Synthesis and application of alizarin complexone functionalized polyurethane foam: Preconcentration/separation of metal ions from tap water and human urine

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ABSTRACT

A new chelating sorbent has been synthesized by the covalent condensation of alizarin complexone (ALC) to polyurethane foam (PUF) through –N=C– group. The material was characterized by IR, ^{1}H NMR and chemical proof. Iminodiacetic acid groups are found in the prepared sorbent and the reaction proceeded via condensation between the toluidine moieties in the PUF and non-hydrogen bonded carbonyl group in ALC. Also, the possibility of elimination reaction between the groups (NH_2, NH and OH) in the polymer and carboxylic groups in the reagent was excluded. The material has been used to separate/preconcentrate Cu^{2+}, Zn^{2+} and Cd^{2+} prior to their determination by flame atomic absorption spectrometry (FAAS). Chemical and flow variables such as sample pH, sorbent capacity, sample flow rate and interference from co-existing ions were investigated. All metal ions are quantitatively desorbed by $0.1\,mol\,L^{-1}$ nitric acid solution. The procedure provides concentration factor 100 and limits of detection $0.013\,\mu g\,mL^{-1}$. The method was validated by the analysis of certified reference materials and real samples such as tap water and human urine.

1. Introduction

In recent years, solid-phase extraction has become one of the most common techniques for preconcentration and sample preparation since it enables achievement of higher concentration factor, the ability to handle larger volume samples in a closed system, and the possibility of combination with different modern analytical systems such as atomic absorption spectrometry [1,2]. Several solid sorbents could be utilized in solid-phase extraction applications such as polyurethane foam (PUF) [3], silica gel [4], styrene-divinylbenzene [5,6], chitosan [7] and other sorbents [8]. The interesting about PUF has increased significantly, and it has been used as a solid sorbent for preconcentration and separation of a wide variety of inorganic and organic compounds in different media [9,10]. The PUF is an excellent sorbent material due to high available surface area, cellular structure and extremely low cost. In addition, it is stable in acids (except concentrated nitric and sulfuric acids), bases and organic solvents and also, it will not change its structure when heated up to 180 °C [9]. The membrane structure and the available surface area of the polyurethane foams make it very suitable stationary phase and as a column filling material. Ion exchange polyurethane foams (IEPUFs), unloaded PUFs and PUFs immobilizing specific reagents have been successfully employed for the separation and determination of metal ions [10].

Many organic ligands have been immobilized on PUF and utilized for preconcentration and separation of trace elements in various environmental samples. Among those, 4-(2-pyridylazo)-resorcinol (PAR) for Zn [11], Cd in drinking water [12]; 2-(2-benzothiazolylazo)-p-cresol (BTAC) for Cd determination in environmental and biological samples [13]; 2-(6′-methyl-2′-benzothiazolylazo)-chromotropic acid (Me-BTANC) for Cu in food [14] and Cd in black tea and spinach leaves [15]; 2-[2-(6-methyl-benzothiazolylazo)]-4-bromophenol (Me-BTABr) for Zn in natural water [16] and O,O-diethyl-dithiophosphate (DDTP) for Cd [17] in natural water samples.

The terminal amine group in the toluidine moiety in PUF has been utilized in covalent coupling of a ligand compound to PUF backbone through a spacer arm –N=N– group was investigated in many articles [18–20]. However, the instability of diazonium salt and loss of reactivity during filtration, washing step and on standing and incomplete coupling of the coupling compound with diazonium salt due to steric hindrance, are the main problems of diazo coupling route [21]. Elimination reactions have been used

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also to immobilize imino diacetic acid moiety to PUF [22]. Another trial has been done to anchor the ligand molecules via condensation of the terminal amino groups in PUF to the formyl groups in the ligand compound. Lemos et al. [23] have applied pyrocatechol functionalized polyurethane foam in an on-line preconcentration system for determination of cobalt, copper and nickel in food samples. The sorbent was prepared by covalent coupling of 2,3-dihydroxybenzaldehyde with the polyurethane foam through –N=C– group.

Alizarin complexone (ALC) or alizarin-3-methyliminodiacetic acid is known as selective spectrophotometric reagent for determination of fluoride [24] via formation of blue colored complex. Therefore this compound is also called alizarin blue fluorine. However, its complex with copper is well investigated [25]. Mrzljak et al. [26] have reported selective spectrophotometric method for determination of Zn(II) at low pH 4.3 by alizarin complexone to remove interference from Mn(II) and Mg(II). The ALC molecule provides a four coordinate chelation environment with two acetic acid groups, the 2-hydroxyl group and the nitrogen atom [27], and has been used to chelate many metal ions for chemical analysis in aqueous solution [28].

In this paper, ALC–PUF was synthesized by a simple and fast reaction between the terminal amine groups in PUF and ALC through a Schiff base (–C=N–) bond formation. It deserves mentioning that the immobilization of the ALC compound on the PUF was accomplished in a single step reaction. Parameters that can influence the adsorption and elution efficiency of the metal ions were investigated in batch and column modes. Validation of the proposed method was investigated by analyzing two standard reference materials. Finally, the possible application of the new methodology for trace Cu, Zn and Cd determination in tap water and human urine samples was evaluated.

2. Experimental

2.1. Apparatus and reagents

Flame atomic absorption spectrometer model AA-6200 (Shimadzu, Japan) equipped with single element hollow cathode lamps and air-acetylene burner was used for the determination of the metals. Air-acetylene flame (fuel $1.8 \, L \, min^{-1}$, oxidant $8 \, L \, min^{-1}$) and 0.7 mm slit width were used. The wavelengths and lamp current selected for the determination were as follows: Cu(II) 324.8 nm and 6 mA; Zn(II) 213.40 nm and 8 mA; and Cd(II): 228.56 nm and 8 mA. ^{1}H nuclear magnetic resonance spectra were recorded on a Varian mercury 300 model ^{1}H NMR spectrometer (Hansen Way, USA) using tetramethylsilane (TMS) as internal standard and deutrated dimethylsulfoxide (DMSO-d$_6$) as solvent and transferred into sample tube. The chemical shift was reported in δ units. Infrared spectra ($4000–700 \, cm^{-1}$) were recorded on Mattson Satellite FTIR spectrometer (Madison, USA) model 2000 using KBr technique at 25 °C. A Metrohm (Herisau, Switzerland) pH meter model 780 was used for the pH adjustments. A mechanical shaker having an oscillating speed and time control facility was used for batch equilibration experiments. Millipore water was supplied from Elix UV water purification system (Billerica, USA). Deionized water was used for washing purposes. The glasswares were cleaned by keeping it overnight in nitric acid solution. Afterwards, it was rinsed thoroughly with deionized water and dried in a dust-free environment. Standard solutions of copper, zinc and cadmium ($1000 \, \mu g \, mL^{-1}$ each) were prepared by the appropriate dilution from $1000 \, mg \, mL^{-1}$ atomic absorption standards (Merck, Germany). Working solutions were prepared immediately before use by diluting the standard solutions with millpore water to the required concentration. Other chemicals were of analytical grade. ALC and Sodium nitrite were purchased from Fluka

chemicals (Buchs SG, Switzerland). Nitric acid (Merck, Germany), hydrochloric acid (Aldrich, USA) and dioxane (Fluka) were used without any further purification. Buffer solutions of pH 4–6, and 7–9 were prepared by mixing appropriate ratios of $0.5 \, mol \, L^{-1}$ acetic acid and sodium acetate or $0.5 \, mol \, L^{-1}$ ammonia and NH_4Cl solutions, respectively. Open-cell polyether-type PUF having density $55 \, kg \, m^{-3}$ was supplied from the ContiTech Foampolster GmbH Company for foam production (Löhne, Germany).

2.2. Synthesis of ALC–PUF

An untreated PUF sheet was solidified in by putting it in a liquid nitrogen reservoir then it was cut into a uniform plugs by a metal slicer. The dimension of each plug was 1 cm length and 3 mm diameter. One gram of the dried plugs was soaked in $50 \, mL \, 5 \, mol \, L^{-1}$ hydrochloric solutions, stirred for 2 h and subsequently washed with water till free from acid. Acid treatment permits the liberation of additional amine groups in PUF by the hydrolysis of the terminal isocyanate groups. Anchoring of ALC to PUF was carried out according to the method reported by Lemos et al. [23]. The PUF plugs were suspended in 100 mL dioxane and stirred at room temperature for 12 h to allow complete swelling of the polymer. Then, the plugs were separated from dioxane and mixed with 0.2 g ALC dissolved in 20 mL dioxane and the mixture was reacted at 90 °C for 72 h with continuous stirring. Afterwards, the canary yellow solid plugs from ALC–PUF were filtered, washed several times with dioxane, ethanol and finally with water then dried in air.

2.3. Recommended procedures

2.3.1. Batch procedure

A sample solution containing 20 μg metal ion in a volume of 20 mL was taken and its pH was adjusted to optimum pH for maximum extraction. ALC–PUF polymer (100 mg) was added to the above solution and shaken for sorption of metal ion at 500 rpm speed and room temperature. The foam containing the adsorbed metal ion was filtered. The extracted amount from the metal ion was desorbed and recovered elements were determined by flame atomic absorption spectrometry (FAAS). The influence of extraction time on sorption capacity was investigated at various shaking periods (2, 5, 10, 15, 20 and 30 min) at the selected pH of maximum extraction. Also, the maximum capacity of ALC–PUF for was determined under "static" batch conditions. A 20 mL solution containing $100 \, \mu g \, mL^{-1}$ each element was shaken with 100 mg ALC–PUF for 1.0 h after adjusting the sample to optimized pH.

2.3.2. Column procedure

The column method was used to investigate an optimum condition for the sorption and desorption of the metals ions. The influence of sample flow rate, concentration of stripping solution, eluent volume and preconcentration study were evaluated in triplicate. The minicolumn was fabricated from polyethylene tube 50 mm length and 3.0 mm internal diameter. A schematic diagram for the column apparatus is shown in Fig. 1. An accurately weighted 600 mg from ALC–PUF plugs were packed in the tube using vacuum suction for one hour to compress the foam and minimize channels to ensure homogenous packing. Then, the minicolumn was connected to peristaltic pump with 1.52 mm i.d. Tygon tubes and millipore water was pumped through it at $3 \, mL \, min^{-1}$ for 1 h in order to replace air in both of the foam cells and channels (if any) in addition to the salvation of the chelating groups. After that the minicolumn was treated with $1.0 \, mol \, L^{-1}$ nitric acid solution and washed by millipore water until the effluent is free from any acid. Lastly, the metal ion solution containing Cu(II), Zn(II), and Cd(II) in the concentration range from 0.008 to $0.050 \, \mu g \, mL^{-1}$ was adjusted to pH 8.5 and passed through the column at a controlled flow rate
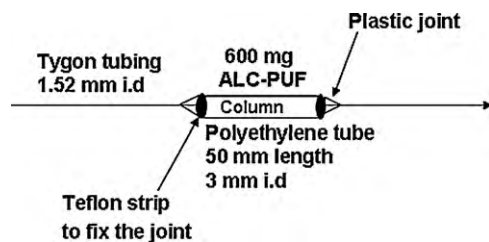
Fig. 1. A schematic diagram for the column apparatus.

of 1.5 mL min^{-1}. Finally, the minicolumn was washed with little amount of millipore water to remove unbounded metal ions. The sorbed metal ions were eluted and the recovered amounts of the metal ions in the eluate were determined by FAAS.

2.4. Sample preparation

2.4.1. Reference materials

Two certified reference materials, NIST-SRM 1577b Bovine liver and SRM 1643d river water were analyzed. Decomposition of bovine liver reference material was carried out according to the method [29]: Accurately weighed 0.400 g from the material was treated with 4.0 mL from 50% (v/v) nitric acid (doubly distilled in a quartz sub-boiling system) and kept overnight in Teflon vessel. Afterwards, the vessel was closed and put into a pressurized digestion system. After heating the mixture in a stove at 170 °C for 16 h and cooling at room temperature, the solution was adjusted to pH 6.0 with a 10% (w/v) sodium hydroxide solution and Tris buffer then the final volume was made up to 25 mL by millipore water. River water reference sample was obtained as a water matrix in 0.5 mol L^{-1} nitric acid. Therefore, it was neutralized to pH 2 with NH$_4$OH and the volume was made up to 100 mL with Millipore water. This solution was adjusted to pH 8.5 and used for preconcentration step given in Section 2.3.2. Analysis of certified reference samples was carried out four replicates.

2.4.2. Tap water

For application of the method to real samples, tap water was collected from our research laboratory at Fayoum University. A 200 mL sample was placed in clean polyethylene beaker. Then, it was filtered through 0.45 μm cellulose nitrate membrane filters to remove suspended fine particles and acidified to pH 2 by nitric acid. Afterwards, the sample was spiked with 5.0 μg from each metal ion and the pH was adjusted to pH 8.5 by 1 mol L^{-1} NaOH. Finally, the preconcentration procedure was applied and the concentration of the elements in the eluate solution was determined by FAAS.

2.4.3. Urine sample

Urine is a matrix of variable composition representing excretory end products of endocrine and metabolic processes. As a result, urine contains a wide variety of organic and inorganic substances. It is usually clear to pale yellow when voided, but major changes soon occur in specimens kept at room temperature and even at 4 °C, because of bacterial action. Microbial degradation of urine may result in either increase or decrease in pH. Both alterations could promote separation of solid phase [30]. To analyze urine, 50 mL human urine sample was taken directly from healthy people and put into an acid-washed polyethylene bottles. Then, 0.5 mL of concentrated nitric acid was added to acidify the sample. When analysis was not performed immediately, the urine samples were kept in a fridge at temperature 4 °C. To each 50 mL sample, 2.5 μg from each metal ion was added and the samples were analyzed before and after addition of the metal ion.
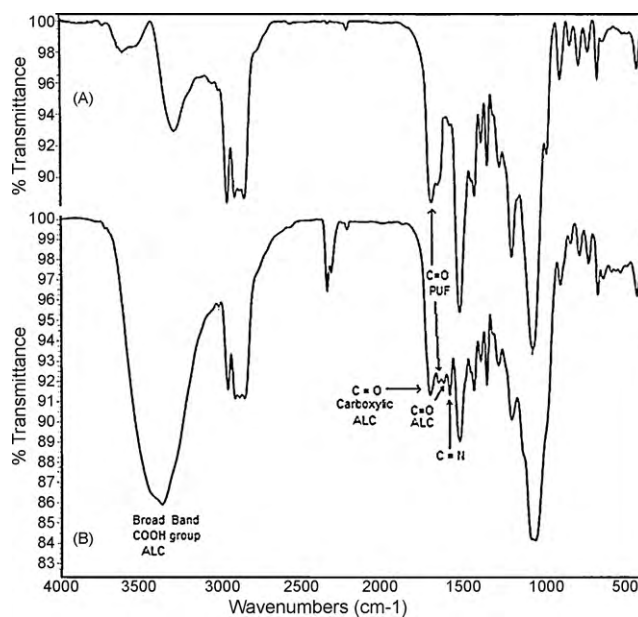

Fig. 2. Infrared spectra of untreated PUF (A) and ALC–PUF (B).

3. Results and discussion

3.1. Characterization of ALC–PUF

The IR spectra of the untreated PUF and ALC–PUF materials were compared as presented in Fig. 2. Both kinds of foams were cleaned by washing several times in ethanol then by millipore water and finally dried at 80 °C. Lastly, each sample was powdered by grinding it in a clean porcelain mortar then it was mixed with KBr and taken for IR test. Untreated PUF showed a broadband at 3600–3000 cm^{-1} corresponding to NH$_2$, N–H and O–H stretching frequencies and a spectral band at 1707 cm^{-1} corresponding to the C=O stretching frequency. However, the IR spectrum of ALC–PUF revealed a more broadband than untreated PUF corresponding to the COOH, N–H and OH stretching frequencies at 3581–3045 cm^{-1}. In addition, two new absorption bands have appeared at 1641 and 1720 cm^{-1} assigned for the hydrogen bonded C=O frequency at position **9** in the ALC moiety and C=O in carboxylic group, respectively. These results are in good agreement to the previously observed values for ALC [31]. In particular, it must be pointed out that the disappearance of spectral band characteristic for the non-hydrogen bonded C=O group at position **10** in the ALC part at 1667 cm^{-1} [31] indicating its involvement in the condensation reaction with the NH$_2$ group in PUF. Moreover, the appearance of new band at 1597 cm^{-1} for –N=C– stretching provides an additional evidence. A schematic diagram for the synthesis reactions of ALC–PUF is shown in Fig. 3.

^{1}H NMR spectra for the ALC–PUF were compared before and after addition of deutrated water (D$_2$O) to the foam dissolved in DMSO-d$_6$ as shown in Fig. 4. Four characteristic peaks were observed at 2.55, 4.47, 9.42 and 10.54 ppm standing for the chemical shifts of H in aliphatic –OH (labelled b), phenolic –OH (labelled f), –NH (labelled g) and –COOH (labelled h), respectively as shown in spectrum (A). However, by addition of D$_2$O to the dissolved ALC–PUF, these four peaks have been disappeared (spectrum B). Only one type of NH protons exists based on the integrated area under this peak (spectrum A). The results show that the integration of the peak for the carboxylic protons equivalent to two H. Hence, two carboxylic groups exist and none of them participating in the reaction to the NH$_2$ group in PUF. In the spectra, two multiples in the region 7.50–7.66 and 7.99–8.04 ppm were appeared which imply the H of target compound is belong to eight aryl protons (Ar–H)
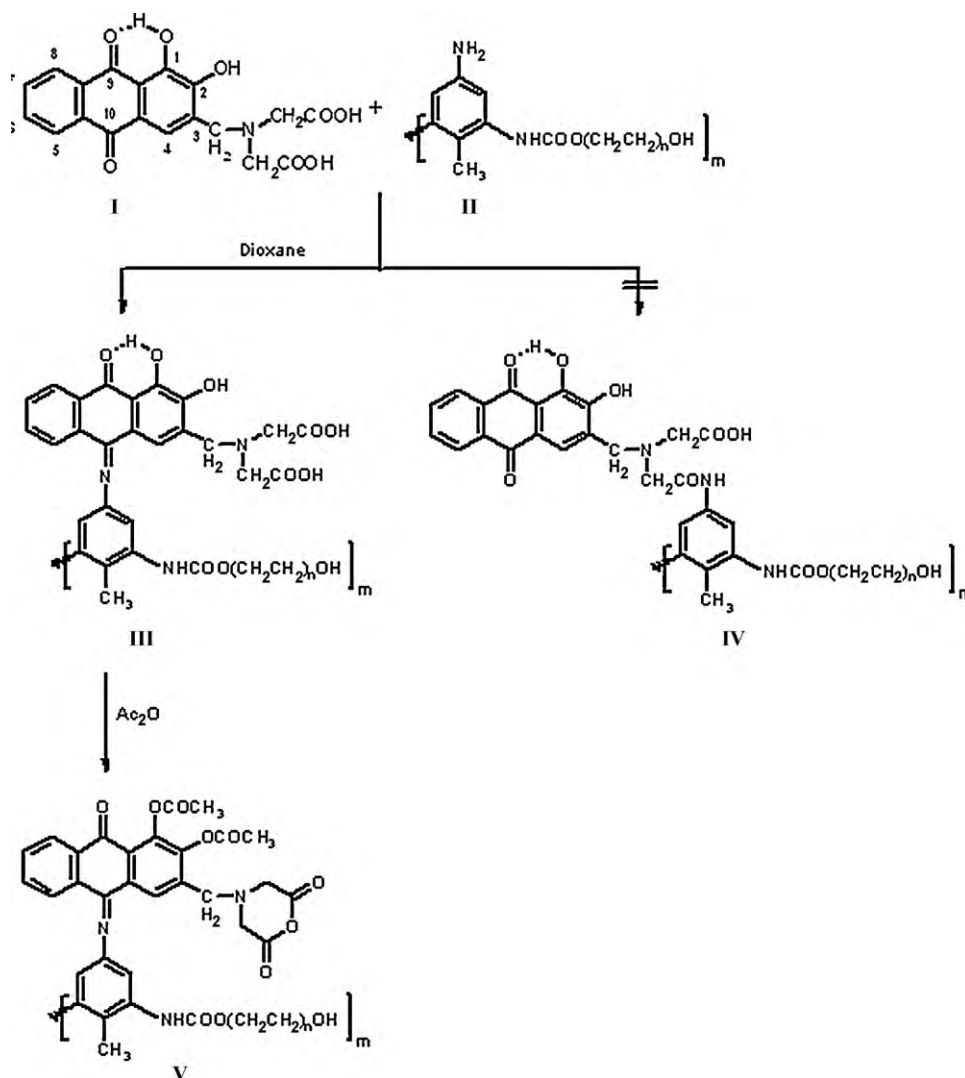
Fig. 3. Chemical structure of ALC (I), PUF (II), proposed ALC–PUF (III), unexpected amide derivative (IV) and anhydride derivative (V).
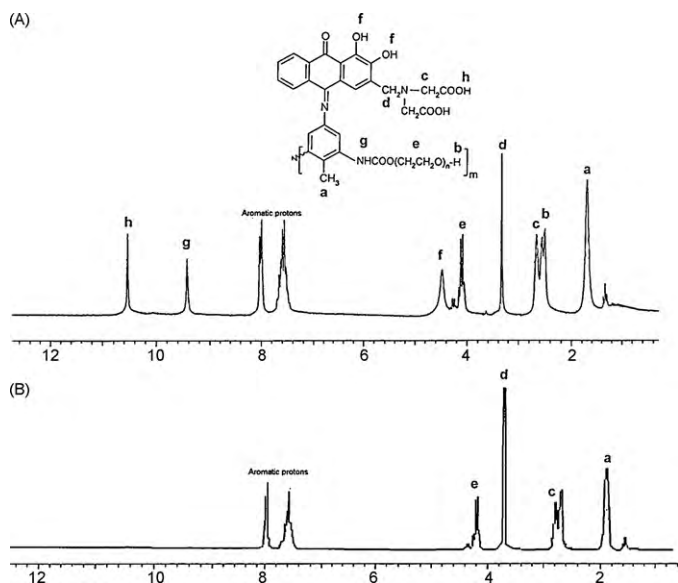

Fig. 4. ^{1}H NMR spectrum of ALC–PUF dissolved in deutrated DMSO (A) and after addition of D_2O (B).

at $\delta \approx 7.30$. The shift from ideal value is due to the effect of the electron-withdrawing and the electron-donating groups present in ALC.

Other peaks at 2.65, 3.33 and 4.05–4.15 ppm are attributed to ($\underline{CH_2}$–CO_2H), ($\underline{CH_2}$–N) and ($\underline{CH_2CH_2}$), respectively. Therefore, the spectra indicated that the ALC–PUF has nine kinds of H. Based on these data; we could conclude that the spectra are corresponding to the proposed structure **III**. A Further supporting chemical evidence for the formation of the Schiff base **III**, not the amide **IV**, was obtained by mixing the dried ALC–PUF (0.3 g) with acetic anhydride (20 mL) in a round-bottom flask fitted with a condenser. The vessel was heated in an oil path at 90 °C. The reaction was allowed to proceed at 90 °C and the product was followed by IR analysis. Typically, after 2 h heating, the absorption bands corresponding to OH and COOH groups have been disappeared and the absorption bands due to the stretching vibration of the carbonyl groups in the anhydride and ester groups have appeared at 1790 and 1728 cm^{-1}, respectively. Also, a new absorption band has appeared at 1660 cm^{-1} which was assigned for the free carbonyl group at position **9** in the ALC part. This indicates the formation of the anhydride **V**, a compound which cannot be obtained from the amide **IV**. Lastly, the spectral data and chemical evidence support the hypothesis that structure **III** was proposed as the reaction product and is presumed to be formed via nucleophilic attack of the nitrogen lone pair of the

amino group in PUF to the non-hydrogen bonded carbonyl group at position **10** in ALC followed by elimination of water molecule to afford the final isolable Schiff base **III** and the formation of the amide **IV** is excluded [32].

3.2. Chemical stability of ALC–PUF

The chemical stability of ALC–PUF was determined using acidic and basic solutions (1, 3 and 6 mol L^{-1} HCl or NaOH). The foam was stirred in these solutions for 24 h, filtered off, washed several times with millipore water and finally dried in air. After this, the change in the sorption capacity was calculated by batch experiment before and after the chemical treatment. It was found that the foam can withstand acids or bases and no large decrease in capacity was observed. The maximum decrease in capacity was less than 1% when the sorbent was treated with 6 mol L^{-1} HCl. Other solutions showed undetectable influence on the capacity.

3.3. Batch experiments

3.3.1. Effect of sample pH

Hydrogen ion concentration plays an important role in the process of solid-phase extraction since it exchanges with metal ions in the chelating groups in the sorbent. The effect of sample pH on the sorption behavior of the tested elements was studied in the pH range 4–9 using 20 mL sample solution containing individual element at 1.0 μg mL^{-1} concentration level. The samples were processed according to the recommended batch experiment. The percentage sorption of metal ion by the foam was calculated from the relation:

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

where C_o and C are the initial, and remaining concentrations (μg L^{-1}) of the metal ion, respectively. As can be seen in Fig. 5, extraction of metal ions by ALC–PUF occurred at pH range 8–9 for Cu, Zn and Cd. Hence, ammonia buffer pH 8.5 was selected for subsequent experiments. Although, better extraction might be achieved at pH 9 but a lower value of pH 8.5 was recommended to avoid the possibility for metal precipitation. In Fig. 5, by increasing the pH in the range 4–7, the sorption of metal ions increases regularly with all elements. However, Cu was found to be more extracted than Zn or Cd. The obtained results confirm approximately similar sorption mechanism for all metal ions. Since both of carboxylic and hydroxyl groups present in ALC molecule, it was expected that metal ions would be completely extracted by the sorbent at pH ≥ 4 (ionization of COOH groups). However, low extraction efficiency was obtained around this pH value. This revealed the importance
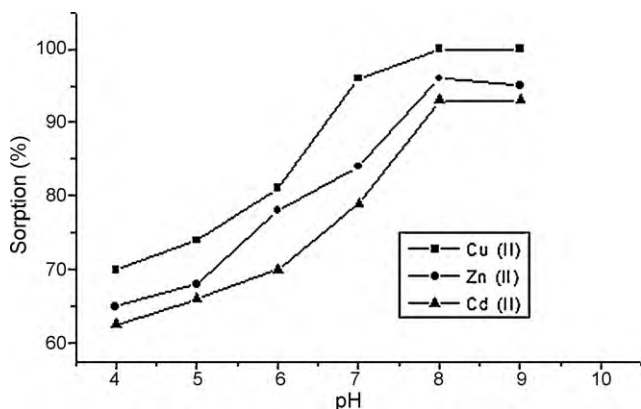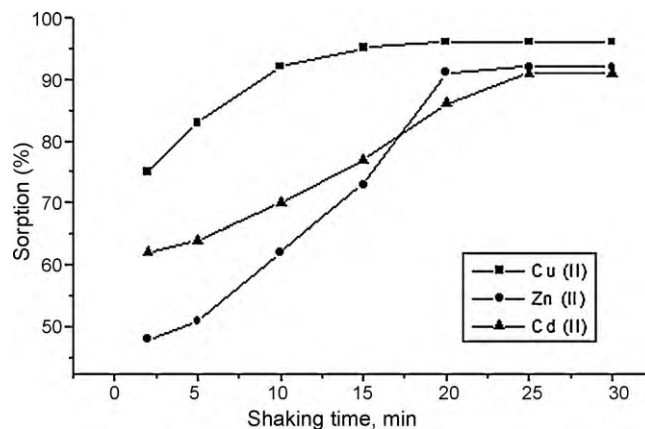

Fig. 6. Effect of shaking time on the sorption of Cu, Zn and Cd (20 mL, 1.0 μg mL^{-1} each) by 100 mg ALC–PUF in batch mode.

of participation of hydroxyl groups (ionize at pH ≥ 8) in extraction process. Therefore, it is concluded that the metal ion is bounded by hydroxyl groups in addition to the carboxylic one. Although the elements might be precipitated at higher pHs, there is no major change in the sorption capacity was observed which confirm more complexation stability between the sorbed metal ions and the ligand functional groups in the sorbent.

3.3.2. Sorption kinetics

The influence of shaking time on the percentage of sorption is recognized of significant importance to determine the possible discrimination order of ALC–PUF behavior towards Cu(II), Zn(II) and Cd(II). Variation of sorption against shaking time has showed dramatic profile. It is evident from the results represented in Fig. 6 that the equilibrium between copper ions and the phase is faster than zinc and cadmium ions. An equilibration time of about 15 min was sufficient to achieve 95% sorption of Cu but about only 66 and 71% from Zn and Cd, respectively. Shaking for 25 min was necessary to achieve 95, 88, and 86% sorption for Cu(II), Zn(II) and Cd(II), respectively. Thus, shaking for 15 min is quite enough to quantitatively extract Cu ions. However, Zn and Cd needed the double of this period (30 min) to asses efficient sorption. The slower rate of sorption Zn and Cd ions by ALC–PUF reflects the low stability of Zn or Cd complexes compared to highly stable Cu-complex. This low stability in case of Zn and Cd could be attributed to the nearly filled d-orbital in Zn ion and the too large size of Cd ions. The sorption of metal ions by ALC–PUF was found to be rapid and reached equilibrium within about 25 min shaking time. The Lagergren plots are depicted in Fig. 7 which confirms first-order kinetics of sorption. The sorption rate constants were found to be 0.237, 0.066 and 0.056 min^{-1} and the correlation coefficient are 0.9957, 0.9810 and 0.9800 for Cu(II), Zn(II) and Cd(II), respectively. Noteworthy, the half time $t_{1/2}$ for sorption, defined as the time required for attaining 50% of the maximum sorption value, was estimated from the obtained rate constant and it was found to be 2.9, 10.5 and 12.3 min for Cu(II), Zn(II) and Cd(II), respectively. In all, 30 min shaking was fixed in carrying out batch experiments because the three elements are present together in the sample.

The sorbed metal ion concentration q_t (μmol g^{-1}) at time t was plotted against the square root of time to test the applicability of the Weber–Morris equation [33].

$$q_t = R_d(t)^{1/2}$$

where R_d is the rate constant of intraparticle diffusion with dimension of μmol g^{-1} min$^{-1/2}$. The obtained results are shown in Fig. 8. Obviously, the rate of diffusion is fast in the early stages of sorption

Fig. 5. Effect of sample pH on the sorption of Cu, Zn and Cd (20 mL, 1.0 μg mL^{-1} each) and 100 mg ALC–PUF in batch mode.
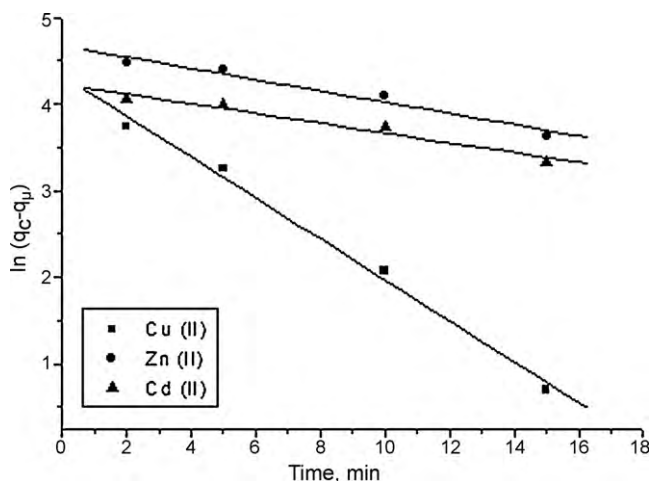
Fig. 7. Lagergren plots of the kinetics of Cu(II), Zn(II) and Cd(II) sorption at pH 8.5 at 25 °C onto ALC–PUF sorbent.
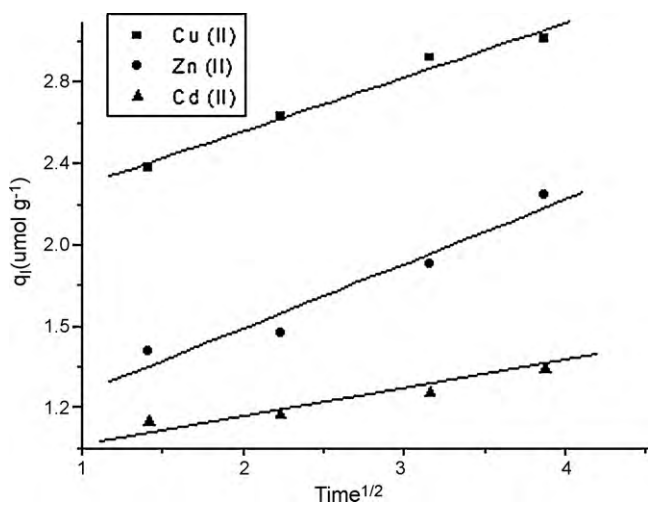

Fig. 8. Intraparticle diffusion profile depicted as variation of the sorbed amount of metal ion ($1.0\,\mu g\,mL^{-1}$) from 20 mL sample at pH 8.5 and 100 mg ALC- PUF sorbent as function of square root of shaking time.

and a linear relationship was verified where the diffusion constant was found to be 0.26607, 0.31732 and 0.13661 $(\mu mol\,g^{-1})\,min^{-1/2}$. By extension of shaking period, the relation becomes no longer linear and deviation has been observed.

3.3.3. Exchange capacity

In order to determine the mass of sorbent necessary to concentrate analyte ions from a given sample, the adsorptive capacity have to be estimated. For this purpose, 20 mL from each metal ions solution at 100 $\mu g\,mL^{-1}$ was shaken with 100 mg ALC–PUF for 30 min after adjusting of the sample to pH 8.5. This experiment was repeated four times for each analyte ions separately. The obtained results are compromised in Table 1. It is evident from the achieved results the developed sorbent exhibits greater capacity towards copper ions than either zinc or cadmium. The order of capacity is

Table 1
Adsorption capacity of ALC–PUF sorbent.

Element	Capacity[a] ($\mu g\,g^{-1}$ (mean ± S.D.))	Capacity ($\mu mol\,g^{-1}$)
Cu(II)	2079.8 ± 11	33.0
Zn(II)	837.0 ± 3.0	12.9
Cd(II)	564.6 ± 1.5	5.0

[a] Mean value ± S.D. based on four replicates ($n = 4$) determinations.

Cu > Zn > Cd. The capacity ($\mu mol\,g^{-1}$) for Cu is more than the double for Zn which in turn doubly exceeds that for Cd. The hard donor oxygen (carbonyl and hydroxyl groups) and nitrogen atoms (imine groups) have greater tendency for coordination to copper ions than zinc or the large ionic radius cadmium ions. Finally, the total sorption capacity in case of the three metal ions is quite sufficient to quantitatively collect these elements from natural samples since they usually exist at low concentration levels.

3.3.4. Selectivity

To assess the validity of the proposed sorbent for analytical applications as separation/preconcentration procedure, the adverse effect of some contaminant species which might has significant effect on the efficiency of sorption and consequently interfere with the determination of trace amounts from the investigated metal ions and/or co-exist with these ions in various natural samples was examined under the optimized conditions. Generally, real samples contain, in addition to elements under consideration, various kinds of species that may compete to the available adsorption sites in the sorbent. In addition, the atomic absorption spectrometric determination of heavy elements at low concentration levels in presence of foreign ions is a significant problem [34]. Therefore, it is necessary to keep in mind this effect when switching to analyze real samples. A selected group of foreign ions were tested for their potential influence on the sorption of the investigated elements. Synthetic mixtures of solution containing metal ion ($1.0\,\mu g\,mL^{-1}$) and excess amounts of diverse ions were preconcentrated and analyzed. Then, their recovery was compared with the recovery of metal ion solution in the absence of contaminant species. The results are compromised in Table 2. The maximum concentration of foreign ions that produced an error in sorption (%) not exceeding 5% is recognized as the tolerable limit when combining both of the preconcentration and the determination steps. No effect on the recovery of the investigated metal ions was found from alkali metals Na$^+$ (10,000 mg L^{-1}) and K$^+$(5000 mg L^{-1}) and alkaline earth elements Ca^{2+} (2000 mg L^{-1}) and Mg^{2+} (1500 mg L^{-1}). The anions Cl$^-$, SO$_4^{2-}$ and PO$_4^{3-}$ have showed little interference with tolerance limit ≥ 150 mg L^{-1}. The strongest interference effect was noticed in the presence of ethylenediamine tetraacetic acid (EDTA). Its tolerable limit was found to be 10, 5 and 5 mg L^{-1} for Cu(II), Zn(II) and Cd(II), respectively. Finally, the developed sorbent is quite suitable to analyze real samples since it remain selective and capable to extract these metal ions even in the presence of the interfering ions up to several thousands folds.

3.4. Dynamic experiments

3.4.1. Sample flow rate

The sample flow rate is critical parameter since the contact time should be enough for complete extraction of the element but

Table 2
Influence of the diverse ions on the recovery of metal ions ($1\,\mu g\,mL^{-1}$, $N = 3$).

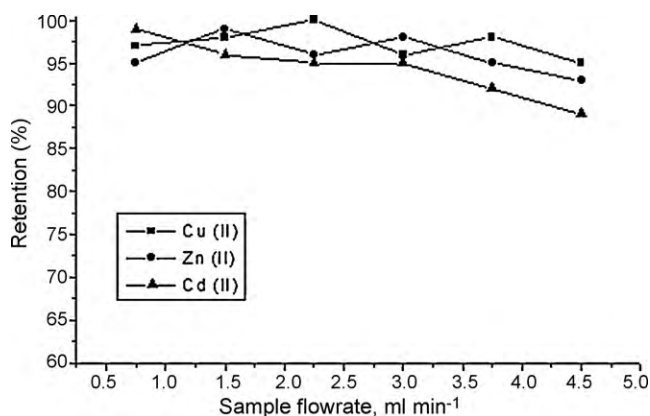| Interfering ion	Maxiumum tolerance limit (mg L^{-1})		
	Cu	Zn	Cd
Na+	10,000	10,000	5000
K$^+$	5000	3000	2000
NH$_4^+$	1500	1000	1000
Cl$^-$	8000	10,000	5000
Ca^{2+}	2000	500	200
Mg^{2+}	1500	200	200
EDTA	10	5	5
Citrate	100	100	200
Mn^{2+}	100	50	100
Fe^{3+}	50	150	100
SO$_4^{2-}$	500	500	300
PO$_4^{3-}$	150	100	100

Fig. 9. Influence of sample flow rate on the retention of Cu, Zn, and Cd (1 μg mL^{-1}) at pH 8 and desorption with 20 mL 0.1 mol L^{-1} nitric acid.

should be also short enough for effective preconcentration step. The extraction of 20 mL metal ion solution at concentration 1.0 μg mL^{-1} and pH 8.5 was investigated at flow rates within the range from 0.8 to 4.0 mL min^{-1}. A peristaltic pump was utilized to control the flow rate. The obtained results are illustrated in Fig. 9. The recovery is 95 to 98% at flow rates varying from 0.8 to 3.0 mL min^{-1}. Increasing sample flow rate than 3.0 mL min^{-1} has led to gradual decrease in the retention efficiency. This decrease could be explained by the insufficient contact time between the metal ions in the mobile phase and the chelating groups in the foam stationary phase. Accordingly, the flow rate 2 mL min^{-1} was recommended in performing the dynamic experiments.

3.4.2. Choice of eluent

In order to choose the proper eluent for desorbing the metal ion from the sorbent surface, a series of selected eluent solution such as hydrochloric acid, nitric acid, acetic acid, thiourea, and sodium thiosulfate at concentration 0.1 mol L^{-1} each were examined individually. Aliquots of 20 mL of 1.0 μg mL^{-1} metal ion solution were passed through the ALC–PUF minicolumn at flow rate 2 mL min^{-1}. The amount of metal ion back-extracted into eluate by 5 mL individual eluent was measured using FAAS and the recovery was calculated for each sample. The results are given in Fig. 10. Best recovery was obtained when nitric acid was used as eluent. Furthermore, higher concentrations of hydrochloric and acetic acids (up to 0.5 mol L^{-1}) solutions were tested. Quantitative recovery was achieved by hydrochloric acid ≥0.4 mol L^{-1} while no improvement was observed at higher concentrations from acetic acid. Accordingly, hydrochloric acid was excluded as eluent to avoid the use of high concentration acids. Therefore, the low concentration (0.1 mol L^{-1}) nitric acid was recommended as eluent because it elongates the lifetime of the mincolumn.

3.4.3. Eluent concentration and volume

Acids are recommended in desorption of metal ions from solid materials because they rapidly decrease the pH of the medium and assist the H$^+$ exchange to replace the bounded metal
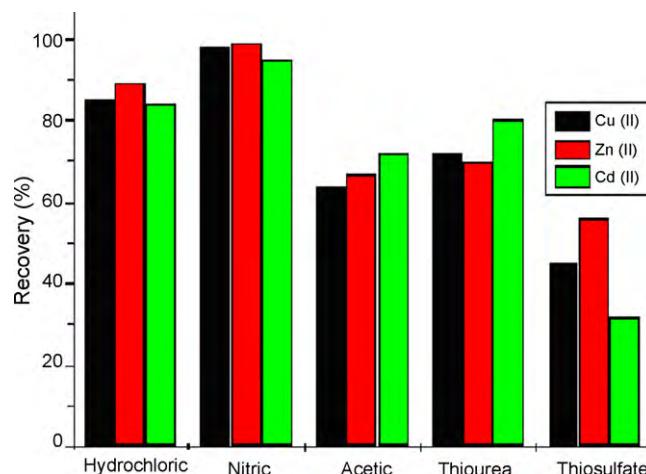

Fig. 10. Influence of the eluent nature of the rceovery of Cu, Zn and Cd using 5 mL 0.1 mol L^{-1} nitric acid, hydrochloric acid, acetic acid, thiourea or thiosulfate for 20 mL of 1.0 μg mL^{-1} metal ion solution passed at flow rate 2 mL min^{-1} and pH 8.5.

Table 4
Recovery of copper, zinc and cadmium in tap water and human urine samples by the proposed procedure.

Analyte	Sample	Added (μg L^{-1})	Found^a (μg L^{-1})	R%
Cu	Tap water	0	6.5 ± 0.4	
		5.0	11.3 ± 0.7	96
	Human urine	0	0.33 ± 0.03	
		2.5	2.68 ± 0.13	94
Zn	Tap water	0	8.6 ± 0.3	
		5.0	13.7 ± 1.2	101
	Human urine	0	0.82 ± 0.06	
		2.5	3.4 ± 0.2	104
Cd	Tap water	0	4.3 ± 0.4	
		5.0	8.9 ± 0.3	92
	Human urine	0	0.03 ± 0.01	
		2.5	2.51 ± 0.12	99

^{a} Mean value ± S.D. based on four replicates (n = 4) determinations.

ions in the solid phase. Nitric acid at varying concentrations (0.05–1.00 mol L^{-1}) was tested as eluting agent in desorption of 20 μg retained element in the ALC–PUF minicolumn. The results indicated the superiority of nitric acid in obtaining higher recovery rates with lower concentration levels of the acid. The data revealed that the recovered amount of elements increases by increasing nitric acid concentration and reached maximum recovery at 0.1 mol L^{-1}. Higher acid concentrations than 0.1 mol L^{-1} have showed nearly constant recovery as leveling off which is followed by a decrease when the concentration >0.5 mol L^{-1}. The decline in recovery might be due to the increased ionic strength in the medium by nitrate ions furnished by the eluent. These nitrate ions may undergo synergistic effect thus promote stronger sorption of metal ions by the foam. Moreover, high concentrations from nitric acid should be avoided since it can decompose the polyurethane foam material by its oxidative action. In addition, the influence of

Table 3
Analytical results of copper, zinc and cadmium in certified reference materials.

Metal ion	NIST – SRM 1577b bovine liver			SRM 1463d river water		
	Certified (μg g^{-1})^a	Found^b	R%	Certified (μg L^{-1})	Found^b	R%
Cu	160 ± 8	152 ± 5.0	95	20.5 ± 3.8	19.3 ± 0.8	94
Zn	127 ± 16	130 ± 7.5	102	72.48 ± 0.65	68.4 ± 3.7	94
Cd	0.50 ± 0.03	0.53 ± 0.06	106	6.47 ± 0.37	6.2 ± 0.7	96

^{a} Certified value and uncertainty as given in the certificate.
^{b} Mean value ± S.D. based on four replicates (n = 4) determinations.

Table 5
Comparison of sorption capacity and preconcentration factor.

Matrix	Capacity ($\mu mol\,g^{-1}$)			CF[a]		
	Cu	Zn	Cd	Cu	Zn	Cd
Support: Polyurethane foam						
Alizarine complexone [this work]	33.0	12.9	5.0	100	100	100
4-Hydroxytoluene [18]	–	3.9	2.8	–	100	100
2-Aminophenol [19]	–	–	5.9	–	–	125
Acetylacetone [19]	–	–	6.9	–	–	288
Pyrochatechol [23]	29.6	–	–	–	–	–
Support: Silica gel						
Salicylaldoxime [35]	50	40	60	40	40	40
Support: Amberlite XAD-2						
Chromotropic acid [36]	134.0	147.5	83.4	100	200	100
Support: Polyvinyl chloride						
PBI[b] [37]	42.8	41.5	–	90	90	–

[a] Preconcentration factor.
[b] PBI: 2-phenyl-1H-benzo[d] imidazole.

eluent volume on the recovery of the elements was also investigated by using fixed HNO_3 concentration at 0.1 mol L^{-1}. It was found that 2.0 mL from the acid is sufficient to achieve quantitative recoveries with 95% confidence limit. Hence, the volume of 2.0 mL eluent was used in the subsequent experiments.

3.4.4. Column reuse

Reusability is one of the most important factors necessary to assess the effectiveness of certain sorbent. Therefore, the mini-column was tested for reuse after being regenerated with 10 mL 0.5 mol L^{-1} HNO_3 and 50 mL millipore water, respectively. It was found to be stable up to at least ten consecutive cycles of adsorption/desorption without obviously decrease in the recovery and sorption capacity for the studied ions.

3.4.5. Preconcentration and limit of detection

For investigating the capability of the sorbent for enriching low concentrations of the elements from large sample volumes was explored. The maximum applicable sample volume must be determined. For this purpose sample solutions of different volumes of 50, 100, 150, 200, 250 and 300 mL containing 2.5 μg of each element were passed through columns under optimized conditions. The sorbed amounts from the elements were further eluted with 2.0 mL, 0.1 mol L^{-1}. The recovery was found to be quantitative with maximum sample volume up to 200 mL with the 95% recovery. A preconcentration factor (CF) of 100 (200/2) was achieved for each element and the detection limit was 0.013 μg mL^{-1}.

4. Accuracy of the method and application to real samples

The accuracy of presented procedure was tested by measuring the content of copper, zinc and cadmium ions in two certified reference materials NIST-SRM 1577b (Bovine Liver) and SRM 164d river water. Aqueous standard solutions were used for calibrations. The certified and observed analytical values were compromised in Table 3. The results for the percentage of recovery ($R\%$) were satisfactory for the certified samples (94–106%). This showed that the method could be applied to the determination of these elements in complex matrices such as natural and biological samples. At the end, the developed method was applied to the analysis of tap water and human urine by spiking or addition/recovery test. As can be seen in Table 4, the analyte ions were quantitatively recovered from the samples. The recovery percentage obtained for analysis of real samples varies from 92 to 104%. This is a comparable result with that obtained for the reference materials indicating the good analytical performance of the proposed procedure in the analysis of the tested samples.

5. Comparison to other sorbents

The sorption capacity of ALC–PUF is comparable to those for modified PUF sorbents but lower than silica gel and amberlite based sorbents. The preconcentration factor of the present polymer was compared with other matrices in Table 5. The preconcentration factors achieved with the ALC–PUF sorbent for the three elements are better or comparable to all the important chelating matrices.

6. Conclusions

Synthesis of a new functionalized polymeric material was obtained from the condensation reaction between PUF and ALC. From IR and ^{1}H NMR studies it could be concluded that the inclusion of ALC in the PUF structure was occurred via –C=N– linkage not by the amide formation. The new sorbent could be used for establishment of rapid, simple and economic alternative preconcentration/separation procedure for the determination of copper, zinc and cadmium in tap water and urine samples. The sorbent showed adequate capacity and relevant preconcentration factor. The high tolerance to interfering substances has presented advantage towards the sorbent. The recovery results for both of certified reference materials and real samples were comparable. Finally, the low acid concentration required for desorption of metal ions avoid any further dilution step for FAAS measurement and it elongates the lifetime of the column thus allow recycling of the polymer many times without affecting its sorption capacity.

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