Development of a method for cadmium ion removal from the water using nano $\gamma$-alumina/β-cyclodextrin

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**A R T I C L E  I N F O**

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**A B S T R A C T**

Cadmium is one of the heavy metals, which is harmful to humans and animals. The toxicity of this metal in the body has caused many studies to remove it in water and soil. Because according to WHO, the maximum concentration of cadmium in drinking water is 3 $\mu$g/L. In this study, trace amount of Cd ion or Cd(II) in water and in the industrial effluent sample were determined via the solid phase extraction approach based on the $\gamma$-Alumina/β-Cyclodextrin as a sorbent followed by flame atomic absorption spectrometry. The effects of various parameters such as pH, the Cd(II) concentration, amount of sorbent, and type and concentration of the eluting agents were determined on the removal efficiency. Maximum removal of Cd(II) was obtained at pH 7. The limit of detection (LOD) and repeatability (RSD%) values (0.389) obtained were found to be in the ranges of 6.77–6.81 $\mu$g/L. The results showed adsorbed cadmium ions are recovered on the nano $\gamma$-alumina/β-cyclodextrin surface with an optimum amount of 16 mL of 0.3 M nitric acid as eluting agent at pH 7.

1. Introduction

Designing and developing a method for concentration, isolation and measurement of cadmium ions is a basic need due to its importance in various industries and low concentration of this ion in most samples [1]. Because of the excessive consumption of cadmium in industry and its widespread use in batteries, plating and pigments has caused serious damage to water and soil resources [2–4]. Increased cadmium in the body causes severe liver and gastrointestinal symptoms [2,3,5]. Several methods have been proposed to remove cadmium from water [6]. Among this method, adsorption with nano sorbents has shown better performance [7].

Nano $\gamma$-alumina has been studied adsorption trace levels of toxic metals such as Ni(II), Zn(II), Cu(II) and Cd(II) due to high specific surface area, very good thermal stability, high hardness and high adsorption capacity [3,8].

Nonetheless, due to the poor bonding with heavy metals, its surface needs to be modified [9]. To overcome this problem, surface modification of nano-alumina with biocompatibility compounds has been studied. One of the best modification of nano $\gamma$-Al$_2$O$_3$ to adsorb Cd(II) as toxic metal in water is magnetic/alumina nanocomposite [10]. Ebrahimpour et al. synthesized / iron oxide nanoparticles in presence of different concentration of tangerine peel extract as surfactant and stabilizer for Cd ions removal from contaminated solution [5]. The results showed maximum removal of cadmium ions (90 %) occurred at pH 4 and adsorbent dose of 0.4 g/100 mL. While, Mahmoud Abd El-Latif et al. demonstrated the maximum removal of cadmium ions on magnetic alumina nanocomposite (MANC) was obtained at pH 6 [2].

Also, high efficiency Cd(II) removal from groundwater using nano $\gamma$-Al$_2$O$_3$ modified by glycerol was explored in Koju et al. study [3]. They demonstrated the hydroxyl group of $\gamma$-Al$_2$O$_3$ participated in the sorption and remove toxicity of Cd(II) from groundwater.

Gržađka in 2015 investigated the adsorption properties of $\beta$-cyclodextrin/ Al$_2$O$_3$ in the presence of some surfactants such as CTAB, SDS, TX-405 and TX-100. The surfactants prevent the accumulation of nano-alumina and improve their properties by forming complex with $\beta$-cyclodextrin [11].

Solid phase extraction (SPE) have been more studied in recent years, due to advantages such as no need for solvent, and high solubility in organic and aqueous solutions [7,12]. Also, by application various ligands having donor atoms including sulphur, oxygen, and phosphorous, SPE can be easily used for selectivity determination of heavy metals by FAAS [8,11]. Alizadeh et al. were determined some toxic metal ions with nano $\gamma$-alumina coated with sodium dodecyl sulphate by solid phase
The effects of pH, amount of nano \( \gamma \)-Al\( _2 \)O\( _3 \), SDS, sample and eluent flow rates; and type and concentration of the eluting agent were studied. The results obtained for their work indicated that the nano \( \gamma \)-Al\( _2 \)O\( _3 \) modified with SDS and 5-BrPADAP can be considered as adsorbent for trace amounts of toxic metal ions.

According to Varmazyari et al. [13] the increased concentrations of CdS (0.1 \( \mu \)g/mL) by inhalation lead to increased neurotoxicity both in vitro and in-vivo studies. Various concentrations of CdS studied to evaluate the neurotoxicity of CdS in the rat brain. The results showed atrophy in the brains by severe degeneration of neurons, necrosis and hyperemia in vessels at highest dose of CdS (25 mg/kg). Although, according to Li et al. [14] the toxicity of the pure Cd metal is higher than that CdS. In fact, decrease of Cd concentration leads to increase cellular viability after exposure to Cd [15,16].

Several reports have demonstrated high aquatic toxicity of Cd(II) ion for aquatic organisms such as planktons, bacteria, microalgae, and aquatic plants such as Spirodela polyrhiza [17-19]. These organisms affect the food chains and Cd(II) toxicity investigation on such organism is very important. So, determination of cadmium concentration is

| Table 1 | The measurement condition of Cd(II) via FAAS. |
| --- | --- |
| Acetylene | Air | Type of flame | Lamp intensity (Pb hollow cathode lamp) | The \( \lambda \) of Pb lamp |
| 1/8 mL/min | 0/8 mL/min | Air/ acetylene | 4 mA | 228/8 nm |

| Table 2 | Recovery (%) of Cd(II) added to nano \( \gamma \)-Alumina/\( \beta \)-Cyclodextrin in Various pH. |
| --- | --- | --- |
| pH | Cd(II) concentration | Recovery (%) |
| 4 | 1.001 | 49.95 |
| 5 | 0.554 | 72.3 |
| 6 | 0.292 | 85.4 |
| 6.5 | 0.195 | 90.25 |
| 7 | 0.093 | 95.35 |
| 8 | 0.127 | 93.65 |
| 9 | 0.117 | 94.15 |

| Table 3 | Recovery of Cd(II) with various eluent. |
| --- | --- | --- |
| Type of eluent | Cd\( _2 \)\( ^+ \) concentration | \% Recovery |
| Nitric acid 0.1 M | 3.72 | 18.6 |
| Nitric acid 1 M | 6.89 | 34.45 |
| Nitric acid 2 M | 7.59 | 37.95 |
| Nitric acid 3 M | 13.01 | 65.05 |
| Sodium hydroxide 2 M | 2.42 | 12.1 |
| Sulphoric acid 1 M | 10.4 | 52 |
| Nitric acid + Acetone 2 M | 8.24 | 41.2 |

| Table 4 | Recovery of Cd with Various Eluent Volume. |
| --- | --- | --- |
| Eluent volume | Cd concentration | \% Recovery |
| 7 mL | 8.9 | 62.3 |
| 10 mL | 6.74 | 67.4 |
| 12 mL | 5.49 | 65.88 |
| 14 mL | 4.7 | 65.8 |
| 16 mL | 4.11 | 65.76 |
| 18 mL | 3.65 | 65.7 |

Fig. 1. The diagram of nano \( \gamma \)-alumina/\( \beta \)-cyclodextrin synthesis.
important in controlling toxicity on aquatic organisms, animals and humans [16, 20, 21].

The aim of this study is determination of trace amount of cadmium by efficient, selective, inexpensive and simple SEP method in presence of nanostructure of \( \gamma \)-\( \text{Al}_2\text{O}_3/\beta\)-cyclodextrin as sorbent in different water and electroplating and finishing industries effluent samples. Also, for improvement of Cd(II) adsorption, the ethylene diamine was used as ligand and results was evaluated by FASS technique. Effective parameters including the pH, amount of ligand, amount of adsorbent, type and volume of eluting agent were investigated and optimized. According the results, optimum pH for cadmium ion removal was estimated at 7 and the detection limits (LOD) and repeatability (%RSD) values were obtained 0.00464 and 0.389, respectively. This technique helps determine the amount of Cd(II) in urban water and wastewater so that excess cadmium is removed and does not lead to ecosystem problems.

2. Experimental

2.1. Materials and methods

All the reagents were of the highest purity available from Merck. Nano \( \gamma \)-\( \text{Al}_2\text{O}_3/\beta\)-cyclodextrin was synthesized with co-precipitation method and was used as synthesized (Fig. 1) [3, 11, 22, 23]. Ultrapure organic solvents and Ethylene diamine tetra acetic acid (EDTA) were procured from Merck. Double distilled water was used throughout the experiments.

The stock standard solution of 1000 ppm Cd(II) was procured from Chem. Lab Company. The Cd(II) concentration was determined by flame atomic absorption (FAAS-PG instrument limited PG990 Spectrophotometer) equipped with a high intensity hollow cathode lamp. The condition of measurement via FFAS was listed in Table 1.

The effect of pH on the extraction of Cd(II) from water samples was studded by pH meter (HANNA HI2210) at the range of 2-10. All reagents and solutions were stirred using a Heidolph shaker. Arminad model centrifuge was used to centrifuge the solutions.

The nano \( \gamma \)-\( \text{Al}_2\text{O}_3/\beta\)-cyclodextrin was prepared to enhance capacity their adsorption capacity for Cd(II). The synthesis method was mentioned at Fig. 1.
2.2. Preparation of standards and solutions

First, 100 mg/L (100 ppm) Cd(II) solution was prepared by diluting an appropriate amount of 1000 mg/L stock solution with deionized water. Then the required concentrations were prepared by consecutive dilution of this solution with deionized water. Then, to find the optimal conditions to achieve the highest extraction efficiency, the effect of various factors such as the pH of the solution, the type and amount of eluent solution and the amount of EDTA were investigated.

2.3. Evaluate the effect of pH

To investigate the effect of pH, the 2 ppm of Cd(II) solutions was added in erlenmeyer and the pH was adjusted to 2–9 with a solution of nitric acid and ammonia. Then, 2 m/l of 1000 ppm of EDTA as ligand were contacted with 0.05 g of nano γ-Al₂O₃/β-cyclodextrin. This solution was stirred for 20 min at 400 rpm. The solution was then centrifuged and the supernatant was separated to adsorption study.

2.4. Evaluate the effect of various eluent solutions

50 mL of 2 ppm standard solution was added to the beaker with 0.05 g of nano γ-Al₂O₃/β-cyclodextrin and 2 mL EDTA. This solution was stirred (20 min, 400 rpm) and centrifuged (3500 rpm) after transferring to falun tube. 5 mL of each eluent (nitric acid 0.1 M, nitric acid 2 M, nitric acid 3 M, sodium hydroxide 2 M, sulfuric acid 2 M and nitric acid + acetone 2 M) were added to the precipitated nanostructure in several beakers. After stirring (30 min, 200 rpm) and centrifuging, the supernatant solution was separated for further study.

2.5. Influence of ligand volume

The effect of the ligand volume on the Cd(II) adsorption was studied by keeping the pH, total amount of Cd(II) and eluent constant. 0.05 g of nano γ-Al₂O₃/β-cyclodextrin was contacted with 50 mL of 2 ppm Cd(II) solution in four erlenmeyer. The totals of 2, 4, 6, 8 mL of 1000 ppm EDTA was added to each Erlenmeyer. After stirring (20 min, 400 rpm) and centrifuging, the precipitation was transferred to another Erlenmeyer with 5 mL eluent and stirred (30 min, 200 rpm) and centrifuged, again. The supernatant solution was separated for further adsorption study.

2.6. Evaluate the effect of eluent volume

To test the effect of eluent volume on quantitative Cd(II) adsorption, different volume of eluent with 0.05 g nano γ-Al₂O₃/β-cyclodextrin were added in to six Erlenmeyer. The totals of 2, 4, 6, 8 mL of 1000 ppm EDTA was added to each Erlenmeyer. After stirring (20 min, 400 rpm) and centrifuging, the precipitation was transferred to another Erlenmeyer with 5 mL eluent and stirred (30 min, 200 rpm) and centrifuged, again. The supernatant solution was separated for further adsorption study. This step, the amounts of 5, 7, 10, 12, 14, 16, and 18 mL of solvent were considered as variables. Finally, the sample absorption was read via flame atomic absorption spectrometer.

2.7. Effect of sample volume

In order to test the effect of volume of Cd(II) sample, 50 mL of 2 ppm solution (pH = 7) was prepared in various volume (100, 200, 400, 500, 700, and 1000 mL) and 0.05 g nano γ-Al₂O₃/β-cyclodextrin and ligand were added to each volume. After shaking and centrifuge, the precipitation was added to eluent and 20 min shacked. The supernatant solution was separated for further adsorption study.

2.8. Calibration curve

In order to determination linear range of calibration curve, solution with various concentration (0, 0.2, 0.3, 0.5, 1, 2, 3, 4 mg/l) were prepared and added in erlenmeyer with 8 mL of ligand and 0.05 g sorbent. After shaking and centrifuge, the precipitation was added to 7 mL HNO₃ as eluent and shacked 20 min. The supernatant solution was separated for further adsorption study.

2.9. Preparation of real samples

In order to analyze real samples, 500 mL of Shahre-Ray urban water and electroplating and finishing industries effluent were added to erlenmeyer with 0.05 g sorbent and 8 mL of ligand. After shaking and centrifuging, the precipitation was added to 7 mL HNO₃ as eluent and shacked 20 min. The supernatant solution was separated for further adsorption study.

3. Results and discussions

Some preliminary experiments were performed to evaluate the influence of various factors on cadmium adsorption and optimize these effective factors [7,12]. The results showed well how the removal of cadmium ion can be optimized by solid state chromatography based on nano γ-Al₂O₃/β-cyclodextrin.

3.1. Influence of pH

The effect of pH on the extraction and recovery of Cd(II) from water samples was studied in the pH range of 1.0–9.0. The results of this study are shown in Table 2 and Fig. 2.

As can be seen, at pH < 7, recovery of Cd(II) has not be completed. This is due to the protonation of the nitrogen atoms of the ligand in an acidic environment, which reduces the tendency to complex with cadmium, in which case there is no tendency to inhibit Cd(II) on the adsorbent.

3.2. Influence of the eluent

According to the results (Table 3), sodium hydroxide cannot be used as a suitable eluent, while acids are more suitable as eluent than bases. In other words, the acidic environment causes Cd(II) to dissolve better and recover more. The results (Fig. 3) showed that recovery was more effective when nitric acid 3 M was used as eluent. Nitric acid is a suitable detergent solution and nitrate ion is used as a matrix for atomic absorption and electro-thermal measurements.
3.3. Influence of eluent volume

In order to determine the most effective eluent volume for Cd(II) recovery, different volumes of nitric acid 3 M eluent were examined. The results (Table 4 and Fig. 4) showed that 7 mL of nitric acid 3 M has the highest efficiency in cadmium recovery.

3.4. Influence of the ligand volume

The influence of ligand volume on the recovery of Cd(II) was studied and the results listed in Table 5. As the results in the table show, the maximum recovery percentage is related to the volume of 8 mL of ligand. Fig. 5 exactly show the effect of ligand volume in recovery of Cd (II).

3.5. Effect of the sample volume

The influence of sample volume on the Cd(II) removal efficiency was presented in Fig. 6 and Table 6. For this purpose, the effect of the sample solution volume on the recovery was studied and the optimum volume was obtained for sample volume 500 mL since the concentration factor was 31.25 since the final elution volume was 16 mL.

As the results show, up to 500 mL of Cd(II)-containing sample, the ions were adsorbed by nano sorbent. If the sample volume is less than this limit, all cadmium ions are adsorbed on the adsorbent. While at higher volumes, adsorption of cadmium on nano-adsorbents is not complete and thus recovery is reduced.

3.6. Analytical performance

As mentioned, in order to plot a calibration graph, a series of standard solutions of Cd(II) were treated under optimized experimental conditions. In the range of Cd(II) concentration from 0–4 mg/L, the linear curve with equation \( \Delta A = 2/581C + 0.009 \) and regression coefficient of \( R^2 = 1 \) were obtained (\( \Delta A \) is the absorbance and \( C \) is molar concentration). Fig. 7 showed that the linear diagram range (LDR) was obtained between 0.5–4 mg/L.

By definition, the limit of detection (LOD) is the minimum amount of cadmium ions that the proposed method can detect. LOD was calculated by the following equation:

\[
\text{LOD} = 3 \times \sigma_b / m
\]

That \( \sigma_b \) is blank standard deviation and \( m \) is the slope of calibration graph. According to the results, \( \sigma_b \) of deionized water and m were obtained 0.004 and 2.581, respectively. Therefore, the LOD of this method was obtained 0.00464. The relative standard deviation (RSD%) for 3 times was equal 0.389.

3.7. Analysis for real samples

To determine the applicability of the method to real samples, it was applied to the solid phase extraction and determination of Cd(II) absorption from 500 mL of water samples (Shahre-Ray urban water and electroplating and finishing industries effluent). The results were listed in Table 7 as can be seen from table, in the industrial effluent sample, a significant amount of cadmium was found, which was determined with a flame atomic absorption spectroscopy.

According to the results, the solid phase extraction method with nano-γ-alumina/β-cyclodextrin has been selective and effective for determining of the low concentration of Cd(II) in the urban drinking water and electroplating and finishing industries effluent. The results of this study showed that the applied nano sorbent can have good recovery in \( \text{pH} = 7 \) and in presence of ethylene diamine as ligand and nitric acid 3 M as eluent. The data indicate the limit of detection (LOD) and the relative standard deviation (n = 3) under optimum condition are 0.0046 and 0.389, respectively. Applicability of this method was estimated using test samples of urban drinking water and Electroplating and finishing industries effluent. This selective method can be used for effective and rapid detection of heavy metals in the tested samples. Among other mentioned method in Table 8, this method was reliable through comparing with each other. As we know, prolonged exposure to cadmium can cause lung, kidney and digestive problems. According to WHO, maximum allow of 10 μg/L cadmium ion in drinking water sources [24,25]. Therefore, in this study, considerable attention has been devoted to the study of effective methods to remove low concentrations of cadmium in contaminated water. It is clear that the removal of cadmium reduces the toxicity of cadmium from aqueous sources.

4. Conclusion

Due to importance of Cd(II) removal as a toxic metal, solid phase extraction with nano sorbent can act an effective method for adsorption and determination of trace amount of cadmium ion. Different parameters such as pH, volume of eluent, volume of ligand and sample and Cd(II) standard concentration were investigated. This study indicates that the nano-γ-alumina/β-cyclodextrin can be considered as an effective adsorbent for an efficient completion of SPE of trace amount of Cd(II).

Although, the authors decided to optimize modification of nanomaterial γ-alumina with ethylene diamine, 2-aminopyridine and natural nano polymers for more adsorption efficiency in future studies. Then, the pre concentration and extraction of other toxic metals such as cobalt and copper and measurement of low amounts of cadmium ion using a graphite furnace atomic absorption spectrometer, CP-Mass and ICP-AES will be investigated.

"Author’s contribution" in this study

Dr Nazanin Farhadyar: Professor Assistance, Corresponding Author and supervisor of thesis.
Leila Esfanjani: Msc student, Research and the practical of the thesis.
Hamid Reza Shahbazi: MSc student, Research and the practical of the thesis.
Fereshteh Fathi: Researcher, Interpretation of results and spectra, writing the manuscript.

Conflict of interest

The authors declare no conflict of interest.

Declaration of Competing Interest

The authors report no declarations of interest.

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