Preparation, magnetic properties, and photocatalytic performance under natural daylight irradiation of Fe$_3$O$_4$-ZnO core/shell nanoparticles designed on reduced GO platelet

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**ABSTRACT**

Ternary mesoporous nanocomposites of RGO/Fe$_3$O$_4$-ZnO were prepared successfully via hydrothermal technique. Fe$_3$O$_4$-ZnO core/shell nanoparticles were decorated on the surface of reduced graphene oxide platelet to improve charge separation efficiency and magnetic properties. The phase, microstructure and specific surface area of the prepared samples were determined via X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy/selected area electron diffraction (TEM/SAED) and Brunauer–Emmett–Teller (BET) techniques. A vibrating sample magnetometer (VSM) was used for recording the magnetization hysteresis curves. The methylene blue (MB) degradation and photocatalytic activities of prepared catalysts were examined under natural daylight irradiation. The magnetic properties of the RFZ photocatalyst increased compared with the FZ from 12.45 emu g$^{-1}$ to 20.18 emu g$^{-1}$. The specific surface area ($a_{\text{BET}}$) for the RFZ compared to the FZ increased from 31.56 m$^2$ g$^{-1}$ to 36.05 m$^2$ g$^{-1}$. The RFZ photocatalyst, as a result of synergistic effects, indicated an excellent performance for treatment of MB dye. The photocatalytic reactions obeyed pseudo-first-order kinetics and apparent rate constant ($k_{\text{app}}$) of RFZ photocatalyst increased compared to FZ. Furthermore, the RFZ photocatalyst could be recycling using a common magnet besides to the high efficiency of degradation. The repeatability of the photocatalytic activity after 10 cycles was additionally tested and revealed that the RFZ photocatalyst up to 8 cycles showed a small drop in catalysis efficiency. Thus, it was concluded that the RFZ ternary photocatalyst can be an economical multifunctional photocatalyst for the degradation of unsafe compounds in wastewater.

1. Introduction

Photocatalytic degradation of hazardous substances disposed of factories and houses has attracted intensive interest, due to its excessive performance and low cost for long term uses [1–3]. Among various materials, porous nanomaterials especially ZnO and Fe$_3$O$_4$ are two essential classes of catalysts for this purpose. ZnO as a semiconductor is a practical and environmentally friendly material that has been widely used in photocatalytic applications due to its visible light induced oxidation, wide band gap (∼ 3.37 eV), non-toxicity, chemical stability and proper sensing behavior [4,5]. ZnO nanoparticles exhibit advanced photocatalytic activity through creating defect sites for photon absorption and preventing electron/hole recombination [5–7]. Superparamagnetic Fe$_3$O$_4$ nanoparticles also have proper magnetic properties which can result in high adsorption capacity and easy and rapid separation of adsorbents from solution via its magnetic properties [8,9]. In the past decade, a wide range of approaches such as proper design and metal loading or doping has been used to promote the photocatalytic efficiency of semiconductor photocatalysts [3]. Generally, several efforts have been made to combine graphene with semiconductor materials to improve their photocatalytic performance. In waste water treatment, semiconductors can usually modify the properties of the graphene sheets [10–13]. Graphene is known as a zero band gap semiconductor, which shows excellent electronic characteristics in the storage and transport of electron and proper photocatalytic activity when combined with semiconductor catalysts such as ZnO [14,15], TiO$_2$ [13,16,17], Fe$_3$O$_4$ [13,17,18], and CdS [19]. In graphene–semiconductor nanocomposites, the presence of nanoparticles on the graphene surface prevents the aggregation of graphene layers, and hence increases the surface area for the removal of pollutants from
aqueous solutions [13,17,20,21].

In this regard, Zhang et al. [22] synthesized Graphene-TiO₂ composites via hydrothermal method, which showed great photocatalytic activity for MB degradation in aqueous solutions. In another study, Zhang et al. [23] made ZnO-Graphene composites through a chemical deposition technique with high photocatalytic activity under UV-Vis light radiation. Moreover, Wang and colleagues [10] designed magnetic graphene nanocomposites via in situ chemical co-precipitations of Fe²⁺ and Fe³⁺ in a basic solution in the presence of graphene to remove the organic dye from the aqueous solution. Tian et al. [24] improved the selectivity of formaldehyde gas sensors using ZnO-Zeolitic Imidazolate core/shell hetero-structures, which were synthesized in hydrothermal condition at 70 °C for 24 h using a self-template strategy. These nanorods had excellent response and recovery times for detecting gases. Ma et al. [25] made a gas sensor of nZnO-nIn₂O₃ by sonochemical synthesis, and the increased the electron transferring by surface modification, which in turn improved the variation amplitude of resistance in gas-sensing. Mohamed Reda et al. [26] by solid state reaction route made the heterostructure photocatalyst of Co₉O₄/ZnO p-n with high separation efficiency of photogenerated electron-holes for Rhodamine B removal. Yang et al. [27] hybridized Fe₃O₄ with TiO₂ to enhance conversion between Fe³⁺ and Fe²⁺. Zubir et al. [28] synthesized a heterogeneous catalyst of GO-Fe₃O₄, and discovered that suitable adding of GO to Fe₃O₄ nanoparticles, let to a higher surface area and excellent catalytic efficiency. In another work, Thangavel et al. [29] synthesized a graphdiyne (GD)-ZnO nanohybrid with a high intermolecular interaction between GD and ZnO via the hydrothermal method for removal of azo dyes. They reported that GD generated an extra band gap in the nanohybrid, due to the diacetylene linkage between the hexagonal rings of carbon which enhanced the transferring of electrons from valence to conduction band. Salamat et al. [30] studied Fe₃O₄-TiO₂ core/shell particles obtained from electric arc furnace dust and used them for degradation of steel mill wastewater. They found that the apparent rate constant depends on pH and surface properties. You et al. [31] synthesized ternary nanocomposites of RGO-ZnO-Fe₃O₄ via solvothermal method for degradation of Rhodamine B under visible-light radiation. These nanocomposites had high stability for reuse over five cycles and could be easily retrieved from the treated water by extra magnetic field due to the superparamagnetic properties. Abbas et al. [32] made a ternary nanocomposites of Fe₃O₄-SiO₂-TiO₂ via sol/gel method for MB degradation with two cycles of recovery. Other binary photocatalysts relating TiO₂-Fe₃O₄ [33–35] were also designed to understand the photocatalytic activity of Fe₃O₄. Nevertheless, these composites always suffered considerable reduction in efficiency after several uses, probably due to the chemical instability of Fe₃O₄ induced by the photo-generated electrons transferred from TiO₂ [13].

Due to the superior magnetic properties of Fe₃O₄ and the dielectric properties of ZnO, it is possible to coat the Fe₃O₄ nanoparticles with a ZnO nanoshell, which will take advantages of the superior properties of the two components. Many investigators focusing on this area discovered that the combination of Fe₃O₄ and ZnO led to a rise in the impedance matching, and also significantly improved their absorption performance by making ternary composites with carbon allotropes [36–39]. However, there is not much report on decorating of Fe₃O₄-ZnO core/shell nanoparticle on reduced graphene oxide platelets. The aim of this work is to increase the magnetic performance and durability of recyclable photocatalysts for practical usage particularly photo-degradation efficiency under natural daylight irradiation.

2. Materials and methods

2.1. Materials

For this work, high purity ferric chloride hexahydrate (FeCl₃·6H₂O), polyvinylpyrrolidone (PVP, K30), urea (CO(NH₂)₂), ethylene glycol (EG), zinc acetate dihydrate (C₉H₆O₂Zn·2H₂O), sodium hydroxide (NaOH), ethanol (C₂H₅OH), graphite, potassium permanganate (K₂MnO₄), sulfuric acid (H₂SO₄), nitric acid (HNO₃), hydrogen peroxide (H₂O₂), sodium borohydride (NaBH₄), and chitosan were supplied by Sigma-Aldrich Co. (Germany) and Fluka provided.

2.2. Fe₃O₄ nanoparticles preparation

Fe₃O₄ Nps were prepared using solvo thermal route according to Wang et al. method [40]. Briefly, 1.1 g of FeCl₃·6H₂O, 2 g of PVP, and 4 g of urea were mixed with 45 mL of EG. After homogenization for 10 min the apparent solution was moved to a Teflon™ autoclave mold and heated at 200 °C for 24 h inside an oven. Then, the black precipitate was washed, centrifuged, and dried.

2.3. Preparation of core/shell structure of Fe₃O₄-ZnO

The core/shell structure of Fe₃O₄-ZnO was obtained via the simple sol–gel route. Typically, 0.2 g of Fe₃O₄ nanoparticles was added to a 3-neck round-bottom flask, along with 100 mL of ethanol solution containing 1 g of zinc acetate. Ultrasonic treatment was applied for 10 min, and the mixture was transferred to an ultrasonic bath. Then, 0.25 M of NaOH-ethanol solution was slowly poured into the flask until the pH of the solution reached 8. To complete the coating process, the reaction was retained at 60 °C for 4 h. The dark product after filtering and washing dried at 50 °C in an oven.

2.4. Preparation of GO platelet

Initially, 2 g of graphite powder was taken into a flask, and a mixture of H₂SO₄ (30 mL) and nitric acid (10 mL) was added and slowly stirred for 1 h in the ice bath. Then, 6 g of potassium permanganate was added to the mixture and stirred slowly and vigorously for 1 h at 0 °C. Once the yellow vapors ceased, the mixture was diluted with 100 mL warm water (T = 90 °C) and left for 3 days stirring at ambient temperature. The yellowish green paste obtained was diluted with 500 mL water containing 10 mL hydrogen peroxide of 35% to stop the reaction. After decantation for 24 h, the paste obtained was washed with HCl 3% and then thoroughly with distilled water several times until pH = 7 achieved. The dark brown paste was dried at a temperature of 80 °C during 24 h to get solid GO.

2.5. Preparation of reduced graphene oxide (RGO) platelet

The GO reduced using Z.Q. Li et al. [17] method. Briefly, 0.1 g of GO was dissolved in distilled water (100 mL). After ultrasonic treatment for 1 h, 4 mL of 5% chitosan solution with 2 g of sodium borohydride were added to the flask, respectively. Following that, the suspension was heated and refluxed at a temperature of 100 °C for 4 h. The reaction mixture was filtered, and RGO was rinsed with water and dried at room temperature.

2.6. Preparation of hybrid RGO/Fe₃O₄-ZnO nanocomposite

For this purpose, 0.1 g of RGO was mixed with 25 mL of distilled water and 25 mL of absolute ethanol. Afterwards, ultrasonic treatment was performed for making uniform suspension. Then, 0.4 g of Fe₃O₄-ZnO was added to the solution and after sonication for 1 h the hydrothermal reaction was carried out at a temperature of 105 °C for 24 h. Finally, the product was filtered, washed with water, and dried at a temperature of 50 °C.

2.7. Characterization

Powder X-ray diffraction (XRD) patterns were taken for the prepared Fe₃O₄ nanoparticles, FZ, and RFZ, using an XRD device (Philips,
Cu Kα λ = 1.540 Å, 40 kV, 25 mA). Field emission-scanning electron microscopy (FE-SEM; HITACHI S-4160) and transmission electron microscopy (TEM-CM30, 150 kV) were used for observing the surface morphology and structure of prepared samples. A vibration sample magnetometer (VSM; Lake Shore, VSM 7400) was used to record the magnetization hysteresis curves of Fe₃O₄, FZ, and RFZ. The distribution of the size of particles was analyzed using dynamic light scattering (DLS; Brookhaven-Plus/BT-MAS90). The Brunauer-Emmett-Teller (BET) surface area and Barrette-Joyner-Halenda (BJH) pore size distribution were evaluated by nitrogen sorption using a microtrac analyzer (BELSORP-miniII). Moreover, a UV–Vis spectrometer (PerkinElmer) was used to determine the optical features.

2.8. Preparation of photocatalytic degradation

The photocatalytic MB degradation was used to assess the photocatalytic performance under natural daylight radiation. 10 mg/L of MB solution was used as the simulated MB-contaminated wastewater, and 10 mg of FZ and RFZ was dissolved in 30 mL of polluted water. The suspension was stirred magnetically during 30 min in darkness to achieve an adsorption-desorption equilibrium. Under ambient conditions, the suspension was exposed to daylight radiation in various times (0–120 min). At certain time interval, 2.5 mL of the mixed suspension was taken out and centrifuged to remove the photocatalyst. By using a UV–Vis absorption spectrometer, the degradation process was determined through analysis of MB absorbance in the photo-ink. A concentration of MB dosage and absorbance in the photodegradation were evaluated by nitrogen sorption using a microtrac analyzer (BELSORP-miniII). Moreover, a UV–Vis spectrometer (PerkinElmer) was used to determine the optical features.

The half-life t₁/₂ (min) of the degradation was measured by the following equation [26]:

\[ t_{1/2} = \frac{\ln 2}{k_{ap}} \]  

The photocatalytic degradation rate constant (kₚₐ) was measured using the first-order plot [26]:

\[ \ln \left( \frac{C}{C_0} \right) = -k_{ap}t \]  

where \( C_0 \) and \( C \) denote MB dosage and absorbance in the photocatalytic reaction before and after exposure, respectively. The apparent degradation rate constant (kₚₐ) was measured using the first-order plot [26]:

\[ \eta \% = \frac{C_0 - C_t}{C_0} \times 100 \]  

3. Results and discussion

3.1. Crystalline structure

As shown in Fig. 1a, the diffraction peaks of Fe₃O₄ at 2θ (30.10°, 35.57°, 43.20°, 53.68°, 57.17°, 62.89°, 71.3°, and 74.31°), which relate to miller indices of (220), (311), (400), (422), (511), (440), (020), and (533), respectively, are in accordance with the Fe₃O₄ PDF data (JCPDS file no. 19-0629) [39-41]. No peak of other phase was detected, indicating that pure magnetite had been prepared in solvothermal process. The mean crystallite size of Fe₃O₄ ~ 25 nm was calculated using the Scherrer equation:

\[ L = \frac{Kλ}{βcosθ} \]  

where L is the mean size of the ordered domains, K represents the typical value of the shape factor (nearly 0.9), λ is the wavelength of X-ray, β represents the line broadening at half the maximum intensity (FWHM), and θ represents the Bragg angle (in degrees).

Fig. 1b presents the XRD patterns of FZ in the presence of magnetite cores after coating. In comparison with Fig. 1a, nine new peaks were observed at 31.78°, 34.43°, 36.24°, 47.52°, 56.56°, 62.86°, 66.28°, 67.90°, and 68.91°. The site and relative intensity of these new peaks were in accordance with (10-10), (0002), (10-11), (10-12), (11-10), (10-13), (20-20), (11-12), and (20-21) planes of standard bulk ZnO hexagonal wurtzite crystalline (JCPDS file No., 36-1451) [31,39]. No peaks corresponding to the impurities are detected, signifying that Fe₃O₄-ZnO heterostructure were formed during the coating process. The mean crystalline size of Fe₃O₄-ZnO (FZ) ~ 25.8 nm was estimated with respect to the line broadening of XRD peaks, based on the Scherrer equation. As presented in Fig. 1c, XRD calculations were performed to confirm the presence of FZ on the RGO platelet surface. No clear difference was detected between FZ and RFZ due to the presence of ZnO particles, which became dominant due to the increased weight ratio in comparison with the RGO and Fe₃O₄ particles. Crystal growth of the core-shell Fe₃O₄-ZnO occurs in the interlayers during the hydrothermal process or may be due to the presence of magnetite, which decreases the aggregation of graphene platelets. Thus, more monolayer graphene leads to weaker carbon peaks [6,31,39]. As revealed in Fig. 1c, just very low intensity peak revealed at 2θ = 25.5° were successfully found onto RGO platelets could be attributed to the (002) plane of the reduced graphene [42]. The characteristic topographies of RGO are obviously detected in the TEM images.

3.2. Core/shell structure

Fig. 2 shows the characteristic FE-SEM images. As displayed in Fig. 2a, the Fe₃O₄ nanoparticles formed spherical clusters of fine particles clinging together. DLS graph in Fig. 2b showed the average size of Fe₃O₄ (Dₕ₀ = 30.35 nm) and proved that most of particles are under 50 nm. The clusters of particles is believed to be due to the magnetic- static coupling between the particles [43]. The microstructure of the Fe₃O₄-ZnO core/shell nanoparticles is shown in Fig. 2c. As seen, the spherical structure of FZ without agglomerated particles is detected. Due to the formation of ZnO shells the magnetic attraction and clunging between Fe₃O₄ cores has decreased. Thus, the shell is known as a dead layer [44]. This result is in good accordance with the DLS graph of FZ in Fig. 2d which indicate an increase in particles size distribution (Dₕ₀ = 68.23 nm) and proved that higher percentages of particles are above 50 nm.

The TEM images in Fig. 3a and b provided supplementary insight into the morphology and surface properties of the Fe₃O₄ and FZ and the core-shell structure of the particles. This finding indicates that instead of homogeneous nucleation and growth in solution, ZnO was deposited selectively on the magnetite cores [41]. A ring of ZnO shell was successfully coated via the sol-gel process on the entire surface of Fe₃O₄ nanoparticles which was clearly recognized by the difference in the color intensity.
3.3. Morphological analysis of RGO/Fe₃O₄-ZnO nanocomposite

Different magnifications of TEM images of the RFZ are shown in Fig. 4, which revealed that heterogeneous nanostructures of FZ were deposited completely on RGO platelets. Fig. 4a shows the TEM image of the well-defined single phase and the monolayer structure of the RGO platelets, which was also confirmed by SAED patterns given in Fig. 4b and c. The TEM images of the RFZ nanocomposite with different magnifications can be observed clearly in Fig. 4d, e and f. The TEM images show well separated cluster distribution of the FZ decorated on RGO platelet. The existence of diffraction spots in three parts with different contrast using SAED patterns shown in Fig. 4f₁, 4f₂ and 4f₃, revealed that Fe₃O₄-ZnO nanoparticles are well attached on RGO platelet [39,45]. Due to the hexagonal structure of the RGO and ZnO, the Fig. 4f₁ shows the interaction of hexagonal structures. Remarkably, the RGO platelets are well distributed without agglomeration and have reasonably large surface area, which provides a better contact with solutions [17,42].

3.4. Magnetic properties evaluation

The magnetic properties of the RFZ photocatalyst were examined at room temperature on a magnetometer and compared with the FZ and Fe₃O₄. The magnetization curves in Fig. 5 revealed that Fe₃O₄ has high

Fig. 2. FE-SEM images and DLS graphs of a) FE-SEM of Fe₃O₄; b) DLS graph of Fe₃O₄; c) FE-SEM of Fe₃O₄-ZnO core-shell; d) DLS graph of Fe₃O₄-ZnO.

Fig. 3. TEM images of a) Fe₃O₄; b) Fe₃O₄-ZnO core-shell.
magnetization saturation (Ms) value of 58 emu g$^{-1}$, which is not close to its bulk value of 92 emu g$^{-1}$, but is in good agreement with the result of several recent studies [46–48]. This reduction may be due to the dysfunction of magnetic moments in atoms of the surface layer, surface oxidation, and dead layer thickness [17,49]. Also, the smaller size of particles resulted in the greater influence of this dysfunction in the magnetic layer in comparison to the bulk [50].

Considering the insignificant coercive field value of magnetite nanoparticles, they could not be detected in the M-H curve; therefore, the magnetite nanoparticles showed superparamagnetism behavior [46].

As seen in Fig. 5, the magnetic saturation (M_s) values of the FZ decreased to 12.45 emu g$^{-1}$ compared to that of Fe$_3$O$_4$ nanoparticles (58 emu g$^{-1}$). The magnetic saturation (Ms) values of the RFZ increased to 20.18 emu g$^{-1}$ compared to that of FZ core/shell due to magnetic properties of RGO platelets. The evaluation of the coercive fields (Hc) of the samples is shown in Table 1. The appearance of the coercive filed (Hc) in FZ and RFZ can be attributed to the presence of ZnO shell and RGO sheets. The role of shell and platelets can be considered as the function of domain walls in relation to magnetic materials to the avoidance of magnetic moment rotation. Therefore, due to a low coercivity, magnetization curves for the samples exhibited superparamagnetism. Moreover, considering the Ms value of FZ and RFZ, it is concluded that these nanomaterials can be efficiently removed and recycled from liquid systems, thus signifying their effective use as a recyclable photocatalyst [51].
The concentration of the dyes was investigated using a UV–Vis spectrophotometer [54]. Fig. 7 indicates the effect of different contact times on the adsorption of aqueous MB solution with and without a catalyst, following daylight irradiation.

As clearly seen, an insignificant MB degradation was observed in the solution in the absence of catalysts under daylight irradiation indicating that the MB degradation predominately occurred via photocatalysis rather than photolysis. Nevertheless, by extending the irradiation time, the MB absorption peak intensity declined at 664 nm, thereby revealing MB molecule degradation via catalysis. The optical absorption of MB degradation was 94.8% for FZ after 120 min, to 98.4% for RFZ, which is shown in Fig. 8a and b.

The high photocatalytic rate of RFZ can be related to its high potential for adsorption of organic pollutants, prevention of electron-hole recombination [26], synergistic effects, and considering the RGO properties [1]. Similar to GD, the (r)GO suppressed the pair recombination due to its electron acceptor nature, which increased the photocatalytic efficiency by trapping the electron on RGO sheets, which react with oxygen to form superoxide radicals (O$_2^-$), whereas the holes react with water to form hydroxyl radicals (OH$_-$) that decompose the MB dyes [29]. The next theory of enhancing the degradation process is rapid transferring of photoinduced of electrons and holes form shells to cores [26,55].

Fig. 9 shows the kinetic analysis (first-order degradation rates) for the RFZ nanocomposite and FZ core/shell. The reaction rate constant ($K_{ap}$) and the half-life $t_{1/2}$ (min) of the degradation are given in Table 3. It can be seen that the adsorption reactions followed the pseudo-first order kinetic process. The apparent rate constant ($K_{ap}$) significantly increased due to the more photocatalytic activity in the ternary RFZ compared to the FZ.

### 3.6. Mechanism of photocatalytic activity for the RFZ nanocomposites

In the RFZ nanocomposite, the electrons are excited from the valence band (VB) to the conduction band (CB) of ZnO shell under natural daylight irradiation, forming holes in VB. Since the energy level of the conduction band of ZnO is higher than the Fermi level of Fe$_3$O$_4$, electrons can be quickly transferred from ZnO shells to the cores [56]. Hence, the cores can act as a reservoir for the photoelectrons and extend the lifetime of the photogenerated charge due to the reduction of Fe$^{3+}$ to Fe$^{2+}$, then probably the binary FZ has proper photocatalytic efficiency [57,58]. Furthermore, the enhanced photocatalytic activity can be explained by the difference in the different band gaps (ZnO: $E_g = 3.37$ eV, Fe$_3$O$_4$: $E_g = 0.1$ eV) and work function of ZnO and Fe$_3$O$_4$, which promotes interfacial electron/hole separation in the photocatalytic process, thereby increasing the number of "live" photocharges and enhancing the photocatalytic performance [59]. In addition, due to the intimate contact of FZ core/shell nanoparticles on RGO platelets, the synergistic effects caused the enhancement in the photocatalytic efficiency of the RFZ nanocomposite [60]. The RGO also acted as an electron acceptor and transporter to effectively separate the photogenerated electron-hole pairs and inhibit the recombination of the photogenerated electron-hole pair, causing most of the holes contributes in the photoinduced oxidation process and improving the photocatalytic activity [25,55,60]. The others might be caused by the concentration of oxygen vacancies on the RGO sheets that can trap the photoinduced electrons during the photocatalytic process and then prevent the recombination of the photogenerated electron/hole pairs. In addition, oxygen species such as O$_2$ and OH$^-$ could be easily adsorbed by oxygen vacancies. After reaction with photogenerated carriers, those oxygen species was converted in to O$_2^-$ and OH$^-$ which can enhance the photocatalytic process [58]. Briefly, the degradation reactions for the RFZ can be written as follows:

$$\text{RGO} \cdot (\text{Fe}_3\text{O}_4 + \text{ZnO}) + \text{hv} \rightarrow (\text{Fe}_3\text{O}_4 + \text{ZnO})(e^- + h^+)$$  \hspace{1cm} (5)

$$\text{ZnO} + \text{hv} \rightarrow \text{e}^-(\text{CB}) + h^+(\text{VB})$$  \hspace{1cm} (6)

### Table 1

<table>
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<th>Samples</th>
<th>$M_s$ (emu/g)</th>
<th>$H_c$ (Oe)</th>
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<tr>
<td>Fe$_3$O$_4$</td>
<td>58</td>
<td>–</td>
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<tr>
<td>Fe$_3$O$_4$-ZnO</td>
<td>12.45</td>
<td>3.24</td>
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<td>rGO/Fe$_3$O$_4$-ZnO</td>
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### 3.5. Investigation of specific surface area of the photocatalysts

The surface area of Fe$_3$O$_4$, FZ and RFZ was determined using BET method. The nitrogen (N$_2$) adsorption-desorption isotherm of Fe$_3$O$_4$, FZ and RFZ are shown in Fig. 6. All of samples exhibited a loop hysteresis type of IV isotherm that is referred to mesoporous materials. The change in surface properties is assumed due to the presence of ZnO shell on the surface of Fe$_3$O$_4$ nanoparticles and the presence of RGO platelets, which increased the surface area of RFZ due to nature of the carbon based materials [52,53]. Therefore, the high surface area could promote higher photocatalytic activity by adsorbing a higher number of organic reactant molecules on the catalyst surface [26]. The BET test data is presented in Table 2.

### 3.6. Photocatalytic degradation and adsorption of MB

The FZ and RFZ photocatalytic activities were estimated by measuring the discoloration of methylene blue (MB) under natural daylight irradiation. The concentration of MB was recorded by evaluating the absorbance at 664 nm, which is the characteristic wavelength of MB.

Fig. 5. Magnetic hysteresis curves of Fe$_3$O$_4$ nanoparticles, Fe$_3$O$_4$-ZnO core/shell and RGO/Fe$_3$O$_4$-ZnO nanocomposite.

Fig. 6. Nitrogen adsorption-desorption isotherms of Fe$_3$O$_4$ and the prepared photocatalysts.

Fig. 7 indicates the effect of different daylight radiation, forming holes in VB. Since the energy level of the conduction band of ZnO is higher than the Fermi level of Fe$_3$O$_4$, electrons can be quickly transferred from ZnO shells to the cores [56]. Hence, the cores can act as a reservoir for the photoelectrons and extend the lifetime of the photogenerated charge due to the reduction of Fe$^{3+}$ to Fe$^{2+}$, then probably the binary FZ has proper photocatalytic efficiency [57,58]. Furthermore, the enhanced photocatalytic activity can be explained by the difference in the different band gaps (ZnO: $E_g = 3.37$ eV, Fe$_3$O$_4$: $E_g = 0.1$ eV) and work function of ZnO and Fe$_3$O$_4$, which promotes interfacial electron/hole separation in the photocatalytic process, thereby increasing the number of "live" photocharges and enhancing the photocatalytic performance [59]. In addition, due to the intimate contact of FZ core/shell nanoparticles on RGO platelets, the synergistic effects caused the enhancement in the photocatalytic efficiency of the RFZ nanocomposite [60]. The RGO also acted as an electron acceptor and transporter to effectively separate the photogenerated electron-hole pairs and inhibit the recombination of the photogenerated electron-hole pair, causing most of the holes contributes in the photoinduced oxidation process and improving the photocatalytic activity [25,55,60]. The others might be caused by the concentration of oxygen vacancies on the RGO sheets that can trap the photoinduced electrons during the photocatalytic process and then prevent the recombination of the photogenerated electron/hole pairs. In addition, oxygen species such as O$_2$ and OH$^-$ could be easily adsorbed by oxygen vacancies. After reaction with photogenerated carriers, those oxygen species was converted in to O$_2^-$ and OH$^-$ which can enhance the photocatalytic process [58]. Briefly, the degradation reactions for the RFZ can be written as follows:

$$\text{RGO} \cdot (\text{Fe}_3\text{O}_4 + \text{ZnO}) + \text{hv} \rightarrow (\text{Fe}_3\text{O}_4 + \text{ZnO})(e^- + h^+)$$  \hspace{1cm} (5)

$$\text{ZnO} + \text{hv} \rightarrow \text{e}^-(\text{CB}) + h^+(\text{VB})$$  \hspace{1cm} (6)

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3.6.2. Recycling test of photocatalyst

To investigate the stability of photocatalysts, recycling tests were conducted that shown in Fig. 10. The mean reaction rate constant (K_{ap}) for each cycles was determined and is given in Table 4. After the end of each process, the catalysts were filtered, washed, and dried at 80 °C for 3 h and utilized for the next cycle, keeping other reaction conditions constant. Up to 8 cycles, the RFZ due to excellent properties of RGO especially high surface area, zero band gap and excellent electronic characteristics in the storage and transport of electron showed a slight decrease in catalysis efficiency that compared to FZ. The reduced photocatalytic degradation efficiency between the cycles can be attributed to the catalytic fouling and sediment, caused by the products during the reaction [17].

4. Conclusion

Mesoporous RFZ photocatalyst were synthesized using a simple hydrothermal process. They showed high adsorption potential, favorable magnetism at room temperature, proper specific surface area, and high photocatalytic performance for MB dye degradation under natural daylight irradiation. The improvement in the photocatalytic efficiency is related to the active electron-hole pairs provided by ZnO, the successful transferring of electrons from shells to the cores, the reduction of Fe^{3+} to Fe^{2+}, and the synergistic effects. Furthermore, the RGO platelets provided appropriate sites for the adsorption of MB, thus improving the catalytic degradation. The prepared magnetic RFZ

### Table 2

<table>
<thead>
<tr>
<th>Samples</th>
<th>a_{BET} (m² g⁻¹)</th>
<th>Total pore volume (cm³ g⁻¹)</th>
<th>Mean pore diameter (nm)</th>
<th>a_{Lang} (m² g⁻¹)</th>
<th>a_p (m² g⁻¹)</th>
<th>V_p (cm³ g⁻¹)</th>
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<td>Fe₃O₄</td>
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<td>117.31</td>
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<td>Fe₃O₄-ZnO</td>
<td>31.56</td>
<td>0.151</td>
<td>19.21</td>
<td>39.55</td>
<td>44.17</td>
<td>0.159</td>
</tr>
<tr>
<td>rGO/Fe₃O₄-ZnO</td>
<td>36.05</td>
<td>0.165</td>
<td>18.35</td>
<td>44.78</td>
<td>54.44</td>
<td>0.177</td>
</tr>
</tbody>
</table>

- BET plot data.
- Langmuir plot data.
- BJH plot data.

Fig. 7. Methylene blue degradation with and without photocatalysts (absorbance at 664 nm).

Fe^{3+} + e⁻(CB)shell → Fe^{2+}  \hspace{1cm} (7)

RGO + (e⁻ + h⁺) → RGO(e⁻) + RGO(h⁺)  \hspace{1cm} (8)

e⁻ + O₂ → O₂⁻⁻  \hspace{1cm} (9)

h⁺ + H₂O→OH⁻ + H⁺  \hspace{1cm} (10)

O₂⁻⁻ + OH⁻+MB(dye)→CO₂ + H₂O(decomposition)  \hspace{1cm} (11)

Fig. 8. UV–Vis absorbance of MB at different time intervals in photocatalytic degradation under natural daylight for a) Fe₃O₄-ZnO core/shell and b) RGO/Fe₃O₄-ZnO nano-composite.

Fig. 9. Kinetics of MB photocatalytic degradation under natural daylight irradiation of the prepared photocatalysts.
photocatalyst with high reaction rate exhibited repeatability, and no significant reduction was observed in the photocatalytic efficiency following 8 cycles. The findings indicated the practical and possible use of the RFZ nanocomposites for photocatalytic degradation of wastewaters.

References