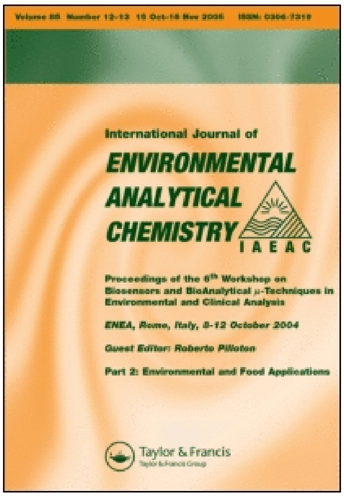

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Determination of lead and cadmium in tap water and apple leaves after preconcentration on a new acetylacetone bonded polyurethane foam sorbent

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The present work describes a rapid, cost-effective analytical procedure for the determination of lead and cadmium in environmental samples by off-line preconcentration with polyurethane foam (PUF) functionalised with acetylacetone by covalent coupling through the –N=N– group. The optimum pH ranges for quantitative uptake were 5–7, 6–7 for lead and cadmium, respectively. The kinetics of metal uptake by the new foam was found to be fast, reaching equilibrium in a few minutes. Metal ions were sorbed in the minicolumn, eluted with acid solutions and determined by flame atomic absorption spectrometer (FAAS). Under the optimum conditions, the preconcentration factors obtained were 288 for Cd and 224 for Pb. The limits of detection of the proposed procedure were 0.09 and 0.07 $\mu g\,L^{-1}$ for Pb and Cd, respectively. The relative standard deviation (RSD) was less than 10%. The accuracy of the method was estimated by using environmental samples that were spiked with Cd and Pb ions. The capacity of the acetylacetone bonded PUF (AA-BPUF) sorbent at optimum conditions has been found to be 4.5, 6.9 $\mu mol\,g^{-1}$ of sorbent for Pb and Cd, respectively.

Keywords: lead; cadmium; polyurethane foam synthesis; preconcentration; separation

1. Introduction

In the determination of trace elements by atomic absorption spectrometry, the use of a preconcentration step is a necessity when the concentration of the analyte is too low to be determined directly, or when the matrix interference cannot be eliminated [1–3]. The most widely used preconcentration technique is the sorption of trace elements on an exchanger, silica gel, activated carbon with or without chelating groups. Several enrichment procedures have been reported in the literature for cadmium and lead determination, involving different analytical techniques, such as precipitation [4], liquid–liquid [5] or solid-phase extraction (SPE) [6]. Liquid–liquid extractions are generally time-consuming, labour-intensive; they require strict control of extraction conditions, such as temperature, pH, and ionic strength. SPE is an attractive alternative because it overcomes many drawbacks of liquid–liquid extraction. Other advantages in the use of

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SPE are disposal costs, achievement of high recoveries, broader range of applications than liquid–liquid extraction due to the large choice of solid sorbents and easy recovery of the solid phase [7]. Chelating resins have been frequently used in SPE as they provide good stability, high sorption capacity for metal ions and good flexibility in working conditions. Iminodiacetate resins such as chelex 100 [8] and Amberlite IRC-718 [9] are widely used for this purpose but lack selectivity [10,11]. Of these, Amberlite-XAD resins have superior physical properties like durability and chemical stability towards harsh environments [12]. Two methodologies are frequently adopted for designing such chelate functionalised Amberlite XAD resins. One involves physical sorption of ligands onto a matrix and the other is based on covalent coupling of a ligand with the polymer backbone through a spacer arm, generally a –N=N– or $–CH_2$ group. The latter strategy renders rugged systems, free from ligand leaching problems but with low sorption capacities.

Among the many available materials that are used for solid phase extraction, polyurethane foam (PUF) has the advantage of smaller resistance for fluid passage. Thus, it results in low overpressure in the system, which reduces the risk of leakage. In addition to this, PUF is available in low cost, simple preparation, high surface area and stability in acidic or basic media. Moreover, this sorbent is resistant to rough changes of pH conditions, despite it swell in the presence of some organic solvents such as ethanol.

PUF was proposed by Braun and colleagues [13] and since then it has been used in many processes operating by batch, off-line column. The importance of PUF in preconcentration of trace metal ions has increased in the past few years. PUF has been used as a solid sorbent to preconcentrate/separate a wide variety of organic and inorganic compounds from different media.

Some reviews have been published about the use of PUF in preconcentration procedures applied to several analytical systems [2,3]. PUF can be directly used without previous pre-treatment [14,15]. On the other hand, several chelating agents were bonded with PUF and used as chelating centres in separation procedures [16–20].

Moody *et al.* [21] reported on the sorption of Co(II), Fe(III), Zn(II), Cd(II) and Mn(II) from potassium thiocyanate solution by using polyether type PUF. Hamon *et al.* [22] published a detailed investigation about Co(II) sorption from thiocyanate solution using PUF. Hamza *et al.* [23] described a quantitative method to collect Zn(II) and Bi(III) from aqueous media, applied for their semi-quantitative determinations. Jesus *et al.* [24] used the PUF-thiocyanate system to separate traces of Zn(II) from Cd(II). Lypka *et al.* [25] proposed the use of benzoylacetone treated PUF for extraction, separation of Cd(II) and Cu(II). El-Shahat *et al.* [26] described the preparation, characterisation of methylene blue-grafted polyurethane foam. The new polymer was used for the preconcentration, separation of Cd(II), Hg(II), Ag(I) from wastewater.

Chakrabarti and Roy [27] proposed a spectrophotometric method for Cd(II) determination after selective extraction onto PUF. Jesus *et al.* [28] proposed the use of PUF as sorbent in an on-line enrichment system. The usages of synthetic adsorption resins on the solid phase extraction of trace heavy metal ions are also very popular [29–31]. In general, metal chelates in the aqueous solutions were adsorbed on the resin, and were desorbed later with a suitable eluent solution.

The purpose of the present work is to apply an acetylacetone bonded PUF (AA-BPUF) in an off-line preconcentration system for the determination of lead and cadmium in tap water and apple leaves samples. The sorbent used as a packing material was prepared by covalent coupling of acetylacetone with the PUF through –N=N– group. The synthesis and characterisation of the new foam was followed by the study of the chemical and hydrodynamic parameters of the off-line system.

2. Experimental

2.1 *Synthesis of modified polyurethane foams*

2.1.1 *Synthesis of one-step coupling bonded polyurethane foam with o-aminophenol (AP-BPUF)*

Untreated foam cubes (20 g) were soaked in a HCl (1 : 1) solution for 3 h to liberate the maximum number of free amino groups by hydrolysis of free isocyanate groups in the foam. The coupling process followed the method previously reported [32]. In short, the foam was suspended in an ice-water mixture, treated with $0.01\,\mathrm{mol\,L^{-1}}$ HCl and $1\,\mathrm{mol\,L^{-1}}$ $NaNO_2$ until the foam attained yellow colour due to the formation of diazonium chloride. Next, the foam was reacted with *o*-aminophenol (AP) at 0–3°C. Finally, the resulting brown coloured foam was washed with doubly distilled water (DDW), acetone and dried in air. To ensure the sufficient concentration of sodium nitrite necessary for the generation of the maximum number of diazonium groups, we examined the effect of nitrite concentration on the uptake of AP-BPUF. One gram of untreated foam was diazotised with varying concentrations of nitrite solutions (0.1–$1.5\,\mathrm{mol\,L^{-1}}$). The products were coupled to AP and the uptake capacity was determined. The results showed that the nitrite solution should be at concentration not less than $1.0\,\mathrm{mol\,L^{-1}}$.

The concentration of the coupling compound (AP) was also studied in order to optimise the possibility of saturating the foam with the ligand moieties. One gram foam samples, previously diazotised by $1.0\,\mathrm{mol}^{-1}$ sodium nitrite solution, was coupled to AP of different concentrations (ranging from 0.1 to $1.0\,\mathrm{mol\,L^{-1}}$) by the sequence stated before. The uptake of these products was determined by testing them for Pb(II) extraction with a batch procedure. The data revealed that, the optimum concentration of AP at maximum sorption capacity was $0.60\,\mathrm{mol\,L^{-1}}$.

2.1.2 *Synthesis of two-steps coupling bonded polyurethane foam with acetylacetone (AA-BPUF)*

The previously prepared AP-BPUF (5 g) was diazotised again by the method mentioned above and then coupled to 2.50 g acetylacetone (AA), leaving for 24h at 0–3°C. After that, the foam was washed repeatedly with DDW and dried in air, in a dust free place, for further use. The *o*-hydroxyphenylazo acetylacetone bonded PUF (AA-BPUF) has reddish yellow colour.

2.2 *Instrumentation*

Flame atomic absorption spectrometric (FAAS) measurements of Pb, Cd were recorded on an AAS5 FL instrument (Carl Zeiss Technology, Germany), equipped with standard burner for air–acetylene flame. The operational conditions for the measurements are listed in Table 1. The FAAS method was used for the determination of the studied metal ions. The pH measurements were carried out using the microprocessor pH metre BT 500 BOECO (Germany), which was calibrated against two standard buffer solutions at pH 4 and 9. A mechanical shaker with up to 200 rpm was used

Table 1. Conditions for flame atomic absorption spectrometer.

	Metal ion	
Parameters	Lead	Cadmium
HC lamp current (mA)	3.0	2.0
Slit width (nm)	1.2	1.2
Wavelength (nm)	217.0	228.8
Fuel flow (mL/h)	65	50
Burner height (mm)	5–10	4–12

Table 2. Elemental analysis of the modified foams.

	Calculated (%)			Experimental (%)		
Sample name	C	H	N	C	H	N
Untreated PUF	62.07	8.8	4.64	62.09	8.9	4.65
o-AP-BPUF	62.01	8.64	5.35	62.12	8.62	4.80
AA – BPUF	61.45	8.5	6.0	61.50	7.98	5.98

(SL 350 Nüve San. Ankara, Turkey). DDW was obtained from two successive distillations using Hamilton laboratory glass instrument (Europe House, Sandwich, England).

2.3 *Chemicals*

Unless otherwise stated, all reagents used were of analytical grade, all solutions were prepared with DDW. Laboratory glassware was kept overnight in chromic acid solution. Stock solutions ($1000\,\mu g\,mL^{-1}$) of the studied metal ions were prepared by dissolving appropriate amounts of analytical reagent grade Lead(II) nitrate (Aldrich, Milwaukee, USA) and cadmium nitrate (Panreac, Barcelona, Spain). Sodium nitrite and sodium hydroxide were obtained from Winlab Company (UK). Hydrochloric acid was purchased from Merck (Darmstadt, Germany), commercial, open cell, polyether-type PUF ($31.6\,kg\,m^{-3}$) was supplied by the Egyptian company for foam production (Cairo, Egypt). All liquids were used without any further purification.

2.4 *Characterisation of the modified foams*

The results of the elemental analysis of the BPUF derivative are given in Table 2. These show good agreement with the calculated CHN values from the proposed formula. The data reveal that the second coupling occurred by ratio (1 : 1) of AP-BPUF to AA.

The significant IR bands of the isocyanate, hydroxyl, carbonyl, amino and azo groups in the BPUF are presented in Table 3. Additional absorption bands for –N=N– and C=O appeared. The disappearance of the band correspondence to NCO group of the untreated foam at $2100\,cm^{-1}$ was observed. The absorption band for NH_2 group has disappeared from the IR charts of the two times coupled BPUF. This confirms that the amino groups of AP-BPUF were exhausted in bonding to the coupling compound in the second step. Figure 1 shows the proposed reactions involved in the preparation of the novel BPUF.

Table 3. Significant IR bands.

Sample designation	IR bands (wavenumber, cm^{-1})				
	υ_{NCO}	υ_{OH}	υ_{CO}	υ_{NH_2}	$\upsilon_{N=N}$
Untreated PUF	2100	3311–3509	1655	3111–3299	–
AP-BPUF	–	3329–3565	1661	2926–3297	1473
AA-BPUF	–	3328–3447	1653, 1716, 1732	–	1473, 1508

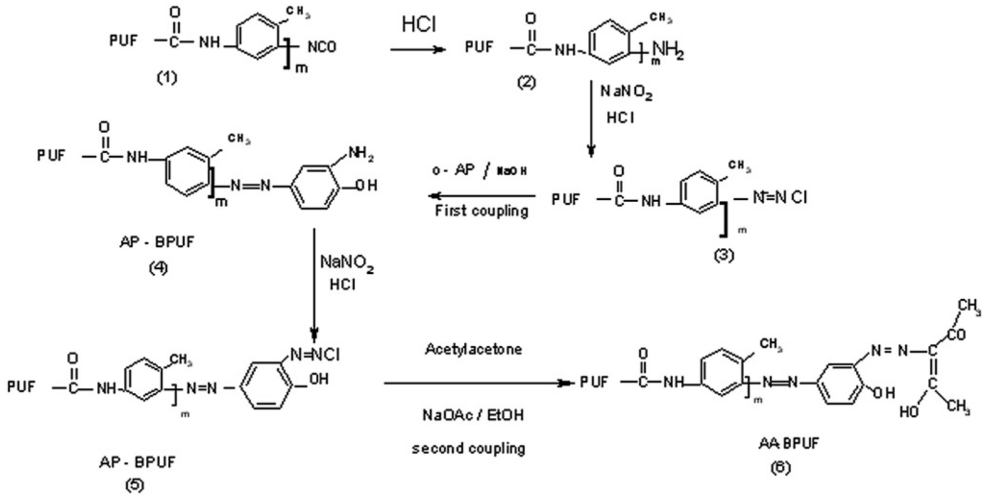

Figure 1. The proposed reactions involved in the preparation of the BPUF.

Additionally, there are absorption bands for the carbonyl groups in case of AA-BPUF which correspond to the amide C=O of the foam material, that of the ligand itself.

2.5 *Stability of the BPUF*

The chemical stability was investigated by measuring the change of sorption capacity for the studied metal ions after successive contact of the modified foams with acids 1–6 M HCl, 1–2 M H_2SO_4, 1–2 M HNO_3, alkaline solutions of 1–4 M NaOH, 1–4M NH_4OH, as well as organic solvents, for example methanol, ethanol, isopropanol, n-butanol, acetone, chloroform and carbontetrachloride. The decomposition was negligibly small. No significant decrease in the sorption capacity was observed, which indicate that these chelating extractors are believed to be sufficiently stable.

3. Recommend procedures

3.1 *Batch experiment*

The separation of Cd and Pb was carried out by a batch technique at 25°C. A portion of 100 mg of the BPUF was mixed with 20 mL of the tested metal ion solution (1 µg mL^{-1})

in a shaker adjusted to the desired shaking speed. After a certain time, the solution was separated and the concentration of metal ion was determined.

3.2 *Dynamic experiments*

In the dynamic experiments 1 g of BPUF was packed into a column (10 cm × 1 cm). The column, filled with water, was packed with gentle pressure on the foam plugs with a glass rod to avoid air bubbles and then capped with glass beads on the top of the bed to prevent foam floating upwards. The bed height of the foam column was about 60 mm. It was washed successively with DDW and then stored in DDW for the next experiment. Test solutions were passed through the foam column at a flow rate of $3\,\mathrm{mL\,min^{-1}}$. The stripping of the metal ions from the foam column was carried out with the eluting agent.

3.2.1 *Tap water analysis*

One litre of tap water was collected from the laboratory and spiked with 20 µg of standard solution of metal ions, adjusted to pH 7 and passed through the modified foam columns at a flow rate of $3\,\mathrm{mL\,min^{-1}}$. The columns were rinsed with 20 mL DDW and the metals were eluted with $0.1\,\mathrm{mol\,L^{-1}}$ HNO_3. The concentration of each metal ion was determined by the recommended method.

3.2.2 *Analysis of apple leaves*

Fresh apple leaves were obtained from Fayoum city (Egypt), washed by DDW until dust free, then put in an oven between two aluminium foil sheets and dried at 105°C for 12 h. The dry leaves were ground in a mortar and sieved through a 0.5 mm sieve in order to obtain an homogenous sample and for easy dissolution. The sample was dried again at 120°C until reaching constant weight. Then we followed up the procedure reported elsewhere [33]. About 4 g of dried sample were heated in 40 mL of concentrated HNO_3 ($14.0\,\mathrm{mol\,L^{-1}}$) until nearly dryness, diluted to 1000 mL with DDW and removing cellulosic residues by filtration. Each 250 mL was adjusted to the optimum conditions and passed through the modified foam column. The retained metal ions in the column were eluted with 0.1M nitric acid and the metal ions were measured by flame AAS. This experiment was repeated three times and the RSD values were calculated.

4. Results and discussion

4.1 *Sorption of metal ions as a function of pH*

Aliquots of varying pH solutions, adjusted in the range 2–9 with HCl or NaOH, containing each metal ion separately were stirred with 100 mg BPUF for one hour. The percentage of metal sorption was calculated by the relation:

$$\text{Sorption }(\%) = [(C_o - C)/C_o)] \times 100$$

Where C_o and C are the initial and remaining concentrations ($\mu g\,L^{-1}$) of the metal ion, respectively.

Generally, it was found that the uptake increases by increasing the pH until reaching a limiting value and then levelling off in a certain range of pH which is usually followed by a decrease (Figures 2 and 3). The optimum pH ranges for Pb and Cd are listed in Table 4. The decrease in percentage sorption at $pH > 8$ may be attributed to the possible precipitation of metal hydroxides. The higher affinity of the two-steps coupled foam AA-BPUF was attributed to the longer arm chelating centres used as metal chelating sites. For example, at pH 6.0, the uptake of Cd with one-step coupled foam AP-BPUF was 52% while it was 85% with AA-BPUF. The maximum uptake of both metals on AA-BPUF reached 98% and 99% for Cd and Pb, respectively.

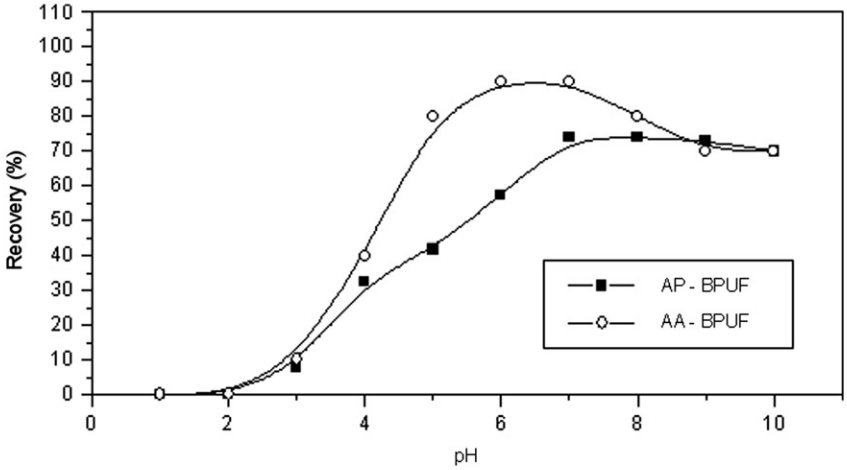

Figure 2. Effect of pH on the recoveries of Cd(II) onto modified BPUFs.

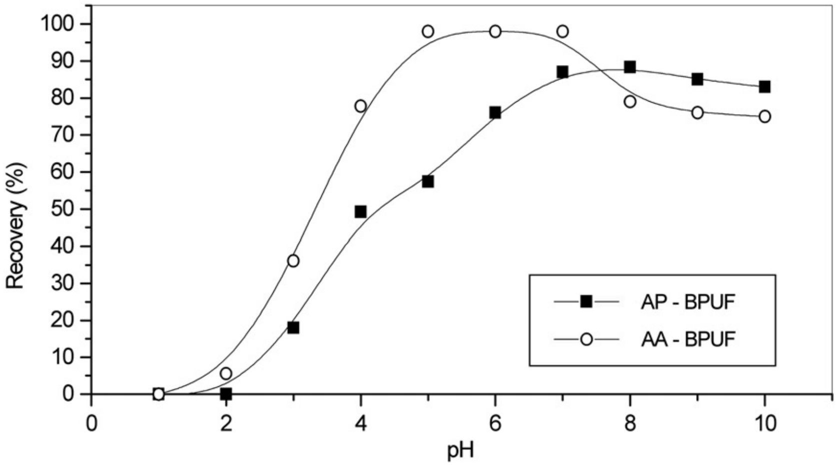

Figure 3. Effect of pH on the recoveries of Pb(II) onto modified BPUFs.

4.2 *Loading kinetics of metal sorption*

The rate of loading of Pb and Cd on the BPUF was investigated by batch experiment at pH 7. The loading half time $t_{1/2}$, defined as the time required for reaching 50% of the BPUF total loading capacity, is estimated from Figures 4 and 5. The time for 50% sorption is very fast. From the uptake kinetics, it is observed that an equilibrium time of about 20 min is required for 93% uptake of Cd and 98% sorption of Pb on AA-BPUF, while 25 min is needed for 75–85% uptake with one-step coupled foam AP-BPUF. The faster uptake of the new modified foam probably reflects a better accessibility of the Cd and Pb ions on the chelating sites (the two OH, the –N=N– groups) in the bonded foam and strong bond formation with the built ligand.

4.3 *Total foam capacity*

The adsorption capacity is an important factor, because it determines how much sorbent is required to quantitatively concentrate the analytes from a given solution. From the results in Table 4, it is obvious that the AA-BPUF has higher capacity than the AP-BPUF. As can

Table 4. Optimum conditions for recoveries of analytes.

Sorbent	Property	Pb(II)	Cd(II)
AP-BPUF	pH range	7–8	7–8
	Loading half time ($t_{1/2}$), min	7.0	12.0
	Capacity (μ mol g^{-1})	3.6	5.9
	RSD (%)[a]	3.2	3.5
AA-BPUF	pH range	5–7	6–7
	Loading half time ($t_{1/2}$), min	3.0	2.5
	Capacity (μ mol g^{-1})	4.5	6.9
	RSD (%)[a]	4.7	2.4

Note: (a) RSD = Relative standard deviation for 10 replicates.

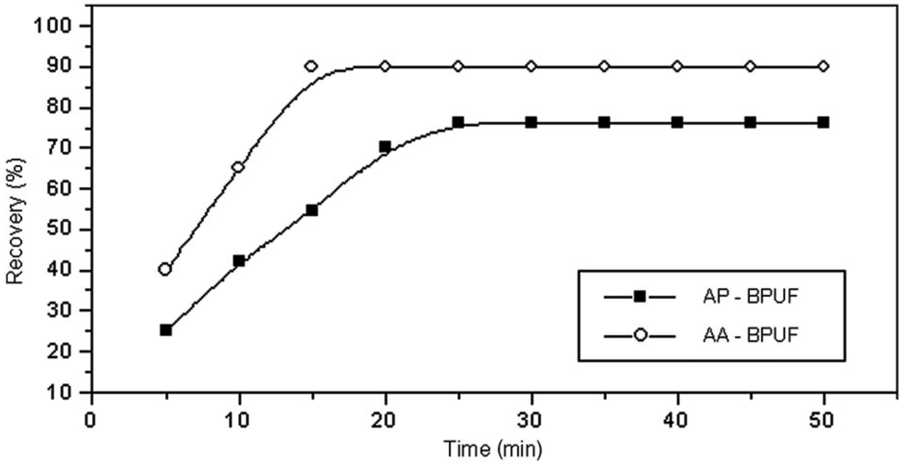

Figure 4. Effect of shaking time on the recoveries of Cd onto modified BPUFs.

be seen in Figures 6 and 7, the amount of Pb or Cd adsorbed per unit mass of the modified foams increased with the initial concentration of Pb or Cd. In order to reach saturation, the initial ion concentrations were increased from 0.5 to 100 µg mL^{-1} until the plateau values (maximum adsorption capacity values) were obtained.

4.4 *Effect of dilution*

Different volumes of DDW were spiked by 20 µg of each metal ion adjusted to the optimum conditions. Using batch experiments, the two BPUF showed constant maximum recovery with increase in the sample volume up to 80 mL.

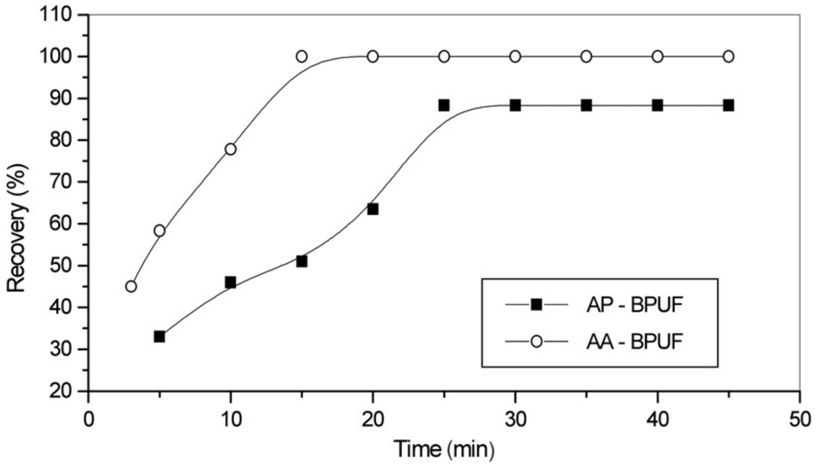

Figure 5. Effect of shaking time on the recoveries of Pb onto modified BPUFs.

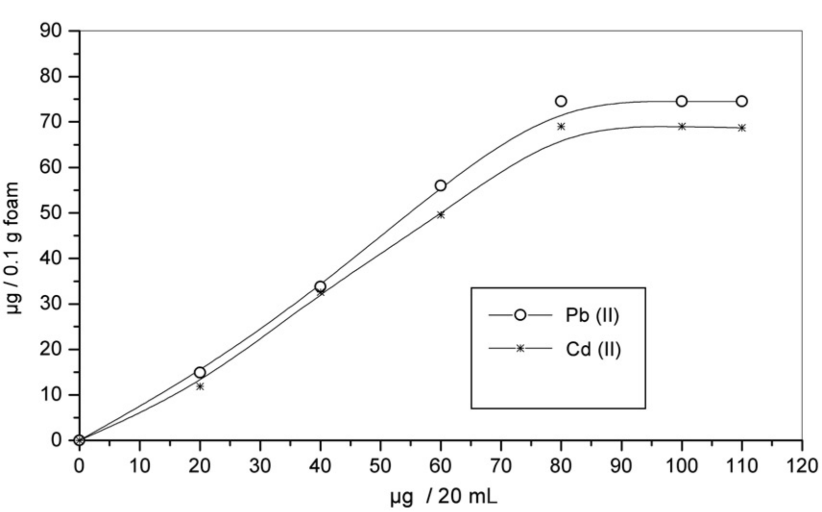

Figure 6. Extraction isotherms onto AP-BPUF.

Increasing the volume greater than 80 mL leads to an observable decline in the recovery percentage. It is clear that the decrease in sorption (%) is gradual in case of AA-BPUF, while this decrease is large in case of AP-BPUF. This suggests that the binding forces in the two-steps bonded sorbent are stronger than the one-step bonded foam (Figures 8 and 9).

4.5 ***Reproducibility of the method***

In order to find the reproducibility in the determination of Pb and Cd ions, the recommended procedure was repeated 10 times under optimum conditions. The relative

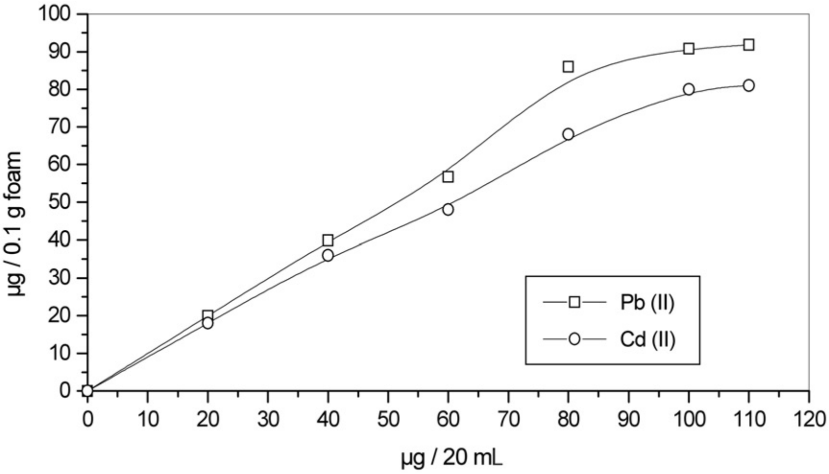

Figure 7. Extraction isotherms onto AA-BPUF.

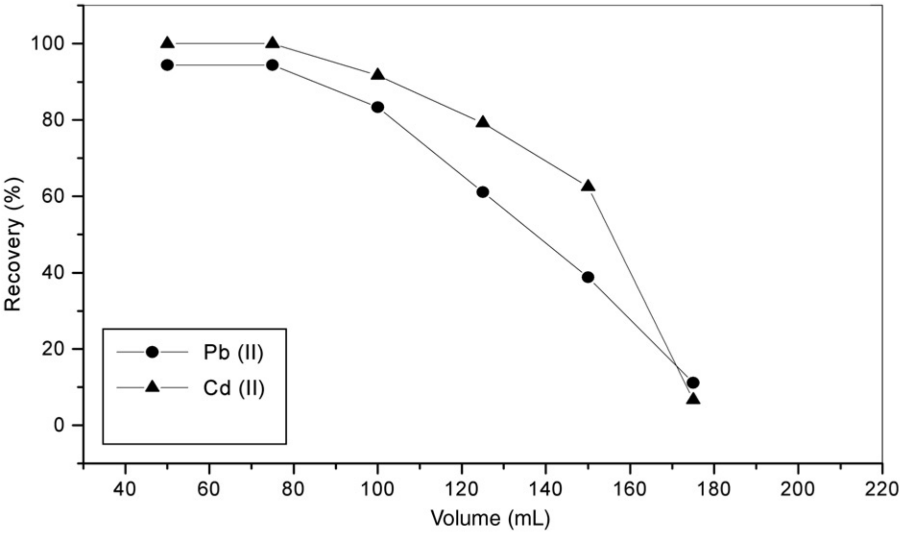

Figure 8. Effect of sample volume on the recoveries of metal ions onto AP-BPUF.

standard deviation (RSD for AA-BPUF was found to be 4.7% and 2.4% for Pb and Cd, respectively (Table 4).

4.6 *Reusability of the BPUFs*

The reusability of the foam was tested by loading Pb and Cd several times on BPUF from 20 mL sample solutions having a concentration of $1.0\,\mu g\,mL^{-1}$ and eluting the sorbed metal by $0.1\,mol\,L^{-1}$ HNO_3 solution. It was found that the sorption capacity after 20 cycles of sorption/desorption does not vary more than 2.5% for AA-BPUF. Therefore, repeated use of the BPUF is feasible. In addition, the uptake capacity of the foam stored for more than 17 months in closed dark bottles under ambient conditions has been found to be practically unchanged.

4.7 *Effect of electrolytes and foreign ions*

The chloride, nitrate, sulphate and phosphate anions (constituents of natural water samples) have the capability to complex with many metal ions. Therefore, in their presence, the efficiency of the ligand built on the foam matrix to bind metal ions may be hampered, resulting in the reduction of overall extraction. Thus, the effects of Cl^-, Br^-, NO_3^-, SO_4^{2-}, PO_4^{3-} and the other foreign species on the sorption efficiency of Pb and Cd onto the novel foams were studied, using the recommended batch method under the optimum conditions.

A species is considered to interfere when it lowers the recovery of metal ions by 5% in comparison to the value observed in its absence. The tolerance limits of various foreign species in the sorption of the studied metal ions are given in Table 5. These values indicate that the extraction on BPUFs is not much sensitive to foreign species, but some of the interfering substances examined were found to impair the quality of the studied metal ions when the chemical variables were maintained at the optimum levels. The results showed that the extraction of Pb and Cd was not affected by the medium composition.

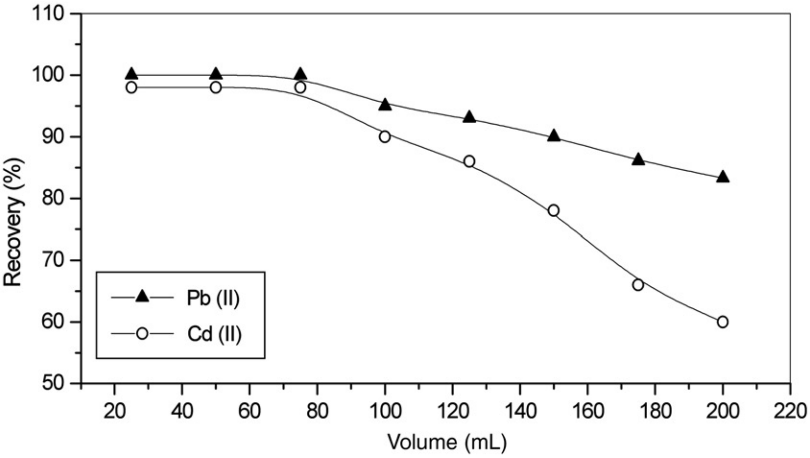

Figure 9. Effect of sample volume on the recoveries of metal ions onto AA-BPUF.

Thus, the Pb and Cd were both separated from other matrices successfully. These results also show that both Cd and Pb could be quantitatively separated in highly saline samples 15,000 mg L^{-1} NaCl, by the proposed preconcentration/separation method.

4.8 *Preconcentration and recovery*

BPUF filled columns were studied to preconcentrate Pb(II) and Cd(II) at a flow rate of 3 mL min^{-1}. The limit of preconcentration was estimated by increasing the dilution of metal ion solution used for sorption by keeping the total amount of the loaded metal ion constant at 20 µg. The uptake was quantitative up to 1500 mL. The sorbed metal ions were eluted by 0.1 mol L^{-1} HNO_3 solution. The volume of desorption was established when the recovery attained 95%. The preconcentration factor was calculated from the ratio of the initial to final volumes. The results are shown in Table 6.

The preconcentration factors of the two steps coupled foams are superior to those of the AP-BPUF. The quantitative recoveries of the present matrices, the faster sorption/desorption, the good reusability and stability are distinct advantages of the procedure. In addition, the acid concentration required for desorption is a dilute solution.

Table 5. Effect of some matrix ions on the recoveries of metal ions on BPUFs.

		Recovery% AP-BPUF		Recovery% AA-BPUF	
Foreign ions	Conc. of foreign ions mg L^{-1}	Pb(II)	Cd(II)	Pb(II)	Cd(II)
Non	–	88.0	74.0	98.0	100.0
NaCl	15,000	75.9	70.3	94.9	95.0
KCl	1000	79.8	72.0	94.0	92.6
$Ca(NO_3)_2$	50	88.7	73.3	95.7	93.3
Mg^{++}	50	88.0	72.8	100.0	96.3
NH_4Cl	1500	76.3	71.3	96.4	97.0
NaBr	100	66.7	71.0	95.9	90.0
NaI	100	81.2	71.0	94.0	93.5
Na_2SO_4	500	86.0	73.3	94.2	94.0
$NaNO_3$	1000	86.4	74.0	97.2	93.0
Na_3PO_4	150	84.0	68.4	94.6	92.0
$FeCl_3$	0.10	86.9	73.1	94.5	98.4
$MnCl_2$	0.10	87.3	74.0	97.0	94.6

Table 6. Enrichment factor of the analytes on the modified BPUFs.

Foam Type	Metal ion	Initial volume (ml)	Desorption volume (ml)	Recovery (%)	CF	RSD (%)
AP-BPUF	Pb(II)	1500	12	96	125	2.4
	Cd(II)	1500	12	98	125	3.0
AA-BPUF	Pb(II)	1500	6.7	98	224	2.6
	Cd(II)	1500	5.2	99	288	3.1

These results show that the tested metal ions can be concentrated effectively from large volumes of dilute aqueous solutions at the $\mu g\,L^{-1}$ level.

4.9 *Determination of limits of detection and quantification*

The limits of detection (LOD) for these metal ions were determined by passing 1500 mL of blank solution through each one of the columns. The detection limits based on three times of the standard deviations of the blank on a sample volume of 1500 mL. The LOD ($\mu g\,L^{-1}$) is defined as blank concentration $+ 3\sigma$, where σ is the standard deviation of blank determinations. In addition, the limit of quantification LOQ ($\mu g\,L^{-1}$) was calculated from blank concentration $+ 10\sigma$ (Table 7).

The detection limit obtained at this work is between 0.03 and 0.09 $\mu g\,L^{-1}$. The LOD values for all metal ions with all BPUFs enable the use of this material in collection of these metal ions at a trace concentration prior to their determination with higher sensitivity.

5. Application

The proposed method was applied to the determination of lead and cadmium content in tap water samples; apple leaves samples and samples of standard solution for the calibration of AAS obtained from Merck (Darmstadt, Germany). These samples were subjected to metal determination using the proposed procedure. The recoveries of spiked samples were also studied (Table 8).

Table 7. Determination of the detection limits of Pb and Cd with modified BPUFs in tap water.

Foam type	Metal ion	Blank $\mu g\,L^{-1}$	$\sigma\,\mu g\,L^{-1}$	LOD $\mu g\,L^{-1}$	LOQ $\mu g\,L^{-1}$
AP-BPUF	Pb(II)	0.0120	0.010	0.04	0.112
	Cd(II)	0.0013	0.011	0.03	0.101
AA-BPUF	Pb(II)	0.0120	0.027	0.09	0.28
	Cd(II)	0.0013	0.024	0.07	0.24

Table 8. Addition–recovery tests in the experiments for Pb(II) and Cd(II) in different samples.

Sorbent	Sample	Metal ion	Added $\mu g\,L^{-1}$ or $\mu g\,g^{-1}$	Found $\mu g\,L^{-1}$ or $\mu g\,g^{-1}$	Recovery %	RSD* %	Materials sources
AA-BPUF	Standard solution	Pb(II)	20.0	20.8	104.0	4.7	Merck chemicals company
		Cd(II)	20.0	19.4	97.02	3.8	
	Tap Water	Pb(II)	20.0	20.9	104.5	1.5	Faculty of science, Fayoum city
		Cd(II)	20.0	19.2	96.0	5.1	
	Apple Leaves	Pb(II)	20.0	20.1	100.5	2.1	Fayoum city
		Cd(II)	20.0	19.1	95.5	7.1	

Note: *Based on three replicate measurements in the same loaded column.

Table 9. Comparison of some chelating resins in literature with the chelating BPUFs proposed in the presented work.

Chelating agent	Sorbent	Enrichment factor Pb	Enrichment factor Cd	Detection limits (μgL^{-1}) Pb	Detection limits (μgL^{-1}) Cd	Precision (%) Pb	Precision (%) Cd	Reference
2-(6-Methyl-2-benzothiazolylazo) hromotropic acid (Me-BTANC)	Polyurethane foam	37	22	0.80	2.04	3.1	2.0	[34]
Cibacron blue F3-GA	Poly(hydroxyethyl methacrylate)	42	52	12.01	1.34	8.9	3.7	[35]
Xylenol orange	Amberlite XAD-7	–	50	–	10	–	2.0	[36]
α-Benzoin oxime	Sepabeads SP70	75	100	16.0	4.2	5.4	5.3	[37]
o-Aminophenol	Polyurethane foam	125	125	0.04	0.03	2.4	3.0	This work
Acetylacetone	Polyurethane foam	224	288	0.09	0.07	2.6	3.1	This work

These results show that the described procedure can be successfully applied to different matrices for the separation and preconcentration of lead or cadmium prior to their determination by flame AAS.

6. Comparison with other chelating matrices

The comparison of the proposed method with other solid phase extraction methods is summarised in Table 9. The performance of AA-BPUF is superior to most of the other adsorbents. Functionalised sorbents such as polyurethane foams are very promising materials for application in off-line preconcentration systems.

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