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APPLICATION OF ZINC FERRITE SILICA GEL COMPOSITE PHOTOCATALYSTS FOR THE TREATMENT OF TEXTILE EFFLUENTS

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ABSTRACT

The photocatalytic activity of the zinc ferrite silica gel composite photocatalysts was evaluated using decolourization of Methylene Blue (MB) which revealed that 30 wt% $ZnFe_2O_4/SiO_2$ was found to have the best photocatalytic activity than 10 wt%, 20 wt% while 40 wt% showed significant reduction in the photocatalytic activity which can be attributed to the increased agglomeration of the zinc particle on silica gel, thereby decreasing the rate of diffusion of photogenerated electron-hole pairs on the MB molecule at the interface of solid photocatalysts and the MB solution. The SiO_2 support improves the photocalytic activity of the $ZnFe_2O_4$ under visible irradiation. The application of the best zinc ferrite silica gel composite photocatalysts to the treatment of real textile effluent resulted more efficiency in the reduction of the effluent's color, COD, BOD than the bare zinc ferrite and the photolysis. 50% color removal, 46% COD and 45% BOD with 30 wt% $ZnFe_2O_4/SiO_2$ while 30% Color removal, 25% COD and 24% BOD with bare $ZnFe_2O_4$ and 14% color removal, 10% COD, 10% BOD using photolysis.

Keywords: Zinc Ferrite, Silica gel, Photocatalysts, Textile effluents.

INTRODUCTION

Water pollution due to the release of chemicals from industrial sectors has been a major concern in recent times. The major constituents of industrial effluents are heavy metals, pesticides, dyes, aliphatic and aromatic compounds, detergents, chlorophenols, e.t.c. many conventional methods (such as sedimentation, chlorination, precipitation, etc.) are used to treat these effluents and each method has its own merits and shortcomings (Nagaveni *et al.,* 2005). Recently, advanced oxidation process (AOPs), especially photocatalysis, have become techniques for wastewater treatment, because they convert organic contaminants to a large extent in to stable less toxic compounds, such as carbon dioxide and water. The high reactivity of hydroxyl radical generated by the AOPs play an important role in oxidizing the organic species present in wastewater in to harmless species (Hameed and Hassan *et al.,* 2009). Heterogeneous photocatalysis by semiconductor materials such as TiO_2, ZnO, Fe_2O_3, CdS, GaP, and ZnS has indeed been widely used for the degradation of various organic and inorganic pollutants (Faber *et al.,* 2005).

Photocatalysts are important materials that provide a relatively simple means for the conversion of light energy including (solar

energy) for use in oxidation and reduction process. They utilize light energy (*hν*) to carry out oxidation and reduction reactions. When irradiated with light energy, an electron (e^-) is excited from the valence band (VB) to the conduction band (CB) of photocatalysts leaving a photogenerated hole (h^+). The produced e^- and h^+enable oxidation and reduction process to occur. When photocatalytic process takes place in aqueous solutions, water and hydroxide ions react with photogenerated h^+ to form hydroxyl radicals (*OH) which is the primary oxidant in the photocatalytic oxidation of organic compounds (Cao *et al.*, 2007).

Zinc ferrite ($ZnFe_2O_4$) has been applied as a visible light responsive photocatalyst for the remediation of hazardous wastes, contaminated groundwater and control of toxic air contaminants (Jadhav *et al.*, 2010). To enhance the photocatalytic activity of $ZnFe_2O_4$, several methods have been proposed for its synthesis with unique size dependent, physical and chemical properties. Various composites of $ZnFe_2O_4$ ($ZnFe_2O_4$ /TiO_2, $ZnFe_2O_4$/ZnO etc) have also been synthesized and their photocatalytic activity is often higher than that of the bare $ZnFe_2O_4$ (Cao *et al.*, 2007)

In this work, $ZnFe_2O_4$ and $ZnFe_2O_4/SiO_2$ was used in varying proportion and the best photocatalys composite with the silica gel $ZnFe_2O_4$ ratio was used to decolorize Methylene Blue (MB) under visible irradiation using 500 W halogen lamps as a model, then applied for the real treatment of textile effluent. Also, in the process the physiochemical content of the textile effluent and water sample was analyzed both before and after the treatment.

MATERIALS AND METHODS

Photocatalytic Decolouration of MB Solution

A 100 ml/L stock solution of MB was prepared using distilled water for all the experiments. The adsorption tests under dark condition were carried out, for the evaluation of the adsorption- adsorption of MB on the surfaces of synthesized photocatalysts. 100ml of solution of MB was taken from the stock solution and poured in to the beaker and kept in the dark at room temperature with continuous stirring for three and half hours. After one hour of continuous stirring in the dark, an aliquot of 5ml was withdrawn from the beaker and then switched on the 500W halogen lamp to provide irradiation for the two and half hours (2:30hours). 5ml of the aliquot was also withdrawn with a syringe at regular interval of time; same procedure was strictly followed for the decolourization of methyl orange. About 100 ml of solution of MB was taken in to a beaker; 0.1g of Photocatalysts was added then the suspension was kept in the dark at room temperature with continuous stirring by the help of magnetic stirrer. After one hour in the dark, 5ml of the suspension was taken and stored in a Vail for the analysis. The suspension was irradiated with source of halogen lamp while stirring of the suspension continued. An aliquot of 5ml was taken for the beaker at regular interval of 30 minutes. Then the catalysts were filtered and the samples were analyzed using UV-vis spectrophotometer. Same procedures were

followed for composite photocatalysts that is ($ZnFe_2O_4$ and $ZnFe_2O_4$/Silica gel) of (10 wt%, 20 wt%, 30 wt%, and 40 wt %)

Photocatalysts Degradation of MB Solution

100 ml of solution of MB was taken in to a beaker, 1.0g of Photocatalysts ($ZnFe_2O_4$ and 30 wt% $ZnFe_2O_4$/Silica gel was added. The suspension was kept in dark at room temperature with continuous stirring with the help of a magnetic stirrer. After an hour in the dark, the suspension was then irradiated with 500 W halogen lamp while stirring of suspension continued. An aliquot of 5 ml was taken from the reactor at an interval of 30 min for 1 hour 40 min then the catalysts was filtered and COD analysis of the sample was then carried out.

RESULTS AND DISCUSSION

Photocatalytic decoulartion of MB as a model using the synthesized photocatalyst

The photocatalytic activity of the prepared photocatalysts was first evaluated using MB dye as a model substrate. MB is widely used dye and is often found in textile effluent. MB is also used as test molecule for evaluating the activity of serries of photocatalyst (Disanto and Wagner,1972). The effect of varying $ZnFe_2O_4$ loading (10, 20, 30 and 40 wt%) on SiO_2support were investigated at an initial MB concentration of 50mg/l with a photocatalyst dosage of 1.0g/l it is clearly seen in Fig.1 that the percentage photocatalytic degradation of MB increases with increase in the $ZnFe_2O_4$ loading from 10 wt% to 30 wt% due to the increase in the number of $ZnFe_2O_4$ active sites because photocatalytic degredation occurs at the active sites. However, percentage photocatalytic degredation of MB decreased when $ZnFe_2O_4$ loading increased to 40 wt%. The significant reduction of the photocatalytic activity of sample containing 40 wt% $ZnFe_2O_4$ can be attributed to the increased agglomeration of $ZnFe_2O_4$ particle on SiO_2 thereby decreasing the rate of diffusion of photogenerated electron-hole pairs onto the MB molecules at the interface of solid photocatalyst MB solution. Retardation of the diffusion of electron-pairs decreases the extent of photocatalytic degredation (Li *et al.,* 2011). Agglomeration of $ZnFe_2O_4$particle on the surface of SiO_2 decreases the specific surface area and light penetration for an efficient photocatalytic degradation. Similar observations were reported for photocatalytic degradation of methyl orange and Orange II dyes on suported α- Fe_2O_3 photocatalyst. Thus, 5 wt% α- Fe_2O_3 /zeolite-HY exhibited the highest acitivty for degredation of methyl orange (Jaafar *et al.,*2012). 25 wt% Fe_2O_3/alumina exhibited the highest degradation of oragne II dyes (Li *et al.,* 2011). in the present work, highest photocatalytic degredation of MB was achieved with 30 wt% $ZnFe_2O_4/SiO_2$. therefore the best loading of $ZnFe_2O_4$ on the SiO_2 support is trade off between good dispersion of $ZnFe_2O_4$ on the support and the amount of the photocatalytic active sites. Moreover Fu *et al.*,(2010) reported that SiO_2 support improves the formation of OH radicals by photocatalysts.

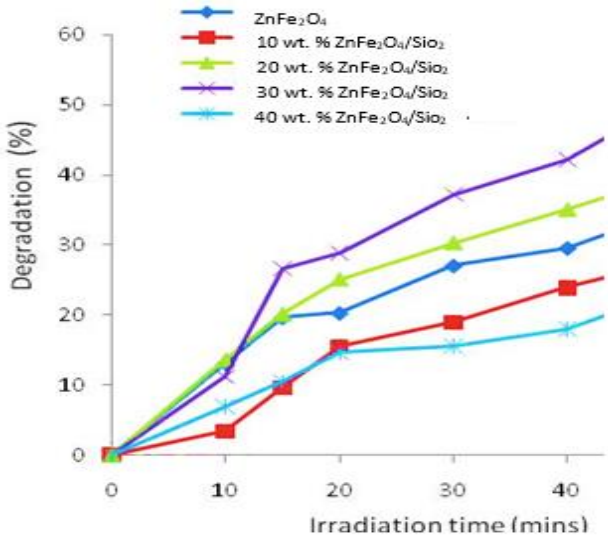

Fig.1: Photocatalytic degradation of MB using $ZnFe_2O_4$ and SiO_2 Supported $ZnFe_2O_4$

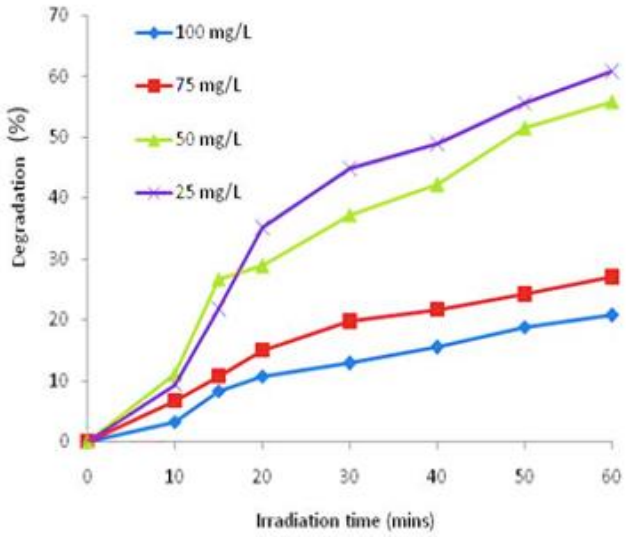

Fig.2: Effect of initial concentration of MB on its photocalytic degradation using 30 wt% $ZnFe_2O_4/SiO_2$

The effect of the initial MB concentration on its photocatalytic degradation using 30 wt% $ZnFe_2O_4/SiO_2$ was investigated by varying MB concentration from 25 to 100mg/l. Fig.2 shows that the photocatalytic degradation decreased with increasing initial concentration of MB, for instance, when the initial concentration of MB was increased from 25 to 100 mg/l, the photocalytic degradation decreased from 59% to 17%, after 60 min of visible light irradiation. This observation can be explained as follows: the generation of electrons and holes is the same for a given dosage of photocatalyst and intensity of the incident radiation. At higher initial concentation, MB molecules can absorb some of the incident radiation. This will decrease the amount of available light photons that will drive the photocalytic process (Jaafar *et.al.*,2012).

Photocatalytic treatment of textile effluent

The properties of the raw treated textile effluent used in the work are presented in Table.1, also presented in the Table are the properties of the treated textile efleunt via photolysis and photocatalysis with $ZnFe_2O_4$ and 30 wt% $ZnFe_2O_4/SiO_2$. Due to the complex nature of most industrial effluents, the organic content of the effluents is measured using lamp parameters such as Chemical Oxygen Demand (COD), Biological Oxyen Demand (BOD) and Total organic carbon (TOC) etc. Conductivity and TDS indirectly measure the amount of in-organic species (such as disolved salts) in the effluent. As seen in Table 1. upon photolysis of the effluent, smaller changes were observed in the properties of the effluent degradation of the organic and inorganic pollutants present in the effluent via photocatalysis. The decrease in the effluent's PH is due to the release of CO_2 during

photocatalytic degradation of organic pollutants. The observed reduction of the effluent's condcutivity and TDS can be attributed to photocatalytic decomposition of inorganic and organometallic dyes and other pollutants

Table 1: Properties of the raw and treated textile effluents

	pH	Conductivity (µs/cm)	Turbidity (NTU)	TDS (mg/l)	BOD (mg/l)	COD (mg/l)
Raw effluent	11.81	3.07	8.80	1520	28.45	784
Effluent treated via photolysis	11.69	3.05	7.00	1510	25.61	706
Effluent treated via photocatalysis and $ZnFe_2O_4$	10.01	2.67	6.52	1505	21.34	588
Effluent treated via photocatalysis with 30 wt% $ZnFe_2O_4/SiO_2$	8.40	2.0	5.01	500	15.65	423

Photocatalytic decolouration of textile effluents

UV-Vis analysis of the treated effluent provides information about the decolourazation of the wastewater caused by photolysis and photocatalytic destruction of the chromophores responsible for the colour of the waster water (Boorman *et.al.*,1999). The results of decolourization of textile effluents are presented in Fig. 3 Irradiation of the textile effluent in the absence of photocatalyst (photolysis) resulted in the removal of only 14% of the effluent's initial colour after 80 mins. When decolourization of the textile effluent via photocatalysis treatment under visible light was performed, percentage decolourization of 30% and 50% were observed for $ZnFe_2O_4$ and 30 wt% $ZnFe_2O_4/SiO_2$ respectively. Thus, 30 wt% $ZnFe_2O_4/SiO_2$ is more effective in colour removal than $ZnFe_2O_4$. This higher adsorption effeciency of 30 wt% $ZnFe_2O_4/SiO_2$ can be attributed to the information of more OH radicals in the presence of SiO_2 as reported by Fu *et al.*, (2010)

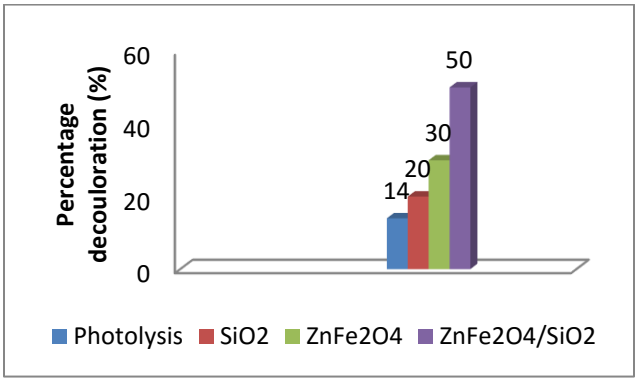

Fig. 3: Decolourization of textile effluent via photolysis and photocatalysis using $ZnFe_2O_4$ and 30 wt% $ZnFe_2O_4/SiO_2$. [Irradiation time – 80 mins. Photocatalysts dose - 0.1 g/L]

Photocatalytic degradation of textile effluent (COD removal)

The results of COD removal from textile effluent via photolysis and photocatalysis are presented in Fig 4. It was found that irradiation of textile effluent for 90 mins in

the absence of photocatalysts (photolysis) resulted in the COD removal of only 10%. This indicates that the organic load of the sample irradiated without photocatalysts did not change much, and the small COD removal observed was due to the photochemical oxidation of the organic compounds present in the textile effluent (Pelantridous *et al.*, 2009). Therefore, irradiation without photocatalysts is not sufficient to efficiently degrade the textile effluent. When the solution was exposed to visible light irradiation in the presence of $ZnFe_2O_4$ and 30 wt% $ZnFe_2O_4/SiO_2$ for 90 mins, 25% and 46% COD was achieved, respectively. This evidently shows that 30 wt% $ZnFe_2O_4/SiO_2$ has better photocatalytic performance than the bare $ZnFe_2O_4$ for the treatment of the textile effluent.

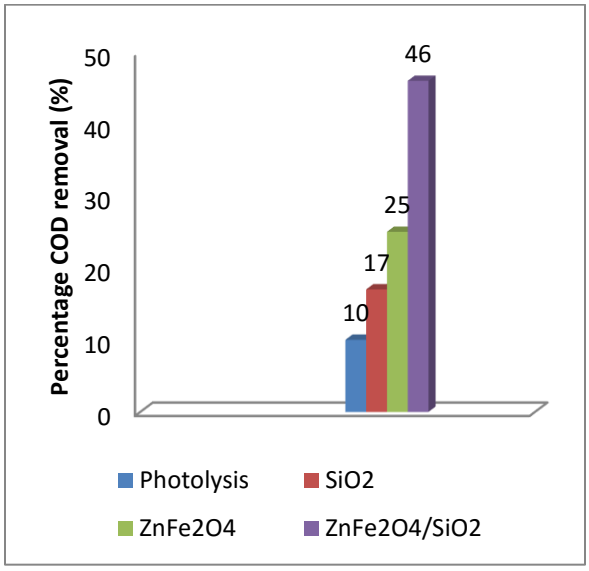

Fig 4: COD removal from textile effluent via photolysis and photocatalysis using $ZnFe_2O_4$ and 30 wt% $ZnFe_2O_4/SiO_2$. [irradiation time – 80 mins. Photocatalyst dose – 0.1 g/L]

Photocatalytic degradation of textile effluent (BOD removal)

The results of BOD removal from textile effluent via photolysis and photocatalysis are presented in Fig 5. It was found that irradiation of textile effluent for 90 mins in the absence of photocatalysts (photolysis) resulted in the BOD removal of only 10%. This indicates that the organic load of the sample irradiated without photocatalysts did not change much, and the small BOD removal observed was due to the photochemical oxidation of the organic compounds present in the textile effluent (Pelantridous *et al.*, 2009). Therefore, irradiation without photocatalysts is not sufficient to efficiently degrade the textile effluent. When the solution was exposed to visible light irradiation in the presence of $ZnFe_2O_4$ and 30 wt% $ZnFe_2O_4/SiO_2$ for 90 mins, 25% and 45% BOD was achieved, respectively. This evidently shows that 30 wt% $ZnFe_2O_4/SiO_2$ has better photocatalytic performance than the bare $ZnFe_2O_4$ for the treatment of the textile effluent.

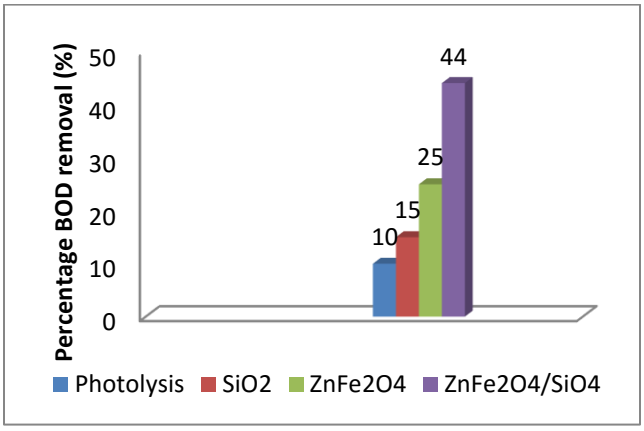

Fig 5: BOD removal from textile effluent via photolysis and photocatalysis using $ZnFe_2O_4$ and 30 wt% $ZnFe_2O_4/SiO_2$. [irradiation time – 80 mins. Photocatalyst dose – 0.1 g/L]

CONCLUSION

Zinc ferrite silica gel composite showed better photocatalytic activity than bare zinc ferrite and photolysis on the treatment of real textile effluent but the best result was achieved through using 30 wt% zinc ferrite silica gel composites photocatalysts.

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