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Retention profile, kinetics and sequential determination of selenium(IV) and (VI) employing 4,4′-dichlorodithizone immobilized-polyurethane foams

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Abstract

Polyurethane foams (PUFs) loaded with the chromogenic reagent 4,4′-dichlorodithizone ($Cl_2H_2D_Z$) have been investigated for the quantitative retention, chemical speciation and sequential determination of traces of inorganic selenium(IV) and (VI) from aqueous media containing bromide ions. The retention profile of selenium(IV) onto the reagent loaded foam followed a dual-mode sorption mechanism involving both absorption related to “solvent extraction” and an added component for surface adsorption. The kinetics and thermodynamic characteristics of selenium(IV) uptake onto PUFs have been studied. The kinetics of selenium(IV) sorption onto PUFs was found fast, reached equilibrium in few minutes and followed a first-order rate constant in presence of bromide ions in the extraction media. The thermodynamic parameters, ΔH, ΔS and ΔG, indicated the exothermic and spontaneous nature of the sorption process. The sorption and the recovery percentages of inorganic selenium(IV) from fresh water by the proposed loaded foam columns were achieved quantitatively. The height equivalent to theoretical plate (HETP), the number of layers (N), breakthrough capacity and the critical capacity for selenium(IV) uptake onto $Cl_2H_2D_Z$ loaded foams columns were found to be 1.3, 103, 8.6 and 7.2 mg/g, respectively. The method was successfully applied for the chemical speciation and sequential determination of inorganic selenium(IV) and/or (VI) species spiked to fresh and industrial wastewaters.

Keywords: Selenium(IV) and (VI); $Cl_2H_2D_Z$; Kinetics; Sorption isotherms; Sorption mechanism; Thermodynamics; PUFs

1. Introduction

Selenium enters into natural waters through seepage from seleniferous soils and industrial waste and liberated into the environment (in soil) through complex biogeochemical reaction forming organoselenium compounds [1]. These compounds are more toxic than inorganic selenium compounds and absorbed by plants such as cabbage and mustard [2,3]. However, trace amounts of selenium have been found to be essential to maintain normal body metabolism [4], since it takes part in the glutathione peroxidase enzyme [4,5]. Selenium(IV) species can also enhance our ability to protect against certain cancer and heart diseases [6,7]. The maximum allowed tolerance limit of selenium is <0.1 mg/m^3 in air, <0.05 μg/ml in water and ≤80 μg/kg in soil [8].

Polyurethane foam (PUF) sorbent represents a cheap and efficient separation and preconcentration media with steadily increasing versatile application in inorganic species analysis [9,10]. Applications of PUFs are of great importance in overcoming many pollution hazards of inorganic pollutants by bringing them to an acceptable concentration in water and other media [9]. Selenium and tellurium have been sorbed from HCl and HBr media by polyether and polyester-based polyurethane foam [11].

Recently, a number of solid sorbents involving untreated and treated foamed plastics have been tested as supports in the reversed-phase extraction chromatography [12–22]. The broad range of surface functional groups present in the basic

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unit of PUF influences its retention properties and reactivity. PUF unloaded or immobilizing specific chromogenic reagents have been successfully employed on-line for the preconcentration, separation and determination of different inorganic species in natural and fresh waters and biological samples [15–19].

The present work is aimed at developing simple, convenient and low cost procedures for the preconcentration, chemical speciation and sequential spectrophotometric determination of inorganic selenium(IV) and (VI) ions in water employing the reagent 4,4′-dichlorodithizone ($Cl_2H_2D_Z$) immobilized PUFs. The kinetics and thermodynamic characteristics of the sorption step onto PUF are critically discussed. Several adsorption models will be used for the retention of randomly distribution sites of equal energy in which Freundlich and Langmuir adsorption isotherms are most commonly used. The mechanism of selenium(IV) sorption employing dithizone or dithizone analogues is a subject of contradictory opinions [23,24].

2. Experimental

2.1. Reagents and materials

All chemicals used were of analytical reagent grade and acids were used without further purification. A stock solution (1000 μg/ml) of $NaHSeO_3$ was prepared in double distilled water. A stock solution of the reagent $Cl_2H_2D_Z$ (0.1%, w/v) was prepared in 10 ml chloroform. The solution was kept refrigerated prior to use under acidified aqueous solution containing sulphuric acid (0.2 M) and sodium sulphate (0.1 M). Commercial white sheets of open cell polyether type PUFs (25 kg/m^3) were used. The foam cubes (10–15 mm edge) were cut from the foam sheets, washed, dried at 80 °C for 2 h [22] and finally stored in plastic bottles for further use. The reagent $Cl_2H_2D_Z$ loaded foam cubes were prepared by mixing the dried foam cubes with chloroform containing $Cl_2H_2D_Z$ at 0.02% (w/v) (50 ml/g dry foam) with efficient stirring in the presence of sulphur dioxide for 30 min and were dried as reported earlier [22]. The reagent $Cl_2H_2D_Z$ immobilized PUFs was found stable for up to 20 h. The $Cl_2H_2D_Z$ immobilized PUFs ($\simeq 4.0 \pm 0.01$ g) were packed in a glass column as reported earlier [22].

2.2. Synthesis of 1,5-di-(4-chlorophenyl)-3-mercaptoformazan ($Cl_2H_2D_Z$)

The reagent $Cl_2H_2D_Z$ was prepared by the nitroformazyl method [25]. The nitroformazan was recrystallized from ethanol, converted to 1,5-di-(4-chlorophenyl)-3-mercaptoformazan and finally purified by dissolution in chloroform. The chloroform extract was stripped with dilute sodium hydroxide solution (2%, w/v) and finally pouring the extract into sulphuric acid (0.5 M). The solid reagent was washed with ethanol until it became acid free, dried, dissolved in chloroform, precipitated with cyclohexane and finally dried in vacuum (mp 125 °C). Elemental analysis of $C_{13}H_{10}N_4SCl_2$—required: C = 53.2%, H = 3.4%, N = 19.1% and Cl = 24.2%; found: C = 53.9%, H = 3.5%, N = 19.4% and Cl = 25.1%.

2.3. Apparatus

A Soxhlet extractor and a lab-line Orbital mechanical shaker SO1 (UK) were used for the foam purification and batch retention experiments. Glass columns (18 cm × 15 mm i.d.) were used in the flow experiments. A single beam Digital Spectro UV–VIS RS Labomed, spectrophotometer with quartz cell (10 mm path length) and a pH meter model 3305 (JENWAY) were used for the absorbance and pH measurements of the test solutions, respectively.

2.4. General extraction procedures

2.4.1. Batch experiments

In a dry 100 ml polyethylene bottle, an accurate weight (0.5 ± 0.01 g) of the reagent $Cl_2H_2D_Z$ loaded foam cubes was shaken on a mechanical shaker for 2 h with 50 ml of an aqueous solution containing selenium(IV) ions at 5 μg/ml concentration level at 20 ± 0.1 °C and at the required pH adjusted by diluted HCl or NaOH. After phase separation, a 10 ml aliquot was assayed spectrophotometrically at 435 nm [23]. The amount of selenium(IV) retained on the foam cubes was determined from the difference between the absorbance of selenium(IV) solutions before (A_b) and after (A_f) shaking with the reagent $Cl_2H_2D_Z$ foam cubes. The extraction percentage (%E) and the distribution ratio (D) of the selenium(IV) uptake on the loaded foam were calculated employing the equations:

$$\%E = \left(\frac{A_b - A_f}{A_b}\right) \times 100 \quad (1)$$

$$D = \frac{\%E}{100 - \%E} \times \frac{v\,(\text{ml})}{w\,(\text{g})} \quad (2)$$

where v is the sample volume in milliliters and w is the weight of the reagent foam cubes in grams. Following these procedures, the kinetics, retention and thermodynamic studies were adopted. All experiments were performed in triplicate at ambient temperature (20 ± 0.1 °C). The results are the average of three independent measurements and the precision in most cases was ±2%. The expected statistical error in the %E and D calculations is within the range of ±2.4.

2.4.2. Column experiments

An aqueous solution (2–3 l) of tap, deionized or industrial wastewater samples spiked with selenium(IV) at 0.05–1 μg/ml level at the optimum experimental conditions was percolated through the foam (4.0 ± 0.01 g) packed column at 2.5 ml/min flow rate. Under these conditions sorption of selenium(IV) took place. The selenium(IV) content before percolation and in the effluent solution was measured at

435 nm against a reagent blank [23]. The sorbed selenium(VI) species on the foam column were then eluted with 20 ml chloroform at 3 ml/min flow rate and measured [23].

2.5. *Sequential determination of selenium(VI)*

Transfer an aliquot (10 ml) of the aqueous solutions containing 0.5–10 μg/ml of selenium(VI). The solutions were then reduced to selenium(IV) with HCl (6 M) by boiling for 15 min in a closed system (to avoid the evaporation of selenium species) and cooled as reported earlier [11]. The pH of the test solution was then adjusted to pH $\simeq$ 0–1 by few drops of saturated NaOH. The produced selenium(IV) solutions were diluted to 10 ml and analyzed as reported [23] via their standard curves prepared under the same experimental conditions.

3. Results and discussion

3.1. *Absorption spectra*

The electronic spectra of the reagents H_2D_Z, $Cl_2H_2D_Z$ and their selenium(IV) chelates in $CHCl_3$ are summarized in Table 1. The characteristic infrared (IR) frequencies of the solid reagents and their selenium(IV) chelates in chloroform and in parallelpiped PUFs are also included in Table 1. The electronic spectra of the reagents showed two well resolved absorption bands in the region of 454–429 and 615–627 nm, whereas their selenium(IV) chelates showed one well defined single band in the range 416–435 nm with a slight basochromic shift in the PUFs (420–440 nm). The introduction of chlorine atoms into the *para* positions of the two phenyl nuclei of dithizone analogue ($Cl_2H_2D_Z$) leads to a slight hypsochromic shift for the band at 429 nm and basochromic shift for the band at 627 nm compared to dithizone (Table 1). The molar absorptivity (ε) value at λ_{max} 627 nm decreased to 2.43×10^4 l mol^{-1} cm^{-1} and at 429 nm increased to 2.39×10^4 l mol^{-1} cm^{-1} for the reagent $Cl_2H_2D_Z$ compared to H_2D_Z in $CHCl_3$ (Table 1). Since the geometry of the complex $Se[(HD_Z)_2]\,Cl_2$ was found tetrahedral [23,24], the corresponding complex of $Cl_2H_2D_Z$ is most likely tetrahedral. This suggestion was also confirmed from the analytical data of the chelate $[SeC_{26}H_{18}S_2Cl_4]Cl_2$ given in Table 1 (required: C = 42.9, H = 2.5, N = 15.4 and S = 8.8; found: C = 42.8, H = 2.7, N = 15.5 and S = 8.04). The IR spectrum of the isolated solid complex was compared with the IR spectra of the selenium(IV) salt and the free reagent $Cl_2H_2D_Z$ recorded separately in KBr discs and as a mechanical mixture of selenium(IV) with the $Cl_2H_2D_Z$ in 1:2 molar ratio. The characteristic IR frequencies observed at 3436 (br), 1636 (s), 1487 (s) and 440 cm^{-1} are safely assigned to ν(N–H), ν(N–N), σ(N–H) + (–C=N–), ν(N–C–S) and ν(Se–Cl) [24], respectively.

Preliminary investigation has shown that the reagent $Cl_2H_2D_Z$ immobilized PUF forms a red colored complex with selenium(IV) in the aqueous solution containing HCl (4 M) and NaBr (2 M). The produced complex was easily retained from the aqueous solution onto the PUF cubes. The reagent foam combines both the selectivity of the chelating agent and/or the advantageous rapidity of kinetic process between trace metal ions in the aqueous phase and the chromofoam in the foam membranes. Thus, the analytical utility of this reaction for the separation, chemical speciation and sequential determination of inorganic selenium(IV) and (VI) was found possible in both static and dynamic modes.

3.2. *Retention profiles of selenium(IV) sorption onto $Cl_2H_2D_Z$ loaded PUF*

In the aqueous solution containing NaBr (2 M), the amount of selenium(IV) ions sorbed onto the reagent $Cl_2H_2D_Z$ loaded foams was found to depend on the solution pH. Therefore, the sorption profiles of selenium(IV) ions from the aqueous solution onto the reagent loaded foams were investigated at various pH 0–12. The sorption percentage of selenium(IV) decreased with increasing the solution pH and maximum uptake was achieved in the range of pH 0–2 indicating that the protonated active sites of PUF are more compatible sites for the sorption of the complex spices of selenium(IV). The decrease in the selenium(IV) uptake by the reagent loaded foams at pH > 2 is attributed to the instability of the complex formed between selenium(IV) and the reagent $Cl_2H_2D_Z$ and subsequent hydrolysis at higher pH. Thus, in the subsequent work, the solution pH was kept at pH 0–2.

In acidic medium (2 M HCl), the nitrogen atom of the amide (–NH–CO–O–) and/or oxygen atom of ether ($–CH_2–O–CH_2–$) groups of the PUF have strong tendency either to donate the loan pair of electrons to the central metal atom or to take the hydroxonium (H^+) ions to form

Table 1
Characteristic absorption IR (cm^{-1}) and electronic (nm) spectral data for the reagents H_2D_Z and $Cl_2H_2D_Z$ and their selenium(IV) chelate in KBr disc and chloroform, respectively[a]

Compound	Wavenumber (cm^{-1})				λ_{max} (nm)	$\varepsilon \times 10^{-4}$ l mol^{-1} cm^{-1}
	ν(N–H)	ν(N–N)	δ(N–H) + (–C=N–)	ν(N–C–S)		
$Cl_2H_2D_Z$	2942 (br)	2374 (w)	1504 (s)	1490 (s), 1450 (s)	627, 429	2.43, 2.39
H_2D_Z	2960 (br)	2365 (w)	1515 (s)	1505 (s), 1465 (s)	615, 454	3.58, 1.79
$Se(Cl_2HD_Z)_2Cl_2$	3436 (m), 3280 (s)	1636, 1580	1526	1487	416	9.01
$Se(HD_Z)_2Cl_2$	3215 (m), 3280 (m)	1610 (s), 1580 (s)	1513 (s)	1501 (s)	435	7.01

[a] s: strong, m: medium, w: weak, sh: shoulder and br: broad.

ammonium and hydroxyl ions, respectively, to neutralize the charge of the produced complex anion in the retention process [26]. The selenium(IV) ion in its complex is most likely not bonded directly to the active sites of the PUFs but it exists as an entity like quaternary ammonium salt. Thus, the most probable sorption mechanism of selenium(IV) from aqueous bromide media at pH < 2 onto $Cl_2H_2D_Z$ immobilized PUFs could be proceeded as follows [9,26]:

$$H_2SeO_{3(aq)} + 2H^+ + 2Cl^- \rightleftharpoons SeOCl_{2(aq)} + H_2O \quad (3)$$

$$SeOCl_{2(aq)} + 4Br^- \rightleftharpoons [SeOBr_4]^{2-}_{(aq)} + 2Cl^- \quad (4)$$

$$[SeOBr_4]^{2-}_{(aq)} + 2Cl_2H_2D_{Z(foam)} \rightleftharpoons [Se(Cl_2HD_Z)_2Br_4]^{2-}_{(foam)} + H_2O \quad (5)$$

The produced anionic complex of selenium $[Se(Cl_2H_2D_Z)_2Br_4]^{2-}$ on the PUFs is further interacted with the protonated urethane nitrogen (–NH_2COO–) and/or ether oxygen (–CH_2HO–CH_2–) linkages of the PUFs to form a complex ion associate with PUFs as follows:

Urethane group:

$$[Se(Cl_2HD_Z)_2Br_4]^{2-}_{foam} + -{}^{+}NH_2COO- \rightleftharpoons [Se(Cl_2HD_Z)_2Br_4]^{2-} \cdot [-NH_2COO-]^{2+}_{2(foam)} \quad (6)$$

Ether group:

$$[Se(Cl_2HD_Z)_2Br_4]^{2-}_{foam} + -CH_2{}^{+}HO-CH_2 \rightleftharpoons [Se(Cl_2HD_Z)_2Br_4]^{2-}_{foam} \cdot [CH_2HO-CH_2]^{2+}_{foam} \quad (7)$$

The pK_a values of protonation of ether oxygen and amide nitrogen are −3 and −6 [26], respectively. Thus, the ether groups of the PUFs in HCl (2 M) media are easily protonated as compared to the amide nitrogen and the interaction of $[Se(Cl_2H_2D_Z)_2Br_4]^{2-}$ species appears to be more stronger.

The influence of mineral acid, e.g., HCl, HNO_3, $HClO_4$ or H_2SO_4 (1 M), on the selenium(IV) uptake onto $Cl_2H_2D_Z$ immobilized PUFs indicated that the sorption is quantitative in HCl. The sorption percentage of selenium(IV) increases with increasing HCl concentration up to 4 M and in the presence of NaBr (2 M). Increasing the acidity (HCl) higher than 4 M has a negative effect due to the degradation of the foam and the possible reduction of selenium(IV) to elemental selenium. Therefore, in the subsequent experiments, a solution containing HCl (4 M) and NaBr (2 M) was selected as a sorptive medium for further extraction studies of selenium(IV).The results obtained are in a good agreement with the data reported elsewhere [11]. Thus, "solvent extraction" is the most probable mechanism for selenium(IV) uptake by the reagent $Cl_2H_2D_Z$ immobilized foams.

The effect of shaking time on the uptake of selenium(IV) at 10 μg/ml concentration from aqueous media by $Cl_2H_2D_Z$ loaded foams was carried out. The retention of selenite ions by $Cl_2H_2D_Z$ loaded foams was approximately slow and maximum equilibrium has reached a constant value in 2 h shaking time with the PUF and then leveled off with increasing time >2 h. Consequently, 2 h shaking time was adopted in the subsequent experiments. This conclusion was supported by the rate of selenium(IV) sorption by $Cl_2H_2D_Z$ loaded foams and the average half-life time ($t^{1/2}$) of equilibrium sorption as calculated from Fig. 1 was in the range 7.8 min.

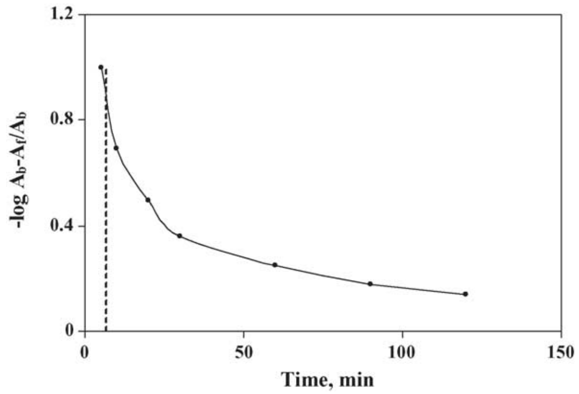

Fig. 1. Rate of sorption of selenium(IV) at 10 μg/ml concentration level onto $Cl_2H_2D_Z$ immobilized foams (0.5 ± 0.01 g).

The effect of the reagent $Cl_2H_2D_Z$ concentration (0.01–0.05%, w/v) immobilized onto the PUF on the extraction of selenium(IV) at concentration level 5 μg/ml was investigated. No significance effect on the sorption of selenium(IV) was observed. Thus, immobilized $Cl_2H_2D_Z$–PUFs of 0.02% (w/v) was selected in the subsequent retention experiments.

The effect of foam dose (w) and batch factor (v/m) on the retention of selenium(IV) at 10 μg/ml concentration level onto $Cl_2H_2D_Z$ loaded foams was also investigated. The sorption of selenium(IV) increased on increasing the foam dose up to 0.5 g of the reagent foam. Thus, in the subsequent work, 0.5 g loaded foam was employed. The extraction percentage of Se(IV) uptake by the reagent loaded foam decreased up to 45% extraction with increasing the sample volume from 25 to 500 ml.

The influence of cation (Li^+, Na^+, Ca^{2+}, Cs^+, K^+ and $NH_4{}^+$) size as metal chlorides and their concentrations on the sorption profile of selenium(IV) at 10 μg/ml concentration level onto the immobilized $Cl_2H_2D_Z$ foam was studied. The results showed no significance effect on the extraction of selenium(IV) in the presence of different concentrations of the salts. Thus, in the subsequent work, the sorption procedures were carried out without salt addition.

3.3. *Kinetic behavior of selenium(IV) sorption onto $Cl_2H_2D_Z$ loaded foams*

The kinetic behavior of selenium(IV) sorption onto $Cl_2H_2D_Z$ immobilized foams depends on two transport act in parallel, i.e., film diffusion and intraparticle diffusion, and the more rapid one will control the overall rate of transport. Thus,

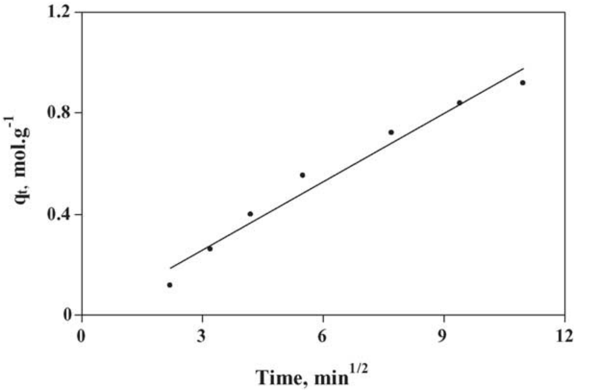

Fig. 2. The sorbed concentration of selenium(IV) onto $Cl_2H_2D_Z$ loaded foams vs. $t^{1/2}$ at 25 ± 0.1 °C.

the sorbed selenium(IV) concentration q_t (mol g^{-1}) at time t was plotted, versus $t^{1/2}$ to test the Weber–Morris equation [27]:

$$q_t = R_d(t)^{1/2} \tag{8}$$

where R_d is the rate constant of intraparticle transport in mmol g^{-1} min$^{-1/2}$. The plot of q_t versus $t^{1/2}$ was found linear (Fig. 2) up to 100 min and deviates as the shaking time increases. In the initial stage, the diffusion rate was slow and decreased with passage of time indicating that the adsorption rate is film diffusion controlled at the early stage of sorption in batch reactor. The value of R_d was computed from the slope of the Weber–Morris plot (Fig. 2). The line does not pass through the origin confirming particle film diffusion along with intraparticle diffusion [26]. The value of R_d was estimated to be 90 mmol g^{-1} min$^{-1/2}$ in good agreement with the data reported by Saeed et al. [28,29].

Moreover, the kinetic data were also determined from the mass action process, which assumes that the movement of selenium(IV) complex into the pores of PUFs is a diffusion process regardless of the mechanism used. This is achieved employing the Lagergren equation [29,30]:

$$\log(q_e - q_t) = \log q_e - \left(k\frac{t}{2.303}\right) \tag{9}$$

where q_e is the sorbed concentration of selenium(IV) onto PUF at equilibrium (mol g^{-1}) and k is the overall rate constant of the sorption process. The plot of $\log(q_e - q_t)$ versus time is shown in Fig. 3. The graph indicated that the process of adsorption is first-order reaction with respect to the adsorbed concentration [31] and the numerical value of the overall rate constant k was found equal to 0.012 min^{-1}.

The value of Bt, which is a mathematical function (F) of q_t/q_e, can be calculated for each value of F employing Reichenburg equation [32]:

$$\text{Bt} = -0.4977 - 2.303\,\log(1 - F) \tag{10}$$

A plot of Bt versus time (Fig. 4) at 25 ± 1 °C was found linear up to 60 min and the line does not pass through the origin as observed earlier [22]. This behavior was observed in

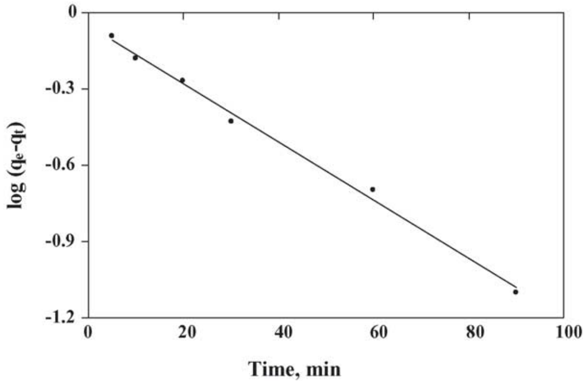

Fig. 3. Lagergren plot of the kinetics of the sorption of selenium(IV) at 10 μg/ml concentration level onto $Cl_2H_2D_Z$ loaded foams (0.5 ± 0.01 g) at 25 ± 0.1 °C.

the case of the Morris–Weber equation [27] test and indicated that a "particle diffusion" mechanism is not only operative for the kinetics of $[Se(Cl_2HD_Z)_2]Cl_2$ retention onto PUF. Therefore, the retention profile of the selenium(IV) chelate involves three steps: bulk transport of $SeOCl_2$ and/or $[SeOBr_4]^{2-}$ in solution, film transfer involving diffusion of these species within the pore volume of the PUFs and/or along the pore wall surface to an active sorption sites and finally formation of $[Se(Cl_2HD_Z)_2]Cl_2$. The actual sorption of $SeOCl_2$ on the interior surface site is slow; hence, it is the rate determining step. Thus, film and intraparticle transport are the main predominating factors controlling the sorption rate.

3.4. Sorption isotherm of selenium(IV)

The sorption profile of selenium(IV) from the bulk aqueous solution containing HCl (4 M) and NaBr (2 M) onto the $Cl_2H_2D_Z$ loaded foam was determined over a wide range of equilibrium concentration (5–100 μg/ml). The amount of selenium(IV) ions retained on the loaded foams is plotted versus their corresponding remaining concentration in the bulk aqueous phase. The data revealed that, at low or moderate

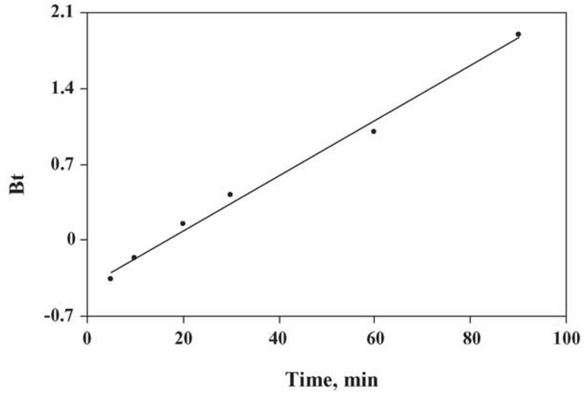

Fig. 4. Reichenburg plot of the kinetics of selenium(IV) uptake at 10 μg/ml concentration level onto $Cl_2H_2D_Z$ loaded foams (0.5 ± 0.01 g) at 25 ± 0.1 °C.

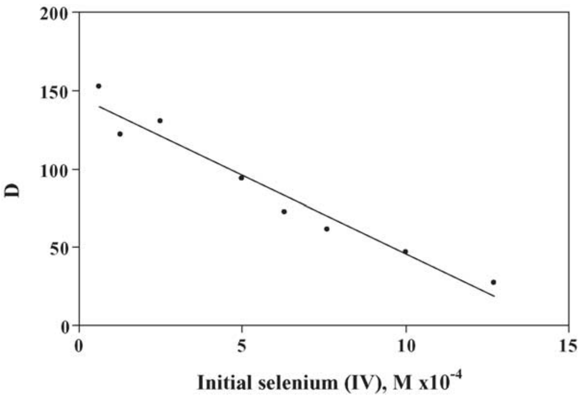

Fig. 5. Plot of the distribution ratio of selenium(IV) uptake onto $Cl_2H_2D_Z$ loaded foams (0.5 ± 0.01 g) vs. the initial concentration of selenium(IV).

selenium(IV) concentration, the amount of selenite ion retained on the $Cl_2H_2D_Z$ loaded foams varied linearly with the corresponding selenium(IV) concentration remaining in the aqueous solution. The equilibrium was approached from the direction that selenium(IV) rich reagent foams suggesting a first-order behavior. These results are in good agreement with data reported [28,29,31]. The extraction capacity of selenium(IV) from the sorption isotherm is relatively low (4.4 mg/g loaded foam) and the equilibrium is approached at low analyte concentration. The distribution ratio (*D*) decreased with increasing selenium(IV) concentration and the foam membranes became saturated with the retained species (Fig. 5). Thus, the *D* fell off as the saturation was approached and the diffusion of the solute through the hydrodynamic boundary layer took place in the sorption step. The most favorable D values were found for more dilute solutions. Thus, intraparticle transport and film diffusion may be the steps controlling molecular diffusion at the macropores of the PUF sorbent [29,30]. Therefore, “solvent extraction” is the most probable mechanism for selenium(IV) sorption from the aqueous solution by the reagent loaded foams.

Several models, e.g., Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherms [33–35], were used to describe the variation of the sorption data of selenite ions over a wide range of equilibrium concentrations onto PUFs. Based on the kinetic consideration, the familiar form of Langmuir sorption isotherm can be expressed in the linear form [33]:

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \qquad (11)$$

where C_e is the equilibrium concentration (M) of selenium(IV) in solution, C_{ads} the adsorbed selenium(IV) concentration onto the reagent loaded foams per unit mass of sorbent at equilibrium (mol g^{-1}), Q a constant related to the maximum sorption capacity of solute per unite mass of adsorbent required for monolayer coverage of the surface and b is an equilibrium constant related to the binding energy of solute sorption that is independent of temperatures. The plot of C_e/C_{ads} versus C_e shown in Fig. 6 strictly follows the adsorption model and is a linear graph throughout the entire concentration range of selenium(IV). The sorption parameters Q and b for the system evaluated from the slope and intercept of Fig. 6 were found equal to 0.013 ± 0.003 mol g^{-1} and 16 ± 1.0 dm^3/mol, respectively. The values of Q and b showed good retention of selenium(IV) ions onto the PUF.

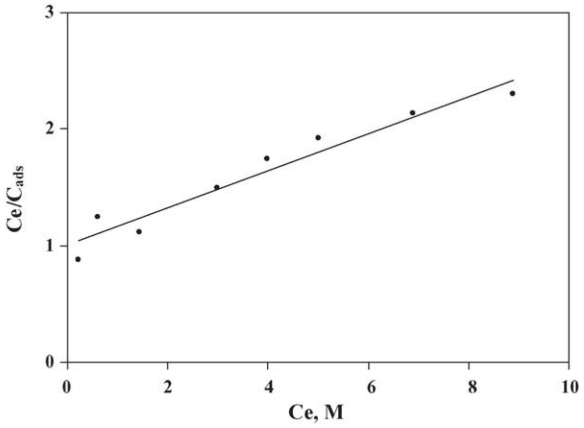

Fig. 6. Langmuir sorption isotherm of selenium(IV) uptake at various concentration levels onto $Cl_2H_2D_Z$ loaded foams (0.5 ± 0.01 g) at 25 ± 0.1 °C.

The sorption data were also subjected to Freundlich sorption isotherm [34] in the following form:

$$\log C_{ads} = \log A + \frac{1}{n} \log C_e \qquad (12)$$

where A and $1/n$ are Freundlich parameters related to the maximum sorption capacity of solute (mol g^{-1}). These parameters encompass maximum sorption capacity of solute (mol g^{-1}), the surface heterogeneity and the exponential distribution of active sites and their energies. The values of A and $1/n$ computed from the intercept and slope of the linear plot of $\log C_{ads}$ versus $\log C_e$ (Fig. 7) over the entire concentration of selenium(IV), were found equal to 0.024 mmol g^{-1}and 0.6, respectively. The value $1/n < 1$ indicates favored adsorption and that the sorption capacity is slightly reduced at lower equilibrium concentration. The isotherm does predict

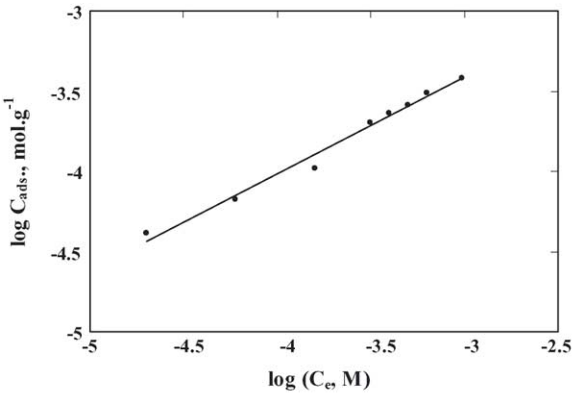

Fig. 7. Freundlich sorption isotherm of selenium(IV) uptake at various concentration levels onto $Cl_2H_2D_Z$ loaded foams (0.5 ± 0.01 g) at pH ∼ 1 and 25 ± 0.1 °C.

saturation of selenium(IV) onto the solid surface of the reagent immobilized PUF and the infinite surface coverage is predicted mathematically indicating a multilayer sorption of the surface.

The Dubinin–Radushkevich isotherm model [35] is postulated within adsorption space close to adsorbent surface to evaluate the sorption free energy and to get some information about the nature of bonding, i.e., either physicosorption or chemisorption. The D–R isotherm can be linearized as follows:

$$\ln C_{\mathrm{ads}} = \ln K_{\mathrm{DR}} - \beta \varepsilon^2 \qquad (13)$$

where K_{DR} is the maximum sorption capacity of selenium(IV) retained, β the activity coefficient constant related to the sorption free energy of the transfer of the solute from the bulk solution to the solid sorbent ($\mathrm{mol}^2\,\mathrm{kJ}^2$) and ε is polanyi potential which is given by the equation:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_{\mathrm{e}}}\right) \qquad (14)$$

where R is the gas constant ($0.0834\,\mathrm{kJ\,mol^{-1}\,K^{-1}}$) and T is the absolute temperature in Kelvin. The plot of $\ln C_{\mathrm{ads}}$ versus ε^2 shown in Fig. 7 is linear indicating that the D–R isotherm is obeyed for selenium(IV) sorption over the entire concentration range. The numerical values of K_{DR} and β calculated from the slope and the intercept were found equal to $25.32 \pm 0.23\,\mu\mathrm{mol\,g^{-1}}$ and $-0.0062 \pm 0.0005\,\mathrm{mmol^2\,kJ^2}$, respectively. Assuming the surface of the reagent foam is heterogeneous and an approximation to a Langmuir isotherm model is chosen as a local isotherm for all sites that are energetically equivalent, the quantity β related to the mean free energy (E) of the transfer of 1 mol of solute from infinity to the surface of PUF can be expressed by the equation:

$$E = \frac{1}{\sqrt{-2\beta}} \qquad (15)$$

The value of E was found within the range of 2.9 ± 0.1 kJ/mol confirming solvent extraction and physical sorption of selenium(IV) complex onto PUF (Fig. 8).

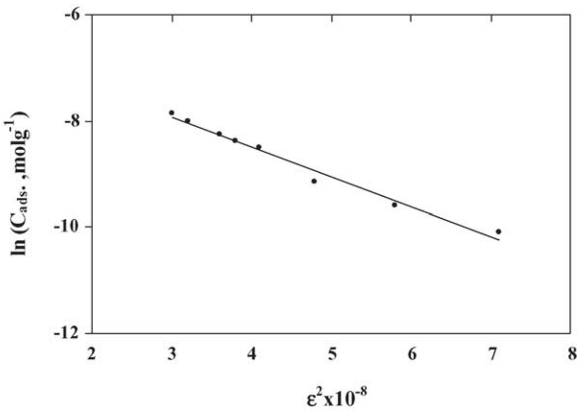

Fig. 8. Dubinin–Radushkevich (D–R) sorption isotherm of selenium(IV) uptake at various concentration level onto $\mathrm{Cl_2H_2D_Z}$ loaded foams (0.5 ± 0.01 g) at pH ∼ 1 and $25 \pm 0.1\,^{\circ}\mathrm{C}$.

3.5. *Thermodynamic characteristics of selenium(IV)*

The sorption behavior of selenium(IV) onto the reagent $\mathrm{Cl_2H_2D_Z}$ immobilized foams was critically investigated at 22, 40 and 60 °C to determine the nature of the retention step of selenium(IV) by the PUF at 10 μg/ml level aqueous sample (100 ml) and the optimum experimental conditions. The thermodynamic parameters of selenium(IV) uptake have been evaluated employing the equations:

$$\ln K_{\mathrm{c}} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \qquad (16)$$

$$\Delta G = \Delta H - T\,\Delta S \qquad (17)$$

$$\Delta G = -RT\,\ln K_{\mathrm{c}} \qquad (18)$$

where ΔH, ΔS and ΔG are the enthalpy, entropy and Gibbs free energy changes, respectively, and K_{c} is the equilibrium constant depending on the fractional attainment (F_{e}) of the sorption process of selenium(IV) onto the $\mathrm{Cl_2H_2D_Z}$ immobilized PUFs at equilibrium. The plots of $\log K_{\mathrm{c}}$ and $\log D$ versus $1/T$ were found linear (Fig. 9) over the entire range of temperature (295–333 K). The numerical values of ΔH and ΔS as calculated from the slope and intercept of $\log K_{\mathrm{c}}$ versus

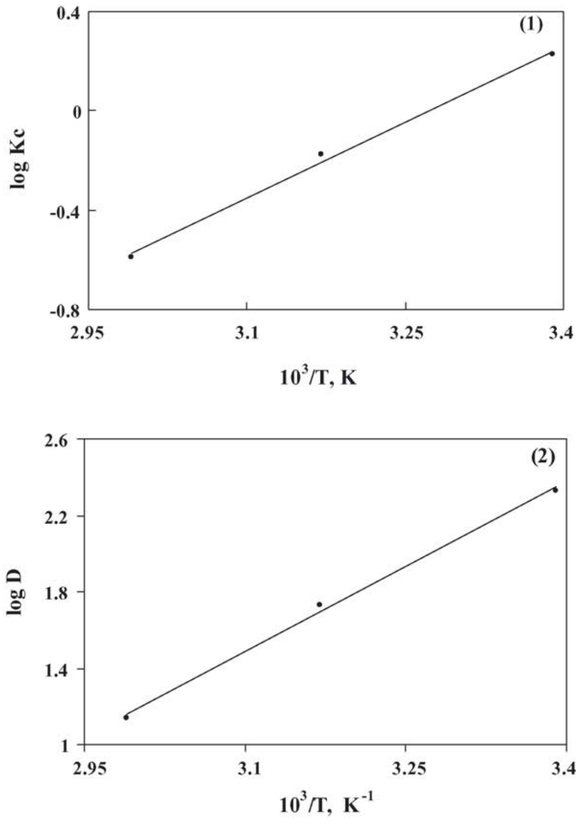

Fig. 9. Plots of equilibrium constant, K_{c} (1), and distribution coefficient, D (2), vs. $1/T$ (K^{-1}) for the sorption of selenium(IV) at 10 μg/ml concentration level from aqueous solution onto $\mathrm{Cl_2H_2D_Z}$ loaded foams (0.5 ± 0.01 g).

$1/T$ (Fig. 9) were found equal to −17.1 and −55.8 kJ/mol, respectively. The negative value of ΔH and the data of K_c and D given in Fig. 9 reflect the exothermic behavior of selenium(IV) uptake from the aqueous solution by the PUFs and non-electrostatic bond formation between the adsorbent and the adsorbate. Similarly, the negative value of ΔS may be indicative of the slow sorption of $Se(Cl_2HD_Z)_2Cl_2$ chelate and ordering of ionic charges without a compensatory disordering of the complex sorbed onto the active sites of the PUF [13]. The negative value of ΔS of selenium(IV) sorption indicates that the freedom of motion of selenium(IV) is more restricted in the foam membrane than in solution. Since the sorption process involves a decrease in free energy, the ΔH is expected to be also negative, which is confirmed by the data obtained. Furthermore, as the temperature increases, the physical structure of membrane may be changing which can affect the strength of the intermolecular interactions between the foam membrane and selenite ions. For example, the higher temperature may cause the membrane matrix to become more unstructured and affect the ability of the polar segments to engage in stable hydrogen bonding with selenite ions, which would result in a lower extraction. The negative value of ΔG (−566 kJ/mol) at 295 K, with a correlation factor of 0.9956, indicates spontaneous and physicosorption nature of retention onto PUF. The increase in the ΔG value with temperature may be due to the spontaneous nature of sorption and is more favorable at low temperature confirming the exothermic sorption process. These results and the flow characteristics of the PUF suggest the possible use of the reagent loaded PUFs in column operations for the enrichment and separation of inorganic selenium(IV) and (VI) species from large sample volumes of water.

3.6. Chromatographic behavior of selenium(IV) retention onto $Cl_2H_2D_Z$ loaded PUFs

Columns packed with $Cl_2H_2D_Z$ loaded foams were successfully employed for the separation of selenium(IV). In these experiments, aqueous solutions (2–3 l) of double distilled water containing selenium(IV) at 0.05–1 μg/ml concentration level, HCl (4 M) and NaBr (2 M) were percolated through the foam packed column at 2.5 ml/min flow rate. A separate blank experiment was also carried out. Analysis of selenium(IV) in the effluent solution of the loaded foam packed column after shaking with $CHCl_3$ [24] against a reagent blank indicated complete sorption of selenium(IV). The sorbed selenium(IV) chelate on the foam membrane was then recovered from the foam column with chloroform (20 ml) at 3 ml/min flow rate. Satisfactorily recovery percentages (≥95%) of the tested selenium(IV) ions were obtained by the proposed loaded foam columns.

The column performance was calculated from the values of height equivalent to theoretical plate (HETP) and N estimated from the breakthrough capacity curve. Thus, aqueous feed solution (5 l) containing selenium(IV) at 0.05 μg/ml concentration level in HCl (4 M)/NaBr (2 M) was percolated through the loaded foam column at 5 ml/min. The S-shaped curve (Fig. 10) represents: (i) the breakthrough volume and (ii) the volume needed to reach bed saturation of selenium(IV). It is clear that the raising position in the curves has a large shape, indicating a high transfer rate of selenium(IV) sorption in the membrane forming the skeleton of the foam material and a high rate of equilibrium attainment between the analyte and the reagent immobilized foams. The HETP and N values for selenium(IV) uptake onto $Cl_2H_2D_Z$ loaded foams were calculated from the breakthrough curve (Fig. 10) employing equation [19]:

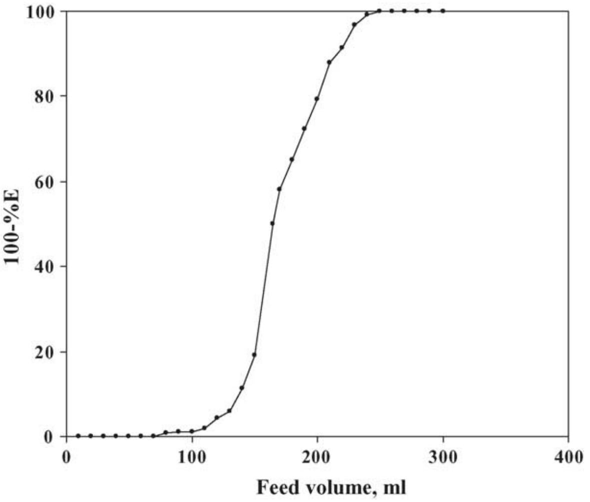

Fig. 10. Breakthrough curve of selenium(IV) uptake at 0.05 μg/ml concentration level from aqueous solution onto $Cl_2H_2D_Z$ immobilized foam (4 ± 0.01 g) packed column at 5 ml/min.

$$N = \frac{V_{50}V'}{(V_{50} - V')^2} = \frac{L}{\mathrm{HETP}} \in \qquad (19)$$

where N is the number of theoretical plates, V_{50} the volume of the effluent solution at center of the S-shaped of the breakthrough curve where the concentration is one-half the initial concentration, V' the volume at which the effluent solution has a concentration of 0.1578 of the initial concentration and L is the length of the foam bed in millimeters. The values of HETP and N were found equal to 1.3 ± 0.1 mm and 103 ± 4, respectively.

The analytical performance of the $Cl_2H_2D_Z$ loaded foam column was also determined from the values of N, HETP, critical and breakthrough (BC) capacities [9,36]. The critical capacity of selenium(IV) ions onto $Cl_2H_2D_Z$ loaded foam column was found equal to 7.2 mg/g at 2.5 ml/min flow rate. The BC of selenium(IV) onto $Cl_2H_2D_Z$ loaded foam was calculated employing the equation [35]:

$$\mathrm{BC} = \frac{V_{50}C_o}{m}\ (\mathrm{mg/g}) \qquad (20)$$

where C_o is the initial concentration (μg/l) of selenium(IV), V_{50} the feed volume (ml) at 50% extraction and m is the mass (g) of the dry foam beds in foam column which was found equal to 8 mg/g for selenium(IV) sorption onto loaded foams at 2.5 ml/min (Fig. 10). This value is quite good as compared to other solid support like Voltalef, silica gel and solid inorganic ion exchanger column [36,37].

3.7. Effect of diverse ions

To assess the selectivity of the proposed reagent $Cl_2H_2D_Z$ immobilized PUFs, the uptake of selenium(IV) at 5–20 μg/ml concentration level from an aqueous solution (50 ml) under the optimum experimental conditions was critically investigated in the presence of some diverse ions. It was found possible to preconcentrate accurately 5–20 μg/ml of selenium(IV) in the presence of up to 500 mg/l of the following ions: $PO_4{}^{3-}$, $N_3{}^{-}$, Mg^{2+}, Ca^{2+}, Cr^{6+}, Na^{+}, K^{+}, Li^{+}, $NH_4{}^{+}$, F^{-}, Cl^{-}, Br^{-}, Al^{3+}, Te^{6+}, Se^{6+}, $WO_4{}^{2-}$, Cr^{3+} and Te^{4+}. In the presence of the ions Cu^{2+}, V^{4+}, Fe^{3+}, $MnO_4{}^{-}$ and $NO_3{}^{-}$ at 100 μg/ml concentration level, the uptake of selenium(IV) was not complete. In case of the ions Cu^{2+}, V^{4+} and Fe^{3+}, simple modifications of the sample solutions involving addition of 0.50 ml of EDTA (0.1 M) and NaF (0.1 M) were introduced to obtain complete sorption of selenium(IV). The addition of NaN_3 removed completely the interference of $KMnO_4$.

3.8. Applications

3.8.1. Removal of inorganic selenium(IV) and/or (VI) in water

The feasibility of the proposed foam method for the collection and recovery of selenium(IV) and/or (VI) and total inorganic selenium(IV) and (VI) after prior reduction of Se(IV) to (VI) from natural and tap water was investigated on five different fresh, natural and wastewater samples. A 1 l of natural water sample spiked with selenium(IV) and/or selenium(VI) at various concentrations (5–10 μg/l) was percolated through the reagent PUF packed column at 2.5 ml/min flow rate at the optimum conditions. Selenium(IV) was quantitatively retained while selenium(VI) was passed through the column without sorption. The retained selenium(IV) species on the foam column were then recovered with 25 ml chloroform at 3 ml/min flow rate and measured [24]. Selenium(VI) was also retained after its prior reduction to selenium(IV) with HCl (6 M) as described [24], recovered with chloroform and determined [11]. In the preconcentration of total inorganic selenium(IV) and (VI), the spiked water samples were initially reduced to selenium(IV) by HCl (6 M). The produced selenium(IV) solution was quantitatively retained on the reagent foam column at 3 ml/min. Good recovery (95–98%) of the retained selenium(IV) species was then obtained. The method is possible to achieve excellent accuracy even in samples with high content of dissolved solids.

3.8.2. Sequential spectrophotometric determination of selenium(IV) and/or (VI)

The validity of the proposed method for the sequential determination of selenium(IV) and (VI) in water was also investigated. An aqueous sample solution (100 ml) spiked with selenite and/or selenate ions at a total concentration of 1–10 μg/ml, HCl (4 M) and NaBr (2 M) was percolated through $Cl_2H_2D_Z$ immobilized foams packed column at 2.5 ml/min. Only selenium(IV) was quantitatively retained as indicated from the analysis of selenium(IV) in the effluent versus reagent blank [23]. The retained selenium(IV) species were quantitatively recovered with chloroform (20 ml) at 2–3 ml/min. The recovered extract was transferred to a 50 ml conical flask containing anhydrous sodium sulphate (1 g). The flask was swirled to mix the contents and the free $Cl_2H_2D_Z$ was then removed from the combined extracts by shaking with dilute solution (10 ml) of NH_3 (two drops of concentrated NH_3 solution in 25 ml of water). The organic extract was then shaken with dilute acetic acid (0.2%) and the chloroform extract was transferred to a 50 ml volumetric flask. The solution was made up to the mark with chloroform. The absorbance of the organic extract was then measured at 435 nm against a reagent blank with the aid of standard curve. Satisfactory results with average recoveries in the range 98 ± 3.2% were obtained for the spiked selenium(IV). Selenium(VI) was also determined by the proposed reagent $Cl_2H_2D_Z$ after prior reduction to selenium(IV) by HCl (6 M). The results (99.6 ± 1.2%) revealed good agreement with the data obtained by the standard dithizone method [23,24].

4. Conclusion

PUF sorbent immobilized with $Cl_2H_2D_Z$ offers unique advantage over granular sorbent in rapid separation and sequential determination of inorganic selenium(IV) and (VI) after reduction to selenium(IV) in extremely dilute aqueous solution (ppb level) by flow mode from fluid water samples. The thermodynamic data confirmed the exothermic nature of selenium(IV) sorption onto the $Cl_2H_2D_Z$ immobilized PUFs. The kinetic data confirmed the intraparticle diffusion process and the first-order model for the sorption step. The results provided a deeper insight into the kinetics and sorption mechanism of selenium(IV) by PUFs. The great potentialities of PUF membranes are attributed to their inexpensiveness and large scale of availability all over the world in many industrial applications. However, work is still continuing for the chemical separation and determination of inorganic and organoselenium(IV) and (VI) species in real samples by solid-phase spectrophotometry. Other study will involve the possible application of on-line preconcentration and determination of selenium(IV or VI) by AAS.

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