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Photodegradation of Methylene Blue Dye in Aqueous Medium by Fe-AC/TiO_2 Composite

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ABSTRACT

A novel magnetic Fe-AC/TiO_2 composite has been synthesized by sol-gel method. The synthesized magnetic Fe-AC/TiO_2 composite was characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), energy dispersive spectroscopy (EDAX) and vibrating sample magnetometer (VSM). The average crystalline size of magnetic Fe-AC/TiO_2 composite was calculated by using Scherrer equation and it was found to be 10.8 nm. The magnetic Fe-AC/TiO_2 composite exhibit paramagnetic property analysed by vibrating sample magnetometer (VSM) at room temperature, which helps to easily separate the composite using an external magnet. The photodegradation activity of magnetic Fe-AC/TiO_2 composite under UV light was studied using the aqueous solution of methylene blue dye. The effect of various parameters such as catalyst loading, pH and initial concentration of the dye on degradation of methylene blue dye in aqueous medium has been investigated. The maximum degradation of methylene blue dye concentration in aqueous medium was obtained at pH=10 and 240mg/L of magnetic Fe-AC/TiO_2 composite for 10mg/L concentration of methylene blue dye. The magnetic Fe-AC/TiO_2 composite was investigated for its recycle efficiency which showed an effective degradation rate of more than 85% even after 5 cycles. Finally, the results prove that photodegradation of methylene blue dye in aqueous solution using magnetic composite was very effective under UV irradiation.

INTRODUCTION

Among various industries, dyeing industries discharge huge amount of coloured wastewater which are highly toxic that pollutes the environment. Over the past few decades, large scale usage of chemicals in various human activities has grown very fast, particularly in a country like India which has to go for rapid industrialization in order to sustain over growing large problem of population. The current pattern of industrial activity alters the natural flow of materials and introduces novel chemicals into the environment (Saritha et al. 2013). The major source of water pollution is domestic waste from urban and rural areas and industrial wastes, which are discharged into natural water bodies. Groundwater is the largest source of freshwater in developing countries and it is also subjected to such danger (Saritha et al. 2011).

Therefore, degradation of the dyes in industrial wastewater has generated considerable attention due to their huge volume of production, slow biodegradation, low decoloration and high toxicity (Xu et al. 2011, Habazaki et al. 2002, Caudo et al. 2006, Amini et al. 2014). Various physico-chemical treatment methods are widely used for treatment of these wastewaters.

Among all the treatment methods, photocatalytic degradation is a promising technique for removal of various toxic chemicals present in wastewaters. Heterogeneous photocatalytic oxidation using TiO_2 as catalyst is an effective method to remove low concentrations of organic contaminants (Lakshmi et al. 1997). The photocatalytic properties of nanoparticles titania (TiO_2) has been extensively investigated due to its application in the field of degradation of pollutants (Hoffmann et al. 1995). Although nanoparticles titania (TiO_2) has very large reactive surface area, it is not an easy process to separate these particles from aqueous pollutants while reusing/recycling the photocatalysts. In order to enhance the process of immobility or separability of the photocatalysts, various researchers prepared titania-coated hollow glass beads (Jackson et al. 1991), titania based thin film (Tada et al. 1997) and titania-coated magnetic particles (Beydoun et al. 2002, Chen et al. 2001). But the activity of titania photocatalysts in the photocatalytic system was reduced to a considerable extent because the effective surface area of photocatalysts was decreased considerably after immobilization.

To maintain the photocatalytic activity, the nanoparticles titania (TiO_2) should be deposited onto supporters with high surface area, such as a porous structure. It is well known that activated carbon (AC) is one of the low-cost and widely available porous materials with relatively large surface area. Commercial activated carbons have been widely used as adsorbents and catalytic supporters in aqueous media to remove pollutants and to recover valuable products. However, in the practical applications, the separation of activated carbons from the aqueous medium commonly involves complex procedures such as filtration or centrifugation. It has been shown that magnetic particles could be easily separated from suspension system (Beydoun et al. 2002, Chen et al. 2001, Fuertes et al. 2006). Thus a composite photocatalyst combining large surface area and magnetic separability is very attractive. This research work has been focused on the synthesis of magnetic Fe-AC/TiO_2 composite by Sol-gel method and characterization of synthesized composite by SEM, XRD, EDAX and VSM. The photodegradation efficiency of the magnetic Fe-AC/TiO_2 composite was investigated using methylene blue dye as test pollutant.

MATERIALS AND METHODS

Textile Dye Methylene Blue

The magnetic Fe-AC/TiO_2 composite was synthesized using different chemicals like ferric nitrate $[Fe(NO_3)_3.9H_2O]$, ethanol, ethylene glycol, titanium isopropoxide, 2-propanol and commercial activated carbon (CAC). All the chemicals used in this study were of the highest purity and of analytical grade. The photodegradation studies were carried out using methylene blue dye as target pollutant. Methylene blue dye is a complex molecule as shown in Fig. 1 with empirical formula $C_{16}H_{18}ClN_3S$

Synthesis of Magnetic Fe-AC/TiO2 Composite

Few grams of activated carbon were immersed in ethanolic ferric nitrate solution and then dried in oven at 100°C for 3 hrs. Ethylene glycol was added to this and heated at 450°C for 3 hrs to get Fe-AC particles. A few mL of titanium isopropoxide with 2-propanol was mixed and then distilled water to obtain TiO_2 nanosol.

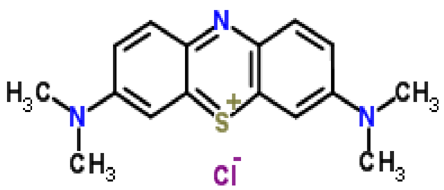


Fig. 1: Methylene blue molecular structure.

Fe-AC particles were mixed with prepared TiO_2 nanosol under sonication for 4 hrs and then the mixture was dried at 100°C for 10 hrs and finally heated at 450°C for 5 hrs. The synthesized Fe-AC/TiO_2 composite was washed with distilled water and after each washing the composite particles were separated using an external magnet. The separated Fe-AC/TiO_2 composite was dried at 100°C for 2 hrs and stored in a desiccator.

Analysis

The magnetic properties, structure and composition of Fe-AC/TiO_2 composite were analysed. The magnetic measurements were carried out with a vibrating sample magnetometer. The structural properties were determined by XRD. The morphologies were characterized with a scanning electron microscope (SEM). The elemental analysis was done by energy-dispersive X-ray spectroscopy.

Photoreactor

Photocatalytic degradation batch experiments were carried out in 500 mL Pyrex batch reactor. An 8 W low pressure lamp was used as the UV light source that was placed in a quartz jacket (50 mm inside diameter and 300 mm height) and submerged at the centre of the cylindrical vessel to provide better irradiation.

Experimental Procedure

Methylene blue dye concentration in aqueous solution was prepared using distilled water and diluted as per the concentration required. The Methylene blue dye aqueous solution was stirred with magnetic Fe-AC/TiO_2 composite dose in 500 mL reactor in the presence of UV light. Few mL of the sample was collected after certain interval of time, magnetic Fe-AC/TiO_2 composite was separated using external magnet and the degradation rates were calculated from absorption values of methylene blue dye concentration measured by UV-visible spectrophotometer.

RESULTS AND DISCUSSION

Characterization of magnetic Fe-AC/TiO_2 composite

Surface morphological studies: SEM provides detailed high resolution images of the sample by rastering a focused electron beam across the surface and detecting secondary or backscattered electron signal. SEM images at various magnifications provide useful information regarding the surface morphology of the synthesized magnetic Fe-AC/TiO_2 composite. The SEM images of magnetic Fe-AC/TiO_2 composite, shown in Fig. 2 (a), (b), (c) and (d), depicts that the particles are agglomerated and are in spherical shape.

Boundaries of particles are clearly observed in the SEM micrographs of the samples. Moreover, it clearly reveals the surface texture and porosity nature. From SEM observations, the magnetic Fe-AC/TiO_2 composite is defined as nanoparticles of few nanometer size in the form of nano clusters.

XRD measurement: X-ray diffraction (XRD analysis) is a unique method in determination of crystallinity of a compound. From X-Ray diffraction data, the particle size can be calculated from the width of the peak by using Scherrer equation:

$$D=K \lambda / \beta \cos \theta \qquad ...(1)$$

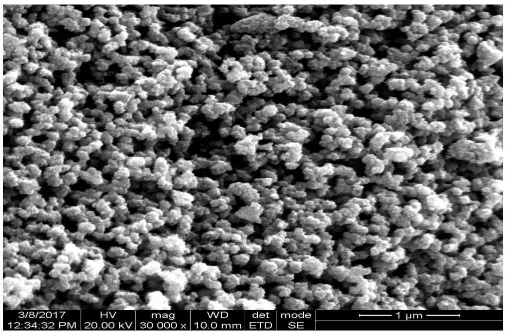
Where, D is the crystallite size, λ is the wavelength of X-ray radiation (Cu Kα-1 radiation = 1.5406 Å), K = 0.9, β is the full width at half maximum (FWHM) and θ is the diffraction angle of the peak (Perumal et al. 2014).

The XRD result for magnetic Fe-AC/TiO_2 composite (Fig. 3) has peaks at 2θ values of 25.29°, 38.34°, 48.23°, 55.21°, 62.91° and 70.42°, which can be assigned to the diffractions of (101), (112), (200), (211), (204) and (220) indicating the formation of anatase phase of TiO_2. From the XRD patterns, the average size of magnetic Fe-AC/TiO_2 composite is found to be 10.8 nm.

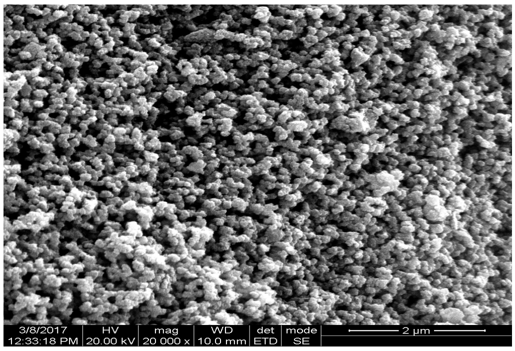
Table 1: Percent degradation and pseudo-first-order kinetic parameters of MB dye

Photocatalyst Fe-AC/TiO_2 dosage (mg/L)	Degradation %	K(min^{-1})	R^2
240	93	0.0159	0.9424
210	88	0.0139	0.9786
180	81	0.0111	0.9888
150	72	0.0090	0.9978
120	69	0.0080	0.9941
90	64	0.0068	0.9849
60	52	0.0054	0.9917
30	41	0.0035	0.9781

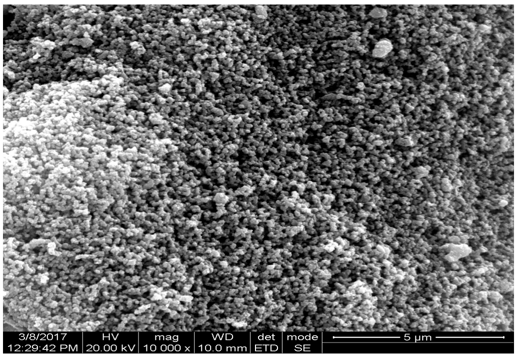
EDAX spectrum: Energy-dispersive X-ray spectroscopy is an analytical technique used for the elemental analysis or chemical characterization of a sample. The EDAX spectrum for magnetic Fe-AC/TiO_2 composite shows different



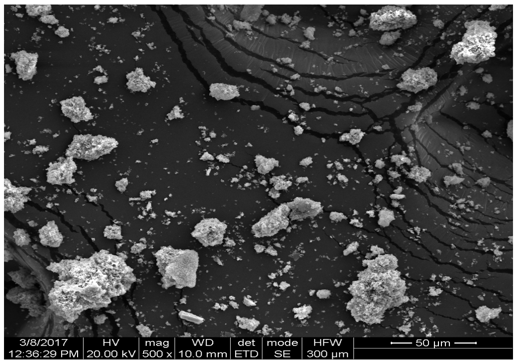
(a)



(b)



(c)



(d)

Fig. 2: SEM images of (a) Fe-AC/TiO_2 (1µm), (b) Fe-AC/TiO_2 (2µm), (c) Fe-AC/TiO_2 (5µm), (d) Fe-AC/TiO_2 (50µm).

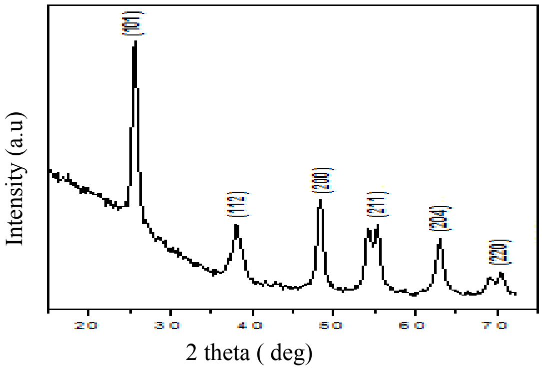


Fig. 3: XRD pattern of Fe-AC/TiO_2 composite.

peaks which clearly depicts the presence of Ti, Fe, C and O. The ESEM micrographs and EDAX (Energy Dispersive Spectroscopy) analysis of Fe-AC/TiO_2 has been shown in Fig. 4 (a) and (b).

Magnetic characterization: The magnetic properties of Fe-AC/TiO_2 composite has been studied by VSM analysis as it consists of magnetic Fe content (magnetite and maghemite) in the catalyst. The magnetic hysteresis loop of Fe-AC/TiO_2 composite has been shown in Fig. 5. Higher saturation magnetization (Ms) is due to Fe content in the photocatalytic composite.

The magnetization of magnetite depends on the size of particles and their distribution. Thus, saturation magnetization (Ms) values lesser than that of bulk magnetite value of 60-70 emu.g^{-1} have been found for magnetite particles of similar sizes of particles found in Fe-AC/TiO_2 composite (10.8 nm) (Rebodos et al. 2010). The remanent magnetization (Mr) values closer to zero show that the composite exhibit paramagnetic property at room temperature, which helps to easily separate the Fe-AC/TiO_2 composite by an external magnet (Pankhurst et al. 2003).

Photodegradation of Methylene Blue Dye

Study of the effect of UV irradiation: To assess the photodegradation by UV irradiation, the methylene blue dye aqueous solution was subjected to UV irradiation without magnetic Fe-AC/TiO_2 composite for 5 hours. The percentage removal of methylene blue dye from aqueous solution by UV irradiation was obtained as 4, 7, 8, 10 and 11% in 1, 2, 3, 4 and 5 hours respectively. This shows that degradation rate under solely UV irradiation was very less.

Study of effect of catalyst loading: Photodegradation batch experiments were carried out with methylene blue dye aqueous solution of concentration 10 mg/L using various dosages of magnetic Fe-AC/TiO_2 composite which has been shown in Fig. 6. The effect of dosage of Fe-AC/TiO_2 composite on the degradation of methylene blue dye was varied from 30 mg/L to 240 mg/L. It was observed that as the composite dose was increased, the percentage degradation of dye concentration also increased. Above 240 mg/L of magnetic Fe-AC/TiO_2 composite dosage, there is no significant increase in the degradation of the dye. Hence, 240 mg/L has been considered as an optimized Fe-AC/TiO_2 composite dose for degradation of methylene blue dye.

The increase in degradation rate with increase in the magnetic Fe-AC/TiO_2 composite loading is due to increase in total active surface area i.e., availability of more active sites on catalyst surface. But higher dose of catalyst results in increase in turbidity of the suspension which decreases the penetration of UV light, and hence photoactivated volume of suspension. Thus, it can be concluded that higher dose of composite may not be efficient in degradation of methylene blue dye.

Study of the effect of pH: Textile industry wastewater is discharged at different pH; therefore, it is important to study the role of pH on degradation of the dye. In order to study the effect of pH, experiments were carried out at various pH values (2 to 12) at constant methylene blue dye concentration (10 mg/L) with magnetic Fe-AC/TiO_2 composite (240

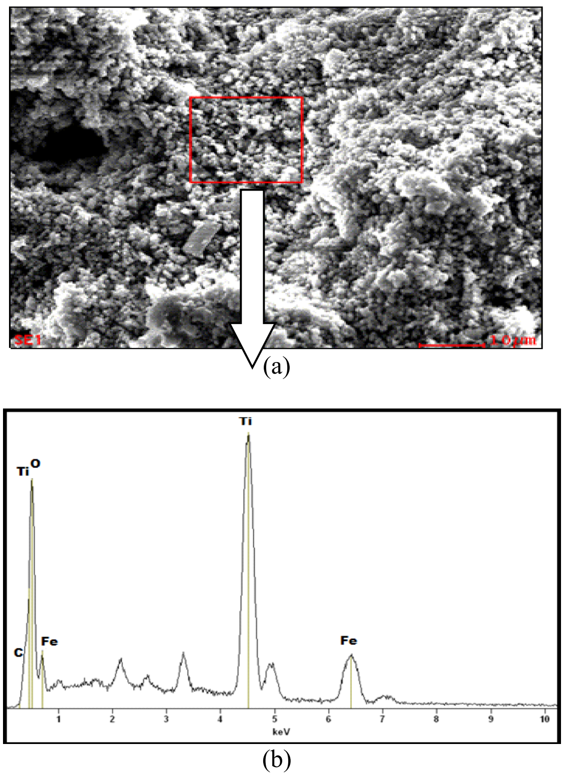


Fig. 4: (a) ESEM image and (b) EDAX spectrum of Fe-AC/TiO_2 composite.

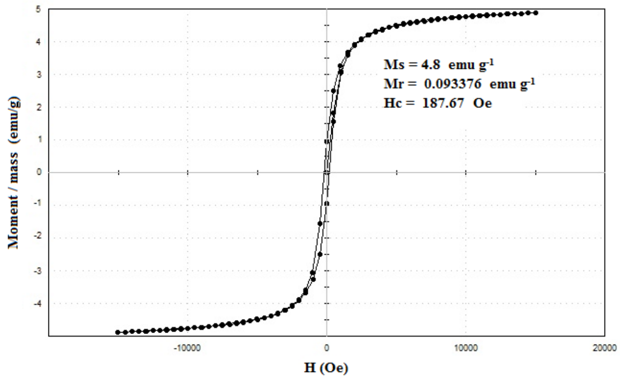


Fig. 5: Magnetization vs. applied magnetic field of Fe-AC/TiO_2 composite.

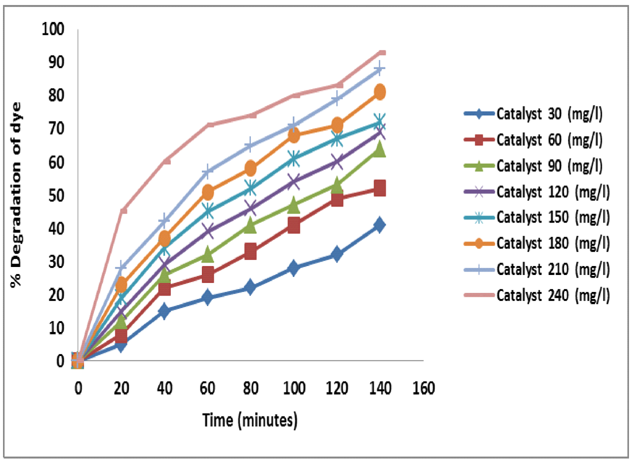


Fig. 6: Effect of catalyst dosage.

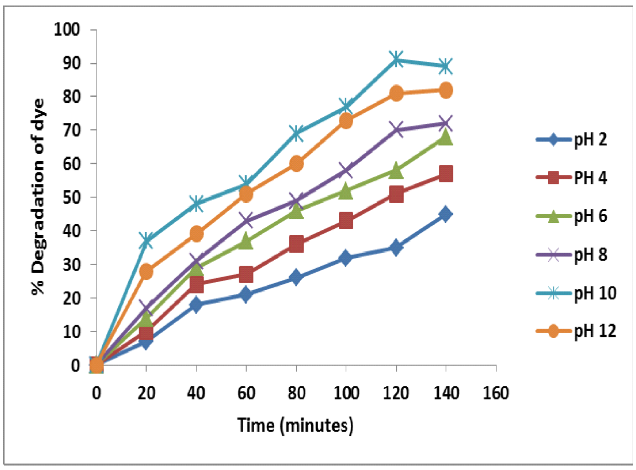


Fig. 7: Effect of pH.

mg/L) which has been shown in Fig. 7. It was observed that the degradation efficiency increases with increase in pH and maximum degradation of 91% was observed at pH 10. When changing to pH 12 there is no significant increase in degradation. This shows the colour removal efficiency of magnetic Fe-AC/TiO_2 composite depends on pH.

Study of effect of initial dye concentration: The influence of initial concentration of dye solution has been investigated with composite dosage (magnetic Fe-AC/TiO2 composite =240 mg/L). The methylene blue dye concentration was varied from 20 to 140 mg/L. The photodegradation activity decreases with increase in dye concentration with constant dosage of composite which has been shown in Fig. 8.

This kind of photodegradation may be due to increase in the extent of adsorption on the magnetic Fe-AC/TiO_2 composite surface which reduces the photoactivity. At high dye concentration, a significant amount of UV light may be absorbed by the dye molecules and these dye molecules prevent the exposure of Fe-AC/TiO_2 composite to light. This may also reduce the magnetic Fe-AC/TiO_2 composite efficiency.

Effect of catalyst loading on kinetics of photocatalytic degradation of dye: Photocatalytic degradation rate constant (k) of the methylene blue dye was calculated using the pseudo-first order kinetic equation:

$$\ln(Co/Ct) = k.t \qquad ...(2)$$

Where, Co and Ct are the concentrations of dye at initial stage and at time *t*, respectively. Plots of ln(Co/Ct) vs irradiation time for photocatalytic degradation of methylene blue dye over various magnetic Fe-AC/ TiO_2 composite dosage has been shown in Fig. 9. The apparent rate constants, K (min^{-1}), % degradation and correlation coefficients for all photoreactions are given in Table 1. The plots show a linear relationship with good correlation coefficient (R^2>0.9424), indicating that the methylene blue dye degradation is best fit to the above kinetic model.

Effect of catalyst reusability on photocatalytic degradation of dye: The reuse of the magnetic Fe-AC/TiO_2 composite is one of the key steps to make heterogeneous photocatalysis technology for practical applications. The separation problem of the TiO_2 nanopowders was solved without depressing the activity of the photocatalyst by depositing it onto Fe-AC. For all samples, the magnetic Fe-AC/TiO_2 composite can be separated completely by an external magnetic field. Subsequently, the magnetic Fe-AC/TiO_2 composite was investigated for its recycle efficiency. The magnetic Fe-AC/ TiO_2 composite was used repeatedly for 5 cycles.

The photocatalytic activity of the magnetic Fe-AC/TiO_2 composite weakened slowly when it was reused and the

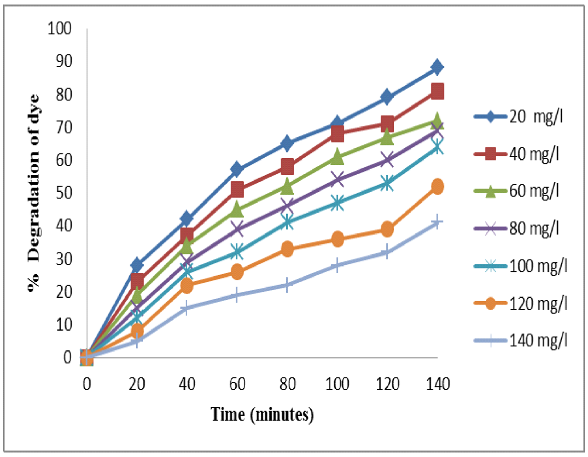


Fig. 8: Effect of initial dye concentration on degradation of the dye.

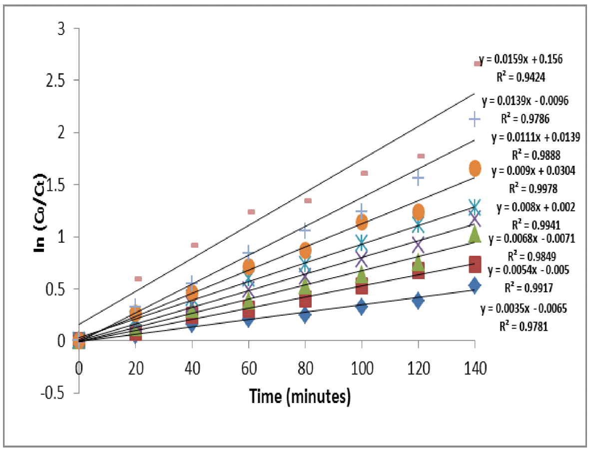


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Fig. 9: Pseudo-first-order degradation rate of MB dye by Fe-AC/TiO_2 composite.

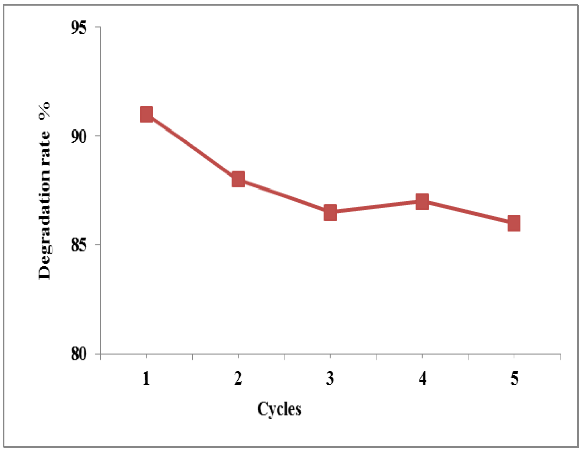

Fig. 10: Effect of catalyst reusability on degradation of the dye.

results have been shown in Fig. 10. It has been very clearly depicted that the degradation rate of methylene blue dye by magnetic Fe-AC/TiO_2 composite was still higher than 85% after 5 cycles. It is very important for the practical detoxification of contaminated water.

CONCLUSION

Photodegradation of methylene blue dye has been carried out over magnetic Fe-AC/TiO_2 composite (prepared by sol-gel method) under UV irradiation and the following findings have been observed:

1. The results showed efficient photodegradation activity and also obey the pseudo first order kinetics.
2. The synthesized magnetic Fe-AC/TiO_2 composite shows good magnetic properties which has been confirmed by VSM analysis, and hence it is found to be easy to separate by an external magnet.
3. The effect of pH, catalyst dosage, initial dye concentration and UV irradiation on degradation efficiency of methylene blue dye were investigated.
4. Experimental results showed that the degradation rate decreased with an increase in the initial concentration of methylene blue dye.
5. It can be concluded that highest degradation efficiency occurred at pH = 10 and 240 mg/L of the composite dosage clearly depicting that magnetic Fe-AC/TiO_2 composite under UV irradiation has higher efficiency for methylene blue dye degradation.

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REFERENCES

Xu, A., Li, X., Ye, S., Yin, G. and Zeng, Q. 2011. Catalyzed oxidative degradation of methylene blue by in situ generated cobalt(II)-bicarbonate complexes with hydrogen peroxide. Applied Catalysis B: Environmental, 102(1-2): 37-43.

Amini, M., Pourbadiei, B., Purnima, T., Ruberu, A. and Keith Woo, L. 2014. Catalytic activity of MnOx/WO_3 nanoparticles: synthesis, structure characterization and oxidative degradation of methylene blue. New Journal of Chemistry, 38(3): 1250-1255.

Beydoun, D., Amal, R., Low, G. and McEvoy, S. 2002. Occurrence and prevention of photodissolution at the phase junction of magnetite and titanium dioxide. Journal of Molecular Catalysis A, 180(2): 193-200.

Caudo, S., Centi, G., Genovese, C. and Perathoner, S. 2006. Homogeneous versus heterogeneous catalytic reactions to eliminate organics from waste water using H_2O_2. Topics in Catalysis, 40(1): 207-219.

Chen, F., Xie, Y.D., Zhao, J.C. and Lu, G.X. 2001. Photocatalytic degradation of dyes on a magnetically separated photocatalyst under visible and UV irradiation. Chemosphere, 44(5): 1159-68.

Fuertes, A.B. and Tartaj, P.A. 2006. Facile route for the preparation of superparamagnetic porous carbons. Chemistry of Materials, 18(6): 1675-1679.

Habazaki, H., Hayashi, Y. and Konno, H. 2002. Characterization of electrodeposited WO_3 films and its application to electrochemical wastewater treatment. Electrochimica Acta, 47(26): 4181-4188.

Hoffmann, M.R., Martin, S.T., Choi, W.Y. and Bahnemann D.W. 1995. Environmental applications of semiconductor photocataly-sis. Chemical Reviews, 95(1): 69-96.

Jackson, N.B., Wang, C.W., Luo, Z., Schwitzgebel, J., Ekerdt, J.G. and Brock, J. 1991. Attachment of TiO_2 powder to hollow micbea ds: activity of the TiO_2-coated beads in the photoassisted oxidation of ethanol to acetaldehyde. Journal of the Electrochemical Society, 138(12): 3660-3664.

Lakshmi, B.B., Patrissi, C. J. and Martin, C.R. 1997. Sol-gel template synthesis of semiconductor oxide micro- and nanostructures. Chemistry of Materials, 9(11): 2544-2550.

Pankhurst, Q.A., Connolly, J., Jones, S.K. and Dobson, J. 2003. Applications of magnetic nanoparticles in biomedicine. Journal of Physics D: Applied Physics, 36(13): 167-181.

Perumal, S., Gnana Sambandam, C., Monikanda Prabu, K. and Ananthakumar, S. 2014. Synthesis and characterization studies of nano TiO_2 prepared via sol-gel method. International Journal of Research in Engineering and Technology, 3(4): 651-657.

Rebodos, R.L. and Vikesland, P.J. 2010. Effects of oxidation on the magnetization of nanoparticulate magnetite. Langmuir, 26(22): 16745-16753.

Saritha, B. and Meikandaan, T.P. 2013. Treatability study of tannery effluent by enhanced primary treatment. International Journal of Modern Engineering Research (IJMER), 3(1): 119-122.

Saritha, B. and Madavan, V. 2011. Study of ground water in Perungudi area of Chennai: Correlation with physico-chemical parameters. Civil and Environmental Research, 1(1): 23-31.

Tada, H. and Tanaka, M. 1997. Dependence of TiO_2 photocatalytic activity upon its film thickness. Langmuir, 13(2): 360-364.