

Effect of pH, Ions and Ionic Strength on TiO₂-mediated Photodegradation of Brilliant Orange

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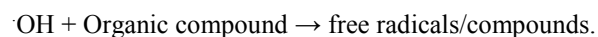
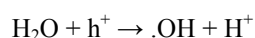
Received on 20.05.2009. Accepted for publication on 05.11.2009.

Abstract

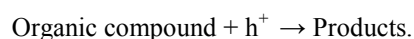
The photodegradation of Brilliant Orange (BO), an anionic mono azo dye used in textile and leather industries, was investigated in aqueous TiO₂ suspension under UV irradiation. The effect of pH on degradation rate was investigated. The experimental results indicated that photocatalytic reaction was favoured in acidic medium. The degradation was minimum at pH 6 which is zero point charge of TiO₂. The effect of different ions and ionic strength on photodegradation was also investigated. Na⁺, Zn²⁺, Al³⁺ and Pb²⁺ ions were used to see the cationic effect and NO₃⁻, CO₃²⁻, Cl⁻ ions were used to see the effect of anions. Pb²⁺ ion enhanced the percent degradation 25 times more than the degradation without it. The effect of ionic strength was studied using different concentrations of Pb(NO₃)₂ solution. Photodegradation was found to increase with the increase of ionic strength.

I. Introduction

The dyes in the effluents discharged from textile dyeing factories and leather industries badly affect the quality of river water. Brilliant Orange H2R (BO) is frequently used in textile industries. Various chemical and physical processes such as precipitation, adsorption, air stripping, flocculation, reverse osmosis and ultrafiltration can be used for color removal from textile effluents^{1,2}. Some oxidation processes such as ozonation and chlorination are also effective in destroying some of dyes³. Semiconductor mediated photodegradation is one of the important advanced oxidation process (AOP), effective for treating organic compounds including dyes⁴⁻⁸. AOPs are based on generation of reactive species such as hydroxyl radicals that oxidizes a broad range of organic compounds quickly and non-selectively^{9,10}. Of all the semiconductors such as TiO₂, ZnO, Al₂O₃, WO₃, etc, TiO₂, because of its nontoxicity and photochemical stability^{11,12}, is being used by a large number of investigators. The electrical character of TiO₂ surface varies with the pH of the medium. Therefore, it is important to investigate the role of pH on degradation. Cu²⁺ ion when added to the suspension of TiO₂, is likely to be adsorbed ($\equiv\text{Ti}-\text{O}-\text{Cu}^+$) and may trap photoelectrons to form $\equiv\text{Ti}-\text{O}-\text{Cu}^{\cdot}$. Similar behaviour is expected from Pb²⁺ ion when added to the suspension of TiO₂. As a result the photoholes will have considerable life time to undergo the following oxidation reactions;



Organic compounds are more likely to be oxidized by holes directly.



So, it will be useful to study the effect of ions on the TiO₂ mediated photodegradation of BO. In the present study, the effect of pH, ion and ionic strength on photodegradation of BO has been investigated.

II. Experimental

Reagents and Chemicals

Brilliant Orange H2R obtained from textile industry was used without further purification. Titania P-25 (anatase) with particle size 0.20-0.25 μm and 99.0 % purity was obtained from Fluka. Double distilled water was used for

preparation of various solutions. Electrolytes, such as NaNO₃, Zn(NO₃)₂, Al(NO₃)₃ and Pb(NO₃)₂ used in all the experiments were obtained from Merck.

The photodegradation reactor was a 100 mL beaker of inside diameter 4.3 cm and height of 5.5 cm and the source of radiation was a horizontal lamp emitting monochromatic radiation corresponding to the wavelength 254 nm. The reactor was placed on a magnetically stirred plate to ensure constant stirring of solution. The total system was enclosed in a wooden box, the inner surface of which was blackened.

Irradiation experiments

To investigate the effect of pH, experiments were carried out using solution of different pH varying from 2 to 11. In this case, the concentration of TiO₂ suspension and the concentration of BO were 1.2 g/100 mL and 1.0×10^{-4} M respectively. 5 mL of TiO₂ suspension and 95 mL of BO solution were added in the reactor. The pH of the suspension was adjusted to a definite value by adding small volume of either NaOH or HCl from a microburette. The solution was irradiated for an hour. During the irradiation time, small volume of irradiated solution was withdrawn after a definite interval of time and this was continued until 5 or 6 samples were collected. The samples were centrifuged and analyzed by UV-Visible spectrophotometer (UV-1610A, Shimadzu, Japan). The experiment was repeated with solution of seven different pH values. The rate of decolorization was estimated. The percent degradation (%) has been calculated as:

$$\text{Percentage of degradation, } = (A_0 - A_t) \times 100/A_0$$

Where, A₀ is the initial absorbance. A_t is the absorbance at any time t. The results have been shown in Fig.1.

To see the effect of cations on photodegradation, the above experiment was performed with 0.1 M nitrates of Na⁺, Pb²⁺, Zn²⁺ and Al³⁺ at pH of the solution. To study the effect of anions, the experiment was repeated with nitrate, carbonate, chloride and sulphates of sodium. The results have been shown in Fig.4 and Fig.5 respectively. The effect of ionic strength was investigated by using Pb(NO₃)₂ solutions with different ionic strengths ranging from 10^{-5} M to 10^{-1} M. The results have been shown in Fig.6.

III. Results and Discussion

Effect of initial pH of the solution

Fig. 1 shows the degradation of dye is favoured by acidic medium. In acidic condition surface of TiO₂ becomes positively charged because the pH_{ZPC} of TiO₂ is 6.25 and in acidic condition, pH is lower than pH_{ZPC} of TiO₂. Anionic BO⁻ molecules are adsorbed on the surface by electrostatic force of attraction and reactions of degradation are favoured. Fig. 1 shows that the maximum photodegradation occurs when the pH of the solution is 3. With the increase of pH the percent photodegradation decreases due to the decrease of adsorption of BO⁻ molecules on the surface. Photodegradation becomes minimum at pH ~6, the zpc of TiO₂. This is because at this pH, the surface of TiO₂ remains uncharged and there is no electrostatic force of attraction between the surface and BO molecule. Above pH 7, although the surface is negatively charged the percent of photodegradation slightly increases. This may be explained by the fact that the alkaline medium favours the formation of ·OH radicals; $h^+ + OH^- \rightarrow \cdot OH$. Higher concentration of active ·OH radicals may cause the higher degradation. Our present studies are in agreement with the results obtained by a group of researchers^{14,10-21}. Sumandeep Kaur¹³ studied degradation of Reactive Red 198 an anionic dye using TiO₂ and UV light and found that the degradation rate was higher in acidic media and decreased with the increase of pH. Chung-Shin Lu²² investigated the degradation of Acridine Orange a cationic dye using TiO₂ and UV light and found that the degradation rate was higher in alkaline media and decreased with the decrease of pH. Fig.1 also shows that the percentage of degradation decreases sharply below pH 3. This might be due to fact that under this condition, TiO₂ suspension starts coagulating reducing the surface area and thereby affecting the production of electron hole pairs.

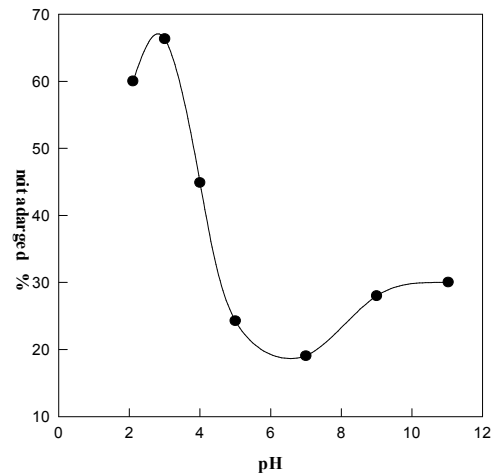


Fig. 1. Effect of pH on percentage degradation of BO during 50 minutes of irradiation

Effect of Cations

Fig.2 shows the effect of cations on photodegradation of BO. All metal ions except lead and aluminium had detrimental effect on the TiO₂ mediated photodegradation of BO.

The results can be explained by the difference of redox potentials of metal ion and conduction band potential of TiO₂. Conduction band potential of TiO₂ is, $E_{CB} = E_{CB}^0 - 0.059pH \text{ V}$ ²³, where E_{CB}^0 , the conduction band potential at pH 0 is $\approx -0.1 \text{ V}$. The redox potential²⁴ of metals and conduction band potential of TiO₂ have been compared in the following table.

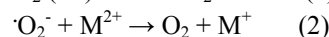
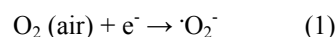
$E^0(M^{2+}/M^+)$	$E_{SR}^0 (V)$	$E_{CB}^0 (V)$	pH	$E_{CB} (V)$
$E^0 (Pb^{2+}/Pb^+)$	-0.06	-0.1	4.10	-0.34
$E^0 (Al^{3+}/Al)$	-1.66	-0.1	3.2	-0.29
$E^0 (Zn^{2+}/Zn^+)$	-0.38	-0.1	3.10	-0.28
$E^0 (Na^+/Na)$	-2.71	-0.1	3.0	-0.28

The redox potential of $E^0 (Pb^{2+}/Pb^+)$ is understandably high than conduction band potential, E_{CB} of TiO₂. So Pb^{2+} ions adsorbed on the surface of TiO₂ ($\equiv Ti-O-Pb^+$) can trap photoelectron to form $\equiv Ti-O-Pb$.

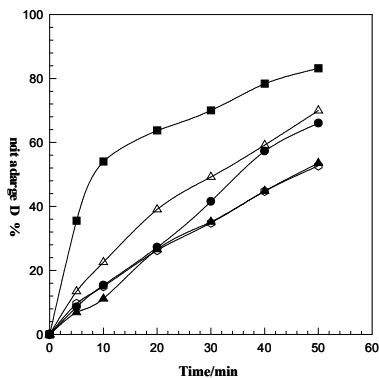
$\equiv Ti-O-Pb^+ + e^- \rightarrow \equiv Ti-O-Pb$, which can be further oxidized by oxygen at the interface.

$\equiv Ti-O-Pb + O_2 \rightarrow \equiv Ti-O-Pb^+ + \cdot O_2^-$. This is possible because of high reduction potential, $E^0 [O_2 (g) / OH^-] = 0.40V$. Superoxide anions acting like superchargers greatly increase the oxidation of organic peroxy radicals to produce H₂O and CO₂. Since the photogenerated electrons can be effectively scavenged by the Pb^{2+} ions photogenerated holes would have more opportunity to participate in the oxidizing reactions. Thus, the overall efficiency of photocatalytic

process is enhanced. Metal ions having redox potential lower than the conduction band potential of TiO₂ are not adsorbed on the surface of TiO₂. Moreover, it is likely that these can scavenge superoxide anions formed by the reduction of oxygen at the interface.



This explains the detrimental effect of some metal ions on the photocatalytic degradation. Rusmidah²⁵ and Ling Zang²⁶ also observed the increased efficiency in the semiconductor mediated photodegradation of organic compound by addition of copper ion. Cu^{2+}/Cu^+ have very high redox potential compared to the conduction band potential of TiO₂.



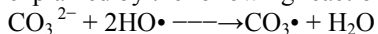
■ = Pb²⁺, △ = Al³⁺, ● = No salt, ▲ = Na⁺, ○ = Zn²⁺

Fig. 2. Percentage degradation of the BO solution with time in presence of different cation.

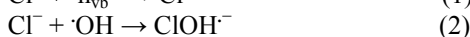
Effect of anions

Fig.3 shows that all the anions have detrimental effect on the degradation efficiency.

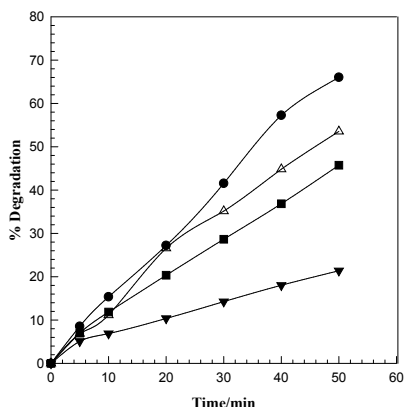
Carbonate had the most negative effect. This may be explained by the following reaction:



In which the most reactive species ·OH radical had been removed. The Cl⁻ ions might act as scavengers of either positive holes or OH radicals or both as shown in equation (1) and (2).



Generally speaking, the detrimental effect of anions might be due to the fact that anions are adsorbed more on the surface at pH lower than zpc of TiO₂ compared to the anionic dye. This hindered the dye molecules to get adsorbed on the surface. This is in agreement with the observations made by Sökmen²⁷ who investigated “Decolourising textile wastewater with modified titania: the effects of inorganic anions on the photocatalysis”. Satyen Gautam¹⁵ studied “Photocatalytic degradation of 3 nitrobenzenesulfonic acid in aqueous TiO₂ suspensions” and found the detrimental effect of chloride, carbonate and bicarbonate on degradation.



● = No salt, △ = NO₃⁻, ■ = Cl⁻, ▲ = CO₃²⁻

Fig. 3. Percentage degradation of BO solution with time in presence of different anion

Effect of ionic strength

The experimental observations of the effect of ionic strength on photodegradation of BO are given in Fig. 4. Results indicate that the increase in ionic strength enhanced the degradation of BO. This enhancement is due to the combination of Pb²⁺ with photoelectrons produced from the surface after irradiation (eq. 1). This causes the easy availability of h⁺ for further reaction as shown below. The higher is the concentration of Pb²⁺ the faster is the formation of ·OH radicals and higher is the rate of degradation.

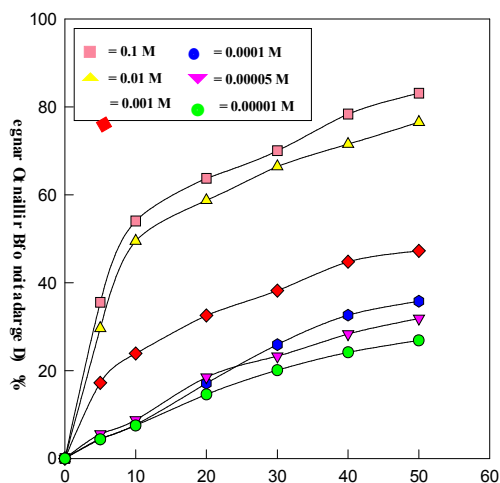
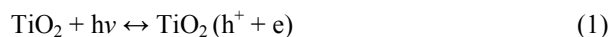


Fig. 4. Percentage degradation of BO with time at various concentration of Pb(NO₃)₂ solution.

IV. Conclusions

Photocatalytic degradation process using UV light and TiO₂ suspension can be efficiently applied for the degradation of non-biodegradable azo dye, BO which is frequently used in textile and leather industries. The photodegradation of BO dye was found to increase with decreasing pH due to easy adsorption of the BO⁻ on positively charged TiO₂ surface. In alkaline medium, the degradation was not satisfactory due to poor adsorption of anionic dye on negatively charged surface. Hence suitable acidic conditions should be used for photodegradation of anionic dye. The cations having higher reduction potential than the conduction band potential of TiO₂ enhanced degradation efficiency. Pb²⁺ ion was found to be most effective. Photodegradation can also be enhanced by increasing the ionic strength of Pb(NO₃)₂ solution. Investigations with Cl⁻, NO₃⁻ and CO₃²⁻ ions showed the remarkable decrease in the rate of photodegradation. Conclusively, semiconductor mediated photodegradation in the presence of ions having high reduction potential than the conduction band potential of TiO₂ can be used for the destruction of organics present in the industrial effluents.

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