

REMOVAL OF CATIONIC AND ANIONIC DYES BY IMMOBILISED TITANIUM DIOXIDE LOADED ACTIVATED CARBON

Chang Sook Keng, Zulkarnain Zainal* and Abdul Halim Abdullah

Department of Chemistry, Faculty of Science, Universiti Putra Malaysia,
43400 UPM Serdang, Selangor, Malaysia

* Corresponding author: zulkar@fsas.upm.edu.my

Abstract

Combination of adsorption and photodegradation processes induces strong beneficial effects in dye removals. Adding high adsorption capacity activated carbon to photoactive titanium dioxide is an attractive solution due to their potential in removing dyes of diverse chemical characteristics. Recently, immobilisation has been an acceptable approach to overcome the drawbacks encountered with powder suspensions. The present study involves the removals of Victoria Blue R (VBR), a cationic dye and Indigo Carmine (IC), an anionic using approximately one gram of immobilised titanium dioxide (TiO₂), activated carbon (AC) and mixture titanium dioxide/activated carbon (TiO₂/AC) from 200 mL solution at the concentration of 20 ppm under UV illumination for 4 hours. Comparisons were made in terms of their removal efficiency by applying first-order kinetics model. Immobilised TiO₂ showed total removal of IC in 40 minutes whereas only 44% of VBR was removed in 2 hours. On the other hand, in the case of immobilised AC, about 87% of VBR and 6% of IC were removed in 2 hours. The results obtained using immobilised TiO₂/AC proved the prominence of this immobilised sample in dealing with VBR and IC by achieving 95% and 62% removal respectively in 2 hours.

Keywords: Adsorption; Photodegradation; Activated carbon; Titanium dioxide; Cationic anionic dyes

Introduction

Textile industry covers pretreatment, dyeing, printing and finishing of textile material. These activities are highly chemically polluting [1]. Dyestuff contributes to the effluent colourization that may lead to the reduction of light transmission to aquatic life. More lives will face the consequences of the development posed by the textile industry. The extend of the destruction caused by the textile industry in releasing large volumes of coloured effluents, has urged environmentalists and worldwide researchers to come hand in hand in controlling the escalating and unsolved problem and pay much attention in developing textile wastewater treatment.

Exploring in various methods such as physical [2-5], chemical [2, 5, 6-10] or biological [11, 12] treatment has drive these researchers to come out with a conclusion whereby each process is applicable in dealing with wastewater and the removal efficiency of the process in a shorter time speaks all. Types of physical treatment methods are such as filtration, sedimentation and degasification while ozonation, coagulation, adsorption, photodegradation and ion exchange are categorized under chemical treatment methods. On the other hand, biological treatment methods like aerobic and anaerobic digestions use microorganisms, mostly bacteria in the decomposition of wastewaters to stable end products. There are tonnes and tonnes of effluents being released every single day and the most effective removal technique is out to be grabbed.

In the chemical classification method, dyes are grouped according to certain common chemical structural features. Cationic and anionic dyes are the two main groups. In order to differentiate cationic and anionic dyes, several points have been studied in detail. Dyes embrace a wide variety of structural types depending on the precise nature of electron donor (A) and electron acceptor (D) groups and can be subdivided into three main categories: cationic ($z = + 1$), anionic ($z = - 1$) and neutral ($z = 0$). Cationic dyes are positively charged and the most important group of this type of dye contains nitrogen atoms in both the D and A groups. On the other hand, a characteristic feature of anionic dyes is the presence of one or more sulfonate ($-\text{SO}_3^-$) groups, usually as sodium (Na^+) salts. These groups ensure that the dyes carry a negative charge.

With the presence of these two main groups of dyes in the wastewater, a method that is able to remove them is essential. Therefore, adsorption-photodegradation process has been proposed by many researchers after realizing the noble potentials in both processes [13-17]. It was proven that activated carbon adsorption works well with photodegradation using TiO₂ in removing various pollutants. The dual effect was capable in increasing the efficiency or performance of the whole removal system. Therefore, in this study, the removal

efficiency of cationic dye, Victoria Blue R (VBR) and anionic dye, Indigo Carmine (IC) using immobilised TiO_2 , AC and TiO_2/AC were compared.

Experimental

Preparation of immobilised TiO_2 , AC and TiO_2/AC

Titanium dioxide powder (specific surface area, BET = $50 \pm 15 \text{ m}^2/\text{g}$, moisture = $\leq 1.5 \text{ wt. \%}$, pH value in 4% dispersion = 3.5 – 4.5, Aeroxide Degussa P25) was mixed with blended and sieved (200 mesh) activated carbon (iodine number = 1150-1200, carbon total content = 70%-80%, bulk density = 0.40-0.44, ash = maximum 5%) with the ratio of 30:70 before adding 15.0 mL of distilled water. The mixture was stirred for 1 hour to ensure homogeneity.

A 6.25 % w/v polyvinylalcohol-formaldehyde binder was prepared to attach TiO_2/AC to the substrate (glass slide with the dimension of 2.54 cm x 7.62 cm). Under continuous stirring in a 70 °C water bath, transparent, sticky polymer glue was formed. This binder was kept in a sealed bottle to prevent it from rapid hardening.

The slide was first applied with a thin layer of binder. Then, TiO_2/AC suspension was brushed onto the layer of binder and let to dry. The samples were kept in a sealed container to prevent preactivation. The same procedure was carried out in the preparation of immobilised TiO_2 and AC.

Dye Solutions

Victoria Blue R and Indigo Carmine stock solutions with the concentration of 200 ppm were prepared by dissolving the dyes powder with distilled water respectively. Dye solution (20 ppm) used in the removal processes was prepared by diluting the stock solution.

Dyes Removal

Photodegradation experiments were run by illuminating Victoria Blue R (VBR) and Indigo Carmine (IC) dye solutions (200 mL) containing immobilised samples using an ultraviolet (UV) lamp and air was continuously pumped into the solution to ensure a constant supply of oxygen. Temperature was maintained at 28 °C using a water bath. UV-Visible analysis was performed on the sample solutions using Perkin Elmer UV/Vis Lambda 20 Spectrophotometer.

Removal Kinetics

In this study, first-order kinetics model is applied to describe the relationship between the initial degradation rate and the initial concentration as photodegradation occurs during the early stage of the process. The kinetic equation of first-order is as shown in Equation (1.1):

$$\ln \frac{C}{C_0} = -k_1 t \quad (1.1)$$

where C is the concentration of the substrate in solution at time t of illumination (ppm),

C_0 is the concentration of the substrate in solution at time zero of illumination (ppm),

k_1 is the first-order rate constant (min^{-1}).

Straight line plots of $\ln \frac{C}{C_0}$ against t gives the values of rate constant, k_1 obtained from the slope. In order to indicate the rapidity of rate processes, the concept of half-life, defined as the time required for a reaction to proceed half-way to completion and usually denoted by $t_{1/2}$. So, if the initial concentration is C_0 , at $t_{1/2}$ it had fallen to $\frac{1}{2} C_0$.

Thus, the half-life time depends on the first-order rate constant and equation below is obtained:

$$t_{1/2} = \frac{\ln 2}{k_1} \quad (1.2)$$

Results and Discussion

Removal of Various Dyes by Immobilised TiO₂

Figure 1 compares the removal of 20 ppm VBR and 20 ppm IC in 4 hours using immobilised TiO₂. IC achieved total removal in 40 minutes while VBR required longer hours to be removed by the immobilised samples. Plots of ln(C/C₀) versus illumination time give straight lines (inset in Figure 1) and the rate constant values for both dye removals were obtained from the slopes. Higher rate constant was observed in IC removal compared to VBR removal with the value of 103.3 × 10⁻³ min⁻¹ for the former and 4.7 × 10⁻³ min⁻¹ for the latter as listed in Table 1. Cationic dye, VBR carries positive charge while anionic dye, IC contains negative charge. It is very difficult to achieve photosensitization with cationic dye because of the positive charge of TiO₂ surface and the resultant electrostatic repulsion between the dye molecules and the TiO₂ surface [18]. This leads to the interpretation of lower removal capability of immobilised TiO₂. This idea is supported by Hasnat and co-workers [19].

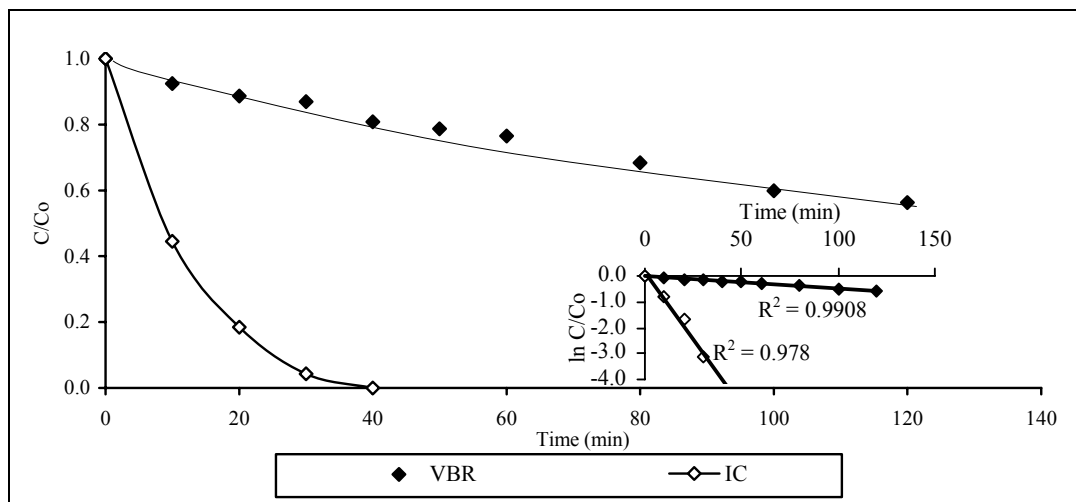


Fig. 1: VBR and IC removals at 20 ppm in the presence of immobilised TiO₂. Inset is the first-order kinetics plot for the removal of both dyes.

Half-life time values and percentage of removal of VBR and IC in the presence of immobilised TiO₂ are tabulated in Table 1. The irradiation from ultraviolet light enhanced oxidation process of adsorbed dye molecules on the surface of TiO₂ particles and the presence of air may speed up the removal process. Immobilised TiO₂ did not show prominent efficiency for the removal of VBR by achieving about 44% of removal in 120 minutes. It can be observed that if the removal process is allowed to proceed for longer time, immobilised TiO₂ is able to remove more dyes. However, immobilised TiO₂ shows its prominence in removing IC by achieving total removal in 40 minutes. It once again proved that immobilised TiO₂ worked well in removing anionic dye due to its positive surface charged. With a faster removal rate, the half-life time for IC removal is shorter than the removal of VBR.

Table 1: First-order rate constant, k_1 , half-life time, $t_{1/2}$ and percentage of removal of VBR and IC in the presence of immobilised TiO_2 .

Dyes	First-order rate constant, k_1 ($\times 10^{-3} \text{ min}^{-1}$)	Half-life time, $t_{1/2}$ (min)	Percentage of removal in 120 minutes (%)
VBR	4.7	147.4	44
IC	103.3	6.7	100

Removal of Various Dyes by Immobilised AC

A different phenomenon was observed in the dye removal systems by applying immobilised AC. VBR removal was much greater and faster compared to IC removal. The removal of this anionic dye was found to be insignificant as shown in Figure 2. On the other hand, the removal of the cationic dye, VBR was prominent. Activated carbon used in this study was prepared commercially by steam activation at 800 °C to 900 °C. In this range of temperature, basic oxides predominate and become acid-adsorbing.

When VBR is dissolved in water and undergoes hydrolysis:



The solution contains equilibrium concentrations of Victoria Blue R chloride, Victoria Blue R hydroxide and hydrochloric acid together with ions of hydrogen, chloride and dye. Activated carbon preferentially adsorbs the basic constituent [20]. This leads to the interpretation of better VBR removal.

However, repulsive force dominates between the AC surface and IC anions and resulted in poor removal efficiency. AC did not have the ability in removing the anionic dye despite of its high adsorption ability. The uptake of IC fluctuates throughout the experiment. The rate constant values for both dye removals were obtained from the slopes of plots of $\ln(C/C_0)$ versus illumination time (inset in Figure 2). As expected, the removal rate shown by VBR is greater than IC as listed in Table 2.

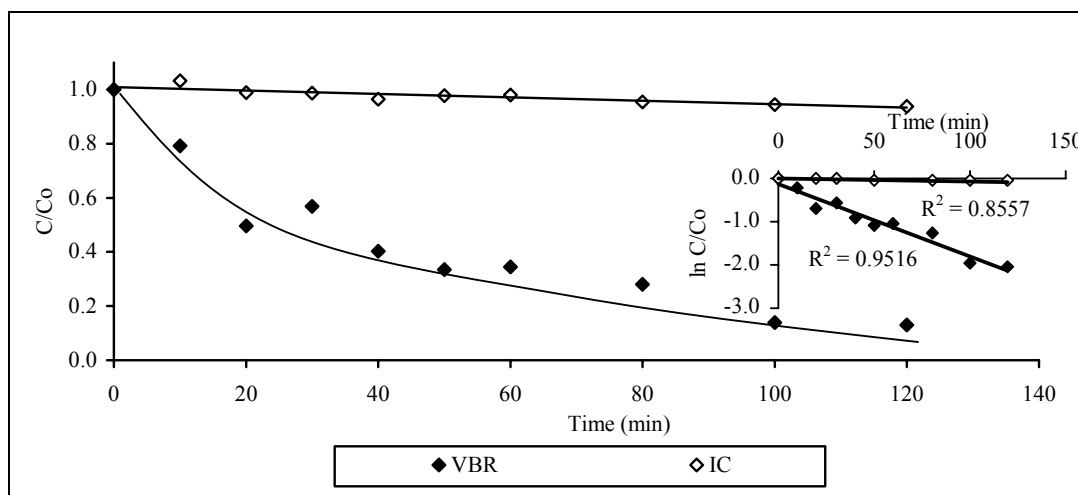


Fig. 2: VBR and IC removals at 20 ppm in the presence of immobilised AC. Inset is the first-order kinetics plot for the removal of both dyes.

A drastic difference was observed in the removal of these two groups of dyes by using immobilised AC as highlighted in Table 2 in terms of the half-life time values and the removal percentage. The percentage of removal of VBR was far higher than IC. This again proved that cationic dye with basic constituent is better removed by immobilised AC. Higher rate constant leads to shorter half-life time for the removal of VBR.

Table 2: First-order rate constant, k_1 , half-life time, $t_{1/2}$ and percentage of removal of VBR and IC in the presence of immobilised AC.

Dyes	First-order rate constant, k_1 ($\times 10^{-3} \text{ min}^{-1}$)	Half-life time, $t_{1/2}$ (min)	Percentage of removal in 120 minutes (%)
VBR	16.5	42.0	87
IC	0.7	990.0	6

Removal of Various Dyes by Immobilised TiO₂/AC

Immobilised TiO₂/AC emphasizes on the combined effect of AC in the adsorption and TiO₂ in the photodegradation as presented in Figure 3. The inset in Figure 3 shows the rate constant values for the removals of both dyes obtained from the slopes of plots of $\ln(C/C_0)$ versus illumination time while the half-life time values are tabulated in Table 3.

AC acts as an adsorbent in adsorbing and removing the dye molecules from the system and some of them which was adsorbed to the surface of AC migrated continuously to TiO₂ where photocatalytic degradation occurs. Upon initiation by UV, high energy electron (e_{CB}^-)/hole (h_{VB}^+) pairs form in TiO₂ from the excitation of electron into the conduction band leaving holes in the valence band. This is followed by formation of hydroxyl radicals, OH· when photogenerated holes reacted with water molecules and hydroxyl ions. On the other hand, the presence of oxygen on the TiO₂ surface responsible for the formation of superoxide radical ion ($O_2^{\cdot-}$) which subsequently forms more hydroxyl radicals. This leads to oxidization of the dye molecules as these hydroxyl radicals are strong oxidizing agents.

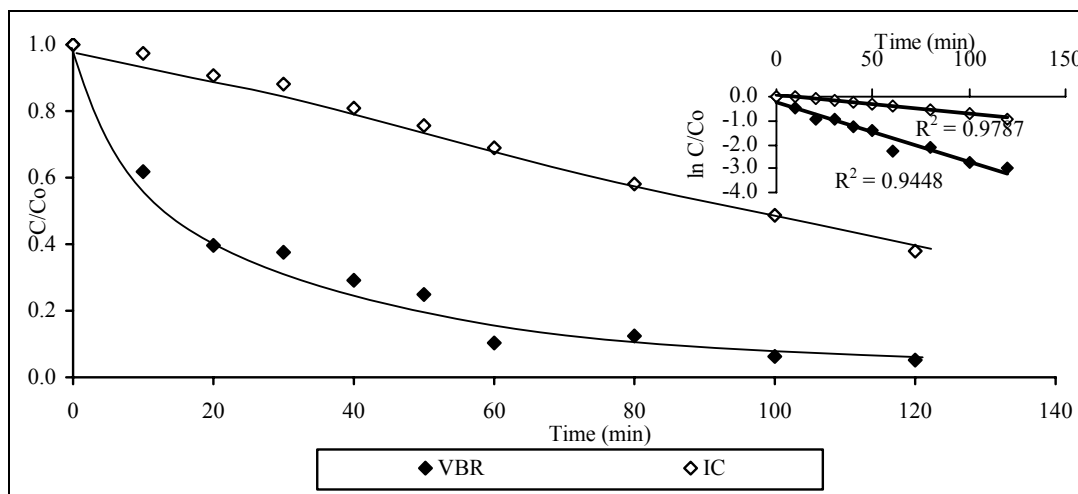


Fig. 3: VBR and IC removals at 20 ppm in the presence of immobilised TiO₂/AC. Inset is the first-order kinetics plot for the removal of both dyes.

Therefore, immobilised TiO₂/AC was introduced to overcome the shortcomings portrayed by immobilised TiO₂ and immobilised AC in removing cationic and anionic dyes. In 120 minutes, immobilised TiO₂/AC was able to remove at approximately 95% of VBR and 62% of IC as listed in Table 3. TiO₂/AC acted as semiconductor and also as an adsorbent gave dual effect to the dye removal systems regardless of their characteristics. AC helps to concentrate the VBR and IC molecules on the surface of TiO₂/AC to enable TiO₂ to degrade the dye molecules. Initialization of UV may lead to the formation of hydroxyl radicals that helps in oxidizing VBR and IC. This resulted in greater dye removals.

Table 3: First-order rate constant, k_1 , half-life time, $t_{1/2}$ and percentage of removal of VBR and IC in the presence of immobilised TiO₂/AC.

Dyes	First-order rate constant, k_1 (x 10 ⁻³ min ⁻¹)	Half-life time, $t_{1/2}$ (min)	Percentage of removal in 120 minutes (%)
VBR	24.3	28.5	95
IC	8.1	85.6	62

Conclusion

This study evaluates the ability and effectiveness of the immobilised system containing TiO₂, AC and TiO₂/AC in removing cationic and anionic dyes. Combination of adsorption and photodegradation processes has better removal capability with various dyes. Immobilised TiO₂/AC showed great potential in dealing with both groups of dyes while TiO₂ and AC worked effectively in the removal of IC and VBR respectively.

Acknowledgement

The authors wish to acknowledge the Department of Chemistry, Universiti Putra Malaysia for the provision of laboratory facilities.

References

1. C., Hessel, C., Allegre, M., Maisseu, F., Charbit and P., Moulin (2007). Guidelines and legislation for dye house effluents. *Environ. Manage.* 83,171-180.
2. K.H., Choo, S.J., Choi and E.D., Hwang (2007) Effect of coagulant types on textile wastewater reclamation in a combined coagulation/ultrafiltration system. *Desalination* 202, 262-270.
3. T.P., Shah, Y., Yoon, C.L., Pederson and R.M., Lueptow (2006) Rotating reverse osmosis and spiral wound reverse osmosis filtration: A comparison. *J. Membr. Sci.* 285, 353-361.
4. G., Capar, L., Yilmaz and U., Yetis (2006) Reclamation of acid dye bath wastewater: Effect of pH on nanofiltration performance. *J. Membr. Sci.* 281, 560-569.
5. T.A., Kurniawan, G.Y.S., Chan, W.H., Lo and S., Babel (2006) Physico-chemical treatment techniques for wastewater laden with heavy metals. *Chem. Eng. J.* 118, 83-89.
6. X., Qu, J., Zheng and Y., Zhang (2007) Catalytic ozonation of phenolic wastewater with activated carbon fiber in a fluid bed reactor. *J. Colloid Interface Sci.* 309, 429-434.
7. S., Barredo-Damas, M.I., Iborra-Clar, A., Bes-Pia, M.I., Alcaina-Miranda, J.A., Mendoza-Roca and A., Iborra-Clar (2005) Study of preozonation influence on the physical-chemical treatment of textile wastewater. *Desalination* 182, 267-274.
8. T.E., Agustina, H.M. Ang and V.K., Vareek (2005) A review of synergistic effect of photocatalysis and ozonation on wastewater treatment. *J. Photochem. Photobio. C: Photochem. Rev.* 6, 264-273.
9. H., Selcuk (2005) Decolorization and detoxification of textile wastewater by ozonation and coagulation processes. *Dyes Pigments* 64, 217-222.
10. A.H., Elshazly and A.H. Konsowa (2003) Removal of nickel ions from wastewater using a cation-exchange resin in a batch-stirred tank reactor. *Desalination* 158, 189-193.

11. D., Paul, G., Pandey, J., Pandey and R.K., Jain (2005). Accessing microbial diversity for bioremediation and environmental restoration. *Trends Biotechnol.* 23(3), 135-142.
12. M.A., Oliveira, E.M., Reis and J., Nozaki (2001) Biological treatment of wastewater from the cassava meal industry. *Environ. Res. Sect. A* 85, 177-183.
13. R. Yuan, R. Guan, W. Shen and J. Zheng (2005) Photocatalytic degradation of methylene blue by a combination of TiO₂ and activated carbon fibers. *J. Coll. Interf. Sci.* 282, 87-91.
14. E. Carpio, P. Zúñiga, S. Ponce, J. Solis, J. Rodriguez and W. Estrada (2005) Photocatalytic degradation of phenol using TiO₂ nanocrystals supported on activated carbon. *J. Mol. Catal. A: Chem.* 228, 293-298.
15. B., Tryba, A.W., Morawski, M., Inagaki, M. (2003) "Application of TiO₂-mounted activated carbon to the removal of phenol from water". *Appl. Catal. B: Environ.* 41, 427-433.
16. J., Matos, J., Laine, J.M. Herrmann (1998) "Synergy Effect in the photocatalytic degradation of phenol on a suspended mixture of titania and activated carbon". *Appl. Catal. B: Environ.* 18, 281-291.
17. T., Torimoto, Y., Okawa, N., Takeda and H., Yoneyama (1997) Effect of activated carbon content in TiO₂-loaded activated carbon on photodegradation behaviours of dichloromethane. *J. Photochem. Photobio. A: Chem.* 103, 153-157.
18. P., Qu, J., Zhao, L., Zang, T., Shen and H., Hidaka (1998) Enhancement of the photoinduced electron transfer from cationic dyes to colloidal TiO₂ particles by addition of an anionic surfactant in acidic media. *Colloids Surf. A: Physicochem. Eng. Aspects* 138, 39-50.
19. M.A., Hasnat, I.A., Siddiquey and A., Nuruddin (2005) Comparative photocatalytic studies of degradation of a cationic and an anionic dye. *Dyes Pigments* 66, 185-188.
20. J.W. Hassler (1974) Purification with Activated Carbon: Industrial, Commercial, Environmental. New York: Chemical Publishing Co., Inc.