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Photosonochemical degradation of phenol in water

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ABSTRACT

The aim of this work is to evaluate the efficiency of the sonochemical effect in conjunction with a photochemical irradiation and the effects of parameters such as pH, ultrasound frequency (35 and 130 kHz), and initial concentration on the degradation processes. The oxidation of a model pollutant, phenol, has been carried out in photosonochemical reactor. It was considerably more effective than ultrasound wave or ultraviolet light alone. It may be the result of three different oxidative processes: direct photochemical action, high frequency sonochemistry and reaction with ozone (produced by ultraviolet irradiation of air). Identification of the first intermediates of the reaction (hydroquinone, catechol, benzoquinone and resorcinol) indicates that hydroxyl radicals are involved in the photosonochemical degradation mechanisms. The disappearance of phenol in each case approximately obeyed first-order kinetics with the apparent first-order decay constant increasing with decreasing solute concentration.

Keywords: Photosonochemistry; Ultrasound; Ultraviolet; Phenol

1. Introduction

In the domain of water purification several techniques have been developed using advanced oxidation processes (AOP) for the degradation of organic pollutants that provide high formation rates of hydroxyl radicals [1]. In recent years, considerable interest has been focused on the application of ultrasound (US) for hazardous chemical destruction, including the degradation of volatile organic compounds, pesticides, humic substances, dyestuffs and polychlorinated biphenyls [2–5]. The effects of ultrasound waves on the hydrophilic chemical oxidations are due to the production of hydroxyl radicals during the cavitation-induced thermal decomposition of water [6]. Sonochemical destruction is also effective for volatile substrates. In this case, the solutes can be directly incinerated in the gas phase of the hot collapsing cavitation bubbles [4]. Most of the studies concerning ultrasound effects relate to the oxidation of aromatic compounds [2,7,8]. In this case, the hydroxyl radical appears as the main reagent that reacts with the organic target [6]. Currently, the sonolysis of this set of compounds in water solution is characterized by a relatively too low rate constant for industrial development. The possible enhancement of organic compound oxidation by combined techniques (O_3/H_2O_2, UV/H_2O_2, and ultrasound/O_3) has been demonstrated in different works [6,8]. Generally, such combined processes are found to enhance hydroxyl radical production, leading to higher oxidation rates and organic matter mineralization [7].

Phenol and other aromatic compounds are ubiquitous contaminants in water [9–12]. The studies on sono-

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chemical degradation of phenol and substituted phenols have been reported [2,7]. The experimental results have showed that phenol could be degraded [13]. However, the decomposition with US does not achieve the target of total destruction since various products such as maleic acid, polyhydroxylbenzenes, quinones, have been identified as a result of its degradation. It is known that US in combination with other conventional methods such as ozonation, wet air oxidation and electrochemical degradation have obtained better results than the conventional method alone [7]. Sonochemistry and photochemistry combined actions have been reported previously. Naffrechoux et al. designed experiments for degradation of phenol using low pressure mercury vapour UV lamp in combination with a 500 kHz ultrasonic transducer [14]. In a similar study Wu et al. studied the use of 9W H-shaped UV lamps and an ultrasonic horn operating combination at a frequency of 30 kHz for phenol degradation [7]. Direct photolysis has been always considered as one possible alternative because it is possible for molecules of most organic compounds to transform, to cleave bonds, and even to undergo complete destruction in the presence of UV irradiation [3,15]. In addition, UV irradiation causes dissociation of the oxidants and formation of highly reactive hydroxyl radicals that attack and destroy the organic pollutants [3].

No study was focused into decomposition of phenol using low frequency (35 and 130 kHz) sonochemical processes and UV radiation (medium pressure mercury vapour lamp, 400 W). The object of this work is to evaluate the potential of combined ultrasound and ultraviolet action, called 'sonuv'. Taking the well-studied organic compound phenol as an example, the oxidation rates obtained in the present study are compared with literature data at different ultrasonic wave frequencies and powers or typical UV irradiance at 254 nm.

2. Materials and methods

Phenol (analytical grade) was obtained from Merck. All other chemicals were of at least 99% purity and were used without further purification. Deionized water was used for preparing all aqueous solutions. In each case, the reaction volume was 2000 ml and the initial concentration of phenol was in the range of 1–100 mg L^{-1}. The pH value of the sample was adjusted to a constant value of 3. The sonodegradation studies were carried out for 5 h. Sonication was achieved at frequency of 35 and 135 kHz (500 W) with an ultrasonic generator (Elma TI-H-5, Germany) with a piezoelectric transducer having a diameter of 8 cm fixed at the bottom of the vessel. Ultrasonic energy dissipated in the reactor was set at 200 W (1.6 W cm^{-2}) through the calorimetric method. The apparatus is open to air. The solution was irradiated with ultrasound for 15 min and then sonication was stopped for the next 10 min. This process was continued till the solution was irradiated for a predetermined time. The photodegradation studies were carried out in a batch reactor system. A 400 W medium pressure mercury lamp (I = 90 μW cm^{-2}, 7 cm long) surrounded by quartz jacket was located in the center of the reactor. The lamp bandwidth was in the range of 185–800 nm. The reactor walls were covered by aluminum foil to avoid release of radiation. The temperature inside the reactor was maintained at 303 K. The apparatus is open to air. The photolysis reactions were carried out for 2 h. The photosonochemical studies were carried out using a 2000 ml (fluid volume) home-made glass water-jacketed sonuv reactor. It consists of a double cylindrical jacket, allowing water cooling of the reaction area. The photosonochemical reactions were carried out for 2 h. All the experiments were carried out in triplicate and the average value were used for further calculations.

Phenol analysis was done according to the direct colorimetric method using 4-aminoantipyrine [16]. However, it should be noted that this method gives a "phenolic index" rather than the actual concentration of phenol. Color was determined spectrophotometrically at 500 nm using UV/VIS Spectrometer (Lambada 25 Perkin Elmer, Shelton). The primary intermediates of phenol degradation were monitored using a high performance liquid chromatograph (KNAUER, USA) equipped with a UV detector. A Spherisorb C18 ODS1 column (250×4.6 mm) was used and the detection wavelength was fixed at 254 for hydroquinone, catechol, resorcinol, and benzoquinone. Eluent consisted of a water/methanol mixture (50%–50%), flow rate 1 ml min^{-1}.

3. Results and discussion

Table 1 shows the degradation of phenol by photolysis, sonication, and the combination of both. In the ultrasonic process, only 23% degradation of phenol has been observed in 300 min of sonication of 100 mg L^{-1} initial phenol concentration at frequency of 130 kHz. Pandit (2005) has reported 17% removal for phenol (Co = 85 mg L^{-1}) by a bath US equipment (120 W, 22 kHz) during 60 min irradiation [17]. Also, 15 % degradation has been reported by Entezari (2003) by means of US at 35 kHz (55 W) for initial phenol concentration of about 0.67 mM during 150 min [18]. This may be because phenol is hydrophilic in nature. Phenol is a moderately soluble compound in water (Cwsat = 0.63 M) with a relatively low vapor pressure (4.6×10^{-4} atm) and Henry's constant of phenol (4.0×10^{-4} L atm M^{-1}). These physicochemical properties preclude significant concentrations of phenol molecule diffusing into the vapor phase of the acoustic cavitation bubbles [18], so it remains in the bulk of the solution during cavitation. Most of the hydroxyl radicals that are formed within the cavity during the sonication might get recombined before they attack the phenol molecules in the bulk liquid. The attack of hydroxyl radicals on phenol was confirmed through the formation of small quantities

Table 1
Degradation efficiency (%) of phenol at the different processes

Type of process	Time (min)	Initial phenol concentration (mg L-1)					
		1	20	40	60	80	100
Sonochemical (35 kHz)	15	10	5	3.3	2.5	2.2	1.8
	30	19	9	6.9	5.4	4.5	3.7
	45	25	12.5	10	7.7	6.4	5.3
	60	37	16	12.5	9.9	8.2	6.8
	75	44	19	15	11.9	9.9	8.3
	90	50	23	17.3	12.7	11.3	9.5
	120	60	27	20	15.5	12.9	11
	180	72	31.5	21.5	17.7	14	11.6
	300	83	36.5	25	20	16	12.9
Sonochemical (130 kHz)	15	23	8	6	4.7	3	2.8
	30	40	14.5	12	8.5	7	6
	45	52	20.5	17	13	10	9
	60	65	25	22	16.2	12.9	11
	75	73	29	24	19.2	15.3	13
	90	80	33	27.5	21.7	17.8	15.6
	120	89	39	33	24.4	21	19
	180	97	43.5	35.2	27.7	23.2	20.4
	300	100	50	40	31.4	25.4	23
Photochemical	5	100	70	54	40	33.5	28
	10	100	92.5	68	53.3	46.5	43
	15	100	100	79	65	58	53
	30	100	100	91	78.3	71	64
	45	100	100	99	88.5	81	73
	60	100	100	100	99	92.5	84
	90	100	100	100	100	99	95
Photosonochemical (35 kHz)	5	100	86.5	67.5	51.5	46.5	42
	10	100	99	85	69.1	60	57
	15	100	100	97.5	84.1	73	69
	30	100	100	100	97.5	87	83.5
	45	100	100	100	100	98	95
	60	100	100	100	100	100	100
Photosonochemical (130 kHz)	5	100	87.5	72	55	50	44
	10	100	99.5	88	71.6	65	58.5
	15	100	100	99	87	80	72
	30	100	100	100	99	93.8	88
	45	100	100	100	100	99	98
	60	100	100	100	100	100	100

of catechol, hydroquinone and resorcinol [17]. The lack of pyrolysis products (e.g., acetylene and methane) during the sonolysis of aqueous phenol indicates that the sonochemical reactions primarily occur within the bulk solution rather than within the superheated regions of the interfacial zone surrounding the cavitation bubble [19]. There are many reports, which have proved the formation of hydroxyl radicals during sonication [19]. Petrier reported this low efficiency is mainly due to the low concentrations of phenol [20]. We observe that initially the rate of ultrasonic degradation of phenol is high but later it reduces substantially. This can be explained by the fact that whatever dissolved air is present in the solution, it is degassed after the initial period of sonication resulting in a decrease in the amount of hydroxyl radicals generated. Also, there could be a competition between the oxidation of the phenol and the intermediates formed resulting into a net reduction in the degradation rate [17].

In the ultraviolet process, the time required for complete degradation increased from 3 to 120 min when the initial concentration was increased from 1 to 100 mg L^{-1}. Chun et al. [21] have reported 96% removal for phenol (C_o = 100 mg L^{-1}) by a bath UV equipment (500 W, $\lambda >$ 200 nm, high pressure) during 60 min irradiation [21]. Also, 92% degradation has been reported by Wu et al. [7] by means of UV at 254 nm (9 W) for initial phenol concentration of about 1.06×10^{-4} mmol L^{-1} during 60 min [7]. It can be concluded that UV light had high potential to degrade the phenol. This may be because UV radiation is strongly absorbed by the phenol which can undergo direct photolysis under UVC [7]. Moreover, it is possible that solvated electrons are present in the system, but it should be specified that they would derive from the photolysis of phenol. This could be the main reason of its fast disappearance under UVC irradiation. This is in agreement with results obtained later [22]. Also, subsequent reactions of solvated electron and H_2O molecules can lead to the formation of hydroxyl radicals that promote the phenol degradation during the UV irradiation. Table 1 shows that the rates of degradation of the phenol at the initial period of the reaction are rapid but the rate slows down later on. The first order degradation rate constants decreased from 0.255 to 0.034 min^{-1} as the concentration increased from 20 to 100 mg L^{-1}. In the initial period of the reaction, the rate wass higher because of the presence of the high concentration of phenol. Afterwards, a number of intermediates were formed which competed with phenol to react with available oxidants and also in absorption of UV radiation. Similar results have been reported by Lathasree et al. [23].

It can be observed from Table 1 that both US and UV light had its potential to degrade phenol and that the highest degradation rate was obtained by the combined effect of US and UV. With the combined effect of UV and US, 100% degradation was achieved within 60 min of irradiation time compared to 95% and 54% achieved with photolysis and sonication, respectively. It is indicated that the synergistic action of UV and US on the substrate exists. However, the involved cooperative reaction paths are not exactly known [7]. Naffrechoux et al. have reported that the synergetic effect can be explained by the combination of three oxidation mechanisms: photodecomposition, sonodecomposition and ozone oxidation [14]. If UV light shorter than 200 nm emitted in the air, O_3 will be produced from O_2. Employing a mercury lamp in the reactor and immersing it partially in the solution will generate ozone right above the liquid surface and its transfer in the liquid is directly dependent on the interfacial area between liquid and gas. Ultrasound stream can considerably enhance the interfacial area by forming a fountain at the surface of the liquid. This can then increase the dissolved ozone concentration, despite the poor quantity formed in the gaseous phase. The effect of both UV irradiation (in air and water) and ultrasound cavitation on phenol decomposition can be explained by direct UV photolysis and by the oxidative action of dissolved ozone and of hydroxyl radicals. Hydroxyl radicals are usually produced by the photolysis and sonolysis of ozone and the cavitation-induced thermal decomposition of water [14].

Another point that is noteworthy for the application of the sonuv system is that it consumes more energy (both transducer and lamp) than the separated techniques. Accordingly, further investigations will be necessary in order to optimize sonuv reactor both for maximizing the degradation and for minimizing the energy consumption.

Table 2 shows the major calculated reaction rate coefficients. As demonstrated in Table 2, degradation of phenol by oxidation processes exhibits first order reaction kinetics. The first order rate constants (*k*) of degradation were obtained from the slope of $-\ln (C/C_0)$ vs. *t* (time) plots

Table 2
First order rate constant for the different phenol degradation processes at different initial phenol concentrations

Type of process		Initial phenol concentration (mg L^{-1})				
		20	40	60	80	100
Sonochemical (35 kHz)	Rate constant (min^{-1})	0.0028	0.002	0.001	0.0013	0.0011
	Correlation coefficient	0.989	0.976	0.968	0.967	0.973
Sonochemical (130 kHz)	Rate constant (min^{-1})	0.0044	0.0036	0.0026	0.0021	0.0019
	Correlation coefficient	0.98	0.981	0.965	0.983	0.989
Photochemical	Rate constant (min^{-1})	0.2554	0.0971	0.0527	0.047	0.0336
	Correlation coefficient	0.991	0.966	0.967	0.967	0.968
Photosonochemical (35 kHz)	Rate constant (min^{-1})	0.4485	0.1967	0.1231	0.0832	0.0664
	Correlation coefficient	0.993	0.986	0.996	0.97	0.974
Photosonochemical (130 kHz)	Rate constant (min^{-1})	0.507	0.22	0.148	0.097	0.0826
	Correlation coefficient	0.981	0.984	0.991	0.978	0.98

where C_0 and C are phenol concentration at time zero and at time *t*, respectively. The rate of phenol degradation was dependent on phenol initial concentration (C_0) and *k* decreased with increasing C_0. First order kinetics with respect to phenol concentrations were found to fit all the experimental data and first order rate constants were estimated as is commonly found in the literature [23–25].

In order to gain a deeper insight into the mechanism of phenol photosonochemical degradation, HPLC analyses of the primary intermediates of the degradation process were performed. Hydroquinone, catechol, benzoquinone, and resorcinol were detected (Fig. 1). The former three compounds have been observed with sonication alone [7]. For the latter, the metasites of the excited phenol resulted from the energy of UV light or US are known to have a reasonable charge density and thus are expected to undergo hydroxyl radical attack. This might explain the cause of the formation of resorcinol. The formation of the primary intermediates as described above clearly demonstrated that the main pathway of phenol oxidation was through hydroxyl radical attack.

Fig. 2 demonstrates the removal of phenol by the photosonochemical process at different pHs. It is clearly shown that lower pH values favored the phenol degradation. The degradation of phenol attained 98% at pH 3, 93% at pH 5, and 75% at pH 7. For samples controlled at pH 11, the extent of phenol degradation was only 52%. These results can be explained from the two sides of UV photolysis and sonication. For direct photolysis of phenol, Wu reported that the rates of the degradation under acid conditions were faster than that in alkaline condition [7]. For sonication, it is reported the sonochemical degradation rate decrease with increasing solution pH [7]. In the present study, the ionic species of phenol are predominant when the pH exceeds 10.0 (pKa value of phenol, at 298 K), but the molecular species predominate when pH is less than the pKa. Therefore, the concentration of phenolate would be very low to negligible at both pH 3, 5 and 7, and could not decrease significantly the possible partitioning of the undissociated phenol into the cavitation bubbles.

Strong hydrophylicity can contribute to an uncomfortable concentration of phenolate ions in the gas-water interfaces of bubble. This does not let phenolate ions vaporize into the cavitation bubbles and therefore they are forced to react only outside of the bubble film with the hydroxyl radicals cleaved from water. Of course phenolate could react more slowly than phenol with hydroxyl radical which could explain why the degradation is slower at pH 11 than at pH 7. However, the pH trend from 3 to 5 likely has another explanation (there is not enough phenolate in that pH interval to significantly modify the reactivity of phenol). Also, phenol in the molecular state can easily enter the gas-water interfaces of bubbles and even vaporizes into cavitation bubbles. Therefore, it can be concluded that pH plays an important part in photolysis and sonolysis of phenol under acid conditions.

4. Conclusion

This study shows the potentialities of US and UV radiation in water and wastewater treatment. In this study, we demonstrated that the percentage of phenol degradation due to the combined effect of UV and US was larger compared to the individual effects of US and UV light. Based on the results, the mineralization was incomplete, as intermediate products existed. Since the toxicity of the primary intermediates threatens human health, it takes sufficient irradiation time to make the

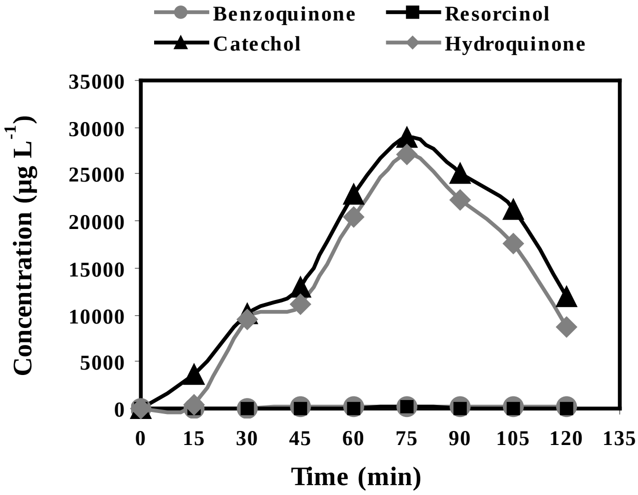

Fig. 1. Concentration of the main intermediate of photosonodegradation of phenol in different reaction time (phenol concentration = 100 mg L^{-1}).

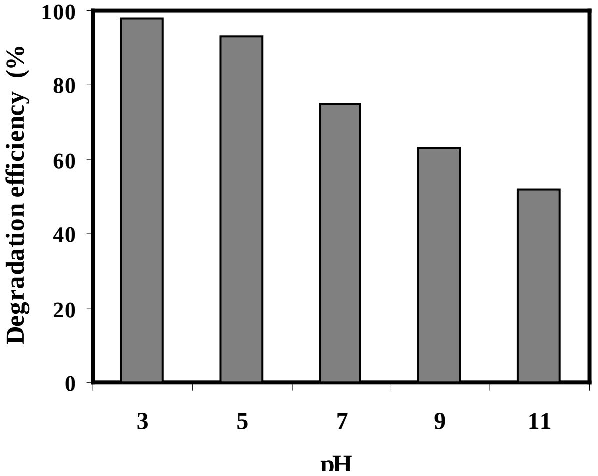

Fig. 2. Effect of pH on phenol photosonodegradation under 130 kHz ultrasound irradiation (phenol concentration = 100 mg L^{-1}, time = 45 min).

intermediates degrade as completely as possible. The rate of phenol degradation increased with decreasing solution pH. Products of the primary intermediates of the reaction (hydroquinone, catechol, benzoquinone and resorcinol) indicated that OH radical was involved in the degradation mechanisms.

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