REMOVAL OF DYE BY IMMOBILISED PHOTOCATALYST LOADED ACTIVATED CARBON

Zulkarnain Zainal*, Chang Sook Keng and Abdul Halim Abdullah

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

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Abstract

The ability of activated carbon to adsorb and titanium dioxide to photodegrade organic impurities from water bodies is well accepted. Combination of the two is expected to enhance the removal efficiency due to the synergistic effect. This has enabled activated carbon to adsorb more and at the same time the lifespan of activated carbon is prolonged as the workload of removing organic pollutants is shared between activated carbon and titanium dioxide. Immobilisation is selected to avoid unnecessary filtering of adsorbent and photocatalyst. In this study, mixture of activated carbon and titanium dioxide was immobilised on glass slides. Photodegradation and adsorption studies of *Methylene Blue* solution were conducted in the absence and presence of UV light. The removal efficiency of immobilised TiO_2/AC was found to be two times better than the removal by immobilised AC or immobilised TiO_2 alone. In 4 hours and with the concentration of 10 ppm, TiO_2 loaded activated carbon prepared from 1.5 g/15.0 mL suspension produced 99.50% dye removal.

Abstrak

Kebolehan karbon teraktif untuk menjerap and titanium dioxida untuk memfotodegrasi bendasing organik dalam sumber air adalah amat diterima. Penggabungan dua teknik ini dipercayai dapat meningkatkan kecekapan penyingkiran disebabkan kesan sinergik. Ini membolehkan karbon teraktif untuk menjerap lebih banyak dan pada masa yang sama tempoh penggunaan karbon teraktif dapat dipanjangkan memandangkan beban kerja penyingkiran pencemar-pencemar organik dikongsi antara karbon teraktif dan titanium dioksida. Sekatan gerak dipilih untuk mengelakkan daripada penapisan bahan penjerap dan fotopemangkin. Dalam kajian ini, campuran karbon teraktif dan titanium dioksida disekat gerak pada kepingan kaca. Kajian fotodegradasi dan penjerapan *Methylene Blue* dilakukan dalam kehadiran dan ketidakhadiran cahaya ultralembahyung (UV). Kecekapan penyingkiran oleh TiO_2/AC tersekat gerak adalah dua kali lebih baik berbanding penyingkiran dengan AC tersekat gerak atau TiO_2 tersekat gerak. Dalam masa 4 jam dan dengan kepekatan 10 ppm, karbon teraktif termuat titanium dioksida yang disediakan dari 1.5 g/15.0 mL ampaian menghasilkan 99.50% penyingkiran pewarna.

Introduction

The idea of conserving the environment does not come in one or two days time. It has become a necessity to enlighten each an everyone of us of the problem faced by the Mother Nature. Pollution in water bodies is escalating and the fear of living in dirty environment has encouraged researchers to come out with or design techniques to overcome the problem. Developing techniques ranging from distillation, ion exchange, filtration, ultrafiltration, reverse osmosis, ultraviolet (UV) radiation to carbon adsorption has become a necessity.

Combined adsorption-photodegradation process is another alternative in the development of wastewater treatment method and is expected to give better results in removing organic pollutants [1-3]. Adsorption can be done by using a variety of materials such as sawdust, coconut shell, rice husk, banana pith, chitosan, chitin, orange peel, activated carbon and so on. On the other hand, photodegradation is applied by using semiconducting compound such as TiO_2, SnO_2, SiO_2, ZrO_2 and many more. It is proven that titanium dioxide photocatalyst, anchored or embedded onto co-adsorbent with large surface area such as activated carbon produced promising results due to the high capacity of activated carbon to adsorb most of the pollutants and the synergistic effect between these two materials [4-8].

In order to ensure the water treatment system works effectively, immobilisation of titanium dioxide loaded activated carbon onto glass slides is introduced in this study. The purposes of immobilising the photocatalyst-

adsorbent are to avoid the filtration step, reduce losses of the materials and increase the efficiency of the whole system [9-12].

Experimental

Preparation of Immobilised Titanium Dioxide Loaded Activated Carbon (TiO_2/AC)

Particle size of titanium dioxide and activated carbon powders were characterized using particle size analyzer Malvern Mastersizer S.

The suspension for TiO_2/AC coating was prepared by mixing 0.30 g titanium dioxide powder (BET surface area = 50 m^2/g, pH 4 suspension, Aeroxide Degussa P25) with 1.20 g AC (iodine number = 1150-1200, carbon total content = 70%-80%, bulk density = 0.40-0.44, ash = maximum 5%) before adding 15.0 mL of distilled water. The mixture was stirred for 1 hour to ensure homogeneity.

The binder was prepared by adding 5.0 g polyvinylalcohol into 80.0 mL formaldehyde at 70 °C under continuous stirring. Transparent, sticky polymer glue was formed and was kept in a sealed bottle to prevent it from rapid hardening.

Later, pieces of glass slides with dimension of 2.54 cm x 7.62 cm were applied with a thin layer of the binder. Then, TiO_2/AC suspension was brushed onto the layer of binder and let to dry. The samples were stored in the dark to prevent preactivation.

Preparation of Methylene Blue

Methylene Blue stock solution with the concentration of 200 ppm was prepared by dissolving 0.2 g Methylene Blue powder in 1000 mL distilled water. Dye solutions used in the removal process were prepared from the stock solution.

Photocatalytic Degradation with Ultraviolet Lamp

The photodegradation experiments were run by illuminating the dye solution (200 mL) containing immobilised TiO_2/AC using an ultraviolet (UV) lamp. Air was continuously pumped into the solution to ensure a constant supply of oxygen. The experimental set-up was covered to avoid unnecessary exposure to light and the temperature was maintained at 28 ºC using a water bath. UV-Visible analysis was performed on the sample solutions using Perkin Elmer UV/VIS Lambda 20 Spectrophotometer.

Results and Discussion

Particle Size of Titanium Dioxide (TiO_2) and Activated Carbon (AC)

TiO_2/AC prepared from TiO_2 and AC powders were studied using Malvern Mastersizer S. Size and characteristics of the particles may affect the stability, chemical reactivity, opacity, flowability and material strength of many materials. This analyzer applied dispersion mechanism whereby particles were accelerated within a compressed air stream and this resulted collision between the particles and wall. Therefore, parameters like feed rate and dispersion air pressure of the particle size analyzer were set at 20% and 3 bar respectively in analyzing both powders. Figure 1 illustrates the size distribution of titanium dioxide and activated carbon. From the figure, it was found that activated carbon has a wide range of sizes whereas titanium dioxide is more uniform whereby it has about the same cumulative percentages in the range of 10 μm to 100 μm. The particle size of titanium dioxide is smaller than activated carbon as it shows higher cumulative percentage at smaller particle size. On the other hand, the cumulative percentage of activated carbon soars higher than titanium dioxide after 350 μm. This shows the compatibility between these two materials when they are mixed together. TiO_2 with smaller particle size will go in between or into the pores of activated carbon that have bigger particle size. This enables TiO_2 and activated carbon to perform effectively in the adsorption-photodegradation process.

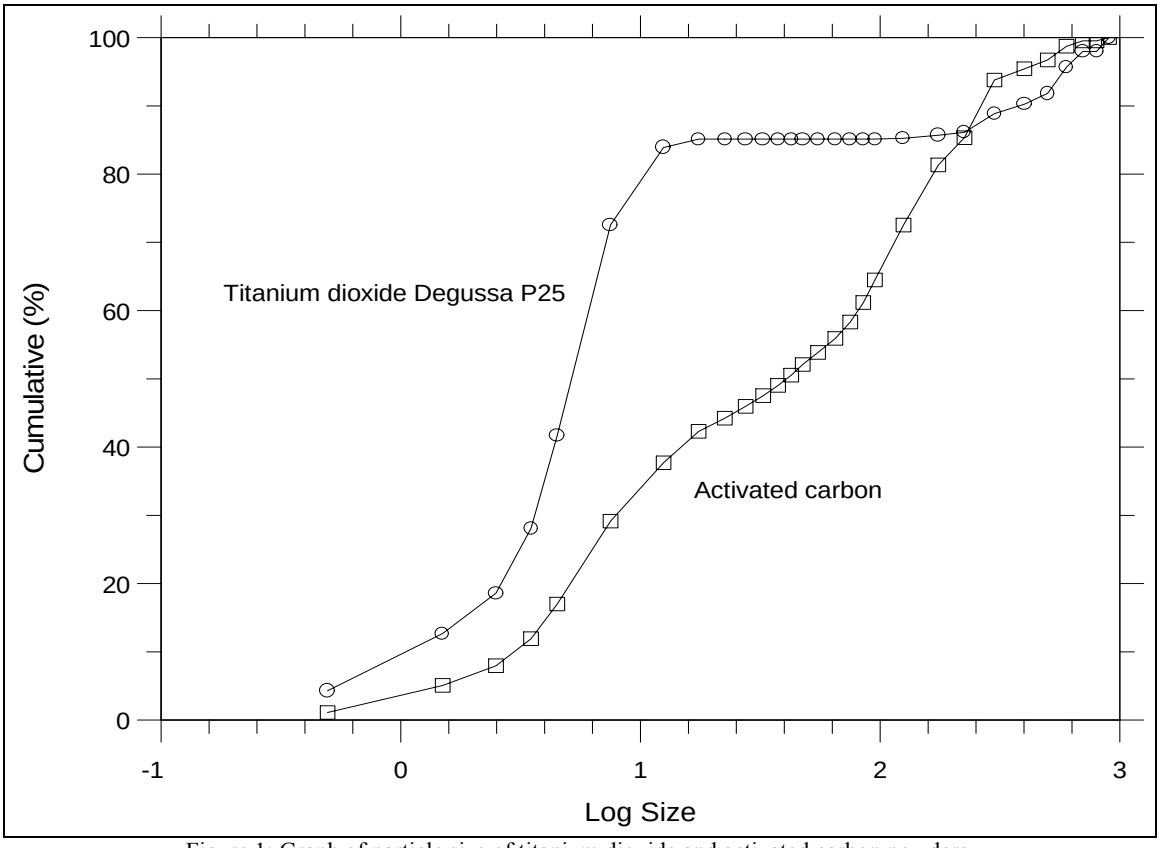

Figure 1: Graph of particle size of titanium dioxide and activated carbon powders.

Comparison between Titanium Dioxide, Activated Carbon and Titanium Dioxide/ Activated Carbon

The removal of Methylene Blue by using the three different samples is depicted in Figure 2. From the graph, it shows that a mixture of TiO_2/AC gives a better efficiency by achieving 99.50% of the dye removed after 4 hours. With the usage of immobilised activated carbon samples, 74.33% of the dye was removed and the percentage of removal goes down to 46.60% by using immobilised TiO_2 samples. These results proved that the combination of titanium dioxide and activated carbon is the best option in removing Methylene Blue. The amount removed by TiO_2/AC is 6.70 x 10^{-6} mol followed by AC (4.65 x 10^{-6} mol) and TiO_2 (2.76 x 10^{-6} mol). Photodecomposition of adsorbed Methylene Blue enhances the adsorption rate of this dye by keeping the adsorptive capacity of activated carbon unsaturated [8]. Dye molecules adsorption by activated carbon followed by a transfer of the molecules to TiO_2 where photocatalysis occurred has created a mutual combination for the enhancement of the dye removal system. This has enabled the adsorption capacity of activated carbon to be maintained and to perform effectively for a longer period of time.

Effect of Suspension Loading in the Preparation of Immobilised TiO_2/AC

Figure 3 shows the effect of suspension loading of TiO_2/AC on the removal of Methylene Blue. Increasing suspension loading of TiO_2/AC resulted the removal system to reach saturation faster as the surface area provided is greater for more adsorption to occur. The removal effect of TiO_2/AC was studied by using kinetics models namely first-order and pseudo-second-order while intraparticle diffusion model was applied to obtain the diffusion rate of the dye molecules into TiO_2/AC. The removal effect of TiO_2/AC by using first-order model is depicted in Figure 4 whereas pseudo-second-order model can be seen in Figure 5. A plot of q_t against the square root of t for the intraparticle diffusion model of Methylene Blue onto TiO_2/AC can be found in Figure 6. The results in Table 1 shows the correlation coefficient, r^2 and first-order apparent rate constant, k compared with correlation coefficient, r^2, sorption capacity, q_2, sorption rate constant of pseudo-second-order rate constant, k_2 and initial sorption rate, h and correlation coefficient, $r^2$and intraparticle diffusion rate constant, k_i at various suspension loading of TiO_2/AC, m. From this table, the results can be better represented by pseudo-second-order based on the correlation coefficients (> 0.990). As the amount of TiO_2/AC increases, sorption capacity, q_2 decreases. This trend is in agreement with Ho and McKay [13] where by these researchers studied the sorption

of Basic Red 22 and Acid Red 114 by biosorbent waste product pith. Correlation coefficients for the intraparticle diffusion parameter are the lowest and this suggests that the diffusion controlled mechanism is not predominant. Figure 7 illustrates the variation of apparent rate constant, k_1 and amount of removal against the suspension loading of TiO_2/AC. 1.5 g/15.0 mL gives the highest apparent rate constant and greatest amount of removal with the value of 4.91×10^{-2} min^{-1} and 6.70×10^{-6} mol respectively. The results revealed that Methylene Blue removal efficiency increases up to the optimum amount (1.5 g/15.0 mL), beyond which the amount of removal decreases. It is due to the difficulty of light penetration into the immobilised samples for photocatalysis to occur.

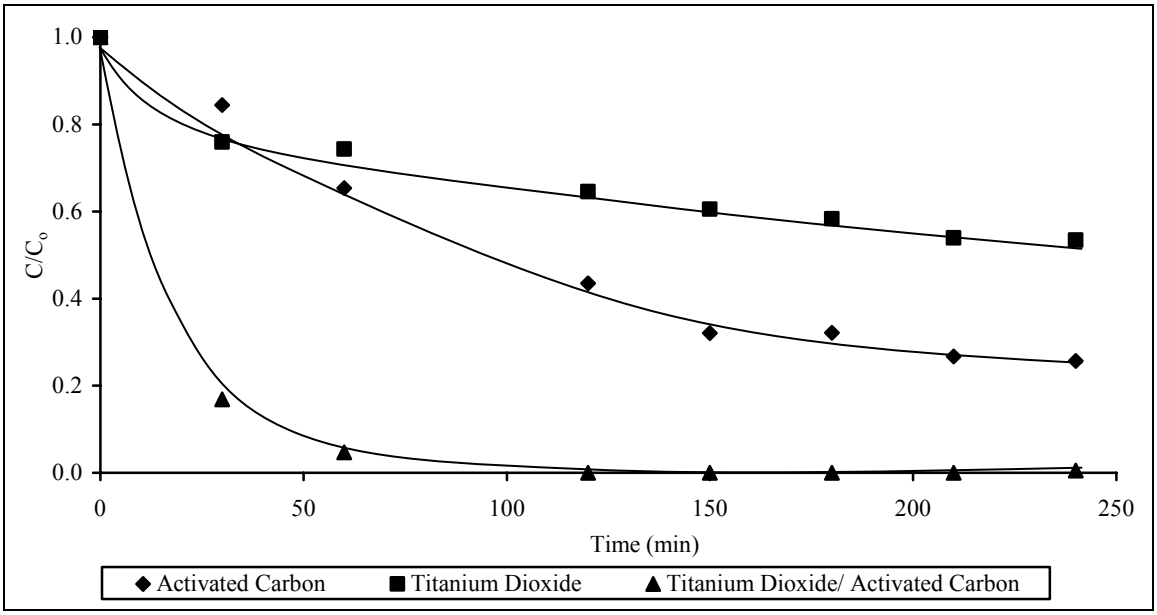

Figure 2: The removal of Methylene Blue by activated carbon, titanium dioxide and TiO_2/AC conducted on 5 pieces of glass slides in 200 mL of 10 ppm Methylene Blue solution at 28 ºC.

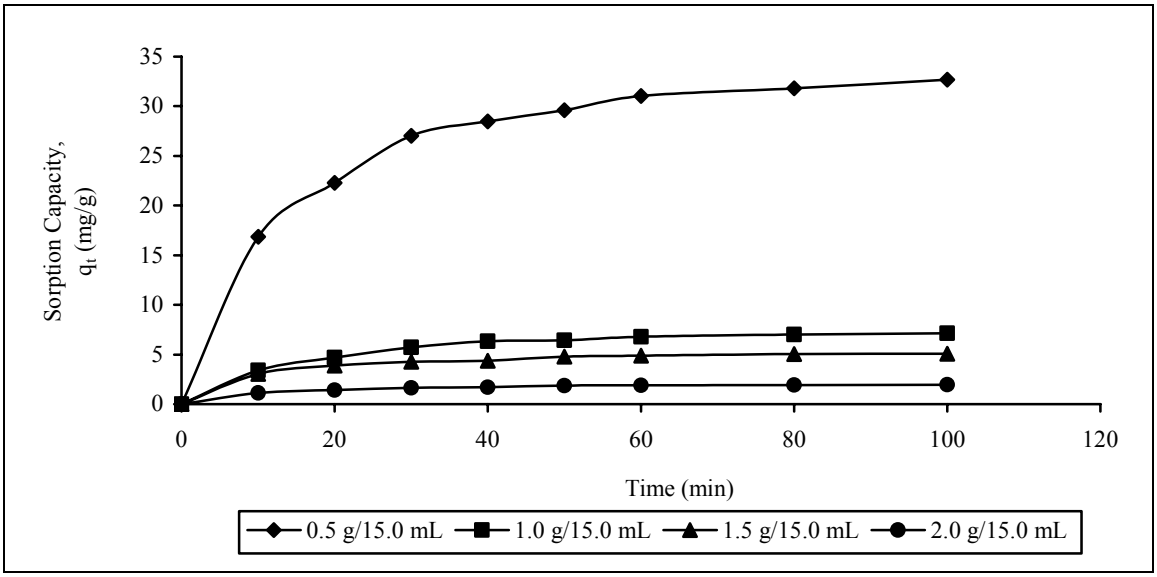

Figure 3: The removal of Methylene Blue by immobilised TiO_2/AC at different suspension loading in the preparation of immobilised TiO_2/AC conducted on 5 pieces of glass slides in 200 mL of 10 ppm Methylene Blue solution at 28 ºC under UV illumination (1 ultraviolet lamp).

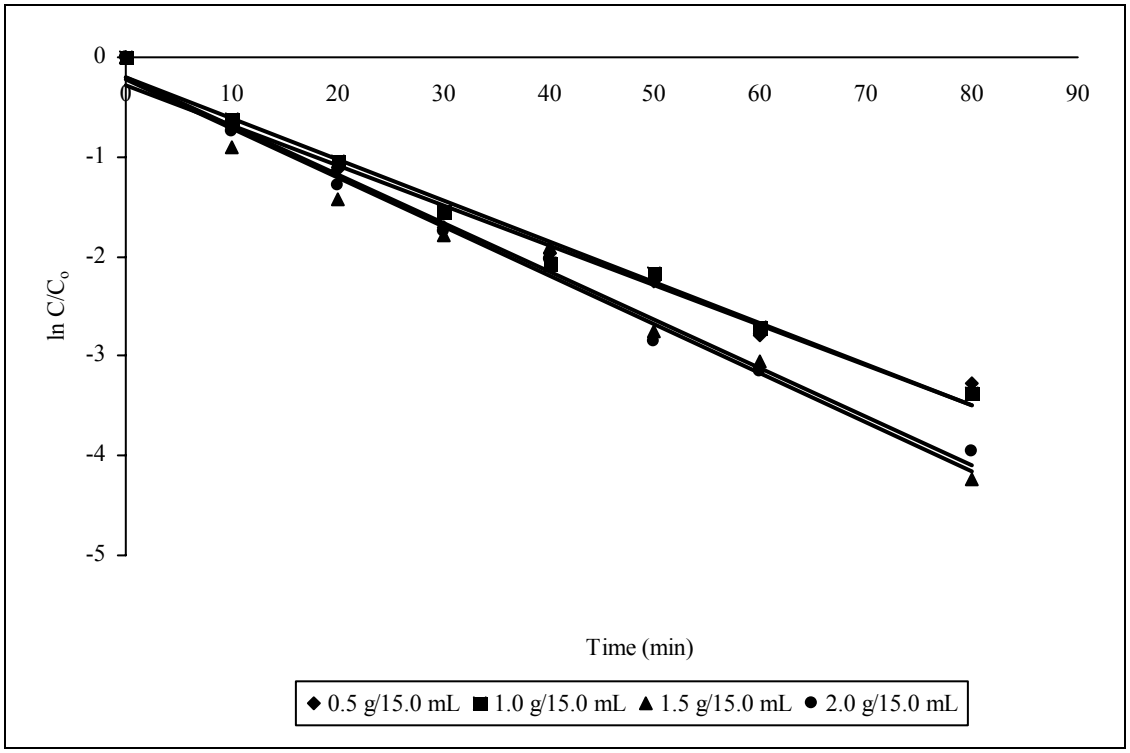

Figure 4: Graph of first-order kinetics of Methylene Blue removal for the effect of suspension loading in the preparation of immobilised TiO_2/AC conducted on 5 pieces of glass slides in 200 ml of 10 ppm Methylene Blue solution at 28 ºC under UV illumination (1 ultraviolet lamp).

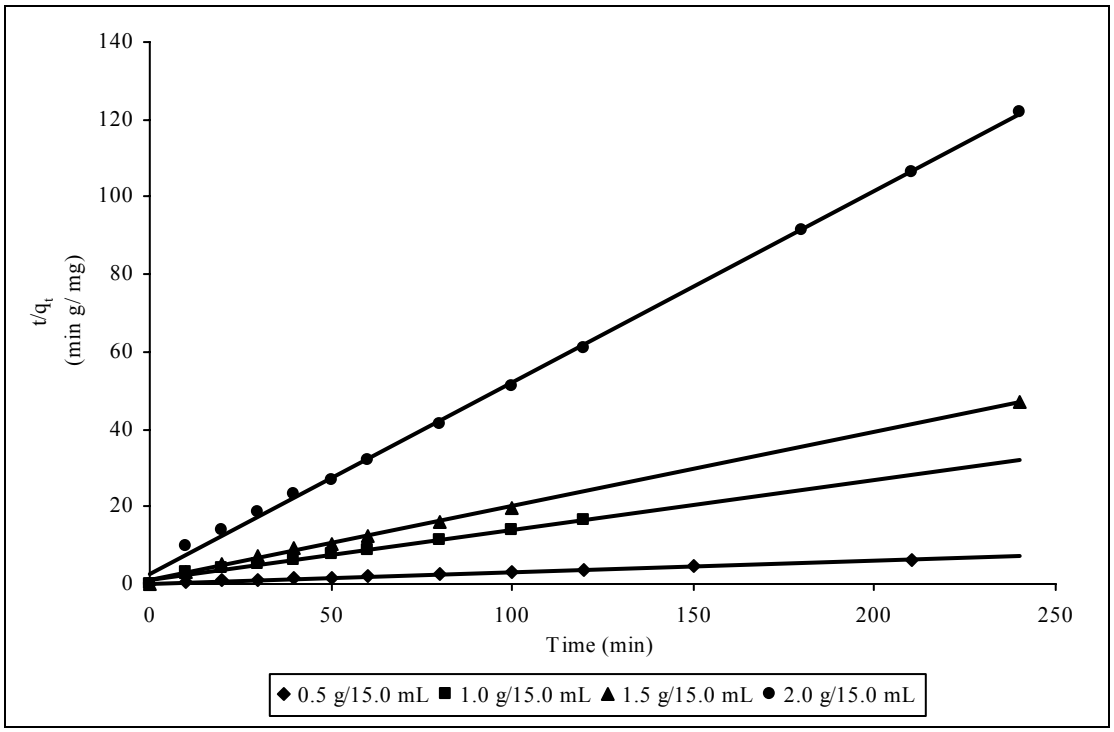

Figure 5: Graph of pseudo-second-order kinetics of Methylene Blue removal for the effect of suspension loading in the preparation of immobilised TiO_2/AC conducted on 5 pieces of glass slides in 200 ml of 10 ppm Methylene Blue solution at 28 ºC under UV illumination (1 ultraviolet lamp).

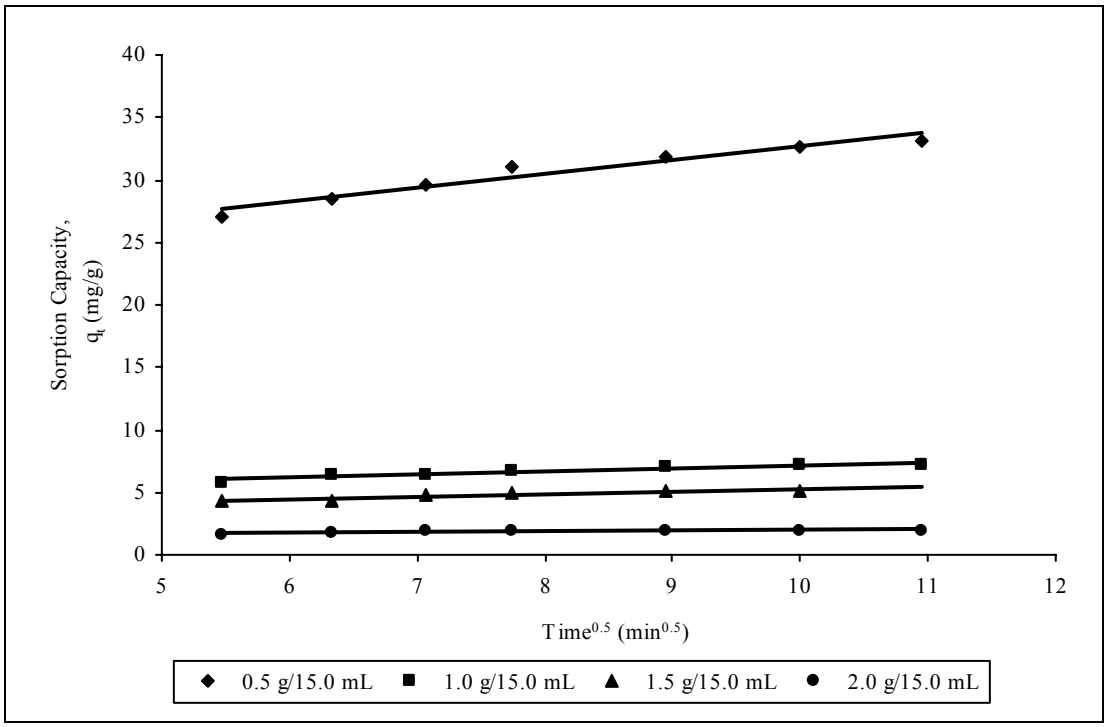

Figure 6: Graph of intraparticle diffussion of Methylene Blue for the effect of suspension loading in the preparation of immobilised TiO_2/AC conducted on 5 pieces of glass slides in 200 ml of 10 ppm Methylene Blue solution at 28 ºC under UV illumination (1 ultraviolet lamp).

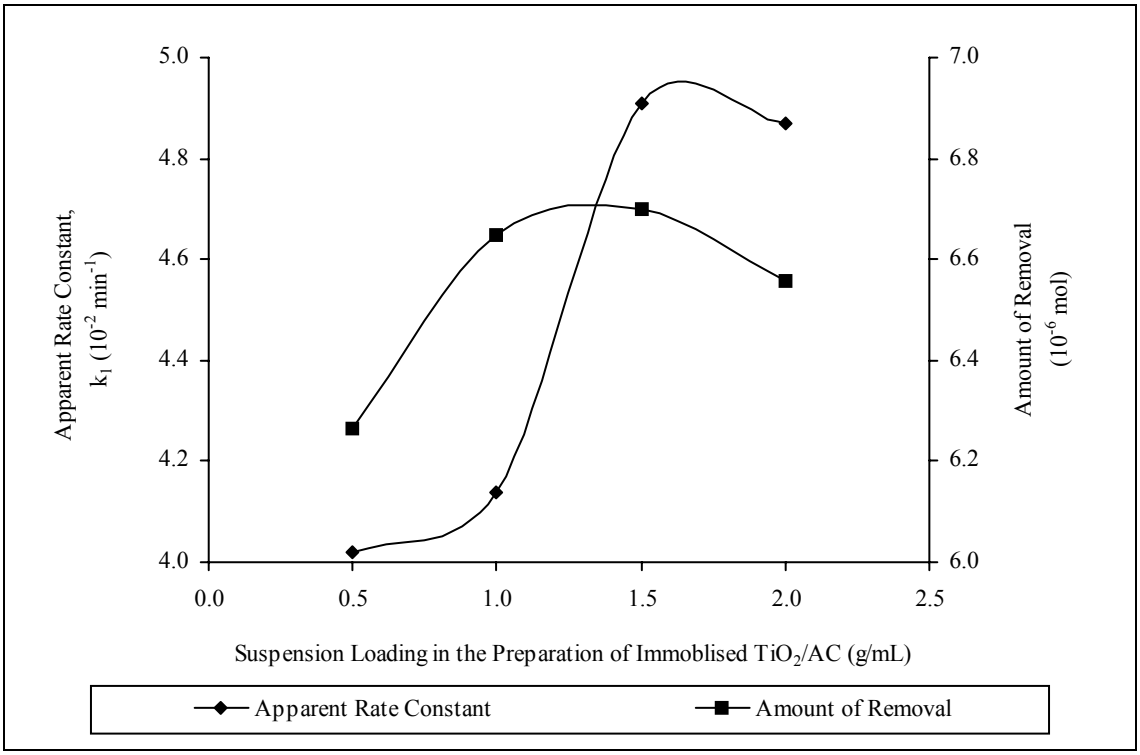

Figure 7: Graph of apparent rate constant and amount of removal versus suspension loading in the preparation of immobilised TiO_2/AC in the removal of Methylene Blue.

Table 1: Parameters for the effect of suspension loading in the preparation of immobilised TiO_2/AC in the removal of Methylene Blue.

m (g /15.0 mL)	First-order Kinetics		Pseudo-second-order Kinetics				Intraparticle Diffusion	
	r_1^2	k_1 ($x10^{-2}$ min^{-1})	r_2^2	q_2 (mg/g)	k_2 ($x10^{-2}$ g/mg per min)	h (mg/g per min)	r_i^2	k_i (mg/g per $min^{0.5}$)
0.5	0.9767	4.02	0.9979	34.2466	0.43	5.01	0.9429	1.1008
1.0	0.9856	4.14	0.9917	7.7220	1.49	0.89	0.8947	0.2577
1.5	0.9797	4.91	0.9987	5.2219	4.00	1.09	0.8762	0.1962
2.0	0.9873	4.87	0.9990	2.0247	9.06	0.37	0.8076	0.0582

Conclusion

Combination of activated carbon and titanium dioxide has proven to be efficient in removing dye molecules compared with neat TiO_2 and neat AC. Moreover, shorter time frame is required in achieving saturation when TiO_2/AC is applied to the dye removal system. TiO_2/AC is able to remove 95.50% of Methylene Blue whereas activated carbon gives 74.33% efficiency and the dye removal by TiO_2 only shows 46.60%. The dye removal system is initialized by the adsorption of Methylene Blue on activated carbon followed by a mass transfer to titanium dioxide to photodegrade the dye molecules. The removal rate of Methylene Blue was affected by the suspension loading used and the removal of this dye followed pseudo-second-order chemical reaction kinetics model in which best correlation coefficients were shown.

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References

1. S., Qourzal, A., Assabbane, Y., Ait-Ichou (2004). Synthesis of TiO_2 via Hydrolysis of Titanium Tetraisopropoxide and its Photocatalytic Activity on a Suspended Mixture with Activated Carbon in the Degradation of 2-naphthol. J. Photochem. Photobio. A: Chem. 163:317-321.
2. N., Takeda, N., Iwata, T., Torimoto, H., Yoneyama (1998). Influence of Carbon Black as an Adsorbent Used in TiO_2 Photocatalyst Films on Photodegradation Behaviors of Propyzamide. J. Catal. 177:240-246.
3. R., Yuan, R., Guan, J., Zheng (2005). Photocatalytic Degradation of Methylene Blue by a Combination of TiO_2 and Activated Carbon Fibers. J. Colloid Interface Sci. 282:87-91.
4. E., Carpio, P., Zúñiga, S., Ponce, J., Solis, J., Rodriguez, W., Estrada (2005). Photocatalytic Degradation of Phenol Using TiO_2 Nanocrystals Supported on Activated Carbon. J. Mol. Catal. A: Chem. 228:293-298.
5. B., Tryba, A.W., Morawski, M., Inagaki (2003). Application of TiO_2-mounted Activated Carbon to the Removal of Phenol from Water. Appl. Catal. B: Environ. 41:427-433.
6. J.-M., Herrmann, J., Matos, J., Disdier, C., Guillard, J., Laine, S., Malato, J., Blanco (1999). Solar Photocatalytic Degradation of 4-chlorophenol Using the Synergistic Effect Between Titania and Activated Carbon in Aqueous Suspension. Catal. Today 54:255-265.
7. 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.
8. P., Fu, Y., Luan, X., Dai, X. (2004). Preparation of Activated Carbon Fibers Supported TiO_2 Photocatalyst and Evaluation of its Photocatalytic Reactivity. J. Mol. Catal. A: Chem. 221:81-88.
9. S., Gelover, P., Mondragón, A., Jiménez (2004). Titanium Dioxide Sol-gel Deposited Over Glass and its Application as a Photocatalyst for Water Decontamination. J. Photochem. Photobio. A: Chem. 165:241-246.
10. K., Ventaka Subba Rao, A., Rachel, M., Subrahmanyam, P., Boule (2003). Immobilization of TiO_2 on Pumice Stone for the Photocatalytic Degradation of Dyes and Dye Industry Pollutants. Appl. Catal. B: Environ. 46:77-85.
11. V.K.S., Rao, M., Subrahmanyam, P., Boule (2004). Immobilized TiO_2 Photocatalyst During Long-term Use: Decrease of its Activity. Appl. Catal. B: Environ. 49:239-249.
12. N., Serpone, E., Borgarello, R., Harris, P., Cahill, M., Borgarello, E., Pelizzetti (1986). Photocatalysis Over TiO_2 Supported on a Glass Substrate. Sol. Energy Mater. 14:121-127.
13. Y.S., Ho, G., McKay (1999). A Kinetic Study of Dye Sorption by Biosorbent Waste Product Pith. Resour. Conserv. Recycl. 25:171-193.