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Photocatalytic Degradation of the Azo Dye "Congo-Red" by $ZnFe_2O_4$/ ZnO Nanocomposite

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Abstract

This paper reports the preparation of $ZnFe_2O_4$/ZnO metal oxide nanocomposite by solution combustion synthesis. Zinc nitrate and ferric nitrate were utilized as oxidizers in this work, while glycine served as fuel. The powder X-ray diffraction pattern indicated that the nanocomposite consisted of $ZnFe_2O_4$ and ZnO having spinel and wurtzite phases respectively. The efficiency of the nanocomposite in the photocatalytic degradation of Congo Red (CR) dye from its aqueous solution was studied. The effects of CR starting concentration, photocatalyst dose, and irradiation duration were investigated. More than 90 % degradation of 10 ppm CR solution was achieved for a photocatalyst dosage of 1.0g/litre of the dye solution in 40 minutes. The excellent photocatalytic activity of the nanocomposite was considered as the result of the synergistic mechanism between its constituent phases, significantly reducing electron-hole recombination. It was noticed that the photocatalyst after the first regeneration was about 85 % efficient compared to the original one. The water contamination with human activity can be reduced by the usage of $ZnFe_2O_4$/ZnO metal oxide nanoparticles.

Keywords: *Congo Red, Nanocomposite, Synergistic Mechanism, $ZnFe_2O_4$/ ZnO Metal Oxide*

1.0 Introduction

Treating polluted water contaminated by human activity will be a challenging task in the future[1]. Azo dyes contain the azo (–N=N–) chromophores and constitute one of the significant classes of dyes used in textile and other industries[2]. Azo dyes such as Congo Red (CR) and their degradation products such as aromatic amines exhibit carcinogenic effects when present in wastewater[3]. Hence, it is of prime importance to treat the effluents containing such dyes to minimize their effect on the environment[4].

Some commonly used methods for removing dyes from wastewater include adsorption, biodegradation, chlorination, ozonation, flocculation, reverse osmosis, etc. Most of these methods are not destructive since they only transfer the contaminant from one phase into the other, requiring further treatment[5].

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Recently, advanced oxidation processes, commonly called AOPs, are being considered as one of the most effective methods for removing toxic and non-biodegradable pollutants from wastewater[6]. Photocatalysis, H_2O_2/UV, and the Fenton process are the commonly used AOPs. AOPs generate hydroxyl radicals (●OH) which are potent oxidizing species responsible for the mineralization of organic matter into H_2O and CO_2[7].

Heterogeneous photocatalysis using metal oxide nanomaterials is considered to be less expensive and more efficient method for removing various pollutants from wastewater. This process involves the oxidation of pollutants on the surface of the photocatalyst. This method results in quick oxidation of the pollutants and does not form polycyclic compounds[8]. The process can efficiently remove inorganic and organic pollutants and microbes from water. However, a significant drawback of this process is the quick recombination of the photogenerated electrons and holes, which decreases the efficiency of the photocatalyst[9].

Semiconductor metal oxide nanoparticle combination is one of the promising techniques to minimize charge recombination. The formation of nanocomposite is an important feature of this technique. A wide band gap semiconductor is coupled with a narrow band gap semiconductor in the nanocomposite material. These two semiconductors should possess matching band potentials. When such a nanocomposite photocatalyst is illuminated with UV or visible light, there is the generation of electrons and holes in the narrow band gap semiconductor, which initiates the photocatalytic reaction, thus increasing the photocatalytic efficiency[9]. Recently, several nanocomposite photocatalysts have been prepared, and their photocatalytic efficiencies in the degradation of dyes have been reported. Some of these include metal oxide composites such as $MgFe_2O_4/TiO_2$, $NiFe_2O_4/TiO_2$, $CuFe_2O_4/TiO_2$, $MnFe_2O_4/TiO_2$ and $ZnFe_2O_4/TiO_2$ [10]. $TiO_2/AgGaS_2$ photocatalyst was synthesized by sol-gel synthesis and solid-state reaction[11]. The photocatalyst exhibited excellent photocatalytic activity in comparison to its constituents. The higher charge separation and quick photogenerated electron transport from $AgGaS_2$ to TiO_2 were credited with this exceptional photocatalytic activity.

The co-precipitation method was employed to successfully synthesize nanocrystalline Fe-Ce mixed metal oxides[12]. The mixed oxide almost completes the degradation of CR from its aqueous solution. This was attributed to the mixed oxide's greater surface area and surface acidity[13].

The synthesis of $ZnFe_2O_4$/ZnO nano composite metal oxide was described in the current work using solution combustion synthesis. Congo Red was successfully removed from its aqueous solution using the nanocomposite. Researchers looked at the effects of photocatalyst dosage, irradiation duration, and starting CR concentration. It was also investigated as to how regeneration affected the photocatalyst's efficiency.

2.0 Materials and Methods

Ferric nitrate [99%, SD Fine Chemicals Ltd., India], Zinc nitrate [99%, SD Fine Chemicals Ltd., India], and Glycine [99%, SD Fine Chemicals Ltd., India] were supplied by SD-Fine Chemicals Limited, India. The chemicals were used as received without further purification.

2.1 Preparation of the $ZnFe_2O_4$/ZnO Metal Oxide Nanocomposite

Appropriate amounts of ferric nitrate, zinc nitrate, and Glycine were transferred into the reaction vessel and were dissolved in a minimum quantity of double distilled water. The solution was stirred on a magnetic stirrer for ~10 minutes and then heated on a hotplate to evaporate excess water. The reaction vessel was then placed into a muffle furnace at ~350°C. Initially, there was dehydration of the reaction mixture followed by combustion, thus forming the nanocomposite. After allowing the nanocomposite to reach room temperature, it was finely crushed into a powder[14,15].

The entire reaction was represented by Equation 1.

$$6Zn(NO_3)_{2(aq)} + 2Fe(NO_3)_{3(aq)} + 10C_2H_5NO_{2(aq)} \downarrow ZnFe_2O_{4(s)} + 5ZnO_{(s)} + 20CO_{2(g)} + 14N_{2(g)} + 25H_2O_{(g)} \quad (1)$$

2.2 Characterization of the $ZnFe_2O_4$/ZnO Nanocomposite

The nanocomposite's PXRD data was acquired using the 40 kV CuKα radiation Philips X'Pert Pro X-ray diffractometer. The nanocomposite's average crystallite

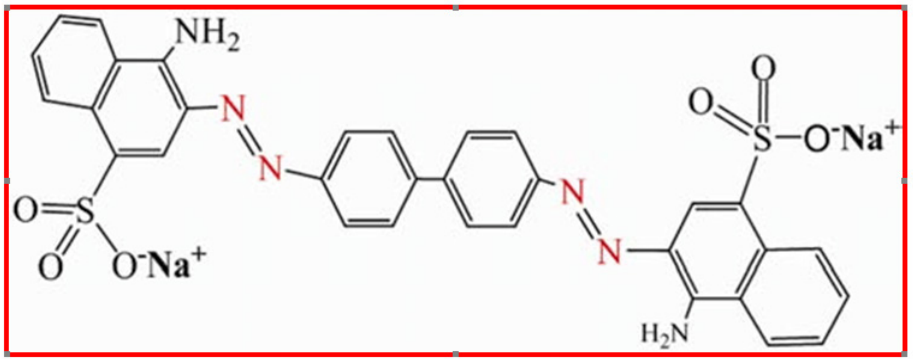

Figure 1. Structure of CongoRed Dye.

size (D) was calculated using Equation 2, also known as Scherer's formula.

$$D = \frac{k\lambda}{\beta cos\theta} \quad (2)$$

Bragg's angle (θ), the full width at half maximum (β), and the wavelength (λ) of the X-rays were obtained from the XRD pattern and the instrument[16].

Using KBr as a reference, the Perkin-Elmer spectrometer (spectrum 1000) was utilized to record the nanocomposite's FTIR spectrum. The scanning electron micrograph of the nanocomposite was captured using a JEOL-2100F (Japan) scanning electron microscope.

2.3 Photocatalytic Degradation of the Congo Red Dye

The Congo Red is a water-soluble azo dye having the structure shown in Figure 1. In human beings, it affects the eyes, skin, respiratory, and reproductive systems. In higher concentrations, it shows cytotoxic, carcinogenic as well as mutagenic effects. Figure 2 depicts the UV-visible spectrum of CR (10 ppm) which showed maximum absorbance at 498 nm[16].

A suitable quantity of the nanocomposite and 50 millilitres of CR solution were added to the reaction vessel. The liquid was centrifuged for ten minutes after being magnetically agitated for thirty minutes while exposed to UV radiation. Equation 3 was used to compute the percentage of dye removal after the UV-visible spectra of the supernatant solution were recorded[17].

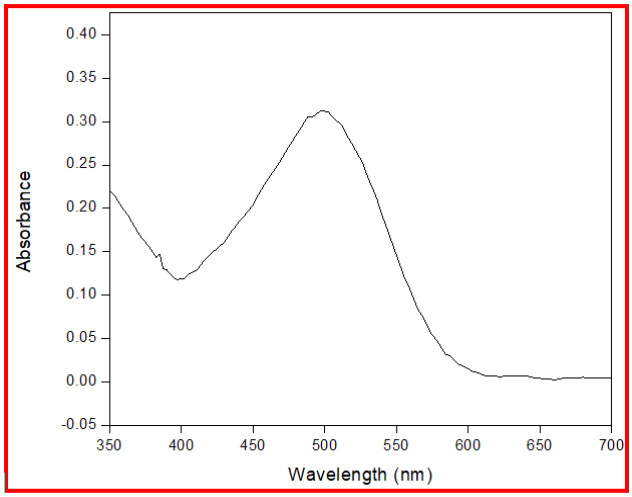

Figure 2. Absorbance of 10 ppm Congo red Dye solution.

$$\%\ dye\ reomval = \frac{(C_0 - C_e)}{C_o}\ x\ 100 \quad (3)$$

C_0 and C_e refer, respectively, to the initial and equilibrium concentrations of the CR solution. The process described above was carried out using different photocatalyst dosages. Figure 6 shows the photocatalyst dosage that works best.

After the ideal dosage was established, 100 mL of CR solution and the ideal quantity of the nanocomposite were added to the reaction vessel to examine the impact of irradiation duration. Under UV light, the slurry was magnetically agitated. A little aliquot of the mixture was taken out and centrifuged every five minutes, and each time the supernatant's UV-visible spectrum was measured. Figure 7 shows the optimal period to be exposed to radiation[18].

2.4 Reusability of the Photocatalyst

Reusability tests were conducted for the $ZnFe_2O_4$/ZnO nanocomposite. After being used in the photocatalytic degradation experiment, the photocatalyst was allowed to settle down naturally in the reactor. The supernatant dye solution was removed by decantation. The residue was washed several times with double distilled water and then dried for 5 hours at 60 °C before being used for new photocatalytic degradation experiments. The studies were carried out after the first and second regeneration. The reusability studies were conducted for 10 ppm CR solution[19].

3.0 Results and Discussions

3.1 Characterization of the $ZnFe_2O_4$/ZnO Nanocomposite

3.1.1 XRD Studies

The $ZnFe_2O_4$-ZnO nanocomposite's PXRD pattern (Figure 3) revealed the existence of the wurtzite phase of ZnO (JCPDS file number: 36-1451) and the spinel phase of $ZnFe_2O_4$ (JCPDS file number: 22-1012). Equation 2 yielded an average crystallite size of around 15 nm[17].

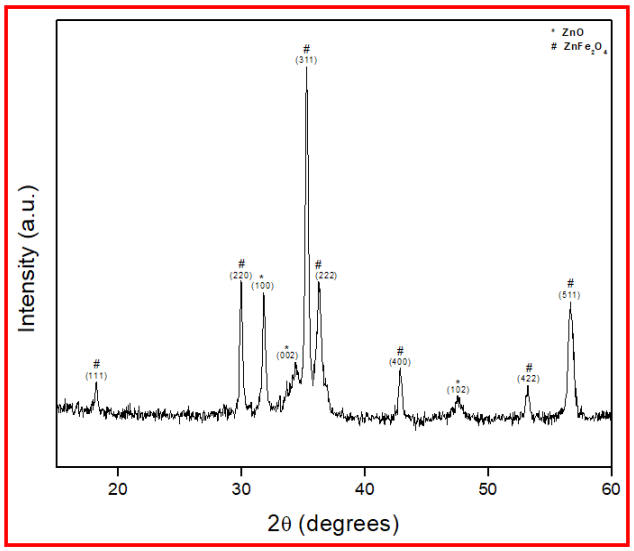

Figure 3. PXRD pattern of the $ZnFe_2O_4$-ZnO nanocomposite.

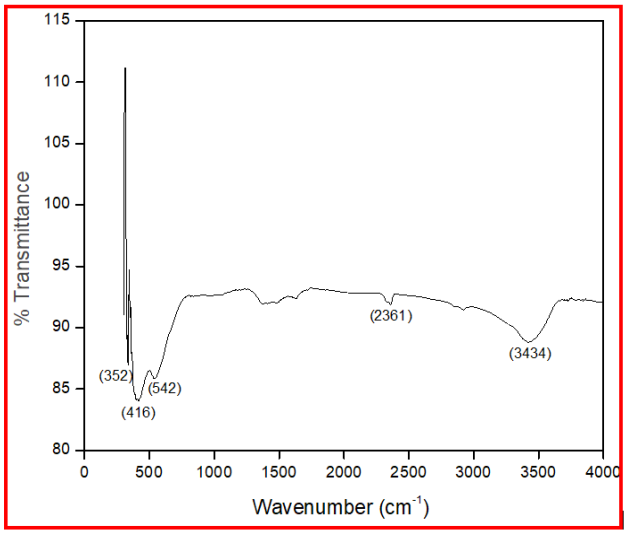

Figure 4. FTIR spectrum of the $ZnFe_2O_4$-ZnO nanocomposite.

3.1.2 FTIR Studies

The $ZnFe_2O_4$-ZnO nanocomposite's FTIR spectra (Figure 4) revealed peaks for both the Zn-O (~352 cm^{-1}) and Fe-O (~416 and ~542 cm^{-1}) linkages. The –OH group of water adsorbed on the photocatalyst surface and ambient CO_2 were responsible for the maxima at approximately 2361 cm^{-1} and 3434 cm^{-1}, respectively[20].

3.1.3 SEM Studies

The SEM micrograph of the nanocomposite (Figure 5) showed that the particles were highly agglomerated. The agglomeration was due to the tendency of the particles to minimize their surface-free energy[21].

3.2 Photocatalytic Degradation Studies

Figures 6 and 7 depict the results of the photocatalytic removal of CR. As the photocatalyst dosage increased, the dye degradation increased until the optimum dosage was reached. The optimum dosage was found to be 1.0 gL^{-1} for both the initial dye concentrations. Beyond 1.0 gL^{-1}, the dye degradation was negligible. It was discovered that 40 minutes was the ideal irradiation time. The photocatalyst's number of active sites rose along with its dosage, which raised the rate at which CR degraded[22].

The photocatalytic degradation of CR decreased with its initial concentration (Table 1). This was because the number of dye molecules increased when the initial CR

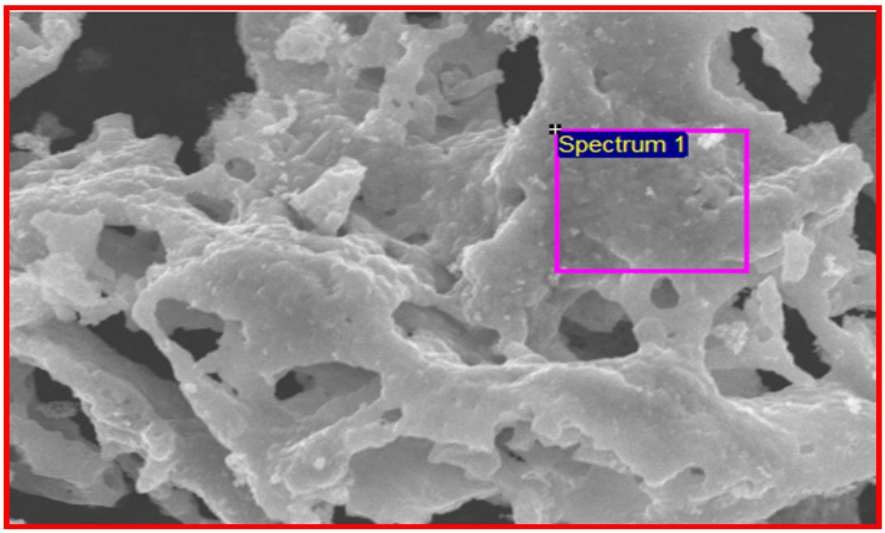

Figure 5. SEM micrograph of the $ZnFe_2O_4$-ZnO nanocomposite.

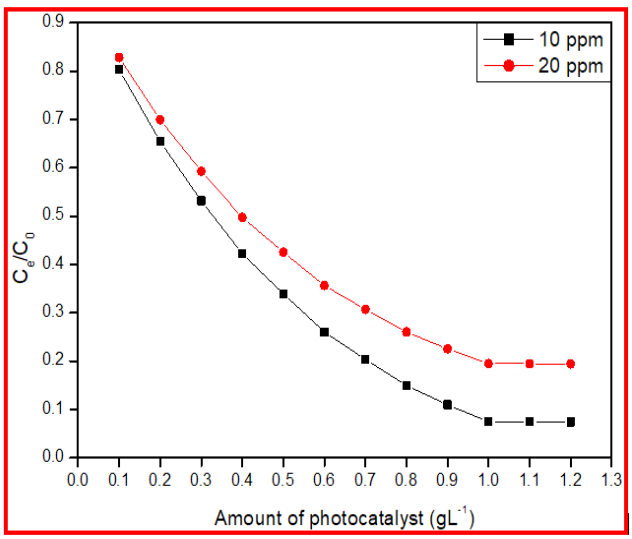

Figure 6. Effect of dosage of the photocatalyst.

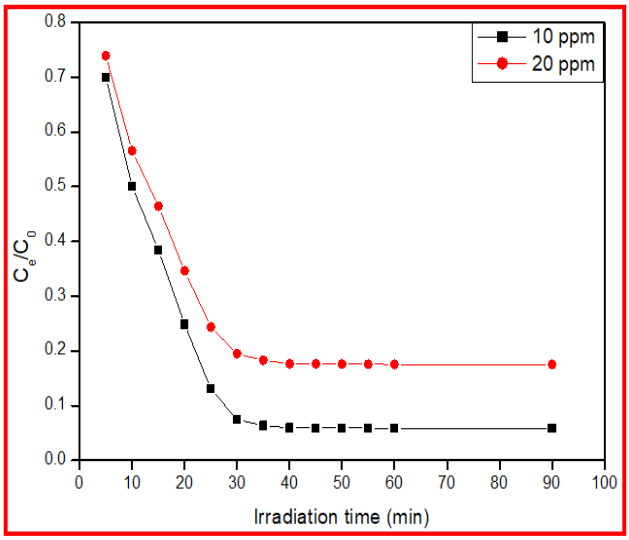

Figure 7. Effect of irradiation time.

concentration was increased for a given dosage of the nanocomposite. Still, the number of active sites remained the same. The competition amongst the dye molecules to adsorb onto the photocatalyst's active sites increased as the initial concentration of the dye increased[22].

3.3 Reusability of the Photocatalyst

Table 2 gives the results of the reusability studies. It was found that the efficiency of the photocatalyst decreased with usage (Figure 8). After the first use, the photocatalyst was almost 85% more efficient in degrading CR than the original one. The efficiency was further reduced after the first and second usage. Also, there was a slight increase in the dosage of the nanocomposite as well as the irradiation time[23].

3.4 Mechanism of Photocatalytic Degradation of Congo Red

As is evident from the results, the $ZnFe_2O_4$/ZnO nanocomposite exhibited excellent photocatalytic

Table 1. Results for the photocatalytic degradation od Congo red dye

Concentration of the Dye solution (ppm)	Optimum Dosage of the Photocatalyst (gL^{-1})	Optimum Irradiation Time (min)	% Dye Removal
10	1.0	40	94.03
20	1.0	40	82.34

Table 2. Reusability of the photocatalyst after first and second recovery

Nature of the photocatalyst	Optimum Dosage of the Photocatalyst (gL^{-1})	Optimum Irradiation Time (min)	% Dye Removal
Original	1.0	40	94.03
First recovery	1.1	45	80.15
Second recovery	1.2	50	75.22

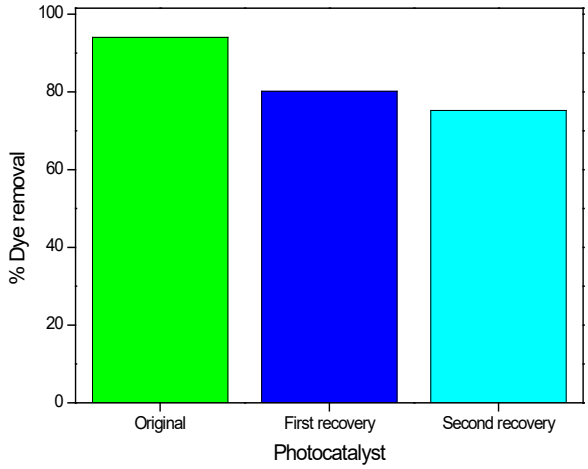

Figure 8. Results of reusability of the photocatalyst.

activity for the removal of CR from its aqueous solution. This was attributed to the presence of both $ZnFe_2O_4$ and ZnO phases, resulting in a synergistic mechanism between them. The synergistic mechanism involved interparticle charge transfer from one phase to another[24].

The $ZnFe_2O_4$/ZnO nanocomposite's photocatalytic degradation mechanism can be explained in the following way. When the nanocomposite is exposed to UV radiation, the semiconductors $ZnFe_2O_4$ and ZnO within it are excited, which causes electron-hole pairs to form in each semiconductor. Every semiconductor has stimulated electrons that move from its Valence Band (VB) to its matching Conduction Band (CB). The CB of $ZnFe_2O_4$ contains electrons that leap into that of ZnO's, boosting the latter's electron concentration[25].

The holes in ZnO's VB shift to that of $ZnFe_2O_4$ at the same time. As a result, there are more holes in the $ZnFe_2O_4$ VB. More charge separation and a notable decrease in electron-hole recombination are the outcomes of this process. The redox processes that take place at the semiconductor surfaces involve both electrons and holes. Overall, this leads to a rise in photocatalytic activity. The improved electron-hole charge separation in the nanocomposite was the cause of its increased photocatalytic activity[26].

4.0 Conclusions

$ZnFe_2O_4$-ZnO nanocomposite was prepared for this study using the solution combustion method. The product was characterised using FTIR, SEM, and PXRD. Excellent photocatalytic effectiveness was demonstrated by the nanocomposite in the extraction of CR from its aqueous solution. As a result, the $ZnFe_2O_4$-ZnO nanocomposite shows promise as a photocatalyst for the efficient extraction of colours from wastewater. So the material we have studied in this work will be a promising combination for effective dye removal from the industrial effluent water.

5.0 Acknowledgement

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