

Synthesis and characterization $\text{ZnFe}_2\text{O}_4@\text{MnO}$ and $\text{MnFe}_2\text{O}_4@\text{ZnO}$ magnetic nanocomposites: Investigation of photocatalytic activity for the degradation of Congo Red under visible light irradiation

Azam Zamani¹, Mirabdullah Seyed Sadjadi^{1,*}, Alireza Mahjoub^{2,*}, Mohammad Yousefi³, Nazanin Farhadyar⁴

¹Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran

²Department of Chemistry, Tarbiat Modares University, Tehran, Iran

³Department of Chemistry, Yadegar-e-Imam Khomeini (RAH) Shahre Rey Branch, Islamic Azad University, Tehran, Iran

⁴Department of Chemistry, Varamin Pishva Branch, Islamic Azad University, Varamin, Iran

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Abstract

In the present investigation, $\text{ZnFe}_2\text{O}_4@\text{MnO}$ and $\text{MnFe}_2\text{O}_4@\text{ZnO}$ magnetic nanocomposites were fabricated by facile hydrothermal method and were calcined at 300 °C for 3 h. Synthesis of $\text{ZnFe}_2\text{O}_4@\text{MnO}$ and $\text{MnFe}_2\text{O}_4@\text{ZnO}$ magnetic nanocomposites optimized by the different weight percentages. The synthesized photocatalyst was characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR), Vibrating Sample Magnetometer (VSM), EDAX (Energy dispersive X-ray Analysis), diffuse reflectance UV-vis spectroscopy (DRS) and field emission scanning electron microscopy (FESEM). The $\text{ZnFe}_2\text{O}_4@\text{MnO}$ nanoparticles were found to have a size of 20-50 nm. Magnetic studies revealed that the $\text{ZnFe}_2\text{O}_4@\text{MnO}$ and $\text{MnFe}_2\text{O}_4@\text{ZnO}$ nanocomposites can be easily separated from the solution by an external magnetic field. The photocatalytic degradation of Congo red dye (CR) was investigated based on the removal of Congo red (CR) in aqueous solution in 35 min of visible light irradiation. Compared with $\text{MnFe}_2\text{O}_4@\text{ZnO}$ nanocomposite, the $\text{ZnFe}_2\text{O}_4@\text{MnO}$ nanocomposite displayed highly photocatalytic performance on the photodegradation of Congo red. Effect of reaction time, pH, and loading of ZnO on degradation of CR was studied. The results demonstrated that the degradation efficiency of $\text{ZnFe}_2\text{O}_4@\text{MnO}$ nanocomposite (98.5%) was better than that of $\text{MnFe}_2\text{O}_4@\text{ZnO}$ nanocomposite (90.32%), which is due to the presence of narrow band gap energy of $\text{ZnFe}_2\text{O}_4@\text{MnO}$. Kinetics studies have displayed that the degradation of CR by the prepared photocatalysts follows the pseudo-first-order kinetics and the rate constant achieved for $\text{ZnFe}_2\text{O}_4@\text{MnO}$ ($k=0.0371 \text{ min}^{-1}$) was much greater than of $\text{MnFe}_2\text{O}_4@\text{ZnO}$ ($k=0.0321 \text{ min}^{-1}$). The synthesized $\text{ZnFe}_2\text{O}_4@\text{MnO}$ nanocomposite can be potentially applied as a magnetically separable photocatalyst to deal with water pollution problems.

Keywords: Congo Red; Hydrothermal Method; Magnetical Nanocomposites; Photocatalytic Activity; Visible Light.

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INTRODUCTION

Dyes are one of the largest groups of organic compounds that exhibit an increasing environmental risk. Textile industries are the most common sectors in the world which uses dye to color the fabrics [1-3]. Waste waters generated by the textile industries contain significant amounts

of non-fixed dyes, especially of azo dyes, and huge amount of inorganic salts. In addition to the drinkable water shortage and drought in the various region of the global, such as water contamination threats to human health [4]. Hence the removal of these dyes from waste water is a main environmental trouble because conventional

* Corresponding Author Email: m.s.sadjad@gmail.com

physicochemical and biological treatment methods are ineffective for decolorization and degradation. Many chemical and physical techniques containing adsorption, coagulation, precipitation, filtration, electrodialysis, membrane separation and oxidation have been utilized efficiently for removal of dye pollutants [5]. Nonetheless, they are non destructive, since they transfer organic compounds from water to another phase, thus causing secondary pollution [6]. Currently, Advanced oxidation processes (AOP's) in which heterogeneous photocatalysis emerges as an appealing harmful method, leading to mineralization of organic water pollutants is widely used [7]. To find an efficient and economically permanent solution to eliminating the water contaminants becomes a pressing subject for every nation. Many research converts to the solar energy, the radiant light, and heat from the sun, which is the most plenty clean energy sources on the Earth. Extensive research studies concentrate on the progress of new materials that can efficiently product solar irradiation and apply it for green environmental contamination management. The photocatalysis process that uses such renewable solar energy to activate the chemical reactions by oxidation and reduction process becomes a sustainable and attractive technology to develop a viable solution for environmental problems [8]. Magnetic and non-magnetic nanoparticles as photocatalysts were made to use in photocatalysis studies. A nanocomposite can be useful in separating nanoparticles from the suspension by making them with magnetic nanoparticles [9-10]. Recently, Magnetic nanoparticles (MNPs) have been attracting a tremendous consideration for their potential use in biomedical applications like controlled drug delivery, cell separation, magnetic resonance imaging and localized hyperthermia therapy of cancer. Iron oxide based magnetic nanoparticles are of special importance because of their suitable biocompatibility and low toxicity. Iron oxides are very ordinary compounds and they are widespread in nature and readily synthesized in the laboratory. In almost everywhere of the global system atmosphere, biosphere, hydrosphere, and lithosphere, iron oxides present. The future of the data storage industry will be worth of wondering by looking at the options available today and the development during the time. Manganese ferrite (MnFe_2O_4) is extraordinarily significant member of the ferrite family with a variety of utilizations in

the modern era of science and engineering [11]. Zinc Ferrite (ZnFe_2O_4) displays superparamagnetic behavior and it has potential application in many fields, such as photocatalysis, magnetic resonance imaging (MRI), Li-ion batteries and gas sensors [12]. Various semiconductor photocatalysts have been considered for the degradation of organic pollutants. Among them, manganese oxide (MnO) is a semiconductor with a wide band gap width ($3.9 \pm 4/0\text{eV}$) at room temperature [13]. Manganese oxides, including MnO, MnO_2 , and Mn_3O_4 , are interesting composites and have been applied in wastewater treatment, catalysis, sensors, supercapacitors, and alkaline and rechargeable batteries [14]. Also, Zinc oxide (ZnO) is a semiconductor with a wide band gap width (3.37 eV) and large excitation binding energy (60 meV) at room temperature, which lead to ZnO has been employed considerable in the degradation of dye pollutant [15]. Despite a large number of studies published on nanocomposites photocatalytic activity, fabrication of $\text{ZnFe}_2\text{O}_4@\text{MnO}$ and $\text{MnFe}_2\text{O}_4@\text{ZnO}$ magnetic nanocomposites via facile hydrothermal method has not yet been reported. And also, we investigated the photocatalytic activity of magnetic nanocomposites for degradation of Congo red dye under the visible light irradiation. In the present study, the magnetic nanocomposites display a high photocatalytic activity under the influence of visible light irradiation at a shorter irradiation time. Furthermore, we have fabricated $\text{ZnFe}_2\text{O}_4@\text{MnO}$ and $\text{MnFe}_2\text{O}_4@\text{ZnO}$ nanocomposites by hydrothermal method and samples were calcined at 300 °C for 3 h with smaller particle size. Our synthesis of $\text{ZnFe}_2\text{O}_4@\text{MnO}$ and $\text{MnFe}_2\text{O}_4@\text{ZnO}$ nanocomposites modified by the different weight percentages of the prepared samples. And also, Effect of reaction time and pH on degradation of CR was investigated. Synthesized nanocomposites were characterized by using XRD, FT-IR, EDAX, UV-DRS, FESEM and VSM. The photocatalytic activity was investigated in an aqueous solution for the photocatalytic degradation of Congo red with the visible light irradiation.

EXPERIMENTAL

Materials

All the chemicals that were employed in the experiments were reagent grade such as 20% NaOH (Merck, Germany), $\text{Mn}(\text{NO}_3)_2$ (Merck, Germany), $\text{Zn}(\text{NO}_3)_2$ (Merck, Germany) and

$\text{Fe}(\text{NO}_3)_3$ (Merck, Germany). All the experiments were performed in aqueous media.

Instrumentation

The crystalline structure of $\text{MnFe}_2\text{O}_4@ZnO$ and $\text{ZnFe}_2\text{O}_4@MnO$ were investigated by XRD (Philips PW 1730 Japan model) with CuK_α radiation (1.5406) °A in 2θ scan range of 10–80°. In order to examine the morphologies of $\text{MnFe}_2\text{O}_4@ZnO$ and $\text{MnFe}_2\text{O}_4@ZnO$ nanomaterials, FESEM measurements were done with a ZEISS DSM-960A analytic microscope (Germany). The magnetic hysteresis loops of samples were performed by a vibrating sample magnetometer with VSM, Lake Shore Model 7404 at room temperature (300 K). Then, A diffuse reflectance spectrum (DRS) of the $\text{MnFe}_2\text{O}_4@ZnO/GO$ and $\text{MnFe}_2\text{O}_4@ZnO/RGO$ nanocomposites were recorded on a UV-2550 Shimadzu UV–vis spectrophotometer equipped

with ISR-2200 DRS accessory (UV-2550 Shimadzu, Japan). Finally, IR spectra were recorded on a Bruker FT-IR instrument using KBr plates.

Synthesis of the $\text{MnFe}_2\text{O}_4@ZnO$ nanoparticles

The fabrication of $\text{MnFe}_2\text{O}_4@ZnO$ was carried out by hydrothermal method [16]. In this regard, 4.75 g $\text{Mn}(\text{NO}_3)_2$, 5.87 g $\text{Fe}(\text{NO}_3)_3$ and 10% NaOH dissolved in 40 ml of distilled water were mixed under magnetic stirring for 30 min. Then, transferred to 50 ml of Teflon lined autoclave and heated to 150 °C for 3 h under autogenous pressure. The reaction mixture was allowed to cool to room temperature. Finally the precipitated solution was washed several times with distilled water and ethanol. Then the brown precipitates were collected and dried at 70°C for 3 hours in hot air oven. Moreover, 1 g of ZnO was calcined at 500 °C for 3 h, followed by dropwise addition of 10%

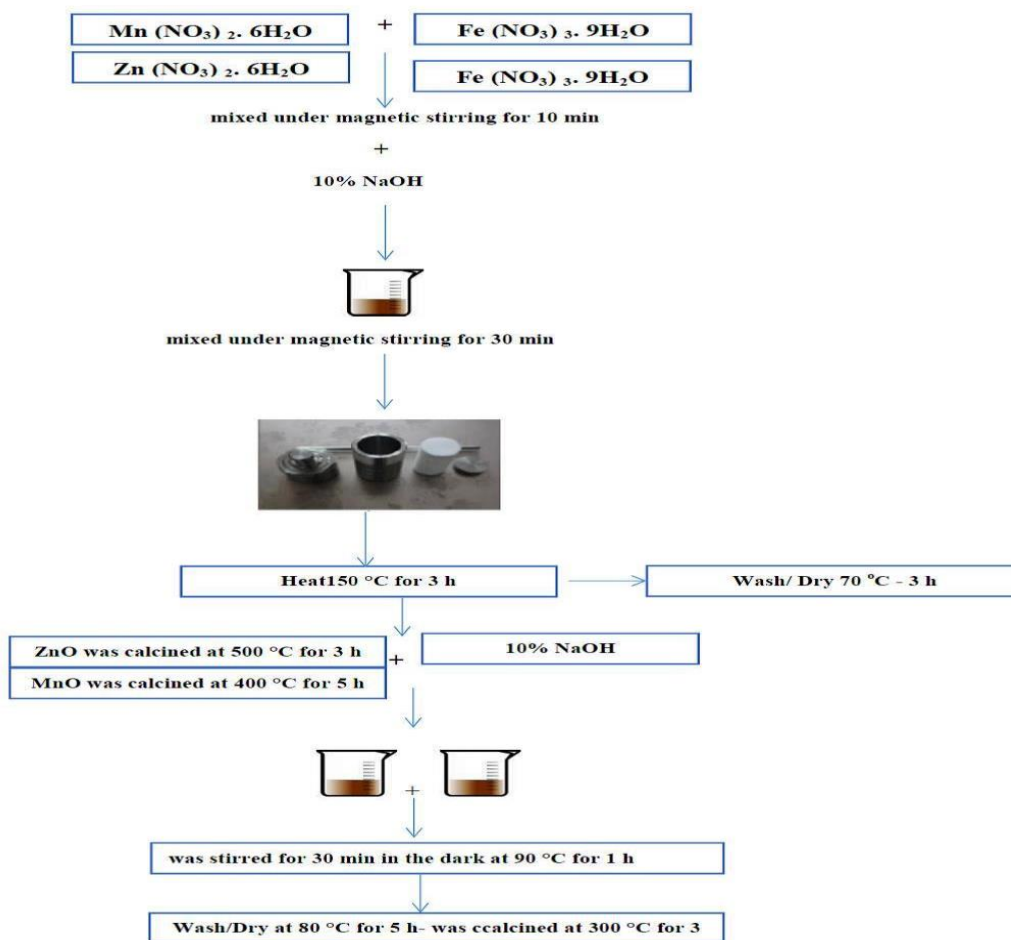


Fig. 1. The preparation steps of $\text{MnFe}_2\text{O}_4@ZnO$ and $\text{ZnFe}_2\text{O}_4@MnO$ nanocomposites.

NaOH solution in calcined ZnO and magnetically stirred for 10 min. After the Mn-Fe precursor solution was added to the suspension, the new mixture was stirred for 30 min in the dark at 90 °C for 2 h. In the following stage, the obtained precipitate was filtered and washed with ultrapure water for various times and was allowed to dry in a vacuum oven at 80 °C for 5h. Finally, the product was calcined at 300 °C for 3 h to form MnFe₂O₄@ZnO nanoparticles.

Synthesis of the ZnFe₂O₄@MnO nanoparticles

ZnFe₂O₄@MnO nanoparticles are synthesized by a hydrothermal method [16]. In this consideration, 3.75 g Zn (NO₃)₂, 4.87 g Fe (NO₃)₃ and 10% NaOH dissolved in 50 ml of distilled water were mixed under magnetic stirring for 30 min. Then, transferred to 50 ml of Teflon lined autoclave and heated to 150 °C for 3 h under autogenous pressure. The reaction mixture was allowed to cool to room temperature. Finally the precipitated solution was washed several times with distilled water and ethanol. Then the solution was collected and dried at 70°C for 3 hours in hot air oven. Furthermore, 1 g of MnO was calcined at 400 °C for 5 h. Then, the calcined MnO was added to 10% NaOH solution and magnetically stirred for 10 min. After the Zn-Fe precursor solution was added to the suspension, the new solution was stirred for 30 min in the dark at 90 °C for 2 h. The resulting precipitate was filtered, followed by washing with ultrapure water for several times and was allowed to dry in a vacuum oven at 80 °C for 5h. Finally, the obtained product calcined at 300 °C for 3 h to form ZnFe₂O₄@MnO nanoparticles. Fig. 1, displays the preparation steps of MnFe₂O₄@ZnO and ZnFe₂O₄@MnO nanocomposites.

Photocatalytic degradation experiments

The Photocatalytic activity of the as-prepared samples were measured by monitoring the degradation rate of CR solution as a model organic pollutants. The experiment was performed under visible light using a 100 W tungsten lamp as a visible light source. The photocatalytic experiments were performed at 25 °C with a concentration of 0.10 g L⁻¹ MnFe₂O₄@ZnO and ZnFe₂O₄@MnO nanocomposites and 50 mg L⁻¹ of CR solution with time intervals of (5–35 min) at pH= 4. In this experiment, 0.10 g L⁻¹ of MnFe₂O₄@ZnO and ZnFe₂O₄@MnO nanocomposites was added to 100 ml of 50mg L⁻¹ CR solution. Before

the photocatalytic reaction, the suspension was stirred in the dark for 30 min for adsorption-desorption equilibrium between the photocatalyst and dye solution. finally, it was irradiated. During irradiation, 5 ml of the suspension was sampled at an interval of 5 min and centrifuged to eliminate the catalyst particles and it was measured by Shimadzu UV-1650PC Model UV-vis spectrophotometer at $\lambda_{max} = 500$ nm. The dye degradation percentage was obtained from the following equation (1):

$$\text{The degradation efficiency (\% of CR)} = \frac{(C_0 - C)}{C_0} \times 100 \quad (1)$$

where C_0 represents the initial CR concentration (mg/L) and C indicates the CR concentration at a certain reaction time (min).

RESULTS AND DISCUSSION

Structural study

XRD patterns of synthesized MnFe₂O₄@ZnO and ZnFe₂O₄@MnO was studied by X-ray diffraction Philips Xpert XRD. Fig. 2 displays the X-ray diffraction patterns in the 2 θ ranges from 5 to 80° for MnFe₂O₄@ZnO and ZnFe₂O₄@MnO. The average crystallite size for prepared samples from the range of 20 nm to 50 nm was computed by using standard Debye-Scherrer equation $D = 0.9\lambda / (\beta \cos\theta)$ [17], where D demonstrates the diameter of the nanoparticles, λ (Cu K α) = 1.5406 Å and β represents the full-width at half maximum of the diffraction lines. Fig.2a and Fig.2b illustrates the X-ray diffraction pattern of the ZnFe₂O₄@MnO and MnFe₂O₄@ZnO, respectively. As portrayed in Fig.2a, diffraction peak of ZnFe₂O₄@MnO was observed at the angles of 18.24, 57.42 and 75.50°, which corresponds to the (111), (511) and (171), respectively. Based on the results, The peaks centered at the angles of 35.34, 56.79, 62.36 and 73.76° indicated (311), (511), (400) and (533) corresponded to the cubic phase of ZnFe₂O₄. These diffraction peaks were remarkably resembled with the standard JCPDS No. 98-003-0547. The peaks centered at the angles of 29.96, 33.52, 37.88, 42.19, 57.84, 64.43 and 65.38° indicated (023), (113), (006), (220), and (212) concurred to the cubic phase of MnO which were directly indexed to JCPDS No. 01-075-0257. The X-ray diffraction pattern of MnFe₂O₄@ZnO was observed in Fig.2b. The peaks centered at the angles of 35.39, 42.93 and 62.30° indicated (113), (004) and (022) respectively, which corresponded to MnFe₂O₄@ZnO. Based on

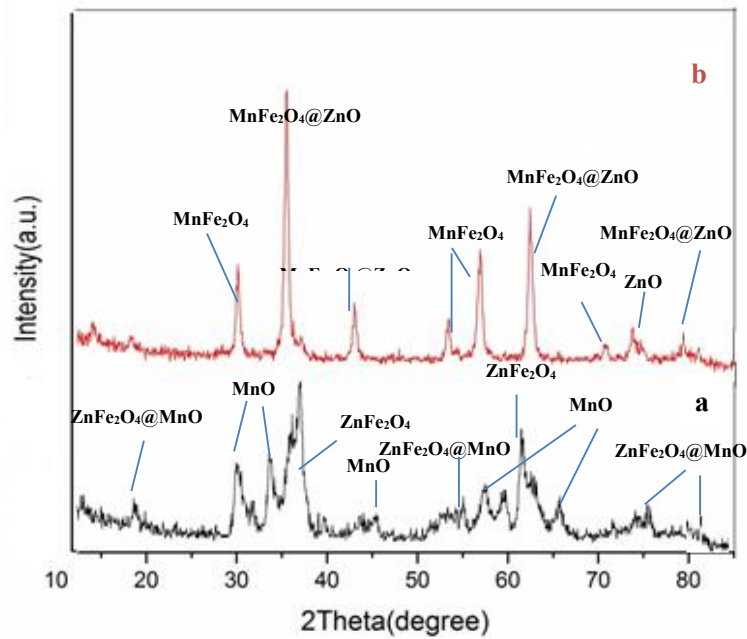


Fig. 2. XRD patterns for (a) $ZnFe_2O_4@MnO$ and (b) $MnFe_2O_4@ZnO$.

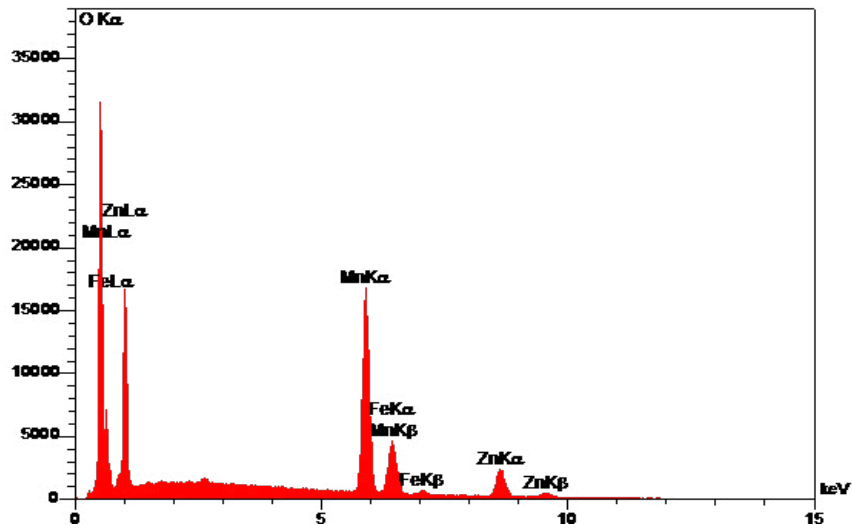


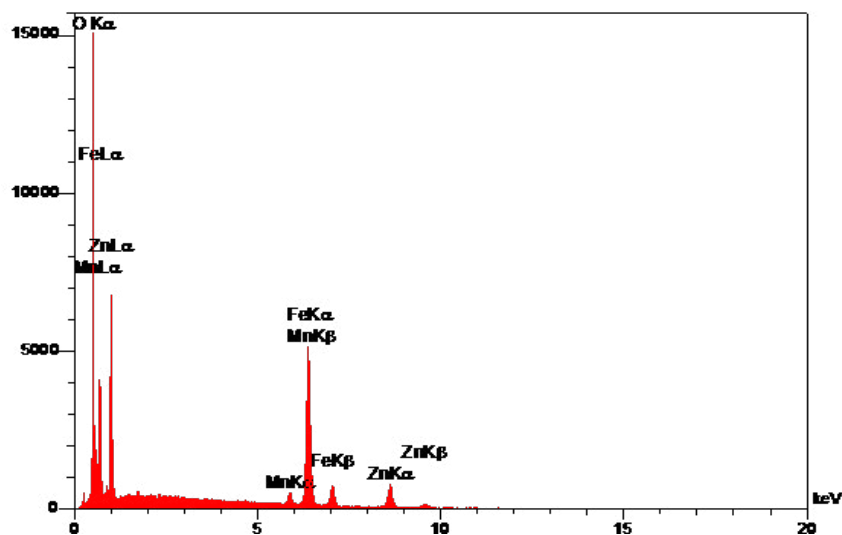
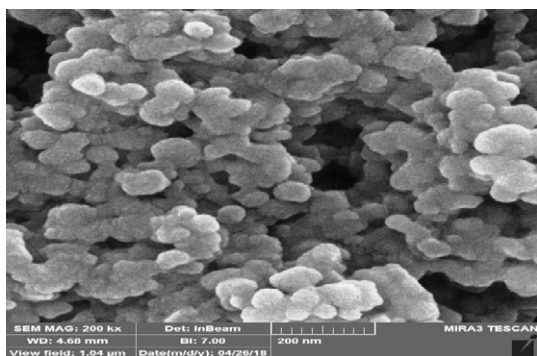
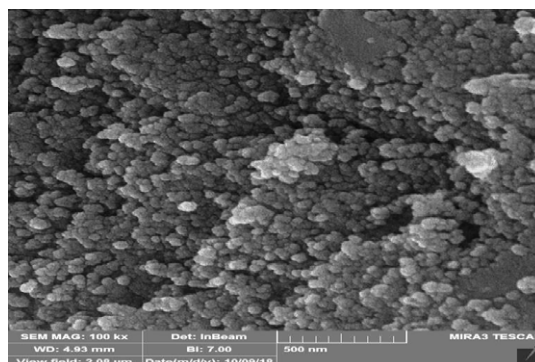
Fig. 3. EDAX analyses of $ZnFe_2O_4@MnO$ nanocomposite.

the results, The peaks centered at the angles of 18.23, 29.99, 35.33, 53.26, 56.77, 70.71 and 74.73 ° indicated (111), (022), (113), (224), (115), (026) and (226) where the $MnFe_2O_4$ belongs to the cubic phase and diffraction peaks were directly indexed to JCPDS No. 98-006-2998. The peaks centered at the angles of 36.94, 42.92, 62.31, 74.70 and 78.64° indicated (111), (002), (022), (113) and (222)

corresponded to the cubic phase of ZnO which were directly indexed to JCPDS No. 98-011-6320. As depicted in **Fig. 2b**, the closer study of EDAX data reveals that Zn, Fe, Mn and O elements were clearly present in the $MnFe_2O_4@ZnO$ and $ZnFe_2O_4@MnO$ nanocomposites, respectively. The amounts of elements are reported for the nanocatalyst $MnFe_2O_4@ZnO$ and $ZnFe_2O_4@MnO$

Table 1. EDX quantification elements of $\text{ZnFe}_2\text{O}_4@\text{MnO}$ nanocomposite.

Element	O	Mn	Fe	Zn	Total
W%W%	40.71	42.12	7.81	9.36	100.00
Atom%	70.80	21.33	3.89	3.98	100.00

Fig. 4. EDAX analyses of $\text{MnFe}_2\text{O}_4@\text{ZnO}$ nanocomposite.Fig. 5. FESEM image of $\text{ZnFe}_2\text{O}_4@\text{MnO}$ nanoparticles.Fig. 6. FESEM image of $\text{MnFe}_2\text{O}_4@\text{ZnO}$ nanoparticles.

in Tables 1 and 2, respectively. Furthermore, as shown in Fig. 3 and Fig. 4, the surface morphology and its chemical composition of the synthesized photocatalyst were examined by using FESEM image. Based on the results, Figs. 5 and 6 reveal the agglomerated spherical shape of $\text{ZnFe}_2\text{O}_4@\text{MnO}$ and $\text{MnFe}_2\text{O}_4@\text{ZnO}$ nanocomposites with an average particle size of < 100 nm, respectively.

Infrared spectral study

FT-IR analysis was done for a detailed investigation of the obtained samples in the synthesized $\text{MnFe}_2\text{O}_4@\text{ZnO}$ and $\text{ZnFe}_2\text{O}_4@\text{MnO}$ as portrayed in Fig. 7. As shown in Fig. 8a, the

solid state FT-IR spectra of the nanocomposites indicated a low intensity bands in the range of 480 and 507 cm^{-1} were assigned to Zn–O and Mn–O stretching vibration band in $\text{ZnFe}_2\text{O}_4@\text{MnO}$ respectively. In addition, another peak appeared at the $650\text{--}540\text{ cm}^{-1}$, which could be assigned to the Fe–O stretching. The absorption band around 1707 cm^{-1} assigned to stretching vibration of carbonyl group C=O. The stretching vibration of the carboxylate group C=O is observed around 1459 cm^{-1} . Also, the bending vibration of H–O–H group appeared at 1625 cm^{-1} . The band at $3500\text{--}3200\text{ cm}^{-1}$ is attributed to the stretching and bending modes of free and absorbed water

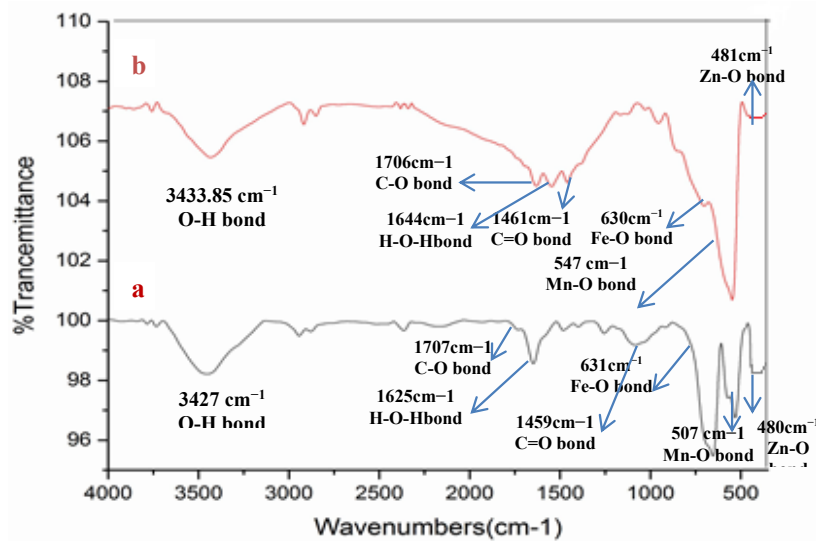


Fig. 7. FT-IR spectra of prepared (a) $\text{ZnFe}_2\text{O}_4@MnO$ and (b) $\text{MnFe}_2\text{O}_4@ZnO$ nanoparticles.

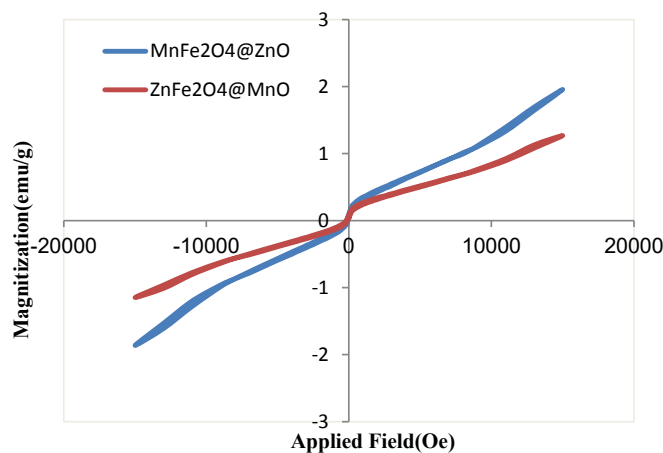


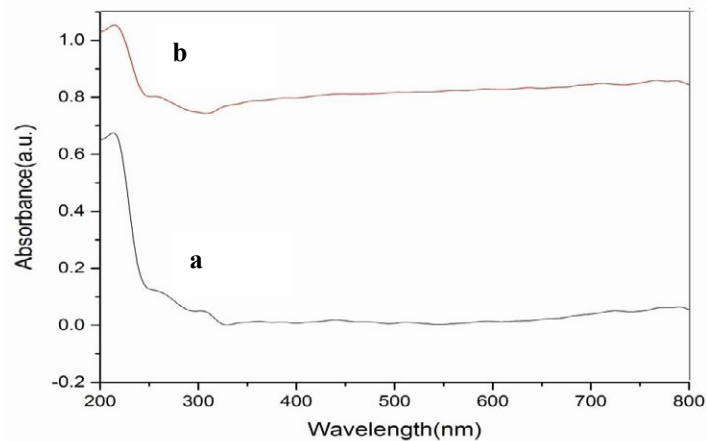
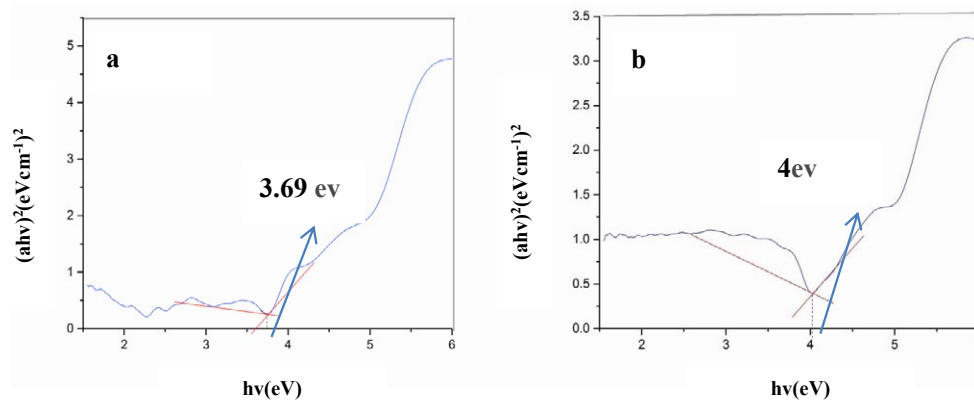
Fig. 8. Hysteresis curves of $\text{MnFe}_2\text{O}_4@ZnO$ and $\text{ZnFe}_2\text{O}_4@MnO$ nanocomposites.

on the surface of the prepared $\text{ZnFe}_2\text{O}_4@MnO$ nanoparticles [18]. As shown in Fig. 8b, the solid state FT-IR spectra of the nanoparticles displayed a low intensity bands in the range of 481 and 547 cm^{-1} were attributed to Zn-O and Mn-O stretching vibration band in $\text{MnFe}_2\text{O}_4@ZnO$. Furthermore, another peak observed at the 650–500 cm^{-1} which could be assigned to the octahedral group Fe-O. The absorption band around 1706 cm^{-1} assigned to stretching vibration of carbonyl group C-O. The stretching vibration of the carboxylate group C=O is shown around 1461 cm^{-1} . Also, The bending vibration of H-O-H group appeared at 1644 cm^{-1} . The broad peak at 3433.85 cm^{-1} is assigned to the stretching and bending modes of free and absorbed water on the surface of the synthesized

$\text{MnFe}_2\text{O}_4@ZnO$ nanocomposites [19-20]. The FT-IR spectra confirm the presence of organic impurities in the synthesized samples due to the preparation conditions.

Magnetic properties of $\text{MnFe}_2\text{O}_4@ZnO$ and $\text{ZnFe}_2\text{O}_4@MnO$

The magnetization measurement for the as-prepared $\text{MnFe}_2\text{O}_4@ZnO$ and $\text{ZnFe}_2\text{O}_4@MnO$ nanoparticles was carried out using a vibrating sample magnetometer (VSM) at room temperature. The magnetic hysteresis loops of the synthesized $\text{MnFe}_2\text{O}_4@ZnO$ and $\text{ZnFe}_2\text{O}_4@MnO$ nanocomposites is observed in Fig. 8, which confirms that the resulting samples showed a characteristic of the superparamagnetic behavior

Fig. 9. Optical Absorption Spectrum Of (a) $\text{ZnFe}_2\text{O}_4@\text{MnO}$ and (b) $\text{MnFe}_2\text{O}_4@\text{ZnO}$.Fig. 10. DRS plots of $(ah\nu)^2$ vs. photon energy $h\nu$ (eV) for (a) $\text{ZnFe}_2\text{O}_4@\text{MnO}$ and (b) $\text{MnFe}_2\text{O}_4@\text{ZnO}$.

with the saturation magnetization of 1.95 and 1.26 emu g^{-1} of $\text{MnFe}_2\text{O}_4@\text{ZnO}$ and $\text{ZnFe}_2\text{O}_4@\text{MnO}$ nanocomposites, respectively. also, the remanent magnetization of $\text{MnFe}_2\text{O}_4@\text{ZnO}$ and $\text{ZnFe}_2\text{O}_4@\text{MnO}$ is 0.102 and 0.089 emu g^{-1} , respectively. Finally, The results demonstrated the superparamagnetic behavior of the nanocomposites because of a decrease in the particle size below a critical value (lower than 100 nm). Thus, the size of the crystalline nature influences the magnetic properties of the nanoparticles [21].

Optical analysis of $\text{ZnFe}_2\text{O}_4@\text{MnO}$ and $\text{MnFe}_2\text{O}_4@\text{ZnO}$

The optical absorption property relevant to the electronic structure formation is indicated as a key factor in demonstrating the photocatalytic activity [22]. The optical properties of the prepared

$\text{MnFe}_2\text{O}_4@\text{ZnO}$ and $\text{ZnFe}_2\text{O}_4@\text{MnO}$ samples were performed by the diffused reflectance UV-vis spectra (DRS), as shown in Fig. 9. The UV-Visible absorption spectra of the synthesized nanocomposites recorded in the range of wavelength 200-800 nm. According to the spectra, all synthesized samples indicated photoabsorption from UV light to visible light region, which displays the possibility of high photocatalytic activity of these nanocomposites under visible light. The band gap of the synthesized nanomaterials calculated from the plot of the transformed Kubelka-Munck function vs. the energy of light [23] is observed in Fig.10. The optical band gap energies of the synthesized $\text{MnFe}_2\text{O}_4@\text{ZnO}$ and $\text{ZnFe}_2\text{O}_4@\text{MnO}$ nanocomposites are 4 and 3.69 eV, respectively. But, this band gap is yet so large that visible light irradiation ($\lambda > 420$ nm) cannot photoexcite electrons in the valence band (VB)

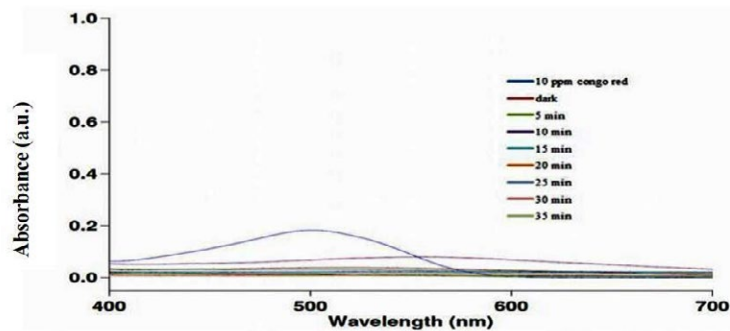


Fig. 11. Photocatalytic degradation of Congo red under visible light in presence of $ZnFe_2O_4@MnO$.

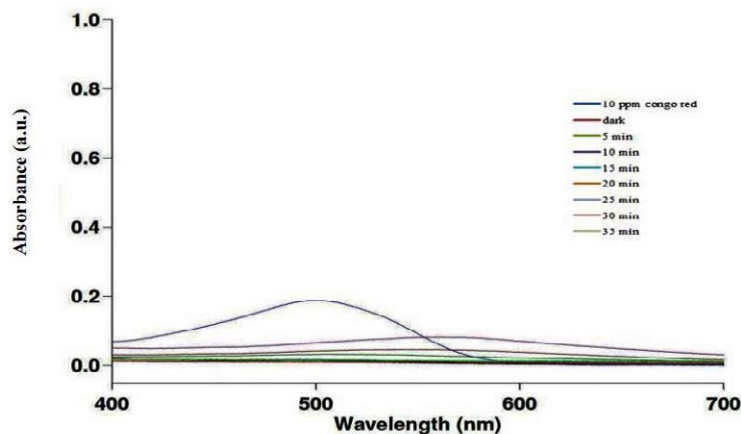


Fig. 12. Photocatalytic degradation of Congo red under visible light in presence of $MnFe_2O_4@ZnO$.

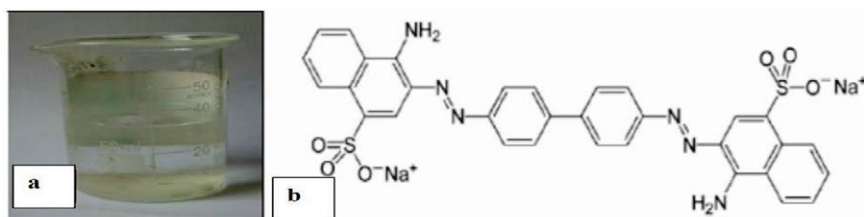


Fig. 13. (a) The degradation of congo red dye [pH region (13-14)] and (b) congo red structure with two sulfonic groups.

to the conduction band (CB) of $ZnFe_2O_4@MnO$. Based on the experimental results, an electron transport mechanism for the photodegradation of the $ZnFe_2O_4@MnO$ composites is suggested. The MnO nanoparticle with a wide band gap of ~ 3.90 eV, is difficult to reach excited states under visible light irradiation. In this work, $ZnFe_2O_4$ act as an electron transfer channel in the $ZnFe_2O_4@MnO$ composite. Therefore, The results revealed that the addition of $ZnFe_2O_4$ can narrow the band gap of MnO ($3.9 \pm 0/4$ eV) to the visible light region of ~ 3.69 eV, which improved the electron-hole separation, leading to enhanced photocatalytic efficiency [13]. Additionally, the addition of

$MnFe_2O_4$ to ZnO structure (3.37eV) causes an increase the band gap width of $MnFe_2O_4@ZnO$ to 4eV for $MnFe_2O_4@ZnO$. Thus, this band gap is so large that visible light irradiation ($\lambda > 420$ nm) cannot photoexcite electrons in the valence band (VB) to the conduction band (CB) of $MnFe_2O_4@ZnO$ [15].

Photocatalytic degradation activities of $MnFe_2O_4@ZnO$ and $ZnFe_2O_4@MnO$ nanocomposites

The photocatalytic activity of synthesized $MnFe_2O_4@ZnO$ and $ZnFe_2O_4@MnO$ nanocomposites was investigated by using CR dye solutions as a model organic pollutant under visible illumination,

Table 2. EDX quantification elements of MnFe₂O₄@ZnO nanocomposite.

Element	O	Mn	Fe	Zn	Total
W%W%	48.09	2.32	42.33	7.26	100.00
Atom%	76.74	1.08	19.35	2.83	100.00

Table 3. Compare the degradation rate, (D%) of ZnFe₂O₄@MnO nanocomposite (0.05-0.20g).

Catalysts	D% 5 min	D% 10 min	D% 15 min	D% 20 min	D% 25 min	D% 30min	D% 35 min
ZnFe ₂ O ₄ @MnO(0.05g)	23.88	33.54	43.23	50.42	54.88	60.31	62.33
ZnFe ₂ O ₄ @MnO(0.1g)	20.23	30.42	40.15	59.25	70.38	85.25	98.5
ZnFe ₂ O ₄ @MnO(0.15g)	10.12	20.23	30.15	40.50	52.19	61.46	85.33
ZnFe ₂ O ₄ @MnO(0.20g)	22.30	35.18	42.55	54.42	59.88	63.33	69.75

Table 4. Compare the degradation rate, (D%) of MnFe₂O₄@ZnO nanocomposite (0.05-0.20g).

Catalysts	D% 5 min	D% 10 min	D% 15 min	D% 20 min	D% 25 min	D% 30min	D% 35 min
MnFe ₂ O ₄ @MnO(0.05g)	15.88	38.15	48.24	53.37	50.88	58.33	65.42
MnFe ₂ O ₄ @ZnO(0.1g)	10.15	20.28	45.56	58.25	78.15	82.23	90.32
MnFe ₂ O ₄ @ZnO(0.15g)	15.32	25.14	38.15	44.28	55.33	68.23	75.55
MnFe ₂ O ₄ @ZnO(0.20g)	22.31	28.19	32.12	38.15	45.55	58.23	68.32

as shown in Figs. 11 and 12. In this regard, 100 ml of 50 mg/l CR solution under pH=13-14 with the presence of 0.10g MnFe₂O₄@ZnO and ZnFe₂O₄@MnO nanocomposites were exposed to the visible light for 35 min. The experiments demonstrated that the percentage of maximum dye degradation in the presence of 0.10g MnFe₂O₄@ZnO and ZnFe₂O₄@MnO nanocomposites were 90.32 % and 98.50 % respectively. The Congo red (CR) main absorption peak happens at 498 nm. The degradation rate was calculated by decreasing in peak intensity at 498 nm in Figs. 11 and 12. When MnFe₂O₄@ZnO and ZnFe₂O₄@MnO nanocomposites are added into solution and exposed to sunlight for 35 minutes, peak intensity gradually decreases. The degradation rate for ZnFe₂O₄@MnO is much higher than ZnFe₂O₄@MnO, as shown in Tables 3 and 4. To study the effect of pH, several experiments were performed on photocatalyst. The pH of the CR dye solution 50ppm is about 7 in the presence of nanocomposites. Calculation of the effect of pH was carried out in the range of 1-14 by adding sodium hydroxide and hydrochloric acid. In the case studies, it was observed that in the pH=1-7, all photocatalysts can only absorb the Congo red, but it does not have the degradation ability and the least photocatalytic activity was found in

the pH regions 8-12. In alkaline pH region 13-14 the degradation of Congo red dye was observed (Fig. 13a). This phenomenon can be illustrated by the surface properties of the MnFe₂O₄@ZnO and ZnFe₂O₄@MnO nanocomposites. Two sulfonic acid groups of Congo red can ionize and make a Congo red anion (Fig. 13 -b). The ZnFe₂O₄@MnO photocatalyst in the high acidic regions (pH=1-7) has a positive small surface potential (Zeta-point charge = +5.84) and in the highly alkaline regions (pH=13-14) has a very high positive surface potential (Zeta-point charge = +15.8). And also, MnFe₂O₄@ZnO photocatalyst in the high acidic regions (pH=1-7) has a positive small surface potential (Zeta-point charge = +3.84) and in the highly alkaline regions (pH=13-14) has a very high positive surface potential (Zeta-point charge = +9.8). A negative surface charge of the Congo red anion is capable to absorb the positive surface of nanocomposite. Therefore, in the region (pH=1-7), photocatalysts only absorbs the Congo red and in the alkaline region (pH=13-14) photocatalysts are capable to degrade the Congo red dye. The photocatalysts in the region between pH=7-13 have a negative surface potential, therefore the interaction and destruction of the Congo red dye in this area has been minimized. The experiments of photocatalysis were carried out at pH= 13-14

owing to this pH is optimized and nanocomposites gave the best efficiency in the photocatalytic degradation of Congo red. $ZnFe_2O_4@MnO$ nanocomposite has a very high positive surface potential compared to the $MnFe_2O_4@ZnO$ nanocomposite in the highly alkaline regions. Therefore, $ZnFe_2O_4@MnO$ photocatalyst gave the best performance in the photocatalytic degradation of Congo red. The effect of initial dye (CR), concentration on its photodegradation was studied from 50-80 ppm at pH=13-14 and nanocomposites dosage of 0.10g/L. It is suggested that the photodegradation decreases with increase of initial CR concentration. At high dye concentrations, the formation reactive oxygen species on the photocatalyst surface is reduced because the photons are interrupted by the dye molecules before they can reach the catalyst surface. Further, nanocomposites dosage is also

same for all initial CR concentration and therefore the formation of $\cdot OH$ remains constant [24]. In the case studies, At high dye concentrations owing to it does not have the degradation ability and the least photocatalytic activity was revealed. We don't cite in this research. The tests of photocatalysis were performed in 10mg/l CR solution due to this concentration is optimized and nanocomposites gave the best activity in the photocatalytic degradation of Congo red.

Effect of catalyst dosage

Figs. 14 and 15 show the loading effect of the $MnFe_2O_4@ZnO$ and $ZnFe_2O_4@MnO$ nanocomposites on the degradation rate of CR solutions. The tests were carried out by varying the weight of photocatalyst from 0.05 g to 0.20 g with optimum CR pH. Based on the results, the

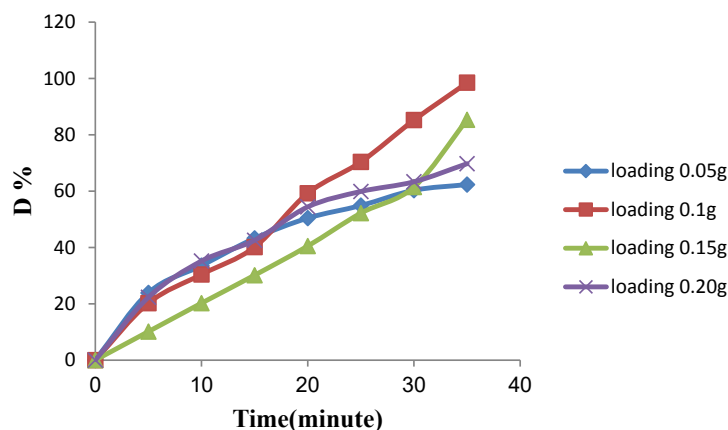


Fig. 14. The effect of loading $ZnFe_2O_4@MnO$ nanocomposite on the CR solutions degradation (Sample: 0.050 g $ZnFe_2O_4@MnO$, initial concentration of CR solution: 50 mg/l, pH of CR solution: 13-14, Volume: 100 ml).

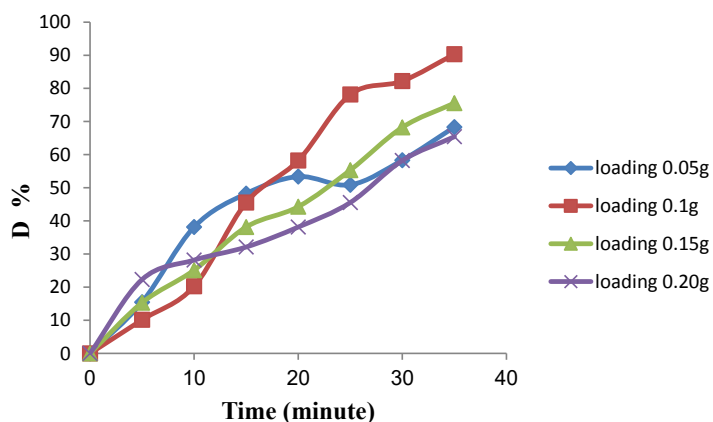


Fig. 15. The effect of loading $MnFe_2O_4@ZnO$ nanocomposite on the CR solutions degradation (Sample: 0.050 g $MnFe_2O_4@ZnO$, initial concentration of CR solution: 50 mg/l, pH of CR solution: 13-14, Volume: 100 ml).

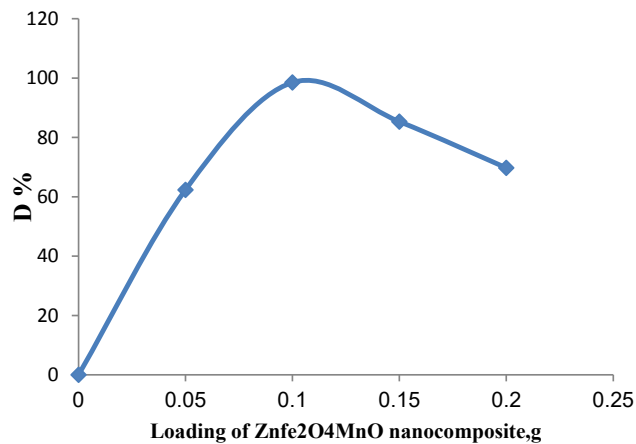


Fig. 16. Relationship between $\text{ZnFe}_2\text{O}_4@\text{MnO}$ nanocomposite loading and degradation rate of CR solution.

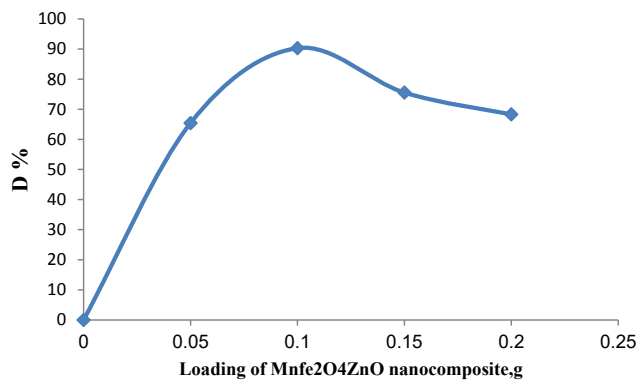


Fig. 17. Relationship between $\text{MnFe}_2\text{O}_4@\text{ZnO}$ nanocomposite loading and degradation rate of CR solution.

CR degradation rate of the $\text{ZnFe}_2\text{O}_4@\text{MnO}$ and $\text{MnFe}_2\text{O}_4@\text{ZnO}$ nanocomposites increased from 62.33% to 98.50% and 68.32% to 90.32%, respectively, along with an increase in the weight of the photocatalyst from 0.05 g to 0.1 g. However, as shown in Figs. 16 and 17, CR degradation rate decreased when the weight increased to 0.15 g and 0.20 g. Moreover, agglomeration happened, leading to an increase in the darkness of solution when the loading of nanoparticles surpassed the optimum amount for the reaction. This situation prevented the influence of visible light, which resulted in losing the activated sites of $\text{MnFe}_2\text{O}_4@\text{ZnO}$ and $\text{ZnFe}_2\text{O}_4@\text{MnO}$ nanocomposites by collision with the ground state $\text{MnFe}_2\text{O}_4@\text{ZnO}$ and $\text{ZnFe}_2\text{O}_4@\text{MnO}$ nanocatalysts [25]. The photocatalytic degradation of Congo red as a function of time by employing the synthesized $\text{MnFe}_2\text{O}_4@\text{ZnO}$ and $\text{ZnFe}_2\text{O}_4@\text{MnO}$ nanocomposites was evaluated under visible light

irradiation, as shown in Fig. 18. It can be seen that the $\text{ZnFe}_2\text{O}_4@\text{MnO}$ nanocomposites compared to $\text{MnFe}_2\text{O}_4@\text{ZnO}$ nanocomposites gave the best efficiency in the photocatalytic degradation of Congo red. The enhanced photocatalytic activity of $\text{ZnFe}_2\text{O}_4@\text{MnO}$ composite is owing to the well optical absorptions in the UV-Vis region with a lower band gap energy giving rise to a higher photocatalytic efficiency.

Kinetics Studies of $\text{MnFe}_2\text{O}_4@\text{ZnO}$ and $\text{ZnFe}_2\text{O}_4@\text{MnO}$ nanocomposites

The dyedegradation percentage of the $\text{MnFe}_2\text{O}_4@\text{ZnO}$ and $\text{ZnFe}_2\text{O}_4@\text{MnO}$ nanocomposites were used from the following equation [25]:

$$R = (C_0 - C_t) / C_0 \times 100\% \quad (2)$$

Where C_0 is the initial CR concentration (mg/l) and C_t is the CR concentration at a certain reaction

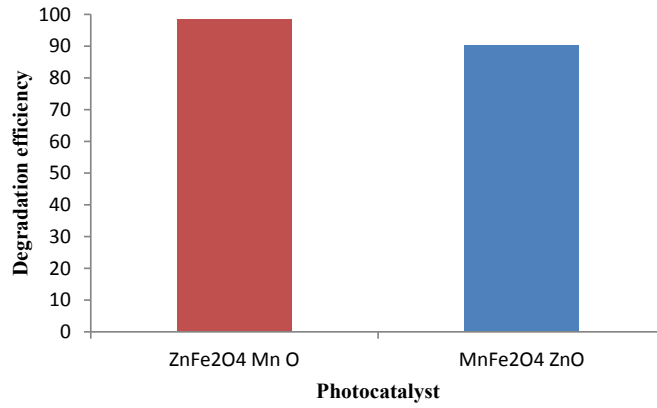


Fig. 18. Comparison of the photodegradation efficiencies of Congo red for ZnFe₂O₄@MnO and MnFe₂O₄@ZnO nanocomposites under visible light irradiation for 35 min.

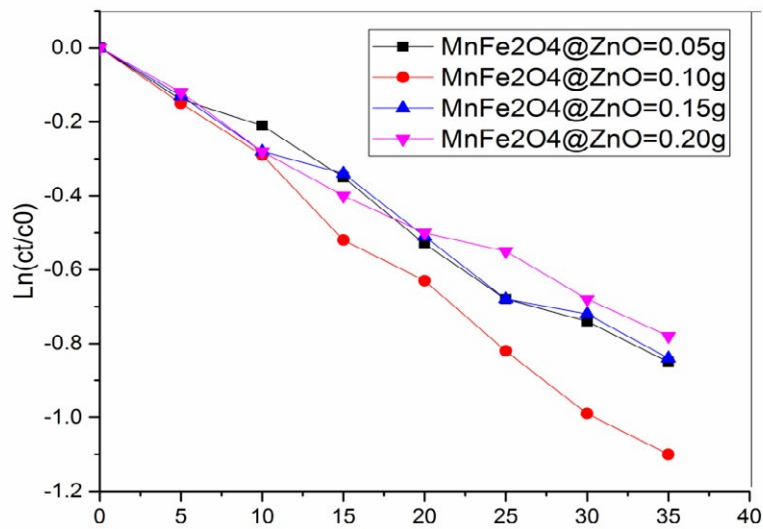
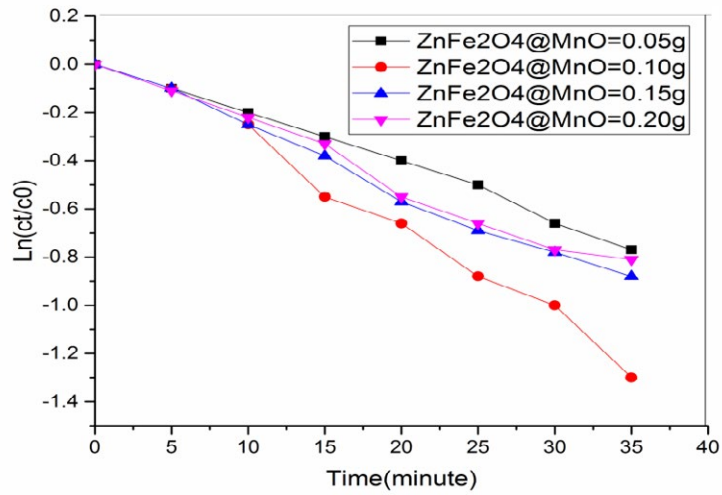


Fig. 19. a) The effect of ZnFe₂O₄@MnO catalyst amount on the photocatalytic degradation of Congo red. b) The effect of MnFe₂O₄@ZnO catalyst amount on the photocatalytic degradation of Congo red.

time (min). A pseudo first order reaction model with respect to CR concentration was presumed to evaluate the degradation rate kinetic and rate constant. First order reaction rate equation can be revealed as follows:

$$-d[C] / dt = k[C] \quad (3)$$

Where k = rate constant, min^{-1} . This equation can be integrated to acquire an integrated form:

$$\ln C_0 / C_t = kt \quad (4)$$

The reaction kinetics of the photocatalysis improved by using the first order kinetic model as follows:

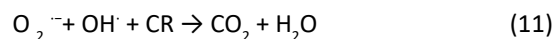
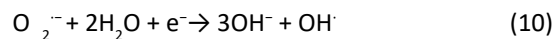
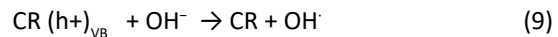
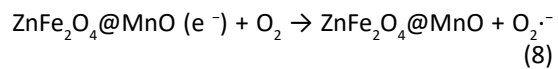
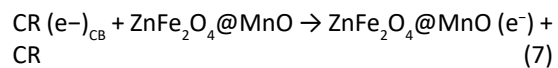
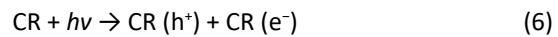
$$\ln C_t = \ln C_0 - kt \quad (5)$$

The plot of $\ln (C_t/C_0)$ versus t can be approached as straight lines (Figs. 19a and b), which means that the photodegradation of CR is fitted as pseudo-first-order kinetics. Table 5 and 6 represent the calculated rate constant and the correlation coefficient under different conditions. The effect of the reaction rate of 0.10g $\text{ZnFe}_2\text{O}_4@ \text{MnO}$ was 0.0371 min^{-1} , which was slightly higher, compared to 0.05g, 0.15g and 0.20g $\text{ZnFe}_2\text{O}_4@ \text{MnO}$ nanocomposite. Additionally, the effect of the reaction rate of 0.10 g $\text{MnFe}_2\text{O}_4@ \text{ZnO}$ was 0.0324 min^{-1} , which was some higher, compared to 0.05 g/L and 0.02 g/L the as-synthesized $\text{MnFe}_2\text{O}_4@ \text{ZnO}$ sample.

Photocatalytic mechanism of $\text{MnFe}_2\text{O}_4@ \text{ZnO}$ and $\text{ZnFe}_2\text{O}_4@ \text{MnO}$ nanocomposites

The acceptable photodegradation mechanism

by applying as-synthesized $\text{ZnFe}_2\text{O}_4@ \text{MnO}$ photocatalyst is showed in Fig.20. In this mechanism, the dye molecules adsorbed on the surface of the catalyst absorb visible radiations and undergo electronic excitation from the highest occupied molecular orbital to the lowest unoccupied molecular orbital (LUMO). Then excited electrons from the LUMO of the dye molecule are injected into the conduction band (CB) of the $\text{ZnFe}_2\text{O}_4@ \text{MnO}$ photocatalyst and the dye is converted into a cationic dye radical. This dye radical undergoes degradation to produce mineralized products. The electron in the CB of the metal oxide is further scavenged by oxygen to produce O_2^- and results in the decolourisation of dyes. This mechanism is important when dye molecules are in an adsorbed state on the catalyst surface [26].



CONCLUSION

In conclusion, magnetically separable $\text{ZnFe}_2\text{O}_4@ \text{MnO}$ and $\text{MnFe}_2\text{O}_4@ \text{ZnO}$ photocatalysts were successfully synthesized through a facile

Table 5. Rate constant of reaction kinetic for $\text{ZnFe}_2\text{O}_4@ \text{MnO}$ photocatalytic degradation by Congo red in different conditions.

pH	Initial CR solution concentration, mg/l	Photocatalyst loading, g	k , min^{-1}	R^2
13	50	0.05	0.0264	0.9879
13	50	0.10	0.0371	0.9877
13	50	0.15	0.0284	0.9919
13	50	0.20	0.0250	0.9833

Table 6. Rate constant of reaction kinetic for $\text{MnFe}_2\text{O}_4@ \text{ZnO}$ photocatalytic degradation by Congo red in different. conditions.

pH	Initial CR solution concentration, mg/l	Photocatalyst loading, g	k , min^{-1}	R^2
13	50	0.05	0.0243	0.9890
13	50	0.10	0.0324	0.9962
13	50	0.15	0.0251	0.9890
13	50	0.20	0.0218	0.9880



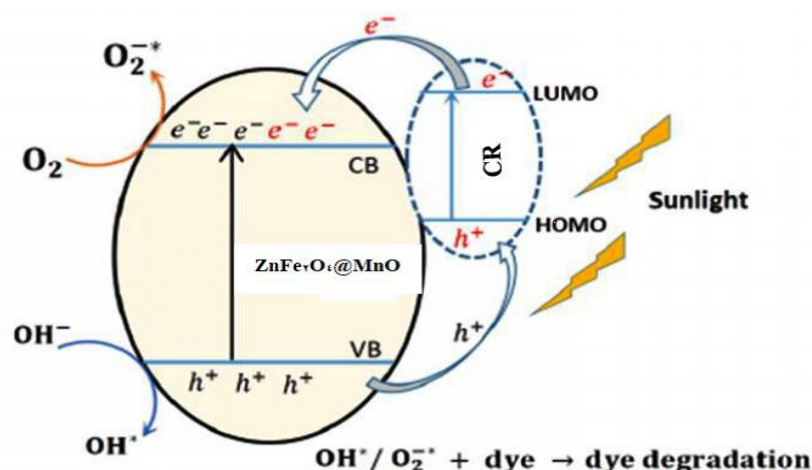


Fig. 20. Photocatalytic mechanism of $\text{ZnFe}_2\text{O}_4@\text{MnO}$ photocatalyst.

hydrothermal method. The photocatalysts were investigated by FESEM, EDAX, XRD, UV-DRS and VSM. The effect of reaction time, pH, and loading of $\text{ZnFe}_2\text{O}_4@\text{MnO}$ and $\text{MnFe}_2\text{O}_4@\text{ZnO}$ nanocomposites on degrading the CR were studied. Regarding the results of photocatalytic, the amount of the catalyst (0.1 g L^{-1}) and initial concentration of CR (50 mg L^{-1}) with $\text{pH}=13\text{-}14$ was considered as the best for Congo red degradation. The experimental data were adequated by calculating the pseudo-first-order kinetic. The prepared $\text{ZnFe}_2\text{O}_4@\text{MnO}$ catalyst revealed significantly enhanced photocatalytic performance toward CR degradation in 35 min of under visible light irradiation compared to that of $\text{MnFe}_2\text{O}_4@\text{ZnO}$ catalyst. The photocatalytic experimental results demonstrated that in the presence of $0.10 \text{ g ZnFe}_2\text{O}_4@\text{MnO}$ and $\text{MnFe}_2\text{O}_4@\text{ZnO}$ degrade Congo red dye as a hazardous pollutant under visible light irradiation in the same reaction condition by 98.50 % and 90.32 % respectively. VSM measurements confirmed the superparamagnetic behavior of the synthesized samples at room temperature and the effect of crystallite size on the magnetic properties. The plot of the Kubelka-Munck function revealed the optical bandgap energy of $\text{ZnFe}_2\text{O}_4@\text{MnO}$ is relatively less than that of $\text{MnFe}_2\text{O}_4@\text{ZnO}$ nanoparticle. Thus the present work concludes that the magnetic and optical properties of synthesized $\text{ZnFe}_2\text{O}_4@\text{MnO}$ nanoparticles and the photocatalytic property of $\text{ZnFe}_2\text{O}_4@\text{MnO}$ nanoparticles makes the nanocomposites promising candidates for the solution of a variety of environmental problems.

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DISCLOSURE STATEMENT

All authors declare that they have no conflict of interest in the publication of this manuscript.

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