



## Parameters effect on heterogeneous photocatalysed degradation of phenol in aqueous dispersion of $\text{TiO}_2$

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### Abstract

Photocatalytic degradation of phenol selected as model compound of organic pollutant had been investigated in aqueous titanium dioxide ( $\text{TiO}_2$ ) dispersion under UV irradiation. The effects of various parameters such as pH, catalyst concentration, phenol concentration, anions, metal ions, electron acceptors, and surfactants on the photocatalytic degradation of phenol were investigated. The degradation kinetics was determined by the change in phenol concentration employing UV-Vis spectrometry as a function of irradiation time. The degradation kinetics of phenol follows pseudo first-order kinetics. The results showed a significant dependence of the photocatalytic degradation of phenol on the functional parameters. The probable promising roles of the additives on the degradation process were discussed.

**Key words:** irradiation; phenol; photocatalytic degradation; titanium dioxide; UV light

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### Introduction

Phenol and phenolic compounds are major pollutants of aquatic environment. Phenol may occur in the aquatic environment due to its widespread use in agricultural, petrochemical, textile, paint, plastic and pesticidal chemical industries. Because of its carcinogenic and mutagenic potential, phenol poses a risk to mammalian and aquatic life (Dionysiou *et al.*, 2000). The toxicity and persistence of organic pollutants in the environment has been the cause of much concern of the societies and regulation authorities (Qamar *et al.*, 2006). When phenol-containing water is chlorinated, toxic polychlorinated phenols can be formed, therefore, such wastewater must be cleaned prior to release into the environment. Owing to its stability and solubility in water, its removal to a safety level (0.1–1.0 mg/L) is not easy (Brown *et al.*, 1967).

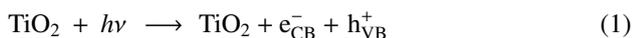
Advanced oxidation processes (AOPs) including heterogeneous photocatalysis have proved to be one of the most effective methods for water treatment. These processes are based on the generation of the strongly oxidizing hydroxyl radicals ( $\cdot\text{OH}$ ), which oxidize a broad range of organic pollutants that could present in water and wastewaters (Akbal and Onar, 2003; Han *et al.*, 2004; Qamar *et al.*, 2006). Heterogeneous photocatalysed degradation using semiconductor powder is an emerging technique for the treatment of toxic pollutants (Kochany, 1993; Herrmann, 1999; Alfano *et al.*, 2000; Fujishima *et al.*, 2000; Peiro

*et al.*, 2001; Akbal and Onar, 2003; Salem, 2003; Barakat *et al.*, 2004; Qamar *et al.*, 2006; Hao *et al.*, 2007). Many semiconductors have photocatalytic properties (Bessa *et al.*, 2001; Salem, 2003; Byrappa *et al.*, 2006). Titanium dioxide ( $\text{TiO}_2$ ) is one of the most efficient and popular photocatalyst (Fujishima *et al.*, 2000) owing to its excellent photocatalytic activity, inertness (Kumara *et al.*, 1999), stability within a wide range of pH (Salem, 2003), and is inexpensive (Braun, 1991; Fabbri *et al.*, 2006).

The efficient photexcitation of  $\text{TiO}_2$  particles requires a photon with energy equal to or greater than its band gap energy (Barakat *et al.*, 2004). An electron may be excited from the valence band to the conduction band ( $e_{\text{CB}}^-$ ) leaving a hole in the valence band ( $h_{\text{VB}}^+$ ). In a photocatalytic process, the generated electron hole pairs must be trapped to avoid recombination (Auguliaro *et al.*, 1997). The electron and hole may migrate to the catalyst surface where they participate in redox reactions. Water or hydroxyl ion ( $\text{OH}^-$ ) is the possible trap for the hole ( $h_{\text{VB}}^+$ ), leading to the formation of  $\cdot\text{OH}$ . It is well known that  $\text{O}_2$  is essential for the photocatalytic oxidation of organic compounds. Its presence depresses the recombination of electron hole pair and degradation of organic substances takes place. Oxygen over the  $\text{TiO}_2$  surface traps the electron ( $e_{\text{CB}}^-$ ) and generates the superoxide radical anion ( $\text{O}_2^{\cdot-}$ ), which is unstable, reactive and involves into more  $\cdot\text{OH}$  (Ilisz *et al.*, 1999). The whole mechanism is given by

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the following Reactions (1)–(5).



In the present work, the effects of various experimental parameters, such as pH, amount of photocatalyst, and amount of phenol, anions, metal ions, electron acceptors and surfactants on the photocatalytic degradation of phenol were examined. UV-Vis spectroscopy was employed to rationalize the result of photocatalytic degradation. Thus the purpose of this work was to study the degradation of phenol with a particular emphasis on experimental parameters.

## 1 Materials and methods

### 1.1 Materials

Photocatalyst  $\text{TiO}_2$  (anatase) was obtained from Jiangsu Hehai Nanometer Science and Technology Co., Ltd., China. Its particle size is  $\leq 30$  nm with a specific surface area of  $120 \text{ m}^2/\text{g}$ . Analytical reagent grade phenol, sodium hydroxide, potassium nitrate, ferric nitrate and potassium peroxydisulfate were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Sodium sulfate, potassium carbonate, potassium chloride, copper nitrate, magnesium sulfate, calcium carbonate and sodium dodecyl sulfate were purchased from Damao Chemical Reagent Co., China. Hydrogen peroxide (50%, W/W, AR grade) was supplied by DC Chemical Co., Ltd., Korea. Sodium dodecyl sulfonate was the product of Xilong Chemical Guangdong, China. Sodium dodecylbenzene sulfonate was obtained from Lingfeng Chemical Reagent Co., China and potassium bromate was purchased from Sigma, USA. All chemicals were used without further purification. Deionized distilled water obtained by Millipore system was used for the preparation of solutions.

### 1.2 Photoreactor

Photocatalytic degradation experiments were carried out in a 500-mL Pyrex-glass cell wrapped in aluminum foil to avoid release of radiation and heat. An aqueous dispersion was prepared by required amount of  $\text{TiO}_2$  (anatase) to a 200-mL solution containing the phenol at appropriate concentration. A magnetic stirrer was used to ensure uniform mixing of solution in vessel. An air pump (BOYU ACQ-001, BOYU Industries Co., Ltd., China) was used to provide oxygen to maintain an aerobic condition. Prior to irradiation the dispersions were magnetically stirred in the dark for ca. 15 min to ensure the establishment of adsorption/desorption equilibrium. The irradiation was carried out using 15 W UV-lamp (Ya Ming Co., China), emitting mainly at 365 nm wavelength. The pH of solutions was measured using 8682 digital pH meter (AZ Instrument Corp., Taiwan, China) and adjusted by HCl (0.1 mol/L)

or NaOH (0.1 mol/L). All experiments were conducted at  $298 \pm 1$  K.

### 1.3 Analysis

At given interval of irradiation, 7 mL of the solution were drawn. The liquid samples were centrifuged at 3000 r/min for 10 min and subsequently filtered to separate  $\text{TiO}_2$  particles. The filtered samples were stored at  $4^\circ\text{C}$  prior to analysis. The experiments were carried out for 600 min. The concentrations of phenol in the filtrates were measured quantitatively through the UV-Vis spectrophotometer (Helios Gamma Thermo Spectronic, England). The UV-Vis spectrophotometer was set at a wavelength of 270 nm for analysis of phenol. A quartz cell with a path length of 1 cm was used for spectrophotometric measurements. The degradation efficiency ( $D_E$ ) of each sample was calculated from Eq. (6):

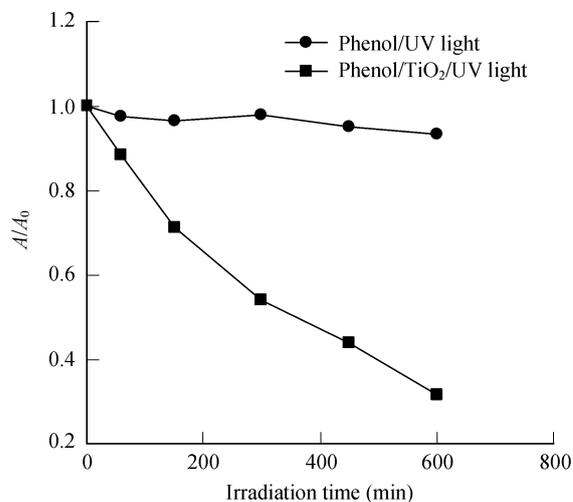
$$D_E = \frac{A_0 - A_t}{A_0} \times 100\% \quad (6)$$

where,  $A_0$  and  $A_t$  are the absorbance at time zero and time  $t$ , respectively.

## 2 Results and discussion

### 2.1 Kinetics of photocatalytic degradation of phenol

Aqueous solution of phenol in the presence or absence of  $\text{TiO}_2$  (anatase) was irradiated by 15 W UV-lamp. The role of photocatalytic degradation and the effect of direct photolysis on the decomposition of phenol were studied. Figure 1 shows the change in absorption intensity as a function of irradiation time of phenol solution. A control experiment was performed by an identical aqueous solution without catalyst. Control experiment showed that degradation of phenol was less than 6.5% within 10 h in the direct photolysis. The result reveals that the degradation of phenol follows pseudo first-order kinetics with respect to



**Fig. 1** Effect of absorption intensity as a function of irradiation time. Phenol:  $3.56 \times 10^{-4}$  mol/L;  $\text{TiO}_2$ : 200 mg/L.

the phenol concentration, i.e.,

$$-\frac{dC_t}{dt} = k_{app} \times C_t \quad (7)$$

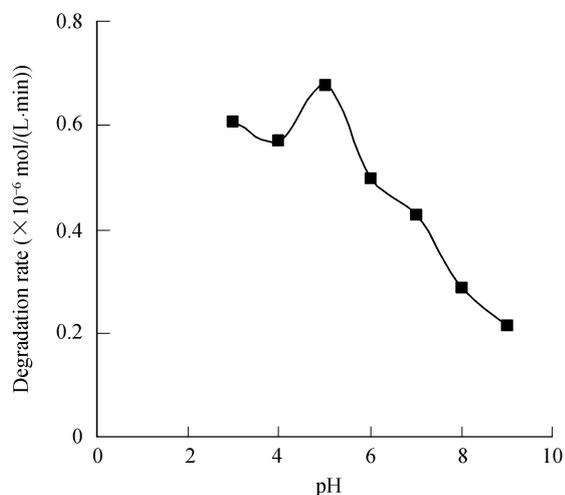
The integration of Eq. (7) with the boundary condition that at the start of irradiation ( $t = 0$ ), the concentration is the initial one,  $C_t = C_0$ , yields Eq. (8):

$$-\ln\left(\frac{C_t}{C_0}\right) = k_{app} \times t \quad (8)$$

where,  $k_{app}$  ( $\text{min}^{-1}$ ) is the apparent first order rate constant,  $C_t$  is the concentration of phenol at time  $t$  (min) and  $C_0$  is the initial concentration of phenol. Kinetic studies were assessed by monitoring the phenol concentration at certain interval of time. The slope of the plot gave the value of  $k_{app}$ . The resulting first order rate constants have been used to calculate degradation rate for phenol and were used for a comparison of the efficiency of photocatalytic process under different experimental conditions.

## 2.2 Optimization of pH, catalyst, and phenol concentration

The pH of the aqueous solution is a key factor for photocatalytic reaction and can affect the adsorption of pollutants on the photocatalyst surface. Figure 2 illustrates the effect of pH on degradation rate of phenol. The degradation rate decreased with increase in pH. The highest degradation efficiency occurred at pH 5 (Table 1) as observed in the literature (Akbal and Onar, 2003). This is attributed to the fact that TiO<sub>2</sub> is amphoteric in aqueous solution. The point of zero charge ( $\text{pH}_{pzc}$ ) of TiO<sub>2</sub> is 6.8, thus below this value the TiO<sub>2</sub> surface is positively charged and above it is negatively charged. At higher pH, phenol exists as negatively charged phenolate species. Low degradation rate at higher pH is attributed to the fact that when the concentration of OH<sup>-</sup> is higher in the solution, it prevents the penetration of UV light to reach the catalyst surface (Qamar *et al.*, 2006). Moreover, high pH favors the formation of carbonate ions which are effective scavengers of OH<sup>-</sup> ions and can reduce the degradation rate (Akbal and Onar, 2003).

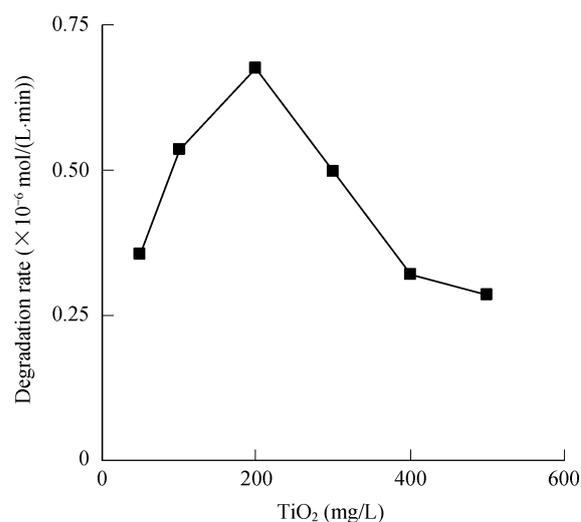


**Fig. 2** Influence of initial pH on photocatalytic degradation of phenol. Phenol  $3.56 \times 10^{-4}$  mol/L; TiO<sub>2</sub> 200 mg/L.

**Table 1** Kinetic results of phenol photocatalytic degradation at 298 K and different pH on TiO<sub>2</sub> catalyst

pH	$k_{app}$ <sup>a</sup> ( $\text{min}^{-1}$ )	Degradation rate ( $\text{mol}/(\text{L}\cdot\text{min}) \times 10^{-6}$ )	$D_E$ <sup>b</sup> (%)
3	0.0017	0.605	63.57
4	0.0016	0.570	61.75
5	0.0019	0.676	68.41
6	0.0014	0.498	55.49
7	0.0012	0.427	49.26
8	0.0008	0.285	35.82
9	0.0006	0.214	32.78

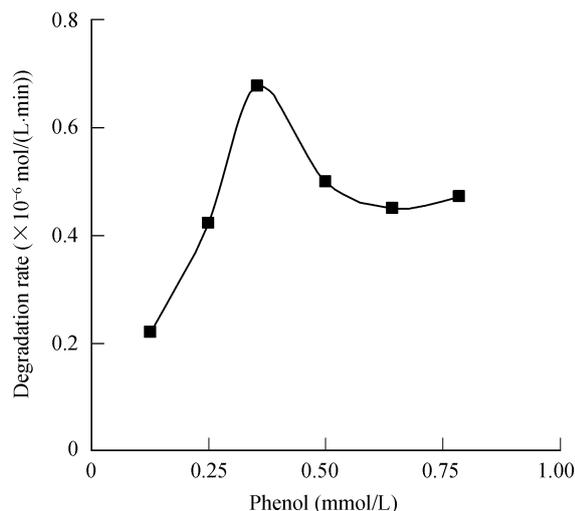
<sup>a</sup> Apparent first order rate constant obtained using Eq. (8); <sup>b</sup> degradation efficiency obtained from Eq. (6).



**Fig. 3** Effect of TiO<sub>2</sub> concentration on the photocatalytic degradation of phenol. Phenol:  $3.56 \times 10^{-4}$  mol/L; pH 5.

The influence of the catalyst concentration on photocatalytic degradation of phenol has been investigated using different TiO<sub>2</sub> concentrations ranging from 50 to 500 mg/L. Figure 3 shows that with the increase in concentration of TiO<sub>2</sub>, the degradation rate increases up to a certain limit (200 mg/L) and further increase of catalyst concentration led to decrease in the degradation as reported earlier (Qamar *et al.*, 2006; Chen *et al.*, 2007). This is due to the fact that the increase in the number of TiO<sub>2</sub> particles will increase the number of photons absorbed and consequently the number of the phenol molecule adsorbed. At high concentrations, decrease in the photodegradation may be due to the aggregation of free TiO<sub>2</sub> particles that results in a decrease in the number of surface active sites (Chen *et al.*, 2007). Further, the excessive opacity and screening effect of excess TiO<sub>2</sub> act as shield as the increased number of particles in solution, and consequently hinder the light penetration. Therefore, there is loss of available surface area for light-harvesting and as a result reduction of the catalytic activity (Lea and Adesina, 1998).

The effect of initial concentration of phenol on the photodegradation in the range of 0.128–0.784 mmol/L is demonstrated in Fig. 4. It reveals that with increase in the concentration of phenol, the degradation rate increases up to a certain limit. Further increase in concentration of phenol led to decrease in the degradation rate after



**Fig. 4** Influence of initial phenol concentration on the photocatalytic degradation of phenol.  $\text{TiO}_2$ : 200 mg/L; pH 5.

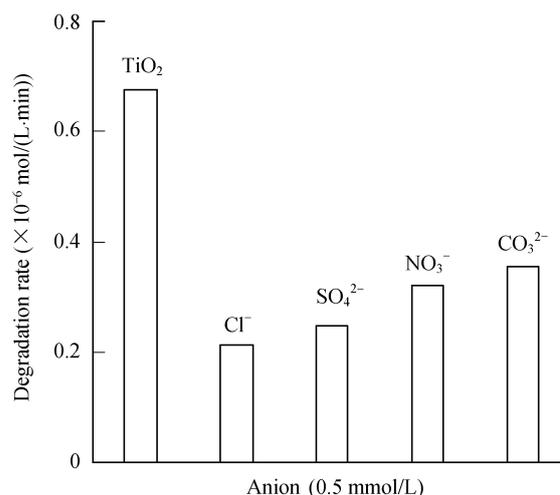
which, it levels off. Decrease in degradation rate at higher concentration is attributed the fact that light absorbed by the phenol is more than that of  $\text{TiO}_2$ . Thus light absorbed by the phenol is not effective to carry out the degradation. Further, the equilibrium adsorption of phenol on the catalyst surface active site increases and more and more molecules of phenol get adsorbed on the surface of the catalyst. Therefore, competitive adsorption of  $\text{OH}^-$  on the same site decreases and consequently the amount of  $\cdot\text{OH}$  and  $\text{O}_2^{\cdot-}$  on the surface of catalyst decreases. For all initial phenol concentrations, the catalyst, irradiation time and intensity of light were constant. Since the generation of  $\cdot\text{OH}$  does not increase, the probability of phenol molecules to react with  $\cdot\text{OH}$  decreases, therefore, a decrease in the degradation efficiency is observed.

### 2.3 Effect of inorganic anions

Wastewater commonly contains significant amounts of inorganic anions, and these anions have serious effect on water properties. The anions can change the ionic strength of the solution, therefore, affect the catalytic activity and hence the photocatalytic degradation (Calza and Pelizzetti, 2001). The effect of chloride, carbonate, nitrate, and sulfate was investigated using corresponding  $\text{K}^+$  as cation except for sulfate where  $\text{Na}^+$  was cation. These anions could be adsorbed on the surface of  $\text{TiO}_2$  in acidic condition by electrostatic attraction. Figure 5 illustrates the effect of these anions on photocatalytic degradation of phenol. All anions were found to inhibit photocatalysis, with the order of  $\text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{CO}_3^{2-}$ . This can be explained on the basis of reaction of  $h\nu_{\text{VB}}^+$  and  $\cdot\text{OH}$  with anions which behave as scavengers, and thus inhibit the degradation (Reactions (9) and (10)):



Carbonate ion has also been reported to scavenge  $\cdot\text{OH}$  radical via a mechanism similar to that of  $\text{Cl}^-$ . The  $\text{SO}_4^{2-}$  played two roles in photodegradation of phenol. First, it



**Fig. 5** Effect of the presence of various anions on photocatalytic degradation of phenol. Phenol:  $3.56 \times 10^{-4}$  mol/L;  $\text{TiO}_2$ : 200 mg/L; pH 5.

affects the photodegradation of phenol by changing the surface charge of  $\text{TiO}_2$ , resulting in a change of distribution of phenol molecules between solution and  $\text{TiO}_2$  surface (Hu *et al.*, 2003). Second, the adsorbed  $\text{SO}_4^{2-}$  reacts with hole and hydroxyl radical to form  $\text{SO}_4^{\cdot-}$  and result in their depletion as follows:



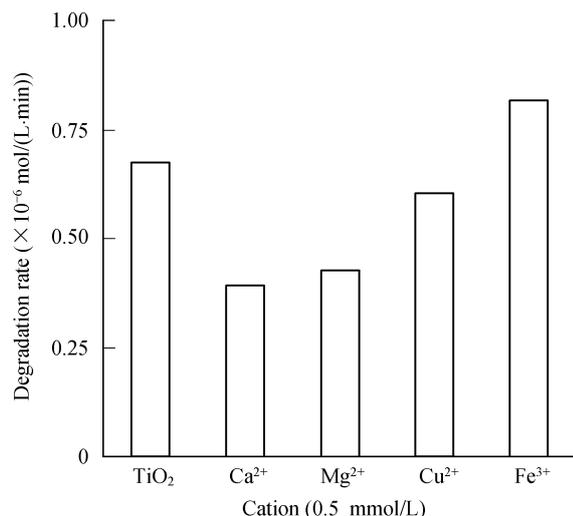
Since  $\text{SO}_4^{\cdot-}$  is less reactive than  $\cdot\text{OH}$  and  $h\nu_{\text{VB}}^+$ , therefore, the excess  $\text{SO}_4^{2-}$  inhibits the photodegradation of phenol. Furthermore, the large size of  $\text{SO}_4^{\cdot-}$  causes it less effective than  $\cdot\text{OH}$  in the oxidation of organic pollutants. Inhibitory effect of  $\text{SO}_4^{2-}$  may be limited by the ability of the sulfate radical itself to oxidize organics (Burns *et al.*, 1999). Nitrate ion has comparatively weaker effect on adsorption and consequently on the photocatalytic degradation (Bhatkhande *et al.*, 2004). In conclusion, the adsorbed anions compete with organic contaminants for the photo-oxidizing species on the surface of catalyst and prevent the photocatalytic degradation of the phenol (Chen *et al.*, 2007).

### 2.4 Effect of metal ions

Dissolved metal ions to a certain extent are common in wastewater, which can significantly affect the photocatalytic reaction for the removal of organic pollutants. As shown in Fig. 6, for the studied system 48.93%, 51.49%, 64.76%, and 74.37% of degradation efficiency with  $\text{TiO}_2$  (anatase) were observed for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$ , respectively. Addition of  $\text{Fe}^{3+}$  is found to be the most effective. It is assumed that positively charged metal ions adsorbed on  $\text{TiO}_2$  surface is easily reduced by conduction band electrons ( $e_{\text{CB}}^-$ ) and thus increase the charge separation as given by following reaction:



The enhancement of degradation by addition of  $\text{Fe}^{3+}$  ion is due to the electron scavenger effect that prevents the re-

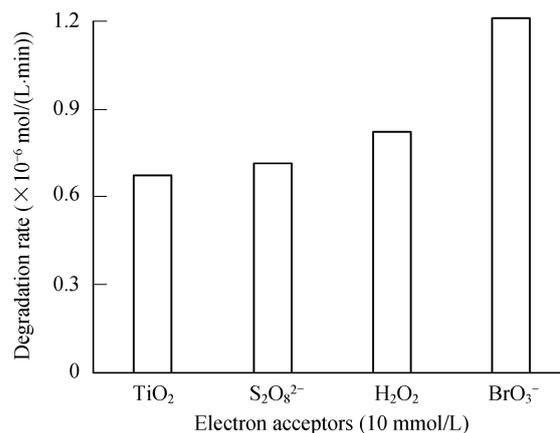


**Fig. 6** Effect of the presence of various metal ions on photocatalytic degradation of phenol. Phenol:  $3.56 \times 10^{-4}$  mol/L; TiO<sub>2</sub>: 200 mg/L; pH 5.

combination of electron-hole pairs. Thus it is favorable for the increasing of the  $\cdot\text{OH}$  and  $\text{O}_2^{2-}$  formation on the TiO<sub>2</sub> surface (Chen and Liu, 2007). Decrease in degradation by other metal ions is attributed to low reduction potential. For example, in the case of  $\text{Cu}^{2+}/\text{Cu}^+$  couple. It is 0.15 eV with respect to normal hydrogen electrode (NHE). The reduction of  $\text{Cu}^{2+}$  by  $e_{\text{CB}}^-$  to  $\text{Cu}^+$  may compete with the formation of superoxide anion radical and consequently reduce the formation of hydroxyl radical (Brezova *et al.*, 1995). Alternatively,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  act to reduce the photodegradation rate by reaction with phenol to create phenol complexes or ligands which are more difficult to be degraded (Zainal *et al.*, 2005).

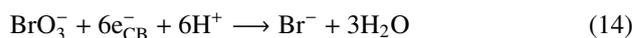
## 2.5 Effect of electron acceptors

One practical problem in using TiO<sub>2</sub> as photocatalyst is the energy wasting in the electron hole recombination which results in low degradation efficiency. Hence the prevention of electron hole recombination becomes very important. The prevention of electron hole recombination can be achieved by adding proper electron acceptors. In heterogeneous photocatalytic reaction, molecular oxygen (air) has been used for this purpose as an electron acceptor for prevention of electron hole recombination, although its role is not just electron scavenging. One approach used by researchers aiming to prevent electron hole recombination is to add electron acceptors into the reaction. The presence of some electron acceptors (oxidants), such as  $\text{H}_2\text{O}_2$ ,  $\text{S}_2\text{O}_8^{2-}$  and  $\text{BrO}_3^-$  can serve as electron scavengers to prevent the recombination and enhance photodegradation efficiency. These electron acceptors have several effects including: (a) avoid recombination of electron-hole by accepting the conduction band electron; (b) increase the concentrations of the hydroxyl radical; and (c) that of other oxidizing species ( $\text{SO}_4^{\cdot-}$ ) to increase the intermediate compound oxidation rate (Muruganandham and Swaminathan, 2006). The effect of these oxidants on photocatalytic degradation of phenol is illustrated in Fig. 7. Irradiation of UV light with the electron acceptors



**Fig. 7** Influence of electron acceptors on the photocatalytic degradation of phenol. Phenol:  $3.56 \times 10^{-4}$  mol/L; TiO<sub>2</sub>: 200 mg/L; pH 5.

enhances the photodegradation of phenol. The order of oxidants on enhancement of degradation rate is  $\text{BrO}_3^- > \text{H}_2\text{O}_2 > \text{S}_2\text{O}_8^{2-}$ . It can be inferred that  $\text{BrO}_3^-$  is most effective oxidant for the degradation of phenol. The higher enhancement of photodegradation efficiency is due to reaction between  $\text{BrO}_3^-$  and conduction band electron (Poulios and Aetopoulou, 1999), which prevents the recombination of electron hole pair:

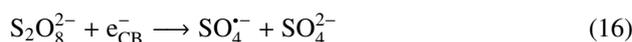


The enhancement in degradation by the addition of  $\text{H}_2\text{O}_2$  is due to its dual function which can act as an electron acceptor and it also increases the  $\cdot\text{OH}$  concentration as given by following reaction:

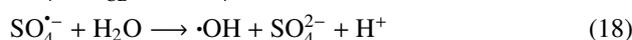


Further, the enhanced degradation rate by  $\text{H}_2\text{O}_2$  is probably due to direct photolysis by UV light. This generates the  $\cdot\text{OH}$ , which are likely to be dominant rate improving mechanism in the process.  $\text{H}_2\text{O}_2$  has two hydrogen atoms bonded to oxygen atoms (H–O–O–H), thus it is more electropositive than  $\text{O}_2$ , suggesting that  $\text{H}_2\text{O}_2$  is a better electron acceptor than oxygen (Chen and Liu, 2007).

In case of  $\text{S}_2\text{O}_8^{2-}$ , the degradation rate was not improved significantly, although  $\text{S}_2\text{O}_8^{2-}$  can generate the sulfate radical anions ( $\text{SO}_4^{\cdot-}$ ), which is very strong oxidizing species, according to following reactions:



The  $\text{SO}_4^{\cdot-}$  may also react with photogenerated electron and with water molecule to produce more sulfate ions as follows:

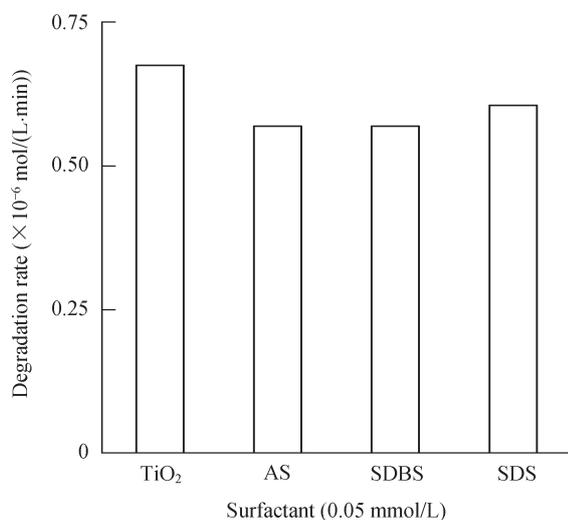


Because  $\text{SO}_4^{\cdot-}$  is less reactive than  $\cdot\text{OH}$  and  $h_{\text{VB}}^+$ , its concentration increases in solution which affects photocatalytic activity. On the other hand, slight increase in degradation by  $\text{S}_2\text{O}_8^{2-}$  may be due to the scavenging of  $\cdot\text{OH}$  and  $h_{\text{VB}}^+$  by  $\text{SO}_4^{2-}$  as reported in the case of anion

such as  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  etc and UV screening of  $\text{TiO}_2$  particles (Burns *et al.*, 1999). Moreover, excess concentration of  $\text{SO}_4^{2-}$  is adsorbed on the  $\text{TiO}_2$  surface and reduces its catalytic activity (Chen and Liu, 2007).

## 2.6 Effect of surfactants

The presence of other compounds may influence the degradation process when we deal with real time contaminated water. Among other substances, the presence of surfactants in wastewater is expected due to their well-known domestic use and industrial applications. The presence of surfactants has been shown to influence the kinetics of degradation process. Hence the effect of some controlled concentration (0.05 mmol/L) of sodium dodecyl sulfate (SDS), sodium dodecyl sulfonate (AS) and sodium dodecylbenzene sulfate (SDBS) on photocatalysis was studied. Figure 8 shows the effect of presence of these surfactants on photocatalytic degradation of phenol. The decreasing order of degradation efficiency is  $\text{SDBS} > \text{AS} > \text{SDS}$  for the studied system. From the results it can be concluded that degradation behavior of irradiated suspension differs only insignificantly when compared with irradiation of target pollutant without surfactant. A decrease of degradation efficiency of phenol ( $\leq 10.3\%$ ) was measured in the presence of surfactants. Slight inhibition of photocatalytic degradation of phenol in aqueous solution of surfactant was also reported (Fabbri *et al.*, 2006).



**Fig. 8** Degradation rate for the decomposition of phenol in the presence of different surfactants. Phenol:  $3.56 \times 10^{-4}$  mol/L;  $\text{TiO}_2$ : 200 mg/L; pH 5.

## 3 Conclusions

We investigated the degradation of phenol as the model pollutant of water by  $\text{TiO}_2$  (anatase) dispersion under irradiation with UV light. The degradation process follows pseudo first-order degradation behavior. The most appropriate condition for degradation of  $3.56 \times 10^{-4}$  mol/L of phenol at  $25^\circ\text{C}$  is determined. The pH is 5 and  $\text{TiO}_2$  is 200 mg/L. The photodegradation rate of phenol was found

to increase along with increasing pH and then decreases. Increasing  $\text{TiO}_2$  concentration beyond 200 mg/L showed a reduction on the photodegradation of phenol due to light shielding effect. The inhibition effect of anions on degradation of phenol was in the order  $\text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{CO}_3^{2-}$ .  $\text{Fe}^{3+}$  at certain concentration boosts the degradation rate whereas  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Mg}^{2+}$  hinder the degradation process. The presence of oxidants such as  $\text{BrO}_3^-$ ,  $\text{H}_2\text{O}_2$  and  $\text{S}_2\text{O}_8^{2-}$  enhance the degradation efficiency appreciably. The controlled concentration of surfactants does not influence the degradation significantly.

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