Talanta 82 (2010) 1974–1979

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Use of amidoximated hydrogel for removal and recovery of U(VI) ion from water samples

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ARTICLE INFO

Article history:
Received 12 May 2010
Received in revised form 12 August 2010
Accepted 17 August 2010
Available online 21 August 2010

Keywords:
Uranium(VI)
Hydrogel
Amidoxime
Sea water
Thermal spring water

ABSTRACT

Poly(acrylamidoxime-co-2-acrylamido-2-methylpropane sulfonic acid) (PAMSA) hydrogel was prepared by copolymerization of acrylonitrile and 2-acrylamido-2-methylpropane sulfonic acid as monomer, N,N′-methylenebis(acrylamide) as crosslinking agent and potassium peroxodisulfate as initiator. Amidoximated copolymer network was prepared by the reaction of copolymer network with hydroxylamine hydrochloride. A batch procedure was used for the determination of the characteristics of the U(VI) solid phase extraction from the amidoximated hydrogel. The determination of U(VI) was performed by spectrophotometric method using arsenazo-III as complexing agent. Optimal pH value for the quantitative preconcentration was 3, and full desorption was achieved with 3 mol L^{-1} $HClO_4$. The adsorption process can be well described by the pseudo-second-order kinetic model, and the equilibrium adsorption isotherm was closely fitted with the Langmuir model. A preconcentration factor of 20 and the three sigma detection limit of 2.8 μg L^{-1} (n = 20) were achieved for uranium(VI) ions. The PAMSA hydrogel was used for separating and preconcentrating the uranyl ion existing in sea water samples, thermal spring water samples and the certified reference materials (TMDA 64; fortified lake water sample).

1. Introduction

Uranium has strategical and economical importance. The latest researches aim to obtain uranium from different resources rather than ores because the uranium resources in lands are expected to exhaust in near future. These resources are coal, ground waters (0.1–10 mg m^{-3}) and especially sea water (2.8–3.3 mg m^{-3}). Atomic power plants continuously require uranium resources, therefore, 4.5 billion tons of total uranium in sea water can be recovered for atomic power utilization [1].

On the other hand, uranium dissolved in aquatic environment is an important environmental problem. The World Health Organization (WHO), Health Canada and Australian drinking water guidelines have fixed the maximum uranium concentration in drinking water to be less than 9, 20 and 20 μg L^{-1}, respectively [2,3]. Otherwise, uranium and its compounds like lead are highly toxic and result in progressive or irreversible renal injury and in acute cases, may lead to kidney failure and death. The tolerable daily intake of uranium established by WHO based on Gilman's studies is 0.6 μg kg^{-1} of body weight per day [2–5].

Hydrogels are three-dimensional cross-linked polymer networks that swell by adsorbing water and may increase their size more than hundred times. When dried, they shrink and recover their original volume. Depending on the type of monomers (i.e., ionic or neutral) incorporated in the gels, they can be made to respond to a variety of external environmental changes such as pH, ionic strength, temperature or specific chemical compounds [6–9]. These materials are of great importance due to their promising applications such as controlled drug-delivery systems, artificial muscles, sensor systems, tissue engineering [10–15]. In addition, they are widely used in the purification of waste water, stabilization of mineral sediments and removal of heavy metals [16–20].

Chelating polymers can be obtained by copolymerization of monomers with different functional groups or by postmodification of polymerized products. The second option is generally preferred to prepare materials which are difficult to obtain by direct polymerization of the corresponding monomers [21]. An example is polyacrylonitrile with nitrile (–CN) groups that can be converted to amidoxime ($-C(NH_2)NOH$) groups by the reacting free hydroxylamine. It is well known that resins or adsorbents containing amidoxime groups as a functional group adsorb U(VI) species in sea water [22]. U(VI) in sea water exists mainly in the form of $UO_2(CO_3)_3^{4-}$. The adsorption mechanism of U(VI) by amidoxime resin has been revealed as a complex formation between UO_2^{2+} and amidoxime functional group [23,24].

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doi:10.1016/j.talanta.2010.08.023

In the present work, the synthesized hydrogels described earlier [25] was investigated for separating trace levels of uranium from sea water with solid phase extraction (SPE). Batch procedure was used at this work. The preconcentrated uranium was determined spectrophotometrically in perchloric acid medium using Arsenazo-III as chromogenic reagent [26,27].

2. Experimental

2.1. Materials and instruments

The monomers 2-acrylamido-2-methylpropane sulfonic acid (AMPS), and acrylonitrile (AN) were obtained from Merck (Darmstadt, Germany) and used without further purification. The crosslinker N,N′-methylene bisacrylamide (BAAm) and potassium peroxodisulfate, $K_2S_2O_8$, were also used as received from Merck (Darmstadt, Germany). A stock solution of uranium(VI) was prepared by dissolving appropriate amount of $UO_2(CH_3COO)_2{\cdot}2H_2O$ from Merck (Darmstadt, Germany) in deionized water. Concentrated HNO_3 (5 mL) was added to 100 mL of solution to suppress hydrolysis. 0.1% (w/v) arsenazo-III (Aldrich, MO, USA) solution was prepared by dissolving 0.1 g of the reagent in 100 mL of deionized water. The following buffer solutions were used for the solid phase extraction procedures: CH_3COOH/CH_3COONa buffer for pH 2–6, Na_2HPO_4/NaH_2PO_4 buffer for pH 7, and NH_3/NH_4Cl buffer for pH 8–9. Other used reagents were also of analytical reagent grade. Distilled–deionized water was used in all experiments.

A Schimadzu UV-1208 model UV–Vis spectrophotometer was used to determine U(VI) as U(VI)–arsenazo-III complex at 653 nm. The pH measurements were made with a Consort C931 model digital pH-meter.

2.2. Preparation of amidoximated hydrogel

Appropriate amounts of AN with AMPS having 70/30 feed composition, 5% N,N′-methylene bisacrylamide (total weight of monomers), 1% $K_2S_2O_8$ (total weight of monomers) and 10 mL deionized water were mixed in a round-bottom flask equipped with a mechanical stirrer and a reflux condenser. The solution was purged with nitrogen for about 10 min, and the reaction mixture was purged again for several minutes prior to heating. The reaction mixture was heated at 70 °C with constant stirring. The mixture was then cooled to room temperature and slowly poured. Solid poly(acrylonitrile-co-2-acrylamido-2-methylpropane sulfonic acid) polymer was purified and finally dried under vacuum. A solution of free hydroxylamine in methanol–water (5:1) was prepared from its hydrochloride salt. Accurately, 3 g of hydroxilamine hydrochloride was dissolved in 30 mL of methanol–water (5:1) mixture. The $NH_2OH{\cdot}HCl$ was neutralized by NaOH solution and the precipitate of NaCl was removed by filtration. The pH of the solution was adjusted to pH 8–8.5 by controlling with 0.1 mol L^{-1} NaOH solution.

An appropriate amount of poly(acrylonitrile-co-2-acrylamido-2-methylpropane sulfonic acid) was kept for swelling in methanol (10 mL) during overnight. The above-prepared free hydroxylamine solution was added to the swollen poly(acrylonitrile-co-2-acrylamido-2-methylpropane sulfonic acid) in a flask fitted with condenser. The amidoximation reaction of the poly(acrylonitrile-co-2-acrylamido-2-methylpropane sulfonic acid) with free hydroxylamine solution was carried out at refluxing temperature of 80 °C for 12 h. The modified resin was filtered off, thoroughly washed with deionized water (five portions of 100 mL) and then dried at 50 °C for 10 h.

2.3. Batch "static" method

Fifty milliliters of sample solution containing 20 μg of uranyl ion was taken and its pH was adjusted to 3. 150 mg of the hydrogel was added to 100 ml of the sample solution in a polyethylene bottle and stirred for 3 h. Then, the hydrogel particles containing uranyl ions were filtered off. The uranyl ions were eluted with 20 mL of 3 mol L^{-1} $HClO_4$ for 2 h. Afterwards, 10 mL of eluent was taken and 1 mL of 0.1% Arsenazo-III solution was added to this solution and the absorbance of uranium(IV)–arsenazo-III complex was measured spectrophotomerically at 653 nm.

2.4. Procedure for the analysis

Sea water and thermal spring water samples were collected from Aegean Sea, İzmir, Marmara Sea, İstanbul and thermal spring water, Yozgat. The polyethylene bottles were cleaned with detergent, water, diluted nitric acid and water in sequence. The samples were immediately filtered through a cellulose filter membrane (pore size 0.45 μm) and then acidified to pH 2 for storage. A 400 mL of water sample was taken into a 500 mL of polyethylene bottle ($n = 4$). Forty milliliters of TMDA 64 standard reference material sample was taken into a 100 mL of polyethylene bottle ($n = 4$) and 15 mL of acetate buffer (pH 3) was added to these sample solutions, respectively. The uranyl ion contents in water samples were determined by standard addition method spiking 25 and 50 μg L^{-1} of uranium(VI) ion. Preconcentration of uranium onto the PAMSA hydrogel and its determination by arsenazo-III procedure were carried out as described in Section 2.3.

2.5. Effect of pH

The effect of pH on the sorption of uranium ion was investigated by the batch method. 50 mL of uranium solutions containing 0.2 μg mL^{-1} of uranium ion was stirred at various pHs changing from 2 to 9. The maximum retention of the U(VI) ions on the PAMSA hydrogel was observed at pH 3. The retained U(VI) ions on the hydrogel were desorbed with 20 mL of 3 mol L^{-1} $HClO_4$ and then determined spectrophotometrically. The optimum pH for maximum sorption was found to be 3 as shown in Fig. 1. Therefore, for all subsequent works, pH 3 was fixed as the optimum for the quantitative separation and preconcentration of uranium(VI) ions.

2.6. Optimization of sorption and elution of uranium(VI)

Optimum pH was found to be 3. Other optimal conditions were ascertained in a similar fashion as given in Table 1. For the sorption of uranium(VI) onto the PAMSA hydrogel, a

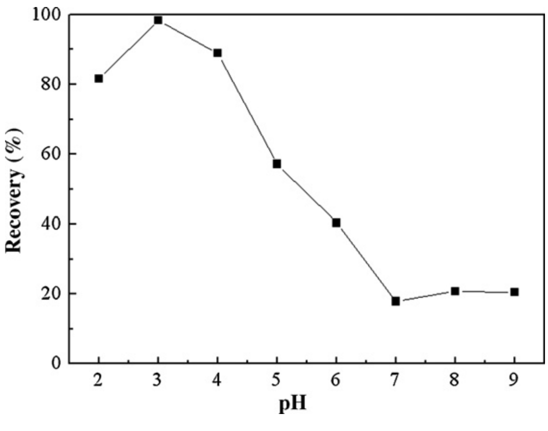

Fig. 1. Effect of pH on the recovery of U(VI).

Table 1
Optimization of experimental parameters for SPE of uranium(VI) (pH 3, sample contact time (min): 3, elution contact time (min): 1, eluent volume: 20 mL, aqueous phase volume: 400 mL).

Parameters									
Sample contact time (min)	15	30	60	120	180	240	300	360	720
Recovery (%)	19.1 ± 1.8	31.1 ± 0.4	54.2 ± 0.5	67.0 ± 2.8	79.9 ± 0.7	91.1 ± 0.7	98.6 ± 0.6	97.8 ± 0.7	96.6 ± 1.0
Elution contact time (min)	15	30	60	120	180	240			
Recovery (%)	62.2 ± 2.4	73.1 ± 0.6	86.2 ± 1.4	96.5 ± 0.9	98.3 ± 0.7	98.1 ± 0.7			
Eluent volume (mL)	10	20	30						
Recovery (%)	81.7 ± 1.6	97.7 ± 1.1	97.9 ± 1.6						
Aqueous phase volume (mL)	50	100	200	300	400	500	600		
Recovery (%)	97.8 ± 0.9	97.6 ± 0.9	98.0 ± 1.6	96.6 ± 0.7	96.4 ± 1.2	90.0 ± 2.5	86.4 ± 1.4		

sample contact time of 3 h was found to be suitable for optimum loading onto the resin. Similarly, the variation of elution contact time from 2 to 4 h show that the elution of sorbed uranium(VI) is quantitative over the entire range. Further, as low as 20 mL of 3 mol L^{-1} $HClO_4$ was enough for quantitative elution of sorbed uranium(VI). Therefore, for complete desorption, 20 mL of 3.0 mol L^{-1} $HClO_4$ was used for convenience. The sorption and desorption of uranium(VI) were found to be quantitative by changing the volume of sample solution in the range 50–400 mL keeping the total amount of loaded uranium(VI) at 20 μg.

2.7. Adsorption isotherm and adsorption capacity

The adsorption capacity of the PAMSA hydrogel for U(VI) was determined by using the batch technique. Therefore, portions of 50 mL of model solutions containing 10–750 mg L^{-1} U(VI) at pH 3 were stirred with 0.15 g of the PAMSA hydrogel at a contact time of 3 h. The retained uranium ions were eluted from the resin with 3 mol L^{-1} $HClO_4$. The concentrations of U(VI) in the eluate were determined spectrophotometrically.

2.8. Matrix effect

The possible influence of matrix ions present in the sea water samples was also examined. The effect of potential interfering ions on the determination of U(VI) was investigated by using the synthetic sea water sample (SSW) [28]. The results are summarized in Table 2. These results show that the proposed preconcentration and separation method could be applied to the sea water samples at the dilution ratios of SSW/4, SSW/2 and SSW (see Table 3).

Table 2
Composition of synthetic sea water (SSW) [28].

Ions	Concentration	
	mg L^{-1}	mmol L^{-1}
Na^+	10569	459.5
Mg^{2+}	1270	52.3
K^+	379	9.7
Ca^{2+}	397	9.9
Sr^{2+}	13	0.15
Cl^-	18990	534.9
$SO_4{}^{2-}$	2648	27.6
$HCO_3{}^-$	139	2.3
Br^-	65.5	0.8
$BO_2{}^-$	18	0.42
F^-	14	0.74
Total	34502.5	1098.3

Table 3
Effect of dilution of synthetic sea water (SSW) on the recovery of uranium (n = 3).

Sample	(1/4) SSW[a]	(1/2) SSW	(1/1) SSW
Recovery (%)	98.4 ± 1.4	97.9 ± 0.8	96.6 ± 2.2

[a] Dilution was performed with distilled–deionized water.

3. Results and discussion

3.1. Evaluation of adsorption isotherm models

It is important to establish the most suitable correlations for the adsorption equilibrium data using isotherm equations as it plays a crucial role in designing adsorption system and optimizing experiment process. Adsorption isotherms are also efficacious to understand adsorption mechanism. Many isotherm models have been proposed to explain adsorption equilibrium, and the most commonly used isotherm models for liquid–solid adsorption are Langmuir, Freundlich and Dubinin–Radusckevich (D–R) isotherms. The equilibrium data obtained were tested with respect to the three isotherm models.

The Langmuir isotherm assumes that the adsorbent surface is homogeneous and the adsorption sites are energetically identical indicating that the adsorbed molecules do not react with each other. The linear form of Langmuir equation can be depicted as [29]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{m1}} + \frac{1}{b \times q_{m1}}$$

where q_{m1} represents the maximal adsorption capacity to form a monolayer (mg/g) in the system; q_e represents the amount of solute adsorbed per unit weight of adsorbent (mg/g) at equilibrium; C_e is the equilibrium solute concentration (mg/L) in solution and b is the Langmuir constant (L/mg). Figs. 2 and 3 show the adsorption isotherms for U(VI) ions, which conforms to the Langmuir equation.

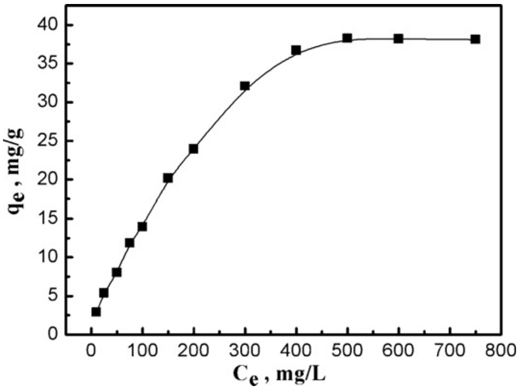

Fig. 2. Effect of uranyl ions concentration on the adsorption of uranyl ions.

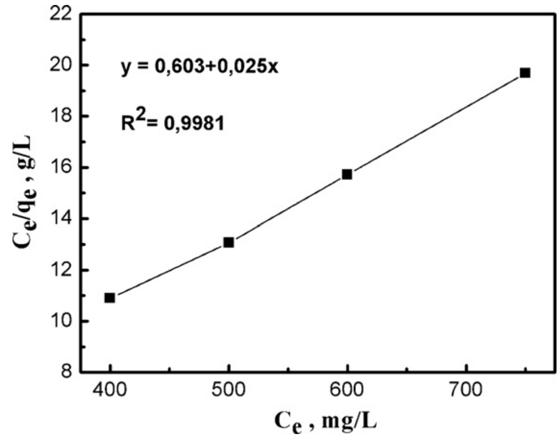

Fig. 3. Langmuir isotherm of the PAMSA hydrogel for uranium(VI).

The plot of C_e/q_e against C_e would be a straight line, and then q_{m1} and b can be obtained from the slope and intercept of the plot.

The Freundlich equation is an empirical equation, which is among the earliest empirical equations applied to predict adsorption equilibrium data. The Freundlich equation can be written in the following form [30]:

$$q_e = K_F C_e^{1/n}$$

where K_F is the constant (mg/g), which indicates the relative adsorption capacity of the adsorbent. The parameter n characterizes the heterogeneity of the system. Fig. 4 shows the adsorption isotherms for U(VI) ions, which conforms to the Freundlich equation.

Langmuir and Freundlich isotherms do not give any idea about adsorption mechanism. D–R isotherm describes adsorption on a single type of uniform pores. In order to understand the adsorption type, D–R isotherms were obtained (Fig. 5). The D–R isotherm which is given with the following equation [31]:

$$\ln q_e = \ln q_{m2} - \beta\varepsilon^2$$

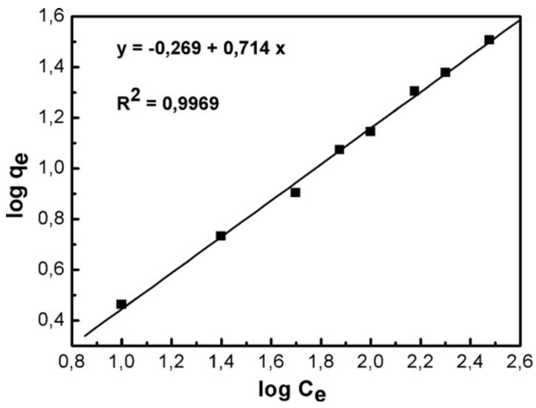

Fig. 4. Freundlich isotherm of the PAMSA hydrogel for uranium(VI).

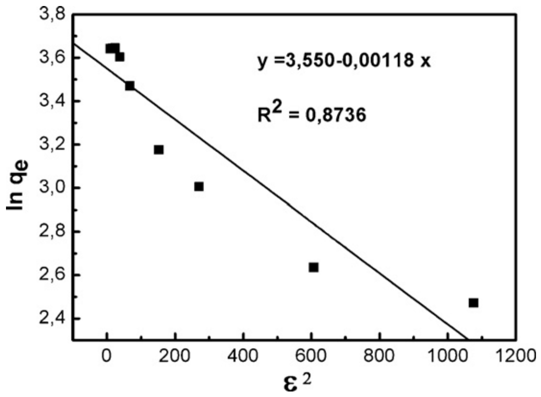

Fig. 5. D–R isotherm of the PAMSA hydrogel for uranium(VI).

where q_{m2} is the D–R monolayer capacity (mg/g), β is a constant correlated to sorption energy ((mol/J)^2), and ε is the Polanyi potential related to the equilibrium concentration (J/mol), illustrated as follows:

$$\varepsilon = RT\ \ln\left(1 + \frac{1}{C_e}\right)$$

where R is the universal gas constant (8.314 J/(mol K)) and T is the absolute temperature (K). The mean free energy, E (J/mol), which is defined as adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution, can be calculated from constant β, and the relationship is presented as:

$$E = (2\beta)^{-0.5}$$

The constant parameters and correlation coefficients were calculated from the Langmuir, Freundlich and D–R equations mentioned above, as summarized in Table 4.

It can be seen that the values of correlation coefficients of Langmuir equation were higher than the other two isotherm values, which indicated the Langmuir isotherm correctly fitted the equilibrium data, confirming the monolayer coverage of uranium onto the hydrogel composites, and the D–R isotherm values were lowest (<0.9), which indicated that the D–R equation represented the poorest fit for the equilibrium data than the other isotherm equations.

The numerical value of mean sorption energy (E) is in the range of 1–8 and 9–16 kJ mol^{-1} forecast the physical adsorption and chemical adsorption, respectively [32], in our study the E value obtained was around 20 kJ/mol. So adsorption proses is chemisorption.

3.2. Kinetics of uranyl ions adsorption

The adsorption kinetics of uranyl ions by the hydrogels were analyzed on the basis of the pseudo-second order kinetic model, which is expressed as [30]: $\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e}$ where t is the contact time (h), q_t and q_e are the amount of uranyl ions adsorbed at an arbitrary time t and at equilibrium (mg/g), respectively, and k is the rate constant (g/mg h). From the data of Fig. 6, plot of t/q_t versus t for the adsorption of uranyl ions is obtained, as shown in Fig. 7. It was observed that the adsorption on hydrogel followed the pseudo-second order kinetic model (the correlation coefficients are larger

Table 4
Langmuir, Freundlich and Dubinin–Radusckevich parameters for uranyl ions adsorption.

Langmuir model			Freundlich model			Dubinin–Radusckevich model			
q_{m1}	b	R^2	K_F	$1/n$	R^2	q_{m2}	β	E	R^2
39.49	0.042	0.9981	0.54	0.714	0.9969	34.81	1.18 10^{-3}	20.58	0.8736

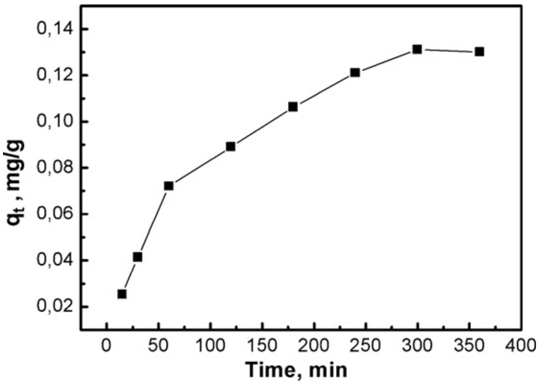

Fig. 6. Effect of time on the adsorption of uranyl ions.

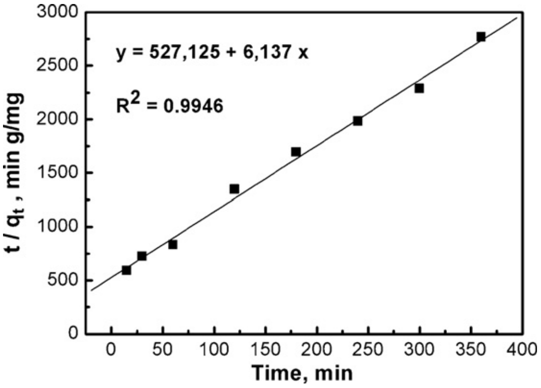

Fig. 7. Plot for pseudo-second order kinetic modelling.

than 0.99). As a result, the q_e and k values were calculated to be 0.163 mg/g and 7.1×10^{-2} min g/mg.

3.3. Validation and application of the proposed method

The proposed method was applied to the sea water and thermal spring water samples. For the validation of the method, the certified reference material (TMDA 64; fortified lake water sample) was analyzed and recovery studies were performed for the sea and thermal spring water samples spiked with UO_2^{2+} at known concentrations. The concentrations of uranium(VI) ion added to the water samples were 25 and 50 μg L^{-1}. The results of analysis of the water samples are shown in Table 5. A good agreement was obtained between the added and found analyte contents. While the recovery values for the uranium ion were found to be 98.8–102.4%, the relative standard deviation value for the samples were in the range 1.2–3.2%. The results obtained by analyzing the CRM for U(VI) ion are given in Table 6. The found and the certified values are in good agreement for the validation of the method.

Table 5
The results for tests of addition/recovery for uranium determinations in water samples (sample volume: 400 mL, final volume: 20 mL, n = 4).

Sample	U(VI)		Recovery (%)
	Added (μg L^{-1})	Found (μg L^{-1})	
Sea water from Aegean Sea	0	4.0 ± 0.5	–
	25.0	28.7 ± 0.8	99 ± 3
	50.0	53.4 ± 0.6	99 ± 1
Sea water from Marmara Sea	0	5.1 ± 0.6	–
	25.0	30.5 ± 0.8	102 ± 3
	50.0	56.2 ± 0.9	102 ± 2
Thermal spring water from Yozgat	0	ND[a]	–
	25.0	25.6 ± 0.8	102 ± 3
	50.0	50.5 ± 0.8	101 ± 1

[a] Not detected.

Table 6
Analysis of CRM (TMDA 64: Fortified lake water sample).

	Concentration (μg L^{-1})		Relative error (%)
	Certified value[a]	Our value[a]	
U(VI)	138.0 ± 2.5	136.2 ± 5.8	−1.3

[a] At 95% confidence level, $\bar{x} \pm t \times s/\sqrt{N}$, n = 4.

4. Conclusions

In this paper, an amidoximated hydrogel was prepared. Then the solid phase extraction (SPE) procedure was developed by using this hydrogel. The SPE method has a good potential for the separation of uranium(VI) from host of co-existing alkali and alkaline earth ions. The proposed method is simple. The adsorption process can be well described by the pseudo-second-order kinetic model, and the equilibrium adsorption isotherm was closely fitted with the Langmuir model. The obtained results show that amidoximated hydrogel (PAMSA) has high adsorption capacity (39.5 mg g^{-1}). The applied method provided good precision with relative standard deviations lower than 4% and high accuracy obtained with quantitative recovery of U(VI). These results showed that the PAMSA hydrogel offers a reliable analysis of U(VI) in water samples and can be used as an effective adsorbent for removing U(VI) ions from aqueous solution, even having high salt matrices like sea water samples.

Acknowledgement

The authors wish to thank the financial support provided by the Erciyes University Research Fund (Project No. EU BAP-FBT-06-04).

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