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Chromatographic Separation, Total Determination and Chemical Speciation of Mercury in Environmental Water Samples Using 4-(2-Thiazolylazo) Resorcinol-Based Polyurethane Foam Sorbent-Packed Column

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Abstract

A simple method has been developed for quantitative retention of traces of mercury(II) ions from aqueous media using polyurethane foams (PUFs) loaded with 4-(2-thiazolylazo) resorcinol (TAR). The kinetics and thermodynamics of the sorption of mercury(II) ions onto PUFs were studied. The sorption of mercury(II) ions onto PUF follows a first-order rate equation with $k = 0.176 \pm 0.010 \text{ min}^{-1}$. The negative values of ΔH and ΔS may be interpreted as the exothermic chemisorption process and indicative of a faster chemisorption onto the active sites of the sorbent. The sorption data followed Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models. The D-R parameters β , K_{DR} and E were $0.329 \text{ mol}^2 \text{ kJ}^{-2}$, $0.001 \text{ } \mu\text{mol g}^{-1}$ and $1.23 \pm 0.07 \text{ kJ/mol}$ for the TAR-loaded PUFs, respectively. An acceptable retention and recovery ($99.6 \pm 1.1\%$) of mercury(II) ions in water at $\leq 10 \text{ ppb}$ by the TAR-treated PUFs packed columns were achieved. A retention mechanism, involving absorption related to “solvent extraction” and an “added component” for surface adsorption, was suggested for the retention of mercury(II) ions by the used solid phase extractor. The performance of TAR-immobilized PUFs packed column in terms of the number (N), the height equivalent to a theoretical plate (HETP), the breakthrough and critical capacities of mercury(II) ion uptake by the sorbent packed column were found to be 50.0 ± 1.0 , $1.01 \pm 0.02 \text{ mm}$, 8.75 and 13.75 mg/g , respectively, at 5 mL/min flow rate.

Keywords: retention of mercury(II) ions, polyurethane foams sorbent, 4-(2-thiazolylazo) resorcinol (TAR), separation mechanism, column chromatography

1. Introduction

Pollution by trace and ultra-trace concentration of heavy metal ions (e.g. mercury, lead, cadmium, arsenic, etc.) in our surroundings (air, soil and water) is an environmental concern due to their toxic effects and accumulation throughout the food chain, leading to serious ecological and health problems [1]. Mercury among the most toxic heavy metals commonly found in the global environment such as lithosphere, hydrosphere, atmosphere and biosphere [1, 2]. It is highly toxic to living cells and a bioaccumulative toxin that attacks the central nervous and endocrine systems [3]. Excessive prolonged exposure to mercury can cause brain damage and, in extreme cases, death [3]. The maximum concentration of mercury in drinking water recommended by the World Health Organization (WHO) is 1 ppb [4]. It can exist in three oxidation states (0, I, II) and all are able to combine with most inorganic and organic ligands to form various complexes e.g. HgX_4^{-2} (where X = Cl, Br and I) and methyl mercury [5, 6]. Mercury compounds are mutagenic and teratogenic in nature [7], and organomercury ones are more toxic than inorganic complex species of mercury(I) or mercury(II).

Techniques for mercury removal include traditional precipitation and coagulation, ion-exchange, solvent extraction, ultra filtration, and adsorption [8]. In recent years, a great deal of attention has been paid to the determination of trace and ultratrace concentrations of mercury by accurate, low-cost and reliable methods without any complicated sample preparation [9]. The most common techniques in analysis of natural water samples are stripping voltammetry [10], gas chromatography [11], spectrophotometry [12, 13], X-ray fluorescence spectrometry [14], and dual-wavelength β -correction spectrophotometric determination and speciation of mercury(II) ions in water using chromogenic reagent 4-(2-thiazolylazo) resorcinol [15].

Polyurethane foams (PUFs) and foams immobilized with supporting solvent extractants, chelating agents, liquid ion exchangers, anchored extracting groups and powdered ion exchangers sorbents have been reported for pre-concentration and separation of various inorganic and organic species from different media [16–22]. The most distinctive features of PUFs as solid sorbents are their membrane-like structure which differentiates them from others [20–22]. The foam membranes act as sorbents, i.e. the ions and/or molecules to be separated or pre-concentrated are retained on/in the membrane-like structure of the foams as shown in **Figure 1** [17–19]. The volume-to-surface ratio of quasi-spherical membrane geometry in comparison with cylindrical or planar one are the most advantageous characteristics of PUFs. Moreover, the PUFs membranes offer a wider range of chemical modifications than normal bulky (granular) solids [17, 20]. The potentialities of the PUF solid quasi-spherical membrane geometry sorbent have been reported [21, 22].

Open cell PUFs are a broad class of polymers having urethane moieties [22–25]. This class of polymers represents one of the most important three-dimensional (3D) products commercially available for fabricating super hydrophobic adsorbents for many organic and inorganic complex species [24–31]. They have excellent hydrophobicity and oleophilicity required for solid phase absorbents for various polar and non-polar species [25–32]. Commercial PUFs also exhibit poor hydrophobicity to some extent, as required for their practical use for clean-up and recovery of organic (e.g. oil spill) and inorganic species [33–39]. Hence, surface

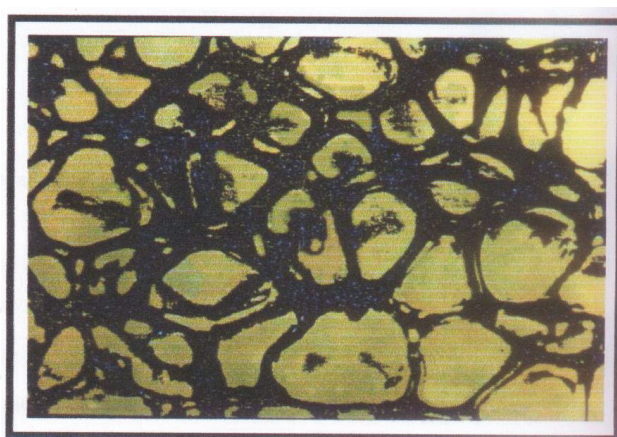


Figure 1. Typical microscopic picture of PUFs.

modification of PUFs is desired to enhance the wettability and hydrophobicity to make it a super hydrophobic and oleophilic absorbent [25–34]. Furthermore, the emergence of nano-materials with excellent properties (particle size and surface area) also makes them ideal for being coupled with PUFs as a model platform towards a target species [37–41].

Recently, much attention has been paid towards thiazole azo compounds as they are sensitive chromogenic reagents and good indicators in acid–base titrations in addition to their being important complexing agents for trace metal ions in aqueous media [10, 40–47]. In continuation to our previous data on the retention of trace metal ions from aqueous media [23, 25, 26], the overall objectives of this chapter are to study: (i) the sorption profile of mercury(II) ions from aqueous media using PUFs physically immobilized with the reagent 4-(2-thiazolylazo) resorcinol (abbreviated as TAR, **Figure 2**) as low-cost solid phase extractor; (ii) the kinetic, thermodynamic and sorption models and mechanism of mercury(II) ion uptake by the used PUF sorbents physically treated with TAR; (iii) chromatographic separation of mercury(II) ions from aqueous media by TAR-immobilized PUF packed column; (iv) a simple, low-cost and precise method based upon TAR-PUF sorbent packed column for separation and sequential determination of mercury(II) ions at ultra-trace level in water; and (v) assigning the most probable retention mechanism of mercury(II) ion retention by the used SPE from aqueous media.

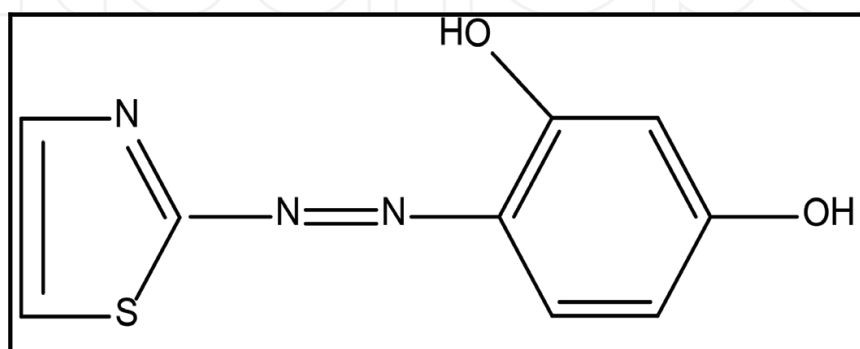


Figure 2. Chemical structure of 4-(2-thiazolylazo) resorcinol, TAR.

2. Experimental

2.1. Reagents and materials

Most of the chemicals were provided by Merck (Darmstadt, Germany). All chemicals were of analytical grade and used without further purification. All solutions were prepared in doubly de-ionized water and kept in a refrigerator. Plastic and glassware bottles were cleaned by soaking in dilute HNO₃ (10% w/v) and subsequently rinsed with distilled water prior to use. Working solutions (1–100 µg mL⁻¹) of mercury(II) ion were freshly prepared from the stock solution of mercury chloride (HgCl₂) (1000 µg mL⁻¹). Britton-Robinson buffers (pH 2–11) were prepared by mixing equimolar concentrations of acetic acid, phosphoric acid and boric acid (0.04 mol L⁻¹), and pH adjusting with NaOH (0.2 M) as reported [48].

2.2. Apparatus

A Perkin Elmer Elan DRC II ICP-MS system (USA) was used under the optimal default conditions. A Perkin Elmer ICP-OES system (Optima 4100 DC Shelton, CT, USA) was operated at the optimum operational parameters for mercury determination (Table 1). A Corporation Precision Scientific mechanical shaker (Chicago, CH, USA) with shaking 10–250 rpm and glass columns (15 cm × 10 mm i.d) (Figure 3) were used, respectively. pH measurements were done with a Thermo Fisher Scientific Orion model 720 pH meter (Milford, MA, USA), and de-ionized water obtained from a Milli-Q Waters Plus system (Milford, MA, USA). A digital micropipette (Volac) was used for solution preparation.

2.3. Preparation of TAR-immobilized PUFs

PUFs cubes (10–15 mm edge) were cut from commercially available white foam sheets, washed and dried as directed previously [25]. TAR reagent in ethanol (50 mL, 0.01% w/v) was shaken with PUFs cubes (4–5 g) with efficient stirring for 30 min. TAR-treated PUFs cubes

Parameter	Unit
Rf power (kW)	1300 W
Plasma gas (Ar) flow rate	15.0 L min ⁻¹
Auxiliary gas (Ar) flow rate	0.2 L min ⁻¹
Nebulizer gas (Ar) flow rate	0.8 L min ⁻¹
Pump rate	1.5 mL min ⁻¹
Observation height	15 mm
Integration time	10 s
Wavelength	327 nm

Table 1. ICP-OES operational parameters for mercury determination.

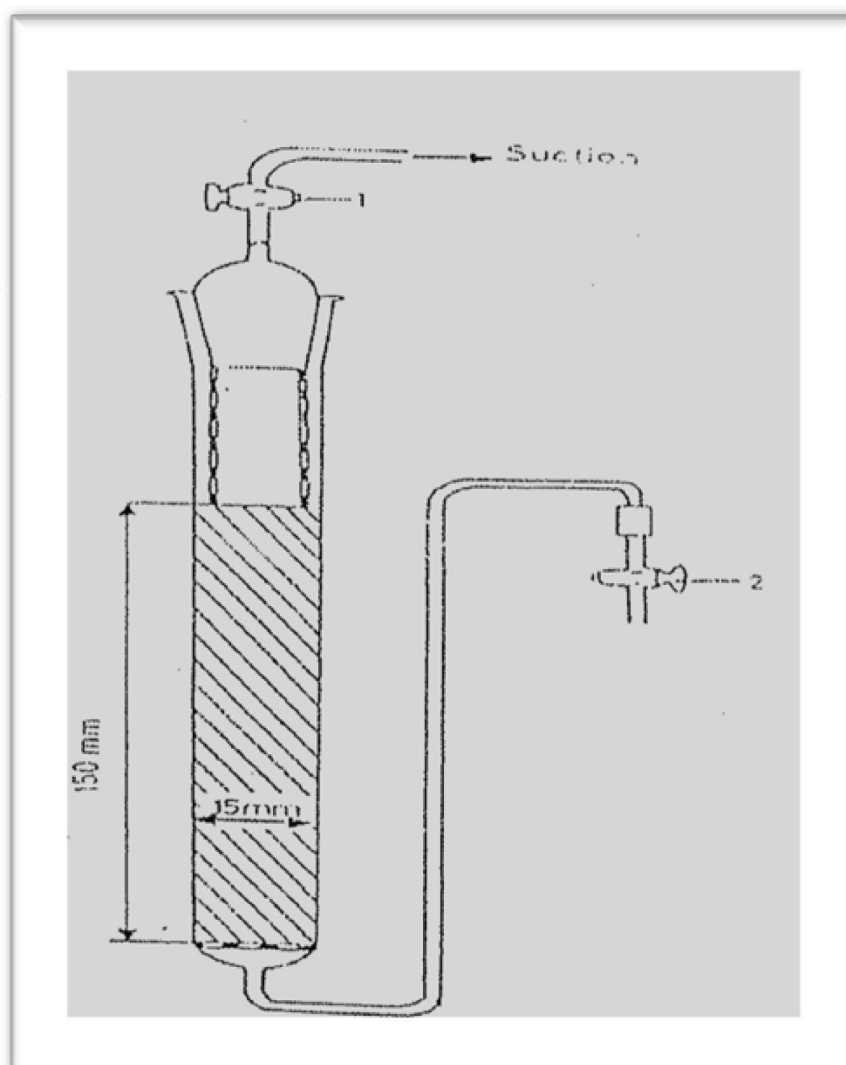


Figure 3. Preparation of PUFs packed column.

were squeezed and dried as reported earlier [25]. The amount of retained (q_e) reagent TAR onto the PUFs cubes was calculated by the following Equation [23, 25].

$$q_e = \frac{(C_b - C_a) \times V}{W} \quad (1)$$

where C_b and C_a are the initial and final concentrations of TAR in solution, respectively; V is the volume of the reagent solution (mL) and W is the mass (g) of the PUFs sorbent.

2.4. General procedures

2.4.1. Batch experiments

In a series of 250-mL conical flasks, an accurate weight (0.10 ± 0.01 g) of the TAR-immobilized PUFs was equilibrated with 200-mL Britton-Robinson buffers pH (2–12) containing mercury(II)

ions $20 \mu\text{g mL}^{-1}$. These solutions were shaken for 60 min at 25°C on a mechanical shaker. After phase separation, the aqueous phase was separated out by decantation and its mercury(II) ion concentration was ICP-OES determined. The concentration of mercury(II) ions retained on the foam solid sorbent was then determined from the difference between mercury(II) ion concentrations before (C_b) and after (C_a) shaking with the TAR-immobilized PUFs. The amount of mercury(II) ions retained at equilibrium q_e , extraction percentage (% E) and distribution ratio (D) of the mercury(II) ion uptake by the used foams were finally calculated as reported earlier [23–26].

Similarly, the effect of different analytical parameters [e.g. shaking time, cation size and monovalent metal ion concentration (Li^+ , Na^+ , K^+ and NH_4^+), sample volume, temperature, TAR and mercury(II) ion concentrations] were critically investigated by batch mode. The %E and D are the average of three independent measurements ($\text{RSD} < 2\%$).

2.4.2. Chromatographic separation of mercury(II) ions on TAR-immobilized PUF sorbent-packed column

A 1-L aqueous solution (pH 6) spiked with mercury(II) ions ($1\text{--}1000 \mu\text{g L}^{-1}$) was percolated through TAR-immobilized PUFs ($0.40 \pm 0.01 \text{ g}$) packed columns at 5 mL min^{-1} flow rate. A blank sample was also tested in the absence of mercury(II) ions. A complete retention of mercury(II) ions took place as indicated by ICP-OES analysis of mercury in the effluent. A complete recovery of mercury(II) ions from TAR-immobilized sorbent packed column was achieved by percolating HNO_3 (20 mL , 1.0 mol L^{-1}) at 2 mL min^{-1} flow rate. Equal fractions of the eluate were then collected and analyzed for mercury content by ICP-OES. The height equivalent to a theoretical plate (HETP) and plate numbers (N) were calculated from the output of the chromatograms. The HETP and N were also determined from the breakthrough capacity curve (S-shaped) of mercury(II) ions at $\mu\text{g/mL}$ level under the optimum condition of mercury(II) ion retention.

2.5. Analytical application

Tap and/or seawater samples ($0.1\text{--}1.0 \text{ L}$) were collected and filtered through a $0.45\text{-}\mu\text{m}$ membrane filter; the solutions were pH adjusted to 6. All sample solutions were then spiked with different mercury(II) ion concentrations ($0.001\text{--}1 \mu\text{g mL}^{-1}$). They were percolated through TAR-loaded foam cubes packed columns at 2 mL min^{-1} flow rate. A complete sorption of mercury(II) ions was achieved as indicated by mercury analysis in the effluents. The amount of retained mercury(II) ions was recovered quantitatively with HNO_3 (20 mL , 1.0 mol L^{-1}) at 5 mL min^{-1} flow rate as noticed by ICP-MS analysis of the eluate.

3. Results and discussion

PUF is an excellent sorbent, which separates and pre-concentrates metal ions rather quickly compared with other solid sorbents [29–32]. It has been used in batch or dynamic techniques for the collection of a variety of chemical compounds, especially cations with harmful effects on humans, animals and plants e.g. Cd(II) and Hg(II) .

3.1. Retention profile of mercury(II) ions onto the PUFs

The amount of mercury(II) ions extracted from the aqueous solution by the reagent TAR-immobilized PUFs was found to be pH dependent. The sorption profile of mercury(II) ions ($20 \mu\text{g mL}^{-1}$) from aqueous media by foams ($0.10 \pm 0.01 \text{ g}$) was investigated by employing Britton-Robinson buffers (pH 2–11). After shaking the test solutions with TAR-immobilized PUFs for 1.0 h at 25°C , the amount of mercury(II) ions remained in the aqueous media was measured by ICP-MS. The uptake percentage (%E) of mercury(II) ions from the aqueous media onto the TAR-immobilized PUFs sorbent was then calculated by the difference between mercury(II) ion concentrations before and after extraction.

As it can be seen in **Figure 4**, the sorption profile of mercury(II) ions by unloaded and TAR-loaded PUFs peaked at pH 6 and decreased progressively on further raising the solution pH. The observed decrease in mercury(II) ion uptake at $\text{pH} > 6$ is most likely attributed to the instability and/or hydrolysis of the complex species formed between mercury(II) complex species and the sorbent Hg-TAR. At $\text{pH} < 6$, the uptake of mercury(II) ions by the solid sorbents reduced. This reduction is probably attributed to TAR's low availability in ionized form and high availability in protonated amine group on the surface of TAR-functionalized PUFs [25].

A comparison between mercury(II) ion uptake from the aqueous media by TAR-treated PUF and untreated PUF (**Figure 4**) showed an excellent extraction performance for the former solid phase extractor. This behavior is most likely due to possible chelation between TAR on/ in the surface and membrane of the PUF and mercury(II) ions in the aqueous media at pH 6 as expressed by the following equation:

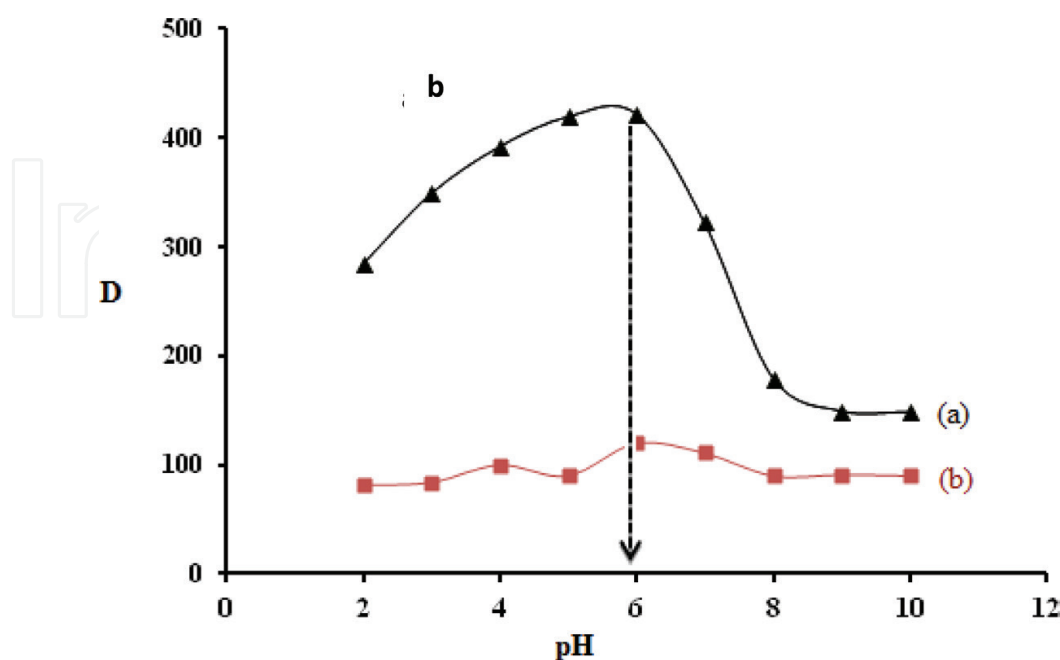


Figure 4. Plot of distribution ratio of mercury(II) ion uptake by TAR-treated PUFs (a) and unloaded PUFs (b) *versus* pH at 25°C after 1-h shaking.

The stability constants of the binding sites of the PUFs with mercury(II) ions were calculated using the Scatchard Eq. [25]:

$$\frac{n}{[Hg]} = K(n_i - n) \tag{3}$$

$$n = \frac{\text{weight of mercury bound to foam (g)}}{\text{weight of foam (g)}} \tag{4}$$

where K is the stability constant of mercury(II) ions on PUFs, n_i is the maximum concentration of mercury(II) ions sorbed by the available sites on the PUFs, and [Hg] is the equilibrium concentration of mercury(II) ions (mol L⁻¹). As shown in **Figure 5**, the curvature of the Scatchard plot demonstrates that more than a mercury(II) complex species could be formed and has its own unique formation constant [23, 25]. The stability constants log K₁ and log K₂ for the sorbed species derived from the respective slopes were 5.365 ± 0.200 and 4.216 ± 0.500. The calculated values of n_{i1} and n_{i2} were 0.022 ± 0.005 and 0.053 ± 0.010 mol g⁻¹, respectively. The values of the stability constants (log K₁ and log K₂) indicate that the sorption of this species took place readily on site K₁, most likely due to the ether group because this group has a greater stability than the amide group (site K₂) [25].

As demonstrated in **Figure 6**, the sorption of mercury(II) ions onto TAR-immobilized PUFs sorbents peaked at about 30 min and remained relatively constant after 60 min. The half-life ($t_{1/2}$) of the equilibrium sorption of mercury(II) ions onto TAR-immobilized PUFs sorbents from the aqueous phase was calculated from the plot of $-\log C_b - C_a/C_b$ versus time (**Figure 7**). The $t_{1/2}$ value of mercury(II) ion uptake by TAR-PUF sorbent was found to be 2.00 ± 0.08 min. It means that most likely gel diffusion is not the only rate-controlling step for TAR-immobilized PUFs sorbent as reported for common ion exchange resins [23, 25]. Therefore, the kinetic

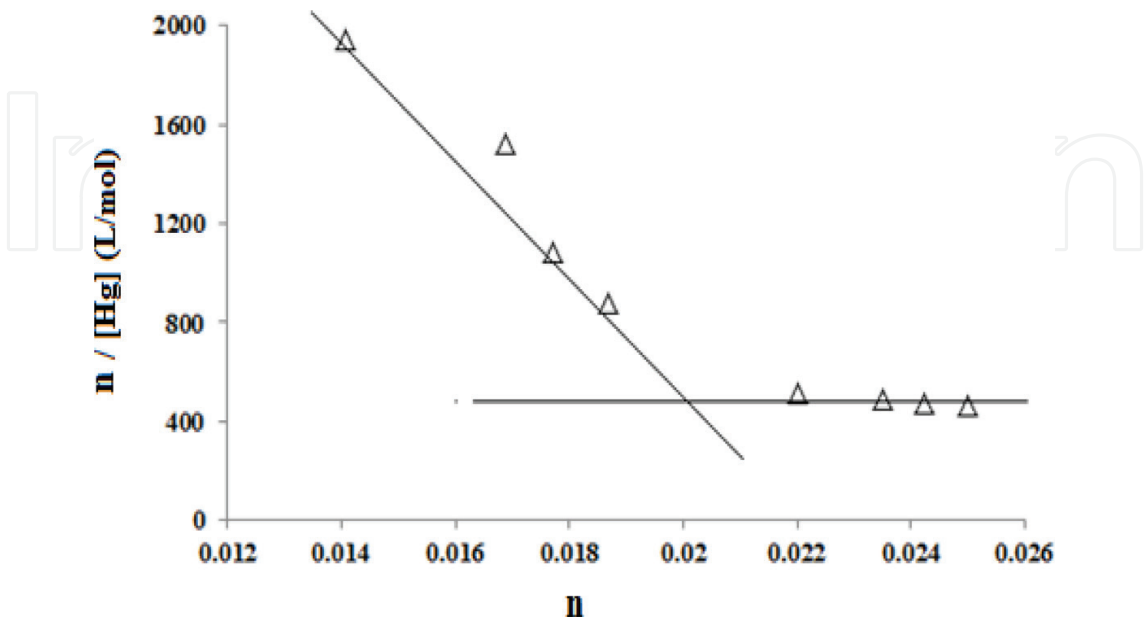


Figure 5. Scatchard plot of the sorption of mercury(II) ions from the aqueous media onto TAR-immobilized PUFs sorbents at 25°C after 1-h shaking.

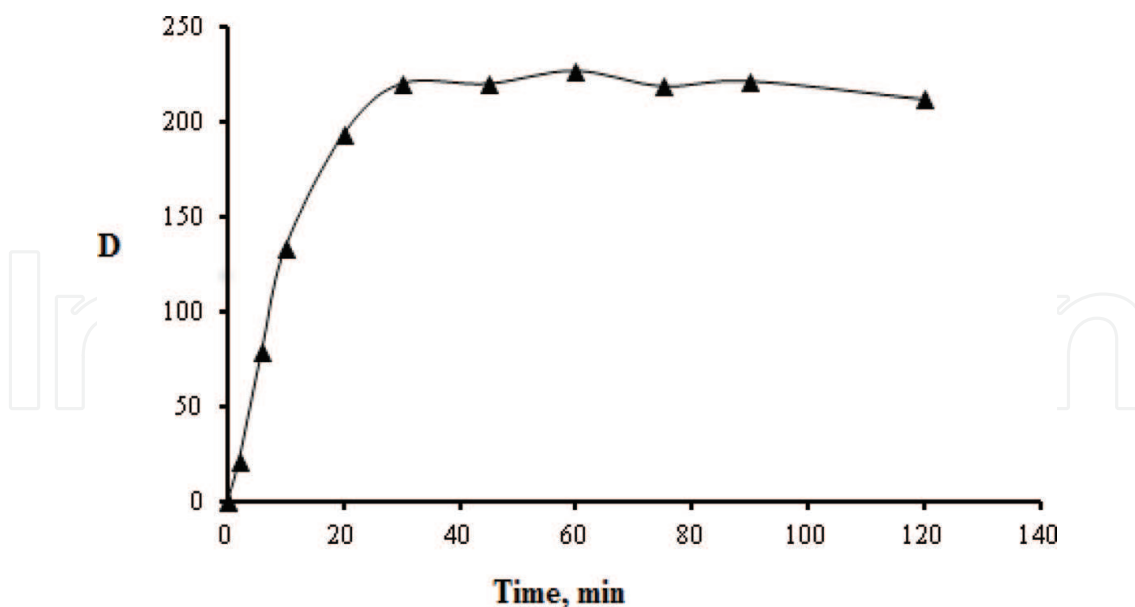


Figure 6. Effect of shaking time on the sorption of mercury(II) ions from the aqueous media onto TAR-immobilized PUFs sorbents at 25°C after 1h shaking time at pH 6.

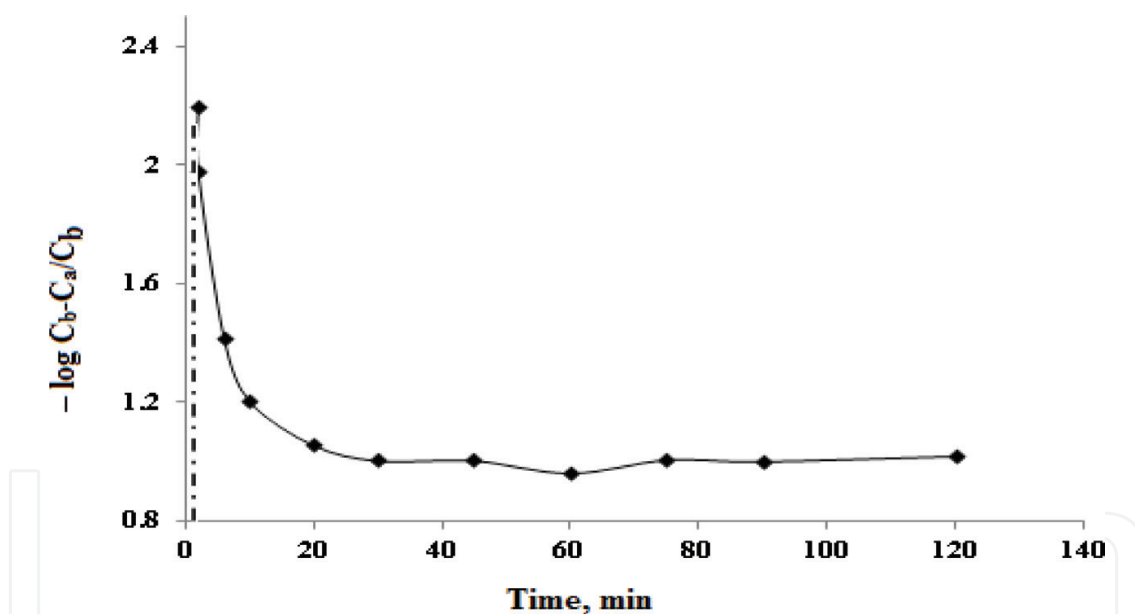


Figure 7. Effect of shaking time on the sorption of mercury(II) ions from the aqueous media onto TAR-loaded PUFs sorbents at 25°C after 1h shaking time at pH 6.

behavior of mercury(II) ion sorption onto the TAR-immobilized PUFs sorbent depends on the film diffusion and intraparticle diffusion that probably control the overall transport of mercury(II) ions in/on the sorbent membrane.

Figure 8 displays the effect of cation size of various monovalent alkali metal ions (Li^+ , Na^+ , K^+ and NH_4^+) as chloride salt (0–2% w/v) on mercury(II) ion uptake (20 ppm) from the aqueous media at the optimized pH 6 onto TAR-loaded PUFs sorbents (0.10 ± 0.01 g) after 1-h shaking. The sorption profile of mercury(II) ions increased with a decrease in the cation size and the overall retention step was in the following order:

$$\text{Li}^+ > \text{Na}^+ \sim \text{NH}_4^+ > \text{K}^+ \quad (5)$$

On the other hand, when monovalent cations were added to the extraction media (0.04–1.2% w/v), the reduction of a number of water molecules available to solvate mercury(II) ions forced the solvent phase out TAR-treated PUF sorbents [23, 25]. This finding is in good agreement with the data reported by El-Shahawi et al., clearly stating that some amount of free water molecules is preferentially used to solvate cations added leading to an analyte uptake enhancement [25]. The ion-dipole interaction of NH_4^+ with the oxygen sites of the PUFs was not a predominating factor in the extraction of mercury(II) ions. This effect is consistent with the “solvent extraction” mechanism with a salting-out agent.

Investigation on the effect of sample volume (20–500 mL) of mercury(II) solution ($20 \mu\text{g mL}^{-1}$) shows that the extraction percentage of mercury(II) ions from the aqueous media slightly decreased (10–15%) when using a sample volume > 200 mL. In contrast, no significant effect on the mercury(II) ion uptake was observed when varying TAR concentration (0.02–0.14% w/v) (Figure 9). As a result, TAR concentration was adopted at 0.05% (w/v) for subsequent work.

3.2. Kinetics of the mercury(II) ion sorption by TAR-treated PUFs

The retention of inorganic pollutants such as mercury(II) species from the aqueous media plays an important role in wastewater treatment. In the present study, data on mercury(II) ion uptake by the used solid sorbents were subjected to many kinetic models e.g. Morris-Weber [49], Lagergren pseudo-first order [50], Bhattacharya & Enkobachar [51], Reichenburg [52] and pseudo-second order rate models [53]. The Weber-Morris model can be mathematically expressed as follows [49]:

$$q_t = R_d (t)^{1/2} \quad (6)$$

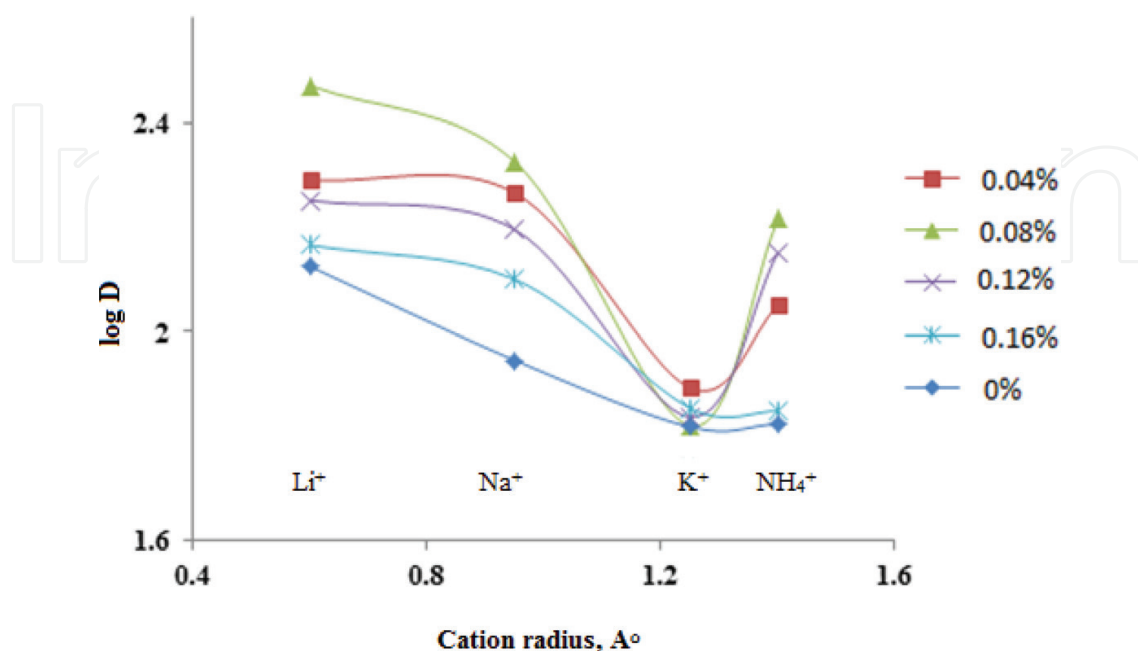


Figure 8. Effect of monovalent cation (Li^+ , Na^+ , K^+ , NH_4^+) size and concentration (1% w/v) on the sorption profile of mercury(II) ions onto unloaded (a) and TAR-loaded PUFs (b) at 25°C after 1-h shaking.

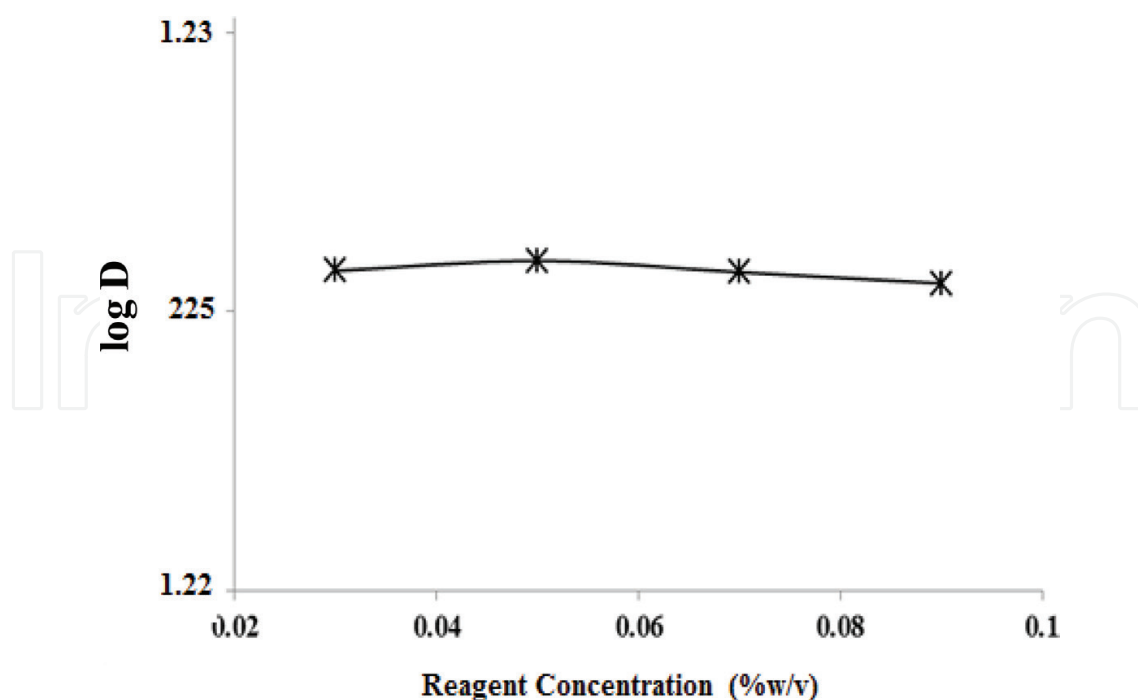


Figure 9. Effect of immobilized-TAR concentration (% w/v) of the loaded foams on mercury(II) ion uptake from the aqueous media pH 6 at 25°C after 1-h shaking.

where R_d is the rate constant of intraparticle transport in $\text{mg g}^{-1} \text{min}^{-1/2}$ and q_t is the sorbed mercury(II) ion concentration (mg g^{-1}) at time t (as shown in **Figure 10**). The plot of q_t versus time were found linear ($R^2 = 0.995$) in the initial stage for mercury(II) ion retention onto the sorbent up to 30.25 ± 0.03 min; on further increasing the shaking time, the straight line did not pass through the origin. It indicates that (i) intraparticle diffusion is not the only rate-controlling step for TAR-immobilized PUFs as in the case of common ion exchange resins [23, 25] and (ii) the retention step is mainly controlled by film diffusion at the early stage of extraction and in the second stage, the diffusion remains fairly constant when the pores volume of PUFs is exhausted [25].

The values of R_d computed from the two slopes in the initial and second stages of the Weber-Morris plots for TAR-loaded PUFs were found to be $0.707 \pm 1.010 \text{ mg (g min)}^{-1}$ and $0.053 \pm 0.020 \text{ mg (g min)}^{-1}$ with $R^2 = 0.995$ and 0.989 , respectively. The change in the slope is most likely related to the existence of different pore sizes [44, 45], further confirming intraparticle diffusion as the rate-controlling step.

Moreover, the rate constant for the retention step of mercury(II) ion retention onto the tested solid sorbent was also evaluated in the light of Lagergren Equation [50]:

$$\log(q_e - q_t) = \log q_e - \frac{K_{\text{Lager}}}{2.303} t \quad (7)$$

where q_e is the amount of mercury(II) ions sorbed at equilibrium per mass unit of sorbent (mmol g^{-1}), K_{Lager} is the first order overall rate constant for the retention process per min and t is the time in min. The value of K_{Lager} calculated from the linear plot of $\log(q_e - q_t)$ versus time (**Figure 11**) was found to be $0.176 \pm 0.010 \text{ min}^{-1}$, suggesting first-order kinetics for the mercury(II) ion retention onto the sorbent. The value of K_{Lager} increases proportionally to the increasing

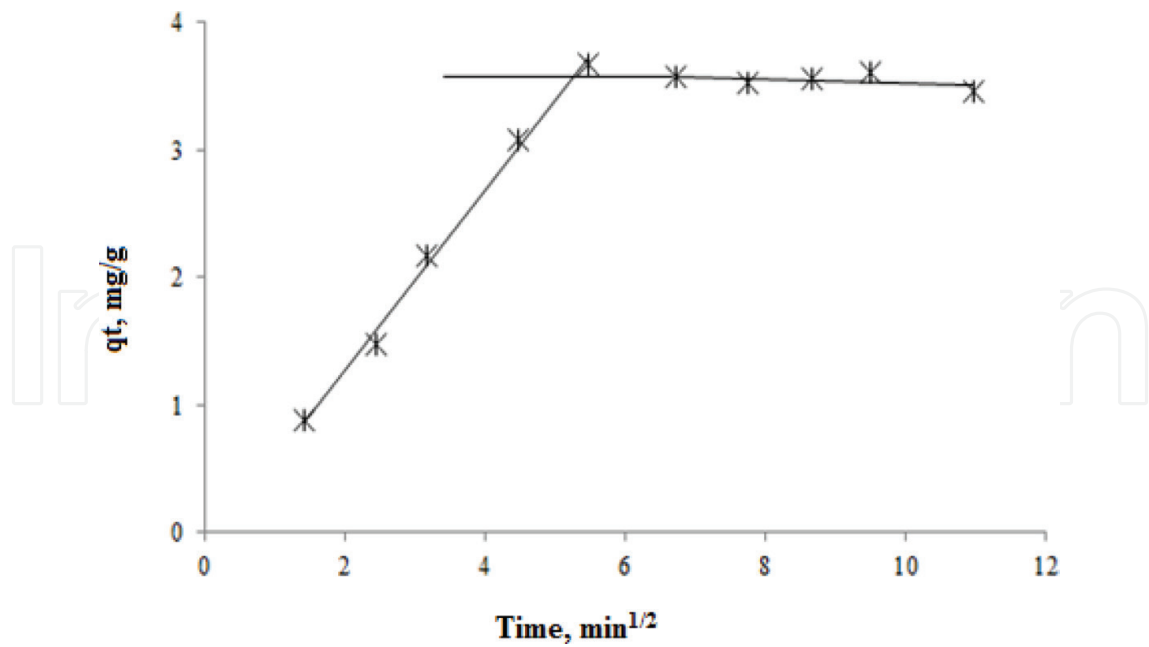


Figure 10. Weber–Morris plot of the sorbed mercury(II) ions onto TAR-immobilized PUFs sorbents versus square root of time at 25°C after 1-h shaking.

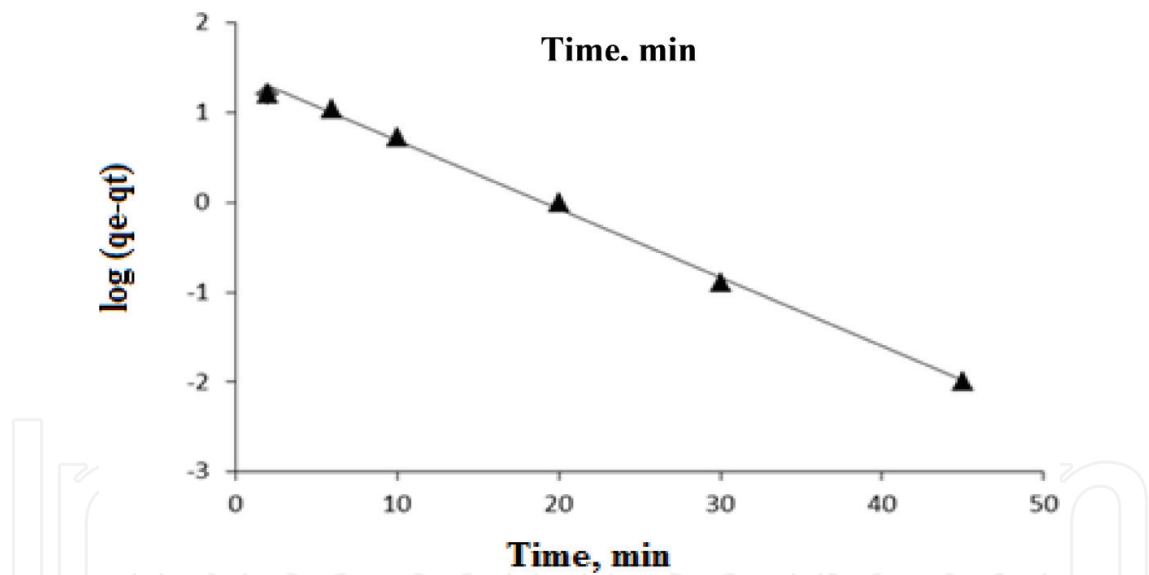


Figure 11. Lagergren plot of mercury(II) ions uptake onto TAR-immobilized PUFs sorbents from the aqueous media versus time at 25°C after 1-h shaking.

sorbate concentration, confirming a monolayer formation of mercury(II) ions onto the surface of the used sorbent as well as the first-order kinetic nature of the retention process [23, 25].

These results were also confirmed by Bhattacharya-Enkobachar kinetic model [51].

$$\log \left(1-U_{(t)} \right) = \frac{-K_{\text{Bhatt}}}{2.303} t \tag{8}$$

where $U_{(t)} = \frac{C_a - C_t}{C_a - C_e}$, K_{Bhatt} = overall rate constant (min^{-1}), t = time (min), C_t = concentration of mercury(II) ions at time t in $\mu\text{g mL}^{-1}$, C_e = concentration of mercury(II) ions at equilibrium in

$\mu\text{g mL}^{-1}$. The value of K_{Bhatt} estimated from the linear region of the plot of $\log (1 - U_t)$ against time (**Figure 12**) was equal to $0.183 \pm 0.002 \text{ min}^{-1}$. This value is quite close to that achieved by Lagergren model, and provides an additional indication of the first-order kinetics for mercury(II) ion retention onto the used sorbent.

The value of Bt , which is a mathematical function (F) of the ratio of the fractions sorbed at time t (q_t) and at equilibrium (q_e) in $\mu\text{mole g}^{-1}$ (i.e. $F = q_t / q_e$), is calculated for each value of F by employing Reichenburg Equation [52, 53].

$$Bt = -0.4977 - 2.303 \log (1-F) \quad (9)$$

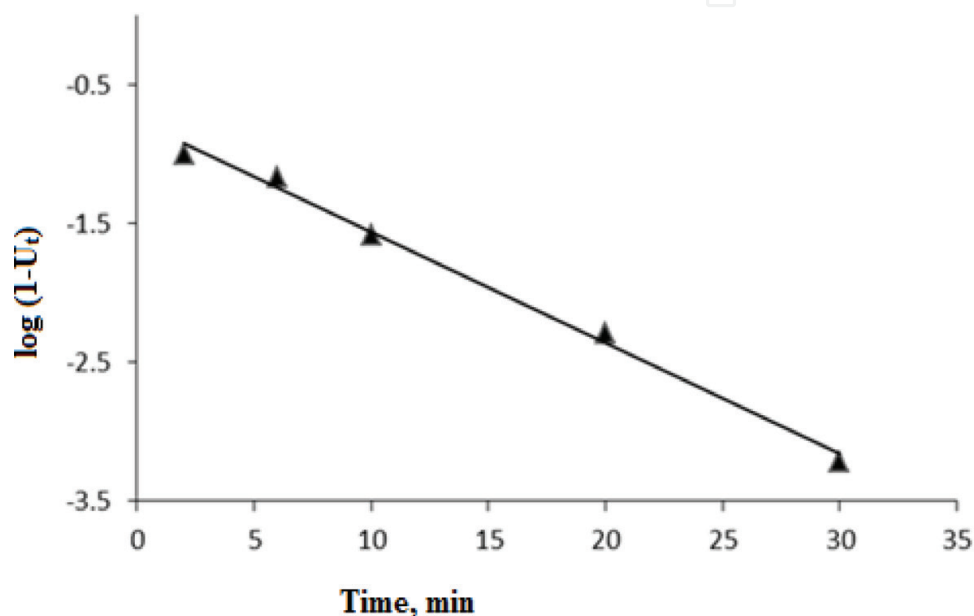


Figure 12. Bhattacharya-enkobachar plot of mercury(II) ion retention from the aqueous media onto TAR-loaded PUFs sorbents at 25°C after 1-h shaking.

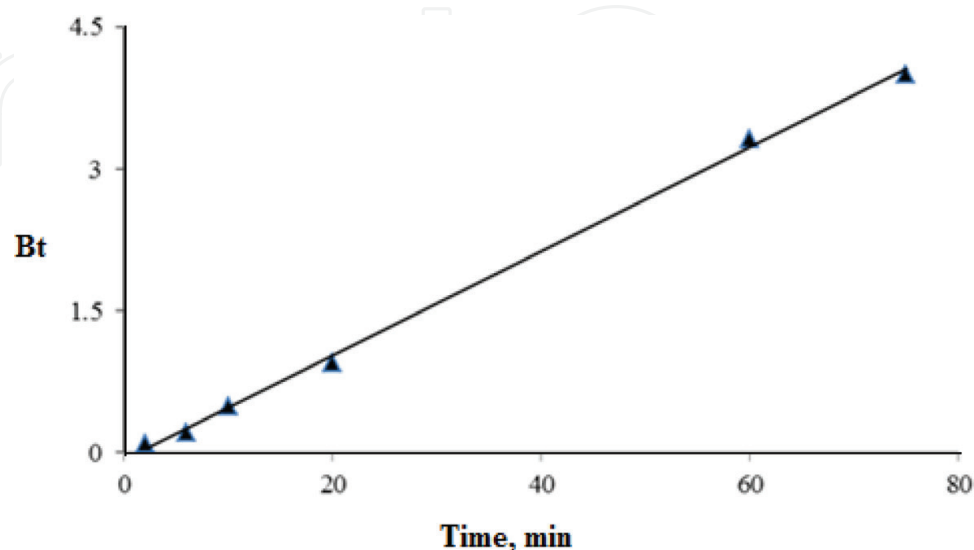


Figure 13. Reichenburg plot of the kinetics of mercury(II) ions retention onto TAR-loaded PUFs sorbents from the aqueous media at 25°C after 1-h shaking.

the plot of Bt versus time at 25°C for mercury(II) ion sorption was linear ($R^2 = 0.998$) up to 80 min (**Figure 13**). The straight line does not pass through the origin, indicating that particle diffusion mechanism is not responsible for mercury(II) ion sorption onto the sorbent. Thus, the uptake of mercury(II) ions onto the sorbent may consist of three steps: (i) bulk transport of mercury(II) ions in solution, (ii) film transfer involving diffusion of mercury(II) ions within the pore volume of TAR-treated PUFs sorbents and/or along the wall surface to the active sorption sites of the sorbent, and (iii) formation of Hg^{2+} -TAR chelate on/in the sorbent. This explains that fact that the sorption of mercury(II) ions on the interior surface is very rapid and hence it is not a rate-determining step.

3.3. Thermodynamic characteristics of the mercury(II) ion retention onto TAR-loaded PUFs sorbents

The sorption behavior of mercury(II) ions by unloaded and TAR-loaded PUFs sorbents was critically studied over a wide range of temperatures (293–353 K) to determine the characteristics of mercury(II) ion retention onto TAR-loaded PUFs sorbents at the established conditions. The thermodynamic parameters (ΔH , ΔS , and ΔG) were evaluated by using the following equations [23, 25]:

$$\ln K_c = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (10)$$

$$\Delta G = \Delta H - T\Delta S \quad (11)$$

$$\Delta G = -RT \ln K_c \quad (12)$$

where ΔH , ΔS , ΔG , and T are the enthalpy, entropy, Gibbs free energy changes and temperature in Kelvin, respectively; and R is the gas constant ($\approx 8.3 \text{ J K}^{-1} \text{ mol}^{-1}$). K_c is the equilibrium constant depending on the fractional attainment (Fe) of the sorption process. The values of K_c for retention of mercury(II) ions from the aqueous media at equilibrium onto unloaded and TAR-loaded PUFs sorbents was calculated by employing the following equation:

$$K_c = \frac{Fe}{1 - Fe} \quad (13)$$

Figure 14 shows a reduction in the values of K_c with increasing temperature, revealing that the retention of mercury(II) ion by the sorbent is an exothermic process. The numerical values of ΔH , ΔS , and ΔG calculated from the slope and intercept of the linear plot were found to be $-41.5 \pm 1.01 \text{ kJ mol}^{-1}$, $-132.8 \pm 0.5 \text{ J mol}^{-1} \text{ K}^{-1}$ and $-1.62 \text{ kJ mol}^{-1}$ (at 298 K), respectively. The ΔH , ΔS , and ΔG values found were equal to $-39.80 \pm 0.01 \text{ kJ mol}^{-1}$, $-128.6 \pm 0.3 \text{ J mol}^{-1} \text{ K}^{-1}$ and $-1.47 \text{ kJ mol}^{-1}$ (at 298 K), respectively.

Considering the Van't Hoff equation in terms of the distribution ratio of mercury(II) ions, D , the following expression is obtained:

$$\log D = \frac{-\Delta H}{2.30 RT} + 1/n C \quad (14)$$

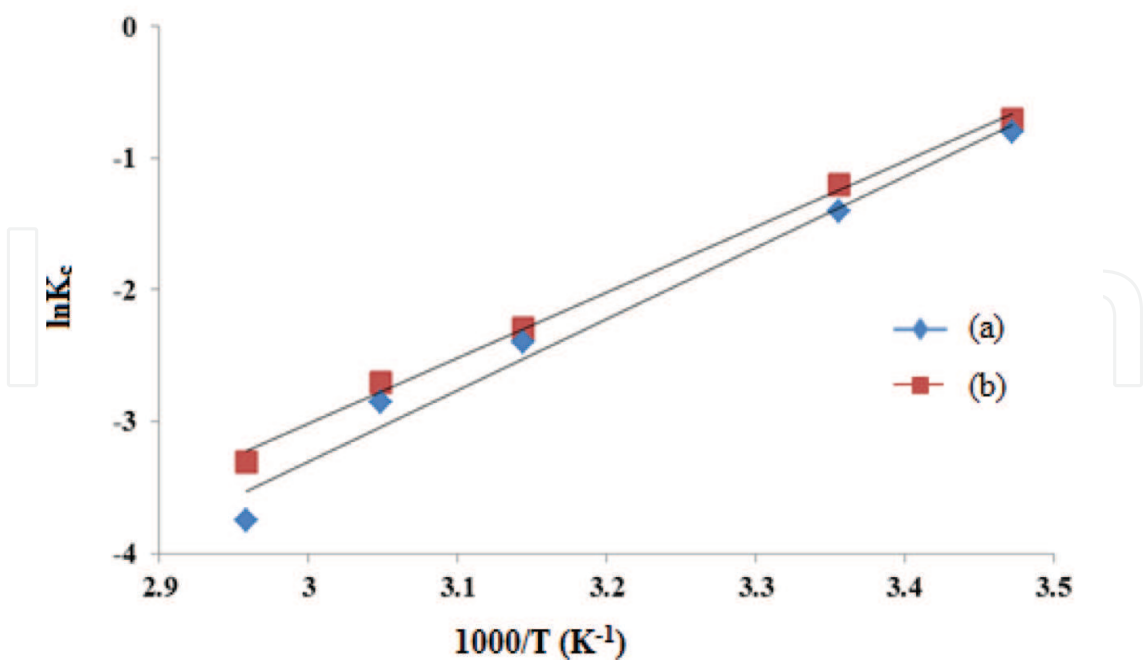


Figure 14. Plot of $\ln K_c$ of mercury(II) ion sorption versus $1000/T$ (K^{-1}) from the aqueous media pH 6 onto unloaded (a) and TAR-loaded PUFs sorbents (b) at $25^\circ C$ after 1-h shaking.

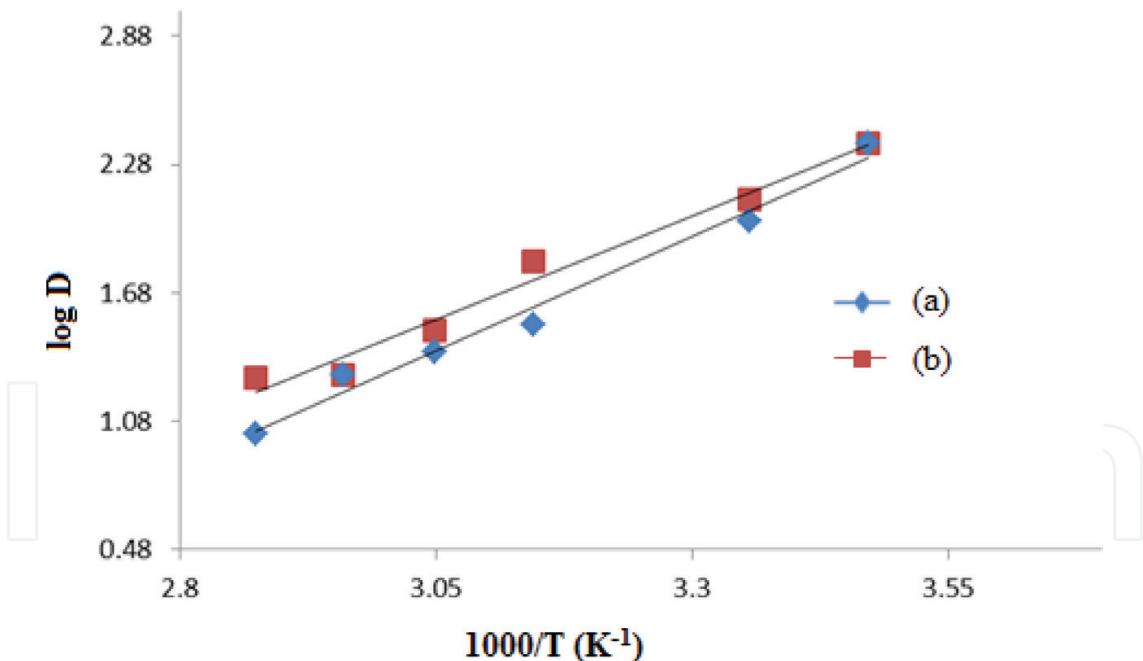


Figure 15. Van't-hoff plot for mercury(II) ion retention onto TAR-loaded PUFs (a) and unloaded sorbents (b) at $25^\circ C$ after 1-h shaking.

where C is a constant. The values of D of mercury(II) ion retention from the aqueous media pH 6 onto unloaded and TAR-loaded PUFs sorbents decreased on raising temperature. The plots of $\log D$ versus $1000/T$ were linear (**Figure 15**). The calculated values of ΔH for mercury(II) sorption were found to be -38.4 and -40.1 kJ mol^{-1} onto unloaded and TAR-loaded PUFs sorbents, respectively.

The negative value of ΔH and the values of D and K_C reflect the exothermic nature of mercury(II) ion uptake by the employed solid PUFs as well as the non-electrostatic bonding formation between the sorbent and adsorbate. The negative values of ΔS may be indicative of the moderate sorption step of mercury(II) complex ion associate and charge ordering without a compensatory disordering of the sorbed ion associate onto the used sorbents. The motion of mercury(II) ions is more restricted in PUF membrane than in solution. Since the sorption process involves a decrease in free energy, the ΔH value is expected to be negative as confirmed above.

The negative value of ΔG at 295 K indicates the spontaneous and physical sorption characteristics of mercury(II) ion retention onto PUFs. An increase in the values of ΔG with temperature may be due to the spontaneous nature of the sorption step, and mercury(II) ion uptake is more favorable at low temperature confirming the exothermic sorption process. The energy of urethane nitrogen and/or ether – oxygen sites of the PUFs with increasing temperature minimizes a possible interaction between the active sites of PUFs and mercury(II) complex ion associates, resulting in a lower sorption percentage of the analyte. Therefore, a sorption mechanism involving “solvent extraction” is most likely responsible for the retention step.

3.4. Sorption isotherms of the mercury(II) ion retention by TAR-treated PUFs sorbents

The sorption characteristics of mercury(II) ions over a wide range of equilibrium concentrations ($1\text{--}80\ \mu\text{g mL}^{-1}$) from the aqueous solution pH 6 onto unloaded and TAR-loaded PUFs were studied. As shown in **Figure 16**, at low or moderate analyte concentrations the amount of mercury(II) ions retained on the sorbent varied linearly with the amount of mercury(II) ions remained in the bulk aqueous solution. The equilibrium was only established for mercury(II) ion rich aqueous phase, confirming the first-order kinetics of the sorption step. A relatively reasonable sorption capacity of mercury(II) ions onto unloaded and TAR-loaded PUFs sorbents (as predicted from the sorption isotherm) was found to be greater than 16.70 ± 0.02 and $24.40 \pm 0.07\ \text{mg g}^{-1}$, respectively. The K_d values decreased on raising mercury(II) ion concentration when the sorbent membrane became more saturated with mercury(II) ions within 15–20 min of shaking (**Figure 17**).

The retention behavior of mercury(II) ions from the aqueous media onto the used sorbents was subjected to Freundlich, Langmuir and Dubinin-Radushkevich (D-R) isotherm models over a wide range of equilibrium concentrations by means of the linear least squares fitting technique. The Freundlich model [54] is expressed in the following form:

$$\log C_{\text{ads}} = \log A + \frac{1}{n} \log C_e \quad (15)$$

where A and $\frac{1}{n}$ are Freundlich parameters related to the maximum sorption capacity of solute (mol g^{-1}) and C_{ads} is the sorbed mercury(II) ion concentration per mass unit of TAR-immobilized PUFs sorbents (mol g^{-1}) at equilibrium. Plot of $\log C_{\text{ads}}$ vs. $\log C_e$ (**Figure 18**) for the mercury(II) ion retention onto TAR-immobilized PUFs was linear ($R^2 = 0.993$) over the entire concentration range of the analyte, indicating a good fit for the experimental data. The Freundlich sorption isotherm encompasses the heterogeneity of the surface and exponential distribution of the sites and their energies. The Freundlich parameters A and $1/n$ computed from

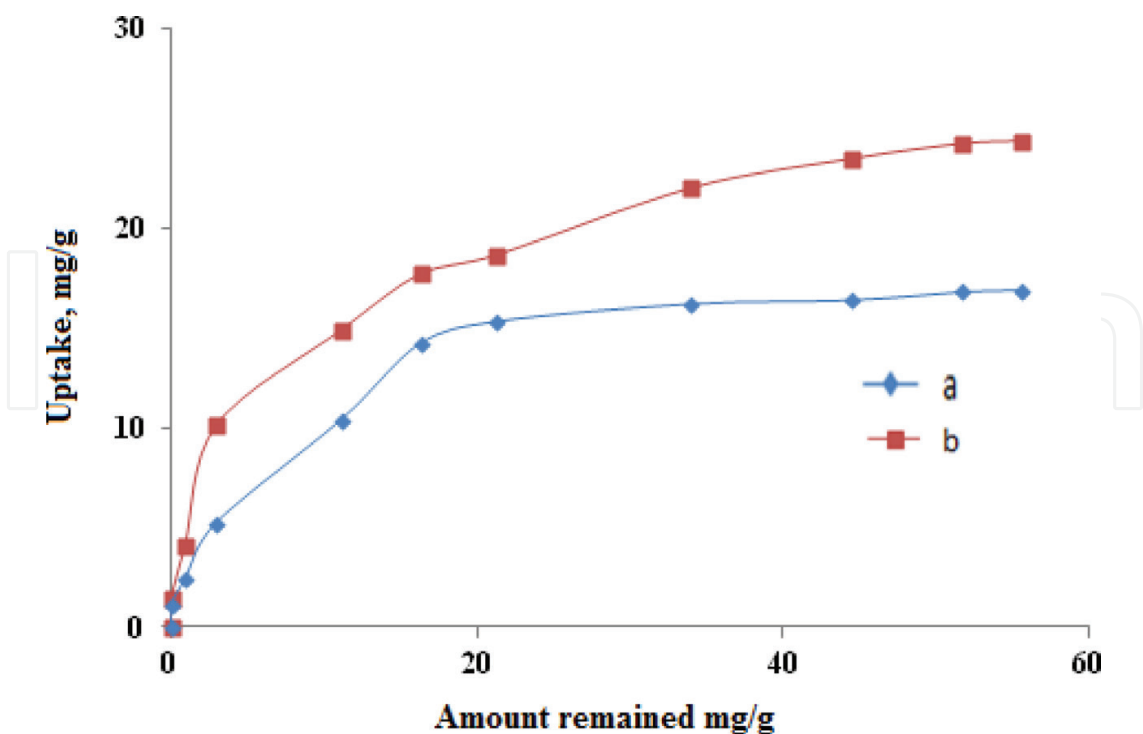


Figure 16. Sorption isotherms of the mercury(II) ion uptake from the aqueous media at optimal conditions onto unloaded (a) and TAR-loaded PUFs sorbents (b) at 25°C after 1-h shaking.

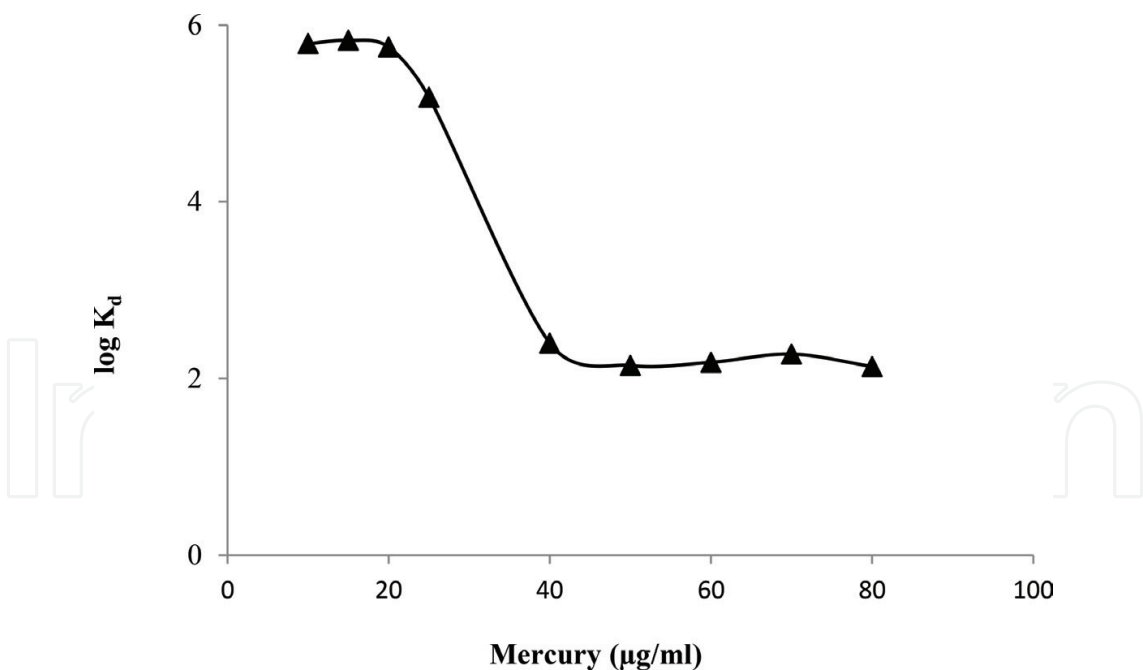


Figure 17. Plot of $\log K_d$ of the mercury(II) ion sorption *versus* mercury(II) ion concentration in the aqueous media pH 6 onto TAR-loaded PUFs sorbents.

the intercept and slope of the linear plot (**Figure 18**) were found to be $0.251 \pm 0.100 \text{ mmol.g}^{-1}$ and 0.25 for TAR-loaded PUFs and $0.501 \pm 0.300 \text{ mmol.g}^{-1}$ and 0.355 for unloaded PUFs. The value of $1/n < 1$ revealing favorable sorption of mercury(II) ions onto the tested solid sorbents.

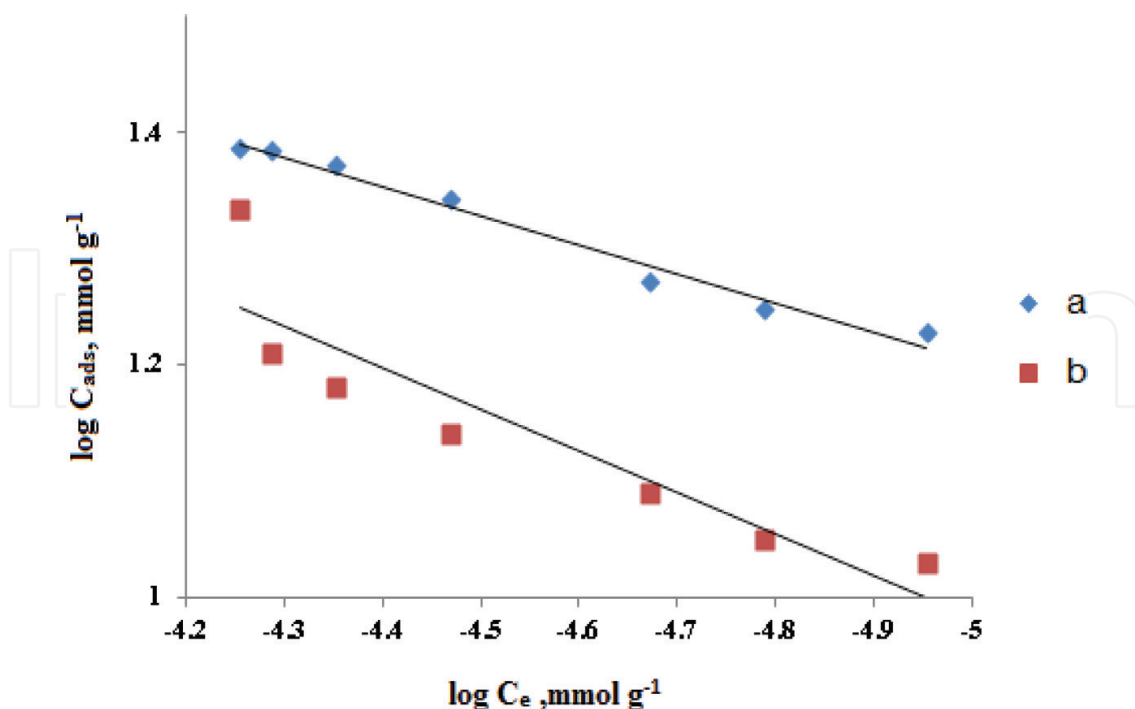


Figure 18. Freundlich sorption isotherms of the mercury(II) ion uptake from the aqueous solution at optimal conditions onto unloaded (a) and TAR-loaded PUFs sorbents (b) at 25°C after 1-h shaking.

At lower equilibrium concentration, the sorption capacity slightly decreased and the isotherm does not predict any saturation of the surface of the PUFs the adsorbate. Thus, an infinite surface coverage is mathematically predicted and a physisorption on the surface of the sorbents is expected.

Langmuir sorption isotherm model is expressed in the following linear form [55].

$$\frac{C_e}{C_{ads}} = \frac{1}{Q_b} + \frac{C_e}{Q} \quad (16)$$

where C_e is the equilibrium concentration (mg L^{-1}) of mercury(II) ions. The constant Q is the Langmuir parameter related to the maximum adsorption capacity of solute per mass unit of adsorbent required for a monolayer coverage of the surface; and b is an equilibrium constant related to the binding energy of solute sorption that is independent of temperature. The plot of C_e/C_{ads} versus C_e over the entire mercury(II) ion concentration was linear (**Figure 19**), confirming the validity of Langmuir adsorption model for analyte uptake onto the sorbent. The parameters Q and b calculated from the slope and intercept of Langmuir plot were found to be $4.89 \pm 0.01 \text{ mmol g}^{-1}$ and 2.61 L mol^{-1} for TAR-loaded PUFs, and $3.20 \pm 0.04 \text{ mmol g}^{-1}$ and 0.74 L mol^{-1} for unloaded PUFs.

The Dubinin-Radushkevich (D-R) isotherm model [56] is postulated within the adsorption space close to the adsorbent surface. The D-R isotherm can be linearized as follows:

$$\ln C_{ads} = \ln K_{DR} - \beta \varepsilon^2 \quad (17)$$

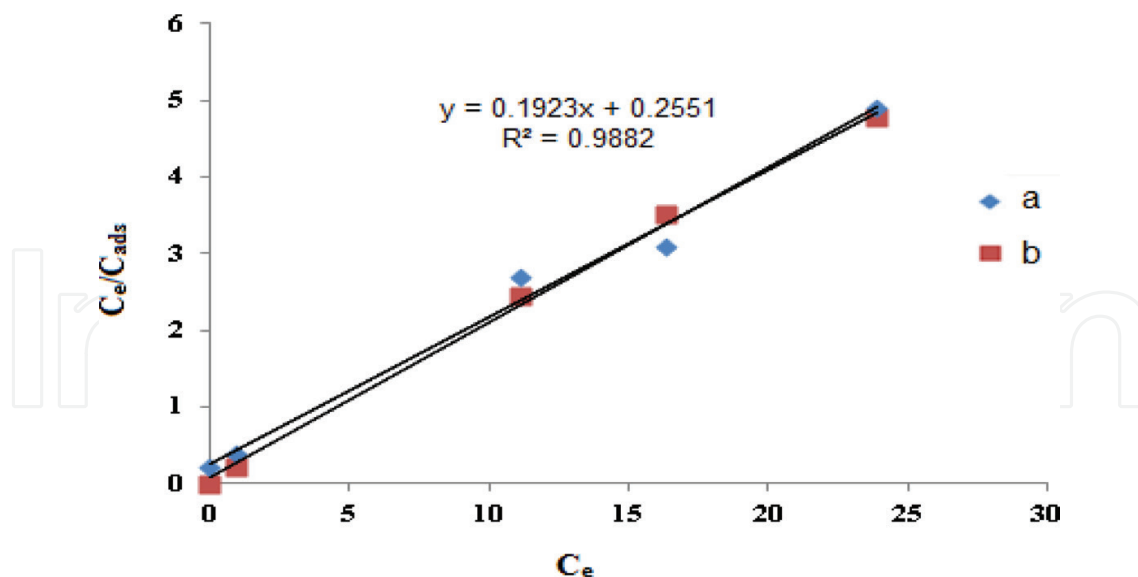


Figure 19. Langmuir sorption isotherm of the mercury(II) ion uptake from the aqueous solution at optimal conditions onto unloaded (a) and TAR-loaded PUFs sorbents (b) at 25°C after 1-h shaking.

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

$$\epsilon^2 = RT \ln(1 + 1/C_e) \quad (18)$$

where R is gas constant in $\text{KJmol}^{-1} \text{K}^{-1}$ and T is the absolute temperature in Kelvin. The plot of $\ln C_{ads}$ versus ϵ^2 was linear with $R^2 = 0.996$ (**Figure 20**) for unloaded and TAR-loaded PUFs, meaning that D-R isotherm model is obeyed for mercury(II) ion sorption onto the sorbents over the entire concentration under study. The values of β and K_{DR} computed from the slope and intercept were equal to $0.008 \text{ mol}^2 \text{KJ}^{-2}$, 4.48 mmol g^{-1} for TAR-loaded PUFs and $0.004 \text{ mol}^2 \text{KJ}^{-2}$, 2.00 mmol g^{-1} for unloaded PUFs.

Assuming that the surface of PUF is heterogonous and an approximation to the Langmuir isotherm model is chosen as a local isotherm for all sites that are energetically equivalent, the quantity β can be related to the mean of free energy (E) of transferring one mole of the solute from infinity to the surface of PUFs. This quantity can be expressed by the following equation:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (19)$$

The value of E was found to be $7.90 \pm 0.07 \text{ KJ/mol}$ for TAR-loaded PUFs sorbents.

With reference to the data reported previously [25], a dual sorption (involving absorption related to “solvent extraction” and an added component for “surface adsorption”) is the most probable retention mechanism for mercury(II) ion uptake by the TAR-loaded foams. Such a proposed model can be written as follows:

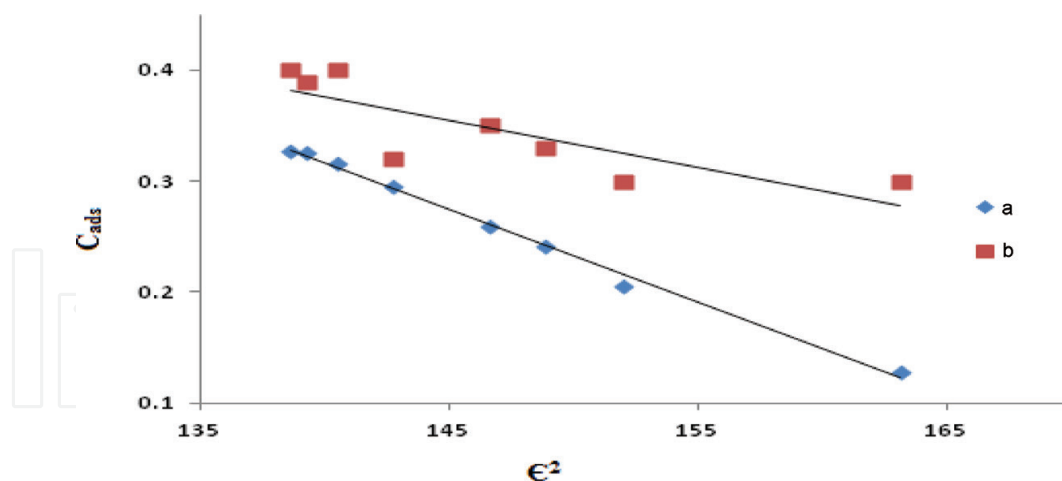


Figure 20. Dubinin-radushkevich (D-R) sorption isotherms of the mercury(II) ion uptake at optimal conditions by unloaded (a) and TAR-loaded PUFs sorbents (b) at 25°C after 1-h shaking.

$$C_r = C_{abs} + C_{ads} = DC_{aq} + \frac{SKLC_{aq}}{1 + KLC_{aq}} \quad (20)$$

where C_r and C_{aq} are the equilibrium concentrations of mercury(II) ions onto the solid sorbent and in the aqueous media, respectively. The parameters C_{abs} and C_{ads} are the equilibrium concentrations of mercury(II) ions onto the tested solid sorbents as absorbed and adsorbed species, respectively. S and K_L are the saturation values for the Langmuir adsorption.

3.5. Chromatographic separation of mercury(II) ions onto TAR-immobilized PUFs packed columns

The cellular membrane structures, excellent hydrodynamic and aerodynamic properties of PUFs [23, 25] enhanced the mercury(II) ion uptake onto TAR-treated PUFs packed columns. **Table 2** shows acceptable extraction and recovery percentages of mercury(II) ions in the range 88.1–103.7% (when percolating the aqueous media spiked with mercury(II) ions through TAR-treated foams packed columns and using HNO_3 as a proper eluting agent).

3.6. Analytical performance of the TAR-immobilized foam packed columns

The performance of TAR-treated PUF packed columns (0.40 ± 0.01 g) was determined by percolating a 2-L aqueous solution containing mercury(II) ions ($20 \mu\text{g mL}^{-1}$) through the packed columns at the optimal conditions (**Figure 21**). The values of HETP and N were calculated from the chromatogram by using Gluekauf Eq. [17]:

$$N = \frac{8 V_{\max}^2}{W^2} = \frac{L}{\text{HETP}} \quad (21)$$

where V_{\max} is the peak elution volume, W is the peak width at $1/e$ times the maximum solute concentration and L is the length of the foam bed in mm. The N and HETP values were found to be 89.00 ± 0.02 and 1.01 ± 0.02 mm, respectively.

The performance of TAR-treated PUF packed columns was also determined from the breakthrough capacity method i.e. percolating 2-L aqueous solution containing mercury(II)

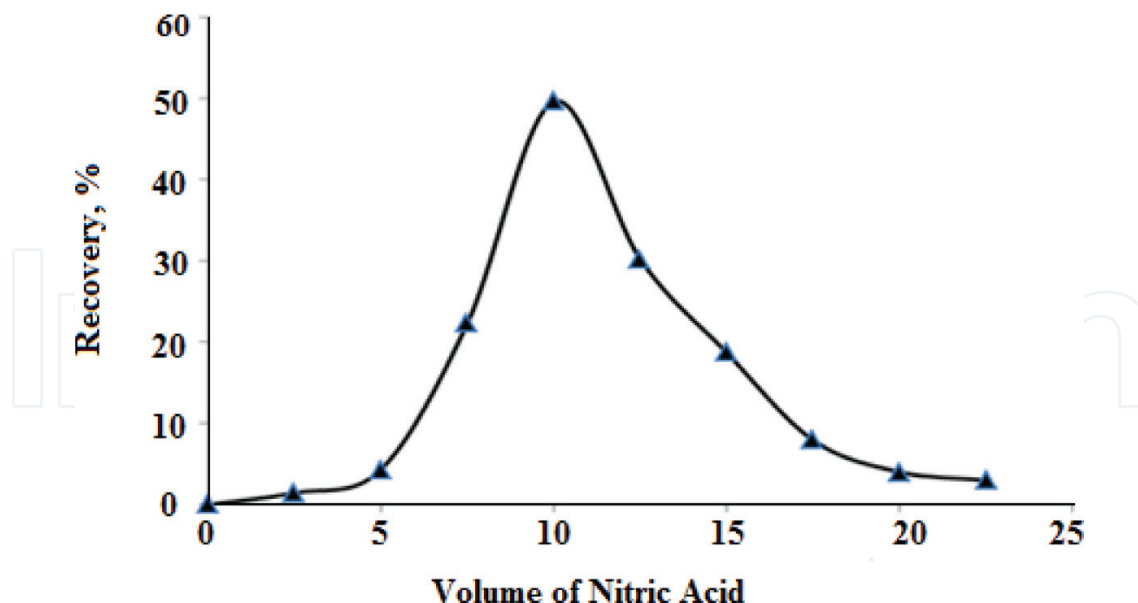


Figure 21. Chromatogram of mercury(II) ion extraction and recovery from the tested TAR- immobilized PUFs packed column using HNO_3 (1 Mol L^{-1}) as eluting agent at 5 mL min^{-1} flow rate.

ions ($5 \mu\text{g mL}^{-1}$) through the TAR loaded PUFs packed column at the optimal conditions (**Figure 22**). The values of HETP and N were then determined by using the Eq. [17]:

$$N = \frac{V_{50} V'}{(V_{50} - V')^2} = \frac{L}{\text{HETP}} \quad (22)$$

where V_{50} is the effluent volume at 50% breakthrough and V' is the volume that the column has a removal efficiency of 15.78% at the initial concentration. The values of N and HETP calculated from **Figure 22** were 90.00 ± 0.03 and $0.99 \pm 0.02 \text{ mm}$ respectively, and had good agreement with data obtained from the chromatogram method. The breakthrough capacity (BC) was also calculated by using the following equation:

$$\text{BC} = \frac{V_{50} \times C_0}{W} \quad (23)$$

the value of BC was found to be 1.27 mg of mercury(II) ion uptake per one gram of the solid sorbent at 5 mL min^{-1} flow rate.

The sensitivity of this method was accessed by limit of detection (LOD) and limit of quantification (LOQ) under the established conditions for mercury(II) ion uptake by TAR- immobilized PUFs packed columns, using the following Equations [57].

$$\text{LOD} = 3 S/b \quad (24)$$

and

$$\text{LOQ} = 10 S/b \quad (25)$$

where S is the standard deviation ($n = 5$) of the blank and b is the slope of the calibration plot. The values of LOD and LOQ were found to be 0.024 and 0.080 ppm, respectively. Such limits

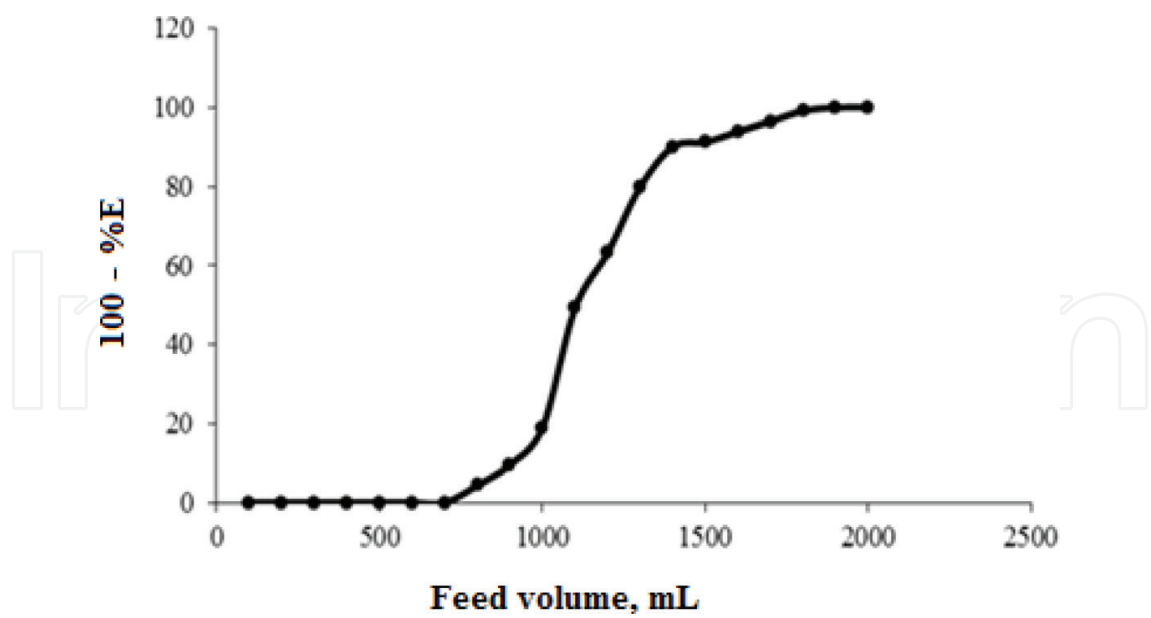


Figure 22. Breakthrough capacity curve for the mercury(II) ion retention onto the investigated columns at optimal conditions.

Hg(II) taken ($\mu\text{g L}^{-1}$)	Hg(II) found ($\mu\text{g L}^{-1}$)	Recovery (%)
500	518.4 ± 1.4	103.7 ± 0.8
100	102.8 ± 0.1	102.6 ± 1.3
10	9.9 ± 1.2	99.6 ± 1.1
5	4.4 ± 1.3	88.1 ± 1.5

Table 2. Analytical data of the extraction and recovery of mercury(II) ions by percolating 1-L deionized water spiked with mercury(II) ions through the tested TAR-PUFs packed columns at 5 mL min^{-1} flow rate (mean \pm SD, $n = 5$).

Type of water	Hg(II) taken, ng mL^{-1}	Hg(II) found, ng mL^{-1}	Recovery %
Tap water	No	0.01	
	1	1.1	110.2 ± 0.1
	10	9.5	95.1 ± 0.1
	1000	825.9	82.5 ± 0.1
Sea water	No	0.03	
	1	0.93	93.6 ± 0.1
	10	7.4	74.5 ± 0.2
	1000	527.9	52.7 ± 0.1

Table 3. Analytical data for the determination of mercury(II) ions (spiked in tap and seawater samples) being removed by the proposed TAR-treated PUFs packed columns (mean \pm SD, $n = 5$).

could be further lowered by increasing the sample volume of the aqueous phase containing ultra-traces of mercury(II) ions at the optimal experimental conditions.

3.7. Analytical applications of the developed TAR-PUFs packed columns

The accuracy of TAR-loaded PUFs packed columns was successfully evaluated by performing recovery tests for 1-L tap and sea water samples spiked with mercury(II) ions in the range 1–1000 ng mL⁻¹. These column proved to satisfactorily remove mercury(II) ions from the tested solutions (>52.7% as displayed in **Table 3**).

4. Conclusion

The kinetic and thermodynamic characteristics of mercury(II) ion uptake by 4-(2-thiazolyl azo) resorcinol-immobilized PUFs sorbents were critically investigated. The kinetic data confirmed the intra-particle diffusion and first-order kinetics of mercury(II) ion retention onto the tested sorbents. Exothermic nature of the retention process of mercury(II) ion onto TAR-treated PUFs is governed by the negative value of ΔH . On the other hand, the negative value of ΔG proves that mercury(II) ion sorption onto the tested sorbents is a spontaneous phenomenon. The developed PUFs packed columns provide a simple, reliable, fairly rapid and low-cost method for the pre-concentration, separation and determination of mercury(II) ion in the aqueous media.

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