conversion of triglycerides increases with the number of holes in the plate. This is due to the fact that the frequency and intensity of turbulence increase for the plates having a large number of small holes. Similar results were obtained by Kumar [53] and Braeutigam [54].

3.5. Hydrodynamic cavitation reactors with a moving element

Hydrodynamic cavitation can also be generated by specially designed rotational devices, such as high pressure or high speed homogenizers [55] and cavitation reactors [23,27,39,49,56]. In such devices, generation of cavitation bubbles is possible due to fast rotations (2200–8000 rpm) and appropriate design of the rotor (arrangement of grooves) (Fig. 9). Compared to conventional methods of cavitational treatment which make use of Venturi tubes, orifice plates or ultrasounds, homogenizers and cavitation reactors are characterized by a low degree of control of the cavitational process. Furthermore, these devices are energy-intensive [55], which in view of the volume of effluents being treated results in high cost of the treatment. Consequently, the use of such devices on an industrial scale is unprofitable and unpopular [57].

During rotations of the rotor, whose surface has a number of indentations, very high surface velocities are created at the surface of the liquid. Liquid at this high velocity enters the indentations and when it leaves them a very low-pressure region is created near the surface of the indentations. The pressure near the surface falls below liquid vapor pressure resulting in the inception of cavitation [49,56].

With an increase in rotational speed of the rotor, the local energy dissipation rate and the intensity of turbulence also increase, which increases the cavitational intensity [49]. After exceeding the critical speed of the rotor, the cavitation number decreases as a result of supercavitation. At higher speeds, a very large number of cavities are generated, which tends to dampen the collapse energy released by the neighboring cavities and lowers the degradation efficiency. In addition, an excessive number of cavities in the system limits diffusion in the direction of implosion event also reducing the degradation rate. A similar phenomenon of occurrence of the optimum rotational speed, below and above of which the degradation efficiency is reduced, was also observed by other authors using cavitation rotors [23,27,39,49,55,56].

The main problem with cavitation rotors is their high-power consumption needed to move them with an appropriate rotational speed [23,55]. This is not an issue on a laboratory scale but in treatment of industrial effluents in volumes often expressed in thousands of m^3 the energy demand is too high and the process becomes unprofitable. It follows from our calculations that 1 J of electric energy allows lowering of COD of 4 L of an effluent by just 0.0023 mg in 20 min, which can be a problem with large effluent volumes. Similar conclusions were drawn by Jyoti [55].

3.6. Acoustic cavitation reactors

Acoustic cavitation reactors use ultrasound energy for the inception of generation of cavities. Ultrasounds are the source of energy which enables the initiation of a cavity growth followed by its collapse which is accompanied by a local increase in pressure and temperature of a solution. Moreover, the generation of an acoustic wave in solution brings about occurrence of local turbulence and microcirculation of fluid, so-called acoustic streaming which further aid physicochemical processes taking place in solution, largely limiting the mass transfer resistance [25]. Phenomena of this type improve the efficiency of generation of hydroxyl radicals and transport of molecules of liquid and contaminants present in it near the collapsing cavities, which results in the effective degradation of organic pollutants (Table 3).

Acoustic cavitation reactors have found a widespread use, among others, in chemical synthesis, biotechnology, treatment of waste streams, degradation of polymeric materials and in the petrochemical industry [58]. When used for waste water treatment, acoustic cavitational reactors presently ensure one of the highest degrees of removal of organic pollutants [59,60]. The efficiency of the process depends largely of the number and type of transducers used, the frequency range (most often 20–520 kHz), amperage (up to 70 A) and the arrangement of transducers in the reactor [5,55,61]. This ensures high cavitational intensity and acoustic streaming. Two types of acoustic cavitational reactors are used most often. They differ with respect to the type and placement of the transducer. The first type is a reactor with an immersed ultrasonic probe (called ultrasonic horn) [62–64]. The cylindrical probe is directly immersed in solution. Most frequently, the probe made of a conducting metal, such as titanium, through vibrations caused by the power supply sends the acoustic wave to the solution. Focusing the energy of the wave on a small surface area of the probe results in the inception of acoustic cavitation through local increases/decreases of pressure and temperature of the solution. The second type of an acoustic cavitational reactor is ultrasonic bath. In this case transducers are placed beneath the container with a solution and the ultrasound energy reaches the medium indirectly through the walls of the container [65]. Detailed investigations of different configurations of sonochemical reactors were described by Csoka et al. [66]. It was demonstrated that the area of irradiation of the probe generating the acoustic wave affects the effectiveness of the transducer. The closer the transducer is to the solution, the better its efficacy is. Therefore, the best distribution of the cavitational activity in the bulk solution is obtained for the reactors with an ultrasonic longitudinal horn. The number and arrangement of transducers in sonochemical reactors should be selected based primarily on the reactor diameter and the height of a liquid inside it. Most often, the power supplied to the solution ranges from 0.03 to 200 W/l [37,58,59]. It is then possible to achieve the maximum cavitational yield distributed throughout the entire solution which improves the effectiveness of removal of organic pollutants [58].

The majority of sonochemical reactors used on a laboratory scale has just one transducer which limits the possibility of distributing cavitation throughout the entire solution. In such a case, even in reactors with the probe immersed directly in solution the cavitation bubbles are generated only in the immediate vicinity of the transducer, making the effectiveness of the physicochemical processes insufficient. Application of a greater number of transducers solves this problem. The transducers can operate with the same frequency of vibrations or the frequencies can be different. An example of such an approach is the sonochemical reactor designed by Parvizian [67], containing four high frequency piezoelectric transducers with a 2.5 cm diameter, operating at 1.7 MHz and installed at the reactor bottom in a way that the fluid was in direct contact with them. This design significantly improved macro- and micromixing of the entire solution compared to the reactor with just one transducer which demonstrates the effect of the number of transducers on the efficiency of acoustic cavitation.

In addition to the number of transducers, the efficiency of acoustic cavitation is also affected by their arrangement. An increase in intensity and power of the acoustic wave through combination of several transducers often requires a new design of sonochemical reactors. Gogate [68] designed a hexagonal reactor with eighteen transducers to improve the degradation of formic acid. Compared to conventional sonochemical reactors, the hexagonal reactor offered an improved distribution of cavitation in three dimensions. Furthermore, cavitational yield and energy efficiency of oxidation of formic acid increased by a factor of four relative to the reactor with an ultrasonic horn and twofold with respect to the process carried out in an ultrasonic bath.

The number and arrangement of transducers in sonochemical reactors should be selected primarily on the basis of reactor diameter and liquid level [58].

3.7. Summary and comparison of degradation effectiveness of selected pollutants using various cavitation equipment

An interesting comparison of the effectiveness of disintegration of bacterial cells using four cavitational devices: high speed homogeniser, high pressure homogeniser, sonochemical reactor and cavitating ball valve was discussed by Jyoti et al. [55]. It was demonstrated that the selection of an optimum pollutant oxidation method should include both economic and process factors (effectiveness, rate, and complexity of oxidation) for a particular effluent volume and type of pollutant.

In the case of high speed homogenization, the maximum disinfection (*ca.* 92%) was achieved at a speed of rotation of 8000 rpm and the time of treatment equal to 20 min [55]. Below these values the effectiveness of generation of cavities was insufficient while above these values the excessive number of cavities limited the collapse energy through dampening effect. In high pressure homogenization, the maximum extent of disinfection (*ca.* 87%) was obtained at discharge pressure of 340.5 atm and the maximum time of treatment [55]. For pressures lower or higher than the optimum one, a drop in the disinfection extent was observed, similarly to high speed homogenization. This effect was explained by the authors as a result of exceeding critical pressure/speed conditions of homogenizers. As the pressure/speed is increased beyond a certain value, the intensity of cavitation also increases; however, due to the corresponding increase in the velocity the residence time (time spent in the cavitational zone) decreases and bacteria can only be partially affected (paralyzed) leading to the decrease in destruction rate. Moreover, above certain pressure/speed values, supercavitation takes place thus limiting the collapse energy. On the other hand, insufficient pressure/speed in the homogenizer lowers the cavitation intensity resulting from too low collapse energy and too small a number of cavities to destroy a bacterial cell.

In the case of hydrodynamic cavitation generated by the cavitating ball valve and ultrasonication the highest degree of disinfection was obtained at 5.1 atm pressure and time of 1 h (44%) and at 22 kHz frequency, 230 W power and 20 min time (85%), respectively [55]. A comparison of rate constants of disintegration for various equipment reveals that the fastest and at the same time most effective method of destruction of bacterial cells is sonochemical cavitation (rate constant $k = 0.06\ [s]^{-1}$), while the least effective method is hydrodynamic cavitation with the cavitating valve ($k = 0.1 \cdot 10^{-6}\ [s]^{-1}$). However, this conclusion is valid only for high concentration of bacterial cells in the treated medium. At lower concentrations or larger volumes of the treated medium, sonochemical cavitation has the lowest overall destruction rates. This is mostly due to a limited area covered by the ultrasonic horn. Thus, the cavitational effect is very high but restricted to the tip of the horn. In the case of high speed and high-pressure homogenizers as well as hydrodynamic cavitation, the liquid is forced to pass through the cavitational zone and individual bacterial cells pass through the disinfection zone several times, thus improving the extent of their destruction. In hydrodynamic cavitation, the liquid goes through the cavitating valve many times causing significant disinfection.

In terms of energy consumption for the various cavitating equipment, the disinfection carried out in a high-speed homogenizer seems to be the best [55]. The number of bacterial cells destroyed per 1 J of energy in this case is equal to 23. For comparison, the respective values for hydrodynamic cavitation with the ball valve, ultrasonic horn and high-pressure homogenizer are 13, 1, and 3. However, in terms of actual energy dissipated which accounts for the energy dissipation efficiency of the equipment (conversion of electrical to mechanical), the hydrodynamic cavitation with the cavitating valve operation at 5.1 atm pressure seems to be the most energy efficient. For this process, the number of destroyed bacterial cells per J of energy dissipated is 310 whereas for sonochemical cavitation, high speed and high-pressure homogenizers the respective values are 45, 55 and 5 CFU killed/J. Based on equipment's electrical/mechanical efficiency, the actual energy dissipated for hydrodynamic cavitation was 32 J/mL while for the other three devices it was greater than 200 J/mL. These calculations lead to a simple conclusion. For treatment of low volumes of effluents, the most economical method in terms of electrical energy consumption involves the high-speed homogenizer whereas for high volumes of industrial effluents the most economical treatment method is hydrodynamic cavitation [69].

The authors using cavitation rotors in treatment of a variety of organic pollutants emphasize that in addition to Venturi tubes and orifice plates cavitation rotors are the most economical method for treatment of aqueous media [49,55,56]. However, if treatment time is of primary importance, the best choice for treatment method is sonochemical cavitation, providing the greatest extent of degradation in the shortest time [49,55]. On the other hand, hydrodynamic cavitation provides the lowest energy consumption. Consequently, the choice of a specific treatment method should depend on which process parameter is of primary importance.

The best method of treatment of high volume of industrial effluents in terms of energy consumption and the number of passes of treated medium through the cavitation zone seems to be hydrodynamic cavitation using a Venturi tube or an orifice plate. Comparing the use of the two methods for specific groups of pollutants one can select the most effective way of cavitational treatment.

Pradhan and Gogate [70] investigated the effectiveness of degradation of *p*-nitrophenol using a Venturi tube and an orifice plate. The Venturi tube had a 12-mm diameter with a throat diameter of 2 mm and an angle of divergent section of 6.4° with a total length of 73 mm while the orifice plate of diameter 25 mm had a single hole with a 2-mm diameter. The two cavitating devices operated at the same inlet pressure. The highest degree of degradation of *p*-nitrophenol was obtained for the highest inlet pressure (2.9 atm) for both the Venturi tube and the orifice plate for the initial concentration of 5 g/L. The observed increase in the extent of removal with an increase in the inlet pressure at various initial concentrations can be attributed to enhanced cavitational activity. The results obtained for 0.5% solution of *p*-nitrophenol revealed that the extent of removal was marginally higher for the Venturi tube (53.4%) than for the orifice plate (51%). The authors attributed this to the fact that at the same operating pressure, the liquid velocity in the Venturi tube (35.5 m/s) is higher than in the orifice plate (21.28 m/s) and hence the number of passes through the cavitation zone will be larger in case of the Venturi tube. The cavitation number is also smaller for the Venturi tube (Venturi tube $C_v = 0.15$; orifice plate $C_v = 0.43$) which results in the increased cavitational intensity. Thus, the orifice plate with a single hole is inferior in the removal of *p*-nitrophenol compared to the Venturi tube. Similar results were obtained by Patil et al. [71] who investigated the effectiveness of removal of an insecticide imidacloprid using hydrodynamic cavitation generated by venturi and orifice plate and carried out under the same operating conditions.

The next example are studies by Badve et al. [38] who disinfected seawater using hydrodynamic cavitation generated by circular and rectangular slit venturi as well as orifice plate. The orifice plate of diameter 25 mm had a single hole with a 2-mm diameter, the cylindrical venturi had a diameter of 18 mm, throat diameter of 2 mm, half angle of divergent section equal to 6.5° and a total length of 106 mm while the slit venturi had a convergent length of 18 mm, dimensions of throat were 3.7 × 0.92 × 0.92 mm, half angle of divergent section was 6.5° and a total length was equal to 86 mm. A maximum of 50 passes of seawater through the cavitating devices were carried out. It was found that the extent of disinfection increased with an increase in inlet pressure up to a certain value above which it decreased as a result of supercavitation. In the absence of cavitation, the sum of pressure and velocity head at the constriction should be equal to pressure head downstream. However, when cavitation takes place, some of the energy is utilized in the generation of the vapor phase. The difference in energy of the medium before and after the constriction determines the force and number of collapsing gaseous bubbles. The higher the inlet pressure, the greater the difference in energy and the greater the intensity of cavitation. For the same inlet pressure, the extent of disinfection was found to be different for different cavitational devices. At 2.96 atm, cavitation numbers obtained for orifice plate, circular and slit venturi were 0.6, 0.2 and 0.1, respectively. The cavitation intensity is much lower for the orifice plate than for the circular and slit venturi which can be attributed to much lower velocity of the fluid in the orifice plate. The Venturi tubes generate a greater number of cavitational events with a higher collapse energy which results in an improved extent of disinfection (Venturi tubes *ca.* 40%, orifice plate *ca.* 12%). It was found that the extent of disinfection obtained with Venturi tubes depended on the ratio of the perimeter of the venturi to the cross-sectional area of its constriction [72,73]. An increase in this ratio caused increased cavitational intensity and efficiency. The numerical values of the ratio for the slit and circular venturi were 15.8, and 4, respectively. Therefore, at the same inlet pressure a higher extent of disinfection was observed for the slit venturi, which is recommended for water disinfection. Similar results for the esterification reaction were obtained by Maddikeri et al. [74] who used the same geometrical parameters of Venturi tubes as Badve [38]. The highest yield was obtained when using a slit Venturi tube which ensures high cavitational efficiency.

4. Effect of process parameters on effectiveness of removal

4.1. Physicochemical properties of pumped medium and initial radius of cavity initiating cavitation

Physicochemical properties of the pumped liquid are among the most important parameters determining the intensity of hydrodynamic cavitation and thus the degree of removal of pollutants. In addition, physicochemical properties of the liquid determine the initial bubble radius which also affects the extent of decomposition and has to be taken into consideration during selection of optimum operating conditions. Energy of collapse of cavities was found to be inversely proportional to the initial bubble radius [75,76]. It is thus advantageous to carry out the process at a high inlet pressure which ensures generation of cavities with the smallest size. This means that physicochemical parameters of the treated effluent should be closely controlled.

The parameters having the greatest effect on cavitational treatment include primarily [77]:

- vapor pressure of treated,
- viscosity,
- temperature,
- surface tension,
- presence of dissolved gases,
- presence of other components, such as surfactants.

Vapor pressure of the treated medium is one of the most important parameters determining the intensity of cavitation. The number of cavities in the reaction system increases with an increase in vapor pressure of the treated. However, the increase in vapor pressure also increases the amount of pollutants in the gaseous phase. Volatile pollutants upon evaporation move into cavities resulting in their excessive accumulation and lowering the number of collapsing bubbles which lowers the extent of removal of pollutants. Senthilkumar [78] demonstrated that in the case of acoustic cavitation an increase in vapor pressure of the treated medium results in a decrease in collapse energy of individual cavities. This can be attributed to an increase in critical cavity radius which lowers the collapse energy. Furthermore, the lifetime of cavitation bubbles increases resulting in a decrease in the extent of pollutant degradation through limitation of the number of cavitational events. The same effect takes place in hydrodynamic cavitation. Interesting results were presented by Mujumdar [79] and Pandit who observed a decrease in the extent of removal of fumaric acid with an increase in vapor pressure of the treated medium by using a mixture of ethanol and water.

Thus, the efficiency of oxidation of pollutants depends to a large extent on the kind of medium in which they are present. When using hydrodynamic cavitation for destruction of bacterial cells in disinfection processes, the best efficiency is achieved at the lower collapse intensities of cavities. The lower collapse energy of cavities allows a more effective disruption of bacterial cells. Consequently, the removal of pollutants requiring lower cavitational intensity, such as simple organic compounds, is best achieved in media having a high vapor pressure whereas for complex organic compounds, requiring high collapse energy to break stable covalent bonds, media with a low vapor pressure are preferred.

The next physicochemical parameter of the treated medium affecting the efficiency of pollutant removal by cavitation is viscosity. Cavitation occurs in a medium when the cohesive forces ensuring continuity of a stream in a fluid are overcome. An increase in this force causes an increase in energy and critical pressure required for the inception of cavitation. After overcoming cohesive forces, it no longer has a major effect on the change in pressure at which cavitation bubbles will collapse.

Senthilkumar [78] performed a numerical simulation of treatment of a variety of viscous liquids in a sonochemical reactor. The author demonstrated that for Newtonian fluids, in which the viscous stresses arising from their flow are directly proportional to the local strain rate, an increase in viscosity of a liquid in a sonochemical reactor does not significantly change the collapse pressure of cavities. For these fluids, it is possible to achieve the maximum cavitational effect. Viscous liquids slightly increase the minimum collapse pressure which can be attributed to an increase in critical pressure needed for the inception of cavitation and overcoming cohesive forces. A slightly higher critical pressure is equivalent to a smaller number of cavitational events which can lead to a substantial decrease in the extent of degradation for a large volume of effluents. Therefore, liquids having a relatively high viscosity will have a much lower cavitation efficiency than liquids with a low viscosity when treating large volumes of effluents. The effect of viscosity on a decrease in cavitation efficiency is even more pronounced for non-Newtonian fluids. Consequently, the maximum cavitational effect can only be achieved for liquids with a low viscosity, such as water.

Surface tension of the pumped medium is the next parameter affecting cavitation efficiency. Liquids characterized by a high surface tension, *e.g.,* water ($\sigma = 0.072\,\mathrm{Nm}^{-1}$ at 20 °C) can achieve the maximum cavitation intensity. The cavities collapse with a higher energy and the number of cavitational events is much greater than in the case of organic liquids, such as glycerol ($\sigma = 0.0637\,\mathrm{Nm}^{-1}$ at 20 °C), acetone ($\sigma = 0.0237\,\mathrm{Nm}^{-1}$ at 20 °C) or ethanol ($\sigma = 0.0223\,\mathrm{Nm}^{-1}$ at 20 °C). Surface tension of a liquid affects primarily the size of stable bubbles which occur in the treated medium during cavitation. The pressure inside the bubble is equal to the outside pressure plus the surface tension. The critical radius at which a stable condition is possible is described by the following equation [77]:

$$R_c = \sqrt{\frac{3GT}{2\sigma}} \tag{3}$$

where G is a measure for the amount of gas in the nucleus; T – temperature of a medium; σ is the surface tension of the liquid.

The higher the surface tension of a liquid, the higher the pressure needed for the generation of a gaseous bubble in accordance with the principle of action of surface tension forces ($dP = 2\sigma/R$; dP – pressure difference, σ – surface tension, R – radius of a gaseous bubble). A higher pressure results in a smaller radius of the bubbles initiating cavitation which entails a higher collapse energy of cavities and a greater number of cavitational events affecting the efficiency of the process. At a high surface tension, the collapsing bubbles are split into smaller fragments which initiate another cycle of generation of cavities. This effect is often considered as negative because the generation of cavities is difficult to control which brings about a large number of cavitational events and can cause damage of the equipment. The effect can be eliminated by an addition of even a small amount of a surfactant.

Senthilkumar [78] demonstrated that an increase in surface tension of a liquid from 0.2 $\mathrm{Nm^{-1}}$ to 0.7 $\mathrm{Nm^{-1}}$ causes an increase in pressure of collapsing bubbles from 20 to about 80 atm. Thus, in order to achieve the maximum cavitation efficiency, the reactions should be carried out in a medium having high surface tension.

4.2. Inlet pressure

Inlet pressure of a treated medium is among the most important parameters determining the efficiency of treatment. The pressure at which a medium enters the constriction causing the inception of cavitation determines the intensity of generation of cavities. In turn, the intensity of generation of cavities determines the extent of degradation of pollutants present in a treated medium. Cavitation is most often described by the cavitation number which includes pressure as an important parameter.

Cavitation number expresses the intensity of cavitation process through the following equation:

$$C_V = \frac{P_2 - P_V}{(1/2)\rho v_o^2} \tag{4}$$

where P_2 is the recovered pressure downstream of the constriction, P_v is the vapor pressure of the liquid, v_o is a velocity at the throat of the cavitating constriction and ρ is the density of the liquid.

An increase in inlet pressure of a medium increases its velocity which reduces the cavitation number. The smaller the cavitation number the greater the number of cavities generated. However, after exceeding a certain inlet pressure value, the extent of degradation of pollutants decreases due to coalescence of cavities which form a so-called cavity cloud thereby decreasing the collapse intensity of individual cavities. This phenomenon is called choked cavitation and it had been described earlier in more detail [80].

A similar effect of decrease in the extent of degradation of organic pollutants present in the aqueous medium and resulting from exceeding limiting inlet pressure values has been described in a number of papers. A narrow range of inlet pressures was observed over which the extent of degradation increased nearly linearly. However, after exceeding the limiting value of inlet pressure, a sharp drop in the extent of degradation was found.

An example of this effect can be found in studies by Chakinala et al. [10]. The effect of inlet pressure of an industrial effluent pumped into a cavitation reactor on the extent of degradation of pollutants expressed as total organic carbon (TOC) was investigated over a pressure range from 47.63 to 102.07 atm. The extent of degradation was found to increase from 39% at 47.63 to 51% at 102.07 atm. Above 102.07 atm the extent of degradation decreased rapidly which can be attributed to choked cavitation.

Similar results were published by Raut-Jadhav et al. [16] who investigated the extent of degradation of a neonicotinoid insecticide Imidacloprid using hydrodynamic cavitation combined with advanced oxidation processes. The investigations were carried out in a narrow pressure range from 4.93 to 19.74 atm. The rate of degradation of the insecticide was found to increase almost linearly with inlet pressure up to 17.27 atm and decrease at the inlet pressure of 19.74 atm. However, increasing the inlet pressure beyond 17.27 atm slightly reduced the extent of degradation of Imidacloprid due to choked cavitation.

The results of studies by Gore et al. [81] on the effect of inlet pressure of a medium in cavitation process on the extent of degradation of orange 4 dye also demonstrated a range of inlet pressures over which the extent of degradation increased. The inlet pressures ranging from 2.96 to 7.9 atm were investigated. The extent of dye degradation was found to increase with an increase in the inlet pressure reaching a maximum at 4.93 atm (37.23% decolorization of the dye) followed by a decrease. The authors attribute this effect to choked cavitation whereby at inlet pressures above 4.93 atm the cavities coalesce forming larger vaporous bubbles which are carried away with the flowing liquid without collapsing. The lack of collapsing cavities results in a rapid decrease in the number of hydroxyl radicals and thus the extent of degradation.

According to the literature data, cavitation takes place when the cavitation number is equal to or less than one. Cavitation can also start at a cavitation number greater than 1 due to the presence of dissolved gases and/or solid particles which act as pre-nuclei and thus accelerate the cavity formation. Many reports indicate that with a decrease in cavitation number below 1, more cavities are formed, eventually resulting in the formation of a cavitation cloud. At this point, the optimum treatment conditions can be achieved [80,82]. Consequently, effluent treatment by cavitation is often carried out at inlet pressures yielding cavitation numbers from 0.1 to 1.

4.3. Hydrogen ion activity

Hydrogen ion activity is another important parameter determining the efficiency of degradation of pollutants in an aqueous medium by hydrodynamic cavitation. As was the case with the inlet pressure, also in this case there are optimum pH conditions for which a high degradation rate is obtained. However, to a large extent it depends on the nature of pollutants and most often the pH is selected by experiment.

According to literature reports, there is no specific range of pH values at which degradation should take place for a particular pollutant in the aqueous medium. Degradation of organic pollutants is most often carried out in an acidic medium (pH < 7). Acidic conditions were found to promote more efficient generation of hydroxyl radicals, mostly through intensified dissociation of hydrogen peroxide and autoprotolysis of water [3]. Furthermore, the oxidation capacity of hydroxyl radicals is higher under acidic condition. This can be attributed to a lower rate of recombination reaction of hydroxyl radicals which is only possible under acidic conditions [70,71].

An example confirming a positive effect of acidic pH on the efficacy of generation of hydroxyl radicals and thus the extent of degradation of contaminants are studies by S. Raut-Jadhav et al. [12]. The effect of pH in the range of 2–6 on the extent of degradation of a pesticide methomyl using hydrodynamic cavitation generated by a Venturi tube was investigated. The extent of degradation of the pesticide was found to increase almost linearly with an increase in acidity of the treated medium according to the first-order kinetics. The rate of degradation of methomyl of $0.72 \times 10^{-3}\,\mathrm{min^{-1}}$ at pH 6 was increased to $22.7 \times 10^{-3}\,\mathrm{min^{-1}}$ by reducing the solution pH to 2.5. However, a further increase in acidity of the solution (at pH 2) the rate of degradation of methomyl slightly decreased. Consequently, pH 2.5 was used as the optimal value. The authors attribute this effect to the fact that acidic conditions favor the generation of hydroxyl radicals by suppressing their recombination reactions. Thus, a greater number of hydroxyl radicals is available at the cavity-water interface for the oxidation of methomyl resulting in increased degradation rates. Similar conclusions were reached by Pradhan and Gogate [70] who investigated the effect of pH on the efficiency of oxidation of *p*-nitrophenol by hydrodynamic cavitation aided by oxidants: hydrogen peroxide and iron (II) sulfate. The extent of removal of *p*-nitrophenol was found to drop from 62.3% at pH 3.75 to 35.7% at pH 8. The effect was attributed to the fact that alkaline conditions hinder decomposition of hydrogen peroxide thus decreasing the concentration of hydroxyl radicals. On the other hand, under acidic conditions decomposition of hydrogen peroxide is more effective and the concentration of hydroxyl radicals, which are responsible for oxidation of *p*-nitrophenol, increases.

Operating parameters for the oxidation of microbiological contaminants are quite different. Treatment aimed at a removal of microorganisms from an aqueous medium is usually carried out under alkaline conditions (pH > 7) [49]. Alkaline conditions improve transport of oxidants into the interior of microorganisms by weakening cell membranes. Moreover, a high pH favors reactions between hydroxyl radicals and phospholipids forming the cell membranes causing their disruption and disintegration of the entire cell. Hydroxyl radicals at an alkaline pH are also more effective in breaking bonds present in metabolic enzymes and responsible for proper functioning of an organism, and in destruction of DNA [83,84].

Examples of efficient degradation of microbial contamination under basic conditions are provided by Badve et al. [38] and Filho et al. [25]. Badve et al. investigated the effect of hydrodynamic cavitation combined with chemical oxidants on degradation of bacteria present in ballast seawater. The process was carried out at different pH values ranging from 4 to 10. The efficacy of disinfection was found to increase with an increase in pH of the seawater. During a 15-min treatment the% disinfection at pH 4 and 10 was equal to 38 and 56%, respectively. The authors attribute this favorable effect of alkaline pH to lethal effects of hydroxide ions to bacterial cells, such as destruction of phospholipids of cell membranes resulting in disintegration of bacterial cells.

4.4. Temperature

Water vapor pressure depends significantly on temperature of the treated medium, increasing exponentially with temperature. Generation of the cavities becomes more intense with an increase in temperature which adversely affects degradation of contaminants when using cavitation alone [50].

According to literature reports, an increase in temperature results in a decrease in cavitation rates due to excessive generation of gaseous bubbles and, consequently, lower energy of their collapse (attenuating effect) [85–88]. The effect of temperature on the degradation rate when using hydrodynamic cavitation alone depends mainly on two opposing phenomena. The first one is related to kinetics of the reactions (increase in their rate) which is advantageous; however, the second one causes the reaction rates to decrease due to the increased solvent vapor pressure inside the bubbles which attenuates the efficacy of cavitational collapse [17].

An increase in temperature decreases the efficiency of cavitation due to formation of an excessive number of the cavities which is related to cavitation suppression and the formation of so-called cloud cavitation.

An example of this effect was provided by the investigations of Wu et al. [89], who observed a decrease in the extent of degradation of chlorocarbons with an increase in temperature of the treated medium when using hydrodynamic cavitation alone. The authors attributed this effect to an increase in volatility of solutes in the treated medium and the formation of an excessive number of the cavities which suppresses degradation by decreasing collapse of the individual cavities.

On the other hand, an increase in temperature favorably affects the kinetics of reaction of oxidation of contaminants by increasing the rate of reaction. Furthermore, the contaminants can get inside the cavities due to increased volatility and degradation during the collapse of the cavitational bubbles. As a result of these opposing effects, it is essential to optimize temperature for specific contaminants and treatment (cavitation only or cavitation combined with additional oxidation). The cost to benefit analysis is important for the treatment to make sure that the increase in extent of degradation at a higher temperature is not outweighed by the cost of heating of the treated medium.

It was demonstrated that if the contaminant has a higher boiling point than the treated medium the effect of decrease in the extent of degradation with an increase in temperature is negligible [71]. In such a case, the change in temperature of the treated medium does not have to be considered during optimization of the treatment process.

When cavitation is combined with advanced oxidation processes, mostly Fenton's reagent, where the kinetics of oxidation plays a more important role then the number of cavitational events, a higher temperature significantly improves the rate of the degradation process [90–93]. Sun et al. [90] demonstrated that the increase in temperature from 20 to 30 °C results in an almost 100% increase in the extent of degradation of *p*-nitroaniline when using Fenton oxidation process. Similar results were obtained by Kavitha and Palanivelu [91] who examined the efficiency of degradation of cresols over a temperature range from 20 to 50 °C using conventional Fenton process. The extent of oxidation of contaminants was higher by 50% for the treatment carried out at 30 °C for 150 min compared with the same reaction carried out at 20 °C. This effect can be attributed to increased oxidation rate of organic contaminants at a higher temperature due to a larger number of hydroxyl radicals generated by Fenton process. Additionally, a decreased force of collapse of the cavitational bubbles at an elevated temperature causes a more efficient generation of hydroxyl radicals in treatments aided by additional oxidants thus enabling more effective oxidation of contaminants.

This conclusion is substantiated by Zhou et al. [94], who observed a stepwise improvement of degradation rate of 2,4-dichlorophenol subjected to acoustic cavitation combined with a Fenton like system with the increase in temperature from 10 to 50 °C. Similar results were described by Sun et al. [95]. A combination of Fenton process and acoustic cavitation for degradation of azo dye Acid black 1 resulted in the increase of degradation efficiency from 92.39% to 99.14% with the increase in temperature from 20 to 40 °C.

4.5. Initial concentration of contaminants

Initial concentration of contaminants present in a treated medium is one of the most important parameters determining the efficiency of degradation process [3]. From the point of view of thermodynamics of reversible reaction an increase of reactant concentration in a system at chemical equilibrium should shift the equilibrium toward more products. Therefore, the increase in concentration of a contaminant in a contaminant-oxidant system at equilibrium should cause the formation of more oxidation products. However, it was observed that actually the increase in pollutant concentration results in lower degradation efficiency of the pollutant, which could be attributed to an insufficient amount of hydroxyl radicals and/or the limited diffusion of hydroxyl radicals out of the interfacial regions of the collapsing cavitational bubbles [71].

The studies confirming the above supposition were carried out by Pradhan and Gogate [70]. The effect of initial concentration of *p*-nitrophenol ($5\,gL^{-1}$ and $10\,gL^{-1}$) on the extent of its removal was investigated using hydrodynamic cavitation combined with advanced oxidation processes – Fenton process and addition of hydrogen peroxide (ensuring the presence of a greater number of hydroxyl radicals in the reaction system) as well as hydrodynamic cavitation alone. When using hydrodynamic cavitation alone it was found that the efficacy of removal of *p*-nitrophenol decreased with an increase in its concentration from 53.4% at $5\,gL^{-1}$ to 44.8% at $10\,gL^{-1}$ at an initial pressure of

2.9 bar. The authors explain that the percent removal of a contaminant will always be higher for its lower concentration due to a smaller number of moles. However, it should be realized that in total the largest number of moles of *p*-nitrophenol was oxidized at its highest concentration, *i.e.* 10 gL^{-1}. Similar results were obtained for hydrodynamic cavitation aided by addition of hydrogen peroxide (5 gL^{-1}) where the greatest extent of removal of *p*-nitrophenol (59.9%) was obtained at its lowest concentration. For the higher initial concentration, the extent of removal dropped to 54.1%. When hydrodynamic cavitation was combined with addition of hydrogen peroxide and Fenton process (1 gL^{-1} $FeSO_4$ + 5 gL^{-1} H_2O_2), the efficacy of removal of *p*-nitrophenol was 61.8% and 53.1% for concentrations of 5 gL^{-1} and 10 gL^{-1}, respectively. Similar results of a decrease in extent of removal of contaminants with an increase in their initial concentration when using hydrodynamic cavitation were reported by Chakinala et al. [61] and Adewuyi [96].

A substantial increase in concentration of a contaminant subjected to oxidation by hydrodynamic cavitation combined with advanced oxidation processes weakens the cavitational effect by suppressing collapse of the gaseous bubbles and hindering the reactions yielding reactive hydroxyl radicals [97]. A larger amount of a contaminant in the reaction system causes diffusion of hydroxyl radicals out of the interfacial regions of the collapsing cavitation bubbles, thus limiting their oxidizing effects and lowering the extent of the treatment process [60].

A decrease of efficiency of degradation with higher concentrations of contaminants due to suppressed collapse of the cavitation bubbles and diffusion of hydroxyl radicals out of the interfacial regions of the collapsing cavities is observed for both hydrodynamic and acoustic cavitation. For example, Neppolian et al. [60] demonstrated that an increase in initial concentration of methyl *tert*-butyl ether from 0.0284 to 0.284 mM resulted in an almost 40% decrease of reaction rate when using an ultrasonic reactor operating at 20 kHz.

Similar results were presented by Özdemir et al. [98]. The effect of initial concentration of a dye RY 145 (50, 125, 250 mgL^{-1}) on the efficiency of its degradation was investigated when using acoustic cavitation combined with Fenton process. Approximately 95% of the degradation was achieved at the lowest concentration. When the initial concentration was increased to 250 mgL^{-1}, the extent of degradation significantly decreased to 71%. A decrease in efficacy of degradation of contaminants due to the increase in their initial concentration when using acoustic cavitation was also described by Babuponnusami and Muthukumar [99], who examined degradation of phenol and Wang et al. [100] investigating the degradation pathway of azo dye reactive brilliant red K-BP.

On the basis of the above results it can be concluded that that the best efficiency of degradation of contaminants by hydrodynamic cavitation or acoustic cavitation combined with advanced oxidation processes is achieved at their low initial concentrations. This is not a problem when treating solutions on a laboratory scale because the solutions can be readily diluted. On the other hand, dilution can become a serious problem on an industrial scale where effluents can have volumes in the order of 10^6 m^3. Initial concentration is one of the more important process parameters affecting the extent of removal of contaminants. However, selection of an appropriate dilution should be preceded by laboratory studies and it should have definite advantages. From the industrial viewpoint, the costs of dilution of effluents should be compared with the increase in efficiency of degradation because dilution of effluent does not always guarantee a significant improvement in the efficiency of degradation. In addition, this practice is not recommended by green chemistry principles. The preferred method of improvement of the extent of degradation involves an increase in intensity of cavitation resulting from optimization of other significant process parameters [71] instead of lowering initial concentration of a contaminant.

4.6. Addition of oxidants

Aiding the cavitation process by addition of various oxidants can greatly improve the efficiency of degradation of organic pollutants. The addition of oxidants to the treated medium increases the rate of generation of highly reactive hydroxyl radicals which are responsible for oxidation and degradation of pollutants. To a large extent, the efficiency of this process depends on the amount of added oxidant.

When using advanced oxidation processes, the decomposition of hydrogen peroxide (H_2O_2) is often used as the source of hydroxyl radicals. Among others, it plays a special role in the Fenton process [101]. The optimum amount of hydrogen peroxide added in this process is usually determined experimentally because insufficient amount of the oxidant results in a substantial decrease of the extent of removal of a pollutant due to insufficient amount of hydroxyl radicals generated in the process of catalytic decomposition of H_2O_2 (Eq. (5)) and participating in the degradation reactions [85].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\cdot} \quad (5)$$

On the other hand, addition of excessive amount of hydrogen peroxide also lowers the efficiency of degradation of a contaminant. This is mostly due to the formation of radicals with a significantly lower oxidation potential than hydroxyl radicals as a result of secondary reactions of hydroxyl radicals with hydrogen peroxide (Eqs. (6)–(9)) [16,29,71].

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2 \quad (6)$$

$$H_2O_2 + OH^{\cdot} \rightarrow HO_2^{\cdot} + H_2O \quad (7)$$

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \quad (8)$$

$$OH^{\cdot} + O_2 \rightarrow HO_2^{\cdot} + O^{\cdot} \quad (9)$$

The effect of decrease or increase of degradation efficiency resulting from various amounts of oxidant added to the treated medium is best seen during preliminary treatment of effluents using the Fenton reagent. The use of Fenton process during pretreatment of an effluent allows a significant reduction of the amount of pollutants by lowering of total parameters such as BOD (biochemical oxygen demand) or COD (chemical oxygen demand). However, this is possible only when proper mole ratios of the reactants are chosen. An excessive amount of hydrogen peroxide results in a significant decrease of performance of microorganisms used in the subsequent stages of biological treatment, thus drastically lowering the extent of degradation [101]. Furthermore, under industrial conditions an increase in the amount of oxidant during treatment of millions m^3 of effluents causes very high production costs. According to the data presented by Grupa Azoty in their financial report for 2014, the average price of hydrogen peroxide in Europe was 900–1000 EUR/ton. Another problem caused by an excessive amount of oxidant during effluent treatment are neutralization reactions (Eq. (7)), resulting in depletion of hydroxyl radicals through reactions with excess hydrogen peroxide [102–108]. This effect significantly reduces the extent of removal of organic contaminants.

When determining the dose of hydrogen peroxide needed to lower pollutant load of an effluent, the kind and concentration of contaminants present in the effluent should be considered. All theoretical calculations should take into account stoichiometry of the reaction and tha actual dose should be slightly larger [101].

The feeding mode of an oxidant to the reaction system is also important. Addition of a specific amount of oxidant can be done stepwise which often improves the efficiency of treatment as exemplified by the study of Zhang et al. [107]. The efficiency of treatment of landfill leachate using the Fenton process with hydrogen peroxide being added stepwise. The stepwise addition of hydrogen peroxide to the reaction system was found improve the efficiency of pollutant removal by 15.6% compared to the single-step addition. Similar results were presented by Gan and Lee [108] who investigated the efficiency of removal of

Rhodamine B using the Fenton process with various amounts of hydrogen peroxide (0.49–2.94 mM) added stepwise. It was demonstrated that after 40 min of the treatment at a H_2O_2 concentration of 0.98 mM almost a 90% decomposition of the dye in the treated medium was achieved.

Stepwise dosage of an oxidant responsible for generation of hydroxyl radicals prevents sudden increases in concentration of hydrogen peroxide which promote depletion reactions described by Eq. (5). Then hydroxyl radicals can freely react with pollutants improving the extent of degradation. Moreover, stepwise addition of hydrogen peroxide prevents its uncontrolled decomposition especially under basic conditions. In acidic media hydrogen peroxide is stable; however, a single-step addition of a large amount of H_2O_2 brings about considerable losses due to uncontrolled decomposition reactions [104]. As a result, the efficiency of oxidation at low concentrations of the oxidant is often comparable to that achieved at much higher concentrations [108].

Ozone is another oxidant added to a treated medium to improve the extent of removal of pollutants. Ozone dissolved in an aqueous medium has a high oxidation potential (2.08 V), which allows degradation of a wide variety of organic pollutants containing in their structure, among others, double bonds (C=C, N=N, C=N) [33,55].

The use of ozone in conventional methods of wastewater treatment is very limited due to its properties and a number of parameters affecting the efficiency of degradation of contaminants, including [81]:

- occurrence of local mass transfer resistance,
- effect of pH on the course of reaction,
- selective nature of redox reactions,
- high production cost.

However, combination of ozonation with an additional physical process, such as hydrodynamic or acoustic cavitation allows elimination of the majority of these problems and a substantial improvement of the efficiency of degradation compared to ozonation alone. This is exemplified by studies by Gogate and Patil [17] who compared the efficiency of degradation of an organophosphorus insecticide triazophos by ozonation combined with hydrodynamic cavitation and by ozonation alone. It was demonstrated that the combination of hydrodynamic cavitation and ozonation improved the percent degradation of triazophos from 56.36% (ozonation only) to 86.68% (ozonation combined with hydrodynamic cavitation) at an ozone flow rate of 0.576 gh^{-1} and from 70.41% to 89.16% at an ozone flow rate of 1.95 gh^{-1}. Similar increases in the extent of degradation by using hydrodynamic cavitation combined with ozonation compared to separate treatments were reported by Raut-Jadhav et al. [12] and Prajapat and Gogate [109].

Process conditions taking place as a result of initiation of cavitation when using the combined treatment can provide an explanation for the increased efficiency of degradation. The occurrence of local mass transfer resistance is eliminated mainly by the forced turbulent flow of a pumped medium through the constriction [110]. One of the essential parameters affecting the degradation pathway of a pollutant subjected to ozonation is the pH of a solution. Under basic conditions ozone undergoes decomposition yielding various types of radicals with a high oxidation potential (hydroxyl and hydroperoxyl radicals), which improves the efficiency of degradation. In contrast, under acidic conditions ozone has an electronic deficit (acts as an electrophile), which limits direct reactions to those with contaminants having a high electron density, such as alkenes [81]. Thus, under acidic conditions degradation reactions involving ozone are selective. Cavitational conditions (collapse of the cavities) enable pyrolysis of ozone at pH < 7 in the gaseous phase to atomic oxygen which reacts with water molecules yielding reactive hydroxyl radicals (Eqs. (10) and (11), thus limiting the selective nature of the reaction [111–117].

$$O_3 \xrightarrow{T,p} O + O_2 \tag{10}$$

$$O + H_2O \rightarrow 2OH^{\cdot} \tag{11}$$

In the bulk aqueous phase, ozone can be decomposed by hydroxide ions to yield hydroxyl and hydroperoxyl radicals participating in oxidation of the majority of organic contaminants (Eqs. (12)–(18)) [117].

$$O_3 + OH^{-} \rightarrow HO_2^{-} + O_2 \tag{12}$$

$$HO_2^{-} + H^{+} \rightarrow H_2O_2 \tag{13}$$

$$O_3 + HO_2^{-} \rightarrow OH^{\cdot} + O_2 + O_2^{-} \tag{14}$$

$$O_2^{-} + H^{+} \rightarrow HO_2^{\cdot} \tag{15}$$

$$O_3 + OH^{\cdot} \rightarrow HO_2^{\cdot} + O_2 \tag{16}$$

$$O_3 + O_2^{-} \rightarrow O_3^{-} + O_2 \tag{17}$$

$$O_3^{-} + H_2O \rightarrow OH^{\cdot} + OH^{-} + O_2 \tag{18}$$

Hydrogen peroxide formed under cavitational conditions (Eq. (13)) along with ozone allows coupled reactions which also contribute to the formation of reactive hydroxyl radicals (Eqs. (19) and (20)).

$$O_3 + H_2O_2 \rightarrow O_2 + OH^{\cdot} + HO_2^{\cdot} \tag{19}$$

$$O_3 + HO_2^{\cdot} \rightarrow OH^{\cdot} + 2O_2 \tag{20}$$

The process of conversion of ozone into radicals responsible for degradation of organic pollutants is terminated upon its complete depletion. Under such conditions, the following chain termination steps take place (Eqs. (21) and (22)).

$$OH^{\cdot} + HO_2^{\cdot} \rightarrow H_2O + O_2 \tag{21}$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2 \tag{22}$$

According to the literature data, an increase in ozone concentration in the reaction system results in an increase in the extent of removal of pollutants [12,17,81,109,111–118]. Research carried out by Raut-Jadhav et al. [12] provides an example of this effect. A detailed comparison of the efficacy of degradation of a commercial pesticide methomyl by hydrodynamic cavitation combined with ozonation at different concentrations of the oxidant was performed. When using ozonation alone (ozone concentration 0.75 gh^{-1}), the% TOC reduction of a 25-ppm methomyl solution after 120 min 5.96%. When using hydrodynamic cavitation alone (inlet pressure 4.93 atm, cavitation number 0.1) under the same operating conditions, the% TOC reduction was 5.45%. The results of this study reveal a serious limitation of ozonation, *i.e.*, mass transfer resistance which was mentioned earlier. When hydrodynamic cavitation was combined with ozonation, the efficiency of degradation at an ozone concentration of 0.5 gh^{-1} increased to 6.98% in just 30 min. With a further increase in ozone concentration to 0.75 gh^{-1}, the extent of degradation was rapidly increased to 41.47%. Further increases of ozone concentration resulted in a gradual improvement of the efficiency of oxidation of methomyl up to 69.87% (at ozone concentration of 2 gh^{-1}). The use of hydrodynamic cavitation combined with ozonation was also found to be the most efficient degradation method compared to hydrodynamic cavitation combined with the Fenton process or addition of hydrogen peroxide.

The selection of optimum concentration of ozone in the reaction system should be carried out experimentally for a particular type of contaminants [119]. If the optimum ozone concentration is exceeded, unreacted ozone could be released from the system [120]. Further increases in concentration of the oxidant causes suppression of diffusion of hydroxyl radicals which entails a gradual decrease of the efficiency of degradation.

This conclusion is supported by the results of study by Gore et al. [81] who observed a steady increase in the percent mineralization of reactive orange dye 4 with an increase in concentration of ozone when using hydrodynamic cavitation aided by ozonation. A maximum extent of degradation of 76.25% was achieved at ozone feed rate of 3 gh^{-1} (5 L of a 40-ppm solution of reactive orange 4). Further increase in the ozone feed rate lowered the extent of degradation down to 64.08% (at ozone feed rate of 8 gh^{-1}) in 60 min.

The extent of degradation of a pollutant was found to depend not only on concentration of the oxidant but also on the location of injection of ozone [12]. Gogate and Patil [17] reported the results of degradation of triazophos by hydrodynamic cavitation combined with ozonation. Ozone was injected at the orifice plate and in the solution tank. The largest extent of degradation was obtained by injecting ozone in solution tank. During 30-min treatment the efficiency was 89.16% whereas under the same conditions when ozone was injected at the orifice plate, the efficiency was less than 80%. The authors attribute this effect to the back pressure induced for introduction of ozone which also results in a lower flow rate of water. The flow rate of water at 4.93 atm inlet pressure without ozone injection was 290 Lh^{-1}. When ozone was injected at the orifice plate the total flow rate of a mixture of ozone and water dropped to 120 Lh^{-1}. This lower flow rate limited the number of passes of liquid thus affecting the dissociation of water and ozone molecules which yields hydroxyl radicals.

4.6.1. Processes of catalytic oxidation of pollutants

When using catalytic processes for degradation of organic contaminants, the efficiency of will also be affected by the amount of catalyst introduced to the reaction system. Consequently, the amount of catalyst should be specified as was the case with the amount of oxidant. For example, in the Fenton process introduction of an excessive amount of catalyst to the reaction system will result in depletion of hydroxyl radicals (Eq. (23)):

$$Fe^{2+} + OH^{\cdot} \rightarrow Fe^{3+} + HO^{-} \tag{23}$$

Therefore, the exact mole ratio of pollutant/oxidant/catalyst should be determined to achieve the most efficient treatment.

In heterogeneous catalysis, the high cost of a solid catalyst is one of the most important parameters determining viability of treatment. In homogeneous catalysis, the use of excessive amounts of a catalyst can result in the formation of a high volume of precipitates which will require additional stages of treatment. Furthermore, the concentration of iron ions in the treated medium can exceed the environmental standards which would preclude its release to the environment. It is thus necessary to design treatment properly and select operating conditions so as to achieve the best economic and environmental effect [102].

When solid catalysts are used, there is a possibility of their regeneration, which can lower the cost of treatment. This is demonstrated by the results of studies by Yang et al. [121] who proved that the efficiency of degradation of methyl orange in Fenton-like process does not deteriorate after several uses of the same synthetic NdFeB catalyst. Following reactivation, it could be used up to five times without deterioration of the extent of degradation.

When removal of pollutants from an aqueous medium is carried out by the Fenton process alone, concentration of a solid catalyst ranges from 1 to 10 gL^{-1} [121]. In the homogeneous process, the concentration of the catalyst ranges from 20 to 60 mgL^{-1}[29,50,85] when treating model effluents. For real effluents, the values increase to 200–500 mgL^{-1} [17,122]. When hydrodynamic cavitation is combined with the Fenton process, the concentration of the solid catalyst decreases to 0.05–5 gL^{-1} [106] while for the homogeneous process it does not exceed 1.7–28 mgL^{-1} [107]. In the case of industrial effluents, the latter values increase to about 120 mgL^{-1} [101].

4.7. Duration of treatment

From a theoretical point of view, the longer the treatment the better its efficiency is. However, when treating industrial effluents, the duration of treatment has an impact on the cost of the process; hence, industrial treatment methods aim at lowering the content of a contaminant in the shortest possible time.

An increase in duration of cavitational treatment improves its efficiency [16,32,123]. This is mostly due to an increased number of passes of the treated medium through the cavitational zone.

The results of investigations demonstrating an improvement in the extent of degradation with the duration of hydrodynamic cavitation have been published by Raut-Jadhav et al. [16], Bagal and Gogate [123] and Gonze et al. [32]. Raut-Jadhav et al. oxidized a neonicotinoid insecticide by hydrodynamic cavitation alone and hydrodynamic cavitation combined with advanced oxidation processes. The authors demonstrated that the extent of degradation of the insecticide increases with the duration of individual treatment processes. When using hydrodynamic cavitation alone at the maximum duration of the treatment (3 h), 27.44% of the neonicotinoid was degraded with the simultaneous 9.65% reduction of TOC. The authors point out one major problem with increasing the time of treatment for complex organic contaminants: the formation of organic byproducts which are hard to degrade by the same method. Neonicotinoid is a moderately stable organic compound which treated by hydrodynamic cavitation yields a number of byproducts having high toxicity and stability (including imidazolone). Extending the time of cavitational treatment results in formation of increasingly more stable and toxic organic compounds which deteriorates the efficiency of the process and cost effectiveness by the need to introduce another stage of treatment. In such a case, a hybrid method combining cavitation with advanced oxidation processes ensuring complete removal of stable byproducts should be considered.

Combination of hydrodynamic cavitation with oxidation by hydrogen peroxide significantly improved the efficiency of degradation of the neonicotinoid while substantially reducing the time needed for complete degradation. Moreover, the toxicity of the solution was also reduced through a more effective decomposition of the byproducts. During a 45-min treatment by cavitation combined with oxidation by hydrogen peroxide 100% of the contaminant was degraded with the simultaneous TOC reduction by 28% (at the mole ratio contaminant: hydrogen peroxide 1:40). In contrast, the use of hydrodynamic cavitation alone under the same operating conditions resulted in a 11.4% removal of the neonicotinoid with a negligible decrease in toxicity of the solution (*ca.* 1% TOC reduction). Therefore, extension of the duration of treatment is not always the best approach to improve the efficiency of degradation of contaminants. A viable alternative is to add an additional process which would allow complete removal of a contaminant in a shorter time. Furthermore, if contaminants tend to form stable and toxic byproducts during the treatment, such an additional stage can lower the toxicity of the medium which is beneficial for the environment and lowers the cost of treatment.

5. Experimental setups using cavitation

5.1. Installation elements

Technological installations used for removal from aqueous media of various kinds of organic pollutants by hydrodynamic/acoustic cavitation typically consists of several basic elements (Fig. 10):

- tank containing a medium being treated, equipped with a stirrer, heat exchanger (important module due to increase in temperature of the medium as a result of cavitation) and a temperature sensor. In the case of hydrodynamic cavitation, the installation can optionally contain two tanks to which the medium is alternately pumped through the throat [124]),
- connecting lines (hydrodynamic cavitation),
- pump (hydrodynamic cavitation),
- venturi, orifice or valve [55] choking flow (hydrodynamic cavitation),
- flow meters and manometers (hydrodynamic cavitation),

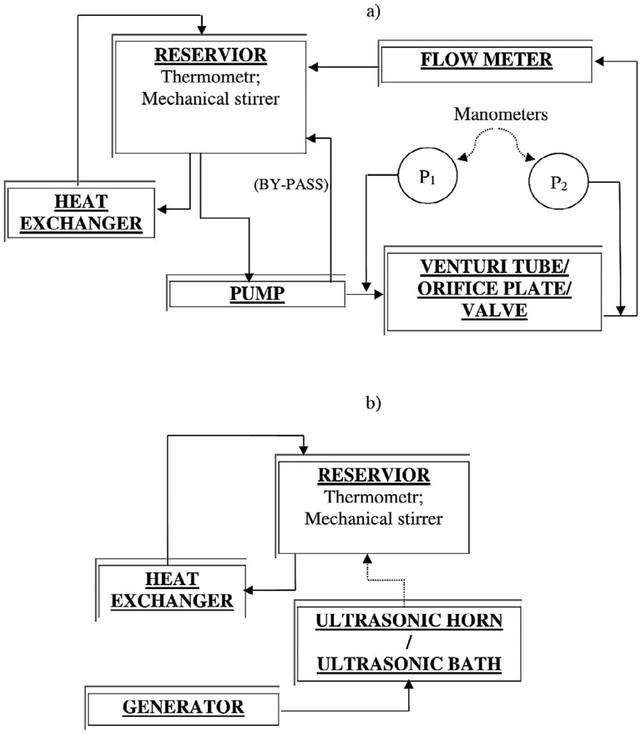


Fig. 10. Scheme of a) hydrodynamic cavitation and b) acoustic systems.

- power source and transducers generating acoustic wave in the medium being treated (acoustic cavitation).

Installation modules are usually made of stainless steel AISI 316, 316L or 316Ti, which resistance to corrosion in aggressive media and enables operation at high temperature and pressure [12,38,125]. In laboratory tests cavitational modules, mostly venturis, are often made of plastics, *e.g.* PMMA – poly(methyl methacrylate) having a good transparency which allows observation of growth and collapse of the cavities in specific cavitational zones [40,126]. It should be pointed out, however, that the autohors of papers on the application of hydrodynamic cavitation to removal of organic pollutants from various aqueous media do not provide information on the wear of materials from which the installation was made. Consequently, it is difficult to discuss strength of particular materials, their applicability to cavitational treatment and the possibility of scaling up the procedure. The information on the state of cavitational modules after the treatment should be provided in each experimental paper dealing with cavitation.

5.2. *Measurement of pressure*

In the case of hydrodynamic cavitation, pressure is most often measured at two different positions, the first one upstream of the throat and the second one downstream of the throat [22–24]. A large pressure drop at the throat initiates the inception of the cavities and it also determines the intensity of cavitation. The control of pressure drop is thus essential during the entire treatment process.

The pressure is measured by digital or analog manometers and pressure transducers which are properly installed in lines [26–29].

5.3. *Measurement of flow rate*

The measurement of flow rate is very important in hydrodynamic cavitation in order to determine the cavitation number which indicates the extent of generation of cavities. Consequently, flow meters are present in almost all installations [48–52]. Most often, they are installed either directly in front of the throat or behind it. At present, the most accurate measurements of a flow rate are carried out by electromagnetic flow meters which are mostly used in studies on hydrodynamic cavitation [56–57].

5.4. *Measurement of efficiency of treatment*

The efficiency of treatment, *i.e.*, the extent of oxidation of organic pollutants present in the treated medium is commonly determined using the reduction of COD in case of effluents having a very complex composition. For model effluents, spectroscopy is used to determine single components or, alternatively, chromatography is employed for mixtures. Chromatographic studies also allow following pathways of oxidation of individual compounds, which enables investigation of the efficiency of treatment towards specific groups of pollutants [127–130].

6. Remarks on the process economics, scale up, limitations and advantages of the cavitation processes combined with AOPs for wastewater treatment

6.1. *Economics and scale up*

Economics of a process is one of the most important criteria of its suitability for industrial application. Hydrodynamic and acoustic cavitation combined with AOPs enables high effectiveness of oxidation of organic contaminants present both in model [18,39,94] as well as real effluents [13,49,122]. However, the results of investigations discussed in this review pertain solely to a laboratory or large-laboratory scale, wherein the volume of the effluent being treated did not exceed 100 L. Cavitation combined with advanced oxidation processes is highly effective in oxidation of, among others, phenol and its derivatives [19,29], which are hard to remove from aqueous media by conventional treatment methods. This is primarily due to high toxicity of these compounds toward the microorganisms present in the activated sludge and to large amounts released in various technological processes, mostly chemical and pharmaceutical [61,94,120]. When analyzing economical feasibility of cavitational processes combined with AOPs in case of scale up, it should be assumed that cavitation would be used in wastewater treatment plants as a preliminary stage prior to biological treatment. This approach would improve the effectiveness of activated sludge, thus increasing the throughput of a WWTP through elimination of toxic chemicals, such as phenol and its derivatives. Cavitational processes can also be applied at the final stage of preparation of the treated effluent for discharge to the environment, following biological treatment. In this case, the use of cavitation ensures water sanitation through destruction of microorganisms left in the effluent after biological processes [22,27,46,65]. The results of investigations reveal that the operational costs of sonolysis of aqueous media are very high [3]. This is mostly related to a low efficiency of conversion of electrical energy to the energy of collapsing cavities in ultrasonic reactors. An additional problem in using such reactors in industrial settings is the emission of noise which accompanies the operation of ultrasonic transducers. This problem must be taken into consideration during evaluation of environmental impact of such an industrial installation. The costs of noise protection, *i.e.,* acoustic insulation of the reactors constitute a significant investment cost. With a scale up of the processes comes the need for usage of a different type of reactors equipped with a greater number of expensive and energy intensive ultrasonic transducers, which will increase operational costs. Mahamuni and Adewuyi [2] demonstrated that the operational cost of removal of phenol from 1 m^3 of water (90% reduction of concentration) using an ultrasonic reactor reaktora sono-kawitacyjnego (flow rate of 1000 $L min^{-1}$) amounts to about 4100 USD. The amount of ultrasonic energy needed for this process is *ca.* 3250 kW. According to the information provided by a leading US manufacturer of ultrasonic devices (Hielscher USA, Inc., Ringwood, NJ 07456, USA) the highest power of a single ultrasonic processor is 16 kW (at an energy conversion efficiency equal to 80%).

The price of this processor is around 200,000 USD. The reaction system presented in the paper [2] requires the use of 204 such ultrasonic transducers in order to achieve the required effectiveness of oxidation of phenol (90%) when treating 1000 $\mathrm{L\,min^{-1}}$ of the effluent. Thus, the total cost of ultrasonic equipment exceeds 40 million USD. The equipment cost significantly raises the total cost of the treatment. It should thus be pointed out that sonolysis used as a standalone process for the removal of organic contaminants from aqueous media can be uneconomical when the process is scaled up. This is mostly due to a high cost of ultrasonic transducers and high consumption of electric energy needed to achieve the effectiveness of degradation comparable to that obtained on a laboratory scale. However, the total cost of wastewater treatment can be reduced by aiding sonolysis with an additional AOP, such as the Fenton process. Mahmuni and Adewuyi [2] demonstrated that the cost of treatment of 1 m^3 of the wastewater containing phenol can be reduced from 4100 USD to 37 USD by combining sonolysis with the Fenton process. Moreover, the time needed to oxidize 90% of a contaminant decreases over 70-fold (the rate constants for oxidation of phenol by sonolysis and sonolysis aided by the Fenton process were equal to 0.0008 $\mathrm{min^{-1}}$ and 0.058 $\mathrm{min^{-1}}$, respectively). An over 100-fold decrease of total costs of treatment for the combined process (Sono: 500 million USD and SonoFenton: 4 million USD) results primarily from lowering the energy costs due to the increase in rate constant and reduction of treatment time as well as a lowered cost of an ultrasonic reactor which consumes less energy when combined treatment processes are used. The cost of an ultrasonic reactor required for effective oxidation of contaminants by sonolysis combined with the Fenton process is *ca.* 1 million USD. In considerations on the possibility of scaling up the treatment and the related issue of economical feasibility it should be remembered that by combining sonolysis with additional AOPs, a fully cost-effective technological process, competitive with the conventional treatment methods, can be achieved [140,141].

In hydrodynamic cavitation, the efficiency of energy conversion is much higher than that of sonolysis [31,41]. Consequently, scaling up these processes is much simpler. Designing an appropriate constriction with optimized operating parameters, such as a pressure drop in the throat, allows a substantial reduction of operating costs of the treatment [3]. The most expensive element of the system affecting the cost of the treatment during scale up is a pump. Selection of a pump providing an appropriate inlet pressure and a volumetric flow rate of the medium being treated in the reaction system is necessary to achieve fully effective cavitation. Jyoti and Pandit [140,141] indicated the possibility of using cavitation for industrial-scale disinfection of drinking water. Due to its low usage of electricity, hydrodynamic cavitation is an excellent alternative to conventional physical methods of treatment [140]. The cost of disinfection of 1 m^3 of water by hydrodynamic cavitation is almost ten times lower than that of acoustic cavitation (hydrodynamic cavitation: 3.7 USD, acoustic cavitation: 35 USD). Combining hydrodynamic cavitation with an additional AOP, such as ozonation, lowers the disinfection cost further, to *ca.* 3 USD per 1 m^3.

Presently, the only commercial cavitational process combined with AOPs, registered by Magnum Water Technology, is the CAV-OX® process [142]. The CAV-OX® process uses a combination of hydrodynamic cavitation, hydrogen peroxide and UV radiation to oxidize contaminants, such as benzene, ethylbenzene, toluene, xylenes, phenol, pentachlorophenol, cyanides and atrazine, in water. The authors of the method report that on a pilot scale the effectiveness of oxidation of organic contaminants exceeded 95%. The cost of treatment of 1 m^3 of water (oxidation of benzene from 50 ppm to 50 ppb) by hydrodynamic cavitation alone using the highly energy efficient CAV-OX® process is 0.45 USD. The cost of a cavitational reactor with a throughput of 94 $\mathrm{L\,min^{-1}}$ with all connections (UV + H_2O_2) is *ca.* 58,000 USD, which includes about 8000 USD for pumps and connections.

Thus, when the economical feasibility of cavitational processes during scaling up is considered, it should be remembered that hydrodynamic cavitation is most promising in this respect. It is energy efficient and the construction elements are inexpensive compared to acoustic cavitation. The most expensive component of a hydrodynamic cavitation reactor is a pump. Moreover, by combining cavitation with an additional AOP in a hybrid method the treatment costs can be reduced further, which allows the hybrid method to compete with conventional wastewater treatment methods.

6.2. *Limitations*

Cavitation used both as a standalone technological process and in combination with advanced oxidation processes offers a high effectiveness of oxidation of a variety of organic contaminants (Tables 2 and 3). However, due to the way the phenomenon is generated (using a constriction or energy of acoustic waves), it has certain limitations which affect its applicability. For acoustic cavitation, the main limitation in oxidation of various organic contaminants is the volume of the treated medium. Usually, the highest effectiveness of oxidation is achieved for solutions ranging from 100 mL to 10 L in volume [19,32,59]. Above these values, a drastic decrease in the effectiveness of oxidation is observed. Large volumes of liquids absorb acoustic waves generated by sonic transducers lowering their energy. This brings about a decrease in the cavitation efficiency and generation of hydroxyl radicals [2,3]. In the treatment of large volumes of liquids by acoustic cavitation generation of the cavities takes place solely in the near vicinity of operation of ultrasonic transducers [143]. Therefore, the treatment of larger volumes of liquids requires the use of a greater number of transducers, which consume more electrical energy and raise the cost of the entire treatment. In order to improve the effectiveness of degradation of contaminants, cavitational zones often have a small volume and a high degree of recirculation of the treated wastewater. However, this significantly limits the applicability of acoustic cavitation.

An increase in volume of the treated solution is not such a big problem in hydrodynamic cavitation. With a properly designed constriction, the intensity of cavitation is greater than that of sonic transducers, which enables effective treatment of wastewater regardless of its volume [81,82]. The only problem is the viscosity of the pumped fluid. Kumar [78] demonstrated that the maximum cavitational effect can only be obtained for liquids with a low density, such as water. For liquids with a higher density generation of the cavities is ineffective. Hence, the use of cavitation is limited to fluids with physicochemical properties similar to those of water.

One of the main problems and limitations of cavitation is a violent nature of this phenomenon. The destructive character of cavitation used in AOPs causes cavitation erosion, which has taken negative connotation and been deterrent to industrial uses. The cavities are formed in a violent phase transition from a liquid to a gas due to lowering of static pressure of the liquid being treated. Abrupt local changes in pressure and the energy of collapsing cavities can be destructive to an almost every construction material [9]. This is a problem which requires periodical control of the inner surface of a cavitation reactor which raises maintenance costs. For many scientists this problem precludes application of cavitation in many technological processes [143]. In addition, treatment of effluents having a complex matrix does not result in a satisfactory total degradation; however, this problem is common to all AOPs [2,3].

6.3. *Advantages*

As the results presented in this review demonstrate, there are some groups of chemical compounds that are almost completely degraded by using cavitation as the standalone AOP process. These include, among others, *p*-nitrotoluene, *p*-aminophenol, 1,4-dioxane, alachlor, chloroform, trichloroethylene and sodium pentachlorophenate. In these cases, the technology can be considered to be fully compliant with green chemistry and can be called a clean technology. Only electrical energy having a low impact on the environment is utilized at the point of use, which is compliant with the principles of sustainable development. Generation of electrical energy is often an added benefit of production processes taking place in industrial facilities, such as refineries. Despite disadvantages and limitations described above, cavitation has a number of advantages, which distinguish it from the commercially available wastewater treatment methods. The main advantages of cavitation include:

1. Low operational costs of hydrodynamic cavitation compared to other AOP processes.
2. The byproducts formed are limited to the expected decomposition products of organic contaminants in the absence of hazardous oxidants, such as chlorine.
3. Effective oxidation of both hydrophilic and hydrophobic organic contaminants due to numerous mechanisms of oxidation (oxidation inside the cavities and in the bulk of solution).
4. Reduction of mass transfer resistance through the formation of microcirculation and turbulence zones in the solution being treated.
5. High synergism of cavitational processes with AOPs allowing an increase in the effectiveness of treatment.
6. Possibility of a variety of combinations of cavitation with AOPs.
7. High effectiveness of treatment of both acidic and basic solutions.
8. Relative ease of scaling up the processes based on hydrodynamic cavitation.
9. Limited use of strong oxidants, such as hydrogen peroxide and ozone, when using cavitation.
10. High effectiveness of oxidation of toxic phenol and its derivatives compared with conventional treatment methods (mainly in combination with AOPs).

7. Suggestions for future work

The literature review and experience of the authors of this paper in the area of wastewater treatment and process analytics incline us to offer a few general rules for the future investigation of cavitation treatment of effluents which should facilitate a comparison with the results of other researchers. The assurance of comparability of the results of investigations of various groups is the key requirement to the comprehensive development of treatment methods for a variety of effluents. The principles of good practice for the investigation of effluent future treatment methods are outlined below.

a) The description of process conditions should include calculated values of the cavitation number and the data needed for this calculation in an appendix. The availability of these data along with geometric dimensions of a cavitation device allows other researchers better planning of their own investigations, including the studies of alternative systems and scale up of processes.
b) The experimental setup should be characterized in detail, including the method of cavitation, types of pumps, inductors, cavitation elements, measurement of pressure and flow rate, location and method of introduction of external oxidants. A clear definition of degree of recirculation of the effluent in flow system is also needed.
c) Raw effluents to be treated should be characterized as much as possible, including their physicochemical form (clarity, occurrence of emulsions, opacity, color), pH, elemental composition and the presence of dissolved organic and inorganic salts. These parameters were shown to have a large effect on the efficiency of cavitation processes and also, to some extent, on the processes aided by UV irradiation. Disregarding these issues for real effluents may diminish the validity of the results and conclusions. When studying model effluents, these issues should be taken into consideration during process optimization and description of the effect of individual parameters on its efficiency.
d) In case of real effluents, the values of total parameters, *i.e.,* COD and BOD, should be monitored, preferably both at the same time. On the one hand, this allows monitoring changes in biodegradability index of the effluent (the COD/BOD ratio) but it also shows the load of pollutants depleting an oxidant when only some contaminants are being studied. When there is a choice between the selection of COD and TOC, COD is preferred. TOC for the processes in which selected organic compounds are converted to other organic compounds would not be a reliable parameter describing the efficiency of degradation.
e) Real effluents can contain organic contaminants which are not oxidized even by the AOPs considered to be very effective. Examples include aliphatic and cyclic hydrocarbons. Their content must be monitored and accounted for in the evaluation of the efficiency of lowering COD. The presence of species resistant to oxidation will constitute "dead" COD, a constant term lowering the efficiency of the investigated process. At the same time, however, in many cases these compounds can be removed by other processes, such as flotation, flocculation, etc. Moreover, they often are not toxic towards strains of bacteria present in the activated sludge of biological module of WWTP. Thus, they will be readily biodegradable and should not be included in the target group of pollutants which are to be removed by AOP processes.
f) Effective process monitoring should include the determination of selected groups of contaminants present in effluents and ensure the possibility of evaluation of toxicity of the byproducts formed (secondary contaminants). Basing evaluation of the effectiveness of treatment solely on total parameters, *i.e.*, COD and BOD, can lead to selection of a technology resulting in the formation of the effluent with a toxicity higher than that of the original effluent despite a decrease in a total pollutant load. The information on the formation of byproducts can be utilized in a comprehensive comparison of the investigated treatment methods facilitating the selection of the optimum approach. Chromatographic techniques are particularly suitable for process control of wastewater treatment. There are chromatographic procedures available for real industrial effluents allowing process control for organic sulfur, nitrogen and oxygen compounds [129,130].
g) The studies of treatment of both model and real effluents should include the description of the effect of individual parameters on degradation pathways and efficiency of contaminants. The reports should include the following parameters: pH, temperature, the ratio of oxidant to COD value, and the method of supplying the oxidant (single-step or sequential).
h) In studies involving catalytic processes, complete characteristics of catalysts should be provided, including particle size, specific surface area, porosity, method of preparation and activation. Otherwise, a comparison of different studies is impossible. The studies should also include optimization of the amount of catalyst and test for the occurrence of permanent adsorption of contaminants, resulting in lowering their content in an effluent by the process different from oxidation (for small-scale studies in batch reactors this can lead to overestimation of the efficiency of degradation). Ultimately, each catalyst exhibiting the desired activity should undergo further studies by using it repeatedly and evaluating its ability to sustain its catalytic properties and the possibility of regeneration.
i) The processes aided by UV irradiation must provide detailed characteristics of the type of lamps and their power, the material of protective coating and its thickness. In addition to specifying the type of lamp (high/medium/low pressure) and input power, the authors should also include the percent of the wavelength at which photooxidation is expected in the spectrum of the lamp. In some cases, the useful region of the spectrum constitutes just several percent of the radiation emitted by the lamp. This is particularly important when trying to assess the cost of various approaches.

Changing the lamp, *e.g.,* by using a mercury lamp doped with iron, can often improve the UV output up to 60% of the input power. In this way, a better compatibility of UV lamps for the selected catalyst can be obtained – for example, different UV regions will be optimal for TiO_2 and ZnO catalysts.

j) The studies of hydrodynamic and acoustic cavitation should include the problems associated with the scaling up of the treatment and the rules allowing achievement of similar values of effectiveness. Currently, there are no papers discussing the effect of scaling up on the effectiveness of oxidation of organic pollutants.

k) The studies should include an improvement in the efficiency of conversion of electric energy in ultrasonic reactors. Thus far, this efficiency is low which prevents a wider applicability of sonolysis.

8. Summary

A literature search has revealed that advanced oxidation processes and cavitation are increasingly used for the removal of a wide variety of organic compounds present in industrial effluents. They are characterized by a high degree of removal of pollutant load and a significant reduction of level of biotoxicity. The use of these methods for treatment of one of the most biotoxic effluents, those from the chemical industry, can significantly improve the efficiency of their treatment. Combination of highly reactive hydroxyl radicals with a great force of implosion of the cavities allows degradation of the majority of organic pollutants which cannot be removed by other, traditional treatment methods.

Hydrodynamic and acoustic cavitation alone were found to achieve at least 10% effectiveness of oxidation of various contaminants in aqueous solutions. The compounds that are readily degradable (over 50% degradation) by cavitation include: *p*-nitrotoluene, *p*-aminophenol, 1,4-dioxane, alachlor, chloroform, trichloroethylene, sodium pentachlorophenate, 1-propanal, 2-pentanone, nonylphenol, methyl parathion, dichlorvos, triazophos, and dye brilliant green. For these compounds, extending the treatment time should allow an almost complete removal of the pollutants. The compounds that are hard to degrade (effectiveness ranging from 10 to 50%) include: pharmaceuticals (ibuprofen, ketaprofen, carbamazepine, diclofenac), organic dyes (reactive orange 4, reactive brilliant red, orange acid II, rhodamine B), phenols (phenol, *p*-nitrophenol, 2,4-dinitrophenol, 2,4-dichlorophenol), insecticides (imidacloprid, dichlorvos, methomyl) and 1-heptanol, 1-hexanol, *m*-cresol, and dimethylhydrazine. In this case, the time needed to reduce the concentration of contaminants could be too long and the process unprofitable. In such cases, the AOP treatment methods combining cavitation with external oxidants, such as ozone, hydrogen peroxide or persulftates provide a high effectiveness of degradation. A high synergism of cavitation combined with the Fenton process and other processes of catalytic and photocatalytic oxidation was demonstrated. The hybrid processes result in a significant increase in the effectiveness of treatment (by combining cavitation with AOPs, the effectiveness of oxidation of hardly degradable contaminants often increases from 10 to 20% for standalone cavitation to over 60% for combined treatment methods) and a reduction of costs and time of the treatment.

As a result of identical physical phenomenon, each of the cavitation methods leads to universal conclusions regardless of the method of its generation even though the intensity of mass and energy exchange associated with hydrodynamics of the reaction system is different for hydrodynamic and acoustic cavitation. The studies on effluent treatment by acoustic cavitation revealed that the efficiency of degradation of contaminants increases with hydrophobicity of the contaminants. The investigations of treatment of real effluents as well as model mixtures should take into consideration the presence of inhibitors decreasing the efficiency of degradation of contaminants. Among these inhibitors are some alcohols – methanol, *n*-butanol and *t*-butanol as well as sodium hydrogen carbonate. Other studies revealed the effect of lowering the efficiency of degradation of contaminants in the presence of inorganic anions. A negative impact of carbonates was established for the processes combining acoustic cavitation with ozonation. In hydrodynamic cavitation, geometry of the cavitation device affects the efficiency of degradation of pollutants. Rectangular slits venturis had a slightly higher efficiency compared with cylindrical venturis (5% difference) and a substantially higher efficiency compared to orifice plates (by 25%). Another important conclusion is the need for a continuous dosage of an oxidant during treatment which results in a better efficiency of degradation compared to a single-step dosage in the beginning of the treatment. A comparison of energy consumption of hydrodynamic and acoustic cavitation for a similar extent of degradation of pollutants in effluents revealed that acoustic cavitation is about 20 times more energy-consuming. Moreover, its high investment costs, complexity of equipment and the difficulty of scale up make it less attractive. Consequently, the preferred technologies of effluent treatment should be based on hydrodynamic cavitation.

Acknowledgments

The authors gratefully acknowledge financial support from the Ministry of Science and Higher Education in Poland for project 0040/IP2/2015/73 in the program, Iuventus Plus" in 2015–2017.

Conflict of interest

The authors have declared no conflict of interest.

References

[1] P.T. Anastas, M.M. Kirchhoff, Origins, current status, and future challenges of green chemistry, Acc. Chem. Res. 35 (2002) 686–694.
[2] N.N. Mahamuni, Y.G. Adewuyi, Advanced oxidation processes (AOPs) involving ultrasound for waste water treatment: a review with emphasis on cost estimation, Ultrason. Sonochem. 17 (2010) 990–1003.
[3] M.V. Bagal, P.R. Gogate, Wastewater treatment using hybrid treatment schemes based on cavitation and Fenton chemistry: a review, Ultrason. Sonochem. 21 (2014) 1–14.
[4] T. Oppenländer, Photochemical Purification of Water and Air: Advanced Oxidation Processes (AOPs)-Principles, Reaction Mechanisms, Reactor Concepts, John Wiley & Sons, 2003.
[5] Y.L. Song, J.T. Li, Degradation of C.I. Direct Black 168 from aqueous solution by fly ash/H2O2 combining ultrasound, Ultrason. Sonochem. 16 (2009) 440–444.
[6] K.S. Suslick, Sonochemistry, Science 247 (1990) 1439–1445.
[7] C.D. Wu, Z.L. Zhang, Y. Wu, L. Wang, L.J. Chen, Effects of operating parameters and additives on degradation of phenol in water by the combination of H2O2 and hydrodynamic cavitation, Desalin. Water Treat. 53 (2015) 462–468.
[8] M.A. Beckett, I. Hua, Elucidation of the 1,4-dioxane decomposition pathway at discrete ultrasonic frequencies, Environ. Sci. Technol. 34 (2000) 3944–3953.
[9] J. Bagieński, Kawitacja w urządzeniach wodociągowych i ciepłowniczych, Politechnika Poznańska, Poznań, 1998.
[10] A.G. Chakinala, P.R. Gogate, A.E. Burgess, D.H. Bremner, Treatment of industrial wastewater effluents using hydrodynamic cavitation and the advanced Fenton process, Ultrason. Sonochem. 15 (2008) 49–54.
[11] A.J. Barik, P.R. Gogate, Degradation of 4-chloro 2-aminophenol using a novel combined process based on hydrodynamic cavitation, UV photolysis and ozone, Ultrason. Sonochem. 30 (2016) 70–78.
[12] S. Raut-Jadhav, D. Saini, S. Sonawane, A. Pandit, Effect of process intensifying parameters on the hydrodynamic cavitation based degradation of commercial pesticide (methomyl) in the aqueous solution, Ultrason. Sonochem. 28 (2016) 283–293.
[13] D.R. Reddy, G.K. Dinesh, S. Anandan, T. Sivasankar, Sonophotocatalytic treatment of Naphthol Blue Black dye and real textile wastewater using synthesized Fe doped TiO2, Chem. Eng. Process. 99 (2016) 10–18.
[14] D.H. Bremner, S. Carlo, A.G. Chakinala, G. Cravotto, Mineralisation of 2,4-dichlorophenoxyacetic acid by acoustic or hydrodynamic cavitation in conjunction with the advanced Fenton process, Ultrason. Sonochem. 15 (2008) 416–419.
[15] I. Grcic, M. Obradovic, D. Vujevic, N. Koprivanac, Sono-Fenton oxidation of formic acid/formate ions in an aqueous solution: from an experimental design to the mechanistic modeling, Chem. Eng. J. 164 (2010) 196–207.
[16] S. Raut-Jadhav, V. Kumar Saharan, D. Pinjari, S. Sonawane, D. Saini, A. Pandit, Synergetic effect of combination of AOP's (hydrodynamic cavitation and H2O2) on the degradation of neonicotinoid class of insecticide, J. Hazard. Mater. 261 (2013) 139–147.
[17] P.R. Gogate, P.N. Patil, Combined treatment technology based on synergism between hydrodynamic cavitation and advanced oxidation processes, Ultrason. Sonochem. 25 (2015) 60–69.
[18] D. Drijvers, H. van Langenhove, L. Nguyen, T. Kim, L. Bray, Sonolysis of an

aqueous mixture of trichloroethylene and chlorobenzene, Ultrason. Sonochem. 6 (1999) 115–121.

[19] A.A. Pradhan, P.R. Gogate, Degradation of p-nitrophenol using acoustic cavitation and Fenton chemistry, J. Hazard. Mater. 173 (2010) 517–522.

[20] Z. XiaoBin, Z. JiaKai, Q. LiMin, Z. XueJun, Calculation and verification of dynamical cavitation model for quasi-steady cavitating flow, Int. J. Mass Transfer. 86 (2015) 294–301.

[21] N. Tran, P. Drogui, L. Nguyen, S.K. Brar, Optimization of sono-electrochemical oxidation of ibuprofen in wastewater, J. Environ. Chem. Eng. 3 (2015) 2637–2646.

[22] M. Zupanc, T. Kosjek, M. Petkovšek, M. Dular, B. Kompare, B. Širok, Z. Blazeka, E. Heath, Removal of pharmaceuticals from wastewater by biological processes, hydrodynamic cavitation and UV treatment, Ultrason. Sonochem. 20 (2013) 1104–1112.

[23] M. Zupanc, T. Kosjek, M. Petkovšek, M. Dular, B. Kompare, B. Širok, M. Strazˇar, E. Heath, Shear-induced hydrodynamic cavitation as a tool for pharmaceutical micropollutants removal from urban wastewater, Ultrason. Sonochem. 21 (2014) 1213–1221.

[24] K.P. Mishra, P.R. Gogate, Intensification of degradation of Rhodamine B using hydrodynamic cavitation in the presence of additives, Sep. Purif. Technol. 75 (2010) 385–391.

[25] J.G.D. Filho, M.P. Assis, A.I.B. Genovez, Bacterial inactivation in artificially and naturally contaminated water using a cavitating jet apparatus, J. Hydro-environ. Res. 9 (2015) 259–267.

[26] P. Li, Y. Song, S. Yu, Removal of Microcystis aeruginosa using hydrodynamic cavitation: performance and mechanisms, Water Res. 62 (2014) 241–248.

[27] M. Petkovšek, M. Mlakar, M. Levstek, M. Strazar, B. Širok, M. Dular, A novel rotation generator of hydrodynamic cavitation for waste-activated sludge disintegration, Ultrason. Sonochem. 26 (2015) 408–414.

[28] A.G. Chakinala, P.R. Gogateb, A.E. Burgessa, D.H. Bremnera, Industrial wastewater treatment using hydrodynamic cavitation and heterogeneous advanced Fenton processing, Chem. Eng. J. 152 (2009) 498–502.

[29] M.V. Bagal, P.R. Gogate, Degradation of 2,4-dinitrophenol using a combination of hydrodynamic cavitation, chemical and advanced oxidation processes, Ultrason. Sonochem. 20 (2013) 1226–1235.

[30] J. Nawrocki, Zaawansowane procesy utleniania w oczyszczaniu wody, Ochr. Sr. 74 (1999) 32–36.

[31] L.J. Xu, W. Chu, N. Graham, Degradation of di-n-butyl phthalate by a homogeneous sono–photo–Fenton process with in situ generated hydrogen peroxide, Chem. Eng. J. 240 (2014) 541–547.

[32] E. Gonze, L. Fourel, Y. Gonthier, P. Boldo, A. Bernis, Wastewater pretreatment with ultrasonic irradiation to reduce toxicity, Chem. Eng. J. 73 (1999) 93–100.

[33] K. Makino, M.M. Mossoba, P. Riesz, Chemical effects of ultrasound on aqueous solutions. Formation of hydroxyl radicals and hydrogen atoms, J. Am. Chem. Soc. 87 (1983) 1369–1377.

[34] J.M. Wu, H.S. Huang, C.D. Livengood, Ultrasonic destruction of chlorinated compounds in aqueous solution, Environ. Prog. 11 (1992) 195–201.

[35] A. Henglein, C. Kormann, Scavenging of OH radicals produced in the sonolysis of water, Int. J. Radiat. Biol. 48 (1985) 251–258.

[36] P.R. Gogate, Cavitation: an auxiliary technique in wastewater treatment schemes, Adv. Environ. Res. 6 (2002) 335–358.

[37] V.S. Moholkar, P. Senthilkumar, A.B. Pandit, Hydrodynamic cavitation for sonochemical effects, Ultrason. Sonochem. 6 (1999) 53–65.

[38] M.P. Badve, M.N. Bhagat, A.B. Pandit, Microbial disinfection of seawater using hydrodynamic cavitation, Sep. Purif. Technol. 151 (2015) 31–38.

[39] M. Petkovšek, M. Zupanc, M. Dular, T. Kosjek, E. Heath, B. Kompare, B. Širok, Rotation generator of hydrodynamic cavitation for water treatment, Sep. Purif. Technol. 118 (2013) 415–423.

[40] S.M. Ashrafizadeh, H. Ghassemi, Experimental and numerical investigation on the performance of small-sized cavitating venturis, Flow Meas. Instrum. 42 (2015) 6–15.

[41] Y. Xiong, F. Peng, Optimization of cavitation venturi tube design for pico and nano bubbles generation, Int. J. Mining Sci. Technol. 25 (2015) 523–529.

[42] H. Ghassemi, H.F. Fasih, Application of small size cavitating venturi as flow controller and flow meter, Flow Meas. Instrum. 22 (2011) 406–412.

[43] T. Jain, J. Carpenter, V.K. Saharan, CFD analysis and optimization of circular and slit venturi for cavitational activity, J. Mater. Sci. Mech. Eng. 1 (2014) 28–33.

[44] T.A. Bashir, A.G. Soni, A.V. Mahulkar, A.B. Pandit, The CFD driven optimisation of a modified venturi for cavitational activity, Can. J. Chem. Eng. 89 (2011) 1366–1375.

[45] A. Ulas, Passive flow control in liquid-propellant rocket engines with cavitating venture, Flow Meas. Instrum. 17 (2006) 94–97.

[46] K. Jung, M. Hwang, Y. Yun, M. Cha, K. Ahn, Development of a novel electric field-assisted modified hydrodynamic cavitation system for disintegration of waste activated sludge, Ultrason. Sonochem. 21 (2014) 1635–1640.

[47] J.B. Parsa, S.A.E. Zonouzian, Optimization of a heterogeneous catalytic hydrodynamic cavitation reactor performance in decolorization of Rhodamine B: application of scrap iron sheets, Ultrason. Sonochem. 20 (2013) 1442–1449.

[48] M.T. Angaji, R. Ghiaee, Decontamination of unsymmetrical dimethylhydrazine waste water by hydrodynamic cavitation-induced advanced Fenton process, Ultrason. Sonochem. 23 (2015) 257–265.

[49] M. Badve, P. Gogate, A. Pandit, L. Csoka, Hydrodynamic cavitation as a novel approach for wastewater treatment in wood finishing industry, Sep. Purif. Technol. 106 (2013) 15–21.

[50] R.K. Joshi, Parag R. Gogate, Degradation of dichlorvos using hydrodynamic cavitation based treatment strategies, Ultrason. Sonochem. 19 (2012) 532–539.

[51] D. Ghayal, A.B. Pandit, V.K. Rathod, Optimization of biodiesel production in a hydrodynamic cavitation reactor using used frying oil, Ultrason. Sonochem. 20 (2013) 322–328.

[52] M. Sivakumar, A.B. Pandit: Hydrodynamic cavitation assisted degradation of rhodamine B: a technologically viable wastewater treatment technique, in: International Conference on Science and Technology under Chemical Society of Canada, October 12–13, 2000, New Delhi, India.

[53] P.S. Kumar, M. Sivakumar, A.B. Pandit, Experimental quantification of chemical efects of hydrodynamic cavitation, Chem. Eng. Sci. 55 (2000) 1633–1639.

[54] P. Braeutigam, M. Franke, Z.L. Wu, B. Ondruschka, Role of different parameters in the optimization of hydrodynamic cavitation, Chem. Eng. Technol. 33 (2010) 932–940.

[55] K.K. Jyoti, A.B. Pandit, Water disinfection by acoustic and hydrodynamic cavitation, Biochem. Eng. J. 7 (2001) 201–212.

[56] M.P. Badve, T. Alpar, A.B. Pandit, P.R. Gogate, L. Csoka, Modeling the shear rate and pressure drop in a hydrodynamic cavitation reactor with experimental validation based on KI decomposition studies, Ultrason. Sonochem. 22 (2015) 272–277.

[57] P.R. Gogate, Cavitational reactors for process intensification of chemical processing applications: a critical review, Chem. Eng. Process. 47 (2008) 515–527.

[58] S. Asgharzadehahmadi, A.A.A. Raman, R. Parthasarathy, B. Sajjadi, Sonochemical reactors: review on features, advantages and limitations, Renew. Sustain. Energy Rev. 63 (2016) 302–314.

[59] A.K. Shriwas, P.R. Gogate, Ultrasonic degradation of methyl Parathion in aqueous solutions: intensification using additives and scale up aspects, Sep. Purif. Technol. 79 (2011) 1–7.

[60] B. Neppoliana, H. Junga, H. Choi, J.H. Leea, J.W. Kang, Sonolytic degradation of methyl tert-butyl ether: the role of coupled fenton process and persulphate ion, Water Res. 36 (2002) 4699–4708.

[61] A.G. Chakinala, D.H. Bremner, P.R. Gogate, K.C. Namkung, A.E. Burgess, Multivariate analysis of phenol mineralisation by combined hydrodynamic cavitation and heterogeneous advanced Fenton processing, Appl. Catal. B: Environ. 78 (2008) 11–18.

[62] D. Liu, E. Vorobiev, R. Savoire, J.L. Lanoisellé, Comparative study of ultrasound-assisted and conventional stirred dead-end microfiltration of grape pomace extracts, Ultrason. Sonochem. 20 (2013) 708–714.

[63] I. Worapun, K. Pianthong, P. Thaiyasuit, Optimization of biodiesel production from crude palm oil using ultrasonic irradiation assistance and response surface methodology, J. Chem. Technol. Biotechnol. 87 (2012) 189–197.

[64] A.S. Badday, A.Z. Abdullah, K.T. Lee, M.S. Khayoon, Intensification of biodiesel production via ultrasonic-assisted process: a critical review on fundamentals and recent development, Renew. Sustain. Energy Rev. 16 (2012) 4574–4587.

[65] I. Lee, J. Han, The effects of waste-activated sludge pretreatment using hydrodynamic cavitation for methane production, Ultrason. Sonochem. 20 (2013) 1450–1455.

[66] L. Csoka, S.N. Katekhaye, P.R. Gogate, Comparison of cavitational activity in different configurations of sonochemical reactors using model reaction supported with theoretical simulations, Chem. Eng. J. 178 (2011) 384–390.

[67] F. Parvizian, M. Rahimi, M. Faryadi, Macro- and micromixing in a novel sonochemical reactor using high frequency ultrasound, Chem. Eng. Processing: Process Intensif. 50 (2011) 732–740.

[68] P.R. Gogate, S. Mujumdar, A.B. Pandit, Sonochemical reactors for waste water treatment: comparison using formic acid degradation as a model reaction, Adv. Environ. Res. 7 (2003) 283–299.

[69] P.R. Gogate, A.B. Pandit, A review and assessment of hydrodynamic cavitation as a technology for the future, Ultrason. Sonochem. 12 (2005) 21–27.

[70] A.A. Pradhan, P.R. Gogate, Removal of p-nitrophenol using hydrodynamic cavitation and Fenton chemistry at pilot scale operation, Chem. Eng. J. 156 (2010) 77–82.

[71] P.N. Patil, S.D. Bote, P.R. Gogate, Degradation of imidacloprid using combined advanced oxidation processes based on hydrodynamic cavitation, Ultrason. Sonochem. 21 (2014) 1770–1777.

[72] W. Jitschin, M. Ronzheimer, S. Khodabakhshi, Gas flow measurement by means of orifices and Venturi tubes, Vacuum 53 (1-2) (1999) 181–185.

[73] G.G. Dastane, M.P. Badve, V.K. Saharan, A.B. Pandit, Numerical optimization and experimental validation of hydrodynamic cavitating device, in: 8th Int. Symp. Cavitation, 2012, pp. 978–981, https://doi.org/10.3850/978-981-07-2826-7.

[74] G.L. Maddikeri, P.R. Gogate, A.B. Pandit, Intensified synthesis of biodiesel using hydrodynamic cavitation reactors based on the interesterification of waste cooking oil, Fuel 137 (2014) 285.

[75] P.R. Gogate, A.B. Pandit, Engineering design methods for cavitation reactors II: hydrodynamic cavitation, AIChE J. 46 (2000) 1641–1649.

[76] V.S. Moholkar, A.B. Pandit, Bubble behavior in hydrodynamic cavitation: effect of turbulence, AIChE J. 43 (1997) 1641–1648.

[77] P.R. Gogate, A.B. Pandit, Hydrodynamic cavitation reactors: a state of the art review, Rev. Chem. Eng. 17 (2001) 1–85.

[78] P.S. Kumar, Studies in cavitation (M. Chem. Engg. Thesis), Univ. of Mumbai, Mumbai, India, 1997.

[79] S. Mujumdar, A.B. Pandit, Study of catalytic isomerisation of maleic acid to fumaric acid: effect of ultrasound, Ind. Chem. Eng. 40 (1998) 187–192.

[80] V.K. Saharan, M.P. Badve, A.B. Pandit, Degradation of Reactive Red 120 dye using hydrodynamic cavitation, Chem. Eng. J. 178 (2011) 100–107.

[81] M.M. Gore, V.K. Saharan, D.V. Pinjari, P.V. Chavan, A.B. Pandit, Degradation of reactive orange 4 dye using hydrodynamic cavitation based hybrid techniques, Ultrason. Sonochem. 21 (2014) 1075–1082.

[82] J.P. Tullis, Choking and supercavitating valves, J. Hydraul. Div. 97 (1971)

1931–1945.
[83] A.F. Carlucci, D. Pramer, An evaluation of factors affecting the survival of Escherichia coli in sea water, Appl. Environ. Microbiol. 8 (1960) 247–250.
[84] C.E. Starliper, B.J. Watten, Bactericidal efficacy of elevated pH on fish pathogenic and environmental bacteria, J. Adv. Res. 4 (2013) 345–353.
[85] P.N. Patil, P.R. Gogate, Degradation of methyl parathion using hydrodynamic cavitation: Effect of operating parameters and intensification using additives, Sep. Purif. Technol. 95 (2012) 172–179.
[86] K.S. Suslick, M.M. Mdleleni, J.T. Ries, Chemistry induced by hydrodynamic cavitation, J. Am. Chem. Soc. 119 (1997) 9303–9304.
[87] M.H. Entezari, P. Kruus, Effect of frequency on sonochemical reactions II. Temperature and intensity effects, Ultrason. Sonochem. 3 (1996) 19–24.
[88] N.P. Vichare, P. Senthilkumar, V.S. Moholkar, P.R. Gogate, A.B. Pandit, Energy analysis in acoustic cavitation, Ind. Eng. Chem. Res. 39 (2000) 1480–1486.
[89] Z.L. Wu, B. Ondruschka, P. Bräutigam, Degradation of chlorocarbons driven by hydrodynamic cavitation, Chem. Eng. Technol. 30 (2007) 642–648.
[90] J.-H. Sun, S.-P. Sun, M.-H. Fan, H.-Q. Guo, L.-P. Qiao, R.-X. Sun, A kinetic study on the degradation of p-nitroaniline by Fenton oxidation process, J. Hazard. Mater. 148 (2007) 172–177.
[91] V. Kavitha, K. Palanivelu, Destruction of cresols by Fenton oxidation process, Water Res. 39 (2005) 3062–3072.
[92] H. Zhang, H.J. Choi, C.P. Huang, Optimization of Fenton process for the treatment of landfill leachate, J. Hazard. Mater. 125 (2005) 166–174.
[93] F.J. Rivas, F. Beltran, O. Gimeno, F. Carvalho, Fenton-like oxidation of landfill leachate, Environ. Sci. Eng. 38 (2003) 371–379.
[94] T. Zhou, Y. Li, F.-S. Wong, X. Lu, Enhanced degradation of 2,4-dichlorophenol by ultrasound in a new Fenton like system (Fe/EDTA) at ambient circumstance, Ultrason. Sonochem. 15 (2008) 782–790.
[95] J.-H. Sun, S.-P. Sun, J.-Y. Sun, R.-X. Sun, L.-P. Qiao, H.-Q. Guo, M.-H. Fan, Degradation of azo dye Acid black 1 using low concentration iron of Fenton process facilitated by ultrasonic irradiation, Ultrason. Sonochem. 14 (2007) 761–766.
[96] Y.G. Adewuyi, Sonochemistry: environmental science and engineering applications, Ind. Eng. Chem. Res. 40 (2001) 4681–4715.
[97] T.H. Wang, S.F. Kang, Y.H. Lin, Comparison among Fenton-related processes to remove 2,4-dinitrophenol, J. Environ. Sci. Health A. 34 (1999) 1267–1281.
[98] C. Özdemir, M.K. Oden, S. Sahinkaya, E. Kalipci, Color removal from synthetic textile wastewater by sono-fenton process, Clean, Soil Air, Water 39 (2011) 60–67.
[99] A. Babuponnusami, K. Muthukumar, Degradation of phenol in aqueous solution by fenton, sono-fenton and sono-photo-fenton methods, Clean Soil Air Water 39 (2011) 142–147.
[100] X. Wang, Z. Yao, J. Wang, W. Guo, G. Li, Degradation of reactive brilliant red in aqueous solution by ultrasonic cavitation, Ultrason. Sonochem. 15 (2008) 43–48.
[101] N. Wang, T. Zheng, G. Zhang, P. Wang, A review on Fenton-like processes for organic wastewater treatment, J. Environ. Chem. Eng. 4 (2016) 762–787.
[102] C.C. Jiang, S.Y. Pang, F. Ouyang, J. Ma, J. Jiang, A new insight into Fenton and Fenton-like processes for water treatment, J. Hazard. Mater. 174 (2010) 813–817.
[103] G. Boczkaj, A. Fernandes, Wastewater treatment by means of advanced oxidation processes at basic pH conditions: a review, Chem. Eng. J. 320 (2017) 608–633.
[104] J.J. Wu, M. Muruganandham, J.S. Yang, S.S. Lin, Oxidation of DMSO on goethite catalyst in the presence of H2O2 at neutral pH, Catal. Commun. 7 (2006) 901–906.
[105] X.F. Xue, K. Hanna, M. Abdelmoula, N.S. Deng, Adsorption and oxidation of PCP on the surface of magnetite: kinetic experiments and spectroscopic investigations, Appl. Catal. B 89 (2009) 432–440.
[106] X.F. Xue, K. Hanna, N.S. Deng, Fenton-like oxidation of Rhodamine B in the presence of two types of iron (II, III) oxide, J. Hazard. Mater. 166 (2009) 407–414.
[107] H. Zhang, X.G. Wu, X.W. Li, Oxidation and coagulation removal of COD from landfill leachate by Fered-Fenton process, Chem. Eng. J. 210 (2012) 188–194.
[108] P.P. Gan, S.F.Y. Li, Efficient removal of Rhodamine B using a rice hull-based silica supported iron catalyst by Fenton-like process, Chem. Eng. J. 229 (2013) 351–363.
[109] A.L. Prajapat, P.R. Gogate, Intensified depolymerization of aqueous polyacrylamide solution using combined processes based on hydrodynamic cavitation, ozone, ultraviolet light and hydrogen peroxide, Ultrason. Sonochem. 31 (2016) 371–382.
[110] L.K. Weavers, M.R. Hoffmann, Sonolytic decomposition of ozone in aqueous solution: mass transfer effects, Environ. Sci. Technol. 32 (1998) 3941–3947.
[111] Z. Wu, M. Franke, B. Ondruschka, Y. Zhang, Y. Ren, P. Braeutigam, W. Wang, Enhanced effect of suction-cavitation on the ozonation of phenol, J. Hazard. Mater. 190 (2011) 375–380.
[112] Z. Wu, H. Shen, B. Ondruschka, Y. Zhang, W. Wang, D.H. Bremner, Removal of blue-green algae using the hybrid method of hydrodynamic cavitation and ozonation, J. Hazard. Mater. 235–236 (2012) 152–158.
[113] L.K. Weavers, F.H. Ling, M.R. Hoffmann, Aromatic compound degradation in water using a combination of sonolysis and ozonolysis, Environ. Sci. Technol. 32 (1998) 2727–2733.
[114] R. Lall, R. Mutharasan, Y.T. Shah, P. Dhurjati, Decolorization of the dye, reactive blue 19, using ozonation, ultrasound, and ultrasound-enhanced ozonation, Water Environ. Res. 75 (2003) 171–179.
[115] H. Destaillats, A.J. Colussi, J.M. Joseph, M.R. Hoffmann, Synergistic effects of sonolysis combined with ozonolysis for the oxidation of azobenzene and methyl orange, J. Phys. Chem. A 104 (2000) 8930–8935.
[116] L.K. Weavers, N. Malmstadt, M.R. Hoffmann, Kinetics and mechanism of pentachlorophenol degradation by sonication, ozonation, and sonolytic ozonation, Environ. Sci. Technol. 34 (2000) 1280–1285.
[117] J.W. Kang, M.R. Hoffmann, Kinetics and mechanism of the sonolytic destruction of methyl tert-butyl ether by ultrasonic irradiation in the presence of ozone, Environ. Sci. Technol. 32 (1998) 3194–3199.
[118] Y.L. Pang, A.Z. Abdullah, S. Bhatia, Review on sonochemical methods in the presence of catalysts and chemical additives for treatment of organic pollutants in wastewater, Desalination 277 (2014) 1–14.
[119] S. Song, M. Xia, Z. He, H. Ying, B. Lu, J. Chen, Degradation of p-nitrotoluene in aqueous solution by ozonation combined with sonolysis, J. Hazard. Mater. 144 (2007) 532–537.
[120] Z. He, S. Song, H. Ying, L. Xu, J. Chen, p-Aminophenol degradation by ozonation combined with sonolysis: operating conditions influence and mechanism, Ultrason. Sonochem. 14 (2007) 568–574.
[121] C.W. Yang, D. Wang, Q. Tang, The synthesis of NdFeB magnetic activated carbon and its application in degradation of azo dye methyl orange by Fenton-like process, J. Taiwan Inst. Chem. Eng. 45 (2014) 2584–2589.
[122] L.P. Ramteke, P.R. Gogate, Treatment of toluene, benzene, naphthalene and xylene (BTNXs) containing wastewater using improved biological oxidation with pretreatment using Fenton/ultrasound based processes, J. Ind. Eng. Chem. 28 (2015) 247–260.
[123] M.V. Bagal, P.R. Gogate, Sonochemical degradation of alachlor in the presence of process intensifying additives, Sep. Purif. Technol. 90 (2012) 92–100.
[124] A. Šarc, T. Stepišnik-Perdih, M. Petkovšek, M. Dular, The issue of cavitation number value in studies of water treatment by hydrodynamic cavitation, Ultrason. Sonochem. 34 (2017) 51–59.
[125] B. Bethi, S.H. Sonawane, G.S. Rohit, C.R. Holkar, D.V. Pinjari, B.A. Bhanvase, A.B. Pandit, Investigation of TiO2 photocatalyst performance for decolorization in the presence of hydrodynamic cavitation as hybrid AOP, Ultrason. Sonochem. 28 (2016) 150–160.
[126] D. Musmarra, M. Prisciandaro, M. Capocelli, D. Karatza, P. Iovino, S. Canzano, A. Lancia, Degradation of ibuprofen by hydrodynamic cavitation: reaction pathways and effect of operational parameters, Ultrason. Sonochem. 29 (2016) 76–83.
[127] G. Boczkaj, A. Przyjazny, M. Kamiński, Characteristics of volatile organic compounds emission profiles from hot road bitumens, Chemosphere 107 (2014) 23–30.
[128] E. Gilgenast, G. Boczkaj, A. Przyjazny, M. Kamiński, Sample preparation procedure for the determination of polycyclic aromatic hydrocarbons in petroleum vacuum residue and bitumen, Anal. Bioanal. Chem. 401 (2011) 1059–1069.
[129] G. Boczkaj, M. Kamiński, A. Przyjazny, Process control and investigation of oxidation kinetics of postoxidative effluents using gas chromatography with pulsed flame photometric detection (GC-PFPD), Ind. Eng. Chem. Res. 49 (2010) 12654–12662.
[130] G. Boczkaj, A. Przyjazny, M. Kamiński, New procedures for control of industrial effluents treatment processes, Ind. Eng. Chem. Res. 53 (2014) 1503–1514.
[131] Y. Lure, P.E. Kandzas, A.A. Mokina, Russ. J. Phys. Chem. 36 (1962) 1422–1425.
[132] K. Inazu, Y. Nagata, Y. Maeda, Decomposition of chlorinated hydrocarbons in aqueous solutions by ultrasonic irradiation, Chem. Soc. Jpn. Chem. Lett. 22 (1) (1993) 57–60.
[133] C. Petrier, A. Francony, Incidence of wave-frequency on the reaction rates during ultrasonic wastewater treatment, Wat. Sci. Technol. 35 (1997) 175–180.
[134] P. Finkbeiner, M. Franke, F. Anschuetz, A. Ignaszak, M. Stelter, P. Braeutigam, Sonoelectrochemical degradation of the anti-inflammatory drug diclofenac in water, Chem. Eng. J. 273 (2015) 214–222.
[135] P.R. Gogate, G.S. Bhosale, Comparison of effectiveness of acoustic and hydrodynamic cavitationin combined treatment schemes for degradation of dye wastewaters, Chem. Eng. Process. 71 (2013) 59–69.
[136] R.H. Jawale, P.R. Gogate, A.B. Pandit, Treatment of cyanide containing wastewater using cavitation based approach, Ultrason. Sonochem. 21 (2014) 1392–1399.
[137] N. Golash, P.R. Gogate, Degradation of dichlorvos containing wastewaters using sonochemical reactors, Ultrason. Sonochem. 19 (2012) 1051–1060.
[138] L.J. Xu, W. Chu, Po-Heng Lee, J. Wang, The mechanism study of efficient degradation of hydrophobicnonylphenol in solution by a chemical-free technology ofsonophotolysis, J. Hazard. Mater. 308 (2016) 386–393.
[139] X. Wang, Y. Zhang, Degradation of alachlor in aqueous solution by using hydrodynamic cavitation, J. Hazard. Mater. 161 (2009) 202–207.
[140] K.K. Jyoti, A.B. Pandit, Effect of cavitation on chemical disinfection efficiency, Water Res. 38 (2004) 2249–2258.
[141] K.K. Jyoti, A.B. Pandit, Hybrid cavitation methods for water disinfection, Biochem. Eng. J. 14 (2003) 9–17.
[142] Y. Benito, S. Arrojo, G. Hauke, P. Vidal, Hydrodynamic cavitation as a low-cost AOP for wastewater treatment: preliminary results and a new design approach, WIT Trans. Ecol. Environ. 80 (2005) 495–503.
[143] Process, CAV-OX Cavitation Oxidation. Application analysis report, magnum water technology, inc. Risk Reduction Engg. Laboratory, Office of Research and Development, USEPA, Cincinnati, Ohio 45268, 1994.
[144] G. Boczkaj, M. Gągol, M. Klein, A. Przyjazny, Effective method of treatment of effluents from production of bitumens under basic pH conditions using hydrodynamic cavitation aided by external oxidants, Ultrason. Sonochem. 40 (2018) 969–979, http://dx.doi.org/10.1016/j.ultsonch.2017.08.032.

Załącznik 2

Publikacja nr 2:

G. Boczkaj, **M. Gągol**, M. Klein, A. Przyjazny, Effective method of treatment of effluents from production of bitumens under basic pH conditions using hydrodynamic cavitation aided by external oxidants, Ultrason. Sonochem. 40 (2018) 969–979.

Ultrasonics - Sonochemistry 40 (2018) 969–979

Contents lists available at ScienceDirect

Ultrasonics - Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

Effective method of treatment of effluents from production of bitumens under basic pH conditions using hydrodynamic cavitation aided by external oxidants

Grzegorz Boczkaj[a,*], Michał Gągol[a,b], Marek Klein[c], Andrzej Przyjazny[d]

[a] *Department of Chemical and Process Engineering, Faculty of Chemistry, Gdańsk University of Technology, Gdansk, Poland*
[b] *Department of Polymer Technology, Gdańsk University of Technology, Faculty of Chemistry, Gdansk, Poland*
[c] *Institute of Fluid-Flow Machinery, Polish Academy of Sciences, Gdansk, Poland*
[d] *Kettering University, 1700 University Avenue, Department of Chemistry & Biochemistry, Flint, MI 48504, USA*

ARTICLE INFO

Keywords:
Hydrodynamic cavitation
Wastewater treatment
Degradation of contaminants
Advanced oxidation processes
Effluents
Bitumen

ABSTRACT

Utilization of cavitation in advanced oxidation processes (AOPs) is a promising trend in research on treatment of industrial effluents. The paper presents the results of investigations on the use of hydrodynamic cavitation aided by additional oxidation processes (O_3/H_2O_2/Peroxone) to reduce the total pollution load in the effluent from the production of bitumens. A detailed analysis of changes in content of volatile organic compounds (VOCs) for all processes studied was also performed. The studies revealed that the most effective treatment process involves hydrodynamic cavitation aided by ozonation (40% COD reduction and 50% BOD reduction). The other processes investigated (hydrodynamic cavitation + H_2O_2, hydrodynamic cavitation + Peroxone and hydrodynamic cavitation alone) ensure reduction of COD by 20, 25 and 13% and reduction of BOD by 49, 32 and 18%, respectively. The results of this research revealed that most of the VOCs studied are effectively degraded. The formation of byproducts is one of the aspects that must be considered in evaluation of the AOPs studied. This work confirmed that furfural is one of the byproducts whose concentration increased during treatment by hydrodynamic cavitation alone as well as hydrodynamic cavitation aided by H_2O_2 as an external oxidant and it should be controlled during treatment processes.

1. Introduction

The production and use of bitumen presents a serious challenge to environmental protection. During the production the problem concerns both the formation of volatile organic compounds (VOCs) [1] and polycyclic aromatic hydrocarbons [2] as well as generation of post-oxidative effluents [3,4] and further utilization of bitumen [5–13]. Waste gases formed during the production (oxidation) of bitumen are cleaned in scrubbers sprinkled with wash oil or an aqueous solution of sodium hydroxide. The latter absorbent in addition to the possibility of condensation of oil mist and absorption of VOCs can also quantitatively trap hydrogen sulfide formed from the oxidized vacuum residue as a result of thermal cracking [3,4]. The remaining gaseous contaminants are utilized thermally whereas the absorbate, so-called post-oxidative effluent, needs to undergo further treatment. In many cases, the treatment of effluents containing such a rich and in some cases hard to define load of pollutants requires a considerable investment associated with an expensive process plant based on complex physicochemical processes. The presence of highly toxic organic and inorganic compounds calls for the use of advanced treatment technologies, ensuring a high degree of oxidation. In the case of bitumens, post-oxidative effluents are sent to a wastewater treatment plant. However, their unique composition precludes the use of biological treatment. A common activated sludge is suitable for treatment of typical petroleum-derived contaminants. On the other hand, post-oxidative effluents contain substantial amounts of oxygenated compounds (ketones, aldehydes, ethers, alcohols) and nitrogen-containing compounds (mainly pyridine derivatives, but also aromatic and aliphatic amines) as well as sulfur compounds [3,4,14–16]. Effluents of this kind require chemical treatment, preferably using advanced oxidation processes (AOPs). A review of recent literature reveals that hydrodynamic cavitation combined with oxidation processes has found increasingly more uses for effluent pretreatment [17–31]. Imploding cavities enable splitting molecules of water and oxidants into highly reactive radicals, including hydroxyl

---

[*] Corresponding author at: Gdansk University of Technology, Faculty of Chemistry, Department of Chemical and Process Engineering, 80 – 233 Gdansk, G. Narutowicza St. 11/12, Poland.
E-mail address: grzegorz.boczkaj@gmail.com (G. Boczkaj).

http://dx.doi.org/10.1016/j.ultsonch.2017.08.032
Received 2 May 2017; Received in revised form 23 August 2017; Accepted 27 August 2017

radicals characterized by the highest oxidation potential. A combination of highly reactive hydroxyl radicals with a high power of implosion allows splitting solid particles into smaller fragments and oxidation of the majority of organic contaminants dissolved in effluents, which cannot be removed by other, traditional methods of treatment. Furthermore, cavities concentrate the number of radicals in a given place of the reaction system thus resulting in homogenization of the entire system and improvement of the effectiveness of oxidation [17]. Cavitation processes have found numerous uses mostly in oxidation of organic contaminants, such as carboxylic acids [18,19], pesticides [20,21], alcohols [22,23], organochlorine solvents [24] or pharmaceutical products [25–27]. In the majority of industrial plants effluent treatment is sequential. Chemical treatment precedes biological processes. The main objective of chemical treatment is the removal of most toxic contaminants which could inhibit the action of activated sludge. Hydrodynamic cavitation combined with advanced oxidation processes (AOP) ensures in many cases a high level of oxidation of organic pollutants (70–100%) [28,29]. The purpose of this work was the investigation of possibility of application and evaluation of the effectiveness of hydrodynamic cavitation combined with ozonation or oxidation using hydrogen peroxide for pretreatment of effluents from the production of bitumens under conditions of basic pH to lower the total organic load and to oxidize persistent organic pollutants.

2. Experimental

2.1. Chemicals

Real effluents from the production of bitumens were obtained from the bitumen oxidation unit using Biturox process (Lotos Asfalt, Grupa Lotos S.A., Gdańsk, Poland), (pH 10.5; COD: 8000–12,000 mg O_2L^{-1}). Deionized water was obtained from the MilliQ water purification system (Millipore Corporation, USA). The following reagents were used: anti-foam agent: Struktol® SB 2032 (Schill + Seilacher, Germany), dichloromethane (for HPLC, Sigma-Aldrich, USA), acetone (for HPLC, Sigma-Aldrich, USA), hydrochloric acid (analytical reagent (AR) grade, Sigma-Aldrich, USA), hydrogen peroxide 30% (POCH S.A., Poland), reagent for COD analysis (sulfuric acid, potassium dichromate, silver sulfate, AR grade, POCH S.A., Poland); standard for COD analysis: sodium hydrogen phthalate (Sigma-Aldrich, USA); standards for quantitative analysis (Sigma-Aldrich, USA): acetaldehyde, propan-1-al, ethyl acetate, methyl acrylate, butan-2-ol, tetrahydrofuran, 2-methylpropan-1-ol, 2-methylbutan-2-ol, butan-1-ol, 2,3-dihydropyran, ethyl acrylate, pentan-2-one, tetrahydropyran, ethyl propionate, 3-methylbutan-1-ol, isobutyl acetate, paraldehyde, pentan-1-ol, hexan-2-one, cyclopentanone, furfural, hexan-1-ol, heptan-3-one, cyclohexanol, anisole, cyclohexanone, 2-methylcyclohexanone, heptan-1-ol, 3-methylcyclohexanone, 2-ethylhexan-1-ol, phenol, benzyl alcohol, acetophenone, o-cresol, 4-methylbenzaldehyde, m-cresol, 2,6-dimethylphenol, 4-ethylophenol, 4-chlorophenol, 4-chlorobutan-1-ol, 3-chlorobutan-1-one. Ozone was produced in a Tytan 32 ozone generator (Erem) at a rate of 9.41 g/h.

2.2. Hydrodynamic cavitation

The treatment of effluents from the production of bitumens by hydrodynamic cavitation aided by oxidation (using hydrogen peroxide or ozone) was carried out in a reaction system shown in Fig. 1. The system consists of a 11-L tank, stirrer, heating and temperature control system, water condenser, vane pump (MS 801-4, 1360 min^{-1}, TECHTOP® MOTOR, Shanghai, China), two digital manometers, electromagnetic flowmeter (MPP 600 by MAGFLO®) and a Venturi tube. The same type of Venturi tube was investigated in previous papers by S. Raut-Jadhav [32] and similar by B. Bethi [33] and M. P. Badve [34]. The tank and connecting elements were made of stainless steel (SS316). Inlet and outlet tubing was made of poly(tetrafluoroethylene) (PTFE). A Venturi tube was made of brass. A vane pump (MS 801-4, 1360 min^{-1}, TECHTOP® MOTOR, Shanghai, China) with a maximum flow rate of 1000 L h^{-1} was used in the reaction system. The volume of effluent treated in the system was 5 L plus 2 mL of anti-foam agent. The effluent temperature was maintained at 40 ± 2 °C by means of an electric heater and condenser cooled with tap water. A Venturi tube had a diameter of 10 mm with a throat diameter of 2 mm (Fig. 2). Effluent treatment was carried out for 360 min at various inlet pressures (6–10 bar) and flow rates 470–590 L h^{-1}. Samples were collected every 15 min during the first hour of the process. After the first hour, samples were collected every hour. Ozonation was performed using a Tytan 32 ozone generator (Erem) at a maximum rate of 9.41 g O_3 h^{-1} at a flow rate of 15 L min^{-1}. Ozone was injected into and behind the throat. Hydrogen peroxide (30%) was fed to the system using a high-pressure pump (S-7110 isocratic pump, Merck-Hitachi, Japan) with a flow rate from 0.5 to 1.5 mL min^{-1}. The pump was connected to the Venturi tube behind the throat (more details in Fig. 1).

2.3. Process control

2.3.1. COD

Chemical oxygen demand was determined using COD cuvette test (HACH®, UK). COD of effluents was monitored using a spectrophotometric method (Spectrophotometer DR2010, HACH®, USA). Samples were combusted in a thermoreactor (HACH®, USA) at 150 °C for 2 h.

2.3.2. BOD

The determination of biochemical oxygen demand was carried out according to ISO 5815-1:2003 (E) standard. Oxygen content was measured using a dissolved oxygen probe COG-1 (ELMETRON®, Poland).

2.3.3. Analysis of composition of VOCs

Identification and quantitative analysis were carried out by gas chromatography-mass spectrometry using a QP2010SE GC–MS (Shimadzu, Japan). Samples were prepared for analysis using dispersive liquid–liquid microextraction (DLLME). The exact experimental procedure was described previously [15].

2.3.4. Investigation of ozone emission from the reactor

The determination of emission of unreacted ozone from the reactor was carried out using the ozone wet-chemistry test reported by Rakness [35]. A piece of PTFE tubing was connected to a tightly closed reactor. The tubing directed unreacted ozone to two scrubbers, each one containing 400 mL of a 2% potassium iodide solution. Before the scrubbers the stream was split into two streams having the same flow rate. One of them was fed directly to the scrubbers and the other to the ventilation system. Unreacted ozone was collected during the entire treatment and the solution in the scrubbers was replaced every hour. Next, the collected solutions were titrated with 0.1 N $Na_2S_2O_3$ to determine the emission of unreacted ozone from the reactor during every hour of the treatment.

3. Results and discussion

3.1. Hydrodynamic cavitation

A Venturi tube whose design was described in paper [32] was used in the investigations. Due to the fact that the industrial effluents investigated had a complex composition, a tested tube geometry was used to ensure that the cavitation conditions allow effective degradation of organic compounds. The use of a previously validated design also allows a comparison of efficiency of degradation of other types of contaminants for AOP processes combined with cavitation which provides information on the applicability of this approach for a wide variety of contaminants. The main parameter used to evaluate the effectiveness of

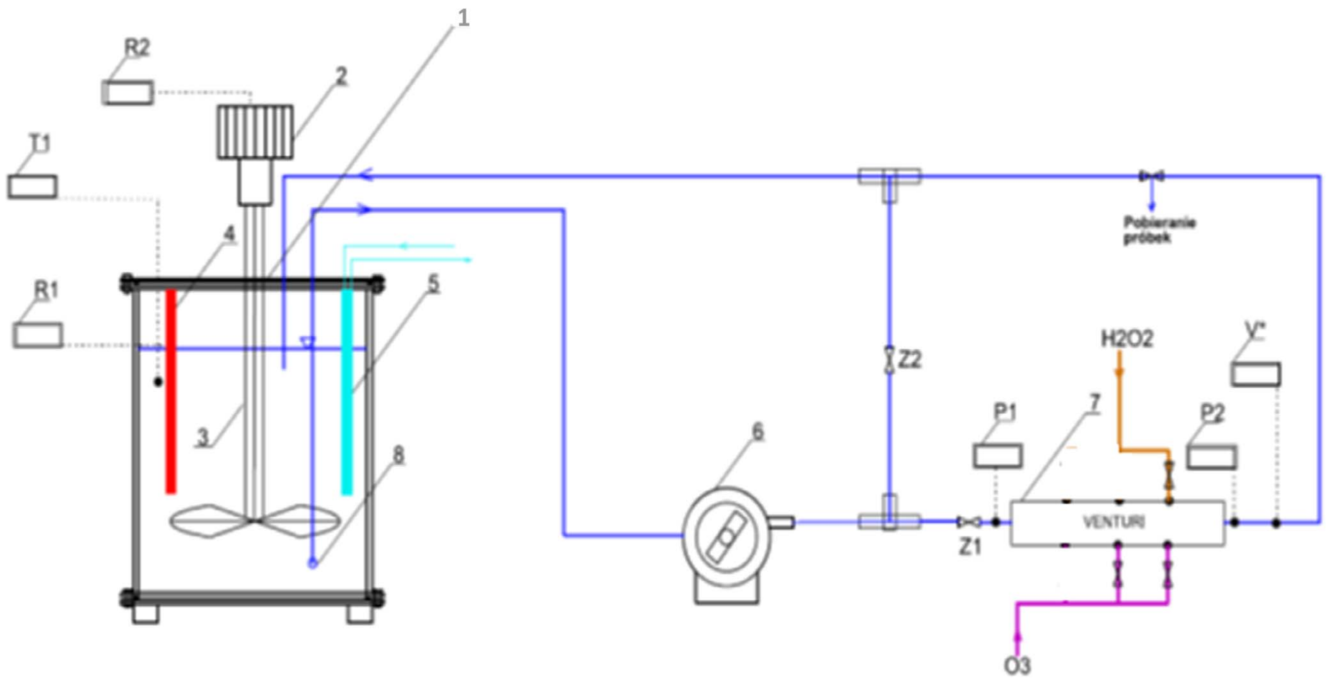


Fig. 1. Schematic diagram of hydrodynamic cavitation system with Venturi tube. 1 – tank, 2 – stirrer motor, 3 – stirrer arm, 4 – temperature sensor, 5 – water condenser, 6 – vane pump, 7 – Venturi tube, 8 – suction side of the pump, T1 – connection of temperature sensor to control panel; R2 – connection of stirrer motor to control panel; R1 – connection of lighting to control panel, Z2 – bypass line valve, Z1 – main line valve, P1, P2 – digital manometers, V* – flowmeter.

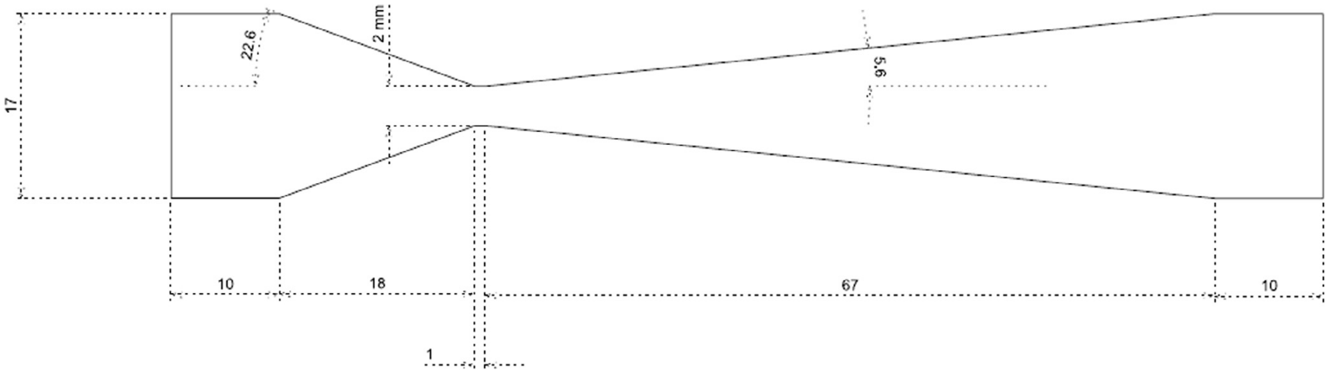


Fig. 2. Schematic of Venturi tube.

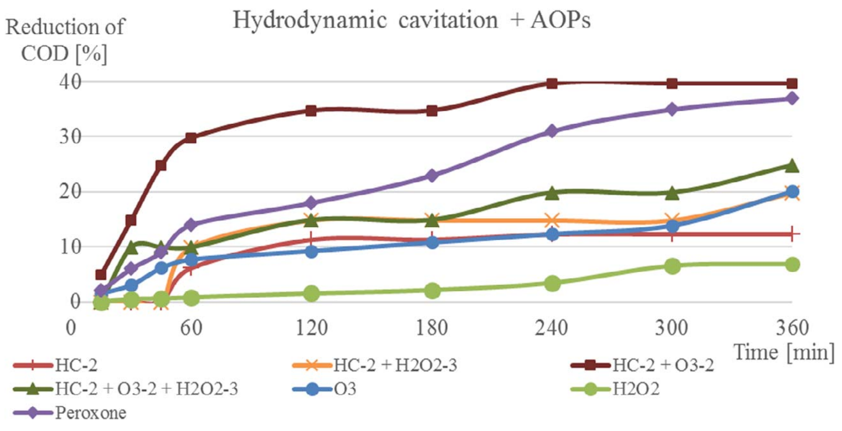


Fig. 3. Comparison of effectiveness for studied hydrodynamic cavitation processes aided by external oxidant.

decreasing total pollution load was chemical oxygen demand. The effectiveness of lowering COD of the effluent solely by hydrodynamic cavitation is depicted in Fig. 3. Three variants of the treatment process were used whereby inlet pressure, cavitation number and volumetric flow rate of the pumped effluent were varied. Process parameters for the experiments are listed in Table 1. It follows from the data in Table 1 that the most effective treatment was HC-2. At a flow rate of 520 L h^{-1}, inlet pressure of 8 bar and a cavitation number of 0.103, the effluent COD was lowered by almost 13% during 120 min of the treatment. This result is not as good as some of the data reported in the literature.

Table 1
Operating conditions for hydrodynamic cavitation process aided by external oxidant.

Process	Flow rate [Lh^{-1}]	Temperature [°C]	Time [min]	Upstream pressure P [bar]	Cavitation number*	H_2O_2 flow rate [$mLmin^{-1}$]	O_3 flow rate [gh^{-1}]	COD reduction [%]	r_{ox} (molar)
HC-1	590	40	360	10	0.08	X	X	9.9	X
HC-2	520	40	360	8	0.14	X	X	12.9	X
HC-3	395	40	360	6	0.18	X	X	11.9	X
HC-2 + H_2O_2-1	520	40	360	8	0.14	0.5	X	17.9	2.1
HC-2 + H_2O_2-2	520	40	360	8	0.14	1.5	X	18.8	6.2
HC-2 + H_2O_2-3	520	40	360	8	0.14	1.0	X	19.7	4.1
HC-2 + O_3 (to the throat)-1	520	40	360	8	0.14	X	9.41	38.5	1.4
HC2 + O_3 (behind throat)-2	520	40	360	8	0.14	X	9.41	39.7	1.4
HC-2 + O_3-2 +H_2O_2-3	520	40	360	8	0.14	1.0	9.41	24.8	1.3
O_3	124	40	360	0.65	1.81	X	9.41	20.1	X
H_2O_2	120	40	360	0.31	1.82	1.0	X	6.8	X
Peroxone (H_2O_2/O_3)	125	40	360	0.71	1.79	1.0	9.41	37.0	X

*$C_v = \frac{(P_2 - P_v)}{2^1 u^2 \times \rho}$, p_2-downstream pressure [Pa], p_v – water vapor pressure at 40 °C [Pa], u – linear velocity at the throat of Venturi tube [ms^{-1}], ρ – density of the pumped medium at 40 °C [$kg\ m^{-3}$].

Padoleya et al. [28] treated distillery wastewater having a similar total pollution load (COD 35,000 mg L^{-1}) and obtained a 34.3% reduction of COD during 150 min; however, the treatment was carried out at a neutral pH. Moreover, composition of the effluent was much less aggressive than the effluent from the production of bitumen. Similarly, Matusiewicz et al. [29] using hydrodynamic cavitation of brewery spent grain diluted by wastewater with a COD of 630 mg L^{-1} achieved a decrease in COD of 24% in 30 min. In the case of effluents from the production of bitumens pH cannot be lowered owing to a high content of sulfides which would be released to the atmosphere as hydrogen sulfide at a neutral or acidic pH. Furthermore, the plot in Fig. 3 reveals that the COD of the effluent does not change during a certain period of the treatment. This can be attributed to the presence in the effluent of organic compounds that are both easy and difficult to oxidize. Readily oxidizable compounds are oxidized first after just a few passes through the cavitation zone which causes a substantial reduction of COD of the effluent in a short time (60–120 min). Next, the effluent COD remains at the same level (for 2–3 h) until another reduction in COD due to oxidation of resistant compounds. Compounds resistant to oxidation require much longer residence time in the cavitation zone. The results are also affected by the cavitation number, which determines the degree of cavity generation in the throat and intensity of the phenomenon. Hence, at the same recirculation the intensity of oxidation of pollutants will be different which results in a nonlinear trend of COD reduction of the effluent during cavitation. The cavitation number (C_v) describes the intensity of cavitation phenomenon. An increase in inlet pressure of the treated medium results in an increase in its flow rate which decreases the cavitation number. The smaller the cavitation number the greater the number of cavities generated and the lower the effectiveness of degradation of pollutants after exceeding the limiting value of inlet pressure. This is attributed to the generation of a large number of cavities at a high inlet pressure which results in their coalescence and formation of a cavity cloud, which hinders an implosion of the generated cavities. This phenomenon is called choked cavitation and it has been described in detail [31]. According to the literature data, cavitation takes place when the cavitation number is equal to or less than one but in some cases cavities can be generated at a cavitation number greater than one due to the presence of dissolved gases and suspended particles which provide additional nuclei for the cavities to form. However, the effectiveness of generation of cavities is the highest when C_v is less than 1 [31,36]. Consequently, oxidation of pollutants is often carried out at inlet pressures allowing the cavitation number to range from 0.1 to 1. No changes in pH were observed during the effluent treatment with respect to the initial pH of the effluent which was 10.5. Many AOP processes take place at a neutral or acidic pH due to much higher effectiveness of oxidation than at basic pH values. This is the case in, among others, Fenton process. However, effluents from the production of bitumens require basic pH values in order to completely retain hydrogen sulfide, which under such conditions occurs in the form of sulfide ions S^{2-}. Correction of pH prior to treatment of these effluents is not recommended due to the possibility of release of H_2S. Consequently, this paper reports the results of investigations on the effectiveness of treatment of the effluents under basic conditions.

3.2. Hydrodynamic cavitation + H_2O_2

The effectiveness of lowering COD load of the effluent by hydrodynamic cavitation aided by oxidation with hydrogen peroxide is depicted in Fig. 3. The most effective HC conditions were used along with three different doses of hydrogen peroxide. In each case hydrogen peroxide was introduced continuously during the entire treatment process. Specific process parameters are listed in Table 1. The greatest reduction in COD (by 20%) of the effluent was achieved when hydrogen peroxide was fed at 1.0 mL·min^{-1}. Hydrogen peroxide is a weak acid with a relatively high oxidation potential dependent on pH (1.80 V at pH = 0; 0.87 V at pH = 14), which does not undergo spontaneous decomposition yielding hydroxyl radicals in the reaction medium [37]. In the case of this study, the efficiency of the process can be affected by three different mechanisms of oxidation of organic contaminants:

- direct reactions between contaminants and oxidant,
- reactions between hydroxyl radicals (generated through cavitation and decomposition of external oxidant) and contaminants,
- thermal decomposition resulting from collapse of gaseous bubbles.

The use of cavitation involves the last two mechanisms for degradation of organic contaminants. At the same time, the results of studies on degradation of organic compounds by cavitation alone reveal that the process reduces COD by 13%. A much improved reduction of COD for the processes aided by external oxidants demonstrates that the most important role in degradation is played by the reactions of contaminants with hydroxyl radicals and direct reactions with the oxidant. Hydrogen peroxide as a single oxidant can react directly mostly with chlorinated alkanes (absent from the investigated effluent), carboxylic acids and polycyclic aromatic hydrocarbons [38,39]. The mechanism of direct oxidation involves primarily the reaction of contaminants with the perhydroxyl anions formed through decomposition of hydrogen peroxide ($H_2O_2 \rightarrow H^+ + {}^-OOH$). Decomposition of hydrogen peroxide is most effective in an acidic medium. However, in case of a basic pH (the effluent studied has a pH 10.5), hydrogen peroxide reacts with hydroxide anions yielding the perhydroxyl anions (Eq. (1)). Under these conditions it is the perhydroxyl anion that is responsible for oxidizing properties of hydrogen peroxide. It reacts with organic contaminants forming adducts which can undergo internal rearrangements to split an anion or to promote migration of the alkyl radical with an electron pair to form an oxidation intermediate. An example of such a reaction is the Baeyer-Villiger reaction of a ketone with hydrogen peroxide yielding an ester [40]. Consequently, all the oxygenated intermediates are much more resistant to oxidation by hydrogen peroxide and must remain much longer in the reaction medium to be completely degraded [37]. Therefore, the mechanism of direct oxidation of organic contaminants by hydrogen peroxide alone causes lowering of initial concentrations of the pollutants in the course of the reaction but the reduction of total pollutant load of the effluent (COD) requires a much larger dose of the oxidant and a much longer time of the reaction.

In the studied process the main mechanism of oxidation of organic contaminants involving hydroxyl radicals formed due to decomposition of hydrogen peroxide under conditions of hydrodynamic cavitation, which are much better oxidants (oxidation potential 2.8 V) than the perhydroxyl anions. Hydroxyl radicals react non-selectively with the contaminants present in the effluent; thus, these are mostly oxidation reactions which occur in the effluent being treated and are responsible for the reduction of COD of the effluent. The main mechanisms of oxidation of selected organic contaminants by hydroxyl radicals are described in detail in a paper by Bhattacharjee [37]. Combination of cavitation with oxidation aims at an increase in the number of hydroxyl radicals in solution (Eqs. (2) and (3)). In this case, the main source of hydroxyl radicals in the aqueous medium being treated is decomposition of hydrogen peroxide (H_2O_2). Most commonly, the amount of hydrogen peroxide added is selected by calculating the amount of oxidant needed to lower the COD of the effluent. For the 5 L of effluent with a COD around 11,000 mg $O_2 \cdot L^{-1}$, the amount of 30% hydrogen peroxide needed to lower COD (complete reduction – 100%) during a 360-min process is equal to about 166 mL (volumetric flow rate during the treatment is 0.46 mL min^{-1}). The mole ratio of the amount of oxidant provided by hydrogen peroxide added to COD of the effluent is $r_{OX} = \frac{HO^{\cdot}\ (oxidant)}{COD\ (waste)} = 1.9$ (detailed calculation below). Addition of an insufficient amount of the oxidant will cause a substantial decrease in efficiency of oxidation of pollutants due to too small a number of hydroxyl radicals formed as a result of decomposition of H_2O_2 participating in the oxidation process [34].

Calculation of r_{ox} parameter:

COD reduction: 100%; volumetric flow rate of 30% H_2O_2: 0.46 $ml \cdot min^{-1}$; density of 30% H_2O_2: 1.11 $g \cdot mL^{-1}$; time of process: 360 min,

COD of the effluent: 11,000 mg $O_2 \cdot L^{-1}$,

For 5 L of the effluent: oxygen demand = 5 * 11,000 = 55 g O_2; 55/32 = 1.7 mol of O_2,

The mass of introduced 30% hydrogen peroxide: $m = 0.46 * 360 * 0.3 * 1.11 = 55.1$ g H_2O_2

The mass of introduced $HO^{\cdot}$ radicals (stoichiometric reaction): $m_r = 55.1$ g; 55.1/17 = 3.2 mol of oxidant,

$r_{ox} = HO^{\cdot}/COD = 3.2/1.7 = 1.9$

$$H_2O_2 + OH^- \rightarrow H_2O + HO_2^- \quad (1)$$

$$H_2O_2 \xrightarrow{cavitation} 2HO^{\cdot} \quad (2)$$

$$HO^{\cdot} + pollutants \xrightarrow{cavitation} degradation\ product \quad (3)$$

Addition of an excessive amount of hydrogen peroxide is also undesirable as it lowers the degree of degradation of pollutants. This is mostly due to generation of radicals with a significantly lower oxidation potential than hydroxyl radicals (Eqs. (4)–(7)) as well as reactions of the radicals with hydrogen peroxide molecules [20,41,42].

$$HO^{\cdot} + HO^{\cdot} \xrightarrow{cavitation} H_2O_2 \quad (4)$$

$$HO^{\cdot} + H_2O_2 \xrightarrow{cavitation} H_2O + HO_2^{\cdot} \quad (5)$$

$$HO_2^{\cdot} + HO_2^{\cdot} \xrightarrow{cavitation} H_2O_2 + O_2 \quad (6)$$

$$HO^{\cdot} + O_2 \xrightarrow{cavitation} HO_2^{\cdot} + O^{\cdot} \quad (7)$$

The two opposite effects, *i.e.* decomposition of H_2O_2 in a basic medium without the formation of hydroxyl radicals and decomposition of H_2O_2 under cavitation conditions to yield hydroxyl radicals were studied in this work. The desired effect of reducing COD by addition of hydrogen peroxide would take place if the latter effect (generation of hydroxyl radicals under cavitation conditions) was predominant. However, the results of this study reveal that the predominant path for decomposition of hydrogen peroxide in a basic medium yields the products with a low oxidation potential. Thus, in order to obtain efficient degradation of contaminants in the investigated system, excess H_2O_2 with respect to COD of the effluent has to be used. However, this solution is not economically justifiable.

Consequently, the most effective lowering of COD of the effluent was observed at a flow rate of 1 $ml \cdot min^{-1}$ ($r_{OX} = 4.1$). Hydrodynamic cavitation combined with hydrogen peroxide allows a higher degree of oxidation of organic pollutants present in the real effluent than the HC alone: COD reduction of 20% as compared with 13%. Similar results of an increased effectiveness of effluent treatment by adding an external oxidant were reported earlier [17–33]. As was the case for HC alone, also for HC aided by an external oxidant COD of the effluent was found not to be decreased between 120 and 300 min of the treatment process. Most likely, under experimental conditions readily oxidizable pollutants are completely oxidized in 120 min. Additionally, no changes in pH were observed during the treatment process. During the treatment the effluent gradually became cloudy, followed by a gradual color change from light yellow to dark brown (until 120 min), which can be attributed to formation of new chemical structures by the chemical compounds being oxidized, and then a complete decolorization and clarification. GC–MS analysis revealed only the formation of furfural as a byproduct generated during the treatment. The majority of compounds undergo oxidation to nonvolatile or slightly volatile organic compounds. For example, aromatic compounds containing several hydroxyl groups (formed from benzene or phenol) cannot be determined by GC. Similarly, the opening of an aromatic ring during oxidation yields compounds having two aldehyde groups which will then be oxidized to compounds with two carboxyl groups [37]. Such compounds are nonvolatile so they cannot be detected by GC–MS. At the same time, their formation from VOCs is advantageous in terms of lowering malodorousness of effluents.

3.3. Hydrodynamic cavitation + O_3

The effectiveness of lowering COD load of the effluent using hydrodynamic cavitation aided by ozonation is shown in Fig. 3. Two independent processes were investigated in which the location of ozone feed was changed. The process was carried out at a maximum rate of the ozone generator (9.41 $g \cdot h^{-1}$). Ozone wet-chemistry test was carried out according to the procedure reported by Rakness [35], which determined the amount of unreacted ozone in the gas leaving the reaction system. The studies revealed that no ozone is emitted from the reactor during the first 2.5 h. However, after this period about 3 g of unreacted O_3 is released from the reactor which constitutes 32% of the introduced dose. Thus, during the initial 2.5-h period saturation of the aqueous phase with ozone takes place in addition to oxidation and the ozone dose used is justified. One of the factors affecting the efficiency of ozonation is the limited mass transfer between the gaseous phase and the effluent. A positive effect of combination of ozonation with cavitation is that the flow of the effluent in the setup including the Venturi tube is turbulent which intensifies the mass transfer between the gaseous and the aqueous phase. Ozone undergoing decomposition to hydroxyl radicals and reacting directly with organic contaminants must first be dissolved in the effluent. Only then the majority of desirable chemical reactions can take place. At the same time the solubility of ozone in the effluent is limited. Thus the optimum approach is to obtain saturation of the effluent with ozone under operating conditions. The results of this study indicate that such an effect is obtained gradually during the first two hours of the treatment. Details of process parameters for the investigations are provided in Table 1. A 40% reduction of COD of the real effluent was achieved during 6 h of the treatment at an inlet pressure of 8 bar and a flow rate of 520 $L\,h^{-1}$. The highest rate of removal of COD was observed during the first 60 min of the process (close to 30% of COD reduction). Doubling this time improved the removal efficiency by another 5% for both the time period 60–120 min and 120–240 min. No changes in the effluent pH were observed (pH = 10.5 during the entire treatment). Similarly to application of hydrogen peroxide, the effluent gradually became cloudy, followed by a gradual color change from light yellow to dark brown (until 120 min), and then a complete decolorization and clarification (Fig. 4).

Similarly to hydrodynamic cavitation aided by hydrogen peroxide, also for HC + O_3 three different mechanisms of oxidation can be proposed:

- direct reactions pf contaminants with ozone,
- reactions of contaminants formed as a result of decomposition of ozone under conditions of hydrodynamic cavitation and
- thermal degradation of contaminants.

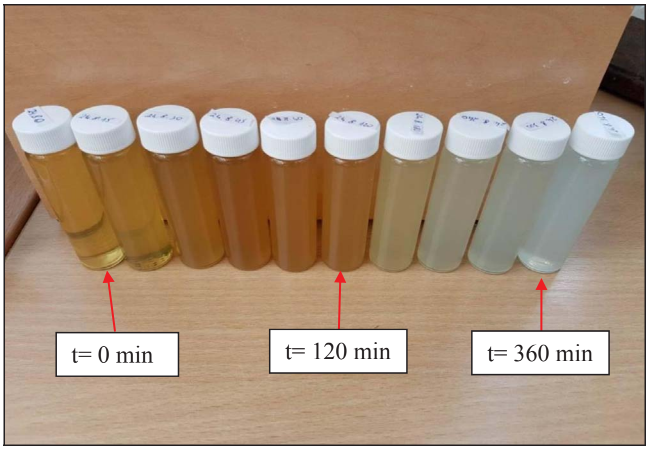


Fig. 4. Color change of effluent samples in hydrodynamic cavitation + O_3 pretreatment process.

The main mechanisms are direct reactions of contaminants with ozone and with hydroxyl radicals. The mechanism of direct oxidation with ozone is mainly associated with its chemical structure. Ozone is a 1,3-dipole and can thus behave as a nucleophile or an electrophile. Therefore, during direct ozonation three different types of reaction with organic contaminants in the effluent can take place [43–45]. In the case of dipolar structure ozone forms with contaminants containing double or triple bonds ozonides, which are converted in the aqueous medium to ketones or aldehydes (Fig. 5). In the case of electrophilic reactions ozone reacts with contaminants having high electron density (mostly compounds containing the aromatic ring). Aromatic compounds having electron donating groups, such as –OH or $-NH_2$ have high electron density on the carbon atoms in the ortho and para positions, which results in the electrophilic attack of ozone on these positions and opening of the aromatic ring. An example of oxidation of phenol by ozone in the reaction medium is provided by Fig. 5. The last possibility of direct oxidation by ozone are nucleophilic reactions. These reactions take place ozone and contaminants containing electron withdrawing groups, such as –COOH or $-NO_2$. Ozone reacts in a highly selective manner oxidizing contaminants to simple organic forms [45]. However, the main mechanism of oxidation of contaminants in the treatment process described in this work is the reaction with hydroxyl radicals formed through decomposition of ozone under conditions of hydrodynamic cavitation [37].

The energy of imploding cavities converts water molecules to reactive radical species which, reacting with ozone, result in the formation of reactive hydroxyl radicals responsible for oxidation of the majority of organic pollutants. At the same time, ozone is converted to reactive chemical species which are further converted to hydroxyl radicals (Eqs. (8)–(10)).

$$O_3 + pollutants \xrightarrow{cavitation} degradation\ product \tag{8}$$

$$O_3 \xrightarrow{cavitation} O_2 + O^{\cdot} \tag{9}$$

$$O^{\cdot} + H_2O \xrightarrow{cavitation} 2HO^{\cdot} \tag{10}$$

A significant improvement in the effectiveness of hydrodynamic cavitation by combining it with ozonation was reported by Gogate and Patil [21] (50% degradation of triazophos by hydrodynamic cavitation alone versus complete degradation by combination of HC and ozonation), Raut-Jadhav et al. [32] (5% versus 70%) and Prajapat and Gogate [46] (30% versus 90%). Location of the place for injecting ozone is also an important parameter affecting the degree of COD removal. The highest effectiveness was obtained by injecting ozone in tank where the flow is undisturbed (1% increase) although the differences in the effectiveness are small for the same times. Similar results were obtained by Gogate and Patil [21] who improved the % degradation of triazophos by 8% by introducing ozone in tank instead of at orifice. The authors attribute this effect by a drop in inlet pressure of the medium before the orifice resulting from the introduction of ozone and thus limitation of the cavitation phenomenon. At the same time, a lowered pressure decreases the solubility of ozone and oxygen in the liquid, thus reducing the amount of oxidant available for reactions in solution. At an inlet pressure of 5 bar the flow rate was around 290 $L\,h^{-1}$. When ozone was introduced at the orifice plate the flow rate dropped drastically to 120 $L\,h^{-1}$. A decreased flow rate limited the number of passes of liquid thus affecting the dissociation of water molecules and ozone resulting in the formation of hydroxyl radicals. A similar effect was observed in this work although the differences were small. Our results reveal that the location of ozone injection had no significant effect on the % removal of organic pollutants present in the effluents from bitumen production under conditions of basic pH. An important difference between this research and the references cited is the fact that the effluents investigated in this study are real effluents having a complex composition. Thus, the effectiveness of removal of pollutants observed is the

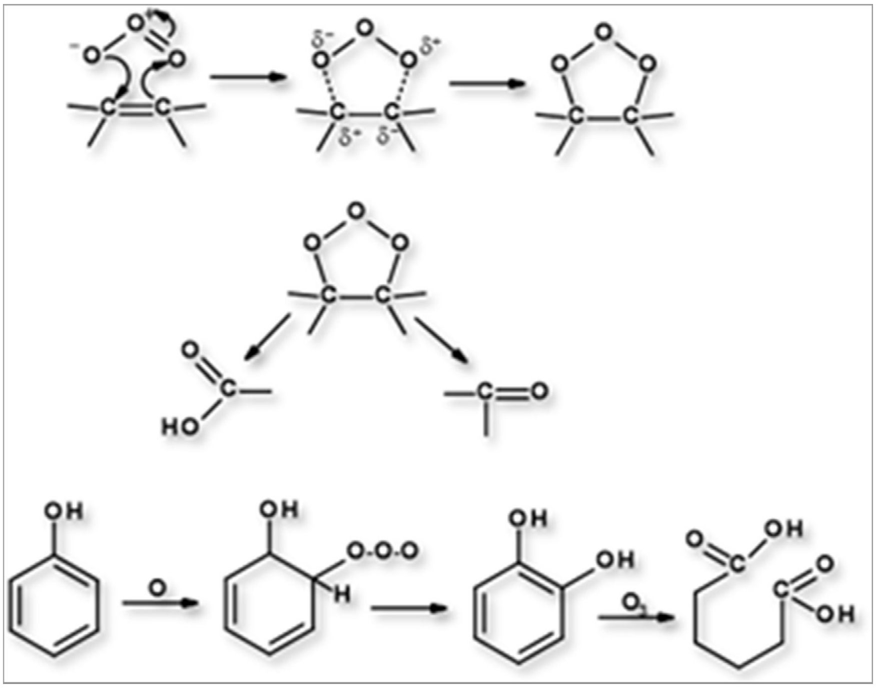


Fig. 5. Reaction of dipolar structure ozone forms with contaminants containing double bonds.

resultant for chemical compounds belonging to different groups. Hydroxyl radicals react nonselectively with contaminants present in the effluent and the reactions are characterized by large values of rate constants. Detailed studies of the reaction rates of hydroxyl radicals with 25 organic contaminants present in drinking water were published by Haag and Yao [47]. The high efficiency of oxidation of hydroxyl radicals does not include all contaminants present in a real effluent which contains both readily oxidizable and refractory compounds. Contaminants that are readily oxidized by hydroxyl radicals include, among others, 1-propanal, 2-pentanone or phenol. Compounds for which hydroxyl radicals exhibit zero or minimal effectiveness of oxidation include, among others, chlorinated compounds [47,48], 4-chloro-2-nitrobenzene [49], benzene with linear alkyl chains [50,51] as well as saturated and cyclic hydrocarbons or furfural. In the course of the treatment the rate of degradation by oxidation decreases due to removal from the reaction medium of readily oxidized compounds. Hydroxyl radicals are still generated; however, their excess in the reaction medium results in consumption in side reactions (reactions (11)–(13)) [48]:

$$H_2O_2 + HO^{\cdot} \xrightarrow{cavitation} H_2O + HO_2^{\cdot} \qquad (11)$$

$$O_3 + HO^{\cdot} \xrightarrow{cavitation} O_2 + HO_2^{\cdot} \qquad (12)$$

$$HO_2^{\cdot} + HO^{\cdot} \xrightarrow{cavitation} H_2O + O_2 \qquad (13)$$

Consequently, oxidation reactions are terminated and COD of the effluent is no longer reduced after 240 min of the treatment.

3.4. Hydrodynamic cavitation + peroxone (O_3 + H_2O_2)

The effectiveness of lowering COD of the effluent by means of hydrodynamic cavitation aided by the peroxone process (combination of hydrogen peroxide and ozone) was also investigated. The results of investigations are shown in Fig. 3. The treatment process was carried out by introducing the oxidants behind the throat due to the results described in paragraph 3.3. The COD value of the effluent was lowered by 25%. Compared with hydrodynamic cavitation combined with ozonation alone, the % removal decreased by 15%. This can be attributed mainly to depletion of reactive forms of ozone by hydrogen peroxide molecules. Alkaline conditions (the effluent pH 10.5) promote the reactions of ozone with hydrogen peroxide hydroperoxyl radicals (which have a lower oxidation potential than hydroxyl radicals), which in subsequent reactions consume reactive hydroxyl radicals in reactions yielding water and oxygen (Eq. (14) and (15)). This results in a decrease of the effectiveness of oxidation of organic pollutants and, consequently, a lowered% COD removal of the effluent.

$$O_3 + H_2O_2 \xrightarrow{cavitation} O_2 + HO_2^{\cdot} + HO^{\cdot} \qquad (14)$$

$$HO_2^{\cdot} + HO^{\cdot} \xrightarrow{cavitation} H_2O + O_2 \qquad (15)$$

3.5. Synergism of combined processes and their energy efficiency

The synergism of combined processes was calculated from Eq. (16) (using hydrodynamic cavitation combined with ozonation as an example).

$$S_{coefficient} = \frac{COD\ reduction\ (cavitation + O_3)}{COD\ reduction\ (cavitation) + COD\ reduction\ (O_3)} = \frac{39.7}{13 + 20.1} = 1.2 \qquad (16)$$

The results of calculation (Table 4) reveal that the greatest synergism is for hydrodynamic cavitation aided by ozonation (S = 1.2). There is no synergism for cavitation aided by hydrogen peroxide (S = 1.0) whereas for the peroxone process the effect of combined treatment is worse than the sum of efficiencies of individual processes (S = 0.5). The synergism for cavitation combined with ozonation is mostly due to the favorable effect of hydrodynamic cavitation on generation of turbulence and microcirculation in the liquid. The additional motion of the liquid limits mass transfer resistance and improves intensification of mixing thus increasing the rate of dissolution of ozone in the liquid. The larger the amount of dissolved ozone the greater the number of hydroxyl radicals which improves the efficiency of oxidation of organic pollutants and reduction of COD of the effluent. Moreover, the pH of the reaction medium (strongly basic) enhances the chemistry of treatment by ozonation.

In order to compare energy efficiencies of the investigated processes in terms of reduction of COD of the effluent, the average power

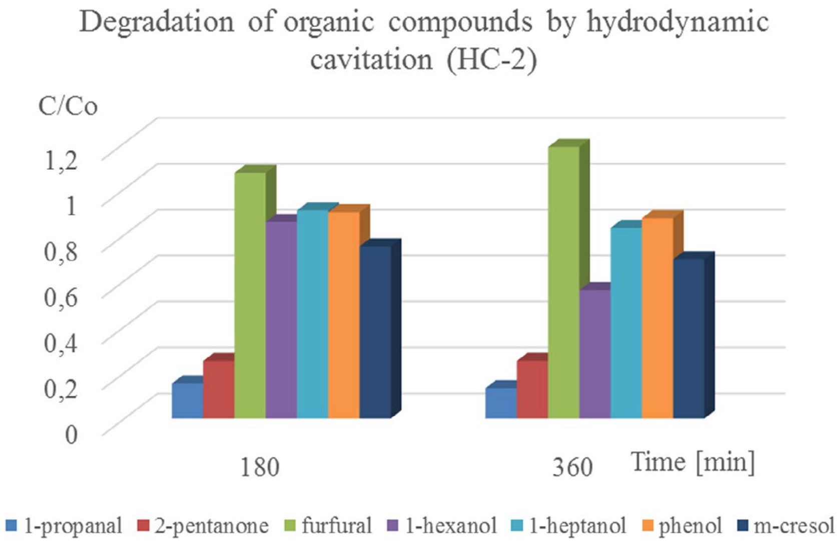


Fig. 6. Degradation of organic compounds by hydrodynamic cavitation.

consumption (in watts) of the devices was used: vane pump – 1100 W; ozone generator – 450 W. In the case of hydrogen peroxide treatment, power consumption by small pumps used at low flow rates is negligible. The energy consumption was related to reduction of COD. The results of calculations are provided in Table 4. It was demonstrated that the most energy efficient process was ozonation (lowering COD of the effluent by 1.13 mg O_2/dm^3 per kJ of energy used) while the least effective process was hydrodynamic cavitation alone (lowering COD of the effluent by 0.24 mg O_2/dm^3 per kJ of energy used). Both hydrodynamic cavitation and ozonation are preferred treatment methods in many industrial facilities as they limit operating costs to electric energy alone and no additional chemicals, such as hydrogen peroxide, have to be purchased. Oil refineries often have surplus of electric energy as a result of cogeneration of steam and electric energy. In this case such a surplus can be utilized for treatment of effluents.

3.6. *Degradation of organic compounds by hydrodynamic cavitation*

The results of quantitative analysis of organic compounds present in the effluent treated by hydrodynamic cavitation are depicted in Fig. 6. The results are shown for the untreated effluent as well as for the effluent treated for 180 and 360 min. Parameters of the investigated process are listed in Table 1 (process HC-2). A detailed description of the procedure was provided in previous papers [15,16]. The plots represent the ratio of concentration of a pollutant after time *t* to its initial concentration. The majority of the pollutants present in the effluent were oxidized. The highest effectiveness of oxidation was achieved after 180 min of the process. Almost 85% of propan-1-al and 70% of pentan-2-one were oxidized. However, for the remaining pollutants the% oxidation was less than 50%. On the other hand, the furfural content in the effluent increased which can be attributed to a number of radical reactions of fragments of the pollutants being oxidized resulting in the formation of new, secondary organic pollutants.

3.7. *Degradation of organic compounds by hydrodynamic cavitation + H_2O_2*

The results of determination of organic pollutants present in the effluent treated by hydrodynamic cavitation aided by hydrogen peroxide are shown in Fig. 7. Parameters of the investigated process are shown in Table 1 (process HC-2 + H_2O_2-3). The majority of the pollutants present in the effluent were oxidized. The highest effectiveness of oxidation was achieved after 180 min of the treatment. Over 60% of the majority of pollutants present in the effluent were oxidized. Hydrodynamic cavitation aided by hydrogen peroxide was found to be least effective for the oxidation of 1-hexanol and 1-heptanol. Similarly to the case of hydrodynamic cavitation alone, the content of furfural in the effluent increased. The results of this investigation reveal that furfural is one of the oxygenated pollutants whose concentration should be controlled during treatment processes. The formation of by-products (secondary pollutants) is one of the aspects that have to be considered during evaluation and selection of the optimum technology of effluent treatment.

3.8. *Degradation of organic compounds by hydrodynamic cavitation + O_3*

The results of determination of organic pollutants present in the effluent treated by hydrodynamic cavitation combined with ozonation are shown in Fig. 8. Parameters of the investigated process are shown in Table 1 (process HC-2 + O_3-2). All the volatile oxygenated pollutants present in the effluent were oxidized. During 180 min of the process the content of the investigated organic pollutants was reduced by close to 100%. Hydrodynamic cavitation aided by ozonation is the most effective treatment among the investigated ones for lowering COD of the effluent from the production of bitumen. Consequently, it should be selected for the treatment of an industrial effluent with a COD of 8000–12,000 mg O_2L^{-1}.

Seven out of 41 oxygenated organic compounds present in the database of the analytical procedure used were determined in the effluent. The results presented are for the compounds determined by GC–MS. However, it follows from our previous work that this is the most important group among VOCs (also with the highest content) occurring in effluents of this kind. The remaining, high-molecular-weight, compounds are oxidized less efficiently than the VOCs identified in this study. Effluents of this kind also contain aliphatic and aromatic hydrocarbons which are more resistant to oxidation. Furthermore, as demonstrated in this investigation, secondary contaminants can be formed during the treatment. For these reasons, there is no correlation between changes in COD and VOCs during the treatment of the effluent.

3.9. *Changes in effluent biodegradability*

The efficiency of degradation of organic contaminants present in effluents from the production of bitumens by the investigated treatment processes was also studied in terms of changes in BOD_5. The knowledge of COD and BOD of an effluent allows calculation of the so-called biodegradability index of an effluent. The biodegradability index of the effluent from the production of bitumens treated by hydrodynamic cavitation combined with additional oxidation processes (O_3 and H_2O_2) is listed in Table 2. The biodegradability index (BI) of an effluent

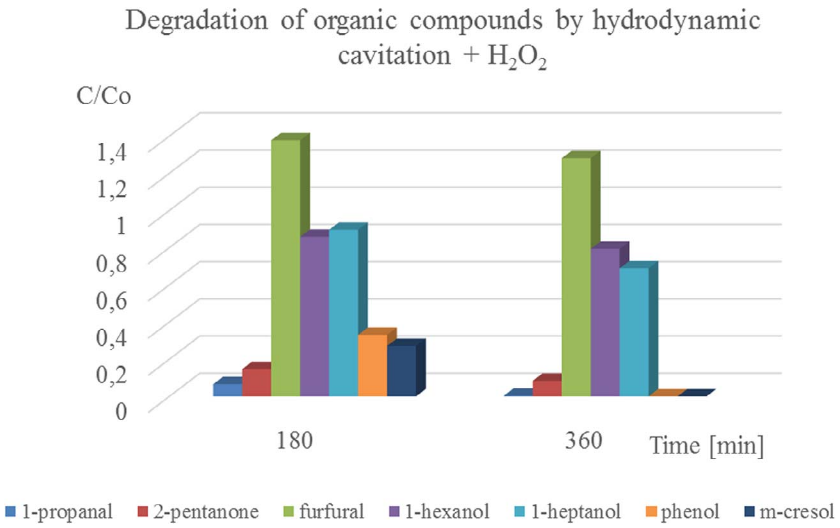


Fig. 7. Degradation of organic compounds by hydrodynamic cavitation + H_2O_2.

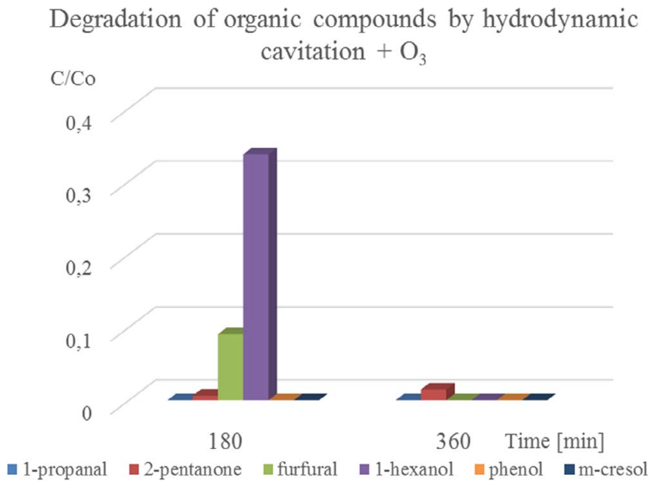


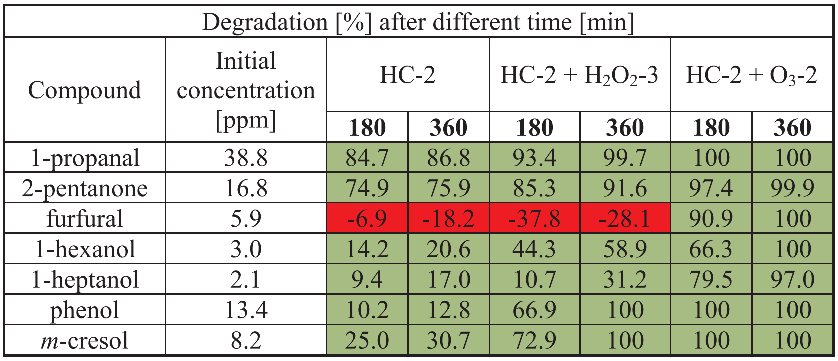
Fig. 8. Degradation of organic compounds by hydrodynamic cavitation + O_3.

provides information on susceptibility of dissolved compounds to degradation by way of biochemical reactions carried out by microorganisms. Most often, BI is expressed as the ratio of BOD_5 to COD of an effluent. According to literature reports an effluent having the BOD/COD index a minimum of 0.3–0.4 is highly susceptible to biodegradation (the greater the value is, the better the effects of treatment by the activated sludge method) [28]. Therefore, a pretreatment resulting in a BI value of 0.3–0.4 will improve the efficiency of the activated sludge treatment. The results presented below reveal that both hydrodynamic cavitation alone as well as hydrodynamic cavitation combined with an additional oxidation process ensure maintaining the BI index of the effluent at an optimal level of 0.3–0.4. Preliminary oxidation of organic compounds having substantial biotoxicity by hydrodynamic cavitation combined with additional oxidation using hydrogen peroxide or ozone enables proper activity of activated sludge and degradation of the remaining organic contaminants during the subsequent stages of biological treatment. The least favorable treatment in terms of biodegradability of the effluent involves hydrodynamic cavitation aided by hydrogen peroxide oxidation (lowering BI from 0.41 to 0.26). This treatment reduces susceptibility of the effluent to biodegradation by

Table 2
Effect of cavitation pretreatment on biodegradability index of effluent.

Reaction conditions	Time (min)	COD (mg L^{-1})	BOD_5 (mg L^{-1})	COD reduction [%]	BOD_5 reduction [%]	BOD_5/COD
Hydrodynamic cavitation, 8 bar	0	8874	3721	0	0	0.42
	180	7892	3212	11.1	13.7	0.40
	360	7723	3069	13	17.5	0.39
Hydrodynamic cavitation (8 bar) + H_2O_2 (1.0 mL min^{-1})	0	11055	4535	0	0	0.41
	180	9419	2478	14.8	45.4	0.26
	360	8874	2275	19.7	49.8	0.26
Hydrodynamic cavitation (8 bar) + O_3 (9.41 g h^{-1})	0	11020	4488	0	0	0.41
	180	7190	2438	34.8	45.7	0.34
	360	6642	2241	39.7	50.1	0.34
Hydrodynamic cavitation (8 bar) + O_3 (9.41 g h^{-1}) + H_2O_2 (1.0 mL min^{-1})	0	11020	4469	0	0	0.41
	180	9379	3405	14.9	23.8	0.36
	360	8284	3042	24.8	31.9	0.37
O_3	0	11035	4358	0	0	0.39
	180	9843	3517	10.8	19.3	0.36
	360	8828	2846	20.1	34.7	0.32
H_2O_2	0	11015	4419	0	0	0.40
	180	10784	4123	2.1	6.7	0.38
	360	10266	3650	6.8	17.4	0.36
Peroxone (O_3/H_2O_2)	0	11041	4255	0	0	0.39
	180	8501	2919	23.0	31.4	0.34
	360	6956	2493	37.0	41.4	0.36

Table 3
Degradation of organic compounds at different times by hydrodynamic cavitation + AOPs.



Degradation [%] after different time [min]							
Compound	Initial concentration [ppm]	HC-2		HC-2 + H_2O_2-3		HC-2 + O_3-2	
		180	**360**	**180**	**360**	**180**	**360**
1-propanal	38.8	84.7	86.8	93.4	99.7	100	100
2-pentanone	16.8	74.9	75.9	85.3	91.6	97.4	99.9
furfural	5.9	-6.9	-18.2	-37.8	-28.1	90.9	100
1-hexanol	3.0	14.2	20.6	44.3	58.9	66.3	100
1-heptanol	2.1	9.4	17.0	10.7	31.2	79.5	97.0
phenol	13.4	10.2	12.8	66.9	100	100	100
m-cresol	8.2	25.0	30.7	72.9	100	100	100

Table 4
Synergetic effect of the combination of AOPs with cavitation and energy efficiency evaluation.

Process	Cavitation	H_2O_2	O_3	H_2O_2/O_3	Cavitation + O_3	Cavitation + H_2O_2	Cavitation + Peroxone
COD reduction [%]	13	6.8	20.1	37.0	39.7	19.7	25
$S_{coefficient}$	–	–	–	1.4	1.2	1.0	0.5
COD reduction [mg]	5755	3745	11035	20425	21890	10905	13680
P elec [W]	1100	–	450	450	1550	1100	1550
P elec for 6-h process [kJ]	23760	–	9720	9720	33480	23760	33480
Energy efficiency [mg COD/kJ]	0.24	–	1.13	2.10	0.65	0.46	0.41

almost 64%. The most efficient treatment of the effluent from the production of bitumens in terms of obtaining the optimal BI value is hydrodynamic cavitation combined with ozonation. In addition to obtaining favorable biodegradability, this treatment results in the greatest reduction of total contaminant load. It should also be noted that due to the treatment method used BOD is reduced to a greater extent than COD and, consequently, the BI index must go down.

4. Conclusions

Wastewater treatment in basic pH conditions by means of AOPs needs further studies. A literature about this topic lacks of many important data, especially in the case of real industrial effluents [39,52]. One of the solutions which can provide good effectiveness are cavitation based processes. Hydrodynamic cavitation, used as a separate process for pretreatment of effluents or combined with additional oxidation processes, constitutes a good method of lowering pollutant load of effluents from chemical processes. The results of investigations presented in this paper revealed that the most effective process for pretreatment of the effluent from bitumen production is hydrodynamic cavitation aided by ozonation, which reduces COD and BOD values of the effluent by 40 and 50%, respectively. The other processes investigated (hydrodynamic cavitation + H_2O_2 and hydrodynamic cavitation alone) ensure reduction of COD by 20 and 13%, respectively and reduction of BOD by 49 and 18%, respectively. Additionally, the treatment resulted in complete removal of all investigated oxygenated organic compounds with the simultaneous decolorization of the effluent and reduction in its malodorousness (Table 3). An especially important conclusion from this part of the work is a very effective degradation of phenol and its derivatives. Hydrodynamic cavitation combined with additional oxidation processes can be used as the second step of effluent pretreatment following currently used physical methods, *i.e.* plate separators and flotators. Degradation of organic pollutants during pretreatment can protect activated sludge from toxic organic compounds and enable effective biodegradation. In the case of the investigated effluent, oxidation of oxygenated organic contaminants prior to biological treatment (using AOP combined with hydrodynamic cavitation) ensures optimum activity of the activated sludge which is especially sensitive to this kind of contaminants. The use of hydrodynamic cavitation aided by external oxidants does not require complicated apparatus and is based on conversion of electric energy to inlet pressure of the medium and usage of elements generating cavitation, which allows unattended operation and easy process control.

Acknowledgments

The authors gratefully acknowledge financial support from the Ministry of Science and Higher Education in Poland for project 0040/IP2/2015/73 in the program “Iuventus Plus” in 2015 – 2017. The authors would like to thank also ICSO Chemical Production, Poland for providing the STRUKTOL SB 2032, antifoam agent.

The authors would like to thank also the Lotos Asfalt, Ltd. (Grupa Lotos) for their cooperation on this project.

References

[1] G. Boczkaj, A. Przyjazny, M. Kamiński, Characteristics of volatile organic compounds emission profiles from hot road bitumens, Chemosphere 107 (2014) 23–30.
[2] E. Gilgenast, G. Boczkaj, A. Przyjazny, M. Kamiński, Sample preparation procedure for the determination of polycyclic aromatic hydrocarbons in petroleum vacuum residue and bitumen, Anal. Bioanal. Chem. 401 (2011) 1059–1069.
[3] G. Boczkaj, M. Kamiński, A. Przyjazny, Process control and investigation of oxidation kinetics of postoxidative effluents using gas chromatography with pulsed flame photometric detector (GC-PFPD), Ind. Eng. Chem. Res. 49 (2010) 12654–12662.
[4] G. Boczkaj, A. Przyjazny, M. Kamiński, New procedures for control of industrial effluents treatment processes, Ind. Eng. Chem. Res. 53 (2014) 1503–1514.
[5] F. Deygout, Volatile emissions from hot bitumen storage tanks, Environ. Prog. Sustainable Energy 30 (2011) 102–112.
[6] D.C. Trumbore, Estimates of air emissions from asphalt storage tanks and truck loading, Environ. Prog. 18 (1999) 250–259.
[7] A. Ventura, A. Jullien, P. Moneron, Polycyclic aromatic hydrocarbons emitted from a hot-mix drum, asphalt plant: study of the influence from use of recycled bitumen, J. Environ. Eng. Sci. 6 (2007) 727–734.
[8] S.K. Chauhan, S. Sharma, A. Shukla, S. Gangopadhyay, Recent trends of the emission characteristics from the road construction industry, Environ. Sci. Pollut. Res. 17 (2010) 1493–1501.
[9] E. Gasthauer, M. Maze, J.P. Marchand, J. Amouroux, Characterization of asphalt fume composition by GC/MS and effect of temperature, Fuel 87 (2008) 1428–1434.
[10] A. Jullien, V. Gaudefroy, A. Ventura, C. de la Roche, R. Paranhos, P. Moneron,

Airborne emissions assessment of hot asphalt mixing methods and limitations, Road Mater. Pavement 11 (2010) 149–169.

[11] A.J. Kriech, L.V. Osborn, D.C. Trumbore, J.T. Kurek, H.L. Wissel, K.D. Rosinski, Evaluation of worker exposure to asphalt roofing fumes: Influence of work practices and materials, J. Occup. Environ. Hyg. 1 (2004) 88–98.

[12] D. Breuer, J.U. Hahn, D. Hober, C. Emmel, U. Musanke, R. Ruhl, A. Spickenheuer, M. Raulf-Heimsoth, R. Bramer, A. Seidel, B. Schilling, E. Heinze, B. Kendzia, B. Marczynski, P. Welge, J. Angerer, T. Bruning, B. Pesch, Air sampling and determination of vapours and aerosols of bitumen and polycyclic aromatic hydrocarbons in the Human Bitumen Study, Arch. Toxicol. 85 (2011) 11–20.

[13] I. Burstyn, P. Boffetta, T. Kauppinen, P. Heikkila, O. Svane, T. Partanen, I. Stucker, R. Frentzel-Beyme, W. Ahrens, H. Merzenich, D. Heederik, M. Hooiveld, S. Langard, B.G. Randem, B. Jarvholm, I. Bergdahl, J. Shaham, J. Ribak, H. Kromhout, Estimating exposures in the asphalt industry for an international epidemiological cohort study of cancer risk, Am. J. Ind. Med. 43 (2003) 3–17.

[14] G. Boczkaj, P. Makoś, A. Przyjazny, Application of dynamic headspace and gas Chromatography coupled to mass spectrometry (DHS-GC-MS) for the determination of oxygenated volatile organic compounds in refinery effluents, Anal. Methods 8 (2016) 3570–3577.

[15] G. Boczkaj, P. Makoś, A. Przyjazny, Application of dispersive liquid-liquid microextraction and gas chromatography with mass spectrometry for the determination of oxygenated volatile organic compounds in effluents from the production of petroleum bitumen, J. Sep. Sci. 39 (2016) 2604–2615.

[16] G. Boczkaj, P. Makoś, A. Fernandes, A. Przyjazny, New procedure for the control of the treatment of industrial effluents to remove volatile organosulfur compounds, J. Sep. Sci. 39 (2016) 3946–3956.

[17] K.P. Mishra, P.R. Gogate, Intensification of degradation of Rhodamine B using hydrodynamic cavitation in the presence of additives, Sep. Purif. Technol. 75 (2010) 385–391.

[18] D.H. Bremner, S. Carlo, A.G. Chakinala, G. Cravotto, Mineralisation of 2, 4-dichlorophenoxyacetic acid by acoustic or hydrodynamic cavitation in conjunction with the advanced Fenton process, Ultrason. Sonochem. 15 (2008) 416–419.

[19] I. Grcic, M. Obradovic, D. Vujevic, N. Koprivanac, Sono-Fenton oxidation of formic acid/formate ions in an aqueous solution: from an experimental design to the mechanistic modeling, Chem. Eng. J. 164 (2010) 196–207.

[20] S. Raut-Jadhav, V. Kumar Saharan, D. Pinjari, S. Sonawane, D. Saini, A. Pandit, Synergetic effect of combination of AOP's (hydrodynamic cavitation and H_2O_2) on the degradation of neonicotinoid class of insecticide, J. Hazard. Mater. 261 (2013) 139–147.

[21] P.R. Gogate, P.N. Patil, Combined treatment technology based on synergism between hydrodynamic cavitation and advanced oxidation processes, Ultrason. Sonochem. 25 (2015) 60–69.

[22] D. Drijvers, H. van Langenhove, L. Nguyen, T. Kim, L. Bray, Sonolysis of an aqueous mixture of trichloroethylene and chlorobenzene, Ultrason. Sonochem. 6 (1999) 115–121.

[23] A.A. Pradhan, P.R. Gogate, Degradation of p-nitrophenol using acoustic cavitation and Fenton chemistry, J. Hazard. Mater. 173 (2010) 517–522.

[24] Z. XiaoBin, Z. JiaKai, Q. LiMin, Z. XueJun, Calculation and verification of dynamical cavitation model for quasi-steady cavitating flow, Int. J. Mass Transfer 86 (2015) 294–301.

[25] N. Tran, P. Drogui, L. Nguyen, S.K. Brar, Optimization of sono-electrochemical oxidation of ibuprofen in wastewater, J. Environ. Chem. Eng. 3 (2015) 2637–2646.

[26] M. Zupanc, T. Kosjek, M. Petkovšek, M. Dular, B. Kompare, B. Širok, Z. Blazˇeka, E. Heath, Removal of pharmaceuticals from wastewater by biological processes, hydrodynamic cavitation and UV treatment, Ultrason. Sonochem. 20 (2013) 1104–1112.

[27] M. Zupanc, T. Kosjek, M. Petkovšek, M. Dular, B. Kompare, B. Širok, M. Strazˇar, E. Heath, Shear-induced hydrodynamic cavitation as a tool for pharmaceutical micropollutants removal from urban wastewater, Ultrason. Sonochem. 21 (2014) 1213–1221.

[28] K.V. Padoleya, Virendra Kumar Saharanb, S.N. Mudliara, R.A. Pandeya, Aniruddha B. Panditb, Cavitationally induced biodegradability enhancement of a distillery wastewater, J. Hazard. Mater. 219–220 (2012) 69–74.

[29] A. Montusiewicz, S. Pasieczna-Patkowska, M. Lebiocka, A. Szaja, M. Szymańska-Chargot, Hydrodynamic cavitation of brewery spent grain diluted by wastewater, Chem. Eng. J. (http://dx.doi.org/10.1016/j.cej.2016.10.132).

[30] M.M. Gore, V.K. Saharan, D.V. Pinjari, P.V. Chavan, A.B. Pandit, Degradation of reactive orange 4 dye using hydrodynamic cavitation based hybrid techniques, Ultrason. Sonochem. 21 (2014) 1075–1082.

[31] V.K. Saharan, M.P. Badve, A.B. Pandit, Degradation of Reactive Red 120 dye using hydrodynamic cavitation, Chem. Eng. J. 178 (2011) 100–107.

[32] S. Raut-Jadhav, D. Saini, S. Sonawane, A. Pandit, Effect of process intensifying parameters on the hydrodynamic cavitation based degradation of commercial pesticide (methomyl) in the aqueous solution, Ultrason. Sonochem. 28 (2016) 283–293.

[33] B. Bethi, S.H. Sonawane, G.S. Rohit, C.R. Holkar, D.V. Pinjari, B.A. Bhanvase, A.B. Pandit, Investigation of TiO_2 photocatalyst performance for decolorization in the presence of hydrodynamic cavitation as hybrid AOP, Ultrason. Sonochem. 28 (2016) 150–160.

[34] A.A. Pradhan, P.R. Gogate, Removal of p-nitrophenol using hydrodynamic cavitation and Fenton chemistry at pilot scale operation, Chem. Eng. J. 156 (2010) 77–82.

[35] K. Rakness, G. Gordon, B. Langlais, W. Masschelein, N. Matsumoto, Y. Richard, C.M. Robson, I. Somiya, Guideline for measurement of ozone concentration in the process gas from an ozone generator, Ozone Sci. Eng. 18 (1996) 209–229.

[36] J.P. Tullis, Choking and supercavitating valves, J. Hydraul. Div. 97 (1971) 1931–1945.

[37] S. Bhattacharjee, Y.T. Shah, Mechanisms for advanced photooxidation of aqueous organic waste compounds, Rev. Chem. Eng. 14 (1998) 1–46.

[38] E.M. Aieta, K.M. Reagan, J.S. Lang, L. McReynolds, J. Kang, W.H. Glaze, Advanced oxidation processes for treating groundwater contaminated with TCE and PCE: Pilot-scale evaluations, J. Am. Water Works Assoc. 80 (1988) 64–72.

[39] W.H. Glaze, K.W. Kang, Advanced oxidation processes for treating groundwater contaminated with TCE and PCE: laboratory studies, J. Am. Water Works Assoc. 80 (1988) 57–63.

[40] P. Sykes, Guidelines to Mechanisms in Organic Chemistry, 5th ed., Orient-Longman, New-Delhi, 1982.

[41] M.V. Bagal, P.R. Gogate, Degradation of 2, 4-dinitrophenol using a combination of hydrodynamic cavitation, chemical and advanced oxidation processes, Ultrason. Sonochem. 20 (2013) 1226–1235.

[42] P.N. Patil, S.D. Bote, P.R. Gogate, Degradation of imidacloprid using combined advanced oxidation processes based on hydrodynamic cavitation, Ultrason. Sonochem. 21 (2014) 1770–1777.

[43] Urs. Von Gunten, Ozonation of drinking water: Part I. Oxidation kinetics and product formation, Water Res. 37 (2003) 1443–1467.

[44] Urs. Von Gunten, Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine, Water Res. 37 (2003) 1469–1487.

[45] W. Gujer, Urs. Von Gunten, A stochastic model of an ozonation reactor, Water Res. 37 (2003) 1667–1677.

[46] A.L. Prajapat, P.R. Gogate, Intensified depolymerization of aqueous polyacrylamide solution using combined processes based on hydrodynamic cavitation, ozone, ultraviolet light and hydrogen peroxide, Ultrason. Sonochem. 31 (2016) 371–382.

[47] W.R. Haag, C.C.D. Yao, Rate constants for reaction of hydroxyl radicals with several drinking water contaminants, Environ. Sci. Technol. 26 (1992) 1005–1013.

[48] G. Boczkaj, A. Fernandes, Wastewater treatment by means of advanced oxidation processes at basic pH conditions: a review, Chem. Eng. J. 320 (2017) 608–633.

[49] P. Saritha, C. Aparna, V. Himabindu, Y. Anjaneyulu, Comparison of various advanced oxidation processes for the degradation of 4-chloro-2 nitrophenol, J. Hazard. Mater. 149 (2007) 609–614.

[50] H. Zangeneh, A.A.L. Zinatizadeh, M. Feizy, A comparative study on the performance of different advanced oxidation processes (UV/O3/H2O2) treating linear alkyl benzene (LAB) production plant's wastewater, J. Ind. Eng. Chem. 20 (2014) 1453–1461.

[51] N.N. Mahamuni, G.A. Yusuf, Advanced oxidation processes (AOPs) involving ultrasound for waste water treatment: a review with emphasis on cost estimation, Ultrason. Sonochem. 17 (2010) 990–1003.

[52] G. Boczkaj, A. Fernandes, P. Makoś, Study of different advanced oxidation processes for wastewater treatment from petroleum bitumen production at basic, Ind. Eng. Chem. Res. 56 (2017) 8806–8814.

Publikacja nr 3:

M. Gągol, A. Przyjazny, G. Boczkaj, Highly effective degradation of selected groups oforganic compounds by cavitation based AOPs under basic pH conditions, Ultrason. Sonochem. 45 (2018) 257–266.

Ultrasonics - Sonochemistry 45 (2018) 257–266

Contents lists available at ScienceDirect

Ultrasonics - Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

Highly effective degradation of selected groups of organic compounds by cavitation based AOPs under basic pH conditions

Michał Gągol[a], Andrzej Przyjazny[b], Grzegorz Boczkaj[a,*]

[a] Gdańsk University of Technology, Faculty of Chemistry, Department of Chemical and Process Engineering, Gdańsk, Poland
[b] Kettering University, 1700 University Avenue, Department of Chemistry & Biochemistry, Flint, MI 48504, USA

ARTICLE INFO

Keywords:
Hydrodynamic cavitation
Wastewater treatment
Acoustic cavitation
Aromatic hydrocarbons
Effluents
Advanced oxidation processes (AOPs)

ABSTRACT

Cavitation has become on the most often applied methods in a number of industrial technologies. In the case of oxidation of organic pollutants occurring in the aqueous medium, cavitation forms the basis of numerous advanced oxidation processes (AOPs). This paper presents the results of investigations on the efficiency of oxidation of the following groups of organic compounds: organosulfur, nitro derivatives of benzene, BTEX, and phenol and its derivatives in a basic model effluent using hydrodynamic and acoustic cavitation combined with external oxidants, *i.e.*, hydrogen peroxide, ozone and peroxone. The studies revealed that the combination of cavitation with additional oxidants allows 100% oxidation of the investigated model compounds. However, individual treatments differed with respect to the rate of degradation. Hydrodynamic cavitation aided by peroxone was found to be the most effective treatment (100% oxidation of all the investigated compounds in 60 min). When using hydrodynamic and acoustic cavitation alone, the effectiveness of oxidation was diversified. Under these conditions, nitro derivatives of benzene and phenol and its derivatives were found to be resistant to oxidation. In addition, hydrodynamic cavitation was found to be more effective in degradation of model compounds than acoustic cavitation. The results of investigations presented in this paper compare favorably with the investigations on degradation of organic contaminants using AOPs under conditions of basic pH published thus far.

1. Introduction

Over the last several decades, a number of new technologies enabling efficient utilization of energy of physical phenomena to initiate chemical reactions in gases, liquids and solids have appeared in chemical engineering [1]. Hydrodynamic cavitation along with acoustic cavitation by generation, growth and rapid collapse of the cavities in liquids allows effective breaking up of chemical bonds in water molecules yielding the reactive hydroxyl ($HO\cdot$) and hydroperoxyl ($HO_2\cdot$) radicals. The presence of cavities in a liquid is primarily due to:

- natural presence of a gas in a liquid either in the dissolved form or trapped at the liquid-solid phase boundary,
- abrupt drop of liquid pressure below the vapor pressure of water.

In water treatment technology, the drop of pressure below the vapor pressure of the treated medium can be accomplished by special chokes, including Venturi tubes, orifice plates, and mechanical rotors [2]. This approach is called hydrodynamic cavitation. When the energy of ultrasounds causing vibrations of molecules of a liquid or solid particles present in a liquid results in a decrease in static pressure of the liquid below its vapor pressure, then the phenomenon is called acoustic cavitation. In either case, the presence of collapsing cavities in the bulk of a treated solution facilitates the generation of radicals with a high oxidation potential. Hydroxyl and hydroperoxyl radicals effect lowering the content of organic contaminants in the treated liquid primarily by the nonselective nature of redox reactions. According to literature reports, cavitation is an effective method of oxidation of organic contaminants present in tap water, groundwater or industrial effluents [3]. The efficiency of oxidation of organic contaminants by cavitation alone generally ranges from 20 to 50% [1]. For readily oxidizable compounds it is possible to achieve a 100% degradation effectiveness. If the treatment is aided by external oxidants (hydrogen peroxide, ozone, Fenton process, peroxone, monopersulfates, persulfates), an 80–100% degradation efficiency can be attained for the majority of the investigated pollutants [4]. Cavitation is an effective method of oxidation of carboxylic acids [5], pesticides [6], nitro compounds [7], organohalogen compounds [8], pharmaceuticals [9,10] as well as

---

* Corresponding author at: Gdansk University of Technology, Faculty of Chemistry, Department of Chemical and Process Engineering, 80 – 233 Gdansk, G. Narutowicza St. 11/12, Poland.
E-mail address: grzegorz.boczkaj@pg.edu.pl (G. Boczkaj).

https://doi.org/10.1016/j.ultsonch.2018.03.013
Received 24 November 2017; Received in revised form 19 March 2018; Accepted 24 March 2018
Available online 05 April 2018
1350-4177/

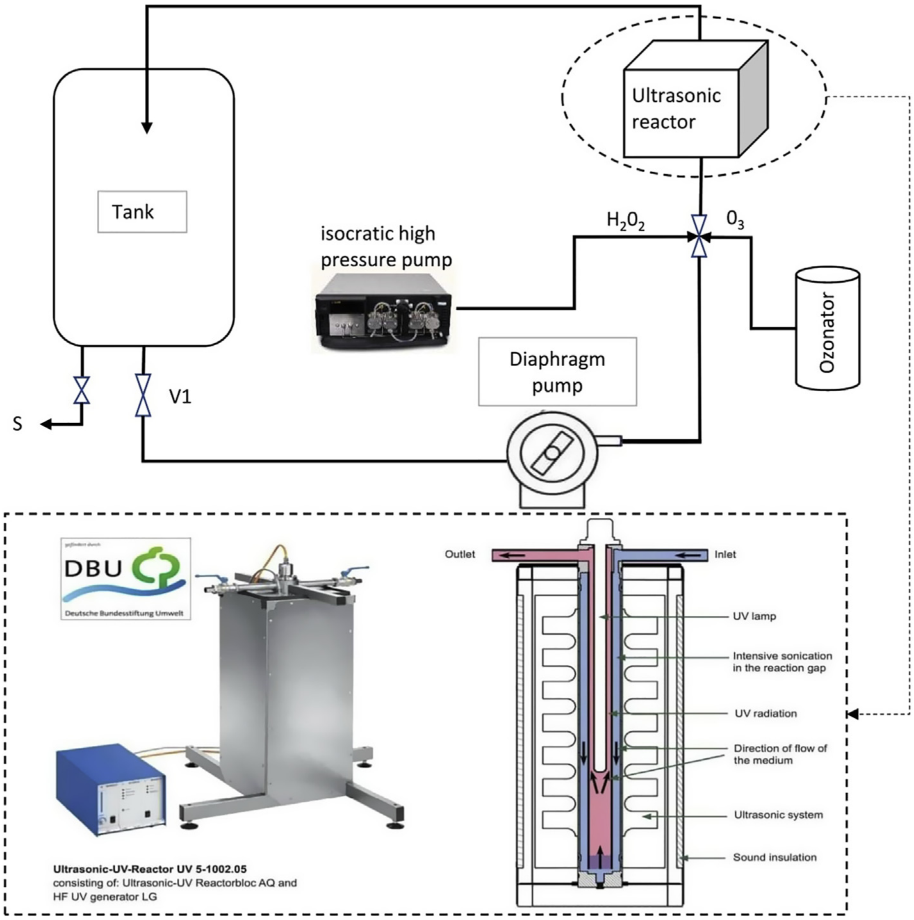


Fig. 1. Acoustic cavitation system (S – sampling; V1 – control valve).

disintegration of cells of microorganisms and bacteria [11,12]. However, the efficiency and effectiveness of the method depend to a large extent on optimization of the process, which is affected by a number of parameters, including proper design of the choke (inlet and outlet pressure), temperature and pH of the medium, kind and concentration of a contaminant or the time of the treatment [13–15].

The present paper describes the results of investigations on the effectiveness of hydrodynamic and acoustic cavitation in degradation of 15 model organic contaminants in a model effluent, mostly those occurring in industrial effluents. The reaction systems used in this work included a hydrodynamic cavitation system described in a previous paper on the treatment of industrial effluents [16] and an ultrasonic reactor. Our previous studies on this topic focused on real effluents from the production of bitumens [16–22]. A very complex composition of the bitumen effluents makes the evaluation of the effectiveness of the investigated AOPs very difficult in relation to individual groups of contaminants [16–23]. Consequently, in the present study, a model effluent having a controlled composition was used. This facilitates the investigation of the effectiveness of oxidation of selected groups of organic contaminants by cavitation processes combined with AOPs without influence of other organic contaminants present in a complex matrix of real effluents from the production of bitumens whose oxidation and formation of by-products would complicate correct interpretation of the results. The effectiveness of hydrodynamic and acoustic cavitation used alone and aided by external oxidants (hydrogen peroxide, ozone and their mixture, so-called peroxone) was investigated. A detailed comparison of the two cavitation methods is also presented.

2. Materials and methods

2.1. Chemicals

The following model contaminants were used in the study: 2-ethylthiophene, dibutyl sulfide, di-*tert*-butyl sulfide, nitrobenzene, 2-nitrophenol, 2-nitrotoluene, benzene, ethylbenzene, toluene, *o*-xylene, phenol, 4-ethylphenol, *m*-cresol, *o*-cresol, and naphthalene (Sigma-Aldrich, USA). Standards for quantitative analysis by GC–MS: 4-chlorophenol, 4-chlorobutan-1-ol, 2-chlorothiophene, and 2-chloropyridine (Sigma-Aldrich, USA). Ozonation was performed using a Tytan 32 ozone generator (Erem) at a rate of 12.32 $g\,h^{-1}$. In addition, the following reagents were used: dichloromethane (for HPLC, Sigma-Aldrich, USA), acetone (for HPLC, Sigma-Aldrich, USA), hydrochloric acid (analytical reagent grade, POCH S.A., Poland) and hydrogen peroxide 30% (POCH S.A., Poland).

2.2. Experimental setup

A model effluent was prepared by dissolving 6.2 mL of the stock solution (concentration of each analyte was 31250 ppm) in 5 L of a NaOH solution (pH = 10.5) in deionized water from the MilliQ water purification system (Millipore Corporation, USA). The concentration of each model compound in 5 L of the treated model effluent was about 40 ppm. The organic contaminants for the model effluent were selected based on previous investigations of real effluents from the production of bitumens, wherein the contaminants occurring in them were identified [16–18,21]. These real effluents are characterized by a strongly basic pH (pH = 10.5) [16–18], which is mostly due to the presence of sodium hydroxide used at the stage of treatment of waste gases to trap quantitatively hydrogen sulfide and acidic sulfur compounds [16]. Therefore, the pH of the effluents cannot be corrected due to a possible release to the atmosphere of acidic components of the absorbate, including hydrogen sulfide. Consequently, the studies of the effectiveness of oxidation of model contaminants were carried out in a basic medium (pH = 10.5).

2.2.1. Acoustic cavitation

The treatment of the model effluent was carried out in an ultrasonic reactor model Ultrasonic-UV-Reactor UV 5-1002.05 (1000 W, 25 kHz, 16 A) (Bandelin electronic GmbH & Co. KG, Germany) shown in Fig. 1. The reaction system included a 5-L tank for the effluent equipped with a stirrer and a temperature control system consisting of an electric heater and a water condenser. The flow of the effluent through the ultrasonic reactor in a closed system was forced by a diaphragm pump operating at a rate of 5.9 L min^{-1}. The tank and connecting elements were made of stainless steel (SS316). The tubing connecting the tank to the pump and the reactor was made of PTFE. When acoustic cavitation was aided by external oxidants (ozone, hydrogen peroxide and a mixture of hydrogen peroxide and ozone – peroxone), ozone was produced using a Tytan 32 ozone generator (Erem) at a rate of 12.32 g h^{-1} at a flow rate of 20 L min^{-1} and injected directly before the reactor. Hydrogen peroxide (30%) was fed through a second valve placed before the ultrasonic reactor using an isocratic high pressure pump S-7110 (Merck-Hitachi, Japan) at a flow rate of 3.0 mL min^{-1}. The treatment of the effluent was carried out at a maximum power of the reactor.

2.2.2. Hydrodynamic cavitation

The treatment of the model effluent using hydrodynamic cavitation aided by external oxidants (hydrogen peroxide, ozone and peroxone) was carried out using the reaction system shown in Fig. 2. The entire system, including a Venturi tube, was described in detail in a previous paper [16]. The treatment was carried out under optimum cavitational conditions resulting in the highest effectiveness of oxidation, *i.e.*, cavitation number 0.14, inlet pressure 8 bar and an effluent flow rate of 520 L h^{-1} (for the reaction system used, previous investigations revealed that the highest effectiveness of oxidation of organic contaminants was achieved at a cavitation number equal to 0.14) [16]. When hydrodynamic cavitation was aided by additional oxidants, the same amount of oxidants was added to the system as in the case of acoustic cavitation (hydrogen peroxide – 3 mL min^{-1}, ozone – 12.32 g h^{-1}, peroxone – H_2O_2 3 mL min^{-1}/O_3 12.32 g h^{-1}). The oxidants were injected to the Venturi tube directly after the throat, into the divergent section using an isocratic high pressure pump (H_2O_2) and an ozone generator (O_3).

2.3. Experimental procedure

The treatment processes for both hydrodynamic cavitation and acoustic cavitation were carried out using 5 L of the model effluent, in which the concentration of each model contaminant was about 40 ppm. The treatment of the effluent was performed at 40 ± 2 °C (the temperature of real effluent from the production of bitumens [16]) for 360 min. Samples of the effluent (22 mL) were collected at the beginning of the treatment and then after 60, 180 and 360 min. A sampling valve was located in the lower part of the effluent tank (S in Figs. 1 and 2). Acoustic cavitation was carried out at a maximum power of the reactor (200 W L^{-1}) – constant frequency and power with no possibility of change. In the case of hydrodynamic cavitation, the operating conditions and the amounts of oxidants added were the ones that had provided the maximum effectiveness of oxidation of organic contaminants in previous studies [16]. Three independent runs were carried out for each process and the results were repeatable (RSD < 5%).

2.4. Analytical procedure

2.4.1. Quantitative analysis by GC–MS

The investigation of changes in concentrations of model

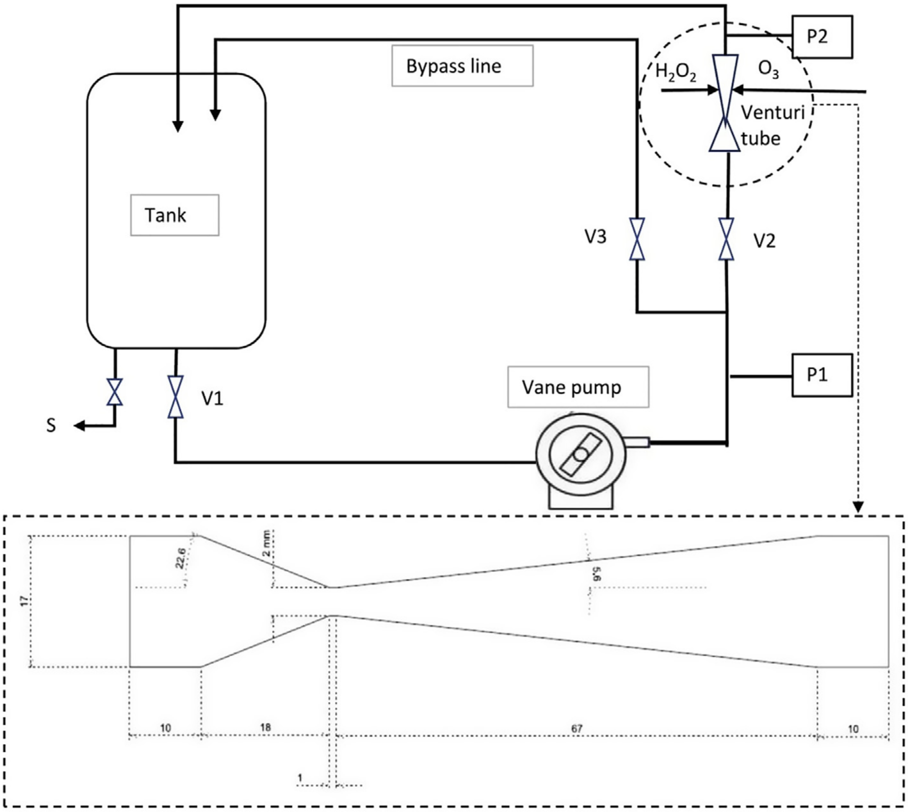


Fig. 2. Hydrodynamic cavitation system (S – sampling; V1, V2, V3 – control valves; P1, P2 – pressure gauges.

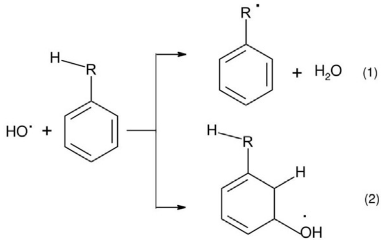
contaminants during the treatment process were carried out by gas chromatography–mass spectrometry using a QP2010SE GC–MS (Shimadzu, Japan). Samples were prepared for analysis using dispersive liquid-liquid microextraction (DLLME). The exact experimental procedure was described previously [17].

3. Results and discussion

3.1. Removal of model contaminants by acoustic cavitation and hydrodynamic cavitation

3.1.1. Acoustic cavitation

The treatment of the model effluent by acoustic cavitation alone was carried out for 360 min. During the treatment the effluent circulated in a closed loop with a volumetric flow rate of 5.9 L min^{-1} (the entire volume of the effluent was pumped 424 times through the cavitational zone of the reactor). The change in concentration of the model contaminants was determined after 60, 180 and 360 min of the treatment. The model contaminants included organic compounds from three groups: organosulfur compounds (2-ethylthiophene, dibutyl sulfide, and di-*tert*-butyl sulfide), nitro derivatives of benzene – (nitrobenzene, 2-nitrophenol, and 2-nitrotoluene) and hydrocarbons most often present in aqueous medium: BTEX (benzene, toluene, ethylbenzene, *o*-xylene), naphthalene, phenol, 4-ethylphenol, *m*-cresol, and *o*-cresol. The effectiveness of degradation of the contaminants is shown in Tables S1 and S2 (Tables S1 and S2 – please refer to Supporting information). The percent oxidation of organic compounds (x), listed in Tables S1 and S2, were calculated using the following formula: $x = (1 - C/C_o) * 100\%$, where C_o is the initial concentration, a C is the concentration in a sample collected after a specified time of treatment. Acoustic cavitation used as a standalone treatment method for model contaminants in water allowed degradation of 7 out of 15 of the investigated compounds. During the first hour of the treatment 66.1% of 2-ethylthiophene, 66.5% of di-*tert*-butyl sulfide, 63.9% of ethylbenzene and 60.6% of toluene were removed (Figs. 3–6). For benzene and *o*-xylene, the percent degradation after the first hour of the treatment was 56.5% and 56.2%, respectively. After the next 2 h of the treatment, over 90% of these contaminants was degraded whereas the 6-hour treatment resulted in an almost complete degradation. The third organosulfur compound, dibutyl sulfide, was completely removed from the effluent after a 60-min treatment (an additional analysis of dibutyl sulfide content after 30 min of the treatment revealed a 23% degradation) (Fig. 3). On the other hand, the effectiveness of degradation of naphthalene after 360 min of the treatment was only 46.7%. For the remaining model contaminants, an increase in concentration in the effluent with respect to the initial value was observed during and after the treatment. Acoustic cavitation is an effective method of oxidation of organosulfur and aromatic compounds (benzene, toluene, xylene and naphthalene). The effectiveness and rate of oxidation of the investigated organic contaminants containing an aromatic ring or having a chain structure depends primarily on the presence of additional moieties, which affect the attack of a hydroxyl radical. Hydroxyl radicals, being strong electrophiles with a deficit of electrons prefer reactions with the contaminants containing bonds or moieties with higher electron density, such as an aromatic ring or a double bond. In the case of contaminants containing an aromatic ring, two major routes of oxidation reaction can be distinguished. The first mechanism involves abstraction of hydrogen atom from the C–H bond of alkyl substituent group yielding a radical and a water molecule (reaction (1)). The second route involves addition of the hydroxyl radical to one of double bonds from the benzene ring (reaction (2)) [24].



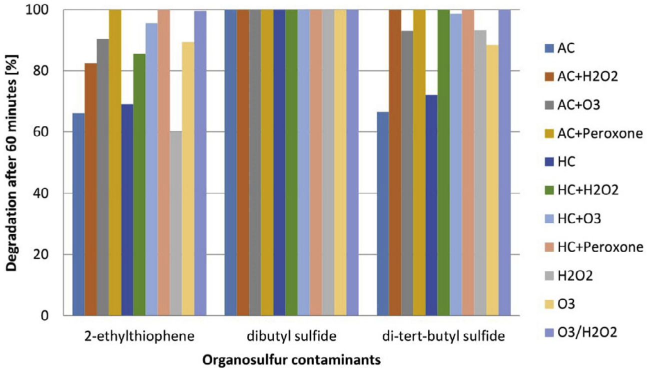


Fig. 3. Percent degradation of organosulfur contaminants after 60-minute treatment process.

Aromatics with electron-donor groups (such as $-NH_2$; –OH; $-OCH_3$; $-CH_3$) possess higher degradation rates compared to benzene or benzene substituted with electron-withdrawing groups (*e.g.,* –CN: benzonitrile) [24]. Electron-donor groups activate benzene ring by increasing its electron density, making the attack of a hydroxyl radical more likely. Similar effects are observed for organosulfur contaminants having a linear structure. The presence of a sulfur atom in the structure of a contaminant increases the rate of attack of hydroxyl radicals due to electron-donating properties of sulfur, which results in a high effectiveness of oxidation [25]. In contrast, electron-withdrawing groups, such as $-NO_2$ present in an aromatic ring and linear molecules decrease reactivity of contaminants [24]. Consequently, among the organic contaminants studied the highest effectiveness of oxidation was observed for BTEX-N and organosulfur compounds, as they contain only electron-donor moieties which increase the probability of attack of hydroxyl radicals.

Ramteke and Gogate [26] demonstrated that acoustic cavitation applied as a standalone treatment process enables an approximately 15% effectiveness of oxidation of BTX + N compounds after only 40 min of sonication (reactor operating at a power of 120 W L^{-1}; C_o = 20000 ppm V = 2 L; T = 24 °C) for the solution with a pH = 3. The effectiveness of oxidation of BTEX + N compounds achieved in this work by using acoustic cavitation was 60% after 60 min. The results of the two studies cannot be directly compared, however, since they differ in several process parameters, including pH and temperature, but much lower effectiveness in Ref. [26] can be mostly attributed to the high concentration of contaminants (20,000 ppm) which at the limited number of hydroxyl radicals generated during acoustic cavitation alone restricts the effectiveness of degradation over the discussed period. It should also be noted that BTEX + N compounds have a limited solubility in water. For most of them, the solubility does not exceed several hundred ppm (except for benzene – *ca.* 1800 ppm at 20 °C). For example, for toluene and ethylbenzene the solubility values are 520 ppm and 150 ppm, respectively, at 20 °C. The concentration reported suggests that some fraction of the contaminants was not dissolved in the effluent or was emulsified. Under real conditions, such an effluent would be subjected to preliminary treatment involving physical separation of the organic phase prior to chemical treatment which would decrease the load of contaminants. Thus, the results of our investigations better characterize the effectiveness of cavitation under real conditions. The authors pointed out that by using a higher power of ultrasonic transducers and a longer sonic cavitation time it should be possible to increase the concentration of hydroxyl radicals in the bulk of the medium being treated, which would result in a much improved

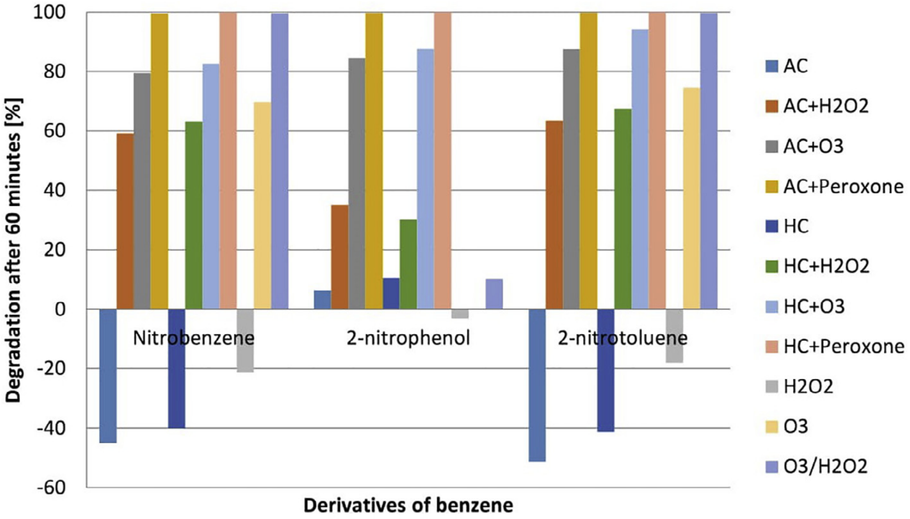


Fig. 4. Percent degradation of benzene derivatives (with nitro group) after 60-minute treatment process.

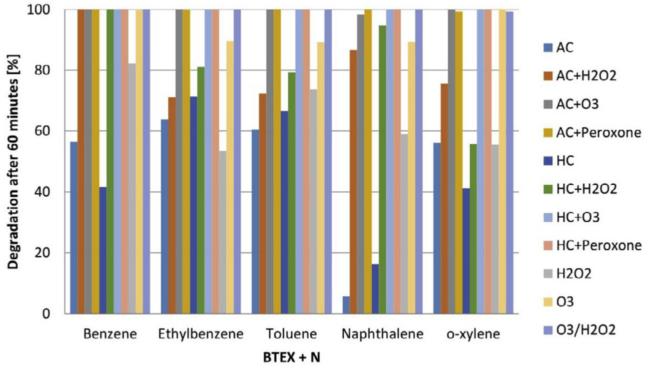


Fig. 5. Percent degradation of BTEX + N compounds after 60-min treatment process.

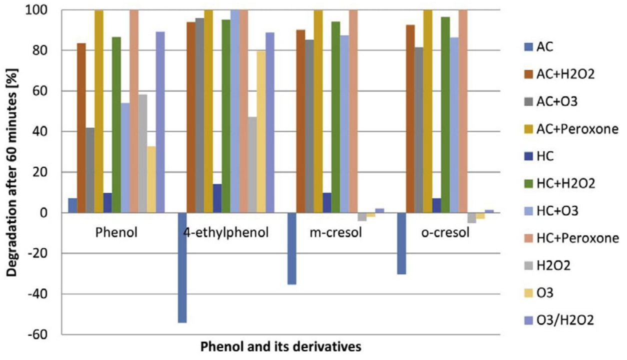


Fig. 6. Percent degradation of phenol and its derivatives after 60-min treatment process.

effectiveness of oxidation. In the system used in this study, the ultrasonic reactor (200 W L^{-1}) operated for 360 min at a power almost twice that of the reactor of Ramteke and Gogate. This allowed much more effective decomposition of water molecules to hydroxyl radicals, thus achieving almost 100% oxidation of BTX + N and organosulfur compounds.

At the same time, the results obtained in this study revealed that acoustic cavitation is ineffective in degradation of phenol and its derivatives as well as nitro derivatives of benzene. For phenol and its derivatives, the results are consistent with those obtained earlier for real effluents treated using hydrodynamic cavitation [16]. An increase in phenol content in real effluents treated by cavitation alone was caused by its generation as a secondary contaminant. Interesting examples of investigations on the effectiveness of oxidation of *p*-nitrotoluene and *p*-aminophenol by means of cavitation were reported by Song et al. [27] and He et al. [28]. He et al. obtained a 4% effectiveness of oxidation of *p*-aminophenol during 30 min of acoustic cavitation (reactor 300 W L^{-1}; C_o = 1000 ppm^{-1}; V = 500 mL; T = 25 °C; t = 60 min) at pH 11 while Song et al. achieved an 8% effectiveness of oxidation of *p*-nitrotoluene during 90 min of the treatment using the same power of the reactor (300 W L^{-1}; C_o = 100 ppm; V = 500 mL; T = 50 °C; t = 25 min) at pH 10. In this work, an over 50% increase in concentration of 2-nitrotoluene compared to the initial sample was observed during the first 60 min of acoustic cavitation while for hydrodynamic cavitation a 41% increase was noted. Only after the first 60 min of the treatment 2-nitrotoluene was partially oxidized. Between 60 and 360 min of the treatment by hydrodynamic cavitation and acoustic cavitation, 32.5% and 43.4%, respectively, of 2-nitrotoluene was oxidized. However, due to a large increase in concentration of 2-nitrotoluene during the first hour of the treatment, the concentration of 2-nitrotoluene in a sample collected after 360 min of the treatment was higher by 7.9% and 8.8% for acoustic cavitation and hydrodynamic cavitation, respectively, compared with the initial concentration . Furthermore, the authors presented a possible degradation pathway of nitro derivatives of benzene, indicating, among others, that hydroxyl radicals (HO·) preferably attack the C–N bond with release of *p*- and *o*-cresol and NO_3^-. Due to pyrolytic conditions during collapse of the cavities, the free NO_3^- group can form other nitro compounds in reactions with aromatic compounds and their intermediates. This provides a tentative explanation of an increase in concentration of phenol and its derivatives and nitro derivatives of benzene in the effluent after 360 min of acoustic cavitation. The acoustic cavitation system used at a power of 200 W L^{-1} enables generation of a large number of radicals which can form new chemical compounds in nonselective radical reactions with the model contaminants and their intermediates.

3.1.2. Hydrodynamic cavitation

The treatment of the model effluent by hydrodynamic cavitation was carried out under operating conditions which afforded the highest effectiveness of oxidation of organic compounds in a previous work [16]. The model effluent was pumped in a closed system at an inlet pressure of 8 bar at a flow rate of 520 L h^{-1} (cavitation number 0.14). The number of passages of the effluent through the cavitational zone of the Venturi tube during the treatment was 624 during 360 min. The effectiveness of oxidation of model organic contaminants by hydrodynamic cavitation alone is higher than that by acoustic cavitation, mostly for phenol and its derivatives. After 360 min of the treatment, the effectiveness of oxidation of phenol, 4-ethylphenol, *m*-cresol and *o*-cresol was 15.4%, 60.1%, 30.6% and 21.4%, respectively. The *ca.* 10% difference in the effectiveness of oxidation of *m*-cresol and *o*-cresol can be attributed mainly to the number and ease of formation of intermediates in the presence of hydroxyl radicals during oxidation. Olariu et al. [29] observed the following 3 products for *o*-cresol: 3-methyl-1,2-dihydroxybenzene, methyl-1,4-benzoquinone and 6-methyl-2-nitrophenol and 5 products for *m*-cresol: 3-methyl-1,2-dihydroxybenzene, 4-methyl-1,2-dihydroxybenzene, methyl-1,4-benzoquinone, 5-methyl-2-nitrophenol and 3-methyl-4-nitrophenol, which were formed during the attack of hydroxyl radicals. In addition, the authors indicated that the conversion yield of *o*-cresol was lower than that of *m*-cresol, amounting to 87% and 98%, respectively. It follows from these data that the meta position of substituents of an aromatic ring is more susceptible to the attack of hydroxyl radicals, which results in a higher efficiency of oxidation of isomers with substituents in this position.

Phenol and its derivatives are among the compounds that are hardest to remove from aqueous media by conventional biological treatment methods. This is mostly due to their high toxicity toward activated sludge and large amounts of these compounds discharged from various technological processes, mostly chemical and pharmaceutical. Consequently, the removal of compounds of this type prior to biological treatment is essential. Chakinala et al. [30] demonstrated that both hydrodynamic cavitation alone and combined with the Fenton process are effective tools for oxidation of phenol and its derivatives. After 105 min of the treatment, the effectiveness of phenol removal ($C_o = 220$ ppm; V = 4 L; T = 35 °C; inlet pressure: 103 bar; pH = 2.5) by hydrodynamic cavitation alone and hydrodynamic cavitation aided by the Fenton process were about 25% and 60%, respectively. The effectiveness of oxidation of phenol achieved in this work was 15.4% after a 6-hour treatment by hydrodynamic cavitation for an effluent with pH = 10.5. Higher effectiveness of oxidation of phenol and its derivatives by hydrodynamic cavitation compared with acoustic cavitation is mostly due to a greater number and higher intensity of cavitational events and thus a greater number of hydroxyl radicals present in the medium being treated. The intensity of generation of cavities in the process of abrupt change in the nature of flow of a liquid and the drop in its pressure below the vapor pressure is much more effective when using a constriction than energy of ultrasonic transducers [14]. Additionally, during the entire treatment by hydrodynamic cavitation, the number of passes of the model effluent through the cavitational zone was greater by 32% than in the case of acoustic cavitation. No significant differences in the effectiveness of oxidation between hydrodynamic and acoustic cavitation were observed for the remaining model contaminants. An increase in concentration of nitro derivatives of benzene was observed which, as described above, was likely due to secondary reactions of chemical compounds present in the effluent and the products of their degradation with the nitrite and nitrate ions as well as the nitrate radicals which can be formed during cavitation. The latter species are characterized by high reactivity, including the ability to undergo addition reactions [31]. On the other hand, hydrodynamic cavitation, similarly to acoustic cavitation, is ineffective toward oxidation of nitro compounds containing an aromatic ring. This is primarily due to the presence of an electron-acceptor moiety ($-NO_2$), which deactivates the aromatic ring thus limiting the probability of attack of hydroxyl radicals [44,45]. Bagal and Gogate [32] found just 12.4% degradation of 2,4-dinitrophenol after a 120-min treatment by hydrodynamic cavitation ($C_o = 20$ ppm; V = 4 L; T = 35 °C; inlet pressure: 4 bar; cavitation number 0.43). In this work, a 31% increase in concentration of 2-nitrophenol was observed after a 6-hour treatment by hydrodynamic cavitation compared to the initial concentration. This can be attributed mainly to numerous radical reactions and the presence of free NO_3^- groups in the treated medium, which leads to the formation of new, secondary chemical contaminants. For organosulfur compounds, a 180-min treatment resulted in 91.4% oxidation of 2-ethylthiophene and 94.1% oxidation of di-*tert*-butyl sulfide and 100% oxidation of dibutyl sulfide after 60 min of the treatment (complete degradation of dibutyl sulfide was achieved after about 30 min of the process). Detailed results of the investigations are compiled in Table S1 (Please refer to Supporting information) and Figs. 3–6.

3.2. Removal of model contaminants by acoustic cavitation and hydrodynamic cavitation aided by H_2O_2

Hydrogen peroxide is among the most common oxidizing agents used in technological processes. Its oxidation potential strongly depends on the pH of the reaction medium and is highest for the reactions carried out in acidic solutions (1.8 V at pH 0; 0.87 V at pH 14) [33]. In technological processes it used mostly in direct oxidation reactions of carboxylic acids, polycyclic aromatic hydrocarbons and haloalkanes [34]. Under alkaline conditions, hydrogen peroxide decomposes to the perhydroxyl anion and water (Eq. (3)) [4].

$$H_2O_2 + HO^- \xrightarrow{pH>7} HO_2^- + H_2O \tag{3}$$

The use of hydrogen peroxide as a sole oxidizing agent in a basic medium is disadvantageous due to formation of perhydroxyl anions [35]. The perhydroxyl anion combines with organic contaminants yielding adducts which can undergo internal rearrangements resulting in a loss of an anion or promotion of migration of an alkyl radical with a free electron pair and formation of an oxidized form of an intermediate. An example is the mechanism of the Baeyer-Villiger reaction of a ketone with hydrogen peroxide described by Sykes [35]. An oxidized intermediate requires a much longer decomposition time than the primary contaminant. Consequently, in order to effectively use the oxidation potential of hydrogen peroxide in basic media, an additional mechanism is needed to increase the amount of hydroxyl radicals in the treated medium, which would allow an effective oxidation of primary contaminants and their intermediates. Only a few reports can be found in the literature in which hydrogen peroxide was used as an oxidant in a basic medium [36,37]. Saritha et al. [36] achieved about 50% oxidation of 4-chloro-2-nitrophenol using hydrogen peroxide (pH 10) when the maximum effect of the oxidant was investigated ($H_2O_2 = 700$ ppm; V = 1L; $C_o = 630$ ppm; t = 300 min). Zangeneh et al. [37] reduced the COD of linear alkyl benzene wastewater by 27% after a 180-min treatment at pH 11 (UV/H_2O_2 process; $COD_o = 350\,mg\,L^{-1}$; UV = 15 W; $H_2O_2 = 20\,mmol\,L^{-1}$; V = 2L). In hydrodynamic and acoustic cavitation (pyrolytic conditions), the majority of hydrogen peroxide is decomposed to hydroxyl radicals (instead of perhydroxyl anions), which are mostly responsible for the effective oxidation of organic contaminants (Eq. (4)).

$$H_2O_2 \xrightarrow{CAVITATION} 2HO\bullet \tag{4}$$

Hydroxyl radicals initiate a chain of oxidation reactions of organic contaminants resulting in the majority of cases in their complete degradation. However, the pathways and mechanisms of the majority of oxidation reactions have not been completely elucidated. The first step of oxidation of halogenated compounds yields intermediates, such as aldehydes, ketones or carboxylic acids. This is due to abstraction of chlorine atom followed by addition of oxygen to the organic radical formed. The final step involves formation of CO_2, H_2O_2 and a halogen anion. Nitrogen present in structures of organic contaminants is oxidized to nitrate ions or released as gaseous N_2. Sulfur in organosulfur compounds is oxidized to sulfate ions [36]. Degradation index of organic contaminants in various groups of compounds is comparable to the rate constant for the reaction of a contaminant with HO· radical [24–27]. The rate constants (k, M^{-1}, s^{-1}) for the reactions of hydroxyl radicals with selected organic contaminants are listed in Table 1.

An increase in number of hydroxyl radicals in the treated medium

Table 1
Reaction rate constants of hydroxyl radicals with selected pollutants [38]

Pollutants	$HO^{\cdot}$ (k, M^{-1}, s^{-1})
Alcohols	10^8–10^9
Ketones	10^9–10^{10}
Aromatics	10^8–10^{10}
N-containing organics	10^8–10^{10}
Phenols	10^9–10^{10}
Chlorinated alkenes	10^9–10^{11}

results in an improved effectiveness of degradation of organic compounds present. Both hydrodynamic and acoustic cavitation aided by hydrogen peroxide afforded a 100% degradation of all the investigated model compounds and their intermediates after 360 min of the treatment. A comparison of the effectiveness of the treatment after the first hour reveals that hydrodynamic cavitation combined with hydrogen peroxide improves degradation of the model contaminants by *ca.* 5–10% (Figs. 3–6). This is primarily due to a higher intensity of cavitation in a choke compared with the area of operation of ultrasonic transducers [23]. In addition, after 1 h of the treatment by hydrodynamic cavitation (HC) the effluent (5-L volume) passed through the cavitational zone about 104 times whereas in the case of acoustic cavitation (AC) the respective number was about 70. Longer residence time in the cavitation zone increases the probability of reaction with hydroxyl radicals thus improving the effectiveness of degradation. After 3 h of the treatment, both acoustic and hydrodynamic cavitation combined with hydrogen peroxide yielded over 95% oxidation of all of the investigated model compounds except for 2-nitrophenol (66.9% – AC + H_2O_2; 62.9% – HC + H_2O_2), *o*-xylene (90.8% – AC + H_2O_2; 80.8% – HC + H_2O_2) and phenol (93.8% – AC + H_2O_2; 96.8% – HC + H_2O_2). The slowest oxidation for the investigated cavitational processes combined with H_2O_2 was observed for 2-nitrophenol (after 60 min, removal of 35.1% and 30.1% for AC + H_2O_2 and HC + H_2O_2, respectively). This can mostly be attributed to depletion of hydroxyl radicals through reactions with numerous intermediates which are formed during oxidation of organic compounds releasing the reactive nitro group [27,28]. The effectiveness of hydrodynamic and acoustic cavitation aided by hydrogen peroxide in the removal of organic contaminants is confirmed by literature reports [7,39]. However, most often the treated medium is acidic. Pradhan and Gogate [7] achieved a 59% effectiveness of oxidation of *p*-nitrophenol in a 90-min treatment by acoustic cavitation aided by hydrogen peroxide (pH 3.7; $C_o = 1\%$ solution; V = 7 L; T = 28 °C; $H_2O_2 = 5\ gL^{-1}$; AC = 25 kHz, 1 kW). In this work, degradation rates of 2-nitrophenol during a 90-min treatment were *ca.* 39% for hydrodynamic cavitation + H_2O_2 and 44% for acoustic cavitation + H_2O_2. These values were estimated from the oxidation curve. Patil et al. [39] observed complete degradation of imidacloprid after a 120-min treatment by hydrodynamic cavitation ($C_o = 20$ ppm; V = 4 L; T = 34 °C; $H_2O_2 = 80$ ppm; inlet pressure: 4 bar ($C_v = 0.37$)) combined with hydrogen peroxide (pH 3). The data reported in this paper reveal that cavitation aided by hydrogen peroxide can be an effective method of oxidation of organic contaminants also in basic reaction media. Detailed results of the investigations are compiled in Table S1 (please refer to supporting information).

3.3. Removal of model contaminants by acoustic and hydrodynamic cavitation aided by O_3

Ozone is characterized by a high oxidation potential equal to 2.08 V. As a result, it is often used as an oxidizing agent for organic contaminants present in aqueous media. The oxidation of organic contaminants by ozone can take place by two routes: (1) at basic pH, ozone rapidly decomposes to yield hydroxyl and other radicals in solution which then react with contaminants (reaction (5), (6), and (7)); (2) under acidic conditions, ozone is stable and can react directly with organic compounds as an electrophile (reaction (8) [40].

$$O_3\ (basic\ solution) \xrightarrow{CAVITATION} O\bullet + O_2 \tag{5}$$

$$O\bullet + H_2O \xrightarrow{CAVITATION} 2HO\bullet \tag{6}$$

$$2HO\bullet + pollutants \xrightarrow{CAVITATION} Oxidation\ products\ (intermediates,\ CO_2,\ H_2O,\ etc.) \tag{7}$$

$$O_3\ (acid\ solution) + pollutants \xrightarrow{CAVITATION} Oxidation\ products \tag{8}$$

The effective utilization of ozone in modern water treatment facilities requires overcoming a number of limitations related to its chemical properties and parameters affecting the course of oxidation reactions. These include [40]:

- problems with overcoming local mass transfer resistance, *i.e.,* effective injection of ozone from a stream of gas to the aqueous phase of an effluent,
- selective nature of oxidation reactions (ozone preferentially reacts with sites with high electron density, such as double bonds C=C, N=N, C=N),
- dependence of degradation pathways on pH of the reaction medium,
- high cost of ozone production (high energy requirement to generate ozone on an industrial scale).

The results of investigations reveal that the combination of ozonation with an additional physical process, such as hydrodynamic cavitation [16] or acoustic cavitation [27], allows overcoming the majority of the process limitations and carrying out an effective treatment process. The energy of collapsing cavitation bubbles in hydrodynamic and acoustic cavitation results in formation in the treated medium of microcirculation and turbulence zones which significantly reduces mass transfer resistance [41]. Additionally, decomposition of ozone to hydroxyl radicals under conditions of basic pH and cavitational energy changes the nature of redox reactions from selective to nonselective, thus improving the effectiveness of removal of organic contaminants. When using both hydrodynamic and acoustic cavitation aided by ozonation (at a maximum ozonator rate of 12.32 g h^{-1}), an oxidation effectiveness of over 85% for all the investigated model contaminants was observed after 1 h of the treatment except for nitrobenzene (79.4% for AC + O_3; 82.6% for HC + O_3), phenol (41.9% for AC + O_3; 54.1% for HC + O_3) and *o*-cresol (81.5% for AC + O_3) (Figs. 3–6). As discussed above, these compounds are hardly oxidizable and secondly a formation of their numerous intermediates and free chemical groups yields in presence of secondary contaminants. Rate constants for their degradation have the smallest value. As a result of a very high efficiency of oxidation of the investigated compounds during the first 60 min of the treatment, additional determination of the concentration of model compounds was carried out after 30 min. High effectiveness of oxidation was found for organosulfur and BTX + N compounds, both for hydrodynamic and acoustic cavitation combined with ozonation (over 80% oxidation except for 2-ethylthiophene). Over 50% of the nitro derivatives of benzene were oxidized after 30 min of cavitational processes combined with ozonation: nitrobenzene (55% for AC + O_3; 56% for HC + O_3), 2-nitrophenol (68% for SK + O_3; 71% for HC + O_3) and 2-nitrotoluene (64% for AC + O_3; 65% for HC + O_3). The least effective oxidation after 30 min of the treatment was observed for phenol (5% for AC + O_3; 7% for HC + O_3). Hydrodynamic cavitation and acoustic cavitation combined with ozonation are effective in the oxidation of all the investigated model compounds and the effectiveness is not significantly different for the two processes (see details in Table S1 – Support information). The fastest oxidation takes place for BTEX + N, organosulfur compounds and nitro derivatives of benzene in the following order: *nitrobenzene* < *2-ethylthiophene* < *2-nitrotoluene* < *2-*

Table 2
Comparison of treatment costs of hydrodynamic/acoustic cavitation and AOPs for BTEX-N complete degradation.

Process	Time (min)	Amount of oxidant (g)	Cost of oxidant (US dollars)	Energy consumption [kJ]	Cost of energy (US dollars)	Total cost of treatment process (USD L^{-1})
HC	360	0	0	23,760	0.73	0.15
AC	360	0	0	21,600	0.66	0.13
O_3	180	36.96	0	4860	0.15	0.03
H_2O_2	360	1198.8	8.86	0	0	1.77
O_3/H_2O_2	60	12.32 (O_3), 199.8 (H_2O_2)	1.48	1620	0.05	0.31
HC/O_3	60	12.32	0	5580	0.18	0.04
AC/O_3	60	12.32	0	5220	0.16	0.03
HC/H_2O_2	180	599.4	4.43	11,880	0.37	0.96
AC/H_2O_2	180	599.4	4.43	10,800	0.33	0.96
$HC/H_2O_2/O_3$	30	6.2 (O_3), 99.9 (H_2O_2)	0.74	2790	0.09	0.17
$AC/H_2O_2/O_3$	60	6.2 (O_3), 199.8 (H_2O_2)	1.48	5220	0.16	0.33

nitrophenol < *di-tert-butyl sulfide* < *ethylbenzene* < *naphthalene* < *o-xylene* < *dibutyl sulfide* < *benzene* < *toluene*. The slowest degradation was observed for phenol and its derivatives for both hydrodynamic and acoustic cavitation applied alone and combined with ozonation: *phenol* < *o-cresol* < *m-cresol* < *4-ethylphenol*. He et al. [28] in their investigations on oxidation of *p*-aminophenol (reactor $300\,W\,L^{-1}$; $C_o = 1000$ ppm; V = 500 mL; T = 25 °C; t = 60 min; pH = 11) also observed a low effectiveness (< 10% degradation) when using acoustic cavitation alone. Complete oxidation of *p*-aminophenol was achieved only by combining acoustic cavitation with ozonation. The rate constants for degradation of *p*-aminophenol by standalone acoustic cavitation and ozonation were lower by an order of magnitude in comparison with the combined treatment.

3.4. Removal of model contaminants by acoustic and hydrodynamic cavitation aided by peroxone

Peroxone is an oxidizing agent consisting of hydrogen peroxide and ozone. Such a combination produces a large number of hydroxyl radicals responsible for oxidation of organic contaminants. Zaviska et al. [42] demonstrated that the use of peroxone results in more effective oxidation than ozonation alone. This is due to improvement of the effectiveness of decomposition of ozone in the aqueous medium by hydrogen peroxide and thus an increase in concentration of hydroxyl radicals available. The mechanism of decomposition of ozone in the presence of hydrogen peroxide was presented in 1988 by Paillard et al. [43]. In a basic aqueous medium hydrogen peroxide occurs in its ionized form (HO_2^-, pKa = 11.6) which combines with ozone in a violent decomposition reaction yielding reactive hydroxyl radicals (Eq. (9)).

$$O_3 + HO_2^- \rightarrow HO\bullet + O_2 + O_2^- \tag{9}$$

However, the use of peroxone in the technology of treatment of aqueous solutions is limited by several important factors [44], including:

- low water solubility of ozone,
- high energy consumption related mainly to the generation of ozone,
- dependence of ozone decomposition reaction on pH and temperature of solutions, presence in solution of microcontaminants and their kinds as well as the consumption of hydroxyl radicals in side reactions.

As discussed earlier, cavitation intensifies mass transfer thus increasing the water solubility of ozone [16]. Generation of a large number of hydroxyl radicals in reaction with the ionized form of hydrogen peroxide improves the effectiveness of treatment. A detailed compilation of research on highly effective oxidation of various model contaminants using peroxone only is provided in a review on wastewater treatment by advanced oxidation processes (AOP) [4,45]. The treatment by cavitation aided by peroxone was carried out at a maximum rate of the ozonator ($12.32\,g\,h^{-1}$) (it was demonstrated in a previous paper that about $5.6\,g\,h^{-1}$ of ozone dissolves in the treated solution [16]) and a flow rate of $3.0\,mL\,min^{-1}$ H_2O_2 (such a flow rate effected maximum oxidation of organic contaminants) for both acoustic cavitation and hydrodynamic cavitation. Over 99.5% and 100% of all the investigated model contaminants were found to be oxidized after 60 min of the treatment by acoustic cavitation and hydrodynamic cavitation, respectively (Figs. 3–6). Additional analyses of the content of model contaminants after 30 min of the treatment revealed over 90% oxidation of all the model contaminants except for nitrobenzene (86.5% for AC + peroxone; 88.9% for HC + peroxone). Both hydrodynamic and acoustic cavitation combined with peroxone are highly effective in oxidation of the groups of organic contaminants studied (organosulfur compounds, nitro derivatives of benzene, BTEX + N and phenol and its derivatives). Ĉehovin et al. [46] also demonstrated the effectiveness of hydrodynamic cavitation aided by peroxone in the removal of natural organic matter from drinking water (initial dissolved organic carbon (DOC) 1.1–3.4 $mg\,L^{-1}$; $O_3 = 14\,mg\,L^{-1}$; V = 83 L; t = 60 min; T = 18–24 °C; $H_2O_2 = 7\,mg\,L^{-1}$; pH = 7.8; $C_v = 0.11$). DOC was lowered by 41% after 60 min of hydrodynamic cavitation combined with peroxone.

4. Comparison of treatment cost of cavitation processes with AOPs

The cost of effluent treatment by hydrodynamic or acoustic cavitation as well as "classic" AOPs depends on a number of factors, including the volume of an effluent, kind and concentration of contaminants or the desired effectiveness of degradation [4,45]. A comparison of costs of treatment by cavitational and AOP processes of 5 L of an effluent to completely remove organic contaminants belonging to BTEX-N compounds are compiled in Table 2 (individual processes – Table 1). The calculations include treatment time needed for complete oxidation, cost of oxidants used and cost of electric energy. The hydrodynamic cavitation system and acoustic cavitation reactor were found to have a power of 1100 W and 1000 W, respectively. In the case of ozonation, the oxidant was generated by an ozone generator consuming a power of 450 W. For the pump introducing hydrogen peroxide to the system at a low flow rate the energy consumption was negligible. The cost of electricity for industrial customers in Poland in 2018 is 0.11 US dollars (USD) per 1 kWh (3600 kJ). The cost of 30% hydrogen peroxide in 2018 (Avantor Performance Materials Poland S.A.) is 8.2 US dollars (USD) for 1 L. The cost of treatment of 1 L of a model effluent to remove BTEX-N compounds using hydrodynamic cavitation and acoustic cavitation alone is 0.15 and 0.13 USD, respectively. It was demonstrated that cavitation aided by ozonation is the most economical method of oxidation of BTEX-N compounds. The cost of treatment of 1 L of a model effluent by hydrodynamic or acoustic cavitation combined with ozonation is 0.04 and 0.03 USD, respectively, and the time needed for complete oxidation is about 60 min. For individual AOP processes: H_2O_2, O_3 and peroxone (H_2O_2/O_3), the cost of treatment is 1.77, 0.03 oraz 0.31 USD, respectively. A comparison of the costs of treatment revealed that the use of cavitation increases the effectiveness of ozonation with a negligible increase in treatment costs. At the same time, the use of cavitation reduces the time of treatment nearly threefold. This is mostly due to intensification of dissolution of ozone in the effluent and its effective decomposition to hydroxyl radicals under cavitation conditions [16]. Despite low cost of hydrodynamic/acoustic cavitation alone, the treatment time needed to achieve 100% oxidation is excessively long in comparison with individual AOP processes except H_2O_2 (HC/AC – 360 min/H_2O_2 – 360 min/O_3 – 180 min/O_3 + H_2O_2 – 60 min). The long time required for complete oxidation of BTEX-N compounds by H_2O_2 alone is primarily due to conversion of a large fraction of the oxidant to poorly reactive perhydroxyl anions under conditions of basic pH. Thus, from the point of view of economics of treatment, the best process would combine cavitation with an additional AOP process [2,16,45]. In technological installations, in which the rate of generation of effluents is low, a large buffer tank would allow the treatment to be limited to cavitation alone. An increased cost of treatment related to the use of additional oxidants is compensated by the reduced treatment time. An example of economical application of cavitation in industrial wastewater treatment is the CAV-OX® process (hydrodynamic cavitation/UV/H_2O_2) [47], which allows effective removal of organic contaminants (including BTEX-N compounds at 0.25–0.50 ppm) at a total treatment cost of 0.45 USD per 1 m^3 of effluent.

5. Conclusions

Hydrodynamic and acoustic cavitation combined with hydrogen peroxide, ozone and/or peroxone ensures high effectiveness of oxidation of organic contaminants present in a basic model effluent. The most efficient treatment involved hydrodynamic or acoustic cavitation combined with peroxone (100% oxidation of all the investigated model contaminants after the first 60 min of the treatment). This is mostly due to the effective generation of hydroxyl radicals under cavitational conditions in the presence of hydrogen peroxide and ozone at a basic pH of the solution being treated. The studies reported in this paper reveal that the use of cavitation allows an effective utilization of hydrogen peroxide as an external oxidant under conditions of strongly basic pH. As a result of known decomposition reactions in basic media, hydrogen peroxide was disqualified by many researchers as an effective oxidant under these conditions. Introduction of H_2O_2 into the cavitational zone ensures its effective conversion to hydroxyl radicals. The second best treatment method consisted of hydrodynamic or acoustic cavitation combined with ozonation wherein a 100% oxidation of the investigated model contaminants was observed after *ca.* 180 min of the treatment. The cavitation phenomenon reduces mass transfer resistance as a result of formation of zones of microcirculation and turbulence in the bulk of solution, which leads to an increase in concentration of ozone dissolved in the treated effluent. This in turn increases the amount of hydroxyl radicals which makes the degradation process more efficient. For hydrodynamic and acoustic cavitation combined with hydrogen peroxide, over 90% oxidation of all the investigated model contaminants was observed after 180 min of the treatment except for 2-nitrophenol (66.9% – AC + H_2O_2; 62.9% – HC + H_2O_2). The rate constants for degradation of nitro derivatives of benzene and phenol and its derivatives were found to be the smallest among all the investigated organic contaminants. This can be mostly attributed to the numerous intermediates formed during their oxidation (*p*-, *o*-xylene, among others) and the secondary contaminants produced owing to the presence of free chemical groups, such as NO_3^-. When hydrodynamic cavitation and acoustic cavitation are used as standalone treatment methods for the degradation of model contaminants, the effectiveness of oxidation of BTEX + N and organosulfur compounds exceeded 90% after 180 min of the treatment. The effectiveness of hydrodynamic cavitation compared with acoustic cavitation is higher by about 5–10% for the individual model compounds, which can be attributed to a higher intensity of cavitation in the throat of a Venturi tube than in the operating zone of ultrasonic transducers. Hydrodynamic cavitation and acoustic cavitation used alone, without an addition of external oxidants, are ineffective in oxidation of nitro compounds and phenol and its derivatives. Phenol and its derivatives are particularly hazardous to the environment due to their high biotoxicity and large amounts released in many technological processes, such as drug manufacturing. Consequently, the content of these compounds should be closely controlled at each stage of treatment of industrial wastewater.

From the point of view of economics of cavitational processes and AOPs, the most economical are hybrid treatments combining cavitation with an additional advanced oxidation process. This allows an almost three-fold reduction of time needed for effective oxidation of contaminants. Consequently, the total cost of a treatment is either comparable or much lower than in the case of individual AOP treatments. It was demonstrated that the most economical treatment of organic contaminants belonging to BTEX-N compounds involves hydrodynamic or acoustic cavitation aided by ozonation (0.04 and 0.03 USD L^{-1}).

Acknowledgments

The authors gratefully acknowledge financial support from the Ministry of Science and Higher Education in Poland for project 0040/IP2/2015/73 in the program "Iuventus Plus" in 2015–2017 *and* National Science Center, Warsaw, Poland – decision no. UMO-2017/25/B/ST8/01364.

The authors would like to thank Lotos Asfalt, Ltd. (Lotos Group, Inc.) for their cooperation on this project as well as SHIM-POL A.M. Borzymowski (a Shimadzu representative in Poland) for lending a GC-MS system QP2010 GC–MS SE for these studies.

The authors also thank Bandelin electronic GmbH & Co. KG along with Ingenieurbüro Peter Wagner for making available a SONOREX Technik AQ 5-1002.5 sono-cavitational reactor for this study.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.ultsonch.2018.03.013.

References

[1] Y.T. Shah, A.B. Pandit, V.S. Moholkar, Cavitation Reaction Engineering, Springer Science & Business Media, New York, 1999.

[2] M. Gągol, G. Boczkaj, Przegląd metod wytwarzania kawitacji do degradacji zanieczyszczeń organicznych w środowisku wodnym (A review of methods of generation of cavitation for degradation of organic pollutants in aqueous medium), Aparatura Badawcza i Dydaktyczna 22 (2017) 62–71.

[3] P.R. Gogate, M.K. Abhijeet, A review of applications of cavitation in biochemical engineering/biotechnology, Biochem. Eng. J. 44 (1) (2009) 60–72.

[4] G. Boczkaj, A. Fernandes, Wastewater treatment by means of advanced oxidation processes at basic pH conditions: a review, Chem. Eng. J. 320 (2017) 608–633.

[5] I. Grcic, M. Obradovic, D. Vujevic, N. Koprivanac, Sono-Fenton oxidation of formic acid/formate ions in an aqueous solution: from an experimental design to the mechanistic modeling, Chem. Eng. J. 164 (2010) 196–207.

[6] P.R. Gogate, P.N. Patil, Combined treatment technology based on synergism between hydrodynamic cavitation and advanced oxidation processes, Ultrason. Sonochem. 25 (2015) 60–69.

[7] A.A. Pradhan, P.R. Gogate, Degradation of p-nitrophenol using acoustic cavitation and Fenton chemistry, J. Hazard. Mater. 173 (2010) 517–522.

[8] D. Drijvers, H. van Langenhove, L. Nguyen, T. Kim, L. Bray, Sonolysis of an aqueous mixture of trichloroethylene and chlorobenzene, Ultrason. Sonochem. 6 (1999) 115–121.

[9] M. Zupanc, T. Kosjek, M. Petkovšek, M. Dular, B. Kompare, B. Širok, Z. Blazeka, E. Heath, Removal of pharmaceuticals from wastewater by biological processes, hydrodynamic cavitation and UV treatment, Ultrason. Sonochem. 20 (2013) 1104–1112.

[10] M. Zupanc, T. Kosjek, M. Petkovšek, M. Dular, B. Kompare, B. Širok, M. Strazˇar, E. Heath, Shear-induced hydrodynamic cavitation as a tool for pharmaceutical

micropollutants removal from urban wastewater, Ultrason. Sonochem. 21 (2014) 1213–1221.

[11] J.G.D. Filho, M.P. Assis, A.I.B. Genovez, Bacterial inactivation in artificially and naturally contaminated water using a cavitating jet apparatus, J. Hydro-environ. Res. 9 (2015) 259–267.

[12] M. Petkovšek, M. Mlakar, M. Levstek, M. Strazar, B. Širok, M. Dular, A novel rotation generator of hydrodynamic cavitation for waste-activated sludge disintegration, Ultrason. Sonochem. 26 (2015) 408–414.

[13] P.R. Gogate, A.B. Pandit, Hydrodynamic cavitation reactors: a state of the art review, Rev. Chem. Eng. 17 (2001) 1–85.

[14] S. Asgharzadehahmadi, A.A.A. Raman, R. Parthasarathy, B. Sajjadi, Sonochemical reactors: review on features, advantages and limitations, Renewable Sustainable Energy Rev. 63 (2016) 302–314.

[15] Y. Xiong, F. Peng, Optimization of cavitation venturi tube design for pico and nano bubbles generation, Int. J. Mining Sci. Technol. 25 (2015) 523–529.

[16] G. Boczkaj, M. Gągol, M. Klein, A. Przyjazny, Effective method of treatment of effluents from production of bitumens under basic pH conditions using hydrodynamic cavitation aided by external oxidants, Ultrason. Sonochem. 40 (2018) 969–979, http://dx.doi.org/10.1016/j.ultsonch.2017.08.032.

[17] G. Boczkaj, P. Makoś, A. Fernandes, A. Przyjazny, New procedure for the control of the treatment of industrial effluents to remove volatile organosulfur compounds, J. Sep. Sci. 39 (2016) 3946–3956.

[18] G. Boczkaj, P. Makoś, A. Przyjazny, Application of dynamic headspace and gas chromatography coupled to mass spectrometry (DHS-GC-MS) for the determination of oxygenated volatile organic compounds in refinery effluents, Anal. Methods 8 (2016) 3570–3577.

[19] G. Boczkaj, A. Przyjazny, M. Kamiński, Characteristics of volatile organic compounds emission profiles from hot road bitumens, Chemosphere 107 (2014) 23–30.

[20] E. Gilgenast, G. Boczkaj, A. Przyjazny, M. Kamiński, Sample preparation procedure for the determination of polycyclic aromatic hydrocarbons in petroleum vacuum residue and bitumen, Anal. Bioanal. Chem. 401 (2011) 1059–1069.

[21] G. Boczkaj, M. Kamiński, A. Przyjazny, Process control and investigation of oxidation kinetics of postoxidative effluents using gas chromatography with pulsed flame photometric detector (GC-PFPD), Ind. Eng. Chem. Res. 49 (2010) 12654–12662.

[22] G. Boczkaj, A. Przyjazny, M. Kamiński, New procedures for control of industrial effluents treatment processes, Ind. Eng. Chem. Res. 53 (2014) 1503–1514.

[23] F. Deygout, Volatile emissions from hot bitumen storage tanks, Environ. Prog. Sustainable Energy 30 (2011) 102–112.

[24] Z. Chen, X. Yu, X. Huang, S. Zhang, Prediction of reaction rate constants of hydroxyl radical with organic compounds, J. Chil. Chem. Soc. 59 (1) (2014) 2252–2259.

[25] E.S.C. Kwok, R. Atkinson, Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure-reactivity relationship: an update, Atmos. Environ. 29 (1995) 1685–1695.

[26] L.P. Ramteke, P.R. Gogate, Treatment of toluene, benzene, naphthalene and xylene (BTNXs) containing wastewater using improved biological oxidation with pretreatment using Fenton/ultrasound based processes, J. Ind. Eng. Chem. 28 (2015) 247–260.

[27] S. Song, M. Xia, Z. He, H. Ying, B. Lu, J. Chen, Degradation of p-nitrotoluene in aqueous solution by ozonation combined with sonolysis, J. Hazard. Mater. 144 (2007) 532–537.

[28] Z. He, S. Song, H. Ying, L. Xu, J. Chen, p-Aminophenol degradation by ozonation combined with sonolysis: operating conditions influence and mechanism, Ultrason. Sonochem. 14 (2007) 568–574.

[29] R.I. Olariu, B. Klotz, I. Barnesa, K.H. Becker, R. Mocanu, FT–IR study of the ring-retaining products from the reaction of OH radicals with phenol, *o*-, *m*-, and *p*-cresol, Atmos. Environ. 36 (2002) 3685–3697.

[30] A.G. Chakinala, D.H. Bremner, P.R. Gogate, K.C. Namkung, A.E. Burgess, Multivariate analysis of phenol mineralisation by combined hydrodynamic cavitation and heterogeneous advanced Fenton processing, Appl. Catal. B: Environ. 78 (2008) 11–18.

[31] P.Y. Jiang, Y. Katsumura, J.K. Ishigure, Y. YoshidaIb, Reduction potential of the nitrate radical in aqueous solution, Inorg. Chem. 31 (1992) 5135–5136.

[32] M.V. Bagal, P.R. Gogate, Degradation of 2,4-dinitrophenol using a combination of hydrodynamic cavitation, chemical and advanced oxidation processes, Ultrason. Sonochem. 20 (2013) 1226–1235.

[33] S. Bhattacharjee, Y.T. Shah, Mechanisms for advanced photooxidation of aqueous organic waste compounds, Rev. Chem. Eng. 14 (1998) 1–46.

[34] E.M. Aieta, K.M. Reagan, J.S. Lang, L. McReynolds, J. Kang, W.H. Glaze, Advanced oxidation processes for treating groundwater contaminated with TCE and PCE: Pilot-scale evaluations, J. Am. Water Works Assoc. 80 (1988) 64–72.

[35] P. Sykes, Guidelines to Mechanisms in Organic Chemistry, fifth ed., Orient-Longman, New-Delhi, 1982.

[36] P. Saritha, C. Aparna, V. Himabindu, Y. Anjaneyulu, Comparison of various advanced oxidation processes for the degradation of 4-chloro-2 nitrophenol, J. Hazard. Mater. 149 (2007) 609–614.

[37] H. Zangeneh, A.A.L. Zinatizadeh, M. Feizy, A comparative study on the performance of different advanced oxidation processes (UV/O_3/H_2O_2) treating linear alkyl benzene (LAB) production plant's wastewater, J. Ind. Eng. Chem. 20 (2014) 1453–1461.

[38] R. Munter, Advanced oxidation processes – current status and prospects, Proc. Estonian Acad. Sci. Chem. 50 (2001) 59–80.

[39] P.N. Patil, S.D. Bote, P.R. Gogate, Degradation of imidacloprid using combined advanced oxidation processes based on hydrodynamic cavitation, Ultrason. Sonochem. 21 (2014) 1770–1777.

[40] M.M. Gore, V.K. Saharan, D.V. Pinjari, P.V. Chavan, A.B. Pandit, Degradation of reactive orange 4 dye using hydrodynamic cavitation based hybrid techniques, Ultrason. Sonochem. 21 (2014) 1075–1082.

[41] L.K. Weavers, M.R. Hoffmann, Sonolytic decomposition of ozone in aqueous solution: mass transfer effects, Environ. Sci. Technol. 32 (1998) 3941–3947.

[42] F. Zaviska, P. Drogui, G. Mercier, J.F. Blais, Procédés d'oxydation avancée dans le traitement des eaux et des effluents industriels: Application á la dégradation des polluants réfractaires, Rev. Sci. Eau 22 (4) (2009) 535–564.

[43] H. Paillard, R. Brunet, M. Doré, Optimal conditions for applying an ozone-hydrogen peroxide oxidizing system, Water Res. 22 (1) (1988) 91–103.

[44] M.A. Oturan, J.J. Aaron, Advanced oxidation processes in water/wastewater treatment: principles and applications. A review, Environ. Sci. Technol. 44 (2014) 2577–2641.

[45] M. Gągol, A. Przyjazny, G. Boczkaj, Wastewater treatment by means of advanced oxidation processes based on cavitation – a review, Chem. Eng. J. 338 (2018) 599–627.

[46] M. Čehovin, A. Medic, J. Scheideler, J. Mielcke, A. Ried, B. Kompare, A.Z. Gotvajn, Hydrodynamic cavitation in combination with the ozone, hydrogen peroxide and the UV-based advanced oxidation processes for the removal of natural organic matter from drinking water, Ultrason. Sonochem. 37 (2017) 394–404.

[47] Y. Benito, S. Arrojo, G. Hauke, P. Vidal, Hydrodynamic cavitation as a low-cost AOP for wastewater treatment: preliminary results and a new design approach, WIT Trans. Ecol. Environ. 80 (2005) 495–503.

SUPPORTING INFORMATION FOR MANUSCRIPT

Highly effective degradation of selected groups of organic compounds by cavitation based AOPs under basic pH conditions

Michał Gągol[1], Andrzej Przyjazny[2], Grzegorz Boczkaj[1*]

[1]Gdańsk University of Technology, Faculty of Chemistry, Department of Chemical and Process Engineering,

[2]Kettering University, 1700 University Avenue, Department of Chemistry & Biochemistry, Flint, MI 48504, USA.

** Dr Grzegorz Boczkaj, PhD. Sc. Eng. Gdansk University of Technology, Faculty of Chemistry, Department of Chemical and Process Engineering, 80 – 233 Gdansk, G. Narutowicza St. 11/12, Poland. Fax: (+48 58) 347-26-94; Tel: (+48) 697970303; E-mail: grzegorz.boczkaj@gmail.com*

Table S1. Percent degradation of model pollutants in hydrodynamic and acoustic cavitation processes with AOPs

Process / Pollutant	AC			AC + AOPs											HC			HC + AOPs							
				H_2O_2			O_3				Peroxone							H_2O_2			O_3			Peroxone	
Time [min]	60	180	360	60	180	360	30	60	180	360	30	60	180	360	60	180	360	60	180	360	30	60	180	30	60
Organosulfur																									
2-ethylthiophene	66.1	92.5	97.5	82.5	100	100	62.3	90.4	100	100	99.2	100	100	100	69.1	91.4	93.4	85.5	100	100	65.1	95.6	100	100	100
dibutyl sulfide	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
di-tert-butyl sulfide	66.5	86.2	97.7	100	100	100	81.8	93.0	100	100	100	100	100	100	72.1	94.1	100	100	100	100	83	98.7	100	100	100
Derivatives of benzene (with nitro group)																									
nitrobenzene	-45.0	-26.9	-9.1	59.2	95.2	100	54.9	79.4	98.0	100	86.5	99.5	100	100	-40.1	-30.7	-8.2	63.2	97.2	100	56	82.6	100	88.9	100
2-nitrophenol	6.2	-26.6	-48.3	35.1	66.9	100	68	84.6	100	100	96.3	99.7	100	100	10.4	-15.7	-31.2	30.1	62.9	100	71	87.6	100	98	100
2-nitrotoluene	-51.3	-31.1	-7.9	63.5	95.4	100	64.3	87.5	99.1	99.9	92.5	99.8	100	100	-41.3	-28.1	-8.8	67.5	98.4	100	65	94.1	100	94	100
BTEX+N																									
benzene	56.5	91.1	100	100	100	100	100	100	100	100	100	100	100	100	41.6	93.5	100	100	100	100	100	100	100	100	100
ethylbenzene	63.9	91.4	100	71.1	100	100	88	100	100	100	99.4	99.8	96.4	92.6	71.4	95.4	100	81.1	100	100	89	100	100	100	100
toluene	60.6	91.5	100	72.3	100	100	100	100	100	100	99.3	100	100	100	66.7	96.4	100	79.3	100	100	100	100	100	100	100
naphthalene	5.7	21.4	46.7	86.7	96.8	100	93	98.4	99.4	99.8	98.8	99.9	100	100	16.2	36.9	51.4	94.7	100	100	95	100	100	99	100
o-xylene	56.2	87.7	99.7	75.7	90.8	100	94	100	100	100	98.8	99.3	96.9	93.4	41.2	51.4	63.7	55.7	80.8	100	96	100	100	100	100
Phenol and its derivatives																									
phenol	7.2	-13.1	-6.6	83.5	93.8	100	5.1	41.9	98.7	100	91.6	99.6	98.4	97.3	9.7	11.5	15.4	86.5	96.8	100	7	54.1	100	93	100
4-ethylphenol	-54.2	-43.8	-18.4	94.0	99.2	100	62	95.9	99.9	100	94.8	99.9	100	100	14.2	41.5	60.1	95.0	100	100	66	99.8	100	96	100
m-cresol	-35.4	-24.1	-7.0	90.1	99.4	100	43.9	85.3	99.7	100	94.7	99.7	99.4	98.7	9.8	21.0	30.6	94.1	100	100	51	87.4	100	98	100
o-cresol	-30.4	-27.1	-8.1	92.5	98.8	100	37.7	81.5	100	100	92.9	99.9	100	100	7.1	14.2	21.4	96.5	100	100	42	86.4	100	94	100

Table S2. Percent degradation of model pollutants in individual cavitation processes and AOPs

Process / Pollutant	AC			HC			H_2O_2			O_3			H_2O_2/O_3		
							Flow rate 3 mlmin^{-1}			Rate 12.32 gh^{-1}			O_3 12.32 gh^{-1}/H_2O_2 3 mlmin^{-1}		
Time [min]	60	180	360	60	180	360	60	180	360	60	180	360	30	60	180
Organosulfur															
2-ethylthiophene	66.1	92.5	97.5	69.1	91.4	93.4	59.9	92.3	99.8	89.4	100	100	89.3	99.5	99.6
dibutyl sulfide	100	100	100	100	100	100	100	100	100	100	100	100	92.1	100	100
di-tert-butyl sulfide	66.5	86.2	97.7	72.1	94.1	100	93.2	100	100	88.4	100	100	100	100	100
Derivatives of benzene (with nitro group)															
nitrobenzene	-45.0	-26.9	-9.1	-40.1	-30.7	-8.2	-21.1	24.4	99.1	69.7	99.1	99.6	79.1	99.6	99.8
2-nitrophenol	6.2	-26.6	-48.3	10.4	-15.7	-31.2	-3.2	-1.7	6.6	-0.2	5.5	7.1	1.8	7.3	10.2
2-nitrotoluene	-51.3	-31.1	-7.9	-41.3	-28.1	-8.8	-18.1	66.1	99.1	74.6	99.4	99.5	76.1	99.3	99.7
BTEX+N															
benzene	56.5	91.1	100	41.6	93.5	100	82.3	87.3	99.8	99.7	100	100	100	100	100
ethylbenzene	63.9	91.4	100	71.4	95.4	100	53.5	92.1	100	89.7	100	100	100	100	100
toluene	60.6	91.5	100	66.7	96.4	100	73.7	88.4	100	89.2	99.8	100	89.4	100	100
naphthalene	5.7	21.4	46.7	16.2	36.9	51.4	59.1	93.1	99.9	89.4	99.8	100	88.8	99.9	100
o-xylene	56.2	87.7	99.7	41.2	51.4	63.7	55.5	91.7	99.6	89.7	99.8	99.8	88.9	99.3	99.8
Phenol and its derivatives															
phenol	7.2	-13.1	-6.6	9.7	11.5	15.4	58.4	94.1	99.7	32.7	89.8	99.8	89.2	99.4	99.4
4-ethylphenol	-54.2	-43.8	-18.4	14.2	41.5	60.1	47.2	94.6	99.9	79.7	89.8	100	88.8	99.9	100
m-cresol	-35.4	-24.1	-7.0	9.8	21.0	30.6	-4.1	-1.71	6.61	-2.1	1.7	8.6	2.1	3.1	11.4
o-cresol	-30.4	-27.1	-8.1	7.1	14.2	21.4	-5.1	-1.71	6.61	-3.1	-1.1	7.2	1.4	2.8	9.4

Załącznik 4

Publikacja nr 4:

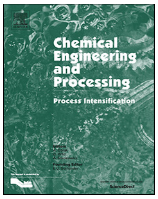
M. Gągol, A. Przyjazny, G. Boczkaj, Effective method of treatment of industrial effluents under basic pH conditions using acoustic cavitation – a comprehensive comparison with hydrodynamic cavitation processes, Chem. Eng. Process. 128 (2018) 103-113.

Chemical Engineering & Processing: Process Intensification 128 (2018) 103–113

Contents lists available at ScienceDirect

Chemical Engineering & Processing: Process Intensification

journal homepage: www.elsevier.com/locate/cep



Effective method of treatment of industrial effluents under basic pH conditions using acoustic cavitation – A comprehensive comparison with hydrodynamic cavitation processes

Michał Gągol[a], Andrzej Przyjazny[b], Grzegorz Boczkaj[a,*]

[a] Gdańsk University of Technology, Faculty of Chemistry, Department of Chemical and Process Engineering, Poland
[b] Kettering University, 1700 University Avenue, Department of Chemistry & Biochemistry, Flint, MI 48504, USA

ARTICLE INFO

Keywords:
Acoustic cavitation
Hydrodynamic cavitation
Sonocavitation
Wastewater treatment
Industrial effluents
Advanced oxidation processes (AOP)

ABSTRACT

The use of acoustic cavitation in advanced oxidation processes (AOPs) is a promising trend in research for treatment of industrial effluents. The paper presents the results of investigations on the use of acoustic cavitation aided by additional oxidation processes (ozonation/H_2O_2 oxidation/Peroxone/UV-C) for the treatment of effluents from the production of bitumens. Under these conditions, the total contaminant load, expressed as chemical oxygen demand (COD), could be lowered by 51%. In addition, changes in concentrations of volatile organic compounds identified in the effluents following the treatment are discussed. The investigations revealed that by using acoustic cavitation combined with the Peroxone process, the majority of oxygenated organic compounds were oxidized. The paper also compares AOPs based on acoustic cavitation with hydrodynamic cavitation-aided processes. This study revealed that the use of acoustic cavitation results in a higher effectiveness of degradation of organic compounds using AOPs based on hydrogen peroxide. On the other hand, hydrodynamic cavitation is generally a slightly more effective method for degradation of organic compounds for ozone-based AOPs. Furthermore, furfural and 2-methylcyclohexanone were discovered as secondary pollutants whose concentration increased during the treatment.

1. Introduction

Acoustic cavitation is a physical phenomenon in which passage of ultrasounds through the cavitating medium generates cavities, promotes their growth and their collapse [1–4]. Cavitation generates localized high temperatures and pressures in the medium. Such conditions promote the reactions of formation of reactive hydroxyl radicals (·OH), which are responsible for oxidation of contaminants present in the treated medium [5–8]. Furthermore, propagation of ultrasonic waves in the liquid medium generates local turbulence and microcirculation in liquid which is known as acoustic streaming, which can mainly cause physical effects and also influence chemical processes limited by mass transfer [2]. These effects increase the rate of generation of hydroxyl radicals and the transport of molecules of liquid and contaminants toward the collapsing cavities, which causes a high degree of oxidation of organic contaminants [9–12].

Acoustic cavitation has found a widespread use in, among others, chemical synthesis, biotechnology, treatment of waste streams (such as industrial effluents), degradation of polymeric materials or the petrochemical industry [3]. In the case of treatment of effluents, acoustic cavitation presently offers one the highest degradation rates compared with other physical methods [4,5]. Efficiency of the process depends to a large extent on the number and type of transducers, frequency range (most often 20–520 kHz), amperage (up to 70 A) and the arrangement of transducers in the reactor [6–8]. This ensures high cavitational intensity and acoustic streaming. Two types of acoustic cavitational reactors are used most often. They differ with respect to the type and placement of the transducer. The first type is a reactor with an immersed ultrasonic probe (called ultrasonic horn) [9–11]. The second type of an acoustic cavitational reactor is ultrasonic bath. In this case transducers are placed beneath the container with a solution and the ultrasound energy reaches the medium indirectly through the walls of the container [12]. Detailed investigations of different configurations of sonochemical reactors were described by Csoka et al. [13]. Most often, the power supplied to the solution ranges from 0.03 to 200 W/l [2,4,14]. It is then possible to achieve the maximum cavitational yield distributed throughout the entire solution which improves the effectiveness of removal of organic pollutants [2]. At present, acoustic

---

[*] Corresponding author at: Gdansk University of Technology, Faculty of Chemistry, Department of Chemical and Process Engineering, 80 – 233 Gdansk, G. Narutowicza St. 11/12, Poland.

E-mail address: grzegorz.boczkaj@pg.edu.pl (G. Boczkaj).

https://doi.org/10.1016/j.cep.2018.04.010
Received 15 December 2017; Received in revised form 9 April 2018; Accepted 9 April 2018

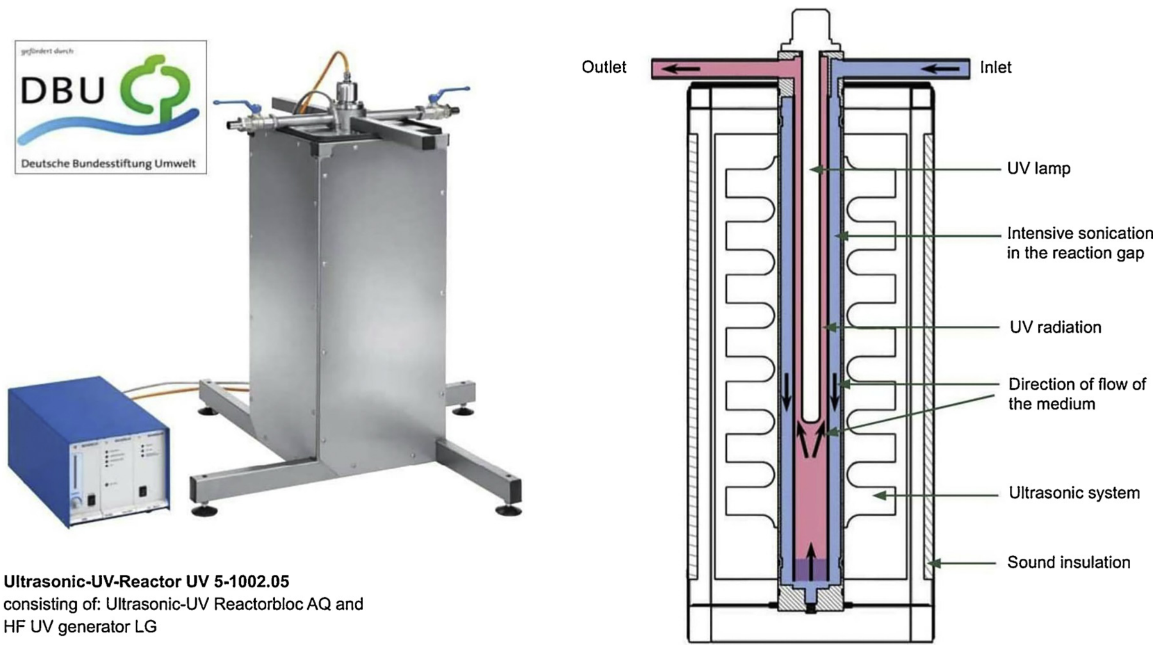


Fig. 1. Experimental setup for acoustic cavitation.

cavitation along with hydrodynamic cavitation are increasingly used for degradation of toxic organic contaminants adversely affecting activated sludge in wastewater treatment plants [15,16]. Wastewater treatment plants of oil refineries are an example of such use. The activated sludge used for biological treatment is adapted to biodegradation of typical petroleum-derived contaminants. However, one of the streams of strongly contaminated effluents fed to WWTP is the effluent from the production (oxidation) of bitumens. Post-oxidative effluents contain large amounts of organic compounds with hetero atoms, such as oxygen (ketones, aldehydes, ethers and alcohols) or sulfur [17–21]. Effluents of this type are highly toxic to activated sludge, therefore, they must be diluted prior to biological treatment or subjected to a preliminary chemical treatment in order to degrade toxic groups of chemical compounds.

The purpose of the present work was to investigate the possibility of use and evaluation of effectiveness of acoustic cavitation combined with ozonation or oxidation with hydrogen peroxide for preliminary treatment of effluents from the production of bitumens in order to lower their total organic load and to oxidize persistent organic contaminants which would allow effective biological treatment by activated sludge in the next stage of effluent treatment. This paper is one of the few publications dealing with the investigation of real effluents generated as a waste during the oxidation of bitumens. The importance of this work consists in the possibility of evaluation of effectiveness of advanced oxidation processes based on cavitation for degradation of organic contaminants in aqueous matrices with a heavy organic load. The effectiveness of the treatment processes of alkaline effluents from the production of bitumens was compared for acoustic-cavitation based AOPs with the results obtained for the previously studied hydrodynamic cavitation-based process [22].

2. Materials and methods

2.1. Chemicals

Real effluents from the production of bitumens were obtained from the bitumen oxidation unit using Biturox process (Lotos Asfalt, Grupa Lotos S.A., Gdańsk, Poland). Characteristics: pH 10.5, COD: 20000–22000 mg $O_2\,L^{-1}$, BOD$_5$: 3400–5200 mg $O_2\,L^{-1}$, S^{2-}: 1000–2000 mg L^{-1}. Deionized water was obtained from the MilliQ water purification system (Millipore Corporation, USA). The following reagents were used: dichloromethane (for HPLC, Sigma-Aldrich, USA), acetone (for HPLC, Sigma-Aldrich, USA), hydrochloric acid (analytical reagent, Sigma-Aldrich, USA), hydrogen peroxide 30% (POCH S.A., Poland), reagent for COD analysis (sulfuric acid, potassium dichromate, silver sulfate, analytical reagent, POCH S.A., Poland), anti-foam agent Struktol SB 2032 (Schill Seilacher, Germany), standard for COD analysis: sodium hydrogen phthalate (Sigma-Aldrich, USA); standards for quantitative analysis: (Sigma-Aldrich, USA): acetaldehyde, 1-propanal, ethyl acetate, methyl acrylate, 2-butanol, tetrahydrofuran, 2-methylpropan-1-ol, 2-methylbutan-2-ol, 1-butanol, 2,3-dihydropyran, ethyl acrylate, 2-pentanone, tetrahydropyran, ethyl propionate, 3-methylobutan-1-ol, isobutyl acetate, paraldehyde, 1-pentanol, 2-hexanone, cyclopentanone, furfural, 1-hexanol, 3-heptanone, cyclohexanol, anisole, cyclohexanone, 2-methylcyclohexanone, 1-heptanol, 3-methylcyclohexanone, 2-ethylhexan-1-ol, phenol, benzyl alcohol, acetophenone, *o*-cresol, 4-methylbenzaldehyde, *m*-cresol, 2,6-dimethylphenol, 4-ethylphenol, 4-chlorophenol, 4-chlorobutan-1-ol, 3-chlorobutan-1-one. Ozone was produced in a Tytan 32 ozone generator (Erem) at a rate of 12.32 g/h.

2.2. Acoustic cavitation

Treatment of effluents from the production of bitumens by acoustic cavitation aided by oxidation (addition of hydrogen peroxide and ozonation) was carried out in an Ultrasonic-UV-Reactor UV 5–1002.05 (Bandelin electronic GmbH & Co. KG, Germany) depicted in Fig. 1. The ultrasonic reactor used in this study had four transducer sections located along a circumference of a flow pipe – parallel to the sonication zone. Each of the sections contained seven transducers with a total power of about 250 W (power of a single transducer was 36 W; length of a caviation zone 50 cm). A diagram of arrangement of the transducers is shown in Figure S1 (Supporting Information). The actual (total) power of the transducers in all four sections was about 1000 W. The energy introduced into the aqueous phase is smaller due to the heat losses in the generator and transducer. According to the data from the manufacturer, the energy loss of generator unit is 9% and the energy loss of transducer is 5%. The maximum energy in the water at the maximum setting of power control is about 8645 W. The effluent volume was 5 L. During the treatment process the transducers were operated at a

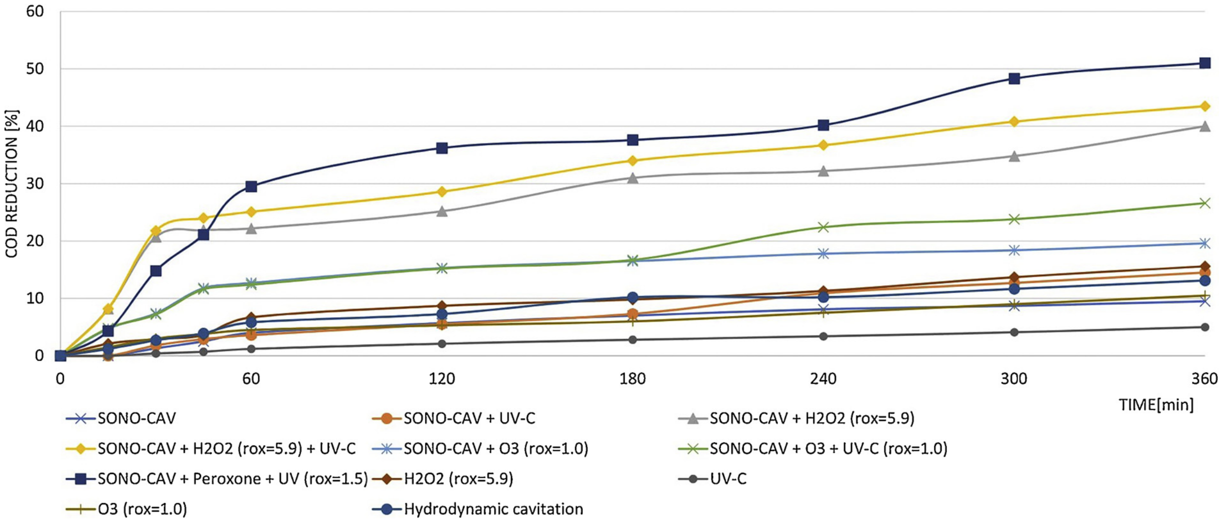


Fig. 2. Comparison of effectiveness of COD removal for studied acoustic cavitation processes with AOPs.

maximum power (100%) which means that the energy supplied to the effluent was about 172.9 W/L. The reactor also contained a 20-W UV lamp (input power 64 W) emitting UV-C radiation at 254 nm. The system consisted of a 5-L storage tank, stirrer, temperature controller, diaphragm pump (effluent pumped at 5.9 L min^{-1}). The tank and connecting elements were made of SS316stainless steel. Inlet and outlet pipes were made of poly(tetrafluoroethylene) (PTFE). The reaction system was used to treat 5 L of effluent from the production of bitumens. Temperature of the effluent was maintained at 40 ± 2 °C by means of an electric heater and a condenser made of SS316 stainless steel to which tap water was fed. Effluent treatment was carried out for 360 min at a maximum power and a flow rate of 5.9 L min^{-1}. For the first hour of treatment, the effluent was sampled every 15 min. Thereafter, samples were collected every hour. Ozonation was carried out by means of a Tytan 32 ozone generator (Erem) at a rate reaching 12.32 gh^{-1} and a flow rate of 20 L min^{-1}. Hydrogen peroxide (30%) was introduced to the system by a S-7110 isocratic high pressure pump (Merck-Hitachi, Japan) at a flow rate ranging from 1.0 to 3.0 mL min^{-1}. Additionally, due to intense foaming of the effluent during ozonation, 2 mL of an anti-foam agent Struktol 2032 were added to each sample.

2.3. *Process control*

2.3.1. *COD*

Chemical oxygen demand was determined using COD cuvette test (HACH®, UK). Samples were combusted in a thermoreactor (HACH®, USA) at 150 °C for 2 h. COD of effluents was monitored using a spectrophotometric method (Spectrophotometer DR/2010, HACH®, USA).

2.3.2. *BOD*

The determination of biochemical oxygen demand was carried out according to ISO 5815-1:2003 (E) standard. Oxygen content was measured using a dissolved oxygen probe COG-1 (ELMETRON®, Poland).

2.3.3. *Analysis of composition of VOCs and VSCs*

Identification and quantitative analysis of VOCs (alcohols: 1-propanol; 2-butanol; 1-hexanol; 1-heptanol; aromatic compounds: phenol; *o*-cresol; *m*-cresol; 2,6-dimethylphenol; 4-ethylphenol; 4-methylbenzaldehyde; aldehydes/ketones: acetaldehyde; 2-pentanone; 2-hexanone; cyclopentanone; furfural; 3-heptanone; cyclohexanone; 2-methylcyclohexanone; 3-methylcyclohexanone; acetophenone) were carried out by gas chromatography-mass spectrometry using a GCMS-QP2010SE GC–MS (Shimadzu, Japan) equipped with a capillary column: Rxi-624Sil MS (60 m x 0.25 mm x 1.40 μm, Restek, USA). Samples were prepared for analysis using dispersive liquid-liquid microextraction (DLLME). The exact experimental procedure was described previously [20]. The investigation of VSCs (ethanethiol; dimethyl sulfide; carbon disulfide; 3-methyl-1-butanethiol; 1,2-ethanedithiol; thiophenol; thioanisole; benzylthiol) was performed using an Autosystem XL gas chromatograph equipped with a flame photometric detector, an autosampler (Perkin Elmer, USA) and a column: DB-1 (60 m x 0.32 mm x 1.0 μm, BGB, Switzerland). Similarly to the analysis of VOCs, samples were prepared using DLLME. A detailed description of the procedure was provided elsewhere [21].

3. Results and discussion

The effluent having a basic pH (10.5) was subjected to treatment by acoustic cavitation alone using the maximum power of transducers as well as by acoustic cavitation aided by the addition of oxidants. The effluent was pumped through the acoustic-cavitational reactor (Fig. 1) by means of a diaphragm pump at a flow rate of 5.9 L min^{-1}. The treatment was continued uninterruptedly for 6 h. A high content of organic compounds in the effluent resulted in formation of large amounts of foam (*ca.* 2 L) during pumping which necessitated addition of an anti-foam agent. Throughout the entire treatment process the temperature was maintained at around 40 °C by circulation of tap water through the heat exchanger. The main parameters used to evaluate the efficiency of removal of total contaminant load were COD and BOD_5. For individual treatment processes, the reduction of COD was studied at the following points of time: raw effluent at 0, 15, 30, 45, 60, 120, 180, 240, 300 and 360 min of the treatment process. BOD_5 was measured for raw effluent and effluent after 180 and 360 min of treatment (Table S1 – please refer to supporting information).

3.1. *Acoustic cavitation*

The effectiveness of removal of COD load of the effluent by means of acoustic cavitation alone and by acoustic cavitation aided by UV-C radiation is shown in Fig. 2. Three independent runs were carried out for each process and the results were repeatable (RSD < 5%). The plots in Fig. 2 represent average values.

It follows from the investigations that acoustic cavitation alone carried out at the maximum power of transducers (1000 W, 16 A, 25 kHz; the actual delivered power (after the efficiency including): 172.9 W/L) allows a COD reduction of the post-oxidative effluents from the production of bitumens by 9.5% (energy efficiency: 0.46 mg COD/kJ) (hydrodynamic cavitation 13%; energy efficiency 0.52 mg COD/kJ).

Table 1
Operating conditions for acoustic cavitation process with addition of external oxidant.

Process	Flow rate [L min^{-1}]	Temperature [°C]	Time [min]	H_2O_2 flow rate [m L min^{-1}]	O_3 flow rate [g h^{-1}]	r_{OX} (molar)	COD reduction [%]
SONO-CAV	5.9	40 ± 2	360	X	X	X	9.5
SONO-CAV + UV-C	5.9	40 ± 2	360	X	X	X	14.5
SONO-CAV + H_2O_2	5.9	40 ± 2	360	0.46	X	0.9	16.0
SONO-CAV + H_2O_2	5.9	40 ± 2	360	1	X	1.9	16.3
SONO-CAV + H_2O_2	5.9	40 ± 2	360	2	X	4.0	33.5
SONO-CAV + H_2O_2	5.9	40 ± 2	360	3	X	5.9	40.0
SONO-CAV + H_2O_2 + UV-C	5.9	40 ± 2	360	3	X	5.9	43.5
SONO-CAV + O_3	5.9	40 ± 2	360	X	12.32	1.0	19.6
SONO-CAV + O_3 + UV-C	5.9	40 ± 2	360	X	12.32	1.0	26.6
SONO-CAV + Peroxone + UV-C	5.9	40 ± 2	360	3	12.32	1.5	51.0
UV-C	5.9	40 ± 2	360	X	X	X	5.0
H_2O_2	59	40 ± 2	360	3	X	5.9	15.6
O_3	5.9	40 ± 2	360	X	12.32	1.0	10.5

This is mostly due to the process of generation of hydroxyl radicals which takes place during collapse of the cavities. Hydroxyl radicals are produced by the dissociation of water, when water vapors are heated to 3000 K and above during the cavitational collapse. Comparing the results of the COD reduction of the acoustic cavitation and hydrodynamic cavitation, it can be observed that the use of hydrodynamic cavitation process allows obtaining a slightly higher COD removal than acoustic cavitation (by about 3.5%). In the case of treatment of large effluent volumes (more than 2 L), the acoustic wave that forces local drops of static pressure below the vapor pressure of the treated liquid is less effective in the intensification of cavitation than the Venturi tube in hydrodynamic cavitation. The most effective collapse of cavities occurs near the sonic transducers. With the increasing distance of the acoustic wave from the excitation space (large volumes of treated effluent) the energy decreases, causing a decrease in the intensity of cavitation and a lower number of generated hydroxyl radicals [2,3]. Acoustic cavitation results in generation of a smaller number of cavities but they have a significantly higher collapse energy compared to hydrodynamic cavitation.

When the effluent was additionally irradiated with a UV-C lamp, the COD reduction increased to 14.5%. The plots in Fig. 2 reveal that significant differences in the COD reduction without and with UV-C irradiation are only observed after 3 h of the treatment.

It is due to the gradual decolorization of the effluent, which allows more effective irradiation by UV-C light as well as the formation of by-products, after 180 min of treatment, that are susceptible to oxidation by UV-C light.

UV-C radiation improves the efficiency of oxidation of organic compounds containing C═C double bonds, such as phenol and its derivatives [24], naphthol dyes [23] as well as chlorinated ethylenes [26]. In this case, during the first three hours of the treatment hydroxyl radicals are consumed mostly for oxidation of simple organic compounds, such as alcohols. Recalcitrant compounds require a much longer oxidation time and undergo oxidation to simpler organic compounds only after 3 h of the treatment. Simple organic compounds often contain double C═C bonds, which allows their effective decomposition by the energy of UV-C radiation. Consequently, the COD of the effluent is lowered by additional 5%. These results indicate validity of sequential treatment of effluents. The first stage would involve acoustic cavitation alone followed by photooxidation using UV. This approach would allow lowering the cost of electric energy used during the treatment. For the reaction system discussed, sequential treatment allows lowering the energy used by about 3% in comparison with the combined processes (acoustic cavitation (6 h) + UV-C lamp (6 h) = 22,982.4 kJ; acoustic cavitation (6 h) + UV-C lamp (3 h) = 22,291.2 kJ). At an average energy cost of 0.18 US dollars (USD) per 1 kW h (3600 kJ), a 6-hour sequential treatment saves *ca.* 6 US dollars/m^3 effluent treated.

3.2. Acoustic cavitation + H_2O_2

The efficiency of COD removal from the effluent using acoustic cavitation aided by an external oxidant (hydrogen peroxide) with and without UV-C irradiation is shown in Fig. 2.

Acoustic cavitation was combined with hydrogen peroxide at four different doses $r_{ox} = \frac{OH\bullet\,(oxidant)}{COD\,(waste)}$ = 0.9; 1.9.; 4.0; 5.9 – molar ratio of the amount of oxidant provided by hydrogen peroxide to COD of the effluent). The exact method for calculation of the r_{ox} molar ratio was given in a previous work [22].

Chemical oxygen demand refers to the amount of oxygen (O_2) in mg/L needed to oxidize contaminants present in the effluent. Conversion of mg of oxygen to moles and expression of the amount of oxidant as moles of hydroxyl radicals allows calculation of r_{ox}. An example of such a calculation is shown below. Calculation of r_{ox} parameter:

Assumption: 100% COD reduction.

Process parameters: volumetric flow rate of 30% H_2O_2: 3.0 ml min^{-1}; density of 30% H_2O_2: 1.11 g mL^{-1}; time of process: 360 min; COD of the effluent: 22,865 mg O_2 L^{-1}.

For 5 L of the effluent: oxygen demand = 5 * 22,865 = 114.3 g O_2; 114.3/32 = 3.57 mol of O_2,

The mass of introduced 30% hydrogen peroxide: m = 3.0 * 360 * 0.3 * 1.11 = 359.6 g H_2O_2

The mass of introduced HO· radicals (stoichiometric reaction): m_r = 359.6 g; 359.6/17 = 21.2 mol of oxidant,

r_{ox} = 21.2/3.57 = 5.9

In each case hydrogen peroxide was introduced continuously during the entire treatment process. Specific process parameters are listed in Table 1. The greatest reduction in COD (by 40%) of the effluent was achieved when hydrogen peroxide was fed at 3.0 mL min^{-1} (r_{ox} = 5.9). With UV-C irradiation turned on, this value increased to 43.5%. This can be attributed to the increased number of hydroxyl radicals generated through decomposition of hydrogen peroxide. For a similar process using hydrodynamic cavitation in combination with hydrogen peroxide (r_{ox} = 6.2), a 20% reduction of COD was obtained [22]. Acoustic cavitation aided by hydrogen peroxide is about twice as effective in COD removal as hydrodynamic cavitation. The local concentration of hydrogen peroxide, in the case of acoustic cavitation based processes, is significantly lower which limited the undesirable reactions of hydroxyl radicals with hydrogen peroxide molecules [27]. As a result, hydroxyl radicals react more effectively with the molecules of the organic pollutants present in the effluent.

Enhancement of acoustic cavitation by additional oxidation aims at the increase in number of hydroxyl radicals in solution. In this case, the main source of hydroxyl radicals in the aqueous medium being treated is decomposition of hydrogen peroxide. Most commonly, the amount of hydrogen peroxide added is selected by calculating the amount of oxidant in the form of HO• needed to lower COD of the effluent.

Addition of an insufficient amount of oxidant results in a substantial decrease in efficiency of oxidation of contaminants due to an insufficient number of hydroxyl radicals formed in decomposition of H_2O_2 participating in the oxidation process [28].

Accordingly, the effluent treatment carried out with an insufficient amount of oxidant ($r_{ox} = 0.9$ and 1.9) resulted in substantially lowered efficiency of COD removal than the treatment with excess oxidant (difference by about 30%). Treatment with an insufficient amount of oxidant lowered COD of the effluent by about 16%. A significant increase in the efficiency of COD removal was observed only after introducing a twofold excess of the oxidant with respect to COD ($r_{ox} = 4.0$) when the lowering of COD changed from 16% to 34%. On the other hand, the use of an excessive amount of oxidant often results in undesirable chemical reactions which deplete hydroxyl radicals, primarily responsible for oxidation of organic contaminants. This is mostly due to reactions of H_2O_2 with hydroxyl radicals present in solution and generation of radicals with a significantly lower oxidation potential than hydroxyl radicals, as well as reactions of the radicals with hydrogen peroxide molecules [29,30].

The most efficient lowering of COD of the effluent was observed at a flow rate of 3 ml min^{-1} ($r_{ox} = 5.9$), *i.e.,* at a more than threefold excess of the oxidant with respect to COD. However, the difference in the efficiency of degradation between twofold and threefold excess of $HO\cdot$ is only 5% whereas for the process with deficiency of the oxidant it is as much as 30%. This could possibly be attributed to partial depletion of hydroxyl radicals and formation of less reactive chemical species which cannot degrade persistent organic contaminants in the process with threefold excess of the oxidant. The actual or absolute degradation increases with oxidant concentration and reduction occurs due to greater interaction between pollutants molecules and oxidizing radicals. Acoustic cavitation combined with hydrogen peroxide allows a higher degree of oxidation of organic contaminants in the real effluent than acoustic cavitation alone: COD reduction 40% *vs.* 9.5%, respectively. Similar results of an increase in COD reduction of the effluent by adding an external oxidant were reported earlier [14–16]. However, it should be pointed out that there is a need to control the amount of the oxidant introduced to strike a balance between the cost of the process and its efficiency. No changes in pH of the effluent (pH = 10.5) during its treatment were observed. During the treatment aided by hydrogen peroxide the effluent first became cloudy (until 60 min), which could be attributed to the formation of new chemical structures by the compounds being oxidized, followed by gradual decolorization from light yellow color to completely clear solution.

3.3. Acoustic cavitation + O_3 and peroxone

One of the main factors affecting the effectiveness of ozone based processes is the ability to achieve a high dissolution rate of the gaseous oxidant in the bulk of the treated effluent. This is mainly due to overcoming the limited mass transfer between the gaseous phase and the effluent. Cavitating conditions allow intensification of the dissolution of ozone in the liquid by providing fluid mixing and maximization of the mass transfer area, intensifying the process of generation of hydroxyl radicals. Two basic mechanisms of oxidation of organic pollutants can be identified in the treated effluent: direct reactions of the pollutants with ozone and oxidation reactions with hydroxyl radicals produced from ozone [22].

Peroxone is an advanced oxidation process based on the use of ozone in conjunction with hydrogen peroxide [31]. According to the literature reports, the use of peroxone improves the efficiency of oxidation of organic contaminants by more efficient conversion of O_3 to $HO\cdot$ and by higher solubility of ozone in the treated aqueous phase [32,33]. The mechanism of action of peroxone involves decomposition of O_3 *via* electron transfer with hydrogen peroxide or activation of hydrogen peroxide in the presence of ozone. This results in formation of reactive radicals $HO\cdot$ and $HO_2\cdot$ responsible for oxidation of organic compounds. The mechanism of decomposition of peroxone leading to the formation of reactive chemical species is represented by reactions ([1)-(3]).

$$H_2O_2 + O_3 \xrightarrow{cavitation} HO\bullet + HO_2\bullet + O_2 \tag{1}$$

$$HO\bullet + O_3 \xrightarrow{CAVITATION} HO_2\bullet + O_2 \tag{2}$$

$$\mathrm{HO_2\bullet + O_3 \xrightarrow{cavitation} HO\bullet + 2O_2} \tag{3}$$

It should be noted that at a basic pH of the treated aqueous medium hydrogen peroxide is largely decomposed to the HO_2^{-}, which is more effective in conversion of O_3 to hydroxyl radicals ($HO\cdot$) [34]. Therefore, the use of peroxone to aid acoustic cavitation in oxidation of organic contaminants present in the effluent with a basic pH can bring tangible benefits.

The efficiency of COD reduction of the effluent by acoustic cavitation combined with ozonation and peroxone process (hydrogen peroxide + ozone) is depicted in Fig. 2.

Ozonation was carried out at a maximum rate reaching 12.32 g h^{-1}. Operating conditions used in the investigations are provided in Table 1.

The results of the investigations reveal that the highest efficiency of the effluent COD reduction for the acoustic cavitation processes in combination with AOPs was obtained for acoustic cavitation aided by peroxone process (51%). In the case of hydrodynamic cavitation combined with peroxone ($r_{ox} = 1.5$), under the same temperature and r_{ox} as for acoustic cavitation, it achieved a 59% reduction in COD (the actual delivered power: ultrasonic system 172.9 W/L; hydrodynamic system 220 W/L). These results of effectiveness can be considered as comparable. Probably a slightly higher effectiveness for hydrodynamic cavitation results is due to the fact that ozone was introduced into the overpressure zone, which increases its solubility in the treated liquid medium. The increased dose of "available" ozone for reaction with both hydrogen peroxide and its secondary products of decomposition at alkaline pH as well as direct reactions with organic pollutants results in a slightly higher decrease of COD. In both processes, an intensification of mass transfer took place, which makes AOPs based on cavitation superior to classical AOPs. As a result of dynamic flow of liquid through the throat, hydrodynamic cavitation, similarly to the acoustic wave energy in acoustic cavitation, results in the formation of so-called microcirculation zones and fluid turbulence zones. In the case of acoustic cavitation, these zones are so-called “acoustic streaming” [35]. Acoustic streaming enhance physicochemical processes taking place in solution, reducing mass transfer resistance, improving intensity of mixing and increasing the surface of mass transfer, which increases the effectiveness of dissolution of gases in the liquid. This, as well as overpressure in the zone of the Venturi tube [22] where the oxidant is injected, results in an increase in solubility of ozone in the bulk of effluent and, consequently, an increase in the concentration of hydroxyl radicals. This gives a nearly 8% more efficient treatment process for hydrodynamic cavitation compared to acoustic cavitation. Similarly, in the case of acoustic cavitation combined with ozonation process only, a 20% reduction of COD was achieved (hydrodynamic cavitation 27% [22]). In the case of combination of acoustic cavitation with ozonation and UV-C irradiation, an increase in process efficiency was approximately 7%.

3.4. Synergism of combined processes and energy efficiency evaluation

Synergism of combined processes was calculated on the basis of COD reduction effectiveness [mg L^{-1}] for 5 L of real effluent from the production of bitumens after 360 min of the treatment. In addition, for each of the processes, energy efficiency was calculated based on the consumption of 1 kJ of energy needed to reduce as much COD as possible (in mg) (Table 2). In order to compare energy efficiencies of the investigated processes in terms of reduction of COD of the effluent, the following average power consumption (in watts) of the devices was

Table 2
Synergetic effect of the combination of AOPs with acoustic cavitation.

Process								
	SONO-CAV	Hydro-CAV	UV-C	H_2O_2 (r_{OX} = 5.9)	O_3 (r_{OX} = 1.0)	SONO-CAV + H_2O_2 (r_{OX} = 5.9)	SONO-CAV + O_3 (r_{OX} = 1.0)	SONO-CAV + Peroxone + UV-C
COD reduction after 6 h [mg]	10445	12460	5015	15,100	10300	45730	19245	56050
$S_{coefficient}$	–	–	–	–	–	1.79	0.93	1.38
P elec. [W]	1000	1100	64	–	450	1000	1450	1514
P elec. for 6 h process [kJ]	21600	23760	1382	–	9720	21600	31320	32702
$E_{effectiv.}$ [mg COD/ kJ]	0.48	0.52	3.63	–	1.06	2.12	0.61	1.71

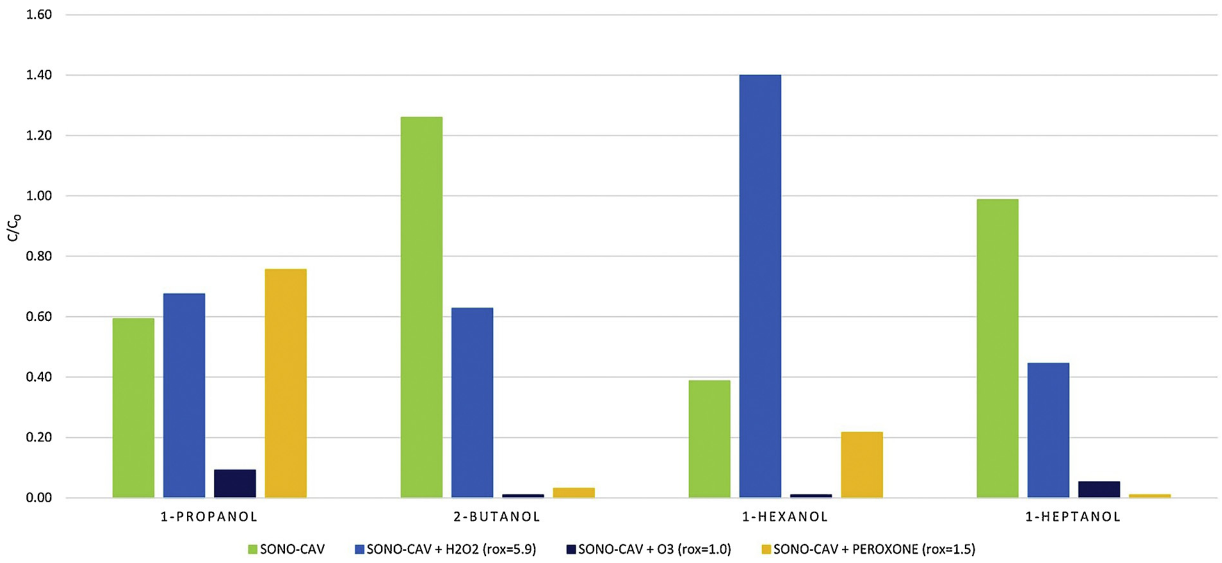


Fig. 3. Degradation of alcohols after 6 h process - acoustic cavitation + AOPs.

used: acoustic cavitation reactor with pump – 1000 W; ozone generator – 450 W; UV lamp – 64 W. In the case of hydrogen peroxide treatment, power consumption by small pumps used at low flow rates is negligible. The synergism of combined processes was calculated from Eq. (4) (using acoustic cavitation combined with H_2O_2 as an example).

$$S_{coefficient} = \frac{COD\ reduction\ (acoustic{-}cav + H_2O_2)}{COD\ reduction\ (acoustic{-}cav) + CODreduction\ (H_2O_2)} = \frac{45730}{10445 + 15100} = 1.79 \tag{4}$$

High synergism was observed in the case of acoustic cavitation combined with hydrogen peroxide (S = 1.79) and peroxone (S = 1.38). No synergism was reported for the acoustic cavitation process combined with ozonation. In the case of hydrodynamic cavitation combined with ozonation / H_2O_2 / peroxone (without UV lamp), the synergism of 1.20, 1.43 and 1.51 was noted (for the same process conditions as in the case of acoustic cavitation). A comparison of the results obtained by hydrodynamic cavitation and acoustic cavitation reveals that the greatest difference in synergism is with the ozonation process. As explained in Section 3.3, hydrodynamic cavitation conditions (overpressure at the site of ozone injection [22]) increase the solubility of ozone in the liquid effluent, which has a beneficial effect on the efficiency of oxidation of organic pollutants thereby increasing the synergism of the combined processes. As far as the energy efficiency is concerned, the most economical cavitation process is acoustic cavitation combined with hydrogen peroxide (2.11 mg COD / kJ – compared with hydrodynamic cavitation + H_2O_2 - 0.92 mg COD / kJ). This is mainly due to the efficient dissipation of hydrogen peroxide molecules by the energy of the ultrasound stream. In the case of hydrodynamic cavitation, the most energy efficient process was the one combined with peroxone (1.71 mg COD / kJ; acoustic cavitation + peroxone – 1.79 mg COD / kJ). On the laboratory scale, the use of acoustic cavitation as a method of pretreatment of effluent from the production of bitumens is a more economical approach [2,3,36]. On a semi-technical or technical scale, when large volumes of wastewater (> 50 L) are treated, the limiting factor of acoustic cavitation usage are the rising prices of reactor components (mainly transducers and their instrumentation) with increased processing capacity. In the case of hydrodynamic cavitation based on Venturi tube, investment costs are related mainly to purchase of high-pressure pumps [36].

The use of combined treatment aims primarily at the reduction of time required to achieve the desired extent of oxidation and cost of the treatment. The treatment time is often shortened by a factor of two but the total effect of lowering COD of the effluent remains at the same level (compared with summation of the effectiveness for the individual treatments). Therefore, the synergism values calculated for the majority of treatment processes are close to one or only slightly greater than one.

3.5. *Degradation of organic compounds by acoustic cavitation + AOPs*

3.5.1. *Acoustic cavitation*

The results of investigations on changes in content of volatile organic compounds in the effluent treated by acoustic cavitation are shown in Figs. 3–5. The results are presented in terms of the fraction of initial concentration present in the effluent after 30, 60, 180 and 360 min of the treatment. Operating conditions of the process are compiled in Table 1. A detailed description of the analytical procedure used was provided in previous papers [37,38]. Contaminants were divided into three groups: alcohols (1-propanol; 2-butanol; 1-hexanol; 1-heptanol), aromatic compounds (phenol; o-cresol; m-cresol; 2,6-

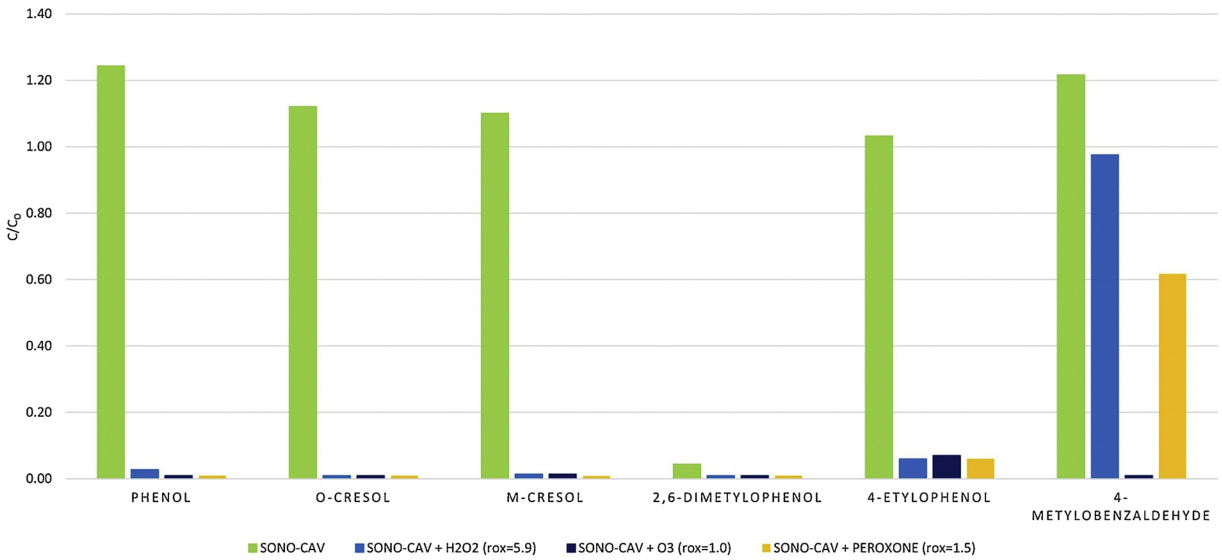


Fig. 4. Degradation of aromatic compounds after 6 h process - acoustic cavitation + AOPs.

dimethylphenol; 4-ethylphenol; 4-methylbenzaldehyde) and aldehydes and ketones (acetaldehyde; 2-pentanone; 2-hexanone; cyclopentanone; furfural; 3-heptanone; cyclohexanone; 2-methylcyclohexanone; 3-methylcyclohexanone; acetophenone).

Using acoustic cavitation alone resulted in oxidation of both 1-hexanol (60%) and 1-propanol (40%). It can be seen that 40% of 1-hexanol was oxidized after only 60 min of the treatment. In the case of hydrodynamic cavitation, 21% oxidation of 1-hexanol was observed [22]. In contrast, oxidation of 1-propanol by acoustic cavitation began only after 180 min of the treatment. The two compounds were present in untreated effluent at concentrations close to 10 ppm (a detailed comparison of concentrations of all the analytes is provided in Table S2). The investigations also revealed that the formation of secondary contaminants took place for some alcohols. The concentration of 2-butanol (initial concentration *ca.* 0.91 ppm) present in the untreated effluent increased during the first 180 min of the treatment. After this time, the formation of 2-butanol as a secondary contaminant increased and a decrease in its concentration was observed over the next 180 min. However, the negative effect is an increase in its concentration as a result of the treatment. Hydrodynamic cavitation also proved to be a better method for degradation of 1-heptanol. In the case of acoustic cavitation, the concentration of 1-heptanol (initially *ca.* 0.84 ppm) remained practically unchanged. Oxidation of this compound likely took place during the treatment, because such effects were observed for the other alcohols, but its secondary generation from other contaminants being oxidized resulted in a constant level of this analyte during 360 min of the treatment. For the hydrodynamic cavitation process, 17% of this compound was oxidized in 360 min.

Alcohols are an effective scavengers of hydroxyl radicals [39]. Thus, in the case of sole use of cavitation phenomena (acoustic- or hydrodynamic cavitation) for oxidation of compounds from this group, the main mechanism of its degradation will be not radical-based (as commonly it is for other groups of compounds) but thermal decomposition will be a dominant. A thermolysis/ thermal decomposition of pollutants in cavitation conditions results from high temperature induced by implosion of cavitation bubbles. During the implosion, the temperature exceeds 4700 °C [1]. Gaseous pollutants due to their different vapor pressure will be degraded inside the cavitation bubbles as well as on the gas-liquid boundary. Studied alcohols have different vapor pressure. The main place and mechanism of degradation of less volatile alcohols (*i.e.* 1-hexanol and 1-heptanol), having vapor pressure lower than 1 kPa, will be the bubble-liquid boundary where thermal degradation

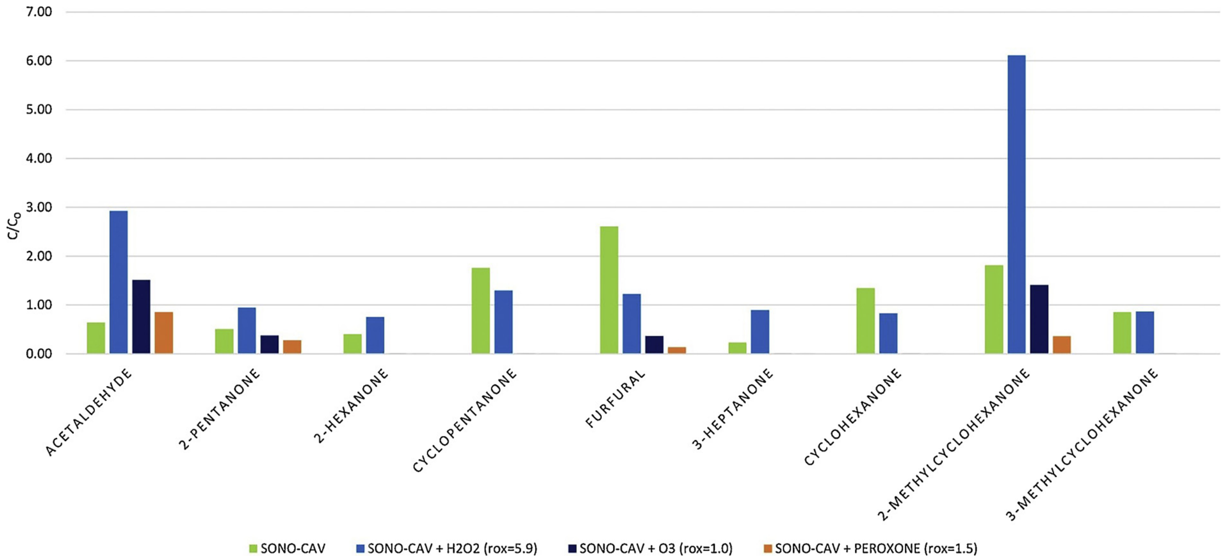


Fig. 5. Degradation of aldehydes and ketones after 6 h process - acoustic cavitation + AOPs.

will take place. Consequently, more volatile alcohols (1-propanol and 2-butanol), having vapor pressure higher than 1 kPa will be thermally degraded inside the bubble.

Among the investigated aromatic compounds, acoustic cavitation allows oxidation of 2,6-dimethylphenol alone (initial concentration below 0.35 ppm). This is the only phenolic compound that was degraded which can be attributed to the presence of methyl groups susceptible to oxidation. Almost 100% of this contaminant was oxidized during 360 min of the treatment. The remaining aromatic compounds had concentrations either unchanged (0.4–15 ppm) or increased by several to several tens of percent due to numerous radical reactions generating secondary contaminants from this group. In the case of aromatic compounds oxidized in the hydrodynamic cavitation process, both phenol (13%) and m-cresol (31%) were partially oxidized. Based on the results obtained, it can be concluded that hydrodynamic cavitation is a more efficient oxidation process for compounds containing the aromatic ring in the structure.

Acoustic cavitation is effective in treatment of other groups of oxygenated organic compounds, *i.e.,* aldehydes and ketones. Five out of the ten identified carbonyl compounds with concentrations ranging from 0.1 to 22 ppm were oxidized. The most effective oxidation was observed for 3-heptanone (78%), 2-hexanone (60%), 2-pentanone (49%), acetaldehyde (36%) and 3-methylcyclohexanone (15%). For the hydrodynamic cavitation process, the degradation efficiency of 2-pentanone was 76%. This part of studies revealed that cavitation is not effective for all pollutants from aldehydes and ketones group. For the remaining compounds there was an increase in the initial concentration after 6 h of the acoustic cavitation process. In addition, both acoustic cavitation and hydrodynamic cavitation processes increased furfural concentration by 260 and 20%, respectively. Furfural is a by-product formed in a number of radical reactions [22].

3.5.2. Acoustic cavitation + H_2O_2 (r_{ox} = 3.17)

The use of hydrogen peroxide to aid acoustic cavitation aims at increasing the number of hydroxyl radicals in the effluent which entails a greater extent of oxidation of organic contaminants. This part of the studies revealed that acoustic cavitation is more effective than hydrodynamic cavitation in combined processes with hydrogen peroxide as an external oxidant. In this case, the direct impact of the ultrasounds on H_2O_2 molecules allows to obtain a more effective conversion of hydrogen peroxide to the radicals responsible for the oxidation reactions with the pollutants present in the effluent. Degradation of selected groups of organic compounds by acoustic cavitation combined with addition of hydrogen peroxide is depicted in Figs. 3–5. In comparison with acoustic cavitation alone, this combined treatment improved the efficiency of oxidation of individual alcohols (Fig. 3). The largest difference in the extent of oxidation can be observed for 1-heptanol. Supplementing hydroxyl radicals by the addition of hydrogen peroxide lowered the concentration of this compound by 56%. Likewise, 2-butanol whose content was increased by 30% when using acoustic cavitation alone, had the concentration lowered by 38% of the initial value by combined acoustic cavitation and hydrogen peroxide. Oxidation of 1-propanol remained at the same level (30–40%). Addition of hydrogen peroxide makes the amount of oxidant available sufficient for degradation of alcohols originally present in effluents as well as those formed as the products of side reactions. On the other hand, the content of 1-hexanol increased by 40% which can be attributed to enhanced degradation of 1-heptanol resulting in formation of an alcohol shorter by one carbon atom. Comparison of the effectiveness of the two cavitation processes combined with hydrogen peroxide for degradation of 1-heptanol and 1-hexanol reveals that acoustic cavitation combined with H_2O_2 generates more secondary oxidation products in the form of alcohols, which increases the concentration of pollutants in the effluent after the treatment process. The positive influence of ultrasounds on the efficiency of conversion of hydrogen peroxide to hydroxyl radicals in the acoustic cavitation process results in an increase in their concentration in the bulk of effluent, which leads to an increase in the number of oxidation reactions leading to the formation of alcohols, mostly 1-hexanol.

Acoustic cavitation aided by hydrogen peroxide enables oxidation of the majority of identified volatile oxygenated compounds containing an aromatic ring (Fig. 4). Six out of seven compounds were oxidized. Similarly to the case of acoustic cavitation alone, 4-methylbenzaldehyde was not oxidized. This compound belongs to the group of compounds that are difficult to oxidize. However, the efficiency of oxidation of the remaining aromatic compounds was increased. Oxidation yield close to 100% was obtained for phenol and its derivatives: 2,6-dimethylphenol, *m*-cresol, *o*-cresol, and 4-ethylphenol. In case of acetophenone, about 33% oxidation yield was obtained after 6-hour treatment. As was the case with acoustic cavitation alone, almost 100% of 2,6-dimethylphenol was oxidized after just 60 min of the treatment. Increasing the number of hydroxyl radicals in the effluent enabled more efficient oxidation of aromatic compounds. Degradation of these compounds is important due to their toxicity toward activated sludge of the refinery WWTP. The oxidation effectiveness of aromatics compounds by acoustic cavitation is comparable to hydrodynamic cavitation. However, in the acoustic cavitation process, the rate of degradation is higher. For the hydrodynamic cavitation process, nearly 70% oxidation of phenol and m-cresol was achieved in 180 min. For acoustic cavitation, the oxidation effectiveness of these compounds for a similar treatment time is almost 78%. Thus, the effective conversion of the oxidant molecules results in the formation of a larger amount of hydroxyl radicals in the acoustic cavitation + H_2O_2 process. This leads to faster oxidation of aromatic pollutants present in the effluent.

Acoustic cavitation combined with hydrogen peroxide is not an effective method of degradation of aldehydes and ketones. The results of oxidation of these organic compounds are shown in Fig. 5. Increasing the concentration of hydroxyl radicals results in efficient oxidation of other organic compounds, such as alcohols, which yields secondary contaminants including aldehydes and ketones. Consequently, in order to remove this group of compounds from the effluent, acoustic cavitation alone is a better choice of the method of treatment. In case of hydrodynamic cavitation, more than 90% oxidation of 1-propanal and 2-pentanone has been reported. Hydrodynamic cavitation combined with hydrogen peroxide is therefore a more effective method of oxidation of aldehydes and ketones.

3.5.3. Acoustic cavitation + O_3

Acoustic cavitation aided by ozonation is also an efficient method of oxidation of organic contaminants occurring in the aqueous phase. The only problem involves appropriate dispersion of gaseous ozone in the liquid. Acoustic cavitation eliminates this problem through the generation of the acoustic wave. Microcirculations generated in the bulk liquid provide effective dispersion of ozone while at the same time they limit mass transfer resistance. The occurrence of micro-circulation and turbulence of liquid in the treated effluent is more effective in hydrodynamic cavitation. In addition, overpressure in the ozone introduction zone under hydrodynamic cavitation increases the solubility of ozone and oxygen in the treated effluent. Therefore, the oxidation effectiveness of individual compounds for acoustic cavitation combined with ozonation is expected to be lower. The efficiency of oxidation of alcohols by acoustic cavitation combined with ozonation is depicted in Fig. 3. Similarly to the treatments discussed above, also in this case oxidation of alcohols was found to be highly efficient. All the investigated alcohols were completely oxidized; however, in contrast with the previous treatments acoustic cavitation aided by ozonation enabled oxidation of 1-propanol, 2-butanol and 1-heptanol in a much shorter time. Over 50% of these contaminants were oxidized after just 60 min. On the other hand, the content of 1-hexanol increased for the first 180 min followed by degradation after that. This can be attributed to depletion of chemical compounds which were converted to 1-hexanol upon oxidation and subsequent degradation of 1-hexanol through oxidation. The degree of degradation obtained with hydrodynamic cavitation + O_3 confirms its higher effectiveness compared with acoustic cavitation + O_3. In the case of hydrodynamic cavitation + O_3, over 95% of the oxidation efficiency was obtained for all alcohols.

Acoustic cavitation and hydrodynamic cavitation aided by ozonation are also very efficient methods of oxidation of aromatic compounds (Fig. 4). In contrast with acoustic cavitation combined with hydrogen peroxide all aromatic compounds, including 4-methylbenzaldehyde, were oxidized. The majority of aromatic compounds were oxidized with the efficiency better than 50% after just 60 min of the treatment. 4-Methylbenzaldehyde, which was not oxidized after 180 min of the previous treatments, was now oxidized in 20%. After the next 3 h its content dropped from 80% to 0%. In case of hydrodynamic cavitation + O_3 process, 40% oxidation of 4-methylbenzaldehyde and 100% oxidation of phenol and m-cresol was obtained during the first 180 min of the treatment. Acoustic cavitation aided by ozonation was also found to be highly effective in oxidation of aldehydes and ketones (Fig. 5). Acetophenone, cyclohexanone, 3-methylcyclohexanone, cyclopentanone and 3-heptanone were completely oxidized. The content of furfural and 2-pentanone was lowered by more than 50%. In this case, the byproducts of oxidation are acetaldehyde and 2-methylcyclohexanone. Hydrodynamic cavitation + O_3 treatment process allowed obtaining over 90% oxidation of furfural and other aldehyde and ketone pollutants in less than 180 min.

3.5.4. Acoustic cavitation + Peroxone

Peroxone, which is a mixture of two oxidants: hydrogen peroxide and ozone, combined with acoustic cavitation was found to lower COD of the effluent by over 50% (hydrodynamic cavitation 59%). Chromatographic analysis also confirmed its high efficiency of this treatment. Only in the case of oxidation of alcohols (Fig. 3) the treatment was less efficient than acoustic cavitation combined with ozonation. The oxidation yields for 1-propanol, 1-hexanol, 2-butanol and 1-heptanol were 25%, 80%, 100% and 100%, respectively. Hydrodynamic cavitation combined with peroxone resulted in over 85% oxidation effectiveness of alcohols. Acoustic cavitation combined with the Peroxone process effectively degraded all the tested aromatic compounds (Fig. 4). Their content decreased by 50% or more in just 60 min of the treatment with the exception of 4-methylbenzaldehyde. It takes about 180 min of the treatment to completely oxidize the majority of them. In the case of 4-methylbenzaldehyde, a compound resistant to oxidation, the efficiency of degradation was *ca.* 40%. Similarly to acoustic cavitation, also hydrodynamic cavitation combined with peroxone is an effective method of oxidation of aromatic compounds. Over 70% oxidation of pollutants belonging to this group of organic pollutants was achieved. Acoustic cavitation combined with Peroxone is the best method of oxidation of aldehydes and ketones (Fig. 5). Complete degradation of these compounds was achieved in the majority of cases. Only for two compounds – furfural and 2-methylcyclohexanone, the final reduction of concentration was below 40%. The concentrations of these two compounds increased at first during the treatment due to their formation as secondary contaminants followed by gradual oxidation during the treatment. Similar results were obtained for hydrodynamic cavitation + peroxone process (over 87% oxidation of aldehydes and ketones).

4. Biodegradability of wastewater

The efficiency of the investigated methods of preliminary treatment of effluents from the production of bitumens by acoustic cavitation combined with additional oxidants was also studied by examining changes in BOD_5. Knowledge of COD and BOD_5 of an effluent allows calculation of so-called biodegradability index. The biodegradability index of the effluent from the production of bitumens treated by acoustic cavitation aided by additional oxidation processes (O_3 / H_2O_2 / Peroxone) is listed in Table S1. The biodegradability index (BI) of an effluent provides information on susceptibility of contaminants present in the effluent to degradation effected by microorganisms and bacteria. Most often, the index is expressed as the ratio of BOD_5 to COD and it should be as large as possible. According to the literature data, an effluent with a BOD_5/COD value between 0.3 and 0.4 is susceptible to biodegradation under aerobic conditions, *i.e.* the conditions under which activated sludge operates [40]. The minimum BI value of an effluent which undergoes biodegradation is equal to 0.14. The results of present investigations reveal that none of the treatments used has a significant effect on the BI value of the effluent which is kept in all the investigated cases at a value greater than 0.14. The same situation was observed for hydrodynamic cavitation-based AOPs. The advantage of acoustic cavitation and hydrodynamic cavitation combined with additional oxidants is mostly lowering the total pollutant load and oxidation of toxic organic compounds which facilitates degradation of the remaining organic compounds by the activated sludge.

5. Degradation of volatile organosulfur compounds (VSCs)

In the case of acoustic cavitation, additional studies were carried out which demonstrated a high oxidation efficiency for degradation of sulfur compounds during the treatment processes described in this paper. Eight chemical compounds (ethanethiol; dimethyl sulfide; carbon disulfide; 3-methyl-1-butanethiol; 1,2-ethanedithiol; thiophenol; thioanisole; benzylthiol) out of 38 available in the database of the procedure used were identified. Changes in concentration of the identified contaminants were determined over the 6-h oxidation for each of the investigated treatment processes. Characteristics of response of the flame photometric detector to volatile organosulfur compounds allow the use of universal calibration for unidentified species. Therefore, to obtain additional information on the investigated processes, changes in concentration of the five unidentified VSCs (X1-X5) during the treatment were determined along with summation of peak areas of the remaining unidentified compounds with conversion of their total peak area to concentration of one of the standards – thiophene. Details are provided in Table S3.

The data compiled in Table S3 reveal that volatile organosulfur compounds are very quickly oxidized by acoustic cavitation and by acoustic cavitation aided by additional oxidants. In the majority of cases concentrations of the investigated compounds decrease by 60–100% after just 30 min of the treatment. After the next 30 min the majority of compounds is completely oxidized. Such a high efficiency of oxidation was also found for the unidentified sulfur compounds. The highest oxidation efficiency for organosulfur compounds was observed for acoustic cavitation combined with hydrogen peroxide. All organosulfur compounds were completely oxidized after 30 min of this treatment. For the remaining treatment methods the sum of all peak areas of organosulfur compounds indicates the continuing presence of this kind of contaminants even after completion of the treatment. This can be attributed to the conversion paths of VSCs which depending on the initial form leads to formation of sulfonic acids (in case of oxidation of thiols and disulfides) or sulfoxides and sulfones (in case of oxidation of sulfides) [17]. In the course of oxidation some intermediate species are formed, such as disulfides from oxidation of thiols, which results in a temporary increase in content of some VSCs during the treatment. Furthermore, interactions with hydroxyl radicals as well as direct reactions with ozone cause conversion of high-molecular-weight organosulfur compounds, undetected by GC-FPD, to lighter compounds which results in the formation of many new VSCs and a temporary increase in their content (thiophenol and X1). Complete degradation of the reactants which formed byproducts is the moment when the trend is reversed and the byproducts undergo further reactions which eventually leads to almost complete removal of VSCs.

6. Conclusions

Acoustic cavitation used as a separate process of pretreatment of effluents from the production of bitumens or combined with additional oxidation processes, constitutes a good method of lowering pollutant load. The results of investigations presented in this paper revealed that the most efficient process for pretreatment of effluents from the production of bitumens involves acoustic cavitation aided by the peroxone and UV-C irradiation, which reduces COD and BOD values by 51% and 60%, respectively. This is a very effective treatment compared with those described in the literature for treatment of industrial effluents at a basic pH [25], especially considering the fact that the effluents investigated in this paper are real industrial effluents having a very complex composition. The remaining treatment methods (acoustic cavitation + H_2O_2 / acoustic cavitation alone/ acoustic cavitation + O_3) reduce COD by 40, 10 and 19.5%, respectively, and BOD by 40, 11 and 19.6%, respectively. It should be noted that the high synergism was observed for acoustic cavitation combined with hydrogen peroxide ($S_{coefficient} = 1.79$). A slightly higher effectiveness of COD and BOD_5 reduction was obtained for hydrodynamic cavitation-based processes (HC: 13%, 15% for COD and BOD_5 reduction; HC + H_2O_2: 20%, 49% for COD and BOD_5 reduction; HC + O_3: 27.4%, 30.1% for COD and BOD_5 reduction respectively). In the case of the investigated treatment processes, the biggest difference was observed for the processes associated with ozonation (reduction of COD and BOD_5 by acoustic cavitation 19.5% and 19.6% and hydrodynamic cavitation 27.4% and 30.1%, respectively). It results mostly from the overpressure in the oxidant introduction zone, which increases the ozone solubility in the liquid phase. This would also be feasible in the case of acoustic cavitation process if a high-pressure pump would be used for the circulation of effluent, and if a restriction that allows obtaining the overpressure in the reactor would be used at the outlet of the acoustic reactor. This would, however, require a specially designed reactor allowing the use of overpressure conditions. On the other hand, acoustic cavitation provides a greater oxidation efficiency compared to hydrodynamic cavitation, when hydrogen peroxide is used as an oxidation reagent. The effect of ultrasound on H_2O_2 molecules allows increasing the efficiency of hydroxyl radicals generation under alkaline conditions, where most of the peroxide would decompose to less active species. In addition, acoustic cavitation and hydrodynamic cavitation combined with the peroxone process resulted in complete removal of all investigated oxygenated organic contaminants with the simultaneous decolorization of the effluent and reduction in its malodorousness. An especially important conclusion from this part of the work is a very effective degradation of phenol and its derivatives. Degradation of organic pollutants during pretreatment can protect activated sludge from toxic organic compounds and enable effective biodegradation. In the case of the investigated effluents, degradation of oxygenated organic compounds observed in this work prior to biological treatment ensures optimal activity of the activated sludge which in refinery WWTP plants is especially effective toward hydrocarbon contaminants. The study also revealed formation of a number of secondary contaminants belonging to O-VOCs. The most important secondary contaminants include furfural (hydrodynamic cavitation and acoustic cavitation) and 2-methylcyclohexanone (acoustic cavitation). Their concentration during AOP treatment should be especially controlled due to their high toxicity toward the activated sludge from a WWTP. It has also been shown that the cavitation phenomenon in combination with AOPs is an effective method of oxidation of organic sulfur compounds. Almost 100% of organosulfur compounds were oxidized after less than 30 min of the treatment.

Acknowledgments

The authors gratefully acknowledge financial support from the Ministry of Science and Higher Education in Poland for project 0040/IP2/2015/73 in the program “Iuventus Plus” in 2015–2017 and National Science Center, Warsaw, Poland – decision no. UMO-2017/25/B/ST8/01364.

The authors would like to thank also the Lotos Asfalt, Ltd. (Grupa Lotos) for their cooperation on this project.

The authors would like to thank Bandelin electronic GmbH & Co. KG and Ingenieurbüro Peter Wagner for lending the acoustic-cavitational reactor SONOREX Technik AQ 5-1002.5 for this study.

The authors have declared no conflict of interest.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.cep.2018.04.010.

References

[1] M. Gągol, G. Boczkaj, Przegląd metod wytwarzania kawitacji do degradacji zanieczyszczeń organicznych w środowisku wodnym, Aparatura Badawcza i Dydaktyczna 22 (2017) 62–71.

[2] S. Asgharzadehahmadi, A.A.A. Raman, R. Parthasarathy, B. Sajjadi, Sonochemical reactors: review on features, advantages and limitations, Renew. Sustain. Energy. Rev. 63 (2016) 302–314.

[3] N.N. Mahamuni, G.A. Yusuf, Advanced oxidation processes (AOPs) involving ultrasound for waste water treatment: a review with emphasis on cost estimation, Ultrason. Sonochem. 17 (2010) 990–1003.

[4] A.K. Shriwas, P.R. Gogate, Ultrasonic degradation of methyl Parathion in aqueous solutions: intensification using additives and scale up aspects, Sep. Purif. Technol. 79 (2011) 1–7.

[5] B. Neppoliana, H. Junga, H. Choi, J.H. Leea, J.W. Kang, Sonolytic degradation of methyl tert-butyl ether: the role of coupled Fenton process and persulphate ion, Water Res. 36 (2002) 4699–4708.

[6] Y.L. Song, J.T. Li, Degradation of CI Direct Black 168 from aqueous solution by fly ash/H_2O_2 combining ultrasound, Ultrason. Sonochem. 16 (2009) 440–444.

[7] K.K. Jyoti, A.B. Pandit, Water disinfection by acoustic and hydrodynamic cavitation, Biochem. Eng. J. 7 (2001) 201–212.

[8] A.G. Chakinala, D.H. Bremner, P.R. Gogate, K.C. Namkung, A.E. Burgess, Multivariate analysis of phenol mineralisation by combined hydrodynamic cavitation and heterogeneous advanced Fenton processing, Appl. Catal. B: Environ. 78 (2008) 11–18.

[9] D. Liu, E. Vorobiev, R. Savoire, J.L. Lanoisellé, Comparative study of ultrasound-assisted and conventional stirred dead-end microfiltration of grape pomace extracts, Ultrason. Sonochem. 20 (2013) 708–714.

[10] I. Worapun, K. Pianthong, P. Thaiyasuit, Optimization of biodiesel production from crude palm oil using ultrasonic irradiation assistance and response surface methodology, J. Chem. Technol. Biotechnol. 87 (2012) 189–197.

[11] A.S. Badday, A.Z. Abdullah, K.T. Lee, M.S. Khayoon, Intensification of biodiesel production via ultrasonic-assisted process: a critical review on fundamentals and recent development, Renew. Sustain. Energy. Rev. 16 (2012) 4574–4587.

[12] I. Lee, J. Han, The effects of waste-activated sludge pretreatment using hydrodynamic cavitation for methane production, Ultrason. Sonochem. 20 (2013) 1450–1455.

[13] L. Csoka, S.N. Katekhaye, P.R. Gogate, Comparison of cavitational activity in different configurations of sonochemical reactors using model reaction supported with theoretical simulations, Chem. Eng. J. 178 (2011) 384–390.

[14] V.S. Moholkar, P. Senthilkumar, A.B. Pandit, Hydrodynamic cavitation for sonochemical effects, Ultrason. Sonochem. 6 (1999) 53–65.

[15] F. Parvizian, M. Rahimi, M. Faryadi, Macro- and micromixing in a novel sonochemical reactor using high frequency ultrasound, Chem. Eng. Processing: Process Intensif. 5 (2011) 732–740.

[16] P.R. Gogate, S. Mujumdar, A.B. Pandit, Sonochemical reactors for waste water treatment: comparison using formic acid degradation as a model reaction, Adv. Environ. Res. 7 (2003) 283–299.

[17] G. Boczkaj, M. Kamiński, A. Przyjazny, Process control and investigation of oxidation kinetics of postoxidative effluents using gas chromatography with pulsed flame photometric detection (GC-PFPD), Ind. Eng. Chem. Res. 49 (2010) 12654–12662.

[18] G. Boczkaj, A. Przyjazny, M. Kamiński, New procedures for control of industrial effluents treatment processes, Ind. Eng. Chem. Res. 53 (2014) 1503–1514.

[19] G. Boczkaj, P. Makoś, A. Przyjazny, Application of dynamic headspace and gas chromatography coupled to mass spectrometry (DHS-GC-MS) for the determination of oxygenated volatile organic compounds in refinery effluents, Anal. Methods 8 (2016) 3570–3577.

[20] G. Boczkaj, P. Makoś, A. Przyjazny, Application of dispersive liquid–liquid microextraction and gas chromatography with mass spectrometry for the determination of oxygenated volatile organic compounds in effluents from the production of petroleum bitumen, J. Sep. Sci. 39 (2016) 2604–2615.

[21] G. Boczkaj, P. Makoś, A. Fernandes, A. Przyjazny, New procedure for the control of the treatment of industrial effluents to remove volatile organosulfur compounds, J. Sep. Sci. 39 (2016) 3946–3956.

[22] G. Boczkaj, M. Gągol, M. Klein, A. Przyjazny, Effective method of treatment of effluents from production of bitumens under basic pH conditions using hydrodynamic cavitation aided by external oxidants, Ultrason. Sonochem. 40 (2018) 969–979, http://dx.doi.org/10.1016/j.ultsonch.2017.08.032.

[23] D.R. Reddy, G.K. Dinesh, S. Anandan, T. Sivasankar, Sonophotocatalytic treatment of Naphthol Blue Black dye and real textile wastewater using synthesized Fe doped TiO_2, Chem. Eng. Process. 99 (2016) 10–18.

[24] R. Kidak, N.H. Ince, Catalysis of advanced oxidation reactions by ultrasound: a case study with phenol, J. Hazard. Mater. 146 (2007) 630–635.

[25] L.P. Ramteke, P.R. Gogate, Treatment of toluene, benzene, naphthalene and xylene (BTNXs) containing wastewater using improved biological oxidation with pretreatment using Fenton/ultrasound based processes, J. Ind. Eng. Chem. 28 (2015) 247–260.

[26] A. Hirvonen, T. Tuhkanen, P. Kalliokoski, Formation of chlorinated acetic acids during UV/H2O-oxidation of ground water contaminated with chlorinated ethylenes, Chemosphere 32 (1996) 1091–1102.

[27] M. Gągol, A. Przyjazny, G. Boczkaj, Highly effective degradation of selected groups of organic compounds by cavitation based AOPs under basic pH conditions, Ultrason. Sonochem. 45 (2018) 257–266.

[28] A.A. Pradhan, P.R. Gogate, Removal of p-nitrophenol using hydrodynamic cavitation and Fenton chemistry at pilot scale operation, Chem. Eng. J. 156 (2010) 77–82.

[29] M.V. Bagal, P.R. Gogate, Degradation of 2, 4-dinitrophenol using a combination of hydrodynamic cavitation, chemical and advanced oxidation processes, Ultrason. Sonochem. 20 (2013) 1226–1235.

[30] P.N. Patil, S.D. Bote, P.R. Gogate, Degradation of imidacloprid using combined advanced oxidation processes based on hydrodynamic cavitation, Ultrason. Sonochem. 21 (2014) 1770–1777.

[31] G. Boczkaj, A. Fernandes, Wastewater treatment by means of advanced oxidation processes at basic pH conditions: a review, Chem. Eng. J. 320 (2017) 608–633.

[32] J.J. Wu, M. Muruganandham, S.H. Chen, Degradation of DMSO by ozone-based advanced oxidation processes, J. Hazard. Mater. 149 (2007) 218–225.

[33] M.A. Alsheyab, A.H. Munoz, Reducing the formation of trihalomethanes (THMs) by ozone combined with hydrogen peroxide (H_2O_2/O_3), Desalination 194 (2006) 121–126.

[34] J. Staehelin, H. Jurg, Decomposition of ozone in water: rate of initiation by hydroxide ions and hydrogen peroxide, Environ. Sci. Technol. 16 (1982) 676–681.

[35] J.G.D. Filho, M.P. Assis, A.I.B. Genovez, Bacterial inactivation in artificially and naturally contaminated water using a cavitating jet apparatus, J. Hydraul. Res. 9 (2015) 259–267.

[36] M. Gągol, A. Przyjazny, G. Boczkaj, Wastewater treatment by means of advanced oxidation processes based on cavitation – a review, Chem. Eng. J. 338 (2018) 599–627.

[37] G. Boczkaj, P. Makoś, A. Przyjazny, Application of dispersive liquid–liquid microextraction and gas chromatography with mass spectrometry for the determination of oxygenated volatile organic compounds in effluents from the production of petroleum bitumen, J. Sep. Sci. 39 (2016) 2604–2615.

[38] G. Boczkaj, P. Makoś, A. Fernandes, A. Przyjazny, New procedure for the control of the treatment of industrial effluents to remove volatile organosulfur compounds, J. Sep. Sci. 39 (2016) 3946–3956.

[39] L.J. Xu, W. Chu, N. Graham, Sonophotolytic degradation of phthalate acid esters in water and wastewater: influence of compound properties and degradation mechanisms, J. Hazard. Mater. 288 (2015) 43–50.

[40] K.V. Padoley, S.N. Virendra Kumar Saharan, R.A. Mudliar, Aniruddha B. Pandey, Pandit, Cavitationally induced biodegradability enhancement of a distillery wastewater, J. Hazard. Mater. 219 (2012) 69–74.

SUPPORTING INFORMATION FOR MANUSCRIPT

Effective method of treatment of industrial effluents under basic pH conditions using acoustic cavitation – a comprehensive comparison with hydrodynamic cavitation processes

Michał Gągol[1], Andrzej Przyjazny[2], Grzegorz Boczkaj[1*]

[1]Gdańsk University of Technology, Faculty of Chemistry, Department of Chemical and Process Engineering,

[2]Kettering University, 1700 University Avenue, Department of Chemistry & Biochemistry, Flint, MI 48504, USA.

** Dr Grzegorz Boczkaj, PhD. DSc. Eng., Assoc. Prof., Gdansk University of Technology, Faculty of Chemistry, Department of Chemical and Process Engineering, 80 – 233 Gdansk, G. Narutowicza St. 11/12, Poland. Fax: (+48 58) 347-26-94; Tel: (+48) 697970303; E-mail: grzegorz.boczkaj@gmail.com or grzegorz.boczkaj@pg.edu.pl*

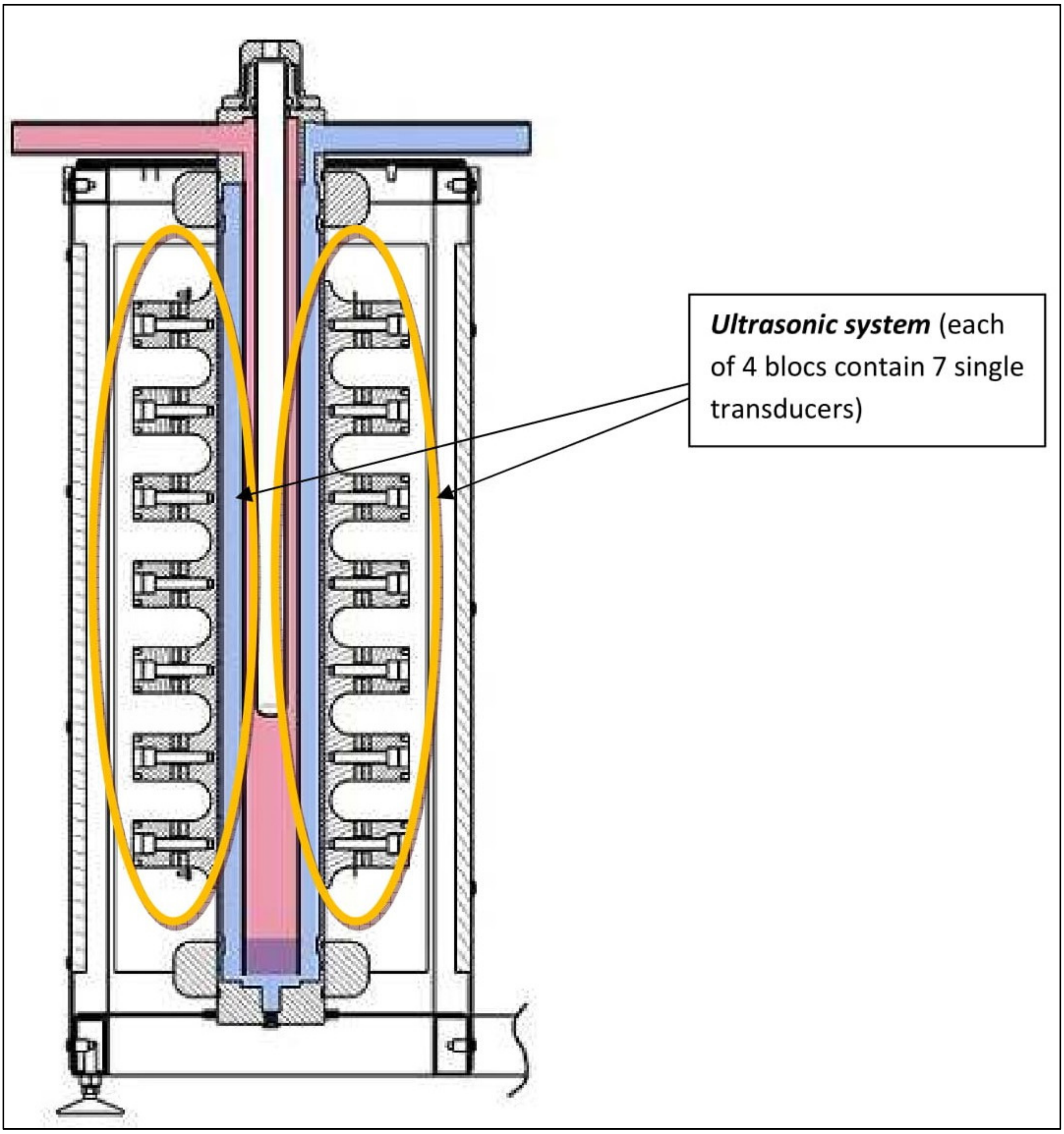


Figure S1. A detailed scheme of ultrasonic system.

Table S1. Effect of acoustic cavitation pretreatment on biodegradability index of wastewater

Reaction condition	**Time (min)**	**COD (mgL^{-1})**	**BOD$_5$ (mgL^{-1})**	**COD reduction [%]**	**BOD$_5$ reduction [%]**	**BOD$_5$/COD**
SONO-CAV	0	21981	4076	*0*	*0*	0.19
	15	21981	-	*0*	-	-
	30	21695	-	*1.3*	-	-
	45	21431	-	*2.5*	-	-
	60	21102	-	*4.0*	-	-
	120	20728	-	*5.7*	-	-
	180	20442	3847	*7.0*	*5.6*	0.19
	240	20201	-	*8.1*	-	-
	300	20069	-	*8.7*	-	-
	360	19892	3619	*9.5*	*11.2*	0.18
SONO-CAV + UV-C	0	21126	3390	*0*	*0*	0.16
	15	21126	-	*0*	-	-
	30	20746	-	*1.8*	-	-
	45	20513	-	*2.9*	-	-
	60	20365	-	*3.6*	-	-
	120	19964	-	*5.5*	-	-
	180	19583	3115	*7.3*	*8.1*	0.16
	240	18823	-	*10.9*	-	-
	300	18443	-	*12.7*	-	-
	360	18063	2795	*14.5*	*17.5*	0.15
SONO-CAV + H_2O_2 (r_{ox}=5.9)	0	22865	4259	*0*	*0*	0.19
	15	20990	-	*8.2*	-	-
	30	18132	-	*20.7*	-	-
	45	17858	-	*21.9*	-	-
	60	17789	-	*22.2*	-	-
	120	17103	-	*25.2*	-	-
	180	15777	3070	*31.0*	*27.9*	0.19
	240	15502	-	*32.2*	-	-
	300	14908	-	*34.8*	-	-
	360	13719	2567	*40.0*	*39.7*	0.19

Reaction condition	**Time (min)**	**COD (mgL^{-1})**	**BOD$_5$ (mgL^{-1})**	**COD reduction [%]**	**BOD$_5$ reduction [%]**	**BOD$_5$/COD**
SONO-CAV + H_2O_2 (r_{ox}=5.9) + UV-C	0	21686	4670	*0*	*0*	0.22
	15	19908	-	*8.2*	-	-
	30	16958	-	*21.8*	-	-
	45	16481	-	*24.0*	-	-
	60	16243	-	*25.1*	-	-
	120	15484	-	*28.6*	-	-
	180	14313	2978	*34.0*	*36.2*	0.21
	240	13727	-	*36.7*	-	-
	300	12838	-	*40.8*	-	-
	360	12252	2704	*43.5*	*42.1*	0.22
SONO-CAV + O_3	0	19622	4213	*0*	*0*	0.21
	15	18700	-	*4.7*	-	-
	30	18170	-	*7.4*	-	-
	45	17307	-	*11.8*	-	-
	60	17130	-	*12.7*	-	-
	120	16620	-	*15.3*	-	-
	180	16384	3756	*16.5*	*10.9*	0.23
	240	16129	-	*17.8*	-	-
	300	16012	-	*18.4*	-	-
	360	15773	3390	*19.6*	*19.5*	0.21
SONO-CAV + O_3 + UV-C	0	21096	4899	*0*	*0*	0.23
	15	20083	-	*4.8*		
	30	19577	-	*7.2*	-	-
	45	18649	-	*11.6*	-	-
	60	18480	-	*12.4*	-	-
	120	17889	-	*15.2*	-	-
	180	17573	4122	*16.7*	*15.9*	0.23
	240	16370	-	*22.4*	-	-
	300	16075	-	*23.8*	-	-
	360	15484	3436	*26.6*	*29.9*	0.22

Reaction condition	**Time (min)**	**COD (mgL^{-1})**	**BOD_5 (mgL^{-1})**	**COD reduction [%]**	**BOD_5 reduction [%]**	**BOD_5/COD**
SONO-CAV + Peroxone + UV	0	21981	3481	*0*	*0*	0.16
	15	21036	-	*4.3*	-	-
	30	18728	-	*14.8*	-	-
	45	17343	-	*21.1*	-	-
	60	15497	-	*29.5*	-	-
	120	14024	-	*36.2*	-	-
	180	13716	1698	*37.6*	*51.2*	0.12
	240	13145	-	*40.2*	-	-
	300	11364	-	*48.3*	-	-
	360	10771	1378	*51.0*	*60.4*	0.13
H_2O_2 (r_{ox}=5.9)	0	19359	4716	*0*	*0*	0.24
	15	18952	-	*2.1*	-	-
	30	18798	-	*2.9*	-	-
	45	18662	-	*3.6*	-	-
	60	18061	-	*6.7*	-	-
	120	17675	-	*8.7*	-	-
	180	17462	4211	*9.8*	*12.1*	0.24
	240	17171	-	*11.3*	-	-
	300	16706	-	*13.7*	-	-
	360	16339	4031	*15.6*	*16.4*	0.25
O_3	0	19622	4168	*0*	*0*	0.21
	15	19328	-	*1.5*	-	-
	30	19033	-	*3.0*	-	-
	45	18876	-	*3.8*	-	-
	60	18739	-	*4.5*	-	-
	120	18582	-	*5.3*	-	-
	180	18445	3847	*6.0*	*7.7*	0.21
	240	18150	-	*7.5*	-	-
	300	17856	-	*9.0*	-	-
	360	17562	3573	*10.5*	*14.3*	0.20
UV-C	0	20067	4105	*0*	*0*	0.21
	15	20067	-	*0*	-	-
	30	19987	-	*0.4*	-	-
	45	19927	-	*0.7*	-	-
	60	19826	-	*1.2*	-	-
	120	19646	-	*2.1*	-	-
	180	19505	4019	*2.8*	*2.1*	0.21
	240	19385	-	*3.4*	-	-
	300	19244	-	*4.1*	-	-
	360	19064	3916	*5.0*	*4.6*	0.21

Table S2. Comparison of studied acoustic cavitation methods with different external oxidants for degradation of organic compounds.

Groups of compounds	**Co [ppm]**	C/Co				C/Co				C/Co				C/Co			
		SONO-CAV [min]				SONO-CAV + H_2O_2 ($r_{OX} = 5.9$) [min]				SONO-CAV + O_3 ($r_{OX} = 1.0$) [min]				SONO-CAV + Peroxone [min]			
		Concentration [ppm]															
ALCOHOLS	**0**	30	60	180	360	30	60	180	360	30	60	180	360	30	60	180	360
1-propanol	**12.87 ± 1.88**	0.89	0.87	0.85	0.59	0.92	0.80	0.67	0.68	0.85	0.40	0.38	0.09	0.83	0.83	0.83	0.76
2-butanol	**0.91 ± 0.11**	1.04	1.12	1.39	1.26	0.98	0.96	0.64	0.63	0.72	0.20	0.18	0	0.91	0.47	0.09	0.03
1-hexanol	**6.87 ± 1.74**	0.91	0.62	0.46	0.39	1.35	1.83	1.44	1.40	0.87	0.99	1.36	0	0.70	0.40	0.40	0.22
1-heptanol	**0.84 ± 0.12**	1.00	0.95	0.95	0.99	0.73	0.72	0.45	0.45	0.31	0.06	0.05	0.05	0.55	0.32	0	0
AROMATIC COMPOUNDS																	
phenol	**15.64 ± 3.89**	1.07	1.15	1.20	1.24	0.45	0.44	0.22	0.03	0.91	0.43	0.41	0	0.87	0.26	0	0
o-cresol	**2.61 ± 0.31**	1.03	1.05	1.12	1.12	1.08	0.72	0.07	0	0.78	0.25	0.24	0	0.79	0.06	0	0
m-cresol	**10.16 ± 1.54**	1.13	1.19	1.23	1.10	1.07	0.99	0.23	0.01	0.90	0.29	0.16	0.01	0.86	0.15	0.01	0.01
2,6-dimethylphenol	**0.35 ± 0.05**	0.57	0.37	0.13	0.04	0.89	0	0	0	0.95	0.83	0.01	0	0.07	0	0	0
4-ethylphenol	**2.12 ± 0.21**	1.06	1.06	1.09	1.03	0.72	0.66	0.23	0.06	0.72	0.25	0.24	0.07	0.68	0.21	0.07	0.06
4-methylbenzaldehyde	**0.41 ± 0.04**	1.04	1.15	1.21	1.22	0.95	0.95	0.94	0.98	0.95	0.88	0.77	0	0.80	0.73	0.67	0.62
ALDEHYDES / KETONES																	
acetaldehyde	**21.68 ± 5.41**	0.95	0.90	0.83	0.64	0.93	1.17	1.42	2.93	0.32	0.60	1.50	1.51	0.16	0.30	0.86	0.86
2-pentanone	**1.12 ± 0.10**	0.83	0.79	0.78	0.51	1.31	1.10	1.01	0.95	0.06	0.08	0.36	0.37	0.17	0.17	0.24	0.28
2-hexanone	**0.33 ± 0.07**	0.91	0.79	0.67	0.41	1.44	1.32	0.98	0.76	0	0	0	0	0	0	0	0
cyclopentanone	**0.15 ± 0.01**	1.51	1.41	1.40	1.77	0.79	0.90	0.87	1.30	0.92	0.07	0.91	0	1.63	1.12	0.33	0
furfural	**1.02 ± 0.12**	1.50	1.89	2.29	2.61	1.21	2.27	1.56	1.23	0.89	0.72	1.34	0.37	1.44	1.43	0.15	0.14
3-heptanone	**0.80 ± 0.24**	0.75	0.50	0.44	0.23	1.55	1.29	0.91	0.90	0.87	0.99	1.36	0	0	0	0	0
cyclohexanone	**1.10 ± 0.17**	1.09	1.18	1.27	1.35	1.29	1.25	0.87	0.83	0	0	0	0	0	0	0	0
2-methylcyclohexanone	**0.29 ± 0.04**	1.21	1.30	1.42	1.82	3.70	5.38	5.40	6.11	0.49	1.44	1.42	1.41	1.05	0.78	0.39	0.36
3-methylcyclohexanone	**0.10 ± 0.01**	1.13	1.08	1.09	0.86	1.64	1.58	1.03	0.87	0.86	0.65	0.39	0	0.49	0.25	0.23	0
acetophenone	**0.44 ± 0.07**	1.08	1.18	1.31	1.33	1.03	0.98	0.82	0.67	0.74	0.30	0.25	0	0.77	0.49	0	0

Table S3. Concentrations of identified VSCs in samples for each of tested treatment processes.

Organosulfur compounds	***Concentration [ppm]***																			
	SONO_CAV [min]					SONO_CAV + O_3 [min]					SONO_CAV + PEROXONE [min]					SONO_CAV + H_2O_2 [min]				
	0	30	60	180	360	0	30	60	180	360	0	30	60	180	360	0	30	60	180	360
ethanethiol	4.18	1.81	1.02	0.06	0.00	3.51	<LOD	<LOD	<LOD	<LOD	4.96	<LOD	<LOD	<LOD	<LOD	4.51	<LOD	<LOD	<LOD	<LOD
dimethyl sulfide	1.30	0.12	0.09	<LOD	<LOD	0.72	<LOD	<LOD	<LOD	<LOD	1.00	<LOD	<LOD	<LOD	<LOD	0.71	<LOD	<LOD	<LOD	<LOD
carbon disulfide	0.59	0.12	0.09	<LOD	<LOD	0.72	0.01	0.01	1.38	0.20	1.02	0.20	0.65	1.95	1.02	1.10	<LOD	<LOD	<LOD	<LOD
3-methyl-1-butanethiol	1.16	0.62	0.14	<LOD	<LOD	0.44	<LOD	<LOD	<LOD	<LOD	0.21	<LOD	<LOD	<LOD	<LOD	0.53	<LOD	<LOD	<LOD	<LOD
1,2-ethanedithiol	<LOD	0.10	0.03	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.04	<LOD	<LOD	<LOD	<LOD
thiophenol	<LOD	2.10	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
thioanisole	0.16	0.14	0.05	<LOD	<LOD	<LOD	0.02	0.02	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.05	<LOD	<LOD	<LOD	0.02
benzylthiol	0.19	0.48	0.27	<LOD	<LOD	0.15	<LOD	<LOD	<LOD	<LOD	0.27	<LOD	<LOD	<LOD	<LOD	0.31	<LOD	<LOD	<LOD	<LOD
X1	<LOD	0.77	0.63	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.27	<LOD	<LOD	<LOD	<LOD	0.73	<LOD	<LOD	<LOD	<LOD
X2	0.02	0.14	0.03	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.13	<LOD	<LOD	<LOD	<LOD
X3	1.74	0.52	0.25	<LOD	<LOD	0.15	<LOD	<LOD	<LOD	<LOD	0.22	<LOD	<LOD	<LOD	<LOD	0.71	<LOD	<LOD	<LOD	<LOD
X4	1.04	0.36	0.17	<LOD	<LOD	0.02	<LOD	<LOD	<LOD	<LOD	0.36	<LOD	<LOD	<LOD	<LOD	1.54	<LOD	<LOD	<LOD	<LOD
X5	0.09	0.05	0.01	<LOD	<LOD	0.96	<LOD	<LOD	<LOD	<LOD	1.09	<LOD	<LOD	<LOD	<LOD	0.71	<LOD	<LOD	<LOD	<LOD
Sum of remaining unidentified VSCs	11.65	8.81	4.44	0.08	0.01	9.04	4.49	1.15	<LOD	<LOD	7.39	0.00	0.31	<LOD	<LOD	9.76	<LOD	<LOD	<LOD	<LOD
TOTAL VSCs	22.12	16.13	7.23	0.14	0.02	15.72	4.52	1.18	1.38	0.20	16.78	0.20	0.96	1.95	1.02	20.82	0	0	0	0.02