



Alumina coated with oxazolone derivative for extraction of trace amounts of cadmium and copper from water and plant samples

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ABSTRACT

A solid phase extraction procedure is proposed for simultaneous separation and preconcentration trace amounts of Cu(II) and Cd(II) using alumina coated with N'-{4-[4-{1-[4-(dimethylamino)phenyl]methylidene}-5-(4-H)oxazolone]phenyle}acetamide and determination by flame atomic absorption spectrometry. Using 0.1 g of the sorbent, the metal ions were sorbed at pH 7 and recovered with 5.0 mL of 0.5 mol L⁻¹ HNO₃. It was found that extraction can be performed from the sample volumes of 2000 and 800 mL for Cu and Cd, respectively (preconcentration factors of 400 for Cu and 160 for Cd). Obtained sorption capacities for 1 g sorbent were 8 mg Cu and 14 mg Cd. The linearity was maintained in the concentration range of 0.1 ng mL⁻¹ to 7.0 µg mL⁻¹ for Cu and 0.13 ng mL⁻¹ to 2.0 µg mL⁻¹ for Cd in the original solution. Eight replicate determinations of a mixture containing 1.0 µg mL⁻¹ each of the elements in the final solution gave relative standard deviation ±1.6 and ±1.3% for Cu and Cd, respectively. The detection limit was calculated as 0.06 and 0.05 ng mL⁻¹ for Cu and Cd, respectively. The proposed method was successfully applied to the determination trace amounts of Cu and Cd in the water and plant samples.

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1. Introduction

Cadmium is one of the most toxic elements and accumulates in humans mainly in the kidneys and liver. A prolonged intake of cadmium leads to calcium regulation in biological systems, which induces cell injury and death. It also inhibits the action of zinc enzymes by substitution. Cd is also a teratogenic and carcinogenic agent [1].

Cd enters the organism primarily via the alimentary and/or respiratory tract. The sources of this metal are food, drinking water and air [2]. Due to that, trace and ultra-trace determinations of Cd in environmental and biological samples have become of increasing interest [3].

Copper is a heavy metal extensively examined in environmental, industrial and biological applications. Copper is vital and toxic for many biological systems [4,5], so that its determination in water samples is warranted by the narrow window of concentration between essentiality and toxicity [6,7]. On the other hand, copper is an important element in geochemistry. It can be easily released from silicate, sulfites and oxides after some physical and chemical weathering and then transferred by water into soil and sediments

[8]. Thus, the determination of trace amounts of copper in different matrices is of great importance.

Despite the sensitivity and selectivity of analytical techniques such as flame atomic absorption spectrometry (FAAS) and inductively coupled plasma optical emission spectrometry (ICP-OES), there is a great necessity for preconcentration of copper and cadmium prior to their determination, basically due to their low concentration or the effects of matrix in aqueous samples. Preconcentration procedures such as liquid–liquid extraction [9,10], cloud point extraction [11–14], coprecipitation [15–18], ion exchange [19], liquid phase microextraction [20] and solid phase extraction [21–27] have been applied to extract copper and cadmium ions.

Solid phase extraction (SPE) is an attractive method that reduces consumption of and exposure to solvent, disposal costs and extraction time. The nature and the properties of the sorbent materials are of prime importance for effective retention of materials in SPE.

Aluminum oxide is one of the most widely used adsorbents, as it does not swell and has good mechanical strength, small solubility and stability in a broad pH range [28]. Immobilization of organic compounds on the surface of the solid support is usually aimed at modifying the surface with certain target functional groups for a higher selectivity of the extraction. The selectivity of the modified solid phases towards certain metal ions is attributed to several well-known factors, such as the size of the organic compound used to modify the sorbent, the activity of the loaded surface groups and the type of the interaction of functional group [29].

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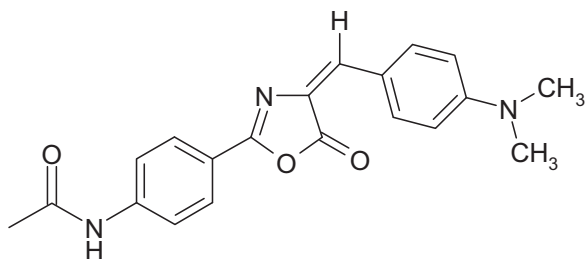


Fig. 1. *N'*-(4-[4-{1-[4-(dimethylamino)phenyl]methylidene}-5-(4-H)oxazolone]phenyle)acetamide (DMOA).

In this work, the analytical potential of alumina coated with *N'*-(4-[4-{1-[4-(dimethylamino)phenyl]methylidene}-5-(4-H)oxazolone]phenyle)acetamide [DMOA] (Fig. 1) was examined for simultaneous separation and preconcentration trace amounts of Cu(II) and Cd(II) in real water and plant samples. The analytical conditions for the preconcentration of analyte elements were investigated.

2. Experimental

2.1. Reagents and solutions

The stock solutions of Cu(II) and Cd(II) were prepared by dissolving 0.2950 g of copper nitrate $\text{Cu}(\text{NO}_3)_2$ 99.99% (Merck, Darmstadt, Germany), and 0.2770 g $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ 99.99% in distilled water and diluting to 100.0 mL, separately. The standard working solutions were diluted daily prior to use. The oxazolone ligand DMOA was synthesized and purified as recommended method in the section 2.3. A 0.2% (m/v) solution of the ligand was prepared by dissolving 0.20 g of DMOA in DMF and diluting to 100.0 mL with ethanol. Buffer solution was prepared from 0.2 M potassium dihydrogen phosphate and 0.2 M dipotassium hydrogen phosphate (Aldrich, Milwaukee, USA) for pH 7. Al_2O_3 (0.063–0.2 mm or 70–230 mesh ASTM) (Merck) was used as sorbent.

2.2. Instruments

An atomic absorption spectrometer model Sens AA (Dandenong, Australia, <http://www.gbcaustralia.com>) equipped with deuterium lamp background corrector was used for the determination of Cd and Cu in air–acetylene flame. The instrumental settings of the spectrometer were as follows: wavelength, 324.8 and 228.8 nm; slit width, 0.5 and 0.5 nm; lamp current, 4 and 4 mA; acetylene flow, 1.5 L min^{-1} and air flow, 3.5 L min^{-1} for copper and cadmium, respectively. A mechanical shaker KS 130 basic (Deutschland, Germany, www.ika.net) having speed control and timer was used for preparation of the sorbent. Funnel-tipped glass tubes (5 mm × 100 mm) equipped with stopcock were used as column for the preconcentration purposes. A 691 Metrohm pH meter (Herisau, Switzerland, <http://www.metrohm.com>) was employed for pH measurements.

2.3. Preparation of the ligand DMOA

4-Aminohippuric acid (0.01 mol) (Merck, >98%), anhydrous sodium acetate (0.01 mol) (Merck, 99.99%), 4-(*N,N*-dimethylbenzaldehyde (0.01 mol) (Merck, >99%), and acetic anhydride (40 mL) (Merck, >98%) were heated under reflux (temperature $\sim 150^\circ\text{C}$) with intermittent shaking until the mixture is transformed from an orange, semi-solid mass to a deep red liquid (2 h). Then the mixture was cooled to room temperature and the

crystalline product was separated by filtration. The crude product was recrystallized and purified from ethanol.

2.4. Preparation of the alumina coated with DMOA

3.0 g of the alumina was added to 50 mL of the solution containing 0.2% DMOA and the mixture was shaken at room temperature for 2 h. The reagent coated alumina was filtered, washed with water and dried at room temperature for 24 h.

2.5. General procedure

A small amount of glass wool was placed in the end of the columns to prevent loss of the sorbent during sample loading. Then, the columns were packed with 100 mg of the alumina coated with DMOA and conditioned with a buffer solution at pH ~ 7 . An aliquot of the sample solution containing Cu(II) (0.2–35.0 μg) and Cd(II) (0.1–10.0 μg) was taken in a 50 mL beaker and to it was added 2 mL phosphate buffer solution with pH 7. The total volume of the solution was made up to about 30 mL with distilled water. It was then passed through the column with flow rate of 1 mL min^{-1} . The retained metal ions were eluted from the solid phase with 5.0 mL of $0.5 \text{ mol L}^{-1} \text{ HNO}_3$. This solution was aspirated into an air–acetylene flame for the determination of Cu and Cd by FAAS.

3. Results and discussion

The preliminary experiments showed that the bare alumina can adsorb a lot of metal ions, but, adsorption was not selective and the recoveries were incomplete (for example Ni: 72%, Cu: 84%, Co: 78%, Fe: 90%, Mn: 80%, Zn: 85%, Ag: 30%, Cd: 87%). By immobilization of the ligand DMOA on the alumina, only, Cu and Cd can be adsorbed in the specific pH. On the other hand, the coating of alumina with the ligand increases the adsorption capacity for Cu and Cd.

In order to achieve the best performance, the separation/preconcentration procedure was optimized for various analytical parameters, such as pH of the sample, the flow rate of eluent and sample solution, amount of adsorbent, volume and type of the eluent solution, volume of the buffer and volume of the sample solution. Various ion interference effects were also investigated.

3.1. Effect of the sample pH

Since the pH of the aqueous solutions is an important analytical factor in the solid phase extraction studies of metal ions, the influence of pH on the recovery of analyte ions was examined in the pH range of 1–10 using the diluted solution HNO_3/NaOH or the proper buffers. The same results were obtained using buffer or HNO_3/NaOH . Cu(II) ions were quantitatively recovered at pH range of 3.0–9.0, while Cd(II) ions were recovered at pH range of 6.5–7.5. In subsequent studies, the pH was kept at 7 using potassium dihydrogen phosphate buffer solution.

3.2. Effect of type and concentration of eluent

Different acids such as HNO_3 , H_2SO_4 and HCl were tested for desorption of Cu and Cd. It was observed that all of them can desorb Cu and Cd from the column. Among the tested acids, the nitric acid provided higher recovery compared to the other acids. It seems that oxidation capability of HNO_3 is the reason for high recovery, as the concentration of hydronium ion in acids such as HCl and HNO_3 is the same. Thus, HNO_3 was selected and its concentration was varied between 0.05 and 2 mol L^{-1} . It was found that 5.0 mL of $0.5 \text{ mol L}^{-1} \text{ HNO}_3$ was sufficient for simultaneous desorption Cu

and Cd. Therefore, in all the experiments 5.0 mL 0.5 mol L⁻¹ HNO₃ was used for desorption.

3.3. Effect of flow rate of sample and eluent solution

The retention of an element on a sorbent also depends on the flow rate of the sample solution. Thus, the effect of flow rate of the sample and elution solution on the retention and recovery of ions was investigated under optimum conditions. The solution containing Cu and Cd was passed through the column with the flow rates adjusted in the range of 0.5–3 mL min⁻¹. It was observed that, at flow rates greater than 3 mL min⁻¹, there was a decrease in the recovery of copper and 1 mL min⁻¹ for cadmium. The reason for this decrease is probably insufficient contact of the metal ions and the sorbent to reach equilibrium. Therefore, a flow rate of 1 mL min⁻¹ was applied for Cu and Cd in subsequent experiments.

For desorption of metal ions, flow rate was varied between 0.5 and 3 mL min⁻¹. The flow rate of 2 mL min⁻¹ was adequate for simultaneous desorption of Cu and Cd.

3.4. Effect of amount of the sorbent

The amount of sorbent is another important parameter that affects the recovery. A quantitative retention is not obtained when the amount of sorbent is less. On the other hand, an excess amount of sorbent prevents the elution of the retained chelates by a small of eluent quantitatively. For this purpose, different amounts of the sorbent (5–100 mg) were examined. The results showed that quantitative recoveries (>95%) of the metal ions were obtained when the sorbent quantity was greater than 30 mg. With 100 mg of the sorbent, the highest recovery was obtained. Therefore, 100 mg was selected for further experiments.

3.5. Breakthrough volume

The measurement of breakthrough volume is important in solid phase extraction because breakthrough volume represents the sample volume that can be preconcentrated without the loss of analyte during elution of the sample. The volume of the first aqueous phase, containing a fixed amount of analytes (5.0 µg Cu and 5.0 µg Cd), was varied in the range of 50–2000 mL under the optimum conditions, keeping other variables constant, and was passed through column for preconcentration. It was found that recovery was quantitative to 2000 mL for copper and 800 mL for cadmium. At higher sample volumes, the recoveries decreased gradually with increasing volume of sample solution. Because of the elution volume was 5.0 mL, preconcentration factors were obtained 400 for Cu and 160 for Cd.

3.6. Sorption capacity of the sorbent

The sorption capacity of the sorbent was determined by the batch process, by equilibrating 0.5 g of the sorbent with the solution containing 5.0 mg copper or 10.0 mg cadmium at pH 7 separately, at room temperature for 2 h to ensure complete equilibration. The mixture was filtered and the concentration of Cd and Cu in the supernatant solution was determined by FAAS. The loading capacity of the sorbent for metal ions was calculated from the difference between the metal ion concentration before and after sorption. The sorption capacities were found 8.0 mg Cu²⁺ and 14.0 mg Cd²⁺ for 1.0 g sorbent.

3.7. Analytical performance

Calibration curves for the determination of copper and cadmium were prepared according to the proposed procedure under the opti-

Table 1
Effect of different salts and metal ions.

| Salt or metal ion | Concentration (mg L ⁻¹) | |
|--|-------------------------------------|--------|
| | Cu | Cd |
| NaHCO ₃ , KH ₂ PO ₄ , KBrO ₃ | 50,000 | 50,000 |
| Na ₂ SO ₄ , NH ₄ SO ₄ | 20,000 | 20,000 |
| Na ₂ CO ₃ | 25,000 | 20,000 |
| Na ₂ SO ₃ | 1,000 | 20,000 |
| NaF | 30,000 | 30,000 |
| NaI | 50,000 | 10,000 |
| NaCl | 30,000 | 25,000 |
| NaBr | 15,000 | 15,000 |
| Pb(II), Zn(II) | 30 | 30 |
| Cr(III), Co(II) | 25 | 30 |
| Ni(II) | 30 | 25 |
| Fe(III) | 10 | 10 |
| Ag(I) | 30 | 7 |

Conditions: 5.0 µg Cu and 5.0 µg Cd; sorbent, 100 mg; pH 7; HNO₃, 5.0 mL 0.5 mol L⁻¹; flow rate, 1 mL min⁻¹.

imum conditions. The linearity was maintained in the concentration range of 0.04–7 µg mL⁻¹ in the final solution or 0.10 ng mL⁻¹ to 7.0 µg mL⁻¹ in the original solution for Cu and 0.02–2 µg mL⁻¹ in the final solution or 0.13 ng mL⁻¹ to 2.0 µg mL⁻¹ in original solution for Cd. The equations of the lines are $A = 0.0743C + 0.0018$ for Cu(II) and $A = 0.2504C + 0.0088$ for Cd(II) in the final solution, respectively where A is the absorbance and C is concentration of the metal ions (µg mL⁻¹). The regression coefficients for the lines are 0.998 and 0.997 for Cu(II) and Cd(II), respectively.

The preconcentration factors for Cu and Cd according to 5.0 mL eluent and the workable maximum sample volumes (2000 and 800 mL) were calculated as 400 and 160, respectively. Eight replicate determination of 5.0 µg copper and 5.0 µg cadmium in the 5.0 mL final solution gave a relative standard deviation of ±1.6% for Cu and ±1.3% for Cd. The limit of detection (LOD) for the analyte ions based on $3\sigma_{bl}/m$ ($n = 8$) was 0.06 ng mL⁻¹ for Cu and 0.05 ng mL⁻¹ for Cd in initial solution.

3.8. Effect of diverse ions

Various salts and metal ions were added to a solution containing 5.0 µg of Cu(II) and 5.0 µg of Cd(II) and the general procedure was applied. The tolerance limit was set as the concentration of the ion required to cause ±3% error. It was found from Table 1 that ions which often coexisted with Cu(II) and Cd(II) in various real samples did not interfere. This suggests that the new solid phase extractant has good selectivity for the recovery of Cu and Cd. Thus, this method is selective and can be used for the determination of Cu and Cd in the plant and water samples.

3.9. Analysis of copper and cadmium in standard samples

The accuracy of the proposed method was tested for the determination of copper and cadmium in standard samples: National Institute for Environment Studies (NIES) No. 2 pond sediment and No. 3 Chlorella. A 0.1000 g standard sample was taken in a beaker and dissolved in concentrated nitric acid with heating. The solution was cooled, diluted and filtered. The filtrate was made to 100.0 mL with distilled water in a calibration flask. A suitable aliquot of the pre-treated sample solution was taken and analyzed by the proposed procedure. The results are given in Table 2, which are in good agreement with the certified values.

3.10. Analysis of copper and cadmium in the plant samples

The applicability of the proposed method was evaluated in the plant samples. A 0.50 g of the dry plant samples (Pistachio, Car-

Table 2
Analysis of copper and cadmium in standard samples.

| Sample | Composition | Found ^a | Recovery (%) |
|---------------------------|---|--|---------------|
| NIES, No. 2 Pond sediment | Fe: 6.53 ± 0.35, Ca: 0.81, K: 0.68, Al: 10.6 ± 0.5%, Zn: 343, Ni: 40, As: 12, Pb: 105, Cu: 210, Cr: 75, Co: 27, Cd: 0.82 (μg g ⁻¹) | Cu: 207.6(μg g ⁻¹) ± 2.7 Cd: 0.799(μg g ⁻¹) ± 0.011 | 98.8 97.4 |
| NIES, No. 3 Chlorella | K: 1.24 ± 0.06, Mg: 0.33 ± 0.02, Ca: 0.46 ± 0.03, Fe: 0.185 ± 0.010, P: (1.7)%, Cu: 3.5 ± 0.3, Zn: 20.5 ± 1.0, Sr: 40 ± 3, Co: 0.87 ± 0.05, Cd: (0.026), Mn: 69 ± 5 (μg g ⁻¹) | Cu: 3.53(μg g ⁻¹) ± 0.05 Cd: 0.0256 ± 0.0005 | 100.8 98.5 |

NIES: National Institute of Environmental Studies.

Conditions: Sorbent, 100 mg; pH 7; HNO₃, 5.0 mL 0.5 mol L⁻¹.^a Average of three determination, ±S.D.**Table 3**
Determination of Cu and Cd in the plant samples.

| Sample | Added (μg g ⁻¹) | | Found (μg g ⁻¹) ^a | | Recovery% | |
|-----------|-----------------------------|------|--|--------------|-----------|-------|
| | Cu | Cd | Cu | Cd | Cu | Cd |
| Pistachio | 0.0 | 0.0 | 3.28 ± 0.05 | ND | – | – |
| | 5.0 | 5.0 | 8.31 ± 0.12 | 5.08 ± 0.03 | 100.6 | 101.6 |
| | 10.0 | 10.0 | 13.4 ± 0.18 | 10.1 ± 0.15 | 101.2 | 101.0 |
| Carrot | 0.0 | 0.0 | 4.88 ± 0.07 | 0.70 ± 0.01 | – | – |
| | 5.0 | 5.0 | 9.85 ± 0.14 | 5.80 ± 0.08 | 99.4 | 102.0 |
| | 10.0 | 10.0 | 14.87 ± 0.26 | 10.9 ± 0.018 | 99.9 | 102.0 |
| Mint | 0.0 | 0.0 | 7.58 ± 0.11 | 0.40 ± 0.01 | – | – |
| | 5.0 | 5.0 | 12.60 ± 0.19 | 5.5 ± 0.09 | 100.4 | 102.0 |
| | 10.0 | 10.0 | 17.57 ± 0.25 | 10.4 ± 0.15 | 99.9 | 100.0 |
| Rice | 0.0 | 0.0 | 2.20 ± 0.04 | ND | – | – |
| | 5.0 | 5.0 | 7.23 ± 0.18 | 4.98 ± 0.08 | 100.6 | 99.6 |
| | 10.0 | 10.0 | 12.17 ± 0.24 | 10.1 ± 0.15 | 99.7 | 101.0 |

Conditions: Sorbent, 100 mg; pH 7; HNO₃, 5.0 mL 0.5 mol L⁻¹; flow rate, 1 mL min⁻¹.

ND: not detected.

^a Average of three determination, ±S.D.

rot, Mint and Rice) was taken separately in beaker and dissolved in concentrated nitric acid and perchloric acid (3:1) by heating on a heater. The solution was cooled, diluted and filtered in to a calibration flask. A 25.0 mL of the pretreated sample solution was taken individually and cadmium and copper were determined by the proposed procedure. The related results are presented in Table 3.

3.11. Analysis of copper and cadmium in the water samples

The proposed method was applied for the determination of copper and cadmium in water samples.

A 50.0 mL of water sample was filtered to remove suspended materials. The filtered solution was analyzed by the proposed pro-

Table 4
Determination of Cu and Cd in the water samples.

| Sample | Added (ng mL ⁻¹) | | Found by ET-AAS (ng mL ⁻¹) ^a | | Found (ng mL ⁻¹) ^a | | Recovery% | |
|---------------------------|------------------------------|------|---|---------------|---|---------------|-----------|-------|
| | Cu | Cd | Cu | Cd | Cu | Cd | Cu | Cd |
| River water ^b | 0.0 | 0.0 | 5.65 ± 0.06 | 3.52 ± 0.08 | 5.60 ± 0.08 | 3.50 ± 0.07 | – | – |
| | 5.0 | 5.0 | 10.64 ± 0.16 | 8.50 ± 0.15 | 10.62 ± 0.14 | 8.50 ± 0.13 | 100.4 | 100.0 |
| | 10.0 | 10.0 | 15.57 ± 0.23 | 13.56 ± 0.21 | 15.57 ± 0.23 | 13.53 ± 0.21 | 99.7 | 100.3 |
| Spring water ^b | 0.0 | 0.0 | 4.27 ± 0.05 | 1.71 ± 0.03 | 4.24 ± 0.06 | 1.70 ± 0.03 | – | – |
| | 5.0 | 5.0 | 9.20 ± 0.12 | 6.69 ± 0.10 | 9.21 ± 0.12 | 6.71 ± 0.11 | 99.4 | 100.2 |
| | 10.0 | 10.0 | 14.43 ± 0.30 | 11.75 ± 0.19 | 14.25 ± 0.20 | 11.71 ± 0.19 | 100.1 | 100.1 |
| Well water ^c | 0.0 | 0.0 | 1.57 ± 0.04 | 1.72 ± 0.04 | 1.55 ± 0.03 | 1.75 ± 0.04 | – | – |
| | 5.0 | 5.0 | 6.52 ± 0.08 | 6.74 ± 0.12 | 6.54 ± 0.10 | 6.70 ± 0.10 | 99.8 | 99.0 |
| | 10.0 | 10.0 | 11.56 ± 0.21 | 11.80 ± 0.25 | 11.55 ± 0.19 | 11.77 ± 0.22 | 100.0 | 100.2 |
| Tap water ^d | 0.0 | 0.0 | 8.33 ± 0.11 | 0.085 ± 0.004 | 8.30 ± 0.12 | 0.088 ± 0.002 | – | – |
| | 5.0 | 5.0 | 13.30 ± 0.20 | 5.13 ± 0.13 | 13.31 ± 0.22 | 5.10 ± 0.10 | 100.1 | 100.4 |
| | 10.0 | 10.0 | 18.28 ± 0.33 | 10.6 ± 0.24 | 18.28 ± 0.31 | 10.2 ± 0.20 | 99.8 | 101.1 |
| River water ^c | 0.0 | 0.0 | 2.91 ± 0.04 | 0.055 ± 0.001 | 2.89 ± 0.05 | 0.058 ± 0.001 | – | – |
| | 5.0 | 5.0 | 7.86 ± 0.15 | 5.10 ± 0.13 | 7.88 ± 0.13 | 5.06 ± 0.11 | 99.8 | 100.0 |
| | 10.0 | 10.0 | 12.93 ± 0.27 | 10.08 ± 0.20 | 12.90 ± 0.25 | 10.08 ± 0.23 | 100.1 | 100.2 |

Conditions: Sorbent, 100 mg; pH 7; HNO₃, 5.0 mL 0.5 mol L⁻¹; flow rate, 1 mL min⁻¹.^a Average of three determination, ±S.D.^b Ravar, Kerman, Iran.^c Baft, Kerman, Iran.^d Kerman, Iran.

Table 5
Comparative data from some recent studies on preconcentration of analyte ions.

| Sorbent/reagent | Analyte | PF | Sorption capacity (mg g ⁻¹) | LOD (μg L ⁻¹) | RSD% | Breakthrough volume (mL) | PT (min) | Reference |
|---|---------|------|---|---------------------------|------|--------------------------|----------|-----------|
| Alumina/DMOA | Cu | 400 | 8.0 | 0.06 | 1.6 | 2000 | 2000 | This work |
| | Cd | 160 | 14.0 | 0.05 | 1.3 | 800 | 800 | |
| XAD-2000/diethyldithio carbamate | Cu | 100 | 5.63 | 0.2 | – | 500 | 250 | [22] |
| | Cd | 100 | 4.41 | 0.2 | – | 500 | 250 | |
| XAD-4/dithiocarbamate | Cu | 200 | 10.8 | 1.0 | 2.8 | 2000 | 3330 | [30] |
| | Cd | 150 | 9.2 | 0.7 | 3.1 | 500 | 2500 | |
| Chromosorb108/bathocuproine disulfonic acid | Cu | 80.0 | 7.5 | 0.16 | 1.9 | 400 | 80 | [31] |
| | Cd | 80.0 | 3.5 | 0.24 | 1.4 | 400 | 80 | |
| XAD-2/2-aminothiophenon | Cu | 35 | 4.6 ^a | 0.54 | 3.7 | – | 180 | [32] |
| | Cd | 74 | 3.7 ^a | 0.14 | 2.2 | – | 180 | |

PF: Preconcentration factor.

PT: Preconcentration Time (for breakthrough volume).

^a mmol g⁻¹.

cedure. The data are reported in Table 4 and reflect the suitability of the present sorbent for water analysis.

4. Conclusions

The new sorbent DMOA/alumina could be successfully applied for simultaneous separation and preconcentration of copper and cadmium in plant and water samples. Comparative data from some papers on solid phase extraction of trace Cu and Cd are summarized in Table 5. This solid phase extractant has the following advantages: Preparation of the sorbent is simple, rapid and low cost. The analytical performance of the presented method is comparable with other methods. The detection limits of investigated elements are superior to those of some preconcentration/separation methods [22,30–32]. The sorption capacities are also better than or comparable with the other methods. The elution was easily performed with 0.5 mol L⁻¹ HNO₃. The preconcentration factor is the highest among the methods given in Table 5. High tolerance to interferences from the matrix ions and good precision are the additional advantages of the present method.

The only disadvantage of the proposed method is the long duration of the preconcentration step due to high breakthrough volume. The short time preconcentration, for the references [22,31,32] in Table 5 is due to small breakthrough volume.

It is to be noted that for the determination of Cu and Cd in real samples, it is not necessary to be used from large volume sample except, very dilute samples.

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