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Effective degradation of sulfide ions and organic sulfides in cavitation-based advanced oxidation processes (AOPs)

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ABSTRACT

The paper presents the results of investigations on the effectiveness and reaction rate constants of the oxidation of sulfide ions and organic sulfides in real industrial effluents from the production of bitumens (2000 mg S²⁻ L⁻¹) using hydrodynamic and acoustic cavitation. The content of the effluents was analysed in terms carbon disulfide, dimethyl sulfide, and di-*tert*-butyl disulfide concentration. A possibility of complete oxidation of sulfides by cavitation alone as well as by its combination with external oxidants such as hydrogen peroxide, ozone or perozone was demonstrated. The oxidation time for the most effective processes is as little as 15 min. Due to the presence of sulfide ions, the effluents from the production of bitumens were oxidized at a strongly alkaline pH. The results of this study reveal the advantage of performing advanced oxidation processes (AOPs) at a basic pH. The effective degradation of sulfide ions enables performance of further degradation of organic contaminants at an acidic pH, ensuring high efficiency of treatment based, for example, on the Fenton reaction without the risk of release of hydrogen sulfide to the atmosphere. The results of this research are applicable to all kinds of caustic effluents for which the lack of possibility of pH adjustment limits their efficient treatment.

1. Introduction

Recent years have witnessed a rapid increase of interest in the application of cavitation in chemical engineering, including treatment of various industrial effluents [1–4]. Cavitation is a physical phenomenon involving the rapid formation and collapse of cavities in a liquid in regions of very low pressure, resulting in formation of the reactive hydroxyl radicals ([•]OH), reacting with the target contaminants present in liquid phase [5–8].

Cavitation has found numerous applications, including chemical synthesis, petrochemical industries, biotechnology, treatment of various wastewaters (e.g., industrial effluents) [9,10], and decomposition of polymeric materials [11,12]. The methods most commonly used for the treatment of aqueous effluents include cavitation affected by ultrasound (so-called acoustic cavitation [13]) and hydrodynamic cavitation resulting from fluid flow in a constricted section of a pipe (e.g., Venturi tube) [14].

Sulfides belong to the group of contaminants whose concentration should be monitored during assessment of the quality of aqueous solutions. They are characterized by a very unpleasant odor and they constitute a serious threat to equilibrium of the entire ecosystem, mostly due to their acid properties. Thus, sulfides cause surface water acidification, thereby negatively the fauna and flora. They are also responsible for the corrosion of metal and concrete elements and the substantial depletion of water oxygenation, causing irreversible environmental damages. Sulfur compounds are anthropogenic pollutants, their major sources being processing of fossil fuels [15]. Industrial effluents rich in sulfides must be treated prior to discharge into aquatic and terrestrial environments. Additionally, effluents containing even trace concentrations of sulfides can poison catalysts, thus making it impossible to perform catalytic reactions [16].

The methods used so far to remove sulphides from aqueous solutions are based mainly on the use of strong, low-molecular-weight oxidants [15]. The most common for this purpose are chlorine, sodium hypochlorite, air, ozone, oxygen or hydrogen peroxide [17–19]. How-

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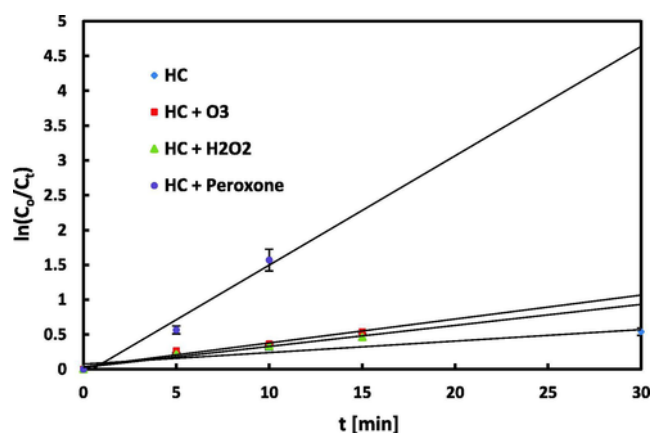


Fig. 1. Decomposition of sulfide ions during first 30 min of hydrodynamic cavitation treatment processes.

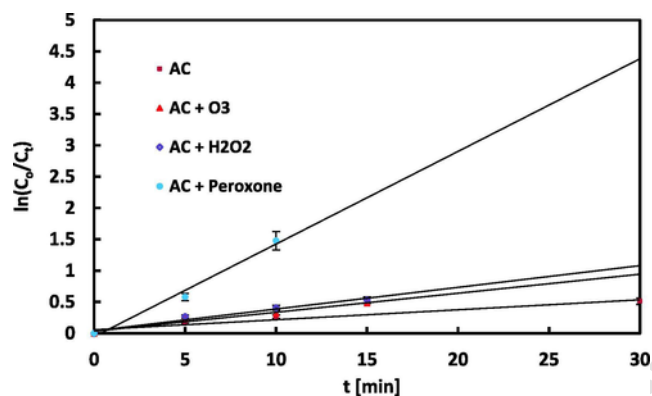


Fig. 2. Decomposition of sulfide ions during first 30 min of acoustic cavitation treatment processes.

ever, the use of these types of oxidants is limited to the total reduction of the sulphide content. In addition, strong oxidants, in the case of usage of excess of oxidants, additionally contaminates the treated solution [16,17]. Furthermore, chlorine based oxidants increase the risk of corrosion, thus are not popular in industrial practice. To completely remove sulfides, expensive heterocyclic oxidizing agents, such as, copolymers, should be used. However, this forces the need for additional operations to recover the copolymer so that it can be reused [15]. The phenomenon of cavitation does not require the use of any additional chemical oxidants. The effectiveness of hydroxyl radicals generated in the cavitation process allows for the complete remove the sulphides from treated solutions. In many cases, the treatment processes using cavitation phenomenon are not adequately effective for the complete degradation of various contaminants present in effluents; however, they can efficiently eliminate a specific group of chemical compounds whose presence limits the possibility of the application of effective treatment technologies. An interesting example of such a case is the presence of sulfide ions in strongly caustic effluents from the production of bitumens. There are various industrial effluents with alkaline conditions containing sulfide ions as well as organic species. In such cases, the use of highly effective AOPs, such as those based on the Fenton reaction, is impossible. The adjustment of the initial pH from strongly basic to acidic would result in the emission of hydrogen sulfide gas. Hence, there is an urgent need to develop an effective method for the reduction of total load of contaminants under basic conditions [20–23] or, alternatively, the use of sequential treatment, wherein in the first stage the contaminant precluding pH adjustment (i.e., sulfide ions) would be eliminated.

The present paper demonstrates that the cavitation used as a sole treatment process as well as in combination with AOPs enables very effective degradation of sulfide ions and organic sulfides. Thus far, no literature reports are available in which changes in sulfide ion concentrations in industrial effluents during AOPs has been investigated. The effluents from the production of bitumens containing ca. 2000 mg S²⁻/L were investigated. The efficiency of the cavitation phenomenon regarding the degradation organic sulfides present in the effluents was also investigated.

2. Materials and methods

2.1. Chemicals

Effluents from the production of bitumens and rich in sulfides was obtained from a bitumen oxidation installation based on the Biturox process (Lotos Asphalt, Grupa Lotos S.A., Gdańsk, Poland), (pH: 10.5; COD: 20,000 mg O₂L⁻¹, BOD: 6000 mg O₂L⁻¹, S²⁻: 2000 mg L⁻¹; content of the investigated organosulfur contaminants: carbon disulfide: 0.6–1.0 mg L⁻¹; dimethyl sulfide: 1.0–1.5 mg L⁻¹; di-tert-butyl disulfide: 1.0–2.0 mg L⁻¹). Ozone was produced in a Tytan 32 ozone generator (Erem) at a rate of 12.32 g h⁻¹. A 30% hydrogen peroxide solution (Avantor Performance Materials Poland S.A., Poland) was used for the experiments.

2.2. Acoustic and hydrodynamic cavitation

The removal of sulfides (including the following organosulfur contaminants: carbon disulfide, dimethyl sulfide and di-tert-butyl disulfide) from the effluents using acoustic and hydrodynamic cavitation combined with other oxidizing agents such as hydrogen peroxide, ozone and peroxone (ozone & hydrogen peroxide) was carried out in an experimental set-up described in our previous reports [20–22]. 5-L samples of the effluent containing 2000 mg S²⁻L⁻¹ and organosulfur concentration of up to 2 ppm were treated. Treatment by the acoustic cavitation was carried out for 360 min in a 1000-W acoustic cavitation reactor at the maximum power of 173 WL⁻¹ and a flow rate of 355 Lh⁻¹. Hydrodynamic cavitation was also performed in an experimental set-up described previously [17–21] at a flow rate of 520 Lh⁻¹ allowing achievement of a maximum oxidation effect (cavitation number 0.140). Effluent samples were withdrawn at a three-hour interval (0, 5, 10, 15, 30, 45, 60, 120, and 180 min). Hydrogen peroxide (30%) was fed into the treatment system by a S-7110 isocratic high pressure pump (Merck-Hitachi, Japan) at a flow rate of 3 ml min⁻¹.

2.3. Analytical procedures

2.3.1. Sulfide ions analysis

The concentration of sulfide ions was measured using a EA9/S-01 silver/sulfide ion-selective electrode (Hydromet, Poland) and a CP-505 pH-meter (Elmetron, Poland). A 5-point calibration curve was applied for the quantitation.

2.3.2. Volatile sulfur compounds (VSCs) analysis

The concentration of VSCs was measured using an Autosystem XL gas chromatograph equipped with a flame photometric detector (FPD) and an autosampler (Perkin Elmer, USA). Separation conditions: DB-1 column (60 m × 0.32 mm × 1.0 μm, BGB-1 Switzerland), carrier gas: helium at 2.0 cm³ min⁻¹, injection port temperature: 300 °C, injection mode: split 1:5, temperature program: 40 °C (4 min)-ramped at 10 °C min⁻¹ to 300 °C (10 min), total analysis time 40 min. FPD operating conditions: temperature 390 °C, gas flow rates: H₂ 75 ml min⁻¹, air 90 ml min⁻¹. Sample preparation was carried out using dispersive liquid-liquid microextraction (DLLME) described in an earlier study [24].

Table 1
Effectiveness of the decomposition of sulfide ions, dimethyl sulfide, carbon disulfide and di-*tert*-butyl disulfide by the various treatment processes.

	Time [min]	Treatment processes							
		HC	HC + O ₃	HC + H ₂ O ₂	HC + Peroxone	AC	AC + O ₃ *	AC + H ₂ O ₂ **	AC + Peroxone**
S ²⁻		<i>Decomposition [%]</i>							
	5	17.5 ± 0.3	23.4 ± 0.4	19.5 ± 0.3	43.2 ± 0.5	15.3 ± 0.3	21.6 ± 0.5	23.5 ± 0.7	44.1 ± 0.2
	10	26.8 ± 0.4	30.6 ± 0.3	28.5 ± 0.6	79.2 ± 1.5	23.5 ± 0.5	27.2 ± 1.0	33.5 ± 0.4	77.2 ± 0.3
	15	36.2 ± 0.2	41.7 ± 0.5	37.1 ± 2.1	99.9 ± 0.1	37.2 ± 0.3	38.2 ± 1.6	41.2 ± 1.2	99.9 ± 0.1
	30	41.8 ± 0.6	100 ± 0.2	100 ± 0.4	100 ± 0.1	40.2 ± 0.4	99.8 ± 0.1	100 ± 0.1	100 ± 0.1
	45	67.2 ± 0.4				66.6 ± 1.4	100 ± 0.1		
	60	71.5 ± 0.5				71.6 ± 0.6			
	120	99.4 ± 0.2				97.5 ± 0.5			
	180	100 ± 0.1				100 ± 0.1			
Dimethyl sulfide	5	14.5 ± 0.6	19.5 ± 0.5	24.4 ± 2.0	33.3 ± 1.1	12.2 ± 0.5	18.5 ± 0.9	21.6 ± 1.4	26.2 ± 0.2
	10	32.3 ± 0.3	39.5 ± 0.5	37.5 ± 1.3	59.2 ± 2.0	29.5 ± 1.8	34.3 ± 1.1	41.2 ± 1.1	54.6 ± 1.0
	15	44.2 ± 0.2	63.2 ± 0.6	62.5 ± 1.2	81.2 ± 1.3	36.3 ± 1.3	55.3 ± 1.1	64.2 ± 0.7	78.6 ± 2.1
	30	76.2 ± 0.2	100 ± 0.1	100 ± 0.5	100 ± 0.6	72.3 ± 1.2	100 ± 0.2	100 ± 0.2	100 ± 0.3
	45	89.2 ± 1.6				84.3 ± 0.6			
	60	94.3 ± 2.1				93.1 ± 2.2			
	120	100 ± 0.3				100 ± 0.3			
Carbon disulfide	5	17.2 ± 0.3	33.2 ± 0.7	27.6 ± 0.6	44.6 ± 1.2	18.3 ± 0.3	26.3 ± 0.2	31.2 ± 1.0	39.3 ± 0.6
	10	33.3 ± 0.6	46.3 ± 0.5	46.6 ± 1.7	61.3 ± 1.2	32.2 ± 0.3	44.2 ± 0.7	45.3 ± 0.6	51.2 ± 1.1
	15	58.3 ± 0.6	80.3 ± 0.2	78.3 ± 0.6	100 ± 0.3	59.6 ± 0.5	76.2 ± 0.4	81.2 ± 1.0	100 ± 0.3
	30	81.2 ± 1.1	100 ± 0.3	100 ± 0.2		79.7 ± 1.4	98.1 ± 0.9	100 ± 0.4	
	45	83.2 ± 1.3				81.6 ± 1.4	100 ± 0.2		
	60	86.3 ± 1.1				84.7 ± 0.6			
	120	100 ± 0.2				99.8 ± 0.1			
180					100 ± 0.7				
Di- <i>tert</i> -butyl disulfide	5	26.2 ± 0.2	38.2 ± 0.3	47.7 ± 0.3	48.5 ± 0.8	24.6 ± 2.0	33.2 ± 0.3	49.6 ± 0.7	51.2 ± 0.3
	10	31.2 ± 0.7	66.3 ± 1.4	65.2 ± 0.9	99.8 ± 0.1	34.6 ± 1.5	56.6 ± 0.6	71.6 ± 0.6	100 ± 0.4
	15	63.3 ± 1.1	92.2 ± 0.7	99.8 ± 0.1	100 ± 0.1	62.6 ± 1.2	87.6 ± 0.2	100 ± 0.2	
	30	74.2 ± 0.4	100 ± 0.1	100 ± 0.2		69.6 ± 1.5	100 ± 0.3		
	45	85.2 ± 0.4				82.2 ± 0.4			
	60	93.2 ± 0.5				89.6 ± 1.2			
	120	99.9 ± 0.1				100 ± 0.1			
180	100 ± 0.2								

*Ozone dose (O₃ and peroxone processes): 2.4 g/dm³·h.

**Hydrogen peroxide dose (H₂O₂ and peroxone processes): 12 g/dm³·h.

3. Results and discussion

3.1. Degradation of sulfide ions (S²⁻) in hydrodynamic and acoustic cavitation treatment processes combined with O₃, H₂O₂ and peroxone

The effectiveness of oxidation of sulfide ions present in bitumens effluent treated by the investigated cavitation processes is depicted in Figs. 1 and 2. Rate constants for the first-order oxidation reaction were determined from the following relationship: $\ln(C_0/C_t) = kt$, where C_0 and C_t are concentrations of the target contaminant in raw effluent and in the treated effluent after a specific time of oxidation, respectively. Moreover, k and t are defined as rate constant and oxidation time, respectively. The data on rate constant values of the oxidation reactions are compiled in Table 2. The results demonstrate that the first-order model of the reaction describes well the changes in the concentration of the target contaminant during cavitation process. Complete oxidation of the sulfide ions was achieved after 15 min of hydrodynamic or acoustic cavitation combined with peroxone. For the other treatment processes, the decomposition efficiency of sulfide ions did not exceed 45% at the same reaction time. After 30 min of the treatment process, the complete oxidation of sulfide ions was observed for hydrodynamic and acoustic cavitation aided by ozone or hydrogen peroxide. For hydrodynamic or acoustic cavitation alone, the time required to achieve the complete oxidation of sulfide ions was 3 h. It should be pointed out that the number of passes of the entire volume of the effluent being

treated through the cavitation zone of ultrasonic (transducer zone) and hydrodynamic (constriction zone) reactors at the flow rates used was 1.1 and 1.7 pass/min, respectively. This means that in the HC reactor organosulfur contaminants were present in the collapse zone more often, which resulted in slightly higher efficiencies of oxidation for the same times of treatment compared with AC. A detailed course of oxidation for individual cavitation processes is shown in Table 1. Both hydrodynamic and acoustic cavitation are violent physical phenomena which allow an efficient generation of [•]OH in the bulk solution for the decomposition of the target contaminant. The thermal decomposition of water molecules taking place during the collapse of gas bubbles formed in the cavitation zones results in the generation of [•]OH [25–26]. Conventional methods for the removal of sulfides or other reducing compounds (such as cyanides) from water or wastewater involve their oxidation using low-molecular-weight oxidants, e.g., oxygen, air, sodium chlorate, ozone or hydrogen peroxide as well as their direct precipitation by flocculation and coagulation [15,16]. However, the application of these individual oxidation/precipitation methods does not allow the removal of trace amounts of contaminants [15]. Furthermore, addition of excessive oxidizing or precipitating agents is often practiced, resulting in the re-contamination of the solution being treated. In such a case, the use of so-called heterogeneous oxidizing agents is indicated [15,16]. These agents allow sulfide oxidation to proceed to completion and subsequent separation of excess of the oxidant. Examples of such reagents include reactive synthetic polymers, e.g., *N*-chlorosulfonamide, *N*-dichlorosulfonamide or *N*-bromosulfon-

Table 2Reaction rate constants (k) obtained during the oxidation of sulfide ions, dimethyl sulfide, carbon disulfide and di-*tert*-butyl disulfide by the various treatment processes.

Contaminant	Treatment processes							
	HC	AC	HC + H ₂ O ₂	AC + H ₂ O ₂	HC + O ₃	AC + O ₃	HC + Peroxone	AC + Peroxone
	k [min ⁻¹]							
S ²⁻	0.0165 ± 0.0015	0.0159 ± 0.0011	0.0302 ± 0.0019	0.0347 ± 0.0025	0.0343 ± 0.0024	0.0304 ± 0.0026	0.1570 ± 0.0140	0.1478 ± 0.0094
Carbon disulfide	0.0348 ± 0.0033	0.0331 ± 0.0025	0.1051 ± 0.0154	0.1140 ± 0.0180	0.0619 ± 0.0040	0.0579 ± 0.0045	0.095 ± 0.0145	0.0722 ± 0.0041
Dimethyl sulfide	0.0501 ± 0.0033	0.0449 ± 0.0036	0.0662 ± 0.0023	0.0671 ± 0.0017	0.0678 ± 0.0021	0.0530 ± 0.0030	0.1102 ± 0.0111	0.1057 ± 0.0091
Di- <i>tert</i> -butyl disulfide	0.0443 ± 0.0022	0.0372 ± 0.0016	0.1061 ± 0.0099	0.1267 ± 0.0097	0.1090 ± 0.0356	0.0842 ± 0.0034	0.1331 ± 0.0112	0.1442 ± 0.0102



Table 3
Calculations of wastewater treatment cost for complete degradation of sulfide ions by cavitation processes combined with AOPs.

Process	Treatment time [min] S ²⁻ degradation (100%)	Amount of oxidant [g]	Cost of oxidants [USD]	Energy consumption [kJ]	Cost of energy [USD]	Total cost of treatment process [USD L ⁻¹]
HC	180	0	0	11,880	0.363	0.073
AC	180	0	0	10,800	0.330	0.066
HC + H ₂ O ₂	30	30	0.74	1980	0.061	0.161
AC + H ₂ O ₂	30	30	0.74	1800	0.055	0.159
HC + O ₃	30	6.16	0	2790	0.085	0.017
AC + O ₃	45	9.24	0	3915	0.120	0.024
HC + Peroxone	30	6.16 + 30	0.74	2790	0.085	0.165
AC + Peroxone	30	6.16 + 30	0.74	2610	0.080	0.164

USD – US Dollars.

amide copolymers containing active halogen atoms at a +1 oxidation state in their structure [15]. The presence of halogen atoms enhances oxidation reactions. The amount of reagents needed to quantitatively oxidize sulfides to sulfates is used up and any excess amount recovered. This type of reagents enables removal of even trace amounts of sulfides. However, each unit operation increases the cost of treatment. Application of hydrodynamic and acoustic cavitation alone allows complete removal of sulfides without any additional oxidants during a reaction time of 3h without any deterioration of wastewater quality. For individual cavitation processes, ca. 40% of sulfide ions were oxidized during a reaction time of 15 min. The highest reaction rate constant of the sulfide ions oxidation was found for the HC process combined with peroxone ($k = 0.1570 \text{ min}^{-1}$). For the treatment based on the sole use of cavitation, oxidation of the sulfide ions was comparable for the HC process ($k = 0.0165 \text{ min}^{-1}$) and the AC process ($k = 0.0159 \text{ min}^{-1}$). This is mostly due to the great number of passes of the effluent through the cavitation zones per unit time. It should be pointed out that during the treatment of the effluent by the cavitation, a number of other organic contaminants are also oxidized, including aldehydes, ketones, and carboxylic acids, improving the quality of the effluent undergoing treatment [5,17–19].

3.2. Degradation of dimethyl sulfide

Dimethyl sulfide (C₂H₆S) is an organosulfur contaminant whose concentration in industrial effluents should be closely controlled. Recent studies indicate that the release of excessive amounts of dimethyl sulfide to the atmosphere aggravates the problem of global warming [24–26]. The main source of the emission of dimethyl sulfide to the atmosphere is the oceans. In natural environments, this contaminant is removed by way of photo-oxidation. Chromophoric dissolved organic matter present in seawater is the source of oxidants, such as oxygen, hydroxyl radicals or ozone, which degrade dimethyl sulfide and the resulting products are used up in biological processes [27,28]. During the first 15 min of the treatment processes, more than 60% of the contaminant was oxidized using the cavitation combined with supplemental oxidants (over 80% for the target contaminant was oxidized when the HC process was combined with peroxone. Extension of the treatment to 30 min resulted in the complete oxidation of dimethyl sulfide. The removal efficiency of dimethyl sulfide was obtained to be 70% by using cavitation processes alone (without external oxidants) within the reaction time of 30 min. The complete oxidation of dimethyl sulfide by the sole use of cavitation process took place after 120 min. As results, rate constants of the oxidation of dimethyl sulfide in individual treatment processes are similar. The fastest oxidation occurs during the HC process combined with the peroxone ($k = 0.1101 \text{ min}^{-1}$). No significant difference between the reaction rate constants of HC/AOPs and AC/AOPs was observed. The rate constants of oxidation reactions are listed in Table 2. It should be indicated that a significant slowing down of the oxidation reaction was observed between 60 and 120 min for the

sole use of cavitation. This could be attributed to an excessive consumption of $\cdot\text{OH}$ for the oxidation of intermediate byproducts of other organic contaminants present in the refinery effluent. Their presence was reported in previous papers [5,17–19]. Therefore, it can be expected that in the case of effluents with a lighter load of organic contaminants and less complex matrix, the efficiency of the decomposition of organosulfur contaminants and sulfide ions would be still higher.

3.3. Degradation of carbon disulfide

Anthropogenic sources of water contamination with carbon disulfide (CS₂) are mainly effluents of the synthetic fiber plants. Additionally, as a result of its physicochemical properties, CS₂ is often used as a solvent in the production of rubbers, waxes and various resins [29]. It also occurs naturally in crude oil; thus, it can be detected in refinery effluents. Carbon disulfide has an intense odor and acute toxicity towards animals and aquatic organisms. Bacteria and microorganisms present in activated sludge of the biological wastewater treatment plants are adversely affected by the carbon disulfide [27]. Furthermore, CS₂ hydrolyzes to hydrogen sulfide (H₂S) and carbonyl sulfide (COS) in aqueous solutions, which are malodorous and corrosive [30,31]. Consequently, this contaminant is likely to be removed from wastewater before being discharged into the biological wastewater treatment plants. Nearly 80% of carbon disulfide was oxidized during the first 15 min of the cavitation processes combined with external oxidants, while the sole use of cavitation process requires at least 30 min for the same removal efficiency. During the short reaction time of 15 min, the complete removal of CS₂ was observed by the cavitation processes combined with the peroxone, while the cavitation processes combined with hydrogen peroxide or ozone required a reaction time of 30 min for the complete oxidation of CS₂. Except for AC/O₃ process which needs a longer reaction time of 45 min for the complete oxidation of CS₂. The complete removal of CS₂ by the cavitation processes alone required 120 min. A decrease in the reaction rate was observed as the reaction time increased from 15 to 30 min and 30 to 120 min for the cavitation aided by hydrogen peroxide or ozone and the sole use of cavitation, respectively. This may be attributed to the presence of chemical species with higher affinity to $\cdot\text{OH}$, such as intermediates byproducts of the oxidation of organic contaminants occurring in the effluent, containing electrophilic centers (aldehydes and ketones). An increase in the amount of oxygenated organic compounds during the treatment of bitumens effluents by the AOPs has been observed and reported in another study [32]. This phenomenon results in increasing the consumption of $\cdot\text{OH}$ and consequently, decreasing the reaction rate constant of the CS₂ oxidation [28]. The sonochemical oxidation of CS₂ considering the kinetic and reaction pathways has been investigated by Adewuyi and Appaw [30]. They were found that the reaction rate constant of the CS₂ oxidation depend on, among others, ultrasonic frequency and the kind of oxidant. At a power of 280 W/L (20 kHz), the removal efficiency of CS₂ with the initial concentration of 0.03 M was

100% during the reaction time of 30 min. They were used air as the oxidant. In the presence of hydroxyl radicals, CS₂ was oxidized to hydrogen sulfate anion (VI) (HSO₄⁻) [30]. In the AC system used in this research the power used was 173 W/L (25 kHz). Under such conditions, the complete oxidation of CS₂ with the initial concentration of 1 mgL⁻¹ by the AC and HC processes was achieved within the reaction time of 180 and 120 min, respectively. The time required for the complete oxidation of CS₂ decreased to lower than 45 min when both AC and HC processes were combined with external oxidants. Another aspect of lower rates of degradation reactions is the concentration level of organic sulfides studied in this work. The concentration level of 1 mgL⁻¹ results in much lower probability of encounter of hydroxyl radicals with these contaminants compared with other organic contaminants present in the effluent [5]. It should be indicated that the reaction rate constants of the oxidation of CS₂ by the cavitation processes in combination with H₂O₂ was twice as much as those for dimethyl sulfide. The absence of methyl groups in the structure of CS₂ molecule facilitates its decomposition by hydroxyl radicals being added to the sulfur atom [29,30].

3.4. Degradation of di-tert-butyl disulfide

Di-tert-butyl disulfide is another organosulfur contaminant of anthropogenic origin. It is extracted from petroleum which can be produced as a relatively inexpensive intermediate during the synthesis of valuable organic compounds, such as chiral amines [31,33]. There is scarce information in the literature on hazards or physicochemical properties of this compound. However, its presence in the effluent of the production of bitumens as well as its structure (the presence of two sulfur atoms and a reactive tert-butyl group of a nucleophilic nature) indicate the need to monitor the concentration of this contaminant in the refinery effluents. It was found that cavitation processes aided by peroxone lead to the complete oxidation of this compound within the first 15 min. Over 90% of the contaminant was oxidized within the first 15 min of the treatment process when cavitation processes were combined with ozone or hydrogen peroxide, while the unaided cavitation processes yielded over 60% oxidation at the same reaction time. After the reaction time of 15 min, a substantial decrease in the oxidation rate of t-Bu₂S₂ by the cavitation processes took place. This can be attributed to the interaction of hydroxyl radicals by intermediates generated during the oxidation of other organic contaminants present in the effluent. The complete oxidation of t-Bu₂S₂ by the cavitation processes alone took place after 120 min of the treatment. It is worth noting that the oxidation rate of t-Bu₂S₂ by the AC combined with peroxone or hydrogen peroxide was higher than that of the combination of HC with peroxone or hydrogen peroxide. Sonic energy is more effective in breaking down and oxidation of this contaminant [4,20].

4. Calculation of wastewater treatment costs for cavitation processes with AOPs

The cost of the removal of sulfide ions S²⁻ from 1 L of the effluents using the cavitation processes is listed in Table 3. Cost analysis was based on consumption and current prices of chemical reagents, time of treatment and the costs related to consumption of electric energy. The study was carried out using HC and AC installations with powers of 1100 W and 1000 W, respectively. Ozone was obtained from a 450 W generator. The energy consumption of the LC pump used for the addition of hydrogen peroxide was negligible in comparison with other devices; thus, its energy cost was neglected. An average cost of electric energy for industrial recipients in Poland – 0.11 USD/kWh was used in calculations. Current price of 1 L of 30% hydrogen peroxide is 8.20 USD (price offer of Avantor Performance Materials Poland S.A.). The cost of the treatment of 1 L of the effluent containing up to

2000 mg S²⁻ for the investigated cavitation processes ranges from 0.017 to 0.165 USD. According to our results, the most economical processes are cavitation combined with the ozonation (HC + O₃ 0.017 USD L⁻¹; AC + O₃ 0.024 USD L⁻¹). This is due to a low cost of the oxidant produced in a generator with a low consumption of electric energy as well as to high synergism of cavitation (especially HC) and ozonation. It was reported in previous studies that the ozonation process alone can achieve the same effect of oxidation of various organic contaminants as the hybrid process; however, it requires at least twice as much time [17–19]. Therefore, the use of hybrid process is to be preferred. The least economical treatment processes are cavitation processes combined with hydrogen peroxide. Their cost is almost ten times as high as that of processes aided by ozonation. Hydrogen peroxide is a relatively expensive oxidant. Additionally, under alkaline conditions it is converted to less reactive radical species, which is partially eliminated by cavitation through H₂O₂ conversion to hydroxyl radicals [20]. The cost of oxidation of sulfides by cavitation processes alone is almost the same (HC 0.073 USD; AC 0.066 USD). The use of cavitation methods on a larger scale requires consideration of the cost of equipment. In the case of HC the most expensive item is the pump; however, it is considerably lower than the cost of sonochemical cavitation reactors equipped with sonic transducers. Consequently, the high cost of ultrasound reactors using current technology limits their full scale application for the treatment of real industrial wastewaters [20].

5. Conclusions

The presence of sulfide ions and organic sulfides in industrial wastewaters is a serious environmental problem. Acidic properties result in poisoning of production lines and corrosion of the equipment used. Their presence in effluents deactivates the activated sludge used during biological treatment. Hence, various oxidants and precipitating agents are used to remove sulfur compounds from wastewater. The main problem in removing sulfides from wastewater by conventional methods is their complete elimination. Such methods are ineffective at ppm concentration levels. The complete removal of sulfur compounds was obtained within the reaction time of lower than 3 h by the unaided cavitation processes (without the addition of external oxidants) with the number of passes through the cavitation zone equal to 198 (acoustic cavitation) and 306 (hydrodynamic cavitation) by using just one cavitation device. The reaction time needed for the oxidation of the target contaminant decreased to 30 min when the cavitation processes were combined with the peroxone process. The cavitation methods exhibited the high efficiency regarding the oxidation of organosulfur contaminants, including dimethyl sulfide, carbon disulfide and di-tert-butyl disulfide. About 60% of organosulfur compounds was oxidized by the cavitation processes within the short reaction time of 30 min. The complete oxidation took place within 30 min when the cavitation processes aided by external oxidants (ozone, hydrogen peroxide and peroxone), while, in the case of the cavitation processes alone, the oxidation was completed after about 120 min. The reaction rate constants for the oxidation of organosulfur contaminants by the investigated AOP processes were found to be similar for hydrodynamic and acoustic cavitation. The use of much technologically simpler hydrodynamic cavitation systems instead of acoustic cavitation reactors allows achievement of the same efficiency with the same treatment time considering practical point of view for full-scale applications.

The combination of AC and HC with the ozonation led to the least total treatment cost in comparison with even the individual AC and HC processes. Conclusively, the combination of acoustic and hydrodynamic processes with ozone, hydrogen peroxide and peroxone presented the great potential of applicability with high efficiency to be used for the treatment of caustic industrial effluents containing sulfide ions and organosulfur compounds, which is a major problem in various indus-

trial effluents such as bitumens effluent. In fact, the rapid removal of sulfide ions eliminates the need for the treatment of alkaline effluents, allowing the use of highly efficient AOPs such Fenton, which are efficient in neutral or acidic media.

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