A Preconcentration Procedure Using 1-(2-Pyridylazo)-2-naphthol Anchored to Silica Nanoparticle for the Analysis of Cadmium in Different Samples

ANUPREET KAUR* and USHA GUPTA

Department of Chemistry,
Punjabi University Patiala, Punjab, India.

ushagupta_doc@yahoo.co.in. Fax: +91-0175-5006185

Received 25 March 2008; Accepted 10 May 2008

Abstract: A new analytical method using 1-(2-pyridylazo)-2-naphthol modified SiO₂ nanoparticles as solid-phase extractant has been developed for the preconcentration of trace amounts of Cd(II) in different water 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-PAN was found to be 60.57 µmol/g at optimum pH and the detection limit (3σ) was 0.76 µg/L. The extractant showed rapid kinetic sorption. The adsorption equilibrium of Cd(II) on nanometer SiO₂-PAN was achieved just in 15 minutes. Adsorbed Cd(II) was easily eluted with 6 mL of 6 M hydrochloric acid. The maximum preconcentration factor was 50. The method was applied for the determination of trace amounts of Cd(II) in various synthetic samples and water samples.

Keywords: Chemically modified SiO₂-nanoparticles, 1-(2-Pyridylazo)-2-naphthol, Preconcentration, Separation.

Introduction

Toxic heavy metals in the environment are a global problem that causes growing concern to humanity. There are hundred of anthropogenic sources of heavy metal pollution including the mining coal, natural gas, paper and chloro-alkali industries. Metals are prevalent in the environment. 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 highly 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 by 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 intake for cadmium from all sources of 1-1.2 $\mu\text{g/Kg}$ body mass. 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 metals¹⁻⁶. Nowadays, many separation/preconcentration techniques for metal ions determination include liquid-liquid extraction⁷⁻⁹, ion-exchange resins^{10,11}, resin chelation and solid-phase extraction¹²⁻¹⁴. Of all these methods, solid phase extraction has been widely used in comparison with traditional extraction techniques; since it is simple, rapid and inexpensive, less polluting to the environment and can be easily automated. Many adsorption 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. One of the specific properties of nanomaterials is that a high percent of atoms of the nanoparticle is on the surface. 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^{14,15}. Nanoparticles such as TiO_2 ^{16,17}, Al_2O_3 ¹⁸, ZrO_2 ¹⁹, CeO_2 ²⁰ 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 SiO_2 -PAN nanoparticles were prepared by sol-gel 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.

Experimental

Apparatus

Absorbance of Cd(II) 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.

Reagents and standard solutions

Unless otherwise stated, all reagents used were of analytical reagent grade and all solutions were prepared with double distilled deionized water. The 3-aminopropyltriethoxysilane of GR grade was supplied by Acros Organics (USA). 1-(2-pyridylazo)-2-naphthol (PAN) was obtained from Fluka (Switzerland).. Nanometer SiO_2 was synthesized according to the method reported²¹.

The average diameter of the nanoparticles is 100 nm as confirmed by Scanning Electron Microscopy. The pH adjustments were made with hydrochloric acid or ammonia /ammonium chloride and pH was maintained with acetic acid /sodium acetate buffer. Stock solution of Cd(II) was prepared by dissolving spectral pure-grade $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ 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.

Sample preparation

Tap water samples taken from research laboratory were analyzed without pretreatment. The pH value was adjusted to 9.2 with 0.5 M ammonia and 0.5 M ammonium chloride buffer prior to use.

Modification process

Surface modification of SiO_2 nanoparticles were performed in a 250 mL flask. Nanometer SiO_2 (1g) was dispersed into dry toluene (30 mL), and then 3-aminopropyltriethoxysilane (4 mL) was gradually added, with continuous stirring. The mixture was refluxed for 6 hours. The silylated nanometer SiO_2 was filtered off, washed with toluene and ethanol and dried at 60°C for 3 hours. The product was transferred into the flask, and then 100 mL absolute ethanol was added followed by 20 mL formaldehyde, 2.5 mL concentrated hydrochloric acid and 1g PAN and refluxed at 72°C for 4 hours. Reaction mixture was filtered under vacuum.

General procedure

Aliquots of sample solutions containing the analytes of interest were prepared and pH was adjusted to the desired value with 0.5 M ammonia and 0.5 M ammonium chloride buffer. Then, 25 mg of SiO_2 -PAN particles were added, and the mixture was shaken vigorously for 15 minutes to facilitate adsorption of metal ion onto the adsorbent. Cd(II) retained on the adsorbent was eluted with 6 M hydrochloric acid, and the elution was neutralized with 2 M sodium hydroxide. Then, these metal ions were filtered and were determined by standard spectrophotometric method²².

Results and Discussion

Characterization of SiO_2 -PAN modified nanometer sized SiO_2

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, for the purpose of separation, 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 nanometer SiO_2 -PAN was characterized by FT-IR and SEM.

Scanning electron microscopy

The average diameter of the nanoparticles SiO_2 , SiO_2 -APTES and SiO_2 -PAN was 100 nm, 1 μm and 2 μm confirmed by Scanning Electron Microscopy. Figure 1, 2 and 3 reveals the average size of SiO_2 nanoparticle, SiO_2 -APTES and SiO_2 -PAN respectively.

Figure 1. SEM micrograph of SiO₂ nanoparticle.

Figure 2. SEM micrograph of SiO₂-APTES nanoparticles.

Figure 3. SEM micrograph of SiO₂-PAN nanoparticles.

FT-IR spectrum analysis

The chemical grafting of 1-(2-pyridylazo)-2-naphthol on the surface of nanometer SiO_2 was confirmed by FT-IR spectrum. FT-IR spectra of 1-(2-pyridylazo)-2-naphthol, nanometer- SiO_2 , nanometer SiO_2 -PAN, respectively (Figure 4). It reveals that 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 ²³. Many new peaks appeared in Figure 4(b) which are assigned as follows: the peak at 1683.5 cm^{-1} is due to N=N stretching vibration of 1-(2-pyridylazo)-2-naphthol, the peaks of C=C stretching vibration for the benzenoid and pyridyl unit in 1-(2-pyridylazo)-2-naphthol occurs at 1590, 1540, 1500 and 695.9 cm^{-1} , the peak of 1381.6 cm^{-1} is due to CH_2 shear deformation vibration, the peak at 1329.4 cm^{-1} is C-N stretching vibration for the benzenoid unit in 1-(2-pyridylazo)-2-naphthol, the peak at 1098.1 cm^{-1} is caused by C-O stretching vibration in 1-(2-pyridylazo)-2-naphthol. The above experimental results suggest that nanometer SiO_2 has been successfully modified by 1-(2-pyridylazo)-2-naphthol.

Figure 4. FTIR spectra (a) PAN (b) nanometer SiO_2 -PAN (c) nanometer SiO_2 – APTES (d) nanometer SiO_2 .

Effect of pH on enrichment recovery

The adsorption of Cd(II) on nanometer SiO₂-PAN was studied at different pH value (3.4 to 10.0) following the recommended procedure. The results of effect of pH on the recoveries of the metal ions were shown in Figure 5. It can be seen that a quantitative recovery ($\geq 95\%$) was found for Cd(II) in the pH range of 9.2-10.0.

Figure 5. Effect of pH on analyte recovery.

Effect of eluent concentration and volume

Elution of Cd(II) from nanometer SiO₂-PAN extractant was investigated by using various concentrations of hydrochloric acid. It can be seen that quantitative recoveries ($\geq 95\%$) of Cd(II) can be obtained using 6 mL of 6M hydrochloric acid as eluent. Therefore, 6 mL of 6 M hydrochloric acid was used as eluent in subsequent experiments. The results of effect of eluent concentration and volume are given in Table 1 and Table 2.

Table 1. Effect of concentration of HCl solution on elution of Cd(II) (n=3)

Concentration of eluent, M	2.0	4.0	6.0	8.0	10.0
Recovery, %	16.44	28.37	96.04	80.47	43.07

Table 2. Effect of volume of HCl solution on elution of Cd(II) (n=3)

Volume of elution, mL	2.0	4.0	6.0	8.0	10.0
Recovery, %	17.46	36.37	94.58	83.61	81.49

Effect of nanometer SiO₂-PAN amount

To test the effect of amount of extractant on quantitative retention of analyte, different amount (5-35 mg) of nanometer SiO₂-PAN were added into the solution following the experimental method. Quantitative extraction of the Cd(II) was obtained in the range of 5-35 mg of nanometer SiO₂-PAN. 25mg of nanometer SiO₂-PAN as extractor was found to be sufficient for further studies. The results are shown in Figure 6.

Figure 6. Effect of sorbent mass on analyte recovery.

Effect of shaking time

The adsorption of Cd(II) on 25mg of nanometer SiO₂-PAN was studied for different shaking time (5-30mins). The results indicated that within 15 minutes the extraction percentage of Cd(II) $\geq 95\%$ was achieved. The results are shown in Figure 7.

Figure 7. Extraction percentage of Cd(II) at different shaking time.

Adsorption capacity (Q_s)

The adsorption capacity²⁵ 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 μmol of Cd(II) adsorbed per gram. From the breakthrough curve the amount of modified nanometer SiO₂-PAN for Cd(II) was found to be 60.57 $\mu\text{mol/g}$ at pH 9.2 respectively. The results are shown in Figure 8.

Figure 8. Adsorption capacity of Cd(II) on nanometer SiO₂-PAN

Effect of sample volume

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 20, 50, 100, 150, 200, 250, 300 and 400 mL of the sample solutions containing 1.0 μg Cd(II) was shaken, quantitative recoveries ($\geq 95\%$) were obtained for sample volume of ≤ 300 mL for Cd(II). Therefore, 50 mL of sample volume solution was adopted for the preconcentration of analytes from sample solutions. The results are given in Figure 9.

Figure 9. Effect of sample volume on analyte recovery.

Effect of coexisting ions

The effect of common coexisting ions on the sorption of Cd(II) was investigated. In these experiments, a solution of 5.0 μg/mL of Cd(II) that contains the added interfering ion was analyzed according to the recommended procedure. The tolerance of coexisting ions defined as the largest amount making the recoveries of Cd(II) less than 90%. In the determination of Cd(II), interfering ions like Hg(II), Cu(II) Fe(II) and Fe(III), were masked with 1 mL of 5% of sodium fluoride solution and Bi(III), Pb(II), Co(II) and Ni(II) were masked with 2 mL of

1 M sodium citrate. Besides, a lot of anions NO_3^- , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, $\text{C}_2\text{O}_4^{2-}$, H_2PO_4^- , I^- , CO_3^{2-} and Cl^- etc did not interfere in preconcentration and determination of Cd(II).

Analytical precision and detection limit

Under the optimized conditions, three portions of Cd(II) standard solutions were enriched and analyzed simultaneously following the experimental method. The relative standard deviation (RSD) of the method was 3.0 % for the determination of 5.0 μg Cd(II) in 100 mL water samples. The detection limit of this method for Cd(II) was 0.76 $\mu\text{g/L}$.

Applications

The developed method has been applied for the determination of trace Cd(II) in tap water, mineral water, waste water and synthetic samples. For analysis, 200 mL of tap water or industrial effluents were studied by the developed method. The results are given in Table 3 and Table 4.

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

Samples	Added, $\mu\text{g/L}$	Found, $\mu\text{g/L}$	Recovery, %
Tap water	20.0	19.70	98.50
Mineral water	20.0	19.85	99.25
Waste water	0.0	8.57	---
	10.0	18.46	98.90

Table 4. Cd(II) content in nail polish.

Sample,	Added, $\mu\text{g/L}$	Found, $\mu\text{g/L}$	Recovery, %
Orange	---	19.23	---
Nail polish	5.0	23.98	95.0
Brown	---	23.98	---
Nail polish	5.0	25.12	96.0
Red	---	37.40	---
Nail polish	5.0	42.15	95.0

Table 5. Figure of merit of comparable methods for the determination of Cd(II) by solid-phase extraction.

Support	Reagent	Preconcentration Factor	Ref
Amberlite XAD-2	2-Aminothiophenol	28.0	26
Polyurethane foam	2-(6-Methyl-2-benzothiazolylazo)chromotropic acid	37.0	27
Polyurethane foam	2-(2'-benzothiaolylazo)- <i>p</i> -cresol	41.0	28
Amberlite XAD-2	Chromotropic acid	21.0	29
Silica Gel	Ammonium diethyldithiophosphate	11.0	30
Silica nanoparticles	1-(2-pyridylazo)-2-naphthol	50.0	This work

Conclusions

1-(2-Pyridylazo)-2-naphthol- anchored silica nanoparticles were prepared and used as solid sorbent for preconcentration and separation of trace Cd(II) prior to their determination. These analytes can be easily screened at $\mu\text{g mL}^{-1}$ level with preconcentration times of 15 minutes and preconcentration factor of 50 for Cd(II).

The method can be used as screening to estimate the total concentration of Cd(II) present in a large number of samples and thus avoiding the continuous use of expensive instrumentation in routine analysis. The 1-(2-pyridylazo)-2-naphthol-anchored silica nanoparticles have been found to be much selective for preconcentration of these analytes and showed great capacity, and rapidness. The proposed method has been used for the determination of these metal ions in various water and synthetic samples. The results of determination have been found to be accurate and reproducible. Comparative information from some studies on preconcentration of Cd(II) by various methods for figure of merits is given in Table 5. The proposed method developed using SiO₂-PAN nanoparticle had a relatively high preconcentration factor compared to other methods reported in Table 5.

References

1. Yaman M, *J Anal At Spectrom.*, 1999, **14**, 275.
2. Anezaki K, Chen X Z, Ogasawara T, Nukatsuka I and Ohzeki K, *Anal Sci.*, 1998, **14**, 523.
3. Zolotov Y A, Maksimova I M, Morosanova E I and Velikorodxy A A, *Anal Chim Acta*, 1995, **308**, 378.
4. Karadjova I, *Mikrochim Acta*, 1999, **130**, 185.
5. Shar G A and Soomaro G A, *The Nucleus*, 2004, **41**, 77.
6. Qufen H, Yang G, Yang J and Yin J, *J Environ Monit.*, 2002, **4**, 956.
7. Liska J, *J Chromatogr. A*, 1993, **655**, 163.
8. Martinez D, Cugat M J, Borrull F and Callul M, *J Chromatogr. A*, 2000, **65**, 902.
9. Bruzzoniti M C, Sarzanini C and Mentassi E J, *J Chromatogr. A*, 2000, **902**, 289.
10. Cao G H and Fang Z L, *Fresenius J Anal Chem.*, 1998, **360**, 156.
11. Yang D, Cheng X J, Liu Y W and Wang S, *Microchim Acta*, 2004, **147**, 219.
12. Alonso E V, De Torres A G and Pavon J M C, *Talanta*, 2001, **55**, 219.
13. Henglein A, *Chem Rev.*, 1989, **89**, 1861.
14. Xue Q J and Xu K, *Prog Chem.*, 2000, **12**, 431.
15. Okuyama K and Lenggoro I W, *Chem Eng Sci.*, 2003, **58**, 5377.
16. Vassileva E and Furuta N, *Fresenius J Anal Chem.*, 2001, **370**, 52.
17. Hosono E, Fujihara S, Kimura T and Imai H, *J Sol-Gel Sci Tech.*, 2004, **29**, 71.
18. Hiraide M, Wasawa J I and Kawaguchi H, *Talanta*, 1997, **44**, 231.
19. Sarkar S, Cara P W, Mcneff C V and Subramanian A, *J Chromatogr B*, 2003, **790**, 143.
20. Ragai J and Selim S T, *J Colloid Interface Sci.*, 1987, **115**, 139.
21. Stober W, Fink A and Bohn E, *J Colloid Interface Sci.*, 1968, **26**, 62.
22. Toral M I, Lara N, Narvaez J and Richter P, *J Chilean Soc.*, 2004, **49**, 163.
23. Silverstein R M and Morrill T C *Spectrometric identification of organic compounds*, 3rd Ed.; Wiley and sons: New York, 1974; 115.
24. Kvitek J R, Evans J F and Care P W, *Anal Chim Acta*, 1982, **144**, 93.
25. Maquieira A, Elmahadi H and Puchades R, *Anal Chem.*, 1994, **66**, 3632.
26. Lemos L A and Baliza P X, *Talanta*, 2005, **67**, 564.
27. Gama E M, Lima A S and Lemos L A, *J Hazard Mater.*, 2006, **136**, 757.
28. Lemos V A, Santelli R E, De Carvalho M S and Ferreira S L C, *Spectromchim Acta B*, 2000, **55**, 1497.
29. Lemos V A, Nunes L S, Baliza P X, Santos J S, Yamaki R T and De Jesus A A, *Can J Anal Sci Spectrosc.*, 2004, **49**, 24.
30. Fernandes A P, De Moraes M and Neto J A G, *Atom Spectrosc.*, 2003, **24**, 179.