Photo-oxidation of phenol over titania pillared zirconium phosphate and titanium phosphate

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Abstract

The photodegradation of phenol was studied in the aqueous solutions over titania pillared zirconium phosphate and titanium phosphate under solar radiation and compared with that of the UV-radiation (6 W low pressure Hg vapor lamp). This reaction was studied by varying different parameters such as catalyst dose, initial phenol concentration, pH of solution and irradiation time. The degradation rate of phenol was favourable under neutral pH condition. The degradation process approximately obeyed first-order kinetics with apparent rate of degradation constant increasing with decreasing the initial phenol concentration.
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1. Introduction

The importance of phenol (photo) oxidation in industrial and environmental (photo) chemistry as well as biological systems is well recognized. Oxidation reactions involving phenols and related compounds (for example quinines) are of interest by virtue of their important roles as antioxidants [1] and polymer photosensitizers [2]. Phenol poses a significant treat to the environment and are mainly found as dilute contaminants in ground waste as well as in surface water [3–6]. Phenolic compounds are toxic to aquatic life and have the ability to impart tastes and odours to drinking water even at parts per billion levels [7].

The simultaneous coupling of photolysis with an oxidant often referred to as advanced oxidation processes (AOPs) or advanced oxidation techniques (AOTs) has demonstrated its usefulness in new routes for the photo-oxidation and photodegradation of organic substrates (OSs) as well as

in a approach to solve environmental problems. Vigorous research has demonstrated that TiO_2 as catalyst causes complete photo-oxidation of phenols (as well as many number of different other pollutants) to non-hazardous products, such as water, carbon dioxide and simple mineral acids [8–12]. Heterogeneous photocatalysis is one of the techniques used for this purpose. Photochemical and photocatalytic properties of semiconductor microcrystallites in solution have become popular due to quantum size effects [13–15]. Recently, the photochemical properties of modified ZrP [16], zirconia incorporated titania [17] and titania pillared zirconium phosphate and titanium phosphate [18] have been reported. Semiconductor photocatalysis appears to be the promising technology that has a number of applications towards air and water purification, water disinfections and hazardous waste remediation. In addition, the basic research underlies the application of these technology is forgoing a new understanding of complex heterogeneous photochemistry of metal oxide system in multiphasic environments where semiconductor photosensitizers like TiO_2 act as catalyst for irreversible oxidation of impurities present in the wastewater using sunlight.

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The present work deals with the photodegradation of phenol in aqueous solution over titania pillared zirconium phosphate and titanium phosphate by varying reaction conditions.

2. Experimental

2.1. Material preparation

Titania intercalated ZrP and TiP were prepared by the procedure reported by Parida and Das [18] using Na-form of zirconium phosphate and titanium phosphate. First,titania sol was prepared by dropwise addition of titanium(IV) isopropoxide to a vigorously stirred 1 M HCl solution to give a molar ratio of 0.25 between alkoxide and HCl solution. The resulting slurry was stirred for 3 h to get a clear titania sol. Then the aqueous suspension of sodium exchanged ZrP or TiP was added slowly to the sol. The resultant suspension was further stirred for 3 h at 50 °C. Then it was filtered and washed thoroughly with deionised water and dried at different temperatures for further studies.

2.2. Physicochemical characterization

The X-ray powder diffraction pattern was taken in the Philips PW 1710 diffractometer fitted with an automatic control. The patterns were run with a monochromatic CuKα radiation with a scan rate of $2°\,min^{-1}$.

The BET-surface area analysis was carried out using Quantasorb instrument (Quantachrome, USA) by nitrogen adsorption–desorption isothems at liquid nitrogen temperature (77 K). Prior to adsorption–desorption measurements, samples were degassed at 110 °C and 10^{-5} torr for 5 h in vacuum.

UV–vis DRS was taken in the Varian UV–vis spectrophotometer in the range of 200–800 nm. The spectra were recorded against boric acid reflectance standard as base line. The computer processing of spectra with CARY 1.5E software consisted calculation of Kebulka–munk function $F(R\infty)$ from the absorbance. This diffused reflectance spectroscopy has been utilised to characterize the bulk structure. This is used to probe the band structure or molecular energy levels in the materials since UV–vis light excitation creates photo-generated electrons and holes. The UV–vis absorption band edge is strong function of cluster size diameter less than 10 nm, which can be attributed to quantum size effect for these semiconductors.

The FT-IR spectra were taken using JASCO FT-IR-5300 in KBr matrix in the range 400–4000 cm^{-1}.

2.3. Experimental procedure

The photo-oxidation of phenol was performed in batch reactors by taking 10 mg/L of the substrate (phenol in water) and 0.2 g/L of the catalyst. The solution was exposed to sunlight in closed pyrex flasks at room temperature with constant stirring. The solar experiments were compared in dark and also under UV-irradiation with 6 W low pressure Hg vapor lamp (90% of light is 254 nm) as a source (Quartz Emersion Well Photoreactor, SAIC, India). The phenol analysis was done by the spectrophotometric method at 500 nm [19].

3. Results and discussion

3.1. Physicochemical characterization

From XRD analyses, the basal spacing of 2 wt% titania loaded zirconium phosphate and 4 wt% titania loaded titanium phosphate showed the highest value, i.e. 19.3 and 25.9 Å, respectively. Again the pillaring was confirmed by FT-IR and UV–vis DRS. Details of which has been published elsewhere [18].

3.2. Photocatalytic oxidation of phenol

3.2.1. Effect of pH

The role of pH on the photocatalytic degradation of phenol was studied in the pH range 3–8 (Fig. 1). It was observed that phenol degradation was favourable at mild acidic and neutral
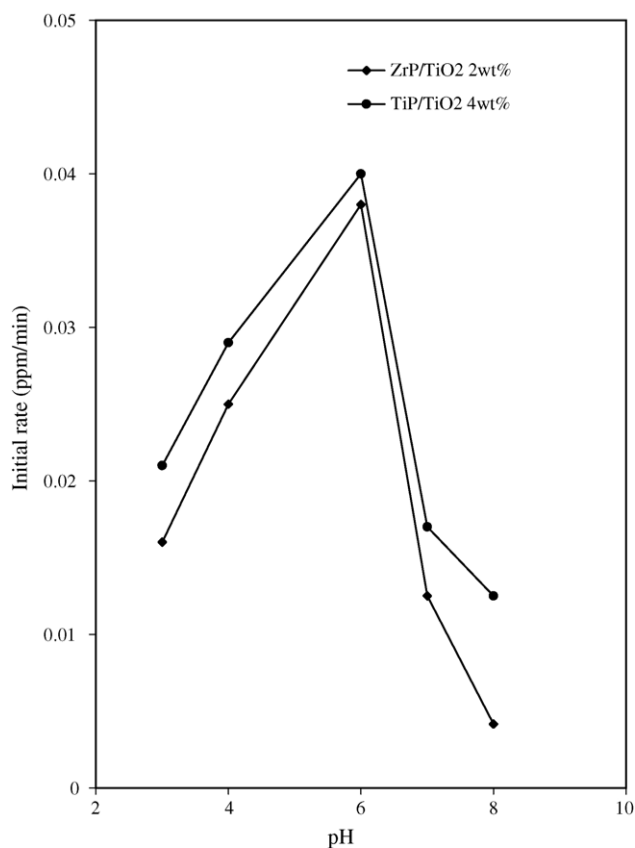

Fig. 1. Effect of pH on the initial rate of degradation of phenol. [Phenol] = 10 mg/L; catalyst dose = 0.6 g/L; time = 240 min.

conditions. Similar results were reported by Wei and Wan [20] for the photodegradation of phenol over titania surface. At higher pH, phenol exists as negatively charged phenolate species. Higher removals of phenol in slightly acidic or in other words almost neutral condition may be attributed to the increased amount of undissociated phenol adsorbed on the catalyst surface. However, the pH_{pzc} of titania pillared zirconium phosphate and titanium phosphate was found to be 5–6 [18]. When the $pH > pH_{pzc}$ the surface of titania pillared zirconium phosphate and titanium phosphate is negatively charged which may repel the phenolate species. Hence, the initial rate of photodegradation of phenol decreases with increasing the pH. From Fig. 1, it was found that pH 6.0 is the optimum value where the initial rate of photodegradation of phenol was found to be 0.038 and 0.04 ppm/min over 2 wt% titania loaded zirconium phosphate and 4 wt% titania loaded titanium phosphate, respectively.

Again the photocatalytic degradation is influenced by acid sites [21]. Generally, acidic sites were beneficial for the adsorption of phenol molecules and inhibition of the recombination process between photo-induced electrons and holes, since photo-induced electrons could be captured by these acidic sites [22]. However, with increasing the wt% of titania, loading was found to be harmful for the photocatalytic activity of titania pillared zirconium phosphate and titanium phosphate possibly due to surface coverage [18].

3.2.2. Effect of titania loading

From Fig. 2, one can see with increase in the titania loading upto 2 wt% for zirconium phosphate and 4 wt% for titanium phosphate, the initial rate phenol degradation increases to 0.038 and 0.04 ppm/min, respectively, and thereafter it decreases to 0.027 and 0.029 ppm/min range. The promoting effect of titania on the activity of zirconium phosphate and titanium phosphate could be understood considering the following factors: (1) pillaring of titania resulted in higher surface area, basal spacings which allows more phenol molecules to be adsorbed on the catalyst surface and ultimately fascilitating the photodegradation process, (2) titania pillaring enhances the acidic sites on the catalyst surface which in turn enhances the adsorption as well as photodegradation of phenol [as explained in Section 3.2.1].

3.2.3. Effect of substrate concentration

The photocatalytic degradation of phenol over titania pillared zirconium phosphate and titanium phosphate was studied in the range of 2–50 mg/L. Hundred percent conversion was observed at low phenol concentrations, such as 2 and 5 mg/L under solar radiation (Fig. 3). With increase in the phenol concentration, the percentage of degradation decreases from 100 to 46.6 and 55% for titania pillared zirconium phosphate (2 wt%) and titanium phosphate (4 wt%), respectively, with the catalyst dose remaining constant. This is mainly because at higher concentration of substrate, the light absorbed by the substrate is more than that of the cat-
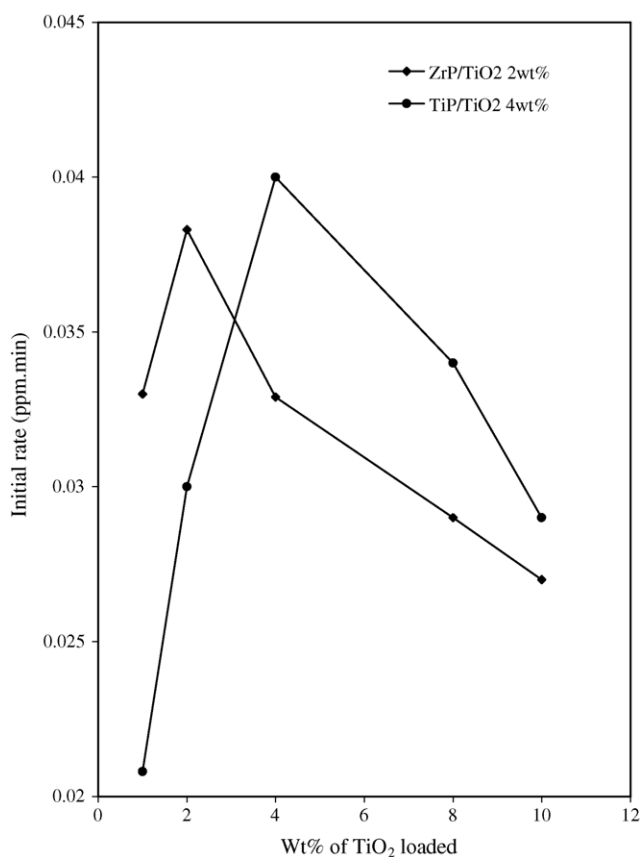

Fig. 2. Effect of titania load on the initial rate of degradation of phenol. [Phenol] = 10 mg/L; catalyst dose = 0.6 g/L; pH 6.0; time = 240 min.

alyst. The light absorbed by the substrate is not effective in bringing the photodegradation. For a fixed catalyst dose, the active sites remaining the same, the number of substrate ions accommodated in the interlayer space increases, so there is a decrease in the percentage of degradation (Fig. 3).

3.2.4. Kinetic analysis

The variation of initial concentration in the range of 10–50 mg/L on the photodegradation of phenol was studied under constant conditions of pH, catalyst weight. Photocatalytic degradation of phenol at low concentration followed pseudo first-order kinetics. A linear relationship was observed between phenol concentration and irradiation time as shown in the Fig. 4(a) and (b) [log C_0/C versus time, where C_0 is the initial concentration of phenol and C is the concentration at time t] for titania pillared zirconium phosphate and titanium phosphate, respectively. The calculated data for pseudo first-order rate constants "k" at different phenol concentration were given in the Tables 1 and 2, respectively, for the titania pillared zirconium phosphate and titanium phosphate. The rate constant values in both the cases were found to decrease with increase in the phenol concentration [23]. The further evidences for this kinetics were obtained from the studies of phototransformation of chlorophenols on ZnO by Sehili et al. [24] and Lemaire et al. [25].

Table 1
Rate constant values for photodegradation of phenol over titania pillared zirconium phosphate (2 wt%)

Time (min)	Concentration (10 mg/L)		Concentration (30 mg/L)		Concentration (50 mg/L)	
	Degradation (%)	$\log C_0/C$	Degradation (%)	$\log C_0/C$	Degradation (%)	$\log C_0/C$
30	60	0.39	21	0.10	18.5	0.08
60	72	0.55	35	0.18	25.2	0.12
120	80	0.69	40	0.22	30.9	0.16
180	84	0.79	49	0.29	41.3	0.23
240	92	1.1	58	0.37	46.6	0.27
300	93	1.15	60	0.39	50	0.30
Apparent rate constants, k (min^{-1})		$k = 0.016$		$k = 0.0048$		$k = 0.0036$

Table 2
Rate constant values for photodegradation of phenol over titania pillared titanium phosphate (4 wt%)

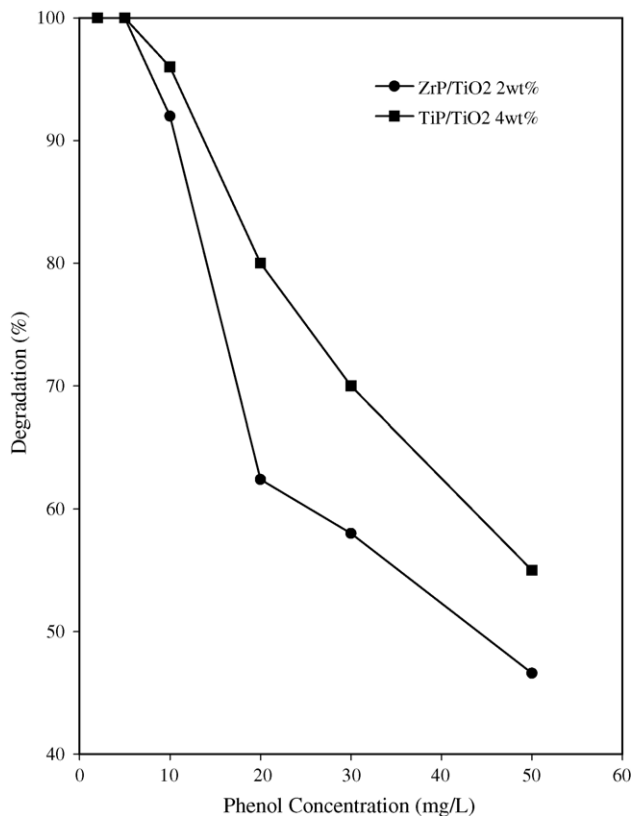| Time (min)	Concentration (10 mg/L)		Concentration (30 mg/L)		Concentration (50 mg/L)	
	Degradation (%)	$\log C_0/C$	Degradation (%)	$\log C_0/C$	Degradation (%)	$\log C_0/C$
30	59	0.38	30	0.15	20	0.09
60	65	0.45	41	0.22	29.5	0.15
120	80	0.69	55	0.34	40.2	0.22
180	88	0.92	63	0.43	48.3	0.28
240	96	1.39	70	0.52	55	0.34
300	97	1.52	70.5	0.53	56	0.36
Apparent rate constants, k (min^{-1})		$k = 0.016$		$k = 0.00675$		$k = 0.00438$

Fig. 3. Effect of initial concentration of phenol on the percentage of degradation. Catalyst dose = 0.6 g/L; pH 6.0; time = 240 min.
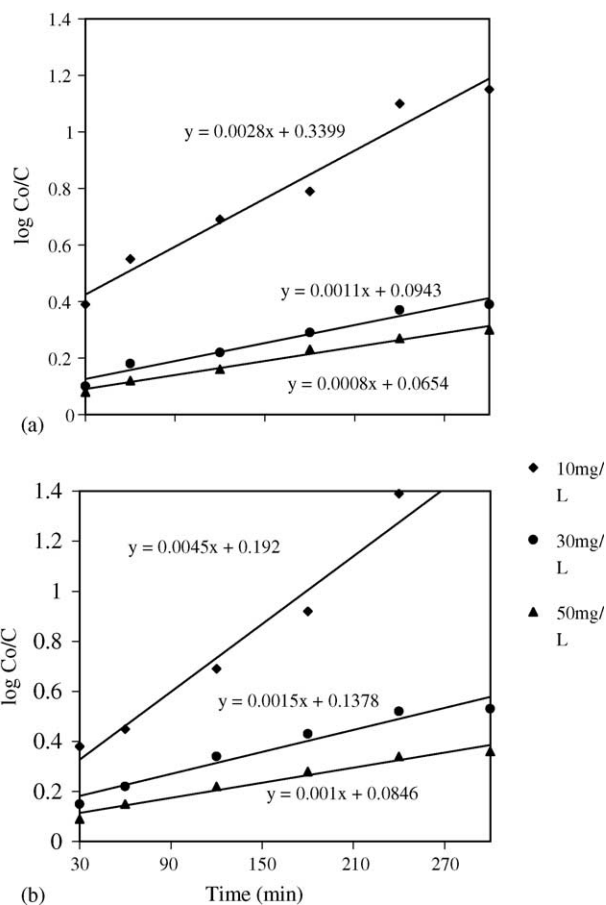

Fig. 4. Plot of log C_0/C vs. time for photocatalytic degradation of phenol: (a) for 2 wt% titania pillared zirconium phosphate, (b) for 4 wt% titania pillared titanium phosphate. Catalyst dose = 0.6 g/L; pH 6.0.
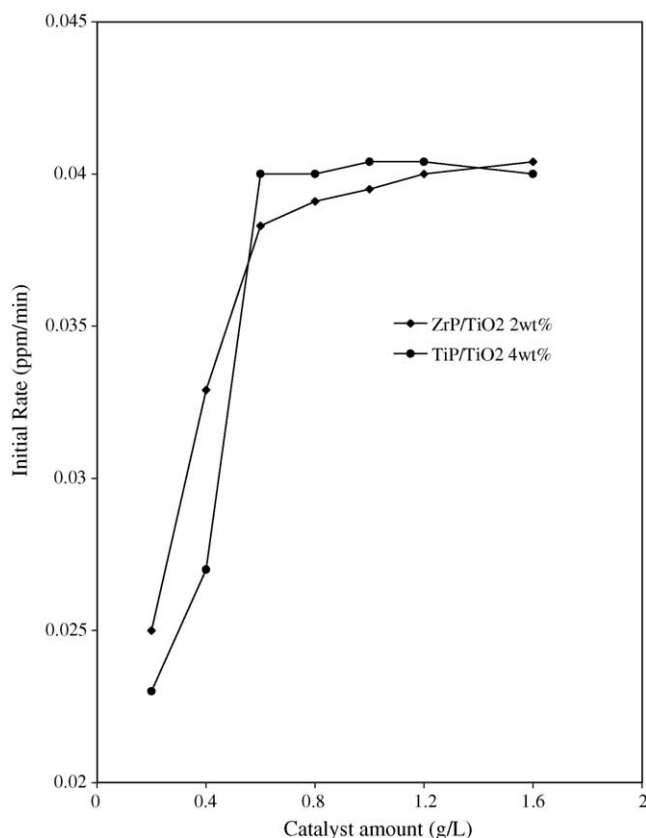
Fig. 5. Effect of catalyst amount on the initial rate of photodegradation of phenol. [Phenol] = 10 mg/L; pH 6.0; time = 240 min.
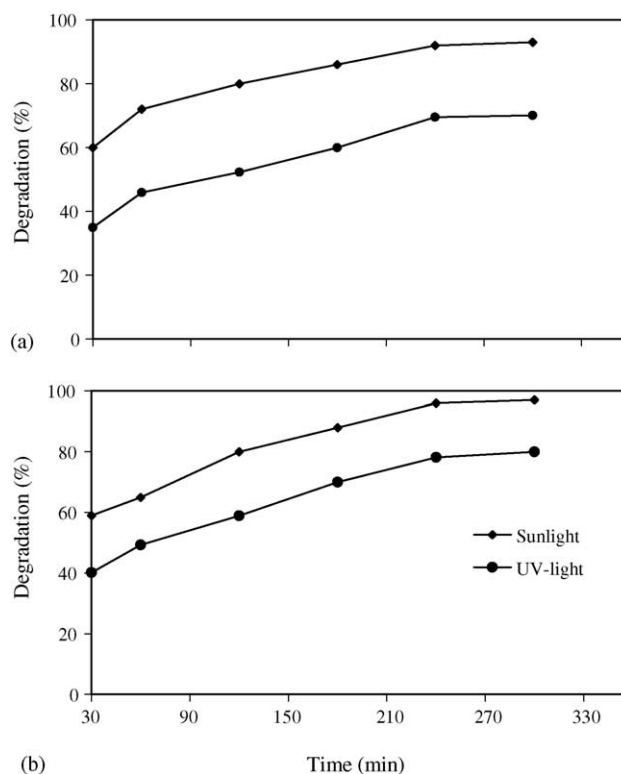

Fig. 6. A comparison plot between the solar and UV-irradiation time for the degradation of phenol. [Phenol] = 10 mg/L; catalyst dose = 0.6 g/L; pH 6.0.

3.2.5. Effect of catalyst dose

The effect was studied in the range of 0.2–1.6 g/L of the catalyst. Fig. 5 shows the variation of initial rate of photodegradation of phenol as a function of catalyst dose (g/L). The values indicated that with increase in the catalyst amount, the initial rate of degradation of phenol increases from 0.025 to 0.038 ppm/min thereafter it remains constant for titania pillared zirconium phosphate and similar observations were seen in case of titania pillared titanium phosphate [0.023–0.04 ppm/min]. This is mainly because of the fact that with increase in the catalyst dose, the phenol adsorbed is more and ultimately this leads to more phenol photodegradation.

3.2.6. Effect of irradiation time

Fig. 6(a) and (b) show the comparison between the effects of irradiation time under solar radiation and UV-source (6 W low pressure Hg vapor lamp). It shows that under solar radiation with increase in the time of irradiation upto 4 h, the percentage of degradation of phenol increases from 60 to 92% and 59 to 96% for 2 wt% titania loaded zirconium phosphate and 4 wt% loaded titanium phosphate, respectively. Then it remains almost constant. This is because of the fact that with increase in the irradiation time, the photons absorbed on the surface of catalyst is more which in turn helps in the photodegradation process. In case of UV-irradiation, one can see

the photodegradation of phenol increases from 35 to 70.1% and 40.2 to 80% for titania pillared zirconium phosphate and titanium phosphate, respectively (Fig. 6(a) and (b)). From this, we can say the photodegradation of phenol takes place almost completely in presence of sunlight rather than UV-light.

4. Conclusions

1. Phenol was oxidized almost completely by photocatalytic process over titania pillared zirconium phosphate and titanium phosphate.
2. The phenol degradation is favourable in neutral pH range.
3. The initial rate of degradation of phenol increases with increasing the amount of catalyst upto 0.6 g/L and thereafter it remains almost constant.
4. The photocatalytic degradation of phenol was studied in the wide range of phenol concentration from 2 to 50 mg/L. It was observed that the initial rate of degradation is high in case of 10 mg/L of phenol concentration, for higher concentration the rate decreases.
5. The photodegradation of phenol over titania pillared zirconium phosphate and titanium phosphate follow pseudo first-order kinetics.
6. The apparent rate constant values (k) were found to decrease with increase in the initial concentration of phenol.

Acknowledgements

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