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Photocatalytic degradation of phenol in water using TiO_2 and ZnO

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Abstract: *Photocatalytic degradation of chemical pollutants in water was investigated using semiconductor oxide catalysts, zinc oxide (ZnO) and titanium dioxide (TiO_2) and phenol as the substrate. Influence of various parameters such as characteristics of the catalyst, irradiation time, substrate and catalyst concentrations, pH etc. has been studied and optimum conditions for the complete degradation of phenol in water have been identified. In terms of activity and durability, TiO_2 is far superior to ZnO. Mixing ZnO with TiO_2 does not affect its activity significantly. The process is especially relevant in view of its potential for the treatment of wastewater containing pollutants, using solar radiation as the energy source.*

Key words: *Photocatalysis, Titanium dioxide, Zinc Oxide, Wastewater, Phenol, Solar irradiation*
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Introduction

Semiconductor mediated photocatalysis is fast emerging as an important technology for the treatment of organic contaminants in wastewater (Li *et al.,* 2008; Hosseini *et al*., 2007; Yesodharan and Devipriya, 2005; Celik *et al.,* 2008; Madhu *et al*., 2009). Suspended n-type semiconductors such as titanium dioxide, zinc oxide and cadmium sulphide have been receiving particular attention as photocatalysts in this context. In this paper, the comparative efficiency of ZnO, TiO_2 and their mixtures is evaluated for the complete degradation of traces of phenol in water under various reaction conditions like pH, irradiation time, substrate and catalyst concentrations *etc.*

Materials and Methods

Phenol Analar grade (99.5% purity) from Qualigens (India) was used without further purification. The water used in all the experiments was purified by double distillation. Other chemicals used were of reagent grade and used as such without further purification. The photocatalysts TiO_2 and ZnO were supplied by Merck India limited.

In a typical experiment, the catalyst is suspended in an aqueous solution of phenol in a Pyrex round bottomed flask. The reaction system was continuously stirred to achieve a homogeneous suspension and thermostated by circulating water to keep the temperature at 27 ±1°C. The water also served as a filter to remove IR light. The suspension was illuminated by a 500 W super high-pressure mercury lamp, mounted axially. For solar experiments, 250 ml solution was exposed to sunlight for a fixed time daily between 09:30 and 16:00 hr. Experiments were conducted on the roof top of laboratory in Kochi, India in April 2008. After illumination for the specified period, the suspension was centrifuged and the supernatant was analyzed for its phenol content by spectrophotometry (APHA, 2005), using Varian UV-VIS spectrophotometer. H_2O_2 was analyzed by iodometry. Experiments were done in triplicate and their average values are reported.

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Results and discussion

The results comfirm that the simultaneous presence of catalyst and light is essential for the photodegradation of organics in water. The results reveal that both ZnO and TiO_2 are effective for the removal of phenol from water and the latter is superior in activity. The optimum catalyst loading was found to be 1 g l^{-1}.

The effect of initial concentration of phenol on the rate of degradation in presence of both ZnO and TiO_2 catalysts was studied, by varying the concentrations over a wide range. The initial rate was calculated from the degradation pattern in the first 30 minutes of irradiation. The results are presented in Fig. 1. In the case of both catalysts, the rate increases with increase in initial concentration of the substrate at lower concentration range (0.5 to 2 x 10^{-5} M for ZnO and 0.5 to 4x10^{-5}M for TiO_2) and the results are consistent with first order kinetics. However at higher concentrations, the increase in rate slows down, suggesting a reduction in the order of the reaction, as the substrate concentration increases. Interestingly, while the rate of degradation almost levels off in the case of TiO_2, it picks up slowly again in the case of ZnO.

A number of reports have suggested a reduction in the reaction order at higher substrate concentrations in TiO_2 photocatalysis (Krosley *et al*., 1993; Yesodharan *et al*., 2003). At high substrate concentrations, all the catalytic sites of the semiconductor surface are occupied and zero order kinetics can be observed, while at low concentrations, the number of catalytic sites is not the limiting factor of the degradation rate, which is now

proportional to the substrate concentration, in accordance with apparent first order kinetics. Reaction orders smaller than unity is reported in the TiO_2 photocatalysis of phosphonic acids as a result of slow diffusion of the products from the surface of the catalyst (Krosley *et al.*, 1993). In the case of phenol, the photodegradation products include a number of intermediates which are expected to remain strongly adsorbed on to the surface of the catalyst through hydrogen bonding with the hydroxylated surface of the catalyst. The effective number of active sites available for phenol adsorption is drastically reduced and this contributes to the reduction in rate of degradation at higher substrate concentrations.

pH of the solution is an important parameter in the photo-catalysed degradation of organic wastes as it is known to influence the surface charge of the semiconductor thereby affecting the interfacial electron transfer and the photoredox process (Lu *et al*., 1993). In this context, the effect of pH on the degradation of phenol in presence of both ZnO and TiO_2 reveal that, in the case of TiO_2, maximum degradation is observed at pH 4 and 10, with the degradation almost complete in the alkaline region. In the case of ZnO, the degradation is not varying much in the pH range of 4-7, even though in this case also, the maximum is observed in the alkaline pH range. The surface functional groups of TiO_2 in water may be $TiOH_2^+$, >TiOH (surface titanol groups) and TiO^-. The isoelectric point for TiO_2 in water is about pH = 6 and the positive surface charge is expected at lower pH and negative surface charge is predicted at higher pH values. Thus, under neutral and weak alkaline conditions, TiO^- is the predominant species of TiO_2 and phenol remains primarily in its molecular state (Wang *et al.,* 1998). Both of them may combine by hydrogen bonding leading to an increase in the adsorption of phenol. Under acidic conditions, the TiO_2 surface carries a net positive charge while the phenols and the intermediates may be primarily negatively charged. This also facilitates adsorption. However, the observed degradation under acidic, neutral and mild alkaline conditions is lower compared to more alkaline systems, suggesting that better adsorption is not necessarily the main driving force for higher degradation of phenol. Previous reports also suggested that, in aqueous solutions, very small amount of phenol are adsorbed by TiO_2 because it has to compete with water for adsorption sites (Stafford *et al*., 1994). The low reactivity on ZnO, under acidic conditions can also be due to the photo-corrosion of ZnO in acidic aqueous suspensions. Significant amounts of Zn^{2+} have been detected in ZnO suspensions, irradiated for 1 hr (Okamoto *et al.,* 1985). On the other hand, TiO_2 was found to be extremely stable with no Ti^{4+} ions detected in solution, even after prolonged irradiation and the phenol has been completely degraded. We have observed that the degradation leads to complete mineralization and the final product is CO_2. The intermediates formed in the reaction have already been identified by earlier workers (Okamoto *et al*., 1985). These intermediates such as hydroquinone, pyrocatechol, 1, 2, 4-benzene triol, pyrogallol, 2-hydroxy-1, 4-benzoquinone and 1,4-benzoquinone, which are primary or secondary hydroxylated products of phenol confirm the role of hydroxyl radicals as the reactive species.

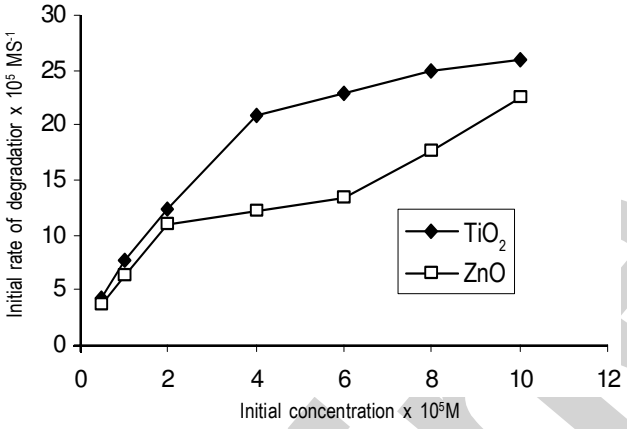

Fig. 1: Rate of degradation of phenol in water at different initial concentrations on ZnO and TiO_2 catalysts

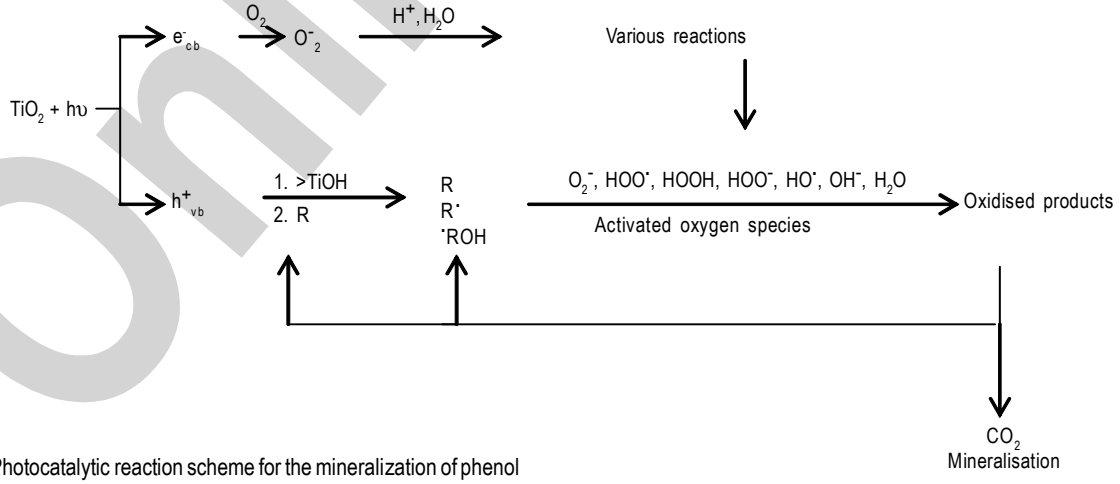

Fig. 2: Photocatalytic reaction scheme for the mineralization of phenol

They undergo further oxidation to yield polar intermediate products like aldehydes and carboxylic acids.

The overall reaction leading to the mineralization of phenol may be presented in accordance with the scheme suggested as in Fig. 2.

In short :

$$C_6H_5OH + 7\ O_2 \longrightarrow 6\ CO_2 + 3\ H_2O$$

It has been reported by many researchers that coupled semiconductor systems, in which illumination of one of the semiconductors produces a response in the other, is an effective method for promoting the degradation of organic pollutants (Doong *et al.,* 2001). The increased efficiency is attributed to interparticle electron transfer. In view of this, we examined the effect of mixing ZnO and TiO_2 on the photocatalytic activity towards the degradation of phenol has been examined. The results show that the activity of the mixture is an average of the activities of individual oxides. They do not have any inhibitive or synergic effect. In a standard experiment in which half of the TiO_2 is replaced by ZnO, the photodegradation is reduced by approximately 20% after 60 minutes of irradiation.

Semiconductors such as TiO_2 and ZnO are found to be efficient photocatalysts for the degradation of phenol in water. Based on the data generated from the current study, a general mechanism applicable for the photocatalytic degradation of a number of organic pollutants in water is proposed. Mixing ZnO and TiO_2 does not produce any synergic or inhibitive effect on the catalyst. The catalyst system is active under solar radiation as well.

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