Research Article

Adsorption Characteristics and Electrochemical Behaviors of Methyl Blue onto Magnetic Mg$_x$Co$_y$Zn$_{(1-x-y)}$Fe$_2$O$_4$ Nanoparticles

Zhixiang Lv$^1$, Xin Yang$^2$, Jihong Han$^2$, Yingyao Wang$^2$, Jiao Zou$^2$, Anqi Yang$^2$, Haoda Zhang$^2$, and Nan He$^2$

$^1$The People’s Hospital of Danyang, Affiliated Danyang Hospital of Nantong University, Zhenjiang 212300, China
$^2$School of Pharmacy, Jiangsu University, Zhenjiang 212013, China

Correspondence should be addressed to Zhixiang Lv; dylvzhixiang@163.com

Received 15 September 2022; Revised 17 April 2023; Accepted 4 May 2023; Published 15 May 2023

Copyright © 2023 Zhixiang Lv et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Magnetic Mg$_x$Co$_y$Zn$_{(1-x-y)}$Fe$_2$O$_4$ nanoparticles were successfully prepared by the rapid combustion approach, and SEM, XRD, VSM, EDX, and FTIR techniques were applied for their characterization. The influence of the element ratios (Mg$^{2+}$, Co$^{2+}$, and Zn$^{2+}$) in magnetic Mg$_x$Co$_y$Zn$_{(1-x-y)}$Fe$_2$O$_4$ nanoparticles on their properties was explored. To acquire a larger specific surface area for better adsorption of methyl blue (MB), magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles calcined at 400°C for 2 h with 25 mL anhydrous ethanol were selected, and their average particle size and the saturation magnetization were about 81.3 nm and 13.5 emu·g$^{-1}$, respectively. Adsorption kinetics models and adsorption isotherm models were applied to research the adsorption characteristics of MB onto magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles. The pseudo-second-order kinetics model ($R^2 > 0.99$) and Temkin isotherm model ($R^2 = 0.9887$) were the most consistent with the data, indicating that the adsorption was the chemical multilayer adsorption mechanism, and the process was an exothermic reaction. The E of the Dubinin-Radushkevich (D-R) isotherm model was 0.2347 KJ·mol$^{-1}$, indicating the adsorption involved physical adsorption besides chemical adsorption. The $\Delta G^0$ and $\Delta H^0$ ($\Delta H^0 = -10.38$ KJ·mol$^{-1}$) of the adsorption process of MB adsorbed onto magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles measured through the thermodynamic experiment were both less than 0, which proved that the process was a spontaneous exothermic reaction. The adsorption capacity of MB onto magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles increased with the pH of MB solution increasing from 2 to 4 at room temperature, and it had no significant change when the pH of MB solution was 4-12, while the relative removal rate was 98.75% of the first one after 2 cycles. The electrochemical impedance spectroscopy (EIS) and the cyclic voltammetry (CV) data further demonstrated that MB was adsorbed onto magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles.

1. Introduction

Dyes have been widely used in textiles, coatings, paint, plastic, and other industries which make people’s lives become colorful [1–6]. Meanwhile, environmental pollution has become increasingly serious owing to the discharge of a great deal of dye wastewater, especially, the nondegradable substances and aromatic and other organics of dyes that make the water eutrophication and absorbed by plants; many of them have serious harm to the environment and eventually enter the human body through the food chain that has a great threat to human health [7–11]. Hence, solving dye pollution has become a serious problem. Many methods of treating dye wastewater have been widely used, such as the membrane separation method [12, 13], photodegradation [14, 15], electrochemical oxidation method [16, 17], and adsorption method [18, 19]. Considering the low cost, no secondary pollution, recycling, and other influence factors, the adsorption method stands out from these methods [20–22].

The adsorbent is a key factor in the adsorption process, and many usual adsorbents, for instance, activated carbon [23], silica gel [24], resin [25], zeolite [26], and activated alumina [27], are applied to treat dye wastewater. With the development of nanotechnology, for larger specific surface area and high adsorption capacity,
nanomaterials are applied for adsorption. Whereas, the difficult separation revealed the disadvantage of nanomaterials for adsorption. To solve the question, magnetic nanomaterials are used for adsorption, and they can be facilely separated from wastewater with an external magnetic field [28–31].

Many approaches can be applied for the preparations of magnetic nanomaterials, such as coprecipitation [32, 33], sol-gel [34], rapid combustion [35], and hydrothermal methods [36]. The coprecipitation method is easy to cause a high local concentration of solution owing to precipitant, leading to agglomeration [37]; and the sol-gel method has the disadvantages of a long preparation cycle and high cost [38], while the hydrothermal method has high requirements on the reaction temperature and pressure and has great safety risks [38]. Compared to these methods, the rapid combustion method has advantages such as low cost, a short preparation period, low equipment requirements, and other advantages.

Spinel ferrites (MFe$_2$O$_4$, M=Mg, Co, Zn, Cu, Ni, etc.) are a kind of magnetic nanomaterials which have been widely studied due to their unique magnetic properties and electrical resistances [39–41]. MgFe$_2$O$_4$, CoFe$_2$O$_4$, and ZnFe$_2$O$_4$ are often used as adsorbents. MgFe$_2$O$_4$ has high adsorption capacity and strong stability. Saturated magnetization and coercivity of MgFe$_2$O$_4$ could be improved by permeating Co into MgFe$_2$O$_4$ due to the saturated magnetization of CoFe$_2$O$_4$ being greater than MgFe$_2$O$_4$ [42, 43]. The specific surface area ratio of MgFe$_2$O$_4$ could be increased by permeating Zn into MgFe$_2$O$_4$ because ZnFe$_2$O$_4$ has a large specific surface area [44]. Although magnetic Mg$_{x}$Co$_{y}$Zn$_{(1-x-y)}$Fe$_2$O$_4$ nanoparticles have some advantages, they have not been widely applied because of their less mature technology.

In this work, magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles were successfully prepared by the rapid combustion approach, and MB was selected as the dye adsorption model which was a complex aromatic and typical anionic dye, the adsorption mechanism of MB onto Mg$_{x}$Co$_{y}$Zn$_{(1-x-y)}$Fe$_2$O$_4$ nanoparticles was investigated [1].

2. Experimental Detail

2.1. Materials. Absolute ethanol, ferric nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O, AR), cobalt nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O, AR), magnesium nitrate hexahydrate (Mg(NO$_3$)$_2$·6H$_2$O, AR), zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O, AR), and methyl blue (MB, BS) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

2.2. Preparation and Characteristic of Magnetic Mg$_{x}$Co$_{y}$Zn$_{(1-x-y)}$Fe$_2$O$_4$ Nanoparticles. The rapid combustion approach was employed to prepare magnetic Mg$_{x}$Co$_{y}$Zn$_{(1-x-y)}$Fe$_2$O$_4$ nanoparticles. At room temperature, Mg(NO$_3$)$_2$·6H$_2$O, Co(NO$_3$)$_2$·6H$_2$O, Zn(NO$_3$)$_2$·6H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O, and anhydrous ethanol (15 mL, 25 mL, 35 mL, 45 mL, 55 mL, and 100 mL) were added to a beaker according to the design ratio (x:y:(1-x-y):2). Then, the beaker was magnetically stirred until a homogeneous solution was formed. The homogeneous solution was moved to a crucible for combustion until the flame went out. Then, the crucible was placed in a calcinatory with programed temperature controlling for calcination and ground after calcination.

The phase identification of magnetic Mg$_{x}$Co$_{y}$Zn$_{(1-x-y)}$Fe$_2$O$_4$ nanomaterials was analyzed by X-ray diffraction (XRD, Rigaku D/max 2500 PCX), a vibrating sample magnetometer (VSM, HH-15, Physcience Opto-electronics Co., Ltd., Beijing, China), and the scanning electron microscopy (SEM, JSM-TOOIF, JEOL Ltd., Japan) that were used to investigate their hysteresis loops and morphology, respectively; the energy dispersive spectroscopy (EDS) was selected to analyze the corresponding element composition, and magnetic Mg$_{x}$Co$_{y}$Zn$_{(1-x-y)}$Fe$_2$O$_4$ nanoparticles were added to the milled KBr for grinding and analyzing their Fourier transform infrared spectroscopy (FTIR, Nicolet Avatar, America) at 4000 cm$^{-1}$-400 cm$^{-1}$.

2.3. Adsorption Experiments of MB onto Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ Nanoparticles. To investigate the adsorption kinetics characteristics of MB onto Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles, each of 5 mg magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles was added into 2 mL MB solution (1900-2200 mg·L$^{-1}$) at room temperature and pH of 4, sonicated for 5 min and stirred for a corresponding time, then centrifuged at 10000 rpm for 5 min. The absorbance of supernatant after centrifugation of magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles was measured by ultraviolet spectrophotometer. To research the adsorption relationship of MB and magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles, similarly, each 5 mg magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles were added into 2 mL MB solution with various initial concentrations of 400-2200 mg·L$^{-1}$ and the gradient of 200 mg·L$^{-1}$ and kept for 24 h. Then, centrifuged and the supernatants were taken for measurements. To investigate the effect of MB solution temperature on the adsorption capacity of magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles, the experimental steps of isotherm were repeated at 303 K, 313 K, and 323 K, respectively. To study the effect of pH on the adsorption capacity, 1 M NaOH solution and 1 M hydrochloric acid were used for accommodating the pH of MB solutions (2, 4, 6, 8, 10, and 12), and the adsorption capacities under various pH values were examined under with 2000 mg·L$^{-1}$ of the initial MB solution. To investigate the adsorption reusability of MB onto magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles, 100 mg of magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles were added to 40 mL MB solution (2000 mg·L$^{-1}$), and when the adsorption was finished, the magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles that adsorbed MB were separated and calcined again at 400°C for 2 h, and the adsorption was repeated. Formula (1) was employed to calculate the adsorption capacity of Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles for MB [45].

\[
q_t = \frac{(C_0 - C_t) \cdot V}{m},
\]

where $C_0$ (mg·L$^{-1}$) and $C_t$ (mg·L$^{-1}$) were the initial concentration of MB and the concentration after adsorption, respectively.
m (g) was the weight of magnetic Mg0.4Co0.5Zn0.1Fe2O4 nanoparticles, and V (L) was the volume of the MB solution.

2.4. Electrochemical Performances of MB onto Magnetic Mg0.4Co0.5Zn0.1Fe2O4 Nanoparticles. To investigate the electrochemical changes for the adsorption process of MB onto Mg0.4Co0.5Zn0.1Fe2O4 nanoparticles. At room temperature, 1 mg magnetic Mg0.4Co0.5Zn0.1Fe2O4 nanoparticles and 1 mg magnetic Mg0.4Co0.5Zn0.1Fe2O4 nanoparticles adsorbing MB were put into 100 μL ultrapure water to make suspension liquids, then ultrasound for 30 min, respectively. The two suspension liquids mentioned above of 8 μL were sucked and added onto the magnetic glassy carbon electrodes which were ground by alumina, respectively, and then dried to obtain the electrodes to be tested. Then, magnetic glassy carbon electrode, Ag/AgCl electrode, and platinum wire electrode were regarded as the working electrode, the reference electrode, and the counter electrode, respectively; 0.1 M KCl was used as the electrolyte which contained 5 mM [Fe(CN)6]3-/4-.

3. Results and Discussion

3.1. Characterization of Magnetic Mg0.4Co0.5Zn0.1Fe2O4 Nanomaterials. Mg0.4Co0.5Zn0.1Fe2O4 nanomaterials calcined at 400°C for 2 h with 25 mL anhydrous ethanol. The corresponding EDS spectogram of Mg0.4Co0.5Zn0.1Fe2O4 nanoparticles was displayed in Figure 1(b), and the proportions of all elements were consistent with the hypothesis before the experiment which proved the formation of Mg0.4Co0.5Zn0.1Fe2O4 nanoparticles. The XRD pattern of Mg0.4Co0.5Zn0.1Fe2O4 nanoparticles calcined at 400°C for 2 h with anhydrous ethanol of 25 mL were characterized as displayed in Figure 1(c). The cell parameters of Mg0.4Co0.5Zn0.1Fe2O4 nanoparticles were a = b = c = 8.3919 Å, α = β = γ = 90°, and...
the volume of $590.99 \text{ Å}^3$, which suggested that Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles were cubic type [49]. The hysteresis loops of Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles were shown in Figure 1(d), and the saturation magnetization ($M_s$) was 13.5 emu·g$^{-1}$, which contributed to being separated after adsorption.

3.2. Optimum Preparation Conditions of Mg$_x$Co$_y$Zn$_{1-x-y}$Fe$_2$O$_4$ Nanoparticles. To acquire a larger specific surface area, the element ratios (Mg, Co, and Zn) of magnetic Mg$_x$Co$_y$Zn$_{1-x-y}$Fe$_2$O$_4$ nanoparticles were investigated, and their XRD patterns, average grain sizes, and the hysteresis loops of magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ ($x = 0.1$ and $y = 0.5$) nanoparticles were shown in Figure S1(A-C), respectively. The wider and the lower the peak was, the lower the crystallinity was, the smaller the average grain diameter was, the larger the specific surface area of the nanomaterials was, and the better the adsorption efficiency of the nanomaterials was. It was obvious that the peak was the widest when $y$ was 0.5. The average grain size was calculated by the Scherrer formula [50] and was 10.8-11.4 nm, and the average grain size was the smallest when $y$ was 0.5. With the increase of Co content and the decrease of Zn content, the saturation magnetization generally presented a rising trend, the reason for which was that the saturation magnetization of CoFe$_2$O$_4$ was higher than that of ZnFe$_2$O$_4$ [51]. The XRD patterns, average grain diameter, and the hysteresis loops of magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ ($y = 0.5$ and $x = 0.1-0.4$) nanoparticles were revealed in Figure S1(D-F), respectively. It was obvious that the peak was the widest when $x$ was 0.4. The average grain diameter decreased from 10.8 nm ($x = 0.1$) to 10.0 nm ($x = 0.4$), indicating that the average grain diameter of magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles had a strong dependence on the content of Zn. Because the $M_t$ value of MgFe$_2$O$_4$ was lower than that of ZnFe$_2$O$_4$, the $M_t$ value of magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles decreased gradually with the increase of Mg content [52]. Hence, the magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles with a larger saturation magnetization were selected to investigate the property and employed to adsorb MB.

The influences of anhydrous ethanol volume and calcination temperature on magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles were investigated. The XRD patterns, average grain diameter, and the hysteresis loops of magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles calcined at different temperatures for 2 h with 25 mL anhydrous ethanol were displayed in Figure S2(A-C), respectively. It was obvious that the peak of the calcination temperature at 400 °C was the widest. While, with the calcination temperature increasing from 400 °C to 800 °C, the diffraction peak intensity of 35.57° gradually increased, and the average grain diameter increased from 10.0 nm to 30.1 nm. The calcination temperature had a larger influence on the average grain size. The reason was that the sintering degree was getting better with the increase in calcination temperature. The $M_t$ value of nanoparticles was related to their XRD patterns, average grain sizes, and the hysteresis loops of magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles were cubic type [49]. The hysteresis loops of magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles were shown in Figure 1(d), and the saturation magnetization ($M_s$) was 69.52 emu·g$^{-1}$ when anhydrous ethanol was 45 mL. To adsorb more MB and for easy separation, after comprehensive consideration, the calcination temperature of 400 °C and the absolute ethanol dosage of 25 mL were the best optimums for preparing magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles.

3.3. Adsorption Characteristics of MB onto Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ Nanoparticles

3.3.1. Adsorption Kinetics. The relationships between different initial concentrations of MB solution and the adsorption capacities of magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles were shown in Figure 2; the adsorption capacity of magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles for MB increased gradually with the increase of initial MB concentration. The reason was that the adsorption sites of magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles were much more than the required adsorption sites of MB in the solution with
the low initial concentration of MB, and MB was adsorbed onto magnetic Mg_{0.4}Co_{0.5}Zn_{0.1}Fe_{2}O_{4} nanoparticles and reached saturation soon. And the required adsorption sites of MB augmented with the increase of initial MB concentration; most of the adsorption sites of magnetic Mg_{0.4}Co_{0.5}Zn_{0.1}Fe_{2}O_{4} nanoparticles were rapidly occupied by MB, and the adsorption rate gradually decreased. Magnetic Mg_{0.4}Co_{0.5}Zn_{0.1}Fe_{2}O_{4} nanoparticles had a large number of effective adsorption sites in a short adsorption time. With the extension of the adsorption time, the effective adsorption sites decreased, and the adsorption rate gradually decreased until it stabilized, which reached the maximum saturated adsorption capacity.

Three frequently used kinetics models, pseudo-first-order, pseudo-second-order, and intraparticle models [53–55], were applied to investigate the adsorption process of MB onto magnetic Mg_{0.4}Co_{0.5}Zn_{0.1}Fe_{2}O_{4} nanoparticles. Equations (2)–(4) of the pseudo-first-order model, pseudo-second-order model, and intraparticle model were as follows:

\[ q_t = q_e \left( 1 - e^{-kt} \right), \]  

(2)
where $q_e$ (mg·g$^{-1}$) and $q_t$ (mg·g$^{-1}$) were the adsorption capacity of MB adsorbed at equilibrium and at any time ($t$), respectively; $k_1$ (min$^{-1}$), $k_2$ (mg·g$^{-1}$·min$^{-1}$), and $k_i$ (mg·g$^{-1}$·min$^{-1}$) were the adsorption rate constants for the corresponding model; $x_i$ was the constant of the intraparticle diffusion model.

Table 1: Fitted kinetics parameters for adsorptions of MB in aqueous solution onto Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles at room temperature.

<table>
<thead>
<tr>
<th>Kinetics models</th>
<th>Equations</th>
<th>Parameters</th>
<th>1900</th>
<th>2000</th>
<th>2100</th>
<th>2200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order model</td>
<td>$q_t = q_e \left(1 - e^{-k_1 t}\right)$</td>
<td>$q_e$</td>
<td>754.9470</td>
<td>792.9734</td>
<td>832.3179</td>
<td>871.1886</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_1$</td>
<td>0.4740</td>
<td>0.48560</td>
<td>0.4208</td>
<td>0.2963</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.7752</td>
<td>0.6888</td>
<td>0.7231</td>
<td>0.7961</td>
</tr>
<tr>
<td>Pseudo-second-order model</td>
<td>$q_t = q^2 e k_2 t / 1 + qek_2 t$</td>
<td>$q_e$</td>
<td>756.3431</td>
<td>794.3882</td>
<td>835.0674</td>
<td>880.4483</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_2$</td>
<td>0.0125</td>
<td>0.0126</td>
<td>0.0064</td>
<td>0.0018</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.9927</td>
<td>0.9911</td>
<td>0.9964</td>
<td>0.9966</td>
</tr>
<tr>
<td>Intraparticle diffusion model</td>
<td>$q_t = x_i + k_i t^{1/2}$</td>
<td>$x_i$</td>
<td>749.7993</td>
<td>787.7387</td>
<td>822.2724</td>
<td>837.7911</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_i$</td>
<td>0.5401</td>
<td>0.5546</td>
<td>1.0581</td>
<td>3.4625</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.6983</td>
<td>0.7482</td>
<td>0.7158</td>
<td>0.6591</td>
</tr>
</tbody>
</table>

$q_e$ (mg·g$^{-1}$) and $q_t$ (mg·g$^{-1}$) were the amounts of MB adsorbed at equilibrium and at any time ($t$), respectively; $k_1$ (min$^{-1}$), $k_2$ (mg·g$^{-1}$·min$^{-1}$), and $k_i$ (mg·g$^{-1}$·min$^{-1}$) were the adsorption rate constants for the corresponding model; $x_i$ was the constant of the intraparticle diffusion model.
The first stage was the surface adsorption process of Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_{2}$O$_{4}$ nanoparticles, namely, MB diffusion adsorption on the surface of Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_{2}$O$_{4}$ nanoparticles. The second stage was the diffusion process within the Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_{2}$O$_{4}$ nanoparticle, which was the process of MB diffusion into the nanoparticles, and the third stage was the process of slow adsorption to adsorption equilibrium. The results showed that the control steps of the adsorption process of MB onto Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_{2}$O$_{4}$ were carried out through the coupling of external diffusion and internal diffusion [57–59].

3.3.2. Adsorption Isotherms. The adsorption isotherm was used to investigate the interaction between MB and magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_{2}$O$_{4}$ nanoparticles. The experimental data were fitted with the Langmuir model, Freundlich model, Temkin model, and D-R model, respectively, as displayed in Figure 5. The Langmuir model assumed that monolayer adsorption on uniformly distributed adsorbent at active sites [60]. The Freundlich model assumed that multilayer adsorption was performed on heterogeneous surfaces [61]. The Temkin model assumed that monolayer and multilayer adsorption was performed on heterogeneous surfaces [62]. The D-R model assumed that adsorption was related to surface porosity and pore volume. D-R isotherm models examined adsorption in terms of energy to determine physical or chemisorption processes [63]. Equations (5)–(9) of the isotherms were as follows:

$$q_e = \frac{q_{\text{max}} K_L C_e}{1 + K_L C_e}$$

$$q_e = K_F C_e^{1/n}$$

$$q_e = B \ln (A_T C_e)$$

$$q_e = \frac{q_{\text{max}} e^{-\beta RT \ln (1 + 1/C_e)}}{E}$$

where $q_e$ (mg·g$^{-1}$) and $q_{\text{max}}$ (mg·g$^{-1}$) were the adsorption equilibrium capacity and maximum adsorption capacity of MB adsorbed onto magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_{2}$O$_{4}$ nanoparticles, respectively. $K_L$, $K_F$, and $1/n$ were constants for the corresponding model. $B$, $A_T$, and $E$ were constants of the Temkin isotherm model. $\beta$ was a constant related to the adsorption energy, and $E$ (KJ·mol$^{-1}$) was the mean adsorption energy. The relevant parameters of the isotherm models were listed in Table 2. The correlation coefficients ($R^2$) of the Langmuir model, Freundlich model, and Temkin model were 0.9859, 0.9665, and 0.9887, respectively, and the $R^2$ of the Temkin model was greater than that of the

<table>
<thead>
<tr>
<th>Model</th>
<th>Equation</th>
<th>$R^2$</th>
<th>Adj. $R^2$</th>
<th>Parameters</th>
<th>Estimated value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$q_e = \frac{q_{\text{max}} K_L C_e}{1 + K_L C_e}$</td>
<td>0.9859</td>
<td>0.9841</td>
<td>$q_{\text{max}}$</td>
<td>1192.3575</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$q_e = K_F C_e^{1/n}$</td>
<td>0.9665</td>
<td>0.9623</td>
<td>$K_F$, $1/n$</td>
<td>192.5846</td>
</tr>
<tr>
<td>Temkin</td>
<td>$q_e = B \ln (A_T C_e)$</td>
<td>0.9887</td>
<td>0.9873</td>
<td>$B$, $A_T$</td>
<td>268.8678</td>
</tr>
<tr>
<td>D-R</td>
<td>$q_e = \frac{q_{\text{max}} e^{-\beta RT \ln (1 + 1/C_e)}}{E}$</td>
<td>0.8929</td>
<td>0.8795</td>
<td>$\beta$, $E$</td>
<td>759.5958</td>
</tr>
</tbody>
</table>

$q_{\text{max}}$ was the maximum adsorption capacity of MB onto magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_{2}$O$_{4}$ nanoparticles; $K_L$, $K_F$, and $1/n$ were constants for the corresponding model.

Table 3: Comparison of the maximum adsorption capacities of MB onto Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_{2}$O$_{4}$ nanoparticles with other adsorbents.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Dose (mg·mL$^{-1}$)</th>
<th>Temperature (°C)</th>
<th>$q_{\text{max}}$ (mg·g$^{-1}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>SNCs-PEI</td>
<td>1</td>
<td>25</td>
<td>337.84</td>
<td>[35]</td>
</tr>
<tr>
<td>GO-CS aerogel</td>
<td>0.8</td>
<td>25</td>
<td>110.9</td>
<td>[71]</td>
</tr>
<tr>
<td>CNF/P-70 aerogel</td>
<td>0.5</td>
<td>25</td>
<td>598.8</td>
<td>[72]</td>
</tr>
<tr>
<td>TPP-PP</td>
<td>0.5</td>
<td>25</td>
<td>160.01</td>
<td>[73]</td>
</tr>
<tr>
<td>GO</td>
<td>0.01</td>
<td>30</td>
<td>419.5295</td>
<td>[74]</td>
</tr>
<tr>
<td>APG</td>
<td>0.01</td>
<td>30</td>
<td>821.05</td>
<td>[74]</td>
</tr>
<tr>
<td>Mg$<em>{0.4}$Co$</em>{0.5}$Zn$<em>{0.1}$Fe$</em>{2}$O$_{4}$ nanoparticles</td>
<td>2.5</td>
<td>RT</td>
<td>1162.3431</td>
<td>This work</td>
</tr>
</tbody>
</table>
Langmuir and Freundlich models, indicating that the Temkin model was fitter for explaining the adsorption relationship between MB and magnetic $\text{Mg}_{0.4}\text{Co}_{0.5}\text{Zn}_{0.1}\text{Fe}_{2}\text{O}_{4}$ nanoparticles. The adsorption of MB onto magnetic $\text{Mg}_{0.4}\text{Co}_{0.5}\text{Zn}_{0.1}\text{Fe}_{2}\text{O}_{4}$ nanoparticles was a monolayer and multilayer chemical adsorption mechanism. Moreover, $B$ of the Temkin model was positive, indicating that the adsorption was an exothermic process [64–66].

D-R isothermal model was employed to calculate the average adsorption energy. When $E < 8 \text{kJ mol}^{-1}$, the physical adsorption occurred; when $8 \text{kJ mol}^{-1} < E < 16 \text{kJ mol}^{-1}$, the chemisorption occurred. When $E > 16 \text{kJ mol}^{-1}$, the ion exchange occurred. It could be seen from Table 2 that $E$ of the adsorption process of MB onto $\text{Mg}_{0.4}\text{Co}_{0.5}\text{Zn}_{0.1}\text{Fe}_{2}\text{O}_{4}$ nanoparticles was 0.2347 KJ mol$^{-1}$, which was less than 8 KJ mol$^{-1}$, indicating that physical adsorption existed in the adsorption process. In conclusion, physical and chemical adsorption both existed in the adsorption process of MB onto $\text{Mg}_{0.4}\text{Co}_{0.5}\text{Zn}_{0.1}\text{Fe}_{2}\text{O}_{4}$ nanoparticles [67].

Table 3 showed the maximum adsorption capacities of magnetic $\text{Mg}_{0.4}\text{Co}_{0.5}\text{Zn}_{0.1}\text{Fe}_{2}\text{O}_{4}$ nanoparticles and other adsorbents for MB. The adsorption capacity of MB adsorbed onto magnetic $\text{Mg}_{0.4}\text{Co}_{0.5}\text{Zn}_{0.1}\text{Fe}_{2}\text{O}_{4}$ nanoparticles was more than those of other adsorbents. The reason for the better adsorption capacity of magnetic $\text{Mg}_{0.4}\text{Co}_{0.5}\text{Zn}_{0.1}\text{Fe}_{2}\text{O}_{4}$ nanoparticles might be that magnetic $\text{Mg}_{0.4}\text{Co}_{0.5}\text{Zn}_{0.1}\text{Fe}_{2}\text{O}_{4}$ nanoparticles with positive charge may have electrostatic adsorption with MB and their surface was rich in hydroxyl groups. Moreover, magnetic $\text{Mg}_{0.4}\text{Co}_{0.5}\text{Zn}_{0.1}\text{Fe}_{2}\text{O}_{4}$ nanoparticles had the advantages of facile preparation and easy separation after adsorption with an external magnetic field, indicating that magnetic $\text{Mg}_{0.4}\text{Co}_{0.5}\text{Zn}_{0.1}\text{Fe}_{2}\text{O}_{4}$ nanoparticles had a wide application prospect in wastewater treatment.

### 3.3.3. Thermodynamic Study

The effect of MB solution temperature on the adsorption capacity of magnetic $\text{Mg}_{0.4}\text{Co}_{0.5}\text{Zn}_{0.1}\text{Fe}_{2}\text{O}_{4}$ nanoparticles was studied to verify the spontaneity of the process [68]. Equations (10)–(12) were used to calculate the thermodynamic parameters ($\Delta G^0$, $\Delta H^0$, and $\Delta S^0$).

\[
\ln K_0 = \frac{q_e}{C_e}, \quad (10)
\]

\[
\Delta G^0 = -RT \ln K_0, \quad (11)
\]

\[
\ln K_0 = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}, \quad (12)
\]

where $K_0$ was the distribution coefficient, $R$ (8.314 J mol$^{-1}$) was the gas constant, and $K$ was the Kelvin temperature. The values of $\Delta H^0$ and $\Delta S^0$ were calculated using the slope and intercept of the $\ln K_0$ and $1/T$ curves. The relationship between $\ln K_0$ and $1/T$ was shown in Figure 6, and it was obvious that $\ln K_0$ had a good linear relationship with $1/T$. $\Delta G^0$, $\Delta H^0$, and $\Delta S^0$ were shown in Table 4, and $\Delta H^0$ was -10.38 KJ mol$^{-1}$; the result showed that the adsorption of MB onto magnetic $\text{Mg}_{0.4}\text{Co}_{0.5}\text{Zn}_{0.1}\text{Fe}_{2}\text{O}_{4}$ nanoparticles was an exothermic process. $\Delta G^0$ was less than 0 KJ mol$^{-1}$, indicating that the process was a spontaneous reaction process. The thermodynamic experiment proved that the adsorption process of MB adsorbed onto magnetic $\text{Mg}_{0.4}\text{Co}_{0.5}\text{Zn}_{0.1}\text{Fe}_{2}\text{O}_{4}$ nanoparticles was a spontaneous exothermic reaction.

![Figure 6: Adsorption thermodynamic of MB onto $\text{Mg}_{0.4}\text{Co}_{0.5}\text{Zn}_{0.1}\text{Fe}_{2}\text{O}_{4}$ nanoparticles at 303 K, 313 K, and 323 K.](image)

![Figure 7: FTIR spectra of $\text{Mg}_{0.4}\text{Co}_{0.5}\text{Zn}_{0.1}\text{Fe}_{2}\text{O}_{4}$ nanoparticles (a), MB (b), magnetic $\text{Mg}_{0.4}\text{Co}_{0.5}\text{Zn}_{0.1}\text{Fe}_{2}\text{O}_{4}$ nanoparticles after adsorption (c), and magnetic $\text{Mg}_{0.4}\text{Co}_{0.5}\text{Zn}_{0.1}\text{Fe}_{2}\text{O}_{4}$ nanoparticle-adsorbed recalcination (d).](image)
3.4. Adsorption Mechanism of MB onto Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ Nanoparticles

3.4.1. FTIR Analysis. The FTIR spectra of magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles, MB, magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles after adsorption, and magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticle-adsorbed recalcination were shown in Figure 7. The Fe-O bond appeared at 578 cm$^{-1}$, the O-H bond appeared at 3423 cm$^{-1}$ which belonged to H$_2$O, and the -SO$_3$Na bond appeared at 1031 cm$^{-1}$, indicating that MB was adsorbed onto magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles [1]. As shown in Figure 7 (D), after magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles were recalcined, most of the MB characteristic peaks disappeared, but the peak of 1124 cm$^{-1}$ appeared as a wide peak, indicating that MB was removed during the process of magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles recalcination and MB was adsorbed onto magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles utilizing chemical bonding. Hence, the calcined of magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles had an obvious adsorption effect and regeneration.

3.4.2. Influence of pH and Cycle Number. The pH of the MB solution had a great influence on the adsorption capacity of magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles. Figure 8(a) showed that the adsorption capacity of magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles increased rapidly with the pH of MB increasing from 2 to 4. The adsorption capacity of magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles did not change significantly when the pH of MB increased from 4 to 12, and the saturated adsorption capacity of magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles increased from 792.42 mg·g$^{-1}$ to 797.73 mg·g$^{-1}$. The reason was that the isoelectric point of MB was 4. MB and the magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles of the surface had a positive charge, and when pH was less than 4, with the pH increasing, the positive charge on the surface of MB decreased gradually, and the adsorption capacity gradually increased. The number of negative charges of MB was equal to the positive charges of magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles when the pH of MB solution was in 4-12, and the applied force between MB and magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles canceled out.

Cycle number was an important index to evaluate an adsorbent. Common regeneration methods included calcination regeneration, chemical regeneration, and biological regeneration. The retention of chemical solvents on the adsorbent and the residual of biological intermediates on the adsorbent would hinder the adsorption of pollutants on the adsorbent in subsequent cycles, and the regeneration efficiency would be significantly reduced after multiple cycles [69]. In contrast, the calcination method was the most widely used and the most mature regeneration method with simple operation and high regeneration efficiency. Therefore, the regeneration of magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles adsorbing MB was completed by calcination.

Figure 8(b) showed that the removal rate of magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles could still reach 98.75% of the first after 2 cycles. But the removal rate decreased significantly after 3 cycles, only 64.17% of the first. The reason was that with the cycle number increasing, the number of calculations increased, and the collapse of adsorption voids of magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles resulted in the decrease of specific surface area; the adsorption sites decreased, and the adsorption effect deteriorated. The result suggested that magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles had good reusability.

The characterization of the recycled Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles after calcination was shown in Figure 9. According to Figure 9(a), compared to fresh Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles, the XRD of calcined nanoparticles had lower diffraction peaks. It could be seen from Figures 9(a) and 9(c) that the morphology of
calcined Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles had not changed obviously. All these characterizations indicated that Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles had excellent cyclic properties.

3.4.3. Electrochemical of MB onto Magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ Nanoparticles. CV was used to investigate the change of electrical signals interacting with magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles. The CV curves of bare MGCE, MGCE/Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$, and MGCE/Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$/MB scanned between -0.1 V and 0.7 V were shown in Figure 10(a). The peak value of current decreased significantly when magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles were added to the electrode, and the reason was that magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles obstructed the flow of [Fe(CN)$_6$]$_{3-/4-}$ to the surface of the electrode. The peak value of current was further reduced when magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles adsorbing MB were added to the electrode, and the reason was that the interaction between MB and magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles further obstructed the flow of [Fe(CN)$_6$]$_{3-/4-}$ to the surface of the electrode.

EIS was a method to study charge transfer characteristics at the electrode interface. The Nyquist plot was a semicircular curve not centered on the real axis, and this kind of decentralization belonged to the non-Debye type relaxation process [70]. The Nyquist plot of bare MGCE (a), MGCE/Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ (b), and MGCE/Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$/MB (c) was shown in Figure 10(b). The size of the sample resistance was determined by the diameter of the semicircle. Magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticle suspension was dropped onto the bare electrode, and the radius of the curve increased after magnetic Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles were added to the electrode. Comparing Figure 10(b) C with Figure 10(b) B, the radius of the circle

\[ \text{Intensity (a.u.)} \]

\[ \theta (°) \]

\[ 20 30 40 50 60 70 80 \]

(a) Calcined Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles

(b) Fresh Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles

(c) Figure 9: XRD (a), SEM (b), and TEM (c) of calcined Mg$_{0.4}$Co$_{0.5}$Zn$_{0.1}$Fe$_2$O$_4$ nanoparticles.
increased further. The results indicated that MB adsorbed onto magnetic Mg\textsubscript{0.4}Co\textsubscript{0.5}Zn\textsubscript{0.1}Fe\textsubscript{2}O\textsubscript{4} nanoparticles further increased the resistance. The electrochemical analysis further verified that MB was adsorbed onto magnetic Mg\textsubscript{0.4}Co\textsubscript{0.5}Zn\textsubscript{0.1}Fe\textsubscript{2}O\textsubscript{4} nanoparticles.

4. Conclusion

1. Magnetic Mg\textsubscript{0.4}Co\textsubscript{0.5}Zn\textsubscript{0.1}Fe\textsubscript{2}O\textsubscript{4} nanoparticles were successfully prepared by the rapid combustion approach. The average particle size and the magnetic saturation intensity of the nanoparticles calcined at 400°C for 2 h with 25 mL anhydrous ethanol were 81.28 nm and 13.5 emu·g\textsuperscript{-1}, respectively.

2. The adsorption of MB onto Mg\textsubscript{0.4}Co\textsubscript{0.5}Zn\textsubscript{0.1}Fe\textsubscript{2}O\textsubscript{4} nanoparticles conformed to the pseudo-second-order model and Freundlich model, indicating that the adsorption process was a chemical multilayer adsorption mechanism. The D-R model indicated that the adsorption involved physical adsorption. Adsorption thermodynamics and the Temkin model demonstrated that the adsorption process was a spontaneous exothermic reaction.

3. The adsorption capacity of magnetic Mg\textsubscript{0.4}Co\textsubscript{0.5}Zn\textsubscript{0.1}Fe\textsubscript{2}O\textsubscript{4} nanoparticles reached 792.42 mg·g\textsuperscript{-1} when pH was 4, and the removal rate of magnetic Mg\textsubscript{0.4}Co\textsubscript{0.5}Zn\textsubscript{0.1}Fe\textsubscript{2}O\textsubscript{4} nanoparticles could still reach 98.75% of the first after 2 cycles, indicating that magnetic Mg\textsubscript{0.4}Co\textsubscript{0.5}Zn\textsubscript{0.1}Fe\textsubscript{2}O\textsubscript{4} nanoparticles had good application value.

Data Availability

The research data used to support the finding of this study are included within the article.

Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary Materials

Supplementary data associated with this article can be found in the online version (Supplementary Materials).

References


[35] J. H. Chen, Z. Wang, and Z. X. Lv, "Adsorption of reactive red 2BF onto Ni0.3Co0.2Zn0.5Fe2O4 nanoparticles fabricated via the ethanol solution of nitrate combustion process," Materials Research Express, vol. 8, no. 1, article 015006, 2021.


T. Dabbebi, S. Hcini, B. Alzahrani et al., "Investigations of microstructural and impedance spectroscopic properties of Mg_{0.5}Co_{0.5}Fe_{1.6}Al_{0.4}O_{4} ferrite prepared using sol-gel method," Journal of Materials Science: Materials in Electronics, vol. 32, no. 9, pp. 12521–12534, 2021.