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Photodegradation of Methylene Blue Mediated by Rice Husk Ash (RHA)-TiO$_2$ Composite

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Abstract

A photo-catalytic composite material incorporating rice husk ash (RHA) and TiO$_2$ (RHA:TiO$_2$ = 75:25 and 50:50) has been developed and used to investigate the photodegradation of the well-known dye pollutant, methylene blue (MB). Photodegradation was monitored in the dark and under illumination using a halogen lamp as well as sun light to facilitate photodegradation. Both the dark reaction and photo- mineralization processes were evaluated in terms of kinetic study which revealed the validation of first-order kinetics. A parallel measurement of chemical oxygen demand (COD) was also performed for a better understanding of the degradation process. The higher degradation rate in the sun light offers an easy-to-use and environment friendly approach for the treatment of dye stuffs. However, the overall phototdegradation mechanism involved the participation of both the anodic (h^+ consumption) and cathodic (e^- consumption) processes which were responsible for the degradation of MB and consumption of dissolved oxygen respectively.

Key words: Photo-degradation, Composite plate, Rice husk ash, Methylene blue, Adsorption.

Introduction

Serious water pollution caused due to direct discharge of various industrial wastes, particularly dye pollutants, has been recognized as a threat to the environment. This has prompted researchers throughout the world to develop new, efficient and cost-effective cleaning technologies for the treatment of waste water containing dye stuffs. Dyes are extensively used in textile, leather, newsprint recycling and the dye-house wastewater usually comprises various dyes, which are toxic and harmful for both human and aquatic lives. Hence, before discharging into the environment, treatment of dye waste water is an important issue (Malik, 2003, Suteu and Biba, 2005, Zheng *et. al.,* 2007, Mahmoodi and Arami, 2009, Mahmoodi and Arami, 2008, Arami *et. al.* 2008). Due to its stable nature and presence of large degree of organics in the dye stuffs, conventional physico-chemical and biological treatment procedures often become less effective to remove them from water (Malik, 2003). Although simple adsorption process and membrane separation technology are still preferred by the researchers for the treatment of dye waste water, the technological improvement of such processes will no doubt be highly beneficial.

Application of photo-catalytic method has become the state-of-the-art in treating a variety of environmental problems (Gaya and Abdullah, 2008, Rajeshwar *et. al.* 2001, Fujishima *et. al.* 2000, Fujishima and Zhang, 2006). This method has already been recognized as an alternative but attractive and efficient pathway for water purification because of its simple and easy-to-use facility. In this process the non hazardous semiconductor photo- catalyst is sensitized by the natural UV component of the sunlight or a UV source to initiate the degradation process. The photo-catalyst is usually applied in suspended (Rashed, and El-Amin, 2007, Sauer *et. al.* 2002) or in immobilized form (Mahmoodi and Arami, 2009, Ahmed, 2003, Bhattacharyya *et. al.,* 2004, Kuo and Ho, 2006). Although the suspended system provides large surface area of the catalyst to precede the reaction with high efficiency, the separation and recycling of the catalyst after the treatment becomes difficult. This problem has been minimized by using the photo-catalyst in the immobilized form. However, to diversify the range of photo-sensitized degradation process, a number of products (tiles, glass, ceramic balls etc.) with photo-catalytic property have been developed for

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environmental applications (Fujishima *et. al.* 2000, Fujishima and Zhang, 2006).

Bangladesh is a developing country where discharge of industrial waste is a major problem and most of the industries are directly releasing the unwanted toxic, hazardous wastes into the rivers and or in nearby ponds. The increasing urbanization and industrialization in Bangladesh have negative impact for water quality and at present it has reached to an alarming proportion (Chowdhury, and Clemett, 2006, Sultana *et. al.* 2009). In this research work an attempt has been made to develop a simple but highly active and environment friendly process for the treatment of industrial waste water which is expected to have a greater impact in the economic development of the country. Primarily, photo-catalyst incorporating low cost composite material has been developed which can be used to treat industrial waste water before flushing to the environment. Since rice husk ash (RHA) is a waste material and acts as an adsorbent (Malik,2003, Mahvi *et. al.* 2004), the approach was to use RHA with TiO_2 (Degussa P25, one of the most active photo-catalyst) to develop such composite material to follow the degradation and adsorption of the pollutants. To examine the efficacy of this newly developed composite material methylene blue (MB) [Alzaydein, 2009, Mills and Wang, 1999] was treated using halogen lamp and sun light. Since no high temperature is required to produce the photo-catalytic composite material and the sun light initiates the photo-sensitized reaction, this method is expected to be beneficial in two ways: (i) easy-to-use procedure for dye waste water treatment, and (ii) utilization of RHA is a promising material recycling technology for future waste management.

Materials and Methods

Chemicals

MB and TiO_2 were obtained from Aldrich and Degussa respectively; RHA was collected from local rice mill which was a waste product obtained through uncontrolled burning in the mill. All the solutions of desired concentrations were prepared using double distilled water.

Fig. 1: Photograph of RHA-TiO_2 (top - 25% TiO_2, bottom - 50% TiO_2) composite

Preparation of RHA-TiO_2 composite photo-catalytic material

RHA-TiO_2 photo-catalytic composite materials were prepared by a simple method. A requisite amount of RHA was mixed with TiO_2 maintaining the photo-catalyst ratio at 0%, 25% and 50%. It was then mixed thoroughly in a ball mill under aqueous suspended condition. After completing the ball mill operation the mixture was heated at 10^oC just to evaporate the excess water and ~ 5.0 mL of sodium silicate solution was added to it as the binder. The mixture was then shaped into 5.0 cm x 5.0cm x 0.625 cm rectangular size using mold and dried at ambient temperature. A pressure of 3 ton was applied to make it in compact form and final product was obtained by further heating at 10^oC for an hour. Figure 1 shows the photograph of these finished composites.

Adsorption of MB (dark reaction)

Since adsorption phenomenon is an important parameter in the photo-catalytic process, prior to the photo-degradation study, the dark reaction of MB in the presence of RHA-TiO_2 composite was carried out at an initial dye concentration of $1.0x10^{-5}$ mol dm^{-3} in monomer form (Mills and Wang, 1999). This monomeric form of MB exhibits the absorption maximum at ~660nm. The composite was placed vertically into the pyrex reactor (10 cmx10 cmx10cm) containing 100 mL MB solution and was kept in the dark for 2½ hrs followed by measuring the residual dye concentration at a regular time interval of 30 mins.

Treatment of model dye pollutant using RHA-TiO_2 composite

The photodegradation of MB was investigated using the same pyrex reactor and the composite was placed vertically into the reactor as described in the previous section. 1.0 $x10^{-5}$ mol dm^{-3} aqueous solution of MB was chosen for the treatment providing indoor illumination through a halogen lamp while the sun light facilitated the out door irradiation. An infrared filter filled with ultra-pure water was used to avoid heating of the reactor during irradiation and this also defined the wavelength of the illumination source as between 200 - 800 nm. Maximum illumination was achieved by using a focusing lense. A magnetic stirrer was used to facilitate continuous stirring of the substrate solution during reaction. For both cases the fate of the photodegradation reactions were monitored as a function of time using the RHA composite

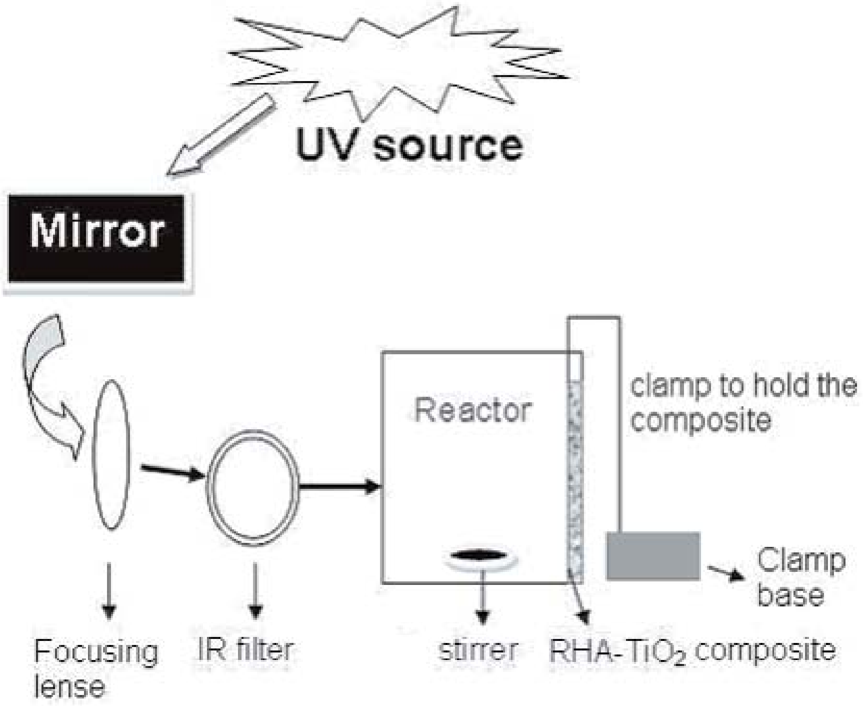

Fig. 2: Schematic of the photo-catalytic experimental set up

plate containing 0% TiO_2, 25 % TiO_2 and 50% TiO_2 as photo-catalyst. Chemical oxygen demand (COD) of the on going photo-process was measured by using the potassium dichromate method (Taicheng *et. al.* 2001). Figure 2 shows the schematic diagram of the experimental set up. The intensity of the halogen lamp and sun light was determined by potassium ferrioxalate actinometry method (Hatchard and Parker, 1956).

Method of analyses

The molar extinction co-efficient of MB at 660 nm is 10^5 $dm^3\ mol^{-1}\ cm^{-1}$ (Mills and Wang, 1999). The concentration of the residual dye at the time interval (t) was obtained by measuring the absorbance at λ_{max}=660 nm using the UV/visible spectrophotometer. The performance of the composite material toward the dark and illumination reactions was monitored in terms of percent of degradation according to the following equation:

$$\text{\% of adsorptial or degradtion} = \frac{C_0 - C_1}{C_0} \times 100 \tag{1}$$

where C_o = initial concentration and C_t = concentration at time t

However, in case of the dark reaction the amount of MB adsorbed per unit mass (q_t, mg g^{-1}) was calculated as,

$$q_t = \frac{C_0 - C_1}{m}\ V \tag{2}$$

where, m = mass of the composite (25 g) and V = volume of MB solution (100 mL).

The kinetics of the adsorption was investigated due to its importance in waste water treatment process. Hence the adsorption kinetics was interpreted in terms of both first-order rate equation based on the solution concentration (Equation 3) and pseudo-second-order kinetic model based on the sorption equilibrium capacity (Equation 4) (Bhakat *et. al.* 2006).

$$\text{In} = \frac{C_0}{C_t} = k_1 t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_2 q_e^2} \tag{4}$$

where, k_1 (min^{-1}) and k_2 (g µ g^{-1} min^{-1}) are the first-order and pseudo-second-order rate constants respectively, q_e = amount of MB adsorbed after reaching the equilibrium (µ g g^{-1}).

However, on the other hand it is well known that TiO_2 sensitized complete photo-degradation process occurs *via* the simultaneous oxidation (h^+ consumption) and reduction (e^- consumption) reactions at the excited catalyst surface. The photogenerated h^+ reacts with H_2O resulting the strong oxidizing agent $OH^\bullet$ radical (standard redox potential +2.8 V) which actively decomposes MB to the mineral end products. While the photogenerated e^- reacts with the dissolved oxygen producing super oxide anions which also participates in the degradation process as shown in equation (7).

The overall degradation of MB proceeds through the following reaction,

$$C_{16}H_{18}N_3SCl + 25.5\,O_2 \xrightarrow{h\nu + T_iO_2} HCl + H_2SO_4 + 3HNO_3 + 16CO_2 + 6H_2O \tag{5}$$

where, anodic and cathodic reactions can be expressed as follows:

Anodic (oxidation) reaction: $h^+ + H_2O \rightarrow H^+ + OH^\bullet \rightarrow$ Degradation of MB (6)

Cathodic (reduction) reaction:

$$e^- + O_2 \rightarrow O_2^{-\bullet} \rightarrow H_2O_2 \rightarrow H_2O \tag{7}$$

It is clear from the above degradation stoichiometry that to complete the reaction, 25.5 molecule of O_2 reacts with per MB molecule, which also ensures the simultaneous consumption of dissolved oxygen throughout the degradation process. Previous investigation (Mills and Wang, 1999) also discussed that for complete mineralization of 1.0×10^{-5} mol dm^{-3} aerated MB solution, all the dissolved oxygen (2.5×10^{-4} mol dm^{-3}) present in the solution was required. Simultaneous consumption of oxygen during the photodegradation of 4-chlorophenol has also been reported by others (Ahmed, 2003, Fonseca *et. al.* 2004, Fonseca *et. al.* 2003). However, the possible reaction mechanisms which contribute the degradation of MB is a combination of oxidation and reduction processes involving (i) direct oxidation of MB by hydroxyl radical (h^+ consumption), and (ii) reduction of oxygen by the superoxide anion (e^- consumption). Hence, the overall degradation process will be a combination of anodic and cathodic (oxidation and reduction) reactions. Considering this critical point, MB degradation and oxygen consumption were monitored with time and the data were analyzed through the apparent first-order rate equation (equation 8) which is the simplified form of Langmuir-Hinshelwood kinetic model (Rashed *et. al.*,2007).

$$\ln\frac{C_0}{C_t} = k_{app}\, t \qquad (8)$$

Where k_{app} is the apparent first-order rate constant (min^{-1})

Results and Discussion

Analysis of RHA

The major elemental composition of RHA was determined by conventional methods which revealed the presence of SiO_2 (91.3%), Al_2O_3 (0.15%), Fe_2O_3 (0.12%), CaO (0.21%), MgO (0.31%), Na_2O (1.52%), K_2O (2.65%), TiO_2 (0.15%), SO_3 (0.24%) and loss on ignition (2.7%) (Farooque, 2006). This RHA is porous in nature which is responsible for its high specific surface (Farooque, 2006). For this reason RHA was chosen with TiO_2 to develop the highly efficient photocatalytic composite material to treat the dye pollutants.

Adsorption of MB

The adsorption efficiency of the composite is shown in Fig. 3. It is clearly evident from Fig. 3 that the adsorption process increased linearly up to 1½ hrs then reached the equilibrium by 2½ hrs time.

The kinetics of adsorption process was analyzed through the first- and second-order adsorption kinetic models (Equations 3 and 4). The experimental data plotted in the graphs as shown in Figs. 4a and 4b respectively. For both models the corresponding adsorption parameters were derived from the respective slopes and intercepts which are summarized in Table I. The calculated regression values (R^2) in Table I shows that the first-order kinetics describe the adsorption phenomenon better than that of the pseudo second-order kinetic model.

Photodegradation of MB without TiO_2

The observed percent of photodegradation of MB in the presence of only RHA (i.e. 0% TiO_2) was very close to that

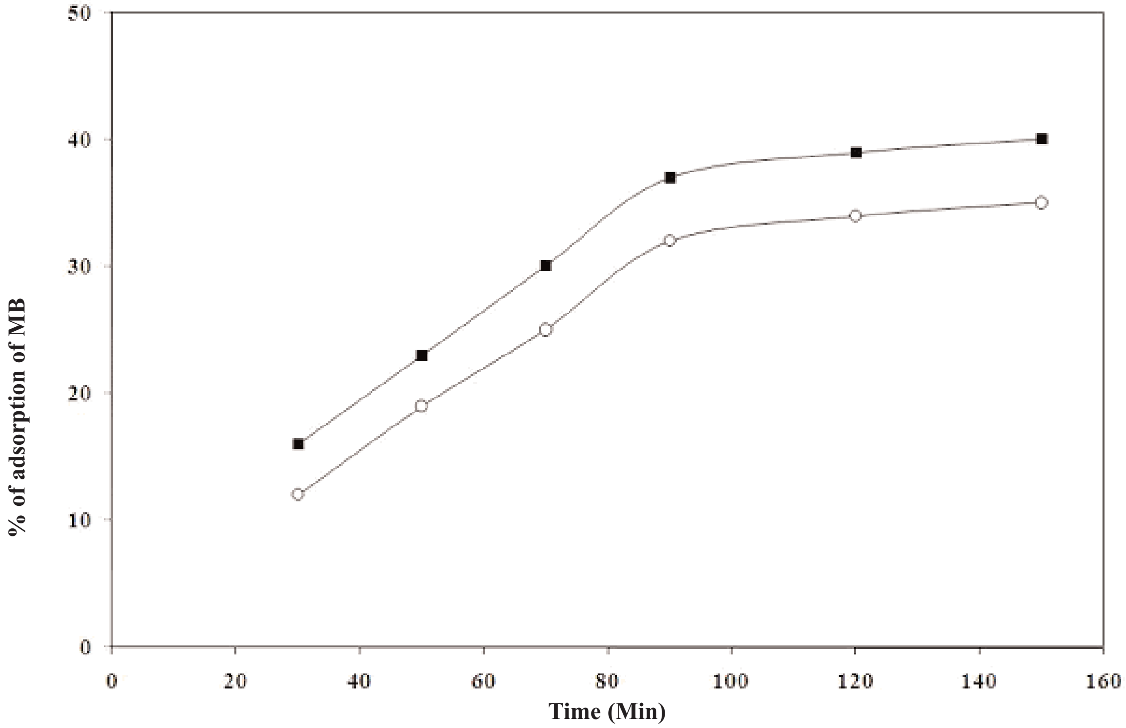

Fig. 3: % of adsorption of MB on RHA-TiO_2 composite (○= 25% TiO_2 and ■ = 50% TiO_2).

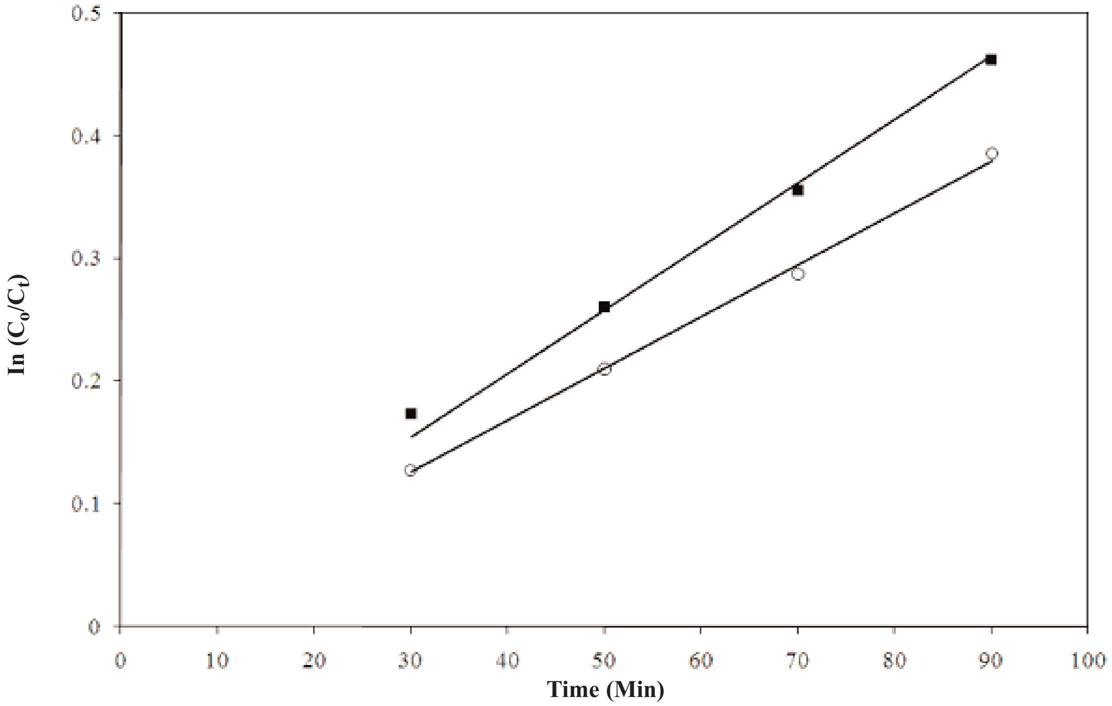

Fig. 4a: First-order adsorption kinetics of MB on RHA-TiO$_2$ composite (○= 25% TiO$_2$ and ■= 50% TiO$_2$).

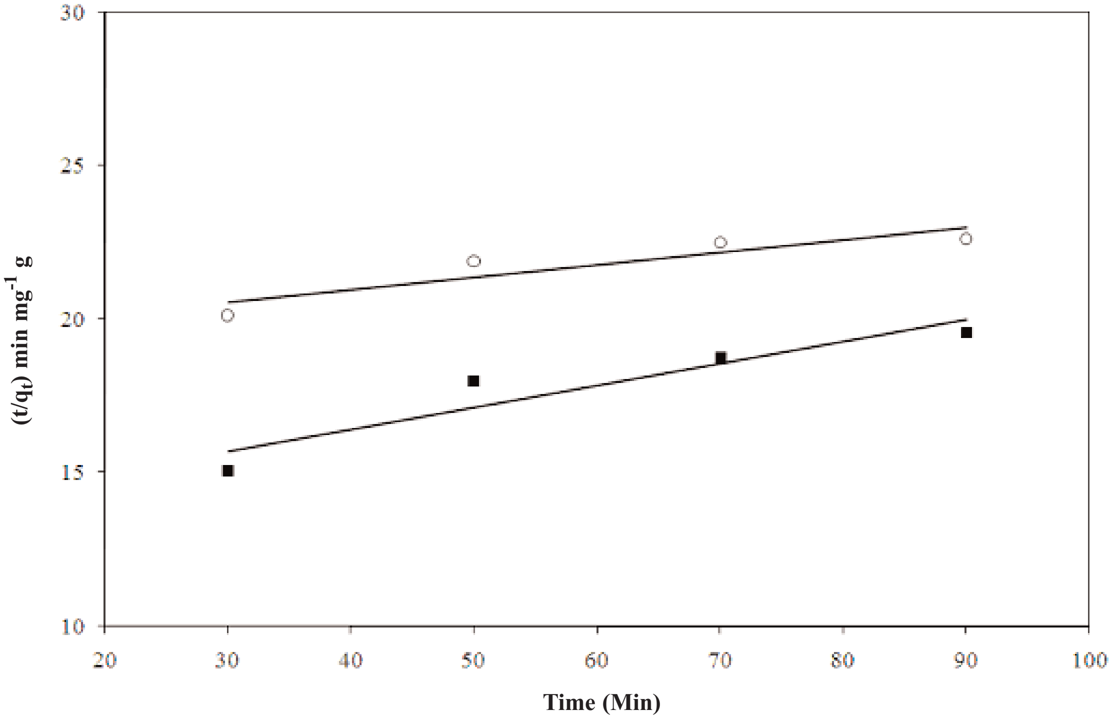

Fig. 4b: Pseudo-second-order adsorption kinetics of MB on RHA-TiO$_2$ composite (○= 25% TiO$_2$ and ■= 50% TiO$_2$).

Table I: Adsorption kinetic parameters.

% of TiO_2 in composite plate	First-order kinetics		Pseudo-second-order kinetics		
	Rate constant k_1 (min^{-1})	R^2	q_e $\mu g\ g^{-1}$	Rate constant k_2 ($g\ \mu g^{-1}\ min^{-1}$)	R^2
25	0.004	0.997	25.0	8.26×10^{-5}	0.821
50	0.005	0.991	14.08	3.71×10^{-4}	0.878

value as observed in case of the adsorption or dark reaction. This indicated that even though illumination was facilitated, the percent of degradation of MB did not increase from that adsorption value due to the absence of TiO_2.

Photodegradation of MB in the presence of TiO_2

Upon illumination the photogenerated h^+ being a very strong oxidizing agent started decomposing MB promptly. The percent of photodegradation of MB at the RHA-TiO_2 composite (containing 25% and 50% TiO_2) was recorded as a function of time and the resulting graphs are shown in Fig. 5. In case of both the illumination sources (halogen lamp, intensity 1.68×10^{16} q cm^{-3} s^{-1} and sun light, intensity 4.94×10^{16} q cm^{-3} s^{-1}) the observed photodegradation increased with reaction time and the corresponding plots showed a rapid increase in degradation up to 1½ hrs, then the rate of the reaction became slow. It is evident from the Fig. 5 that although both indoor and out door illumination favoured the photo-degradation process, yet the effect of different irradiation sources is a major factor, since the photo-generation of e^-/h^+ pair depends on the energy of the source light. Hence, the treatment procedure using the sun light having an effective intensity of 4.94×10^{16} q cm^{-3} s^{-1} resulted a high degradation as observed in previous study performed by Rashed *et. al.*, 2007. In-order to further examine the activity of the developed composite, percent of COD consumption was measured only for the case of MB degradation under sun light using RHA-TiO_2 (50%) composite and based on Equation (1) and the corresponding graph (Figure 5) showed that the percent of COD consumption followed similar trend to that of the MB degradation percent. However, it is evident

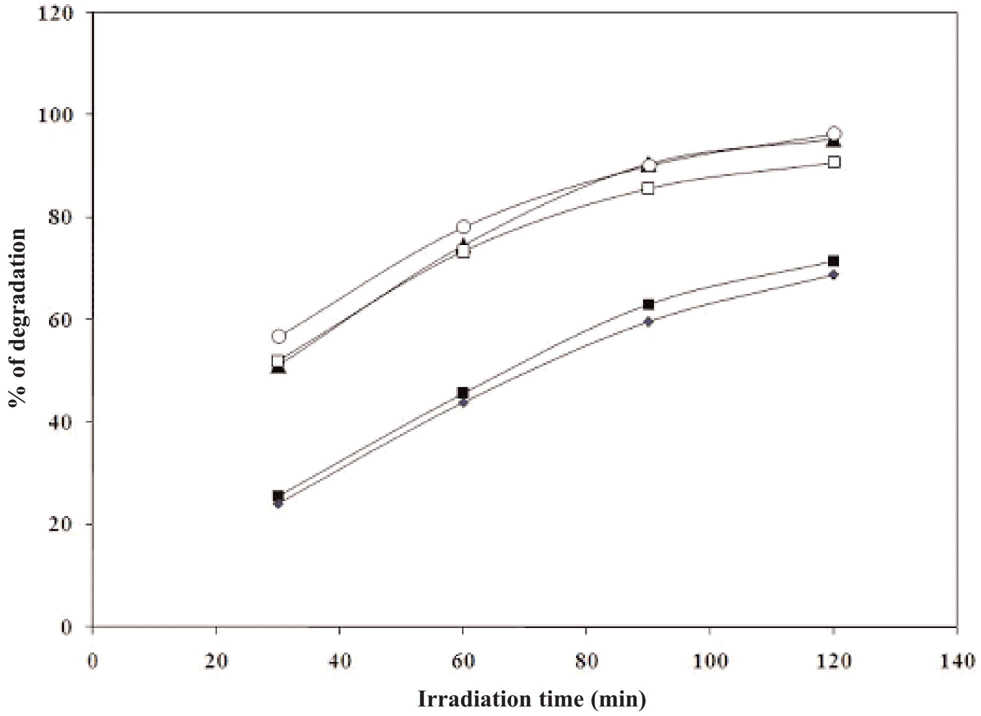

Fig. 5: % of degradation of MB and O_2 on RHA-TiO_2 composite (MB degradation under halogen lamp using 25% TiO_2 =u, and 50% TiO_2 =n MB degradation under sun light using 25% TiO_2 =s, and 50% TiO_2 = O.   = O_2 consumption under sun light using 50% TiO_2).

from Fig. 5 that the degradation percentage of MB is slightly higher than that of COD removal percentage. The experimental data for MB degradation (h^+ consumption by anodic reaction) and oxygen depletion (e^- consumption by cathodic reaction) were interpreted in terms of first-order kinetic model as discussed in the previous section. For both cases, the plots of ln (C_0/C_t) vs time (Fig. 6) resulted in straight lines as expected and the gradients of these plots upon linear regression equals the apparent first-order rate constants which are summarized in Table II. The rates of the photo-processes were obtained using the following equation:

$$\text{rate} = \text{gradient}\ [C_0] \qquad (9)$$

It is clear from the data of Table II that in case of MB degradation (using 50% RHA-TiO_2 composite and sun light), the observed degradation rate is 2.6×10^{-7} mol dm^{-3} min^{-1} while the corresponding oxygen consumption rate is 5.6×10^{-6} mol dm^{-3} min^{-1} which is almost 22 fold higher. This indicates that to decompose one MB molecule 22 molecule of oxygen was required. This value is very close to the theoretical value (Equation 5) which showed that 25.5 molecule of oxygen is consumed per MB molecule decomposition. The discrepancy between the theoretical and observed value could be due to the involvement of various unknown intermediates in the oxidative photo-destruction of MB, since it adsorbs on the surface of the adsorbent (Rashed *et. al.*,2007). The observed depletion in dissolved oxygen concentration indicated that the presence of oxygen is necessary for a photodegradation reaction. Thus the photodegradation reaction must proceed towards the mineral end products through the participation of both anodic and cathodic reactions.

It is obvious from the present results that the efficiency of the composite material toward adsorption and photo-mineralisation of MB, achieved by using RHA-TiO_2 (either 50% or 25% TiO_2) were almost same under the present experimental condition. However, further work is needed to optimize the photodegradation experimental protocol with regard to catalyst dose, initial concentration, pH of the solution etc. and works in this direction are in progress.

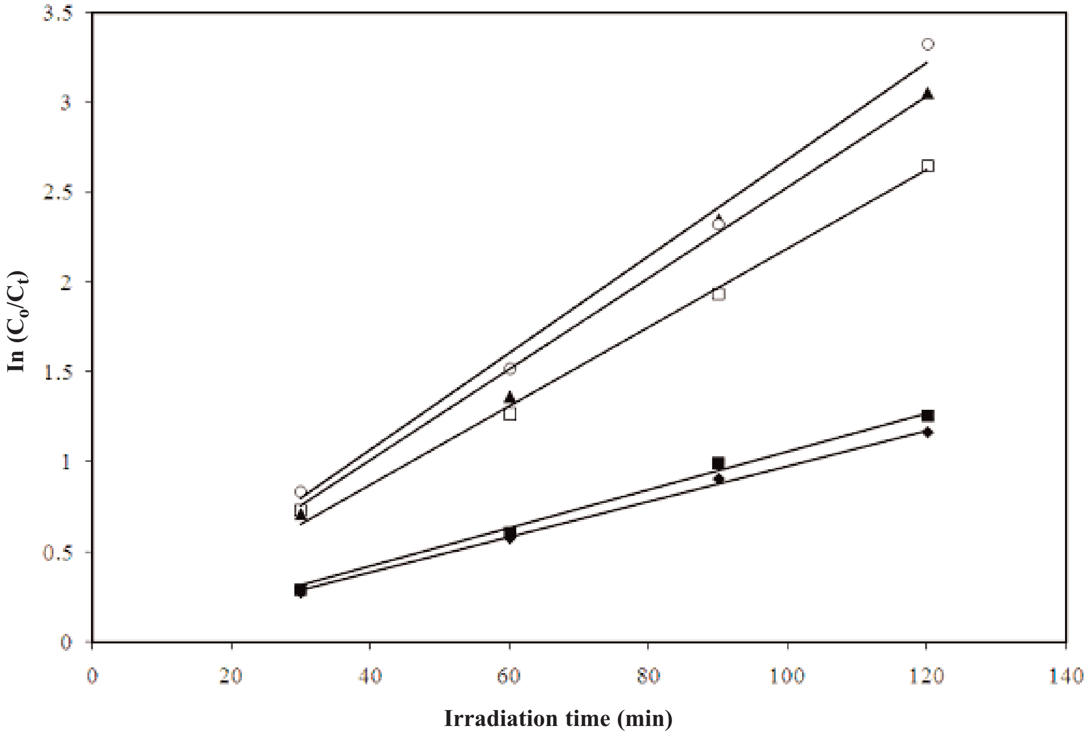

Fig. 6: First-order photo-degradation kinetics of MB degradation and O_2 consumption on RHA-TiO_2 composite (MB degradation under halogen lamp using 25% TiO_2 =u, and 50% TiO_2 = n. MB degradation under sun light using 25% TiO_2 =s, and 50% TiO_2 = O. = O_2 consumption under sun light using 50% TiO_2)

Table II: First-order kinetic parameters for MB degradation and O_2 consumption.

% of TiO_2 in composite material	Halogen lamp			Sun light		
	Rate constant k_{app} (min^{-1})	Degradation rate ($mol\ dm^{-3}\ min^{-1}$)	R^2	Rate constant k_{app} (min^{-1})	Degradation / consumption rate ($mol\ dm^{-3}\ min^{-1}$)	R^2
	Degradation of MB ($C_0 = 1.0\ x10^{-5}\ mol\ dm^{-3}$)					
25	0.009	$9.0x10^{-8}$	0.997	0.025	$2.5x10^{-7}$	0..990
50	0.01	$10.0x10^{-8}$	0.993	0.026	$2.5x10^{-7}$	0..991
				Consumption of O_2 ($C_0 = 2.5\ x\ 10^{-4}\ mol\ dm^{-3)}$		
				0.022	$5.6x10^{-6}$	0.995

Conclusion

The developed cost-effective RHA-TiO_2 composite material effectively treats MB the well known representative of the polluting dye stuffs. Both adsorption and photo-catalytic destruction revealed that this could be a potential approach in treating the industrial waste water which will have a great impact in the economic development of the country. The experimental value of MB photodegradation and O_2 consumption rates showed simultaneous involvement of h^+ (oxidation of MB through anodic process) and e^- (reduction of O_2 through cathodic process) during the photo-degradation process. However, to optimize this technology, effect of various parameters *i.e.* dose of the photo-catalyst, pH of the solution, concentration of the substrate etc. need to be considered.

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