Photocatalytic destruction of organic pollutants in a Pt/TiO$_2$ semiconductor particulate system

Debabrata Chatterjee* & Chandan Bhattacharya
Chemistry Section, Central Mechanical Engineering Research Institute, Durgapur-713209, India

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Photo-oxidation of phenol, chlorophenol and trichloroethylene in water has been studied by using Pt/TiO$_2$ semiconductor photocatalyst in presence of FeCl$_3$. After 5 h of irradiation with a 50 W tungsten lamp, over 80-90% degradation of pollutants is achieved. A working mechanism involving the formation of a hydroxyl radical is proposed.

A number of organic pollutants that are emitted from various industrial sectors, agricultural and even domestic fields cause contamination of water (even when they are present in low concentrations) as well as air and pose severe ecological problem as the biodegradation of the above pollutants is often very slow. The photocatalytic route using semiconducting TiO$_2$ particle towards detoxification of water contaminated with organic pollutants is of current interest. However, the main drawback of TiO$_2$ semiconductor is that it absorbs a small portion of solar spectrum in the UV region (band gap energy of TiO$_2$ is 3.2eV). Hence, in order to harvest maximum solar energy, it is essential to shift the absorption threshold towards visible region. Dye sensitization is an alternative method in which dye (sensitizer) adsorbed on TiO$_2$ surface gets excited by absorbing visible light and effects charge transition at sub-bandgap excitation to permit photocatalytic processes. In presence of visible light, ferric ions are believed to behave as sensitizers in photoassisted electron transfer process. Therefore, in order to examine the TiO$_2$ catalysed photocatalysis of organic pollutants using visible light we have undertaken the present investigation. We wish to report herein the preliminary results on photocatalysis of some common organic pollutants, viz., phenol, chlorophenol and trichloroethylene catalysed by suspended Pt/TiO$_2$ system in presence of FeCl$_3$ by using a 50W tungsten lamp.

Experimental
Semiconductor grade TiO$_2$ (Degussa p25) was loaded with platinum (4%) by following the procedure reported by Erbs et al. All other chemicals used were of A.R. grade. Doubly-distilled water was used throughout the studies. In a typical photocatalytic experiment aqueous suspension (50 ml) of pollutant ($10^{-3}$ M) containing 10mg of Pt/TiO$_2$ photocatalyst and 25mg of FeCl$_3$ was taken in a flat-surfaced glass reactor. A 50 W tungsten lamp (Philips Medical Spot Lamp; inner diameter of the focus tube was 5.1 cm) was used for the irradiation. The distance between the lamp and the glass-reactor containing reaction mixture was fixed at 8 inch. The reaction mixture was magnetically stirred during photolysis. Aliquots of the reaction mixture were withdrawn at chosen intervals of time and subjected to GC (CE 8000 Series) analysis. A Tenex column operating at FID detector was used for this purpose. Production of CO$_2$ was demonstrated by the precipitation of BaCO$_3$ in the Ba(OH)$_2$ solution used to scrub the effluent gas. The time course of photodegradation reaction was followed gas chromatographically by monitoring the disappearance of GC-peak corresponding to the reacting pollutant (i.e. phenol, chlorophenol and trichloroethylene).

Results and discussion
Results of photodegradation of water bound organics are summarized in Table 1. A series of control experiments reveals the fact that at about 15-20% of the initial concentration each organic compound under investigation, viz., phenol, chlorophenol and trichloroethylene is adsorbed on the surface of TiO$_2$ catalyst in the dark under specified conditions. Both TiO$_2$ and FeCl$_3$ are essential for effective photodegradation of these compounds in presence of visible light. However, slow photodegradation of pollutants was also observed (Fig. 1) in presence of FeCl$_3$ alone. The decline in yield was observed after 5h. This may be due to deactivation of TiO$_2$ powder caused by the physico-chemical change during the course of irradiation.
Based of the above experimental results and considering that ferric ion complex (Fe$^{3+}$OH$^-$) is reduced to ferrous ion and hydroxy radical, the following working mechanism is proposed.

\[ \text{hv} \quad (\text{Fe}^{3+}\text{OH}^-) \rightarrow (\text{Fe}^{2+}) + (\text{OH})^- \quad \ldots (1) \]

\[ \text{Fe}^{2+} + \text{O}_2 \rightarrow \text{O}_2^- + \text{Fe}^{3+} \quad \ldots (2) \]

\[ \text{hv} \quad \text{TiO}_2 (\text{Fe}^{3+}\text{OH}^-) \rightarrow \text{TiO}_2 (\text{Fe}^{2+}\text{OH}^-) \quad \ldots (3) \]

\[ \text{TiO}_2 (\text{Fe}^{3+}\text{OH}^-) \rightarrow e_{\text{CB}} (\text{TiO}_2) + \text{TiO}_2 (\text{Fe}^{3+}\text{OH}^-) \quad \ldots (4) \]

\[ e_{\text{CB}} (\text{TiO}_2) + \text{O}_2 \rightarrow \text{O}_2^- \rightarrow \text{HO}_2^- \quad \ldots (5) \]

\[ \text{P} + \text{OH}^- \rightarrow \text{Products} \quad \ldots (6) \]

\[ \text{HO}_2^- + \text{P} \rightarrow \text{Products} \quad \ldots (7) \]

\[ (\text{P} = \text{pollutant}) \]

In FeCl$_3$ catalysed reaction, photosensitization of ion-complex (Fe$^{3+}$OH$^-$) results in the formation of hydroxyl radical (OH$^-$) and Fe$^{3+}$ which subsequently react with dissolved oxygen to produce superoxide radical and Fe$^{1+}$ (Eqn 1-2). In TiO$_2$ / FeCl$_3$ system, photoactivation of surface adsorbed Fe$^{3+}$OH$^-$ takes place to yield hydroxyl radical (Fe$^{2+}$OH$^-$) species adsorbed on the surface of TiO$_2$ (Eq. 3). The TiO$_2$(Fe$^{3+}$OH$^-$) species effects charge injection in the conduction band (CB) of TiO$_2$ as shown in Eq. 4. It is presumed that the repeated attacks of OH$^-$ and HO$_2^-$ radicals on the aromatic ring cause the deep oxidation of aromatics leading to the formation of carbon dioxide as an end product. The higher activity observed in case of TiO$_2$ / FeCl$_3$ system may be explicable in terms of rapid scavenging of conduction band electron (e$_{\text{cb}}$) by molecular oxygen (Eq. 5) leading to the formation of superoxide and hydroperoxide radicals (Eq. 5). The rate controlling step of photocatalytic process is most likely a surface chemical step (electron transfer) probably coupled with adsorption of reactants.

In conclusion, the present work implies technical feasibility of using solar light with small amount of a sensitizer in conjunction with TiO$_2$ semiconductor to elminate water-bound organic pollutants.

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**References**