See discussions, stats, and author profiles for this publication at: [https://www.researchgate.net/publication/273496210](https://www.researchgate.net/publication/273496210_Determination_of_aluminum_from_water_samples_and_dialysis_fluids_after_separationpreconcentration_on_Duolite_XAD-761_polymeric_resin?enrichId=rgreq-d830780d2a74c7516fcf6ebee47432ff-XXX&enrichSource=Y292ZXJQYWdlOzI3MzQ5NjIxMDtBUzo0NDY3NjU3OTYyMDQ1NDdAMTQ4MzUyODY3NDI0OQ%3D%3D&el=1_x_2&_esc=publicationCoverPdf)

[Determination of aluminum from water samples and dialysis fluids after](https://www.researchgate.net/publication/273496210_Determination_of_aluminum_from_water_samples_and_dialysis_fluids_after_separationpreconcentration_on_Duolite_XAD-761_polymeric_resin?enrichId=rgreq-d830780d2a74c7516fcf6ebee47432ff-XXX&enrichSource=Y292ZXJQYWdlOzI3MzQ5NjIxMDtBUzo0NDY3NjU3OTYyMDQ1NDdAMTQ4MzUyODY3NDI0OQ%3D%3D&el=1_x_3&_esc=publicationCoverPdf) separation/preconcentration on Duolite XAD-761 polymeric resin

Article in Desalination and Water Treatment · February 2015

Project

Some of the authors of this publication are also working on these related projects:

: Developing of A New Analytical Method Based Solid Phase Extraction for Separation/Enrichment of Indium in Some Food and Water Samples [View project](https://www.researchgate.net/project/Developing-of-A-New-Analytical-Method-Based-Solid-Phase-Extraction-for-Separation-Enrichment-of-Indium-in-Some-Food-and-Water-Samples?enrichId=rgreq-d830780d2a74c7516fcf6ebee47432ff-XXX&enrichSource=Y292ZXJQYWdlOzI3MzQ5NjIxMDtBUzo0NDY3NjU3OTYyMDQ1NDdAMTQ4MzUyODY3NDI0OQ%3D%3D&el=1_x_9&_esc=publicationCoverPdf)

Desalination and Water Treatment

ISSN: 1944-3994 (Print) 1944-3986 (Online) Journal homepage:<http://www.tandfonline.com/loi/tdwt20>

Determination of aluminum from water samples and dialysis fluids after separation/ preconcentration on Duolite XAD-761 polymeric resin

Harun Ciftci, Cigdem Er & Mustafa Ozkan

To cite this article: Harun Ciftci, Cigdem Er & Mustafa Ozkan (2016) Determination of aluminum from water samples and dialysis fluids after separation/preconcentration on Duolite XAD-761 polymeric resin, Desalination and Water Treatment, 57:15, 6916-6924, DOI: [10.1080/19443994.2015.1011704](http://www.tandfonline.com/action/showCitFormats?doi=10.1080/19443994.2015.1011704)

To link to this article: <http://dx.doi.org/10.1080/19443994.2015.1011704>

Published online: 11 Feb 2015.

[Submit your article to this journal](http://www.tandfonline.com/action/authorSubmission?journalCode=tdwt20&show=instructions) \mathbb{Z}

III Article views: 63

 \overrightarrow{Q} [View related articles](http://www.tandfonline.com/doi/mlt/10.1080/19443994.2015.1011704) \overrightarrow{C}

[View Crossmark data](http://crossmark.crossref.org/dialog/?doi=10.1080/19443994.2015.1011704&domain=pdf&date_stamp=2015-02-11) \mathbb{Z}

Full Terms & Conditions of access and use can be found at <http://www.tandfonline.com/action/journalInformation?journalCode=tdwt20>

Determination of aluminum from water samples and dialysis fluids after separation/preconcentration on Duolite XAD-761 polymeric resin

Harun Ciftci*, Cigdem Er, Mustafa Ozkan

Faculty of Science and Arts, Department of Chemistry, Ahi Evran University, Kirsehir, Turkey, Tel. +90 386 2804552; Fax: +90 386 280 4525; emails: harunciftci@yahoo.com (H. Ciftci), cigdemer86@gmail.com (C. Er), mustafaozkancan@gmail.com (M. Ozkan)

Received 15 April 2014; Accepted 15 January 2015

ABSTRACT

In the present study, a new solid-phase extraction method was developed for the separation and preconcentration of trace aluminum in various water samples. The 4-(2-pyridylazo) resorcinol was used as a chelating agent for adsorption of aluminum ions from aqueous solutions on Duolite XAD-761 polymeric resin. Various experimental parameters such as pH of sample solution, volume, and concentration of eluent, flow rate of sample solution, sample and solution volume, amount of ligand and adsorbent, matrix effects for preconcentration, and capacity of adsorbent were investigated. The developed procedure was successfully applied to dialysis fluids and some water samples.

Keywords: Separation; XAD-761; Aluminum; Dialysis fluids; Resorcinol

1. Introduction

Aluminum has a lot of advantages due to its specific characteristics, and its use in the industry is increasing day by day. For example, it is used in sectors such as medicine, food, and beverage as an ideal packaging material because of its homogeny and intransitive structure, malleability, longevity, and low economy.

Aluminum may assemble in the human body directly or indirectly, so it degenerates brain cells and causes Parkinson and Alzheimer diseases [\[1,2](#page-9-0)]. Serious toxic effect of aluminum was observed on patients with renal failure subjected to dialysis, such as anemia, encephalopathy, and dialysis dementia [\[3](#page-9-0)]. Besides, the removal of aluminum from organisms is difficult because it spreads widely and is attached to

protein abundantly in organisms. Recently, in spite of many suggestions for its removal from organism, it is announced that the most effective way is decreasing of the aluminum amount taken by organism. The dialysis fluids are prepared from dialysis concentrates that are mixed with pure water. If aluminum is present as a contaminant in these fluids, it is able to diffuse through the dialysis membranes and penetrate into the blood stream of the patient [[4](#page-9-0)]. The official pharmacopoeias [[5\]](#page-9-0) require an accurate control of the trace levels of aluminum in commercial dialysis solutions, which must be lower than 10 μ g L⁻¹ and World Health Organization (WHO) has suggested that the maximum amount of aluminum in drinking water should be 0.05 mg L^{-1} [\[6\]](#page-9-0).

It was confirmed that decrease in aluminum content under critical level has a preventive effect. Hence, a simple and sensitive method is of primary impor- *Corresponding author. tance for determination of aluminum in various

^{1944-3994/1944-3986} 2015 Balaban Desalination Publications. All rights reserved.

samples such as food, biological, water, and dialysis solutions. Direct determinations of metal ions at those levels in environmental samples by many spectroscopic techniques are limited not only due to insufficient sensitivity, but also in connection with matrix interference. Matrix separation and/or analyte preconcentration stages in analysis are usually required to overcome matrix interference or to improve the detectability in order to achieve accurate analytical results of trace elements [\[7](#page-9-0),[8](#page-9-0)]. Among various separation and preconcentration techniques, solid-phase extraction (SPE) is the most common technique for the removal and separation of metal ions from environmental samples. It has advantages such as high recovery, fast extraction, high enrichment factor, low cost, and low consumption of organic solvents [\[9\]](#page-9-0).

The basic principle of SPE for trace elemental ions is the transfer of analyte from the aqueous phase to the active site of the adsorbent. Thus, the type of adsorbent is very important for the extraction efficiencies of analytes. Due to the unique properties (e.g. large specific surface area, high adsorption capacity, and low temperature modification) amberlite resins, activated carbon, cellulose, modified silica gel, polymeric resin, and biomass are most commonly used as adsorbents for efficient preconcentration/separation of analytes in current research into SPE [[10,11\]](#page-9-0).

Polymeric resins have some advantages such as low cost, simple preparation, high porosity, the larger surface area, stability against acidic or basic media, and selectivity for some analytes [[12](#page-9-0)]. In order to increase the selectivity and adsorption capacity of the sorbent, sometimes ligands or chelating agents were used to obtain metal chelates before SPE procedure [\[7\]](#page-9-0).

In the present work, a new solid-phase extraction method was developed for separation, removing, and preconcentration of trace aluminum in water samples. Some experimental and analytical parameters were investigated and optimized. The 4-(2-pyridylazo) resorcinol (PAR) that contains a heterocyclic nitrogen group, azo group, and o-hydroxyl group, which provides various numbers of different potential binding sites for metal ion under investigation was used as ligand (Fig. 1). Duolite XAD-761 (one of the macroporous

Fig. 1. Molecular formula of 4-(2-pyridylazo) resorcinol.

organic ester acrylic polymers with a large surface area) was used as adsorbent. It is easily regenerated for multiple adsorption–desorption cycles with good reproducibility in the sorption characteristics [\[13\]](#page-9-0). The developed procedure was successfully applied to dialysis fluids and some water samples.

2. Experimental section

2.1. Apparatus

The analysis was performed by ContrAA 300 a high resolution-continuum source flame atomic absorption spectrometer (HR-CS FAAS) (GLE, Berlin, Germany) equipped with a 50 mm burner head and an injection module (SFS-6). All absorption lines of an element in the spectral range of 185–900 nm can be analytically evaluated using a Xe short-arc lamp as a continuum lamp source. The spectral background of the sample in the HR-CS FAAS is always corrected directly on the analysis line simultaneously and independently. All measurements were carried out under optimum conditions in three replicates using an injection module (SFS-6) enabling the computer controlled aspirations of blank solutions, analytical solutions, and samples. All pH measurements were made with an Orion Star (Thermo Fisher, USA) model pH meter. The operating conditions for Al by HR-CS FAAS are given in Table 1.

2.2. Reagents

All solutions were prepared using ultrapure water (specific resistance 18 M Ω cm) from a Milli-Q purification system (Millipore Corporation, Massachusetts, USA). Standard solutions of analytes were prepared from their 1,000 mg L^{-1} stock solutions (Merck). In the study buffer solutions (Merck) of sodium acetate– acetic acid (for pH 3–5.8), sodium monohydrogen phosphate–potassium dihydrogen phosphate (for pH 6–8), and ammonium chloride–ammonia (for pH 9) were used. Duolite XAD-761 which is an ester acrylic

Table 1 The operating conditions for atomic absorption spectrometer

polymer (Sigma–Aldrich) was used as polymer resin. The size of polymeric resin particles was between 20 and 60 mesh. The chelating agent PAR (inforn of monosodium salt hydrate) was purchased from Aldrich and a standard PAR solution of 0.02% (w/v) was prepared by dissolving 0.01 g of PAR in 50 mL of methanol.

All glassware was cleaned using ultrapure water, kept in nitric acid for 24 h, and washed again with ultrapure water.

2.3. Preparation of separation column

Glass column which was 10.0 cm in length and 0.8 cm in internal diameter was used in order to separation/preconcentration of metal ions. Separation column had a 250 mL reservoir on top of the column and a stopcock at the bottom of the column. Column system was prepared by placing a small portion of cleaned glass wool as a plug at one end of the column holding a certain amount $(0.4-0.6 \text{ g})$ of adsorbent. This system was cleaned with water, 2 mol L^{-1} HCl, and 2 mol L^{-1} $HNO₃$ solutions by following given order [[14–16\]](#page-9-0).

2.4. Preconcentration procedure

The proposed preconcentration procedure was tested with model solutions prior to the determination of trace aluminum in water samples. In order to prepare model solution 2.5 mL of 2.0 mg L⁻¹ Al³⁺ solutions were added to 1.0 mL of 0.02% (w/v) PAR solution and 4 mL of buffer solutions (sodium acetate–acetic acid, sodium monohydrogen phosphate–potassium dihydrogen phosphate, and ammonium chloride–ammonia) (to give the desired pH between 3 and 9) in a flask, and adjusted to a pH range of 3–9 with 0.1 mol L^{-1} of each HCl/NaOH. Then, final volume was completed to 50 mL by deionized water. The column was preconditioned by passing the aqueous solutions of working pH through column, and then, the model solution was passed through the column at a flow rate of 5 mL min^{-1} . Afterward, the column was rinsed with of deionised water of 10 mL, and the Al-PAR chelates adsorbed on the resin were eluted with 5 mL of 2 mol L^{-1} HCl solutions. The eluent was analyzed for the determination of metal concentrations by HR-CS FAAS.

2.5. Analysis samples

Tap water and river water (Kızılırmak) were collected from Kırsehir, Turkey. Dam water was collected from KesikKopru dam lake (Kırsehir-Kırıkkale, Turkey). Commerical drinking water was bought directly in local supermarket. Hemodialysis solutions (concentrated acidic solution and concentrated basic solution) obtained from the Ahi Evran University Training and Research Hospital, Department of Hemodialysis. The concentration $(g L^{-1})$ of each component was as follows:

- (1) Concentrated acidic solution for haemodialysis (Renasol BA, Fresenius); NaCl: 215; KCl 5.20; CaCl₂·2H₂O: 7.71; MgCl₂·6H₂O: 3.55; Acetic acid: 6.30, and Glucose monohydrate: 38.50.
- (2) Concentrated basic solution for haemodialysis (Renasol BB-8.4, Fresenius); NaHCO₃: 84.0 g.

Haemodialysis solutions were diluted by deionized water $(1/4 \text{ v/v})$. Before the analysis, the samples were filtered through a cellulose membrane filter (Millipore) of pore size 0.45 μm. Appropriate amounts of PAR solution and buffer solution of sodium acetate–acetic acid (pH 5.5) and known amounts of analyte ions were mixed in volumetric flasks. Then, the preconcentration procedure was applied to the obtained sample solutions.

3. Results and discussion

3.1. Effect of pH on the recovery of Al

The dependence of the sorption conditions on the pH of solution is one of the important parameters that can have a significant influence on the overall recovery of analytes. The recoveries of the analytes were determined by applying the preconcentration procedure by changing the pH of model solution in the

Fig. 2. pH effect of sample solution on the recovery of aluminum (sample volume: 50 mL, amount of aluminum: 5 μg, eluent: 5 mL of 2 mol L−¹ HCl solution, sample flow rate: 5 mL min−¹ , amount of adsorbent: 400 mg, chelating agent, 1.0 mL of 0.02% (w/v) PAR).

range of 3.0–9.0. The quantitative recoveries (above 95%) of analyte ions were obtained at pH 5.5–7.5. The recoveries of Al^{3+} ions were decreased when the sample solution pH is over 7.5 and less than 5.5 (Fig. [2](#page-4-0)). Hence, pH 5.5 was selected as an optimum pH for adsorption and recovery of the analyte ions for further experiments.

3.2. Effect of eluent type and concentration on the recovery of Al

In order to choose the most effective eluent for desorbing of Al^{3+} ions from the adsorbent, different concentrations and different volumes of HCl and HNO₃ solutions were tested. Quantitative recovery (>95%) has been obtained by using 5 mL of 2 mol L−¹ HCl solution (Table 2).

3.3. Effect of the sample flow rate on the recovery of Al

The flow rate of the sample solution also effects on the recovery of aluminum ions. Therefore, the effect of flow rate was also investigated under the optimum conditions (pH 5.5, eluent 5 mL of 2 mol L^{-1} HCl). As shown in Fig. 3, the optimum value for the flow rate of the sample solution was found up to 5 mL min^{-1} . Above 5 mL min−¹ , the recovery decreased gradually. Therefore, to decrease the duration of analysis without decreasing recovery values, a flow rate of 5 mL min^{-1} was chosen as the optimum flow rate for subsequent experiments.

3.4. Effect of eluent flow rate on the recovery of Al

The flow rate effect of eluent solution (5 mL of 2 mol L^{-1} HCl) on the recovery of Al^{3+} ions was examined in the range of 2.0–5.0 mL min⁻¹ at optimum conditions. The recovery of analyte ions ranged between 95 and 100% at the eluent flow rates varying up to 5.0 mL min−¹ . To decrease the analysis time, eluent flow rate was selected as 5 mL min^{-1} .

Table 2 The effect of eluent type/concentration/volume on recovery of aluminum

Eluent	Recovery $(\%)^a$
1 mol L^{-1} HCl, 5 mL	92 ± 1
$2 \text{ mol } L^{-1}$ HCl, 5 mL	98 ± 2
1 mol L^{-1} HNO ₃ , 5 mL	90 ± 2
2 mol L^{-1} HNO ₃ , 5 mL	$95 + 2$

a Results are mean ± standard deviation of three replicate analyses.

Fig. 3. Effect of flow rate of sample solution on the recovery of aluminum (sample volume: 50 mL, amount of aluminum: 5 μg, eluent: $\overline{5}$ mL of 2 mol L⁻¹ HCl solution, sample solution pH 5.5, amount of adsorbent: 400 mg, chelating agent, 1.0 mL of 0.02% (w/v) PAR).

3.5. Effect of sample volume on the recovery of Al

For the preconcentration purposes, to achieve the higher preconcentration factor, the eluent volume should be as small as possible, and the volume of sample solution should be as high as possible [\[7\]](#page-9-0). In order to obtain the maximum applicable sample solution (or analyte concentration), the model solutions with different volumes including the same amount of analyte ions were used. For this purpose, aqueous solutions containing $5 \mu g$ Al^{3+} were preconcentrated by using sample volumes of 50, 100, 250, 500, 750, and 1,000 mL corresponding to analyte concentrations of 0.100, 0.050, 0.020, 0.010, 0.006, and 0.005 μ g mL⁻¹, respectively. The recoveries of Al^{3+} ions were quantitative (>95%) for sample volumes up to 500 mL (Fig. 4). The preconcentration factor (PF) is calculated by the ratio of the highest sample volume with the analytes under study (500 mL) and the lowest eluent volume (5 mL). The PF was 100.

Fig. 4. Effect of sample volume on the recovery of aluminum (sample flow rate: 5 mL min−¹ , amount of aluminum: $5 \mu g$, eluent: 5 mL of 2 mol L⁻¹ HCl solution, sample solution pH 5.5, amount of adsorbent: 400 mg, chelating agent, 1.0 mL of 0.02% (w/v) PAR).

3.6. Effect of chelating agent amount on the recovery of Al

In the separation/preconcentration studies, various ligands which have high affinity to metal ions were used widely for the adsorption process. In this study, the effect of the amount of PAR on the recoveries of Al^{3+} ions were also investigated. Different amounts of PAR in the range of 0–2 mg (by using 0.02% (w/v) PAR solution with different volumes) were added to each model solution containing same amount of analyte, and preconcentration procedure was applied. The results are given in Fig. 5. When PAR was used, the adsorption of analyte ions on XAD-761 resin, thus the performance of proposed procedure increased the optimum amount of PAR was found as 0.2 mg or higher. In case of adding of PAR less than this value, the recovery was below 95%. Therefore, 0.2 mg of PAR (1.0 mL of 0.02% (w/v) PAR solution) was added to the solutions in subsequent studies.

3.7. Effect of adsorbent amount on the recovery of Al

The effect of the amount of XAD-761 resin on recoveries of analytes was also studied. For this purpose, different amount of sorbent (200–600 mg) was tested into adsorption columns. Fifty milliliter of model solution containing 5 μg of analyte was passed through the column at optimum experimental conditions (pH 5.5, flow rate 5 mL min^{-1} , eluent 5 mL of 2 mol L⁻¹ HCl, chelating agent 1.0 mL of 0.02% (w/v) PAR). The results showed that the recovery of the analytes increased up to 400 mg XAD-761 value and remained about constant above this value (Fig. 6). Therefore, 400 mg minimum sorbent amount providing maximum recovery of analytes was selected for further studies.

Fig. 5. Effect of amount of chelating agent on the recovery of aluminum (sample solution volume: 50 mL, sample flow rate: 5 mL min−¹ , amount of aluminum: 5 μg, eluent: 5 mL of 2 mol L−¹ HCl solution, sample solution pH 5.5, amount of adsorbent: 400 mg).

Fig. 6. Effect of sorbent amount on the recovery of aluminum (sample flow rate: 5 mL min⁻¹, amount of aluminum: 5 μg, eluent: 5 mL of 2 mol L⁻¹ HCl solution, sample solution pH 5.5, chelating agent, 1.0 mL of 0.02% (w/v) PAR).

3.8. Matrix effect on the recovery of Al

Matrix effects are important problems during adsorption, separation, and recovery of heavy metals in the water samples. Therefore, the effects of common coexisting ions on recovery of aluminum ions were investigated. The maximum concentrations of the various metal ions as their nitrate or chloride salts which are tolerable within the 5% relative error were determined by adding them to a solution containing of analyte ions and by applying the proposed procedure. The results indicated that the foreign ions tested having concentrations given in Table 3 did not interfere recovery of aluminum ions.

3.9. The equilibrium experimental data and adsorption capacity

The equilibrium experimental data was obtained by batch technique. The equilibrium was achieved

Table 3

Effects of the some foreign ions on the recovery of aluminum (sample solution: 50 mL, amounts of Al: 5 μg, pH 5.5)

Foreign ions	Concentration $(mg L^{-1})$	Recovery $(\%)^a$	
$\rm K^+$	5,000	98 ± 2	
$Na+$	20,000	96 ± 2	
$Ca2+$	2,000	101 ± 2	
$\frac{Mg^{2+}}{Zn^{2+}}$	2,000	98 ± 2	
	10	95 ± 2	
$Cu2+$	10	97 ± 2	
Co^{2+}	10	95 ± 2	
$Ni2+$	10	98 ± 2	
	10	96 ± 2	
	10	103 ± 1	
$\begin{array}{c} \mathrm{Cd}^{2+} \\ \mathrm{Cr}^{3+} \\ \mathrm{Fe}^{3+} \end{array}$	10	97 ± 2	

^aResults are mean ± standard deviation of three replicate analyses.

within a short period of 10 min (resin 0.1 g, pH 5.5, Al concentration $1 \text{ mg } L^{-1}$; solution volume 50 mL at 150 rpm) (Fig. 7).

The adsorption capacity of the sorbent is an important factor in the evaluation of the properties of a sorbent. Because, it determines how much sorbent is required to concentrate Al^{3+} quantitatively from a given solution [[17–19\]](#page-10-0). To be determination of adsorption capacity, 100 mg of resin was added into a 250 mL flask containing 100 mL of model solution, which has various concentrations of analyte ions under the optimum experimental conditions. The prepared solutions containing different amounts of analytes were shaken for 1 h at 150 rpm at room temperature. Then, 10 mL of supernatant was taken from each solution and the amount of residual Al^{3+} in the solution was determined by using HR-CS FAAS.

There are several isotherm equations available for analyzing experimental adsorption equilibrium data. In this study, the equilibrium experimental data for adsorbed Al^{3+} ions on resin were analyzed using the Langmuir and Freundlich models. These isotherms are as follows:

3.9.1. Langmuir isotherm model

The linearized equation form of the Langmuir model used to evaluate maximum metal uptake is expressed by the following equation:

$$
C_{\rm e}/q_{\rm e} = C_{\rm e}/q_{\rm max} + 1/K_{\rm L}q_{\rm max} \tag{1}
$$

where C_e is the final metal concentrations in the solution at equilibrium (mg L⁻¹), q_e is the amount of sorbed metal ions per gram of sorbent at equilibrium (mg g−¹), K^L is a constant related to the energy of adsorption/desorption (Lg^{-1}) , and q_{max} is the maximum adsorption capacity of sorbent (mg/g).

Fig. 7. Time course of aluminum recovery by XAD-761.

3.9.2. Freundlich isotherm model

$$
\log q_{\rm e} = \log K_{\rm F} + (1/n) \log C_{\rm e} \tag{2}
$$

where K_F and *n* are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

Langmuir model had been shown to fit the experimental data well, with the correlation coefficients (R^2) 0.9935 for Al ions. The Langmuir monolayer adsorption capacities (q_{max}) were estimated as 22.5 mg g⁻¹. Constants of the energy (K_I) for Al-PAR chelate was calculated as $0.05 \, \text{L g}^{-1}$ (Figs. 8 and 9).

High correlation coefficients indicate that the adsorption of Al chelates on the sorbent comply with the Langmuir adsorption isotherm. This means that the solid surface presents a finite number of identical sites which are genetically uniform, and there are no interactions between adsorbed species, and a monolayer adsorption is formed when the solid surface reaches saturation [\[20\]](#page-10-0).

The equilibrium data also fitted to Freundlich equation, a fairly satisfactory empirical isotherm can

Fig. 8. Langmuir isotherm obtained from the aluminum adsorption on XAD-761.

Fig. 9. Linearized Langmuir isotherm plot for the adsorption of aluminum on XAD-761.

be used for non-ideal adsorption. K_F relates the multilayer adsorption capacity and n intensity of adsorption, which varies with the heterogeneity of the sorbent [[21](#page-10-0)]. A relatively $n < 1$ indicates that adsorption intensity is favorable over the entire range of concentrations studied, while $n > 1$ means that adsorption intensity is favorable at high concentrations but much less at lower concentrations [[22](#page-10-0)]. The Freundlich adsorption capacitiv (K_F) was found to be 1.21 $(mg^{(1-1/n)}L^{1/n}g^{-1})$. In the adsorption system, the *n* values are calculated as 1.38 from slopes of curves in Fig. 10. Those values indicate that adsorption intensities are favorable at high concentrations.

3.10. Analytical features

Under the optimum experimental conditions, linear dynamic range, correlation coefficient, LOD, precision, and accuracy were examined.

By using direct aspiration in FAAS without applying the preconcentration system the linear dynamic range for aluminum was 0.1 to 20.0 mg L^{-1} $(R^2 = 0.999)$.

LOD of the proposed was determined as the concentration corresponding to three times of the standard deviation (σ) of blank measurements ($N = 15$). LOD [$3\sigma/(m \times \text{PF})$] was found as 0.18 $\mu g L^{-1}$. Where m
is slope of calibration curve obtained without preconis slope of calibration curve obtained without preconcentration procedure and PF is preconcentration factor for the proposed procedure.

The precision of the proposed was examined by seven replicate measurements of 50 mL of sample solution containing 100 μ g L⁻¹ Al³⁺. The mean recovery for aluminum was obtained as 98.2 with the relative standard deviation (RSD) of 2.4%.

3.11. Reusability of the sorbent

The stability and reusability of the sorbent were evaluated by determining the recovery of the analyte by applying adsorption—elution cycles. One adsorption—elution cycle was considered as follow: the

Fig. 10. Freundlich isotherm plot for adsorption of aluminum on XAD-761.

passage of 50 mL of the model solution, 5 mL of eluent solution, and 50 mL of ultrapure water through the column loaded with 400 mg of sorbent, respectively. The adsorbent was always stored in water when it was not in use. The capacities of the adsorbents did not significantly change up to 100 cycles.

3.12. Comparison of the method with others

The data from the present method have been compared with those of recent reported methods on preconcentration of aluminum (Table 4). Some parameters obtained are comparable to those presented by other methods. The present work has relatively low LOD and RSD when compared to other methods [\[23–26](#page-10-0)]. Another parameter, PF (100) is relatively high enough when compared to some of the other methods [\[23,24\]](#page-10-0).

3.13. Analytical applications

In order to show the applicability of the proposed method, it was applied for the determination of aluminum in water samples and dialysis solutions for haemodialysis under optimal experimental conditions. The accuracy of the method was checked by determining the percent relative error the of spiked

Table 4

Comparison of the proposed method for preconcentration of Al ions in aqueous solution with other methods described in the literature

Procedure/material	Ligand	PF	LOD $(\mu g L^{-1})$	$RSD(\%)$	Ref.
SPE/Activated silica gel	8-hydroxyquinoline	20	0.5	4.53	[23]
SPE/N ano ZrO_2/B_2O_3	Ligandless	10	7.71	3.8	[24]
$SPE/Poly S_{15} - g-EMA_{120}$	AHPMAPDAB	133	0.32	1.8	$[25]$
SPE/Activated silica gel	2-methyl-8-hydroxyquinoline	200	0.34	<6.0	$\lceil 26 \rceil$
$SPE/XAD-761$	4-(2-pyridylazo) resorcinol	100	0.18	2.4	Current paper

Table 5 Levels of aluminum in water samples (sample volume: 250 mL)

Sample	Added $(\mu g L^{-1})$	Found ^a (μ g L ⁻¹)	Relative error $(\%)$
Commerical drinking water	0	20.4 ± 1.4	
	20.0	41.6 ± 2.4	3.0
Tap water	0	24 ± 1.5	
	20	45 ± 2.8	2.3
River water	0	58.1 ± 2.6	
	50.0	105.4 ± 4.8	-2.5
Dam water	0	42.9 ± 3.8	
	20.0	60.4 ± 7.6	-3.9
Acidic haemodialysis solution	0	ND^b	
	10.0	10.1 ± 0.4	1.0
Basic haemodialysis solution	0	11.2 ± 0.6	
	10.0	20.8 ± 1.2	-1.9

^aMean and standard deviation from three determinations.

^bNon-detectable for below detection limit.

real samples. The results obtained are given in Table 5. A good agreement was obtained between added and found values of the analytes.

4. Conclusion

The proposed SPE method method presented is simple, efficient, and sensitive preconcentration in water samples and dialysis solutions for haemodialysis. Under the optimum experimental conditions, quantitative recoveries were achieved for a PF of 100. The recoveries of elements in the presence of the most common matrix elements containing the alkaline and alkaline earth metals and transition metals were fairly good. Sorbent material was also stable with a period greater than 100 cycles. The developed method can be recommended a powerful technique for simple separation and selective determination of aluminum ions in water samples and the dialysis fluids

Acknowledgment

Authors would like to thank the Scientific and Technological Research Council of Turkey (TUBITAK Grant no. 110T111).

References

- [1] E. Onur, Evaluation of aluminum toxicity the point of view of quality control, official, J. Turkish Nephrology, Assoc. 1 (1997) 74–79.
- [2] R.A. Yokel, The toxicology of aluminum in the brain: A review, Neurotoxicol. 21 (2000) 813–828.
- [3] K. Berend, G.B. van der Voet, F.A. de Wolff, D.M.P. Mingos (Ed.), Group 13 Chemistry II—Biological Aspects of Aluminum, vol. 104, Springer, Berlin, 2002, pp. 1–58.
- [4] J. Komárek, R. Červenka, T. Růžička, V. Kubáň, ET-AAS determination of aluminium in dialysis concentrates after continuous flow solvent extraction, J. Pharm. Biomed. Anal. 45 (2007) 504–509.
- [5] European Pharmacopeia, third ed., Council of Europe, Strasbourg, 1997, pp. 1540–1542.
- [6] WHO, Guidelines for Drinking Water Quality, vol. 1, Recommendation, World Health Organization, Geneva, 2008.
- [7] A.R. Türker, Separation, preconcentration and speciation of metal ions by solid phase extraction, Sep. Purif. Rev. 41 (2012), 169–206.
- [8] S. Baytak, A.R. Türker, The use of immobilized on Amberlite XAD-4 as a new biosorbent for the column preconcentration of iron(III), cobalt(II), manganese(II) and chromium(III), Talanta 65 (2005) 938–945.
- [9] H. Ciftci, Separation and preconcentration of cobalt using a new Schiff base derivative on XAD-7, Clean 38 (2010) 657–662.
- [10] H. Ciftci, M.M. Temuz, E. Ciftci, Simultaneous preconcentration and determination of Ni and Pb in water samples by solid-phase extraction and flame atomic absorption spectrometry, J. AOAC Int. 96 (2013) 875–879.
- [11] S. Jaggi, U. Gupta, Solid phase extraction and preconcentration of Ni(II) using 1-(2-pyridylazo)-2-naphthol) (PAN) modified β-cyclodextrin butanediol diglycidyl ether polymer as a solid phase extractant, Maced. J. Chem. Chem. Eng. 32 (2013) 57–67.
- [12] Ö. Yalçınkaya, H. Erdoğan, H. Çiftçi, A.R. Türker, Preconcentration of aluminum on nano $ZrO₂$ /B₂O₃ and its determination by flame atomic absorption spectrometry, Spectrosc. Lett. 45 (2012) 344–351.
- [13] V. Tharanitharan, K. Srinivasan, Removal of Ni(II) from water and wastewater using modified Duolite XAD-761 resin, Indian J. Chem. Technol. 16 (2009) 245–253.
- [14] V.N. Bulut, D. Arslan, D. Ozdes, M. Soylak, M. Tufekci, Preconcentration, separation and spectrophotometric determination of aluminium(III) in water samples and dialysis concentrates at trace levels with 8-hydroxyquinoline–cobalt(II) coprecipitation system, J. Hazard. Mater. 182 (2010) 331–336.
- [15] S. Khan, T.G. Kazi, J.A. Baig, N.F. Kolachi, H.I. Afridi, A.Q. Shah, G.A. Kandhro, S. Kumar, Separation and preconcentration of trace amounts of aluminum ions in surface water samples using different analytical techniques, Talanta 80 (2009) 158–162.
- [16] H. Ciftci, C. Er, Solid-phase extraction and separation procedure for trace aluminum in water samples and its determination by high-resolution continuum source flame atomic absorption spectrometry (HR-CS FAAS), Environ. Monit. Assess. 185 (2013) 2745–2753.
- [17] G. Kaya, I. Akdeniz, M. Yaman, Solid phase extraction and preconcentration of nickel in water samples with activated carbon-PAR and flame atomic absorption spectrometry, At. Spectrosc. 29 (2008) 150–155.
- [18] E. Eren, O. Cubuk, H. Ciftci, B. Eren, B. Caglar, Adsorption of basic dye from aqueous solutions by modified sepiolite: Equilibrium, kinetics and thermodynamics study, Desalination 252 (2010) 88–96.
- [19] H. Ciftci, T. Tunc, I.H. Tasdemir, E. Ciftci, Development of a new enrichment method for simultaneous determination of copper and zinc in water samples, Environ. Toxicol. Chem. 30 (2011) 616–621.
- [20] E. Eren, H. Gumus, A. Sarihan, Synthesis, structural characterization and Pb(II) adsorption behavior of Kand H-birnessite samples, Desalination 279 (2011) 75–85.
- [21] P. Baláž, A. Aláčová, J. Briančin, Sensitivity of Freundlich equation constant 1/n for zinc sorption on

changes induced in calcite by mechanical activation, Chem. Eng. J. 114 (2005) 115–121.

- [22] Y.S. Al-Degs, M.I. El-Barghouthi, A.A. Issa, M.A. Khraisheh, G.M. Walker, Sorption of Zn(II), Pb(II), and Co(II) using natural sorbents: Equilibrium and kinetic studies, Water Res. 40 (2006) 2645–2658.
- [23] S. Khan, T.G. Kazi, J.A. Baig, N.F. Kolachi, H.I. Afridi, A.Q. Shah, G.A. Kandhro, S. Kumar, Separation and preconcentration of trace amounts of aluminum ions in surface water samples using different analytical techniques, Talanta 80 (2009) 158–162.
- [24] O. Yalçınkaya, H. Erdoğan, H. Çiftçi, A.R. Türker, Preconcentration of aluminum on nano $ZrO₂$ /B₂O₃ and its determination by flame atomic absorption spectrometry, Spectrosc. Lett. 45 (2012) 344–351.
- [25] H. Çiftçi, C. Er, O. Yalçinkaya, M.M. Temuz, A.R. Turker, High-resolution continuum source flame atomic absorption spectrometric (HR-CS FAAS) determination of trace aluminium and lead in water and some beverage samples after separation and preconcentration procedure, Int. J. Environ. Anal. Chem. 94 (2014) 579–593.
- [26] T.G. Kazi, S. Khan, J.A. Baig, N.F. Kolachi, H.I. Afridi, A.Q. Shah, Determination of trace quantity of aluminium in dialysate concentrates using solid phase and cloud point extraction methods, Anal. Methods 2 (2010) 558–563.