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Short Communication

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Preparation and characterization of rice husk ash (RHA)-TiO_2 / ZnO composites and its application in treating effluents from textile industries

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Abstract

Photocatalytic composite materials incorporating the photocatalysts (TiO_2, ZnO) with rice husk ash (RHA) have been developed to investigate the photodegradation of real textile dye effluent. The structural characterization of the composite materials was performed using XRD (X-Ray Diffractometer). The characteristic XRD peaks together with the 2θ values for both TiO_2 and ZnO were in excellent agreement with the standard JCPDS *d*-values. The efficacy of these composites was examined through the degradation of a textile dye, collected from a local dye house. The sun light was used as the source of illumination for the preceding degradation reaction.

Keywords: Photocatalyst; Composite; Illumination; Photodegradation; Decolourization.

Introduction

Semiconductor mediated photocatalytic technology for the destruction and decomposition of toxic and hazardous compounds has now received significant attention (Khataee and Kasiri 2010; Patil *et al.,* 2010; Gaya *et al.,* 2008). Indeed, over the past two decades, researchers throughout the world have particularly focused their attention on this emerging photocatalytic technology. The reason behind such attention is its significant efficacy and easy-to-use operating procedure over the conventional biological and physico-chemical approaches.

Although a number of catalysts have been used for the photodegradation of a wide variety of hazardous compounds, TiO_2 and ZnO are considered as the most promising photocatalysts due to their high photosensitivity, large band gap and non-toxic nature (Ebrahimi *et al* 2012, Imajo *et al* 2008, Khataee and Kasiri 2010). The most common forms of TiO_2, anatase and rutile (Khataee and Kasiri 2010) are photoactive because of the presence of higher degree of surface hydroxylation. However a special form of TiO_2 (Degussa P25) is used in many studies as the most effective standard (Ahmed 2000). It is a typical non-porous composition of anatase : rutile, 70 : 30. On the other hand, the presence of large number of active sites on the crystal surface makes ZnO a highly active photocatalyst.

Dye-stuffs are an important source of water pollution. Commercially, there are more than 100,000 dyes exist and globally over $7x10^5$ tons of dyes are produced in a year and 15% of which is lost during the dyeing process (Yogendra *et al.,* 2011). Dyes can easily contaminate the water bodies through their discharge from the dye-manufacturing plants, textile plants, plastic industries etc. Such coloured water bodies are obviously undesirable to both human and aquatic lives.

Discharge of industrial waste water is a major problem in Bangladesh and at present it has reached to an alarming proportion (Kabir 2012, Sultana *et al.,* 2009). Considering the waste water situation of Bangladesh (which urges immediate treatment), the aim of this present research work is to introduce photocatalytic technology for the treatment of dye effluents in our country. Hence, an attempt has been made to develop a cost-effective composite material incorporating TiO_2 and ZnO as photocatalysts with rice husk ash (RHA) to treat dye effluents before discharging into the aquatic environment. Since RHA is porous in nature with high specific surface, it is widely used as an adsorbent (Mahvi *et al.,* 2004), RHA was chosen with the photocatalyst (TiO_2 and ZnO) to develop the photocataytic composite materials for the treatment of textile effluent. Hence incorporation of the photocatalysts (TiO_2 and ZnO) with RHA would provide a dual active (adsorption and photodegradation) process for waste water treatment. However in addition to the treatment procedure, utilization of RHA would be a promising material recycling technology for future waste management.

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Materials and methods

Analar grade reagents (either from E. Merck or BDH) and double distilled water were used to prepare all the solutions. RHA was collected from local rice mill and textile effluent was collected from a local dyeing industry. All the solutions were prepared freshly prior to each experiment.

Preparation of RHA - photocatalytic composite material

Photocatalytic composite materials were prepared as described previously (Ahmed *et al* 2011). However, in brief, a mixture of RHA and photocatalyst (75 : 25, w/w) was ball milled under aqueous suspended condition and then heated at 100°C just to evaporate the excess water. At this stage ~ 5.0 mL of sodium silicate solution was added to it as the binder. The mixture was then shaped into desired size (3.5cm x 3.5cmx 0.5cm) 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 100 °C for an hour.

Characterisation of the RHA - photocatalytic composite material

The photocatalytic composite materials were characterized by phase analysis using x-ray diffraction spectrophotometer (PANalytical X'Pert PRO XRD PW 3040). The phases of TiO_2 and ZnO present in the photocatalytic composite materials were determined from the respective x-ray diffraction patterns and confirmed using standard JCPDS files. The lattice parameters of RHA-TiO_2 and RHA-ZnO composites were calculated by using Equation 1 (for tetragonal system, http://www.abdn.ac.uk/~che241/y3-2002/handouts/3ho3.pdf) and Equation 2 (for hexagonal system, Kabir 2009) respectively.

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (1)$$

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2} \quad (2)$$

Photodegradation efficacy of the composite materials for the treatment of dye pollutants

Photocatalytic efficiency of composite materials was investigated through the degradation of textile effluent. The degradation was initiated through the illumination of sun light (intensity ~47 Klux, measured by Light Meter, Model no CEM, DT-1308, Taiwan) and the performance of the photocatalytic composite materials was measured using following equation:

$$\%\text{ of photodegradation} = \frac{A_0 - A_t}{A_0} \times 100 \quad (3)$$

where, A_0 = initial absorbance, A_t = absorbance at time *t*

Results and discussion

Characterization of RHA - photocatalytic composite materials

The XRD diffraction patterns of the prepared RHA - TiO_2 and RHA - ZnO composites are given in Figs 1a and 1b respectively. In case of RHA - TiO_2 composite, the

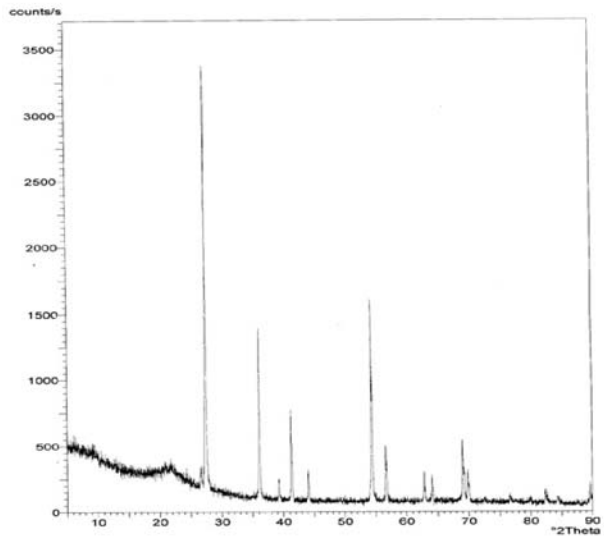

Fig. 1a. XRD diffraction patterns of prepared RHA - TiO_2 composite

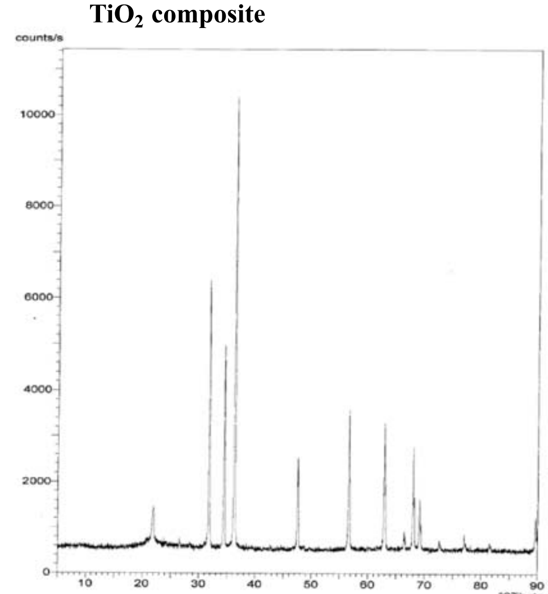

Fig. 1b. XRD diffraction patterns of prepared RHA - ZnO composite

characteristic peak (100% intense, 1 1 0 plane) was observed at 2θ position 27.44° while for RHA - ZnO composite, the most intense peak was at 2θ position 36.25° (1 0 1 plane). However, for both of the cases, the experimental *d*-values and the corresponding intensities are summarized in Table I. The experimental *d*-values and their corresponding intensities are in excellent agreement with the JCPDS standard values (Khataee and Kasiri 2010, Yakuphanoglu *et al* 2007, Lupan *et al* 2008). Moreover, since RHA contains silica, the diffraction spectra of the composites also showed the characteristic peak of silica (Malek *et al* 2007) at 2θ position ~23°. However, in case of RHA - TiO_2 composite the XRD spectrum attributed to the tetragonal rutile phase (Lee *et al* 2011) while the spectrum of RHA - ZnO composite ensured the ZnO as hexagonal wurtzite (Yakuphanoglu *et al* 2007, Lupan *et al* 2008).

Table I. Characteristic d-spacing and 2 values observed for RHA - TiO_2 and RHA - ZnO composites

RHA - ZnO photocatalytic composite				RHA - TiO_2 photocatalytic composite			
d-spacing	2θ	Intensity	h k l	*d*-spacing	2θ	Intensity	*h k l*
2.815	31.76	59.42	1 0 0	3.248	27.44	100.00	1 1 0
2.603	34.42	44.91	0 0 2	2.487	36.08	39.26	1 0 1
2.476	36.25	100.00	1 0 1	2.187	41.25	21.31	1 1 1
1.911	47.53	20.07	1 0 2	2.054	44.06	6.71	2 1 0
1.625	56.59	30.80	1 1 0	1.687	54.33	46.02	2 1 1
1.477	62.85	28.08	1 0 3	1.479	62.79	7.39	0 0 2
1.378	67.94	22.90	1 1 2				
1.359	69.07	11.59	2 0 1				

The lattice parameters for tetragonal TiO_2 and hexagonal ZnO were calculated using the Equations 1 and 2 respectively and are summarized in Table II. A very good agreement between the calculated and standard JCPDS values was found. It is attributed from the data presented in the Table II that the phases of photocatalysts (TiO_2, ZnO) did not change during the preparation of the composite material, which was expected.

Table II. Lattice parameters of TiO_2 and ZnO

Lattice parameters of the photocatalysts			
ZnO (in RHA - ZnO composite)		TiO_2 (in RHA - TiO_2 composite)	
Calculated value	JCPDS standard	Calculated value	JCPDS standard
a = 3.250°A	*a* = 3.249°A	*a* = 4.593°A	*a* = 4.594°A
c = 5.206°A	*c* = 5.206°A	*c* = 2.957°A	*c* =2.959°A

Photodegradation of textile dye

A typical UV-Vis spectrum of 50% diluted aqueous solution of the textile effluent is shown in Fig. 2 with two major peaks at 293 nm and 511 nm. The spectra of this sample after irradiation at several time intervals (in the presence of RHA - TiO_2 and RHA - ZnO composites) showed gradual decrease in absorbance. Moreover, no other new peak was observed. This indicated that photodegradation of the textile effluent occurred within the present experimental set up. The degradation efficiency of both the composites was measured using equation 3. Maximum degradation (25 - 30%) was achieved at 3 hours. It is evident that the degradation efficiency is comparatively low for both cases. The reason for this less efficiency is yet not identified.

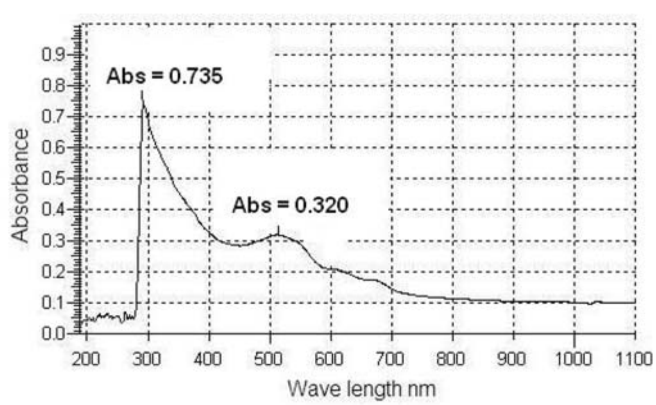

Fig. 2. UV-Vis spectrum of 50% diluted natural textile dye (without irradiation)

Conclusion

Photocatalytic composite materials incorporating the photocatalysts (TiO_2, ZnO) with rice husk ash (RHA) have been developed to investigate the photodegradation of real textile dye effluent. The structural characterization of the composite materials was performed using XRD which was in good agreement with the standard JCPDS data. The prepared composite materials were used to investigate the photodegradation of textile dye effluent. However, in order to scale up this methodology for industrial application, optimization of this technology with high efficiency is no doubt the most significant step. This is speculated that after scaling up this methodology, it would be possible to develop photocatalytic reactor or effluent treatment plant (ETP) using the photocatalytic composite materials which would provide an efficient, cost-effective and environment friendly pathway for the treatment of textile effluents, where natural sun light would act as the UV-source. Moreover, utilization of RHA with the photocatalysts would be a promising material recycling technology for future waste management.

Acknowledgement

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