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Removal of Cd^{2+} ions from water and wastewater by complex formation with cadion2b and extraction the complex with magnetic nano particles

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ABSTRACT

The objective of this research is the promotion of new ways of removal of Cd (II) ions from water and wastewater that may cause hazardous health effects. In this study, was used cadion-2B(4-(4-Nitro-1-naphthyl-2-triazeno) for complex formation with cadmium and extraction the complex with magnetic nanoparticle. Synthesized magnetite nanoparticles with co-precipitation method and TEM, XRD were used to characterization of the synthesized magnetite nanoparticles. XRD results showed that the synthesized magnetite particles and TEM results showed that the diameter of the particles is 40-60 nm. For better extraction of cadmium ions parameters such as pH, contact time, amount of magnetite nanoparticles, and concentration of cadion-2B were optimized. Maximum removal of Cd(II) ions was obtained at pH=6,magnetic nanoparticles =50(mg/L),cadion-2B=40(mg/L) and adsorption equilibrium was achieved in 30 min. The adsorption data obeyed the Langmuir equation with a maximum adsorption capacity of 151.5(mg/g) at 25°C. Absorbent after reaction with cadmium ions by a magnet outside from environment. The amount of cadmium ions removed by FAA determined. The results indicated that magnetic nanoparticles (MNPs)can be used as an effective adsorbent for extraction of cadmium ions complex from contaminated water and wastewater sources.

KEYWORDS

Clays;
Adsorption;
Heavy metal;
Landfill leachate;
Tunisia.

INTRODUCTION

Use of municipal and industrial wastewater in irrigation suburban areas in many parts of the world has become commonplace and ordinary. Wastewater can be used to restore degraded areas and vegetation growth. Sewage, including refined and unrefined, waters from rains and industrial and domestic wastewater can be used as water to urban parks and forest margins of cities and industrial complexes. On the other hand, waste water often contain considerable quantities of heavy metals and toxic. Long-term use of waste water in irrigation water often lead to increased levels of heavy metals in soil. And finally can entered in biological cycle by plants and the effects appear. The usual method for removing metal ions from aqueous streams including chemical deposition, reverse osmosis, membrane processes, ion exchange, adsorption methods, electrochemical methods, and each method has been presented as a process. However, this method when the concentration is low, inefficient and expensive and may produce secondary waste treatment plant that it is difficult, however, these processes may be ineffective or too expensive. Cadmium is a bluish-white metallic soft element. It is well known that cadmium metal itself is not toxic, but most of its compounds have a very high toxicity on inhalation. High concentrations related to industrial activity in some areas have been found. Cadmium is also an important pollutant in soils. It is absorbed easily by plants, enters the human body by the food chain and is harmful to health. Cadmium is a major pollutants for which the need for better analytical methods has attracted the attention of many workers in recent years. Cadmium, absorbed easily by plants, is generally present as available cadmium in soils. Cadmium is a toxic heavy metal of significant environmental and occupational concern[1]. It has been released to the environment through the combustion of fossil fuels, metal production, application of phosphate fertilizers, electroplating, and the manufacturing of batteries, pigments, and screens[2, 3, 4]. In this study, cadmium ions in water and wastewater by a ligand called cadion2B complex formation and complex from environment extraction by magnetite nanoparticles. One of The main advantages this method is was that low cost and its application is simple and the speed of extraction is high.

MATERIALAND METHODS

Chemicalsandreagents

Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), Ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), cadion2B,Ethanol 99.8%,ammonia---, cadmium (II) nitrate(1000mg/L)were all analytical grade from Merck Chemical Co. Triton X-114 from Applichem Co, Cadion-2B from sigma Aldrich Co, Ultra-pure water was used throughout the work. The pH of the solutions was adjusted by dropwise addition of nitric acid (0.01 mol L^{-1}) and sodium hydroxide solutions (0.01 mol L^{-1}).

Synthesis of magnetite nanoparticles

In this method, magnetite nanoparticles were prepared by the chemical co-precipitation method. Individually, 2.73 g of $FeCl_3.6H_2O$ and 1.004 g of $FeCl_2.4H_2O$ were dissolved in 25 mL of deionized water for prepare the stock solution of ferrous and ferric chloride in a Balloons which was thendegassed by argon gas for 3 min. At this moment, 250 mL ofNaOH (1mol L^{-1}) solution was degassed (for 10 min). Then, soda solution was added dropwise to the mixture of ferrous and ferric chloride by using the dropping funnel during 60 min under argon gas protection and vigorous stirring (500 rpm) by a stirrer. During reaction process, the solutionpH was checked. When reaction be completed the solution it is alkaline. Magnetite nanoparticles separated from the solution by a magnet and then washedwith 250 mL doubly distilled water three times. Finally, the obtained Fe_3O_4 NPs were re-suspended in 250 mL of degasseddeionized water. The synthesized magnetite nanoparticles in this study characterized by using TEM and XRD techniques.

Instrumentation

Varian Spectra AA 420 (Springvale, Victoria, Australia)flame atomicabsorptionwithair–acetylene flame Hollow cathod elampswasused for determination ofCd(II). The calibration Curves forCd(0.5–5.0 mg/mL). Separation of magnetite particles by a magnet done with power 1.4Tesla, N35 model (5 × 3 × 2 cm) from Tehran Magnet (Tehran, Iran). A hotplate and stirrer 1100 series model (Jenway, England) was applied for stirring of the metal ion solutions.

Optimization of cadmium ions adsorption

To optimize the test conditions Change a parameter, and other parameters remained constant: At first, 50 mL aqueous solution of the cadmium ions (200 mg/L) was prepared in a 250 mL Erlen Mayer by addition of the appropriate amount of the cadmium ions standard solutions and then differing amounts of magnetite NPs was added to the metal ion solution. At this stage pH of the solution was adjusted to the desired value and then 1mL of different concentrationscadion-2B (cadion-2Bsuspention in The optimal amount of Tritonx-114)was added into the metal ion solution and the mixed solution was stirred for a desired time andafter that the cadmium complex adsorption on the magnetite nanoparticles were separated by magnet and the residual metal ion concentration in the supernatant clear solution was determined by FAAS.

Adsorption experiments

Laboratory batch experiments were carried out to study the adsorption of cadmium on cadion-Fe_3O_4 nanoparticles. The experiments were performed at room temperature (25±2 °C) using 250 balloon containing 50 mL cadmium solution. The Cadmium solution was prepared by diluting the standard cadmium solution (1000 ppm) Merck. A known amount of Cadion2B and Fe_3O_4 nanoparticles was added to 50 mL of the corresponding cadmium solution over a period of time on a shaker at 120 rpm. After the aqueous phase was separated magnetically, the concentration of Cd(II) in the solution was determined by using an atomic absorption spectrometer. The adsorption of cadmium by Cadion2B-Fe_3O_4 nanoparticles was investigated at pH range of 2-12. The initial pH of the solution was adjusted by using HCl (0.1mol L^{-1}) or NaOH (0.1mol L^{-1}). The effects of contact time (10, 20, 30, 40 and 50min), initial concentration of cadmium (40, 80, 120, 160,200,240 and 280 (mgL^{-1}) and amount of magnetite nanoparticles (0.03, 0.04, 0.05and 0.06 gr) were also examined throughout the experiments at 25±2 °C and 120 rpm shaking speed. The amount of Cd^{+2} ions removal was calculated from the difference between Cadmium take and that remained in the solution. The removal efficiency (R)of cadmium was calculated as$R\%=\frac{Co-Ci}{co}\times 100$. Where Co and C_i are the initial and residual concentrations of the metal ion in the solution (mg L^{-1}). The amount of cadmium adsorbed on the sorbent phase (mg g^{-1}) was calculated as:$q_e = \frac{Ci-Cf}{co}\times V$

Where q_e is the amount of cadmium adsorbed per unit weight of adsorbent, Vis the volume of the liquid phase(L), mis the weight of adsorbent (g) and C_i and C_f are the initial and final concentrations of cadmium (mg L^{-1}) in water

Adsorption isotherm models

Using isotherm models can determine how much solute were be absorbed by the absorbent also to evaluate the absorption capacity of adsorbent can be used. Generally the information obtained from material balance in solution known as adsorption isotherms. The information of absorption can be explained by simple models such as Langmuir and Freundlich. Isotherm describes the fraction of adsorbate molecules that are partitioned between liquid and solid phases at equilibrium in the Langmuir model is assumed that in the absorption layer consists of a layer of adsorbed molecules all of the adsorbent sites have same energy. Adsorption of Cd(II)by cadion2B -Fe_3O_4 nanoparticles was modelled using two adsorption isotherms. The linearized Langmuir equation can be expressed as:$\frac{1}{q_e} = \frac{1}{K_L q_{max}}\frac{1}{C_e} + \frac{1}{q_{max}}$

Where K_L is a constant related to affinity of the binding sites with the metal ions (L mg^{-1}) and Ce is the equilibrium cadmium concentration (mg L^{-1}) in the solution and q_e is the equilibrium cadmium concentration (mg g^{-1}) on the adsorbent. q_{max} is the maximum amount of metal ion adsorbed per unit weight of absorbent to form a complete monolayer on the surface (mg g^{-1}).

Freundlich isotherm based upon sorption on heterogeneous surfaces was applied freundlich isotherm (1906) is applicable to both monolayer (chemisorption) and multilayer adsorption (physisorption) and is based on the assumption that the adsorbate adsorbs onto the heterogeneous surface of an adsorbent (Yang, 1998). In the linear form Log q_e =log $k_f + \frac{1}{n}$ Log c_e

Where 1/n (dimensionless) and K_f ($mg^{1-(1/n)}\ g^{-1}\ L^{1/n}$) are the freundlich constants indicating the relative adsorption intensity and the capacity of adsorption, respectively. Parameters related to each isotherm for the adsorption of the metal ions on the adsorbent were determined by using linear regression analysis, and square of the correlation coefficients (R^2) were calculated. The essential characteristics of the

Langmuir isotherm can also be expressed in terms of a dimensionless constant of separation factor or equilibrium parameter, R_L, which is defined as

$$R_L = \frac{1}{1+K_L C_0}$$

Where K_L is the Langmuir constant and C_0 is the initial concentration of metal ions. The R_L value indicates the shape of isotherm[5]. R_L values between 0 and 1 indicate favorable adsorption, while $R_L>1$, $R_L = 1$, and $R_L = 0$ indicate unfavorable, linear, and irreversible adsorption isotherms.

RESULTS AND DISCUSSION

Characterization of Fe_3O_4 NPs

The XRD analysis of the Fe_3O_4 nanoparticlesis shown in Figure. 1. The peaks at 2θ values of 18.30, 35.2, 37, 43, 53.5, 57, 62.8,71,74,75 and79 that are maximum peaks corroborate the presence of Fe_3O_4. XRD results showed that the synthesized magnetite particles

As shown in Figure. 2, Fe_3O_4 nanoparticles prepared are in the range of 40–60 nm in diameter.

Adsorption studies

Optimization of adsorbent

The percentage of cadmium ions removed by adsorbent (Cadion-2B-Fe_3O_4) shown in Figure.3. To optimize of the cadion-2B amounts 20, 30, 40 and 50(mgL^{-1})and optimize of the magnetite nanoparticles amounts 30,40,50and60 ($mg\ L^{-1}$) were added to the solution(containing 200 ppm cadmium ions) individually(Ligand of Cadion-2B is insoluble in

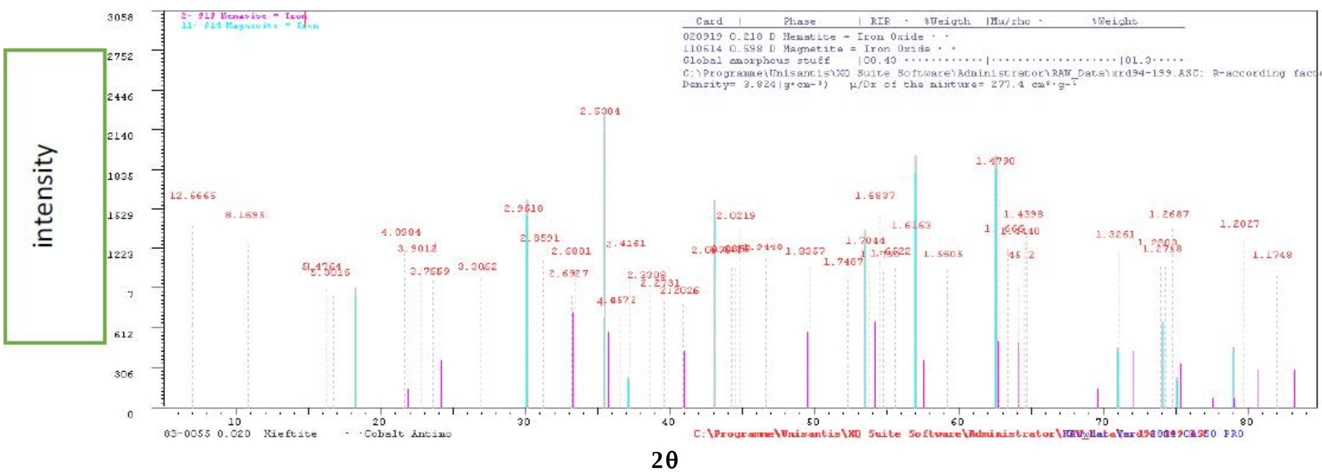

Figure 1 : XRD image of the Fe_3O_4 NPS

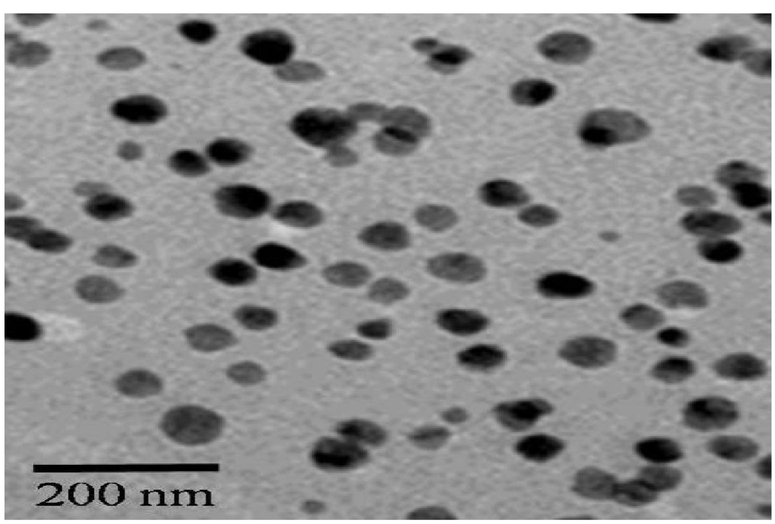

Figure 2 : The TEM image of Fe_3o_4nanoparticles

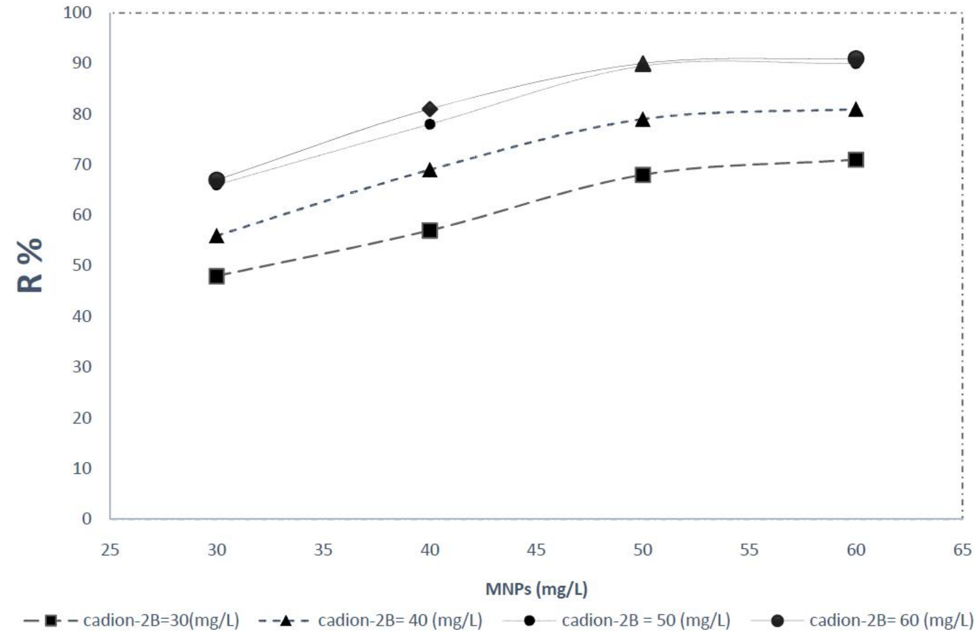

Figure 3 : The effect of adding Cadion-2B and Fe_3O_4nanoparticles on the adsorption of cadmium ions (cadmium initial concentration 200 mg L^{-1}, pH=7,contact time =25min,rpm=120,Temp=25±2 °C)

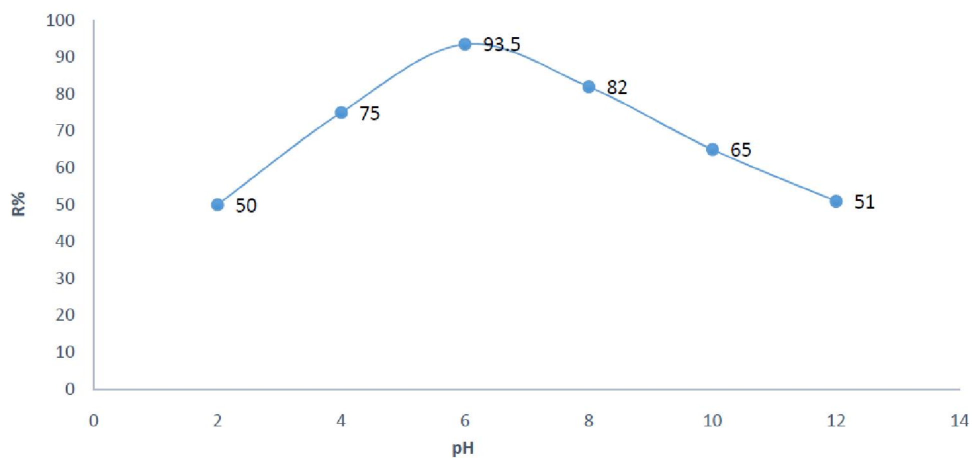

Figure 4 : Effect of pH on the adsorption of Cd^{2+} ion by cadion-2B-Fe_3O_4 nanoparticles adsorbent (cadmium initial concentration 200 mg L^{-1}, contact time=25min,MNPs=50ppm,cadion-2B=40 ppm,Temp=25±2 °C)

aqueous solution then Triton x-114 is added to the solution until ligand dissolved)the absorbent by magnet was collected and remaining metal in solution was analyzed. The results Shown in Figure 3 that the best removal efficiency of cadmium ions from 50(mgL^{-1})MNP$_S$ and 40(mgL^{-1})Cadion-2B is made.

Effect of sample's pH

The pH is an important factor affecting the removal of metal ions from aqueous solutions. Dependence of metal sorption on pH is related to both the metal chemistry in the solution and the ionization state of functional groups of the adsorbent which affects the availability of binding sites[6,7].

The percentage of cadmium (II) ion removed by cadion-2B-Fe_3O_4 nanoparticlesas a function of equilibrium solution pH is shown in Figure. 3. Because pH affects the surface charge magnetite nanoparticles and cadion-2B ligand. Under different pH conditions, the removal efficiency of Cadmium ions by the cadion2B-Fe_3O_4 nanoparticles was measured. As presented in Figure. 4, the removal efficiency (R %) increased from 50 % to 93.5%when the initial pH varied from 2 to 6, then at pH>6removal efficiency decreased with increasing solution pH. Thus, the optimal pH for Cd^{2+} ions removal was found to

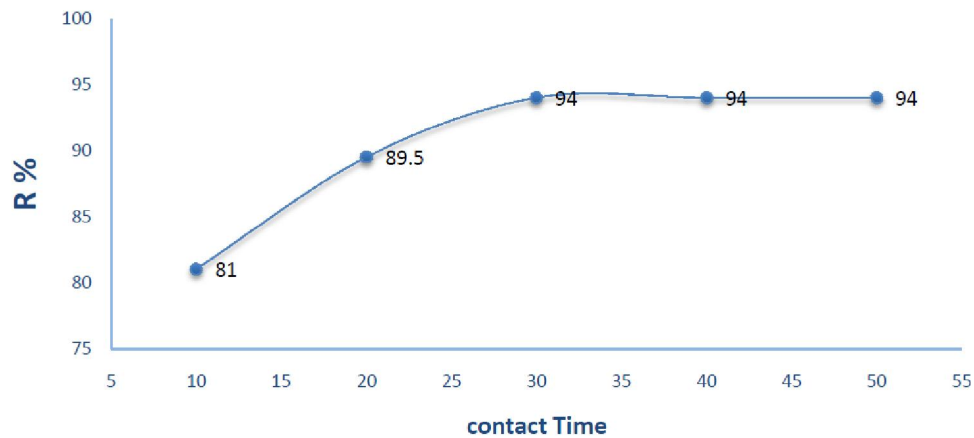

Figure 5 : Effect of contact time on the adsorption ofCd^{+2} ion by Cadion-Fe_3O_4nanoparticles adsorbent(cadmium initial concentration=200 ppm, MNPs =50ppm,cadion-2B=40ppm, pH=6,rpm=120,Temp=25±2 °C)

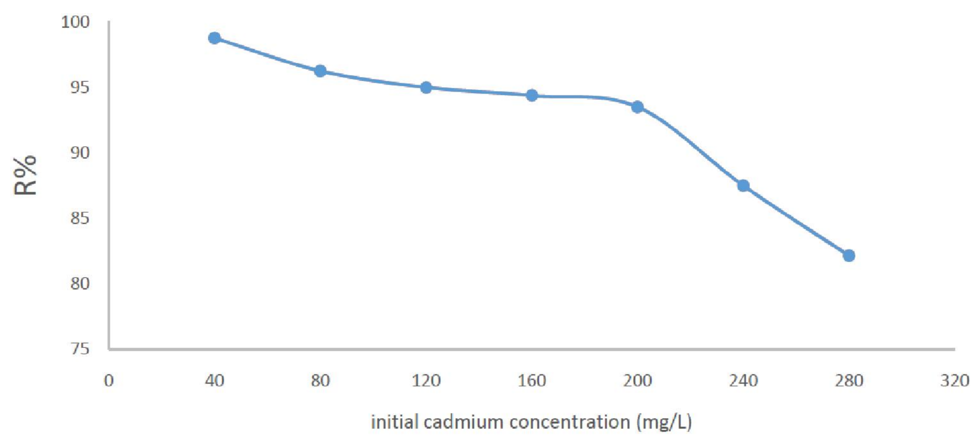

Figure 6 : Effect of increasing concentration ofcd^{2+}ions on the removal efficiency

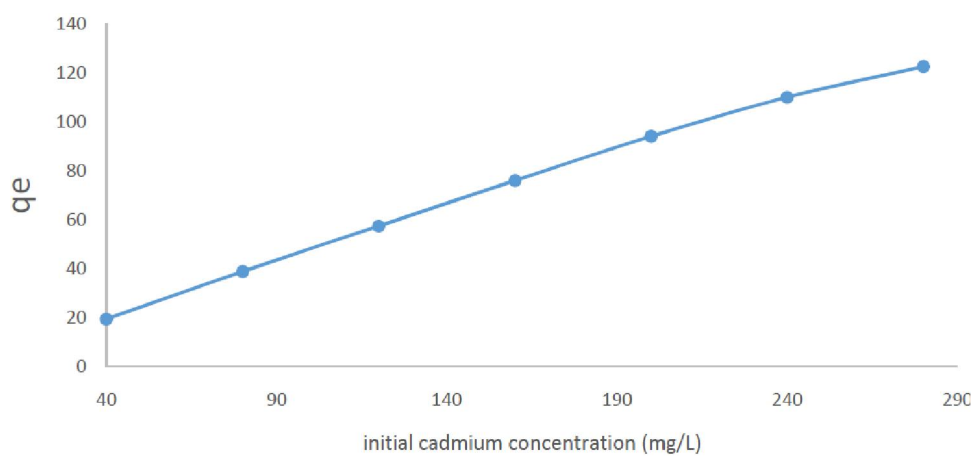

Figure 7 : The increase dq_e at higher initial concentration

be 6.0. Acidic environment leads to better connectivity will be surfactant and complex to nanoparticles But causes competition between H^+ and Cd^{+2} ions in reaction with Cadion2B and cd^{+2}ion extraction reduced. Decrease of cadmium adsorption at pH>6 was due to formation of dissolved hydroxyl groups[8, 9,10]. With the formation of hydroxyl Cadmium ions was reduced free cadmium ions in the solution.

Effect of contact time

Figure. 5 illustrates the variation in the amount adsorbed as a function of time for Cd^{+2}ions. The remova lefficiency increases with time in the first 30 min. Then the adsorption curve reached equilib-

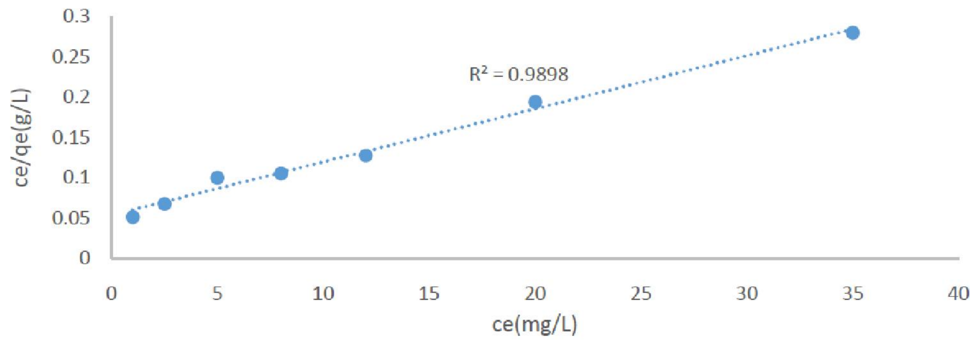

Figure 8 : Langmuir isotherm

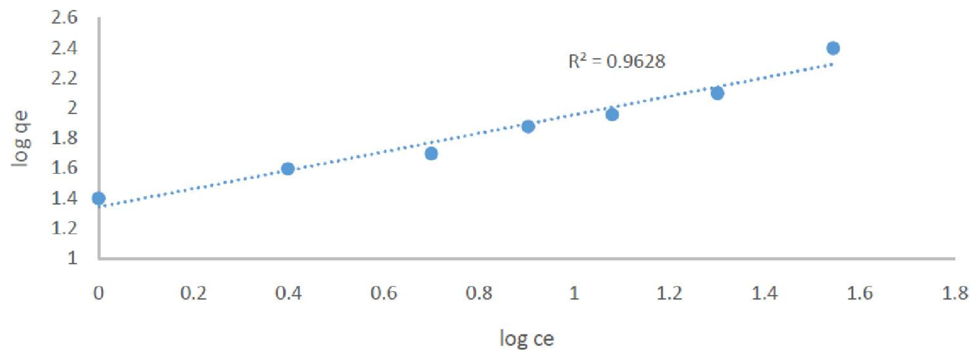

Figure 9 : Freundlich isotherm

TABLE 1 : Equilibrium model parameters for adsorption of complex by MNPs

Langmuir isotherm	Freundlich isotherm
q_{max} (mgg^{-1}) $k_L R_L$ R^2	K_F nR^2
151.50.123 0.039 0.989	4.1241.625 0.9628

rium after this time[11].

Effect of initial Cd (II) concentration

Investigate the effect of concentration on the removal of Cd(II), Different concentrations of cadmium ions was made (40, 80, 120, 160,200, 240,280 mgL^{-1})and in each of these concentrations 50(mgL^{-1}) magnetite nanoparticles and 40(mgL^{-1}) cadion-2B was added andwas adjusted pH in 6. Aspresented in Figure 6. The percentage of removal efficiency (%)cadmium ions were decreased when increasing concentration of solution. Although percent of adsorption (%)cadmium ions decreased bute quilibrium adsorption capacity ofcadion-2B-Fe_3o_4nanoparticles increased with increasing initialCd(II) ionconcentration. At low initial solution concentration, available adsorption sites for cadmium ions is high and the cadmium ions were easilyadsorbed. At higher initial solution concentration, the total available adsorption sites are limited, therefore will be

TABLE 2 : Removal of the Cd (II) ions from different wastewater samples by applying the proposed method

Sample	Input Cd^{2+} ions ($mg\ L^{-1}$)	Removal (%)
1	80	95.5
2	160	93.5
3	240	86

decreased removal efficiency of Cd(II)ions.

Adsorption isotherm

Figure 8 and Figure 9. Displays a comparison of the fitting of the experimental data with Langmuir and Freundlich adsorption isotherms; It suggests that the Langmuir model is more suitable in simulating the adsorption isotherm of Cd^{2+}ion onto adsorbent. The related parameters have also been summarized in TABLE 1. It is observed that the Langmuir model possesses higher R^2 than the Freundlich model, which means the monolayer coverage around of adsorbent. The parameters values are presented in TABLE 1.

Application for real samples

Under optimum conditions, removal of the cadmium ions from the wastewater samples was studied Wastewater samples were collected from the wastewater of bushehr I. R. Iran. The samples were filtered before analysis through a 0.45μm membrane filter. In first part, waste water samples spiked with 80,160 and 240mgL^{-1}of theCd^{2+} ions. The parameters values are presented in TABLE 2. The concentrations of these spiked cadmium ions in the three samples were determined by flame atomic absorption. The results showed that applicable is this method for wastewater samples. And can be used for complex matrices such as wastewater. And Remove cadmium ions was done with a high percentage.

CONCLUSION

In this research the capability and effectiveness of the adsorbent (Cadion2B- Fe_3O_4 NPs) for removal of Cd(II) ions from various water and wastewater samples. Parameters such as pH, contact time, concentrations of cadion2B and magnetite nanoparticle influenced the removal of cadmium ions were optimized. The cadmium removal was optimal at pH=6, MNPs=50 (mgL^{-1}),cadion-2B=40(mgL^{-1}) and 30 minutes equilibrium time in experiments. Higher initial cadmium concentration led to lower removal percentages but higher adsorption capacity. The cadmium adsorption data was fitted to the Langmuir model that means the monolayer coverage around of adsorbent. Studies on batch adsorption using real samples in order to remove the cadmium ions indicated that the adsorbent has a good potential to remove the heavy-metal ions from wastewater samples in practical applications.

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