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Development of an extractive spectrophotometric method for uranium using MWCNTs as solid phase and arsenazo(III) as chromophore

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Abstract Multiwalled carbon nanotubes (MWCNTs) based sorptive extraction method for uranium (U) from aqueous solutions has been developed. The proposed method was optimized by evaluating the analytical parameters including pH, eluent type, flow rates of sample and eluent, etc. The adsorption capacity of MWCNTs was found to be 9.80 μg g^{-1}, while the detection limit based on 3σ criterion was 1.9 μg L^{-1}. The presented method was applied for the estimation of U in ore sample. Effect of potentially interfering ions was also studied and were found to inert not interfering with U during the analysis. The results suggest that MWCNTs can be used as reliable solid phase for preconcentration and arsenazo-III as chromophore for U spectrometric determination from aqueous solutions.

Keywords Carbon nanotubes · Uranium · Solid phase · Pre-concentration · Arsenazo-III

Introduction

Due to its chemical toxicity and radioactive nature, uranium (U) is one of the most hazardous heavy metals in the environment. U in trace amount is found almost everywhere in water, soil and rocks [1]. It is also known as responsible to cause toxicological effects in mammals and is potential occupational carcinogen [2].

Uranium assessment in trace quantity is important task to estimate the performance of different nuclear processes and thus its determination in environmental samples is a matter of concern for safety reasons [3]. A number of various methods have been developed for U determination in different samples. These various techniques are laser fluorimetry [4], gamma spectrometry [5], stripping voltammetry [6], fluorimetry [7], potentiometry [8], polarography [9], X-ray fluorescence [10], inductively coupled plasma mass spectrometry [11, 12], neutron activation analysis [13], and alpha spectrometry [4, 14]. Although all these techniques are sensitive and capable of fast measurement, but requires expensive instruments, perfect experimental conditions and complicated sample-pretreatment steps. For U determination spectrophotometric methods are widely because it is quite simple and reliable accuracy [7, 8]. Spectrophotometry is still a requisite technique for the determination of trace U and a variety of different chromogenic agents have been used in this regard. The chromogenic reagents commonly used for U determination are arsenazo-III (A-III) [15], 4,4-diaminophenylmethane [16], *p*-carboxychlorophosphonazo [17], chromazurol S [18], 4-(2-pyridylazo) resorcinol [19], meloxicam [20], dimethylphenylazosalicylfluorone [21], 8-quinolinol [22], anthranilic acid and rhodamine 6G [23], pyrocatechol [24], 2-(5-bromo-2-pyridylazo-5-diethylaminophenol) [25], dibenzoylmethane [26], and thiocyanate [27], although most of them are not selective.

A number of different methods have been developed for the removal of uranium from aqueous solutions based on various adsorbents such as activated carbon [28], olivine-rock [29], montmorillonite [30], carbon fiber [31], algae

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and biomass of fungus [32], attapulgite [33], manganese coated zeolite [34] and carbon nanotubes (CNTs) [35].

Carbon nanotubes (CNTs) have been used earlier as sorbents in solid phase extraction [36]. Depending on the layers, CNTs are divided into single walled (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). CNTs have a great potential as advanced sorbents for the extraction and pre-concentarion of different contaminants like phenols [37], dyes [38], pesticides [39], metal ions [40] drugs [41, 42], natural organic matter [43, 44] and many other chemicals [45].

Because of its dynamic oxidation state, U has a unique nature as compared to many other metals. U has the capability to be a part of positive, neutral and negatively charged complexes, nearly at neutral pH. Due to the strong association of U with other elements, its determination needs selectivity. Because of simplicity and selectivity, organic dyes have been widely investigated and reported for the spectrophotometric determination of U [45–47]. Among a variety of these organic reagents which are largely based on azo-dyes for U determination, sodium salt of A-III is reported as a responsive chromogenic reagent. Because of U-(A-III) high stability its quantitative determination even in very low pH became possible, where neither hydrolysis, nor the formation of polynuclear species can take place [48].

In this work, we studied the sorption of uranium on MWCNTs as function of the following parameters: pH, sample volume, eluent nature and volume, flow rate and A-III concentration. The basic objectives of present work are to investigate the sorption behavior of uranium on MWCNTs and its spectrophotometric determination using A-III as chromogenic reagent.

Experimental

Apparatus

Absorbances were measured using Hitachi Model 150-20 UV–Vis double beam spectrophotometer carrying a 10 mm optical path cell. For pH adjustments, pH meter, Nel pH 900 (Ankara-Turkey) Model glass-electrode was used. To measure the concentrations of interfering ions Perkin-Elmer Model 3110 atomic absorption spectrometer (Norwalk, CT, USA) was used.

Reagents

Standard solutions of U were prepared by the dilution of certified standard solution (1000 mg L^{-1}) HIGH-PURITY standards (Charleston, SC). Arsenazo-III (3,6-bis[(2-arsonophenyl)azo]-4,5-dihydroxy-2,7-naphthalenedisulfonic acid) (Fluka Chemie, Buchs, Switzerland), solution was prepared by dissolving 0.1 g of the reagent in 100 mL distilled water. Working solutions were prepared by adequate dilution of the stock solution. All reagents and solvents used in experimental work were of analytical grade.

Sample preparation

0.5 g of ore samples were weighed into a PTFE Teflon beakers of 100 mL capacity and adding 10 mL of HNO_3 followed by heating on hot plate for 3 h at 70 °C. 5 mL of $HClO_4$ were added to this mixture and the temperature was raised to 90 °C and left overnight. Further HNO_3 (10 mL), $HClO_4$ (5 mL) and HF (5 mL) were added again and the mixture was heated for 24 h at 70 °C until a semi dried mass was obtained. The obtained residue was redissolved in 15 mL of acid mixture of HNO_3, HCl and HF (1:1:1) and heated overnight at 70 °C. At last, the residue was dissolved in 10 mL of 1 N HNO_3 and diluted to the desired sample volume with deionized water [49].

Adsorption studies

In batch adsorption experiments, 0.2 g of MWCNTs was introduced into 100 mL Erlenmeyer flasks, containing 50 mL of 150 µg mL^{-1} stock solution at pH 5. Flasks were shaken in a mechanical shaker at 150 rpm for 24 h on a pre-settled temperature. Then the mixture was filtered and the maximum amount of U thus pre-concentrated was eluted with 1.5 N HCl and determined spectrophotometrically adding A-III. The capacity of MWCNTs was found to be 9.80 mg g^{-1}.

Adsorption capacity (q) was calculated as:

$$q = V(C_0 - C_e)/W$$

where C_o is initial concentration and C_e is the equilibrium concentration of U (µg mL^{-1}). V represents the volume of the solution (mL), and W is the mass of adsorbent, 0.2 g in our case.

Procedure

In column study, column with 1 cm diameter and 15 cm length was loaded with 0.2 g of MWCNTs. An aliquot of U solution containing 10–150 µg of the metal ion was taken in a beaker and diluted in the range of 20–500 mL with deionized water. The test solution, whose pH was already adjusted to 5 by using acetate buffer, was passed through the MWCNTs column at 1–5 mL min^{-1} flow rate. The effluent carrying the analyte was collected in a volumetric flask and washing the column three times with 5 mL of acetate buffer. A mixture of acid and methanol was used for the elution of U retained in the column. For rapid and quantitative elution of U from the column the best choice is a mixture of HCl and methanol and quantitative elution for retained U was observed with 10 mL of methanol containing 1 mL of 1 N HCl [50].

The column was washed with deionized water and the washings were also collected in a flask where U was determined spectrophotometrically at 649.1 nm by adding A-III. Deionized water was used for repeatedly washing the column and in the usual mode the U retained in the column was eluted out and determined. For 10 min the solutions were kept until the complete color development and followed by measuring the absorbance at 649.1 nm against a blank. The calibration curve was fitted by taking average of five similar measurements (samples with different concentration) of each standard solution.

Results and discussion

To attain maximum U recovery from aqueous solution and its best determination, it is obligatory to optimize the experimental parameters like pH, sample and eluent volume, eluent nature and flow rates and effects of interfering ions, etc.

Effect of pH

The pH has a key role in the determination of U retained on MWCNTs because the changing the pH affects both the stability of the U and the MWCNTs surface morphology (e.g. protonation of the functional groups causing the sorption). The sorption competence of MWCNTs for U was strongly influenced by the initial pH of aqueous solution. Initially the effect of pH on the adsorption of U ions on MWCNTs was studied in the pH range of 1–7 for the U. The results regarding the pH effect on the adsorption yield of the U are shown in Fig. 1. When pH is lower (pH = 1), the functional groups on MWCNTs will be protonated and may not freely interact with U ions. At pH 5, due to deprotonation of the metal-binding sites, the negative charge density on the surface of MWCNTs increases resulting in the increase of attraction between metal ions and negative charge, which allows the sorption on the MWCNTs surface [7, 8, 14, 43]. It was observed that adsorption efficacy increased as pH was increased from 1 to 5. Maximum adsorption was observed at pH 5 and this was used for adsorption for U in column.

The absorbance of the A-III complex is dependent on pH. The optimum pH where maximum absorbance occurs is dependent on the ionic medium used. Finally after elution pH was maintained at 1.5 with HCl for spectrometric determination step as the U-(A-III) complex is stable at this pH [47].

Effect of sample volume

To get high enhancement factor, the effect of sample volume on U sorption in the solid phase extraction system was investigated by passing varying volume of solution containing 10 μg L^{-1} of U through MWCNTs under the optimum conditions. Uranium was recovered from different volumes of aqueous solutions of different concentrations. In this study, initial volume of the solution was selected as 400 mL. When the sample volume increases a gradual decrease in the recoveries can be seen, at 500 mL of sample volume only 82 % of recovery was obtained (Fig. 2). Final

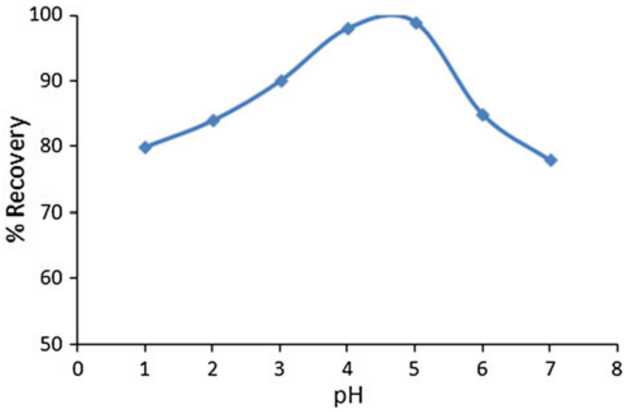

Fig. 1 Effect of pH on % recovery of Uranium

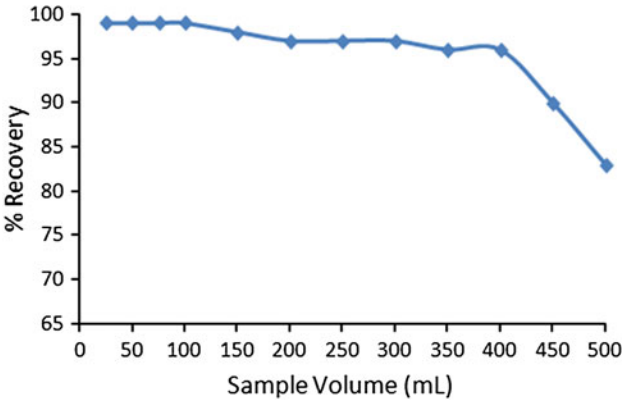

Fig. 2 Effect of sample volume (mL) on % recovery of Uranium

Table 1 Effect of eluents combination on desorption of U

Eluent$_{(\text{Acid Concentration}=1\text{ N})}$	Ratio	% Recovery
Methanol	–	70
Methanol+HCl	1:1	82
Methanol+HCl	1:2	91
Methanol+HCl	1:3	100
Methanol+HNO_3	1:1	79
Methanol+HNO_3	1:2	83
Methanol+HNO_3	1:3	91
Methanol+H_2SO_4	1:1	69
Methanol+H_2SO_4	1:2	78
Methanol+H_2SO_4	1:3	82

volume of the solution was considered as 10 mL, a 40-fold pre-concentration factor was obtained for the U. The results have shown that U can be quantitatively recover even from a small volume of solution while recovery greater than 96 % can be obtained from a solution volume of 400 mL.

Effect of type and volume of the eluent

Acidified methanol can be used for the quantitative elution of U retained in the column. Though, the recoveries were dependent on the nature and concentration of eluent. The elution of sorbed U, MWCNTs was also studied by using methanol, HCl, HNO_3 and H_2SO_4 of various concentrations in methanol. An aliquot of 100 mL containing 10 µg of U was taken in beaker and after the adjustment of its pH was passed through the column at optimum flow rate. Elution was carried out with HCl, HNO_3 and H_2SO_4 with methanol in different ratios. The results were given in Table 1. The recovery increased with the increase in concentration of the eluent. Quantitative recovery (100 %) of U was achievable while using a mixture of and 1 N HCl in methanol but declined when HNO_3 or H_2SO_4 were used in place of HCl. Maximum recovery was obtained when 10 mL of I N HCl with methanol in 1:3 was used as eluent (Fig. 3). Similarly another problem with HNO_3 as elutant is its high blank values in the spectrophotometric determination of U while using A–III.

Flow rates of sample and eluent

Sample solutions can be passed through the MWCNTs column at a higher flow rate without affecting the adsorption as a bulk volume of sample solution is required in solid phase extraction procedures. The effect of the flow rate of the sample and eluent solutions on the adsorption was examined in the wide range of 1–10 mL min^{-1}. The results are given in Fig. 4. The effect of flow rate of the sample solutions had no obvious effect on the adsorption of U at the range of 1–5 mL min^{-1}, while the case of eluent was quite different. At lower flow rate of eluent (1–3 mL min^{-1}), the recoveries were quantitative while at higher flow rates the recoveries decreased. Thus 5 mL min^{-1} was chosen as the flow rate of the sample and 2 mL min^{-1} for eluent solutions in the following experiments.

Effect of reagent concentration

Uranium reacts with A-III in a wide pH range to form a 1:1 complex [51]. The effect of A-III concentration on the absorbance of the complex was investigated with changing the volume of 0.1 % concentration. Effect of ligand was studied in the range of 200–1,000 µL; at 200 µL the recovery was about 85 % which increased with increasing the volume. It is clear from Fig. 5 that the maximum recovery was attained with 500 µL of 0.1 % A-III; above this volume up to 1,000 µL the absorbance remained

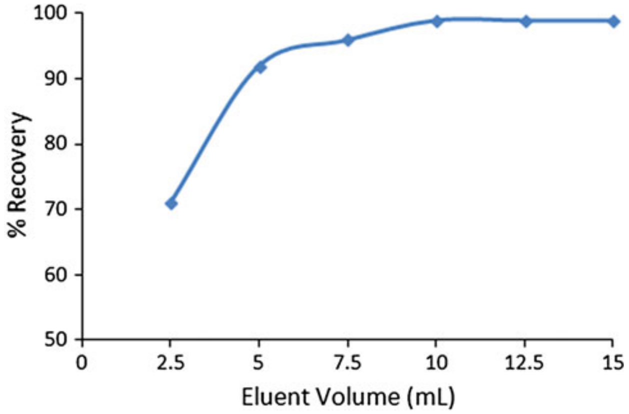

Fig. 3 Effect of eluent volume (mL) on % recovery of Uranium

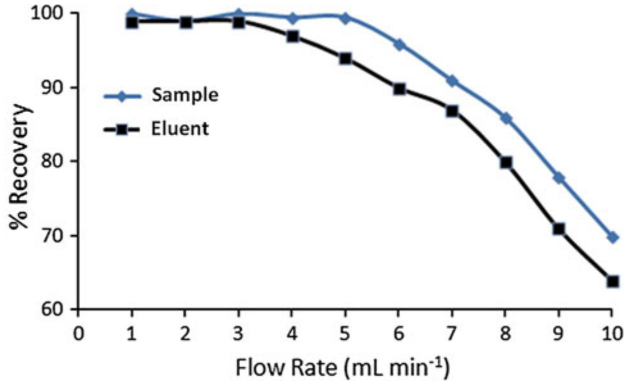

Fig. 4 Effect of flow rates of sample and eluent (mL min^{-1})

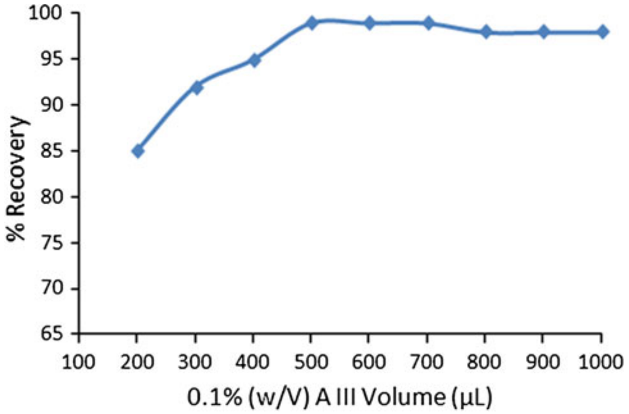

Fig. 5 Effect of 0.1 % (w/v) A-III volume (µL) on % recovery of Uranium

Table 2 Influence of interfering ions in the determination of U

Foreign ions	Amount (μg)	% Recovery
Na^+, Mg^{+2}	6000	99
Ca^{+2}	3000	99
Fe^{+3}, Al^{+3}, Cu^{+2}	2500	100
Ni^{+2}, Zn^{+2}, Mn^{+2}, Pb^{+2}, Co^{+2}, Cd^{+2}	1000	97
Th^{+4}	500	97
Cl^-	4000	100
F^-	3000	98
NO_3^-, CO_3^-	1000	100
PO_4^-, SO_4^-	500	100

Table 3 Accuracy of analytical method based on added/observed concentration of U (μg g^{-1}) in ore samples ($n = 5$)

Added	Observed	% Recovery
–	2.83 ± 0.02	–
2	4.85 ± 0.01	101
4	6.79 ± 0.04	99
6	8.71 ± 0.05	98

unchanged. Therefore, 500 μL of 0.1 % A-III was used in all further experiments.

Effect of diverse ions on the recovery

The tolerance for diverse ions on U determination was scrutinized separately by adding a rather higher concentration of different foreign ions. The probable interference expected from various ions, which may be present in mineral samples, was examined by adding them in the aqueous solutions of U and following the above discussed procedure. We found that a number of foreign ions were not interfering in the analysis of U even at higher concentrations and the recoveries were quantitative (Table 2).

Analytical features of the method

The accuracy of the proposed procedure was evaluated by U determination in ore sample solutions collected from Sivas region of Turkey. Ore samples were digested and spiked with a known amount of U. 10 mL of sample was taken in calibrated flask and the proposed procedure was applied.

Linear plot was obtained between the measured absorbance and the U concentrations. The concentration range of 6–250 μg L^{-1} of U was selected as linear calibration range. Pre-concentration factor of 80 is achievable if sample volume of 400 mL and eluent of 5 mL is passed through column. The detection limit (LOD) and quantification limit (LOQ) were 1.9 and 6.0 μg L^{-1}, respectively. The accuracy of our developed method was checked by determining U in samples by standard addition method (Table 3). Different authors have used different combinations of solid phases and detection procedures for U pre-concentration followed by determination. So far our proposed procedure for U pre-concentration and determination is simple, cost effective and quicker and additionally, analytical features of our proposed methods are comparable with them (Table 4).

Table 4 Figures of merits of comparable methods for U determination

SPE details	Detection	Linear range (μg L^{-1})	LOD (μg L^{-1})	Reference
Multiwalled carbon nanotubes (MWCNTs)	UV–Vis	–	–	[35]
Naphthalenemethyltrioctylammonium chloride modified with Arsenazo(III)	UV–Vis	0.5–6	0.045	[52]
Duolite XAD761	ICP-MS	–	4.5	[53]
Xylenol orange modified Silica	LIF*	–	0.1	[54]
8-hydroxyquinoline immobilized on surfactant coated alumina	UV–Vis	–	0.12	[55]
Polymer-based cartridge modified with 2-(2-benzothiazolylazo)-3-hydroxyphenol	UV–Vis	2–125	0.6	[56]
Silica gel functionalized with Sulfasalazine	UV–Vis	20–2,700	1.0	[57]
5,7-Dichloroquinoline-8-ol modified napthalene	UV–Vis	0.4–20	2.0	[58]
Ion-imprinted chitosan resin	UV–Vis	5.0–100	2.0	[59]
Geobacillus thermoleovorans, immobilized on an Amberlite XAD-4	UV–Vis	17.5–250	2.7	[60]
Multiwalled carbon nanotubes (MWCNTs)	UV–Vis	6–250	1.9	Present study

* *LIF* Laser induced fluorimeter

Conclusions

Though a number of different techniques have been reported for U determination, but our proposed procedure is relatively rapid, convenient, low cost, sensitive and selective for U determination at trace amount. Additionally, because of eliminating the synthesis and use of any complexing ligand in column for sorption has reduced the risk of contamination to a higher extent. Furthermore, the detection limit and relative standard deviation of our proposed method are better than those techniques which were developed earlier. The possible interference of foreign ions like, alkaline, earth alkaline and other ions was investigated and no prominent effect was encountered. The accuracy was authenticated by analyzing the spiked ore samples.

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