



Preparation of magnetic chitosan/Fe-Zr nanoparticles for the removal of heavy metals from aqueous solution

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Original Article

Abstract

Copper and hexavalent chromium are heavy metals that are harmful to human health. Natural adsorbent chitosan, due to its considerable properties such as the presence of functional groups of $-NH_2$ and $-OH$, non-toxicity, low cost, and biocompatibility, has gained much attention in pollutant removal. Therefore, in the present study, adsorption of chromium (VI) and copper (II) ions was conducted in a batch system using magnetic chitosan/Fe-Zr nanoparticles. In addition, the effect of different variables such as contact time, pH, adsorbent dose, initial concentration of heavy metals, and temperature were investigated. The results of the present study indicated that the highest efficiency in removal of chromium (VI) and copper (II) in pH of 4 were 99.52% and 97.72%, respectively. Moreover, adding 0.4 g of the composite at concentration of 5 mg/l can result in up to 97.43% removal of copper (II) and adding 1 g of this composite at the same concentration can result in more than 91% removal of chromium (VI). In addition, it was concluded that increasing the density of the heavy metals did not have a remarkable effect on the removal efficiency. The equilibrium related to adsorbent capacity and the amounts of nanoparticles were obtained using the plots of Langmuir and Freundlich adsorption isotherms for chromium (VI) and copper (II), respectively. The studied adsorbent had a high level of efficiency in the removal of heavy metals from aqueous solutions.

KEYWORDS: Magnetic Chitosan, Adsorption, Chromium, Copper

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Introduction

One of the most important toxic heavy metals is hexavalent chromium [Cr (VI)] and it enters water resources mostly through industrial effluents. Cr (III) is needed for natural carbohydrate metabolism of mammals, but Cr (VI) is highly toxic, carcinogenic, and

mutagenic and is considered to be of high risk for humans and animals.¹ Copper is another heavy metal that is harmful to human health. Cu (II) is toxic and can increase complications like anemia, gastrointestinal discomfort, and risk of lung cancer.² The recommended limits of Cr (VI) and Cu (II) in drinking water are 0.05 mg/l and 1 mg/l, respectively.³ There are various methods to remove heavy metals from water resources, including precipitation,

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solvent extraction, reverse osmosis, restoration, and adsorption. Among these methods, adsorption has been highly examined in the removal of heavy metals from aqueous solutions due to its simplicity and the availability of numerous adsorbing materials like nanomaterial, and carbonic, polymeric, and biological materials.^{1,2} Chitin is an abundant natural compound made of mono-polysaccharide derived from the skeleton of insects, crustacea shells, the cell wall of fungi, and snails. Through the deacetylation process of chitin, a type of poly-amino-saccharides called chitosan is formed.⁴

Chitosan has attracted the attention of scholars due to its properties like hydrophilic quality, biological compatibility, biodegradability, non-toxicity, good adsorption, and broad application range. As chitosan contains high amounts of amine and hydroxyl groups, it has a high adsorption capacity in both physical and chemical removal of different types of metals like copper, chromium, silver, platinum, and lead. In fact, chitosan has the capacity of bonding with heavy metals up to more than 1 mmol/g, which is much higher than that of active carbon.²⁴ The tendency of chitosan to adsorb heavy metals is highly dependent on chitosan source, degree of deacetylation, nature of the given metal, amount of crystallization, amine content, and pH of the solution. Combining chitosan with other materials is also extensively applicable in removing heavy metals.⁵ Chitosan in combination with alginate,⁶ cellulose,⁷ and clinoptilolite^{8,9} has been utilized to remove copper.

To remove chromium, magnetic chitosan with a capacity of 69.40 mg/g and chitosan/montmorillonite with adsorption capacity of 41.67 mg/g were utilized.¹⁰ However, to enhance the adsorption capacity of the adsorbents, much attention has been paid to the designing and synthesis of new adsorbents. Various types of hydrogels of magnetic chitosan have been prepared and utilized to treat contaminated water. For example, magnetic chitosan hydrogel

bed/polyvinyl alcohol with fast coagulation have been successfully used in the removal of color.¹¹ Magnetic chitosan complex-coated Fe₃O₄ is used to remove Alizarin Red (AR) from aquatic environments.¹² Recently, Wang et al. have studied the application of magnetic chitosan composites (MCCs) in the removal of heavy metals and colors.¹³ Compared to other adsorbents, processes using MCCs have a high capacity of adsorption, and rapid adsorption even in small amounts and short contact time.¹ The aim of the present study was to synthesize magnetic chitosan/Fe-Zr nanocomposite and investigate Cr (VI) and Cu (II) removal from aqueous solutions.

Materials and Methods

This experimental study was performed in Birjand University of Medical Sciences, Iran, (Environmental Chemistry Laboratory). The utilized materials were produced by Merck Company (Germany). The utilized chitosan had a deacetylation rate of 91.04% and was produced by Sigma-Aldrich Company (MO, USA). The utilized devices included Varian AA240 Atomic Adsorption Spectrometer (Varian Inc., Australia), PG T80+ UV/VIS spectrophotometer (PG Instruments Ltd, UK), fourier transform infrared spectroscope (FTIR) model Tensor 27 with spectrometry range of 400-4000 1/cm (Bruker Corporation, MA, USA), X-ray powder diffraction (XRD) model Panalytical Philips-XPERT-PRO (Philips, Amsterdam, Netherlands), scanning electron microscope (SEM) device model KYKY-EM3200, and vibrating sample magnetometer (VSM) (7400 series, Lake Shore Cryotronics Inc., Westerville, OH, USA).

Synthesis and Preparation of MCh/Fe-Zr Nanoparticles

Preparation of Magnetic Fe-Zr Nanoparticles

The most common method of producing magnetic nanoparticles is using chemical methods especially co-precipitation. In this method, to produce magnetic nanoparticles (Fe₃O₄), divalent and trivalent iron solutions are utilized along with an appropriate alkaline agent like soda or mixed ammonia in

controlled test conditions to produce a dark magnetic hydrophilic solution of water which contains magnetic particles with negative charge attached to the ions of alkaline material. In the present study, first Fe₂ and Fe₃ salts were dissolved with proportion of 1:2 in distilled water, and then, soda (1.5 mol) that was exposed to N₂ at 80 °C for 30 minutes was gradually added to it. To this solution, 30 CC of ZrOCl₂ 0.5 mol/l solution was added, and the mixture was stirred for 8 hours, and the resultant dark sediment was washed with deionizer water several times and dried at 70 °C.¹³

Preparation of Magnetic Fe₃O₄@Zr(OH)₄ Covered on the Surface of MCh/Fe-Zr Bead

First, 4 g chitosan was mixed in 400 ml citric acid with shaker for 1 hour. Then, 8 g magnetic Fe₃O₄Zr(OH)₄ nanoparticles was added to chitosan gel within 3 hours so that a slurry solution formed. NaOH 2 mol/l solution was added to this solution drop by drop with a glass syringe while stirring hard. The resulting macrosphere gel was allowed to settle in NaOH solution for 60 minutes, and then, the formed bead separated from NaOH was washed with deionizer water so that its pH was neutralized. In the next phase, the MCh/Fe-Zr synthesized adsorbent was dried using freeze dryer for 1 day.

Stock solutions (100 mg/l) of the chromium ion and copper under study were prepared by dissolving an appropriate weight of pure K₂Cr₂O₇ salt and copper nitrate in distilled water, respectively. Using HCL and NaOH solutions, pH was set at 0.1 mol. Afterwards, a certain dose of the adsorbent was added to the sample containing a certain density of metal ions, and the sample was mixed using a shaker for a certain time. To measure the density of the remaining Cr (VI), colorimetric analysis was conducted using a spectrophotometer at wavelength of 540 nm, and the remaining density of Cu²⁺ was measured using atomic adsorption device at wavelength of 324.8 nm. The studied parameters included pH (2-12), adsorbent rate (0.4-2 g/l), temperature (15.25

and 35 °C), concentration of heavy metals (0-10 mg/l), and contact time (0-720 minutes). All of the parameters were chosen according to previous studies. The balanced adsorption capacity of the adsorbent was measured using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (\text{Eq. 1})$$

where q_e is the amount of adsorbed ions per unit mass of the adsorbent, C_0 is the initial density of metal ions in the solution in mg/l, C_e is the balanced density of metal ions in the solution in mg/l, and m is the weight of the adsorbent in g. The adsorption performance and capacity of the adsorbent in adsorbing the heavy metal ions from water solutions were measured using the Langmuir and Freundlich isotherm models. The Langmuir model proposes that adsorption occurs in a single layer or in a constant number of adsorption sites, all adsorption sites have equal energy, and the structure of the adsorbent is homogenous.¹⁴ The Langmuir equation is provided bellow (Equation 2):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (\text{Eq. 2})$$

Where q_e is the number of the balanced metal ions in mg/g, q_m is the maximum superficial adsorption capacity in mg/g, C_e is the balanced density of metal ions in the solution in mg/l, and K_L is the Langmuir constant in l/mg that shows the superficial energy and integration tendency of joint sites. The Freundlich isotherm model describes adsorption in heterogeneous systems. This model is shown in the following equation (Equation 3):¹⁵

$$q_e = k_F C_e^{\frac{1}{n}} \quad (\text{Eq. 3})$$

Where q_e is the amount of the balanced metal ions in mg/g, C_e is the balanced density of metal ions in the solution in mg/l, K_F is the Freundlich constant which determines the adsorption capacity, and n is the Freundlich capacity that expresses the hardness or intensity of adsorption.

Results and Discussion

Fourier Transform Infrared Spectroscopy Spectrum

To observe the chemical structure of chitosan and the resulting changes in the composite of magnetic chitosan/Fe-Zr nanoparticles, FTIR technique was utilized. As indicated in figure 1, the presence of the down peaks proves the presence of the target functional groups in the structure of nanoparticles. Adsorbing peak of chitosan in 3459.9 was related to tensile proof of O-H, in 1415 to tensile proof of amide I and N-H, in 1339 to amide II and CH₃, 1272 to vibrating tensile proof of C-O carbonyl group, in 2993.2 to vibrating proof of C-H, in 570 to vibrating proof of Fe-O, in 1139.8 to tensile proof of C-O-C, and in 788 to vibrating proof of Fe-O available in chitosan. These changes in FTIR spectrum indicate that magnetic Fe₃O₄ nanoparticles have successfully been modified by chitosan.

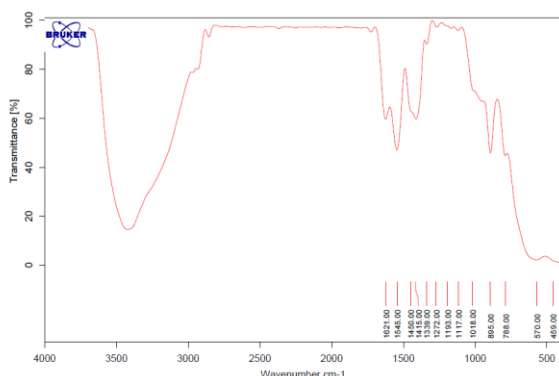


Figure 1. Fourier transform infrared spectroscopy (FTIR) spectrum of composite of MCh/Fe-Zr nanoparticles

Examining the Magnetic Properties of Composite of MCh/Fe-Zr Nanoparticles

Vibration sample was examined at room temperature to examine the magnetic properties of MCh nanoparticles using magnetometer. Magnetic moment in magnetic field in 300 K for MCh is presented in figure 2. The magnetic curve indicates that MCh is super-paramagnetic and its magnetic saturation is 25.037. The synthesized adsorbent is dispersed and can be dispersed

again. Moreover, these particles have good magnetic properties which refer to the potential application of magnetic adsorbent.

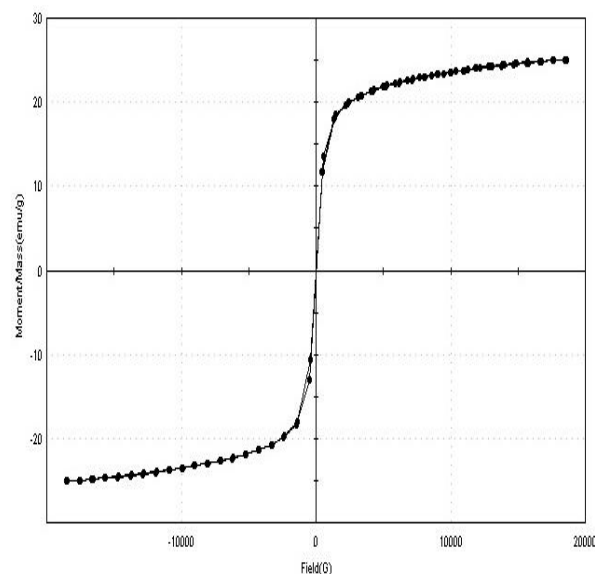


Figure 2. Vibrating sample magnetometer (VSM) curve of MCh/Fe-Zr nanoparticles

Examining the X-ray Diffraction Spectrum

The crystal structure of MCh composite is presented in figure 3. XRD patterns indicated certain peaks for MCh at 2 θ , 30.313 (2 2 0), 35.707 (3 1 1), 43.401 (4 0 0), 53.85 (4 2 2), 57.41 (5 1 1), 63.05 (4 4 0), 75.64 (6 2 2), 32.155 (0 1 1), 36.613 (6 1 1), 57.33 (0 3 0), and 63.17 (18 1 1). This is in agreement with data presented by the Inorganic Crystal Structure Database (ICSD). XRD indicated that modification of chitosan-zirconium on magnetic nanoparticles has no effect on changing the phase of Fe₃O₄. The results also indicated high crystallization of MCh/Fe-Zr nanoparticles.

Examining Scanning Electron Microscope Images

The shape and size of MCh/Fe-Zr nanoparticles composite were determined using SEM. Figure 4 illustrates SEM images of the nanoparticles that have irregular shapes, spherical particles of Fe₃O₄ attached to the surface of the MCh-Zr particles with high density, and the size of the synthesized nanoparticles ranging from 31.9 to 140.4 nm.

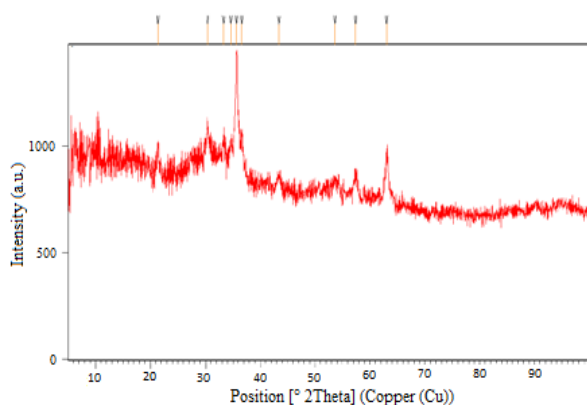


Figure 3. X-ray powder diffraction (XRD) spectrum of MCh/Fe-Zr nanoparticles composite

The Effect of Initial pH of the Solution on the Removal Rate of Cr (VI) and Cu (II)

The impact of initial pH of the solution in the range of 2-12 was investigated on the adsorption rate of metal ions of Cr (VI) and Cu (II) by the composite of MCh/Fe-Zr nanoparticles (Figures 5 and 6). It was observed that the highest adsorption rate for Cr (VI) ions using the proposed adsorbent in pH of 4 was 99.52% and for Cu (II) in pH of 9 was 97.72%.

Adsorption of heavy metal ions is highly reliant on protonation and non-protonation of amine and carboxylic groups available in chitosan nanoparticles.¹⁶ As pH of the solution drops, amine groups existing in the

composite of chitosan nanoparticles are protonated to different degrees. Therefore, the number of available sites for chelating of metal ions will decrease, which in turn causes the removal of electrostatic metal cations.¹⁷ However, in high pH, the available ligands in the adsorbent like COO⁻ enhance the density of negative charge on the surface of the ligands. Therefore, electrostatic adsorption of metal ions with positive charge will increase on the surface of the ligands and the rate of adsorption will rise. Due to the concentration of OH⁻ ions in pH rates of higher than 9, deposition of metal ions is observed in the form of hydroxides and causes increase in the rate of adsorption.¹⁸

The effect of pH on adsorption of metal ions using chitosan and its derivatives has been investigated in different studies. Vasconcelos et al. reported pH of 6 as the optimal rate in experiments of adsorption of Cu (II) ions using cross-linked chitosan.¹⁸ Alejandra Perez-Fonseca studied the removal of Cr (VI) using the composite of chitosan-covered agave fiber and high-density polyethylene (HDPE) wastes.²⁰ The optimal pH reported in their study was 4 and the maximum capacity of Cr (VI) adsorption was 200 mg Cr (VI)/g.²⁰

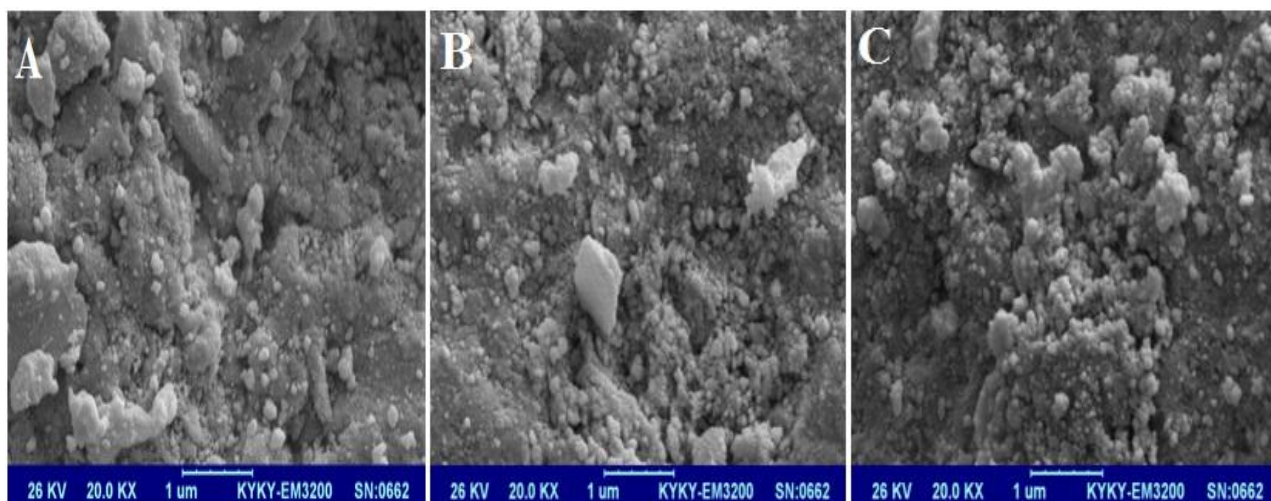


Figure 4. A: Scanning electron microscope image related to composite of MCh/Fe-Zr nanoparticles before adsorption of metal ions, B: scanning electron microscope image related to composite of MCh/Fe-Zr nanoparticles after adsorption of copper, C: scanning electron microscope image related to composite of MCh/Fe-Zr nanoparticles after adsorption of chromium

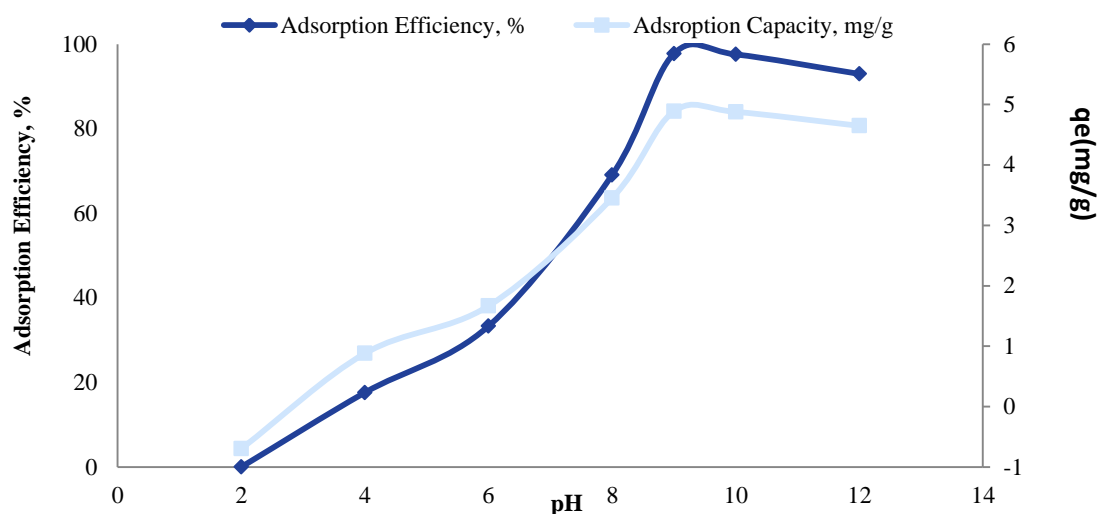


Figure 5. Comparison of the effect of pH changes on removal efficiency of copper using MCh/Fe-Zr nanoparticles

(Cu^{2+} = 5 ppm, speed = 300 rpm, time = 30 minutes, temperature = 25 °C, and adsorbent dose = 1 g/l)

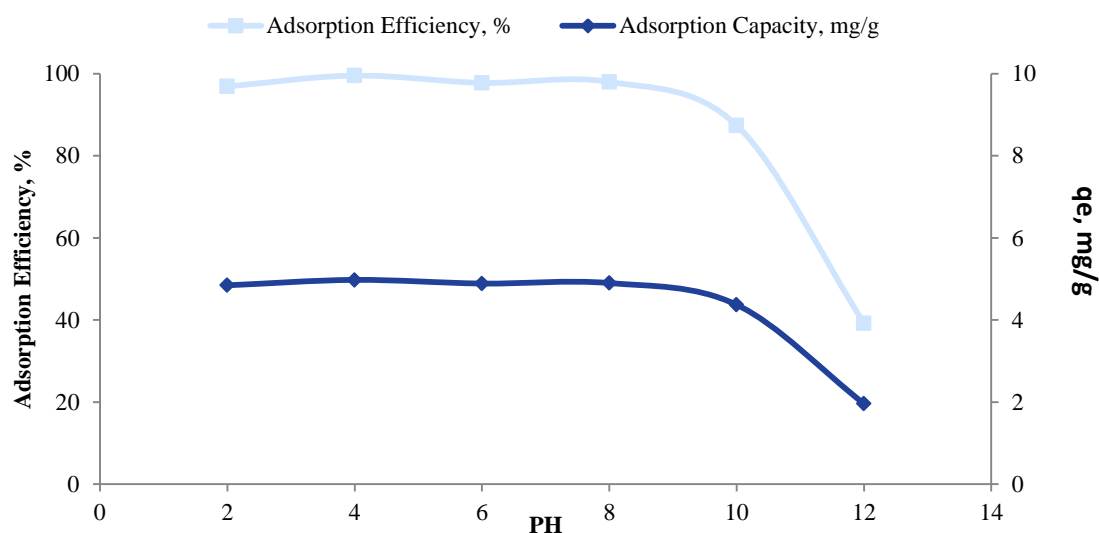


Figure 6. Comparison of the effect of pH changes on removal efficiency of copper using MCh/Fe-Zr nanoparticles (Cr⁶⁺ = 5 ppm, speed = 300 rpm, time = 30 minutes, temperature = 25 oC, and adsorbent dose = 1 g/l)

Tingyi Liu et al. investigated the removal of Cr (VI), Pb (II), Cd (II), and Cu (II) from industrial wastewater.²⁰ They concluded that the rate of Cr (VI) removal increases as pH decreases, and the removal efficiency of copper and lead increase as pH increases.²¹

Examination of the effect of the dose of MCh/Fe-Zr nanoparticles composite on removal rate of Cr (VI) and Cu (II) ions

Examination of the effect of adsorbent amount on the adsorption process of Cr (VI) and Cu

(II) metal ions by the composite of MCh/Fe-Zr nanoparticles was carried out to determine the effective dose of the adsorbent. Considering the minimum amount of the adsorbent that has the highest rate of adsorption, the range of 0.4-2 g/l of adsorbent dosage was determined in the initial concentration of 10 mg/l. Figures 7 and 8 indicate the effect of adsorbent amount on the removal percentage of the ions. For Cr (VI), as the amount of the adsorbent increased from 0.4 to 2 g/l, the removal

percentage increased from 63.06% to 96.22% and the adsorption capacity decreased from 7.88 to 2.4 g/g, respectively. Yu et al. conducted a study of magnetic chitosan-Fe hydrogel in the removal of Cr (VI) and concluded that as the amount of magnetic Fe_3O_4 nanoparticles rises, the adsorption capacity drops.²² They also found that the adsorption capacity of Cr (VI) after contact time of 30 minutes was 144.9 mg/g.²² For Cu (II), the maximum removal efficiency obtained was 97.43 in adsorption dose of 0.4 g/l. As the amount of the adsorbent rises, the number of available adsorption sites increases, which enhances the amount of adsorbed metal. Decreased adsorption capacity and increased amount of adsorbent were mostly due to the fact that the adsorption sites, during the adsorption process and collection of particles, are not saturated in high amounts of adsorbent which results in surface area reduction.²⁴ In real applications, the minimum amount of the adsorbent that can respond to the requirements should be selected. In the study conducted by Dragan et al., the chitosan/clinoptilolite composite was used to remove copper ions, and the adsorbent amount in 100 mg/l was 2 g/l. under these conditions, the adsorption capacity was 719.39 mg/g.⁸

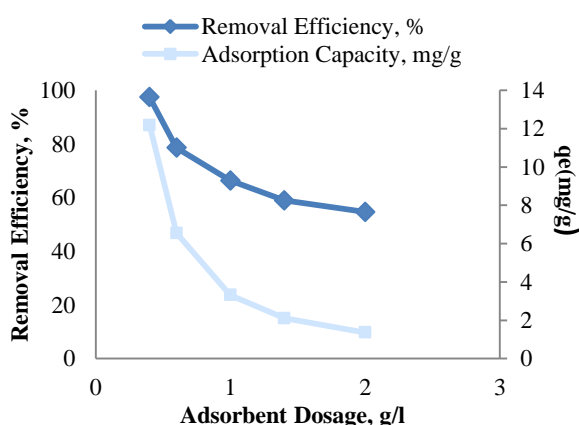


Figure 7. Comparison of the effect of adsorbent dose changes on the removal efficiency of copper using MCh/Fe-Zr nanoparticles (density Cu^{2+} = 5ppm, speed = 30 rpm, time = 30 minutes, temperature = 25 °C, and pH = 9)

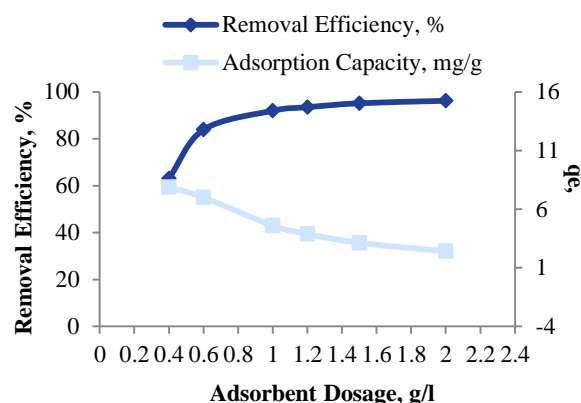


Figure 8. Comparison of the effect of adsorbent dose changes on the removal efficiency of chromium using MCh/Fe-Zr nanoparticles

(density Cr^{6+} = 5ppm, speed = 300 rmp, time = 30 minutes, temperature = 25 °C, and pH = 4)

Examination of the Effect of the Initial Concentration of Metal Ions on Adsorption Rate

The removal percentage of Cr^{6+} and Cu^{2+} using MCh/Fe-Zr nanoparticles under the effect of the initial concentration of metal ions ranging between 2 and 10 g/l was investigated for Cr^{6+} in pH of 4 and the adsorbent amount of 2 g/l, and for Cu^{2+} in pH of 9 and the adsorbent amount of 0.4 g/l. Figures 9 and 10 indicate the effect of the initial concentration of metal ions on removal percentage and adsorption capacity. As the initial concentration of the metal ions increased, the removal percentage dropped.

An increase in the initial concentration of metal ions causes gradient driving force of concentration to rise and enhance adsorption capacity. At low concentrations, all metal ions react with adsorption sites in the adsorbent; however, there are still free adsorption sites on the surface of the adsorbent. In high concentrations of metal ions, each active adsorption sites is surrounded by more metal ions; therefore, adsorption capacity increases as more adsorption sites are occupied. In higher concentrations, adsorption capacity is almost fixed, which is due to the saturation of adsorption sites.^{18,19} Swayampakula et al. studied the removal of copper ions and reported similar results.²⁴ They found that as the concentration of ionic solution increased

from 50 to 200 mg/l, adsorption capacity also increase.²⁴ They reported a maximum adsorption capacity of 196 mg using 5 g/l adsorbent and time of 4 hours.²⁴ Zareie et al. studied the removal of copper using nano-chitosan and reported an increase in concentration from 10 to 100 mg/l, a decrease in removal efficiency, and 26.88 mg/g maximum removal capacity in concentration of 100 mg/l.²⁵

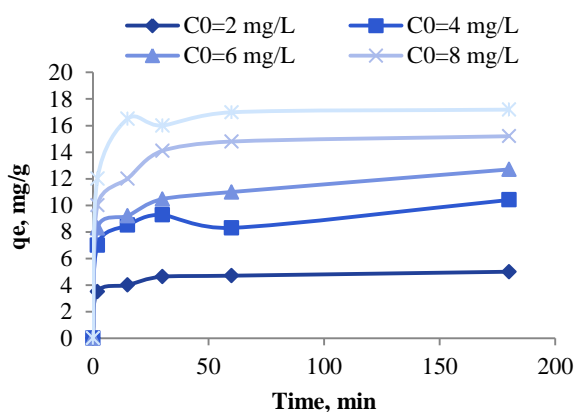


Figure 9. The effect of time and initial concentration on adsorption of copper on MCh/Fe-Zr nanoparticles in temperature 25 °C, adsorption dose of 0.4 g/l, speed of 300 rpm, time of 300 minutes, and pH of 9

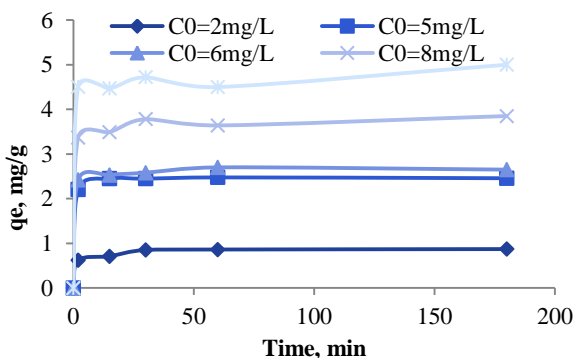


Figure 10. Comparison of the effect of time and initial concentration on adsorption of chromium on MCh/Fe-Zr nanoparticles in temperature of 25 °C, adsorption dose of 2 g/l, speed 300 of rpm, time of 60 minutes, and pH of 9

Adsorption Isotherm Models

As seen in figure 11 and table 1, the empirical data are in agreement with both equations. Therefore, it can be concluded that the surface of the adsorbent is homogeneous, and superficial adsorption occurs both physically and chemically.

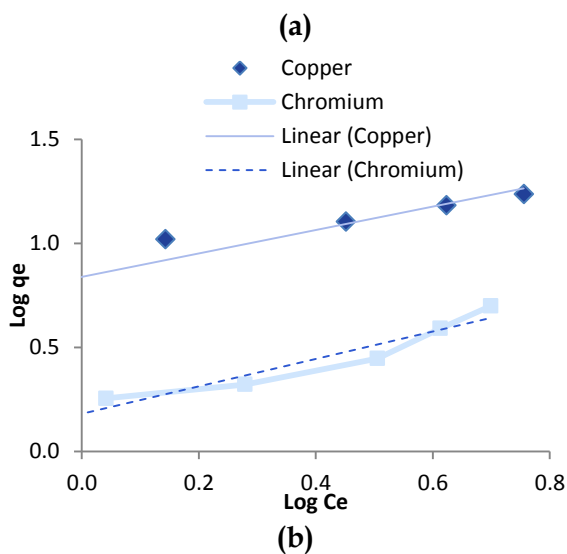
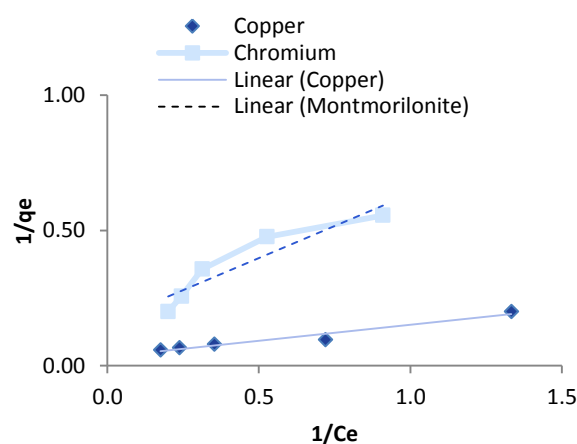


Figure 11. Langmuir (a) and Freundlich (b) adsorption isotherms of Cr and Cu ions using MCh/Fe-Zr nanoparticles in adsorbent dosage of 0.4 g/l for copper and 2 g/l for chromium, initial concentration of metal ions of 2-10 mg/l, temperature of 25 °C, Cu solution pH of 9 and Cr solution pH of 4

Table 1. Resulting parameters from adsorption isotherm models

Metal ion	Freundlich			Langmuir		
	K_f (l/mg)	n	R^2	K_1 (l/mg)	q_{max} (mg/g)	R^2
Cr ⁶⁺	1.52	1.52	0.91	3.99	6.19	0.87
Cu ²⁺	6.91	1.78	0.91	0.28	30.07	0.95

Conclusion

In this study, the adsorption of Cu (II) and Cr (VI) ions onto MCh/Fe-Zr nanoparticles was studied. The effects of adsorption parameters, such as adsorbent dosage, pH, metal ion concentration, and adsorption isotherm, were investigated. The results indicate that due to having large superficial area and possessing amine and carboxyl functional groups, chitosan nanoparticles are effectively able to remove the metal ions of chromium and copper. Factors like pH, adsorption amount, and initial concentration of metal ions influence the maximum adsorption capacity. The maximum adsorption capacity of Cr⁶⁺ was obtained in pH of 4, adsorbent amount of 2 g/l, and concentration of 10 mg/g. The adsorption capacity of copper was the same in pH of 9, adsorbent amount of 0.4 g/l, and concentration of 10 mg/g.

Conflict of Interests

Authors have no conflict of interests.

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