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Ionic liquid-modified silica as sorbent for preconcentration of cadmium prior to its determination by flame atomic absorption spectrometry in water samples

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ABSTRACT

A new method based on a microcolumn packed with ionic liquid-modified silica combined with flame atomic absorption spectrometry has been developed for the determination of trace amount of cadmium (Cd) in environmental samples. The ionic liquid-modified silica sorbent was prepared by the surface of commercial silica was chemically modified with ionic liquid. Several factors influencing the preconcentration efficiency of Cd and its subsequent determination, such as pH of the sample, sample flow rate and volume, concentration of chelating agent, eluent and interfering effect, have been investigated. Cd could be quantitatively retained by ionic liquid-modified silica in the pH range of 9–12, then eluted completely with 2.0 mL of 1.0 mol L^{-1} HCl. The detection limit of this method for Cd was 0.60 μg L^{-1} with an enrichment factor of 75, and the relative standard deviation (RSD) was 3.7% at the 100 μg L^{-1} Cd level. The method has been applied for the determination of trace amount of Cd in water samples with satisfactory results.

1. Introduction

Cadmium (Cd) is a highly toxic non-essential element, and may result in bioaccumulation, mainly in the kidneys and liver for a relatively long time [1]. Prolonged intake of Cd leads to severe dysfunction of the kidneys, and it can also inhibit the action of the zinc enzymes by displacing the zinc. Moreover, the possible role of Cd in human carcinogenesis has been also studied [2,3]. The most exposure of human to Cd comes from the tobacco smoke and from ingestion of food, which arises from the uptake of Cd by plants from fertilizers, sewage sludge, manure and atmospheric deposition [4,5]. Determination of Cd in environmental and biological materials is an important screening procedure in the studies of environmental pollution and occupational exposure.

Flame atomic absorption spectrometry (FAAS) has been widely used for the determination of trace quantities of Cd because of the low costs, operational facility and high sample throughput. However, the direct determination of Cd at trace level by FAAS is limited not only by insufficient sensitivity, but also by matrix interference. The most effective way to avoid these problems is to perform appropriate sample pretreatment, aimed at lowering the limit of detection, by both removal of interferences and increasing the concentration of the analyte. Various techniques for Cd separation and preconcentration have been proposed, such as coprecipitation [6,7], liquid–liquid extraction [8,9], cloud point extraction [10–12], solid-phase extraction [13–18], liquid phase microextraction [19,20] and electrochemical deposition [21], etc. Recently, solid-phase extraction (SPE) have been extensively used for separation and determination of trace elements because this approach offers a number of important benefits, such as reducing of disposal costs, achievement of high recoveries and the sorbent easy to recover. SPE also offers broader range of applications than liquid–liquid extraction due to the large choice of sorbent.

Room temperature ionic liquid (IL) is a kind of burgeoning green solvent, and has aroused increasing interest for their promising role as alternative media in synthesis, separation, and electrochemistry applications as a result of its unique chemical and physical properties [22–24]. Its non-inflammability and non-volatility provided advantages for using it as a replacement to volatile organic compounds in solvent extraction processes [25,26]. Moreover, the higher extraction efficiency of metal ions in some IL-based extraction system brought it more attention. As a novel separation technology, IL-based extraction was found to have some disadvantages need to be overcome, such as lower rate of mass transfer, longer equilibrium time, difficulty in separate-phase and entraining loss of IL to aqueous phase [27]. These problems can be ameliorated by immobilizing ionic liquids on different solid substrates. Supported ionic liquid phase combine the advantages of ionic liquids with those of heterogeneous support materials. Some studies have successfully confined various ionic liquids phases to the surface

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of support materials and explored their potential catalytic applications [28,29]. On the analytical chemistry applications of supported ionic liquid phase, ionic liquid-modified silica particles were used as HPLC stationary phase to separate some familiar organic compounds [30,31], and as sorbent for solid phase extraction of organic compounds [32–34]. Ionic liquid impregnated resins were prepared for solid–liquid extraction of rare earth elements and noble metal ion [35,36]. However, there is not the report of the application of supported ionic liquid phase for the preconcentration of trace metal ions.

In this work, ionic liquid-modified silica (IL-silica) was synthesized and characterized by FT-IR. The potential of ionic liquid-modified silica for the preconcentration of trace Cd was assessed using column method. A new method using a microcolumn packed with ionic liquid-modified silica as sorbent has been developed for the preconcentration of trace amount of Cd after forming complex with dithizone, which reacts with metallic ions forming a very stable complex and has found numerous applications in trace element separation and preconcentration [37,38], and determination by FAAS.

2. Experimental

2.1. Apparatus

A TAS-990 atomic absorption spectrophotometer (Beijing Purkinge General Instrument Co. Ltd., Beijing, China) equipped with deuterium lamp background correction was used for the determination of Cd. A Cd hollow cathode lamp operating at 228.8 nm was used as the radiation source. The lamp current, spectral band pass and observation height were set at 2.0 mA, 0.4 nm and 5.0 mm, respectively. Other instrumental parameters were adjusted according to the manufacturer's recommendation. The pH values were measured with a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, China). A HL-2 peristaltic pump (Shanghai Qingpu Huxi Instrument Factory, Shanghai, China) was used in the separation/preconcentration process. A laboratory-made PTFE microcolumn (20 mm × 3.0 mm i.d.), packed with IL-silica, was used in the manifold for separation/preconcentration. A minimum length of PTFE tubing with i.d. of 0.5 mm was used for all connection. A MK-III microwave digestion system (Shinco institute of microwave digestion technology, Shanghai, China) was used to dissolve the solid samples.

2.2. Standard solution and reagents

Stock standard solution (1000 mg L^{-1}) of Cd was obtained from the National Institute of Standards (Beijing, China). Working standard solutions were obtained by appropriate dilution of the stock standard solutions. 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4MIM][PF_6]$) was purchased from Shanghai Chengjie Chemical Co., Ltd. (Shanghai, China). Silica gel (200–300 mesh, Qingdao Ocean Chemical Factory, Qingdao, China) was boiled with (1 + 1) nitric acid for 3 h, then immersed in (1 + 1) hydrochloric acid for 24 h, finally washed with doubly distilled water until no chloride appeared in the washings. The cleaned silica gel was dried at 120 °C for 24 h. 0.01 mol L^{-1} stock solution of dithizone was prepared by dissolving appropriate amount of dithizone (AR, Shanghai Chemistry Reagent Company, Shanghai, China) in tetrahydrofuran. All reagents used were of analytical reagent grade or better. Doubly distilled water was used throughout. The following buffers were used to control the pH of the solutions: sodium acetate–acetic acid (pH 3–6), ammonium acetate–ammonia (pH 6–8), and ammonium chloride–ammonia (pH 8–10).

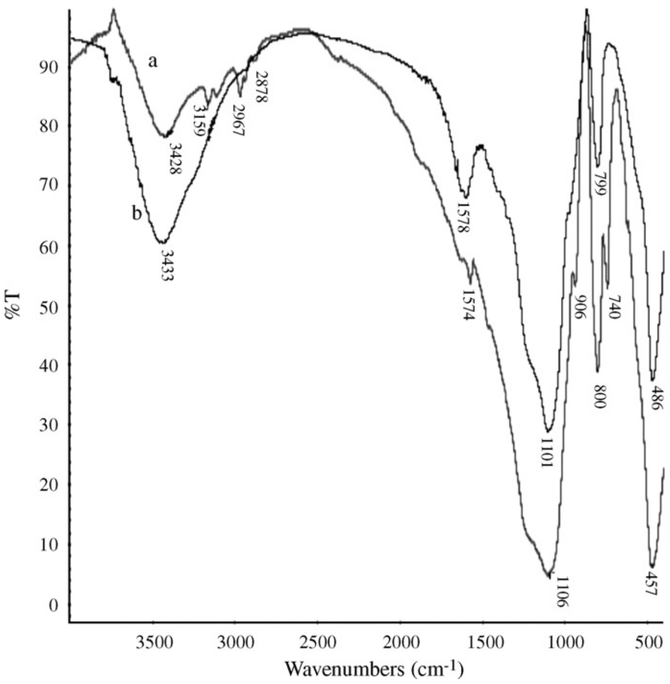

Fig. 1. FT-IR spectrums of ionic liquid-modified silica (a) and silica (b).

2.3. Preparation of ionic liquid-modified silica

IL-silica was prepared as described previously [39]. A typical example is as follows: to a stirred solution of $[C_4MIM][PF_6]$ (0.500 g) in acetone, 1.5 g of silica powder was added. After stirring for 2.5 h, the volatile components of the mixture were evaporated by water bath. Then the resulting material was washed thoroughly with methylene chloride and distilled water, and dried under vacuum at 150 °C for 3 h, leading to a white powder. The total weight of the IL-silica is 1.8 g, so 0.3 g of ionic liquid was grafted on the surface of silica.

Fig. 1 shows the FT-IR spectrums of $[C_4MIM][PF_6]$ modified silica (a) and silica gel before modification (b). It can be seen that a new absorption peak at the position of about 1574 cm^{-1} appeared after silica gel being treated with $[C_4MIM][PF_6]$. This absorption peak could be attributed to the C=C vibration of imidazole ring. The peak at the position of 3159 cm^{-1} could be attributed to C–H vibration of aromatic cycle. The peak at the position of 2967 and 2878 cm^{-1} could be attributed to C–H vibration of saturated hydrocarbon. These peaks indicated that ionic liquid has been grafted on the surface of silica.

2.4. Column preparation

Thirty milligrams of IL-silica was introduced into a PTFE microcolumn (20 mm × 3.0 mm i.d) plugged with a small portion of glass wool at both ends. Before use, 2.0 mol L^{-1} HCl solution and doubly distilled water were passed through the column to clean and condition it. Then, the column was conditioned to the desired pH by passing 10 mL of the corresponding buffer solution through the column.

2.5. General procedure

A portion of aqueous sample solution containing Cd and 8×10^{-6} mol L^{-1} of dithizone was prepared, and the pH value was adjusted to the desired value with corresponding buffer solution. The solution was passed through the column by using a peristaltic pump at a flow rate of 2.0 mL min^{-1}. Afterwards, the retained Cd ion was eluted with 2.0 mL of 1.0 mol L^{-1} HCl solution at a flow rate of 0.2 mL min^{-1}. The analyte in the effluent was determined by FAAS. A blank was always taken through the whole procedure. The column could be used repeatedly after regeneration with 2.0 mol L^{-1} HCl solution and doubly distilled water, respectively.

2.6. Sample preparation

A portion (1.0000 g) of a stream sediment reference material (GBW07307, obtained from Perambulation Institute of Physical Geography and Geochemistry of Geological and Mineral Ministry, Langfang, China) was accurately weighed into a PTFE vessel, treated with 9 mL of concentrated HCl and 3 mL of concentrated HNO_3. Then the vessel was submitted to a power program in the microwave oven. There heating steps with a duration of 5 min each, with 250, 400 and 650 W were applied. The program was repeated twice to obtain a clear solution. The solution was heated to near dryness and the residue dissolved in 0.1 mol L^{-1} HNO_3. The final volume was made up to 100 mL with doubly distilled water after adjusting of pH to 10.0.

Lake water sample was collected from East Lake (Wuhan, PR China), and tap water sample was freshly collected from our laboratory, after allowing the water to flow for 5 min. All water samples were filtered through a 0.45 μm membrane filter and analyzed as soon as possible.

3. Results and discussion

3.1. Effect of pH

In order to evaluate the effect of pH on the adsorption of Cd, the pH values of sample solutions were adjusted to a range of 3–12 with corresponding buffer solution and processed according to the recommended procedure. The adsorption percentage of Cd was calculated based on a difference between the amounts of Cd in the starting sample and the solution out flowing from the column. The results were shown in Fig. 2. As can be seen, quantitative adsorption (>95%) was found for Cd in the pH range of 9–12. In this work, a pH of 10.0 was selected as the compromise condition.

3.2. Effect of flow rate of sample solution

The flow rate of sample solution affects the retention of Cd on the adsorbent and the duration of analysis. Therefore, the effect of flow rate of sample solution on the adsorption of Cd was examined in the range of 0.5–2.0 mL min^{-1} under the optimum pH condition according to the recommended procedure. It was found that the flow rate in the range of 0.5–2.0 mL min^{-1} had no significant influence on the adsorption of Cd. Thus, all subsequent experiments were performed at a flow rate of 2.0 mL min^{-1}, the highest flow rate of the manifold used in this experiment.

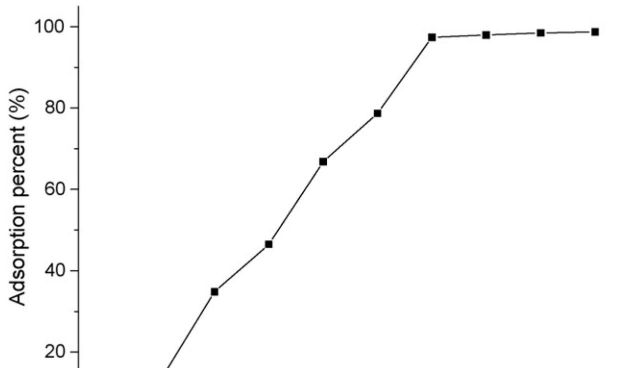

Fig. 2. Effect of pH on the adsorption of Cd on IL-silica. Cd: 0.5 μg mL^{-1}; dithizone: 8×10^{-6} mol L^{-1}; sample volume: 20 mL; flow rate: 2.0 mL min^{-1}.

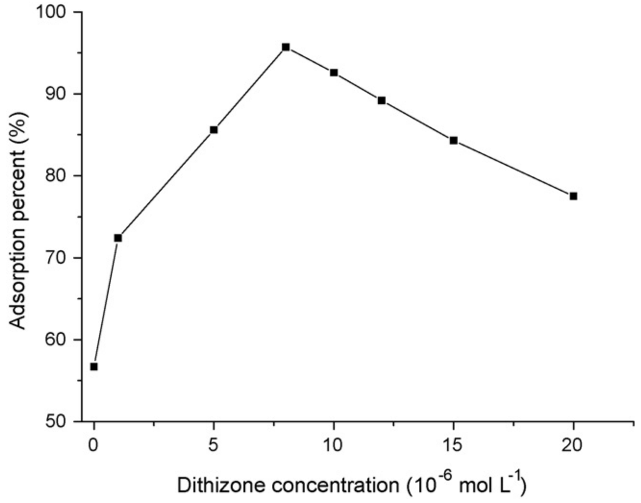

Fig. 3. Effect of the concentration of dithizone on the adsorption of Cd on IL-silica. Cd: 0.5 μg mL^{-1}; pH 10.0; sample volume: 20 mL; flow rate: 2.0 mL min^{-1}

3.3. Effect of dithizone concentration

The influence of the concentration of dithizone on the adsorption process was investigated in the range from 1.0×10^{-6} to 2.0×10^{-5} mol L^{-1} and the results were shown in Fig. 3. The adsorption percentage of Cd increased along with the dithizone concentration. However, further increase in the concentration of dithizone, beyond 8×10^{-6} mol L^{-1}, caused a significant decrease in the adsorption of Cd. This is most probably due to the competition of dithizone itself with Cd-dithizone complex to transfer into the IL-silica. Hence, 8×10^{-6} mol L^{-1} was employed as the optimum concentration of dithizone.

3.4. Elution of the adsorbed Cd

As shown in Fig. 2, the adsorption of Cd is negligible at low pH. For this reason, various concentrations HCl and HNO_3 were studied for the elution of retained Cd from the microcolumn at the flow rate of 0.2 mL min^{-1}. The results obtained are given in Table 1. As can be seen, quantitative recovery (>95%) could not be achieved when HNO_3 was used as eluent, and 1.0 mol L^{-1} HCl was sufficient for complete elution of Cd.

The effect of eluent volume on the recovery of Cd was also studied by keeping the HCl concentration of 1.0 mol L^{-1}. It was found that quantitative recovery (>95%) could be obtained with 2.0 mL of 1.0 mol L^{-1} HCl. Therefore, 2.0 mL eluent was used in the following experiments.

Table 1
Eluent data (%) for Cd adsorbed on IL-silica.

Eluent (mol L^{-1})	0.5	1.0	2.0	3.0	4.0
HCl	80.4	95.3	95.1	95.5	96.1
HNO_3	15.7	22.0	26.9	43.5	47.3

(Eluent volume: 2.0 mL)

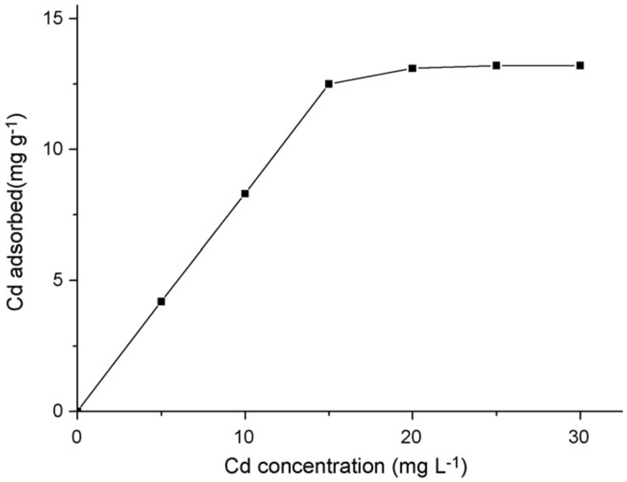

Fig. 4. Breakthrough curve of Cd on IL-silica. Sample volume: 25 mL, other parameters are similar to the recommended procedure

3.5. Effect of sample volume

In order to explore the possibility of enriching low concentrations of analyte from large volume, the effect of sample volume on the recovery of Cd was investigated. For this purpose, 25, 50, 100, 150 and 200 mL of sample solutions containing 0.5 μg of Cd were processed according to the recommended procedure. It was found that quantitative recovery (>95%) was obtained up to a sample volume of 150 mL, and the adsorbed Cd could be eluted with 2.0 mL eluent, so an enrichment factor of 75 was achieved by this method.

3.6. Adsorption capacity

To determine the adsorption capacity, 25 mL sample solutions with the different Cd concentration (from 0 to 30 mg L^{-1}) was adjusted to pH 10.0, and the proposed preconcentration procedure was applied. The amount of Cd adsorbed at each concentration level was determined. The breakthrough curve for Cd was gained by plotting the concentration (mg L^{-1}) of Cd solution versus the milligrams of Cd adsorbed per gram IL-silica, and shown in Fig. 4. From the adsorption isotherm, the adsorption capacity of IL-silica for Cd was found to be 13.3 mg g^{-1}.

3.7. Column reuse

The stability and potential regeneration of the column were investigated. The column can be reused after regenerated with 10 mL 2.0 mol L^{-1} HCl and 20 mL double distilled water, respectively, and stable up to at least 20 adsorption–elution cycles without significant decrease in the recovery of Cd.

Table 2
Tolerance limits for coexisting ions for the adsorption of Cd.

Coexisting	Tolerance limit of ions (mg L^{-1})
Na^+, K^+	5000
Ca^{2+}, Mg^{2+}	2000
Cu^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}	500
Fe^{3+}, Al^{3+}	100
SO_4^{2-}, Cl^-	2000
PO_4^{3-}	500

3.8. Effect of interferences

The effects of common coexisting ions on the adsorption of Cd on IL-silica were investigated. In these experiments, the solutions of 100 μg L^{-1} of Cd containing the interfering ions were treated according to the recommended procedure. The tolerance limits of the coexisting ions, defined as the largest amount making the recovery of Cd less than 95%, are given in Table 2. It can be seen that the presence of major cations and anions has no significant influence on the preconcentration of Cd ion under the selected conditions.

3.9. Detection limits and precision

Under the optimum experimental conditions, the calibration curve for Cd was linear in the concentration range from 1.0 to 800 μg L^{-1} with a correlation coefficient of 0.9982. The calibration function was A (absorbance) = 0.0005c (μg L^{-1}) + 0.0065. The detection limit of this method, evaluated as the concentration corresponding to three times the standard deviation of eleven replicate measurements of blank solution using the preconcentration method, was found to be 0.60 μg L^{-1} for Cd. The precision of this method (RSD), examined by eleven replicate measurements of 100 μg L^{-1} of Cd solution, was found to be 3.7%.

Table 3 compares the characteristic data of the present method with those reported in literatures. Generally, the detection limit obtained by the present method is comparable to those reported method, and the adsorption capacity and the enrichment factor of IL-silica are better than other sorbents for Cd.

3.10. Analytical application

In order to establish the validity of the proposed procedure, the method has been applied to the determination of Cd in the sediment certified reference materials (GBW07307, China). The analytical value (1.01 ± 0.05 μg g^{-1}, n = 5) is in good agreement with the certified value (1.05 ± 0.08 μg g^{-1}).

The proposed method was applied to the determination of Cd in lake water and tap water samples. In addition, the recovery experiments of different amounts of Cd were carried out, and the results are shown in Table 4. The results indicated that the recoveries were reasonable for trace analysis, in a range of 95–103%.

Table 3
Comparison of the published methods with the proposed method in this work.

Adsorbent	Adsorption capacity (mg g^{-1})	Enrichment factor	Detection limit (μg L^{-1})	Reference
Naphthalene	–	40	0.6	[13]
Chelating resin	7.3	50	0.42	[14]
Activated carbon	0.08	–	1.0	[15]
Al_2O_3	0.89	21.9	0.08	[16]
Biosorbent	–	32	1.7	[17]
Modified Wool	1.3	39	0.037	[18]
IL-silica	13.3	75	0.6	this work

Table 4
Determination of Cd (μg L^{-1}) in water samples[a].

Samples	Added	Found[b]	Recovery (%)
Lake water	0	4.50 ± 0.13	–
	10	14.16 ± 0.27	97
	20	23.58 ± 0.45	95
Tap water	0	2.18 ± 0.11	–
	10	11.75 ± 0.25	96
	20	22.73 ± 0.33	103

[a] Sample volume: 100 mL.
[b] Mean ± S.D., $n = 5$.

4. Conclusions

It can be concluded from the results that ionic liquid-modified silica is an effective sorbent for Cd and can be used for its preconcentration from aqueous solutions. The proposed method based on preconcentration with IL-silica microcolumn and determination by FAAS showed enough sensitivity for trace Cd determinations in various samples. The precision and accuracy were satisfactory. The method can be applied to the separation, preconcentration and determination of Cd in real samples.

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