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

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## 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

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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 $\text{min}^{-1}$, 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 $\text{min}^{-1}$, 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 $\text{min}^{-1}$. 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 $\text{min}^{-1}$. 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

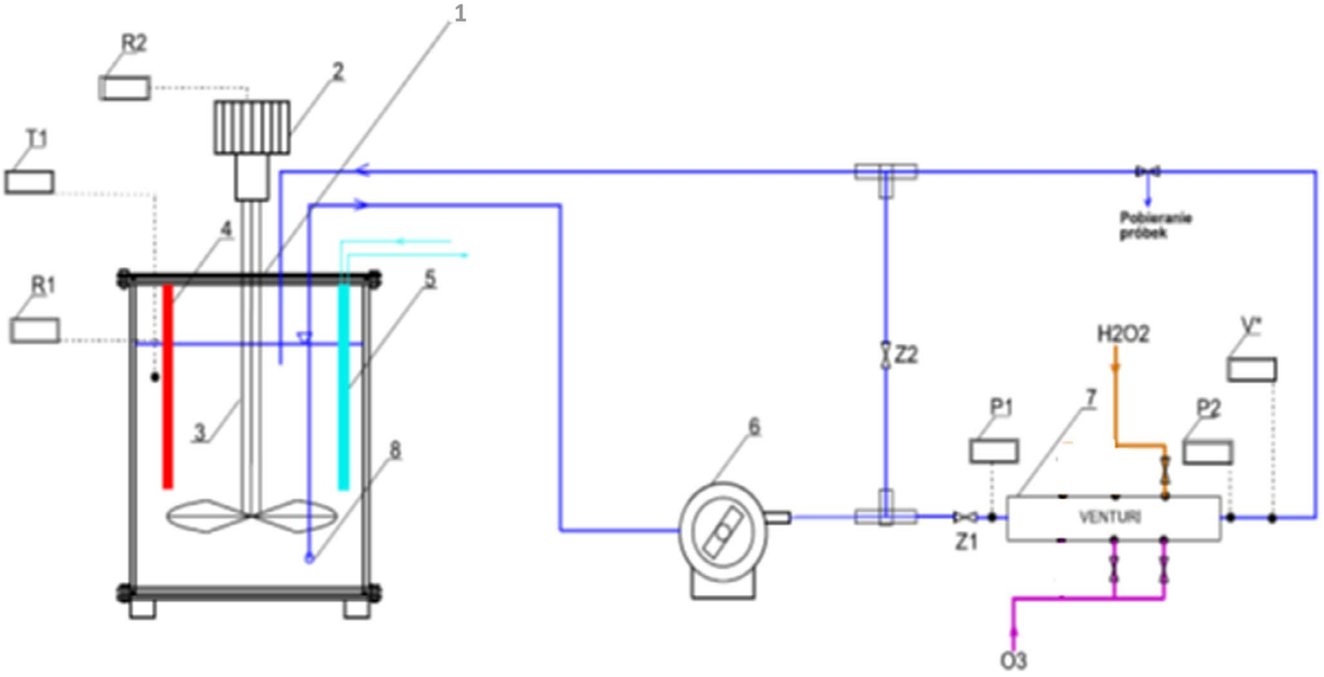

**Fig. 1.** Schematic diagram of hydrodynamic cavitation system with Venturi tube. 1 – tank, 2 – stirrer motor, 3 – stirrer arm, 4 – temperature sensor, 5 – water condenser, 6 – vane pump, 7 – Venturi tube, 8 – suction side of the pump, T1 – connection of temperature sensor to control panel; R2 – connection 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.

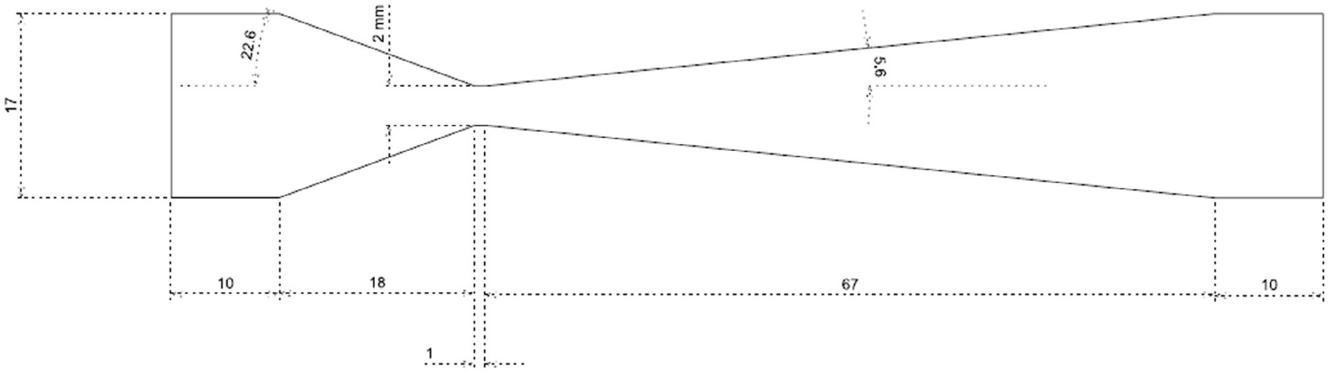

**Fig. 2.** Schematic of Venturi tube.

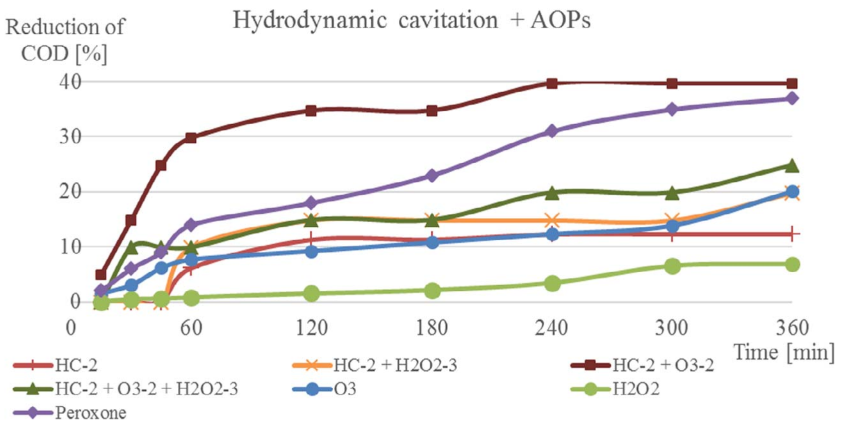

**Fig. 3.** Comparison of effectiveness for studied hydrodynamic cavitation processes aided by external oxidant.

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 [$^oC$] | 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,

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

$$H_2O_2 + OH^- \rightarrow H_2O + HO_2^- \tag{1}$$

$$H_2O_2 \xrightarrow{cavitation} 2HO^{\cdot} \tag{2}$$

$$HO^{\cdot} + pollutants \xrightarrow{cavitation} degradation\ product \tag{3}$$

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].

$$HO^{\cdot} + HO^{\cdot} \xrightarrow{cavitation} H_2O_2 \tag{4}$$

$$HO^{\cdot} + H_2O_2 \xrightarrow{cavitation} H_2O + HO_2^{\cdot} \tag{5}$$

$$HO_2^{\cdot} + HO_2^{\cdot} \xrightarrow{cavitation} H_2O_2 + O_2 \tag{6}$$

$$HO^{\cdot} + O_2 \xrightarrow{cavitation} HO_2^{\cdot} + O^{\cdot} \tag{7}$$

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.

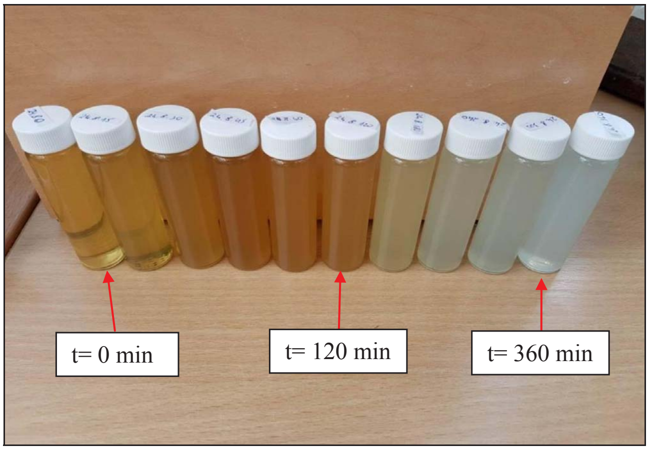

**Fig. 4.** Color change of effluent samples in hydrodynamic cavitation + $O_3$ pretreatment process.

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

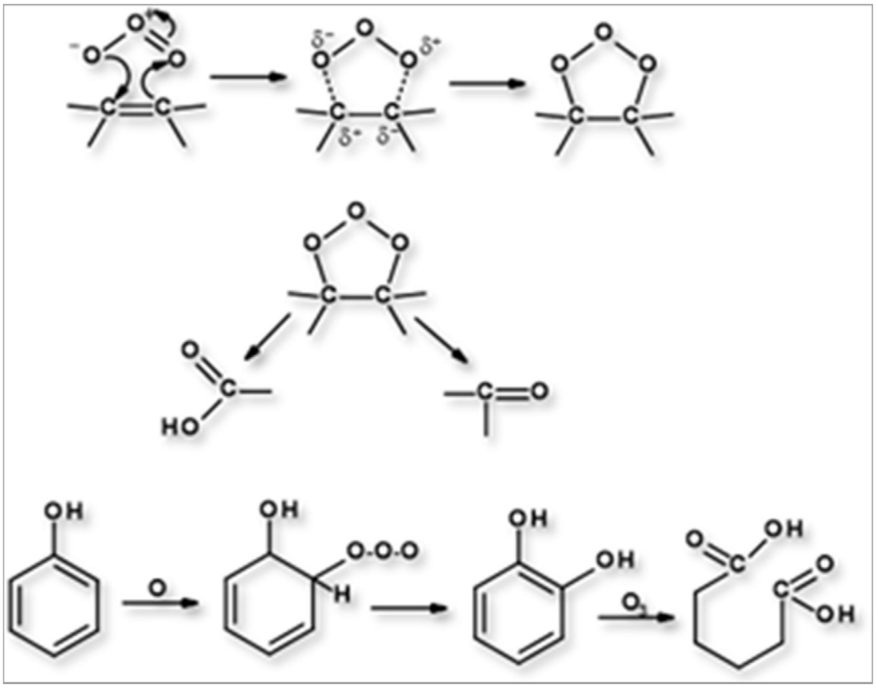

**Fig. 5.** Reaction of dipolar structure ozone forms with contaminants containing double bonds.

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]:

$$H_2O_2 + HO^{\cdot} \xrightarrow{cavitation} H_2O + HO_2^{\cdot} \tag{11}$$

$$O_3 + HO^{\cdot} \xrightarrow{cavitation} O_2 + HO_2^{\cdot} \tag{12}$$

$$HO_2^{\cdot} + HO^{\cdot} \xrightarrow{cavitation} H_2O + O_2 \tag{13}$$

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.

$$O_3 + H_2O_2 \xrightarrow{cavitation} O_2 + HO_2^{\cdot} + HO^{\cdot} \tag{14}$$

$$HO_2^{\cdot} + HO^{\cdot} \xrightarrow{cavitation} H_2O + O_2 \tag{15}$$

### 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).

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

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

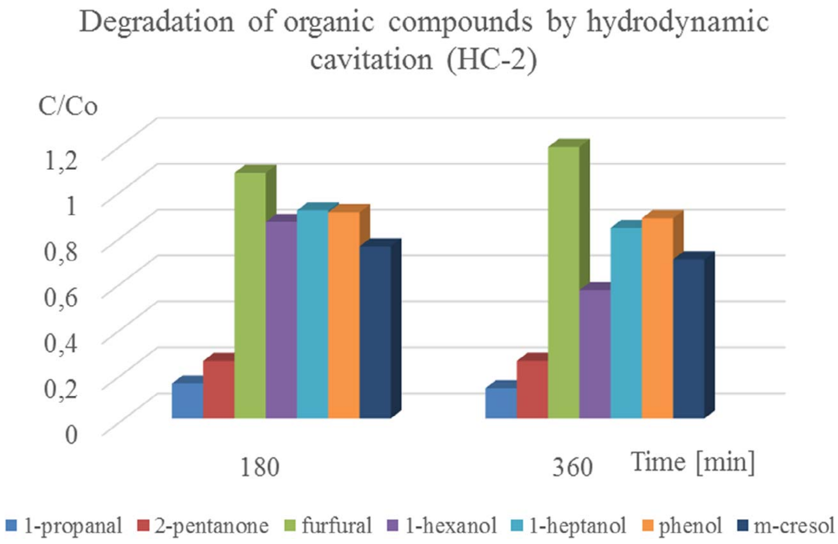

**Fig. 6.** Degradation of organic compounds by hydrodynamic cavitation.

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

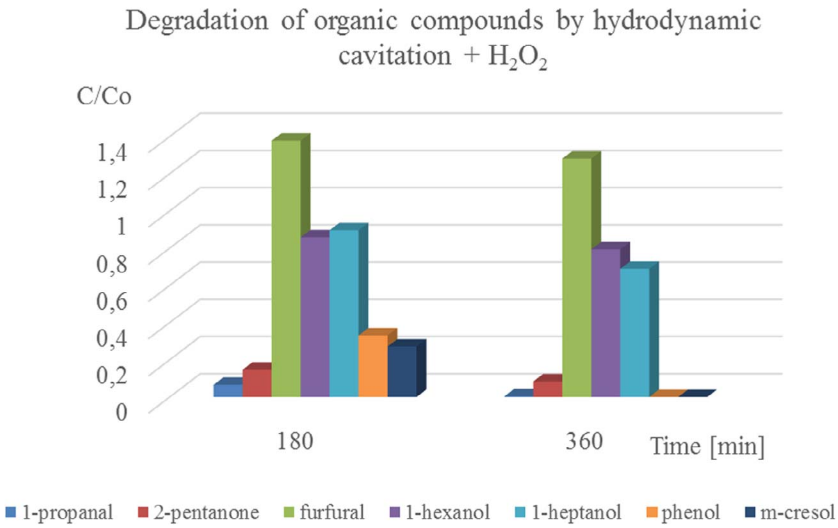

**Fig. 7.** Degradation of organic compounds by hydrodynamic cavitation + $H_2O_2$.

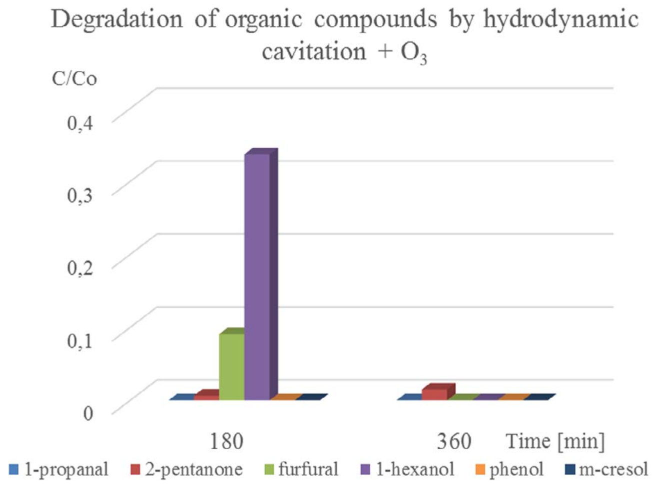

**Fig. 8.** Degradation of organic compounds by hydrodynamic cavitation + $O_3$.

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.

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## 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.