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Solar photocatalytic treatment of phenolic wastewaters: influence of chlorides, sulphates, aeration, liquid volume and solar light intensity

S. Adishkumar[a,*], S. Kanmani[b], J. Rajesh Banu[a]

[a]*Department of Civil Engineering, Regional Centre of Anna University, Tirunelveli, India*
Email: adishk2002@yahoo.co.in
[b]*Department of Civil Engineering, Centre for Environmental Studies, Anna University, Chennai, India*

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ABSTRACT

The solar photocatalytic treatment of phenolic wastewater over TiO_2 suspensions was investigated. The study focused on the effect of various operating parameters on the treatment efficiency including chlorides (50–200 mg/L), sulphates (50–200 mg/L), aeration (pre-aeration, with and without aeration), liquid volume (0.25–1.5 L) and solar light intensity (throughout the year). The presence of chloride and sulphate ions decreased the degradation rate of phenol due to a decrease in the adsorption of the pollutant and act as hydroxyl ion scavengers. It was observed that the phenol removal efficiency was 30, 85 and 77% for pre-aeration, with and without aeration, respectively. The phenol removal efficiency was 99, 94 and 79% and 46% for wastewater volume of 0.25, 0.50, 1.0 and 1.5 L, respectively. It was observed that as the volume of wastewater was increased, the phenol removal was found to decrease. The phenol removal efficiency reached its maximum of 95% at maximum UV light intensity of 32 W/m^2 and the minimum phenol removal efficiency of 59% at minimum UV light intensity of 20 W/m^2.

Keywords: Solar photocatalysis; Phenolic wastewater; Inorganic ions; Aeration; Liquid volume; Solar light intensity

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1. Introduction

Over the past several years, heterogeneous semiconductor photocatalysis using TiO_2 as the photocatalyst has received considerable attention for water and wastewater treatment. TiO_2 photocatalysis is an emerging wastewater treatment technology with key advantages including the lack of mass transfer limitations when nanoparticles are used as photocatalysts; operation at ambient conditions and the possible use of solar irradiation. The catalyst itself is inexpensive, commercially available in various crystalline forms and particle characteristics and photochemically stable. However, there are two potential drawbacks associated with the use of TiO_2, namely: (i) its possible toxic effects on human health, and (ii) reduced activity due to the complexity of water matrix (i.e. presence of solids or inorganic ions) [1].

The mechanism of heterogeneous photocatalytic degradation can briefly be described as follows:

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*Corresponding author.

illumination of an aqueous TiO_2 suspension with irradiation with energy greater than the band gap energy of the semiconductor (i.e. 3.2 eV in the case of anatase TiO_2) generates valence band holes and conduction band electrons. Due to this wide gap energy, TiO_2 can be activated by UV-A irradiation below 385 nm. Holes and electrons may either undesirably recombine liberating heat or make their separate ways to the surface of TiO_2, where they can react with species adsorbed on the catalyst surface. Valence band holes can react with water and the hydroxide ion (e.g. under alkaline conditions) to generate hydroxyl radicals $HO^{\bullet}$, while electrons can react with adsorbed molecular oxygen reducing it to superoxide radical anion which, in turn, reacts with protons to form peroxide radicals. Organic compounds can then undergo both oxidative degradation through their reactions with valence band holes, hydroxyl and peroxide radicals and reductive cleavage through their reactions with electrons yielding various by-products and eventually mineral end products [2–4]. The aim of this work was to study the photocatalytic treatment of phenolic wastewater over TiO_2 suspensions regarding the effect of various operating conditions such as chlorides, sulphates, aeration, liquid volume and solar light intensity.

2. Materials and methods

2.1. Titanium dioxide

The photocatalyst employed was commercial titanium dioxide supplied by Degussa P25. According to the manufacturer's specifications, P25 has an elementary particle size of 30 nm, a Brunauer–Emmett–Teller specific surface area of 50 m^2/g and its crystalline mode is 80% anatase and 20% rutile. The catalyst was used as received.

2.2. Photocatalytic experiments

All photocatalytic experiments were carried out at Anna University campus in Chennai, (13˚00.57´´N; 80˚ 14.12´´E), Tamil Nadu. An open borosilicate glass tray of 1.5 L capacity was used as the reaction vessel. Fig. 1 depicts the photographic view of solar photocatalytic reactor. The suspensions were magnetically stirred in the dark for 30 min to attain adsorption–desorption equilibrium between phenol and TiO_2. Irradiation was carried out in the open air and continuously aerated by a pump to provide oxygen and for the complete mixing of reaction solution. In all cases, 1 L of reaction mixture was irradiated. At specific time intervals, the required amount was withdrawn and filtered to separate the catalyst. The samples were analysed for phenol removal as per standard methods [5].

Fig. 1. Photographic view of solar photocatalytic reactor.

3. Results and discussion

3.1. Effect of chloride

The real industrial wastewaters contain chloride up to 200 mg/L. Based on that, the effect of chloride for the removal of phenol was studied by varying the chlorides concentration by adding sodium chlorides in the range of 50–200 mg/L. Blank controls were also run without addition of salts. The results of the experimental run are depicted in Fig. 2. It was observed that phenol removal efficiency was 48, 46, 30 and 15% for chloride concentration of 50, 100, 150 and 200 mg/L, respectively; whereas in the absence of chloride, the phenol removal efficiency of 79% was

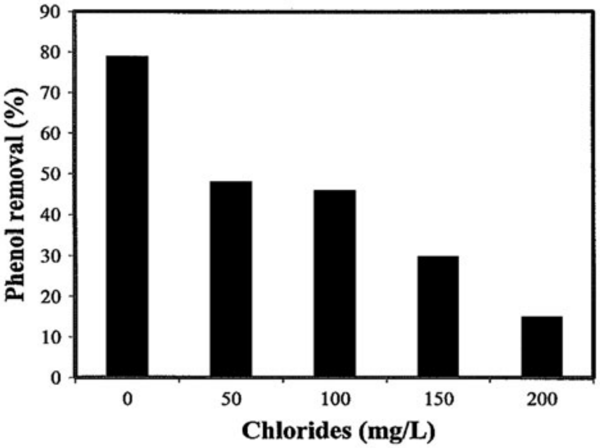

Fig. 2. Effect of chlorides on SPCO of phenol (pH = 6, TiO_2 = 0.25 g/L, phenol = 50 mg/L, contact time = 5 h).

observed. It was observed that the chloride ions give negative impact on the phenol removal efficiency even at low concentration of 50 mg/L. Previous studies reported by Kamble et al., Alhakimi et al. and Bhatkhande et al. [6–8] also observed negative effects for the degradation of benzene sulphonic acid, 4-chlorophenol and nitrobenzene, respectively. The negative effects might be due to the following reasons: at low pH levels, the catalyst exists primarily as $TiOH^+$ and TiOH. Under these conditions, the negatively charged chloride ions are attracted to the catalyst surface therefore competing with pollutant species for active sites, resulting in low removal efficiency. And also, the chloride ions in the suspension could act as electron scavengers, competing with molecular oxygen. This will inhibit the formation of the superoxide radicals that are essential for the formation of the actual oxidation agent, the hydroxyl radicals. Another possible reaction of the chloride ions could be with the free radicals in the suspensions, leading to the consumption of the radicals that are desired in high concentration in order to react with organic pollutants [7].

3.2. Effect of sulphate

The real industrial wastewaters contain sulphate up to 200 mg/L. Based on that, the effect of sulphate was studied by varying the sulphate concentration by adding sodium sulphate in the range of 50–200 mg/L. Blank controls were also run without addition of salts. The results of the experimental run are depicted in Fig. 3. It was observed that phenol removal efficiency was 28, 22, 20 and 19% for sulphate concentration 50, 100, 150 and 200 mg/L, respectively; whereas in the absence of sulphate, the phenol removal efficiency of 79% was observed. It was observed that the phenol removal decreased with increase in sulphate concentration. It might be due to a decrease in the adsorption of the pollutant, which acts as hydroxyl ion scavenger and may also absorb UV light. Also, the surface bound sulphate ions could lose an electron to TiO_2 valence band holes or to a hydroxyl radical and become sulphate radicals. Although these radicals have a high oxidation potential, their larger size and the fact that the radical function could be distributed over a resonance structure may render them less effective than $OH^{\cdot}$ [9]. At low pH, attractive forces between the TiO_2 surface and the negative charge materials, such as sulphates, will favour adsorption. Photocatalytic activity can be decreased by these anions that may hinder OH^- production and prevent substrates from reaching or nearing surface active site and the TiO_2 surface is negatively charged and repulsive forces will lead to decreased adsorption at high pH [10].

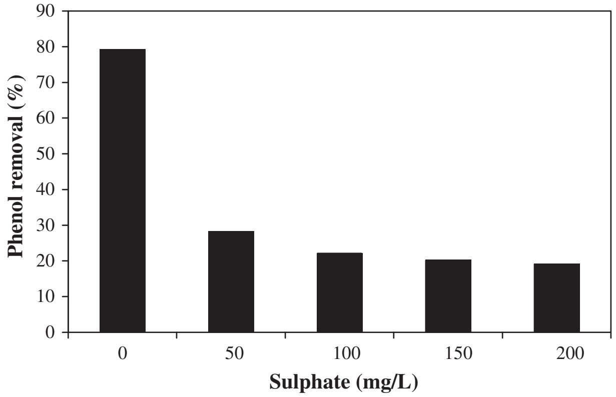

Fig. 3. Effect of sulphate on SPCO of phenol (pH = 6, phenol = 50 mg/L, TiO_2 = 0.25 g/L, contact time = 5 h).

3.3. Effect of aeration

In order to study the effects of aeration, three sets of experiments were carried out, viz. aeration before reaction, aeration during reaction and that without aeration. The results of the experimental studies are depicted in Fig. 4. It was observed that the phenol removal efficiency was 30, 85 and 77% for aeration before reaction, aeration during reaction and without aeration, respectively. In the case of aeration before reaction, in the presence of oxygen, the catalyst surface may become highly hydroxylated to the point of inhibiting the adsorption of phenol, and thus slows down the reaction rate. This effect was also referred by Tay et al. [11] for removal of colour substances. When compared to aeration during reaction and without aeration, not much difference was observed; it indicates that oxygen from atmosphere is sufficient for photocatalytic degradation. Even though, aeration is

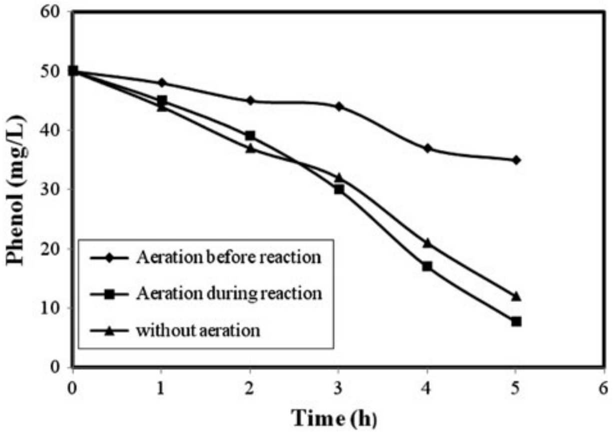

Fig. 4. Effect of aeration on SPCO of phenol (pH = 6, phenol = 50 mg/L, TiO_2 = 0.25 g/L, contact time = 5 h).

recommended so as to prevent the recombination reaction between the generated positive holes and electrons in the photocatalytic degradation. Generally aeration is used for this purpose as it also provides uniform mixing, suspension of the catalyst in the case of slurry reactors and economical source of oxygen [2]. Similar results were observed by Pekakis et al. [12], and it was found that the decolouration of textile dye was about 80 and 93% for without and with aeration, respectively, and stated that lack of air was found to decrease only the extent of colour removal, and the presence of excess molecular oxygen positively influenced photocatalytic degradation.

It was reported that the use of air gives more degradation as compared to pure oxygen indicating that oxygen is required only at minimum concentrations [13]. It was also observed that when the wastewater was not aerated, the phenol decreased much faster than when aerated at the initial stage at $t \leqslant 2$ h, but the rate becomes extremely slower after that at $t \geqslant 2$. The difference at the initial stage is obviously attributed to the numerous bubbles generated by aeration, which should scatter the light before arriving at the catalytic surface of the reactor. At later stage, when not aerated, the initial dissolved oxygen is exhausted and a large percent of excited electrons should recombine with positive holes and get back to the ground state [14]. Hence, for continuous operation of the reactor, aeration is thus required. In this subsequent studies, the amount of air bubbles were controlled adequately so as not to scatter much light.

3.4. Effect of liquid volume

In order to study the effect of liquid volume, SPCO experiments were performed at four different volumes of wastewater from 0.25 to 1.5 L. The results of the experimental studies are depicted in Figs. 5 and 6 and furnished in Table 1. The phenol removal efficiency was 99, 94, 79 and 46% for wastewater volume of 0.25, 0.50, 1.0 and 1.5 L, respectively. It was observed that as the volume of wastewater was increased, the phenol removal was found to decrease. And also, it was observed that the kinetic constant (k) decreases when the wastewater volume increases. Of course, it seems not to be a logical behaviour because, as general rule, kinetic constants have to be independent on the volume. An explanation to this behaviour is that the reactor can be divided into two theoretical zones, where the reaction can proceed in a different manner. The two zones were: the illuminated zone (equal for all reactors), where radiation is absorbed by the catalyst and a dark zone (larger as the volume increases), where radiation cannot penetrate. In this case, the reactions assume to occur only in the illuminated zone [15]. Hence, the penetration depth of light decreases causing reduction in phenol removal efficiency.

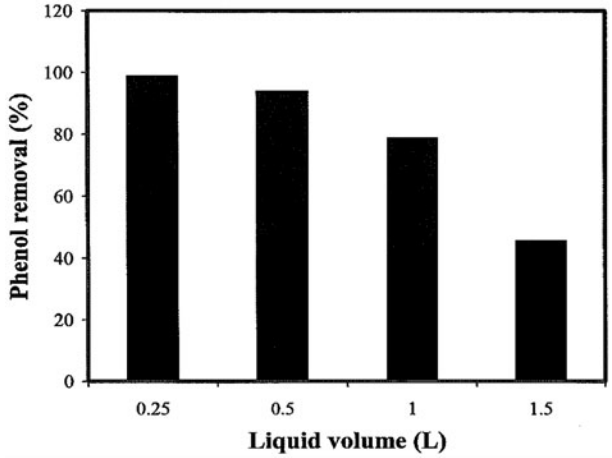

Fig. 5. Effect of liquid volume on SPCO of phenol (pH = 6, phenol = 50 mg/L, TiO_2 = 0.25 g/L, contact time = 5 h).

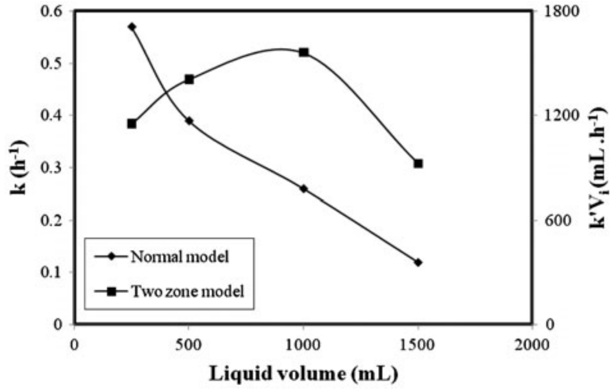

Fig. 6. Effect of liquid volume of normal and two zones model.

If it is assumed that the luminic step is the controlling one, that is, the reaction occurs only in the illuminated zone, the equation of the mass balance for phenol is change. Thus, the volume considered for the rate of phenol removal (V_T.dc/dt) is the total volume, because the measured concentration of phenol is referred to the total volume. However, if reaction only occurs in the illuminated zone, the reaction rate is referred only to the volume of this zone (V_i). Thus, the mass balance for phenol removal $dc/dt = -k \cdot c$ can be rewritten in the following manner $V_T \cdot dc/dt = -k'c\, V_i$, where V_T is the total volume of the reactor and V_i is the volume of the illuminated zone. Integrating the equation becomes $V_T \cdot \ln(C_o/C) = -k' V_i$. As it can be

Table 1
First-order rate constant for normal and two zones model

Sl.no.	Volume of wastewater (mL)	C_o (mg/L)	C_f (mg/L)	Phenol removal (%)	k (h^{-1})	$k'V_i$ ($mL\,h^{-1}$)
1	250	50	0.5	99	0.57	1,151
2	500	50	3	94	0.39	1,406
3	1,000	50	10.5	79	0.26	1,560
4	1,500	50	27	46	0.12	924

seen from Fig. 5 and Table 1, the product $V_T \cdot \ln(C_o/C)$ remains practically constant and does not depend on the volume. This implies that the product $-k'V_i$ is constant. In addition, it can be said that V_i was also constant, because the catalyst dosage and reactor surface area are constant. This means that k' was really a constant. It seems that reaction occurs only in the illuminated zone.

3.5. Effect of solar irradiation and TiO_2

In order to study the effect of solar irradiation and TiO_2, three sets of experiments were conducted, viz. photolysis (without TiO_2), dark adsorption (without solar) and photocatalysis (solar/TiO_2). The results of the experimental studies were depicted in Fig. 7. About 93% of phenol removal in photocatalysis (solar/TiO_2) at 5 h irradiation time was observed. This was contrasted with 0% removal of phenol for the same experiment performed in the absence of TiO_2 (photolysis) and the negligible 1.1% of phenol removal was observed without solar light(dark adsorption). These experiments demonstrated that both solar light and a photocatalyst such as TiO_2 were needed for the degradation of phenolic wastewaters.

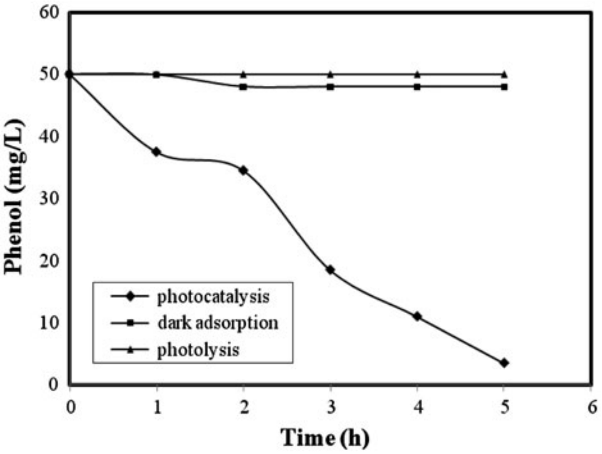

Fig. 7. Effect of solar irradiation and TiO_2.

This might be due to the fact that when fine suspensions of TiO_2 are irradiated at wavelengths less than 380 nm, it causes electron excitation from the valence band to the conduction band and a vacancy or hole is left in the valence band. Such holes have the effect of a positive charge. This in turn generates the formation of holes on the surface of the semiconductor, which can react with oxygen, water and hydroxide ion to form hydroxyl radical. Furthermore, superoxide and perhydroxyl radicals are formed from the reaction of excited electrons with oxygen molecules. The highly reactive oxygen species so formed then react with the organic pollutants resulting in their extensive oxidation [16]. Previously, several authors Daneshvar et al. [17] and Alqaradawi et al. [18] have studied the photocatalytic degradation of various organic pollutants and the mechanistic scheme leading to the degradation of the organics according to the following reactions (Eqs. (1)–(6)):

$$TiO_2 + h\nu(<380\ \text{nm}) \rightarrow TiO_2(e^- + h^+) \tag{1}$$

$$TiO_2(e^-) + O_2 \rightarrow TiO_2 + O^-_{2^\circ} \tag{2}$$

$$TiO_2(h^+) + H_2O_{(ad)} \rightarrow TiO_2 + H^+ + OH_{(ad)^\circ} \tag{3}$$

$$TiO_2(h^+) + OH^- \rightarrow TiO_2 + OH_{(ad)^\circ} \tag{4}$$

$$\begin{aligned} TiO_2(H^+) + OM &\rightarrow \text{degradation intermediates} \\ &\rightarrow TiO_2 + OM^{\circ +} \end{aligned} \tag{5}$$

$$\begin{aligned} OM + OH_{(ad)^\circ} &\rightarrow \text{degradation intermediates} \\ &\rightarrow CO_2 + H_2O \end{aligned} \tag{6}$$

3.6. Effect of solar light intensity

In order to study the effect of solar light intensity, the experiments were conducted daily for a period of one year. The radiation intensity received by the

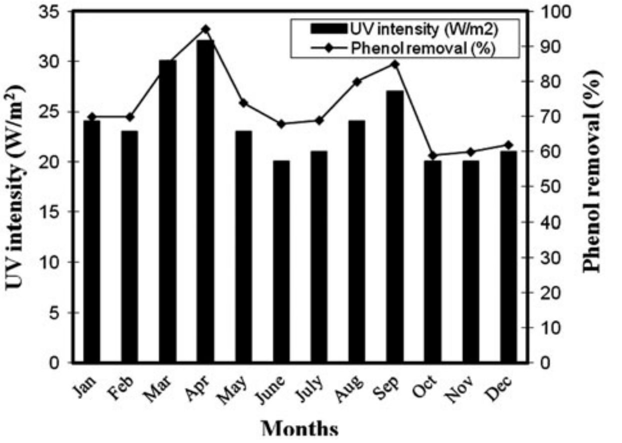

Fig. 8. Effect of solar light intensity on SPCO of phenol (pH = 6, phenol = 50 mg/L, TiO2 = 0.25 g/L, contact time = 5 h).

samples was measured. The results of the experimental studies were depicted in Fig. 8. An average phenol removal efficiency of 73% was observed at an average UV light intensity of 23 W/m^2. It was also observed that the phenol removal efficiency reaches its maximum of 95% at the maximum UV light intensity of 32 W/m^2 and the minimum phenol removal efficiency of 59% was observed at the minimum UV light intensity of 20 W/m^2. It might be because the higher the UV light intensity, the faster the formation of OH free radical, which leads to higher degradation of phenol wastewater [19–21]. The results suggest that photocatalytic process with solar light irradiation is a feasible technique for phenol removal. The use of solar light could be an excellent alternative since this natural source of energy could reduce the costs for the treatment of phenolic wastewaters [22–25].

4. Conclusions

(1) The chloride and sulphate ions give negative impact on the phenol removal efficiency even at low concentration of 50 mg/L.
(2) When compared to aeration during reaction and without aeration, not much difference was observed; it indicates that oxygen from atmosphere is sufficient for photocatalytic degradation.
(3) It was observed that as the volume of wastewater was increased, the phenol removal was found to decrease due to penetration depth of light decrease.
(4) The average phenol removal efficiency of 73% at an average UV light intensity of 23 W/m^2 was observed.

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