PRECONCENTRATION OF Cd²⁺ IN DIFFERENT SAMPLES BY CHEMICALLY MODIFIED SiO₂-DHAQ NANOPARTICLES

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(Received: March 18, 2010 - Accepted: March 18, 2010)

ABSTRACT

A new analytical method using 1,8-dihydroxyanthraquinone modified SiO₂ nanoparticles as solid-phase extractant has been developed for the preconcentration of trace amounts of Cd²⁺ in different samples. Conditions of the analysis such as preconcentration factor, effect of pH, sample volume, shaking time, elution conditions and effects of interfering ions for the recovery of analyte were investigated. The adsorption capacity of nanometer SiO₂-DHAQ was found to be 85.83 µmol/g at optimum pH and the detection limit (3σ) was 0.60 ng/mL. The extractant showed rapid kinetic sorption. The adsorption equilibrium of Cd²⁺ on nanometer SiO₂-DHAQ was achieved within 20 min. Adsorbed Cd²⁺ was easily eluted with 6 mL of 1M hydrochloric acid. The maximum preconcentration factor has been found to be 66.70. The method was applied for the determination of trace amounts of Cd²⁺ in different samples.

Keywords: Chemically modified SiO₂-nanoparticles, 1,8-dihydroxyanthraquinone, Preconcentration, Separation.

INTRODUCTION

In recent years, the toxicity and effects of trace elements to the danger of public health and environment have attracted increasing attention in the fields of pollution and nutrition. Metals are prevalent in the environment. There are hundred of natural and anthropogenic sources of heavy metal pollution including the mining coal, natural gas, paper and chloro-alkali industries. They are derived from natural and anthropogenic sources. Cadmium is considered a non-essential and highly toxic element with a series of cumulative effect. Its toxicity is comparable to that of arsenic and mercury but its lethal potential is higher than that of any other metallic element. In the recent years there has been an increased concern over the concentration of cadmium in drinking and natural water due to its high toxicity and pollution to the environment especially the aquatic system. Nowadays there are many known sources of contamination of cadmium owing to the large number of its inorganic salts, which are used in catalytic and synthetic reactions, in Ni-Cd battery manufacturing and as stabilizers for plastics and additives. The FAO-WHO joint expert committee on food additives recommended a provisional maximum tolerance daily in take for cadmium of 1-1.2 µg/Kg body mass from all sources^[1]. Therefore, accurate and reliable methods sometimes must be developed for cadmium determination. Because of their extremely low concentration, a preliminary concentration step i.e. preconcentration is usually necessary prior to the determination of the metals.^[2-3] Nowadays, liquid-liquid extraction^[4-6], ion-exchange resins⁷ and solid-phase extraction^[8-9] are used for the preconcentration of different metal ions. Of all these methods, solid phase extraction has been widely used since it is simple, rapid and inexpensive, less polluting to the environment and can be easily automated. Many materials such as organic chelate resin, silica gel, activated carbon, activated alumina, zeolites and microcrystalline materials are commonly used as adsorbents.

Nowadays, nanometer materials have become more important owing to its special physical and chemical properties. The field of nanocomposite materials has received the attention, imagination and close scrutiny of scientists and engineer in recent years. These particles fall within the colloidal range, exhibiting typical colloidal properties. The surface atoms are unsaturated and can therefore bind with other atoms, possess high chemical activity. Nanoparticles exhibit intrinsic surface reactivity and high surface areas and can strongly chemisorb many substances. The size, surface structure and interparticle interaction of nanomaterials determine their unique properties and the improved performances and make their potential application in many areas. Nanoparticles such as TiO₂^[10], Al₂O₃^[11], ZrO₂^[12], CeO₂^[13] and modified silica nanoparticles have been used for the preconcentration of many metal ions and give promising results when used for trace element analysis of different samples. In present work, chemically grafted SiO₂-DHAQ nanoparticles were prepared by sol-gel^[14] method and characterized by Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FT-IR). These nanoparticles have been used for the preconcentration and separation of cadmium prior to their determination by spectrophotometric method.^[15]

EXPERIMENTAL

Absorbance of Cd²⁺ was measured with UV-Vis Shimadzu-1700 spectrophotometer. The pH values were controlled by century Cp-901 digital pH meter. Infrared spectra was recorded on a Perkin Elmer FT-IR analysis.

Unless otherwise stated, all reagents used were of analytical reagent grade and all solutions were prepared with double distilled water. 3-aminopropyltriethoxysilane of GR grade was supplied by Acros Organics (USA). 1,8-dihydroxyanthraquinone(DHAQ) was obtained from Merck (Mumbai). Nanometer SiO₂ was synthesized according to the method reported.¹⁴ The average diameter of the silica nanoparticles is 100nm as confirmed by Scanning Electron Microscopy. Stock solution of Cd²⁺ was prepared by dissolving spectral pure-grade CdSO₄·8H₂O and diluted as and when required. The glassware was washed with chromic acid and soaked in 5% nitric acid overnight and then cleaned with double distilled water before use.

Surface modification of SiO₂ nanoparticles were performed in a 250mL flask. Nanometer SiO₂ (1g) was dispersed into dry toluene (30mL), and then 3-aminopropyltriethoxysilane (4mL) was gradually added, with continuous stirring. The mixture was refluxed for 6h. The silylated nanometer SiO₂ was filtered off, washed with toluene and ethanol and dried at 60°C for 3h. The product was transferred into the flask, and then 30mL diethyl ether was added followed by 2g of DHAQ and refluxed at 72°C for 4h. Reaction mixture was filtered under vacuum and the chemically modified nanoparticles were stored in dessicator.

Aliquots containing 0.5 µg of Cd²⁺ were prepared and pH was adjusted to 7.0 with 0.2 M Sodium tetraborate/boric acid buffer, 25mg of SiO₂-DHAQ particles were added, and the mixture was shaken vigorously for 20mins to facilitate adsorption of metal ion onto the adsorbent. 6mL of 1M hydrochloric acid was used for elution of Cd²⁺ from the adsorbent. Eluent was filtered with cellulose nitrate membrane (47mm and 0.1 µm) and determined by standard spectrophotometric method.¹⁵ The results of analysis are given in Table 1.

Table 1. Various parameters studied for preconcentration of Cd(II) using SiO₂-DHAQ nanoparticles as extractant.

Parameters	Results
Eluent concentration (M)	1.0
Eluent volume (mL)	6.0
pH	7.0
Adsorption capacity (µmol/g)	85.83
Sample volume (mL)	100.0
Shaking time (mins)	20.0
Extractant amount (mg)	25.0
Preconcentration factor	66.70
LOD (ng/mL)	0.60

RESULTS AND DISCUSSION

The modification of nanometer-sized material is usually required in order to prevent a conglomeration of particles and to improve its consistency in relation to other materials, such as organic polymers. In addition, the modification of nanometer-sized materials can improve the selectivity of nanometer-sized materials towards metal ions. Organosiloxane is the most often used modifiers, in which one side is linked with the inorganic nanometer-sized materials, and the exposed end is the analytical functional group. The modified nanoparticles SiO_2 -DHAQ were characterized by FT-IR and SEM.

The average diameter of the nanoparticles SiO_2 , SiO_2 -APTES and SiO_2 -DHAQ was 100nm, 1 μm and 2 μm confirmed by Scanning Electron Microscopy. Figure 1, 2 and 3 show the scanning electron micrographs of these nanoparticles respectively.

Fig 1. SEM micrograph of SiO_2 nanoparticles.

Fig 2. SEM micrograph of SiO_2 -APTES nanoparticles.

Fig 3. SEM micrograph of SiO_2 -DHAQ nanoparticles.

The chemical grafting of 1,8-dihydroxyanthraquinone on the surface of nanometer SiO_2 was confirmed by FT-IR spectrum. The main absorption peaks of nanometer SiO_2 (3448.0, 1642.5, 1404, 1070.2, 964.2, 798.8 cm^{-1}) are in agreement with standard spectrum of SiO_2 .¹⁶ Many new peaks appeared in FT-IR spectrum by grafting with DHAQ as peak at 1652 cm^{-1} arises both from C=O and C≡N stretching. The phenyl ring vibrations appear at 1500, 1467.5, 1377.5 and 1349.7 cm^{-1} .

The adsorption of Cd^{2+} on SiO_2 -DHAQ nanoparticles was studied in pH range of 3.4 to 10.0 following the recommended procedure. The results of effect of pH on the recoveries of the metal ions are shown in Figure 4. It can be seen that a quantitative recovery ($\geq 95\%$) was found for Cd^{2+} in the pH range of 7.0-10.0. Cd(II) is a soft acid and has good affinity towards hard base ligands containing the oxygen, sulphur and nitrogen groups.

Fig 4. Effect of pH on analyte recovery.

The buffer solution containing increases the selectivity and does not affect the sensitivity. Therefore, the progressive decrease in the progressive decrease in the retention of Cd(II) at low pH is due to competition between the hydrogen ion and Cd(II) for adsorption on SiO_2 -DHAQ Nanoparticles.

Elution of Cd^{2+} from SiO_2 -DHAQ nanoparticles extractant was investigated by using various concentrations of hydrochloric acid. Quantitative recoveries ($\geq 95\%$) of Cd^{2+} were obtained using 6mL of 1M hydrochloric acid as eluent. Therefore, 6mL of 1M of hydrochloric acid was used as eluent in subsequent experiments. The results of effect of eluent concentration and volume are given in Table 2 and Table 3.

Table 2. Effect of concentration of eluent solution on elution of Cd(II) (n=3).

Concentration of eluent (M)	0.25	0.5	1.0	2.0	4.0	5.0	6.0
Recovery (%)	28.23	44.45	99.09	57.47	31.14	27.85	16.73
Volume of eluent (mL)	2.0	4.0	5.0	6.0	7.0	8.0	
Recovery (%)	27.79	73.19	87.45	99.09	57.33	21.10	

Table 3. Analytical recovery of Cd(II) added to some water samples(n=3).

Samples	Added ($\mu\text{g/L}$)	Found ($\mu\text{g/L}$)	Recovery (%)
Tap water	5.0	4.90	98.0
	10.0	9.75	97.50
	20.0	19.40	97.0
Mineral water	5.0	4.86	97.20
	10.0	9.80	98.0
	20.0	19.49	97.45
Waste water	0.0	8.40	---
	5.0	13.15	97.08
	10.0	18.35	99.40

To test the effect of amount of extractant on quantitative retention of analyte, different amount of nanometer SiO_2 -DHAQ were taken by the general procedure. Quantitative adsorption of the Cd^{2+} was obtained in the range of 5-40mg of SiO_2 -DHAQ nanoparticles. 25mg of adsorbent was found to be sufficient for further studies. The results are shown in Figure 5.

Fig 5. Effect of sorbent mass on analyte recovery.

The adsorption of Cd^{2+} on 25mg of nanometer SiO_2 -DHAQ was studied for different shaking time (10-45min). The results indicated that within 20mins the extraction percentage of Cd^{2+} $\geq 95\%$ was achieved. The results are shown in Figure 6.

Fig 6. Extraction percentage of Cd(II) at different shaking time.

The adsorption capacity^[17] is an important factor as it determines how much adsorbent is quantitatively required to concentrate the analytes from a given solution. A breakthrough curve was obtained by plotting the concentration (mg/L) vs. the mmol of Cd^{2+} adsorbed per gram. From the breakthrough curve the amount of modified nanometer SiO_2 -DHAQ for Cd^{2+} was found to be $85.83 \mu\text{mol/g}$ at pH 7.0. The results are shown in Figure 7.

Fig 7. Adsorption capacity of Cd(II) on nanometer SiO_2 -DHAQ.

In order to explore the possibility of concentrating low concentration of analytes from large volumes, the effect of sample volume on the retention of metal ions was also investigated. For this purpose 50, 100, 150, 200, 250, 300 and 400mL of the sample solutions containing $1.0 \mu\text{g}$ Cd^{2+} was shaken, quantitative recoveries ($\geq 95\%$) were obtained for sample volume of $\leq 300\text{mL}$ for Cd^{2+} . Therefore, 50mL of sample volume solution was adopted for the preconcentration of analytes from sample solutions. The results are shown in Figure 8.

Fig 8. Effect of sample volume on analyte recovery.

The effect of common coexisting ions on the sorption of Cd^{2+} was investigated. In these experiments, a solution of 5.0 mg mL^{-1} of each analyte that contains the added interfering ion was analyzed according to the recommended procedure. The tolerance limit (mg L^{-1}) for anions such Cl^{-} , Br^{-} , NO_3^{-} , SO_4^{2-} , PO_4^{3-} and EDTA were 0.12, 0.008, 0.06, 0.07, 0.04 and 1.1 respectively. The tolerance limits in mg mL^{-1} for Ca^{2+} , Mg^{2+} , Co^{2+} , Ni^{2+} , Fe^{3+} , Al^{3+} , Cr^{3+} , Pb^{2+} , Mn^{2+} and Zn^{2+} were 0.41, 0.40, 0.67, 0.02, 0.03, 0.24, 0.11, 0.07, 0.06 and 0.07 respectively. These results demonstrate that SiO_2 -DHAQ nanoparticles can be used for the preconcentration Cd^{2+} in different samples, because common cations and anions at their normal levels do not affect the sorption efficiency of nanoparticles for the cadmium ions.

Under the optimized conditions, five portions of Cd^{2+} standard solutions were enriched and analyzed simultaneously following the experimental method. The relative standard deviation (RSD) of the method was 2.2 % for the determination of $5.0 \mu\text{g Cd}^{2+}$ in 100mL water samples respectively. The detection limit of this method for Cd^{2+} was 0.60 ng/mL.

APPLICATIONS

The developed method has been applied for the determination of trace amounts of Cd^{2+} in food samples (potato chips, biscuits) and spiked tap water, mineral water, waste water, synthetic (nail paints). For analysis, 200mL of sample solution was taken and studied by general procedure.

In order to establish the validity of the proposed procedure, the method was applied to the determination of the content of the studied elements in the standard reference material – Oriental Tobacco Leaves. The results are given in Table 4, 5 and Table 6.

Table 4. Determination of Cd(II) in certified reference material (tobacco leaves) (n=3).

Analyte	Concentration of metal ($\mu\text{g g}^{-1}$) tobacco leaves	
	Certified value	found value
Cd(II)	1.12±0.12	1.06±0.05
Cd(II)	14.1±0.5	14.0±0.6

Table 5. Cd(II) content in nail polish (n=3).

Sample	Added ($\mu\text{g/L}$)	Found ($\mu\text{g/L}$)	Recovery (%)
Orange	---	19.30 ^a	---
nail polish	5.0	23.99	98.72
	10.0	29.94	98.77
Brown	---	20.11 ^a	---
nail polish	5.0	24.65	98.16
	10.0	29.56	98.17
Red	---	31.24 ^a	---
nail polish	5.0	35.68	98.45

CONCLUSIONS

The preconcentration method described by using 1,8-dihydroxyanthraquinone anchored silica nanoparticles for the determination of Cd^{2+} in water samples has a good accuracy, repeatability and sensitivity. The preparation of sorbent is easy and the preconcentration factors obtained are sufficiently large. The results of comparison of preconcentration factor are given in Table 7.

Table 6. The results of comparison of preconcentration factor are given in this table.

Support	Reagent	Preconcentration Factor	Ref
Amberlite XAD-2	2-aminothiophenol	28.0	18
Amberlite XAD-2	pyrocatechol	22.0	19
Polyurethane foam	2-(6-methyl-2-benzothiazolylazo)chromotropic acid	37.0	20
Metal alkoxide glass	8-quinolinol	55.0	21
Chitosan biopolymer	5-sulphonic acid-8-hydroxyquinoline	14.0	22
Naphthalene	ammonium pyrrolidine dithiocarbamate	53.0	23
Silica nanoparticles	1,8-dihydroxyanthraquinone	66.70	present work

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