

Research Article

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Synthesis, characterization, and application of the novel nanomagnet adsorbent for the removal of Cr(VI) ions

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Abstract: The synthesis of an efficient adsorbent to remove chromium ions from water is challenging. Therefore, in this study, a new nanomagnet composite (Fe_3O_4 /biochar/ZIF-8) was synthesized by a one-pot hydrothermal method using a metal–organic framework (MOF, ZIF-8) as a sacrificial template, citrus peels as a source of biochar, and iron oxide nanoparticles for magnetization. The synthesized nanocomposite showed a high efficiency toward the adsorption of Cr(VI) ions. The adsorption study showed that the experimental data were well-described using the Langmuir isotherm model and pseudo-second-order model. According to the Langmuir model, the adsorption capacities toward Cr(VI) adsorption were 77 and $125 \text{ mg} \cdot \text{g}^{-1}$ for Fe_3O_4 /biochar and Fe_3O_4 /biochar/ZIF-8, respectively, indicating the role of MOF in improving the adsorption performance. The Fe_3O_4 /biochar/ZIF-8 showed an excellent adsorption performance in the presence of coexisting ions at a wide pH range using different eluents to study reusability up to five successive cycles. We can conclude from this study that this nano-adsorbent is a promising material for removing pollutants from environmental water samples.

Keywords: ZIF-8, nanocomposite, metal–organic framework

1 Introduction

The heavy metals, dyes, and pharmaceuticals pollution released from industrial effluents easily penetrate the water environment and cause a long-term threat to human and aquatic life. Particularly, dangerous heavy metals such as hexavalent chromium ions Cr(VI) cause severe problems [1]. Chromium (Cr) is a crucial element that is extensively used in a variety of sectors, including alloy production, leather tanning, and electroplating [2]. Naturally, chromium has two oxidation states, hexavalent and trivalent, of which the hexavalent state shows a higher toxicity due to its mutagenicity, carcinogenicity, and greater mobility [3]. On the other hand, the trivalent state can be utilized by the cell for many biological processes [4]. Therefore, the World Health Organization and environmental protection organizations in various nations have imposed tight restrictions on the amount of Cr ions in surface or drinking water [5,6]. As a result, it is now of utmost importance to effectively remove Cr(VI) ions from aqueous solutions. Several techniques have been applied for the removal of Cr(VI) ions from aqueous solutions such as ion exchange [7,8], membrane separation [9], phytoremediation [10], microbial remediation [11], and electrochemical reduction [12]. Adsorption technology is crucial in the removal of Cr(VI) ions owing to its exceptional advantages such as simplicity, high efficiency, cost-effectiveness, and flexibility [13] and uses a range of adsorbents, including carbon nanotubes [14,15], activated carbon [16], metal oxides [17], graphene oxide [18], and clay minerals [19]. However, the majority of adsorbents are not suitable for practical applications due to their poor selective characteristics and limited adsorption capabilities in hostile environments [20]. Therefore, the need for novel nanomaterials that can sustain strong adsorption performance in challenging practical environments is critical.

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Metal–organic frameworks (MOFs) have attracted attention over the last few years due to their intriguing structural properties, such as variable pore size, programmable functionalities, abundant functional groups, and high specific surface areas [21]. These properties allowed their wide applications in different fields including environmental remediation [22], catalysis [23], supercapacitors [24], sensors [25], energy storage [26], and adsorption [27–30]. The zeolitic imidazolate framework-8 (ZIF-8) is a member of the MOF family of materials and has comparatively high thermal stability than other MOFs [31]. Through chelation interactions, the metal coordination site (Zn^{2+}) in ZIF-8 may create metal complexes with the adsorbate, and the N heteroatom might enhance adsorption chelation sites [32]. However, the application of MOFs in water treatment is still restricted due to many factors such as the difficult and complicated recyclability of most MOFs, poor stability, and weak selectivity [33]. By encapsulating functional nanoparticles into MOFs, researchers can create MOF-containing nanocomposites that combine the benefits of two different components and improve synergistic effects in the resulting hybrid products. Subsequently, MOFs must be modified to be widely used. Having the potential for regeneration and reuse, biochar is a novel type of environmentally friendly material that is rich in carbon [34]. It can be made from a variety of substances, including industrial biowastes, marine and aquatic species, and agricultural and forestry leftovers (such as wood chips, rice straw/husk, fruit peels, leafy litter, *etc.*) [35–38]. In recent years, biochar has attracted considerable interest as an adsorbent from environmental media because of its inexpensive cost, relatively high porosity, porous qualities, possibility of regeneration, and reuse. For instance, biochar from crab shells could efficiently remove dye from water [39], human hair-derived biochar is utilized to adsorb tetracycline antibiotics [40], and biochar from coconut shells acts as an efficient adsorbent for the removal of methylene blue [41]. However, using traditional separation techniques like centrifugation, filtering, and gravity sedimentation to separate biochar is laborious, time-consuming, and expensive [42]. Subsequently, there is an urgent need for the magnetization of biochar to produce magnetic biochar adsorbent that exhibits a predominant future due to the easy separation using an external magnet instead of traditional methods [43]. For eliminating inorganic and organic contaminants from aquatic environments, magnetic biochar has been widely used. In general, ferric and ferrous compounds are used as precursors to precipitate and link magnetic media, such as zero-valent iron, magnetite (Fe_3O_4), and maghemite ($\gamma\text{-Fe}_2\text{O}_3$), onto biochar matrix [44,45]. With the addition of the biochar matrix and magnetic iron, the magnetic biochar typically displays a relatively high

adsorption capability and stability [46]. Since iron oxide is more oxidatively stable than zero-valent iron, iron oxide-doped magnetic biochar has many advantages for real-world use. Due to their strong magnetic and adsorptive properties, Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ are excellent candidates for the synthesis of iron oxide-doped magnetic biochar. Therefore, the preparation of MOF-magnetic biochar-based composites is a promising approach due to the ability to attain complementary effects between the 3-D MOFs and carbon-based materials. Due to the abundance of active sites, hierarchical porosity, and increased specific surface area, MOFs conjugated with biochar formed from naturally renewable biomass might significantly improve the physical and chemical performances of the biochar. The addition of biochar to the MOF can significantly enhance MOF agglomeration and increase the number of exposed active sites, which ultimately results in MOFs with a relatively high adsorption capacity and stability. Additionally, the recycling of adsorbents was aided by magnetic modification, and the ability of carbon-based materials to successfully prevent secondary contamination brought on by the dissolution of metal ions made them suitable for use in genuine large-scale applications.

The novelty of this study is the synthesis of a new magnetically modified MOF-based nanocomposite from three different components having a porous architecture that was characterized and investigated for efficient water treatment. Herein, a novel magnetic ZIF-8/biochar nanocomposite was prepared and investigated for the removal of Cr(VI) ions from an aqueous solution. To assess the removal efficiencies under various conditions, batch adsorption tests were carried out, and the mechanisms were also investigated. The particular points were to synthesize and characterize magnetic ZIF-8/biochar nanocomposite, assess and compare the adsorption capacities toward Cr(VI) ions using different adsorbents by studying the effect of key factors (pH and ionic strength) on adsorption capacity, explore the adsorption mechanisms through a series of experiments, such as kinetics, isotherms, and physicochemical characterization analysis, and investigate the regeneration and reusability of the adsorbent. The findings of this work would serve as a guide for the synthesis of functionalized biochar and the removal of Cr(VI) ions from contaminated water. It will also provide an effective approach for constructing new MOF-based adsorbents with excellent adsorption capacity, and attract MOF's attention for the water treatment. Furthermore, it will help researchers to overcome the limitations of using MOF-based materials as adsorbents such as poor mechanical stability, difficulty of connecting MOFs with matrix, poor reusability, and high water solubility.

2 Materials and methods

2.1 Chemicals

The citrus fruits as carbon precursors were bought from local supermarkets (Mansoura, Egypt). Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 2-methylimidazole, and potassium hydroxide (KOH) were purchased from Sigma-Aldrich. Ammonium iron(III) sulfate dodecahydrate ($\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) was supplied by Shanghai Chemical Reagent Co., Ltd. (Shanghai, China). Ammonium ferrous sulfate ($(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$) was obtained from Chongqing Beibei Chemical Reagent (Chongqing, China). Sodium hydroxide (NaOH), hydrochloric acid (HCl), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), etc. were obtained from Sinopharm Chemical Reagent Co., Ltd. China. All chemicals used were of analytical grade and used without any additional purifications. A stock solution of $\text{K}_2\text{Cr}_2\text{O}_7$ was prepared using distilled water and diluted for further experimental purposes.

2.2 Synthesis of ZIF-8

To synthesize MOFs (ZIF-8), the steps in Liu *et al.* [47] were followed with some modifications. Briefly, two separate volumes (40 mL) of methanol were used to dissolve Zn ($\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.587 g) and 2-methylimidazole (1.298 g). Then, the metal solution was stirred for 1 h under sonication. Finally, the ligand solution was added to the metal solution at room temperature with sonication.

2.3 KOH-activated-citrus peel powder

The carbon precursor was extracted from citrus peels. First, citrus peels that had been cleaned were chopped into pieces and dried at 80°C before being processed into powder. Then, KOH (30%) was used to activate the citrus peel powder in a ratio of 1:2 (W/V) to KOH. It was allowed to stand for 30 min before being dried for 3 h at 70°C in an oxygen-free environment.

2.4 Synthesis of Fe_3O_4 nanoparticles

The magnetic Fe_3O_4 nanoparticles were synthesized by the co-precipitation method as described in the literature [48]. Briefly, 300 mL of distilled water was used to disperse 3.36 g

of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 8.1 g of $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ at a temperature of 50°C under an N_2 atmosphere. Then, ammonium solution (20 mL, $8 \text{ mol} \cdot \text{L}^{-1}$) was added drop by drop to the solution reaction to precipitate the magnetic particles. After that, the pH of the solution reaction was adjusted to 11 using NaOH solution under an ultrasonicator for 15 min. Using an external magnet, the precipitated product was separated and washed several times using distilled water until the pH of the filtrate became 7. Finally, the magnetic nanoparticles were dried at 45°C under a vacuum.

2.5 Synthesis of the magnetic ZIF-8/biochar nanocomposite

The nanocomposite of magnetic ZIF-8/biochar was synthesized by a one-pot hydrothermal method. Briefly, 100 mL of ZIF-8 suspensions were used to dissolve 10 g of Fe_3O_4 and KOH-activated citrus peel powder while stirring at room temperature for 13 h. After that, using an external magnet, the precipitate was collected and dried under a vacuum at 65°C. Then, the resulting product was inserted into a tube furnace for slow continuous pyrolysis under an N_2 atmosphere at 600°C for 2 h using a rate of $5^\circ\text{C} \cdot \text{min}^{-1}$. The product was dipped in HCl solution (1 M) after cooling to room temperature to remove the impurities and alkali. Then, the product was washed using ethyl alcohol and water several times until the pH of the filtrate reached 7. The resulting composite was then dried and ground. The synthesized nanocomposite magnetic ZIF-8/biochar was then stored for the next experiments. Additionally, the composite Fe_3O_4 /biochar was synthesized using the typical steps but without adding the ZIF-8 MOF during the synthesis.

2.6 Batch adsorption experiments

The efficiency of synthesized adsorbents for the removal of $\text{Cr}(\text{VI})$ ions was evaluated using batch adsorption experiments. In brief, 20 mL of $\text{Cr}(\text{VI})$ solution in the concentration range of $0\text{--}500 \text{ mg} \cdot \text{L}^{-1}$ was added to 0.05 g of adsorbent in a flask while the solution pH was 2. Using a shaking water bath, the solution was shaken for 24 h at 180 rpm. To study the kinetics of the adsorption process, 200 mL of $300 \text{ mg} \cdot \text{L}^{-1}$ $\text{Cr}(\text{VI})$ solution was added to 0.5 g of the adsorbent in a flask at pH 2 and the solution was shaken for 24 h at 180 rpm. Then, at different time intervals, part of the solution was withdrawn and analyzed for the presence of $\text{Cr}(\text{VI})$ ions and Cr using UV-vis spectrophotometer at

$\lambda = 540$ nm after a complex formation with 1,5-diphenylcarbazine with a flame atomic absorption spectrometer, respectively. The difference between total Cr and Cr(VI) ions is used to calculate the concentration of Cr(III) ions. Before each analysis and after the completion of the adsorption process, the adsorbent was collected using an external magnet. Additionally, the effect of different parameters on adsorption was investigated including ionic strength (0–0.1 M), pH (1:10), and 0.01 M competing ions (PO_4^{3-} , SO_4^{2-} , Cl^- , Fe^{3+} , Ca^{2+} , and Na^+). During these adsorption experiments, the solid/liquid ratio was fixed at $2.5 \text{ g}\cdot\text{L}^{-1}$ (20 mL solution). Moreover, desorption and reusability were investigated using different eluents including NaOH, NaHCO_3 , Na_2EDTA , HNO_3 , and NaNO_3 at a concentration of 0.01 M. In this experiment, 20 mL of Cr(VI) solution at pH 2 and a concentration of $50 \text{ mg}\cdot\text{L}^{-1}$ was mixed with the adsorbent, which was then collected with a magnet, washed with distilled water, and dipped in an eluent solution for 24 h to study the desorption efficiency. In the reusability experiment, the desorbed adsorbents using NaOH were used to adsorb Cr(VI) ions for five successive cycles to determine the adsorption capacity. All previously described adsorption experiments were performed in triplicate to approve the quality of results.

2.7 Characterization of synthesized adsorbents

To characterize the synthesized materials, different techniques have been used. The essential functional groups on the surface of synthesized materials were investigated using Fourier transform infrared spectroscopy (FT-IR; IRTracer-100 Shimadzu, Japan) in the range of $400\text{--}4,000 \text{ cm}^{-1}$. The magnetic behavior of materials was identified using a vibrating sample magnetometer (VSM; Lake Shore 7404, USA). The thermal gravimetric analysis (TGA; STA409PC, DSC404F3, Germany) was used to investigate the thermal stability of the synthesized materials under an N_2 environment in the range of $30\text{--}1,000^\circ\text{C}$ at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$. Moreover, the surface morphology was investigated using a scanning electron microscope (SEM, Zeiss Genimi500, Zeiss, Germany). The Raman spectra were analyzed using a Raman spectrometer (Renishaw, UK). The specific surface area (S_{BET}) was determined using the Brunauer–Emmett–Teller method via the adsorption/desorption isotherms of N_2 at a temperature of 77 K. The pH drift method was used to calculate the point of zero charge (pH_{PZC}) at which $\Delta\text{pH} = 0$ (where ΔpH is the difference between the initial and final pH values).

3 Results and discussion

3.1 Characterization of the synthesized materials

To achieve the successful characterization of the synthesized materials, several common techniques have been applied. In this section, we used different techniques to verify the successful fabrication of the desired materials. First, the scanning electron microscope (SEM) was used to detect the morphologies of the synthesized materials and follow the surface change resulting from the added materials. Figure 1a shows the SEM image of the citrus peel-derived biochar that appeared to have several pores on its rough structure surface. Figure 1b shows the SEM image of the Fe_3O_4 /biochar composite in which the composite has a stacked and smooth structure surface holding several nanoparticles with diameters in the range of 25–30 nm. The appeared nanoparticles to confirm the successful precipitation of magnetic Fe_3O_4 nanoparticles on the surface of the biochar.

Figure 1c shows the SEM image of the Fe_3O_4 /biochar/ZIF-8 composite. Figure 1c shows that the introduction of the ZIF-8 MOF to the composite has a great effect on the structure, which is clearly shown via the morphology change. The Fe_3O_4 /biochar/ZIF-8 composite appeared to have wrinkled edges with smooth surfaces and a multi-layer structure, which could be the result of ZIF-8 decomposing at a higher pyrolysis temperature. Additionally, to sustain the framework, the partially decomposed ZIF-8 was distributed between the sheets that resemble graphene as a sacrifice template. Also, the crystallinity of the synthesized materials was studied using XRD patterns as shown in Figure 2a. According to the XRD patterns, the synthesized magnetic Fe_3O_4 nanoparticles showed the appearance of characteristic planes (440), (511), (422), (400), (311), and (220) at $2\theta = 62.9^\circ$, 57.2° , 53.7° , 43.4° , 35.5° , and 30.2° , respectively [49]. When the XRD patterns of the Fe_3O_4 nanoparticles and Fe_3O_4 /biochar composite were compared, it was noticed that the crystallinity remained unchanged, which indicated the stability of the Fe_3O_4 /biochar composite crystal structure even after loading of magnetic nanoparticles on the biochar surface. After the addition of the ZIF-8 MOF to the Fe_3O_4 /biochar composite, several new peaks appeared, which were attributed to the addition of the MOF. The results of the XRD patterns revealed the crystal structures of the Fe_3O_4 nanoparticles and Fe_3O_4 /biochar composite, suggesting that the synthesized Fe_3O_4 /biochar/ZIF-8 composite was well fabricated. The presence of functional groups and information about chemical bonding can

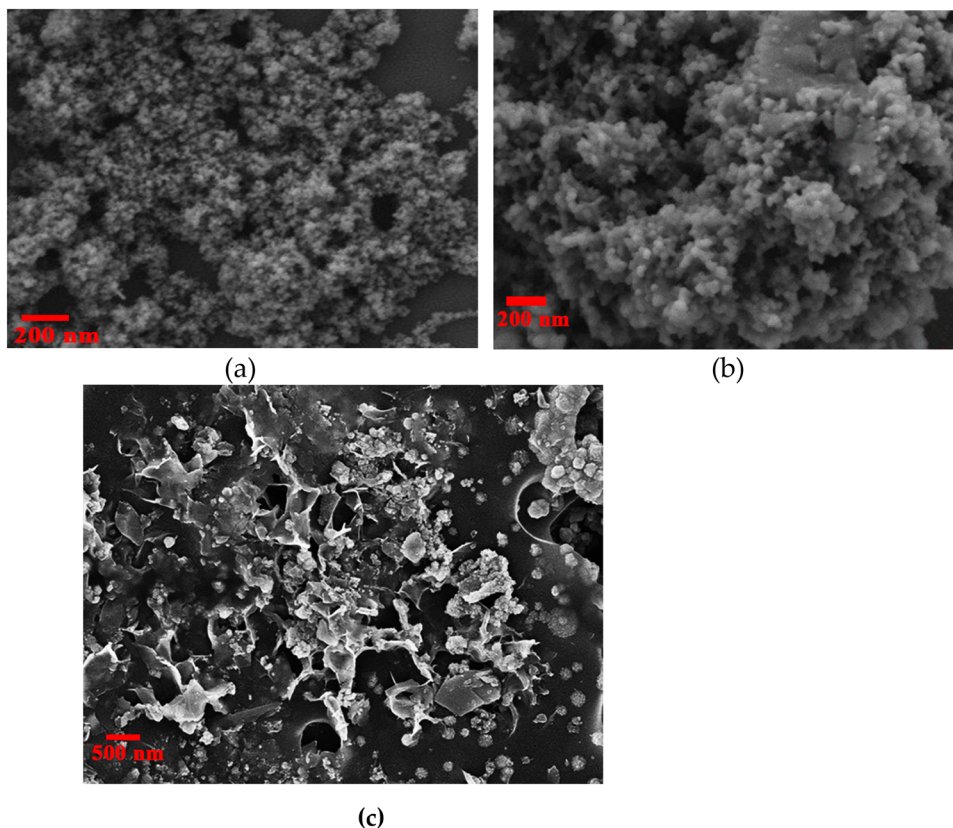


Figure 1: SEM images of the biochar (a), $\text{Fe}_3\text{O}_4/\text{biochar}$ (b), and $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ (c).

be obtained using FT-IR spectra, as shown in Figure 2b. Generally, the characteristic peak at $1,621\text{ cm}^{-1}$ was attributed to the $\text{C}=\text{N}$ bond in the ZIF-8 MOF or to the $\text{C}=\text{C}$ bond in the aromatic ring. Also, the broad peaks at $3,421\text{ cm}^{-1}$ were attributed to the $\text{N}-\text{H}$ stretching vibration or the $\text{O}-\text{H}$ stretching vibration [50,51]. Additionally, the $\text{C}-\text{O}$ stretching vibration of carboxylic acids and aromatic ethers is usually represented by the band at $1,095\text{ cm}^{-1}$. These oxygen-containing functional groups and double bonds of aromatic rings are very effective in pollutant removal via hydrogen bonding and $\pi-\pi$ interactions, respectively [50,52,53]. Moreover, that ZIF-8 MOF was well introduced into the nanocomposite was confirmed from the appearance of the peak at 480 cm^{-1} that was attributed to $\text{Zn}-\text{N}$ vibrations [54]. Also, that Fe_3O_4 was well introduced into the nanocomposite was confirmed from the appearance of the peak at 568 cm^{-1} that was attributed to $\text{Fe}-\text{O}$ vibrations.

Furthermore, the Raman spectra of the synthesized materials are shown in Figure 2c. In Raman spectra, there are two bands G- and D-bands, which are attributed to the ordered graphitic sp^2 hybridized carbon and disordered sp^3 hybridized carbon, respectively. The degree of graphitization can be obtained from the total peak area of the

Raman spectra [55]. As a result, it is possible to use the peak area rate from the D-band to the G-band (I_D/I_G) as a guideline when determining the degree of structural disorder in carbon materials [56]. According to Figure 2c, the I_D/I_G of the $\text{Fe}_3\text{O}_4/\text{biochar}$ is higher than that of the $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ nanocomposite, indicating the increase of sp^2 -hybridized domains. The Raman spectra results indicated the successful introduction of the ZIF-8 MOF to the composite $\text{Fe}_3\text{O}_4/\text{biochar}$. Additionally, the magnetic properties of the synthesized materials were investigated using VSM, as shown in Figure 3a. According to Figure 3a, Fe_3O_4 , $\text{Fe}_3\text{O}_4/\text{biochar}$, and $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ have excellent magnetic properties. The saturation magnetization values were 24.53, 32.30, and $67\text{ emu}\cdot\text{g}^{-1}$ for $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$, $\text{Fe}_3\text{O}_4/\text{biochar}$, and Fe_3O_4 , respectively. According to the results, the saturation magnetization of pure Fe_3O_4 nanoparticles is the highest and this value was decreased after the incorporation of non-magnetic biochar and ZIF-8. However, by using an external magnet, these composites still exhibited magnetic properties and could be easily collected from the solution.

As the specific surface area is very important in determining the adsorption properties of the materials, the N_2 adsorption/desorption isotherm method was used for the

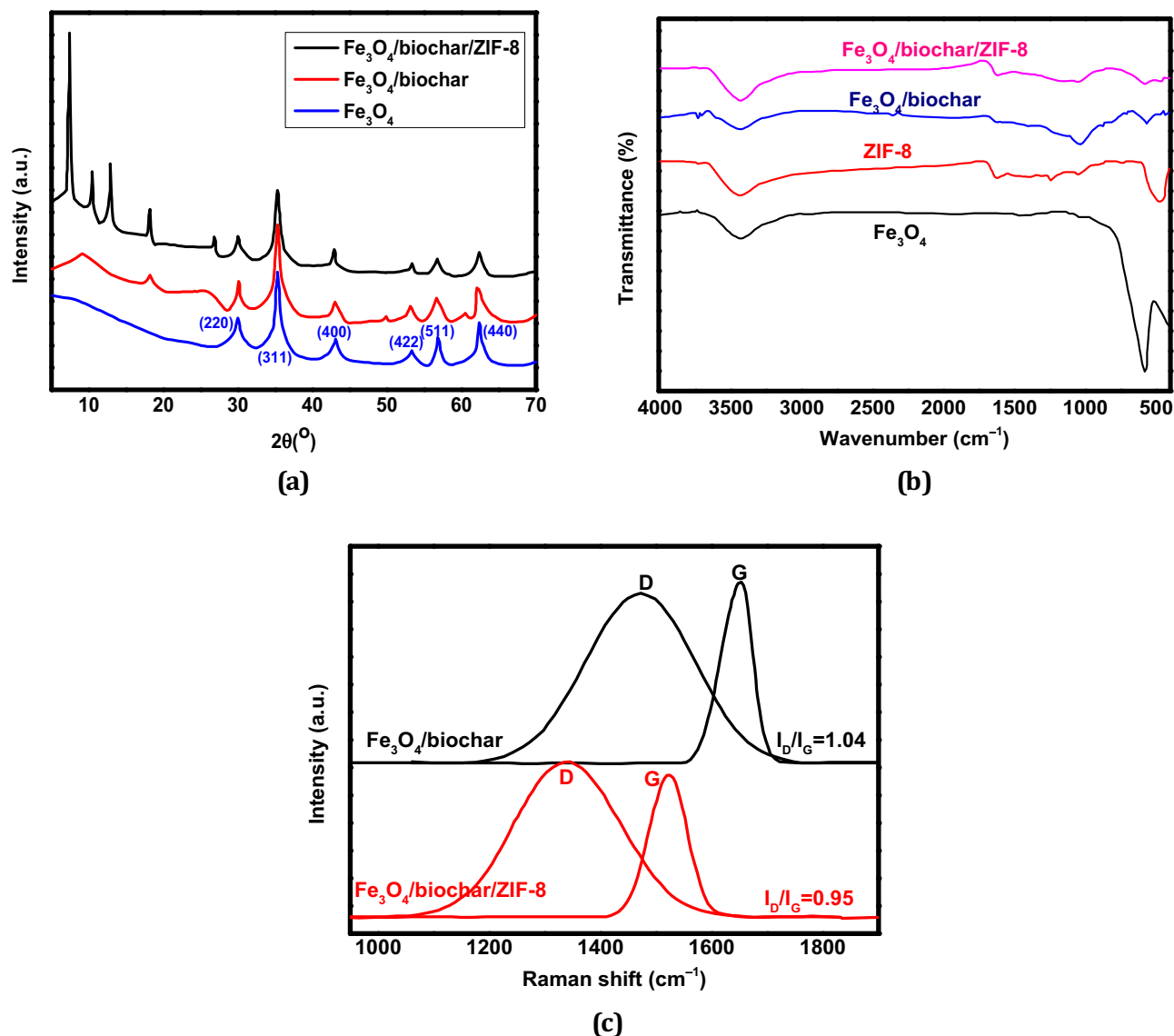


Figure 2: XRD patterns (a), FT-IR spectra (b), and Raman spectra (c) of the synthesized materials.

investigation of the S_{BET} surface area of synthesized materials [57] as shown in Figure 3b. According to Figure 3b, the synthesized biochar showed an S_{BET} of $8.97 \text{ m}^2\text{g}^{-1}$. The addition of magnetic nanoparticles to the biochar showed an increase in the S_{BET} to reach $280.55 \text{ m}^2\text{g}^{-1}$. Additionally, further addition of MOF ZIF-8 to the magnetic biochar increased the S_{BET} to reach $940.25 \text{ m}^2\text{g}^{-1}$. The S_{BET} of $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ is about two times higher than that of $\text{Fe}_3\text{O}_4/\text{biochar}$. It appears that the addition of ZIF-8 facilitated the expansion of the surface area. The $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ nanocomposite showed a combined feature of type I and IV phenomena, indicating the co-occurrence of micropores and mesopores that interpret the enhanced surface area. Additionally, the $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ nanocomposite

shows an H4-type hysteresis loop at a relative pressure $p/p^0 > 0.4$, indicating the higher content of mesopores. In contrast, at a relative pressure $p/p^0 < 0.01$, the importance of micropores is very clear as the adsorption capacity was significantly increased. The mesoporous and microporous construction will aid in the improved migration of the adsorbate particles *via* the porous arrangement, increasing the capillary effect and improving the adsorption behavior of nanocomposites [58]. Therefore, the N_2 adsorption/desorption isotherms showed the significant effect of ZIF-8 MOF on the nanocomposite. The thermal stability of synthesized materials was determined using TGA analysis in the temperature range from 30 to $1,000^{\circ}\text{C}$, as shown in Figure 3c. According to the TGA curves of $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ and

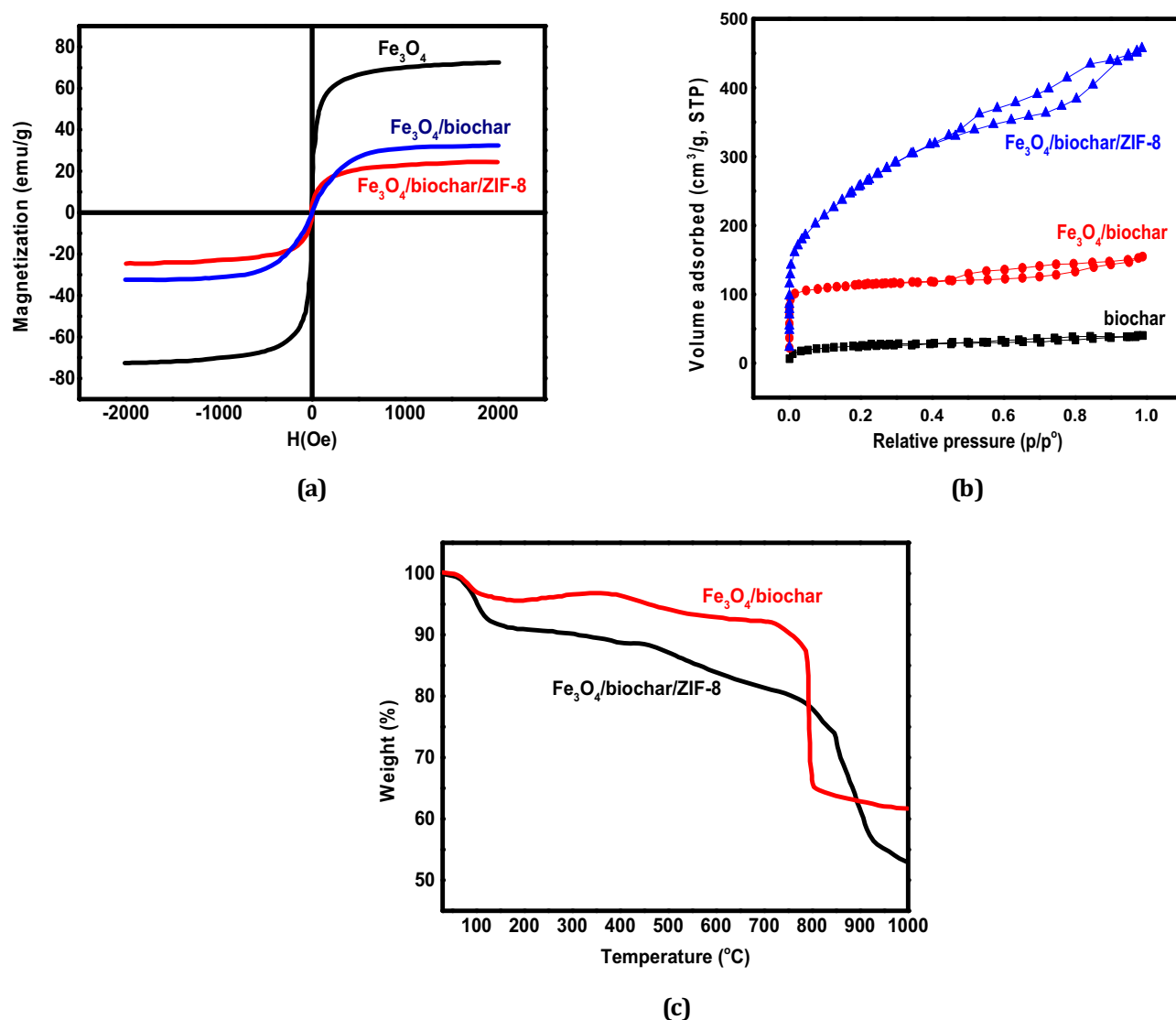


Figure 3: Magnetic hysteresis loops (a), the N_2 adsorption–desorption isotherms (b), and thermogravimetric analysis (TGA) (c) of the synthesized materials.

$\text{Fe}_3\text{O}_4/\text{biochar}$ composites, the adsorbed surface water was evaporated in the temperature range from 30 to 100°C ; however, the decomposition of functional groups in the composites was observed in the temperature range from 100 to 780°C . It is clear that the weight loss of the $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ nanocomposite was higher than that of the $\text{Fe}_3\text{O}_4/\text{biochar}$ in the temperature range from 100 to 780°C by about 11%, which was attributed to the evaporation of the ZIF-8 MOF from the surface of the nanocomposite. The $\text{Fe}_3\text{O}_4/\text{biochar}$ composite showed a rapid weight loss at 780°C , resulting from the decomposition of its carbon backbone. At a temperature higher than 900°C , the weight loss in the $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ nanocomposite was attributed to the decomposition of the metallic Zn from the MOF. Therefore, the $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ nanocomposite has a higher thermal stability than the

$\text{Fe}_3\text{O}_4/\text{biochar}$ composite, which was attributed to the ZIF-8 MOF acting as a sacrificial template. All characterization results indicated the good fabrication of the nanocomposite $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$.

3.2 Adsorption study

3.2.1 Adsorption isotherm and kinetics

To understand the adsorption behavior of $\text{Cr}(\text{VI})$ ions on the surface of the synthesized nanocomposites, the adsorption isotherm and kinetics were studied. Figure 4a shows the adsorption isotherms in which the initial concentration of $\text{Cr}(\text{VI})$ ions was varied with the adsorption capacities of the

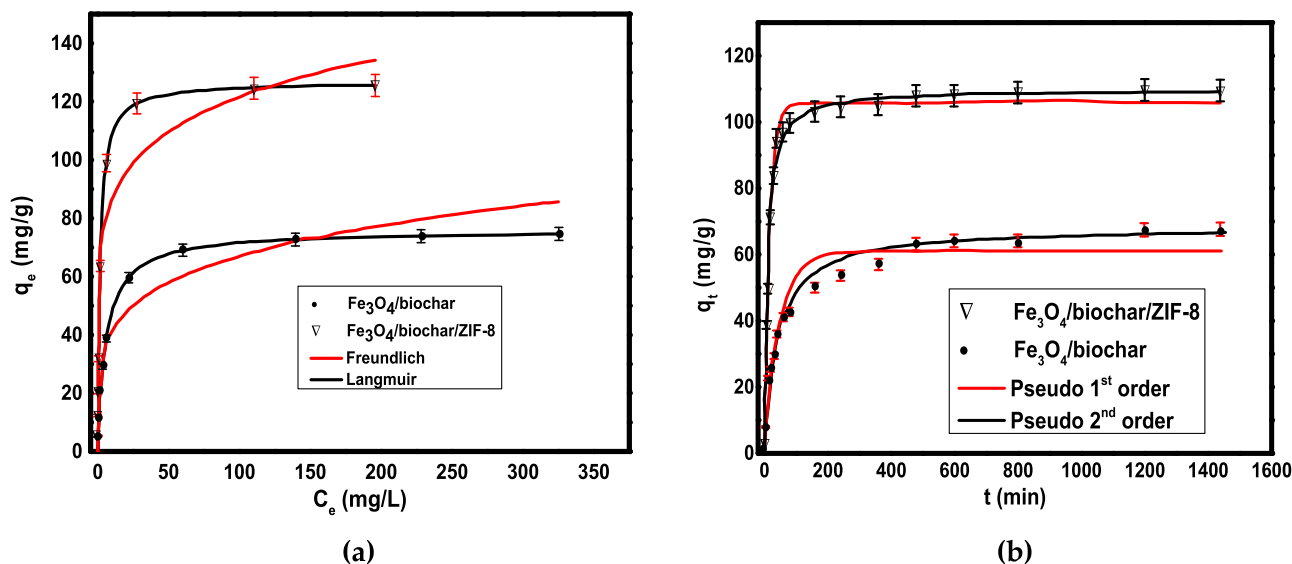


Figure 4: Adsorption isotherms models (a) and adsorption kinetics models (b) for the removal of Cr(vi) ions on the surface of the synthesized materials (initial concentration = $300 \text{ mg}\cdot\text{L}^{-1}$, pH = 2, temperature = 25°C , adsorbent dose = 0.5 g, and contact time = 24 h).

prepared adsorbents. For both nanocomposites, $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ and $\text{Fe}_3\text{O}_4/\text{biochar}$ as adsorbents, the increase in the Cr(vi) initial concentration caused a rapid increase of the adsorption capacities until an equilibrium was reached at which the adsorption remains unchanged. Figure 4a shows the fitting of experimental adsorption data using the Freundlich equation – Eq. (1) – and Langmuir equation – Eq. (2) – for the better understanding of isotherms:

$$q_e = K_F C_e^{1/2}, \quad (1)$$

$$q_e = \frac{Q_{\max} K_L C_e}{1 + K_L C_e}, \quad (2)$$

where q_e is the adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$) at equilibrium, K_F is the Freundlich equilibrium adsorption constant ($\text{mg}^{1-n}\cdot\text{L}^n\cdot\text{g}^{-1}$), K_L is the Langmuir equilibrium adsorption constant ($\text{L}\cdot\text{mg}^{-1}$), and $Q_{\max}$ is the maximum adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$). The Freundlich and Langmuir isotherm coefficients are presented in Table 1.

According to Figure 4a, the adsorption isotherms of Cr(vi) on the surface of both nanocomposites were better

defined using the Langmuir model than the Freundlich model, which is also from the R^2 values presented in Table 1. This indicated that the adsorption of metal on the surface of adsorbents occurred as a monolayer over the identical adsorption sites [59,60]. The coefficients presented in Table 1 indicate that the maximum adsorption capacities according to the Langmuir isotherm were 125 and $77 \text{ mg}\cdot\text{g}^{-1}$ for $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ and $\text{Fe}_3\text{O}_4/\text{biochar}$, respectively. The results of adsorption experiments show that even without ZIF-8 doping, the $\text{Fe}_3\text{O}_4/\text{biochar}$ nanocomposite has a good adsorption capacity, which is attributed to the porous structure, large specific surface area, abundant mineral components, and surface functional groups. For comparison, Table 2 shows the maximum adsorption capacities of different MOF adsorbents in the Cr(vi) removal from water. The adsorption capacity of $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ toward the removal of Cr(vi) ions is higher than many previously prepared adsorbents. The adsorption of Cr(vi) ions on the surface of $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ and $\text{Fe}_3\text{O}_4/\text{biochar}$ nanocomposites was favorable, as

Table 1: Adsorption isotherm and kinetic parameters for the adsorption of Cr(vi) ions on the surface of the synthesized materials

Adsorbent	Langmuir			Freundlich			Pseudo-first order			Pseudo-second order		
Parameters	q_m (mg·g ⁻¹)	K_L (L·mg ⁻¹)	R^2	N	K_F (mg·g ⁻¹) (L·mg) ^{-1/n}	R^2	K_1 (min ⁻¹)	q_e	R^2	K_2 (g·mg·h ⁻¹)	q_e	R^2
Fe ₃ O ₄ /biochar	77.0	0.15	0.998	4.77	25.6	0.844	0.03	67.7	0.930	0.0005	68.7	0.997
Fe ₃ O ₄ /biochar/ ZIF-8	125.0	0.54	0.998	6.50	61.0	0.768	0.07	111.0	0.981	0.0010	111.0	0.999

Table 2: Comparison of the $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ nanocomposite with previously reported adsorbents for the adsorption of $\text{Cr}(\text{VI})$ ions

Adsorbent	pH	Removal capacity ($\text{mg}\cdot\text{g}^{-1}$)	Reference
$\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$	2.0	125.0	This study
$\text{Fe}_3\text{O}_4/\text{MIL-100}$	2.0	18.0	[67]
MIL-100	2.0	30.4	[68]
Amine-MIL-101	4.0	44.0	[69]
Mn-UiO-66	—	32.77	[70]
MOF BUC-17	4.0	121.0	[71]
GO-CS@MOF	3.0	144.9	[72]
ZIF-67	5.0	13.3	[73]
ZIF-8	7.0	0.15	[74]
Cu-BTC	7.0	40.0	[75]

indicated by the separation factor (R_L) values (from 0–1) [61,62]. Moreover, the stronger adsorption affinity of $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ toward $\text{Cr}(\text{VI})$ ions than $\text{Fe}_3\text{O}_4/\text{biochar}$ was evident from the higher R_L values. This was because the introduction of the MOF (ZIF-8) to the nanocomposite provided more adsorption active sites. Additionally, the adsorption kinetics was investigated using pseudo-first- (Eq. (3)) and pseudo-second-order kinetics (Eq. (4)):

$$q_t = q_e(1 - e^{-k_1 t}), \quad (3)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}, \quad (4)$$

where q_t ($\text{mg}\cdot\text{g}^{-1}$) represents the adsorption capacity of the adsorbent at the reaction time t , k_1 (min^{-1}) represents the rate constant of the pseudo-first-order kinetics, and k_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$) represents the rate constant of pseudo-second-order kinetics. The pseudo-first- and pseudo-second-order kinetic model coefficients are presented in Table 1.

The effect of time on the removal of $\text{Cr}(\text{VI})$ ions on the surface of $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ and $\text{Fe}_3\text{O}_4/\text{biochar}$ nanocomposites is shown in Figure 4b. Similar adsorption behavior was observed for both adsorbents. According to Figure 4b, the adsorption equilibrium for the removal of $\text{Cr}(\text{VI})$ ions on the surface of $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ and $\text{Fe}_3\text{O}_4/\text{biochar}$ nanocomposites was achieved at 300 and 500 min, respectively. Under high concentrations of $\text{Cr}(\text{VI})$ ions, it was a quick initial stage of adsorption aided by ion diffusion. After this stage, the rate of adsorption was decreased due to the saturation of adsorption sites with metal adsorbate ions. The effect of time indicated a faster adsorption of $\text{Cr}(\text{VI})$ ions on the $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ than $\text{Fe}_3\text{O}_4/\text{biochar}$ because the presence of a higher number of abundant functional groups facilitated the rapid uptake of ions. According to Table 1, the adsorption of $\text{Cr}(\text{VI})$ ions on

$\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ than the $\text{Fe}_3\text{O}_4/\text{biochar}$ adsorbent was best described using a pseudo-second-order kinetic model as indicated by the correlation coefficient (R^2) values. This indicated that the adsorption of both adsorbents was achieved using chemical and physical methods [63]. In the physical method, the diffusion of ions was achieved within the pores of nanocomposites; whereas, in the chemical method, by complexation of ions was achieved by the functional groups and reduction. This kinetic behavior of $\text{Cr}(\text{VI})$ adsorption was observed with previously reported adsorbents [64–66].

3.2.2 Effect of competing ions and the ionic strength

To understand the efficiency of any adsorbent for the removal of contaminants, the effect of competing ions should be investigated to determine the selectivity of the adsorbent toward targeted ions. Therefore, the competition between $\text{Cr}(\text{VI})$ ions and competing ions for the adsorption active sites on the surface of $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ and $\text{Fe}_3\text{O}_4/\text{biochar}$ was investigated, as shown in Figure 5a. According to Figure 5a, the adsorption of $\text{Cr}(\text{VI})$ ions on the surface of the $\text{Fe}_3\text{O}_4/\text{biochar}$ nanocomposite was slightly affected by the presence of Ca^{2+} , Fe^{3+} , and Cl^- ions, as well as slightly affected by the presence of PO_4^{3-} and SO_4^{2-} .

Also, the adsorption of $\text{Cr}(\text{VI})$ ions on the surface of $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ was significantly affected by the competing ions and the effect was in the order $\text{SO}_4^{2-} > \text{Fe}^{3+} > \text{PO}_4^{3-} > \text{Ca}^{2+} > \text{Cl}^-$. The SO_4^{2-} ions had a higher effect on the removal of $\text{Cr}(\text{VI})$ ions than PO_4^{3-} ions. This is attributed to the less net charge of PO_4^{3-} than $\text{Cr}_2\text{O}_7^{2-}$ at pH 2, as it exists as HPO_4^{2-} and H_3PO_4 while SO_4^{2-} carries two negative charges, such as $\text{Cr}_2\text{O}_7^{2-}$ with the same molecular structure producing a higher competition for adsorption sites [76,77]. The complexation of $\text{Cr}(\text{VI})$ oxyanions with Fe^{3+} and Ca^{2+} ions was the reason for the high effect on the adsorption process [78]. Another important factor affecting the adsorption of $\text{Cr}(\text{VI})$ ions is the ionic strength, as shown in Figure 5b, in which the adsorption was studied on the surface of $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ and $\text{Fe}_3\text{O}_4/\text{biochar}$ nanocomposites at different concentrations of NO_3^- ions. According to Figure 5b, the increase of NO_3^- concentration caused a decrease in the adsorption efficiency of the $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ nanocomposite. The increase of NO_3^- concentration to $0.1\text{ mg}\cdot\text{L}^{-1}$ caused a decrease in adsorption efficiency by 39%. However, for the $\text{Fe}_3\text{O}_4/\text{biochar}$ nanocomposite, the reduction in the adsorption efficiency was only 11%. The main cause of the decreased $\text{Cr}(\text{VI})$ removal at an increased ionic strength was the competition between $\text{Cr}(\text{VI})$ and NO_3^- ions for the adsorption sites [79].

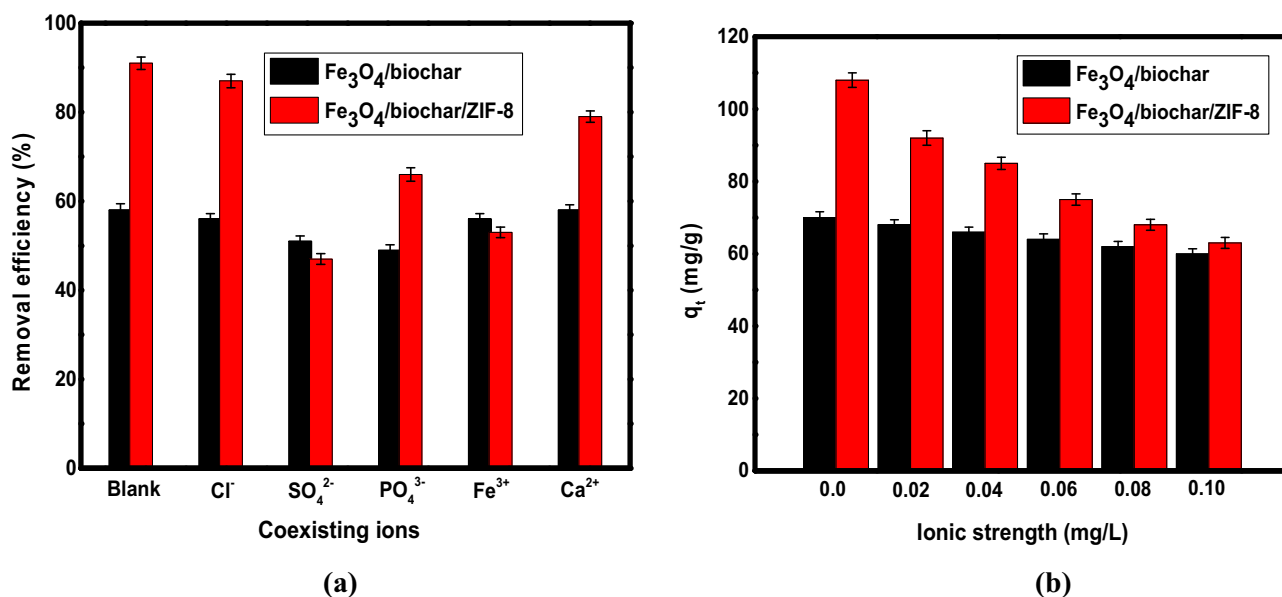


Figure 5: The effect of 0.01 M competing ions (a) and the effect of the ionic strength (b) on the adsorption of Cr(VI) ions on the surface of the synthesized materials.

3.2.3 Effect of pH values

It is well-known that one of the key elements that greatly affects the removal of Cr(VI) from aqueous solution is the pH value [80] because the solution pH also influences the charge of the adsorbent surface in addition to the species and redox potential of Cr(VI) that are already present [81,82]. Therefore, the effect of solution pH on the removal of Cr(VI) from aqueous solution on the surface of Fe₃O₄/

biochar/ZIF-8 and Fe₃O₄/biochar nanocomposites was investigated, as shown in Figure 6a.

While the adsorption behavior between Fe₃O₄/biochar/ZIF-8 and Fe₃O₄/biochar nanocomposites was different, the solution pH clearly had a great effect on the removal of Cr(VI) ions. According to Figure 6a, Fe₃O₄/biochar nanocomposites exhibited a limited pH range for the removal of Cr(VI) ions (pH = 1–4) while the Fe₃O₄/biochar/ZIF-8 nanocomposite exhibited a wide pH range (pH = 2–10) for the

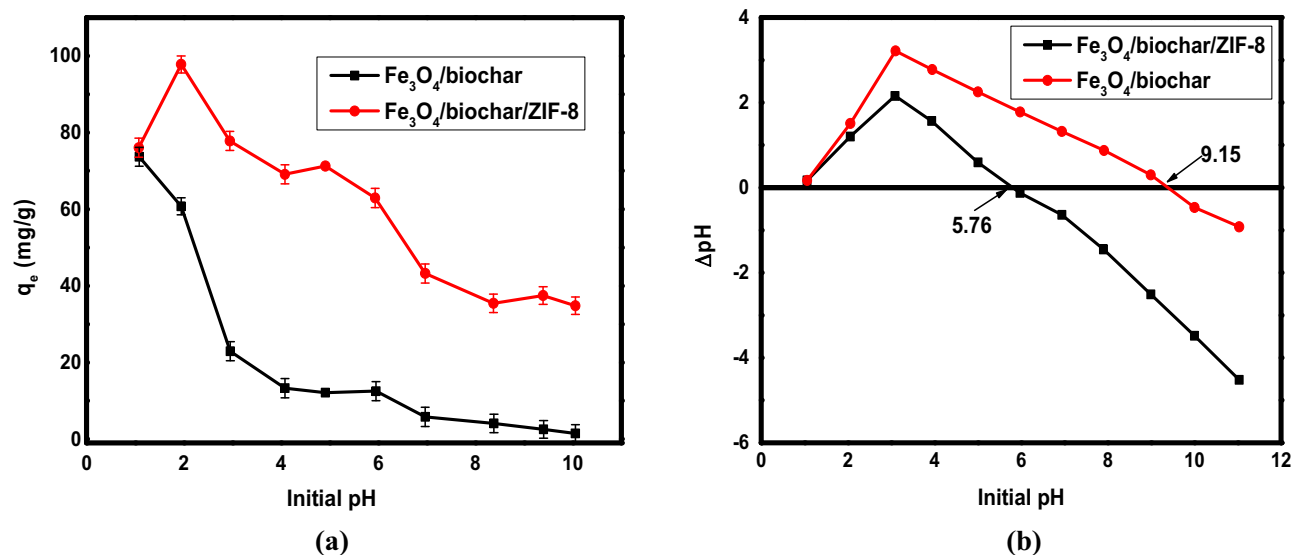


Figure 6: The effect of pH (a) and the point of zero charge (pH_{pzc}) (b) for the adsorption of Cr(VI) ions on the surface of the synthesized materials.

Cr(vi) adsorption. For the $\text{Fe}_3\text{O}_4/\text{biochar}$ nanocomposite, the increased pH value from 1 to 3 caused an increased adsorption efficiency toward Cr(vi) ions, and this adsorption efficiency was decreased at pH 7. For the $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ nanocomposite, the adsorption capacity was still high even after the pH increased up to 10, and higher than that of the $\text{Fe}_3\text{O}_4/\text{biochar}$ nanocomposite by about 31%. However, the increased pH value also reduced the adsorption efficiency of the pollutant over both the adsorbents. To better understand the pH effect, the point of zero charges (pH_{pzc}) of the two prepared adsorbents was investigated, as shown in Figure 6b. According to Figure 6b, the pH_{pzc} values were 9.15 and 5.76 for $\text{Fe}_3\text{O}_4/\text{biochar}$ and $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$, respectively. The higher value of $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ was attributed to the introduced MOF. After adsorption, pH variations in the solution were also noticed. The pH of the solution after adsorption on the surface of $\text{Fe}_3\text{O}_4/\text{biochar}$ was a little lower than the pH_{pzc} value, thereby reducing its adsorption efficiency. Apart from the changes in the Cr(vi) percentage with the increasing solution pH, the electrostatic repulsion between the negatively charged $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ surface and Cr(vi) anions was the primary cause of the decrease in the adsorption efficiency at $\text{pH} > 6$. Additionally, the higher adsorption efficiency of $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ at low pH values than $\text{Fe}_3\text{O}_4/\text{biochar}$ was attributed to the protonated functional groups on its surface. When the adsorption solution was analyzed after adsorption at low pH values, the presence of Cr(III) ions was approved, indicating the reduction of Cr(vi) ions. This reduction of Cr(vi) ions to Cr(III) ions is well known with the biochar adsorbents due to their role as electron donors and electron acceptors as discussed in the literature [83,84].

Subsequently, the removal of Cr(vi) ions on the surfaces of $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ and $\text{Fe}_3\text{O}_4/\text{biochar}$ was achieved via different mechanisms.

3.2.4 Regeneration and reusability study

Regeneration and reusability study for any adsorbent is very important economically as it decreases the overall cost of the treatment process [85–87]. Before reusing the adsorbents, the desorption of adsorbed pollutants should be investigated first. Therefore, many eluents have been explored to desorb Cr(vi) ions from the surface of the synthesized $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ and $\text{Fe}_3\text{O}_4/\text{biochar}$ as adsorbents, as shown in Figure 7a.

According to Figure 7a, the desorption efficiency toward Cr(vi) ions from the surface of $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ was in the order of $\text{NaNO}_3 < \text{NaHCO}_3 < \text{NaOH} < \text{HNO}_3 < \text{Na}_2\text{EDTA}$, whereas for $\text{Fe}_3\text{O}_4/\text{biochar}$, the desorption efficiency toward Cr(vi) ions was in the order of $\text{NaOH} < \text{HNO}_3 < \text{NaNO}_3 < \text{NaHCO}_3 < \text{Na}_2\text{EDTA}$, as shown in Figure 7a. It is clear that the sodium EDTA salt has the highest desorption capacity toward Cr(vi) ions. The acids HCl and HNO_3 showed good desorption capacities toward Cr(vi) ions from the surface of $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ and $\text{Fe}_3\text{O}_4/\text{biochar}$, which was similar to the literature [88,89]. However, the commonly used desorption eluent for Cr(vi) ions is the basic solution of NaOH [90,91]. According to the desorption experimental results, the Na_2EDTA solution was used as an eluent to desorb Cr(vi) ions from the surface of $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ and $\text{Fe}_3\text{O}_4/\text{biochar}$ during the

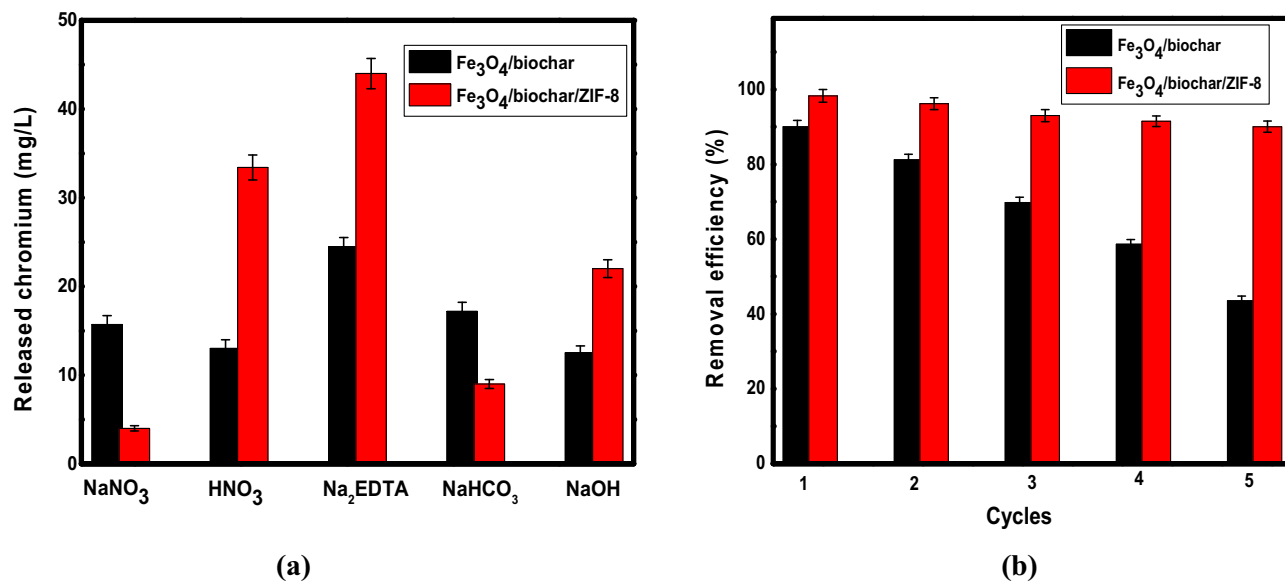


Figure 7: The desorption of total Cr ions using different eluents (a) and the reusability study (b) for the adsorption of Cr(vi) ions on the surface of the synthesized materials.

reusability study. The reusability of $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ and $\text{Fe}_3\text{O}_4/\text{biochar}$ for the removal of $\text{Cr}(\text{VI})$ ions was investigated for five successive adsorption–desorption cycles as shown in Figure 7b. According to Figure 7b, the $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ showed higher reusability results than $\text{Fe}_3\text{O}_4/\text{biochar}$. For both adsorbents, the removal efficiency was the highest in the first cycle due to the availability of vacant adsorption sites. After that, the removal efficiency was decreased cycle by cycle until it reached its minimum in the fifth cycle due to the destroyed adsorption sites resulting after each cycle. The removal efficiency of $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ toward $\text{Cr}(\text{VI})$ removal remained higher than 90.0% even after the last cycle, whereas for $\text{Fe}_3\text{O}_4/\text{biochar}$, the removal efficiency was decreased gradually from 90.5 to 45% in the last cycle.

The reusability results indicated that $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ is a promising adsorbent to eliminate pollutants from water with cost-effective properties.

3.2.5 Suggested mechanism of adsorption

To study the mechanism of adsorption of $\text{Cr}(\text{VI})$ ions on the surface of $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$, XPS spectra of $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ before and after adsorption were recorded, as shown in Figure 8a and b, respectively, to provide information regarding the surface chemistry of the adsorbent. Comparing Figure 8a and b showed a change in the metal (Zn) binding energy after and before adsorption, indicating

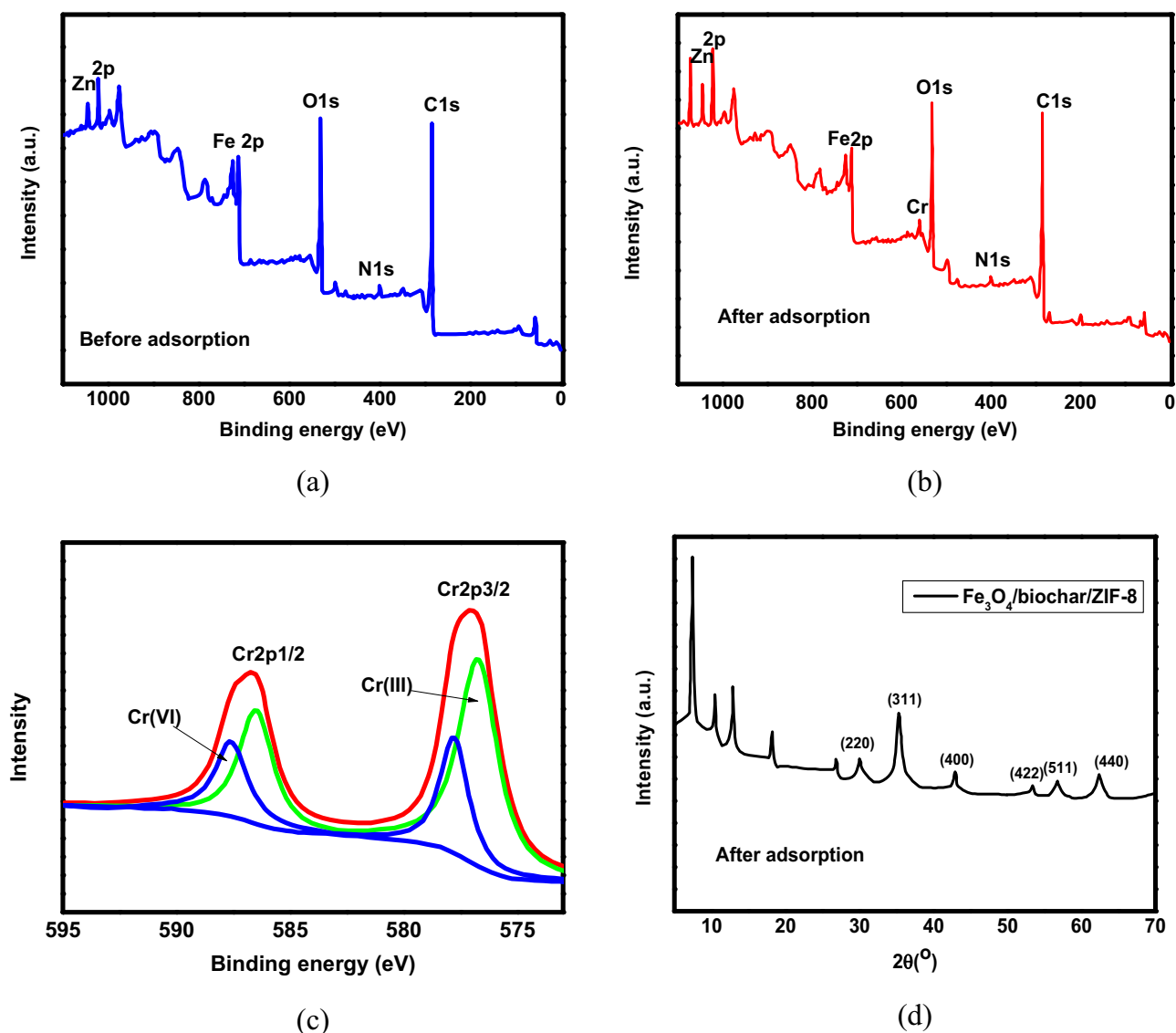


Figure 8: The XPS survey spectra of $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ before adsorption (a) and after adsorption (b). XPS high-resolution Cr 2p spectra of $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ after the removal of $\text{Cr}(\text{VI})$ ions (c), and XRD patterns of $\text{Fe}_3\text{O}_4/\text{biochar}/\text{ZIF-8}$ after adsorption (d).

that metal sites were involved in the chelation process. Also, the XPS spectra after adsorption showed the appearance of a new binding energy peak at 580 eV, which belongs to Cr(vi) ions, confirming their presence on the surface of the adsorbent. Additionally, the identification of the adsorbed species of chromium ions was achieved using high-resolution XPS spectra as shown in Figure 8c. According to Figure 8c, the high-resolution XPS spectra showed the presence of two satellite bands of Cr(III) and Cr(vi) ions at 587 and 577 eV, respectively. Subsequently, the presence of two chromium species Cr(III) and Cr(vi) on the surface of Fe₃O₄/biochar/ZIF-8 indicated the removal of Cr(vi) ions on the adsorbent surface by adsorption and by the chemical reduction to Cr(III). In this regard, the mechanism of Cr(vi) removal can be explained as follows: the protonated nitrogen and oxygen functional groups on the surface of adsorbent under acidic conditions can adsorb Cr(vi) species (HCrO₄⁻) via electrostatic interactions and chemical bonding. This chemical bonding on the surface of adsorbent was also associated with the chemical reduction of Cr(vi) to Cr(III). The chemical bonding also occurred through the metal sites (Zn) of the MOFs. The resulting Cr(III) ions could be removed by complexation with functional groups on the adsorbent surface and others may be dissolved in water.

The study of adsorbent stability is very important. Therefore, the stability of Fe₃O₄/biochar/ZIF-8 as an adsorbent was determined by XRD after adsorption, as shown in Figure 8d. According to Figure 8d and comparing with the results of XRD before adsorption, there is no change in the XRD patterns before and after adsorption. These results indicate the good stability of Fe₃O₄/biochar/ZIF-8 as an adsorbent. To confirm this stability of Fe₃O₄/biochar/ZIF-8 as an adsorbent, the concentration of Fe and C in the solution after equilibrium was measured. Carbon was found to be 0.51–0.71% and Fe was found to be 0.2–0.3% under acidic conditions. These results also confirmed the high stability of Fe₃O₄/biochar/ZIF-8 and the gained stability by MOF modification.

The present MOF-based adsorbent has several advantages such as excellent designability with the control of pore size, pore type, adsorption sites, and surface area that affect the adsorption capacity. This MOF-based adsorbent with a controlled chemical design and pore structure allows its application in water treatment. Another advantage is the reusability with high adsorption efficiency, which reduces the overall cost of treatment so it is cost-effective. Also, it is very stable and easily collected from the reaction medium due to its magnetic properties. It can capture pollutants with different mechanisms due to the diversity of functional groups on its surface. It is very

selective and can be used in the presence of competing ions and at a wide pH range. However, like any adsorbent material, it has some disadvantages such as the difficulty of connecting the MOFs with the matrix, high cost of synthesis, long time synthesis, and high accuracy and skill during the synthesis.

4 Conclusions

In summary, Fe₃O₄/biochar, and Fe₃O₄/biochar/ZIF-8 nanocomposites were synthesized by the one-pot hydrothermal method. The citrus fruits as a source of biochar were mixed with magnetic nanoparticles and MOFs to synthesize a novel nanocomposite of Fe₃O₄/biochar/ZIF-8. The nanocomposite was well characterized using different techniques including SEM, XRD, FT-IR, Raman spectroscopy, the N₂ adsorption–desorption isotherm, TGA, and magnetization curves. All these results showed an excellent combination between the three components of the nanocomposite. The nanocomposite was employed as a recyclable ecological adsorbent for the effective removal of Cr(vi) ions from the aqueous solution. The Fe₃O₄/biochar/ZIF-8 nanocomposite showed improved adsorption capacities toward the examined pollutant. The adsorption data were well-described using the Langmuir isotherm model and pseudo-second-order kinetic model, indicating monolayer and physicochemical adsorption. The adsorption capacities were found to be 77 and 125 mg·g⁻¹ for Fe₃O₄/biochar and Fe₃O₄/biochar/ZIF-8, respectively, according to the Langmuir model. The results indicated the role of MOFs as a matrix that holds the nanoparticles and improves their properties. The effect of different parameters on adsorption has been investigated, including pH, ionic strength, and competing ions. The results showed that the studied material has a good adsorption capacity at different ionic strength values and in the presence of different competing ions, indicating its applicability in real water treatment. Moreover, the Fe₃O₄/biochar/ZIF-8 nanocomposite showed excellent reusability toward Cr(vi) removal. The removal mechanism of Cr(vi) ions on the surface of the nanocomposite was studied and the results indicated the removal of ions by chemical bonding with the zinc metal, nitrogen, and oxygen centers, chemical reduction of Cr(vi) ions to Cr(III) ions, and electrostatic interaction. The XRD results of the nanocomposite after adsorption showed its good stability as an adsorbent. We can conclude that the Fe₃O₄/biochar/ZIF-8 nanocomposite is a promising recyclable adsorbent for the removal of pollutants from water.

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