

Photocatalytic decomposition of leather dye Comparative study of TiO₂ supported on alumina and glass beads

S. Sakthivel^a, M.V. Shankar^b, M. Palanichamy^b, B. Arabindoo^b, V. Murugesan^{b,*}

^a Institut für Solarenergieforschung Hameln/Emmerthal (ISFH), Aussenstelle Hannover, Sokelant str. 5, Hannover 30165, Germany

^b Department of Chemistry, Anna University, Chennai 600025, India

Received 24 July 2001; received in revised form 25 September 2001; accepted 25 September 2001

Abstract

TiO₂ supported on alumina and glass beads were prepared and their photocatalytic activities were determined by photo-oxidation of commercial leather dye, Acid brown 14 in aqueous solution illuminated with solar light. The progress of photocatalytic degradation of the Acid brown 14 was studied by monitoring the change in the concentration of the dye employing HPLC and measuring the absorbance with UV–Vis spectrophotometer for decolourisation. The photodegradation rate was determined for each experiment and the highest efficiency was observed for TiO₂ supported on alumina beads suggesting that the dye molecules are adsorbed on the alumina supports to make high concentration environment around the loaded TiO₂. The effect of pH on the rate of degradation was followed in the pH range 3–11. Acidic pH range was found to favour the degradation rate. Comparative study of different advanced oxidation methods applied to degrade Acid brown 14 in aqueous solution was made and solar light/TiO₂/Fenton system was found to be very effective. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Photodegradation; Acid brown 14; TiO₂–alumina beads; TiO₂–glass beads; Fenton reagent; Hydrogen peroxide

1. Introduction

In recent years, photocatalytic degradation attracts increasing attention as a promising technology for the removal of toxic organic and inorganic contaminants from water and wastewater [1–4]. However, the development of a practical photocatalytic system has not yet been achieved successfully because many operational parameters are to be considered. The success of photocatalytic degradation process in wastewater treatment will depend on how much energy cost can be brought down. This can be achieved by improving photocatalytic degradation efficiency by catalytic modification and optimisation of process conditions. The practical limitation in the use of catalyst powder in solar reactor for photodegradation is the separation of the fine catalyst powder from the treated wastewater. Thus the development of a viable solar reactor will hinge to a large extent on the degree of success that can be achieved in immobilizing the powder catalyst on a support in such a way as to afford a reasonably high surface area and accessibility of the immobilised catalyst for photodegradation of the contaminants. Among the various semiconductors employed, anatase phase of TiO₂ is the most preferable material for the photocatalytic

process [2,5–7] due to its high photosensitivity, non-toxic nature, large bandgap and stability. The improvement in the photocatalytic behaviour of particulate TiO₂ by intimate incorporation of adsorbent material (alumina) is ascribed to the adsorptive properties of this material. Although TiO₂ has large bandgap (3.2 eV), the main drawback is the charge carrier recombination which occurs within nanoseconds. To circumvent this particular limitation, number of strategies have been proposed to improve the lifetime of charge carriers such as the deposition of metal and coupled semiconductor systems [8–12]. Apart from these, one more approach for the prevention of recombination of the photogenerated electron (e⁻) and hole (h⁺) is to increase the rate of transfer of electron (e⁻) and hole (h⁺) to solution species. This can be accomplished by the use of charge transfer medium nearer to the photocatalyst surface. Rapid scavenging of holes can also be promoted by adsorption of the reductant and any oxidised intermediates from the solution by incorporation of more effective adsorption sites. These sites must be nearer to the catalyst active sites so that the hole-generated oxidants (hydroxyl radicals) can reach them before these intermediates are lost through a reaction. This has been accomplished in the presence of strong adsorbents [13]. Unfortunately TiO₂ has low adsorption abilities for organic substances and furthermore target organic substances being in such low concentrations, the rate of photodecomposition of target organic

* Corresponding author. Fax: +91-44-2200-660.

E-mail address: v.murugu@hotmail.com (V. Murugesan).

substances is usually very low. One of the main strategy proposed recently to enhance the rate of photodegradation is the use of adsorbent as the support for photocatalyst to provide high concentration environment of organic molecules around the catalysts. In order to obtain high decomposition rates of target organic substances of very low concentration, the target substances must be exclusively adsorbed on the adsorbent supports which must be quickly oxidised at the loaded TiO_2 . A number of investigators have reported the photodegradation of various organic compounds with various supported materials such as silica, glass beads, alumina, ceramics, zeolites, rare earth oxides, magnesia, etc. [13–22].

In this investigation, photocatalytic degradation of leather dye, Acid brown 14 over TiO_2 catalyst supported on two different materials, namely alumina and glass beads have been studied in batch experiments to compare their efficiencies. Acid brown 14 used as a model pollutant poses unique environmental problems [23]. Coloured dye effluents pose a major problem for manufacturing plants as well as water treatment plants downstreams, as dyes constitute more complex entities and present a significant challenge to environmental scientists because of the persistent environmental health risks.

2. Experimental details

2.1. Materials

The commercially available TiO_2 (Degussa P-25 having 70% anatase and 30% rutile, surface area $50 \text{ m}^2/\text{g}$, and particle size 30 nm) was obtained from Degussa Chemical,

Germany. It was used as a standard photocatalyst without any further treatment unless otherwise stated. Acid brown 14 obtained from Clariant Chemical was used as a model pollutant. It shows intense absorbance both at 212 nm (aromatic group) and 465 nm (azo group) (Fig. 1). H_2O_2 (30%), FeSO_4 and FeCl_3 were obtained from E. Merck. Alumina and glass beads (3–5 mm diameter) were purchased from market. All other chemicals were extra pure grade and used as-received.

2.2. Immobilisation of TiO_2

TiO_2 (P-25) was supported onto alumina and glass beads (3–5 mm diameter) by heat attachment method and designated here afterwards as $\text{TiO}_2\text{-AB}$ and $\text{TiO}_2\text{-GB}$. Glass beads were etched with dilute hydrofluoric acid for 24 h and washed thoroughly with distilled water for making rough surface for better contact of TiO_2 on glass surface. Alumina beads were initially washed with dilute nitric acid and then with distilled water. TiO_2 slurry was prepared with known amount of TiO_2 (2 g) in 100 ml distilled water and stirred overnight before introducing the support. The sample was thoroughly mixed for 20 min. The mixture was then placed in an oven for 24 h at 120°C . The samples were thoroughly washed with distilled water for the removal of free TiO_2 particles. The TiO_2 content in alumina and glass beads was nearly 7–8%.

2.3. Adsorption study

The adsorption isotherm of Acid brown 14 on support was determined by mixing 100 ml aliquot of aqueous solutions of the dye at various initial concentrations C_i at

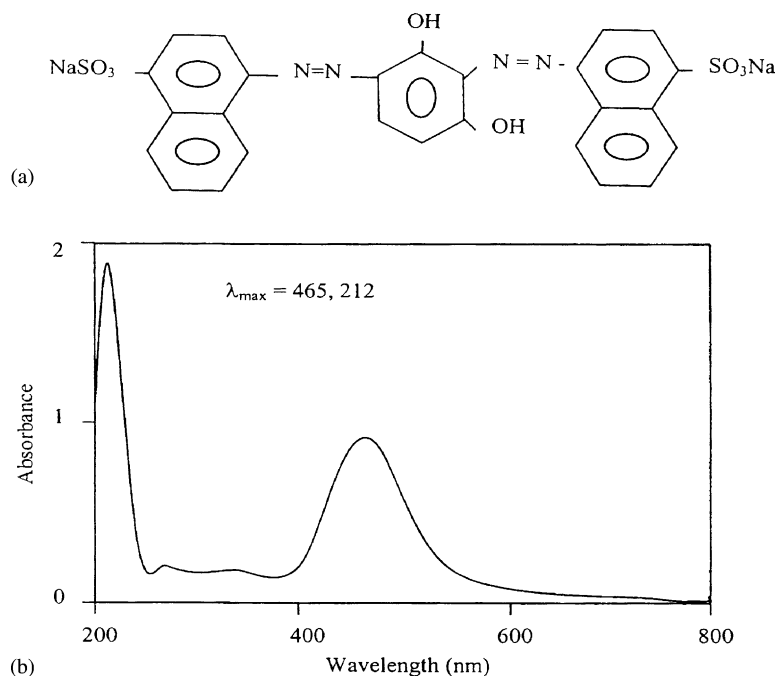


Fig. 1. (a) Structure of Acid brown 14; (b) absorbance spectrum.

solution pH (8.67) with 100 g of respective support materials (alumina, glass, TiO₂-alumina (or) TiO₂-glass). The mixtures were kept in dark room overnight. The change in dye concentration was measured by HPLC. The extent of equilibrium adsorption was determined from the decrease in dye concentration. From the adsorption, induced decrease in the molarity (ΔC) and the amount of dye moles adsorbed on the supported material were determined through Eq. (1). All the isotherm measurements were made in the dark:

$$n = \frac{V \Delta C}{W} \quad (1)$$

where n is the number of dye moles adsorbed per gram of supported material, ΔC the decrease in the dye concentration in moles, W the weight of supported material in grams and V the volume of dye solution in ml.

2.4. Photocatalytic study

The experiments were carried out with TiO₂ supported on alumina and glass beads in two separate borosilicate photochemical batch reactors (surface area: 163 cm²; capacity: 100 ml) under identical conditions. Sunlight was used as the energy source. The experiments were performed at ambient temperature between 25 and 30 °C at solution pH 8.67. The dye solutions were prepared using double distilled water. pH of the dye solution was adjusted by adding 0.01 N NaOH or 0.01 N H₂SO₄. In all the experiments, the dye solution of appropriate concentration was taken in the reactor and covered with glass plates to avoid evaporation of dye solution in the sunlight. The whole set-up was placed in sunlight between 9 AM and 2 PM and average intensity of sunlight during this period was 1.315 × 10⁵ lx unit. The progress of photocatalytic degradation of the Acid brown 14 was monitored by withdrawing definite quantity of aliquot at regular intervals and measuring the absorbance in UV-Vis spectrophotometer (Hitachi UV-2000) for decolourisation and degradation using HPLC (Shimadzu LC-10 AT VP series, RP 18 ODS column; analysis conditions: eluent—methanol:water (10:90), flow rate of eluent: 1 ml/min, UV detector range: 212 nm). The rate of photodegradation was calculated for each experiment.

3. Results and discussion

3.1. Adsorption isotherm

The dye was adsorbed strongly onto both alumina and TiO₂-coated alumina beads from aqueous solution. A measurable decrease in the concentration of the dye solution was observed upon equilibrating them overnight with respective beads in the dark. The adsorption isotherms for Acid brown 14 on different beads (alumina, glass, TiO₂-AB and TiO₂-GB) are illustrated in Fig. 2. The number of dye moles (n) adsorbed per gram of supported material is plotted

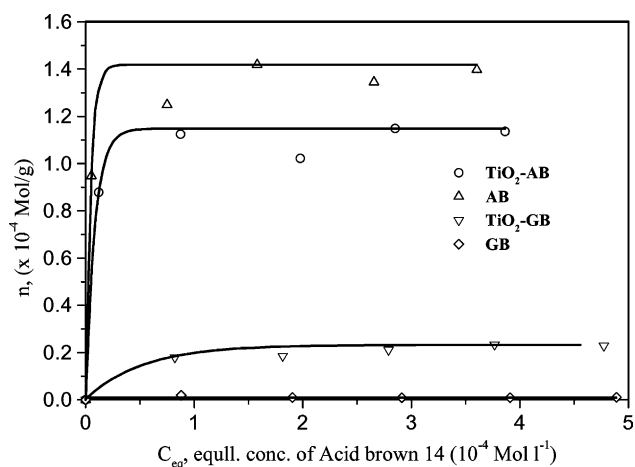


Fig. 2. Adsorption of Acid brown 14 at different initial concentration on alumina, glass, TiO₂-AB and TiO₂-GB beads. Acid brown 14 = $2 \times 10^{-4} \text{ mol l}^{-1}$; TiO₂-supported beads: 100 g/100 ml.

against the equilibrium concentration of the dye solutions (C_{eq}). The adsorption isotherm is a typical Langmuir adsorption model. The maximum number of dye moles adsorbed per gram of TiO₂-AB beads is 1.124×10^{-4} on average but in the case of TiO₂-GB beads it is only 0.207×10^{-4} . The adsorption capacity of TiO₂ supported on alumina beads is five times greater than TiO₂ supported on glass beads.

3.2. Solar photocatalysis

The change in dye concentration vs time profile observed during the photocatalytic degradation of Acid brown 14 is shown in Fig. 3. It has been observed that the Acid brown 14 degradation proceeds rapidly with higher degradation rate in TiO₂-AB system than in TiO₂-GB system. Both degradation curves can be fitted reasonably well by an exponential decay curve thus suggesting first-order kinetics. The resulting first-order rate constant (k_1) multiplied by the initial dye concentration has been used in all subsequent

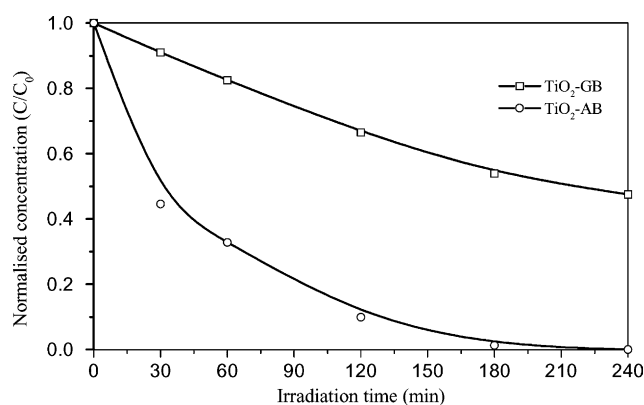


Fig. 3. Comparison of TiO₂-AB and TiO₂-GB for the photocatalytic degradation of Acid brown 14. Acid brown 14 = $2 \times 10^{-4} \text{ mol l}^{-1}$; TiO₂-supported beads: 100 g/100 ml.

plots to calculate the degradation rate. Under the experimental conditions, complete decolourisation of the dye has occurred within an hour with the removal efficiency of 76.2% of the dye stuff. The degradation rate has decreased after 1 h irradiation in both the systems evincing the formation of long-lived reaction intermediates. The complete degradation of the dye occurred within 240 min irradiation in TiO₂-AB system whereas only 52.53% degradation occurred in TiO₂-GB system for the same period. It is also noticed that the rate of photocatalytic degradation is high with adsorbent material such as alumina beads. Anderson and Bard [13,16] have also observed similar kind of rate enhancement in the photocatalytic degradation of Rhodamine 6G and salicylic acid TiO₂/SiO₂ and on TiO₂/Al₂O₃, respectively.

3.3. Effect of pH

The amphoteric behaviour of many metal oxides influences the surface charge properties of the catalyst as well as support material. The effect of pH on the rate of photocatalytic degradation was studied in the pH range 3–11 for the supported system (TiO₂-AB/TiO₂-GB). The quantity of Acid brown 14 adsorbed at various pH values are illustrated in Fig. 4. In the case of TiO₂-AB system, higher degradation rate and adsorption are observed at low pH values (pH 3–6) with maximum at pH 4. Increasing the solution pH diminishes the adsorption, which decreases rapidly after pH 9. The possible explanation for this behaviour may be that pH can affect either the surface properties of the photocatalyst or the support material. Titania as well as alumina have amphoteric character [2]. The zero-point charge pH_{zpc} is 6.8 for TiO₂ particles (Degussa P25) [24] and 9.1 for alumina [2]. In TiO₂-AB system, both TiO₂ and alumina are more positive in acidic medium (TiO₂: pH < 6.8; alumina: pH < 9.1) whereas in the alkaline medium (TiO₂: pH > 6.8; alumina: pH > 9.1) both are negatively charged based on their zero point charge (zpc). Acid brown 14 is a dianionic species in aqueous solution. Hence in acidic pH range, electrostatic

interactions between the positive (TiO₂/alumina)⁺ and dye anion (dye²⁻) lead to strong adsorption and the corresponding high rate of degradation. Above the pH 9, both TiO₂ and alumina surfaces acquire negative charges and hence electrostatic repulsion between (TiO₂/alumina)⁻ and dye anion (dye²⁻) retards adsorption. Hence the degradation rates are lowest at pH 10 and 11. With TiO₂-GB-supported system, the highest degradation rate is observed at pH 3–6 as in TiO₂-AB system. It is also observed that the rate of degradation is not correlated with adsorption and very little quantity of dye is adsorbed in this system. The observed results could be Nernstian shift of the band edges to more negative values with increase in pH leading to a diminishing oxidation potential of h_{νB}⁺ at high pH [25].

3.4. Sunlight–TiO₂-AB/TiO₂-GB–H₂O₂ system

Experiments were conducted to examine the effect of H₂O₂ on the rate of degradation of Acid brown 14 in the sunlight-irradiated TiO₂-AB/TiO₂-GB systems. The effect of H₂O₂ concentration on the degradation of Acid brown 14 in all the systems (sunlight–H₂O₂, sunlight–TiO₂-AB/TiO₂-GB, sunlight–TiO₂-AB/TiO₂-GB–H₂O₂) are presented in Table 1. The addition of H₂O₂ to sunlight–TiO₂-AB/TiO₂-GB system has increased the degradation rate. H₂O₂ is suitable for trapping electrons [26,27] by preventing the recombination of e⁻ and h⁺ pairs and thus increasing the chances of formation of •OH and O₂•⁻ on the surface of catalyst. The rate of degradation increases rapidly with increase in H₂O₂ concentration up to 4.4 × 10⁻² mol l⁻¹. Many investigators [28–30] have already explained the enhanced photocatalytic oxidation rate in the presence of hydrogen peroxide by the following reactions:

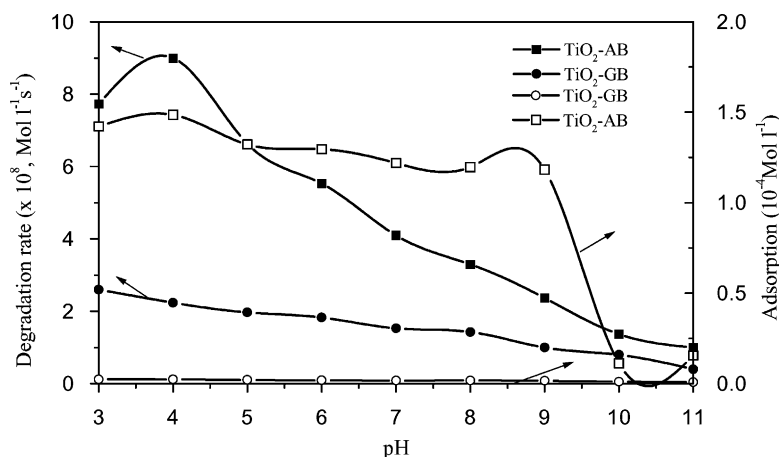
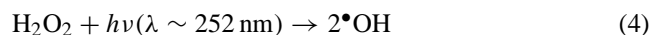
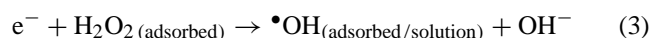


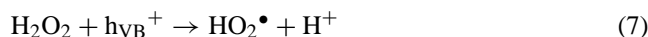
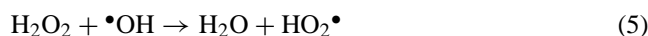
Fig. 4. Influence of pH on the adsorption and rate of degradation of Acid brown 14 on TiO₂-AB and TiO₂-GB beads. Acid brown 14 = 2 × 10⁻⁴ mol l⁻¹; irradiation time: 240 min; TiO₂-supported beads: 100 g/100 ml.

Table 1
Sunlight–TiO₂-AB/TiO₂-GB–H₂O₂^a

System	H ₂ O ₂ (10 ⁻² mol l ⁻¹)	Degradation rate (×10 ⁸ mol l ⁻¹ s ⁻¹)
Sunlight–H ₂ O ₂	4.41	1.10
Sunlight–TiO ₂ -AB–H ₂ O ₂	0.0	7.67
Sunlight–TiO ₂ -AB–H ₂ O ₂	0.88	8.69
Sunlight–TiO ₂ -AB–H ₂ O ₂	4.41	10.78
Sunlight–TiO ₂ -AB–H ₂ O ₂	8.82	9.21
Sunlight–TiO ₂ -AB–H ₂ O ₂	13.23	7.29
Sunlight–TiO ₂ -GB–H ₂ O ₂	0.0	1.17
Sunlight–TiO ₂ -GB–H ₂ O ₂	0.88	1.81
Sunlight–TiO ₂ -GB–H ₂ O ₂	4.41	3.44
Sunlight–TiO ₂ -GB–H ₂ O ₂	8.82	2.56
Sunlight–TiO ₂ -GB–H ₂ O ₂	13.23	1.41

^a Acid brown 14 = 2 × 10⁻⁴ mol l⁻¹; TiO₂-supported beads: 100 g/100 ml; irradiation time: 240 min.

Reactions (2) and (3) suggest that either superoxide (or) conduction band electrons can initiate radical formation from hydrogen peroxide. Since hydrogen peroxide is photosensitive, illumination of light of wavelength 252 nm produces •OH (reaction (4)). Sunlight contains 4.3% of UV (3.9% UVA and 0.4% UVB) mostly in the region 315–365 nm (UVA) which does not have sufficient energy to cleave hydrogen peroxide [30]. Hence production of •OH radicals by a homogeneous pathway (reaction (4)) may be ruled out in this system, suggesting that hydrogen peroxide effect in improving reaction rate is through heterogeneous pathway (reactions (2) and (3)). Further increase of H₂O₂ after the optimum level (4.4 × 10⁻² mol l⁻¹) decreases the rate of degradation slowly. The negative effect of high concentration of H₂O₂ may be due to the formation of HO₂•. When H₂O₂ concentration is higher, HO₂• formed is significantly less reactive than •OH. Wang and Hong [27] reported that H₂O₂ sorbed on the catalyst surface can effectively scavenge not only the catalyst surface formed •OH (reactions (5) and (6)) but also the photogenerated holes (h_{VB}⁺) (reaction (7)) and thus inhibit the major pathway for heterogeneous generation of •OH radicals:



Peroxy radical is significantly less reactive than •OH with respect to organic oxidation. Mengyue et al. [31] and Weichgrebe [32] have observed beneficial effect of the addition of H₂O₂ reagent on the photocatalytic degradation of pesticides and landfill leachate.

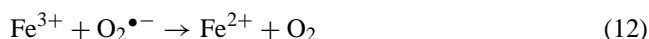
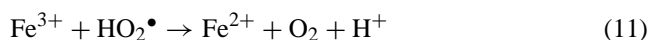
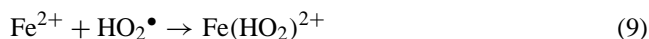
3.5. Sunlight–TiO₂-AB/TiO₂-GB–Fenton system

Fenton reagent [33], a mixture of hydrogen peroxide and ferrous salt, has been a powerful oxidant for many organic

compounds and has attracted interest in wastewater treatment [34–36]. The hydroxyl radical is generally invoked as the primary reactive species generated according to the following reaction [37]:



This is one of the possible mechanisms to increase the reaction rate by increasing the concentration of •OH radicals present in the photocatalytic system. The addition of organic oxidants such as ClO₂⁻, ClO₃⁻, BrO₃⁻, H₂O₂, IO₄⁻ and S₂O₈²⁻ in the TiO₂ photocatalyst has been explored by Grätzel et al. [38], Pelizzetti et al. [39] and Martin et al. [40]. Grätzel et al. [38] reported that H₂O₂, IO₄⁻ and S₂O₈²⁻ additives have significant rate-enhancing effect in TiO₂ photocatalysis of organic compounds. Pelizzetti et al. [39] reported similar rate-enhancing effect of inorganic oxidants such as H₂O₂, IO₄⁻ and S₂O₈²⁻. The rate-enhancing effect of inorganic oxidants in the UV/TiO₂/oxidant system was reported by many investigators based on the comparison of TiO₂ photocatalysis with and without the presence of inorganic oxidants [38–40]. The presence of Fenton's reagent in the reaction mixture plays a key role in the photocatalytic degradation of the dyes [41–43]. The effect of Fenton reagent on TiO₂-AB/TiO₂-GB photocatalysis on Acid brown 14 is illustrated in Table 2. The rate of photodegradation of Acid brown 14 in sunlight–TiO₂-AB/TiO₂-GB–Fenton system is faster than all other systems. When suitable amount of Fe²⁺/H₂O₂ is present, reaction (8) becomes significant. When Fe²⁺/H₂O₂ concentration is increased above the optimum concentration (FeSO₄ (0.5 × 10⁻⁴ mol l⁻¹) + H₂O₂ (4.4 × 10⁻² mol l⁻¹), the rate of photodegradation slowly decreases. However, as Fe²⁺/H₂O₂ increases, •OH produced from reaction (8) reacts with H₂O₂ more than before thus producing HO₂• which can participate in the following reactions [44]:



Another reason for this negative effect due to the addition of more amount of Fenton reagent is the formation of Fe³⁺ (reaction (8)) which initially forms complexes with both water and organic compounds [45,46]. Hence the active sites of the catalyst are covered with both Fe²⁺ and Fe³⁺ ions and thus the photon absorption by the catalyst decreases and it may affect •OH formation through the photocatalytic process on TiO₂. This has been identified by inductive-coupled plasma (ICP) analysis.

3.6. Sunlight–TiO₂-AB/TiO₂-GB–Fe³⁺ system

The effect of the addition of Fe³⁺ towards the photodegradation of Acid brown 14 in systems TiO₂-AB/TiO₂-GB is

Table 2
Sunlight–TiO₂-AB/TiO₂-GB–Fenton system^a

System	H ₂ O ₂ (10 ⁻² mol l ⁻¹)	FeSO ₄ (10 ⁻⁴ mol l ⁻¹)	Degradation rate (×10 ⁸ mol l ⁻¹ s ⁻¹)
Sunlight–FeSO ₄	–	0.5	^b
Sunlight–H ₂ O ₂	4.41	–	1.10
Sunlight–Fenton	4.41	0.5	1.47
Sunlight–TiO ₂ -AB–Fenton	0.0	0.0	7.67
Sunlight–TiO ₂ -AB–Fenton	0.88	0.1	9.15
Sunlight–TiO ₂ -AB–Fenton	4.41	0.5	12.40
Sunlight–TiO ₂ -AB–Fenton	8.82	1.0	11.19
Sunlight–TiO ₂ -AB–Fenton	13.23	1.5	8.11
Sunlight–TiO ₂ -GB–Fenton	0.0	0.0	1.17
Sunlight–TiO ₂ -GB–Fenton	0.88	0.1	2.95
Sunlight–TiO ₂ -GB–Fenton	4.41	0.5	5.77
Sunlight–TiO ₂ -GB–Fenton	8.82	1.0	4.11
Sunlight–TiO ₂ -GB–Fenton	13.23	1.5	3.63

^a Acid brown 14 = 2 × 10⁻⁴ mol l⁻¹; TiO₂-supported beads: 100 g/100 ml; irradiation time: 240 min.

^b Degradation not occurred.

illustrated in Table 3. Photodegradation of Acid brown 14 in sunlight–TiO₂-AB/TiO₂-GB–Fe³⁺ system is significantly faster than sunlight–Fe³⁺ and sunlight–TiO₂-AB/TiO₂-GB. The sunlight–TiO₂-AB/TiO₂-GB–Fe³⁺ system improved the rate of photocatalytic processes via the following reaction:



Fe³⁺ behaves as an electron scavenger thus preventing the recombination of e_{CB}⁻ and h_{VB}⁺. Mengyue et al. [31] have also observed similar kind of rate enhancement in the photocatalytic degradation of organophosphorus pesticides using thin films of TiO₂. Sclafani et al. [47] have reported that when suitable amounts of Fe³⁺ are present, the following reactions become significant:

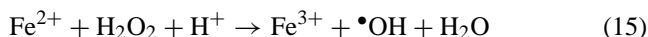
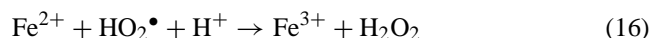


Table 3
Sunlight–TiO₂-AB/TiO₂-GB–Fe³⁺ system^a

System	Fe ³⁺ (10 ⁻⁴ mol l ⁻¹)	Degradation rate (×10 ⁸ mol l ⁻¹ s ⁻¹)
Sunlight–Fe ³⁺	0.5	^b
Sunlight–TiO ₂ -AB–Fe ³⁺	0.0	7.67
Sunlight–TiO ₂ -AB–Fe ³⁺	0.1	7.95
Sunlight–TiO ₂ -AB–Fe ³⁺	0.5	9.38
Sunlight–TiO ₂ -AB–Fe ³⁺	1.0	7.73
Sunlight–TiO ₂ -AB–Fe ³⁺	1.5	7.18
Sunlight–TiO ₂ -GB–Fe ³⁺	0.0	1.17
Sunlight–TiO ₂ -GB–Fe ³⁺	0.1	1.81
Sunlight–TiO ₂ -GB–Fe ³⁺	0.5	2.97
Sunlight–TiO ₂ -GB–Fe ³⁺	1.0	2.41
Sunlight–TiO ₂ -GB–Fe ³⁺	1.5	1.75

^a Acid brown 14 = 2 × 10⁻⁴ mol l⁻¹; TiO₂-supported beads: 100 g/100 ml; irradiation time: 240 min.

^b Degradation not occurred.



The above reactions increase the amounts of •OH and H₂O₂ and thus improve the rate of the photocatalytic process. It has been observed in the present investigation that when Fe³⁺ concentration is in excess of 0.5 × 10⁻⁴ mol l⁻¹, the rate of degradation decreases gradually due to the deposition of iron on semiconductor particle as in the case of Fenton system. Hence it is presumed that the decrease of photocatalytic activity by the addition of an excess amount of Fe³⁺ may be due to the coverage of Fe²⁺ and Fe³⁺ ions on the active site of the catalyst.

4. Conclusion

The results of this investigation clearly indicate the importance of adsorption characteristic of supported system to obtain high degradation rates of pollutants. Higher degradation rate was observed for TiO₂-AB- than TiO₂-GB-supported system. The possible reason for this behaviour is that the dye molecules are mainly adsorbed on the adsorbent sites to make high concentration environment around the loaded TiO₂. This enhances the photodegradation efficiencies. In TiO₂-AB system, pH markedly influences the overall efficiency of the degradation process which correlates with the adsorption behaviour of Acid brown 14 on the TiO₂-AB system. This is indicative of the significant role of the surface property of both TiO₂ and alumina beads. In the case of TiO₂-GB, pH is not a significant factor and hence no significant adsorption is observed in this system. The comparative study of advanced oxidation methods applied to degrade Acid brown 14 in aqueous solution reveals the following. The order of reactivity in the presence of TiO₂-AB and in the absence of TiO₂-AB is sunlight–TiO₂-AB–Fenton > sunlight–TiO₂-AB–H₂O₂ > sunlight–TiO₂-AB–Fe³⁺ > sunlight–TiO₂-AB > sunlight–Fenton > sunlight–H₂O₂.

A synergic effect also exists when two (or) more simple oxidation systems are combined. This synergy is reflected in the marked increase in the free radical reaction pathway.

Acknowledgements

The authors gratefully acknowledge the financial support by the Ministry of Environment and Forests, Government of India, New Delhi, for this project.

References

- [1] D.F. Ollis, C.S. Turchi, *Environ. Prog.* 9 (1990) 229.
- [2] D.W. Bahnemann, in: E. Pelizzetti, M. Schiavello (Eds.), *Photochemical Conversion and Storage of Solar Energy*, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1991, pp. 251–276.
- [3] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.* 95 (1995) 69.
- [4] A. Mills, S.L. Hunt, *J. Photochem. Photobiol. A* 108 (1997) 1.
- [5] K.I. Okamoto, Y. Yamamoto, H. Tanaka, M. Tanaka, *Bull. Chem. Soc. Jpn.* 58 (1985) 2015.
- [6] H. Ohnishi, M. Matsumura, H. Tsubomura, M. Iwasaki, *Ind. Eng. Chem. Res.* 28 (1989) 719.
- [7] S. Sakthivel, B. Neppolian, A. Banumathi, M. Palanichamy, V. Murugesan, *Indian J. Sci. Ind. Res.* 59 (2000) 556.
- [8] T. Sakata, T. Kawai, K. Hashimoto, *Chem. Phys. Lett.* 88 (1982) 50.
- [9] J. Abrahams, R.S. Davidson, C.J. Morrison, *Photochem. Photobiol. A* 29 (1985) 353.
- [10] N. Serpone, E. Borgarello, M. Grätzel, *J. Chem. Soc. Commun.* (1983) 342.
- [11] D.W. Bahnemann, *Isr. J. Chem.* 33 (1993) 115.
- [12] C. Martin, G. Solana, V. Rives, G. Marci, L. Palmisano, A. Sclafani, *Catal. Lett.* 49 (1997) 235.
- [13] C. Anderson, A.J. Bard, *J. Phys. Chem.* 99 (1995) 9882.
- [14] R. Matthews, *J. Catal.* 111 (1988) 264.
- [15] N.B. Jackson, C.M. Wang, Z. Luo, J. Schwitzgebel, J.K. Ekerdt, J.R. Brock, H. Heller, *J. Electrochem. Soc.* 138 (12) (1991) 3660.
- [16] C. Anderson, A.J. Bard, *J. Phys. Chem. B* 101 (1997) 2611.
- [17] K. Kato, *J. Ceram. Soc. Jpn.* 101 (3) (1993) 245.
- [18] Y. Xu, H. Langford, *J. Phys. Chem.* 99 (1995) 11501.
- [19] J. Lin, J.C. Yu, *J. Photochem. Photobiol. A* 116 (1998) 63.
- [20] L. Palmisano, M. Schiavello, A. Sclafani, *New J. Chem.* 12 (1988) 847.
- [21] N. Takeda, T. Torimoto, S. Sampath, S. Kuwabata, H. Yoneyama, *J. Phys. Chem.* 99 (1995) 9986.
- [22] T. Torimoto, S. Ito, S. Kuwabata, H. Yoneyama, *Environ. Sci. Technol.* 30 (1996) 1275.
- [23] H. Zollinger (Ed.), *Color Chemistry: Synthesis, Properties and Applications of Organic Dyes and Pigments*, VCH, New York, 1987.
- [24] J. Zhao, T. Wu, K. Wu, K. Oikawa, H. Hidaka, N. Serpone, *J. Environ. Sci. Technol.* 32 (1998) 2394.
- [25] D. Duonghong, J. Ramsden, M. Grätzel, *J. Am. Chem. Soc.* 104 (1982) 2977.
- [26] P. Pichat, C. Guillard, L. Amalric, A.C. Renard, O. Plaidy, *Solar Energy Mater. Solar Cells* 38 (1995) 391.
- [27] Y. Wang, C.S. Hong, *Wat. Res.* 33 (1999) 2031.
- [28] K. Tanaka, T. Hisanaga, K. Harada, *New J. Chem.* 13 (1989) 5.
- [29] M.W. Peterson, J.A. Turner, A.J. Nozik, *J. Phys. Chem.* 95 (1991) 665.
- [30] M.C.R. Symons, in: J.O. Edwards (Ed.), *Peroxide Reaction Mechanisms*, Interscience, New York, 1961, pp. 137–149.
- [31] Z. Mengyue, C. Shifu, T. Yaowu, *J. Chem. Technol. Biotechnol.* 64 (1995) 339.
- [32] D. Weichgrebe, *Beitrag zur chemison-oxidativen abwasserbehandlung*, Ph.D. Dissertation, TU Clausthal, Germany, 1994.
- [33] H.J.H. Fenton, *J. Chem. Soc.* 65 (1894) 899.
- [34] H.R. Einsenhauer, *J. WPCF* 36 (1964) 1117.
- [35] D.F. Bishop, G. Stern, M. Fleisschman, L.S. Marshall, *Ind. Eng. Chem. Des. Dev.* 7 (1968) 110.
- [36] M. Barbeni, C. Minero, E. Pelizzetti, E. Borgarello, N. Serpone, *Chemosphere* 16 (1987) 2225.
- [37] C. Walling, *ACC Chem. Res.* 8 (1975) 125.
- [38] C.K. Grätzel, M. Jirousek, M. Grätzel, *J. Mol. Catal.* 60 (1990) 375.
- [39] E. Pelizzetti, V. Carlin, C. Minero, M. Grätzel, *New J. Chem.* 15 (1990) 351.
- [40] S.T. Martin, A.T. Lee, M.R. Hoffmann, *Environ. Sci. Technol.* 29 (1995) 2573.
- [41] S. Sakthivel, B. Neppolian, B. Arabindoo, M. Palanichamy, V. Murugesan, *Indian J. Eng. Mater. Sci.* 7 (2000) 87.
- [42] S. Sakthivel, B. Neppolian, B. Arabindoo, M. Palanichamy, V. Murugesan, *Indian J. Sci. Ind. Res.* 59 (2000) 556.
- [43] S. Sakthivel, B. Neppolian, B. Arabindoo, M. Palanichamy, V. Murugesan, *Wat. Sci. Technol.* 44 (5) (2001) 211.
- [44] J.D. Rush, B.H.J. Bielski, *J. Phys. Chem.* 89 (23) (1985) 5062.
- [45] E. Oliveros, O. Legrini, M. Hobl, T. Muller, A.M. Braun, *Chem. Eng. Proc.* 36 (1997) 397.
- [46] B.G. Kwon, D.S. Lee, N. Kong, N. Yoon, *Wat. Res.* 33 (9) (1999) 2110.
- [47] A. Sclafani, L. Palmisano, E. Davi, *J. Photochem. Photobiol. A* 56 (1991) 113.