Hydrodynamic cavitation based advanced oxidation processes: Studies on specific effects of inorganic acids on the degradation effectiveness of organic pollutants

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ABSTRACT

The use of cavitation in advanced oxidation processes (AOPs) to treat acidic effluents and process water has become a promising trend in the area of environmental protection. The pH value of effluents – often acidified using an inorganic acid, is one of the key parameters of optimization process. However, in the majority of cases the effect of kind of inorganic acid on the effectiveness of degradation is not studied.

The present study describes the results of investigations on the use of hydrodynamic cavitation (HC) for the treatment of a model effluent containing 20 organic compounds, representing various groups of industrial pollutants. The effluent was acidified using three different mineral acids. It was demonstrated that the kind of acid used strongly affects the effectiveness of radical processes of oxidation of organic contaminants as well as formation of harmful secondary pollutants. One of important examples is a risk of formation of p-nitrotolune. Sulfuric acid was the only chemical used for acidification which caused effective treatment with lack of formation of monitored type of secondary pollutants. The best treatment effectiveness – during a 6-hour cavitation process - in most cases much above 80% along with 90% TOC removal was obtained in the case of sulfuric acid. Nitric acid provided lower effectiveness (above 60% for most of the compounds). The worst performance are reported for hydrochloric acid – below 50% of degradation for most of the compounds.

1. Introduction

Due to high energy of collapse of gaseous bubbles, cavitation caused by ultrasounds (sonocavitation) or by various constrictors, such as orifices, venturi tubes or valves (hydrodynamic cavitation) enables effective decomposition of a wide variety of organic contaminants [1–3]. Degradation of organic compounds present in the treated medium takes place through thermal decomposition of the contaminants occurring in the center of collapse of cavities, so-called "hot spots", but the primary mechanism of decomposition/oxidation involves reactions with the radical species being formed, mostly hydroxyl radicals, which are strong oxidizing agents [4–6]. The combination of highly reactive hydroxyl radicals with the high impact of cavity collapse allows breaking and oxidation of the majority of organic contaminants, which cannot be removed by other, traditional treatment methods. Additionally, the

force of collapse increases the number of radicals in a constriction, thus improving homogenization of the system and efficiency of the oxidation process [7–9]. Cavitational processes have found wide applicability in oxidation of organic contaminants containing oxygen, nitrogen and sulfur atoms [1–9]. Based on the literature, treatment processes are usually carried out under acidic conditions (pH 2–5) [10–12]. Remarkably, in the papers discussing these problems no attention is paid to the kind of inorganic acid used to adjust the pH of the solution, which can influence the degradation efficiency of organic contaminants. This is mostly due to the possibility of generation of additional radicals by recombination of ions and formation of new radical species or by scavenging of free oxidizing radicals in reactions with inorganic ions, resulting either in enhancement or in deterioration of the degradation efficiency of the target organic contaminants.

Most industrial effluents have an acidic pH. In some cases, this is due to addition of a mineral acid. Sometimes the presence of anions, i.e. Cl^-, NO_3^- and SO_4^{2-} results from the process itself. However, in other cases their presence is due to the acid used to acidify a solution. Thus, in the latter case it is possible to select an inorganic acid for acidification of an effluent. Acidification could be needed for absorption of specific

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groups of pollutants in the aqueous phase. Otherwise, it could be due to acidic nature of process water used to this end.

The present paper discusses the results of studies on comparison of the effectiveness of degradation of organic pollutants under cavitation conditions depending on the kind of inorganic acid present in effluents. Three inorganic acids most commonly used for acidification of treated solutions were used: hydrochloric acid – containing a reactive chlorine atom, nitric acid – containing a reactive nitrate group and sulfuric acid – containing a reactive sulfate group. The term reactive used in this context refers to chemical processes taking place under cavitation conditions, wherein the anions mentioned above can be converted to active radical species, which can improve the efficiency of the treatment process. The investigated contaminants included 20 organic compounds containing oxygen, sulfur and nitrogen atoms, which are most commonly determined in industrial effluents.

2. Materials and methods

2.1. Chemicals

Model effluent was prepared by dissolving in deionized water the following standards: tetrahydrofuran, benzene, pyridine, toluene, ethylbenzene, furfural, 3-methylpyridyne, o-xylene, 2,4-dimethylpyridine, 2,4,6-trimethylpyridine, phenol, dibutyl sulfide, o-cresol, m-cresol, 4-methylbenzaldehyde, tert-butyl disulfide, 2-nitrophenol, 4-ethylphenol, naphthalene and p-nitrotoluene (Sigma-Aldrich, USA) – at a concentration of 50 ppm of each analyte. Listed pollutants were mixed together in the defined concentration. The following internal standards were used during quantitation by GC–MS: 4-chlorophenol, 2-chlorothiophene, and 2-chloropyridine (Sigma-Aldrich, USA). Inorganic acids included hydrochloric acid (35–38%), sulfuric acid (95%) and nitric acid (95%) (Avantor Performance Materials Poland S.A, Poland).

2.2. Hydrodynamic cavitation

Treatment of model effluents containing 20 organic contaminants in deionized water was carried out using hydrodynamic cavitation (based on Venturi) under acidic conditions at a temperature 40 ± 2 °C. A Venturi tube was made of brass and had a diameter of 10 mm (inlet and outlet) with a throat diameter of 2 mm (length of 1 mm). The convergent part (inlet-throat) had a length of 18 mm and angle of 22.6°, while divergent (throat-outlet) part had a length of 67 mm and angle of 5.6°. In the investigations, 5-L samples of the model effluent having an initial pH of 2 and containing about 50 ppm of each of the contaminants were treated. According to our previous studies, most of organic pollutants used in this research often is present in industrial effluents at 10–100 ppm level, thus 50 ppm was used as a corresponding concentration to evaluate proposed influence of type of acid used. Acidic conditions were obtained by an addition of appropriate amounts of hydrochloric, nitric or sulfuric acid. The treatment was carried out for 360 min at a flow rate of 520 L h^{-1} affording a maximum oxidation effect (cavitation number 0.140), as described in our previous papers [4–6]. Samples of the effluent were collected over a 6-hour period at the following points of time: 0, 60, 180, and 360 min.

2.3. Analytical method – gas chromatography coupled with mass spectrometry (GC–MS)

The analysis was performed using gas chromatography–mass spectrometry (GC–MS, model QP2010SE, Shimadzu, Japan). Sample preparation involved dispersive liquid-liquid microextraction (DLLME). Separation conditions: capillary column DB-624 (60 m × 0.25 mm ID × 1.40 μm), carrier gas: helium at 1.1 cm^{3}min^{-1}, injection port temperature: 300 °C, temperature program: 50 °C (5 min)- ramped at 5 °C min^{-1} to 115 °C- ramped at 10 °Cmin^{-1} to 250 °C (10 min). Mass

spectrometric conditions: ion source temperature (EI, 70 eV): 220 °C, GC/MS transfer line temperature: 280 °C, MS mode: Single Ion Monitoring (SIM) for selected ions and SCAN over the range 33–350 m/z. Details of the experimental procedure were described in an earlier work [7]. Total organic carbon was measured by a TOC-L analyzer (Shimadzu Corporation) using a standard program of the instrument.

3. Results and discussion

3.1. Hydrochloric acid

Presence of hydrochloric acid in the effluents can result from its application in the industry I it is a one of the most important inorganic acids used especially in chemical and pharmaceutical industries as well as in metallurgy. The occurrence of chloride ions in effluents can be a consequence of hydrochloric acid application as well as addition of salts containing this ion. Chloride anions are stable in aqueous solutions and have reducing properties [13]. Cavitational treatment of aqueous solutions aims at increasing the content of hydroxyl radicals generated by thermal decomposition of water molecules. Hydroxyl radicals oxidize organic contaminants in direct reactions; however, if a solution contains excessive amounts of chloride anions, a gradual quenching of the oxidation reactions takes place and the so-called "chlorine pathway" opens [13,14]. In this pathway chloride anions remove hydroxyl radicals, thus slowing down the decomposition efficiency of the target organic contaminants. The reaction of chloride anions with hydroxyl radicals yields hypochlorous acid (HClO) – reaction (1).

$$HO\cdot + Cl^- \rightarrow HClO \qquad (1)$$

Hypochlorous acid is chemically stable in aqueous solutions. Its oxidizing properties are weak in comparison with hydroxyl radicals [14]. The experimental data shown in this paper support the notion of chlorine pathway for the depletion of hydroxyl radicals generated by hydrodynamic cavitation after acidification of the effluent using hydrochloric acid. The addition of hydrochloric acid significantly hinders the oxidation of organic contaminants due to excessive consumption of hydroxyl radicals through the reaction with chloride anion. The degradation efficiency of the target organic contaminants by the HC process in the presence of hydrochloric acid is compiled in Table 1. The removal efficiency of the majority of 20 organic contaminants treated by the HC/HCl process did not exceed 50% after 180 min of the treatment process except for phenol (100% oxidation), tetrahydrofuran (100% oxidation) and benzene (80.7% oxidation). As was demonstrated in previous research papers, the three exceptions are compounds that are most readily degraded by cavitation phenomenon. Even a small amount of hydroxyl radicals generated by cavitation in solution can oxidize these contaminants. Moreover, these organic compounds are characterized by high reaction rate constants with as-generated hydroxyl radicals [15]. No changes in concentration were observed for m-cresol and naphthalene. The effectiveness of oxidation of these compounds depends upon a long exposure to hydroxyl radicals. On the other hand, higher reaction time is required to acceptably degrade these organic pollutants. In the case of gradual scavenging of hydroxyl radicals by chloride ions, chemically stable organic contaminants are not oxidized. An increase in concentration of 4-methylbenzaldehyde (−7%) and p-nitrotoluene (−34%) with respect to their initial concentrations in the model effluent was observed. 4-Methylbenzaldehyde is formed mostly through oxidation of toluene followed by addition of free methyl groups removed firstly from degradable organic contaminants [5]. On the other hand, p-nitrotoluene is formed as a result of recombination of atmospheric nitrogen, converted in an aqueous oxidizing medium to nitrates and nitrites, with derivatives of aromatic hydrocarbons [5]. Detailed information on changes in the concentration of contaminants in the model effluent during hydrodynamic cavitation is provided in Fig. 1. It

Table 1
Degradation efficiency of the organic contaminants by various HC processes.

Contaminant	C₀ [ppm]	HC			HC + HCl			HC + HNO₃			HC + H₂SO₄		
					Time [min]								
		60	180	360	60	180	360	60	180	360	60	180	360
		Degradation [%]											
Tetrahydrofuran	44.9 ± 5.2	44.1	82.4	95.3	91.2	100	100	100	100	100	62.6	69.6	76.0
Benzene	22.4 ± 3.2	22.2	34.4	59.2	71.5	76.1	80.7	−16.5	−33.7	−36.6	47.1	77.5	85.3
Pyridine	43.8 ± 7.1	9.3	19.8	31.9	25.5	44.2	43.8	26.5	54.5	92.0	35.0	68.2	89.8
Toluene	20.8 ± 3.6	8.2	20.2	42.1	29.7	45.4	46.9	−11.1	−11.9	−12.5	32.0	34.3	86.5
Ethylbenzene	15.7 ± 1.4	14.9	20.1	31.8	27.3	30.0	35.6	7.4	33.2	77.9	31.7	45.6	95.6
Furfural	17.4 ± 0.8	7.0	13.1	30.9	10.0	14.3	22.6	3.2	50.1	93.0	33.2	39.2	92.3
3-methylpyridine	39.4 ± 5.5	11.5	25.6	37.8	19.5	34.2	42.7	44.1	53.1	73.1	27.3	65.3	88.2
o-xylene	19.6 ± 2.1	15.5	20.1	34.8	20.8	38.3	40.3	6.5	11.2	16.2	26.1	42.5	93.2
2.4-dimethylpyridine	54.2 ± 8.6	6.1	8.8	15.3	9.3	19.7	21.6	33.8	41.2	96.5	58.3	76.8	91.2
2.4.6-collidine	36.1 ± 4.6	7.3	8.0	10.2	11.2	14.2	16.7	49.2	55.7	76.9	55.4	59.7	89.0
Phenol	22.6 ± 1.8	19,6	59.4	75.9	2.8	41.1	100	29.4	17.6	−1.5	26.4	35.7	82.9
Dibutyl sulfide	22.6 ± 0.4	13.0	16.7	27.8	4.7	16.2	37.0	50.2	50.6	49.5	29.7	80.8	96.7
o-cresol	26.6 ± 0.6	1.5	3.9	5.5	3.9	4.5	−0.2	−13.0	−13.6	−14.8	26.0	42.9	88.7
m-cresol	19.3 ± 0.5	1.5	2.5	2.8	2.2	2.5	2.7	27.4	41.1	52.8	25.5	41.6	91.1
4-methylbenzaldehyde	27.5 ± 0.4	2.2	3.8	5.3	−4.0	−5.0	−7.3	−21.6	−1.2	−0.8	35.7	65.1	84.8
Tert-butyl disulfide	21.8 ± 0.1	3.6	4.8	8.1	3.8	9.4	11.2	14.8	14.4	14.7	31.3	85.5	97.4
2-nitrophenol	25.9 ± 1.1	8.4	13.8	17.1	14.8	27.2	25.8	−25.5	−16.3	93.4	10.2	41.7	88.8
4-ethylphenol	29.6 ± 0.5	1.4	2.0	3.8	7.4	6.5	4.1	5.1	8.0	59.9	31.9	47.9	79.1
Naphthalene	32.6 ± 0.2	0.7	1.4	1.8	0.6	0.5	0.5	−15.7	−11.5	−13.7	22.1	55.4	95.8
p-nitrotoluene	36.8 ± 0.8	13.0	35.7	48.9	−20.1	−25.0	−34.3	−14.6	−14.4	−19.3	15.7	58.2	84.4

should be pointed out that the treatment of organic contaminants using hydroxyl radicals is usually carried out in an acidic medium [10–12], mostly to prevent absorption of CO₂ in water. At a neutral pH, the effluent absorbs atmospheric CO₂, yielding a weak and labile carbonic acid. Carbonic acid is recognized as a powerful radical scavenger compound

[16]. It lowers the concentration of hydroxyl radicals in the treated effluent through the direct reactions with carbonate and bicarbonate ions, thereby lowering the efficiency of the treatment process (reactions (2) and (3)). The radical species formed in reactions 2 and 3 are characterized by low reactivity; therefore, they do not promote the
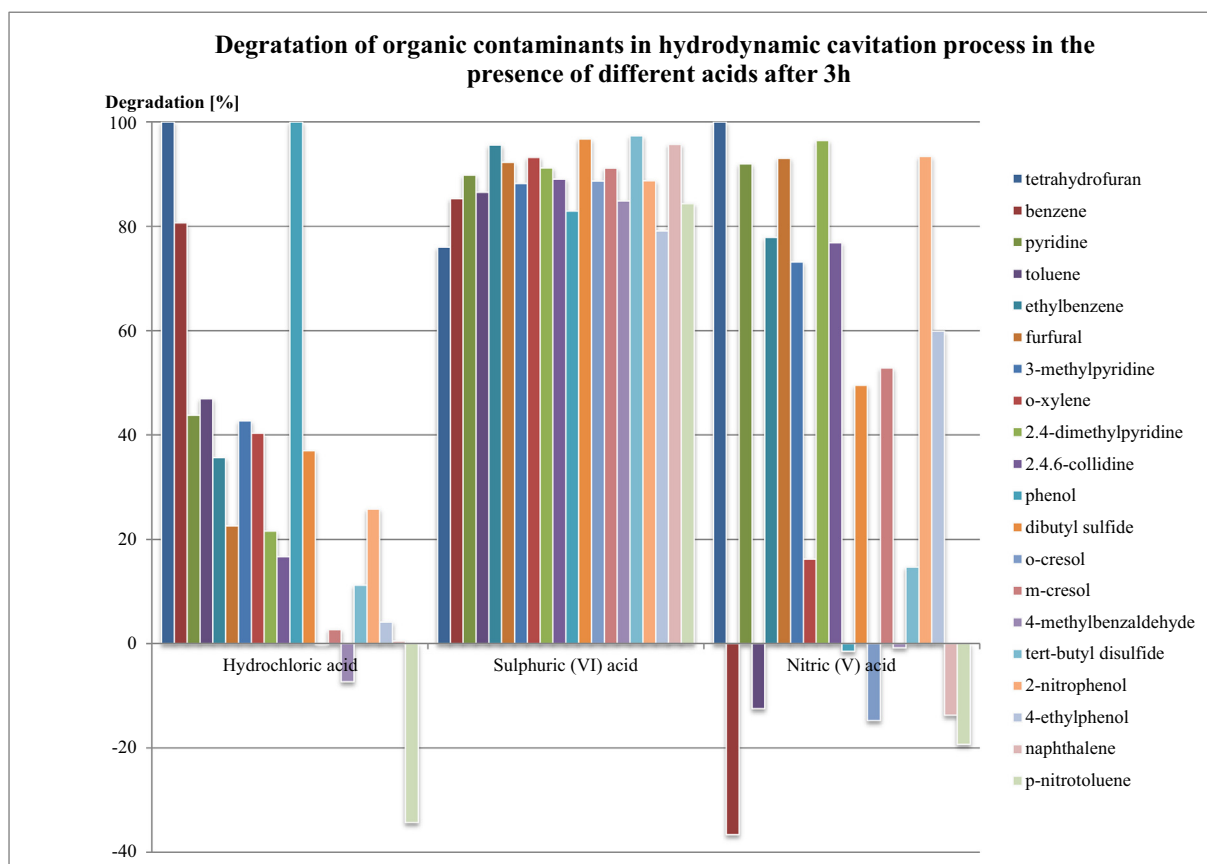
Fig. 1. Degradation of organic contaminants in hydrodynamic cavitation process in the presence of different acids after 3 h.

degradation efficiency of the target organic contaminants by the HC process [17]:

$$HCO_3^- + HO\cdot \rightarrow CO_3^- \cdot + H_2O \qquad (2)$$

$$CO_3^{2-} + HO\cdot \rightarrow CO_3^- \cdot + OH^- \qquad (3)$$

Consequently, radical processes are preferably carried out in the presence of a mineral acid which eliminates the problem of CO_2 absorption by decreasing the pH of water. In such a case, hydroxyl radicals can react directly with the contaminants in an effluent being treated. However, as demonstrated by the results discussed above, hydrochloric acid should not be selected as it causes a significant reduction in the degradation efficiency of organic contaminants under cavitation conditions.

3.2. Nitric acid

Nitric acid was the next compound investigated in terms of its effectiveness of oxidation of organic contaminants present in an acidified effluent under hydrodynamic cavitation conditions. Nitric acid is a strong oxidizing agent, in high concentrations and elevated temperatures can oxidize even some nonmetals, such as sulfur [18]. The nitrate anion has oxidizing properties due to the presence of nitrogen with a 5+ oxidation number [18,19]. In case of this study the concentration of nitric acid was relatively low. The results presented in this paper revealed that, contrary to chloride ions, nitrate ions have minor effect on the oxidation of organic contaminants in the presence of hydroxyl radicals. The concentration of nitric acid in the solution is not significant, thus its oxidative properties cannot play the major role in this system. However, in overall its effect can be described as positive in respect to obtained degradation effectiveness. It follows simply from the pH lowering, which increases the effectiveness of cavitational process. This can be observed especially for heterocyclic organic contaminants. In this regard, a substantial increase in the degradation efficiency of heterocyclic amines by the HC process was observed: pyridine 92% (HC+HCl 44%), 3-methylpyridine 73% (HC+HCl 43%), 2,4-dimethylpyridine 97% (HC+HCl 22%), 2,4,6-trimethylpyridine 77% (HC+HCl 17%) as well as furfural 93% (HC+HCl 23%) after 6 h of the treatment as compared to the treatment by HC + HCl. Heterocyclic compounds contain at least one heteroatom (most often O, N or S) in the ring. As a result of their electron configuration, they readily undergo substitution reactions and in the presence of strong acids they are easily converted into salts. The combination of highly reactive hydroxyl radicals and a strong nitric acid results in conversion of organic contaminants to less stable organic compounds followed by their effective degradation. Among the other model organic contaminants, a significant increase in the concentration of benzene (−37%), toluene (−13%), o-cresol (−15%), naphthalene (−14%) and p-nitrotoluene (−19%) was observed within the reaction time of 6 h. Benzene and its derivatives are highly stable even in the presence of strong nitric acid and hydroxyl radicals [19]. An increase in their concentration during the HC process can be attributed to the decomposition of other organic contaminants, converted in a strongly acidic medium (primarily to degradation of phenol and benzene derivatives) [20,21]. Detailed results of the studies on effectiveness of the oxidation of organic contaminants by the HC+HNO₃ process are shown in Table 1 and Fig. 1.

3.3. Sulfuric acid

Among the three inorganic acids studied, sulfuric acid was found to be the most effective inorganic acid in aiding oxidation in the presence of hydroxyl radicals. Advanced oxidation processes (AOPs), including hydrodynamic cavitation, enable conversion of sulfate ions to sulfate radicals ($SO_4^{\bullet -}$) [22–24]. Generation of sulfate radicals is advantageous for the oxidation process, mainly due to its high oxidation potential, equal to 2.6 V (for hydroxyl radicals it is 2.8 V) [25,26]. Moreover, the

period of activity of sulfate radicals in the bulk solution is much longer than that of hydroxyl radicals. This is mostly associated with the tendency of sulfate radicals to transfer electrons in chemical reactions rather than to abstract protons as is the case with hydroxyl radicals. Moreover, as-generated sulfate radicals are readily converted into hydroxyl radicals as a result of their interaction with water molecules as exhibited via the following reaction [27–30]:

$$SO_4^{\bullet -} + H_2O \rightarrow HO\bullet + HSO_4^- \qquad (4)$$
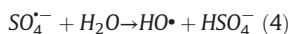
The presence of two highly reactive chemical species in the solution greatly improves the degradation efficiency of individual organic contaminants. This is mostly attributed to an increase of rate constants of oxidation reactions (Table 2). It follows from the presence of both hydroxyl and sulfate radicals as well as the absence of ions being scavengers of hydroxyl radicals. A detailed comparison of the oxidation efficiency of the target organic contaminants using HC + HCl, HNO₃ and H₂SO₄ is depicted in Table 1 and Fig. 1. For the refractory organic compounds, the addition of sulfuric acid shortens the time needed for their oxidation. For all 20 investigated organic contaminants oxidized by the sulfuric acid-aided HC process, over 75% degradation efficiency was achieved after the reaction time of 6 h. This is the most effective treatment process compared to both hydrochloric acid and nitric acid-aided HC processes.

3.4. Comparison of overall performance and reaction rate constants (k) of oxidation reactions of tested model contaminants in the presence of chloride, nitrate and sulfate anions

The reaction rate constants of oxidation reactions of the investigated organic contaminants by hydroxyl radicals generated by hydrodynamic cavitation in the presence of chloride, nitrate and sulfate ions are compiled in Table 2. It was assumed that the oxidation of organic contaminants by the HC process is first order, which is confirmed by the consistency of the results.

Under conditions of hydrodynamic cavitation + HCl, the most rapidly oxidized contaminants from the investigated group were in turn: phenol (0.0181 min⁻¹) > tetrahydrofuran (0.0137 min⁻¹) > benzene (0.0036 min⁻¹) pyridine and 3-methylpyridine (0.0015 min⁻¹). These

Table 2
Reaction rate constants (k) obtained during the oxidation of model contaminants by the HC treatment process aided by hydrochloric, nitric and sulfuric acids.

Contaminant	Treatment processes		
	HC + HCL	HC + HNO₃	HC + H₂SO₄
	k [min⁻¹]		
Tetrahydrofuran	0.0137	0.0190	0.0033
Benzene	0.0036	x	0.0052
Pyridine	0.0015	0.0070	0.0063
Toluene	0.0016	x	0.0053
Ethylbenzene	0.0010	0.0043	0.0085
Furfural	0.0006	0.0076	0.0068
3-methylpyridine	0.0015	0.0033	0.0060
o-xylene	0.0013	0.0005	0.0073
2,4-dimethylpyridine	0.0006	0.0090	0.0063
2,4,6-collidine	0.0004	0.0036	0.0055
Phenol	0.0181	x	0.0047
Dibutyl sulfide	0.0013	0.0013	0.0097
o-cresol	0.0001	x	0.0059
m-cresol	0.0001	0.0019	0.0066
4-methylbenzaldehyde	x	0.0002	0.0051
Tert-butyl disulfide	0.0003	0.0003	0.0105
2-nitrophenol	0.0008	0.0078	0.0062
4-ethylphenol	0.0001	0.0025	0.0041
Naphthalene	0.00001	x	0.0088
p-nitrotoluene	x	x	0.0053

x – determination of rate constant was not possible.

are compounds most susceptible to oxidation by cavitation. Despite low concentration of hydroxyl radicals, which are scavenged by chloride ions, the contaminants are degraded by radical reactions due to their structure, which makes them susceptible to be attacked by free oxidizing radicals [15]. The reaction rate constants for the oxidation of the remaining organic contaminants are <0.0015 min^{-1} (Table 2).

In the case of nitric acid-aided HC process, the organic contaminants that are degraded most rapidly are: tetrahydrofuran (0.0190 min^{-1}) > 2,4-dimethylpyridine (0.0090 min^{-1}) > 2-nitrophenol (0.0078 min^{-1}) > furfural (0.0076 min^{-1}) and pyridine (0.0070 min^{-1}). The presence in solution of additional ions having oxidizing properties (nitrate anions: NO_3^-), which aid the reactions of hydroxyl radicals to degrade the target pollutants, which results in the increased reaction rate constants of the oxidation process. According the results, the oxidation of furfural and 2-nitrophenol had the highest reaction rate constants (almost 70-fold increase in the reaction rate constant of HC + HNO$_3$ process compared with HC + HCl process). This is mostly caused by a greater availability of hydroxyl radicals in the solution as well as the interaction of contaminants with nitrate ions resulting in the enhanced degradation of the target organic contaminants.

The next investigated treatment process was hydrodynamic cavitation aided by H$_2$SO$_4$. The following contaminants were found to be oxidized most rapidly: *tert*-butyl disulfide (0.0105 min^{-1}) > dibutyl sulfide (0.0097 min^{-1}) > naphthalene (0.0088 min^{-1}) > ethylbenzene (0.0085 min^{-1}) and *o*-xylene (0.0073 min^{-1}). Under pyrolytic conditions occurring during cavitation, sulfate ions are converted to sulfate radicals ($SO_4^{\cdot-}$). Then, as-generated sulfate radicals react with water molecules to be converted into hydroxyl radicals in the bulk solution. Thus, if the effluent treated by the HC is acidified with sulfuric acid, there are two sources of hydroxyl radicals in the liquid phase: 1) decomposition of water molecules by the cavitation and 2) conversion of sulfate ions. This leads to a significant increase in the number of free oxidizing radicals in the solution, which brings about the enhanced degradation efficiency together with the increased degradation rates of the organic contaminants. Consequently, the degradation rate of the investigated contaminants by the HC + H$_2$SO$_4$ process was the highest in comparison with the HC+HCl and HC/HNO$_3$ treatment processes. The reaction rate constants for the oxidation of the studied organic contaminants by the HC + HCl, HC+HNO$_3$ and HC+H$_2$SO$_4$ processes are compiled in Table 2.

A comprehensive comparison of the results, revealed that the best inorganic acid to acidify the reaction medium is sulfuric acid. In this case, the reaction rate constants for the oxidation were the highest for the majority of target contaminants. Compared to the acidification by the other two inorganic acids (HCl and HNO$_3$), the rates of degradation in the presence of sulfuric acid were higher by a factor of several to several dozen. In some cases, higher rates were observed for nitric acid, but the differences were small and it can be stated that for these contaminants both acids have a similar effect on the effectiveness of degradation. The results of the investigations also demonstrated that for the decomposition of aromatic compounds the use of sulfuric acid is preferred.

A comparison of obtained data with literature is difficult, due to the differences in process conditions. Some data are provided only for sonocavitation systems, in some cases exclusively for very high frequencies (>200 kHz). In other studies the experiments were performed exclusively in deionized water. This also indicate the importance of studied aspect of cavitation processes relating to the type of mineral acid present in the effluent. However few attempts were performed to fit the obtained results into the current state of the art. In case of phenol k calculated in this study in the range of 0,0047 to 0,0181 min^{-1} (depending on the type of acid) is comparable with the one (0,0151 min^{-1}) obtained in sonocavitation system (358 kHz, 100 W; no data about pH) [31]. The values obtained for benzene (0,036–0,052 min^{-1}) are comparable to one found in the literature - 0,025 min^{-1} (US system 850 kHz, 40 W; no data about pH) [32] and 0,046 (US system 20 kHz, 750 W; deionized water) [33]. Similarly, rate constant values determined for pyridine (0,0015–0,007 min^{-1}) were on the same order of magnitude as reported in the literature - 0,0044 min^{-1} (US system 40 kHz, 360 W, deionized water with NaCl addition), however in this case the degradation effectiveness was lower than 50% during 180 min of treatment and no further degradation was observed (degradation was inhibited after first 100 min of treatment) [34].

Studied processes differ also in respect to removal of total organic carbon (TOC). This parameter allows to evaluate the potential of treatment method to mineralize the pollutants, i.e. to degrade not only the primary pollutants but also the intermediates formed during the process. This part of the studies revealed, that TOC removal correspond to overall degradation effectiveness of studies processes. The most effective degradation was obtained for HC performed with sulfuric acid. In this case a 90% removal of COD (primary 748 mg/dm^3 vs 76 mg/dm^3 after the treatment process) is reported. Treatment performed in deionized water resulted in 18% removal of TOC. In case of nitric acid and hydrochloric acid the TOC removal was 52% and 21% respectively.

4. Conclusions

Hydrodynamic cavitation, as one of the advanced oxidation processes, allows effective degradation of organic contaminants in aqueous solutions. The main mechanism of the oxidation involves radical reactions. Direct reactions of as-generated hydroxyl radicals with contaminants can be aided or hindered by various types of ions present in solution. The presence of some ions is due to technological processes or it is intentional – related to acidification of effluents. Consequently, this study is focused on the effect of inorganic acid (HCl, HNO$_3$, and H$_2$SO$_4$) on the degradation efficiency of organic contaminants present in the model effluent by the hydrodynamic cavitation process. The pollutants selected for these studies are present in several types of industrial effluents. Such a wide variety of organic pollutants in same time can be found in refinery effluents, such as effluents from bitumen production [35,36]. The obtained results reveal that the presence of chloride ions precludes effective oxidation of the target organic contaminants. However, comparing to experiments performed in deionized water, even addition of hydrochloric acids improve in some manner the degradation effectiveness. This can be attributed to scavenging of hydroxyl radicals in so-called chlorine pathway, which results in formation of species with a substantially lower oxidation potential. Nitrate ions having nitrogen at a 5+ oxidation state are characterized by strong oxidation properties without hydroxyl radical scavenging effect. In the presence of refractory organic contaminants, such as heterocyclic compounds, nitrate ions facilitate their conversion into salts with easier degradability. However, a side effect is the generation of secondary pollutants.

Oxidation of the organic contaminants through radical reactions is aided by the presence of sulfate ions. In aqueous media, sulfate ions are converted into additional sulfate and hydroxyl radicals. Under cavitation conditions, sulfate ions are to some extent converted to sulfate radicals having remarkable oxidation potential. Moreover, sulfate radicals have a longer activity period than that of hydroxyl radicals, which allows a longer exposure of refractory contaminants to their attacks and thus an increase in the effectiveness of degradation. The result of a larger number of hydroxyl radicals in a treated solution, which depends on the kind of acid used for acidification of the effluent, is an increase in rate constants of oxidation reactions of the target organic contaminants, according to the following order: HCl < HNO$_3$ < H$_2$SO$_4$.

These studies highlight the risk of by-products formation – in few cases an increase of concentration was reported (negative values of % degradation on Fig. 1). Sulfuric acid was the only acidifier which allowed to eliminate the problem of by-products formation in respect to

monitored compounds. In other cases this phenomenon is of significant concern. In case of typical process control performed in the industry – based on measurement of parameters describing reduction of total load of pollutants, such differences couldn't been reported, thus increase of content of harmful compounds like p-nitrotoluene overlooked. Application of GC–MS allowed for detailed analysis of these effects. It revealed, that in case of hydrochloric acid 4-methylbenzaldehyde and p-nitrotoluene are formed as by-products.

In case of hydrochloric acid, along with main degradation route, a several side-reactions related to a so-called chlorine pathway can take place leading to formation of additional by-products. This explains increase of content of 4-methylbenzaldehyde, which can be formed by main route (oxidation of toluene with formation of benzaldehyde group) combined with addition of methyl group as a consequence of presence in treated media of methyl radicals which can be formed during several reaction of chloride radicals. Increase of nitro- containing organic compounds follows from the atmospheric nitrogen fixation, converted to nitrates and nitrites available for reactions with treated organic pollutants. In case of nitric acid, nitrate ions had minor effect on the oxidation of organic contaminants in the presence of hydroxyl radicals and in overall application of this acid had positive effect on HC process. The increase of concentration of aromatic hydrocarbons simply follows from the degradation of other compounds present in the treated medium. In applied conditions their degradation was slow, thus in total their concentration slightly increased. This drawbacks were overcome by application of HC process with addition of sulfuric acid. In this case positive effect of pH lowering along with possibility of sulfate ions conversion to sulfate radicals allowed to obtain satisfactory performance of treatment process.

While, in case of nitric acid several by-products were formed. In both cases formed by products are aromatic hydrocarbons with peripheral functional groups. Especially in case of nitric acid, analysis of concentration changes of monitored pollutants reveals that these by-products also undergo degradation via AOP studied, however its rate is much slower, comparing to primary pollutants, thus for studied period of treatment their final concentration is reported as increased comparing to primary composition. Two alternative approaches are available for application in real case scenario. Firstly, prolongation of treatment time should result in further degradation of formed by-products. Second option demands analysis of the applicability of microorganisms in the activated sludge of biological treatment plant for final purification of the effluents. In case of their usefulness this solution should be preferred due to much lower costs of biological treatment comparing to AOPs.

The most favorable conditions for degradation of organic contaminants by hydrodynamic cavitation were obtained after acidification of the effluent with sulfuric acid. This approach is preferred considering both process and economic point of view. Effective degradation of studied pollutants correspond also to high – 90% of TOC removal. Using hydrochloric acid leads to the issue of the presence of corrosive chloride ions while the use of sulfuric acid instead of nitric acid is preferred as being a less expensive solution.

CRediT authorship contribution statement

Michał Gągol: Investigation, Formal analysis, Writing - original draft. **Elvana Cako:**Investigation, Formal analysis, Writing - original draft, Conceptualization, Methodology, Validation, Data curation.**Kirill Fedorov:**Investigation, Conceptualization, Writing - original draft, Methodology, Validation, Data curation.**Reza Darvishi Cheshmeh Soltani:**Validation, Writing - review & editing.**Andrzej Przyjazny:**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 no conflict of interest.

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