

Removal of 2,5-Dichlorophenol from Aquatic Environment Using TiO₂ as Photocatalyst

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Received on 12.01.2009. Accepted for Publication on 12.05.2009

Abstract

To investigate the photodegradation of organics in the aqueous suspension of photocatalyst, 2,5-dichlorophenol (2,5-DCP) was taken as organic pollutant, TiO₂ was used as photocatalyst and monochromatic UV light of wavelength 254 nm was used for irradiation. The photodegradation was found to be affected by the initial concentration of 2,5-DCP, the concentration of TiO₂ suspension and the initial pH of the solution. The optimum conditions for the photodegradation were pH 4.8 and the concentration of the suspension 0.8 g /100 mL of solution. The complete photodegradation of 8×10^{-4} M 2,5-DCP solution was observed after 4 hours of irradiation in the suspension under optimum conditions. The photodegradation ended up by mineralization, which was confirmed by the presence of Cl⁻ ion and by the increased concentration of hydrogen ion.

Key words: Photodegradation, dichlorophenol, TiO₂ suspension, mineralization.

I. Introduction

Semiconductor mediated photocatalytic degradation of organic and inorganic compounds is a promising method for waste water treatment. Many investigators have reported the removal of pollutants from aqueous solution by photocatalytic method¹⁻⁴. Under favourable conditions, it is possible to mineralize specific organic hazards completely with the production of mineral acids. Phenols and chlorophenols are common pollutants in industrial waste water particularly in effluents from petrochemicals, agrochemicals, plastic industries, paper industries, preservative industries, coal distillation plants, pharmaceutical industries etc. Huge tannery waste in Hazaribag area of Dhaka city, Bangladesh is another important source of these toxic chemicals. Through the discharge of these industrial wastes and also through the decomposition of pesticides, herbicides, the pollutants enter into soil and aquatic environment.

Phenols and phenolic compounds are carcinogenic and penetrate through the skin. The presence of toxic chemicals on earth is threat for living beings. It is necessary to treat effluents containing chlorinated phenol prior to the discharge into the receiving water. The degradation of these compounds to simple harmless compounds is possible via chemical, photochemical and biological processes. In the present investigation TiO₂ (rutile) has been selected as a photocatalyst.

Titanium dioxide or titania is a non-stoichiometric transition metal oxide. Titanium dioxide has been widely used as a catalyst in the photodegradation of many compounds. The band gap energy of TiO₂ ranges from 3.0 to 3.2 eV depending on its nature and the equivalent wavelength ranges from 376 to 410 nm⁵.

Photodegradation of many organic pollutants including phenols, chlorinated phenols and other chlorinated compounds have been extensively studied^{1,4,6-9} in the presence of TiO₂ and ZnO. Primarily, the organics are adsorbed on the surface of semiconductor due to electrostatic force of attraction. Adsorption of chlorophenols on various oxides e.g. ZnO, Al₂O₃, MnO, Fe₂O₃ was also carried out^{1,10-12}.

The present work explores the possibility of utilizing TiO₂ (rutile) suspension to remove 2,5-dichlorophenol from aqueous phase by studying photodegradation through laboratory experiments. In the first part of this work, adsorption of 2,5-dichlorophenol on TiO₂ has been carried out

at different pH. In the second part, photodegradation of 2,5-dichlorophenol on aqueous suspension of TiO₂ has been investigated by varying the parameters such as amount of TiO₂, initial pH of the medium and the initial concentration of 2,5-DCP in the presence of monochromatic UV light of wavelength of 254 nm.

II. Experimental

Chemicals used in the experiments were of analytical grade and commercially available reagent. 2,5-dichlorophenol (2,5-DCP) and titanium oxide (rutile) were procured from Fluka, (Switzerland) and Baker & Baker Ltd., (England), respectively and used without further purification. Deionized double distilled (DD) water was used throughout the present study.

Concentration of 2,5-DCP was determined by UV-Visible Spectrophotometer (UV-160A, Shimadzu, Japan). The reagent bottles containing adsorbent and adsorbate were shaken by a thermostatic mechanical shaker (SW B-20, Fisons Ltd, Germany). The pH of the solutions was recorded before and after the experiments by a pH-meter (HANNA-pH 211, Romania).

Adsorption Process

1×10^{-2} M 2,5-DCP was prepared in aqueous 0.05 M NaNO₃ solution and further dilutions were made by adding DD water whenever necessary. The concentration range used for experiments was 5×10^{-5} M to 5×10^{-4} M.

The equilibrium time of adsorption of 2,5-DCP on TiO₂ adsorbent was estimated, at pH 3.5 and temperature $30 \pm 0.2^\circ\text{C}$. 0.2 g of TiO₂ and 25 ml of 1×10^{-4} M 2,5-DCP solution were used and the pH was adjusted carefully without affecting the volume. The bottles were shaken in a thermostatic mechanical shaker at $30 \pm 0.2^\circ\text{C}$. After a definite time interval, supernatant was centrifuged and a clear solution was taken for spectral analysis. The absorbance of the clear solution was measured spectrophotometrically using $\lambda_{\text{max}} 280 \pm 1$ nm. The equilibrium time for adsorption was found to be 2 hours.

After establishing equilibrium time, the batch adsorption experiments were carried out with 0.2 g of TiO₂ at different initial concentration ranging from 5×10^{-5} M to 5×10^{-4} M of 2,5-DCP in 0.05 M NaNO₃ solution. To study the effect of pH on adsorption of 2,5-DCP on titanium oxide, the adsorption experiments were carried out by varying the solution from pH 3.5 and 5.0 at constant temperature ($30 \pm 0.2^\circ\text{C}$) using the equilibrium time two hours as determined earlier.

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Photodegradation Process

The reactor in which experiments were carried out was a beaker of inner diameter 5.5 cm and height 7.5 cm. The source of radiation was comprised of a lamp emitting monochromatic radiation of 254 nm. The reactor was placed on a magnetically stirred plate and the distance of the solution surface from the lower part of the lamp was fixed at 7.1 cm. The total system was enclosed in a wooden box and its inside surfaces were blackened. A typical experiment was done by the following way:

0.2 g TiO_2 was taken in a beaker containing 5.0 mL water, which was kept overnight. 95.0 mL of 2,5-DCP was added to the beaker. Before illumination, the solution was magnetically stirred for 30 min to ensure that the adsorption process goes to completion on the TiO_2 surface. During photolysis the contents of the reactor were stirred magnetically. After photolysis for a definite time, a small volume of solution was taken to centrifuge. After centrifugation, supernatant liquid was taken for spectral analysis. The above procedure was repeated for different time intervals, different amount of TiO_2 , different pH of the medium and the different initial concentrations of 2,5-DCP.

III. Results and Discussion

Adsorption isotherm

The adsorption of 2,5-DCP on titanium oxide has been investigated under different experimental conditions. The equilibrium time for the adsorption of 2,5-DCP on 0.2 g of TiO_2 adsorbent at pH 3.5 was estimated to be two hours. The adsorption experiments were carried out at pH 3.5 and 5.0 using two hours equilibrium time at 30°C. Fig. 1 shows the two isotherms. At the lower equilibrium concentration ranges, the amount adsorbed increases with increasing the pH. However, at higher equilibrium concentration ranges, both the isotherms coincide with each other.

The zero point charge (pH_{zpc}) of TiO_2 was around 5.5- 6.0¹³ which suggests that, oxide surface at pH 3.5 is more positive than that at pH 5.0. From the effect of pH of the solution, it may be suggested that at lower pH (3.5) the adsorption is mainly due to the bonding of molecular dichlorophenol to surface by weak physical forces. But at pH 5.0, the adsorption is due to strong electrostatic force of attraction, between phenolate ion and the surface¹⁴. This might be the reason of higher adsorption at pH 5.0 than pH 3.5 (Fig. 1).

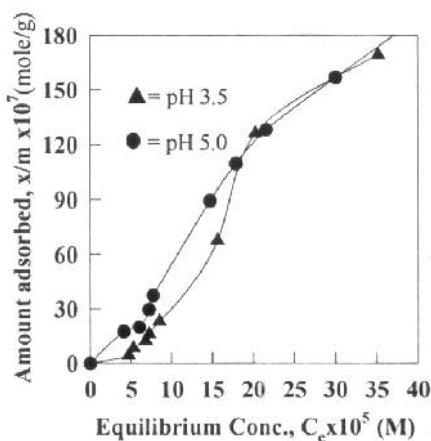


Fig. 1. Adsorption isotherms of 2,5-DCP at different pH at 30°C.

Photodegradation of 2,5-DCP in the presence of TiO_2 suspension

The conditions of photodegradation of 2,5-DCP were optimized by varying the amount of TiO_2 , pH of the solution and initial concentration of 2,5-DCP. For this purpose, the experiments were carried out with one hour irradiation time.

Effect of amount of TiO_2 on the photodegradation of 2,5-DCP

Photodegradation of 2,5-DCP (8×10^{-4} M) was studied in aqueous suspension of TiO_2 by varying the amount of TiO_2 (0.2 g to 1.6 g) by irradiating with 254 nm UV light. The percent degradation of 2,5-DCP increases initially with increasing amount of TiO_2 . The degradation reaches to maximum when the concentration of suspension was 0.8 g TiO_2 /100 mL solution. Then photodegradation decreases with further increase of TiO_2 (Fig. 2). With increasing the amount of TiO_2 more electron-hole pairs introduce in the system. This leads to an increase in the extent of photodegradation of 2,5-DCP up to a certain concentration of TiO_2 (0.8 g TiO_2 / 100 mL). However, in the presence of excess TiO_2 , it is likely that the electron-hole pairs undergo recombination. As a result, the percentage of degradation of 2,5-DCP decreases. Another possibility for decreasing degradation is that the presence of excess TiO_2 does not allow the light to penetrate deep into the bulk of the suspension.

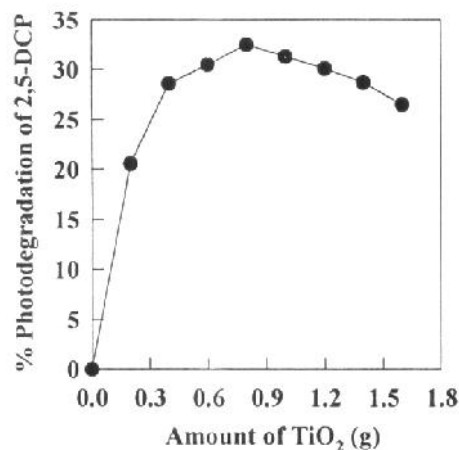


Fig. 2. Photodegradation of 8×10^{-4} M 2,5-DCP with various amount of TiO_2 at pH 5.8.

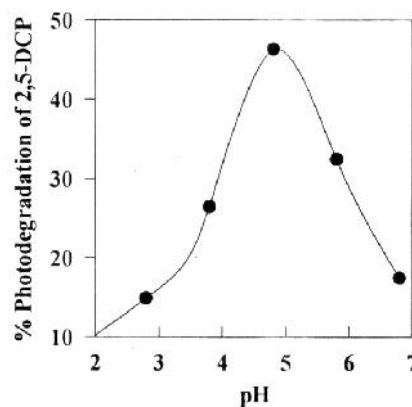
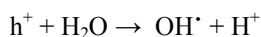
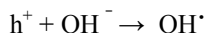


Fig. 3. Effect of initial pH on the photodegradation of 8×10^{-4} M 2,5-DCP by using 254 nm light.

Effect of initial pH on the photodegradation of 2,5-DCP

The role of pH is quite significant in the case of photodegradation, because the surface of TiO₂ and the chemical properties of 2,5-DCP are greatly influenced by the pH of the medium. The effect of pH on the degradation of 2,5-DCP was studied using the 2,5-DCP concentration of 8×10^{-4} M and varying the pH of the solution from 2.8 to 6.8 at 30°C (Fig. 3). The extent of photodegradation increases with increasing initial pH up to 4.8 of the medium. Then it decreases with further increase of pH. The maximum percentage of degradation of 2,5-DCP was found at pH 4.8. This is nearly in agreement with the study of Islam *et al.*¹ who studied ZnO-mediated photodegradation of 2,4-dichlorophenol. The transfer of the photogenerated charged carriers from TiO₂ particles to the adsorbates is dependent on the surface charge of TiO₂ particles.

The point of zero charge of TiO₂ has been found to be in the range of 5.5- 6.0¹³. At pH > p*H*_{zpc} the particle surface becomes negatively charged. The negative electric field formed around the TiO₂ particle is detrimental to the transfer of h⁺ to the adsorbate. As a result, the following reactions producing hydroxyl radical proceed slowly.



It is well known that the hydroxyl radical is the primary oxidizing species involved in the photomineralization of organic pollutants. So, under these conditions, the degradation becomes hindered. At pH < p*H*_{zpc} the particle surface becomes positively charged. So, h⁺ transfer becomes easier, and production of OH[•] increases. Under these conditions, recombination of e⁻ + h⁺ is expected to be slow. So, the photodegradation increases from pH 2 to 5. Similar observation had been obtained during the photodegradation of 2,4-DCP by ZnO¹. Results of adsorption experiments (Fig. 1) also support this observation.

Effect of initial concentration of 2,5-DCP

As the initial concentration of 2,5-DCP had been changed, keeping the concentration of TiO₂ (0.8 g TiO₂/ 100 mL solution) same in suspension, it has been found that the percent photodegradation decreases with increasing the concentration of DCP at pH 4.8.

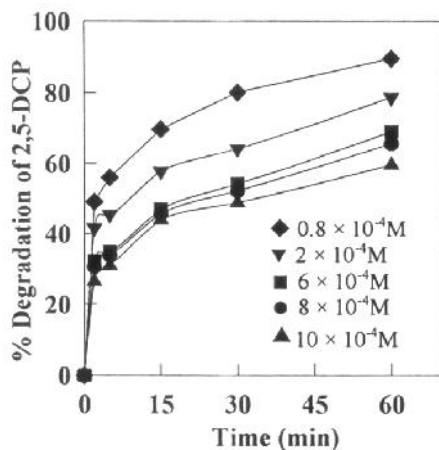


Fig. 4. Change of concentration of 2,5-DCP with time of degradation using different initial concentration of 2,5-DCP at pH 4.8.

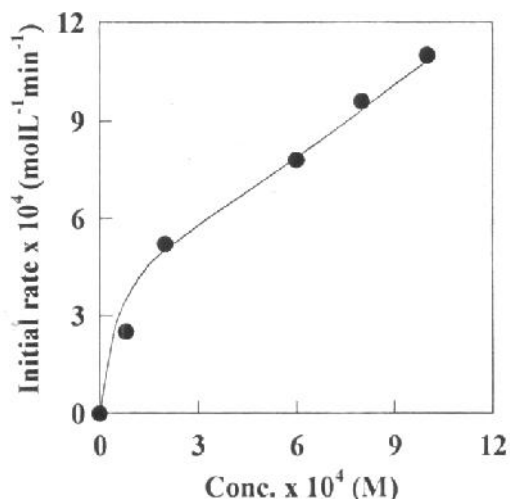


Fig. 5. Initial rate of photodegradation of 2,5-DCP versus initial concentrations.

The percentage of degradation was found to be dependent on both time of irradiation and the initial concentration of 2,5-DCP. Fig. 4 shows that the percent of degradation increases with the time of irradiation at the constant initial concentration of 2,5-DCP.

When initial rate is plotted against initial concentration of 2,5-DCP (Fig. 5), it has been found that the initial rate of photodegradation increases with increasing concentration of 2,5-DCP. This is in agreement with the study of Mahmood *et al.*¹⁵ who studied ZnO mediated degradation of brilliant orange by visible light. The photodegradation of 2,5-DCP at lower concentration is higher than that at higher concentration due to the easy availability of solid surface to adsorbates. The lower degradation rate at higher concentration might be attributed to the consumption of OH[•] by reaction with Cl⁻ produced in the mineralization process. This is in agreement with the observation of Ling Zang *et al.*⁴ who studied the photochemistry of semiconductor particles.

Mineralization by photodegradation

After optimizing the conditions, the photodegradation of 2,5-dichlorophenol from aqueous suspension of TiO₂ was investigated. A definite concentration 8×10^{-4} M of 2,5-DCP was used keeping the volume of solution to be 100.0 mL and amount of TiO₂ 0.8 g. The suspension was irradiated by 254 nm UV light. The progress of the removal i.e. the degradation of 2,5-DCP was monitored by recording the change of absorbance at $\lambda_{\text{max}} \approx 280$ nm with time. The spectra of photodegradation with respect to time are shown in Fig. 6. The percentage of degradation was calculated and presented in Fig. 7. The Fig. 6 & 7 suggest that the mineralization of 2,5-DCP was almost complete within four hours.

After the photodegradation the remaining solution was concentrated to one third of the original volume by heating. The solution was cooled, acidified by HNO₃ and a few drops of AgNO₃ solution were added. A milky white precipitates were obtained. These were soluble in dilute NH₃ solution and were reprecipitated by HNO₃. These results confirmed the presence of Cl⁻ ions produced by the mineralization of 2,5-DCP.

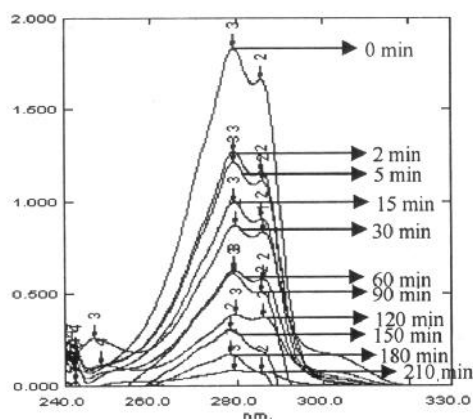


Fig. 6. Spectra of 2,5-DCP after photodegradation by 254 nm light at pH 4.8

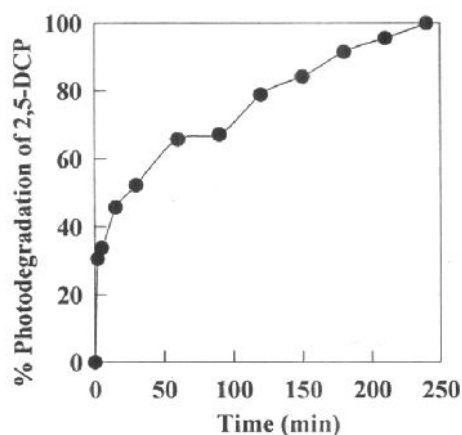
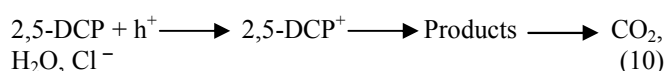
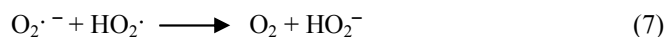
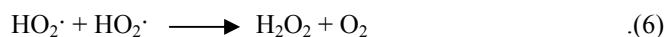
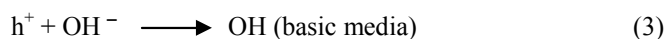
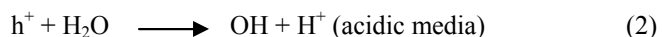


Fig.7. Photodegradation of 8×10^{-4} M 2,5-DCP using 0.8 g TiO_2 /100 ml solution at pH 4.8 by 254 nm light

Mechanism of photodegradation of 2,5-DCP in the presence of TiO_2 suspension

When TiO_2 suspension is illuminated under UV-radiation the electrons are promoted from the valence band to the conduction band and a hole (h^+) is produced in the valence band. Holes are sufficiently energized so that they may oxidize H_2O or OH^- to generate hydroxyl radicals ($\cdot\text{OH}$). The hydroxyl radicals may attack the 2,5-DCP and degrade it (eqn. 11) or h^+ can directly attack 2,5-DCP (eqn. 10). The $\cdot\text{OH}$ may be produced from another route. The conduction band electrons (e^-) may react with the dissolved oxygen (O_2) to form super oxide anions ($\text{O}_2^{\cdot-}$) (eqn. 4). In acidic medium, $\text{O}_2^{\cdot-}$ anions can combine with protons to form HO_2^{\cdot} radicals (reaction 5). This HO_2^{\cdot} radical can produce $\cdot\text{OH}$ via equation 6, 7, 8, & 9. The formation of super oxide anions ($\text{O}_2^{\cdot-}$) inhibits the recombination of electron hole pairs and thus enhances the photodegradation. The possible products of mineralization are CO_2 , H_2O , Cl^- and H^+ .

The main routes for photomineralization are shown below.



The above mechanism for the photodegradation of 2,5-DCP suggests that the mineralization of 2,5-DCP mostly occurs by sequential mechanism^{16, 17}.

IV. Conclusion

TiO_2 mediated photodegradation of 2,5-DCP by UV-light completely mineralized the compound after 4 hours irradiation with 254 nm UV light. This method can be applied for the treatment of waste water containing organic pollutants.

Acknowledgement

Authors gratefully acknowledge the University Grants Commission of Bangladesh for providing financial support to carry out the research work.

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