Abstract: In the present study, a ternary magnetic nanocomposite ($\text{SiO}_2/\text{MnFe}_2\text{O}_4/\text{ZIF-8}$) was synthesized via the embedding of the $\text{SiO}_2/\text{MnFe}_2\text{O}_4$ nanocomposite within the metal–organic framework (ZIF-8). The synthesized nanocomposite was characterized using suitable techniques including FT-IR, XRD, SEM, TEM, VSM, and BET. The nanocomposite showed a high surface area ($S_{\text{BET}} = 831 \text{ m}^2\cdot\text{g}^{-1}$) and superparamagnetic behavior (23.7 emu $\cdot$ g$^{-1}$). All characterization techniques confirmed the successful combination of three nanocomposite parts ($\text{MnFe}_2\text{O}_4$, $\text{SiO}_2$, and ZIF-8). The nanocomposite was examined for the adsorption of organic dyes, malachite green (MG) and methyl red (MR), from aqueous solutions. The adsorption conditions including ionic strength, contact time, pH, and adsorbent dosage were optimized by studying their change effect. The $\text{SiO}_2/\text{MnFe}_2\text{O}_4/\text{ZIF-8}$ nanocomposite showed high adsorption capacities (1000.03 and 1111.12 mg/g) for the removal of MG and MR, respectively, from water. The isotherm and kinetics studies indicated that the adsorption of MG and MR dyes on the surface of the $\text{SiO}_2/\text{MnFe}_2\text{O}_4/\text{ZIF-8}$ nanocomposite followed the Langmuir isotherm model and pseudo-second-order kinetic model, suggesting the monolayer chemisorption mechanism. The reusability study of up to five successive cycles indicated the successful reuse of the $\text{SiO}_2/\text{MnFe}_2\text{O}_4/\text{ZIF-8}$ adsorbent for dye removal from wastewater. The comparison of the present adsorbent to the previously reported adsorbents indicated that it is a promising adsorbent for dye adsorption from wastewater and must be investigated in the future for the removal of additional pollutants.

Keywords: dye adsorption; water treatment; nanomaterials; metal-organic framework

1. Introduction

Nowadays, water pollution represents a major problem in the world [1,2]. Dyes, heavy metals, and herbicides are the most common biological, inorganic, and organic pollutants in water and soil [3]. Among all water-existing pollutants, dyes are the most harmful species to the environment [4]. For example, methyl red (MR) and malachite green (MG) are widely used in different daily activities such as cosmetics, paper industries, food industries, printing, and textiles [5,6]. The release of such dyes may lead to serious problems for human health or the environment due to their high toxicity, mutagenic effect, and carcinogenic effect [7,8]. MR dye has an accumulative tendency due to its low bio-degradability resulting from the existence of a benzene ring in addition to its mutagenic effect under aerobic environments [9]. In addition, MR can cause digestive tract damage, and skin and eye irritations [10]. MG
dye has a mutagenic effect and carcinogenic effect, and can cause damage to the human respiratory system [11]. According to reports from the World Health Organization (WHO), environmental contaminants found in the soil, air, and water cause 25% of human health diseases [12]. Subsequently, these dyes must be treated before being released into the environment. Efforts have been made to develop a rapid, suitable, and effective method for the removal of dyes from wastewater. The decolorization of dyes has been achieved via several technologies including ion-exchange [13], reverse osmosis [14], precipitation [15], degradation [16,17], coagulation [18,19], and adsorption [20–23]. Among all used technologies, adsorption is the widely used method for dye removal due to the availability of a large number of adsorbents, its effectiveness, simple operation, low cost, and versatility [24]. Additionally, the adsorption method is used to separate dyes from waste on an industrial level. However, classical adsorbents such as zeolite, silica, and carbon have several limitations including the requirement of a long contact time, low adsorption capacity, difficult regeneration process, and the resultant secondary pollution [25]. Thus, the magnetic separation methods and large surface adsorbents have attracted attention to avoid secondary pollution and enhance the adsorption capacity in addition to the fast processing and ease of reusability and regeneration [26,27]. For example, different adsorbents have been magnetized for the effective removal of water pollutants such as a magnetic carbonaceous adsorbent for the removal of methylene violet [28], a FeNi\textsubscript{3}/SiO\textsubscript{2}/CuS nanocomposite for the removal of Congo red dye [29], a magnetic-polymer-based nanocomposite for the removal of Congo red dye and hexavalent chromium Cr(VI) ions [30], and a magnetic-lignin-based adsorbent for the removal of several azo dyes [31].

Recently, the attractive properties of metal–organic frameworks (MOFs) have attracted scientists’ attention for application in different fields [32,33]. MOFs are known as porous coordination polymers with magnificent properties that have allowed their use in different fields of application including heterogeneous catalysis [34], adsorptive removal of toxic species [35], membranes [36], magnetism [37], luminescence [38], sensors [39], storage of gases [40], photocatalysis [41], ion exchange [42], and drug delivery [43].

MOFs are formed from inorganic clusters as building blocks and linkers of organic ligands to produce an organic–inorganic hybrid of porous architectures [44]. This mixing of inorganic and organic moieties resulted in the synthesis of more than 10,000 MOF constructions [45]. MOFs have a 3-D network with a high pore volume, homogenous micropores, and a large surface area. The change in inorganic clusters and organic linkers is used to turn their shape and pore size from a microporous to a mesoporous scale that gives them specific attention [46]. MOFs showed an improved adsorption capacity and selectivity toward different pollutants due to the presence of open sites in their structures. These advantages of MOFs including large surface area, tunable pore size, and composition diversity [47] allowed their use as adsorbents for the removal of different types of pollutants such as benzene [48], naphthalene [49], dyes [50], and sulfur compounds [51]. However, MOFs have the limitation of difficult separation from aqueous solutions that hinder their application as adsorbents. This limitation can be overcome through the magnetization of MOFs allowing their separation by applying an external magnetic field. The magnetization of MOFs by filling it with magnetic nanomaterials produces a composite with high adsorption capacity to remove organic dyes from an aqueous solution, and it is also simpler to separate from an adsorption environment that prevents secondary pollution. Recent works have reported the magnetization of MOFs for the efficient removal of water pollutants such as MIL-101(Fe) modified with magnetic Fe\textsubscript{3}O\textsubscript{4} for the removal of malachite green and methyl red [52], a Fe\textsubscript{2}O\textsubscript{3}@MIL-100(Fe) composite for the degradation of methylene blue [53], and magnetic amino-functionalized La-MOF (MOF/NH\textsubscript{2}/Fe\textsubscript{3}O\textsubscript{4}) for the removal of methyl orange dye [54]. These magnetic MOFs showed many advantages such as retaining excellent performance up to several consecutive cycles, exhibiting a significant adsorbent potential, and the ability to be easily removed from liquid media.

In this work, the ZIF-8 MOF as zeolitic imidazolate frameworks was synthesized and embedded with SiO\textsubscript{2}/MnFe\textsubscript{2}O\textsubscript{4} nanoparticles to produce a nanocomposite named Magnetochemistry 2022, 8, 133
SiO$_2$/MnFe$_2$O$_4$/ZIF-8. The synthesized nanocomposite was characterized using proper techniques including Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), transmission electron microscopy (TEM), a scanning electron microscope (SEM), BET, and a vibrating sample magnetometer (VSM). Then, the efficiency of the synthesized adsorbent for the adsorption of MG and MR dyes from aqueous solution was evaluated and optimized by studying the effect of contact time, adsorbent dose, pH, and ionic strength. Additionally, pseudo-first-order and second-order models were used to study the adsorption kinetics. Finally, Langmuir and Freundlich isotherm models were used to study the adsorption mechanism. The reusability of the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite for the removal of MG and MR dyes was studied by applying an external magnet. The possibility of using the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite as an adsorbent for dye removal from an aqueous solution was finally assessed.

2. Materials and Methods

2.1. Chemicals

All reagents were analytical grade and used without any purifications. Tetraethyl orthosilicate (TEOS), 2-methylimidazole, manganese nitrate, iron nitrate, methyl red (MR), malachite green (MG), and zinc nitrate were supplied from Sigma-Aldrich, Germany. Ethyl alcohol, Ethylene Diamine (EDA), aqueous ammonia, hydrochloric acid, and sodium hydroxide were supplied from Elgomhoria Chemical Co, Cairo, Egypt. All solutions were prepared using distilled water.

2.2. Synthesis of SiO$_2$/MnFe$_2$O$_4$ Nanocomposite

For the synthesis of the SiO$_2$/MnFe$_2$O$_4$ nanocomposite, MnFe$_2$O$_4$ nanoparticles were synthesized first using a co-precipitation process as reported in the literature [55]. In a typical method, a mixed solvent of 3.0 mL of EDA and 70.0 mL of distilled H$_2$O was used to dissolve 4.20 g of NaOH followed by the addition of 4.9 g of manganese nitrate and 13.4 g of iron nitrate that previously dissolved in 50.0 mL of distilled H$_2$O. To reach the complete complexation, the previous mixture was heated for 3 h at 100 $^\circ$C. After that, the synthesized magnetic MnFe$_2$O$_4$ nanoparticles were collected using an external magnet and washed many times using H$_2$O and ethyl alcohol followed by the dryness of nanoparticles at room temperature. Secondly, the modified Stöber process was used for the modification of MnFe$_2$O$_4$ nanoparticles using SiO$_2$ as reported in the literature [56]. Typically, a mixed solution of aqueous ammonia (1.2 mL, 25%), 20 mL of deionized H$_2$O, and ethyl alcohol (40 mL, 99.9%) was used to disperse MnFe$_2$O$_4$ nanoparticles (0.15 g) under ultrasonication for 60 min followed by the stepwise addition of TEOs (0.6 mL). The reaction was kept for up to 6 h at 30 $^\circ$C followed by the separation of the synthesized SiO$_2$/MnFe$_2$O$_4$ nanocomposite using an external magnet. The collected nanocomposite was washed several times using ethyl alcohol and finally dried at 60 $^\circ$C in a vacuum.

2.3. Synthesis of SiO$_2$/MnFe$_2$O$_4$/ZIF-8 Nanocomposite

The synthesis of the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite was achieved as detailed in this section. First, the methanol solvent (65 mL) was used to disperse the SiO$_2$/MnFe$_2$O$_4$ nanocomposite (0.2 g) and zinc nitrate hexahydrate (2 mmol) under ultrasonication. After that, methanol (30 mL) was used to dissolve 2-methylimidazole (10 mmol) that was stepwise-added to the previous suspension at ambient temperature in a rotary evaporator under strong stirring. Then, this produced mixture was kept for 1 day at room temperature to give grey powder of SiO$_2$/MnFe$_2$O$_4$/ZIF-8 that was collected using an external magnet. Finally, the synthesized nanocomposite was washed several times with ethyl alcohol and deionized H$_2$O and dried at 60 $^\circ$C in a vacuum. Figure 1 illustrates the synthesis procedures of the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite.
Figure 1. The synthesis scheme of SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite. (TEOS: Tetraethyl orthosilicate).

2.4. Adsorption Experiments

The synthesized SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite was evaluated for the adsorption of MG and MR dyes from an aqueous solution. First, deionized H$_2$O was used for the preparation of the required concentrations of the dyes. The batch adsorption experiments were performed by shaking 50.0 mL of dye solution (50.0 to 500.0 mg/L) with 0.01 g of the adsorbent using a water bath shaker at 250 rpm at 25 °C and the required pH value. The shaking process was continued until reaching equilibrium, which was 60 min for MG and 30 min for MR. The best conditions of the adsorption process were performed by studying the effect of pH, contact time, adsorbent dose, and ionic strength. The effect of pH was investigated in the range of 3–12. The pH values were adjusted using the buffer solution and the measurements were carried out using a digital pH meter. To study the effect of contact time, the adsorption experiments were performed at different time intervals ranging from 0 to 240 min. To study the ionic strength effect, different concentrations of NaCl salt were added to the water samples in the range of 0–0.5 M. To study the effect of adsorbent dose, the adsorption experiments were performed using different masses of adsorbent in the range of 0.15–1 g/L. After each adsorption experiment, the adsorbent was collected using an external magnet and the supernatant was examined for the existence of the MG and MR dyes using a UV-Vis spectrophotometer at $\lambda = 620$ nm and 526 nm, respectively. The adsorption capacity at equilibrium ($q_e$, mg/g) of the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite was calculated according to Equation (1).

$$q_e = \frac{(C_o - C_f)V}{m}$$  

where $m$, $V$, $C_o$, and $C_f$ are the mass of the adsorbent in g, the volume of the solution in L, the equilibrium concentration of the dye (mg/L), and the initial concentration of the dye (mg/L), respectively.

Moreover, the reusability of the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite as an adsorbent for the removal of MG and MR dyes was investigated for up to five cycles. Each cycle consists of an adsorption process followed by the collection of adsorbent using a magnet for the desorption process to be used in the next cycle. The desorption process examined a mixed solvent of ethyl alcohol and H$_2$O with a ratio of 8:2, respectively. During each desorption process, the eluent was mixed with the eluent for half an hour with sonication followed by magnetic separation and dryness at 70 °C. After each cycle, the adsorbent was collected and the solution was examined for the presence of dyes. Finally, the regeneration and reusability of the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite for dye removal were evaluated.
3. Results and Discussion

3.1. Characterization of Synthesized Nanomaterials

For the characterization of the synthesized nanomaterials, MnFe₂O₄ nanoparticles, the SiO₂/MnFe₂O₄ nanocomposite, and the SiO₂/MnFe₂O₄/ZIF-8 nanocomposite, the proper techniques were used, as discussed in this section. TEM and SEM images were used for the identification of particle size and surface morphology, as shown in Figure 2. Figure 2a shows the TEM image of MnFe₂O₄ nanoparticles indicating the nanosize of the synthesized magnetic particles. Figure 2b shows the TEM image of the SiO₂/MnFe₂O₄ nanocomposite that clearly showed the good addition of SiO₂ to the magnetic MnFe₂O₄ nanoparticles. Figure 2c shows the TEM image of the SiO₂/MnFe₂O₄/ZIF-8 nanocomposite that showed the good dispersion of the SiO₂/MnFe₂O₄ nanocomposite inside the structure of ZIF-8 nanostructures. Moreover, the size and morphology of synthesized nanomaterials were confirmed using SEM images. Figure 2d shows the SEM image of the synthesized magnetic MnFe₂O₄ nanoparticles, confirming the nanoscale size of the particles with agglomeration tendency due to the magnetic behavior. Figure 2e shows the SEM image of the SiO₂/MnFe₂O₄ nanocomposite with a larger size than MnFe₂O₄ nanoparticles due to the addition of the SiO₂ layer that confirms the TEM results. Additionally, Figure 2e indicates that the SiO₂/MnFe₂O₄ nanocomposite was uniform. Figure 2f shows the SEM image of the SiO₂/MnFe₂O₄/ZIF-8 nanocomposite, indicating the nanosize scale of the synthesized nanocomposite after the embedding of the SiO₂/MnFe₂O₄ nanocomposite inside the structure of ZIF-8. The SiO₂/MnFe₂O₄/ZIF-8 nanocomposite showed a wide size range distribution from 30.0 nm to 200.0 nm with a rhombic dodecahedral structure. The SEM and TEM images show that the SiO₂/MnFe₂O₄ nanocomposite was well encapsulated by a shell of ZIF-8.

XRD of the synthesized nanomaterials was performed to characterize the composition and crystallinity, and the results are shown in Figure 3a. The XRD of magnetic MnFe₂O₄ nanoparticles indicated the spinel structure of magnetic nanoparticles, as confirmed from the appearance of characteristic peaks at 2θ = 62.30, 56.80, 53.33, 43.06, 35.37, and 30.02, which correspond to the planes (440), (511), (422), (400), (311), and (220) [57]. From the XRD of the SiO₂/MnFe₂O₄ nanocomposite, the amorphous properties of SiO₂ did not change the phase of MnFe₂O₄ magnetic nanoparticles when added, as inferred from the identical XRD patterns. From the XRD of the SiO₂/MnFe₂O₄/ZIF-8 nanocomposite, new characteristic peaks of ZIF-8 appeared at 2θ = 18.20, 16.54, 14.85, 13.00, 10.54, and 7.44, which correspond to the planes (222), (013), (022), (112), (002), and (011) [58]. In addition, characteristic peaks of MnFe₂O₄ appeared in the XRD of the SiO₂/MnFe₂O₄/ZIF-8 nanocomposite. Thus, the XRD results indicated a good combination between the three parts of the nanocomposite MnFe₂O₄, SiO₂, and ZIF-8.

Figure 2. Cont.
bent eases their reuse for water treatment, which reduces the overall cost of the treatment.

Figure 2. The TEM image of (a) MnFe₂O₄ nanoparticles, (b) SiO₂/MnFe₂O₄ nanocomposite, and (c) SiO₂/MnFe₂O₄/ZIF-8 nanocomposite, and SEM images of (d) MnFe₂O₄ nanoparticles, (e) SiO₂/MnFe₂O₄ nanocomposite, and (f) SiO₂/MnFe₂O₄/ZIF-8 nanocomposite.

Figure 3. The XRD patterns (a) and FT-IR spectra (b) of the synthesized MnFe₂O₄ nanoparticles, SiO₂/MnFe₂O₄, and SiO₂/MnFe₂O₄/ZIF-8.

For the identification of functional groups, FT-IR spectra of the synthesized nanomaterials were generated in the range of 450–4000 cm⁻¹, as shown in Figure 3b. According to Figure 3b, the MnFe₂O₄ nanoparticles showed an absorption band corresponding to the oxygen-metal bond at 500–600 cm⁻¹ [59]. In addition, stretching vibrations of hydrogen-
bonded H–O groups showed an appearance of the minor band at 1620 cm\(^{-1}\) and the broad band at 3400 cm\(^{-1}\) [60]. The SiO\(_2\)/MnFe\(_2\)O\(_4\) nanocomposite showed an absorption band corresponding to the OH–Si bond’s bending vibration at 962 cm\(^{-1}\), while the band corresponding to the Si–O–Si bond’s asymmetric stretching vibration appeared at 1100 cm\(^{-1}\)–1080 cm\(^{-1}\) [57]. The spectrum of the SiO\(_2\)/MnFe\(_2\)O\(_4\)/ZIF-8 nanocomposite showed the appearance of characteristic bands of ZIF-8. The hydroxyl groups of ZIF-8 and H\(_2\)O molecules showed the appearance of the band at 3430 cm\(^{-1}\). The bands below 800 cm\(^{-1}\) were attributed to the out-of-plane bending of the ZIF-8 aromatic ring, while the in-plane bending bands were observed at the range of 950–1350 cm\(^{-1}\). The vibration of the entire ring showed the appearance of bands in the range of 1550–1350 cm\(^{-1}\). In addition, the stretching vibrations of the aliphatic chain of H-methylimidazole and aromatic ring C–H bonds showed the appearance of bands in the range of 2930–3135 cm\(^{-1}\) [61–63].

For the determination of magnetic properties, magnetization curves of the synthesized MnFe\(_2\)O\(_4\) nanoparticles, SiO\(_2\)/MnFe\(_2\)O\(_4\), and SiO\(_2\)/MnFe\(_2\)O\(_4\)/ZIF-8 were generated, as shown in Figure 4a. According to Figure 4a, all synthesized nanomaterials showed paramagnetic behavior with saturation values of 40.0, 33.8, and 23.7 emu/g for MnFe\(_2\)O\(_4\) nanoparticles, SiO\(_2\)/MnFe\(_2\)O\(_4\), and SiO\(_2\)/MnFe\(_2\)O\(_4\)/ZIF-8, respectively. The modification of magnetic MnFe\(_2\)O\(_4\) nanoparticles with nonmagnetic SiO\(_2\) caused a drop in saturation magnetization. In addition, the embedding of SiO\(_2\)/MnFe\(_2\)O\(_4\) inside the ZIF-8 caused a drop in the saturation magnetization. However, the SiO\(_2\)/MnFe\(_2\)O\(_4\)/ZIF-8 nanocomposite still had good magnetic properties, allowing its magnetic separation by applying an external magnetic field. After the adsorption of dyes, the magnetic adsorbent could be collected using a magnet from the entire solution (Figure 4a, inset). This magnetic behavior of the adsorbent eases their reuse for water treatment, which reduces the overall cost of the treatment.

![Figure 4. The magnetic curves (a) and N\(_2\) adsorption–desorption isotherm (b) of the synthesized MnFe\(_2\)O\(_4\) nanoparticles, SiO\(_2\)/MnFe\(_2\)O\(_4\), and SiO\(_2\)/MnFe\(_2\)O\(_4\)/ZIF-8 (inset: a photograph for the magnetic separation of synthesized nanocomposite).](image-url)
and 831 m$^2$/g for MnFe$_2$O$_4$ nanoparticles, the SiO$_2$/MnFe$_2$O$_4$ nanocomposite, and the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite, respectively, indicating the enhanced surface area of the nanocomposite after embedding the SiO$_2$/MnFe$_2$O$_4$ nanocomposite inside the framework ZIF-8. This sharp increase in the surface area was attributed to the ideal structure of ZIF-8, which has a very high $S_{BET}$ that is equal to 1485.5 m$^2$/g$^{-1}$. The characterization techniques indicated the successful combination between the three components SiO$_2$, MnFe$_2$O$_4$, and ZIF-8 to produce the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite.

3.2. Optimization of the Adsorption Parameters

To determine the optimum conditions for the removal of MR and MG dyes on the surface of the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite, the effects of different parameters including ionic strength, contact time, adsorbent dose, and pH were studied as shown in Figure 5. The effect of ionic strength on the removal of MR and MG dyes was studied using different NaCl concentrations ranging from $1 \times 10^{-3}$ to 0.5 mol/L, as shown in Figure 5a. With a contact time of 60.0 min for the MG dye and 30.0 min for the MR dye, a stirring speed of 240 rpm at 25.0 °C, an initial dye concentration of 100 ppm, and an adsorbent dose of 0.2 g/L, the influence of ionic strength on adsorption was investigated. According to Figure 5a, the adsorption capacity of MR and MG dyes was decreased by increasing the concentration of sodium chloride. This decrease in adsorption capacity associated with the increase in ionic strength is attributed to the decrease in electrostatic attraction between adsorbent and adsorbate. Additionally, the adsorbent molecules were agglomerated by increasing the ionic strength, causing a decrease in the number of adsorption sites [65]. In addition to this electrostatic influence, the salt ions could compete with the adsorbate ions for the adsorption sites, leading to the weakening of dye adsorption. The second studied parameter that affected the adsorption was the contact time. The adsorption of MR and MG dyes on the surface of the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite was determined at a time ranging from 0 to 250 min, as shown in Figure 5b. According to Figure 5b, the adsorption capacity was increased up to 60 min for MR dye and 30 min for MR dye, and over this time, the adsorption capacity did not change. This increase in the adsorption capacity in the first stage was attributed to the availability of adsorption sites, until equilibrium was reached [66]. After that, there were unavailable adsorption sites to adsorb more ions of the dye due to the occupation of all adsorption sites causing no increase in the adsorption [67]. Subsequently, the optimum contact time was 60 min for MG dye and 30 min for MR dye, after which the adsorption became constant, revealing the saturation of active sites on the adsorbent surface.

Another significant parameter in the adsorption of dyes is the adsorbent dose. Figure 5c illustrates the effect of SiO$_2$/MnFe$_2$O$_4$/ZIF-8 dose on the removal of MG and MR dyes using 240 rpm as a stirring rate and 100 ppm as the initial dye concentration. According to Figure 5c, the adsorption capacity was sharply increased by increasing the adsorbent dose from 0.5 g/L to 2.0 g/L, after which the adsorption capacity declined. Subsequently, the optimum dose of SiO$_2$/MnFe$_2$O$_4$/ZIF-8 as the adsorbent was chosen as 0.2 g/L. This behavior could be attributed to the aggregation of adsorbent particles and overlapping of adsorption sites at a high dosage of the adsorbent, causing a decrease in the surface area and, correspondingly, a decrease in the adsorption capacity [68]. In addition, pH is a vital parameter affecting the adsorption of organic dyes. This importance arises from its effect on the ionization of both adsorbent surface and adsorbate molecules [69]. To study the effect of pH on the adsorption of MG and MR dyes on the surface of SiO$_2$/MnFe$_2$O$_4$/ZIF-8, experiments were examined in the pH range of 3 to 12, as shown in Figure 5d. The pH effect was determined at a stirring speed of 240 rpm and initial dye concentration of 100 ppm. According to Figure 5d, the increasing pH value caused a decrease in the adsorption capacity of SiO$_2$/MnFe$_2$O$_4$/ZIF-8 toward MG dye. At a high pH value, the MG dye was deprotonated, while, at a low pH value, the MG dye was protonated. Thus, at a low pH value (2–5.5), the positively charged MG dye was electrically attracted to the negatively charged SiO$_2$/MnFe$_2$O$_4$/ZIF-8 (more –ve zeta potential, Figure 5e), while at
a higher pH value (8–12), the electrostatic repulsion between the negatively charged MG dye and negatively charged SiO$_2$/MnFe$_2$O$_4$/ZIF-8 surface caused a notable decrease in the adsorption capacity. For the adsorption of MR dye on the surface of SiO$_2$/MnFe$_2$O$_4$/ZIF-8 at different pH values, the adsorption capacity was constant until the pH of 5 and then decreased with the pH increase. This low adsorption capacity of MR anionic dye at pH > 5 was attributed to the repulsive forces between the negatively charged surface of SiO$_2$/MnFe$_2$O$_4$/ZIF-8 and the anionic dye.

Figure 5. The effect of ionic strength (a), contact time (b), adsorbent dose (c), pH (d), and zeta potential measurements (e) on the removal of MR and MG dyes on the surface of SiO$_2$/MnFe$_2$O$_4$/ZIF-8.

3.3. Adsorption Isotherm

The mechanism of the adsorption process can be analyzed using isotherm studies [70,71]. In the current study, the adsorption of MG and MR dyes on the surface of the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite was evaluated using the two familiar adsorption
models, Langmuir and Freundlich. The linear equations of Langmuir and Freundlich models are presented as shown in Equations (2) and (3), respectively.

\[
\frac{C_e}{q_e} = \frac{1}{K_Lq_m} + \frac{C_e}{q_m}
\]

(2)

\[
\log q_e = \frac{1}{n} \log C_e + \log K_F
\]

(3)

where \( q_m, C_e, q_e, \) and \( K_L \) are the maximum adsorption capacity (mg/g), the concentration of dye at equilibrium (mg/L), the amount of the dye adsorbed at the equilibrium (mg/g), and the Langmuir adsorption constant (L/mg), respectively. \( K_F \) and \( n \) are constants of the Freundlich model that are related to the adsorption intensity and adsorption capacity, respectively. The linear plot of \( C_e \) and \( C_e/q_e \) according to the Langmuir model can be used for the determination of \( K_L \) and \( q_m \) from the slope and intercept, respectively. The linear plot of \( \log C_e \) and \( \log q_e \) according to the Freundlich model can be used for the determination of \( K_F \) and \( n \) from the intercept and slope, respectively. The fitting of experimental data for the adsorption of MG and MR dyes on the surface of the SiO\(_2\)/MnFe\(_2\)O\(_4\)/ZIF-8 nanocomposite using Langmuir and Freundlich models is shown in Figure 6. The calculated parameters of Langmuir and Freundlich isotherms are listed in Table 1.

![Figure 6](image)

Figure 6. The fitting of experimental data to Langmuir isotherm (a) and Freundlich isotherm (b) for the adsorption of MG and MR dyes on the surface of SiO\(_2\)/MnFe\(_2\)O\(_4\)/ZIF-8 nanocomposite.

Table 1. The adsorption isotherm and kinetic parameters for the adsorption of MG and MR dyes on the surface of SiO\(_2\)/MnFe\(_2\)O\(_4\)/ZIF-8 nanocomposite.

| Dye   | Langmuir | Freundlich |
|-------|----------|------------|
|       | \( q_m \) (mg/g) | \( K_L \) (L/mg) | \( R^2 \) | \( 1/n \) | \( K_F \) (mg/g)(L/mg)^{1/n} | \( R^2 \) | \( k_1 \) (min^{-1}) | \( q_e \) | \( R^2 \) | \( k_2 \) (g/mg.h) | \( q_e \) | \( R^2 \) |
| MG    | 1000.03  | 0.077      | 0.900 | 0.396 | 8.715 | 0.963 | 0.062 | 445.248 | 0.991 | 0.001 | 555.55 | 0.999 |
| MR    | 1111.12  | 0.040      | 0.979 | 0.501 | 7.338 | 0.965 | 0.160 | 141.70  | 0.941 | 0.001 | 476.20 | 0.999 |

The Langmuir isotherm model states that the adsorbent surface is homogenous and all adsorption sites are energetically equivalent that can adsorb the adsorbate ions as a monolayer, while the Freundlich isotherm model states that the surface of the adsorbent is heterogeneous and the adsorption sites can adsorb the adsorbate ions as multilayers. The correlation coefficient \( R^2 \) of the linear fit was used to evaluate the applicability of the model to describe the adsorption process. From the values of \( R^2 \) of the linear fit, the Langmuir isotherm was better at explaining the adsorption of both dyes MG and MR on the surface of the SiO\(_2\)/MnFe\(_2\)O\(_4\)/ZIF-8 nanocomposite. Moreover, the calculated \( q_m \) values were close to the experimental values. This means that the adsorption of MG and MR dyes...
on the surface of the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite was achieved via homogenous adsorption as a monolayer and confirmed the chemisorption mechanism.

The maximum adsorption capacities ($q_m$) for MR dye and MG dye are 1111.12 mg/g and 1000.03 mg/g, respectively. The Langmuir constant ($K_L$) indicates the degree of interactions between adsorbate ions and the adsorbent surface. In addition, the values of the Freundlich constant ($1/n$) indicate if the adsorption process is favored or not favored. For both dyes, $1/n$ values are less than 1, indicating the favorable adsorption of MG and MR dyes on the surface of the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite. The results indicate the efficiency of the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite as an adsorbent for wastewater treatment, especially after providing excellent results with two structurally different dyes with different electronic characteristics.

3.4. Adsorption Kinetics

For understanding the rate of dye removal from aqueous solution on the surface of the synthesized SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite, kinetic models were used to fit the experimental data of adsorption. In the present study, two kinetic models, pseudo-first-order and pseudo-second-order, were used to fit the experimental data of the MG and MR dyes adsorption on the surface of the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite, as shown in Figure 7. The pseudo-first-order and pseudo-second-order kinetic models can be represented according to Equations (4) and (5), respectively.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where $q_t$, $q_e$, $k_1$, and $k_2$ denote the adsorption amount at time $t$, the adsorption amount at equilibrium, the pseudo-first-order rate constant, and the pseudo-second-order rate constant, respectively.

![Figure 7](image_url)

**Figure 7.** The fitting of experimental data to pseudo-first-order model (a) and pseudo-second-order (b) for the adsorption of MG and MR dyes on the surface of SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite.

The rate constants and coefficients of the pseudo-first-order model and pseudo-second-order model can be calculated from the plot of $\log (q_e - q_t)$ against $t$ and $t/q_t$ against $t$, respectively, as introduced in Figure 7a,b. The rate constants and coefficients of the pseudo-first-order model and pseudo-second-order model are listed in Table 1.

By comparing the correlation coefficient ($R^2$) values of the two kinetic models, the pseudo-second-order model had a higher $R^2$ value than the pseudo-first-order, indicating the greater suitability of the pseudo-second-order kinetic model to describe the adsorption of MG and MR dyes on the surface of the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite.
best fitting of experimental data to the pseudo-second-order kinetic models indicates the chemical interactions between dyes and the adsorbent surface during the adsorption process. Additionally, the calculated value of $q_e$ from the pseudo-second-order model was found to be very close to the experimental value, confirming the greater suitability of the pseudo-second-order model for describing the adsorption of MG and MR dyes than the pseudo-first-order model. This means that the adsorption of MG and MR dyes on the surface of the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite occurred via complicated chemical adsorption that may include many different interactions between the MG and MR dye molecules and the functional groups on the surface of SiO$_2$/MnFe$_2$O$_4$/ZIF-8.

3.5. Regeneration and Reusability Study

For the application of any adsorbent at an industrial scale, it is important to show good reusability results as the reusability of the adsorbent decreases the overall cost of the treatment. After the dye adsorption, the dye is required to be desorbed from the surface for the reactivation of adsorption sites for the next adsorption cycle. After each adsorption process, the adsorbent was collected using a magnet and the solution was examined for the presence of dyes. Then, the adsorbent was washed by the eluent to desorb the dyes for use in the next cycle. In the current study, the used eluent was a mixed solvent of ethyl alcohol and H$_2$O with a ratio of 8:2, respectively. This mixed solvent helps the desorption of MG and MR dyes from the surface of the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite. Ethyl alcohol has a carbon chain that competes with the MG and MR dyes for the surface of the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite and eases the desorption of dyes from the surface of the adsorbent. Ethyl alcohol also reduces the interaction between the dyes and the surface of the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite. Additionally, H$_2$O helps the solubility of dyes and eases their desorption from the surface of the adsorbent. In the present study, the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite was reused for the adsorption of MG and MR dyes for five successive cycles, as shown in Figure 8.

![Figure 8](image_url)

**Figure 8.** The reusability study of SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite for the removal of MG and MR dyes up to five cycles.

According to Figure 8, the highest removal efficiency (%) for both dyes on the surface of the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite was achieved in the 1st cycle. This may be attributed to the availability of a large number of fresh active sites on the surface of the adsorbent to uptake large amounts of MG and MR dyes. The results showed the reduction in removal efficiencies to 93.5% and 865% for the removal of MG and MR dyes, respectively, after the 5th cycle. This decrease in the removal efficiency may be attributed to the damage of some adsorption sites and the blockage of the others due to the failure to desorb the dyes as a result of the strong interaction between MR and MG dyes and the surface of the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite. The reusability results show that the prepared
SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite can be used many successive times for the removal of organic dyes from wastewater.

3.6. Comparative Study

To evaluate the efficiency of the synthesized SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite in the adsorption of MG and MR dyes, a comparative study of $q_{\text{max}}$ of previously synthesized adsorbents used to remove MG and MR dyes is shown in Table 2.

| Adsorbent                  | Pollutant | Removal Capacity (mg/g) | Ref.  |
|----------------------------|-----------|-------------------------|-------|
| SiO$_2$/MnFe$_2$O$_4$/ZIF-8 | MR        | 1111.12                 | This study |
| MIL-53 (Fe) DSAC           | MR        | 384.62                  | [9]   |
| K$_2$CO$_3$@activated carbon | MR     | 226.90                  | [72]  |
| H$_3$PO$_4$@activated carbon | MR     | 435.25                  | [72]  |
| 101(Fe)@PDopa@Fe$_3$O$_4$  | MR        | 625.0                   | [73]  |
| Woody biochar              | MR        | 156.25                  | [74]  |
| SiO$_2$/MnFe$_2$O$_4$/ZIF-8 | MG        | 1000.03                 | This study |
| Cu-MOFs/Fe$_3$O$_4$         | MG        | 125.15                  | [75]  |
| MIL-101-SO$_3$H            | MG        | 113.67                  | [76]  |
| 101(Fe)@PDop@Fe$_3$O$_4$   | MG        | 676                     | [77]  |
| TU-poly(AN-co-AA)          | MG        | 269.54                  | [78]  |
| AC@Fe$_3$O$_3$             | MG        | 311.40                  | [79]  |

According to Table 2, the classical adsorbents showed relatively low adsorption capacities toward MR and MG dyes, for example, carbon-based adsorbents such as K$_2$CO$_3$@activated carbon and woody biochar. However, carbon-based adsorbents were superior to other techniques for the removal of dyes from aqueous solution; the adsorption capacities ranged from 100 mg/g to 500 mg/g. Even after the magnetization of these carbon-based adsorbents, the adsorption capacity was improved but still low. For example, the magnetized activation carbon (AC@Fe$_3$O$_3$) gave an adsorption capacity of 311.40 mg/g. Previously, these adsorption capacities were considered to be high. The advancement of adsorbent synthesis using nanotechnology made these values low. Thus, the fabrication of advanced adsorbents such as magnetic MOFs (101(Fe)@PDopa@Fe$_3$O$_4$) provided an improved adsorption capacity exceeding 500 mg/g. These improved capacities were attributed to the large surface area, tunable pore size, composition diversity, and high selectivity. Compared to previously reported adsorbents, even the adsorbents of similar composition, the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite showed good adsorption capacities toward the removal of MG and MR dyes, making it an effective promising adsorbent to remove organic dyes from wastewater.

4. Conclusions

In the present study, a good ternary adsorbent based on MOFs named SiO$_2$/MnFe$_2$O$_4$/ZIF-8 was synthesized with a very large surface area (831 m$^2$ g$^{-1}$) and paramagnetic properties (23.7 emu g$^{-1}$). The synthesized SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite was investigated for the adsorption of MG and MR dyes from an aqueous solution. The adsorption effective conditions were determined, including the effect of ionic strength, contact time, adsorbent dose, and pH. The fitting of adsorption data to isotherm models showed an agreement with the Langmuir model for the removal of both dyes, indicating that the dyes were adsorbed on the homogeneous surface of SiO$_2$/MnFe$_2$O$_4$/ZIF-8 as a monolayer. According to the Langmuir model, the adsorption capacities were 1111.12 mg/g and 1000.03 mg/g, for MR and MG, respectively. Additionally, the adsorption rate was investigated using the pseudo-first-order and pseudo-second-order models with an agreement to pseudo-first-order model indicating that the adsorption of both dyes
on the surface of the synthesized adsorbent was reached via chemisorption. In addition, the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite can be used many successive times to remove organic dyes with high efficiency, helping decrease the treatment cost. The adsorption capacities of the SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite toward the removal of MG and MR dyes were compared to the other reported adsorbents showing higher values. Subsequently, the synthesized SiO$_2$/MnFe$_2$O$_4$/ZIF-8 nanocomposite is a promising material for the removal of coloring dyes from aqueous solutions and must be investigated for the removal of additional pollutants in the future.

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