Fe$_3$O$_4$ MNPs Adsorbent for Pre-concentration and Determination of Cd (II) ions in Drinking Water using Flame Atomic Absorption Spectrometry

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Abstract—This work terms synthesis, characterization and usage of magnetic nanoparticles Fe$_3$O$_4$ as an adsorbent for pre-concentration of Cd (II) in water. The morphology of Fe$_3$O$_4$ was investigated using FTIR, field emission scanning electron microscopy. The extraction efficiency of Fe$_3$O$_4$ was analyzed using batch process with flame atomic absorption spectrometry. Factors affecting pre-concentration such as pH, dosage of adsorbent, time of extraction, volume of sample, solvent of elution, and interferences were optimized. It was determined that Cd (II) adsorption is highly pH dependent, and a high recovery (94%) was achieved at pH 6.0. The limit of detection (3SDblank/m), limit of quantification (10SDblank/m), pre-concentration factor, and the relative standard deviation of Cd (II) extraction were 1.26 ng/mL, 4.28 ng/mL, 30, and 3.8% (concentration = 10 ng/mL, n = 10), respectively. Good relative recoveries of 82%–97% (percentage relative standard deviation <4.45) were achieved from spiked commercial drinking water and tap water samples.

Index Terms—Cadmium, FAAS, Fe3O4 nanoparticles, Magnetic solid phase extraction.

I. Introduction

Cadmium ion Cd (II), is a poisonous heavy metal ion for organisms, according to the "environmental protection agency (EPA)" priority pollutant index [1-3]. The acceptable concentration level of Cd (II) in standard drinking water is considered 5.0 ng/mL by the EPA and "World Health Organization" chemical fact periodicals is 3.0 ng/mL [4]. Among heavy metal ions present in the environment, Cd (II) ion concentration is increasing rapidly [5]. Many harmful impacts such as high blood pressure, bone breakage, damage of red blood cells, and kidney failure can be attributed to cadmium ion level [3]. Because the amount of Cd (II) existing in water samples is at trace level, so, sample preparation techniques are essential for Pb(II) analysis (that is, extraction and pre-concentration) in water samples. Solid-phase extraction (SPE) is a well-known method that is frequently useful for pre-concentration of Cd (II) ions from water solutions [6]. The SPE approach proposals several benefits, such as easy and simple process, low-cost, flexibility, high recovery, as well as eco-friendly method [6,7]. Despite all the benefits of SPE as a standard method, time-consuming analysis and low breakthrough volume make its user unfavorable. However, utilization of magnetic nanoparticles (MNPs) has been reported as a good technique to overcome those SPEs' drawbacks by prevention of column blocking and channeling as well as fast separation using an external magnet. The extraction method according to magnetic adsorbents is termed magnetic solid phase extraction (MSPE) [7,8] and the usage of MSPE was effectively utilized for extraction and removal of Cd (II) from diverse aquatic and foodstuff samples [9,10].

In this work, MNPs of Fe$_3$O$_4$ without any modification were chosen as SPE sorbents for the separation and pre-concentration of trace level Cd (II) ions from water samples. Synthesized nanoparticle was characterized by FT-IR and field emission scanning electron microscopy (FESEM). Various influencing parameters on the separation and pre-concentration of trace level Cd (II) ions such as pH value, adsorbent dosage, extraction time, sample volume, solvent elution, and the effects of interference ions were examined.

II. Procedure for Paper Submission

A. Chemicals and Reagents

All analytical grade chemicals without further purification were used. Cadmium (II) Nitrate tetrahydrate Cd (NO$_3$)$_2$·4H$_2$O, Ferric chloride 6-hydrate (Iron III Chloride) Fe$_3$Cl$_3$.6H$_2$O, ammonium ferrous sulfate hexahydrate (NH$_4$)$_2$Fe(SO$_4$)$_2$.6H$_2$O, Ammonia solution concentrated (NH$_4$OH 28%), and Sodium hydroxide pellets (NaOH, 98%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Hydrochloric acid (HCl, 37%) was purchased from Fluka Chemika (Buchs, Switzerland). Absolute ethanol (99.8%) was purchased from Merck (Darmstadt, Germany). 0.1 M, HCl, and/or NaOH were used

to adjust the pH of the solution. Working solutions were prepared with deionized water.

B. Instruments

FT-IR spectra (4000–400 cm^{-1}) were recorded on a Perkin- Elmer TM400 FTIR Spectrometer (Waltham, MA, USA) as KBr pellets. The size, morphology, and structure of the nanoparticles were observed using a Carl Zeiss Supra 35-VP FESEM (Oberkochen, Germany) operated at 10 kV, a magnification of 75,000´ and a working distance of 8 mm. A Metrohm pH meter model 713 (Herisau, Switzerland) was used to measure the pH. A Perkin-Elmer A Analyst 400 FAAS (Waltham, MA USA) equipped with a hollow cathode lamp for cadmium and a deuterium lamp for background correction was used to measure the quantities of Cd (II) present. The hollow cathode lamp was operated at 8 mA, and the wavelength was set at 228.8 nm.

C. Preparation of MNPs

Magnetic particles were prepared through a new modification using coprecipitation method. Ferric chloride hexahydrate $FeCl_3 \cdot 6H_2O$ (4.8) g and ammonium ferrous sulfate hexahydrate $(NH_4)_2$ Fe $(SO_4)_2 \cdot 6H_2O$ (2.4) g in the ratio 2:1 were dissolved in 60 mL deionized water under a nitrogen atmosphere with sonication for 5 min at 60°C. Then, 45 mL of ammonia solution (8 mol/L) pH (9–10) was added drop-wise into the reaction mixture. A black precipitate was formed instantly, and the reaction was allowed to proceed for another 5 min. The precipitate was then collected using a magnet, and the supernatant was decanted. The black precipitate was washed with double distilled (5 × 50 mL) water and dried in an oven at 60°C for 6 h [11].

D. General Procedure of MSPE

150 mL of (10 ng/L) sample solution of Cd (II) was taken into a glass beaker, and the solution pH was adjusted to pH 6.0 with the appropriate amount of 0.1 mol/L HCl and NaOH, individually. Then, 40 mg of Fe_3O_4 MNPs was added to the solution to obtain sorption equilibrium. The beaker was mechanically shaken by an orbital shaker for 30 min at 25°C and adsorbent was removed through permanent magnet. 5 mL of 1 mol/L HCl was added into the beaker as desorption solvent shaken using an orbital shaker for 5 min. Then, the adsorbent was collected through an external magnetic field, and the desorbed analyte solutions were analyzed using flame atomic absorption spectrophotometer (FAAS) for determination of Cd (II) ion. Ultrapure water was selected as the blank solution in MSPE process. The MSPE process and FAAS determination were performed in triplicates.

E. Sample Preparation

Two types of drinking and tap water samples were taken from Koya market and Chemistry research laboratory (Koya, Kurdistan region, Iraq), respectively. Drinking and tap water samples were filtered off by using Millipore cellulose acetate membrane filter (pore diameter 0.45 μm) and acidified to pH 2.0 with 2 mol/L HNO_3. The triplicate

measurements of water samples were performed using FAAS analysis.

III. Results and Discussion

A. Characterization of Adsorbent

FT-IR spectroscopy

The FT-IR spectrums (Fig. 1) provide abundant information about the structures of the synthesized adsorbents. The synthesized Fe_3O_4 MNPs is offered two peaks around 472 cm^{-1} and 575 cm^{-1} absorption peaks correspond to the Fe–O bond vibration of Fe_3O_4 nanoparticles [11]. The sample showed peaks around 1631 cm^{-1}, and broad peak at 3322 cm^{-1} which may belong to OH group from water molecules adsorbed on the surface particles [11].

FESEM

The morphology study of the developed magnetic adsorbent (Fe_3O_4 MNPs) was achieved through FESEM image. The morphology of the magnetic Fe_3O_4 nanoparticles synthesized is shown in Fig. 2 as spherical shapes with an average particle of size 12 nm. These findings confirm the successful preparation of the Fe_3O_4 adsorbent by simple chemical coprecipitation method.

B. Optimization of the MSPE Method

Various factors that influencing Cd (II) extraction performance of the developed adsorbent, such as pH of the solution, dosage of adsorbent, time of extraction, volume of sample, solvent of elution, and interference ions were optimized. The percentage recovery (%R) was utilized to assess the MSPE method under optimized conditions.
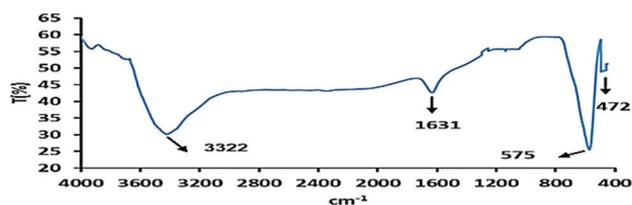
Fig. 1. FT-IR spectrum of synthesized Fe_3O_4 magnetic nanoparticles.
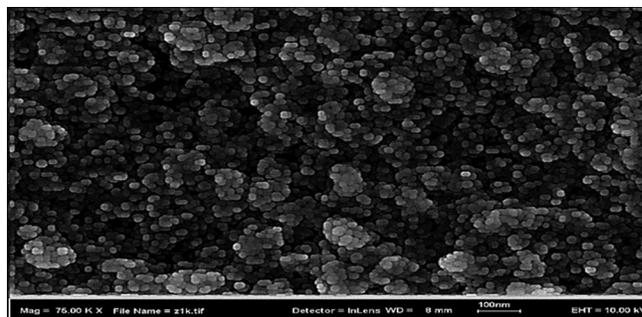
Fig. 2. Field emission scanning electron microscopy image of Fe_3O_4 MNPs.

Effect of pH

The effect of solution pH (2.0–7.0) on the MSPE performance was designed in 150 mL water solution (10 ng/ mL of Cd). Solution pH above 7.0 was not measured because of precipitation of Cd (II) in the samples as Cd $(OH)_2$ [1,4]. The data in Fig. 3a display that maximum Cd (II) recovery that was obtained in the pH range 5.0–6.0. The minimum recovery of Cd (II) is detected at pH 2–4, which is probably due to proton (H^+) competition. In addition, repulsion possibly occurs between Cd (II) and positively charged receptors on the surface of the magnetic adsorbent. Therefore, pH 6.0 is measured as the best working pH for further studies.

Effect of adsorbent dosage

One of the important factors in MSPE method is the quantity of adsorbent dosage. The effect of F_3O_4 MNPs amount on the extraction of the Cd (II) ions was investigated under optimized conditions. Fig. 3b illustrates, the percentage recovery (%*R*) is rapidly improved with the increasing dosage from 10 mg to 40 mg, due to rise of extraction sites [4]. Then, it is reached the extraction equilibrium at 40–200 mg of adsorbent, and no additional uptake was examined. This is probably due to the absence of Cd (II) ions in the samples where most of 10 ng/ mL of Cd (II) ions were extracted by 40 mg of F_3O_4 MNPs. Hence, 40 mg of adsorbent dosage is selected as the best dosage of adsorbent for further examinations.

Effect of extraction time

Extraction time is also a fundamental factor for the percentage recovery of Cd (II) ions. To investigate the loading time of Cd (II) ions on the Fe_3O_4 MNPs adsorbent, different extraction times from 5 to 60 min were studied using the mechanical shaking for extraction of Cd (II) ions. As shown in Fig. 3c, the percentage recovery of Cd (II) ions is rapidly enhanced with over 80% extraction during 20 min and reaches above 91% extraction at 30 min for the Fe_3O_4 MNPs adsorbent.

Effect of sample volume

To achieve a higher pre-concentration factor (PF), a large volume of sample solution is required. As shown in Fig. 3d, measurable recovery of Cd (II) ion- is obtained when sample volume - is <150 mL. Therefore, a sample volume of 150 mL and a desorption volume of 5 mL are utilized so that a (PF) of 30 is achieved in this study. Hence, a sample volume of 150 mL is selected for the rest of the investigations.

Effect of solvent elution

As the extraction of cations at pH <2 is insignificant, one can assume that elution will be preferred in acidic medium. The elution condition was planned through utilizing several concentrations and volumes of HCl for the elution of retained Cd (II). Table I shows that 5.0 mL of 1.0 mol/L HCl is acceptable to complete elution of Cd (II) ions with a shaking time of 30 min. Therefore; 5.0 mL of 1.0 mol/L HCl is utilized as eluent in all next studies.

Effect of interference ions

One of the atomic absorption spectrometry (FAAS) techniques for the quantitative analysis of the metal ions is matrix interference. Several concentrations of cations and anions (Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, K^+, Na^+, Zn^{2+}, Cu^{2+}, Ca^{2+}, Al^{3+}, and Fe^{3+}) were added individually, to the solution containing a fixed concentration of cadmium ions that pre-concentrated using the current MSPE method. A 150 mL sample solution of 0.1 ng/mL Cd (II) ion containing interference ions of 1000-fold of Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, K^+, and Na^+, 500-fold of Al^{3+} and Fe^{3+}, and 200-fold of Zn^{2+}, Cu^{2+}, and Ca^{2+} was spiked into the sample solution, individually and showed that high percentage recovery of 88 % of Cd (II) ion is acquired in the presence of numerous foreign ions.

C. Analytical Application

Under the optimum experimental conditions, the synthesized MSPE Fe_3O_4 adsorbent, showed good linearity (R^2) 0.9993 in the range of 5.0–50.0 ng/mL for determination of Cd (II) ion in drinking water samples. The limit of detection (LOD=3SD_{blank}/m) and limit of quantification (LOQ=10SD_{blank}/m) are 1.26 ng/mL and 4.28 ng/mL, respectively. 10 replicates of 40 mg of prepare Fe_3O_4 in 10 batches were utilized for extraction of Cd (II) ions, and relative standard deviation (RSD) of 3.8 % was obtained for (concentration = 10 ng/mL, *n* = 10) of Cd (II). The value of RSD shows excellent reproducibility of Cd (II) ion extraction by Fe_3O_4 MNPs adsorbent.

Fe_3O_4 MNPs adsorbent was applied to the packed drinking water (Kani and Life brands) and tap water samples for pre-concentration of Cd (II) ions. A 150 mL of each water
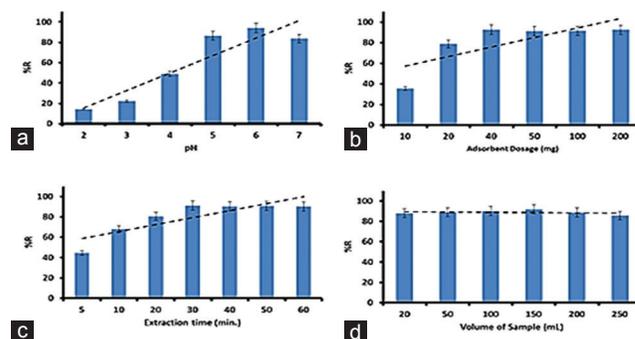
Fig. 3. Effect of (a) pH, (b) adsorbent dosage, (c) extraction time, and (d) volume of sample on percentage recovery of Cd (II).

TABLE I
EFFECT OF CONCENTRATION AND VOLUME OF ELUTION SOLUTION ON THE PERCENTAGE RECOVERY OF CD (II)

HCl concentration (mol/L)	HCl volume (mL)	Cd (II) (R %)
0.10	3.00	32.50
0.10	5.00	76.90
0.50	3.00	78.80
0.50	5.00	82.10
1.00	3.00	84.90
1.00	5.00	91.40

TABLE II

DETERMINATION OF CD (II) IONS USING FAAS TECHNIQUE IN WATER SAMPLES AND USING (Fe_3O_4) AS ADSORBENT; CONDITIONS: pH=6.0; 40.0 MG OF FE_3O_4 MNPS; 150 ML SAMPLE VOLUME; 30 MIN. ADSORPTION TIME; 5 ML HCL ELUTION VOLUME

Element	Spiked (ng/mL)	Tab water		Kani water		Life water	
		[a]Found (μgL^{-1})	[b]R.R (%)	[a]Found (ng/mL)	[b]R.R (%)	[a]Found (ng/mL)	[b]R.R (%)
Cd (II)	0.00	0.00					
	5.00	4.10±4.41	82.00	4.22±4.33	84.40	4.31±4.45	86.20
	5.00	48.80±4.41	97.60	46.30±1.23	92.60	44.13±1.29	88.26

[a]Mean±RSD%; [b]: Relative recovery

TABLE III

COMPARISON BETWEEN THE PROPOSED METHOD AND SOME EXISTING TECHNIQUES OF PRE-CONCENTRATION OF CD (II) IONS USING FAAS TECHNIQUE

Adsorbent type	LOD (ng/mL)	Sample type	Detector	Reference
Silica gel	4.25	Water	FASS	[1]
Fe_3O_4 modified	3.71	Water and food	FASS	[2]
Diphenylcarbazone amine functionalized	1.50	Food	FASS	[3]
Fe_3O_4	1.20	Water	FASS	This work

GMA-MMA-EGDMA: Glycidyl methacrylate - methyl methacrylate - ethylene glycol dimethacrylate

samples were spiked with 5 and 50 ng/mL of Cd (II) metal ions. Table II shows high recoveries percentage between 82.0 and 97.6%. The values of RSD percentage are displayed the effectiveness of Fe3O4 nanoparticles as an adsorbent in the pre-concentration of Cd (II) ions in a water sample.

D. Comparison between the Proposed Method and other Methods

The data of this work were compared with other previous studies with similar target Cd (II) metal ions Table III. Selected factors gained were comparable to those presented by other procedures designated in the literature. The achieved detection limit by the SPE procedure is comparable to most of those reported in the literature. Likewise, the LOD measured by the recommended magnetic adsorbent in this work was lower than the others.

IV. CONCLUSION

Fe_3O_4 MNPs adsorbent was successfully prepared using coprecipitation method to pre-concentrate Cd (II) metal ions before the determination using FAAS. The Fe_3O_4 MNPs adsorbent displays high pre-concentration factor, good sensitivity and ease of operation as well as rapid separation by an external magnet. Fe_3O_4 MSPE adsorbent has a high potential for Cd (II) analysis in water samples.

V. ACKNOWLEDGMENT

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