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PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE IN AQUEOUS SOLUTIONS BYTIO$_2$-SIO$_2$ CATALYST

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Abstract

The research was aimed at studying the Photocatalytic decompositions of methylene blue (MB) in aqueous solutions using titanium-based catalyst.. The catalyst was prepared by supporting titanium (IV) oxide on Silica (SiO_2). The physicochemical characteristic of the catalyst was obtained using Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD) and Fourier Transform infrared spectroscopy (FTIR). The diffraction patterns showed strong peaks that are assigned to titania anatase phase and weaker peak(s) that indicated low rutile phase. The FTIR spectra showed broad peaks of Ti-O-Ti linkages in TiO_2 particles. The catalyst was tested in visible light or UV irradiation at 254 nm or 365nm and was found to be active in the decomposition of Methylene blue from aqueous solutions. The kinetic of decomposition of MB was evaluated and found to be better represented by lagergren pseudo-second order model. The applicability of this model was expressed by the linearized plot of (t/qt) versus t.

Keywords: *Photocatalytic, Methylene Blue, Dye, Degradation, Catalyst*

Introduction

Dyes are the chemicals that are extensively employed to impart colour to various industrial products. After the reactive dyeing process is finished, large part of the dyes is lost in textiles waste water (Zollinger,1991; Vaidya and Datye,1982). The release of this waste water in natural environment is not only hazardous to aquatic life but also in many cases mutagenic to humans (Hao *et al*., 2000 and Boeningo, 1994). Attentions have now been focused on the removal of these toxic wastes (Ollis and Al-Elkabi., 1993; Serphone and Pellizetti ., 1989; Ollis *et al*., 1991; Green and Rudham., 1993).
The traditional treatment of waste water has some limitations. These include cost or formation of hazardous by-products (Patterson, 1985; Autenrieth *et al*., 1991). Biological degradation is cost effective but is usually time consuming (Autenrieth *et al*., 1991) and also some dyes were reported to be biologically resistant (Dai *et al*., 1995; Martin *et al*., 2003; Sarasa *et al*., 1998; Arslan *et al*., 2000).

The traditional waste water treatment plants involve large capital investments and operating costs, resulting to treatment systems which are not proper solutions for small villages that cannot afford such expensive treatment systems (Boeningo, 1994; Jorgensen, 1999). Hence, an alternative method of waste water treatment needs to be developed. Photocatalysis has offered solutions to these problems. Muhammad (2010), has reported the enhancement in photocatalytic activity of Cr (10%)-doped TiO_2 for methylene blue degradation. It was found that 70% of the dye methylene blue could undergo degradation in 240min in the presence of doped catalyst as compared to only 17% degradation in the presence of TiO_2 alone.

Kasanen *et al*, (2011) examined the photocatalytic effect of immersed TiO_2 coating on the degradation of methylene blue in aqueous solution. The percentage of methylene blue degraded during 6 hours UV illumination varied from 80 to 92. The degradation followed pseudo- first order reaction kinetics.

In this study, TiO_2-SiO_2 catalyst was prepared and tested for decomposition of methylene blue under UV irradiation at 254nm. Different degree of decompositions was observed. Our objective was to Study the kinetics of photocatalytic degradation of the organic pollutant.

Materials and Method

Chemicals used in the research such as titanium dioxide, methylene blue and silicon dioxide, were of analar grade and were used without further purification. All glass wares used in this work were well washed with detergent, rinsed with distilled water and dried in an oven at 110^oC. All weighing was done using electric metler balance model AB 54.

Preparation of mixed TiO_2-SiO_2 catalyst

A mixture of 5% TiO_2 (0.42g) and SiO_2 (5g) was suspended in 200cm^3 distilled water. The mixture was continuously stirred while evaporating at about 70 ^oC. The resulting solid was further dried at 110 ^oC overnight and then calcined in air at 500 ^oC for 1hour.

Catalysts characterization

The catalyst synthesised was characterized by X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area and total pore volume measurements and FTIR spectral analysis.

X-ray diffraction analysis

The X-ray diffraction measurements were made using a Philips PW1710 powder diffractometer using Cu Kα radiation at 40mA and 40KV. Samples were run with a continuous scan over the 2θ range of 20-80^o at a scan rate of 0.02/s.

Surface area measurement

The specific surface area of the sample was measured by Brunauer-Emmett-Teller (BET) method using Quantachrome Autosorb-1 nitrogen adsorption apparatus. The sample was degassed at 300 ^oC for 4 hr prior to nitrogen adsorption measurements. The pore size distribution was calculated by applying the Barrett- Joyner-Halenda (BJH) model.

FTIR spectral analysis:

The FTIR spectrum of sample was recorded on Perkin Elmer FTIR spectrum 2000 spectrometer using KBr matrix. The KBr was ground into powder and mixed with the sample. Then, pellet was prepared by pressing the powder at 66,000KPa of pressure using uniaxial press. The background was automatically corrected from the sample spectra by scanning for pure KBr.

Physical Adsorption of Methylene blue (MB)

In order to determine the effect of physical adsorption during the photocatalytic degradation, the initial concentration of the substrate was monitored in the absence of light but in the presence of the catalyst for 1 hour. The adsorption experiments were conducted at room temperature. Generally, 50 mg of catalyst was placed in a beaker containing 150 cm^3 aqueous solution (30 mg/l) of organic compound.. The mixture was magnetically stirred for 1 hour. A 5 cm^3 aliquot was sampled at 15 min intervals, centrifuged for 90 min at 1,000 rpm and filtered using a millipore membrane filter (0.45μm). The absorbance of the sample was measured at 665nm using PYL Unicam SP8-400 UV-visible Spectrophotometer.

Photocatalytic degradation of Methylene blue (MB) using visible light or uv at 254nm or 365nm

The photocatalytic degradation of methylene blue was studied using visible light or uv at 254 or 365nm. The photocatalytic effect was investigated by monitoring the initial concentration of the substrate in the presence of visible or uv lights for 1 hour. The degradation experiments were conducted at room temperature. Certain amount of the catalyst (50 mg) was placed in a beaker containing 150 cm^3 aqueous solution (30 mg/l) of organic compound. The mixture was magnetically stirred for 1 hour. A 5 cm^3 aliquot was sampled at 15 min intervals, centrifuged for 90 min at 1,000 rpm and filtered using a millipore membrane filter (0.45μm). The absorbances of the sample were measured at 665nm using PYL Unicam SP8-400 UV-visible Spectrophotometer.

Results and Discussion

The physicochemical characteristics of the catalysts were determined by Brunauer-Emmett-Teller (BET) surface area measurements, X-ray diffraction (XRD) and FTIR spectral analysis.

Table1 shows the surface area of the TiO_2-SiO_2 catalyst and was determined to be 5.882m^2/g

Table 1: Surface areas of the catalysts

Material	Surface area(m^2/g)
TiO_2-SiO_2	5.882

The FTIR spectrum of the catalyst was measured and the results are presented in Table 2. Bands at 3448cm^{-1}weree assigned to surface adsorbed water and hydroxyl group (Wu *et al., 2004*). Broad band at 798 cm^{-1} are attributed to Ti-O-Ti linkages in TiO_2 ((Zeitler and Brown, 1957). The Bands at 1050cm^{-1} corresponds to the asymmetric stretching vibration of Si-O-Si (Jianjun *et al.*, 2010).

Table 2: The FTIR Spectrum data of the catalyst

Catalyst	V(O-H)cm^{-1}	V(Ti-O-Ti)cm^{-1}	V(Si(Al)-O)cm^{-1}	V(Si-O-Si)cm^{-1}
TiO_2-SiO_2	3448	798		1050

The X-ray diffractions (XRD) of the catalyst was determined and the Diffractogram is as shown in Fig 1.

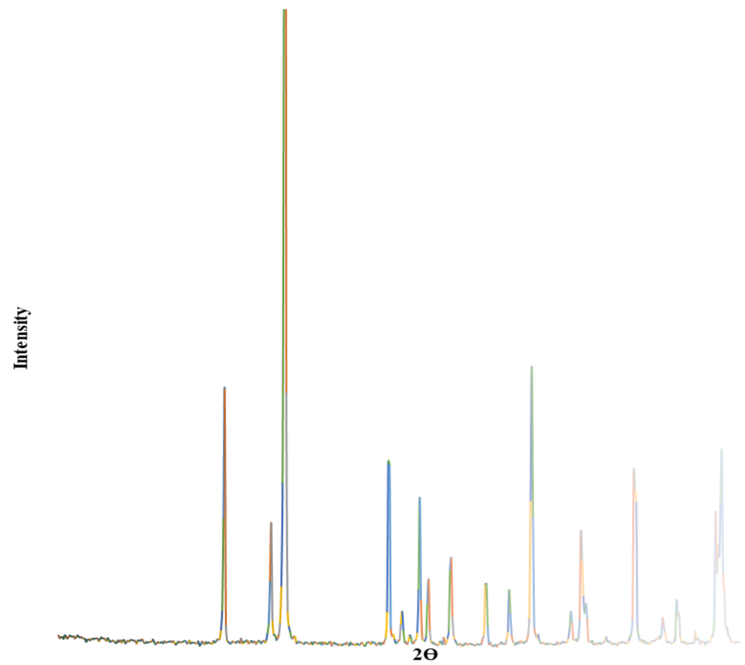

Fig 1: *XRD Diffractogram for the* TiO_2-SiO_2 *catalyst*

The X-ray diffractions (XRD) of the catalyst was measured at scan rate of (2θ) 0.02/s and the profile is shown in Figures 1. The XRD of the catalyst showed peaks at 2θ of 25.29^o, which represent the formation of anatase titania phase (Jianjun *et al*., 2010; Chwei-Huann *et al*., 2007). The catalyst showed peaks at 2θ of 36.45^o, which indicate the formation of rutile phase, the heat treatment at 500 ^{o}C may result in the transformation of the anatase into rutile phase, this is in agreement with the work of Collins-Martinez *et al* (2007), who reported the conversion of anatase titania to rutile phase with temperature.

The profiles for the photodegradation of MB using the catalyst were shown in Fig 2.

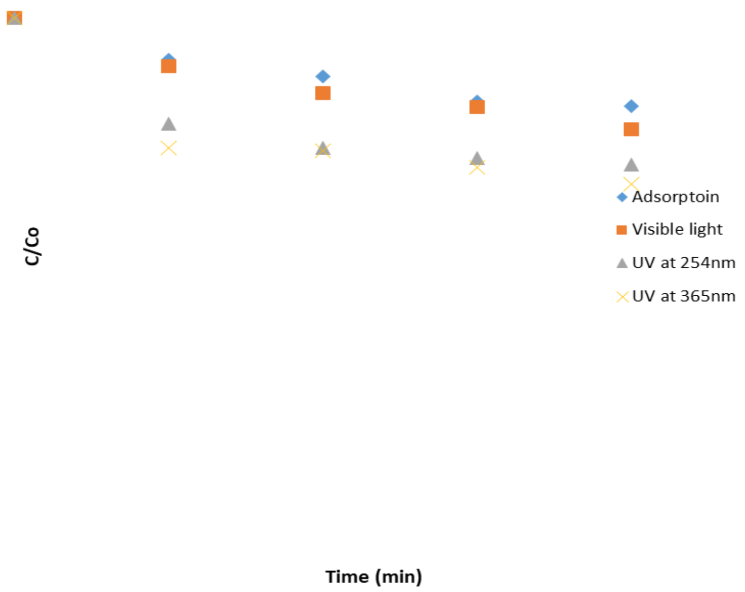

Fig 2: Relative removal of MB using TiO2-SiO_2 *catalyst*

The Photocatalytic activity of the catalyst in the degradation of methylene blue was investigated; the results yield different removal profiles at different light wave length and irradiation time. The removal of methylene blue is represented in term of C/Co (Where Co is the initial concentration and C is the concentration at time t in mg/liter). A plot C/Co against time shows the profile for photocatalytic removal of MB using the catalyst. In the absence of light, the removal due to physical adsorption of MB was very low. Illumination with visible light and UV light at 254 and 365nm, photocatalytically enhances the MB removal. The photocatalytic degradation of MB at 365nm was slightly higher than 254nm. The mineralization rate at 365nm was reported to be slightly higher than at 254 nm, which was attributed to the partial absorption and wasting of light at 254nm by the organic substrate (Venkatachalam *et al*., 2007).

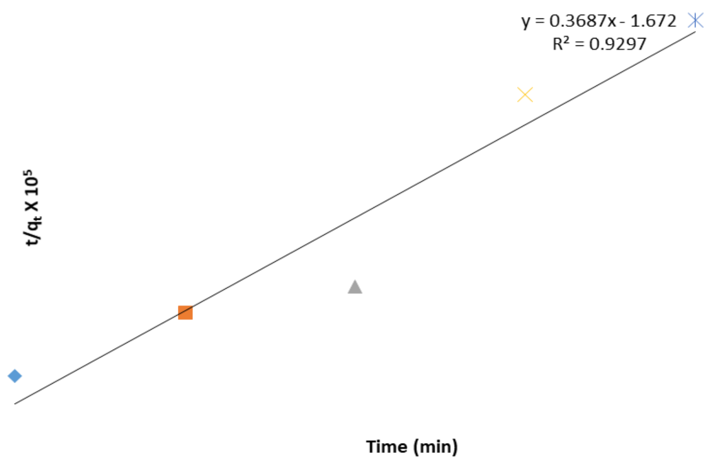

Fig 3: *A plot t/qt versus t for the degradation of Methylene blue using* TiO_2-SiO_2 *(Visible light)*

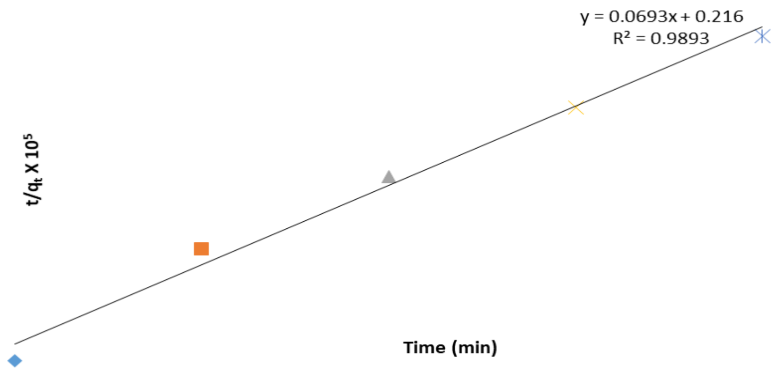

Fig 4: *A plot t/qt versus t for the degradation of methylene blue using* TiO_2-SiO_2 *(UV at 254 nm)*

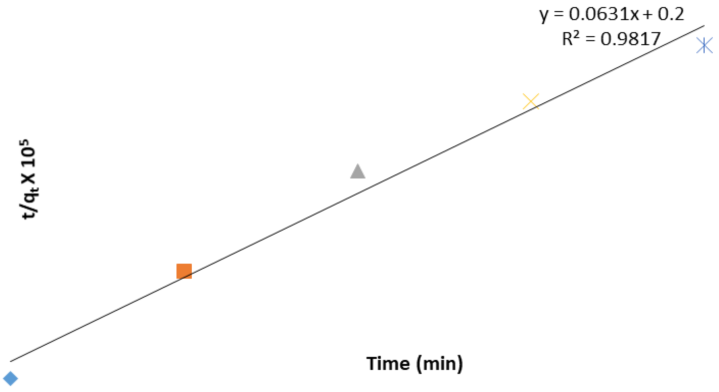

Fig 5 : *A plot t/qt versus t for the degradation of methylene blue using mixed* TiO_2*-*SiO_2 *(UV at 365 nm)*

Kinetics of photodegradation of methylene blue

The kinetics of the removal of MB was explored using well known Lagergren pseudo- second order kinetics model (Mehmet *et al*., 2009). The Pseudo-second second order model is represented as

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2$$

This can be rearranged as

$$\frac{dq_t}{(q_e - q_t)^2} = K_2 dt$$

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

$$\frac{t}{qt} = \frac{1}{K_2 q_e^2} + \frac{t}{qe}$$

k_2 is the rate constant for second-order adsorption (g mol^{-1} min^{-1}), q_t is the amount of MB adsorbed at time t ($molg^{-1}$) and q_e is the amount of MB adsorbed at equilibrium. The value of qt was calculated by a mass balance relationship,

qt = (Co-Ct) V/m (Dogan and Alkhan., 2003;Dogan *et al*., 2004),

Where Co is the initial MB concentration in solution ($moldm^{-3}$); Ct is the residual MB concentration in solution at time t ($moldm^{-3}$), V is the volume of the solution in dm^3 and m is the mass of the catalyst in gram. The pseudo-second-order kinetic model was found to describe the data better, the validity of the model of lagergren and the pseudo-second-order kinetic model was found applicable as the plot of t/qt versus t show a linear relationship with correlation coefficient (R^2) about 0.999. Figures 3-5 show the linearized plot of t/qt versus t.

The second order nature of the adsorption process of MB have been established (Kavita and Namasivayam., 2007; Hamdaoui., 2006; Dogan *et al*., 2004; Dogan *et al*., 2007; Bulut *and* Aydin., 2006).

Conclusion

The TiO_2-SiO_2 catalyst was synthesised and used to study the photocatalytic degradation of methylene blue. The catalysts yield different removal profiles at different light wave length and irradiation time. In the absence of light, less removal of MB due to physical adsorption was observed. In photocatalytic degradation using visible light, the removal of MB was slightly improved. Illumination with UV light at 254 and 365nm, showed better removal, photocatalytic removal using UV at 365nm was slightly higher than UV at 254nm. The removal of MB was evaluated and found to be better represented by pseudo-second-order adsorption rate, which was expressed by the linearized plot (t/qt) versus t.

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