Removal of Cd\textsuperscript{2+} ions from water and wastewater by complex formation with cadion\textsuperscript{2b} and extraction the complex with magnetic nanoparticles

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\textbf{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.

\textbf{KEYWORDS}

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

\textbf{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, cadmium can enter the 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, and 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 environmental 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.

MATERIAL AND METHODS

Chemicals and reagents

Ferric chloride hexahydrate (FeCl$_3$·6H$_2$O), Ferrous chloride tetrahydrate (FeCl$_2$·4H$_2$O), 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$_2$O and 1.004 g of FeCl$_2$·4H$_2$O were dissolved in 25 mL of deionized water for prepare the stock solution of ferrous and ferric chloride in a Balloons which was then degassed by argon gas for 3 min. At this moment, 250 mL of NaOH (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 solution pH was checked. When reaction be completed the solution it is alkaline. Magnetite nanoparticles separated from the solution by a magnet and then washed with 250 mL doubly distilled water three times. Finally, the obtained Fe$_3$O$_4$ NPs were re-suspended in 250 mL of degassed deionized water. The synthesized magnetite nanoparticles in this study characterized by using TEM and XRD techniques.

Instrumentation

Varian Spectra AA 420 (Springvale, Victoria, Australia) flame atomic absorption with air–acetylene flame Hollow cathod elampswas used for determination of Cd(II). The calibration Curves for Cd(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 solu-
tion. At this stage pH of the solution was adjusted to the desired value and then 1 mL of different concentration of cadion-2B (cadion-2B suspension) was added into the metal ion solution and the mixed solution was stirred for a desired time and after 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$_3$O$_4$ nanoparticles. The experiments were performed at room temperature ($25 \pm 2 ^{\circ}C$) using 250 mL 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$_3$O$_4$ 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$_3$O$_4$ nanoparticles was modelled using two adsorption isotherms. The linearized Langmuir equation can be expressed as:

$$\frac{1}{q_e} = \frac{1}{q_{max} K_L c_e} + \frac{1}{q_{max}}$$

Where $K_L$ is a constant related to affinity of the binding sites with the metal ions (L mg$^{-1}$) and $C_e$ 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$^{1-n}$/g$^{1}$ L$^{n}$) 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$_3$O$_4$ NPs

The XRD analysis of the Fe$_3$O$_4$ nanoparticles is shown in Figure. 1. The peaks at 2θ values of 18.30, 35.2, 43, 53.5, 57, 62.8, 71, 74.75 and 79 that are maximum peaks corroborate the presence of Fe$_3$O$_4$. XRD results showed that the synthesized magnetite particles

As shown in Figure. 2, Fe$_3$O$_4$ 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$_3$O$_4$) shown in Figure. 3. To optimize of the cadion-2B amounts 20, 30, 40 and 50 (mg L$^{-1}$) and optimize of the magnetite nanoparticles amounts 30, 40, 50 and 60 (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$_3$O$_4$ NPS](image)

![Figure 2: The TEM image of Fe$_3$O$_4$ nanoparticles](image)
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(mg/L)MNP S and 40(mg/L)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-Fe₃O₄ nanoparticles adsorbent (cadmium initial concentration 200 mg L⁻¹, contact time=25min,MNPs=50ppm,cadion-2B=40 ppm,Temp=25±2 °C) increased from 50 % to 93.5 % when the initial pH varied from 2 to 6, then at pH>6 removal efficiency decreased with increasing solution pH. Thus, the optimal pH for Cd²⁺ ions removal was found to...
Figure 5: Effect of contact time on the adsorption of Cd$^{+2}$ ion by Cadion-Fe$_3$O$_4$ nanoparticles adsorbent (cadmium initial concentration = 200 ppm, MNPs = 50 ppm, cadion-2B = 40 ppm, pH = 6, rpm = 120, Temp = 25 ± 2 °C)

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

Figure 7: The increase $q_e$ 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 removal efficiency increases with time in the first 30 min. Then the adsorption curve reached equilib-
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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 and it was adjusted pH in 6. As presented in Figure 6. The percentage of removal efficiency (%) cadmium ions were decreased when increasing concentration of solution. Although percent of adsorption (%) cadmium ions decreased but the equilibrium adsorption capacity of cadion-2B-Fe\(_3\)O\(_4\) nanoparticles increased with increasing initial Cd(II) ion concentration. At low initial solution concentration, available adsorption sites for cadmium ions is high and the cadmium ions were easily adsorbed. At higher initial solution concentration, the total available adsorption sites are limited, therefore will be 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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Input Cd(^{2+}) ions (mg L(^{-1}))</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>80</td>
<td>95.5</td>
</tr>
<tr>
<td>2</td>
<td>160</td>
<td>93.5</td>
</tr>
<tr>
<td>3</td>
<td>240</td>
<td>86</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>q(_{\text{max}}) (mgg(^{-1}))</td>
<td>K(_L) nR(^2)</td>
</tr>
<tr>
<td>151.50.123 0.039 0.989</td>
<td>4.1241.625 0.9628</td>
</tr>
</tbody>
</table>

TABLE 2 : Removal of the Cd (II) ions from different wastewater samples by applying the proposed method
filtered before analysis through a 0.45 µm membrane filter. In first part, waste water samples spiked with 80, 160 and 240 mg L⁻¹ of the Cd²⁺ 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- Fe₃O₄ 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 (mg L⁻¹), cadion-2B=40 (mg L⁻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.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial and technical support provided by the Persian Gulf University of Bushehr and support research committee bushehr province of water and wastewater company.

REFERENCE