

Retention Profile of Selenium (IV) from Aqueous Media Containing Bromide Ions Employing Polyurethane Foams

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Abstract

A simple and accurate method for the quantitative retention of traces of selenium (IV) from aqueous media was developed employing polyurethane foams (PUFs). The dependences of selenium (IV) uptake by the unloaded and tributyl phosphate (TBP) plasticized PUFs on pH, salt effect, nature and concentration of surfactant, etc. was critically studied. The sorption data have followed Langmuir, and Dubinin - Radushkevich (D-R) type sorption isotherms. Thus, "a dual-mode" sorption mechanism involving both absorption related to "solvent extraction" and an added component for "surface adsorption" may be simultaneously present. The sorption and recovery percentage of selenium (IV) from fresh and natural water by the proposed loaded and unloaded foam columns were quantitatively achieved. The method was applied for the retention and recovery of selenium (IV) species spiked to fresh water employing PUFs packed columns.

Keywords: Selenium (IV), Polyurethane foam, Isotherms and Chromatographic separation

1. Introduction

Selenium is a naturally occurring trace element recognized for its unique intermediate properties between metals and non-metals (Iyengar, 1978, PP. 55 – 82; WHO, 1987). Selenium is distributed in nature in a relatively small concentration in rocks, coal and other fossil fuels. Volcanic eruption, smelting ceramics, and metallurgical operations, manufacture of pesticides, glass and electronic goods are also major sources of selenium in the environment (Shpira, 1971). Selenium enters into natural waters through seepage from seleniferous soils and industrial waste and liberated into soil through complex biogeochemical reaction forming organo selenium compounds (Sitting, 1976). Such class of compounds is more toxic than inorganic selenium compounds and absorbed by plants such as cabbage and mustard (Adriano, 1992). However, trace amounts of selenium have been found to be essential to maintain normal body metabolism (Sitting, 1976), since it takes part in the glutathione peroxidase enzyme etc., (Mertz, 1986). Selenium can also enhance our ability to protect against certain cancer and heart diseases (Holum, 1995).

The analytical applications of tri-n-butyl phosphate (TBP) immobilized PUFs in batch and column operation modes for the preconcentration and separation of trace metal ions have been initiated (Braun, 1985). Since then, several separations and preconcentration of inorganic species in aqueous media have been examined by the foams supported solvent extractants (El-Wakil, 1990, PP. 703 - 716; Palagyi and Braun, 1992; El-Shahawi, 1995, PP. 185 - 190; El-Shahawi, 1997, PP. 483 – 489). A series of organic reagents e.g., TBP, methyl isobutyl ketone, diethyl ether, isopropyl ether and ethyl acetate have been impregnated onto polyurethane foam membranes (Palagyi and Braun, 1992). The produced reagent foams have been used successfully for various analytical purposes (Oleschuk and Chow, 1996, PP. 1545 - 1554; Rzeszutek and Chow, 2001, PP. 265 - 271).

Recent years have seen an upsurge of interest in the application of liquid-solid separation technique for the chemical preconcentration and speciation, removal and subsequent determination of some toxic trace metal species in environmental samples (Ofomaja, 2010; Hosseini, 2009, PP. 807 - 812; Sanchez-Moreno, 2010, 716 - 723). Thus, the present paper describes convenient and low cost liquid-solid extraction procedures for the chemicals separation and subsequent determination of selenium (IV) in water samples employing unloaded and TBP loaded foams from aqueous bromide media. The script also discusses the extraction mechanism, the most probable equilibria and thermodynamic stability of the produced ion-associates on/in the solid sorbent.

2. Experimental

2.1 Reagents and materials

All chemicals used were of analytical reagent grade quality and were used without further purification. Doubly de-ionized distilled water was used throughout the work. Stock solutions (2 % v/v) of TBP were prepared by

dissolving the exact volume of each reagent separately in chloroform. Stock solution (1.00 mg mL^{-1}) of selenium (IV) was prepared by dissolving the appropriate weight of selenium oxide (SeO_2) in de-ionized water acidified with few drops of nitric acid (1.0 mol L^{-1}). Freshly diluted of selenium (IV) solutions were prepared by diluting the stock solution with water. Stock solutions (2 % v/v in benzene) of dioctyl phthalate (DOP) and tri-n-butyl phosphate (TBP) were used.

2.2 Apparatus

A Perkin Elmer (Lambda EZ – 210) double beam UV-VIS (190 – 1100 nm) spectrophotometer with 1 cm (path width) quartz cell was used for recording the electronic spectra and the absorbance of the test selenium (IV) complex. The absorbance of the organic extract of selenium (Marczenko, 1986) was measured with a single beam Digital Spectro UV-VIS RS Labomed, Inc spectrophotometer with glass cells (10 mm). An Orion pH-meter (model 9418) with glass and saturated Calomel electrode was used for the pH measurements. Glass columns (18 cm x 15 mm ID) were used in dynamic mode of extraction. A Lab-line Orbital mechanical shaker SO1 (UK) and a Soxhlet extractor were also used in batch experiments and for the foam purifications.

2.3 Reagent foam and PUFs packed column preparation:

The reagent foam cubes were prepared by mixing the dried foam cubes with chloroform containing TBP or DOP (2 % v/v) (10 mL g^{-1} dry foam) with efficient stirring for 30 min. The plasticized TBP or DOP reagent foam cubes were then squeezed and dried between two filter papers to remove the excess solution as reported (El-Shahawi and Nassef, 2003, PP. 29 - 39). The unloaded and reagent TBP or DOP loaded PUFs were packed in the glass columns by applying the vacuum method of foam packing as described earlier (Braun, 1985).

2.4 Determination of selenium (IV)

Selenium (IV) was determined by iodometry and/or spectrophotometry at wavelength 358 nm as follows: a 10 mL of aqueous solution containing selenium (IV) at concentration level $20 \text{ } \mu\text{g mL}^{-1}$ was adjusted to pH zero with few drops of HCl (2 M) and $\sim 0.2 \text{ g}$ of potassium iodide was then added. The solution was then swirled well and the released iodine was determined spectrophotometrically by 3, 3'- diaminobenzidine method [Marczenko, 1986].

3. Results and Discussion

3.1 Retention profile of selenium (IV) onto PUFs

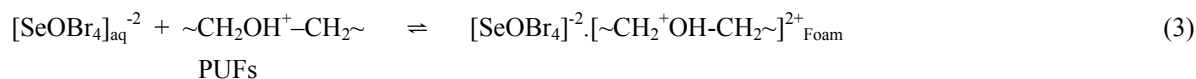
Preliminary investigation on the retention of selenium (IV) ions from the aqueous solution by the unloaded and the reagent TBP immobilized foams was found to depend on the aqueous solution pH. Thus, the sorption profiles of selenium (IV) ions at $10 \mu\text{g mL}^{-1}$ concentration level from the aqueous solutions (50 mL) at different pH and acidity by the unloaded or TBP-immobilized PUFs ($0.2 \pm 0.01 \text{ g}$) were critically investigated. After shaking the test solutions for 1 h, the concentration of selenium (IV) retained on the aqueous solution was then measured [Marczenko, 1986]. The data revealed that, the sorption profile of selenium (IV) by the unloaded and the foam immobilized with TBP foams decreased on increasing the solution pH and shows the highest sorption percentage at pH \sim zero. The decrease in the selenium (IV) uptake by the loaded foams at higher pH is most likely due to the instability or the hydrolysis of the produced complex species formed between selenium (IV) and the reagent immobilized foam.

The sorption profile of selenium (IV) ions by the unloaded was found less than that obtained with the TBP immobilized PUFs. The influence of HCl concentration on the uptake of selenium (IV) from the aqueous solution containing saturated KBr onto unloaded and TBP loaded foams was carried out. A sharp increase in the extraction of selenium (IV) sorption onto PUFs was achieved on increasing the HCl concentration up to 4.0 M. At acidity higher than 4.0 M, the extraction percentage of selenium decreased due to the degradation of the foam and the possible reduction of selenium (IV) to the elemental selenium which has no ability to form complex with the tested reagents. These results are in a good agreement with data reported elsewhere (El-Shahawi, 2005, PP. 806 - 815). Therefore, in the subsequent experiments, a solution of HCl (4.0 M) was used as an excellent extraction media for selenium (IV) sorption.

Moreover, the effect of KBr concentrations on the extraction of selenium (IV) on the unloaded and the immobilized TBP foam was investigated. The sorption of selenium (IV) increased as the concentration of KBr increased up to (2 M) and remained constant (Fig. 1). Thus, in the subsequent work KBr concentration (2.0 M) level was used in the extraction media. The retention of selenium (IV) onto PUFs cubes most likely proceeds as follow:

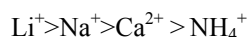


or



The influence of shaking time on the uptake of selenium (IV) from the aqueous media containing HCl (4 M) and KBr (2 M) was carried out employing the unloaded and the reagent TBP loaded PUFs. The sorption of selenium (IV) ions was slow at the initial stage and maximum equilibrium has reached constant values after 80 min shaking time. Maximum sorption was obtained from the extraction media containing HCl (4 M) and KBr (2 M) solution at shaking time ≥ 80 min. Thus, the actual sorption of $(\text{SeOBr}_4)^{-2}$ on the interior surface sites was found slow, and inter particle transport are the main predominating factors controlling the sorption rate (Farg, 2007, PP. 218 - 229). Consequently, 80 min shaking time were adopted in subsequent experiments.

The influence of various concentrations (0.01-0.05 % w/v) and cation size of the of alkali metal (Li^+ , Na^+ , Ca^{2+} and NH_4^+) chlorides on the uptake of selenium (IV) ions from the aqueous media containing HCl (4 M) and KBr (2 M) onto unloaded and TBP immobilized PUFs was studied. The results revealed no significance effect of cation concentration (Li^+ , Na^+ , Ca^{2+} and NH_4^+) as chloride salts on the equilibrium sorption of the tested selenium (IV) ions onto PUFs. The sorption profile of selenium (IV) more or less slightly increased in the following order:



This behavior is characteristics of "solvent extraction" mechanism with the salt acting as salting out. Thus, in the subsequent work the sorption procedures were carried out without salt addition. Similar trends were also obtained in solvent extraction of gold (I, III) ions by PUFs (Farg, 2007, PP. 218 - 229). On the other hand, the effect of some surfactants individually e.g. diallyl phthalate, sodium lauryl sulphate and Triton X-100 on the sorption of selenium (IV) onto unloaded and TBP loaded foam was carried out. A significant increase on the uptake of selenium (IV) onto unloaded and TBP loaded was noticed on the use of diallyl phthalate.

3.2 Sorption isotherms of selenium (IV) onto PUFs

The amount of selenium (IV) uptake from the bulk aqueous solution onto the unloaded and TBP immobilized foam was found to depend on its initial concentration and can be expressed in the form of its diffusion and thermodynamic behavior (Fig. 2). Therefore, the uptake of selenium (IV) from the aqueous solution onto the PUFs was subjected to Langmuir and Dubinin-Radushkevich (Somorjai, 1994) isotherms models. The Langmuir sorption isotherm based on the kinetic consideration is expressed in the following linear form (Somorjai, 1994):

$$C_e/C_{\text{ads}} = 1/Qb + C_e/Q \quad (4)$$

where, C_e is the equilibrium concentration (M) of selenium (IV) in solution, C_{ads} is the adsorbed selenium (IV) concentration onto the unloaded and TBP loaded foam, respectively per unit mass of sorbent at equilibrium (mmol g^{-1}), and Q and b are constants related to the maximum sorption capacity and the binding energy of solute sorption that is independent of temperature. Plots of C_e/C_{ads} versus C_e , are linear throughout the entire concentration range of selenium (IV). The sorption parameters Q and b for the adsorption process evaluated from the slopes and intercepts were found equal 0.06914 ± 0.002 , $0.0792 \pm 0.0029 \text{ mol g}^{-1}$ and 34.223, $38.73 \text{ dm}^3 \text{ mol}^{-1}$ for selenium (IV) sorption onto unloaded and TBP immobilized foam, respectively. The values of Q and b indicating good retention of selenium (IV) onto unloaded and TBP immobilized foam.

The sorption data were also subjected to Dubinin - Radushkevich (D-R) isotherm model (Somorjai, 1994) is postulated within the adsorption space close to the adsorbent surface. The D-R isotherm can be linearized as follows:

$$\ln C_{\text{ads}} = \ln K_{\text{DR}} - \beta C^2 \quad (5)$$

where, C_{ads} is the amount of selenium (IV) retained per unit mass of PUFs, K_{DR} is the maximum amount of selenium (IV) retained, β is a constant related to the energy of transfer of the solute from the bulk solution to the solid sorbent and C is Polanyi potential which is given by :

$$C = RT \ln (1+1/C_e) \quad (6)$$

where, R is gas constant in $\text{KJ mol}^{-1} \text{K}^{-1}$ and T is the absolute temperature in Kelvin. The plots of $\ln C_{\text{ads}}$ versus C^2 were found linear for unloaded and TBP loaded foam. The plots indicate that, the D-R isotherm model is obeyed for selenium (IV) sorption onto the unloaded and TBP loaded foam over the entire concentration range. The values of β and K_{DR} calculated from the slopes and intercept were found 0.0013, 0.0011 $\text{mmol}^2 \text{KJ}^2$ and 93.19, 93.042 $\mu\text{mol g}^{-1}$ for unloaded and TBP loaded foam, respectively. The mean free energy (E) of the transfers of one mole of solute from infinity to the surface of PUF was determined employing the equation:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (7)$$

The value of E was found in range of -17.8, -19.3 KJ mol^{-1} for unloaded and TBP loaded foam, respectively confirming the chemisorption onto the solid PUFs sorbent.

3.3 Chromatographic separation of selenium (IV)

The sorption of selenium (IV) from aqueous solutions onto unloaded and TBP loaded PUFs in batch experiments suggested the use of PUFs in column mode for complete extraction and recovery of selenium (IV) from aqueous solution. Columns (10 cm height and 12 mm ID) were packed with (3 ± 0.1 g) unloaded and TBP loaded foam and were successfully employed for the enrichment of selenium (IV). In these experiments, an aqueous solution (2 L) of doubly distilled water containing selenium (IV) at 5 and 10 $\mu\text{g mL}^{-1}$ level for unloaded and TBP loaded foam respectively, (4.0 M HCl and 2.0 M KBr) was percolated through the foam packed column at 5 mL min^{-1} flow rate. A separate blank experiment was also carried out by passing an aqueous solution (100 mL) free from selenium (IV) ions under the same experimental conditions through the unloaded and TBP loaded foam columns. Spectrophotometric determination of selenium (IV) in the effluent solution of loaded foam column against reagent blank indicated complete sorption of selenium (IV). The sample and blank columns were washed with an aqueous solution (100.0 mL) of HCl (4.0 M) - KBr (2.0 M). The sorbed chelate of selenium (IV) on/in the foam membrane was then recovered with chloroform (10 mL) at 2 mL min^{-1} flow rate. Satisfactory recovery ($\geq 96\%$) of the tested selenium (IV) ions was obtained by the proposed unloaded and TBP loaded foam columns.

The height equivalents to a theoretical plate (HETP) and the number of theoretical plate (N) were calculated from the breakthrough capacity curve (Braun, 1985). Representative results are shown in Fig. 3. The HETP and N values for selenium (IV) uptake onto unloaded and TBP loaded foams calculated from breakthrough curve were found equal 0.92, 13.03 and 0.763, 15.72, for unloaded and TBP loaded foam, respectively.

3.4 Performance of the PUFs packed column

The performance of the unloaded and TBP loaded foam column was also determined from the critical capacity and breakthrough capacity. The critical capacity was defined as the amount of selenium (IV) that could be retained on the unloaded and TBP loaded foam column at rate 2 mL min^{-1} until the selenium (IV) was first detected in the effluent solution. Practically, this value was found equal to the actual volume of the effluent solution collected just before first appearance of selenium (IV) in the effluent minus the free column volume. The S-shaped curve is shown in Fig. 3 represent i- the breakthrough volume and ii- the volume needed to reach bed saturation of selenium (IV). The critical capacities of selenium (IV) ions onto unloaded and TBP loaded foam column were found equal to 0.3 and 0.4 mg g^{-1} , respectively at 1.5 and 2 mL min^{-1} flow rate. The values of the breakthrough capacity (BC) of selenium (IV) uptake was calculated as reported (Ma, 2000, 191 - 196). The values of BC were found equal to 0.65, 0.78 mg g^{-1} for selenium (IV) sorption onto unloaded and TBP loaded foam respectively at 2.0 mL min^{-1} .

The applicability of the proposed method for quantitative collection and recovery of selenium (IV) from natural water was investigated on different samples. The tested sample was spiked with various selenium (IV) concentrations (5-10 $\mu\text{g mL}^{-1}$). A one liter water sample spiked with selenium (IV) was percolated through the PUF column at 1.5 and 2 mL min^{-1} flow rate at optimum conditions of selenium (IV) uptake. The retained selenium (IV) species on the foam column were then recovered by percolating a 20 mL of chloroform at 2-3 mL min^{-1} flow rate. The selenium (IV) content before and after extraction and also after recovery in elute was determined spectrophotometry.

4. Conclusion

The developed extraction procedures provide low cost and precise approach for selenium (IV) preconcentration in various water samples. It compares favorably with many preconcentration methods of selenium (IV) species. The sensitivity of the method could be improved to pico-molar level of selenium (IV) determination by on-line

prior preconcentration from large sample volumes onto TBP immobilized PUFs packed column followed by elution with suitable eluting agent. Work is still continuing on i. studying the on-line preconcentration of selenium (IV) and selenium (VI) after reduction of the latter to the tetra valence in natural water.

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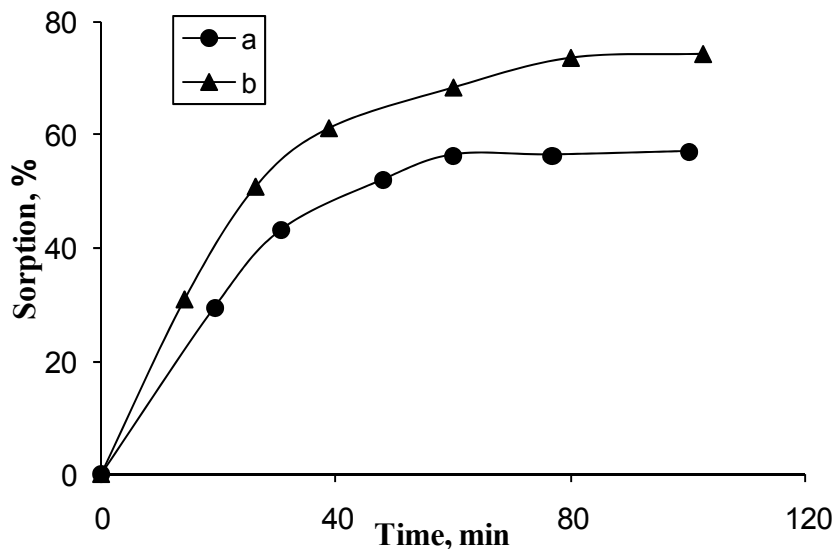


Figure 1. Influence of shaking time on the sorption of selenium (IV) from the aqueous solution onto the unloaded (a) and the TBP immobilized (b) PUFs from aqueous solutions containing HCl (4.0 M) and KBr (2.0 M)

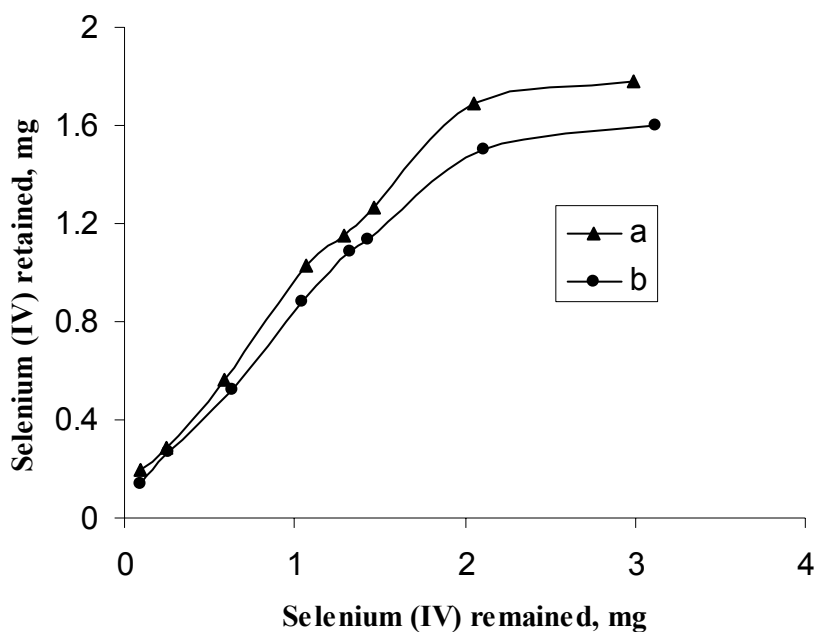


Figure 2. Sorption isotherms of selenium (IV) uptake onto the unloaded (a) and TBP immobilized (b) PUFs from aqueous solutions containing HCl (4.0 M) and KBr (2.0 M) at $25 \pm 1^\circ\text{C}$

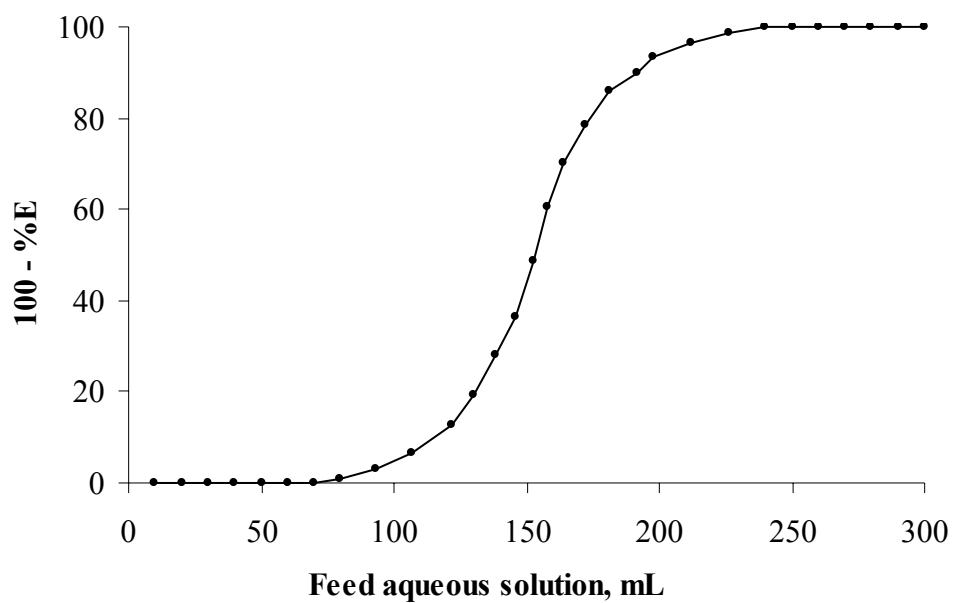


Figure 3. Breakthrough capacity curve of selenium (IV) uptake onto TBP loaded (b) PUFs (4.0 ± 0.01 g) packed columns at 5 ml min^{-1}