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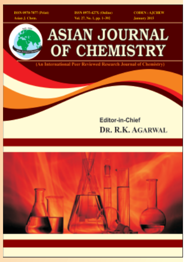

Photocatalytic Degradation of Methylene Blue and Phenol Using TiO_2/Activated-Carbon Composite Catalysts

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Photocatalytic degradation of methylene blue and phenol were conducted separately in aqueous solutions using titania-activated carbon composites. Activated carbon composites of different textural features and light of different wavelength or energy were used in order explore their effects on the performance of titania-activated carbon catalysts. The catalysts (TiAC1, TiAC2 and TiAC3) were prepared by impregnating activated carbon supports with an aqueous suspension of titanium precursor (TiO_2). The catalysts were characterized using BET, XRD and FTIR. The diffraction pattern showed strong peaks that are assigned to titanium anatase phase and weaker peaks that indicated low rutile phase. The FTIR showed broad peaks of Ti-O-Ti linkages in TiO_2 particles. The photocatalytic degradation of methylene blue and phenol was performed separately in visible light and UV irradiation of different wavelengths. Adsorption was dominant in the case of methylene blue removal while photodecomposition was more pronounced in the case of phenol removal.

Keywords: Phenol, Methylene blue, Photocataysis, Titania, Precursors, Activated carbon.

INTRODUCTION

Photocatalytic degradation is of great interest for researchers due to its promising efficient removal of pollutants in water and wastewater treatment processes. Heterogeneous photocatalysis had been extensively studied to degrade or remove wide variety of pollutants in water[1]. UV-irradiated titanium dioxide, in intimate contact with an aqueous solution of organic pollutants, develops a redox environment leading to their total decomposition into harmless substances such as CO_2 and water[2]. The basic mechanism of heterogeneous photocatalysis had been well established[3]. TiO_2 has an appropriate energetic separation between its valance and conduction bands, the valance band and the conduction band energies are estimated to be +3.1 and -0.1 eV, respectively, which means its band gap energy, is 3.2 eV and therefore absorbs in the near UV range ($\lambda < 387$ nm). Photocatalytic degradation reactions are initiated when a photon of energy higher or equal to the band gap energy is absorbed by a semiconductor such as TiO_2, thereby promoting an electron from the valence band to the conduction band with simultaneous generation of a positive hole (h^+) in the valence band[4]. Most of the e^- and h^+ recombine in a few nanoseconds and the energy is dissipated as heat. Only few of the electrons and holes migrate to the surface of the catalyst. In an aqueous suspension, positive holes (h^+) react with the adsorbed water and ^-OH groups to give strong oxidizing hydroxyl radicals. In addition, the free electrons react with adsorbed molecular oxygen to produce O_2^- superoxide anion that may also contribute to the production of more hydroxyl radicals through the formation of $^{\bullet}OH$ radicals and H_2O_2. The reaction of $^{\bullet}OH$ radicals with the organic pollutant is a key reaction step leading to mineralization of these compounds. The electron hole recombination slows down the photodegradation process. It was also established that the oxidizing species ($^{\bullet}OH$) generated by the photocatalyst does not migrate very far from the active center of the TiO_2 and therefore degradation takes place virtually on the catalyst surface[5].

Several attempts have been made to improve the photoefficiency of TiO_2. Doping with ions was reported to have an inhibiting effect due to increase in the electron-hole recombination[6]. In mixing TiO_2 with inorganic co-adsorbent such as silica, alumina and zeolite to enhance photodegradation, it was reported that photogenerated oxidizing species cannot migrate from the original sites to the co-adsorbent to react there with adsorbed pollutant molecule[7]. Ultimately, enhancing the photodegradation process needed optimum adsorption strength on the co-adsorbent and photon energy in its initiation of electron photoexcitation and generation of radicals. Activated carbon support has been used and reported as promising in photodegradation of pollutants. A mixture of activated carbon and TiO_2 has been reported to have a synergistic effect on the photodegradation of organic pollutant[8-11], porosity of activated carbon leads to high adsorption of pollutants on the catalyst surface, which might accelerate the process of decomposition through the transfer of the adsorbed pollutants to the titania active sites. A variation in photon intensities and wavelength or energy has been reported to influence photodecomposition of phenolic compounds, photon of higher energy of illumination was found to be more effective in pollutant decomposition[12].

It has been generally recognized that the presence of surface defects are important for initiating the photocatalytic reactions[13-18]. This is also directly associated with populations of hydroxyl group, surface oxygen and impurities in the catalyst. These and the redox cycle of titanium (Ti^{4+} and Ti^{3+}) as shown below are essential for efficient photocatalysis.

$$TiO_2 + UV \rightarrow TiO_2\ (e^- + h^+) \quad (1)$$

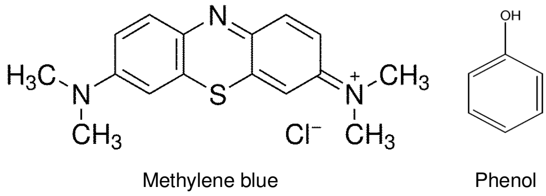
surface active OH^- react with the hole to form an electron donor $^{\bullet}OH$ radicals.

$$h^+ + OH^-_{ad} \rightarrow {}^{\bullet}OH_{ad} \quad (2)$$

$$h^+ + H_2O_{ad} \rightarrow {}^{\bullet}OH_{ad} + H_2 \quad (3)$$

$$2Ti^{4+} + O^{2-}(\text{colloid}) \xrightarrow{UV} \text{anion vacancy} + 2Ti^{3+} + ½O_2 \quad (4)$$

In this work, titanium oxide-based catalyst of three different activated carbon supports were prepared and tested for the decomposition of both facile (methylene blue) and refractory (phenol) pollutants under visible light and UV of different wave lengths ($\lambda = 254$ and 365 nm). Fig. 1 shows the chemical structure of methylene blue and phenol. Different degree of adsorption and photodecomposition were observed. The objective of this study is to determine the role of activated carbon features and light of different wavelength or energy on photocatalytic degradation, with the view to have an insight toward improving its efficiency.



Methylene blue Phenol

Fig. 1. Chemical structures for methylene blue and phenol

EXPERIMENTAL

Reagent grade chemicals were used as purchased without further purification. Titanium dioxide powder and phenol crystals (BDH chemicals limited, Poole, England), methylene blue (Sigma Aldrich, Germany) and the desired concentrations were prepared using distilled water. Spent carbons from refinery were used as activated carbon supports.

Catalyst preparation: The catalysts were prepared by impregnating titania on activated carbons of different surface areas and porosities. A measured amount of TiO_2 to obtain 5 wt % active components on each of the activated carbon support was used. In each case, the TiO_2 suspension in water was mixed with the activated carbonand continuously stirred while evaporating at about 70 °C. The evaporated solid was further dried at 110 °C overnight. It was then calcined in air at 500 °C for 1 h. In the subsequent discussions, the catalysts are referred to as TiAC1, TiAC2 and TiAC3.

Catalysts characterization: The catalysts were characterized by X-ray diffraction (XRD) using a Philips PW1710 powder diffraction with CuK_α radiation (40 % KV, 40 mA) at a scan rate (2θ) of 0.02/s. The Brunauer-Emmett-Teller (BET) surface area and total pore volume were measured using Quantachrome Autosorb-1 nitrogen adsorption apparatus. All samples were degassed at 300 °C for 4 h prior to the measurement. The FTIR spectra of samples in KBr matrix were obtained using Perkin Elmer FTIR spectrum 2000 spectrometer. Mass and energy changes profiles were observed using thermogravimetric analyser SDT 2960, at heating rate of 10 °C/min until maximum temperature of 1000 °C.

Adsorption and photodegradation: The photocatalytic activities of the prepared catalysts were evaluated in a Chromato-vue C-70G viewing system reactor (Ultra violet products, Inc., San Gabriel, CA, USA). At the top portion, it is fitted with visible light and UV lamps which emits UV light at 254 or 365 nm. The reactions were conducted using dissolved oxygen. At room temperature, solubility of oxygen from air is about 8 mg/L. Therefore, the reactor content was vigorously stirred so that oxygen is continuously replenished to maintain its level in the reaction mixture. This also kept the catalyst particles dispersed. Physical adsorption (in the absence of light, later referred to as "no light"or NL) and photodegradation with artificial visible light (VL) or UV light at 254 or 365 nm were performed at room temperature and neutral pH conditions for 1 h. 50 mg of each catalyst was placed in 250 mL beaker containing 150 mL aqueous solution (30 ppm) of either methylene blue or phenol. A 5 mL aliquot was sampled at 15 min intervals. It was centrifuged for 90 min at 1000 rpm. Prior to the analysis, the supernatant was filtered using a millipore membrane filter (0.45 μm). The absorbance of (methylene blue at $\lambda_{max} = 665$ nm and phenol at $\lambda_{max} = 268.4$ nm) the samples were measured using a UV-visible Spectrometer, Perkin Elmer, USA.

RESULTS AND DISCUSSION

Table-1 shows the surface area and total pore volume of the titania-based catalysts, both the surface area and the porosity of the catalysts in ascending order are: TiAC1 < TiAC2 < TiAC3. Fig. 2a shows the XRD profile of the samples and Fig. 2b shows the XRD profile for the activated carbon supports before adding the catalysts. Anatase phase of titania could be observed at 2θ of 25 and 48 on all the samples[19,20]. In addition to anatase, phases evolve at 2θ of 27.5 and 36 due to treatment at 500 °C, new solid solution could be developed[21]. Fig. 3a shows the FTIR spectra of the samples and Fig. 3b shows the FTIR spectra for the activated carbon supports before adding the catalysts. Bands at 3429 and 1630 cm^{-1} are assigned to surface adsorbed water and hydroxyl group[22]. Broad bands at 1000-500 cm^{-1} are attributed to Ti-O-Ti linkages[23] in TiO_2.

Fig. 4a-c shows methylene blue removal in terms of C/C_o for all the catalysts. In control experiment with no light, the removal due to physical adsorption of methylene blue on TiAC1 was about 69 % after 1 h. The combination of both physical adsorption and UV decomposition (UV254 and

TABLE-1
SURFACE AREAS AND TOTAL PORE VOLUMES FOR THE CATALYSTS

Catalyst	Surface area (m^2/g)	Total pore volume (cm^3/g)
TiAC1	41.47	0.01276
TiAC2	204.1	0.06095
TiAC3	1060	0.3265

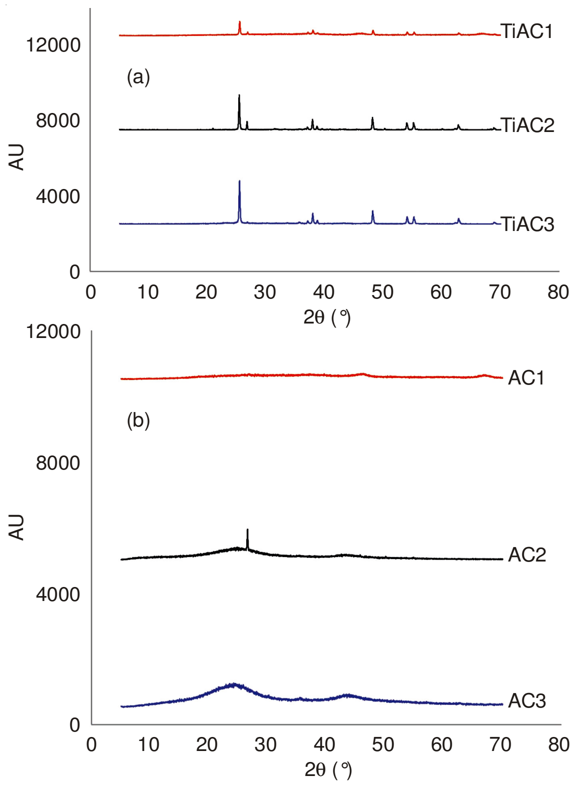


Fig. 2. (a) XRD profile of the catalyst with the three activated carbon supports (b) XRD profile of the three activated carbon supports before adding the catalysts

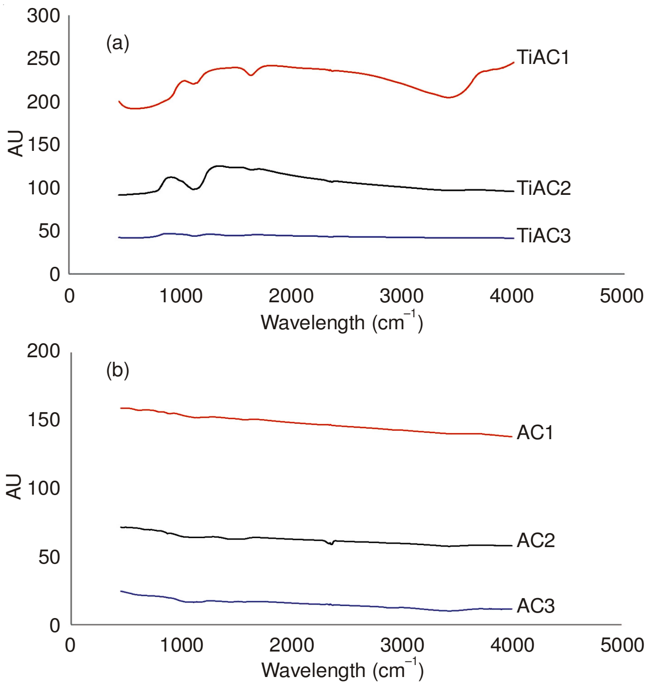


Fig. 3. (a) FTIR spectra of the catalyst with the three activated carbon supports (b) FTIR spectra of the catalyst with the three activated carbon supports

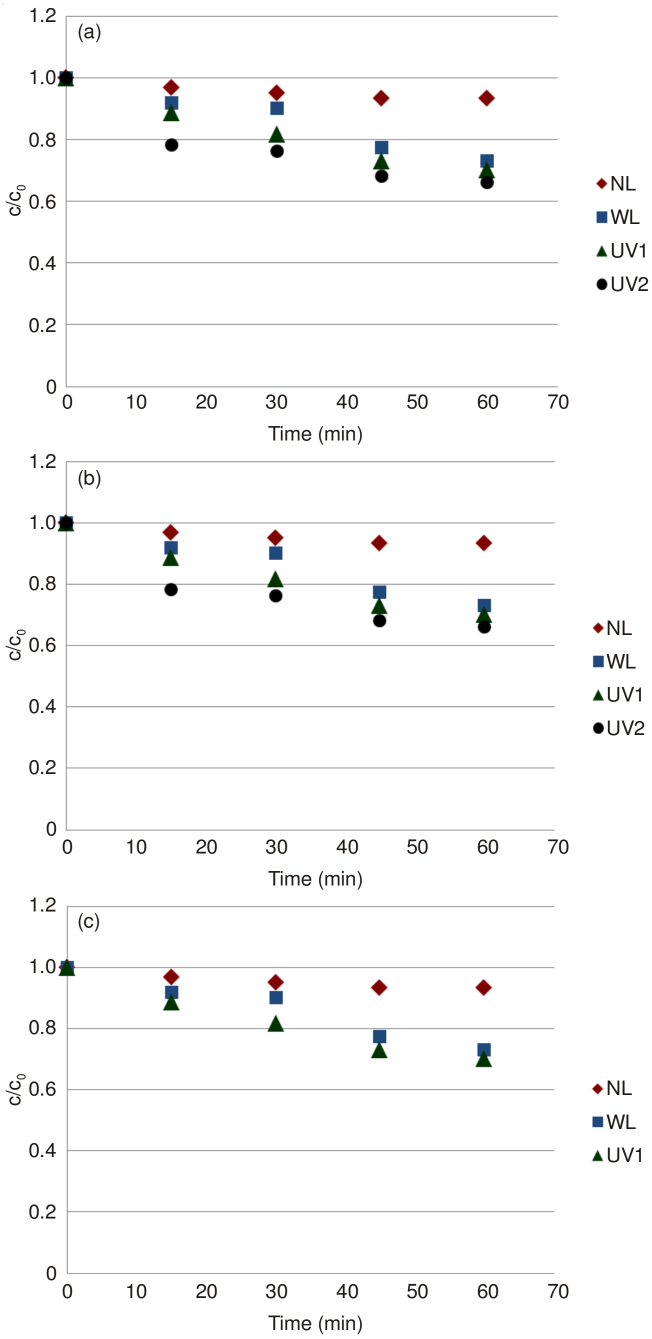


Fig. 4. (a) Methylene blue removal using TiAC1 catalyst (b) methylene blue removal using TiAC2 catalyst (c) methylene blue removal using TiAC3 catalyst

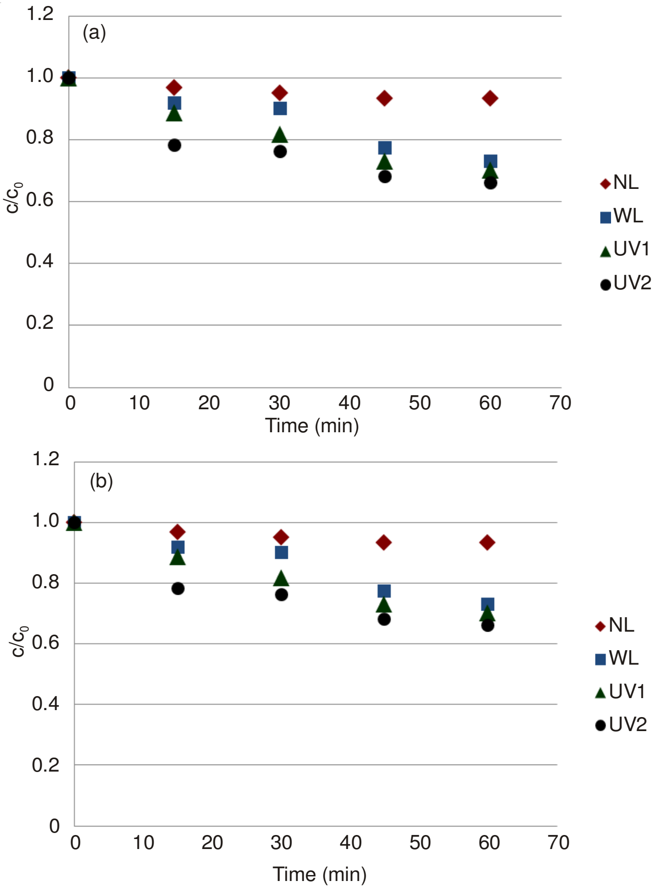
and 365 nm) yielded as high as 78 %. The removal due to physical adsorption of methylene blue on TiAC2 was about 83 % after 1 h, the combination of adsorption and photodecomposition in the presence of UV at different wavelengths was insignificant with only 84 %. Similar trend was observed on TiAC3 with 98 % physical adsorption and 99 % photodecomposition with only UV at 254 nm. This is an indicative of high strength of adsorption on TiAC2 and TiAC3 catalysts as shown by high values of adsorption rate constant (Tables 3b and 4b), which is in agreement with their large surface area and porosity as shown in the in the BET result. Strongly adsorbed pollutants (larger molecular size) may block further adsorption or limit penetration depth of UV photons as in this case where the removal is dominated by physical adsorption. This is contrary to earlier report that shows synergy between physical adsorption and chemical decomposition, the results of this work showed that adsorption must be limited to avoid shielding of photon from reaching the titania active sites.

In addition to methylene blue, removal and photodecomposition of phenol-a refractory organic compound was also demonstrated as shown in Fig. 5a-c. Similar removal due to physical adsorption of 7 and 8 % were obtained on TiAC3 and TiAC2, respectively, but TiAC1 removed up to 11 % of phenol. Under UV irradiation (UV 365 nm) an improvement in the removal due to photodecomposition of 25.6, 34 and 54 % was observed on TiAC1, TiAC3 and TiAC2, respectively. This is in line with the increase in the rate constant upon irradiation as shown in Table-2. Similarly, activated carbon as additive to titania in the photodegradation of organic pollutants has been found to improve photocatalytic activities[8-11].

TABLE-2
APPARENT REACTION RATE CONSTANT (k_{app}, min^{-1})
FROM THE LANGMUIR-HINSHELWOOD MODEL
FOR DECOMPOSITION OF PHENOL (eqn. 6)

	TiAC1		TiAC2		TiAC3	
	k_{app}	R^2	k_{app}	R^2	k_{app}	R^2
NL	0.001	0.952	0.002	0.966	0.001	0.869
VL	0.003	0.896	0.004	0.931	0.005	0.953
UV1	0.010	0.248	0.004	0.973	0.006	0.972
UV2	0.016	0.497	0.005	0.935	0.008	0.803

NL = Experiment in dark room, no light, or NL, VL = visible light, UV = Ultravoilet at 254 or 356 nm



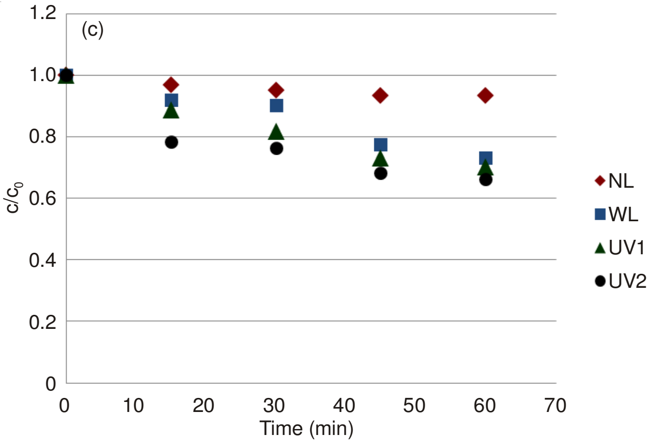


Fig. 5. (a) Phenol removal using TiAC1 catalyst (b) phenol removal using TiAC2 catalyst (c) phenol removal using TiAC3 catalyst

The removal of both methylene blue and phenol reached equilibrium in about 1 h. The efficiencies of the catalysts were further, compared at 15 min of the start of the removal as shown in Figs. 6 and 7. In the absence of UV irradiation, the catalysts shows methylene blue removal of 51.53, 62 and 97.48 % on TiAC2, TiAC1 and TiAC3, respectively (Fig. 6). UV irradiation on both TiAC1 and TiAC2 shows a significant removal of 75.6 and 84.97 %, respectively, while on TiAC3 removal due to photodecomposition was insignificant. Fig. 7 shows only 2.73, 3.2 and 3.3 % phenol removal by physical adsorption on TiAC1, TiAC3 and TiAC2, respectively. Under UV irradiation

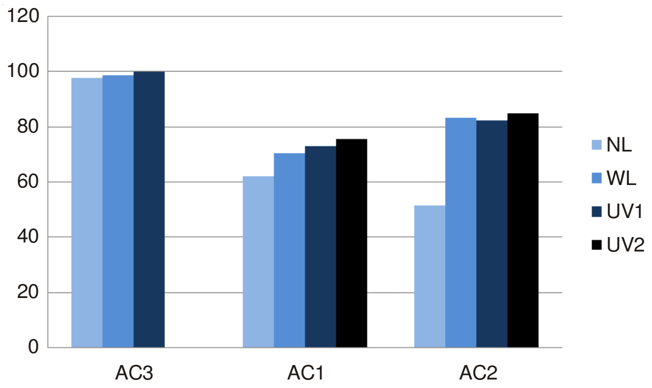


Fig. 6. Efficiencies of the catalysts in removing methylene blue at 15 min

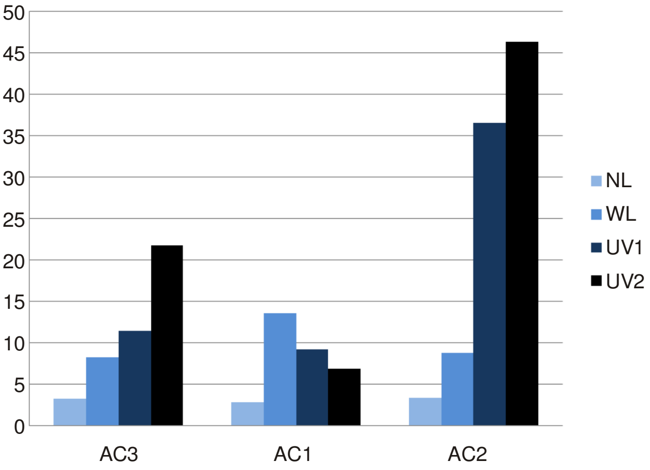


Fig. 7. Efficiencies of the catalysts in removing phenol at 15 min

(365 nm) an improvement of 17.43, 21.67 and 46.3 % was observed on TiAC1, TiAC3 and TiAC2, respectively. There were improvements either with visible light or UV of different wave length, which implies the effectiveness of photon energy in activating the titanium surface to generate radicals that leads to decomposition of the adsorbate.

Although irradiation with UV increases methylene blue removal the effect of difference in photon energy or UV wavelength is lower on the removal. Furthermore, once the physical adsorption of methylene blue reaches about 70 %, the UV irradiation is ineffective in providing additional removal due to chemical decomposition. This implies that high adsorption leads to coverage of the titanium-phase from photons thereby hindering the catalyst reaction, which is contrary to earlier report that suggested synergy between physical adsorption and photodecomposition.

Based on the well known assumptions, the model relate rate of adsorption and/or reaction (r) with the concentration of the adsorbate (C) as follows:

$$r = -\frac{dC}{dt} = \frac{k_r K_{ad} C}{1 + K_{ad} C} \tag{5}$$

where k_r and K_{ad} are constants; indicating rate of reaction and rate of adsorption, respectively. For systems with weak adsorption and/or low reactant concentrations, the equation can be modified and linearized as follows:

$$\ln\left(\frac{C}{C_o}\right) = -k_r K_{ad} C = -k_{app}\, t \tag{6}$$

where k_{app} is the apparent rate constant. Both the methylene blue and phenol data were fitted to eqn. 6. The model was found to be inadequate in describing the methylene blue removal data, indicative of strong adsorption. On the other hand, the phenol results give statistically acceptable regressions as shown in Table-3. In all cases, it shows very low reaction rate under dark condition. There are significant increases in the reaction rates with increase in the light wavelength. This indicates the dominant effect of phenol removal due to photocatalytic reaction rather than physical adsorption.

TABLE-3a
FIRST ORDER KINETIC DATA FOR ADSORPTION OF PHENOL ON A SAMPLE OF THE CATALYSTS

	TiAC1		TiAC2		TiAC3	
	K_2	R^2	K_2	R^2	K_2	R^2
NL	0.067	0.927	0.061	0.813	0.044	0.999
VL	0.142	0.937	0.057	0.922	0.037	0.807
UV1	0.027	0.954	0.029	0.978	0.049	0.921
UV2	0.034	0.993	0.057	0.953	0.057	0.913

TABLE-3b
FIRST ORDER KINETIC DATA FOR ADSORPTION OF METHYLENE BLUE ON A SAMPLE OF THE CATALYSTS

	TiAC1		TiAC2		TiAC3	
	K_2	R^2	K_2	R^2	K_2	R^2
NL	0.106	0.981	0.076	0.891	0.02	0.852
VL	2.37	0.949	0.085	0.733	0.016	0.836
UV1	0.085	0.562	0.067	0.501	6.915	1.000
UV2	0	–	0.156	0.912	–	–

As indicated above, removal of methylene blue could not be described by Langmuir-Hinshelwood adsorption-reaction model, when adsorption was neglected. Therefore, the dominance of physical adsorption is evaluated. The physical adsorption mechanism is explored using well known pseudo-first-order kinetic model of Lagergren and second order kinetics model. The first order is given as

$$\frac{dq_t}{dt} = k_1\,(q_e - q_t) \tag{7}$$

Eqn. 7 may be integrated from initial condition at t = 0 and when the amount adsorbed, $q_t = 0$ to any time t and any value of q_t, gives

$$\ln\,(q_e - q_t) = \ln q_e - k_1 t \tag{8}$$

where q_e is the amount adsorbed at equilibrium and k_1 is the rate constant for pseudo first-order adsorption (min^{-1}).

The second order model is represented as

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \tag{9}$$

this can be rearranged as:

$$\frac{dq_t}{\left(d_e - q_t\right)^2} = k_2 dt \tag{10}$$

and in integrated form using the same condition as indicated in the case of first-order, gives

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{11}$$

k_2 is the rate constant for second-order adsorption (g mol^{-1} min^{-1}). The data of methylene blue and phenol removals were fitted to both eqns 7 and 9. The pseudo-second-order kinetic model was found to describe the data better (Table-4).

TABLE-4a
SECOND ORDER KINETIC DATA FOR ADSORPTION OF PHENOL ON A SAMPLE OF THE CATALYSTS (k_2, g mol^{-1} min^{-1})

	TiAC1		TiAC2		TiAC3	
	K_2	R^2	K_2	R^2	K_2	R^2
NL	0.017763	0.965	0.011079	0.805	0.045406	0.967
VL	0.009894	0.941	0.044669	0.997	0.002556	0.851
UV1	0.312331	1.000	0.004335	0.916	0.004526	0.941
UV2	0.03485	0.999	0.019045	0.989	0.013676	0.982

TABLE-4b
SECOND ORDER KINETIC DATA FOR ADSORPTION OF METHYLENE BLUE ON A SAMPLE OF THE CATALYSTS (k_2, g mol^{-1} min^{-1})

	TiAC1		TiAC2		TiAC3	
	K_2	R^2	K_2	R^2	K_2	R^2
NL	0.011773	0.990	0.048014	0.999	0.371368	1.000
VL	1.6335	1.000	0.131639	0.999	0.4250	1.000
UV1	0.204188	0.999	0.111009	0.999	0.5880	1.000
UV2	0.753923	1.000	0.178349	1.000	–	–

Conclusion

Photocatalytic decomposition of methylene blue and phenol has been demonstrated separately on titanium activated carbon composites, the degree of photocatalytic removal of methylene blue was insignificant with high level of physical adsorption of the catalysts. Therefore adsorbent-adsorbate pair with low physical adsorption exhibited more effective photocatalytic decomposition. Photocatalytic removal of methylene blue was less due to its higher adsorption on all the catalysts as shown by its high adsorption rates constants, while in the case of phenol there was a significant increase in the reaction rates constants on illumination, which is an indicative of removal due photocatalytic decomposition. Therefore, the phenol data was found to be well fitted to Langmuir-Hinshelwood reaction model, when physical adsorption was assumed to be negligible. Methylene blue was dominantly removed by physical adsorption and hence the adsorption mechanism was better described by pseudo-second-order adsorption rate. From this study the degree of photocatalytic decomposition of either methylene blue or phenol depended on the adsorbent-adsorbate pair adsorption strength, which needed to be low enough to allow for efficient photon energy reaching the titania active sites to effect photolysis.

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