Scientific paper

Adsorption of Cr (III) and Cd (II) Ions using Mesoporous Cobalt-Ferrite Nanocomposite from Synthetic Wastewater

Iman Khoshkerdar[1] and Hossein Esmaeili[2,*]

[1] *Department of Chemical Engineering, Dashtestan Branch, Islamic Azad University, Dashtestan, Iran*

[2] *Department of Chemical Engineering, Bushehr Branch, Islamic Azad University, Bushehr, Iran*

* *Corresponding author: E-mail: esmaeili.hossein@gmail.com & esmaeili.hossein@iaubushehr.ac.ir*

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Abstract

In this study, cobalt-ferrite nano-composite (CFNC) is used to adsorb chromium and cadmium ions from synthetic wastewater. Adsorptive characteristics of CFNC are determined by various analysis including SEM, FTIR, VSM and BET. Also, effect of different parameters such as solution pH, buffer volume, electrolyte dose, the initial ion concentration, contact time, the adsorbent dose and temperature were studied on adsorption process. The results showed that the maximum recovery of Cd(II) and Cr(III) ions were determined as C0 = 20 mg/L, t = 50 min, T = 25 °C, CFNC dosage = 20 g/L, and pH = 7 (for Cr(III)) and 6 (for Cd(II)). In these conditions, the amount of 100% Cr(III) and Cd(II) were removed from the aqueous solution. Also, the equilibrium study showed that the adsorption process followed the Langmuir model and the maximum adsorption capacity for Cr(III) and Cd(II) ions were obtained 217 and 303 mg/g, respectively which show very high adsorption capacities. In addition, adsorption kinetics showed that the pseudo first-order kinetic model was better than the pseudo second-order kinetic model. Moreover, thermodynamic studies showed that the adsorption process was possible, spontaneous and endothermic.

Keywords*:* Nano-composite; cobalt-ferrite; heavy metals; synthesis wastewater

1. Introduction

After fast growth of population and industrialized societies, releasing heavy metals in water ecosystem is one of the most important concerns of the environment. Although most of the noxious chemical materials when they are in the atmosphere after some years are less hazardous, when pollution is made by heavy metals ions, removing them are very difficult and maybe gradually accumulated and enter to our body throughout food chains.[1,2] Important heavy metals such as cadmium, zinc, chromium, lead, and copper penetrate to the water throughout industrial wastewater. Cr (III) ions are in modern industrial as leather and oil purification and also Cd (II) ion is widely used in various industries like as metallurgy, dye industry, and making battery, so that wastewater of these industries is polluted by a lot of Cr (III) and Cd (II) ions.[3] Environmental protection agency (EPA) and world health organization (WHO) identify the admissible value of Cr (III) and Cd (II) ions in drinking water as 0.1 and 0.003 mg/L, respectively.[4,5] In oxidation state, Cr (III) is completely insoluble, and then it deposits easily. This ion is less detrimental in nature, but a high concentration of chromium ion (III) is hazardous.[6] Increasing heavy metals concentration in water cause that health on a human is in danger. For example, the presence of heavy metal Cr (III) in the body can cause some illness as skin illness, liver, lung, kidney, brain failure, pancreas, and injuring bowels. Also, Cd(II) can cause some injuries to kidneys, tay-tay, increased blood pressure, and emphysema.[7,8] Therefore, suitable and cheap methods to remove these ions from water are essential.[9,10] There are various methods such as chemical precipitation, ionic exchange, membrane filtration, reverse osmosis, electrical coagulation, solvent extracting and adsorption to recovering and removing ion of heavy metal and pollutions from synthesis wastewater.[11,12] Adsorption is one of the most common methods to remove heavy metals ion due to high efficiency, easy recovery and its cheap cost. Nevertheless, adsorption capacity, selectivity, equilibrium time and recovery depend on characteristics of sorbent materials.

Therefore, recently researches about applications of new materials such as nano-adsorbents are focused on adsorption ion of heavy metals from aqueous solutions.[13,14] Nano-structured adsorbents have strong effects for treatment of contaminants from wastewaters due to a large specific surface area, high adsorption capacities and short diffusion paths.[15] However, it is difficult for recovery of nano-sized adsorbents from aqueous media.[16] The application of nanostructured magnetic adsorbents (such as; Fe_3O_4 nano-particles) is a new technology which has recently received important attention; because of their potency to be easily separated from wastewater using an external magnetic field after adsorption, in this way, their reconstruction and reuse are essential. For practical application of nanoparticles in various potential fields, their surface modification is vital.[17] To improve the magnetic features of adsorbents, we can combine magnetic nanoparticles with different materials such as Co, CaO, MgO and etc. Different methods such as impregnation, ball milling and chemical co-precipitation have been expanded to combine them together to produce magnetic nano-composite. Among them, chemical co-precipitation is the most important method, because of simple procedure and no need of special chemicals.[14] Until now, there are a lot of research to remove heavy metals by using composite that we can note some of them such as CaO/Fe_3O_4 magnetic composite,[14] oxide graphite nanocomposite based on polymer,[18] chitosan/Sulfydryl-functionalized graphene oxide composites,[19] nanofibre membrane of chitosan/hydroxyapatite composite,[20] magnetized nanocomposite coated with manganese oxide,[21] bentonite composite/reformed poly acryl amide by ammines acids of humic acids[22] that show very high efficiencies.

The purpose of this study is to investigate the effect of cobalt-ferrite nanocomposite (CFNC) as a magnetic adsorbent for the removal of chromium (III) and cadmium (II) ions from synthesis wastewater. Cobalt-ferrite ($CoFe_2O_4$) is regarded as an attractive magnetic material, because it has moderate saturated magnetic, terrific chemical stability and mechanical strength.[23] CFNC is used to destroy environmental various contaminants as sorbent and photo-catalyzer.[24] Hence, the effect of important parameters like pH, type and volume of buffer, type and concentration of the electrolyte, initial concentration, contact time, sorbent dose and temperature on adsorption process is investigated. Also, kinetic, equilibrium and thermodynamic behaviors of the adsorbent were studied.

2. Material and Methods

2. 1. Preparation of Solutions

To prepare stock solutions containing chromium (III) and cadmium (II) ions sequentially $Cr(NO_3)_3$ and $3CdSO_4.8H_2O$ with the weight of 0.228 and 0.37 g were added to deionized distilled water to reach the volume of 1000 mL. Then, solutions with lower concentrations were made by dilution of these solutions.

Also, the buffer solution was used to keep the pH of the solutions at the optimized pH. To this end, four buffers such as citrate, phosphate, maleic acid and potassium hydrogen phthalate was used. To prepare buffer solutions of maleic acid, citrate, phosphate and potassium hydrogen phthalate in a pH value of 7, the amounts of 1.16, 2.14, 138 and 2.04 g of maleic acid, sodium citrate and potassium hydrogen phthalate salts were added to the 100 mL balloon containing distilled water and the pH values was regulated by NaOH solution (1 molar).

2. 2. Synthesis of CFNC

A mixture of 25mL of $Fe(NO_3)_3$ with the molarity of 0.4 Mol L^{-1} and 25 mL of $Co(NO^3)^2$ with the molarity of 0.2 Mol L^{-1} was produced and the mixture was stirred with a magnetic stirrer and NaOH solution (3 Mol L^{-1}) was added to the solution until the mixture pH reached 11–12. Then, 0.6mL of olive oil was added to it as a surfactant and was heated at 80 °C for 1 h. The obtained black sediment was separated from the solution using a magnet due to a magnetic property and washed with water and ethanol several times to neutralize its pH. After pulverizing, a soft powder was obtained.[25]

2. 3. Analysis Methods

The concentration of Cr (III) and Cd (II) ions after adsorption process was identified by flame atomic absorption instrument which was equipped with air-acetylene fuel (PLUS SPECTRAA- 10, VARIAN). Also, Scanning Electron Microscopy (SEM) (TESCAN VEGA II, Czech Republic), Fourier Transform Infrared (FTIR) (Perkin-Elmer, Germany), Vibrating Sample Magnetometer (VSM) (Lakeshore VSM 7410, Germany) and Brunauer–Emmett–Teller (BET) (ASAP 2020, USA) analyzers were used to investigate the change of sorbent surface, functional groups in sorbent, magnetic characteristics and specific surface area before and after adsorption process.

2. 4. Batch Experiments

First, 20 mg of CFNC and 10 mL of surfactant were placed into a beaker to reduce surface tension and more adsorption of heavy metals on the sorbent surface[26] and placed on the magnetic stirrer for 3 min until nano-particles distribute uniformly in solution. Produced mixture was transferred to a 100 mL balloon, and then 20 mL of cadmium (II) and chromium (III) solution with the concentration of 100mg/L was added to that. Then, 0.5 mL of hydroxide sodium (0.1 Mol L^{-1}) was added to the solution and finally, 1.5 mL of the maleic acid buffer with the pH value of 6 was added to the solution and the balloon was filled to the marked line with double distilled water. After shaking balloon and unifying solution, the content of balloon was transferred to a beaker with the working volume of 200 mL. Then, to do adsorption process, this solution was located on the magnetic stirrer and the specified value of the adsorbent was added to the solution. After adsorption process, this solution was filtered by Whatman filter paper (No. 42) and centrifuge for 2 min and it then was moved to a test tube. Eventually, the concentration of metal ions in the solution was measured.

2. 5. Desorption Experiment and Reuse of Adsorbent

To study desorption process, 20 mg of magnetic nanocomposite of cobalt-ferrite, 10 mL surfactant (Triton X-100), 0.5 mL solution of 0.1 Mol L^{-1} chloride sodium, and 20 mL of cadmium (II) and chromium (III) solution (with the concentration of 100 mg/L) were added to the 100 mL balloon. After that 1.5 mL of maleic acid buffer with pH of 6 for chromium (III) and pH of 7 for cadmium (II) was added until its volume reached to the mark line (100 mL). After shaking the balloon, the contents of the balloon were transferred to a 200 mL beaker. To perform desorption process, this solution was stirred at different times. Then, the solution filtered by filter paper and was centrifuged for 2 min and it then was transferred to a test tube and concentration of metal ions in final solution were measured by flame atomic absorption apparatus. After that, achieved sorbent was washed with 30 mL acetone/methanol and the aforementioned steps were repeated again on the adsorbent with a solution consist of same cadmium (II) and chromium (III) ions.

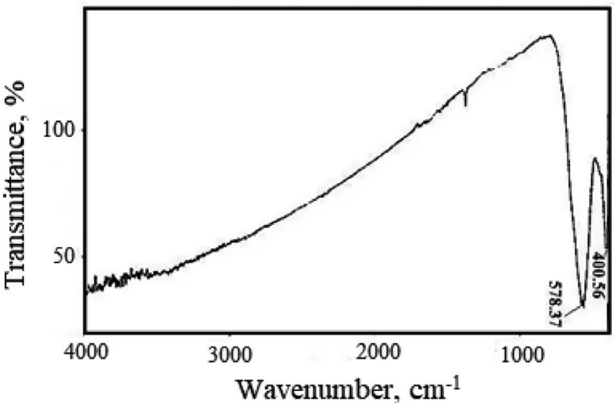
3. Results and Discussion

3. 1. Characteristics

In Fig. 1, the morphology of the adsorbent surface has been shown using SEM. Fig. 1-A shows nano-particles of cobalt-ferrite that they are the as disordered polygon and are accumulated, that the reason of accumulating assign to the magnetic character of nano-particles. The pores and empty spaces are clearly seen in the surface of CFNC. The presence of small grains of magnetic nano-particles is indicating the porous structure and high adsorption capacity. Also, the presence of a lot of pores with disordered sizes in the surface of cobalt-ferrite is suitable to take cadmium (II) and chromium (III) heavy metals ion. Additionally, the morphology and the pores of the adsorbent surface after adsorption of metal ions are shown in Fig. 1-B and C.

Also, Fig. 2 shows FT-IR spectra and functional groups of synthesized cobalt-ferrite at different wavenumbers. As shown in this Fig., two vibration peaks of 578 and 406 cm^{-1} exist that first peak is powerful and related to tension vibration of $Fe^{+3}O^{-2}$ in quadrilateral situation and peak with less intensity assign to tension link $Fe^{3+}O^{2-}$ in octagon situation. As a result, FTIR spectra can prove structure of reverse spinel in synthesized cobalt-ferrite.

Fig. 2. FTIR analysis of CFNC



Additionally, VSM analysis of CFNC is shown in Table 1. The amount of the saturation magnetization (M_s), residual magnetism (M_r) and coercivities (H_c) are 50.5, 23.45 and 848.09 emu g^{-1}, sequentially. The amount of saturated magnetism is based on particles size and is de-

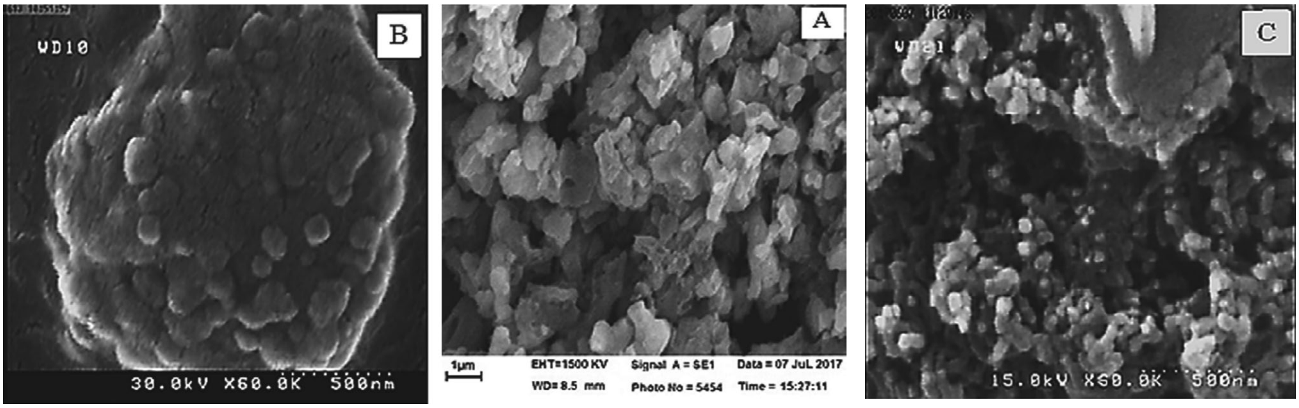


Fig. 1: SEM images (A) CFNC before adsorption of metal ions on a scale of 500 nm, (B) adsorbent after adsorption of chromium(III) ions on a scale of 1 µm, (C) adsorbent after adsorption of Cadmium(II) ions on a scale of 500 nm.

creased with particle size reduction.[27] The values of M_s and M_r are high due to the presence of magnetic properties. Achieved values showed that this material can separate from solution easily by external magnetic force. Also, considering achieved values from Table 1, CFNC is hard based on the type of magnetic material.

Table 1: VSM analysis of CFNC

Hc (Oe)	Mr (emu g^{-1})	Ms (emu g^{-1})
848.1	23.5	50.5

Eventually, the specific surface area of the adsorbent was measured by BET analysis. The BET results are shown in Table S-1. As can be seen in this table, the specific surface area of cobalt-ferrite adsorbent is obtained 17.84 m^2/g and the average diameter of pores achieved 7.53 nm which shows this adsorbent is mesoporous.

3. 2. Effect of pH

Solution pH has a crucial role in the adsorption process.[28,29] Figure 3 shows the effect of pH on chromium (III) and cadmium (II) ion adsorption using CFNC. At low pH values, H$^+$ ion concentration is much more than the metal ions, in this case, H$^+$ ion competes with heavy metal ions to locate on active sites of adsorbent, and creates repulsive force by locating on the adsorbent surface which prevents locating ions on the adsorbent surface and adsorption efficiency decreases. By increasing pH, H$^+$ ion concentration decreases in solution and therefore enough surfaces create to locate heavy metal ions. Increasing solution pH to pH near to 7, the value of the hydrogen ion (H$^+$) into the aqueous solution is decreased and concentration of hydroxide (OH$^-$) will increase. On the other hand, by increasing pH, accessibility of heavy metal ion of chromium (III) and cadmium (II) ion to active sites is increased and therefore adsorption efficiency has been increased. So, adsorption of chromium (III) and cadmium (II) ions sequentially at pH value of 7 and 6 were optimized with 95.3% and 93.1%. At pH larger than optimized values, it is shown that hydroxide ion (OH$^-$) in solution is precipitated as insoluble and cause to decrease of adsorption efficiency.

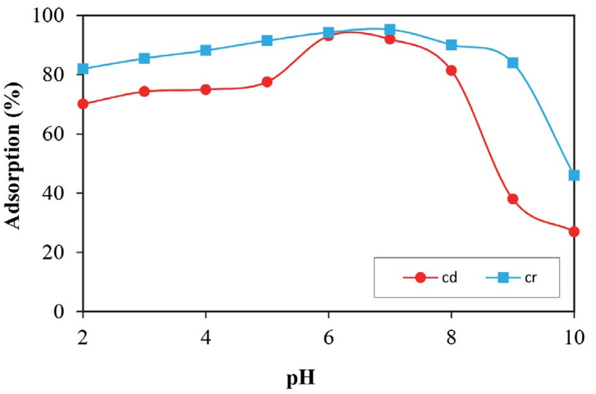


Fig. 3: Effect of pH on chromium (III) and cadmium (II) ion adsorption using CFNC

3. 3. Effect of Buffer Type and Volume

The buffer plays an important role to keep the pH of the solution at a constant value.[30] Effect of different buffers such as citrate, phosphate, maleic acid, potassium hydrogen phthalate was studied on adsorption efficiency of chromium (III) and cadmium (II) ion and results are shown in Table S-2. Among the four types of buffers, it is shown maleic acid has highest adsorption efficiency to chromium (III) and cadmium (II) ion sequentially with 96.4% and 95%, while potassium hydrogen phthalate has the least adsorption efficiency to chromium (III) and cadmium (II) ion with 87.4% and 88.9%. Reducing the adsorption efficiency of Cr (III) and Cd (II) ions by different buffers can be attributed the formation of Cr (III) and Cd (II) ions deposition with anions in the buffer structure.

To determine an optimum volume of maleic acid, various amounts of this buffer were studied in the range of 0, 1, 1.5, 2, 3 and 4 mL based on adsorption efficiency of chromium and cadmium. In Fig. 4, effects of buffer volume on chromium (III) and cadmium (II) ion adsorption have been shown by CFNC. It is seen that by increasing volume of maleic acid, adsorption efficiency of chromium (III) and cadmium (II) ions will be increased. In volume higher than 1.5 mL of maleic acid, the value of adsorption is not change for cadmium ion but efficiency value of adsorption for chromium ion is decreased. Therefore, buffer volume of 1.5 mL is obtained from aqueous solution as optimum value to chromium (III) and cadmium (II) ion adsorption.

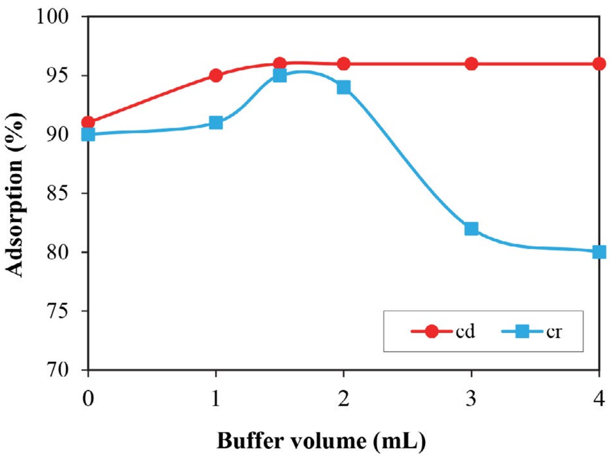


Fig. 4: Effect of buffer volume on removal of chromium (III) and cadmium (II) ions from aqueous solution using CFNC

3. 4. Effects of Electrolyte Type and Concentration

In this study, effects of various electrolytes such as $CaCl_2$, NaCl, KCl, and $NaNO_3$ were investigated on adsorption efficiency of chromium (III) and cadmium (II) ions. The results are given in Table S-3. Among the various electrolytes, NaCl, KCl, and $NaNO_3$ electrolytes had a better adsorption efficiency to remove chromium (III) and cadmium (II) ions with single capacity cations than $CaCl_2$ with bivalency cations. The difference in adsorption efficiency is due to capacities difference between Ca^{2+}, K^+ and Na^+ electrolytes with chromium (III) and cadmium (II) ions existed in solution to fill the active sites. The displacement of ions on active sites cause a competition between them and it reduces adsorption efficiency. Among these materials, NaCl was chosen as a better electrolyte. On the other hand, ions of NaCl, make chromium (III) and cadmium (II) ions to accumulate and from this way increase adsorption efficiency of chromium (III) and cadmium (II) heavy metals ion on the adsorbent.

After determining types of electrolyte, effects of electrolyte NaCl concentration on adsorption efficiency of chromium (III) and cadmium (II) cations were studied in the range of 0.0004 to 0.001 molar that the result has been shown in Fig. 5.

As seen in Fig. 5, after concentration of 0.001, the slope of the Fig. 5 is reduced by increasing concentration of electrolyte NaCl. In fact, by increasing concentration of electrolyte NaCl in aqueous solution, increasing ionic strength cause increasing dissolution of solvent in aquatic phase and as a result adsorption efficiency is decreased. Therefore, the molar concentration of 0.001 is obtained as an optimum concentration for electrolyte NaCl.

3. 5. Effect of Metal Ion Concentration

To investigate the effect of initial ion concentration, adsorption of Cr (III) and Cd (II) ions was studied by CFNC sorbent in the concentration of 10, 20, 30 and 50 mg/L. Fig. 6 shows the effect of initial ion concentration of chromium and cadmium using CFNC sorbent. The other conditions are including an adsorbent dose of 20 g/L, contact time of 50 min and temperature of 25 °C and pH for Cr (III) = 7 and for Cd (II) = 6. Increasing concentration from 10 to 20 mg/L, adsorption efficiency of chromium (III) and cadmium (II) ion has been increased. Because increasing the concentration of chromium (III) and cadmium (II) ions creates the required force for mass transfer between the solid and liquid phase in the solution. For concentrations greater than 20 mg/L, adsorption efficiency of chromium (III) and cadmium (II) ion is changed very slightly because of a high amount of chromium (III) and cadmium (II) ion to saturate active sites on the adsorbent surface of CFNC. Therefore, at low concentrations of metal ion, adsorption process is equilibrated sooner and initial concentration of 20 mg/L for chromium (III) and cadmium (II) ions was optimized sequentially by adsorption efficiency of 91% and 93%.

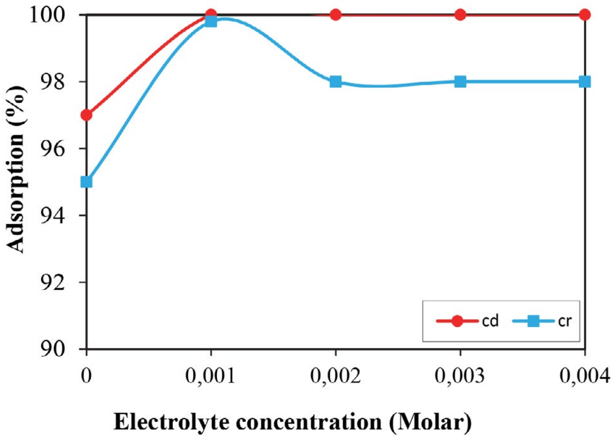


Fig. 5: Effect of electrolyte concentration on removal of Cr (III) and Cd (II) from aqueous solution using CFNC

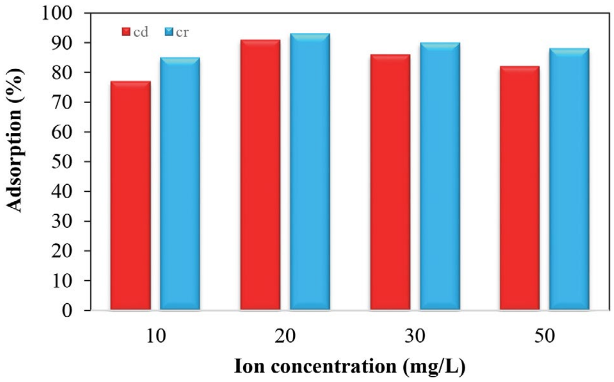


Fig. 6: The effect of initial concentration of cadmium and chromium in conditions in terms of (cadmium pH: 6, chromium pH: 7, adsorbent dosage 20 g/L, time 50 min and temperature 25 °C)

3.6. Effect of Contact Time

The contact time is one of the most important factors that plays an important role in batch adsorption tests.[14] The removal efficiency of chromium (III) and cadmium (II) ions by CFNC in contact period times 10–80 min has been shown in Fig. 7. As can be seen, adsorption efficiency is fast in the beginning and after that process goes forward slowly and after 50 min, the adsorption efficiency remained constant. Increasing adsorption efficiency at early times (time <50 min) is due to the availability of sufficient surfaces and the number of adsorbent unsaturated active sites.[10] At this time, the removal efficiencies of Cr(III) and Cd(II) ions were 100%. So, the contact time of 50 min is selected as optimum time.

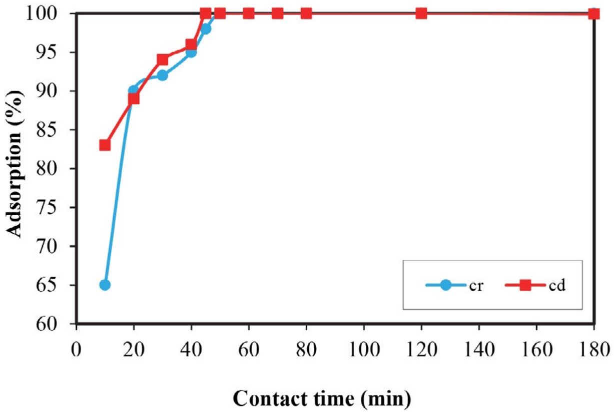


Fig. 7: The effects of time on the cadmium and chromium in conditions in terms of (cadmium pH: 6, chromium pH: 7, initial concentration of metal ions 20 mg/L, adsorbent dosage 20 g/L and temperature 25 °C)

3. 7. Effect of Sorbent Dose

Another important parameter in adsorption processes is the adsorbent dose. This parameter determines the potential and capacity of an adsorbent to adsorb metal ions from aqueous solutions.[14] Effect of CFNC dose is studied in conditions: pH chromium ion (III):7 and cadmium ion (II): 6, initial concentration of metal ions of 20 mg/L, contact time of 50 min and temperature of 25 °C in adsorbent doses of 10, 15, 20, 25 and 30 g/L and results can be seen in Fig. 8. As shown in this Fig., in an adsorbent dose range of 10–15 g/L, adsorption efficiency of chromium (III) and cadmium (II) ion is low due to the lack of sufficient active sites to replace heavy metal ions. On the other hand, adsorption efficiency was increased by increasing sorbent dose of CFNC. At concentrations higher than 20 g/L, adsorption efficiency was not changed. Therefore, an adsorbent dose of 20 g/L was reported as the optimum value. In optimum adsorbent dose, the removal efficiency was obtained 100% for both metal ions.

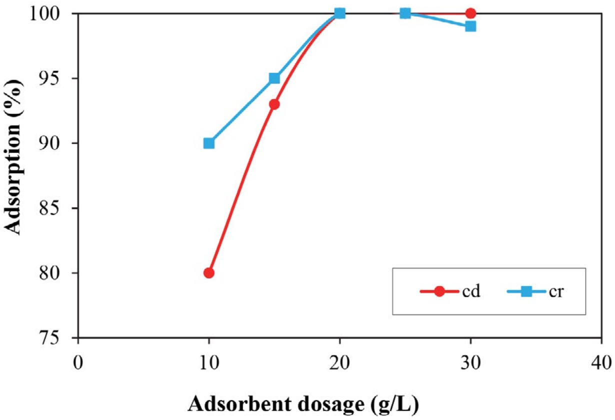


Fig. 8: The effect of cobalt-ferrite magnetic nanocomposite on the percentage remove of cadmium and chromium in conditions in terms of (cadmium pH: 6, chromium pH: 7, initial ion concentration 20 mg/L, time 50 min and temperature 25 °C)

3. 8. Effect of Temperature

To investigate the effect of temperature on adsorption of chromium (III) and cadmium (II) ions by CFNC sorbent, various temperatures such as 25, 30, 40, 50 and 60 °C were checked that the results have been drawn in Fig. 9. Regarding Fig. 9, adsorption efficiency of metal ions was decreased with increasing temperature due to the endothermic adsorption process and destructing active sites. Also, it may be due to the high tendency of metal ions to separate from the adsorbent and release in the solution with the increase of the solution temperature.[14] So, 25 °C was selected as an optimum value for temperature.

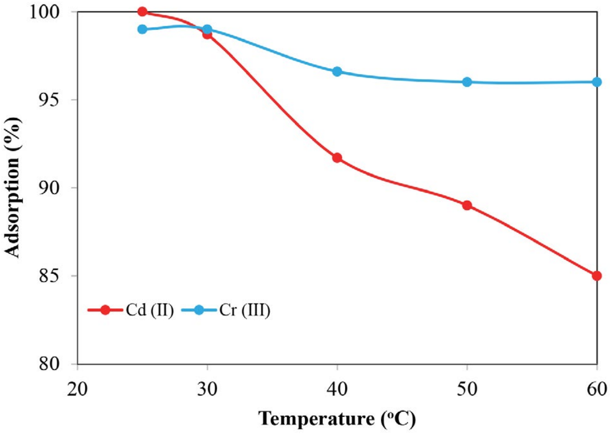


Fig. 9: The effect of temperature on the cadmium and chromium in conditions in terms of (cadmium pH: 6, chromium pH: 7, initial concentration of metal ions 20 mg/L, time 50 min and adsorbent dosage 20 g/L)

3. 9. Study of Adsorption Isotherms

To explain the interaction between sorbent and contaminants, adsorption isotherms are used widely and play an important role in the optimal use of adsorbents.[28] In this study, Langmuir and Freundlich isotherm models are used to explain adsorption process of chromium (III) and cadmium (II) ions using CFNC.[31–33] The details are given in supplementary material.

As it is shown in Table 2, correlation coefficient in Langmuir isotherm model to cadmium (II) and chromium (III) ion is 0.9948 and 0.9999 sequentially. Also, the value of R_L achieved from Langmuir isotherm to remove cadmium (II) and chromium (III) ion from aqueous solution by using CFNC sorbent is obtained 0.049 and 0.083 sequentially that show removing of cadmium (II) and chromium (III) ion by using CFNC is desirable. Additionally, maximum adsorption capacity (q_{max}) of cadmium (II) and chromium (III) ions by using Langmuir isotherm is achieved 303 and 217 mg/g sequentially which are significant amounts. Cadmium (II) and chromium (III) ion have correlation coefficient sequentially 0.9268 and 0.9959 for the Freundlich isotherm model. Moreover, the value of n for cadmium (II) and chromium (III) ion are obtained

Table 2: Langmuir and Freundlich isotherm constants for adsorption of cadmium (II) and chromium (III) using CFNC from aqueous solutions.

Isothermic models	parameters	cadmium	chromium
	q_{max} (mg/g)	217	303
	K_L (L/g)	0.95	0.55
Langmuir isotherm model	R^2	0.99	0.99
	R_L	0.05	0.08
Freundlich isotherm model	n	0.48	2.36
	R^2	0.93	0.99
	K_f	8.15	7.21

0.48 and 2.36 that show the Freundlich isotherm model is sequentially desirable and undesirable to remove cadmium (II) and chromium (III) ions by using of CFNC.

3. 10. Kinetic Study

Kinetic studies of adsorption processes show the interactions between metal ions in aqueous solution and the adsorbent. Also, the kinetic study describes the mechanism of the adsorption process[34]. In this study, in order to explain adsorbent kinetic behavior, pseudo first-order and pseudo second-order kinetic models were applied.[32–34] The details are given in Supplementary material.

Fig. S-3 shows the effect of time (t) against $\log(q_e\text{-}q_t)$ for pseudo first-order kinetic model. Also, the effect of time (t) against t/q_t for the pseudo second-order kinetic model is shown in Fig. S-4. Additionally, constants and parameters of pseudo first-order and pseudo second-order kinetic models for adsorption of cadmium (II) and chromium (III) ions using CFNC are tabulated in Tables S-4 and S-5. Based on the obtained values for correlation coefficient (R^2), adsorption process of Cr (III) and Cd (II) ions using CFNC follow up the pseudo-first order kinetic model and this model has higher R^2 in comparison to pseudo-second order kinetic model. In other word, the pseudo first-order kinetic model is fitted well with the experimental data.

3. 11. Thermodynamic Studies

In this work, a thermodynamic study of cadmium (II) and chromium (III) ions removal using CFNC was done at temperatures of 5, 15, 25, 30, 40, 50 and 60 °C. The other conditions were constant including pH of cadmium ion: 6 and chromium ion (III): 7, sorbent dose of 20 g/L, the initial concentration of 20 mg/L and contact time of 70 min. The details are given in Supplementary material. Constants and thermodynamic parameters are presented in Table 3.

A positive value of enthalpy ΔH° shows that adsorption process of cadmium (II) and chromium (III) ions using CFNC sorbent is endothermic. Also, the value of ΔS° was positive that shows at the solid/liquid interface an increase of randomness occurs after adsorption of Cd(II) and Cr(III) using CFNC adsorbent.[33] Moreover, a negative value of Gibbs free energy shows that cadmium (II) and chromium (III) ions adsorption using ferrite-cobalt sorbent is spontaneous.

3. 12. Desorption

Desorption process gives useful data about the possibilities of adsorbent regeneration after it saturates with heavy metals, and this process is necessary to enhance the economical feasibility of the adsorption process[34]. Fig. 10 shows adsorption efficiency of cadmium (II) and chromium (III) ions due to reusing of CFNC in consecutive adsorption. Desorption process was done in 8 cycles. Adsorption efficiency of heavy metal ions due to desorption in the first eight steps, the peak of the graphs was constant, and after each repetition, no significant change was observed with the ferrite-cobalt magnetic nanocomposite. These results indicate the ability to reuse ferrite-cobalt

Table 3: Thermodynamic properties for cadmium (II) and chromium (III) adsorption

heavy metal ion	Temperature/K	K_C	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)
cadmium (II)	278	2.25	−1.82	39.37	147.85
	288	3.86	−3.23		
	293	5.92	−4.31		
	298	10.17	−5.73		
chromium (III)	278	2.25	−2.86	34.36	133.91
	288	3.86	−4.2		
	293	5.92	−4.87		
	298	10.17	−5.54		

magnetic nanocomposite to recover cadmium (II) and chromium (III) ions from aqueous solutions. Also, the advantage of the CFNC sorbent is that it can be used 4 times consecutively by washing it with 30mL of acetone/methanol (1:1).

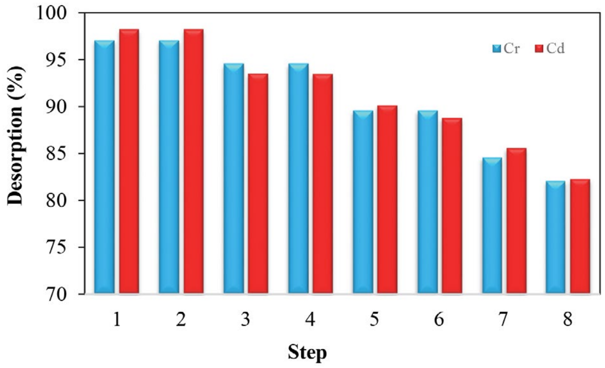


Fig. 10: Desorption of cadmium (II) and chromium (III) ions from solution using acetone/ethanol (1:1)

4. Conclusion

To remove cadmium (II) and chromium (III) ions, cobalt-ferrite nanocomposite (CFNC) was used as a new magnetic adsorbent. To determine characteristics of CFNC sorbent, various analyses such as SEM, FTIR, VSM, and BET were used. By BET analysis, the specific surface area of CFNC was measured 17.84 m^2/g. Also, various parameters such as pH of the solution, type and volume of buffer, type and concentration of the electrolyte, the initial concentration of metal ions in solution, contact time, sorbent dose and temperature were studied on the removal of chromium and cadmium ions from aqueous solution using CFNC. The results showed that the optimum value of pH to remove cadmium (II) and chromium (III) ions were achieved 7 and 6, respectively. The other optimum conditions were including: temperature = 25 °C, initial ion concentration= 20 mg/L, contact time = 50min, type of buffer = maleic acid, type of electrolyte = NaCl and adsorbent dose = 20 g/L. To study adsorption process of cadmium (II) and chromium (III) ions, CFNC sorbent of Langmuir and Freundlich isotherm models were used. Adsorption data follow Langmuir isotherm and show that cadmium (II) and chromium (III) ions adsorption are happened on monolayer surface and homogeneous of CFNC. Moreover, maximum adsorption capacity (q_{max}) of cadmium (II) and chromium (III) is achieved from Langmuir adsorption isotherm model 217 and 303 mg/g, sequentially. In order to study the kinetic behavior of adsorption, pseudo first-order and pseudo second-order kinetic models were used and the results showed that the pseudo first-order kinetic model was more desirable than the pseudo second-order model because of its higher correlation coefficient (R^2). The thermodynamic study also showed that the adsorption of chromium and cadmium ions using CFNC adsorbent is spontaneous and endothermic. Additionally, the desorption process showed that the adsorbent can be used consecutively 4 times by washing it with 30mL of acetone/methanol solution (1:1).

Conflict of Interests Statement

The authors declare that there is no conflict of interests.

5. References

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Povzetek

Študija preučuje možnost uporabe kobalto-feritnih nano-kompozitov (CFNC) za adsorpcijo kromovih in kadmijevih ionov iz odpadnih voda. Adsorpcijske lastnosti smo določali z različnimi tehnikami kot so SEM, FTIR, VSM in BET. Prav tako smo preučevali kako vplivajo na adsorpcijo pH vrednost, volumen pufra, dodatek elektrolitov, začetna koncentracija ionov, kontaktni čas in temperatura. Rezultati so pokazali, da je maksimalna adsorpcija Cd(II) in Cr(III) ionov dosežena pri začetni koncentraciji C0 = 20 mg/L, t = 50 min, T = 25 °C, CFNC koncentraciji 20 g/L ter pH vrednosti pH = 7 (za Cr(III)) oziroma 6 (za Cd(II)). Pod temi pogoji je bila dosežena 100 % odstranitev ionov iz vodne raztopine. Študija je pokazala, da lahko adsorpcijsko ravnotežje opišemo z Langmuirjevo izotermo, pri čemer dosežemo visoke maksimalna adsorpcijske kapacitete, ki znašajo 217 mg/g za Cr(III) ione in 303 mg/g za Cd(II) ione. Kinetiko adsorpcije lahko bolje opišemo z reakcijo psevdo-prvega reda kot z reakcijo psevdo-drugega reda. Adsorpcija je pod preučevanimi pogoji spontana in endotermna.