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Ultrafast degradation of brilliant cresyl blue under hydrodynamic cavitation based advanced oxidation processes (AOPs)

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ABSTRACT

The study highlights effectiveness of hydrodynamic cavitation (HC) in the degradation of effluents polluted by Brilliant Cresyl Blue (BCB) dye. Optimal process parameters were cavitation number 0.27, inlet pressure 1.70 bar, temperature 20 °C and pH 7. The efficiency of HC was investigated in combination with other advanced oxidation processes, including the addition of external oxidants (hydrogen peroxide, ozone, and sodium persulfate) and photooxidation. A detailed investigation of reactive radical species present in the system is also presented. Hybrid processes based on HC revealed the highest synergism. Finally, ultrafast degradation of target oxazine dye (decolorization efficiency of 100%) within the short treatment time of 1 min was developed. The most effective process was a combination of hydrodynamic cavitation and ozonation with a synergistic coefficient of 1.84 and electrical energy per order EEO of 0.03 kWh m^{-3} $order^{-1}$. The presented solution is ready to be implemented as technology for industrial practice.

1. Introduction

The discharge of wastewaters containing organic dyes into aquatic environments causes serious health and environmental issues [1–3]. Brilliant Cresyl Blue (BCB) is an oxazine dye, and it is widely used in the textile, printing industries as well as a tracer within the red blood cells to determine the RNA stain [4]. Studies have shown that BCB is classified considered as a carcinogenic, toxic, and mutagenic compound. Even a low concentration of this dye has adverse effects on the environment [5]. For commercial purposes, more than 10 thousand varieties of synthetic dyes are produced and available on the market worldwide.

Moreover, the usage of synthetic dyes exceeds 70 thousand tonnes per year, and approximately 20% of the dyes are released into the wastewater after the dyeing process [6,7]. These wastewaters contain high amounts of suspended particles and intense colour with high pH and are varied in the residual chemical oxygen demand (COD), the high value of total organic carbon (TOC), and often are discharged directly into the environment [8,9]. Hence, it is essential to treat such effluents and prevent their discharge into freshwater sources. Considering the damage to the aquatic environment caused by the wastewater discharged by textile dyeing industries, it is necessary to develop an environmentally friendly and energy-efficient technique to treat the textile effluent before being discharged

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into the aquatic environment [10,11]. Over the past few years, several conventional techniques consisting of different combinations of physical, chemical, and biological oxidation processes have been developed for the treatment of textile effluent. These treatment processes, however, produce large amounts of secondary pollutants, which are even more carcinogenic than the parent compound.

Recently, many researchers have used hydrodynamic cavitation (HC), one of the advanced oxidation processes (AOPs), to treat wastewater as a versatile hybrid AOPs [12–15]. During the HC, a substantial pressure change occurs when an aqueous solution passes through cavitating devices such as orifice or Venturi, due to the alteration in the fluid flow path [16,17]. Cavitation phenomenon involves nucleation, growth, and subsequent collapse of as-generated microbubbles or cavities that occur at short time intervals at multiple reactor locations and thus release large amounts of energy. A sudden collapse of the cavities creates a hot spot (high localized temperatures (5000–10,000 K) and pressures (500 atm), resulting in the formation of $HO^\bullet$, $^\bullet H$, $HO_2^\bullet$, and H_2O_2 [18]. As generated radicals (non-selective reactive species) are capable of oxidizing organic substances within the cavitating devices and help to mineralize the target compounds [19–21]. However, it has been reported in many studies that HC alone can not provide the necessary removal of organic pollutants present in the treated aqueous phase. As a hybrid AOP, which results in significantly higher degradation in a shorter time of treatment, it is therefore often combined with other processes such as the addition of a photocatalyst, Fenton reagent, H_2O_2, ozone, etc.

Many literature studies have been reported for the treatment of dyes applying individually operated AOPs such as photocatalysis and Fenton reaction, as well as combined treatment schemes such as sonoelectrochemical oxidation, sonophotocatalytic degradation, hydrodynamic acoustic cavitation (HAC) and combined hydrodynamic cavitation - hydrogen peroxide (HC/H_2O_2) approach. The removal efficiency of acid red 88 was investigated using different approaches based on hydrodynamic cavitation [22]. Using HC and combined approach of HC/H_2O_2, it was reported that the removal extent of acid red 88 stands at 92% and 99% within 120 min under the optimized parameters of 4000 μM addition of 30% H_2O_2. The combined operation of HC/H_2O_2 (100 μM) with Fe–TiO_2 (1.8 g/L) resulted in the complete decolorization of the effluent (removal efficiency of 100%). The aforementioned study reported that the degradation rate was enhanced by 45–60% for the combination of HC/H_2O_2 with the addition of an appropriate catalyst. A novel approach to utilizing hydrogel adsorbent and HC was investigated for the degradation of crystal violet dye, as a result of which 73% TOC removal was obtained within 90 min under optimized operational conditions. The observed synergistic index was 1.53 as compared to the addition of individual treatment processes [23]. The removal of Rhodamine-b dye in the presence of HC-assisted hydrogel nanocomposite adsorption was also studied. According to the results, the decolorization efficiency of 65% was obtained under optimized operating conditions such as pH 7.62, 0.5 g clay loaded nanocomposite hydrogel, and 25 g hydrogel loading in the adsorption column. The greater extent of the degradation was observed with the addition of H_2O_2 to the hybrid system, which increased the degradation of Rh–B dye to 72.85% with TOC removal of 45% [24]. In another study, researchers focused their attention on the oxidation of reactive red 4 using an improved hybrid process with a combination of HC, H_2O_2, and ozone. It was reported that almost 99% of the degradation was achieved within 5 min in comparison with the other processes [25]. Among the application of $HO^\bullet$, $H^\bullet$, $HO_2^\bullet$ as oxidizing species to remove organic pollutants, recently sulfate radical $SO_4^\bullet$ sulfate radical $SO_4^\bullet$ is considered as an alternative to $HO^\bullet$radical due to their high oxidation potential 2.5–3.1 (eV), which is capable of destroying various persistent pollutants such as organic dyes. Since sulfate radical $SO_4^\bullet$ has a longer lifetime ($3–4 \times 10^{-5}$ s) than $HO^\bullet$ radical (2×10^{-8} s), their usefulness is already proved in the literature [26]. Two oxidants such as persulfate ($S_2O_8^{2-}$) and peroxymonosulfate (HSO_5^-) are the sources of $SO_4^\bullet$ which can be activated using various activators including, catalysts, UV, base, and heat. Sulfate radicals attack (hydro) peroxide (O–O) bond by homolytic or heterolytic cleavage, and they can transform from/to hydroxyl radicals $HO^\bullet$ [27]. Therefore, the role of $SO_4^\bullet$radicals in the degradation of BCB was investigated. Thermal activation (20°*C*, 50°*C*)and the effect of concentration (0.1 M, 0.5 M, 1.0 M) of PS in model solution was studied.

The literature analysis revealed that there are many studies reported using AOPs for degrading different types of dyes, but no studies are reported based on a combination of HC with other AOPs such as H_2O_2, Ozone and UV treatment for the oxidation of BCB. The present work is aimed at defining possible enhancement in the oxidation of BCB by using HC in the presence of various oxidants such as H_2O_2, ozone, and persulfate. The synergistic effect of various parameters on the oxidation of dye by different combined processes such as HC/H_2O_2, HC/ozone, HC/PS, HC/H_2O_2/ozone, HC/UV and $HC/UV/H_2O_2$ was assessed.

2. Experimental methodology

2.1. Chemicals

The commercial dye Brilliant Cresyl Blue (CAS: 81029-05-2) was purchased from POL-AURA. Hydrogen peroxide 30% was procured from POCH S.A., Poland. Sodium peroxydisulfate (Merck), Methanol (POCH S.A.), Propanol (POCH S.A.), t-butanol (Sigma-Aldrich), p-benzoquinone (Sigma-Aldrich) were bought and used without further purification. Sodium hydrogen carbonate (POCH S.A.), sodium chloride (POCH S.A), sodium carbonate (Chempur), sodium sulfate (Chempur). The experiments were conducted with a dye solution of a concentration of 5 mg/L. All the solutions were prepared using deionized water obtained from the MilliQ water purification system (Millipore Corporation, USA). Sodium hydroxide (Merck) and sulphuric acid (Merck, 95–97%) was used for adjusting the solution pH (2–10). A Tytan 32 ozone generator (Erem) was applied for the generation of ozone gas at a rate of 0.459 g/h. All the chemicals used were of analytical grade.

2.2. Experimental procedure

All the studies were conducted using a 6 dm^3 volume of the dye solution. The solution temperature inside the reactor was maintained at 20 ± 2 °C by circulating cooling water through the cooling coil mounted inside of the mixing chamber. The total reaction time for all the experiments was 180 min, and the aliquots were taken for the analysis at regular time intervals. The effect of the cavitation number on decolorization and COD removal was initially investigated by varying the pressure in the range of 3–10 bar. To study the effectiveness of the hybrid processes based on HC, oxidative reagents such as ozone, hydrogen peroxide, and sodium peroxydisulfate were added to the reactor. HC, in combination with hydrogen peroxide and PS experiments, was conducted at a different feed rate for hydrogen peroxide and PS to find the influence of the oxidants. The oxidants (ozone, hydrogen peroxide, and PS) were directly injected through the nozzle into the throat of the Venturi slit, thus directly exposing to the cavitational effect. Different types of scavengers were used to examine the combined effect of the oxidants and cavitation on decolorization and COD removal.

2.3. Hydrodynamic cavitation set up

The schematic representation of the HC system is illustrated in Fig. 1. The experimental setup is comprised of an 11-L stainless steel tank (SS316) with a closed-loop circuit of the temperature control system, stirrer, an electric heater, a vane pump (MS 801–4, 1360 min^{-1}, TECHTOP® MOTOR, Shanghai, China) and a Venturi slit as a cavitating device. There were two discharge lines from the pump with a maximum flow rate of 1000 L/h, i.e., the primary process line and the bypass line. The primary process line was fitted with digital manometers, a Venturi tube (cavitating device), and an electromagnetic flowmeter (MPP 600 by MAGFLO®). The Venturi tube was made of brass (diameter of 10 mm with a throat diameter of 2 mm), and the connecting elements were made of stainless steel (SS316), while the inlet and outlet tubing were made of polytetrafluoroethylene (PTFE). Geometric details, the dimensions of Venturi, and other operational parameters of the cavitating device and its arrangements have already been reported by our research group [12]. The volume of the dye solution treated in the system was 6 L for the studies involving HC, O_3, H_2O_2, and combinations of them. In experiments with UV light irradiation, an additional 3-L chamber equipped with a UV lamp (UVHQ 250Z; Hg lamp (UV-Technik (Germany)) was attached to the primary process line. The power of the lamp is 250 W with a specific lamp power of 56 W/cm. The UV emission spectrum of the Hg lamp is provided on Fig. S1 (supporting information file). The oxidants (hydrogen peroxide and PS solutions) were injected continuously into the system using a high-pressure pump (S-7110 isocratic pump, Merck-Hitachi, Japan) with a flow rate of 0.22 mL/min. In comparison, ozone was injected directly from the ozone generator at a flow rate of 0.5 L/min, which corresponds to 0.459 g/h of ozone production. The concentration of ozone in inlet gas stream to the reactor was 1.53×10^{-2} g ozone/L

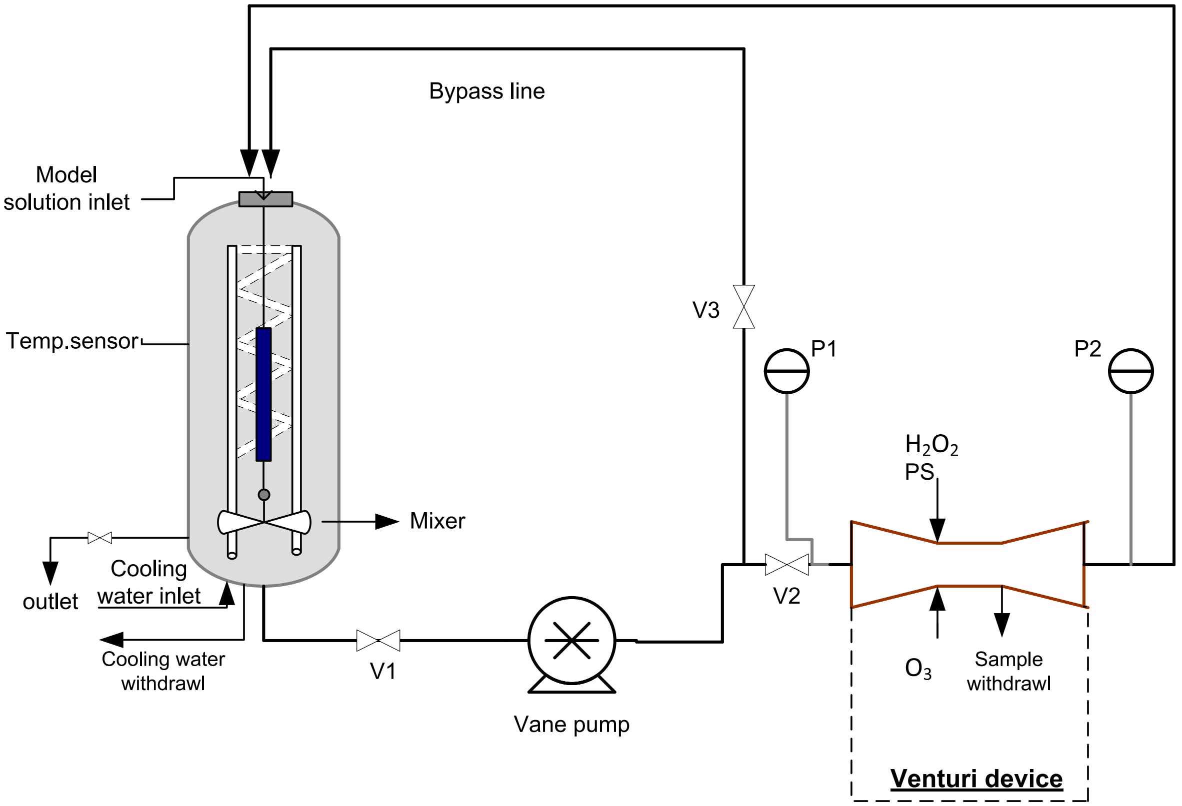


Fig. 1. The schematic representation of the hydrodynamic cavitation system.

of air.

2.4. Analytical procedure

A UV spectrophotometer (DR2010, HACH®, USA) was used to determine the dye degradation in the aqueous media. The absorbance measured for the wavelength of 625 nm corresponded to the maximum absorption wavelength of BCB dye. The degradation efficiency (decolorization efficiency) was calculated through the following Eq. (1):

$$\text{Degradation (\%)} = ((C_i - C_f)/ C_i) * 100 \quad (1)$$

Where, C_i and C_f were concentrations calculated based on absorbance values for the dye solutions before and after the treatment processes, respectively. The COD of the solution was measured with a standard cuvette test method using a HACH COD reactor and a HACH DR/2010 spectrophotometer [28,29]. The effect of scavengers at a set time interval was determined with the RP- HPLC, equipped with a C18 column of dimensions 4.6 × 150 mm obtained from Agilent Technologies (USA), and a UV detector. To detect the presence of intermediate by-products generated during the degradation of BCB, the process samples were analysed with the HPLC-UV/DAD technique. The mobile phase applied in RP-HPLC determination consists of acetonitrile: water mixture (20:80 v/v) with flow rate maintained at 1 mL/min. All the experiments were repeated twice, and the average values of two runs with an experimental error of ±3% were reported.

3. Results and discussion

3.1. Establishing optimal parameters for HC processes

3.1.1. Effect of the cavitation number on dye degradation

The cavitation number describes the intensity of cavitation in hydraulic devices. It is given as a ratio of the difference between the

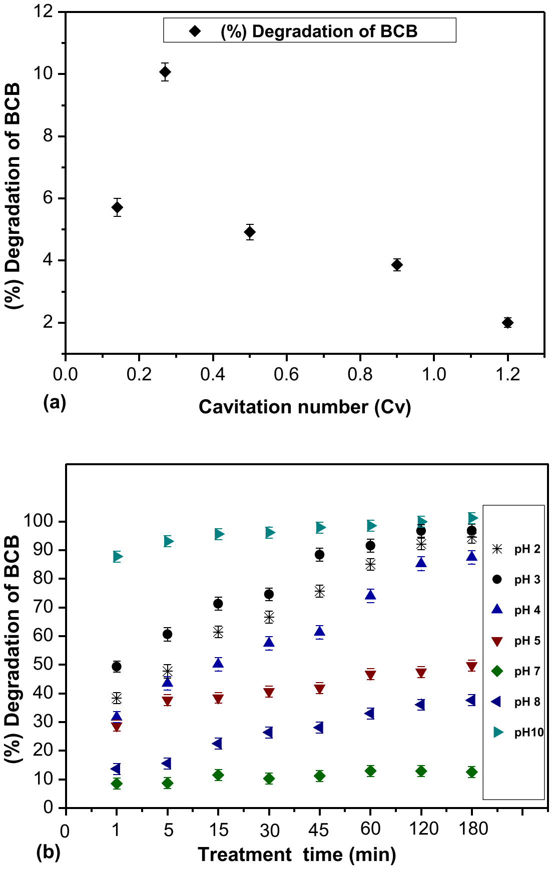


Fig. 2. Illustrates the role of process parameters (cavitation number; pH) in the degradation of 5 mg/L dye, 20 °C (Table 1; Table 2) (a) Graph demonstrates optimization of cavitation number in BCB degradation and highest degradation (10%) is obtained for C_V 0.27 (b) Graph demonstrates the effect of pH media in BCB degradation.

recovered downstream pressure of the throat and the vapor pressure of the liquid over the linear velocity of the fluid at the throat [30]. It is expressed as follows Eq. (2):

$$Cv = \frac{(p_2 - p_v)}{1/2\rho\nu_0^2} \tag{2}$$

where, p_2-downstream pressure [Pa], p_v – water vapor pressure at 20 °C [Pa], ρ– density of the pumped medium at 20 °C [kg/m], ν – linear velocity at the throat of Venturi tube [m/s].

The optimal values depending on the system are in the range of 0–1. The cavitation number is a crucial parameter that directly influences the efficacy of the HC in dye degradation. The interdependence between cavitation number and degradation rate was investigated, experiments were conducted for different cavitation number values C_v (0.14, 0.27, 0.5, 0.9, 1.2).

It was observed that the highest degradation efficiency was obtained for C_v (0.27) with the inlet pressure of 1.70 bar and the outlet pressure of 1.20 bar. As the inlet pressure rises, the cavitation number declines, thus resulting in a greater amount of reactive hydroxyl radicals $HO^\bullet$ that react with the dye molecules. At the same time, the flow rate of the solution will be higher and consequently followed by an increased number of Venturi passes [31]. As a result, a strong interaction between free reactive radicals $HO^\bullet$and dye molecules occurs [32]. Hence, increased degradation efficiency was observed for C_v 0.27 (10%) (Fig. 2a). For lower values of C_v (0.14), degradation efficiency was 5%, and for higher values of C_v (1.2), degradation efficiency was 2%. This leads to a conclusion that at a lower C_v (0.14) a cloudy cavity is formed and the interacting surface between the dye molecules and $HO^\bullet$ is too small to decompose dye molecules, while at higher C_v values (1.2), number of $HO^\bullet$ formed is not sufficient to attack and decompose the target molecules. Therefore, all the experiments were performed at an optimum cavitation number of 0.27 (inlet pressure 1.70 bar and outlet pressure 1.20 bar, flow rate 338 L/h, the velocity at the throat of Venturi 31 m/s, and temperature maintained at 20 °C. Information about the relationship between the parameters and cavitation number can be found in (Table 1). The number of passes is expressed as follows Eq. (3) [33]:

$$\text{Number of passes} = (\text{Flow rate [L/min]} \,/\, \text{V[L]}) * \text{t(min)} \tag{3}$$

This parameter will be used in further discussion to understand the effectiveness of cavitation-based processes fully. Low cavitation numbers, i.e., the high linear velocity of the liquid results in a maximized number of passes of the treated media via the cavitation zone.

3.1.2. Effect of pH on the degradation of BCB

The pH value plays a significant role in the degradation of the dye solution. Hereby during the optimization of process parameters, studies of pH effect on BCB degradation were considered indispensable since this factor influences the physicochemical properties of the dye molecules in the solution. Experiments were conducted in the pH range of 2–10. The results obtained indicate that the highest degradation efficiency was obtained for solutions of pH 3.0 and pH 10.0 (Fig. 2b). Approximately 99.5% of BCB was degraded at a solution pH of 10.0 and 99.8% at a solution pH of 3.0 within the treatment time of 180 min using sole HC ($C_v = 0.27$), meanwhile, if we compare degradation efficiency in 1 min of treatment time, 87.89% degradation corresponds to solution pH of 10.0, and 49.35% degradation corresponds to solution pH of 3.0, i.e., basic circumstances were favorable for the degradation of BCB. The lowest degradation efficiency of 12.58% was obtained in the pH range 6–7. Details of BCB degradation at different pH values and rate constants are provided in Table 2. A rise in the reaction rate constant from 1×10^{-2} min^{-1} to 2.3×10^{-2} min^{-1} was obtained when the solution pH increased from 7.0 to 10.0, respectively. The extent of degradation may occur because of the generation of $HO^\bullet$ increases with an increase in pH media, and this accompanied by higher oxidation potential of $HO^\bullet$ (2.8V), which leads to a higher degradation of BCB.

Meanwhile, the studies also revealed an increase in the degradation of BCB for pH 3 compared to a neutral pH. This fact can be explained by a low ability of hydroxyl radicals $HO^\bullet$ to be recombined in acidic pH. Therefore, more $HO^\bullet$ are disposable in solution and can directly react with pollutant molecules, thus resulting in degradation efficiency of 98.81% in 180 min. A similar effect has been observed by Gore et al. [25]. The results obtained indicate that both acidic and alkaline media enhance the degradation of BCB concerning a neutral pH. However, basic pH is favored since the degradation takes place in only 1-min treatment for HC as a sole treatment process. Phenoxazine groups of dye, such as BCB and Nile Blue, are stable at different pH media [4], therefore degradation of BCB is attributed to the combined effect of acid/basic pH and cavitation conditions related to generation of radical species. Blank experiments of pH effect on BCB without treatment were conducted to check if pH conditions affect the decolorization of BCB. After 180 min incubation of samples at pH 3, pH 7 and pH 10, no change was observed in model samples of BCB. Blank experiments were conducted also to evaluate the role of temperature on BCB degradation. Two different temperatures were selected (20 °C and 50 °C), and after 180 min incubation, no decolorization was observed. Selection of the pH for real wastewater treatment scenario will depend

Table 1
Effect of process parameters in % degradation of BCB.

Nr.exp	Flow rate [L/h]	Inlet Pressure [bar]	Number of passes (min $^{-1}$)	Cavitation number	(%) Degradation of BCB
1	150	1.1	75	1.2	2.01
2	170	1.15	85	0.9	3.86
3	240	1.27	120	0.5	4.92
4	338	1.7	169	0.27	10.07
5	475	1.85	175	0.14	5.71

Table 2
Effect of pH media in % degradation of BCB in 180 min treatment time.

Nr.exp	Treatment time (min)	pH of BCB model solution	$k \times 10^{-2}$ (min^{-1})	(%) Degradation
6	180	2	1.6	97.42
7	180	3	1.9	99.81
8	180	4	1.0	87.44
9	180	5	0.4	49.69
10	180	7	0.1	12.58
11	180	8	0.3	37.6
12	180	10	2.3	99.5

on the type of effluents and their native pH as well as the possibility of their mixing with other effluents having strongly acidic or basic pH. This way, the utilization of external chemicals for pH correction can be minimized, thereby lowering the costs of the treatment process.

3.2. *Effectiveness of ozone as a sole process, and in combination with HC for BCB degradation*

Ozone is a powerful oxidant having a high oxidation potential (2.08 eV). It was used to enhance the degradation of pollutant molecules in the aqueous medium. Ozone can degrade a variety of organic contaminants whose molecules contain unsaturated bonds

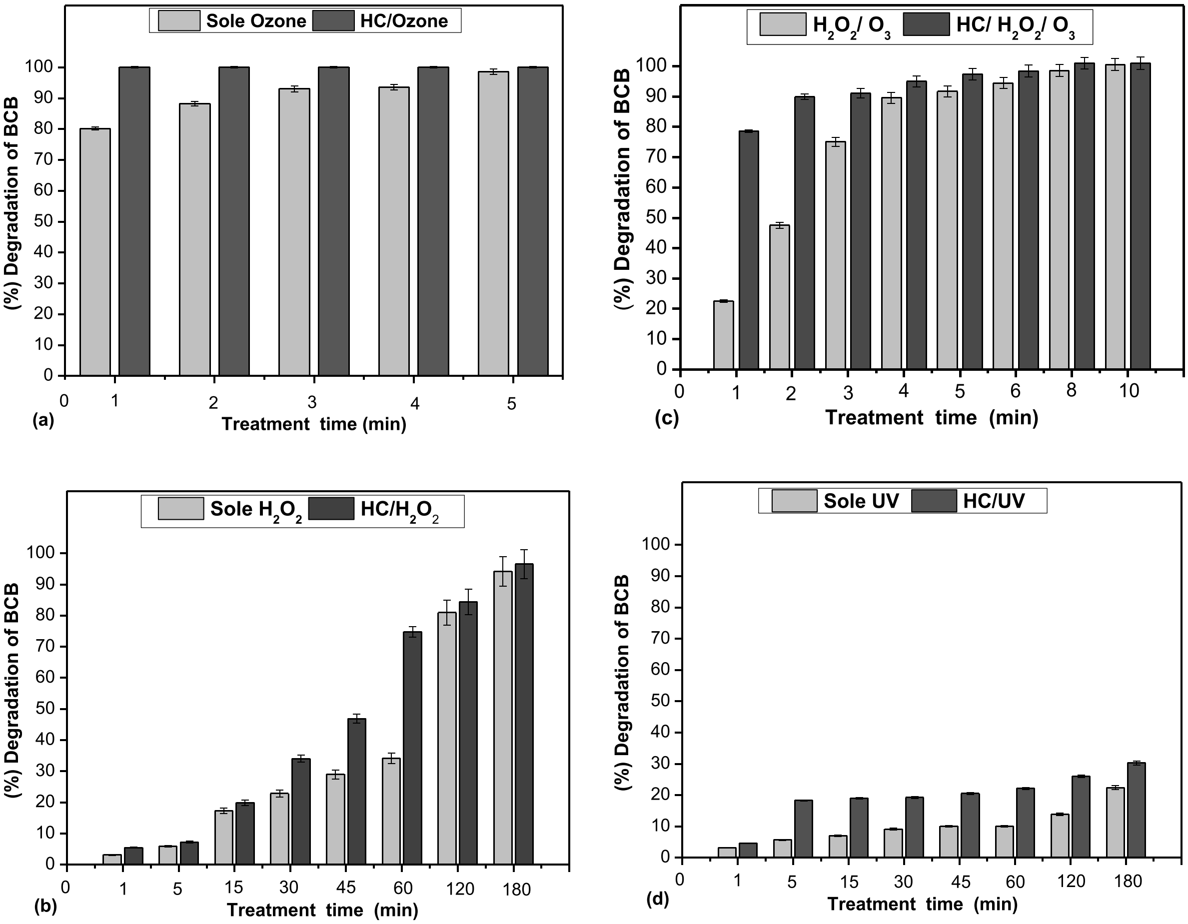


Fig. 3. Illustrates the effect of hydrodynamic cavitation combined with AOPs for degradation of 5 mg/L BCB, 20 °C, Ozone flowrate 0.5 L/min, H_2O_2 flowrate 0.22 mL/min a) Comparison of effectiveness in degradation for sole ozonation (r_{ox} 1.03) (Table 3; exp 14) and combined processes of HC and O_3 (r_{ox} 0.27) (Table 3; exp 15) b) Comparison of effectiveness in degradation for sole H_2O_2 (r_{ox} 8.31) (Table 3; exp 16) and combined processes of HC and H_2O_2 (r_{ox} 8.31) (Table 4; exp 17) c) Comparison of effectiveness in degradation for sole H_2O_2/O_3 (r_{ox} 4.94) (Table 3; exp 22) and combined processes of $HC/H_2O_2/O_3$ (r_{ox} 3.07) (Table 4; exp 23) d) comparison of effectiveness in degradation for sole UV (Table 3; exp 18) and combined processes of HC and UV (Table 3; exp 19).

such as C═C, N═N, and C═N [14]. Cavitation devices ceaselessly generate free reactive radicals, which intensively interact with pollutant molecules contributing, thus in higher degradation rates of contaminants present in wastewater [34].

In order to intensify the degradation of BCB dye, a combination of HC and ozone was studied in the present work. An enhanced mass transfer of ozone molecules from the gas phase to model solution occurs during the combination of HC with ozone gas, where an immediate degradation of dye molecules takes place within the treatment time of 1 min. Under HC conditions, ozone molecules are readily transformed into atomic and molecular oxygen $O_{2,}$ which undergoes in reaction with water molecules to produce superoxide $O_2^{\bullet -}$ and $HO^{\bullet}$ radicals [35]. The reactions that take place are presented in the following Eqs 4–11 [25,35–38]:

$$H_2O \overset{HC}{\rightarrow} HO^{\bullet} + H^{+} + e^{-} \quad (E^{o} = 2.8\ V) \tag{4}$$

$$O_3 \xrightarrow{HC(2H^{+}+2e^{-})} O_2^{\bullet} + H_2O(E^{o} = 2.08V) \tag{5}$$

$$O_3 \overset{HC}{\rightarrow} O_2 + O(^3P) \tag{6}$$

$$H_2O \overset{HC}{\rightarrow} HO^{\bullet} + {}^{\bullet}H \tag{7}$$

$$O(^3P) + H_2O \rightarrow 2\ HO^{\bullet} \tag{8}$$

$$HO^{\bullet} + O_2^{-} \rightarrow OH^{-} + {}^{1}O_2 \tag{9}$$

$$O_3 + OH^{-} \rightarrow HO_2^{\bullet} + O_2^{\bullet -} \tag{10}$$

$$O_2^{\bullet -} + BCB \rightarrow \text{degradation } by - products \rightarrow CO_2 + H_2O \tag{11}$$

In case of ozone based processes it is important to evaluate what is the effectiveness of ozone uptake from the injected gas by the processed liquid. A preliminary studies revealed, that 15 min are needed to saturate the processed liquid with ozone, and that ozone is absorbed quantitatively in the aqueous phase during first 15 min of the barbotage. After this time period ozone starts to be detect at the reactor's gas outlet. Since 100% degradation for HC/O_3 and sole ozone was achieved respectively in 1 min and 5 min treatment time, it is considered that total amount of ozone introduced in the inlet gas was available for treatment process. It can be inferred that the degradation of BCB was 10% using HC as a sole process in 180 min, and 100% degradation was attained in 5 min with the sole use of ozonation (r_{ox} 1.03). It was also possible to achieve 100% degradation in only 1 min by combining HC with ozone (r_{ox} 0.27) (Fig. 3a). A synergistic effect was obtained for the combined process with a respective synergistic coefficient of 1.84. The removal efficiency was also confirmed by the COD analysis results, which showed degradation efficiency of 94% by the sole ozonation process, and degradation efficiency of 97% for the combined process of HC/O_3 (Table 3; exp 13, 14, 15). The synergetic coefficient that examines the efficiency of the combined method is expressed in the following equation Eq. (12):

Table 3

Comparison of effectiveness between sole and combined processes of HC/AOP (neutral pH, 5 mg/L BCB, 20 °C, liquid oxidants flowrate 0.22 mL/min, ozone flowrate 0.5 L/min).

Nr. exp	Processes	Treat. time (min)	Oxidant amount (g)	r_{ox}	Syn. Coeff.	k (min^{-1})	(%) COD Change	(%) Degradation
13	**HC**	180	–	–	1.84	6.0×10^{-4}	10	10.00 ± 0.25
14	**Sole O_3**	5	0.04	1.03		5.2×10^{-1}	94	100 ± 0.20
15	**HC + O_3**	1	0.01	0.27		9.9×10^{-1}	97	100 ± 0.22
16	**Sole H_2O_2**	180	43.96	8.31	1.07	1.3×10^{-2}	85	90.49 ± 0.04
17	**HC + H_2O_2**	180	43.96	8.31		1.5×10^{-2}	90	96.49 ± 0.23
18	**Sole UV**	180	–	–	0.9	1.4×10^{-3}	19	22.00 ± 0.04
19	**HC + UV**	180	–	–		1.9×10^{-3}	26	34.00 ± 0.06
20	**Sole UV + H_2O_2**	180	43.96	8.31	5.91	1.3×10^{-2}	89	93.98 ± 0.13
21	**HC + UV + H_2O_2**	180	43.96	5.54		8.4×10^{-2}	95	100 ± 0.22
22	**Sole H_2O_2+O_3**	15	H_2O_2: 3.3; O_3: 0.11	4.94	0.82	2.7×10^{-1}	85	100 ± 0.20
23	**HC + H_2O_2+O_3**	8	H_2O_2: 1.95; O_3: 0.06	3.07		2.9×10^{-1}	93	100 ± 0.19
24	**UV + O_3+H_2O_2**	10	H_2O_2: 2.2; O_3: 0.07	3.60	1.85	7.7×10^{-1}	96	100 ± 0.16
25	**HC + UV + O_3+H_2O_2**	5	H_2O_2: 1.1; O_3: 0.04	2.26		9.7×10^{-1}	98	100 ± 0.16
26	**Sole UV + O_3**	15	O_3: 0.11	4.02	3.42	2.3×10^{-1}	93	100 ± 0.16
27	**HC + UV + O_3**	5	O_3: 0.04	1.34		4.2×10^{-1}	98	100 ± 0.26
28	**Sole PS (0.1 M; 20°C)**	180	0.94	0.31	2.16	1.0×10^{-3}	13	14.61 ± 0.04
29	**HC + PS (0.1 M; 20°C)**	180	0.94	0.31		3.0×10^{-3}	40	43.94 ± 0.08
30	**Sole PS (0.5 M; 20°C)**	180	4.71	1.68	1.24	3.0×10^{-3}	39	43.98 ± 0.06
31	**HC + PS (0.5M; 20°C)**	180	4.71	1.68		5.0×10^{-3}	52	57.42 ± 0.11
32	**Sole PS (1 M; 20°C)**	180	9.42	3.36	5.00	5.0×10^{-3}	47	51.36 ± 0.10
33	**HC + PS (1 M; 20°C)**	180	9.42	3.36		2.3×10^{-2}	94	98.47 ± 0.17
34	**Sole PS (1 M; 50°C)**	60	3.14	1.12	2.24	3.1×10^{-2}	82	84.36 ± 0.20
35	**HC + PS (1 M; 50°C)**	60	3.14	1.12		7.1×10^{-2}	92	98.61 ± 0.19

$$S = \frac{k_{HC+O_3}}{k_{HC} + k_{O_3}} \tag{12}$$

k_{HC+O_3} is the rate constant of the combined process of HC and ozone,k_{HC} is the rate constant of sole HC process, and $k_{O_3}$is the rate constant of the sole ozonation process.

The degradation of reactive orange 4 (RO4) by the HC-based hybrid treatment techniques have also been studied by other researchers [25]. They reported that the combination of HC with ozone at an optimum feed rate of 3 g/h resulted in the TOC removal efficiency of 76.25% during the treatment time of 60 min. Studies of rhodamine 6G degradation with the hybrid process of HC/ozone were conducted by Rajoriya et al. [35]. They similarly reported the decolorization efficiency of 100% in 5–10 min, TOC removal of 84% using HC/ozone process (3 g/h) in 120 min. **Conclusively, the results of the present study showed a significant improvement in the effectiveness of the treatment process at a much shorter required treatment time in comparison with the already reported data regarding the combined process of HC/O_3.**

3.3. Effect of HC coupled with H_2O_2 on dye degradation

The effect of H_2O_2 with a particular dosage in combination with HC was investigated. H_2O_2, as an oxidant with the oxidation potential of 1.78 eV, under optimum cavitation conditions, can be dissociated, giving rise of a number of $HO^\bullet$ radicals [39]. The sufficient amount of energy needed for the dissociation of H_2O_2 will be produced from the cavitation phenomena because, during cavitation, a sufficient amount of energy is created to dissociate the O–O bond (213 kJ/mol) in H_2O_2 and O–H bond (418 kJ/mol) of H_2O. Therefore, a rise in the amount of $HO^\bullet$generated from H_2O_2 in combination with HC will lead to the degradation of dye molecules as well as other organic pollutants [13,25,39,40]. The reactions taking place are described below Eqs. 13–20 [39,41]:

$$H_2O_2 \overset{HC}{\rightarrow} 2\ HO^\bullet \tag{13}$$

$$H_2O \overset{HC}{\rightarrow} H^\bullet + HO^\bullet \tag{14}$$

$$HO^\bullet + HO^\bullet \overset{HC}{\rightarrow} H_2O_2 \tag{15}$$

$$HO^\bullet + H_2O_2 \overset{HC}{\rightarrow} {}^\bullet OH_2 + H_2O \tag{16}$$

$$HO^\bullet + {}^\bullet OH_2 \overset{HC}{\rightarrow} H_2O + O_2 \tag{17}$$

$${}^\bullet OH_2 + H_2O_2 \rightarrow HO^\bullet + H_2O + O_2 \tag{18}$$

$$BCB + {}^\bullet OH_2 \rightarrow CO_2 + H_2O + \text{other intermediates} \tag{19}$$

$$BCB + H_2O_2 \rightarrow CO_2 + H_2O + \text{other intermediates} \tag{20}$$

We observed that most of the mineralization using the hybrid process of HC/H_2O_2 occurs in the first 60 min. For the sole H_2O_2 process, the degradation efficiency of only 35.74% was obtained for the treatment of 5 mg/L dye, while the degradation efficiency of 74.15% was achieved for the combined process of HC/H_2O_2 (Fig. 3b). Thus, a significant speed-up of the degradation was observed in the first 60 min. The synergistic coefficient of 1.07 obtained in a combination of HC and H_2O_2 proved the effectiveness of HC in making H_2O_2 more suitable for the degradation of organic pollutants. This is due to the high number of $HO^\bullet$ generated by the dissociation of H_2O_2 in the presence of HC, leading to higher degradation efficiency of BCB compared to that obtained for the sole H_2O_2 process. Overall, the degradation effectiveness in both processes (sole H_2O_2 (r_{ox} 8.31) and HC/H_2O_2 (r_{ox} 8.31)) was high and reached 90.49 and 96.49% after 180 min, respectively (Table 3; 16, 17). The effectiveness of the combined method of HC/H_2O_2 was also reported by other researchers in the degradation of different dyes such as methylene blue, methyl orange, and Rhodamine-B [42,43].

3.4. Effect of the combination of HC with UV irradiation on BCB degradation

The combination of HC with UV light irradiation was also investigated in this study. A slight increase in the degradation rate of BCB was observed when the combined process of HC/UV (34%) was used instead of the photolysis alone (22%). Both experiments were performed for 180 min at 20 °C with a rate constant of 1.4×10^{-3} min^{-1} for the sole UV process and 1.9×10^{-3} min^{-1} for HC aided with UV. As generated $HO^\bullet$ in the combined process of HC/UV eventually sped up the degradation rate of the target pollutants compared to individual approaches. Cavitation phenomena and photolysis of water molecules enhanced the generation rate of oxidizing species, consequently, giving rise to the degradation of contaminant molecules [44]. The results of COD analysis exhibited the degradation efficiency of 19% for the sole UV and 26% for the combined process of HC/UV. The synergistic coefficient was 0.9, and this shows that there is no additional efficacy for the combination of both methods (Table 3; exp 18, 19).

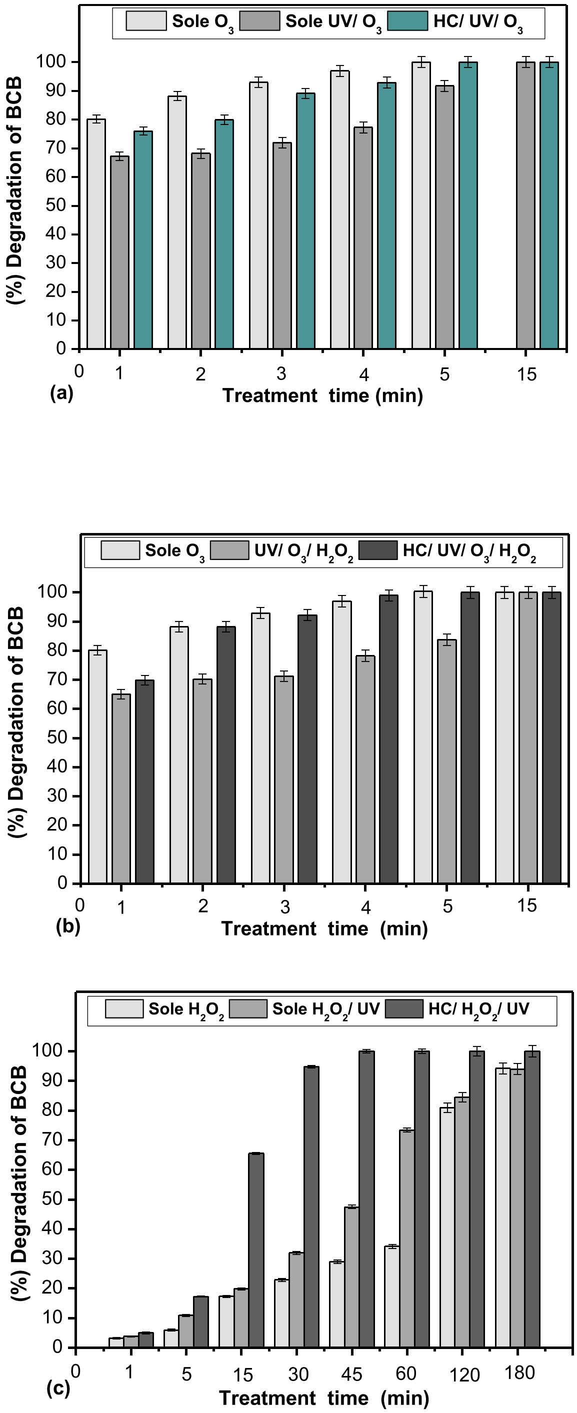


Fig. 4. Effect of hydrodynamic cavitation combined with hybrid AOPs for degradation of 5 mg/L BCB; 20 °C; Ozone flowrate 0.5 L/min; H_2O_2 flowrate 0.22 mL/min a) Comparison of effectiveness in degradation for sole UV/O_3 (r_{ox} 4.02) (Table 3; exp 26) and combined processes of HC and UV/O_3 (r_{ox} 1.34) (Table 3; exp 27) b) Comparison of effectiveness in degradation for sole UV/O_3/H_2O_2 (r_{ox} 3.60) (Table 3; exp 24) and combined processes of HC and UV/O_3/H_2O_2 (r_{ox} 2.26) (Table 3; exp 25) c) Comparison of effectiveness in degradation for sole H_2O_2/UV (r_{ox} 8.31) (Table 3; exp 20) and combined processes of HC and H_2O_2/UV (r_{ox} 5.54) (Table 3; exp 21).

3.5. Dye degradation kinetics

During the degradation studies under the cavitation effect, the concentration of $HO^{\bullet}$ radicals was found to be continuous, extremely reactive, and non-selective, so its concentration impact can be neglected. The kinetic analysis reveals that the degradation of BCB dye with HC fits into the pseudo-first-order kinetic model. It was observed that the pseudo-first-order rate constant increases from 1.3×10^{-2} to $9.3 \times 10^{-2}\ \text{min}^{-1}$ when AOPs are combined with HC. Under cavitation conditions, the degradation occurs due to pyrolytic decomposition of the dye molecules inside the bubble. As a result, contaminant molecules are converted to low toxic substances and even non-toxic compounds [31]. The reaction rate constant determination is expressed in the following Eqs. (21) and (22) [45]:

$$C = C_0 \times e^{-kt} \tag{21}$$

$$k = -\frac{\ln\left(\frac{C}{C_0}\right)}{t} \tag{22}$$

3.6. Effectiveness of HC-based AOPs AOPs-assisted HC process

HC-based AOPs provide efficient degradation of wastewater pollutants; thus, synergistic coefficient values are higher for HC based AOPs compared to sole AOPs processes [25]. In this study, AOPs such as the ozonation process, UV oxidation, and H_2O_2 oxidation were combined with HC for better degradation efficiency of BCB, additionally contributing to the reduction of treatment costs. Reactions that take place are exhibited in the following equations Eqs. 23–25 [34]:

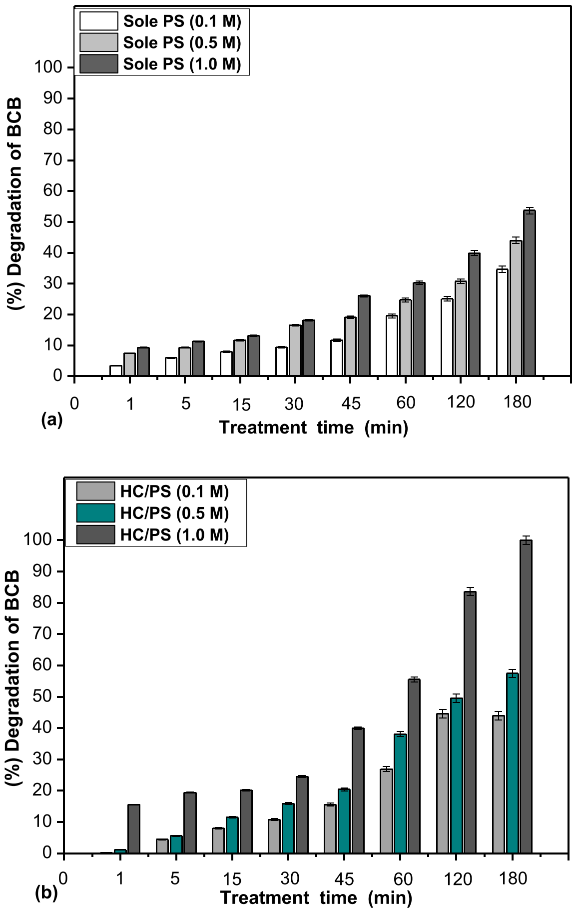


Fig. 5. Effect of hydrodynamic cavitation combined with persulfate PS in different concentrations (0.1 M; 0.5 M; 1 M) for degradation of 5 mg/L BCB; 20 °C; PS flowrate 0.22 mL/min a) Comparison of % degradation of dye for different persulfate concentrations for sole PS processes (r_{ox} 0.31; r_{ox} 1.68; r_{ox} 3.36) (Table 3; exp 28, 30, 32) b) Comparison of % degradation of dye for different persulfate concentrations in combined treatment processes of HC/PS (r_{ox} 0.31; r_{ox} 1.68; r_{ox} 3.36) (Table 3; exp 29, 31, 33).

$$O_3 / UV: \quad O_3 + h\nu + H_2O \rightarrow 2HO^{\bullet} + O_2 \tag{23}$$

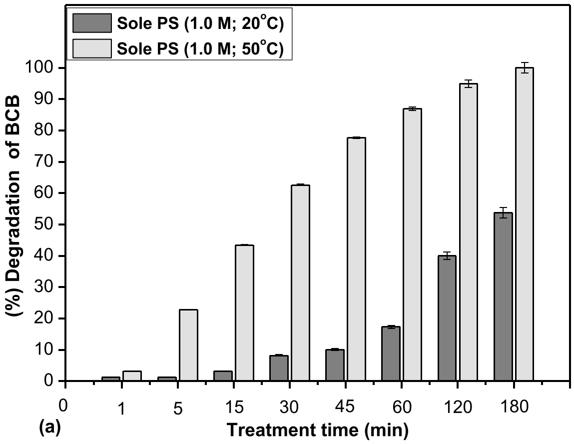
$$UV/H_2O_2: \quad H_2O_2 + h\nu \rightarrow 2HO^{\bullet} \tag{24}$$

$$O_3/UV/H_2O_2: \quad H_2O_2 + O_3 + H_2O(h\nu) \rightarrow 4HO^{\bullet} + O_2 \tag{25}$$

Several experiments were performed to study the effect of the combination of HC with AOPs as hybrid treatment methods. The best processes appeared to be the combined treatment process of HC/UV/O_3, which resulted in the degradation efficiency of 100% in 5 min and a synergistic coefficient of 3.42 (r_{ox} 1.34) and followed then by the combined process of HC/UV/O_3/H_2O_2 with degradation efficiency of 100% in 5 min and a corresponding synergistic coefficient of 1.85 (r_{ox} 2.26). The degradation efficiency of the hybrid process of H_2O_2/UV was increased from 93.98% for the sole process (r_{ox} 8.31) to 100% for the combined process of HC/H_2O_2/UV (r_{ox} 5.54) in 180 min treatment time, with a synergistic coefficient of 5.91 (Fig. 4 a, b, c). The (%) COD removal for processes of HC/UV/O_3, HC/UV/O_3/H_2O_2, and HC/H_2O_2/UV resulted in being 98%, 99%, and 97% respectively. The synergistic coefficients of 3.42, 1.85, and 5.91 for the processes, as mentioned earlier, confirmed the effectiveness of HC-assisted AOPs for the decolorization and mineralization of BCB-contained liquid phase (Table 3; exp 27, 25, 21).

3.7. *Effect of concentration and temperature of persulfate in the degradation of BCB dye*

In the present study, two pairs of experiments were conducted where the effects of PS concentration and temperature of the PS-



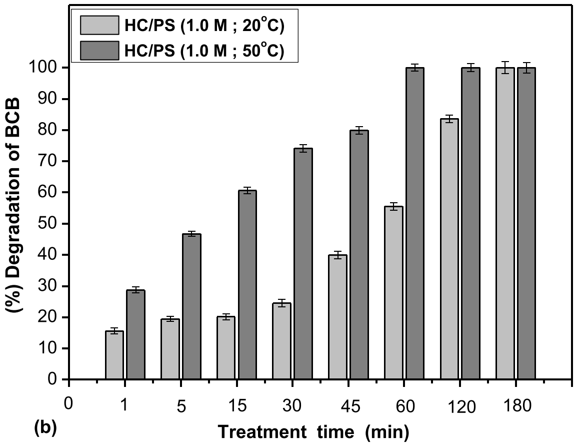


Fig. 6. Effect of hydrodynamic cavitation combined with persulfate PS (1 M) in different temperatures (20 °C; 50 °C) for degradation of 5 mg/L BCB. a) Comparison of % degradation of dye for sole processes of PS in 20 °C (r_{ox} 3.36) (Table 3; exp 32) and 50 °C (r_{ox} 1.12) (Table 3; exp 34) b) Comparison of % degradation of dye for combined treatment processes of HC/PS in 20 °C (r_{ox} 3.36) (Table 3; exp 33) and 50 °C (r_{ox} 1.12) (Table 3; exp 34).

assisted treatment process in the degradation of BCB were studied. For this purpose, three concentrations of PS (0.1 M; 0.5 M; 1.0 M), together with two different temperatures (20 °C and 50 °C), were selected. In the first set of experiments, the temperature was kept constant at 20 °C, and the effect of HC combined with PS for the three concentrations (0.1 M; 0.5 M; 1.0 M) on dye degradation was investigated (Table 3; exp 28–33). We found that as the concentration increases, degradation efficiency increases too. The highest of the achieved degradation (%) corresponds to HC/PS (1.0 M; r_{ox} 3.36), with 98.47% within the treatment of 180 min (Fig. 5). For the second pair of experiments, the concentration of 1.0 M PS was selected as a fixed parameter since the highest degradation (%) was obtained for PS (1.0 M), and the effect of the temperature was investigated in the degradation of BCB for the HC/PS process. At 20 °C, HC contributes to the degradation of BCB increasing from 51.36% (sole PS; r_{ox} 3.36) to 98.47% (HC/PS; r_{ox} 3.36). On the other hand, when PS (1.0 M) is activated by heat at the temperature of 50 °C, HC gives attribute in treatment time, which is reduced from 180 (sole PS; r_{ox} 1.12) to 60 min (HC/PS; r_{ox} 1.12). Degradation values varied from 84.36% to 98.61% respectively (Fig. 6). The amount of COD removed confirmed the extent of dye mineralization (Table 3; exp 32–35). **It is clear that in this case, the application of PS as an oxidant is not justified since less expensive oxidants H_2O_2, as well as O_3, provide much higher effectiveness.**

3.8. Effect of the initial concentration of BCB on its degradation efficiency

The initial concentration of dye has a significant impact on the degradation rate. This study revealed a remarkable decrement in degradation rate as the initial concentration of dye increases. Wang et al. [43], studied the degradation of rhodamine B by swirling jet elicited cavitation, and they stated that with the increase of concentration from 10 mg/L to 50 mg/L, degradation was decreased from 98.9% to 63.4% in 180 min. Thakare et al. [46], claimed that as the concentration of brilliant green increased from 10 to 30 mg/L, its degradation efficiency decreased from 27.92 to 17.34%. The presented results go along closely with results already stated in other researches of dye removal, such as reactive red X-3D [47] and acid orange 7 (AO7) [48].

In the present study, it was observed that with an increase in BCB concentration from 5 to 20 and 50 mg/L, a substantial decrease in degradation (%) was obtained comparing the same time of treatment. The influence of concentration on the degradation rate of BCB is compiled in Table 4. During BCB treatment by the sole HC process, degradation decreased from 10.0 to 4.14% when the initial concentration of BCB increased from 5 to 50 mg/L, respectively (Table 4; exp 13, 42). The most effective process for degradation of 5 mg/L dye was considered HC combined with ozone (r_{ox} 0.27) where degradation efficiency of 100% was achieved in short reaction time of 1 min (Table 4; exp 15), meanwhile complete degradation of 20 mg/L was achieved in 15 min (r_{ox} 1.01) and 99.8% degradation of 50 mg/L BCB was achieved in treatment time of 60 min (r_{ox} 1.21) (Table 4; exp 38, 44). The most effective process for the highest degradation of BCB (20 and 50 mg/L) was the hybrid process of HC/UV/O_3/H_2O_2 where the degradation efficiency of 100% was achieved in only 5 min (r_{ox} 0.57), whereas 99.73% degradation for 50 mg/L BCB was achieved within 30 min of treatment (r_{ox} 1.36) (Table 4; exp 41, 47) (Fig. 7 a, b). In the case of HC processes assisted with the addition of external oxidants, the less effective process was considered HC/H_2O_2 where degradation efficiency of 96.5% was obtained at initial BCB concentration of 5 mg/L (r_{ox} 8.31) to 14.5% (r_{ox} 8.34) and 3.06% (r_{ox} 3.33) for 20 and 50 mg/L in treatment time of 180 min, respectively (Table 4; exp 16, 39, 45) (Fig. 7c). It is clear that H_2O_2, reacting directly or converted mainly to $HO^\bullet$, is not effective for BCB degradation. A comparison of results between O_3 and O_3/H_2O_2 (peroxone process) revealed an interesting difference between these processes. Generally, peroxone is a more effective AOP comparing to ozonation due to the enhanced formation of reactive radicals $HO^\bullet$. Thus, conversion of O_3 by reaction with H_2O_2 (HC/H_2O_2/O_3; r_{ox} 3.07) to produce an increased amount of free reactive radicals was not favored making ozonation combined with HC (HC/O_3; r_{ox} 0.27) the most effective process of this studies (Table 4; exp 15, 23). The same trend was also observed for the higher concentration of dye, such as 20 and 50 ppm (Table 4; exp 37, 40, 44, 46).

Table 4

Effect of the initial concentration of BCB in (%) degradation in different processes of HC combined with AOP. Comparison of (%) degradation for different concentrations of BCB (20 °C).

Nr.exp	Processes	C (mg/L)	Treatment time (min)	pH	Oxidant amount (g)	r_{ox}	k (min^{-1})	(%) Degradation
13	**Sole Cavitation**	5	180	7	–	–	6.0×10^{-4}	10.00 ± 0.25
14	**Sole O_3**	5	5	7	0.04	1.03	5.2×10^{-1}	100 ± 0.20
15	**HC + O_3**	5	1	7	0.01	0.27	9.9×10^{-1}	100 ± 0.22
16	**HC + H_2O_2**	5	180	7	43.96	8.31	1.5×10^{-2}	96.49 ± 0.23
23	**HC + H_2O_2+O_3**	5	8	7	H_2O_2: 1.95; O_3: 0.06	3.07	2.9×10^{-1}	100 ± 0.19
25	**HC + UV + O_3+H_2O_2**	5	5	7	H_2O_2: 1.1; O_3: 0.04	2.26	9.7×10^{-1}	100 ± 0.16
36	**Sole Cavitation**	20	180	7	–	–	2×10^{-4}	4.10 ± 0.03
37	**Sole O_3**	20	30	7	0.23	2.02	1.9×10^{-1}	99.7 ± 0.82
38	**HC + O_3**	20	15	7	0.11	1.01	0.7×10^{-1}	100 ± 0.86
39	**HC + H_2O_2**	20	180	7	43.96	8.34	9×10^{-4}	14.4 ± 0.14
40	**HC + H_2O_2+O_3**	20	30	7	H_2O_2: 7.32; O_3: 0.23	3.41	1.7×10^{-1}	100 ± 0.78
41	**HC + UV + O_3+H_2O_2**	20	5	7	H_2O_2: 1.22; O_3: 0.04	0.57	9.7×10^{-1}	100 ± 0.89
42	**Sole Cavitation**	50	180	7	–	–	3×10^{-4}	4.14 ± 0.04
43	**Sole O_3**	50	60	7	0.46	1.61	0.9×10^{-1}	99.70 ± 1.03
44	**HC + O_3**	50	60	7	0.46	1.21	0.9×10^{-1}	99.80 ± 1.18
45	**HC + H_2O_2**	50	180	7	43.96	3.33	2.0×10^{-4}	3.06 ± 0.04
46	**HC + H_2O_2+O_3**	50	60	7	H_2O_2: 14.65; O_3: 0.46	1.61	0.8×10^{-1}	99.19 ± 1.06
47	**HC + UV + O_3+H_2O_2**	50	30	7	H_2O_2: 7.32; O_3: 0.23	1.36	3.2×10^{-1}	99.73 ± 0.93

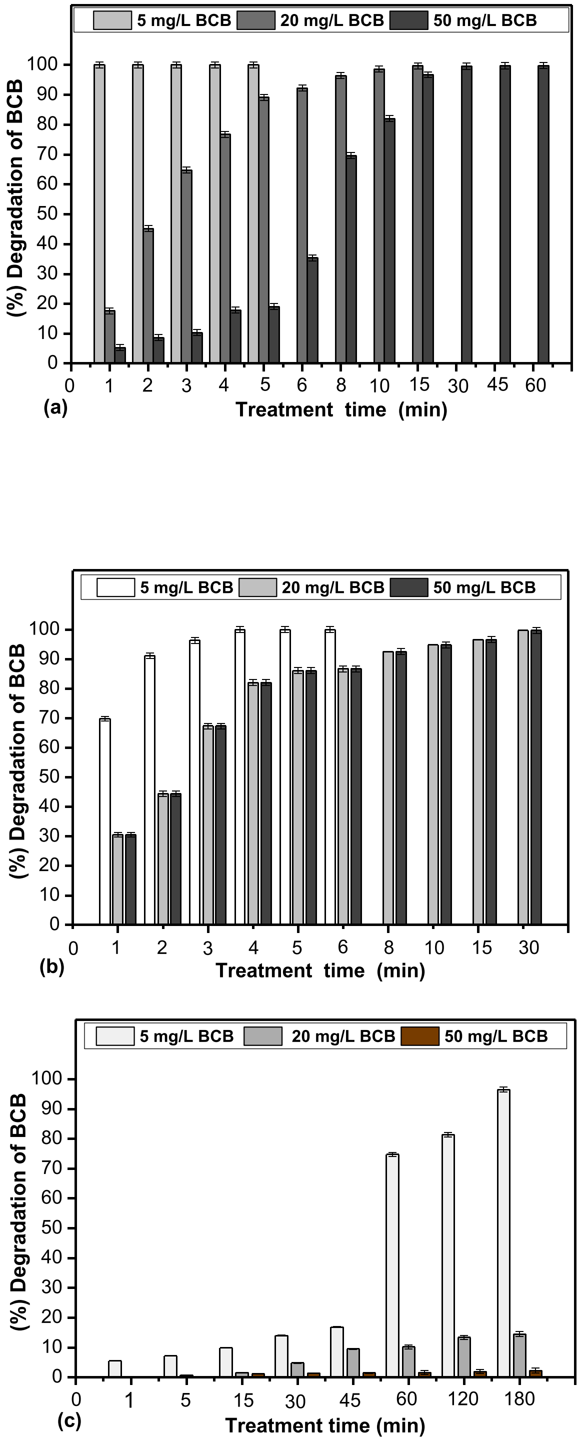


Fig. 7. Effect of initial concentration (5; 20; 50 mg/L) BCB for different processes of HC combined with advanced oxidation processes; 20 °C; neutral pH (6–7); ozone flowrate 0.5 L/min; H_2O_2 0.22 mL/min a) Effect of initial concentration of (5; 20; 50 mg/L) BCB for process of HC/O_3 (r_{ox} 0.27; r_{ox} 1.01; r_{ox} 1.21) (Table 4; exp 15, 38, 44) b) Effect of initial concentration of (5; 20; 50 mg/L) BCB for process of HC/UV/O_3/H_2O_2 (rox 2.26; rox 0.57; 1.36) (Table 4; exp 25, 41, 47) c) Effect of initial concentration of (5; 20; 50 mg/L) BCB for process HC/H_2O_2 (r_{ox} 8.31; r_{ox} 8.34; r_{ox} 3.33) (Table 4; exp 16, 39, 45).

3.9. Role of scavengers in the degradation of BCB

Since the dye degradation under the effect of ozone occurs in the time interval of 1–5 min, ozone was considered as the most effective oxidant used for the degradation of BCB molecules. To study whether the degradation of BCB takes place due to $HO^{\bullet}$ radicals or superoxide radicals $O_2^{\bullet-}$, several scavengers were used. The scavengers selected for this purpose were: methanol, n-propanol, n-butanol, t-butyl alcohol (TBA), and p-benzoquinone (P-BQ). The alcohols were used as scavengers to investigate the formation and role of $HO^{\bullet}$in the dye degradation, whereas P-BQ was used as a $O_2^{\bullet-}$ scavenger. Their role has also been investigated by other researches [49,50].

Since the degradation of BCB by the combined process of HC/O_3 occur in only 1 min, therefore we compared the degradation efficiency (%) of BCB for the first minute of each experimental run with the addition of scavengers. A significant decline in the degradation efficiency (%) occurred in the presence of P-BQ, where the degradation efficiency decreased from 100% for HC/O_3 to only 11.24% for the combined process of HC + O_3/P-BQ. The presence of P-BQ extends the treatment time to 45 min. This can be explained by the presence of superoxide radicals ($O_2^{\bullet-}$) into the model solution formed from the ozone molecule. They are continuously generated; thus, immediate degradation of BCB in the presence of P-BQ was prevented by the fast reaction of superoxide radical ($O_2^{\bullet-}$) with this scavenger (Table 5; exp 53). In the case of alcoholic compounds, a significant decrease in the degradation of BCB takes place in the first minute of reaction in the presence of TBA, but within 3 min the dye faces complete degradation of 100%. Ozone directly reacts with TBA with a relatively high reaction rate constant (10^4-10^5 s^{-1}) [51]; thus the inhibition of BCB degradation is directly related to a competitive reaction of ozone with TBA and lasts until most of the TBA is oxidized (HC + O_3/TBA) (Table 5; exp 48).

Comparing from r_{ox} values for all processes, the lowest r_{ox} $0.27 < 1$ (Table 3; exp 15) corresponds to the HC/O_3 process in which 100% degradation was achieved in 1 min. This means that the excess of O_3 can be converted to other radicals such as ($O_2^{\bullet-}$, $HO^{\bullet}$, $OH_2^{\bullet}$) which contribute to high degradation in short treatment time. The reaction rate was slower with addition of P-BQ such that only 44.23% degradation occurred in 6 min. This compound was used as a commonly known scavenger of superoxide radicals. Significant influence on process effectiveness suggests important role of superoxide radicals in the degradation mechanism. Superoxide radical promotes oxidation reaction by the nucleophile addition of $O_2^{\bullet}$ into the dye molecule. This nucleophile favours a cleavage of benzene ring and subsequent complete mineralization of the compound [52]. Combining all obtained data, we propose that the radical species mainly responsible for the degradation of BCB dye are superoxide radicals ($O_2^{\bullet-}$), but it is worth noting that $HO^{\bullet}$ may also be involved in the degradation of BCB dye molecules.

3.10. Possible degradation mechanism of BCB

It is well known that the identification of by-products formed during AOP based treatment is a one of the important aspects in case of the development of new processes [53]. Thus, we analysed possible pathways of degradation of target pollutant to assess the risk of formation of harmful by-products. The first possible degradation pathway is based on the direct attack of the ozone gas to the azo double bond of the BCB [54], resulting in –N═N- cleavage. Superoxide radicals ($O_2^{\bullet-}$) mainly attack azo bonds, and this is typically reported in the degradation of azo dyes where the main reactive species responsible for dye degradation was found to be ($O_2^{\bullet-}$) [50], nevertheless presence of $HO^{\bullet}$ initiate -N-C- bond cleavage [55]. The cleavage of –N═N- and -C-N- produced the nitrosobenzene, naphthalene ring with the substituent, and 2-Amino-4,6-dichlorotriarine [47]. Superoxide radical ($O_2^{\bullet-}$) initiates cycloaddition reactions with unsaturated bonds in addition to electrophilic assault and leads to the creation of a carbonyl group (–C═O) or nitroso group (–NO) compounds [56]. Cationic dye molecules interact with $O_2^{\bullet-}$, $HO_2^{\bullet}$ or $HO^{\bullet}$ species to generate unstable intermediates. To detect the presence of intermediate by-products, the process samples were analysed by HPLC-UV/DAD technique. Gradient elution program was used in these studies to detect any additional peaks appearing during the HC-assisted degradation of BCB. The analytical method used in this studies is very sensitive - with detection limits for compounds having aromatic rings in their structure below 0.1 ppm). Thus, any intermediate by-products possible to be formed would be detected. The studies revealed that BCB is completely degraded, and there was no intermediate present in the samples. The complete disappearance of peaks on the HPLC chromatogram indicates the absence of any organic moiety. Analysis of final samples revealed that no additional compounds or by-products are present in the treated medium. These results confirmed the high removal efficiency of COD (almost 100%). The dye is a hetero-polyaromatic compound having nitrogen (N), oxygen (O), Zinc (Zn), and chlorine (Cl) atoms attached to the central aromatic ring. Initially, ozone selectively attacks activated aromatic rings or double bonds, which are both present in BCB dye. Owing to the elevated

Table 5
Role of scavengers in (%) degradation of BCB (neutral pH, 20 °C, 5 mg/L).

(%) Degradation of BCB						
Nr.exp	Processes	Time (min)				
		1	3	6	15	45
48	**HC + O_3/TBA**	1.3	40.9	100	–	–
49	**HC + O_3/n-propanol**	30.4	58.7	65.9	98.7	100
51	**HC + O_3/methanol**	59.6	100	–	–	–
52	**HC + O_3/n-butanol**	62.9	85.5	96.9	100	–
53	**HC + O_3/P-BQ**	11.24	21.06	44.23	97.03	98.03

electronic densities on these aromatic carbons replaced with electron-donor groups, they are particularly reactive with ozone, and the reaction will take place mainly concerning the carbon atoms situated in the ortho and para positions. The electron-withdrawing groups (–COOH, $–NO_2$) replaced aromatics are weakly reactive to ozone. The molecular structure of BCB dye contains both electron-donating groups (–OH, –NHR) and electron-withdrawing groups ($ZnCl_2$). Hence, ozone reactions should occur initially in certain preferential sites. Sites with high electronic density have been recognized, and the evaluation has shown that ozone attacks are likely to occur in the azo group [57,58]. The degradation pathway similarly includes the following reactions (i) hydroxylation reaction where deformation of C–H bonds intended to the formation of small carbon chain compounds (ii) direct oxidation cleavage of benzene ring in BCB molecules (iii) cleavage of $C{=}O$ in the hetero-ring of BCB molecule [59] (iv) splitting of the chromophoric azo $C–N{=}C$ bond via the direct oxidation [60]. The proposed degradation pathway of BCB is illustrated in (Fig. 8) .

3.11. *Influence of water matrix on the degradation rate of BCB dye*

The presence of inorganic anions affects the decolorization of dye-polluted wastewater due to their specific properties. NaCl imposes the fiber staining by the ability to enhance the dye diffusion being therefore easily absorbed in fiber; meanwhile, carbonate and bicarbonate ions increase the pH media, which helps in dye-fiber binding assisted through the formation of covalent bonds [61]. Sodium sulfate helps in dye fixation in fabric because it reduces negative charges in fiber [62]. Inorganic anions scavenge $HO^{\bullet}$ and inhibit dye degradation. Thus, these inorganic ions were studied as potential inhibitors of degradation that can be present in real wastewaters.

Since HC/O_3 process was considered as the most effective process to be (Degradation efficiency of 100% in 1 min) therefore, it was seen reasonable to study the effect of the presence of co-existing compounds on its effectiveness in the degradation of BCB. For this purpose, two different concentrations (5 and 10 mM) of salts (NaCl, Na_2SO_4, Na_2CO_3, Ca $(NO_3)_2$ under two different pH values (7.0 and 10.0) were taken into consideration. These studies revealed (Fig. 9) that the presence of the salts, as mentioned above, initiates a slight decrease in the degradation (%) of BCB dye. Comparison of BCB degradation results within the same group of anions concentration (10 mM) under two different pH (7.0 and 10.0) revealed that the lowest degradation was obtained in the presence of sulfate and carbonate

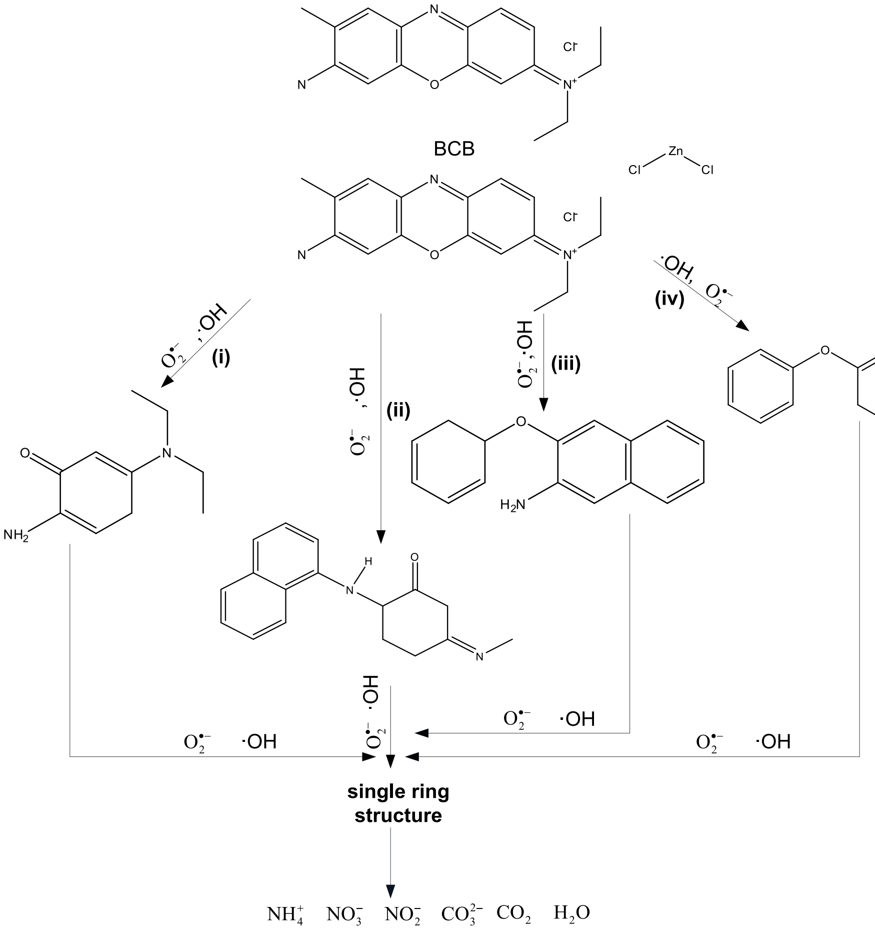


Fig. 8. Proposed degradation mechanism of BCB dye.

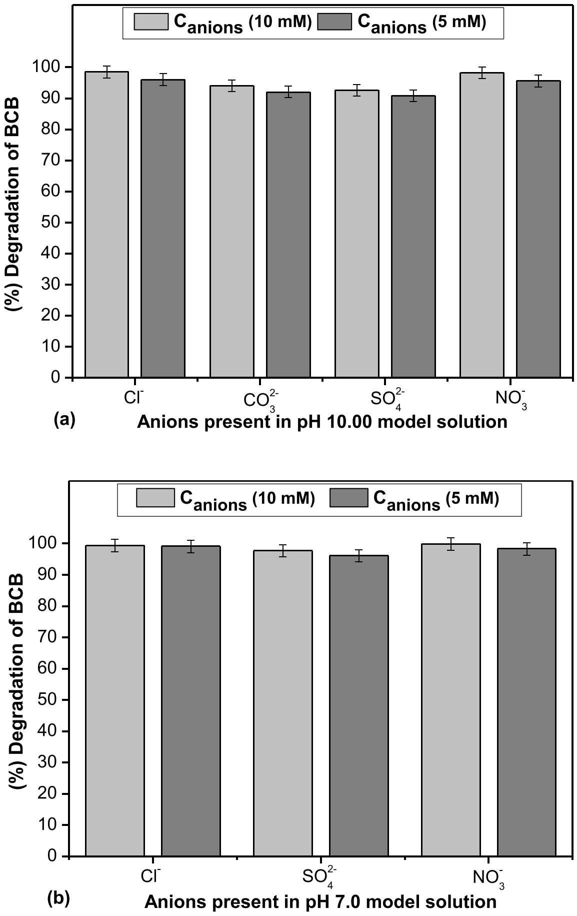


Fig. 9. Effect of water matrix in degradation of 5 mg/L BCB under combined process of HC + O_3 (ozone flowrate 0.5 L/min; 1 min treatment time). Comparison with (100% deg; 1 min treatment time) (Table 3; exp 15). a) BCB degradation in presence of anions and pH 10.0 media (Table 6; exp 54–57) b) BCB degradation in presence of anions and pH 7.0 media (Table 6; exp 58–60).

anions with 91 and 92% degradation in the first minute of treatment, meanwhile complete degradation was achieved within 5 min of treatment time. 100% of degradation was achieved in 5 min of treatment time. Carbonate anion reacts with hydroxyl radical, resulting in the formation of carbonate radical. It is a very selective and strong one-electron oxidant, competing, therefore, with hydroxyl radicals and scavenging them [61]. In a higher concentration of carbonates present in aqueous media, the scavenging effect is more visible [61]. The same effect was also observed for a lower concentration of anions (5 mM), where the lowest degradation (%) of BCB still was obtained in the presence of sulfate and carbonate anions with degradation efficiency (%) of 92.6 and 94%, respectively. The

Table 6
Effect of anions in the degradation of BCB. Comparison of (%) degradation between two different concentrations of anions (10 mM; 5 mM) and two different pH media (10.0; 7.0) in BCB removal under the combined process of hydrodynamic cavitation and ozone (ozone flow rate 0.5 L/min; 20 °C; 1 min treatment time). HC + O_3 (100% degradation; 1 min treatment time).

% Degradation of BCB in 1 min, in the presence of anions					Max treatment time to reach 100% degradation in the presence of anions (min)	
The concentration of present anions in the 5 mg/L model solution of BCB			10 (mM)	5 (mM)		
Nr. exp	Anions	pH	(%) Deg of BCB	(%) Deg of BCB	10 (mM)	5 (mM)
54	Chloride	10	96.0 ± 0.22	98.5 ± 0.21	5	3
55	Carbonate	10	92.0 ± 0.20	94.0 ± 0.22	5	4
56	Sulfate	10	91.0 ± 0.20	92.6 ± 0.20	5	5
57	Nitrate	10	95.0 ± 0.21	98.2 ± 0.22	5	3
58	Chloride	7	99.3 ± 0.22	99.1 ± 0.21	3	2
59	Sulfate	7	96.0 ± 0.21	97.7 ± 0.19	5	5
60	Nitrate	7	97.8 ± 0.23	98.3 ± 0.19	5	3

maximum degradation of 100% was achieved in 5 and 4 min of treatment in the presence of sulfate and carbonate anions, respectively. As it corresponds to the effect of other anions, their inhibition effect was small and comparable in between them, and degradation values varied from 95 to 99.8% for nitrate (10 mM nitrate at initial pH of 10.0) in the first minute of treatment time but it is worth mentioning that removal efficiency of 100% was obtained in only 5 min treatment time. The fastest time to achieve 100% in the presence of anions was 2 and 3 min in case of chloride (pH 7.0; 10 mM and 5 mM) and nitrate (5 mM; pH 10.0 and pH 7.0) anions, respectively.

Further experimental results of the effect of anions on the degradation (%) of BCB dye are compiled in Table 6. Results were compared with the experimental value found in (Table 3; exp15) for HC/O_3 in which the degradation efficiency of 100% was achieved within the short treatment time of 1 min. It can be seen that sulfates and carbonates exhibited the most suppressive effect among the studied anions. From experimental observations, we found out that as the concentration of anion increases, degradation of dye slightly decreased. This effect is even more enforced in basic pH conditions, herewith the treatment process of HC/O_3 can be considered as a promising process for the degradation of organic pollutants such as organic dyes in real industrial wastewaters containing several co-existing inorganic compounds moreover it can be implemented in future studies for treating saline wastewaters containing a high value of TDS.

4. Economic assessment

Treatment costs of the model solution containing BCB dye treated by the HC process combined with AOPs were estimated. The analysis was performed using the same methodology as in the previous study of our research team [63]. The compilation is provided in Table 7. They were calculated considering such factors as treatment time, cost of oxidants, and cost of electric energy. The HC system uses the power of 1100 W, and the ozone generator uses the power of 380 W. The cost of electricity in 2019 for industrial customers in Poland is 0.164 US dollars (USD) per 1 kWh (3600 kJ). The cost of treatment was first estimated for each 6-L batch volume of experiments, and then it was recalculated to 1 m^3 model solution treatment.

Two alternative options for the treatment process were analysed. Higher degradation of the BCB dye takes 0.5 M place at basic pH conditions for the sole use of the HC process with degradation efficiency of 99.5% in treatment time of 180 min (Table 2; exp 12). In this case, the cost of treatment of one cubic meter of effluents containing 5 mg/L of BCB dye was estimated at 15.03 USD ($). In the case of real effluents having a primary, basic pH – the HC should be a process of the first choice.

The second option relates to the treatment of effluents containing BCB dye at neutral pH conditions. Correction of pH to basic conditions to perform the treatment and further back-correction to neutral pH for effluent discharge could be not reasonable from the practical point of view. From the aspect of cost estimation, both experiments share the same cost of treatment of 15.03 USD ($) (Table 7; exp 13, 12). The most economical approach for the degradation of BCB dye by the HC–based AOPs, turned out to be the combined process of HC/O_3 with the total treatment cost of 0.15 USD/m^3, followed by sole O_3 (0.73 USD/m^3) and HC/UV/O_3/H_2O_2 (0.99 USD/m^3) (Table 7; exp 15, 14, 25). It was observed that the lowest treatment costs belong to the processes with a short treatment time (up to 1 min) for HC/O_3, and UV/O_3; HC/UV/O_3/H_2O_2 (up to 5 min). In case of cost evaluation for the highest concentration of BCB dye (20 and 50 ppm), the lowest treatment costs belong to the combined process of HC/UV/O_3/H_2O_2 (0.99 and 5.95 USD/m^3) (Table 7; exp 25, 47).

The efficiency of combined processes of hydrodynamic cavitation and AOPs also was expressed in terms of electrical energy per order (E_{EO}). It was calculated for the most effective processes to give an insight into the significance of usage of hydrodynamic cavitation. Electrical energy per order (E_{EO}) is a parameter that describes the amount of electrical energy needed to decline the concentration of pollutants by one order of magnitude (90% reduction) in a unit of volume water [64,65]. The equation used to determine electrical energy per order (E_{EO}) is the same equation reported by Asaithambi et al. [66], where he determined the removal of the organic pollutant from industrial wastewater using the UV/Fe^{2+}/H_2O_2 process, and he determined the electrical energy per order for processes applied in wastewater treatment. The evaluation of (E_{EO}) was limited to processes that attained 100% degradation of BCB. This analysis revealed that the lowest electrical energy per order (E_{EO}) was obtained for the combined process of HC/O_3 with a value of 0.03 kWh m^{-3} $order^{-1}$ meanwhile (E_{EO}) for the process of sole ozonation was 0.74 kWh m^{-3} $order^{-1}$. These results are followed then by the combined process of HC/UV/O_3/H_2O_2 (0.75 kWh m^{-3} $order^{-1}$) and sole process of UV/O_3/H_2O_2 (3.01 kWh m^{-3} $order^{-1}$). Higher (E_{EO}) values were obtained with an increase in the concentration of BCB from 5 mg/L (HC/O_3; 0.03 kWh m^{-3} $order^{-1}$) to 20 mg/L (HC/O_3; 6.70 kWh m^{-3} $order^{-1}$). This can be explained by the fact that, with an increase in the concentration of dye more time is needed to completely degrade the BCB as a result more energy is required in the system. Effectiveness of hydrodynamic cavitation is once more reinforced by comparing (E_{EO}) for the processes as mentioned above, and it can be understood that by using HC, (E_{EO}) was strongly declined comparing sole processes to hydrodynamic cavitation based combined processes. Evaluated results of electrical energy per order are presented in the (Table 7; exp 14, 15, 22, 23, 24, 25, 38, 40, 41). Therefore, it can be concluded that amount of energy needed for wastewater treatment by hydrodynamic cavitation aided AOPs is less than sole hybrid AOP processes, contributing thus to the cost-effectiveness of wastewater treatment processes.

5. Conclusions

These studies revealed that the combined process of hydrodynamic cavitation and ozone HC/O_3 may be considered as a very effective method in the degradation of BCB dye-containing effluents. Broadly explained, our findings indicate that under optimal parameters such as C_v (0.27), inlet pressure (1.70 bar) the sole process of hydrodynamic cavitation provided only 10% BCB degradation in 180 min treatment time. Meanwhile, the addition of ozone increased degradation of dye to 100% in only 1 min of treatment

Table 7
Evaluation of the cost of treatment for combined processes of HC and AOPs in three different concentrations, neutral pH, 20 °C.

Nr. exp	Processes	C (mg/L)	Time (min)	Amount of O_3 (g)	Amount of H_2O_2; PS (mL)	Cost of oxidant [USD]	Energy Consumption [kJ/1m^3] (100% degradation)	Cost of Energy [USD]	Total cost of treatment [USD/m^3]	E_{EO} (kWh m^{-3} order^{-1})
13	**Sole Cavitation**	5	180	–	–	–	11880	0.541	15.03	–
14	**Sole Ozone**	5	5	0.04	–	–	579	0.026	0.73	0.74
15	**HC + O_3**	5	1	0.01	–	–	116	0.005	0.15	0.03
16	**Sole H_2O_2**	5	180		39.6	0.32	11880	0.541	24.05	–
17	**HC + H_2O_2**	5	180	–	39.6	0.32	11880	0.541	24.05	–
22	**Sole H_2O_2+O_3**	5	15	0.11	3.3	0.03	1737	0.079	17.70	6.70
23	**HC + H_2O_2+O_3**	5	8	0.06	1.76	0.01	926	0.042	9.44	1.91
24	**Sole UV + O_3+H_2O_2**	5	10	0.08	2.2	0.02	1170	0.053	1.98	3.01
25	**HC + UV + O_3+H_2O_2**	5	5	0.04	1.1	0.01	585	0.027	0.99	0.75
37	**Sole Ozone**	20	30	0.23	–	–	3474	0.158	4.40	–
38	**HC + O_3**	20	15	0.11	–	–	1737	0.079	2.20	6.70
39	**HC + H_2O_2**	20	180		39.6	0.32	11880	0.541	24.05	–
40	**HC + H_2O_2+O_3**	20	30	0.23	6.6	0.05	3474	0.158	5.90	26.81
41	**HC + UV + O_3+H_2O_2**	20	5	0.04	1.1	0.01	585	0.027	0.99	0.75
43	**Sole Ozone**	50	60	0.46	–	–	6948	0.317	8.79	–
44	**HC + O_3**	50	60	0.46	–	–	6948	0.317	8.79	–
45	**HC + H_2O_2**	50	180	–	39.6	0.32	11880	0.541	24.05	–
46	**HC + H_2O_2+O_3**	50	60	0.46	13.2	0.11	6948	0.317	11.80	–
47	**HC + UV + O_3+H_2O_2**	50	30	0.23	6.6	0.05	3510	0.160	5.95	–
35	**HC/PS (1M; 50°C)**	5	60	–	13.2	1.23	3960	0.180	16.40	–
12	**HC** (pH **10**)	5	180	–	–	–	11880	0.541	15.03	–

time. The synergistic coefficient of 1.84 for the combined process of HC/O_3 indicated the high effectiveness of both methods as a successful attempt, which led to total dye degradation. Additionally, the rate of BCB degradation for the combined process of HC/O_3 is almost twice the added values of independent processes.

Despite the highest degradation achieved, the time of treatment is also the shortest compared to other processes. Finally, this rapid process revealed to be the cheapest one with a treatment cost of 0.15 USD/m^3 calculated for degradation efficiency of 100% in treatment time of 1 min. These results appear to be consistent with comparison performed for studied processes in terms of electrical energy per order (E_{EO}), where once more, it was proved the effectiveness of combined processes of HC and other external oxidants. A significant difference between E_{EO} for Sole ozone (0.74 kWh m^{-3} order^{-1}) and combined process of HC/O_3 (0.03 kWh m^{-3} order $^{-1}$) reinforce the finding that the use of hydrodynamic cavitation and ozone lower the treatment time and consequently the cost of treatment. Rapid degradation of the target pollutant in the present study allows performing the treatment on-line without the need for high volume tanks due to short retention time needed. Finally, low costs of treatment make the developed method ideal for implementation in real industrial practice.

CRediT authorship contribution statement

Elvana Cako: Conceptualization, Methodology, Validation, Investigation, Formal analysis, Writing - original draft, Data curation, Writing - review & editing. **Kumaravel Dinesh Gunasekaran:** Investigation, Formal analysis. **Reza Darvishi Cheshmeh Soltani:** Validation, Writing - review & editing. **Grzegorz Boczkaj:** Conceptualization, Methodology, Validation, Investigation, Formal analysis, Writing - original draft, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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