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Solid phase extraction of copper, cadmium and lead in environmental samples FAAS using activated carbon modified with 5-(4-dimethyl aminobenzyledeneamino)-2-hydroxy benzoic acid

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Abstract

Sensitive and selective preconcentration procedure was developed for the determination of trace Cu(II), Cd(II) and Pb(II) ions in environmental samples. 5(4-dimethyl aminobezyledeneamino) 2-hydroxy benzoicacid modified with activated carbon was prepared and used as new solid phase extractor. Adsorbed metal ions were eluted with 10ml of 3N HNO_3 at a flow rate of 2 ml/min. The concentration of metal ion determined by flame atomic absorption spectrometry (FAAS). Different factors including pH of the sample solutions, effect of sample volume, the amount of modified activated carbon, type and volume of eluent were examined. The proposed method was applied to the determination of metal ions in water samples and soil samples with satisfactory results (recoveries range from 96 to 99%).

Key words: Solid phase extraction, metals, modified activated carbon, soil, water.

Introduction

The transition of metals including copper, cadmium and lead is an important risk for human and animals, due to the increasing heavy metal concentration in the environment like water, soil and atmosphere by the anthropogenic activities. Copper is widely distributed in nature and micronutrient for living organisms in some of their enzyme system. Copper is used many industrial process like alloy, electroplating, chemical, fungicides and mining industries. Cadmium and lead are toxic heavy metals for plants and animals even at lower concentration. These are used in large number of industries such as battery manufactures, paints and alloys. Their exposes to humans may cause vomiting, irritation, abdomen pain, disorder of respiratory system, brain, nerve system, kidney, description of hemoglobin and reproductive system (1-5). Consequently, sensitive and reliable analytical methods and producer have important role to evaluate the impacts of metal pollutants in environmental samples.

Atomic absorption spectrometry (AAS) with its relative low cost good analytical performance is the main instrument in the laboratories for the determination of heavy metals. Accurate determination of heavy metal ions in real samples is directly difficult by atomic absorption spectrometry because of low concentration of metals, which are near or below detection limit and also matrix ions influence of analyzed samples(6-9). The separation and preconcentration techniques are needed for solving this problem. Among the various preconcentration techniques solid phase extraction (SPE) techniques have been widely used for the determination of trace metal ions in aqueous samples, because of high enrichment factors in short time and low consumption of reagent(10-13). Various solid phase extraction materials including XAD resins (14-16), modified silica gel(17-21), microcrystalline naphthalene(22-24) and alumina(25-26) have been used. Activated carbon is one of the important solid supports that has been used alone or modified due to its large surface area, high absorption capacity, porous stature, selective determination and high purity standards. There are several recent reports on the use of modified activated carbon for metal enrichment (27-33).

In this present work 5(4 dimethyl aminobezyledeneamino)2 hydroxy benzoic acid was prepared and modified with activated carbon for the solid phase extraction of Cu(II), Cd (II) and Pb(II) metal ions by AAS in natural water and soil samples.

Materials and Methods

Experimental

Flame Atomic absorption spectrometer (Perkin-Elmer model 2380, USA) equipped with multi-elemental hallow cathode lamp and air acetylene burner was used for the determination of metals. ELICO deluxe pH meter used for preparation of buffer solution.

Reagents and Materials:

All chemicals were used of Analytical Grade (Merk India). Deionised double distilled water used for through out experimental study. Stock solution of Cu (II), Cd (II) and Pb(II) were dissolving their nitrate salts in small amount of HNO_3 and makeup with double distilled water. Acetate buffer solution was prepared with 0.1M sodium acetate, 0.1 M glacial acetic acid.

Synthesis of 5-(4-dimethylaminobezyledeneamino)-2-hydroxy benzoic acid (DABIHBA)

0.01 mols of paradimethyl amino benzaldehyde were dissolved in methanol added with 0.01 mols of 5-amino salicylaldehyde in methanol. Then the solution was refluxed 3 hours and kept freeze in over night. An orange colour solid was formed, filtered and recrystalized in ethanol.

Elemental analysis, calculated as % of $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85; Found: C, 67.61; H, 5.69; N, 5.82; IR (KBR, cm^{-1}): 3433(COOH), 2919(OH), 1663(C═O), 1604(C=N), 1542(C═C).

Preparation of Activated carbon

Activated carbon (40-60 mesh) was stirred with concentration HCl for 1h, and allowed to stand for 2 hr. After filtration, the AC was washed with distilled water until free from acid and then dried at 120^0C for 1hr.

Purified 5g of activated carbon stirred with 50 ml 0.1% of DMABIHBA solution 30 min and deposited for 2 hours after filtered the solution and dried at 40^0C. Then the 100 mg of modified activated carbon packed in the glass column (11.96 mm id, and 30 cm) with small amount of glass wool because of to prevent the loss of adsorbent during the sample passed through the column.

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Preconcentration procedure

The model solution(25 ml) containing 0.1μg of Cu, 0.05μg Cd, 0.08 of Pb metal ions pH was adjusted to 4 with acetate buffer. Then the solution was passed through the column at a flow rate of 5 ml/min. The adsorbed metal ions on the modified activated carbon in the column were eluted with 10 ml of 3N HNO_3 at the flow rate of 2 ml/min. The concentration of analyses was determined by Flame atomic absorption spectrometry (FAAS).

Preparation of real samples

Tap Water and pond water were collected from Gollapalli village near Tirupathi, Andhra Pradesh, India. Before the analysis, the sample were filtered through cellulose membrane filter (0.45 μm pore size), acidified with 5 ml of concentrated nitric acid. The pH was adjusted to 4.0 with buffer solution. The sample was passed through the mini column. The absorbed metal ions on modified activated carbon in column were eluted with 5 ml of 3N $HNO_{3.}$ Analytes determined by Flame atomic absorption spectrometry (FAAS).

Sea water was collected from Bay of Bengal in Manginapudi beach in Machilepatnam, Andhra Pradesh, India. Before the analysis, the sample were filtered through cellulose membrane filter (0.45 μm pore size), acidified with 5 ml of concentrated nitric acid. Then the above preconcentration procedure was followed to the solution

The soil samples were collected from near industrial areas around Tirupathi. The soil samples dried in an oven at 105^0C and homonized with a sieved. Then 300 mg soil sample was weighted and transferred into porcelain crucible. The samples were burned in oven at 450^0C for 3 hours and the resulting inorganic residues were dissolved with 5 ml of concentrated HNO_3. This solution boil until dryness and 3 ml of conc. HNO_3 was added again. The final solution was transferred to 50 ml volumetric flask and diluted with distilled water. Then the above preconcentration procedure was followed to the solution.

Result and Discussion

Effect of pH

The effect of the pH test solution on the retention of Cu (II), Cd (II), Pb (II) ions studied. Aliquots sample containing 0.1μg of Cu, 0.05μg Cd, 0.08 of Pb metal ions in the pH range 2.0-9.0 were passed through the column and their concentrations were measured after elution. The results are shown fig1. The results of this study showed that metal ions were completely adsorbed on the adsorbent over the pH range of 3.0-5.0. Therefore, the pH 4.0 was selected for further studies.

Amount of activated carbon

The amount of modified activated carbon was also very important factor, because how much adsorbent was required for quantitatively separation of analytes from a aqueous solution. The amount of modified activated carbon loaded on the column varied from 0.050 to 0.300 g. The standard sample (25 ml) containing analytes 0.1 μg Cu (II), 0.08 μg Pb and 0.05 μg were treated by applying preconcentration procedure. As results are given in fig 2, in this study quantitatively recoveries were obtained for 100 mg of modified Ac. Therefore, all the further works 100 mg of modified activated carbon was used.

Effect of sample volume

Effect of sample volume on the adsorption of metal ions on 100 mg of sorbent was studied by passing of sample volume of 10-200 ml solutions containing 0.1 μg Cu (II), 0.05 μg Cd (II) and 0.08 μg Pb (II) metal ions through the column. The amount of metal ions was measured after elution of adsorbed metals in the column by using 10 ml of 3N $HNO_{3.}$ The results are given in fig 3. Quantitatively recoveries were achieved for the analytes from 25 ml of sample volume. Therefore, 25 ml sample volume was chosen for further studies.

Effect of Flow rate

As the retention of analytes on adsorbent depends up on the flow rate of the samples solution, the effect of flow rate was examined under the pH 4 by the passed sample solution through the mini column with the flow rates carrying in the range of 2-5 ml /min and elution flow rate in the range of 0.5-2 ml/min. The quantitative recoveries of metal ions were obtained with a flow rate of 5 and 2 ml/min both sample and eluent.

Effect of type and volume of elution solution

The investigation of effect of eluent solution was tested to elute with HCl and HNO_3 at various concentration and different volumes were adsorbed metal ions in the column. The results are given in table 4. Quantitative recoveries were obtained for analytes by using with the volume of 10 ml of 3N HNO_3 at a flow rate of 2 ml/min other than HCl. Therefore, 10 ml of 3N HNO_3 was selected for further studies.

Effect of foreign ions

In order to examine the effect of various tested metal ions in the optimum conditions, extraction of these metal ions in the presence of some selected metal ions by have been carried out which prompted to perform an intensive selectivity study to evaluate the possible interference of some metal ions in the process of solid phase extraction of Cu(II), Cd(II) and Pb(II). Interferes ions that may be contained with this ions were investigated. The interference effect of calcium, magnesium and other alkali and alkaline earth ion were presented in table 5. The table display that these ions up to 1000 fold are negligible and high selectivity for accurate and precise determination of Cu(II), Cd(II) and Pb(II) metal ions in real samples.

Application of real samples

The pre-concentration of Cu (II), Cd (II) and Pb (II) from aqueous solution on activated carbon impregnated with 5(4 dimethyl aminobezyledeneamino)2 hydroxy benzoic acid (DABIHBA) in environmental samples by FAAS method was developed. The procedures were applied to the determination of analytes in pond water, tap water and sea water samples. Reliability was checked by spiking experiments and independent analysis. The results were presented tables 1-2. The recovery of spiked samples is satisfacily responsible and confirmed using this method, which indicates applicability of the present procedure in the determination of Cu (II), Cd (II) and Pb (II) of natural water samples.

Table 1: Analytical results for determination of Cu (II), Cd (II) and Pb (II) in natural water samples

Element	added (μgL^{-1})	Found^{a} (μgL^{-1})	Recovery (%)
Pond water			
Cu	0	48±0.02	
	5	51.64±2.28	97.4
Cd	0	7.5±1.02	
	5	12.34±2.0	98.7
Pb	0	39±3.6	
	5	43.24±3.03	98.3
Tap water			
Cu	0	5.2±0.54	
	5	9.82±1.13	96.3
Cd	0	N.D	
	5	4.86±0.2	97.2
Pb	0	N.D	
	5	4.96±0.39	99.2

'a' *average value for three determination, "±" standard deviation (n*=3).

This method was also applied to the determination of Cu (II), Cd (II) and Pb (II) in real samples including soil samples. Soil samples were collected from different industrial sites of around Tirupati. The results were presented table 3.

Table 2: Sea Waters- Determination of Cu (II), Cd (II) and Pb (II) in sea water samples

Analyte	Added (μg L^{-1})	Found ^{a} (μg L^{-1})	Recovery (%)
Cu	-	19.08±0.08	
	2.5	21.66±0.76	97.1
Cd	-	13.97±0.34	
	2.5	16.02±0.69	97.3
Pb	-	10.5±0.30	
	2.5	12.88±0.76	99.1

'a' *average value for three determination, "±" standard deviation (n*=3).

Table 3: Soil samples- Determination of Cu (II), Cd (II) and Pb (II) in soil samples

S.No	Soil Sample	Element	Found[a] $\mu g g^{-1}$
1	Near poiner alloy industry	Cu	1.72±0.24
		Cd	0.88±0.08
		Pb	6.19±1.47
2	Near distillery Industry	Cu	4.86±0.95
		Cd	0.42±0.09
		Pb	2.05±1.05
3	Near sugar Industry	Cu	13.63±2.41
		Cd	0.84±0.05
		Pb	0.49±0.24

'a' *average value for three determination, "±" standard deviation (n*=3*).*

Table: 4: Effect of type and concentration of eluent on the recoveries of metal ion s(pH :4, flow rate 2 ml per minute)

Eluent type	Volume (ml)	Recovery (%)
3 N HNO_3	10	98
3 N HNO_3	5	96
3 N HCl	10	92
3 N HCl	5	94
1 N HNO_3	10	89
1 N HNO_3	5	90
2 N HNO_3	10	91
2 N HNO_3	5	93

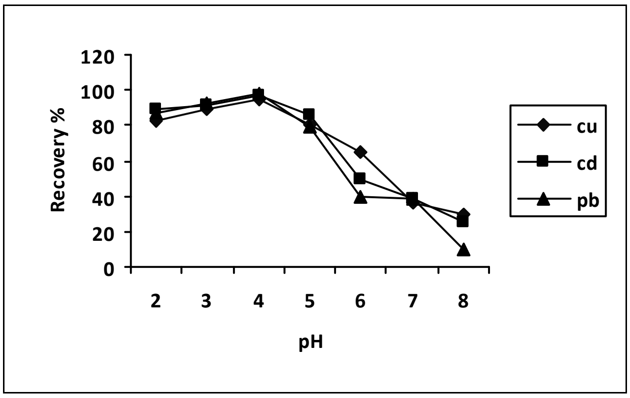


Fig:1 Effect of pH on recovery of metal ions(amount of analytes 0.1µg Cu, 0.05µg Cd, 0.08µg Pb; eluent:3N HNO_3)

Table: 5-Effect of matrix ions on the recoveries of the examined metal ions

ion	Tolerance limit
Na^+	1000
K^+	1000
Cl^-	1000
Mg^+	600
HCO_3^-	1000
PO_4^{3-}	500
Zn^{2+}, Ca^{2+}, Ag^+, Al^{3+}, Cr^{3+}, Hg^{2+}	100

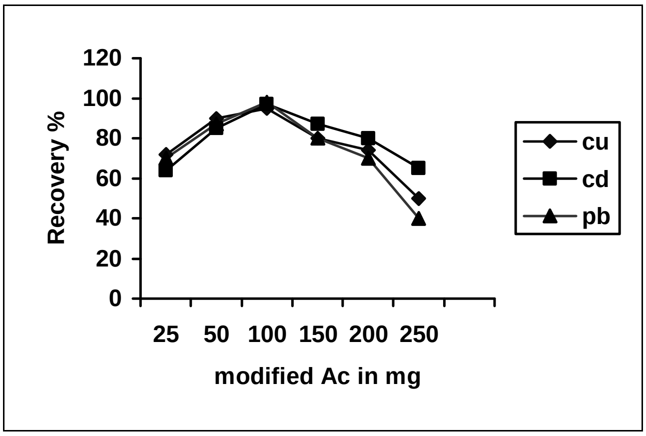


Fig:2 Effect of amount of modified aviated carbon on recovery of metal ions (pH:4; amount of analytes 0.1µg Cu, 0.05µg Cd, 0.08µg Pb; eluent: 3N HNO_3)

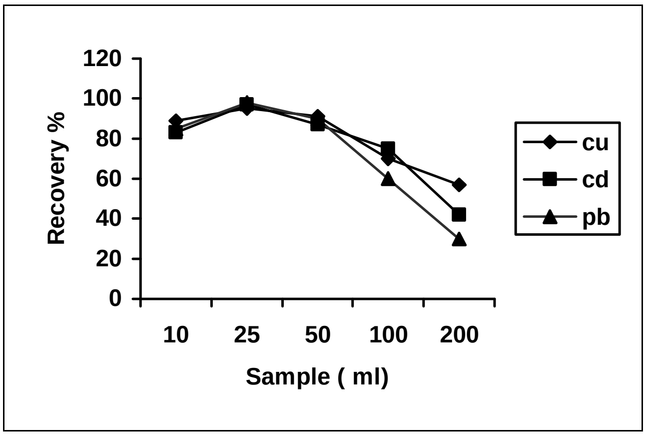
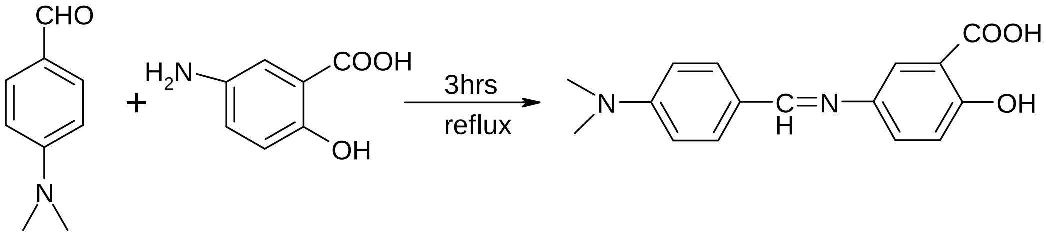


Fig:3 Effect of sample volume on recovery of metal ions (pH:4; amount of analytes 0.1µg Cu, 0.05µg Cd, 0.08µg Pb; eluent:3N HNO_3)

Scheme



Conclusion

The DMBIHBA loaded activated carbon is sensitive and accurate method for determination of trace amount of copper, cadmium and lead ions in low concentrations. The results presented in table1, 2 have confirmed the applicability of the separation and preconcentration of metals. The proposed method shows low reagent consumptions, eco friendly and simple method for the determination of trace metals in natural waters and soil samples.

References

[1] Mustafa Tuzen; Mustafa Soylak. *J. of hazardous materials,* **2009,** 1641; 428-1432.
[2] Mehrorang Ghaedi; Khodabakhsh Niknam; Ardeshir Shokrollahi; Ebrahim Niknam; Hamid Reza Rajabi; Mustafa Soylak. *Journal of Hazardous Materials,* **2008**, 155(1-2); 121-127.
[3] O Hazer; S Kartal; S Tokalıoglu. *Journal of Analytical Chemistry,* **2009**, 64; 6.
[4] K Prasad; P Gopikrishna; R Kala; T Prasada Rao; G R K Naidu. *Talanta,* **2006** *69(4);* 938-945.
[5] M Ghaedi; Montazerozohori; M Soylak. *Journal of Hazardous Materials,* **2007**,142(1-2); 368-373.
[6] Celal Duran;Ali Gundogdu;Volkan Numan Bulut; Mustafa Soylak. *Journal of Hazardous Materials,* **2007,** 146(1-2); 347-355.
[7] Zhenhua Li; Xijun Chang; Xiaojun Zou; Xiangbing Zhu; Rong Nie; Zheng Hu; Ruijun Li. *Analytica Chimica Acta,* **2009**, 632(2); 272-277.
[8] Mustafa Tuzen; Kadriye Saygi; Mustafa Soylak. *Journal of Hazardous Materials,* **2008,** 15(2); 632-639.
[9] Guangyu Yang; Weibo Fen; Chun Lei; Weilie Xiao; Handong Sun. *Journal of Hazardous Materials,* **2009**, 162(1); 44-49.
[10] Mehmet Sayım Karacan; Neslihan Aslantaş. *Journal of Hazardous Materials,* **2008**, *155(3);* 551-557.
[11] M Ghaedi; F Ahmadi; M Soylak *Journal of Hazardous Materials,* **2007,** *147(1-2); 226-231.*
[12] Zhenhua Li; Xijun Chang; Zheng Hu; Xinping Huang; Xiaojun Zou; Qiong Wu; Rong Nie. *journal of Hazardous Materials,* **2009**, 166(1); 133-137.
[13] Ghaedi M; Shokrollahi A; Kianfar AH; Pourfarokhi A; Khanjari N; Mirsadeghi AS; Soylak M. *J Hazard Mater,* **2009**, 162(2-3); 1408-14.
[14] Sharma RK; Pant P. *J Hazard Mater*, **2009**, 163(1); 295-301.
[15] Yong Guo; Bingjun Din; Yongwen Liu; Xijun Chang; Shuangming Meng; Maozhong ian. *Analytica Chimica Acta,* **2004**, 504(2); 319-324.
[16] Duran C; Senturk HB; Elci L; Soylak M; Tufekci M. *J Hazard Mater*, **2009**, 162(1); 292-9.

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[17] B S Garg; R K Sharma; J S Bist; N Bhojak; Sachin Mittal. *Talanta,* **1999**, 48(1); 49-55.
[18] Xijun Chang; Haixia Luo; Yuemei Cui; Xiangbing Zhu; Yunhui Zhai; Zheng Hu Qun He. *Journal of Molecular Structure*, **2008**, 891(1-3) 45-49.
[19] K Jal; S Patel; B K Mishra; *Talanta,* **2004**, 62(5), 1005-1028.
[20] I Hatay; R Gup; M Ersöz. *Journal of Hazardous Materials,* **2008**, 150(3); 546-553.
[21] Madrakian T; Afkhami A; Zolfigol MA; Solgi M. *J Hazard Mater*, **2006**, 128(1); 67-72.
[22] Gopi krishna p; Rao K S; Biju V M; Prasada Rao T; Naidu G.R.K. *Chemia analityczna*, **2004**, 49; 383-393.
[23] M A Taher. *Journal of Analytical Chemistry,* **2001**, 56; 149-155.
[24] B Rezaei; S Meghdadi; N Majidi. *Spectrochimica Acta Part A,* Molecular and Biomolecular Spectroscopy, **2007**, 67(1); 92-97.
[25] M Ghaedi; H Tavallali; A Shokrollahi; M Zahedi; M Montazerozohori; M Soylak .*Journal of Hazardous Materials,* **2009**, 166(2-3); 1441-1448.
[26] Attinti Ramesh; Bobba Aparna Devi; Hiroshi Hasegawa; Teruya Maki; Kazumasa Ueda. *Microchemical Journa,* **2007**, 86(1); 124-130.
[27] R Dobrowolski. *Studies in Surface Science and Catalysis,* **1999**, 120(2); 777-805.
[28] M Ghaedi; A Shokrollahi; A H Kianfar; A S Mirsadeghi; A Pourfarokhi; M Soylak. *Journal of Hazardous Materials,* **2008**, 154(1-3) 128-134.
[29] Mehmet Sayım Karacan; Neslihan Aslantaş. *Journal of Hazardous Materials,* **2008**, 155(3); 551-557.
[30] Barbara Mikuła; Bożena Puzio. *Talanta,* **2007**, 71(1); 136-140.
[31] Ru Gao; Zheng Hu; Xijun Chang; Qun He; Lijun Zhang; Zhifeng Tu; Jianping Shi. *Journal of Hazardous Materials,* **2009**, 172(1); 324-329.
[32] Ayob; Parchehbaf Jadid; Habibollah Eskandari. *E-journal of chemistry*, **2008**, 5(4); 878-883.
[33] M Ghaedi; A Shokrollahi; A H Kianfar; A Pourfarokhi; N Khanjari; A S Mirsadeghi; M Soylak. *Journal of Hazardous Materials,* **2009**, *162(2-3);* 1408-1414.