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Degradation of phenol in water by the combination of sonolysis and photocatalysis

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ABSTRACT

The combination of sonolysis and photocatalysis has been used to degrade an aqueous solution of phenol. The synergistic index for sonophotocatalysis was 1.06, indicating that there was a slightly synergistic effect between sonolysis and photocatalysis, and that the degradation by sonolysis, photocatalysis, and sonophotocatalysis presented a good fit to the pseudo-first-order kinetic model. Additionally, the effects of parameters such as the initial pH value of the solution, dissolved gases, salt addition, Fe^{3+} ions, and metaloxide (CuO and MnO_2) on the sonophotocatalytic degradation were studied. The results shown that acidic/weakly acidic condition is superior to alkaline condition, and higher concentration of dissolved oxygen and the presence of Fe^{3+} favored the phenol degradation, CuO and MnO_2 had no significant effect on the degradation, while $NaHCO_3$ restrained the degradation rate.

Keywords: Sonolysis; Sonophotocatalysis; Photocatalysis; Phenol

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1. Introduction

In the past decades, continuing interest has been focused on the application of ultrasound (US) for the treatment of hazardous contaminants in water, including the degradation of volatile organic compounds [1], azo dyes [2], and pesticides [3]. For many organic contaminants, the ultrasonic process has the advantage of completely converting the organic pollutants to carbon dioxide and water, or converting them to compounds which are less harmful than the original pollutants. In addition, some complicated reactions are performed with inexpensive equipment and often in fewer steps than the conventional methods by using US [4].

The ability of US to promote a chemical reaction can be attributed to the phenomenon of acoustic cavitation which involves the nucleation, growth/expansion and collapse of the microbubbles by implosion [5–8]. Cavitation occurs whenever a new surface, or cavity, is created within a liquid. The sudden collapse of the microbubbles induces localized supercritical conditions: high temperature, high pressure, electrical discharges, and plasma effects. It has been reported that temperatures of the order of 5,000 K have been experimentally obtained [9], and pressures of the order of 1,000 atm have been calculated [10]. The

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consequences of these extreme conditions are the thermal dissociation of water to form hydroxyl and hydrogen radicals, which are the precursors of other chemical reactions induced by US. From the reactions of these entities ($^\cdot O$,$^\cdot H$, and $^\cdot OH$) with each other and with H_2O and O_2 during the quick cooling phase, $HO_2^\cdot$ radicals and H_2O_2 are formed. Therefore, any solute or solvent in contact with or inside these cavities in the vapor form undergo fragmentation generating free radicals which can be used to degrade toxic compounds.

Phenol is an important organic intermediate and also environmentally relevant pollutants, which is widely existed in the effluents from dyestuffs, paint, pharmaceutical, pesticides, petrochemicals, and other industries [11,12]. Its high stability and solubility in water are the main reasons why the degradation of this compound to the acceptable levels is a relatively difficult process. The studies on sonochemical degradation of phenol and its derivatives have been reported [13–15]. The results have shown that phenol could be degraded. However, sonolysis alone does not achieve the target of total degradation particularly in the case of hydrophilic compounds since it is difficult for them to transfer to the hydrophobic regions of the cavitation bubbles where most of the degradation occurs [16]. In order to increase degradation efficiency, hybrid methods constituting two or more individual techniques have been developed. Among those methods, the combination of sonolysis and photocatalysis is known as sonophotocatalysis receiving continuing attention [17–19]. Sonophotocatalysis not only achieves additive effect [20], but also obtains synergistic effect especially when it combines with relatively low frequency US (20–100 kHz) [17,21]. The observed synergistic effect is probably ascribed to the following reasons: (1) for the sonolytic process, photocatalyst particles enhance the cavitation phenomenon through breaking up the microbubbles into smaller ones; (2) for the photocatalytic process, mechanical effects of ultrasonic waves cause the size of catalyst agglomerates to be reduced, which increase mass transfer and surface cleaning. There are several reports available where sonophotocatalysis degradation is possible for chitosan [22], methyl orange [23], and monocrotophos [24]. Those reports demonstrated that considerable enhancement degradation could be obtained with the combination of sonolysis and photocatalysis.

Although sonophotocatalysis has been extensively employed for the remediation of hazardous contaminants, the remediation of phenol in water has received appreciably less attention. The primary objective of this work is to investigate the effects of pH, dissolved gases and the existence of different ions on the degradation rates of phenol. Moreover, this study attempts to gain a deeper insight into the mechanism of phenol sonophotocatalytic degradation by analyzing of the primary intermediates.

2. Materials and methods

2.1. Materials

Phenol (analytical grade) was obtained from Shanghai Chemical Ltd. All other chemicals were of at least 99% purity and were used without further purification. Bubbling gases (air, O_2 and N_2) of five–nine grades were purchased from Shanghai gas factory. Deionized water was used for preparing all aqueous solutions. Two 9 W H-shaped ultraviolet (UV) lamps (Jinguang lamps and lanterns factory, Shanghai, China) emitting at a predominant wave of 253.7 nm were used as a source of UV radiation. Three gas cylinders were used for bubbling air, N_2, and O_2, respectively, through the solution. An ultrasonic horn (No. 726 Institute of Shanghai, China) operating at a frequency of 30 kHz and a rated output power of 100 W was used as the ultrasonic source. A beaker made of quartz was used as the reactor (42 mm i.d., 75 mm high). The amount of titanium dioxide (P-25 TiO_2) was purchased from Degussa AG. Its average particle size was about 30 nm and the surface area measured by BET was 50 m^2/g. Five milligram (per 80 mL of the solution in the reactor), used in these studies, was well-chosen experimentally. The aeration injection was 60 mL/min.

2.2. Methods

The experimental apparatus was shown in Fig. 1. It was basically the same as that used by Wu et al. [25] for the sonophotochemical degradation of phenol. A certain aqueous solution of phenol was placed in a reactor. The probe tip diameter was 15 mm and it was immersed 0.5 cm into the solution. Two UV lamps were located on either side of the sample reactor. A 30˚C water bath was used to offset the heat liberated during sonication or/and illumination and to control the temperature of the solution during the experiments. The aqueous solutions of reactor were continuously purged and replaced with the dissolved gas by bubbling the gases such as N_2, O_2, or air. An amount of 5.0 mg P-25 TiO_2 was used in 80 mL phenol solution. The experiments were first conducted by comparing the degradation effect of sonolysis, photocatalysis, and sonophotocatalysis, respectively, and

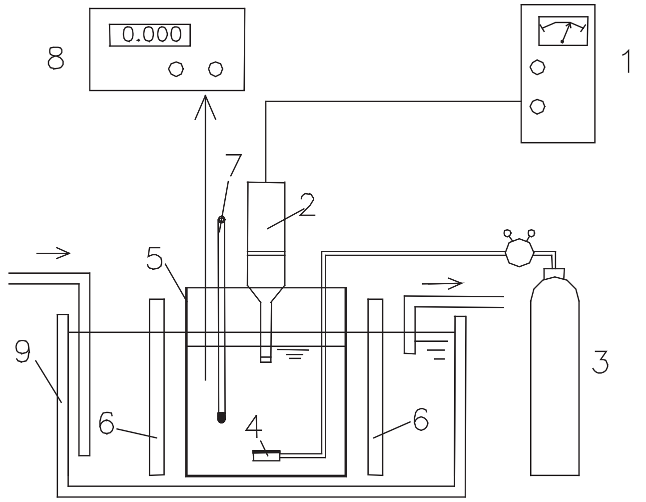

Fig. 1. Schematic diagram of apparatus (1) ultrasonic generator, (2) probe, (3) gas cylinder, (4) gas diffuser, (5) quartz reactor, (6) UV lamp, (7) thermograph, (8) analyzer, and (9) water bath.

then studying the effects of pH, saturating gases, salt, metaloxide, and Fe^{3+} ions on the last process method. Samples were withdrawn at desired time intervals. Before the analysis, all the samples were filtered with 0.22 μm membrane films to remove particles produced by erosion of the sonication probe during sonication and added as a photocatalyst.

2.3. Analysis

The concentrations of phenol were analyzed quantitatively using 4-aminoantipyrine method with a TU-1,800 spc UV spectrophotometer (Beijing) fixed at 510 nm. The primary intermediates of phenol degradation were monitored using a high performance liquid chromatograph (Agilent 1100 Serie, USA) equipped with a 486 absorbency detector. A Hypersil 5 μm C18 ODS column (250 × 5.0 mm) was used and the detection wavelength was fixed at 220 nm for phenol, hydroquinone, catechol, resorcin, and at 254 nm for benzoquinone. Eluent consisted of a water/methanol mixture containing acetic acid (1%).

3. Results and discussion

3.1. Sonolytic, photocatalytic and sonophotocatalytic degradation of phenol

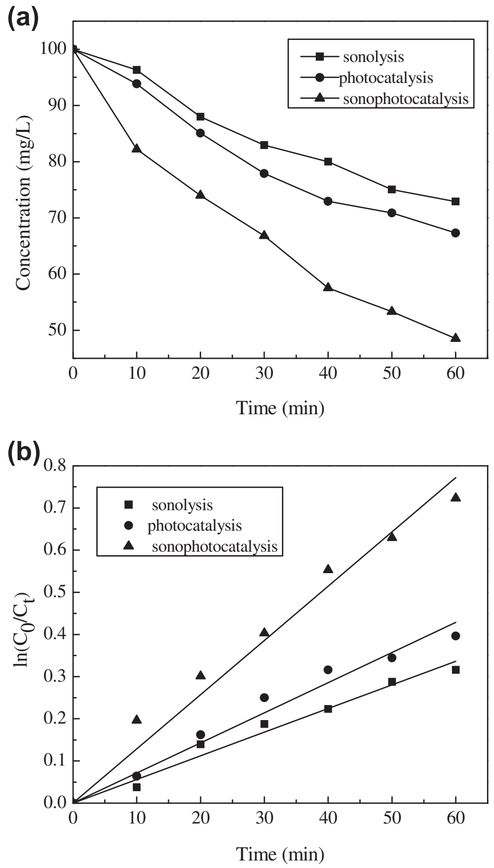

Fig. 2. Comparison of phenol degradation performances in different treatment processes ((a) degradation curves and (b) degradation kinetics curves). Experimental conditions: amount of TiO_2 = 5.0 mg, pH = 6.75, acoustic intensity = 9.73 W/cm^2, and air injection = 60 mL/min.

The degradation of phenol is performed under different experimental conditions including sonolysis, photocatalysis and sonophotocatalysis, and the results are depicted in Fig. 2. It can be observed from Fig. 2 that the efficiency of degradation of phenol increases with an increase in irradiation time, and the highest degradation rate is obtained by sonophotocatalysis. With the combined effect of photocatalysis and sonolysis, 51.48% degradation is obtained within 60 min of irradiation time, compared to 27.1% obtained with sonolysis and 32.71% obtained with photocatalysis.

A pseudo-first-order kinetics model (Eq. (1)) [26] was adopted to describe the degradation performance of the sonolysis, photocatalysis, and sonophotocatalysis processes.

$$\ln\left(\frac{C_0}{C_t}\right) = kt \tag{1}$$

where C_0 is the initial phenol concentration; C_t is the concentration at time t; and k is the rate constant. Fig. 2(b) shows the fitting for the experimental data using the pseudo-first-order. The correlation factor R^2 reaches more than 0.98. This gives good indication for the consistency with the proposed model, which means that our experimental data can be modeled

Table 1
Rate constants corresponding to the sonolytic, photocatalytic, and sonophotocatalytic degradation and synergistic index between sonolysis and photocatalysis

Process	Sonolysis	Photocatalysis	Sonophotocatalysis
k (10^{-3}/min)	5.21	6.91	12.83
R^2	0.994	0.994	0.983
Synergistic index		1.06	

by pseudo-first-order kinetics. Table 1 lists the experimentally obtained rate constants based on a pseudo-first-order treatment of the data. The rate constant k of the different processes reveals a synergistic effect existing in sonophotocatalysis process. When the sum of the rate constants for the photocatalysis and the sonolysis is less than the rate constant of sonophotocatalysis, the combination of photocatalysis with sonolysis produces a synergistic effect on the degradation rates.

Similar to the equation developed by Cheng et al. [27], the synergy between sonolysis and photocatalysis can be directly described as follows:

$$\text{Synergistic index} = \frac{k_{(\text{sonophoto})}}{k_{(\text{sono})} + k_{(\text{photo})}} \tag{2}$$

where $k_{\text{sonophoto}}$, k_{sono} and k_{photo}, are the rate constants for sonophotocatalysis, sonolysis and photocatalysis, respectively. The synergistic index is 1.06 in this study. It appears that there has been a synergistic effect between photocatalysis and sonolysis. It can be explained that the increase of mass transport of chemical species between the solution phase and the catalyst surface, and the additional yields of hydroxyl radicals by acoustic cavitation result in the reinforcement of phenol degradation by sonophotocatalysis [28,29]. Moreover, the continuous cleaning of the TiO_2 surface by acoustic cavitation may also play some part in enhancing the photocatalytic rate [30].

3.2. Effect of pH

Generally, the pH value of the solution has an enormous influence on sonolysis as well as photocatalytic degradation of organic pollutants in aqueous medium. Kidak and Ince [31] reported that the sonochemical oxidation of phenol was faster at lower pH value than at high pH value. Kritikos et al. [18] reported that the photocatalytic degradation of phenol was reinforced under acidic conditions, while hindered under alkaline condition. As expected, the sonophotocatalytic degradation of phenol is relatively faster under acidic/subacid condition than under alkaline condition as shown in Fig. 3. The maximum degradation of phenol obtained 51.48% at pH value of 6.75 within 60 min of irradiation time, while 21.8% obtained at pH value of 11. These results can be explained from the two aspects. On one hand, the enhancement observed at relatively lower pH value is ascribed to the fact that phenol is present in the molecular form at lower pH value ($pK_a < 9.86$). This molecular form of phenol makes it possible to enter the reactive zone (gas-liquid film region), and even easily vaporize into the cavity (gaseous) region from the gas-liquid interface [32]. On the other hand, the adsorption of the pollutant and thus the rates of degradation will be maximum value near the point of zero charge (pzc) of the catalyst [33]. The pzc of TiO_2 surface is at pH_{pzc} 6.5 [34]. This accords with the higher degradation rates observed for the phenol with sonophotocatalysis at pH value of 6.75.

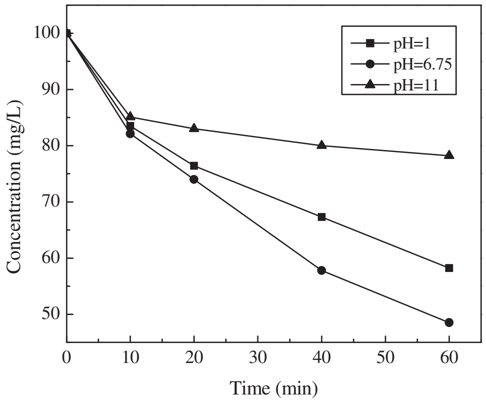

Fig. 3. Effect of initial pH value on phenol degradation. Experimental conditions: amount of $TiO_2 = 5.0$ mg, acoustic intensity = 3.11 W/cm^2 and air injection = 60 mL/min.

3.3. Effect of saturating gases

Fig. 4 presents the effect of different gases (N_2, O_2 and air) on the sonophotocatalytic degradation of phenol. From Fig. 4, it can be observed that the order of degradation ratio is as follows: $N_2 < \text{air} < O_2$, and the sonophotocatalytic degradation rate of phenol increases with increasing dissolved oxygen. This is in striking correspondence with the rate of degradation of phenol, reported by Sivasankar and Moholkar [35]. The results may be partially ascribed to the extra generation of hydroxyl radicals, arisen from dissociation of molecular oxygen in the cavitation bubbles. Moreover, dissolved oxygen chemically participates in the

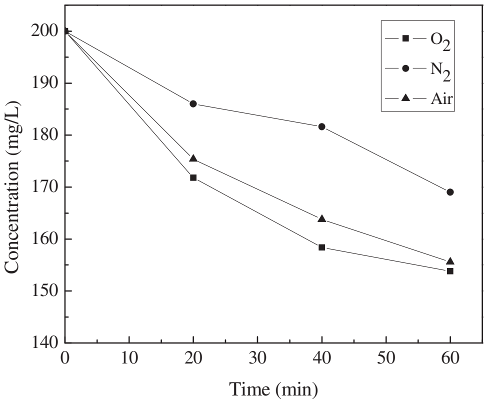

Fig. 4. Effect of saturating gases on phenol degradation. Experimental conditions: amount of $TiO_2 = 5.0$ mg, pH = 6.75, acoustic intensity = 3.11 W/cm^2 and gas injection = 60 mL/min.

electron pathway of photocatalysis and the formation of oxygen radicals of sonolysis, thereby leading to degradation. On the contrary, dissolved nitrogen present in aqueous solution may scavenge the free radicals and inhibit the free radical oxidation of phenol [36].

3.4. Effect of Fe^{3+} ions

In order to investigate the effect of Fe^{3+} on the degradation of phenol during sonophotocatalytic process, a series of experiments were conducted by varying Fe^{3+} concentration from 0 to 0.2 mmol/L. The preliminary experiments proved that there was no change in the absorption spectrum when Fe^{3+} was added into the phenol solution, confirming no complex formation occurred between phenol and the Fe^{3+}. The phenol initial removal rate for various concentrations of Fe^{3+} is presented in Fig. 5. It is noted that the degradation rate of sonophotocatalysis in the presence of Fe^{3+} is significantly enhanced after 20 min of irradiation time, and the best degradation is obtained with 0.025 mmol/L of Fe^{3+}. For example, the combination of sonophotocatalysis with 0.025 mmol/L of Fe^{3+} led to about 57.67% degradation whereas only 30% degradation is observed in the absence of Fe^{3+} within 60 min. These results can be explained as follows. During the sonolysis process, the sonolytic cleavage of water produced an amount of hydroxyl radicals, and two hydroxyl radicals can produce a hydrogen peroxide (Eqs. (3) and (4)). Meanwhile, under UV illumination, the Fe^{3+} existed as an aqua complex $[Fe(OH)(H_2O)_5]^{2+}$ excited by light and an electron is transferred from the ligand to the metal center producing a hydroxyl radical and Fe^{2+} which can initiate the Fenton's reaction for the phenol degradation (Eq. (5)) [37].

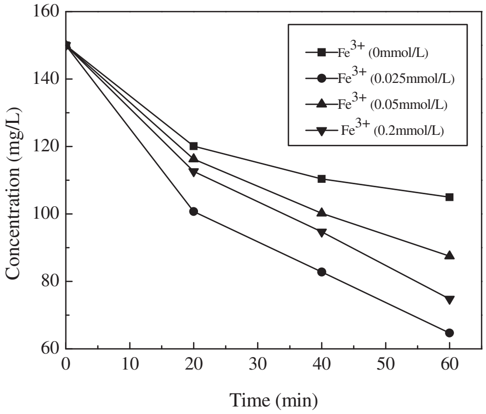

Fig. 5. Effect of Fe^{3+} ions concentration on the phenol degradation. Experimental conditions: amount of $TiO_2 = 5.0$ mg, pH = 6.75, acoustic intensity = 3.11 W/cm^2 and air injection = 60 mL/min.

The generated Fe^{2+} reacts with hydrogen peroxide and produces Fe^{3+} and a hydroxyl radical, which is the traditional Fenton reaction (Eq. (6)). The regenerated Fe^{3+} again forms Fe^{2+} and a hydroxyl radical, and the cycle continues until the complete degradation of phenol and its intermediates is achieved (Eq. (7)). The degradation of phenol will be stopped until all the hydrogen peroxide is consumed by Fe^{2+}. Thus, the additional hydroxyl radicals generated through sono-Fenton and photo-Fenton reactions enhance the sonophotocatalytic degradation in the presence of Fe^{3+}.

$$H_2O \xrightarrow{US} H^{\cdot} + HO^{\cdot} \tag{3}$$

$$2HO^{\cdot} \longrightarrow H_2O_2 \tag{4}$$

$$Fe^{3+} + H_2O \xrightarrow{UV} Fe^{2+} + HO^{\cdot} + H^{+} \tag{5}$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO^{\cdot} + H_2O \tag{6}$$

$$\text{Phenol} + HO^{\cdot} \rightarrow \text{intermediates} \longrightarrow CO_2 + H_2O \tag{7}$$

3.5. Effect of $NaHCO_3$

The effects of addition $NaHCO_3$ (0.1 mol/L) on the sonophotocatalytic degradation of phenol was shown in Fig. 6. Since $NaHCO_3$ retarded the action of sonophotocatalysis, only 26.2% of degradation was observed. Undoubtedly, this inhibition is ascribed to the formation of $CO_3^{\bullet-}$ (Eq. (8)), which reduces

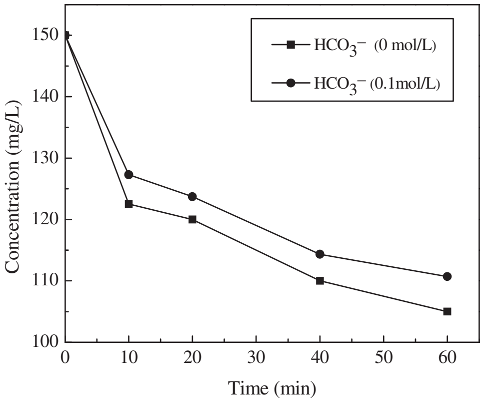

Fig. 6. Effect of $NaHCO_3$ on phenol degradation. Experimental conditions: amount of $TiO_2 = 5.0$ mg, pH = 6.75, acoustic intensity = 3.11 W/cm^2, and air injection = 60 mL/min.

hydroxyl radicals [38]. Additionally, there is a drastic competition between phenol and HCO_3^- with respect to hydroxyl radicals [39].

$$HO^{\cdot} + HCO_3^- \rightarrow CO_3^{\cdot-} + H_2O \tag{8}$$

3.6. Effect of CuO and MnO_2

From Fig. 7, it can be seen that the addition of CuO and MnO_2 has no obvious effect on the degradation of phenol. The main reasons are as follows. On one hand, the adulterant of CuO and MnO_2 on the surface of TiO_2 is benefit for the capture of photoelectron to inhibit the recombination of electron and cavity so as to improve the sonophotocatalytic degradation rate. On the other hand, several modes of reactivity aroused by ultrasonic irradiation have been proposed: pyrolytic decomposition, hydroxyl radical oxidation, plasma chemistry and supercritical water oxidation [40]. CuO and MnO_2 acted as catalysts for supercritical water oxidation to enhance phenol degradation. However, the adulterant may affect the UV light transmit through the solution and holdback the photocatalytic process. Since the positive aspect and the negative aspects were balanced out, no obvious effect obtained on the sonophotocatalytic degradation of phenol.

3.7. The primary intermediates of sonophotocatalytic degradation

In order to gain a deeper insight into the mechanism of phenol sonophotocatalytic degradation, HPLC analyses of the primary intermediates (hydroquinone, catechol, benzoquinone, and resorcin) of the degradation process were performed. It can be seen from Fig. 8 that the concentration of hydroquinone and catechol increased within the irradiation time of 60 min, while benzoquinone, and resorcin were not detected. The possible reason is that benzoquinone and resorcin were converted into other intermediates or carbon dioxides and water as soon as they were generated. The production of hydroquinone and catechol monitored by HPLC prove the degradation mechanism of phenol: The first phase is the production of degradation intermediates, such as benzoquinone and hydroxyl compound with phenyl; the second phase is the subsequent production of organic acid; and the last phase is called complete oxidation, when degradation intermediates mostly decrease and the major production is carbon dioxide. In this study, the figure shows that the concentration of hydroqui-

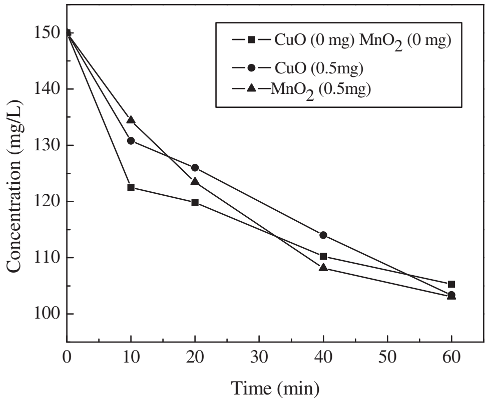

Fig. 7. Effect of CuO, MnO_2 on phenol degradation. Experimental conditions: amount of $TiO_2 = 5.0$ mg, pH = 6.75, acoustic intensity = 3.11 W/cm^2, and air injection = 60 mL/min.

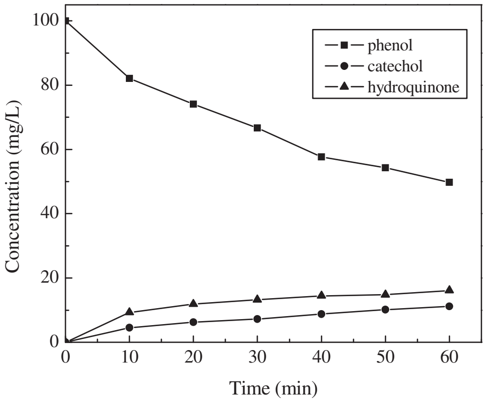

Fig 8. The concentration change of primary intermediates of sonophotocatalytic degradation as a function of irradition time. Experimental conditions: air injection = 60 mL/min.

none and catechol increases gradually as the irradiation time increases, it can be inferred that the phenol degradation is primarily involved in the first phase.

4. Conclusion

The sonophotocatalytic degradation of phenol was studied. Based on our experimental investigation, the following conclusions can be made:

(1) The degradation of phenol with sonophotocatalysis was much higher compared to the individual effects of sonolysis and photocatalysis. The synergy index of 1.06 for sonophotocatalysis suggested that the combination of sonolysis and photocatalysis had a slightly synergistic effect.
(2) The rate of phenol degradation increased with increasing dissolved oxygen in the aqueous solution and the weakly acidic condition favored the degradation process.
(3) Fe^{3+} presented in the aqueous phenol solution enhanced the sonophotocatalytic degradation of phenol greatly, and CuO and MnO_2 presented in the solution made no obvious effect on the degradation, while the presence of $NaHCO_3$ inhibited the degradation of phenol.

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