

## Photodegradation of Congo Red and Reactive Yellow 2 Using Immobilized TiO<sub>2</sub> under Sunlight Irradiation

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**Abstract:** The present study explored the possibility of using immobilized TiO<sub>2</sub> to photodegrade Congo Red and Reactive Yellow 2. Through this immobilization method, the separation process of fine titanium dioxide (TiO<sub>2</sub>) photocatalyst at the end of the treatment can be avoided. The photocatalytic degradation of both dyes was investigated under sunlight irradiation. The results showed that the percentage of dye removal increased with decreasing initial dye concentration and increasing irradiation time. For all the dye solutions studied, higher removal efficiency was obtained under acidic medium. The findings have shown the potential of this application in dye removal from aqueous solution.

**Key words:** Photodegradation • Anionic dye • Immobilization • Titanium dioxide

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### INTRODUCTION

Due to the extensive usage of dyes in many industries, particularly, textile, ceramic, paper, printing and plastic industries, dyes have now become an integral part of industrial wastewater. In fact, there are more than 100,000 commercially available dyes with over  $7 \times 10^5$  tonnes of dyestuffs produced annually [1]. It is estimated that 2% of dyes produced annually are discharged in effluent from manufacturing operations while 10% are discharged in effluent from textile and associated industries [2]. Many dyes are difficult to degrade, as they are generally stable to light and oxidizing agents and are resistant to aerobic digestion. As such, effluent contaminated with dye from these industries has become one of the main sources of environmental pollution.

The presence of dyes even in trace quantities is very undesirable in aqueous environment due to their brilliant appearance. Apart from this, these highly coloured

effluents will also affect the photosynthetic activity in aquatic life as it reduces the transparency of the water and sunlight penetrative ability.

Conventional treatment technologies for dye removal from industrial effluents include biological treatment, coagulation, ozonation, electrochemical processes, nanofiltration and activated carbon adsorption. Although carbon adsorption has demonstrated high efficiency in handling liquid industrial wastewater, the high cost of activated carbon remains as the major drawback. This has led to search for cheaper substitutes. The photocatalytic mineralization of organic pollutants using photocatalyst could be one of the attractive alternatives. It has been reported as a successful and effective technique in removing and destroying dye molecules [3-5].

Anatase-type TiO<sub>2</sub> is a semiconductor that has attracted much attention for its potential application in the decomposition of various environmental pollutants in both gaseous and liquid phases [6]. When TiO<sub>2</sub> is illuminated with light energy greater than the bandgap

energy ( $\lambda < 380$  nm), it can act as a photocatalyst to mineralize toxic and bioresistant organic compounds from aqueous solution to non-toxic and safer compounds. This process can destroy organic matter, transforming organic carbon to  $\text{CO}_2$  and organic N, S, or Cl to diluted inorganic acids such as  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$  [7].

However, due to the small particle size of the  $\text{TiO}_2$ , a post-treatment catalyst recovery stage involving microfiltration is necessary. Post-treatment catalyst recovery would be undesirable on industrial scale as it would add to the capital and operating costs of the treatment. Therefore, the aim of this study is to assess the ability of immobilized  $\text{TiO}_2$  to photodegrade anionic dyes which are commonly used in textile materials.

### MATERIALS AND METHODS

**Sorbates:** The sorbates and their chemical structures (Figure 1) used in this study are listed below.

1. Congo Red, CR (C.I. 22120,  $\lambda_{\text{max}} = 498$  nm)
2. Reactive Yellow 2, RY2 (C.I. 18972,  $\lambda_{\text{max}} = 404$  nm)

Both dyes were purchased from Sigma-Aldrich Chemical Company and used as received without further purification. Synthetic dye solutions with the concentration of 500 mg/L was prepared as stock solution and subsequently diluted when necessary.

**Immobilization of  $\text{TiO}_2$ :** The  $\text{TiO}_2$  powder P-25 (mainly in anatase form, mean particle size of 30 nm, BET surface area of  $50 \text{ m}^2/\text{g}$ ) from Degussa (Frankfurt, Germany) was used as the photocatalyst in this study. The immobilization of  $\text{TiO}_2$  on glass plate (2 inch  $\times$  4 inch  $\times$  0.12 inch) was carried out according to the previously reported method [8]. The resulting mixture was stirred continuously until all the  $\text{TiO}_2$  powders were uniformly dispersely. The glass plate was dipped into the mixture (considered as 1 time dip coating).

**Experimental:** Irradiation experiments of dye solutions were carried out by stirring 500 ml of 10 mg/L dye solution in a 1000 ml beaker with 5 plates of immobilized  $\text{TiO}_2$ . The whole setup was placed under the exposure of sunlight for 4 hours unless otherwise stated. Aeration was provided by bubbling air into the reaction solution

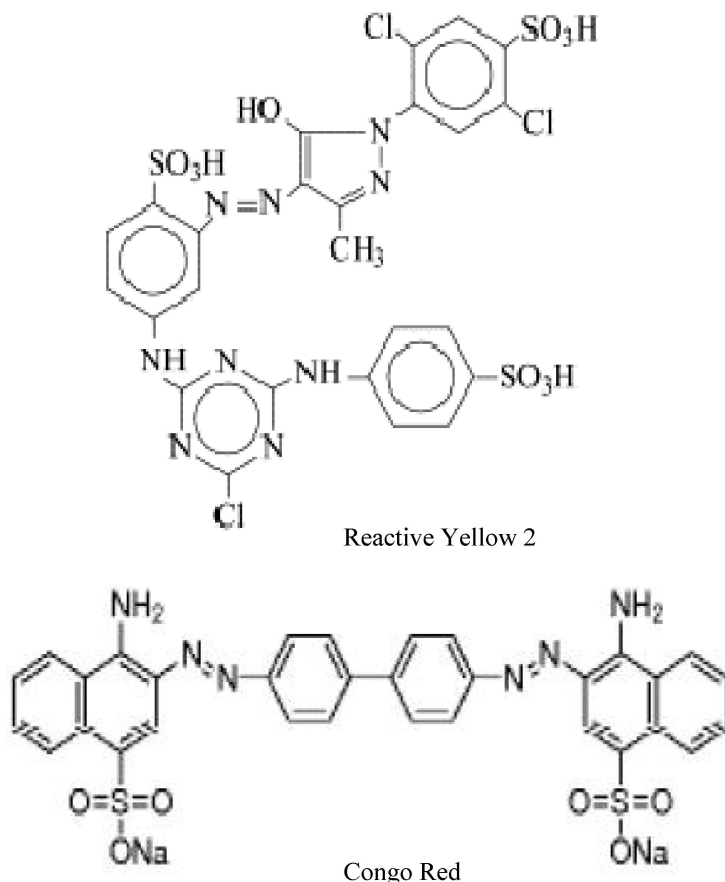


Fig. 1: Chemical structures of the studied dyes

by an air pump to ensure a constant supply of oxygen. For the effect of contact time, at predetermined intervals, aliquots of solution were withdrawn and analysed for its dye concentration using Perkin Elmer Lambda 35 UV-vis spectrophotometer. The effect of pH on dyes removal was studied by equilibrating the solution at different initial pH values, achieved by the addition of 0.1 M HCl or 0.1 M NaOH. The effect of light source was studied by using two different light sources: white fluorescent light (18 watt) and UV-irradiation (high pressure mercury lamp). The reusability of immobilized TiO<sub>2</sub> was studied by repeating the photodegradation experiments for 4 times.

## RESULTS AND DISCUSSION

### Effect of Contact Time and Initial Dye Concentration:

Figure 2 shows the result of contact time and initial dye concentration for the removal of RY2 and CR. The percentage of removal was highly concentration dependent. Increasing concentration of dye solution decreased the percent of removal in both dyes. An explanation for this behavior is that as initial concentration increases, more dye molecules are adsorbed on the surface of TiO<sub>2</sub>. The large amount of adsorbed dye is thought to have an inhibitive effect in photodegradation because it absorbs light and photons, thereby reducing the generation of hydroxyl radicals. As the formation of hydroxyl radicals on the surface of TiO<sub>2</sub> decreases, the relative number of hydroxyl radicals attacking the compound also decreases, thus resulting in lower percent of decolourization. The adverse effect of increasing initial concentration towards photodegradation has been reported previously [9-11].

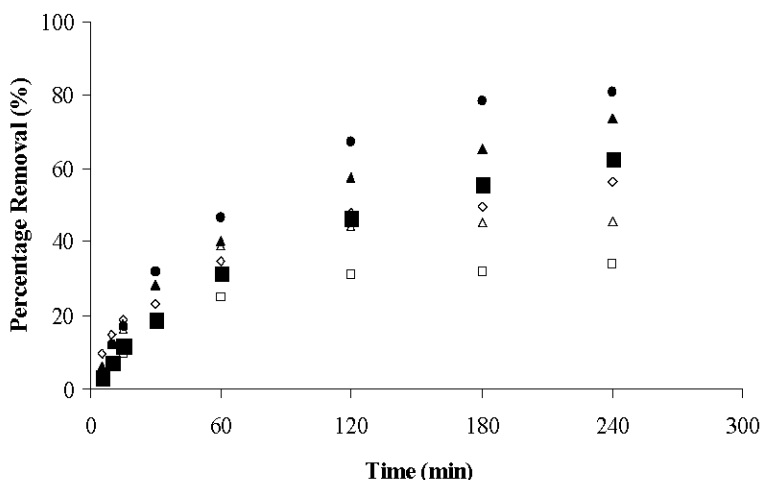


Fig. 2: Effect of initial dye concentration and contact time on the photodegradation of dyes (●, ▲, ■, – 5, 7.5 and 10 mg/L of CR; ○, △, □– 5, 7.5 and 10 mg/L of RY2)

**Effect of pH:** The study of pH on dye removal is important in establishing the optimum pH for the photodegradation of dyes (Figure 3). The interpretation of pH effect on the efficiency of RY2 and CR photodegradation process is related to the ionization state of the surface of TiO<sub>2</sub>. The point of zero charge (pzc) of TiO<sub>2</sub> has been reported as 6.9 [12]. Hence, TiO<sub>2</sub> surface will remain positively charged when pH < 6.9 and negatively charged when pH > 6.9. Since both studied dyes were anionic dyes, therefore under pH < pH<sub>pzc</sub> conditions, which is acidic solutions, the surface of TiO<sub>2</sub> will be positively charged and adsorbs both RY2 and CR molecules readily. Whereas under the alkaline condition, the number of negatively charged surface sites on the TiO<sub>2</sub> increase and this cause a lower photodegradation efficiency due to the electrostatic repulsion.

### Effect of Light Sources:

Figure 4 shows the effect of light sources in the removal of RY2 and CR, respectively. It is evident that the decolourized efficiency of both dyes with solar light irradiation was more efficient than that with artificial UV light irradiation. This phenomenon was partially attributed to a higher temperature of dye solution under solar light irradiation. Similar observation was reported in the removal of Methylene Blue whereby the color removal rate with solar light irradiation was almost twice that of artificial UV light irradiation [13].

### Effect of Reusability:

The regeneration of TiO<sub>2</sub> photocatalyst was one of key steps to make this type of heterogeneous photocatalysis technology applicable for practical usage. Thus, a study on the repetitive usage of dip coated TiO<sub>2</sub> glass plates was carried out.

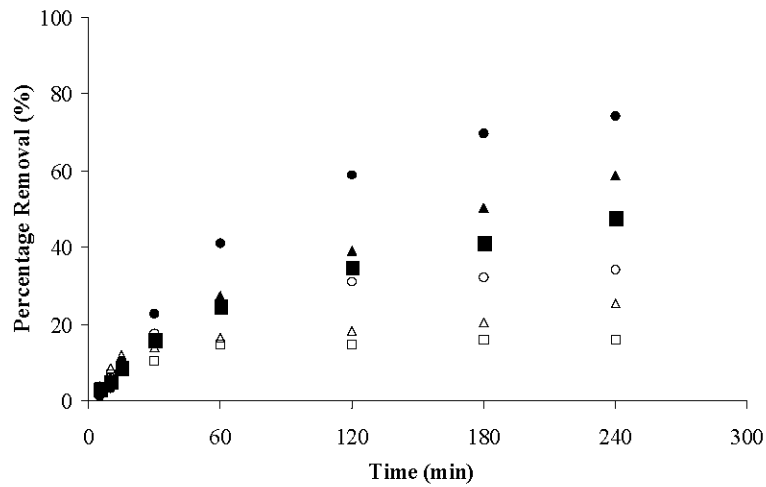


Fig. 3: Effect of pH on the photodegradation of dyes (●, ▲, ■, – pH 5, 9 and 10 for CR; ○, △, □– pH 5, 9 and 10 for RY2)

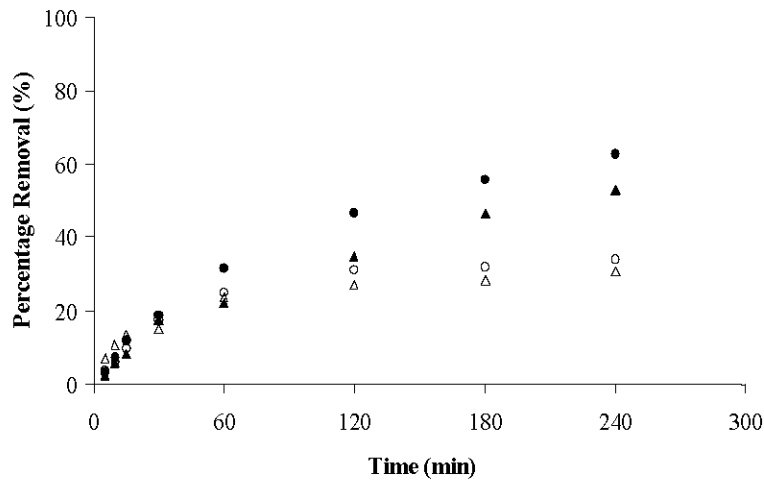


Fig. 4: Effect of different light sources on the photodegradation of dyes (●, ▲, – Sunlight, UV light for CR; ○, △- Sunlight, UV light for RY2)

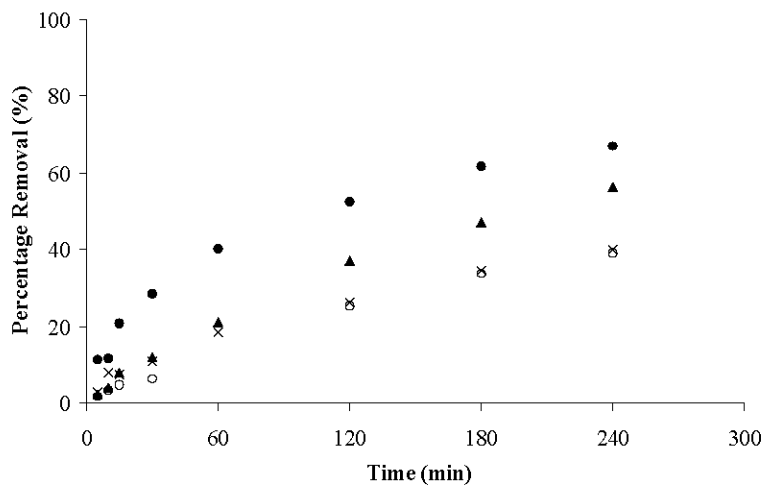


Fig. 5: Effect of repetitive usage of dip coated TiO<sub>2</sub> in the removal of CR (●, ▲, ×, ○ – 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>th</sup> and 4<sup>th</sup> time usage)

For all the dye solutions studied, the percentage of dye removal decreases with increasing number of usage. It was observed that the dye removal efficiency of CR decreased from 66.6% to 38.8% after four times reuse (Figure 5) whereas a decrease of 15% was noted in the case of RY2. This implies that when the dip-coated TiO<sub>2</sub> glass plates were used repetitively for photodegradation of dye solutions with the same initial concentration, the photocatalytic activity of the dip-coated TiO<sub>2</sub> glass plates decayed gradually. The decrease in the dye removal efficiency may be due to the non-negligible adsorbed dye molecules on the TiO<sub>2</sub> glass plates and this will hinder the formation of electron-hole pairs which is crucial in photodegradation of the dyes.

### CONCLUSION

This study explored the feasibility of using an inexhaustible and economical solar light as the main light source to remove dyes from aqueous solution via photodegradation method. From the results, it is evident that immobilized TiO<sub>2</sub> displayed a good performance in the removal of anionic dyes under acidic medium and long illumination time. However, the percentage of dyes removal decreased with increasing number of usages of immobilized TiO<sub>2</sub>. Thus, further studies will focus on the possibility of recycling this immobilized TiO<sub>2</sub> and analysis on the intermediates products formed during the photodegradation process to ensure that no undesirable hazardous compounds were formed before complete mineralization takes place.

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### REFERENCES

1. Wang, X.S., Y. Zhou, Y. Jiang and C. Sun, 2008. The removal of basic dyes from aqueous solutions using agricultural by-products. *J. Hazard. Mater.*, 157: 374-385.
2. Hamdaoui, O. and M. Chiha, 2007. Removal of methylene blue from aqueous solutions by wheat bran. *Acta Chim. Slov.*, 54: 407-418.
3. Baran, W., A. Makowski and W. Wardas, 2008. The effect of UV radiation absorption of cationic and anionic dye solutions on their photocatalytic degradation in the presence TiO<sub>2</sub>. *Dyes and Pigments*, 76: 226-230.
4. Adamek, E., W. Baran and A. Makowski, 2008. The influence of selected parameters on the photocatalytic degradation of azo-dyes in the presence of TiO<sub>2</sub> aqueous suspension. *Chem. Eng. J.*, 145: 242-248.
5. Pouretedal, H.R., A. Norozib, M.H. Keshavarz and A. Semnani, 2008. Nanoparticles of zinc sulfide doped with manganese, nickel and copper as nanocatalyst in the degradation of organic dyes. *J. Hazard. Mater.*, 162: 674-681.
6. Fu, P.F., Y. Luan and X.G. Dai, 2004. Preparation of activated carbon fibers supported TiO<sub>2</sub> photocatalyst and evaluation of its photocatalyst reactivity. *J. Molecular Catalysis*, 221: 81-88.
7. Gelover, S., P. Mondragón and A. Jiménez, 2004. Titanium dioxide sol-gel deposited over glass and its application as a photocatalyst for water decontamination. *J. Photochem. Photobiol. A: Chem.*, 165: 241-246.
8. Ong, S.T., C.K. Lee, Z. Zainal, P.S. Keng and S.T. Ha, 2009. Photocatalytic degradation of basic and reactive dyes in both single and binary systems using immobilized TiO<sub>2</sub>. *J. Fundamental Sci.*, 5: 88-93.
9. Parra, S., S.E. Stanca, I. Guasaquillo and K.R. Thampi, 2004. Photocatalytic degradation of atrazine using suspended and supported TiO<sub>2</sub>. *Appl. Catalysis B: Environ.*, 51: 107-116.
10. Toor, A.P., A. Verma, C.K. Jotshi, P.K. Bajpai and V. Singh, 2006. Photocatalytic degradation of Direct Yellow 12 dye using UV/TiO<sub>2</sub> in a shallow pond slurry reactor. *Dyes and Pigments*, 68: 53-60.
11. Daneshvar, N., D. Salari and A.R. Khataee, 2003. Photocatalytic degradation of azo dye acid red 14 in water: investigation of the effect of operational parameters. *J. Photochem. Photobiol. A: Chem.*, 157: 111-116.
12. Paritam, K.D., K.R. Ajay, K.S. Virender and J.M. Frank, 2004. Adsorption of arsenate and arsenite on titanium dioxide suspensions. *J. Coll. Inter. Sci.*, 278: 270-275.
13. Kuo, W.S. and P.H. Ho, 2001. Solar photocatalytic decolorization of MethyleneBlue in water. *Chemosphere*, 45: 77-83.