



Photocatalytic Removal of Azo Dye and Anthraquinone Dye Using TiO₂ Immobilised on Ceramic Tiles

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Abstract: The photocatalytic activity of TiO₂ immobilized on different supports; cement and ceramic tile, was studied to decolorize two commercial dyes. The catalyst was immobilised by two different techniques, namely, slurry method on ceramic tile and powder scattering on cement. The degradation of the dyes was carried out using UV and solar irradiation. The comparative efficiency of the catalyst immobilised on two different supports was determined. The photodegradation process was monitored by UV-Vis spectrophotometer. The catalyst immobilised on ceramic tile was found to be better than the catalyst immobilised on cement. Experimental results showed that both illumination and the catalyst were necessary for the degradation of the dyes and UV irradiation is more efficient compared to solar irradiation.

Keywords: Photocatalytic degradation, TiO₂, Immobilization, Ceramic tile.

Introduction

The photocatalytic degradation of coloured organic pollutants on semiconductor surfaces has been proved to be a better process for waste water treatment¹⁻³. Among the various semiconductors employed, TiO₂ has been recognized as a good photocatalyst for the degradation of several organic contaminants^{4,5}. Due to its high photo reactivity, chemical stability and low toxicity most studies related to photodegradation reactions have been carried out using suspensions of powdered TiO₂ (usually Degussa P-25) in the polluted aqueous solutions. However, from a practical point of view, the use of catalyst suspensions in slurry photo reactors may constitute a limitation because of filtration problems linked to the small size of the TiO₂ particles that should be removed from the treated stream. In general, such separation processes are expensive in terms of time, reagents and manpower⁶ and this fact remains as a great hurdle in the commercialization of the process. Therefore, several attempts have been made to immobilize the catalyst on rigid and inert supports and this is a very active topic of research on TiO₂ photocatalysis⁷. Pozzo *et al.*⁸ have made an overview of the

research on supported titanium oxide as photocatalyst. The effect of different supporting materials mixed physically with TiO_2 on the photocatalytic degradation of 4-nitrophenol has been studied recently⁹. Since the powder form usually gives better performance than the immobilized thin films in many cases, the search for suitable supports for the immobilisation of the photocatalyst continues to be in search. The aim of the present work is to investigate the performance of TiO_2 supported on cement and ceramic tile for the degradation of two commercial dyes.

Experimental

The commercial azo dye Reactive Red 120 and the commercial anthraquinone dye Vat yellow 4 were obtained from Sivasakthi Dyeing unit, SIPCOT Industrial Estate, Perundurai, India and used as such without any purification. Titania P-25 (surface area $50 \text{ m}^2/\text{g}$) was obtained from Degussa. The titania particles are mixture of both anatase and rutile forms. All the other catalysts and chemicals used were of AR grade. They were obtained from S.D Fine chemicals and were used as received. Required concentrations of dye solutions were prepared by dissolving the dyes in distilled water.

The specific amount of catalyst was coated on ceramic tile by slurry method and the catalyst was supported on cement by powder scattering method. 50 mL of this solution was flooded on the TiO_2 coated tile and the solution was irradiated with a 400 W medium pressure mercury vapour lamp for UV radiation. Solar irradiation was carried out in the same set up, with the system placed on the roof top of the laboratory during sunny days in April-may. Similar procedure was followed for the degradation of the dyes by the catalyst coated on cement. Samples were drawn periodically and analysed for the dye concentration by spectrophotometry. λ_{max} of Reactive Red 120 and vat yellow 4 are 515 nm and 490 nm respectively..

Results and Discussion

Photodecolourisation of the dyes on TiO_2 coated tiles TiO_2

Catalyses the photo decolourisation of both dyes Reactive red 120 and Vat yellow 4 under UV as well as natural sunlight. The comparative photodecolorisation of the dyes on TiO_2 catalyst coated on ceramic tile and cement supports under UV and solar irradiation is given in Table.1. The results show that the catalyst supported on tile serves better for the degradation of the dyes under UV as well as solar irradiation. This may be presumably due to the difference in the method of coating the catalyst on the supports. Powder scattering method on cement resulted in the build-up of layers of the catalyst powder on the support resulting in small surface area and small pores for the catalyst to degrade the dyes. Though this method gives a homogeneous effect in the eye view, but as the supported catalyst was dipped in dye solutions, it is either the powder peeled off from the support that makes the catalyst cannot be used any longer, or the surface area was too small for the dyes to be degraded.

Table 1. Decolorisation of the dyes under UV and solar irradiation by TiO_2 immobilised on cement and ceramic tile

| Dye | Conc mg/L | Decolorisation Percentage | | | |
|------------------|--------------|------------------------------------|----------------------------------|------------------------------------|----------------------------------|
| | | UV irradiation | | Solar irradiation | |
| | | TiO_2 coated on cement | TiO_2 coated on tile | TiO_2 coated on cement | TiO_2 coated on tile |
| Reactive Red 120 | 5 | 87 | 98 | 75 | 84 |
| | 10 | 76 | 94 | 68 | 80 |
| Vat Yellow 4 | 5 | 82 | 96 | 45 | 52 |
| | 10 | 77 | 85 | 34 | 48 |

Whereas the slurry method that was used to coat the catalyst on the tiles gave larger catalyst surface area as it was homogeneously distributed by the paste. This is revealed from the surface morphology of the catalyst supported on cement and tile. The SEM micrographs shown in Figure 1 and 2 show that the catalyst supported on the tile form small particles in uniform size, highly disperse and homogeneously distributed on the surface. It would give larger surface area for photocatalytic activity.

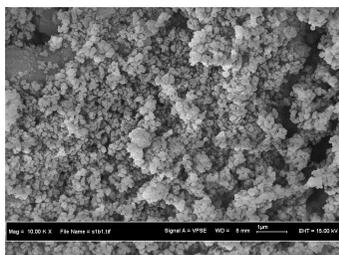


Figure 1. SEM Micrograph of TiO₂ immobilised on cement

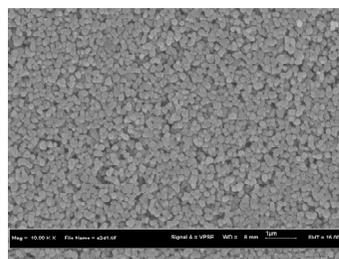


Figure 2. SEM Micrograph of TiO₂ immobilised on ceramic tile

Effect of initial concentration of the dyes

Figure 3 shows the effect of concentration of the dye Reactive Red 120 on the efficiency of decolourisation in presence of UV light. The decolourisation proceeds very fast in the early stages of irradiation and very slowly thereafter. The decolourisation takes place in the absence of the catalyst also, but very slowly. The experiments were carried out under identical conditions in the presence of natural sunlight and the results are presented in Figure 4. Similar studies were conducted using Vat yellow 4 dye solution and the results are presented in Figures 5 & 6.

It is observed that in the case of both dyes, under sunlight as well as UV irradiation, the colour removal efficiency in terms of percentage of the initial dye concentration decreased with increase in the initial concentration of the dye, both in the presence and absence of the catalyst. This is consistent with the observations made in our earlier studies^{10,11} where the catalyst was used in suspension for the decolourisation of the dyes.

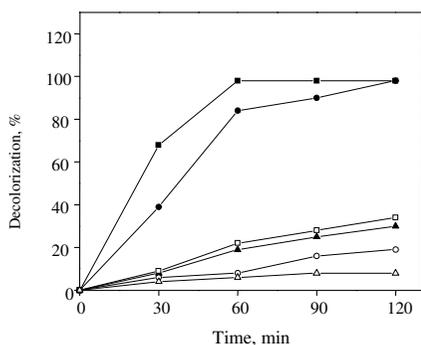


Figure 3. Effect of concentration of Reactive Red 120 on the efficiency of decolourization in UV light. (■) TiO₂/UV 5 mg/L, (●)TiO₂/UV 10 mg/L, (▲)TiO₂/UV 50 mg/L, (□) UV 5 mg/L, (○) UV 10 mg/L, (Δ) UV 50 mg/L

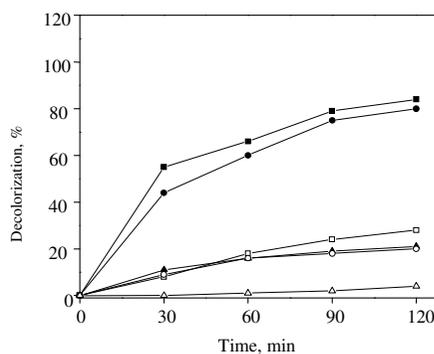


Figure 4. Effect of concentration of Reactive Red 120 on the efficiency of decolourization in Sun light. (■) TiO₂/SL 5 mg/L, (●)TiO₂/SL 10 mg/L, (▲)TiO₂/SL 50 mg/L, (□) SL 5 mg/L, (○) SL 10 mg/L, (Δ) UV 50 mg/L

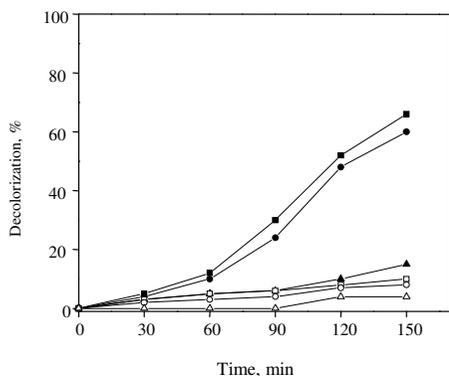


Figure 5. Effect of concentration of Vat yellow 4 on the efficiency of decolorization in UV light. (■) TiO₂/UV 5 mg/L, (●) TiO₂/UV 10 mg/L, (▲) TiO₂/UV 50 mg/L, (□) UV 5 mg/L, (○) UV 10 mg/L, (Δ) UV 50 mg/L

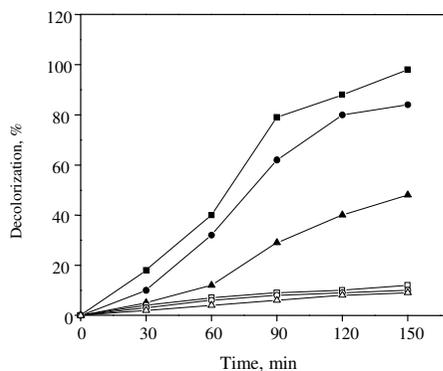


Figure 6. Effect of concentration of vat yellow 4 on the efficiency of decolorization in Sun light. (■) TiO₂/SL 5 mg/L, (●) TiO₂/SL 10 mg/L, (▲) TiO₂/SL 50 mg/L, (□) SL 5 mg/L, (○) SL 10 mg/L, (Δ) UV 50 mg/L

At higher concentration of the dye, the path length of photon entering the solution decreases and at low concentration the reverse effect is observed¹². Higher concentrations lead to a reduction in the light penetration and thus reduction in the exposure of catalyst surface. Major part of the decolorisation occurs at or near the irradiated surface, termed as reaction zone and higher concentration of the dye leads to a decrease in the irradiated surface. Consequently, the reactive OH radicals formed by the illuminated catalyst surface also will be less. This results in lower percentage of decolorisation and degradation.

Comparison of the effect of UV and sunlight on the decolorisation efficiency

Figures 7 and 8 show the comparison of the effect of UV and sunlight on the decolorisation efficiency using 5 mg/L solution of the dyes. The results illustrate that in the absence as well as in the presence of the catalyst, UV irradiation is more efficient for the decolorisation compared to sunlight.

The observed difference in the rate of decolorisation under UV and solar irradiation as shown in Figures 7 and 8 is attributed to the difference in the input energy. The energy of UV irradiation is large compared to the band gap energy of the catalysts. Hence the electron-hole recombination problem, which is more common in semiconductor oxide mediated heterogeneous photocatalysis, is largely avoided, though not fully, with UV irradiation source. But in sunlight, only 5% of the total irradiation possesses the optimum energy for the band gap excitation of the electrons. Hence the percentage degradation is found to be less in solar irradiation of textile dyes¹³. Though sunlight has only 5% of optimum energy for photocatalytic excitation and for the degradation of textile dyes, it could be a safe and cost effective source. Moreover there is no material deterioration in case where sunlight is used as a radiation source. But UV light source may affect the catalyst decomposition¹⁴. UV source is not only hazardous but also expensive because of the large input of electric power to generate UV irradiation. Since intense sunlight is available throughout the year in tropical countries like India, it could be effectively used for the photocatalytic degradation of pollutants in wastewater. In case of large surface demanding photocatalytic degradation sunlight would be the ultimate source. Hence, though not so effective as UV irradiation for the decolorisation of the dyes on immobilised catalyst, using solar irradiation for the process may be helpful in making it economically viable.

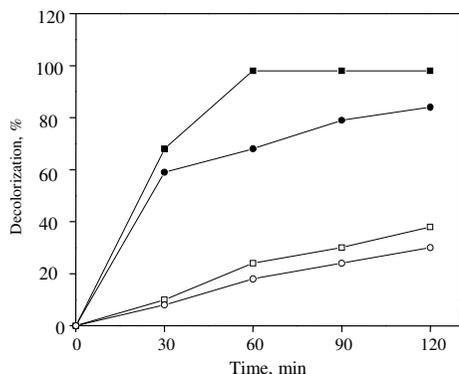


Figure 7. Comparison of the effect of UV and sunlight on the decolorisation of Reactive Red 120: $C_0= 5$ mg/L, (■) UV/TiO₂, (●) SL/TiO₂, (□) UV, (○) SL

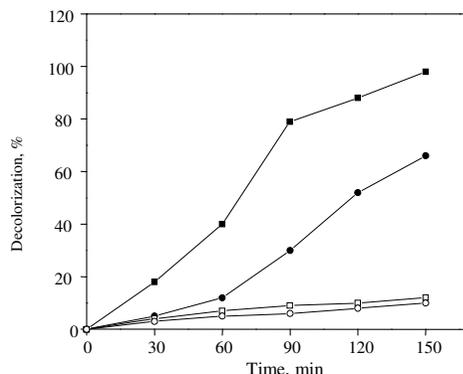


Figure 8. Comparison of the effect of UV and sunlight on the decolorisation of Vat yellow 4: $C_0= 5$ mg/L, (■) UV/TiO₂, (●) SL/TiO₂, (□) UV, (○) SL

Effect of pH

Our studies^{11,12} reported earlier using the catalyst in suspension show that pH of the reaction system plays an important role in the photocatalytic degradation of dyes. In order to examine this for the dyes in the current form of immobilization of the catalyst, the decolorization reactions were studied at varying pH in presence of UV irradiation for both dyes of concentration 5 mg/L. The results are presented in Figures 9 and 10. In the absence as well as in the presence of the catalyst, the maximum decolourisation was observed at pH 4, with the rate decreasing with increase in pH, at both concentrations, for both dyes. This is qualitatively consistent with the findings of Lee *et al*¹⁵ and Kuo and Ho¹⁶. The enhanced rate at acidic pH may be attributed to the adsorption of more (dye⁻) ions on the surface of the electrically positive TiO₂ and increased interaction with the oxidizing radicals. Also, in acidic media (pH ≈ 3.8), the superoxide radical anion O₂^{•-} gets protonated and produces HO₂[•] radicals, which are predominant oxidants in the initial photodegradation stage¹⁷.

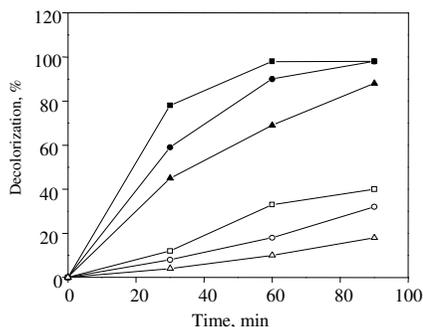


Figure 9. Effect of pH on the efficiency of decolourization of Reactive Red 120 (5 mg/L) under UV light:(■) TiO₂/UV.pH 4, (●)TiO₂/UV pH 7, (▲)TiO₂/UV pH 10, (□) UV pH 4, (○) UV pH 7, (Δ) UV pH 10.

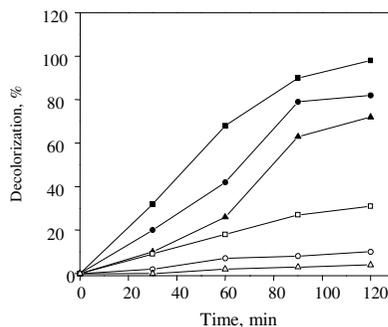


Figure 10. Effect of pH on the efficiency of decolourization of vat yellow 4 (5 mg/L) under UV light:(■) TiO₂/UV.pH 4, (●)TiO₂/UV pH 7, (▲)TiO₂/UV pH 10, (□) UV pH 4, (○) UV pH 7, (Δ) UV pH 10.

The effect of pH is less significant in systems without the catalyst, thereby proving the importance of catalyst in the photodegradation of the dye. Since it is observed that considerable photocatalytic reaction occurred in the alkaline range as well, it is inferred that the reaction occurs not only on the surface but also in its close vicinity. Heterogeneously initiated homogeneous reactions have been observed in earlier studies also¹⁸. Further, alkaline pH favours the formation of more OH radicals due to the presence of large quantity of OH⁻ ions in the alkaline medium, which can enhance the photocatalytic degradation.

Conclusion

The study reveals that both the dyes Reactive Red 120 and vat yellow 4 could be decolourised by TiO₂ immobilised on ceramic tile, thereby reducing the inconvenience of filtration of the catalyst as in the case of suspensions. The decolourisation percentage was more for both dyes in the case where the catalyst was immobilised on ceramic tiles compared to the case where it was immobilised on cement. UV Irradiation of the dye solutions could bring Concentration of the dye and pH of the system were found to have significant effect on the decolorisation. This method can be upgraded to large volume of textile wastes of low concentration, as it may be a viable technique for large volume of textile dye wastes degradation provided strong binding of the photocatalyst particles on the surface of the reactor is possible. If the concentration is high, dilution to the appropriate level is a prerequisite.

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