Enhanced effect of suction-cavitation on the ozonation of phenol

Zhilin Wu [a,b], Marcus Franke [a], Bernd Ondruschka [a,*], Yongchun Zhang [b], Yanze Ren [a], Patrick Braeutigam [a], Weimin Wang [b]

[a] Institute for Technical Chemistry and Environmental Chemistry, Friedrich Schiller University of Jena, Lessingstr. 12, D-07745 Jena, Germany
[b] Nanjing Institute of Environmental Science, MEP of China, Jiangwangmiaostr. 8, 210042 Nanjing, China

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ABSTRACT

800 mL of 1.0 mM phenol-containing aqueous solution was circulated at 20 °C for 30 min in a suction-reactor, while 3.2 mg min^{-1} ozone was introduced into the solution under the suction orifice. The removal rates of phenol vary polynomially with the orifice diameter as well as the suction pressure. The rate constant for the zero-order kinetics achieves the highest value at −0.070 MPa by using 5 mm orifice. Although the suction-cavitation alone cannot remove phenol in 30 min, it can considerably enhance the ozonation of phenol. The rate constants for the zero-order kinetics by the simple ozonation and the combined method are 0.018 and 0.028 min^{-1}, respectively. Furthermore, no ozone was observed in the tail gas during the first 15 min for the ozonation in the suction reactor, and then the concentration of unreacted ozone slowly increased, indicating that the utilization rate of ozone is significantly improved by the suction-cavitation. The increasing input concentration of ozone obviously accelerates the ozonation of phenol, but the total required quantities of ozone are very close by various ozone input concentrations to reach the same degradation rate, indicating the ozonation assisted by the suction-cavitation can be considered as a quantitative reaction.

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1. Introduction

Phenolic compounds are particularly important among organic pollutants, and the removal mechanisms and kinetics of phenol by ozonation in water have been extensively studied [1–5]. The initial attack of ozone and hydroxyl radicals formed in situ on the aromatic ring brings about hydroxylation, which gives predominantly catechol and hydroquinone. The ozonation of catechol and hydroquinone leads to the cleavage of the aromatic ring and the formation of muconaldehyde and muconic acid [2,6,7], which contain the aliphatic double bonds. Then the anomalous ozonolysis of α,β-unsaturated carbonyl groups play an important role in the formation of lower molecules. The major product is formic acid with minor amounts of glyoxal, glyoxylic acid, oxalic acid, and carbon dioxide [2,5]. Direct oxidation occurs primarily through cleavage of the aromatic ring in acidic solutions, while at higher pH values the free-radical pathway is more significant [4]. In recent years, enhancing the reaction kinetics of ozonation as well as increasing mass transfer and utilization rate of ozone have been focused.

In order to enhance the ozonation by using more generated hydroxyl radicals, catalytic ozonation is more effective than ozonation alone. Typical homogeneous catalysts for ozonation are transition metal ions such as Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, Fe^{3+} and Ag^+ [8–10]. To avoid further separation, heterogeneous catalysis could be better than homogeneous one [10]. Hydroxyl radicals were detected in the catalytic ozonation by solid Cu/Mg/Al and probably worked as the active species on the catalyst surface [11]. De-aluminated Y-zeolite also accelerates the transformation from ozone molecules to hydroxyl radicals [12]. The direct oxidation mechanism with molecular ozone was proved in catalytic ozonation with brucite, and hydroxyl radical mechanism plays a main role in catalytic ozonation with magnesia [13].

The ozonation process depends not only on the kinetic of reactions but also on the mass transfer between phases [14]. The ozonation of phenol is a mass transfer limited reaction. Therefore, it is important to develop techniques and reactors, which provide higher mass transfer coefficient of ozone, to increase the kinetics of ozone absorption [4,15]. In order to improve the gas absorption, many diffusers and contactors have been investigated, e.g., turbine, spray, gas-inducing, microbubble and Karman mixers [16–19]. The rate of mass transfer could be increased by as much as 40% with electrostatic spraying [16]. The ozone volumetric mass transfer coefficient increases with the increase of both gas and liquid flow rates owing to fine bubbles generated by the Karman mixer [17]. Compared with the bubble contactor, the total mass transfer coefficient of the microbubble system is 1.8 times higher and the pseudo-first order rate constant is 3.2–3.6 times higher at the same initial dye concentration [18].

* Corresponding author. Tel.: +49 3641 948400; fax: +49 3641 948402.
  E-mail address: bernd.ondruschka@uni-jena.de (B. Ondruschka).

Hydrodynamic and ultrasonic cavitations both enhance the mass transfer coefficient [20,21], and these techniques also intensify the Fenton process by generation of additional free radicals. On the one hand, turbulences produced during hydrodynamic cavitation process increase the mass transfer rates and provide better contact between the pseudo-catalyst surfaces and the reactants [22]. The enhanced mass transfer rates, also achieved due to the recirculatory flows in the liquid whistle reactor, increase the effective utilization of ozone [23]. On the other hand, ozone (ORP 2.08 V) suffers the destruction to form atomic oxygen (ORP 2.42 V) by the collapsing cavitation, yielding more active species with water, hydroxyl radical (ORP 2.80 V) [18,24].

Hydrodynamic cavitation and its chemical effect can be induced by both of positive and negative pressure difference [25–28]. The so-called suction-cavitation is hydrodynamic cavitation induced by negative pressure. Due to the more energy-efficiency and safety, the suction-cavitation was used to assist and enhance the ozonation of phenol in this investigation. By using well-dispersing ozone, atomic oxygen and hydroxyl radicals induced in the cavitation–ozonation system, the remarkable enhanced effect of suction-cavitation on the ozonation of phenol was demonstrated in the absence of additional catalyst and mixer.

2. Materials and methods

2.1. Chemicals

Phenol (99%), hydroquinone (99%), catechol (99.5%), p-benzoquinone (99.5%), oxalic acid (99%), fumaric acid (99.5%), and maleic acid (99%) were provided by Fluka and used as received. Phenol was the only reagent used in the degradation studies. The other reagents provided product identification. Water used for sample preparation was deionized water (conductivity $\leq 1.5\ \mu S\ cm^{-1}$).

2.2. Yield measurement of the ozone generator

To measure the concentration of ozone in the gas, the reaction with potassium iodide solution followed by titration with sodium thiosulphate using starch solution as an indicator was carried out. 200 mL of 0.1 M KI solution was introduced in a washing cylinder fitted with a gas diffuser (16–40 μm pores). Fischer Ozon-Generator 500 (Neckenheim, Germany), with a stabilized voltage supply, was employed and the applied power adjusted appropriately. The flow and pressure of oxygen were set at 0.67 L min^{-1} and 0.1 MPa, respectively; and the ozone/oxygen mixture was passed into the KI solution for 10 min. The yields of ozone were determined as 3.2, 3.8, 9.2, 13.4 mg min^{-1} at 15, 16, 20, 25 W, respectively.

2.3. Device for creating hydrodynamic cavitation by suction

A lab-scale device for creating hydrodynamic cavitation (suction-reactor), induced by suction orifice, with ozone inlet was used and is shown in Fig. 1. The device consists of a centrifugal pump, a suction orifice, a heat exchanger, a water tank, a manometer, a flowmeter and some connecting pipes. All of the contacting materials are constructed from stainless steel (SS316).

The centrifugal pump (Speck GY-028-2, 2750 rpm, Roth, Germany) is capable of generating a pressure of 0.7 MPa and a flow rate of 1980 L h^{-1} at most. The maximal electrical power is 1.1 kW. The total volume of the solution is 800 mL. The temperature of bulk liquid was maintained constant by the cooling circulator and the heat exchanger.

A 21 mm orifice plate (thickness 1 mm) with various single holes (ID 4–21 mm) was attached at the inlet of pump, so that the cavitation can be induced by suction. The inner diameter for the connecting pipes is 21 mm. Cavitation events are controlled by the
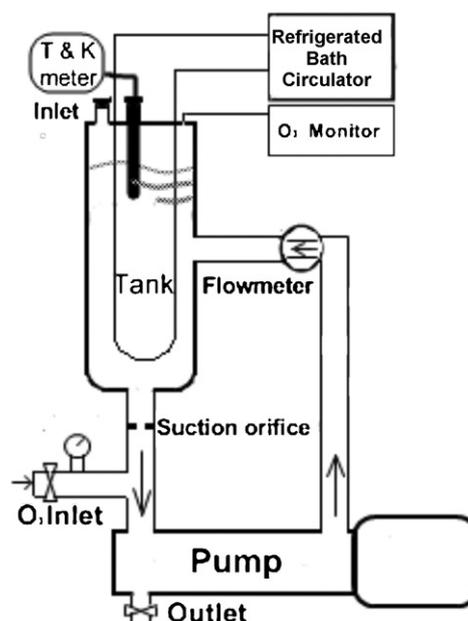
Fig. 1. Lab-scale suction-reactor with Speck GY-028-2 pump, FP50 refrigerated/heating circulator and Greisinger GMH 3430 digital conductivity and temperature meter (T&K meter).

orifice diameter. The suction pressure was measured by a manometer, and the flow rate through the various orifices was determined by a flow meter, as shown in Fig. 1.

Ozone/oxygen gas was introduced into the solution under the suction orifice. Ozone monitor (EG-2001; Fischer Ozotron 37) was connected with the gas outlet of the tank to determine ozone concentration in the residual gas.

2.4. A typical run

800 mL of 1.0 mM phenol-containing aqueous solution was circulated for 30 min at 20 °C through the suction-reactor, while ozone (3.2 mg min^{-1}) was passed into the solution. The flow and pressure of oxygen were set at 0.67 L min^{-1} and 0.1 MPa, respectively. The pH values were not artificially adjusted during the ozonation. The pH values were measured to be 5.2 and 3.6 in 0 and 30 min of ozonation, respectively.

2.5. Ozonation in 3-tandem gas washing cylinders (bubbling-reactor)

In order to determine the effect of ozonation alone, 800 mL of phenol-containing solution was added to 3-tandem gas washing cylinders (300, 250, 250 mL in each 500 mL cylinder) fitted with the gas micro-diffusers (16–40 μm pores), and the ozonation of phenol was performed as normal. Ozone monitor (EG-2001; Fischer Ozotron 37) was connected with the fourth gas washing cylinder to determine ozone concentration in the residual gas. Ozonation was performed for 30 min at 20 °C while ozone (3.2 mg min^{-1}) was passed into the solution. The flow and pressure of oxygen were set at 0.67 L min^{-1} and 0.1 MPa, respectively.

2.6. Analysis

A conductivity meter, immersed in the water-tank, was periodically used for analysis. During the ozonation, aliquots (1 mL) of the processed solution were periodically extracted for some selected reaction procedures and analyzed quantitatively and qualitatively by HPLC [29]. A Fischer Ozone monitor was used to determine the
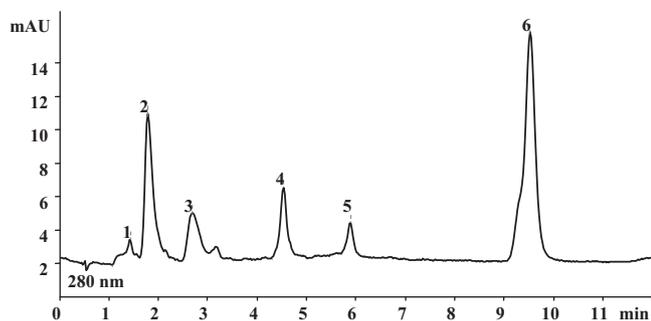
Fig. 2. HPLC chromatogram for the products and intermediates from the ozonation of phenol (peaks 1 and 2: lower dicarboxylic acids; peak 3: maleic acid; peak 4: hydroquinone; peak 5: catechol; peak 6: phenol. Reaction conditions: phenol-containing aqueous solution (1 mM, 800 mL), 5 mm suction orifice, reaction time 30 min, 20 °C, 3.2 mg min^{-1} ozone, and 0.67 L min^{-1} ozone–oxygen flow at 0.1 MPa).

level of unreacted ozone. The results reported are an average of two individual experiments.

3. Results and discussion

Due to the specifications for promoting mass transfer, the jet contactor is very efficient for the ozonation of phenol. The very strong ozone mass transfer performance of the Confined Plunging Liquid Jet Contactor (the overall volumetric mass transfer coefficient $k_L a$ ranged from 0.301 to 0.474 s^{-1}), which is combined with its compact size and safety improvements due to its operation under suction, has been reported [30]. In the Jet Contactor a jet of liquid generates fine gas bubbles that are contacted with the bulk liquid flow. A maximum experimental $k_L a$ value of 0.84 s^{-1} was achieved after improvement of the Jet Contactor [31]. By another comparison of $k_L a$ between ejector and traditional bubble column, $k_L a$ of the ejector (0.072–0.135 s^{-1}) was much greater than that of the bubble column (0.015–0.028 s^{-1}). As a consequence, 98% of ozone introduced was transferred in liquid phase [20].

In addition, cavitation processes can use the indirect action of ozone, in which the generated hydroxyl radicals are much more reactive and less selective than ozone. Under sonolysis the thermolytic destruction of ozone forms atomic oxygen, which reacts with water vapor in cavitation bubbles, yielding gas-phase hydroxyl radicals [24,32,33]. Due to the promotion of mass transfer and an enhanced generation of hydroxyl radicals, the combination of ultrasonic or hydrodynamic cavitation and ozonation synergistically affects during the organic degradation and water disinfection, which reduces to half or one-third of the required concentration of ozone [23,34]. The enhanced effects of suction-cavitation on the ozonation of phenol are illustrated as follows.

3.1. Products and intermediates from the ozonation of phenol

Fig. 2 shows a HPLC chromatogram, in which the major products and intermediates from the ozonation of phenol are presented. Any phenol undegraded is shown as peak 6; peaks 4 and 5 show hydroquinone and catechol, respectively; peak 3 is maleic acid, and peaks 1 and 2 are lower dicarboxylic acids.

The produced acids induce an increase in conductivity so the degree of degradation of the phenol solution can be related to the conductivity measurement. The higher the conductivity, the more phenol has been converted. Fig. 3 shows the linear relationship between conductivity and degradation of phenol. The values used here were selected from different procedures in which HPLC analyses were carried out. As shown in Fig. 3, the conductivity increases while the concentration of phenol decreases. At the start of the experiments the conductivity is very low (<1.5 μs cm^{-1}) but the
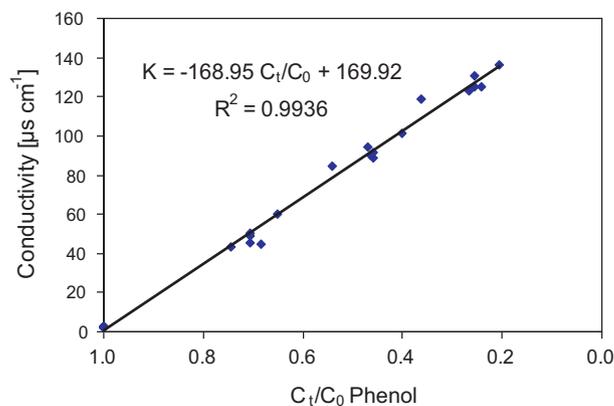
Fig. 3. Relationship between conductivity and degradation of phenol in aqueous solutions (reaction conditions: phenol-containing solutions (1 mM, 800 mL), 20 °C, 3.2 mg min^{-1} ozone, and 0.67 L min^{-1} ozone–oxygen flow at 0.1 MPa).

value reaches 85.5 μs cm^{-1}, 50% of phenol has been degraded and at 136.1 μs cm^{-1} only 20% of phenol remains. As a result of linear regression, the phenol concentrations can also be calculated in terms of the conductivity in the individual experiments.

3.2. Effect of suction orifice

Cleavage of chloroform induced by the suction-cavitation has been demonstrated in our former study, and the observed decomposition rates of chloroform vary polynomially with the diameter of suction orifice [28]. In this investigation, the degradation of phenol was carried out in aqueous solutions with various diameters of the suction orifice. The other conditions were kept constant. 800 mL of 1 mM phenol solution was circulated for 30 min at 20 °C in the suction-reactor. The input of ozone was 3.2 mg min^{-1} during the circulation. For the control experiment, ozonation in the bubbling-reactor, the other reaction conditions are same as described above, but no cavitation affects.

The concentration of phenol steadily declined during the ozonation and the degradation of phenol follows zero-order kinetics in the suction-reactor. Optimal degradation was observed with 5 mm diameter orifice (see Fig. 4). The highest degradation rate constant for the zero-order kinetics was achieved (0.028 min^{-1}) at −0.070 MPa by using 5 mm orifice compared to the worst degradation of phenol solution conducted in the bubbling-reactor (k_0 = 0.018 min^{-1}), in which no hydrodynamic cavitation was used.
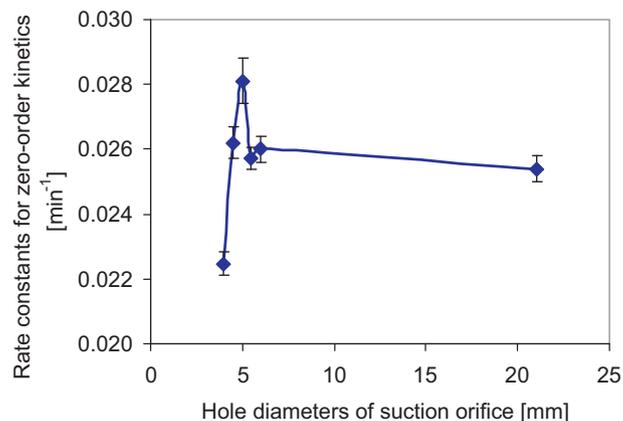
Fig. 4. Effect of orifice diameter on the ozonation rate constants of phenol in the suction-reactor (reaction conditions: phenol-containing aqueous solution (1 mM; 800 mL), reaction time 30 min at 20 °C, 3.2 mg min^{-1} ozone, and 0.67 L min^{-1} ozone–oxygen flow at 0.1 MPa).
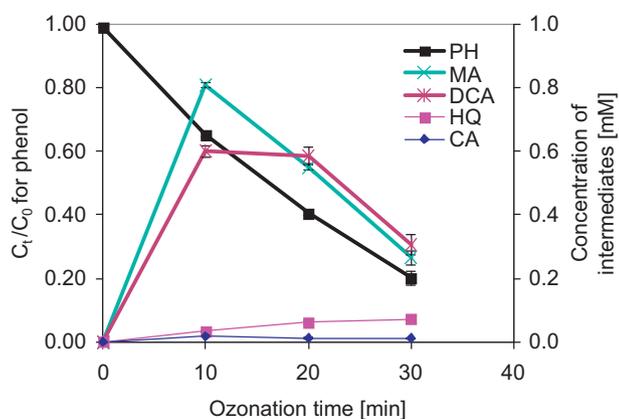
Fig. 5. The concentration gradients of reactant and intermediates under the ozonation with suction-cavitation (reaction conditions: phenol-containing aqueous solutions (1 mM, 800 mL), ozone 3.2 mg min^{-1}, 20 °C, 5 mm orifice. PH = phenol; MA = maleic acid; DCA = dicarboxylic acids, HQ = hydroquinone; CA = catechol).

The orifices with the diameter near 5 mm (4.5 and 5.5 mm) show a weaker performance for the degradation, but are better than 4 mm and 6 mm. The largest hole without orifice plate also has a quite good effect. This is due to the good mass transfer of ozone induced by high water flow and the higher number of cycles in the given time. The effect of suction orifice on the ozonation of phenol is consistent with results seen in the decomposition of chloroform in aqueous solutions [28,35], indicating that the hydrodynamic cavitation plays an important role during the ozonation of phenol, i.e., it accelerates phenol removal by improving mass transfer and generating more hydroxyl radicals.

In addition, as shown in Figs. 5 and 6, the intermediates formed during the combined ozonation/suction-cavitation are obviously different from use of ozonation alone. Minor catechol and hydroquinone were formed by the ozonation in suction-reactor along with the major intermediates of maleic acid and other dicarboxylic acids. The concentration of acids increased during the first 10 min, and then sharply decreased, while hydroquinone almost steadily increased. This means that the intermediates dicarboxylic acids, as well as phenol were fast converted to carbon dioxide and water. On the contrary, the concentrations of intermediates, except catechol, steadily increased during the ozonation in the bubbling-reactor, indicating little phenol was converted to carbon dioxide and water,
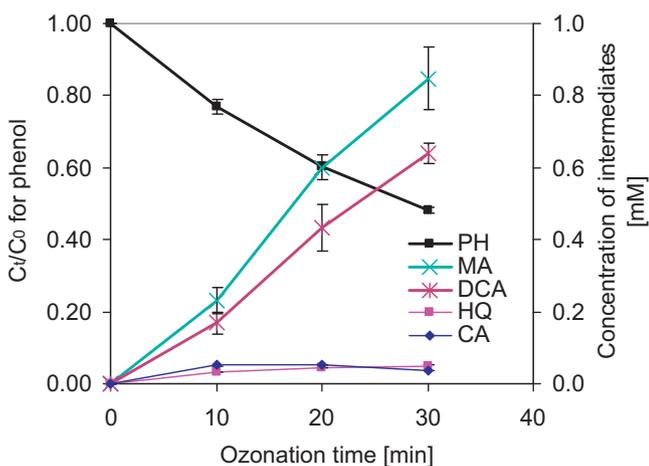
Fig. 6. The concentration gradients of reactant and intermediates under the ozonation in the bubbling-reactor (reaction conditions: phenol-containing aqueous solutions (1 mM, 800 mL), ozone 3.2 mg min^{-1}, 20 °C. PH = phenol; MA = maleic acid; DCA = dicarboxylic acids, HQ = hydroquinone; CA = catechol).
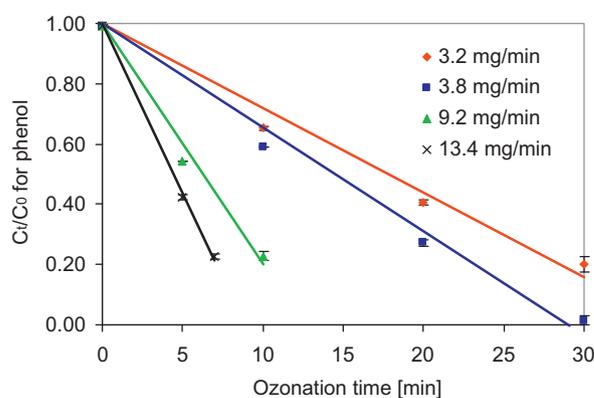
Fig. 7. Effect of ozone concentration on the ozonation rate of phenol in the suction-reactor (reaction conditions: phenol-containing aqueous solutions (1 mM, 800 mL), 5 mm suction orifice, reaction time 30 min at 20 °C, and 0.67 L min^{-1} ozone–oxygen flow at 0.1 MPa).

but rather to intermediates which are accumulated by the ozonation alone.

40% of phenol was degraded in 14 min by the combined method and 20 min by ozonation alone. At this point, maleic acid and other dicarboxylic acids declined into 0.70 and 0.60 mM after peaks in the combined system. As comparison, maleic acid and other dicarboxylic acids climbed into 0.60 and 0.43 mM with the ozonation alone. It indicates that dicarboxylic acids were rapidly produced and oxidized by hydroxyl radicals formed in the combined system. Generally, ozonation alone has been shown to achieve a very limited mineralization of organic compounds. An objective of the combination of ozonation/suction-cavitation is to produce a large amount of radicals to oxidize organic pollutants. Hydroxyl radical (k_{OH} 10^8–10^{10}) is a less selective and more powerful oxidant than molecular ozone (k_{O_3} 10^{-5}–10^2) [36].

This again illustrates the advantages of a combination of ozonation and suction-cavitation. The highest concentrations of most intermediates (except hydroquinone) are achieved in 10 min and then decrease when combined ozonation/suction-cavitation is used, but the concentration of most intermediates continued to increase with ozonation alone. Moreover, the concentrations of all acids are significantly lower at the end of reaction when using the combined method compared to ozonation alone. This demonstrates that the suction-cavitation significantly enhances the mineralization of phenol and its intermediates.

3.3. Effect of ozone input

The effects of ozone concentration were investigated with the optimal orifice (5 mm) and using phenol-containing aqueous solution (1 mM, 800 mL) circulated at 20 °C. The increasing concentration of ozone undoubtedly accelerated the oxidation-removal of phenol, as shown in Fig. 7.

To reach the degradation degree of 80%, 29 min of 3.2 mg min^{-1} ozone sparging are required but this time is considerably reduced when the ozone input concentration is increased. Thus, it needs 24, 10, 7 min to achieve the same degradation degree with 3.8, 9.2 and 13.4 mg min^{-1} ozone input, respectively. Surprisingly, the total required quantities of ozone to reach the degradation degree of 80% by the various concentration of ozone input are very close, i.e., 92.8, 91.2, 92, 93.8 mg ozone, respectively, indicating the utilization rate of ozone is close to 100% and the ozonation of phenol can be considered as a quantitative reaction in the suction-reactor. Moreover, the rising concentration of ozone can reduce the energy consumption for the generation of ozone, due to the shortened reaction time. If the same degradation degree is considered, then
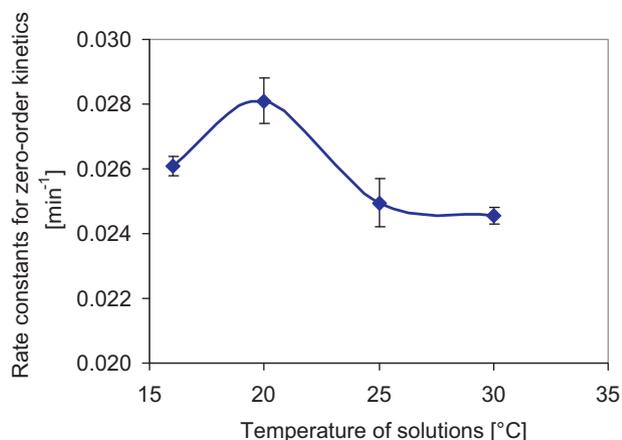
Fig. 8. Effect of temperature on the ozonation rate constant of phenol in suction-reactor (reaction conditions: phenol-containing aqueous solutions (1 mM, 800 mL), 5 mm suction orifice, reaction time 30 min, 3.2 mg min^{-1} ozone, and 0.67 L min^{-1} ozone–oxygen flow at 0.1 MPa).

Fig. 9. Enhancement of the ozonation removal of phenol by suction-cavitation (reaction conditions: phenol-containing aqueous solutions (1 mM, 800 mL), ozone 3.2 mg min^{-1}, 20 °C, 5 mm orifice. HC: by hydrodynamic cavitation alone; O$_3$: by ozonation alone; O$_3$ + HC: by ozonation with hydrodynamic cavitation).

the energy consumptions are: 0.0029 kWh at 25 W (13.4 mg min^{-1} ozone) for 7.5 min; 0.0033 kWh at 20 W (9.2 mg min^{-1} ozone) for 10 min; 0.0075 kWh at 15 W (3.2 mg min^{-1}) for 30 min.

The concentration for the intermediates, such as hydroquinone, maleic acid and the lower dicarboxylic acids, steadily increases during ozonation in the bubbling-reactor, but they begin to decrease after 5 min during the ozonation with more ozone input in the suction-reactor indicating that the intermediates are strongly degraded/mineralized in 5 min ozonation in the suction-reactor.

3.4. Effect of temperature

Ozone solubility in water decreases with increasing temperature, while the reaction rate of phenol with ozone increases with the rising solution temperature. Even more important is the fact that the solution temperature also affects the formation and collapse intensity of hydrodynamic cavitation bubbles, thus affecting the dispersion and decomposition of ozone in water, and the formation of OH radicals.

The solution temperatures were regulated, and the effect of temperature on the degradation kinetics of phenol was observed over 30 min by using 5 mm suction orifice with 3.2 mg min^{-1} ozone, and the results are shown in Fig. 8.

As shown in Fig. 8, the solution temperature obviously influences the ozonation kinetics of phenol in the suction-reactor. With the 5 mm orifice the ozonation rate of phenol enhanced by suction-cavitation is fastest with 20 °C being the optimal value. The rates decrease with increasing solution temperature when the temperature is over 20 °C, due to the increased water vapour pressure inside the bubble. Increasing water vapour pressure attenuates the efficacy of cavitational collapse and resulting worse-dispersion of ozone [25]. Meanwhile, the increasing temperature facilitates the escape of ozone from water. However, faster reaction rates are observed with increasing temperature below 20 °C as higher temperatures enhance the reaction of phenol with ozone.

The solution temperature can also influence the type of intermediates formed: maleic acid and other lower dicarboxylic acids are favoured at the optimal temperature (20 °C) showing, once again, that the degree of mineralization of phenol and its intermediates is dependent on the hydrodynamic cavitation condition.
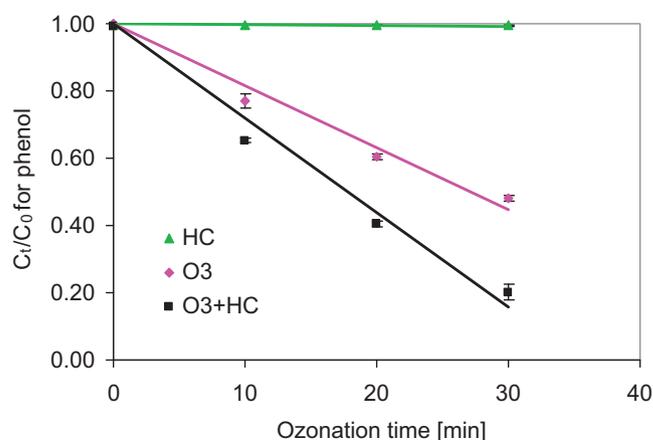
3.5. Enhanced effect of suction-cavitation on the ozonation of phenol

The degradation kinetics of phenol were compared using the treatment by the suction-cavitation alone, the ozonation in the bubbling-reactor, and the ozonation in the suction-reactor, as shown in Fig. 9. The ozonation degradation of phenol in the bubbling-reactor or with suction-cavitation follows the zero-order kinetics, the rate constants are 0.018 and 0.028 min^{-1}, respectively. However, phenol cannot be degraded in 30 min by using suction-cavitation alone. Obviously, suction-cavitation can considerably enhance the ozonation of phenol.

With simple ozonation treatment in the bubbling-reactor, ozone was found in the tail gas even at the beginning of the ozonation and then the concentration of unused ozone sharply rises over 5 min and steadily increases during the ozonation. However, when the combined ozonation/suction-cavitation was applied, no ozone was observed in the tail gas during first 15 min of ozonation, and then the concentration of ozone slowly increased to a very low level indicating that the utilization rate of ozone is significantly improved by suction-cavitation (Fig. 10), again indicating the reason of which is that the ozonation of phenol is a quantitative reaction in the suction-reactor.
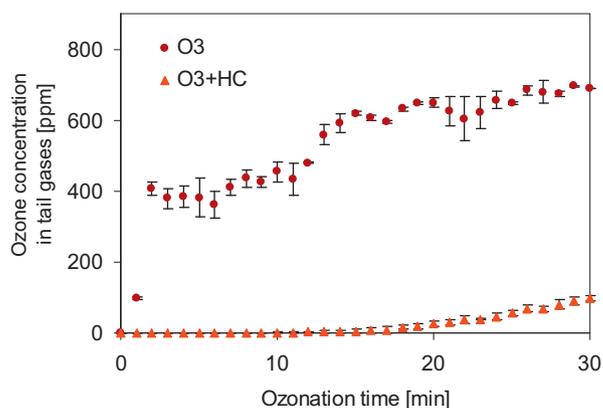
Fig. 10. Comparison of concentrations of ozone in the tail gases between bubbling-reactor and suction-reactor (reaction conditions: phenol-containing aqueous solutions (1 mM, 800 mL), ozone 3.2 mg min^{-1}, 20 °C, 5 mm orifice. O$_3$: by ozonation alone; O$_3$ + HC: by ozonation with hydrodynamic cavitation).

4. Conclusions

Degradation of phenol using a combination of suction-cavitation and ozone is a non-conventional method, producing no secondary pollution. Hydrodynamic cavitation itself is the physical process producing cavitation, which generate strong turbulence during the collapse of the bubbles. A large number of small vortices appear in the flow field, accompanied by high pressure pulses, micro jets and shock waves, all of which improve mass transfer. Meanwhile, due to these physical effects, ozone is well dispersed in water, dissolved and decomposed to enhance the oxidation of phenol.

The following conclusions can be drawn from the investigation:

(1) Hydroquinone, catechol, maleic acid and the lower dicarboxylic acids are the major intermediates from the ozonation of phenol in the suction-reactor. The formed acids lead to an increase of the conductivity of the resulting solutions. The phenol concentrations can be calculated in terms of the conductivity in the individual experiments using linear regression.
(2) The ozonation of phenol in the suction-reactor follows zero-order kinetics. The observed rates polynomially vary with the orifice diameter. The highest degradation rate constant was obtained at −0.070 MPa by using 5 mm orifice. It can conclude that the hydrodynamic cavitation plays a considerable role during the ozonation of phenol.
(3) Lower temperature is favoured to the ozonation of phenol enhanced by the suction-cavitation between 15 and 35 °C. The best temperature was found to be 20 °C, since the optimal oxidation conditions are present for effective hydrodynamic cavitation events.
(4) The enhanced effect of suction-cavitation on the ozonation of phenol has been demonstrated through the comparison of the reaction kinetics of (a) ozonation alone; (b) hydrodynamic cavitation alone, and (c) the combined method. The rate constants for zero-order kinetics of the ozonation alone and the combined method are 0.018 and 0.028 min^{-1} with other constant conditions, respectively. However, phenol cannot be degraded in 30 min by using suction-cavitation alone. The utilization rate of ozone is significantly improved by suction-cavitation as shown by measurements of ozone in the tail gas. The ozonation of phenol in the suction-reactor can be considered as a quantitative reaction.

Acknowledgments

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