

Removal of Pb and Cd from aqueous media and fish liver using novel polyurethane foam functionalized with pyrazolone as a new metal ion collector

Research Article

N. Burham^a*, S.M. Abdel-Azeem^a, M.F. El-Shahat^b

^a Chemistry Department, Faculty of Science,
Fayoum University,
Fayoum City, Egypt

^b Chemistry Department, Faculty of Science,
Ain-Shams University,
Cairo, Egypt

Received 06 October 2008; Accepted 11 March 2009

Abstract: In the present paper, an off-line preconcentration procedure for the determination of cadmium and lead by flame atomic absorption spectrometry (FAAS) is proposed. Polyurethane foam (PUF) functionalized with o-aminophenol (o-AP) followed by Pyrazolone (Pyr) packed in a minicolumn was used as a sorbent material. The metals were retained on the modified PUF, from which it could be eluted and effectively preconcentrated. The detection limits were 0.072 and 0.016 $\mu\text{g L}^{-1}$ for Pb and Cd respectively. Enrichment factors were 250 and 319 for lead and cadmium respectively. The procedure has been applied successfully to metal determination in water samples, fish liver and reference material.

Keywords: Functionalized polyurethane foam • Pyrazolone • Heavy metals • Fish liver • Tap water

© Versita Warsaw and Springer-Verlag Berlin Heidelberg.

1. Introduction

Heavy metals are toxic and harmful even at low concentrations. Adsorption and ion exchange is the most often used processes for heavy metal removal. However, the need exists for low cost, effective and regenerable sorbent materials, which are capable of removing metal ions from waste water [1].

Preconcentration and separation methods for modern analytical chemistry are very important for accurate analysis of geological, biological and industrial materials and natural water samples, especially at trace levels [2]. The pretreatment of aqueous samples by the sorption technique not only increase the ion concentration to a detectable level, but also eliminates matrix effects [3-7]. The use of chelating sorbents can

provide a concentration factor up to several hundred folds [8-10], better separation of interfering ions, increased efficiency and the possibility of combining with different determining methods [11,12]. A variety of solid phase extractors have been developed for metal ions, and there is continued interest in the development of new collectors of high sorption uptake and selectivity [13-17]. In comparison with liquid – liquid extraction of metal ions, the solid phase extractors have two major advantages. They are ecofriendly, and it is easier to reuse them. Ion exchangers and chelating matrices are the two most important classes of solid phase extractors. However, the later ones are attractive due to their selectivity. The basic advantages of such an application lie in the increased selectivity, high preconcentration factors, higher degree of

* E-mail: n_burham@yahoo.com

adsorbent – adsorbate interaction, repetitive use over many cycles of adsorption elution – regeneration, and reproducibility of analytical preconcentration and determination [18]. Generally, chelating sorbents essentially consists of two components: chelate forming functional groups and the polymeric matrix or the support. The properties of both components determine the features and the application of respective material [19].

The primary method of synthesizing chelating sorbents proves to be the incorporation of an active functional group into the polymeric matrix by a chemical reaction on polymer backbone. Polyurethane foam (PUF) -polyether type is of significant interest in analytical chemistry [14-17,20,21]. PUF's are used as solid matrices because of their high sorption capacity to various compounds, chemical and hydrolytic stability, relative availability, and low price. In addition, the components are retained on PUF's due to both absorption and adsorption, which results in a uniform distribution of sorbates in the whole volume of the sorbent.

Our choice was to develop a new kind of bonded foam with high surface area and good chelating centers. Many hydrophobic chelating agents like 1-(2-Pyridylazo)-2-naphthol (PAN), 4-(2-Pyridylazo) resorcinol (PAR) and others are used for the development of loaded foam to increase the sensitivity and specificity of the foam towards metal ions. But the resistance of these loaded foams towards reagent leaching out (especially by organic solvents) limits their applicability. This has led to new methods which can be carried out by building up chelating groups on the terminal amino groups in the PUF. In this work, ligands bonded PUF has been studied as chelating foams. We have built hydroxyl – phenyl azo derivatives in the backbone of the untreated foam by coupling of o-aminophenol (o-AP) to the diazotized foam by the method reported [22]. Then the amino group of o-AP was diazotized and coupled to pyrazolone (Pyr, 3-methyl-1-phenyl-2-pyrazolin-5-one). This chelating group retains free metal ions due to the presence of two azo groups adjacent to the hydroxyl groups of the phenolic coupling component. Modified chelating foam with high selective retention properties has been prepared using this method. This novel chelating foam constitutes the basis of employed chemical separation procedure, with applications ranging from analytical and environmental chemistry. The principle interest of their use in trace analytical chemistry lies on the simplicity of the method for the selective separation of metal ions.

2. Experimental Procedures

2.1. Synthesis of bonded polyurethane foams (BPUF)

2.1.1. Synthesis of one-step coupling bonded polyurethane foam (o-AP – BPUF)

20 grams untreated foam cubes were soaked in one liter 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 reported [22]. The foam was suspended in an ice-water mixture and treated with 300 mL 0.1 mol L⁻¹ HCl and one liter 1 mol L⁻¹ NaNO₂ until the foam attained yellow color due to the formation of diazonium chloride. Then, the foam was left for 1 h at temperature 0 - 3°C. Next, the foam was reacted with o-AP (10.9 g in 100 mL of 10% NaOH solution). Addition was carried out gradually with continuous stirring at 0-3°C. Finally, the resulting brown colored 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 o-AP – BPUF. One gram of untreated foam was diazotized by varying concentrations of nitrite solutions (0.1–1.5 mol L⁻¹) under the optimum conditions. The products were coupled to the o-AP and the uptake capacity was determined. The results showed that the nitrite solution should be at concentration not less than 1.0 mol L⁻¹.

The concentration of coupling compound o-AP was also studied in order to insist the higher possibility to saturate the foam with the ligand moieties. One gram foam samples, previously diazotized, were coupled to o-AP of different concentrations (ranging from 0.1 to 1.0 mol L⁻¹) by the sequence stated before. The uptake of these products was determined by testing them for Cd (II) extraction with the batch procedure. The data revealed that the optimum concentration of o-AP at maximum sorption capacity is 0.60 mol L⁻¹.

2.1.2. Synthesis of two-steps coupling bonded polyurethane foam

The previously prepared AP-BPUF (5 g) was diazotized again by the method mentioned above then coupled to 3.35 g Pyr (in 100 mL ethanol and 20 g sodium acetate) and leaved for 24 h at 0-3°C. After that the foam was washed repeatedly with DDW, dried, and preserved for further use. PUF functionalized with o-Hydroxyphenylazo pyrazolone (Pyr-BPUF) has an orange red color.

2.2. Instrumentation

Flame atomic absorption spectrometric (FAAS) measurements of Pb and Cd were recorded on AAS5 FL (Carl Zeiss Technology, Germany), 1995 equipped with standard burner for air–acetylene flame. The operational conditions for the measurements are depicted 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 meter BT 500 BOECO, Germany, which was calibrated against two standard buffer solutions at pH 4 and 9, and a mechanical shaker with up to 200 rpm (SL 350 Nüve San. Ankara, Turkey). Doubly distilled water (DDW) was obtained from two successive distillations using Hamilton laboratory glass instrument (Europe House, Sandwich, England). All experiments were done at room temperature.

Table 1. Conditions for flame AAS.

Parameters	Metal ion	
	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 ⁻¹)	65	50
Burner height (mm)	5-10	4-12

2.3. Chemicals and solutions

Unless otherwise stated, all reagents used were of analytical grade and all solutions were prepared with DDW. Labware and glassware were used throughout and repeatedly cleaned with chromic acid and rinsed with DDW. Stock solutions (1000 µg mL⁻¹) of the studied metal ions were prepared by dissolving appropriate amounts of analytical reagent grade lead(II) nitrate Pb(NO₃)₂ (Aldrich, Milwaukee, USA), Cadmium nitrate Cd(NO₃)₂•4H₂O (Panreac, Barcelona, Spain). Sodium nitrite and sodium hydroxide were received from Winlab Company, UK for reagents fine chemicals. Hydrochloric acid used was delivered from Merck (Germany). Commercial, open cell, polyether-type PUF (31.6 kg m⁻³) supplied by the Egyptian company for foam production (Cairo, Egypt). All liquids were used without any further purification.

Table 2. Elemental analysis of the modified foams.

Sample name	Calculated (%)			Experimental (%)		
	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
Pyr-BPUF	62.1	8.45	6.32	61.30	7.79	6.42

2.4. Characterization of the modified foams

2.4.1. Elemental analysis

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

2.4.2. IR analysis

The important IR bands are presented in Table 3. An 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 NH₂ group has disappeared from the IR charts of the two steps coupled BPUF. This confirms that the amino groups of AP-BPUF were exhausted in bonding to the coupling compound in the second step. Scheme 1 shows the proposed reactions involved in the preparation of the novel BPUF.

Table 3. Important IR bands.

Sample designation	IR bands (wave number, cm ⁻¹)				
	ν _{NCO}	ν _{OH}	ν _{CO}	ν _{NH2}	ν _{N=N}
Untreated PUF	2100	3311-3509	1655	3111-3299	-
o-AP-BPUF	-	3329-3565	1661	2926-3297	1473
Pyr-BPUF	-	3300-3436	1653, 1705, 1716	-	1473, 1508

2.4.3. Chemical Stability of the BPUF

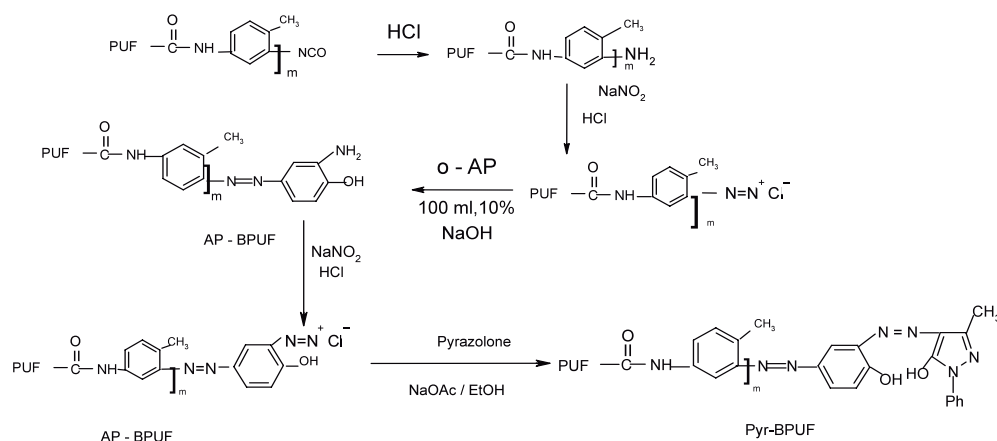
The chemical stability was investigated by measuring the change of sorption capacity for Pb and Cd ions after successive contact of the modified foam with acids 1–6 M HCl, 1–2 M H₂SO₄, 1 M HNO₃ and alkaline solutions of 1–2 M NaOH and 1–2 M NH₄OH, as well as organic solvents e.g. methanol, ethanol, isopropanol, n-butanol, acetone, chloroform and carbontetrachloride. The results show that the foam is highly stable in mineral acid, alkaline medium as well as common organic solvents when the foam shaken for 10 hours, but in ≥ 2 M HNO₃ the foam undergoes degradation and the capacity for Cd or Pb falls rapidly.

2.5. Recommend procedures

2.5.1. Batch Experiments

2.5.1.1. Optimum pH of metal ion uptake

The optimum pH of metal ion uptake was determined by batch equilibrium techniques. Metal ion (20 mL, 1 µg mL⁻¹) was shaken with 100 mg of foam for 1 h. The pH of the metal ion solution was adjusted prior to equilibration over a range of 2–9 with HCl or NaOH.



Scheme 1. The proposed reactions involved in the preparation of the Pyr-BPUF.

After the equilibration, the remained metal ions were determined by flame AAS and the recovery percentage was calculated.

2.5.1.2. Kinetics of metal sorption

To determine the rate of loading of Pb(II) and Cd(II) on the foam, the batch experiments were carried out under the following conditions: 100 mg of foam cubes were stirred with 20 mL of solutions containing the studied metal ions ($1 \mu\text{g mL}^{-1}$) for different time intervals. The remained metal ion was determined and the percentage sorption was calculated.

2.5.1.3. Foam capacity

The total capacity of the BPUF was determined by shaking 20 mL of metal ion solution of different concentration ($0.5\text{--}100 \mu\text{g mL}^{-1}$) with 100 mg foam for 1.0 h at the optimum sorption pH. The foam was filtered off and the concentration of the sorbed metal ion was determined by flame AAS, the uptake was calculated from the difference between the original and remaining concentration.

2.5.1.4. Effect of sample volume

The effect of dilution on the recovery of metal ions by static method was examined. $20 \mu\text{g}$ of each metal ion was placed in solutions of different volume ($50\text{--}1000 \text{ mL}$) at the optimum pH and shaking time with 100 mg foam. After that, the sorbent was filtered off and the collected metal ions were desorbed by stirring the modified foam with $25.0 \text{ mL } 0.1 \text{ mol L}^{-1} \text{ HCl}$ solution. The desorbed metal ions were determined by flame AAS.

2.5.1.5. Reproducibility test

To study the accuracy of the developed procedure, the reproducibility experiment was carried out as follow: ten

sample solutions were prepared equally, 20 mL solution contains the studied metal ions ($1 \mu\text{g mL}^{-1}$) adjusted to the optimum pH and shaking time with 100 mg sorbent. The uptake was calculated for each sample by the concentration difference before and after sorption and the accuracy measured as RSD%.

2.5.1.6. Effect of diverse ions

The tolerance effect of some electrolytes which may affect the determination of the studied metal ion was investigated by testing the uptake percentage in different concentrations of interfering ions on 20 mL solution containing $20 \mu\text{g}$ of the studied metal ions with 100 mg foam. The tolerance limit was considered at ion concentration causing a relative error $< \pm 5\%$. The interfering ions considered are those normally present in water e.g. Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Fe^{3+} , Mn^{2+} , Cl^- , Br^- , I^- , NO_3^- , SO_4^{2-} and PO_4^{3-} were studied.

2.5.2. Dynamic Experiments

2.5.2.1. Column preparation

The glass column, with a stopcock, was 10 cm long, and 1.0 cm in diameter. A small amount of glass beads placed on the disc to prevent loss of the foam during sample loading, the column was packed with 1.0 g of the modified foam. The foam was packed with gentle pressure by glass rod on the foam plugs onto the column filled with water to avoid air bubbles then adding glass beads on the top of the foam 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.

2.5.2.2. Breakthrough capacity

1000 mL samples containing each metal ion separately at concentrations ($10 \mu\text{g mL}^{-1}$), were passed through

foam columns, at flow rates 3.0 mL min^{-1} . Each solution was adjusted to the optimum pH and the effluent was collected in 10 mL fractions where the amount of metal ion in each fraction was determined by the recommended method. The percentage of the metal in each effluent aliquot can be calculated and plotted against the volume of effluent (Bed volume). The dynamic capacities with each metal ion could be calculated. The breakthrough studies were carried out by 1.0 g of different bonded foams each in a separate column.

2.5.2.3. Flow rate effect

The dependence of uptake of the metal on the flow rate was studied for Pb(II) and Cd(II) at the pH chosen for maximum complexation, the solution (50 mL , $1 \text{ } \mu\text{g mL}^{-1}$) flow rate being varied from 1 to 12 mL min^{-1} and the retention percentage of the metal ion into the column was determined.

2.5.2.4. Desorption breakthrough

To determine the volume of acid for quantitative recovery, the following procedure was employed: $50 \text{ } \mu\text{g}$ of each metal was placed in 50 mL solution sample and adjusted to the optimum pH and flow rate. After this, the column was rinsed with 10 mL DDW. The retained metal ions were eluted by 0.1 mol L^{-1} nitric acid solution. The volume of acid at $\geq 95\%$ recovery was chosen for desorption in the determination of the preconcentration factor.

2.5.2.5. Determination of the detection limit

Blank samples (500 mL) were adjusted to the optimum pH of sorption then passed into the column at the suitable flow rate. The column was then eluted with nitric acid of appropriate concentration then the eluate was aspirated into flame for AAS determination. This experiment was performed three times and the standard deviation of the results was calculated. Limit of detection (LOD) defined, as three times standard deviation of blank ($\text{blank} + 3\sigma$) was calculated. In addition, the limit of quantification (LOQ) defined as ten times standard deviation of blank ($\text{blank} + 10\sigma$).

2.5.2.6. Preconcentration and recovery

Pyr-BPUF modified Foam packed in glass columns treated with $0.1 \text{ mol L}^{-1} \text{ HNO}_3$ solution and washed with DDW until free from HNO_3 . A suitable aliquot of the solution containing Pb(II) or Cd(II) in the concentration range $5\text{--}25 \text{ } \mu\text{g L}^{-1}$ was passed through this column after adjusting its pH at the optimum value at a flow rate of 3.0 mL min^{-1} . The stripping of the metal ions from the foam was carried out by $0.1 \text{ mol L}^{-1} \text{ HNO}_3$. The eluate

was aspirated into the flame for AAS determination. The concentration factor (CF) could be calculated from the ratio of the initial volume of the sample to the final volume after concentration.

2.6. Analysis of real samples

2.6.1. Tap and lake water analysis

Lead and cadmium were determined in water samples by additive method. 1500 mL of tap or lake water was collected from our research laboratory in faculty of science or Qaroun Lake at Fayoum city was adjusted to the optimum pH. The water was spiked with cadmium or lead analytes, placed in a glass container and passed through the modified foam columns at flow rate 3 mL min^{-1} . The column was eluted by 0.1 mol L^{-1} nitric acid solution and the metal ions in the collected eluate was measured by flame AAS. The experiment was repeated three times and the recovery percentage and RSD were calculated.

The water samples were collected in polyethylene bottles washed with detergent, pure water, dilute HNO_3 and pure water, respectively. Before the analysis, the samples were filtered.

2.6.2. Analysis of fish sample

Fish sample (alive) obtained from Karon plantations for fish (Fayoum City, Egypt) was cut and the liver was taken, cleaned, washed several times with DDW then put in a clean and dry beaker and dried at 105°C for 24.0 h . After this, the fish liver sample was transferred into a clean, dry crucible and ignited for 6.0 h in a muffle at 200°C then 400°C and finally at 600°C , temperature was changed every 2.5 h . The sample was digested in 20 mL concentrated nitric acid (14.0 mol L^{-1}) till nearly dryness then diluted up to 1000 mL with DDW and made at the optimum conditions then passed into the column. The experiment was repeated three times and the recovery and RSD% values were found.

3. Results and discussion

3.1. Sorption of metal ions as a function of pH

The sorption of metal ions viz. Cd(II) and Pb(II) on the foam was carried out at different pH by the batch equilibrium technique and is shown in Figs. 1 and 2. The percentage of metal sorption was calculated by measuring the metal ion content before and after the chelation by the relation: $\text{Sorption } (\%) = [(C_0 - C) / C_0] \times 100$ Where C_0 and C are the initial and remaining concentrations ($\mu\text{g L}^{-1}$) of the metal ion respectively. The extraction of metal ions increases with increase in pH, reaching

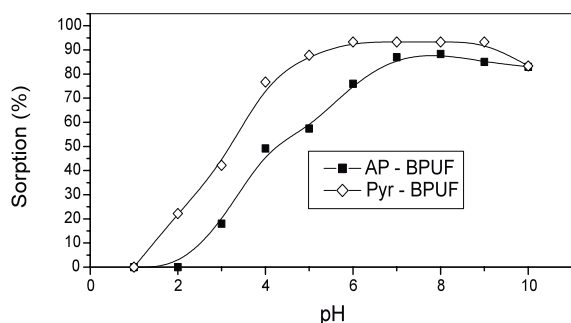


Figure 1. Effect of pH on the removal of Pb(II) with different modified BPUF sorbents.

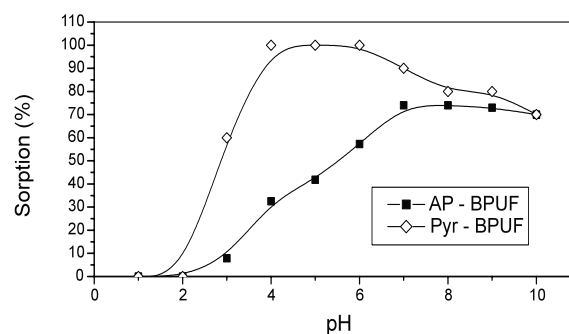


Figure 2. Effect of pH on the removal of Cd(II) with different modified BPUF sorbents.

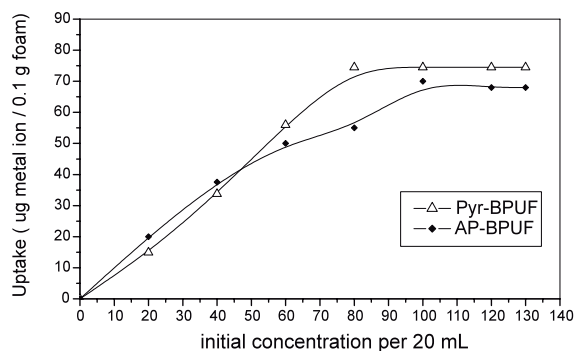


Figure 3. Extraction isotherms of Pb(II) with the new foams.

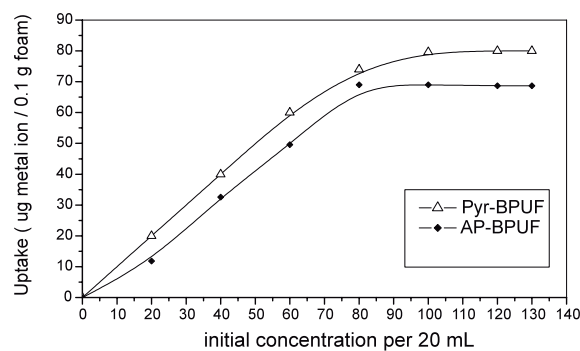


Figure 4. Extraction isotherms of Cd(II) with the new foams.

a limiting value followed by a decrease in the uptake beyond the limiting value. The decrease in uptake at low pH values might be due to the weak nucleophilicity of both the hydroxyl oxygen of the phenolic reagent and nitrogen of the azo group, which are responsible for the chelation to metal ions. This could be explained by the attack of H^+ on these centers in acidic medium. By increasing the pH, the concentration of protons decreases resulting in the ionization of the OH groups to form phenoxides, which have negatively charged oxygen. Thus strong chelating sites in the BPUF sorbent would be available. All subsequences works were preformed at pH 6, which was considered to be the optimum pH.

3.2. Kinetics of Cd and Pb sorption

To determine the retention rate of Pb and Cd on the foam the following batch procedure was applied: 0.1 gm foam were stirred with 20 mL of the studied ion solution at room temperature for 1-120 min. The concentrations of Cd and Pb in the initial and final solution were determined. The loading half time $t_{1/2}$ needed for 50% reduction of the initial solution concentration has been estimated to be 3.5 min for Pb and 2.0 min for Cd (see Table 4). This fast extraction indicates that the new foam is suitable for preconcentration of trace Pb and Cd from dilute solutions.

3.3. Total foam capacity

Figs. 3 and 4 show the effect of initial metal ion concentrations of Pb(II) and Cd(II) ions on the equilibrium sorption capacities. It is clear that the uptake capacities were increased with increasing the initial concentrations and reached a plateau (maximum uptake capacity values) were obtained.

From the results in Table 4, it is obvious that Pyr-BPUF has higher capacities than the one step coupled foam (o-AP-BPUF). This is due to the formation of surface complex with the built legends.

Table 4. Optimum conditions found experimentally for preconcentration of Cd(II) and Pb(II) by the BPUF.

Sorbent	Property	Metal ion	
		Pb(II)	Cd(II)
AP-BPUF	pH range	7-8	7-8
	Loading half time ($t_{1/2}$), min	7.0	12.0
	Capacity ($\mu\text{mol g}^{-1}$)	3.6	5.9
	RSD (%) ^a	3.2	3.5
Pyr-BPUF	pH range	6-8	4-6
	Loading half time ($t_{1/2}$), min	3.5	2.0
	Capacity ($\mu\text{mol g}^{-1}$)	4.3	7.6
	RSD (%) ^a	1.7	3.6

^a RSD = Relative standard deviation for ten replicates

3.4. Effect of electrolytes and foreign ions

The interfering effects of certain salts and ions on the determination of Pb and Cd were examined Table 5. The effect of salts commonly present in water samples such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Fe^{3+} , Mn^{2+} , Cl^- , Br^- , I^- , SO_4^{2-} , NO_3^- and PO_4^{3-} ions on the uptake of 20 μg of Pb and Cd was studied. All the tested electrolytes caused not more than 5% decrease in the retention capacity of the studied ion within the working pH interval and the most ion are tolerated to different degrees.

3.5. Breakthrough capacity

The calculated capacities (Figs. 5 and 6) show that the Pyr-BPUF has greater capacity than the one step o-Aminophenol bonded foam. The breakthrough capacity of these metal ions per one gram of BPUF was calculated according to the equation [uptake = $(V_{50\%} \times C_0)/m$] where $V_{50\%}$ is the effluent volume (mL) at 50% breakthrough, C_0 is the concentration of the feed solution, and m is the mass of foam in grams. The column dynamic capacities for Pb and Cd are

Table 5. Effect of other ions on the recovery of Cd(II) and Pb(II).

Foreign ions	Conc. Of foreign ions mg L^{-1}	Recovery AP - BPUF, %		Recovery pyr- BPUF, %	
		Pb(II)	Cd(II)	Pb(II)	Cd(II)
Non	non	88.0	74.0	98.0	100
NaCl	15000	83.9	70.3	94.7	95.5
KCl	1000	84.0	72.0	99.5	98.0
$\text{Ca}(\text{NO}_3)_2$	50	88.7	73.3	97.8	96.3
Mg^{2+}	50	88.0	72.8	100.0	100.0
NH_4Cl	1500	85.3	71.3	95.0	95.7
NaBr	100	86.0	71.0	95.7	96.4
NaI	100	83.2	71.0	95.0	97.0
Na_2SO_4	500	86.0	73.3	95.0	98.0
NaNO_3	1000	86.4	74.0	97.4	100.0
Na_2PO_4	150	84.0	75.4	95.2	94.4
FeCl_3	0.10	86.9	73.1	96.2	98.0
MnCl_2	0.10	87.3	74.0	95.7	99.3

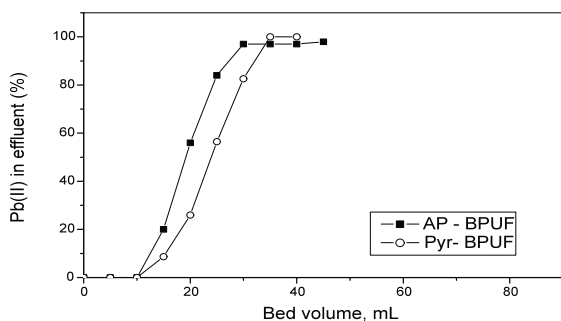


Figure 5. Breakthrough capacity for Pb(II) with BPUF sorbents.

estimated to be $0.087 \mu\text{mol g}^{-1}$ for Pb and $0.133 \mu\text{mol g}^{-1}$ for Cd with AP-BPUF and $0.106 \mu\text{mol g}^{-1}$ for Pb and $0.311 \mu\text{mol g}^{-1}$ for Cd with Pyr-BPUF. The difference in uptake capacity of these bonded foams may be attributed to the chemical stability between the studied metal ions and the new chelating sites built on the foam, and the difference in the ionic sizes of the studied metal ions.

3.6. Effect of flow rate

The results indicated that the optimum flow rate for quantitative recoveries of these metal ions is 3.0 mL min^{-1} with AP - BPUF and 7 mL min^{-1} with Pyr - BPUF. However, at flow rates greater than 3.0 and 7.0 mL min^{-1} there was a decrease in the percentage of retention onto the column between 5-7%. Probably the metal ions could not be significantly equilibrated with the chelating centers of the modified foam as it needs longer contact time with the sorbent.

3.7. Preconcentration and recovery

For the preconcentration of trace elements in natural water samples, the method used must have high preconcentration factor. To obtain high preconcentration factors sample volume is an important factor. The effect of the sample volume on the recoveries of analyt ions was also investigated in the range of 50-1500 mL. The results are depicted in Table 6. The recovery values of cadmium and lead were very efficient (>95%) in the sample volume range of 50-1500 mL.

3.8. Determination of limits of detections and quantifications

The limits of detection (LOD) for Cd and Pb were determined by passing 1500 mL of blank solution through the column. The loaded metal ions on the BPUF column were eluted by $0.1 \text{ mol L}^{-1} \text{ HNO}_3$ and determined by flame AAS. The LOD ($\mu\text{g L}^{-1}$) defined as blank concentration + 3σ where σ is the standard deviation of blank determinations. Also, the limit of quantification LOQ ($\mu\text{g L}^{-1}$) was calculated from blank concentration + 10σ Table 7. The values of LODs enable the use of

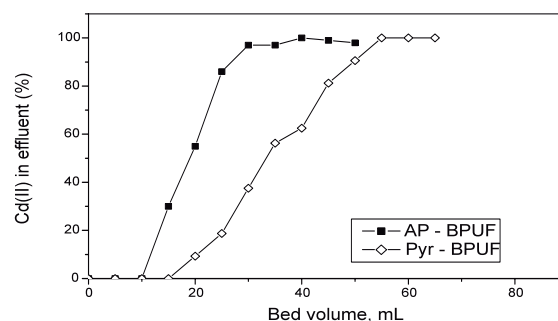


Figure 6. Breakthrough capacity for Cd(II) with BPUF sorbents.

Table 6. Preconcentration factor of Pb(II) and Cd(II) with modified BPUF sorbents.

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
Pyr-BPUF	Pb(II)	1500	6.0	96	250	3.4
	Cd(II)	1500	4.7	96	319	2.8

* Based on three replicate measurements in the same loaded column

this foam in the collection of Cd and Pb ions at a trace concentration prior to their determination with higher sensitivity.

3.9. Reusability of the BPUF

The reusability of the foam was tested by loading Cd and Pb several times on BPUF by column procedure from 50 mL sample solutions having a concentration of $1.0 \mu\text{g mL}^{-1}$ and eluting the sorbed metal by 0.1 mol L^{-1} HNO_3 solution. It was found that the sorption capacity after 23 cycles of sorption and desorption does not vary more than 3%. Therefore, repeated use of the BPUF is feasible. Also, the uptake capacity of the foam stored for more than 20 months in closed dark bottles under ambient conditions has been found to be practically unchanged.

3.10. Analytical Applications

3.10.1. Method validation and analytical performance

In order to establish the validity of the proposed procedure, the method has been applied to the determination of lead and cadmium in reference material (Quality control

standard #1, BDH Cat NO: 456422W). The determined values were not significantly different from the certified values (Table 8).

The present method was also evaluated using spiked tap water, Qaroun lake water and fish liver samples. The recoveries of analytes spiked into the analyzing samples, were studied; satisfactory results were obtained as shown in Table 8. Good agreement was obtained between the added and recovered analyte contents using the experimental procedure. The recovery values calculated for the standard additions were always higher than 95%, thus confirming the accuracy of the procedure and the absence of matrix effects. Also, the high tolerance limits for diverse ions confirm the accuracy of the procedure. An R.S.D% value for the determination of analytes in the spiked sample was less than 10%. It is evident for the reliability of the proposed method for the analysis of high salinity water like Qaroun lake water and the drinking water.

3.10.2 Comparison with other matrices

A comparison between Pyr-PUF capacity and other sorbents reveals that this solid phase has obvious advantages and limitation (Tables 9 and 10). Although the removal capacity of the new extractor is generally lower than that of the other sorbents, it can be used to remove metal ions from relatively dilute solution. As it can be seen, the new developed method has higher preconcentration factor, lower detection limit and allowed a highly sensitive and simple approach for the determination of Cd and Pb at trace levels in

Table 7. Determination of the detection limits of Pb and Cd with modified BPUF sorbents.

Foam Type	Metal ion	Blank $\mu\text{g L}^{-1}$	σ $\mu\text{g L}^{-1}$	LOD $\mu\text{g L}^{-1}$	LOQ $\mu\text{g L}^{-1}$
AP-BPUF	Pb(II)	0.0120	0.010	0.04	0.112
	Cd(II)	0.0013	0.011	0.03	0.101
Pyr-BPUF	Pb(II)	0.0120	0.020	0.072	0.212
	Cd(II)	0.0013	0.005	0.016	0.051

Table 8. Determination of Cd(II) and Pb(II) in various water samples and certified reference material.

Sorbent	Sample	Metal ion	Added or Certified $\mu\text{g L}^{-1}$	Found $\mu\text{g L}^{-1}$	Recovery %	RSD* %
Pyr-BPUF	Quality Control Standard #1, No:456422W	Pb(II)	20.0	20.05	100.25	2.3
		Cd(II)	20.0	20.01	100.05	3.0
	Qaroun lake Water	Pb(II)	20.0	20.1	100.5	1.2
		Cd(II)	20.0	20.6	103.0	2.7
	Tap Water	Pb(II)	20.0	20.1	100.5	4.7
		Cd(II)	20.0	19.8	99.0	3.1
	Fish Liver	Pb(II)	20.0	20.4	102.0	4.6
		Cd(II)	20.0	20.6	103.0	3.9

* Based on three replicate measurements in the same loaded column

Table 9. Comparison of some extractors in literature with Pyr-BPUF.

Solid matrix	Ligand	Metal	CF	LOD $\mu\text{g L}^{-1}$	Sample	Determination technique	Ref.
Chitosan biopolymer	8-hydroxyquinoline	Cd	24	0.10	Water	FAAS	[23]
Amberlite XAD-2	2-aminothiophenol	Cd	74	0.14	Water	FAAS	[24]
Amberlite XAD-4	3,4-dihydroxybenzoic acid	Cd	102	0.028	Biological samples	TS-FF-AAS	[25]
Diaion	A. fumigatus	Pb	50	0.30	Water, dust and black tea	FAAS	[26]
pumice stone	Penicillium digitatum	Pb	50	5.80	Waters and vegetables	FAAS	[27]
Mci Gel Chp 20y Resin	QAMDHB	Pb	300	1.3	biological, water and soil samples	GFAAS	[28]
		Cd	300	1.2			
Foam	pyrazolone	Pb	250	0.072	Waters and fish liver	FAAS	This work
		Cd	319	0.016			

CF: preconcentration factor; LOD: limit of detection; FAAS: Flame Atomic Absorption Spectrometry; TS-FF-AAS: Thermospray Flame Furnace-AAS, QAMDHB: 2-(2-Quinolinil-azo)-4-methyl-1,3- dihydroxidobenzene; GFAAS: graphite furnace atomic absorption spectrometry.

Table 10. Comparative data from some recent studies for the capacity of Pb and Cd with Pyr-BPUF.

System	Studied metals	pH range	Eluent (mol L^{-1})	Flow rate (mL min^{-1})	Resin capacity (mmol g^{-1})	Ref.
Dowex Optipore V-493/dibenzylthiocarbamate	Cd, Pb	2.0	1 HNO_3 in acetone	4.0	65-41	[29]
Amberlite XAD-2010/DDTC	Cd, Pb	6.0	1 HNO_3 in acetone	10	51-30	[30]
Nanometer titanium dioxide immobilized on silica gel	Pb	4-7	1 HCl	2.0	15	[31]
Chinese herb Pang Da Hai (seeds of Sterculia lychnophora Hance)	Cd, Pb	5-8	1 HNO_3	-	156-131	[32]
8-Hydroxyquinoline anchored to silica gel	Cd, Pb	4-7	2 HNO_3	4.0	92-158	[33]
PUF functionalized with pyrazolone	Cd, Pb	7-8	0.1 HNO_3	3	7.6-4.3	This work

DDTC: diethyldithiocarbamate, PUF: Polyurethane foam

different real samples. The analyte elution of the studied metal ions from the new foam is easily performed with $0.1 \text{ mol L}^{-1} \text{ HNO}_3$.

4. Conclusion

The synthesized Pyr-BPUF can be used to remove lead and cadmium ions from relatively dilute solutions. The sorbent is highly stable, inexpensive, and can be used repeatedly without lose of its sorption capacity. The foam is also durable against strongly acidic and

basic solutions. The foam used more than 20 times in succession did not lose its sorption efficiency. The quantitative sorption pH range (6-8 and 4-6) was fairly wide, which implies that careful adjustment of the solution pH is not necessary. The developed methodology in this paper was successfully applied to the determination of lead and cadmium in spiked water samples and fish liver. The method proved to be rapid, reliable and flexible with limited interference. Based on these results, a new method is proposed for the determination of the studied metal ions (Pb and Cd) by flame AAS after preconcentration with the new BPUF.

References

- [1] M. Ghoul, M. Bacquet, M. Morcellet, *Water Research* 37, 729 (2003)
- [2] M. Nicolai, C. Rosin, N. Tousset, Y. Nicolai, *Talanta* 50, 433 (1999)
- [3] V.A. Lemos, S.L.C. Ferreira, *Anal. Chim. Acta* 441, 281 (2001)
- [4] D.S. de Jesus, R.J. Cassella, S.L.C. Ferreira, A.C.S. Costa, M.S. de Carvalho, R.E. Santelli, *Anal. Chim. Acta* 366, 263 (1998)
- [5] D.S. de Jesus, R.J. Cassella, S.L.C. Ferreira, A.C.S. Costa, M.S. de Carvalho, R.E. Santelli, *Anal. Chim. Acta* 378, 287 (1999)
- [6] M. Kumar, D.P.S. Rathore, A.K. Singh, *Talanta* 51, 1187 (2000)
- [7] R. Say, E. Birlik, A. Ersoz, F. Yilmaz, T. Gedikbey, A. Denizli, *Anal. Chim. Acta* 480, 251 (2003)
- [8] Y. Guo, B. Din, Y. Liu, X. Chang, S. Meng, J. Liu, *Talanta* 62, 209 (2004)
- [9] P.K. Tewari, A.K. Singh, *Talanta* 53, 823 (2001)
- [10] A. Goswami, A.K. Singh, B. Venkataramani, *Talanta* 60, 1141 (2003)
- [11] F. Baffi, A.M. Cardinale, R. Bruzzzone, *Anal. Chim. Acta* 270, 79 (1992)
- [12] H. Bagheri, A. Gholami, *Talanta* 55, 1141 (2001)
- [13] B.C. Mondal, D. Das, A.K. Das, *Talanta* 56, 145 (2002)
- [14] E.A. Moawed, *Analytica Chimica Acta* 580, 263 (2006)
- [15] E.A. Moawed, *Acta Chromatographica* 14, 298 (2004)
- [16] E.A. Moawed, M.F. El-Shahat, *React. Funct. Polym.* 66, 720 (2006)
- [17] E.A. Moawed, M.A.A. Zaid, M.F. El-Shahat, *J. Anal. Chem.* 61, 458 (2006)
- [18] M. Dogutan, H. Filik, I. Tor, *Talanta* 59, 1053 (2003)
- [19] S.D. Çekiç, H. Filik, R.S. Apak, *Anal. Chim. Acta* 505, 15 (2004)
- [20] S.G. Dmitrienko, Ya. A. Zolotov, *USP. Kim*, 71, 180 (2002) (In Russian)
- [21] T. Braun, J.D. Navratil, A.B. Farag, *Polyurethane Foam Sorbent in Separation Science* (CRC Press, Boca Raton, 1985)
- [22] N. Burham, S.M. Abdel-Azeem, M.F. El-Shahat, *Anal. Chim. Acta* 579 (2006) 193
- [23] A.O. Martins, E.L. Silva, E. Carasek, N.S. Goncalves, M.C.M. Laranjeira, V.T. Favere, *Anal. Chim. Acta* 521, 157 (2004)
- [24] V.A. Lemos, P.X. Baliza, *Talanta* 67, 564 (2005)
- [25] V.A. Lemos, M.A. Bezerra, F.A.C. Amorim, *J. Hazardous Materials* 157, 613 (2008)
- [26] M. Soylak, M. Tuzen, D. Mendil, I. Turkekul, *Talanta* 70, 1129 (2006)
- [27] S. Baytak, E. Kendüzler, A.R. Türker, N. Gök, *J. Hazardous Materials* 153, 975 (2008)
- [28] G. Yang, W. Fen, C. Lei, W. Xiao, H. Sun, *J. Hazardous Materials*, 162, 44 (2009)
- [29] E. Melek, M. Tuzen, M. Soylak, *Anal. Chim. Acta* 578, 213 (2006)
- [30] C. Duran, A. Gundogdu, V.N. Bulut, M. Soylak, L. Elci, H.B. Sentürk, M. Tüfekci, *J. Hazardous Materials* 146, 347 (2007)
- [31] R. Liu, P. Liang, *J. Hazardous Materials* 152, 166 (2008)
- [32] Y. Liu, X. Chang, Y. Guo, S. Meng, *J. Hazardous Materials*, B135, 389 (2006)
- [33] A. Goswami, A.K. Singh, B. Venkataramani, *Talanta* 60, 1141 (2003)