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Fast, Selective Removal and Determination of Total Bismuth (III) and (V) in Water by Procaine Hydrochloride Immobilized Polyurethane Foam Packed Column Prior to Inductively Coupled Plasma – Optical Emission Spectrometry

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Additional information is available at the end of the chapter

1. Introduction

Bismuth is found in nature in trivalent state as bismuthinite, Bi_2S_3, bismite, Bi_2O_3 and bismuth sulfide- telluric, Bi_2Te_2S. It is also found as a secondary component in some lead, copper and tin minerals [1]. Bismuth (V) compounds do not exist in solution and are important in the view of pharmaceutical analytical chemistry [1]. In the Earth's crust, bismuth presents at trace concentration (8 μg Kg^{-1}) while, bismuth minerals rarely occur alone and are almost associated with other ores [2]. Bismuth appears to be environmentally significant because its physical and chemical properties have led it to be used in different areas of life. Pamphlett et al, 2000 [3] have reported that, bismuth compounds after oral intake enter the nervous system of mice, in particular, in motor neurons [3]. Hence, bismuth species are included in the list of potential toxins [3].

The development of selective, separation, pre-concentration and determination method for bismuth at sub-micro levels is a challenging problem because of its extremely low concentrations in natural samples and of its strong interference from the sample matrices. Several methods e.g. hydride generation atomic absorption spectrometry [4], electro thermal atomic absorption spectrometry [5], atomic fluorescence spectrometry [6], hydride generation atomic absorption spectrometry [7], and cathotic and anodic adsorptive stripping voltammetry [8 - 10] have been reported for bismuth determination. Most of these methods require preconcentration of bismuth for precise determination because most analytical techniques do not possess adequate sensitivity for direct determination.

Solvent extraction in the presence of co-extractant ligands e.g. bis (2, 4, 4-trimethyl pentyl) monothiophosphinic acid [11], pyrolidine dithocarbamate [12] etc has received considerable attention. However, these methods are too expensive, suffer from the use of large volumes of toxic organic solvents, and time-consuming. Thus, recent years have seen considerable attention on preconcentration and/ or monitoring of trace and ultra trace concentrations of bismuth by low cost procedures in a variety of samples e.g. fresh, marine and industrial wastewater [13]. Solid phase extraction (SPE) techniques have provided excellent alternative approach to liquid – liquid extraction for bismuth preconcentration prior to analyte determination step [14 -18].

Polyurethane foams (PUFs) sorbent represent an excellent solid sorbent material due to their high available surface area, cellular and membrane structure and extremely low cost [19]. Thus, several liquid solid separation involving PUFs methods have been employed successfully for separation and sensitive determination of trace and ultra trace levels of metal ions including bismuth (III) [19-29]. The membrane like structure and the available surface area of the PUFs make it a suitable stationary phase and a column filling material [25, 27]. Thus, the main objectives of the present chapter are focused on: i. developing of a low cost method for the removal of bismuth(III) and (V) species after reduction of the latter to tri valence state employing PUFs impregnated $PQ^+.Cl^-$; ii. Studying the kinetics, and thermodynamic characteristics of bismuth (III) sorption by trioctylamine plasticized $PQ^+.Cl^-$ treated PUFs and finally iii. Application of the developed method in packed column for complete removal and / or determination of bismuth (III &V) species in wastewater by $PQ^+.Cl^-$ treated PUFs sorbent.

2. Experimental

2.1. Reagents and materials

All chemicals used were of A.R. grade and were used without further purification. Stock solution (1000 µg mL^{-1}) of bismuth (III) was prepared from bismuth (III) nitrate (Aldrich Chemical Co Ltd, Milwaukee, WC, USA). More diluted solutions of bismuth (III) (0.1 – 100 µg mL^{-1}) were prepared by diluting the stock solution with diluted nitric acid. Stock solutions of procaine [2-(diethylamino)ethyl 4 aminobenzoate] hydrochloride, $PQ^+.Cl^-$ (1.0 %w/v), Fig.1 and KI (10%w/v) were prepared by dissolving the required weight in water (100 mL). A stock solution (1%v/v) of trioctylamine (Aldrich) was prepared in water in the presence of few drops of concentrated HNO$_3$. Sodium bismuthate
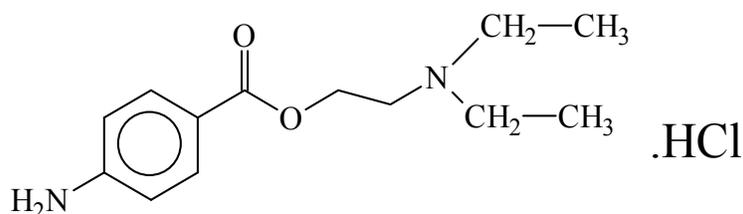

Figure 1. Chemical structure of procaine hydrochloride.

(NaBiO$_3$, 85% purity) (BDH, Poole, England) was used for preparation of stock solution (50 μg mL^{-1}) of bismuth (V) in dark bottle [30] as follows: an accurate weight of NaBiO$_3$ was heated in a suitable volume of HClO$_4$ (20 mL, 0.5 mol L^{-1}) filtered and the solution was made up to 250 mL with deionized water and finally analyzed under the recommended conditions of bismuth determination by ICP-OES (Table 1). The measured concentration was taken as a standard stock solution of bismuth (V) in the next work. Bismuth (V) solution was finally stored in low density polyethylene bottles (LDPE) in dark. Stock solutions (0.1-1% w/v) of PQ$^+$.Cl$^-$ (BDH) and trioctylamine (Merck, Darmstadt, Germany) abbreviated as TOA were prepared in deionized water containing few drops of concentrated HNO$_3$. Sodium diethyldithiocarbamate (Na-DDTC) and PQ$^+$ .Cl$^-$(1% w/v) were purchased from Fluka, AG (Buchs, Switzerland). Commercial white sheets of PUFs were cut as cubes (10 -15 mm), washed, treated and dried. The reagent PQ$^+$ .Cl$^-$ (1.0 % w/v) was dissolved in water, shaken with the PUFs cubes in the presence of TOA (1% v/v) with efficient stirring for 30 min, squeezed and finally dried as reported [21]. The certified reference material (CRM) i.e. trace metal in drinking water standard (CRM-TMDW) was obtained from High-Purity Standard Inc. Sulfuric acid (0.5mol L^{-1}) was used as an extraction medium in the sorption process of bismuth (III) by the PUFs. Commercial white sheets of open cell polyether type polyurethane foam were purchased from the local market of Jeddah City, Saudi Arabia and were cut as cubes (10-15 mm). The PUFs cubes were washed and dried as reported [21, 27]. A series of Britton- Robinson (B-R) buffer (pH 2-11) was prepared as reported [31].

Parameter	
Rf power (kW)	1050 (900.0)
Plasma gas (Ar) flow rate, L min^{-1}	15 (15)
Auxiliary gas (Ar) flow rate, L min^{-1}	0.2 (1.2)
Nebulizer gas (Ar) flow rate, Lmin^{-1}	0.80 (0.93)
Pump rate, mL min^{-1}	1.5
Observation height, mm	15
Integration time, s	10
Wavelength, nm	Bi 223.061

*ICP –MS operational parameters are given in parentheses. Other parameters are: lens voltage =9.0; analog stage voltage 1750 V; pulse stage voltage =750 V; quadrupole rod offset std = =0.0; cell rod offset =-18.0; discriminator threshold =17.0; cell path voltage Std = -13.0 V and atomic mass 208.98 am.

Table 1. ICP-OES operational conditions and wavelength (nm) for bismuth determination*

2.2. Instrumental and apparatus

A Perkin – Elmer (Lambda 25, Shelton, CT,USA) spectrophotometer (190 – 1100 nm) with 10 mm (path width) quartz cell was used for recording the electronic spectra and measuring the absorbance of the ternary complex ion associate PQ$^+$. BiI$_4^-$ of bismuth (III) at 420 nm before and after extraction with the reagent PQ$^+$.Cl$^-$ treated PUFs. A

Perkin Elmer inductively coupled plasma – optical emission spectrometer (ICP- OES, Optima 4100 DC (Shelton, CT, USA) was used and operated at the optimum operational parameters for bismuth determination (Table 1). A Perkin Elmer inductively coupled plasma – mass spectrometer (ICP – MS) Sciex model Elan DRC II (California, CT, USA) was also used to measure the ultra trace concentrations of bismuth in the effluent after extraction by the developed PUFs packed column at the operational conditions (Table 1). A Corporation Precision Scientific mechanical shaker (Chicago, CH, USA) with a shaking rate in the range 10 – 250 rpm and glass columns (18 cm x 15 mm i.d) were used in batch and flow experiments, respectively. De-ionized water was obtained from Milli-Q Plus system (Millipore, Bedford, MA, USA). A thermo Orion model 720 pH Meter (Thermo Fisher Scientific, MA, USA) was employed for pH measurements with absolute accuracy limits being defined by NIST buffers.

2.3. General batch procedures

2.3.1. Preparation of the immobilized reagent ($PQ^+ .Cl^-$) polyurethane foams.

The reagent $PQ^+ .Cl^-$(1% w/v)in water was shaken with the PUFs cubes in the presence of the plasticizer TOA (1% v/v) with efficient stirring for 30 min. The loaded $PQ^+.Cl^-$ PUFs cubes were squeezed and dried between two filter papers [20, 21]. The amount of $PQ^+.Cl^-$ retained onto the PUFs sorbent was calculated using the equation [21]:

$$a = \left(C_0 - C \right) \frac{v}{w} \tag{1}$$

where, C_0 and C are the initial and final concentrations (mol L^{-1}) of the reagent ($PQ^+.Cl^-$) in solution, respectively, v = volume of the reagent solution (liter) and w is the mass (g) of the PUFs sorbent. The reproducibility of $PQ^+.Cl^-$ treated PUFs is fine and the PUFs can be reused many times without decrease in its efficiency.

2.3.2. Batch extraction step

An accurate weight (0.1 ± 0.002 g) of unloaded- or $PQ^+.Cl^-$immobilized PUFs was equilibrated with an aqueous solution (100 mL) containing bismuth (10 µg mL^{-1}) in the presence of KI (10% w/v) , H_2SO_4 (0.5 mol L^{-1})and ascorbic acid (0.1%w/v) to minimize the aerial oxidation of KI. The test solution was shaken for 1 h on a mechanical shaker. The aqueous phase was then separated out by decantation and the amount of bismuth (III) remained in the aqueous phase was then determined spectrohotometrically against reagent blank [32] or by ICP-OES at ultra trace concentrations. The amount of bismuth (III) retained on the foam cubes was then calculated from the difference between the absorbance of $[BiI_4]^-$ in the aqueous phase before (A_b) and after extraction (A_f). The sorption percentage (%E) , the distribution ratio (D), the amount of bismuth (III) retained at equilibrium (q_e) per unit mass of solid sorbent (mol/g) and the distribution coefficient (K_d) of sorbed analyte onto the foam cubes were finally calculated as reported. The %E and K_d are the average of three independent measurements and the precision in most cases was ±2%. Following these procedures, the influence of shaking time and temperature on the retention of bismuth (III) by the PUFs sorbents was fully studied.

2.3.3. Retention and recovery of bismuth (III)

An aqueous solution (100 mL) of bismuth (III) ions at concentration (5 – 100 μg L^{-1}), KI (10%) and H$_2$SO$_4$ (1.0 mol L^{-1}) was percolated through the PQ$^+$.Cl$^-$ loaded PUFs (1.0 ± 0.002 g) column at 2.0 mL min^{-1} flow rate. A blank experiment was also performed in the absence of bismuth (III) ions. Bismuth (III) sorption took place quantitatively as indicated from the analysis of bismuth species in effluent solutions by ICP- OES. After extraction, the ultra trace concentrations of bismuth (III) remained in the test aqueous solutions were estimated by ICP-MS. Bismuth (III) species were recovered quantitatively with HNO$_3$ (3.0 mol L^{-1}, 10 mL) at 2.0 mL min^{-1} flow rate.

2.3.4. Retention and recovery of bismuth (V)

An aqueous solution (100.0 mL) of bismuth (V) at concentration < 10 μg L^{-1} was allowed to react with an excess of KI (10% w/v) - H$_2$SO$_4$ (1.0 mol L^{-1}). The solution was then percolated through PQ$^+$ .Cl$^-$ loaded PUFs (1.0 ± 0.002 g) packed column at 2.0 mL min^{-1} flow rate of 2.0 mL min^{-1}. The retained bismuth (III) species were recovered with HNO$_3$ (10.0 mL, 1.0 mol L^{-1}) at 2.0 mL min^{-1} flow rate and analyzed by ICP- OES.

2.3.5. Sequential determination of total bismuth (III) and (V)

An aqueous solution (100 mL) containing bismuth (III) and (V) at a total concentration ≤ 10 μg L^{-1} was analyzed according to the described procedure for bismuth (V) retention and recovery. Another aliquot portion (100 mL) was adjusted to pH 3 - 4 with acetate buffer and then shaken with Na-DDTC (5 0 mL, 1%w/v) for 2-3 min. Bismuth (III) ions were then extracted with methylisobutylketone (5.0 mL) as Bi (DDTC)$_3$after 2 min [24]. Bismuth (V) remained in the aqueous solution was reduced to bismuth (III) by an excess of KI (10% w/v) in the presence of H$_2$SO$_4$ (0.5 mol L^{-1}) and then percolated through the PQ$^+$.Cl$^-$ loaded PUFs column at 2 ml min $^{-1}$ flow rate at the optimum experimental conditions. The retained bismuth species were recovered and finally analyzed following the recommended procedures for bismuth (III). Thus, the net signal intensity of ICP- OES (or ICP-MS) at ultra trace concentrations of the first aliquot (I$_1$) will be a measure of the sum of the bismuth (III) and (V) ions in the mixture, while the net signal intensity of the of the second aliquot (I$_2$) is a measure of bismuth (V) ions. The difference (I$_1$-I$_2$) of the net signal intensity is a measure of bismuth (III) ions in the binary mixture.

2.4. Analytical applications

2.4.1. Analysis of certified reference material TMDW

The TMDW water sample (2 mL) was digested with nitric acid (10 mL, 3.0. mol L^{-1}) and hydrogen peroxide (10 mL, 10% v/v), boiled for 5 min and diluted by an excess of KI (10% w/v) - H$_2$SO$_4$ (1.0 mol L^{-1}) to 100 mL. After cooling, the test solution was percolated through the PQ$^+$.Cl$^-$ loaded PUFs column at 2 ml min $^{-1}$ flow rate. The retained bismuth species were recovered with HNO$_3$ (10.0 mL, 1.0 mol L^{-1}) at 2.0 mL min^{-1} flow rate and nalyzed by ICP-OES following the recommended procedures for bismuth (III).

2.4.2. Analysis of total bismuth in wastewater

Wastewater samples (1.0 L) were collected and filtered through a 0.45 μm membrane filter (Milex, Millipore Corporation). The test solution was digested with nitric acid (10 mL, 3.0. mol L^{-1}) and hydrogen peroxide (10 mL, 10% v/v), boiled for 5 min and spiked with different amounts (0.05- 0.5 μg) of bismuth (III) in presence of an excess of KI (10% w/v). After centrifugation for 5 min, the sample solutions were percolated through $PQ^+.Cl^-$ loaded PUFs packed columns at 5 mL min^{-1} flow rate. The concentration of bismuth in the effluent solution was determined by ICP - MS. The retained bismuth (III) species on the PUFs were then recovered and analyzed as described above.

2.4.3. Analysis of total bismuth in seawater

The general procedure for the extraction and recovery of bismuth (III) ions from seawater samples onto $PQ^+.Cl^-$ impregnated PUFs was performed as follow: A 100 mL of water samples were filtered through 0.45 μm membrane filter, adjusted to pH zero with H_2SO_4 (0.5 mol L^{-1}) in the presence of KI (0.1% w/v) and ascorbic acid. The sample solution was then passed through $PQ^+.Cl^-$ impregnated PUFs (1.0 ± 0.001 g) packed column (10 cm x 1.0 cm i.d.) at 5 mL $min.^{-1}$ The retained bismuth(III) species were then recovered and analyzed as described above. The recovered bismuth (III) ions were then determined by ICP-OES.

3. Results and discussion

In recent years [28, 29], PUFs immobilizing some ion pairing reagents have received considerable attention for selective separation, determination and / or chemical speciation of trace and ultra trace metal ions. The non-selective sorption characteristic of the PUFs has been rendered and became more selective by controlling the experimental conditions e.g. pH, ionic strength, etc. Preliminary investigation has shown that, on shaking unloaded PUFs and $PQ^+.Cl^-$ immobilized PUFs with aqueous solutions containing bismuth (III) ions , KI (10% w/v) and H_2SO_4 (0.5 mol L^{-1}), considerable amount of bismuth (III) species were retained onto $PQ^+.Cl^-$ treated PUFs in a very short time compared to the untreated PUFs ones. Thus, in subsequent work, detailed study on the application of $PQ^+.Cl^-$ immobilized PUFS for retention of various bismuth (III & V) species to assign the most probable kinetic model, sorption isotherm models, mechanism and thermodynamic characteristics of retention of bismuth (III) from the test aqueous solutions.

3.1. Retention profile of bismuth (III) from the aqueous solution onto PUFs

Bismuth (III) forms an orange – yellow colored tetraiodobismuthate(III) complex, $[BiI_4]^-$ [32] in aqueous solutions containing sulfuric acid (0.5 mole L^{-1}) and an excess of KI (10% w/v). Thus, the sorption profile of aqueous solutions containing bismuth (III) at different pH by $PQ^+.Cl^-$ loaded foams was critically studied after shaking for 1h at room temperature. After equilibrium, the amount of bismuth (III) in the aqueous phase was determined spectrophotometrically [32]. The results are shown in Fig. 2. The %E and K_d of bismuth (III)

sorption onto the PUFs markedly decreased on increasing solution pH and maximum uptake was achieved at pH zero. At pH >1, the sorption of bismuth (III) by $PQ^+.Cl^-$ treated PUFs towards bismuth (III) decreased markedly (Fig.2). This behavior is most likely attributed to the deprotonation of the ether oxygen ($-CH_2 – O– CH_2 –$) and/or urethane nitrogen ($- NH– CO–$) of PUFs, instability, hydrolysis, or incomplete extraction of the produced ternary complex ion associate of $PQ^+.[BiI_4]^-$ on/ in the PUFs sorbent.
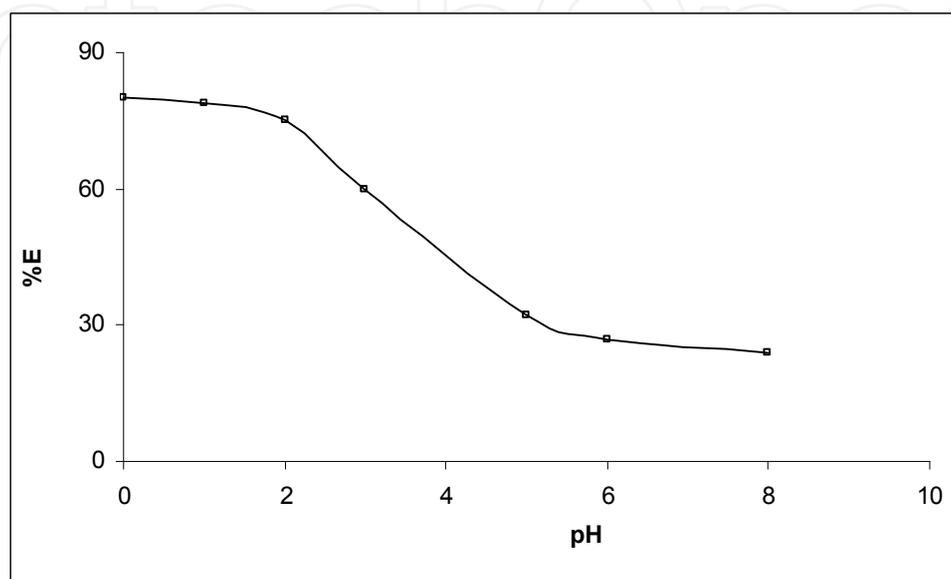
Figure 2. Effect of pH on the sorption percentage of bismuth (III) from aqueous solutions containing KI (10 % m/v) - H_2SO_4 (2.0 mol L^{-1}) onto $PQ^+ .Cl^-$ immobilized PUFs (0.1 ± 0.002 g) at 25 ± 0.1[0]C.

The retention of bismuth (III) at low pH of aqueous media is most likely attributed to sorbent membranes. The pK_a values of protonation of oxygen atom of ether group ($- CH_2- OH^+- CH_2-$) foam and nitrogen atom of the amide group ($- N^+H_2 - COO-$) foam are – 3 and – 6, respectively [32]. Thus, in extraction media containing H_2SO_4 (0.50 mole L^{-1}) and KI, the complexed species of bismuth $[BiI_4]^-$ are easily retained onto the protonated ether group of the PUFs than amide group of PUFs sorbent. The stability constants of the binding sites of the PUFs with $[BiI_4]^-$ were calculated using the Scatchard equation [33]:
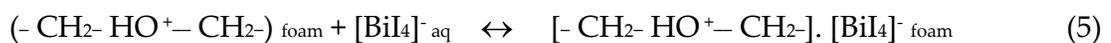
$$\frac{n}{[Bi]} = K(n_i – n) \tag{2}$$

and n is given by the equation:

$$n = \frac{\textit{weight} \text{ of bismuth bound to foam (g)}}{\text{weight of foam (g)}} \tag{3}$$

where, K = stability constant of bismuth (III) on PUF, n_i = maximum concentration of sorbed bismuth (III) by the available sites onto the PUFs, and [Bi] is the equilibrium concentration of bismuth (III) in solution (mol L^{-1}). The plot of n /[Bi] versus n is shown in Fig. 3. The curvature of the Scatchard plot demonstrated that more than one class of complex species of

bismuth (III) has been formed and each complex has its own unique formation constant. The stability constants log K_1 and log K_2 for the sorbed species derived from the respective slopes were 5.56 ± 0.2 and 4.82 ± 0.5, respectively. The values of n_1 and n_2 calculated from the plot were found equal 0.038 ± 0.005 and 0.078 ± 0.01 mol g^{-1}, respectively. The values of the stability constants (log K_1 and log K_2) indicated that, the sorption of bismuth (III) species took place readily on site K_1 that most likely belong to the ether group. The fact that, ether group has a stability greater than the amide group (site K_2) as reported [32]. Moreover, the high values of K_1 and K_2 indicated that, both bonding sites of PUFs are highly active towards $[BiI_4]^-$ species in good agreement with the data reported involving the extraction of the bulky anion $[BiI_4]$ by methyl isobutyl ketone and other solvents that posses ether linkages in their structures e.g. diethyl ether and isopropyl ether [34]. Based on these data and the results reported on the retention of $AuCl_4^-$ and CdI_4 by PUFs [29, 34], a sorption mechanism involving a weak base anion ion exchanger and/ solvent extraction of $[BiI_4]^-_{aq}$ by the protonated ether oxygen or urethane nitrogen linkages of the PUFs as a ternary complex ion associate is most likely proceeded as follows:
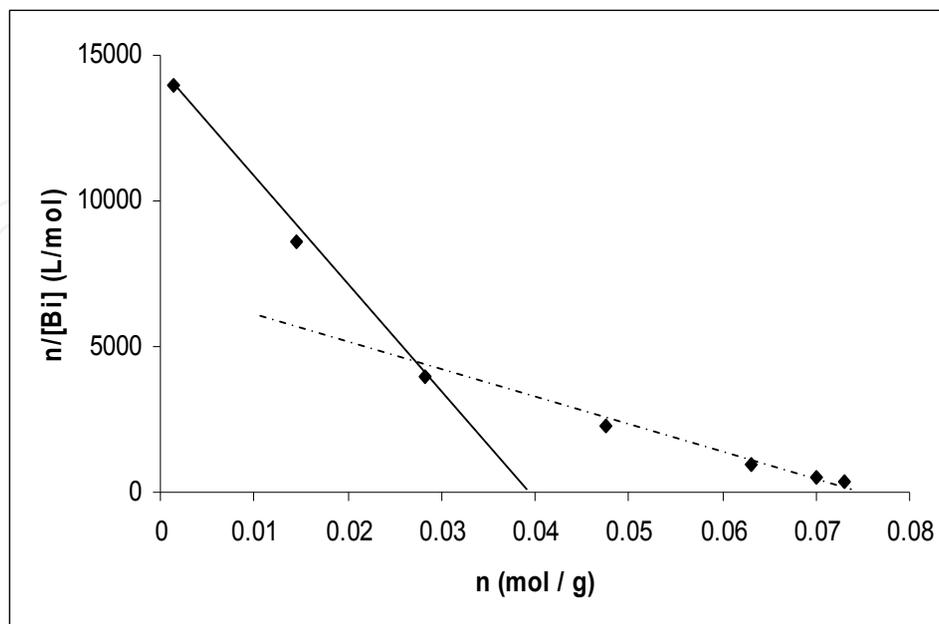
Ether group, PUF:

$$(-CH_2- O- CH_2-) \text{ foam} + H^+ \quad \leftrightarrow \quad (-CH_2- HO^+- CH_2-) \text{ foam} \qquad (4)$$

$$(-CH_2- HO^+- CH_2-) \text{ foam} + [BiI_4]^-_{aq} \quad \leftrightarrow \quad [-CH_2- HO^+- CH_2-].[BiI_4]^- \text{ foam} \qquad (5)$$

Urethane group, PUF:

$$(-NH-COO-) \text{ foam} + H^+ \quad \leftrightarrow \quad (--NH^+_2-COO-) \text{foam} \qquad (6)$$

$$(-N^+H_2-COO-) \text{foam} + [BiI_4]^-_{aq} \quad \leftrightarrow \quad [-N^+H_2-COO-].[BiI_4]^- \text{foam} \qquad (7)$$

Figure 3. Scatchard plot for the binding of $[BiI_4]^-$ species by $PQ^+ .Cl^-$ immobilized PUF (0.1 ± 0.002 g) from aqueous media containing KI (10 % m/v) - H_2SO_4 (0.5 mol L^{-1}) at 25 ± 0.1^0C.

The distribution ratio of bismuth (III) onto $PQ^+.Cl^-$ immobilized PUFs showed high retention (D= 6.17×10^4 mL g^{-1}) compared to the unloaded PUFs (3.05×10^3 mL g^{-1}) due to the formation of the ion associate ($[(PQ^+). (BiI_4)]^-_{foam}$ on/in treated PUFs. Thus, the solution pH was adjusted at pH 0.0 – 1.0 and $PQ^+.Cl^{-1}$ treated PUFs was used as a proper sorbent in the subsequent work.

The influence of the plasticizer e.g. tri-n-octylamine (TOA, 0.5 -2.0 %v/v) and tri-n-butyl-phosphate (TBP,0.01%v/v) on the retention of bismuth (III) from the aqueous solutions onto the $PQ^+.Cl^-$ loaded PUFs was studied. Bismuth (III) sorption onto the PUFs sorbent increased (D = 6.6×10^4 mL g^{-1}) in presence of TOA (1% v/v). The formation of the co ternary complex ion associates $TOA^+.BiI_4^-$ and $PO^+.BiI_4^-$ in acidic media may account for the observed increase.

3.2. Kinetic behavior of bismuth (III) sorption onto $PQ^+.Cl^-$ -TOA loaded PUFs

The influence of shaking time (0 – 60 min) on the uptake of bismuth (III) from the aqueous acidic media at pH zero was investigated. The sorption of bismuth (III) ions onto TOA plasticized $PQ^+.Cl^-$ immobilized PUFs was fast and reached equilibrium within 60 min of shaking time. This conclusion was supported by calculation of the half-life time ($t_{1/2}$) of bismuth (III) sorption from the aqueous solutions onto the solid sorbents PUFs. The values of $t_{1/2}$ calculated from the plots of -log C/C_0 versus time for bismuth (III) sorption onto PUFs, where C_0 and C are the original and final concentration of bismuth(III) ions in the test aqueous solution, respectively . The value of $t_{1/2}$ was found 2.32 ± 0.04 min in agreement with $t_{1/2}$ value reported earlier [19]. Thus, gel diffusion is not only the rate-controlling step for $PQ^+.Cl^-$ immobilized PUFs as in the case of common ion exchange resins [19] and the kinetic of bismuth (III) sorption by $PQ^+.Cl^-$ immobilized PUFs sorbent depends on film and intraparticle diffusion step where, the more rapid one controls the overall rate of transport.

The sorbed bismuth (III) species onto PUFs sorbent was subjected to Weber–Morris model [35]:

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

where, R_d is the rate constant of intraparticle transport in μ mole g^{-1} $min^{-1/2}$ and q_t is the sorbed Bi (III) concentration (μ mole g^{-1}) at time t. The plot of qt *vs.* time (Fig 4) was linear (R^2= 0.989) at the initial stage of bismuth (III) uptake by TOA plasticized $PQ^+.Cl^-$ loaded PUFs sorbents was linear up to 10 ± 1.1 min and deviate on increasing shaking time. The rate of diffusion of $[BiI_4]^-_{aq}$ species is high and decreased on increasing shaking time. Thus, the rate of the retention step of $[BiI_4]^-_{aq}$ onto the used solid sorbent is film diffusion at the early stage of extraction [34, 35]. The values of R_d computed from the two distinct slopes of Weber – Morris plots (Fig.4) for bismuth(III) retention by the solid sorbent were found equal 3.076 ± 1.01 and 0.653 m mole g^{-1} with correlation coefficient (R^2) of 0.989 and 0.995, respectively. The observed change in the slope of the linear plot (Fig.4) is most likely attributed to the different pore size [34, 35]. Thus, intra-particle diffusion step is most likely the rate determining step.
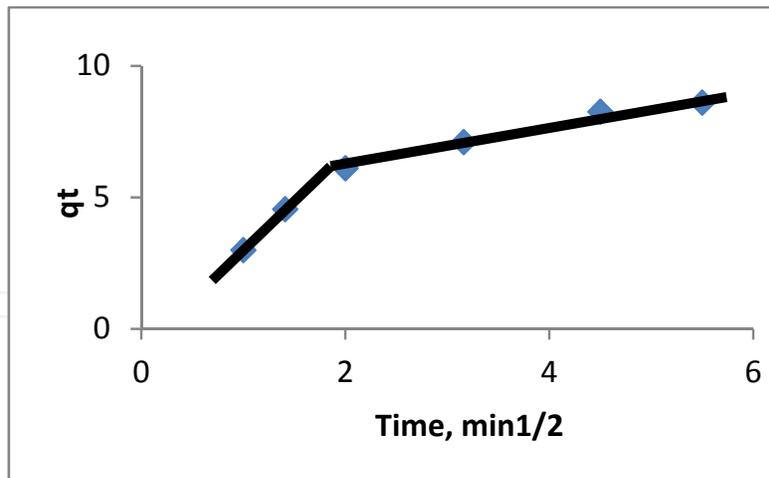
Figure 4. Weber – Morris plot of sorbed bismuth (III) onto PQ$^+$.Cl$^-$ immobilized PUFs $vs.$ square root of time. Conditions: Aqueous solution (100 mL) containing KI (10 % m/v) and H$_2$SO$_4$ (0.5 mol L^{-1}), foam doze = (0.1 ± 0.002 g and 25 ± 0.1^{0}C**.**

The retention step of the [BiI$_4$]$^-$ species onto the loaded PUFs at 25 ± 1 ^{0}C was subjected to Lagergren model [28]:

$$\log\ (q_e - q_t)\ =\ \log q_e\ -\ \frac{K_{Lager}}{2.303}\ t \qquad (9)$$

where, q$_e$ is the amount of [BiI$_4$]$^-$ sorbed at equilibrium per unit mass of PUFs sorbent (μmoles 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 plot of log (q$_e$ – q$_t$) $vs.$ time (Fig.5) was linear. The computed value of K$_{Lager}$ was 0.132 ± 0.033 min^{-1} (R^2= 0.979) confirming the first order kinetic model of sorption of [BiI$_4$]$^-$ species onto the solid sorbent [29]. The influence of adsorbate concentration was investigated and the results indicated that, the value of K$_{Lager}$ increased on increasing adsorbate concentration confirming the first order kinetic nature of the retention process and the formation of monolayer species of [BiI$_4$]$^-$ onto the surface of the used adsorbent [26, 29].
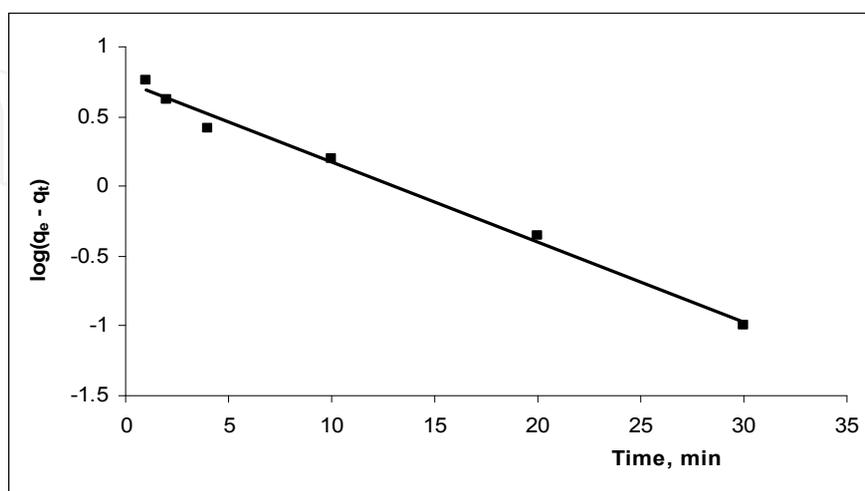

Figure 5. Lagergren plot of bismuth (III) uptake onto PQ$^+$.Cl$^-$ PUFs from aqueous solutions containing KI (10 % m/v) - H$_2$SO$_4$ (2.0 mol L^{-1}) $vs.$ time at 25 ± 0.1^{0}C**.]**

The sorption data was also subjected to Bhattacharya- Venkobachar kinetic model [36].

$$\log \left(1 - U_{(t)} \right) = \frac{- K_{\text{Bhatt}}}{2.303} \, t \qquad (10)$$

$$\text{where, } U_{(t)} = \frac{C_0 - C_t}{C_o - C_e} \, ,$$

where, K_{Bhatt} = overall rate constant (min^{-1}), t = time (min), C_t= concentration of the bismuth (III) at time t in μg mL^{-1}, C_e= concentration of Bi (III) at equilibrium in μg mL^{-1}. The plot of $\log (1-U_{(t)})$ *vs.* time was linear (Fig.6) with R^2= 0.987. The computed value of K_{Bhatt} (0.143 ± 0.002 min^{-1}) from Fig. 6 was found close to the value of K_{Lager} (0.132 ± 0.033 min^{-1}) providing an additional indication of first order kinetic of bismuth (III) retention towards PQ$^+$ .Cl$^-$ loaded PUFs sorbent.
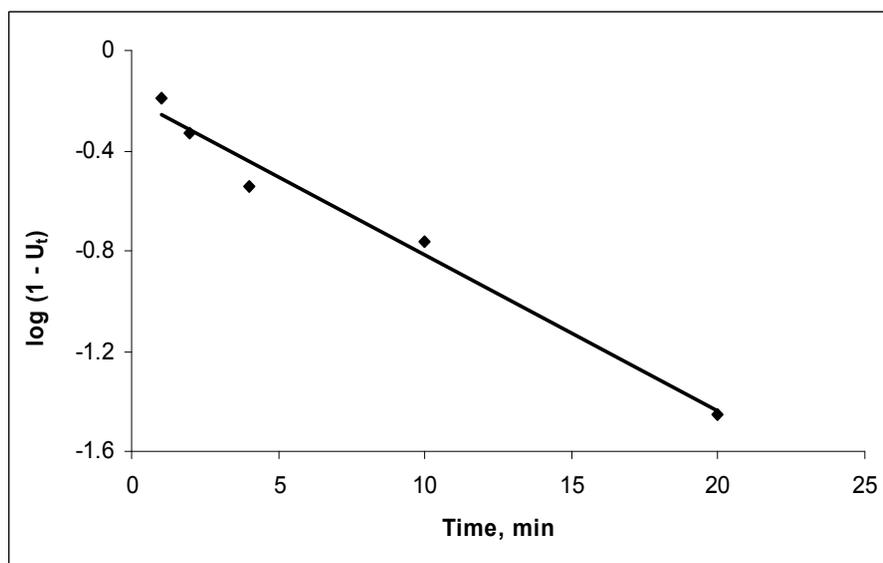

Figure 6. Bhattacharya-Venkobachar plot of bismuth (III) retention from aqueous media containing KI (10 % m/v) - H$_2$SO$_4$ (0.5 mol L^{-1}) at 25 ± 0.1^{0}C onto the PQ$^+$ .Cl$^-$ and TOA loaded PUFs.

The value of BT, which is a mathematical function (F) of the ratio of the fraction sorbed (q_t) at time t and at equilibrium (q_e) in μ mole g^{-1} i.e. F= q_t / q_e calculated for each value of F employing Reichenburg equation [36].

$$BT = - 0.4977 - 2.303 \log (1- F) \qquad (11)$$

The plot of Bt versus time at 25 ± 1 ^{0}C for TOA plasticized PQ$^+$ .Cl$^-$ PUFs towards bismuth (III) species was linear(R^2 = 0.990) up to 35 min (Fig. 7) . The straight line does not pass through the origin indicating that, particle diffusion mechanism is not only responsible for the kinetic of [BiI$_4$]$^-$sorption onto the PQ$^+$ .Cl$^-$ treated sorbents. Thus, the uptake of [BiI$_4$]$^-$ onto the employed sorbents is most likely involved three steps: i- bulk transport of [BiI$_4$]$^-$ in solution, ii- film transfer involving diffusion of [BiI$_4$]$^-$ within the pore volume of TOA plasticized PQ$^+$ .Cl$^-$ treated PUFs and/ or along the wall surface to the active sorption sites of

the sorbent and finally iii- formation of the complex ion associate of the formula [- CH$_2$- HO$^+$— CH$_2$-]. [BiI$_4$]$^-$Foam or [-$^+$NH$_2$ — COO$^-$]. [BiI$_4$]$^-$Foam. Therefore, the actual sorption of [BiI$_4$]$^-$ onto the interior surface of PUFs was rapid and hence particle diffusion mechanism is not the rate determining step in the sorption process. Thus, film and intraparticle transport might be the two main steps controlling the sorption step. Hence, "solvent extraction" and/or "weak base anion ion exchanger" mechanism is not only the most probable participating mechanism and some other processes e.g. surface area and specific sites on the PUFs are most likely involved simultaneously in bismuth (III) retention [37].
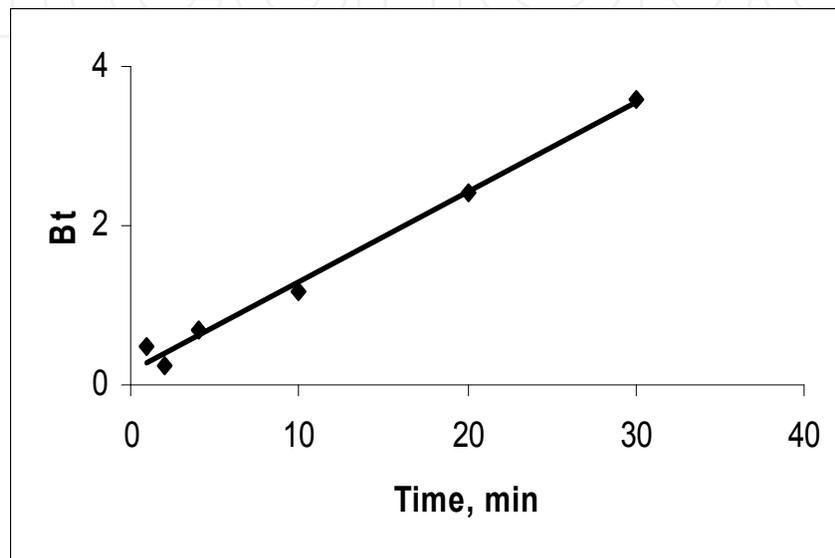

Figure 7. Reichenburg plot of bismuth (III) retention from aqueous media containing KI (10 % m/v) - H$_2$SO$_4$ (0.5 mol L^{-1}) at 25 ± 0.1^{0}C onto PQ$^+$ .Cl$^-$ loaded PUFs.

3.3. Thermodynamic characteristics of bismuth (III) retention onto plasticized PQ$^+$.Cl$^-$ loaded PUFs

Bismuth (III) retention onto TOA plasticized PQ$^+$.Cl$^-$ PUFs was studied over a wide range of temperature (293-353 K) to determine the nature of bismuth (III) retention onto solid sorbent at the established experimental conditions. The thermodynamic parameters (ΔH, ΔS, and ΔG) were evaluated using the equations:

$$\ln K_c = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (12)$$

$$\Delta G = \Delta H - T\Delta S \quad (13)$$

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 (≈ 8.3 J K^{-1} mol^{-1}). K$_c$ is the equilibrium constant depending on the fractional attainment (Fe) of the sorption process. The values of K$_c$ of bismuth (III) retention from the test aqueous solutions at equilibrium onto the plasticized PQ$^+$.Cl$^-$ PUFs were calculated using the equation:

$$K_C = \frac{Fe}{1 - Fe} \qquad (14)$$

Plot of ln K_C *vs.* 1000/T (K^{-1}) for bismuth (III) retention was linear (Fig. 8) over the wide range of temperature range (293- 323 K). The value of K_C decreased on increasing temperature, revealing that, the retention process of $[BiI_4]^-$ species onto the sorbents is an exothermic process [21, 22]. The numerical values of ΔH, ΔS, and ΔG calculated from the slope and intercept of the linear plot Fig. 8 were -18.72± 1.01 kJ mol^{-1} , 54.57± 0.5 J mol^{-1} K^{-1} and -2.46 ± 0.1 kJ mol^{-1} (at 298 K), respectively with a correlation factor of 0.998.
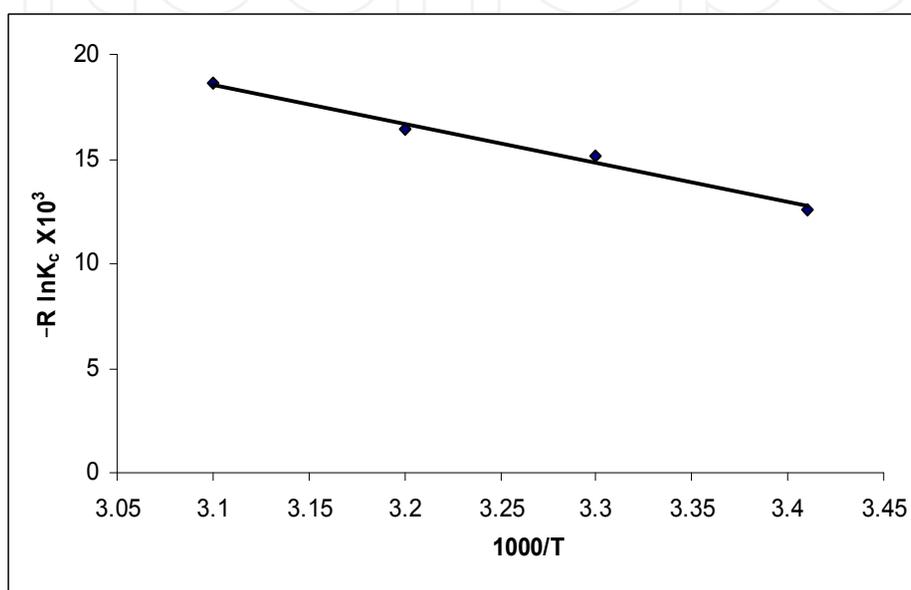

Figure 8. Plot of ln K_C *vs.* 1000/T (K^{-1}) of bismuth (III) sorption from aqueous media containing KI (10 % m/v) - H$_2$SO$_4$ (0.5 mol L^{-1}) onto PQ$^+$ .Cl$^-$ treated PUFs.

The retention of bismuth (IIII) by plasticized PQ$^+$.Cl$^-$ loaded PUFs was also subjected to Vant Hoff model:

$$\log K_d = \frac{-\Delta H}{2.30\ RT} + C \qquad (15)$$

where, C is a constant. Vant - Hoff plot of log K_d *vs.* 1000/T (K^{-1}) of bismuth (III) uptake from the test aqueous media of KI (10 % m/v) - H$_2$SO$_4$ (0.5 mol L^{-1}) onto plasticized PQ$^+$.Cl$^-$ loaded PUFs sorbent was linear (Fig. 9). The value of ΔH calculated from the slope of Fig. 9 was - 20.1 ± 1.1 kJ mol^{-1} in good agreement with the values evaluated from equations 12 and 13. The ΔS of activation were lower than TΔS at all temperature. Thus, the retention step is entropy controlled at the activation state.

The negative value of ΔH and the data of D and K_C reflected the exothermic behavior of bismuth (III) uptake by the employed solid PUFs and non-electrostatics bonding formation between the adsorbent and the adsorbate. The positive value of ΔS proved that, bismuth (III) uptake are organized onto the used sorbent in a more random fashion and may also

indicative of moderated sorption step of the complex ion associate of $[BiI_4]^-$ and ordering of ionic charges without a compensatory disordering of the sorbed ion associate onto the used sorbents. The sorption process involves a decrease in free energy, where ΔH is expected to be negative as confirmed above. Moreover, on raising the temperature, the physical structure of the PUFs membrane may be changing, and affecting the strength of intermolecular interactions between the membrane of PUFs sorbent and the $[BiI_4]^-$ species. Thus, high temperature may make the membrane matrix become more unstructured and affect the ability of the polar segments to engage in stable hydrogen bonding with $[BiI_4]^-$ species, which would result in a lower extraction. The negative of ΔG at 295 K implies the spontaneous and physical sorption nature of bismuth (III) retention onto PUFs. The decrease in ΔG on decreasing temperature confirms the spontaneous nature of sorption step of bismuth (III) is more favorable at low temperature. The energy of urethane nitrogen and/or ether oxygen sites of the PUFs provided by raising the temperature minimizes the interaction between the active sites of PUFs and the complex ion associates of bismuth (III) ions resulting low sorption via "Solvent extraction" [38]. These results encouraged the use of the reagent loaded PUFs in packed column mode for collection, and sequential determination of bismuth (III) and (V) in water samples.
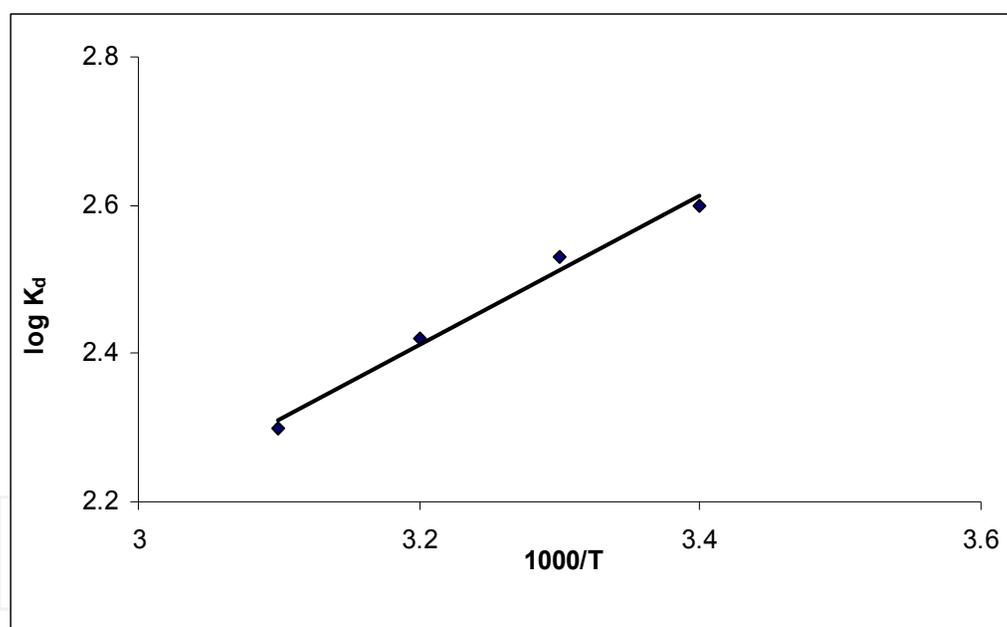

Figure 9. Vant - Hoff plot of log K_d *vs.* 1000/T (K^{-1}) of bismuth (III) retention from aqueous media containing KI (10 % m/v) - H_2SO_4 (0.5 mol L^{-1}) onto $PQ^+ . Cl^-$ loaded PUFs.

3.4. Sorption isotherms of bismuth (III) onto PQ⁺ .Cl⁻ loaded PUFs sorbents

The development of a suitable preconcentration and/ or separation procedures for determination of trace concentrations of bismuth (III) in water is becoming increasingly important. PUFs physically immobilized with a series of quaternary ammonium ion pairireagents e.g. tetraphenyl phosponium chloride, amiloride hydrochloride, tetraheptyl

ammonium bromide or procaine hydrochloride was tested for the separation of bismuth (III) from aqueous iodide aqueous media. The results revealed considerable retention of bismuth (III) onto PQ^+ .Cl^- loaded PUFs compared to other onium cations. Thus, the retention profile of bismuth (III) over a wide range of equilibrium concentrations of bismuth (III) ions onto PQ^+ .Cl^- loaded PUFs sorbent from aqueous KI (10%w/v) -H_2SO_4 (1.0 mol L^{-1}) solutions was investigated. The amount of $[BiI_4]^-$ retained onto the PUFs at low or moderate bismuth (III) concentration varied linearly with the amount of bismuth (III) remained in the test aqueous solution (Fig. 10).The equilibrium was approached only from the direction of $[BiI_4]^-$ species-rich aqueous phase confirming a first- order sorption behavior [39]. The sorption capacity of bismuth (III) species towards PQ^+.Cl^- immobilized PUFs as calculated from the sorption isotherm (Fig.10) was 40.0 ± 1.10 mg g^{-1}. The plot of distribution coefficient (K_d) of bismuth (III) sorption between the aqueous solution H_2SO_4 (0.5 mol L-1) and KI (10% w/v) and PQ^+.Cl^- loaded PUFs sorbent is given in Fig. 11. The most favorable values of K_d of bismuth (III) sorption onto PUFs sorbent were also obtained from more diluted aqueous solutions (Fig. 11). The K_d values decreased on increasing the concentration of bismuth (III) ions in the aqueous phase and the PUFs membranes became more saturated with the retained $[BiI_4]^-$ species.
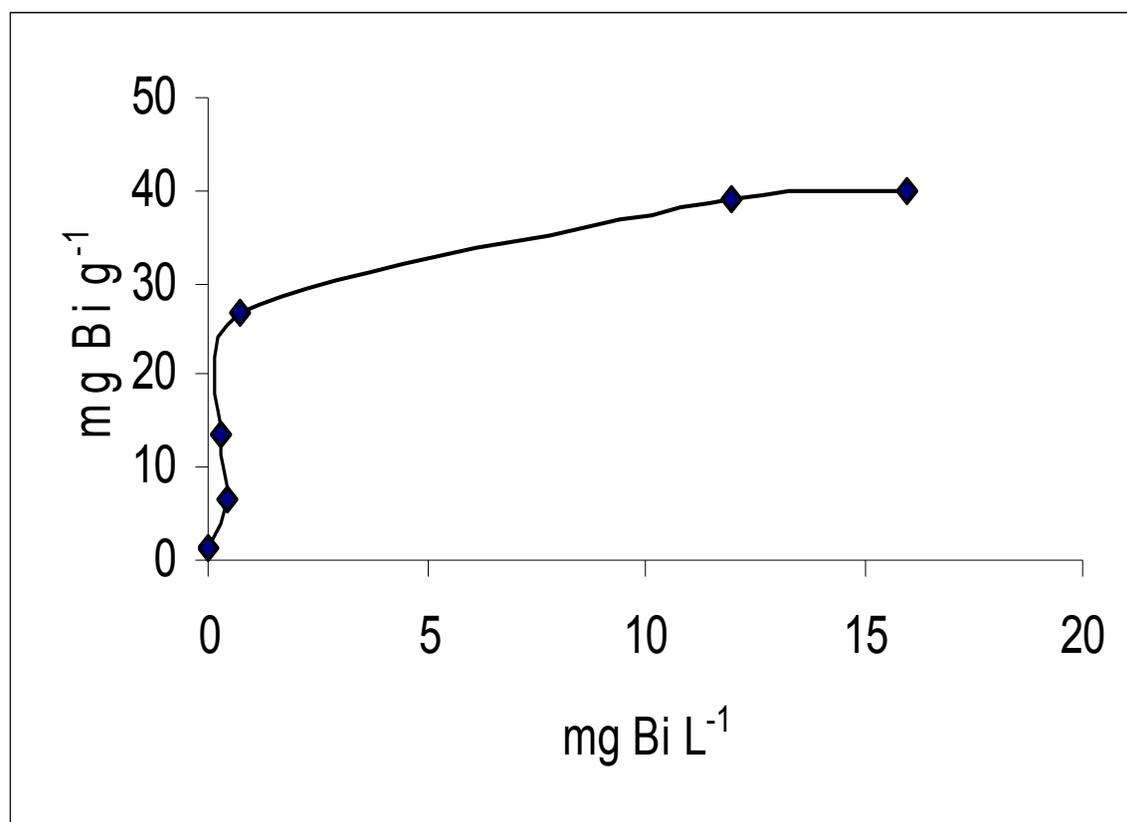

Figure 10. Sorption isotherm of bismuth (III) from aqueous solution of H_2SO_4 (0.5 mol L^{-1}) and KI (10% w/v onto the PQ^+. Cl^- immobilized PUFs.
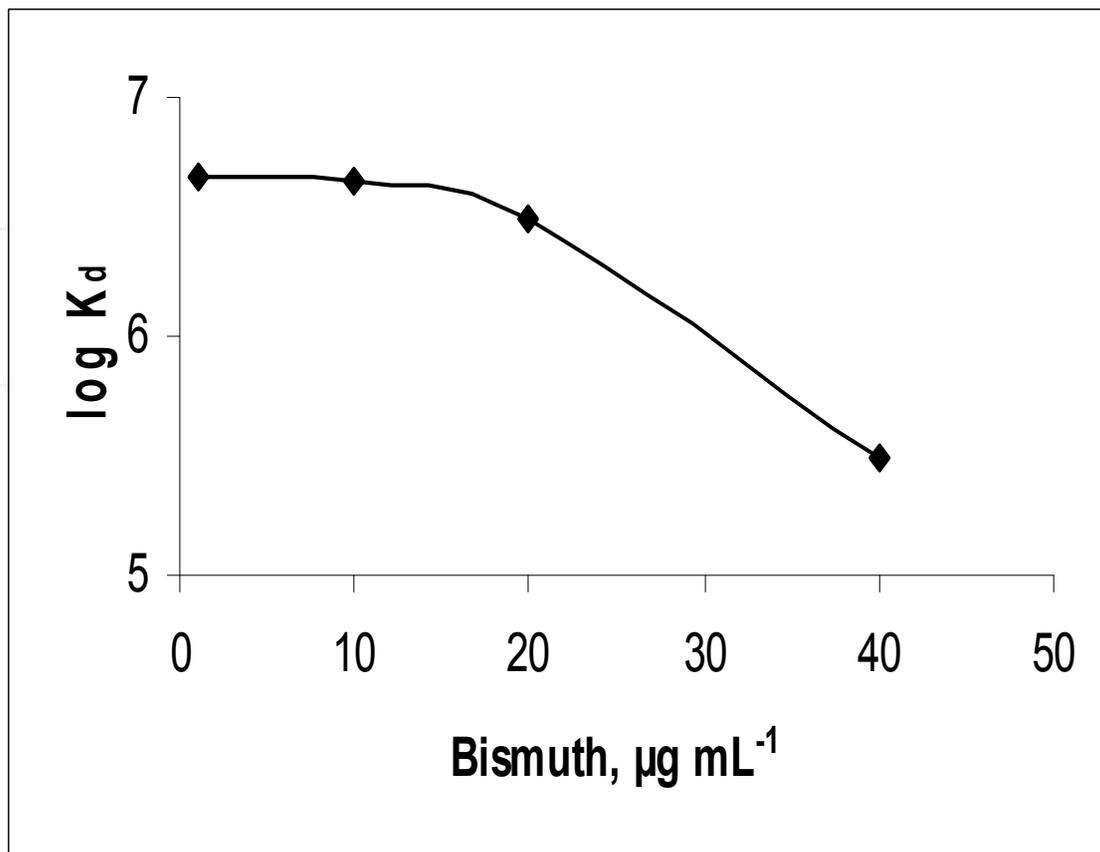
Figure 11. Plot of the distribution coefficient (K_d) of bismuth (III) sorption between the aqueous solution H_2SO_4 (0.5 mol L-1) and KI (10% w/v) and $PQ^+.Cl^-$ loaded PUFs

Sorption of bismuth (III) onto PUFs sorbent was subjected to Langmuir isotherm model expressed in the following linear form [40]:

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \tag{16}$$

where, C_e is the equilibrium concentration ($\mu g\ mL^{-1}$) of bismuth (III) in the test solution, C_{ads} is the amount of bismuth (III) retained onto PUFs per unit mass. The Langmuir parameter Q and b related to the maximum adsorption capacity of solute per unite mass of adsorbent required for monolayer coverage of the surface and the equilibrium constant related to the binding energy of solute sorption that is independent of temperature, respectively. The plot of C_e/C_{ads} *vs.* C_e over the entire range of bismuth (III) concentration was linear (Fig.12) with correlation coefficient of, $R^2 = 0.998$ indicating adsorption of the analyte by $PQ^+.Cl^-$ treated PUFs sorbents followed Langmuir model. The calculated values of Q and b from the slope and intercept of the linear plot (Fig.12) were $0.21 \pm 0.01\ m\ mol\ g^{-1}$ and $5.6 \pm 0.20 \times 10^5\ L\ mol^{-1}$, respectively.

Dubinin - Radushkevich (D - R) isotherm model [41] is postulated within the adsorption space close to the adsorbent surface. The D-R model is expressed by the following equation:

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

where, K_{DR} is the maximum amount of bismuth (III) retained, β is a constant related to the energy transfer of the solute from the bulk solution to the sorbent and ϵ is Polanyi potential which is given by the following equation:

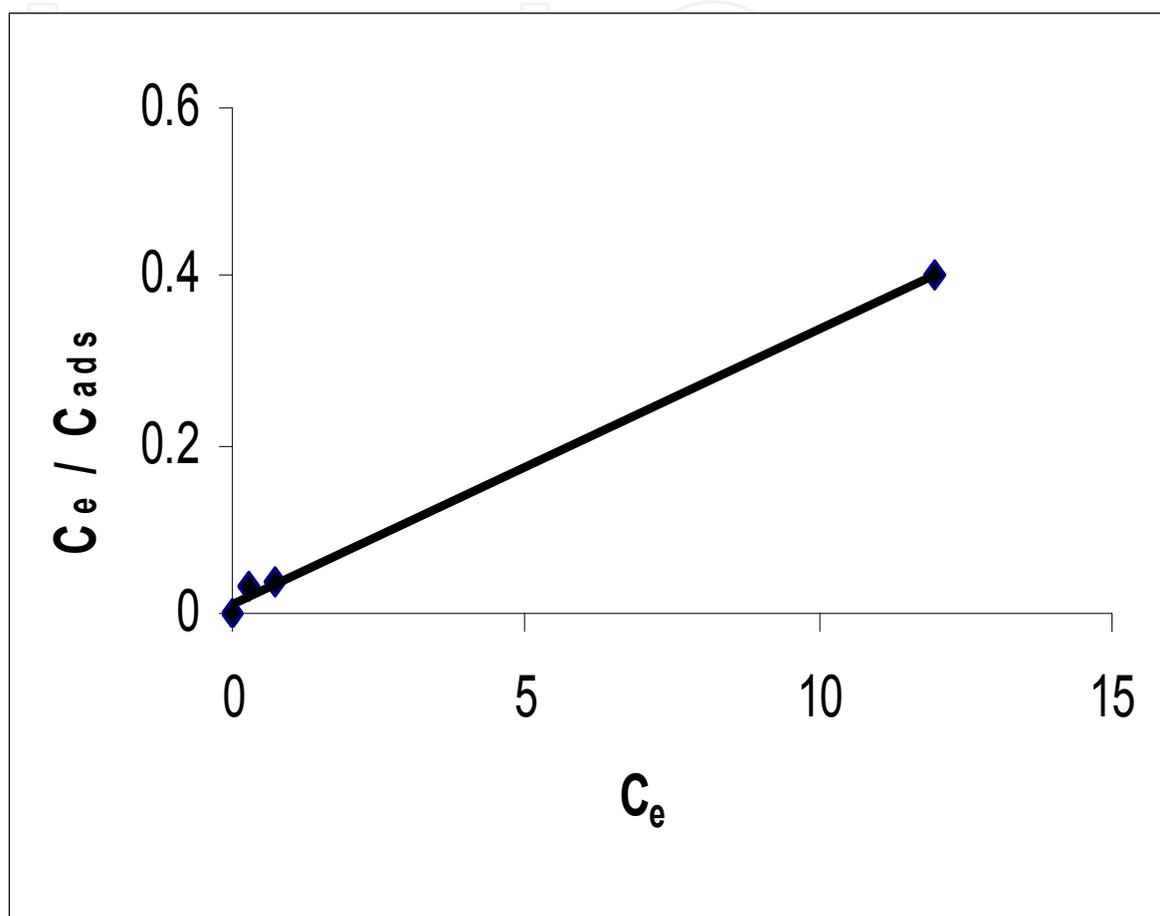$$\epsilon^2 = RT \ln (1 + 1/Ce) \tag{18}$$

Figure 12. Langmuir sorption isotherm of bismuth (III) uptake from aqueous solution onto $PQ^+.Cl^-$ loaded PUFs at optimum conditions.

The plot of $\ln C_{ads}$ versus ϵ^2 was linear with $R^2 = 0.986$ (Fig. 13) for the $PQ^+.Cl^-$ immobilized PUFs indicating that, the D-R model is obeyed for bismuth (III) sorption over the entire concentration range . The values of β and K_{DR} computed from the slope and intercept were found 0.33 ± 0.01 mol^2 KJ^{-2} and 171 ± 2.01 μ mol g^{-1}, respectively. Assuming that, the surface of PUFs is heterogonous and an approximation to 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 the transfer of one mole of solute from infinity to the surface of PUFs. The E value is expressed by the following equation:

$$E = \frac{1}{\sqrt{-2\beta}} \tag{19}$$

The value of E was found 1.23 ± 0.07 KJmol^{-1} for the PQ$^+$.Cl$^-$ loaded foam. Based on these results, the values of Q and b and the data reported [42, 43], a dual sorption sorption mechanism involving absorption related to "weak – base anion ion exchange" and an added component for "surface adsorption" is the most probable mechanism for the uptake of bismuth (III) by the used PUFs. This model can be expressed by the equation:

$$Cr = Cabs + Cads = DC_{aq} + \frac{SK_LC_{aq}}{1 + K_LC_{aq}} \qquad (20)$$

where, C_r and C_{aq} are the concentrations of bismuth (III) retained onto the PUFs and the aqueous solution at equilibrium, respectively. C_{abs} and C_{ads} are the concentrations of the absorbed and adsorbed bismuth (III) species onto the PUFs at equilibrium, respectively and S and K_L are the saturation parameters for the Langmuir adsorption model.
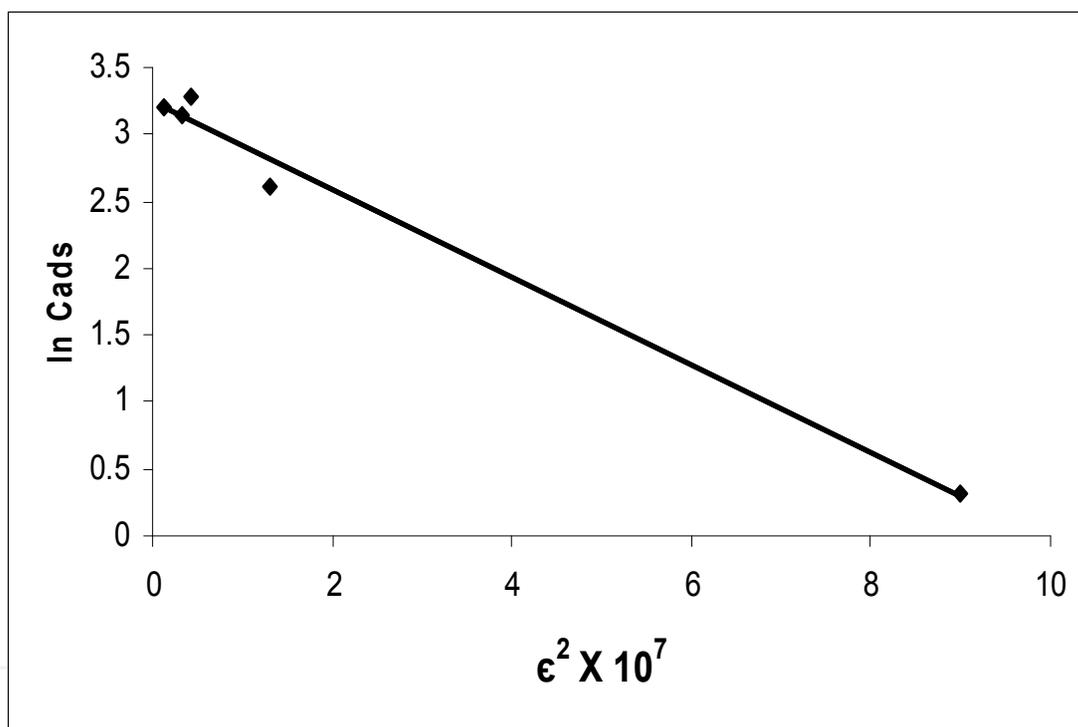

Figure 13. Dubinin-Radushkevich (D-R) sorption of bismuth (III) extraction from aqueous solution onto PQ+.Cl- loaded PUFs at the optimum conditions

3.5. Chromatographic behavior of bismuth (III) sorption

The membrane like structures, the excellent hydrodynamic and aerodynamic properties of PUFs sorbent [42, 43], kinetics, capacity and the sorption characteristics of bismuth (III) retention towards plasticized PQ$^+$.Cl$^-$ PUFs sorbent [39] encouraged the use of the sorbent in packed column for quantitative retention of bismuth (III) from the test aqueous iodide solution. Thus, the test solutions (1.0 L) of the deionized water containing KI (10% w/v) - H$_2$SO$_4$ (1.0 mol L^{-1}) was spiked with various trace concentrations (5 -100 µg L^{-1}) of bismuth (III) and percolated through the PUFs packed columns at 5 mL min^{-1} flow rate. ICP-OES

measurements of bismuth in the effluent indicated complete uptake of bismuth (III). A series of eluting agents e.g. NH_4NO_3, $HClO_4$ and HNO_3 (1-5. mol L^{-1}) was tested for complete elution of the retained bismuth (III). An acceptable recovery (96.0 ± 2.1) of bismuth (III) was achieved using HNO_3 (10 mL, 3 mol L^{-1}) at 2 mL min^{-1} flow rate. Therefore, HNO_3 (3 mol L^{-1}) was selected as a proper eluting agent for bismuth (III) from the packed columns. With HNO_3, reproducibility data even at ultra trace concentrations (0.5 ng mL^{-1}) of bismuth (III) were successfully achieved. The data of pre concentration and recovery of various concentrations of bismuth (III) are summarized in Table 2. A recovery percentage in the range 98.0 ± 1.5 – 104.2 ± 2.3 was achieved confirming the performance of the developed of $PQ^+.Cl^-$ loaded PUFs.

Bismuth (III) taken, μg L^{-1}	Bismuth (III) found, μg L^{-1}	Recovery, % *
100	98.5	98.0 ± 1.5
50	52	104 ± 2.3
10	10.2	101 ± 1.1

* Average (n=5) ± relative standard deviation.

Table 2. Recovery percentage (%) of bismuth (III) ions from deionized water by the developed PUFs packed columns

The proposed PUFs packed columns was also tested for collection and recovery of bismuth (V) species (< 5 μg L^{-1}) from aqueous solutions after reduction to bismuth (III). A series of reducing agents e.g. H_2S, Na_2SO_3, and KI was tested and satisfactory results were achieved using KI. Thus, in the subsequent work, KI was selected as a proper reducing agent for bismuth (V) to bismuth (III) species. Reduction of bismuth (V) to bismuth (III) was found fast, simple and also form a stable $[BiI_4]^-$ species. The solutions were then percolated through PUFs packed column following the described procedures of bismuth (III) retention. The results are summarized in Table 3. An acceptable recovery percentage of Bismuth (V) in the range 94.0 ± 2.1 – 95.0 ± 3.5 was achieved. The proposed PUFs packed column was also tested for chemical speciation and determination of total bismuth (III) and (V) species in their mixtures. An aqueous solution of bismuth (III) and (V) was first analyzed according to the described procedure for bismuth (V). Another aliquot portion was also adjusted to pH 3 – 4 and shaken with Na-DDTC for 2-3 min and extracted with chloroform (5.0 mL) as Bi (DDTC)$_3$ [33]. The remaining aqueous solution of bismuth (V) was reduced to bismuth (III) with KI (10%w/v) - H_2SO_4 (0.5 mol L^{-1}) and percolated through the $PQ^+.Cl^-$ loaded PUFs column. The retained bismuth species were then recovered and finally analyzed following the recommended procedures of bismuth (III) retention. The signal intensity of ICP- OES of the first aliquot (I_1) is a measure of the sum of bismuth (III) and (V) ions in the mixture, while the net signal intensity of the second aliquot (I_2) is a measure of bismuth (V) ions. The difference (I_1-I_2) of the net signal intensity is a measure of bismuth (III) ions in the binary mixture. Alternatively, bismuth (III) as Bi(DDTC)$_3$ in the methylisobutyl ketone phase was stripped to the aqueous phase by HNO_3 (1 mol L^{-1}) and analyzed by ICP-OES The results are given in Table 4. An acceptable recovery percentage in the 92.5 ± 3.01– 104.3 ± 4.5% of bismuth (III) and (V) ions was achieved.

Bismuth (V) added μg L^{-1}	Bismuth (V) found, μg L^{-1}	Recovery,%
100	95 ± 1.5	95.0± 3.5
250	235 ± 50	94.0 ± 2.1

*Average recovery of five measurements ± relative standard deviation.

Table 3. Recovery (%) of bismuth (V) ions from deionized water by PUFs packed columns

Bismuth (III) and (V) taken, μg L^{-1}		Total bismuth found μg L^{-1}	Recovery,% *
Bi (III)	Bi (V)		
20	25	47 ± 3.5	104 ± 4.5
25	100	118± 5	94.4 ± 2.9
10	10	18.5± 1.5	92.5 ± 3.01

* Average recovery of five measurements ± relative standard deviation.

Table 4. Recovery (%) of total bismuth (III) and (V) in their mixture from aqueous media

3.6. Capacity of the PQ$^+$.Cl$^-$ immobilized PUFs

The developed method was assessed by comparing the capacity of the used sorbent towards bismuth (III) sorption with most of the reported solid sorbents e.g. 2, 5- di- mercapto-1, 3, 4-thiadiazol loaded on Silica gel [44] and amionophosphonic dithio-carbamate functionalized polyacrylonitrile [45]. The capacity of the used PQ$^+$.Cl$^-$ loaded PUFs sorbent (40.0 ± 1.10 mg g^{-1}) towards bismuth (III) retention was found far better than the data reported by other solid sorbents e.g. 2, 5- dimercapto-1, 3, 4-thiadiazol loaded on Silica gel (3.5 mg g^{-1}) [44] and amionophosphonic dithiocarbamate functionalized poly acrylonitrile (15.5 mg g^{-1}) [45] and some other solid sorbents.[5]

3.7. Analytical performance of the immobilized PUFs packed column

The performance of the PUFs packed column was described in terms of the number (N) and the height equivalent to the theoretical plate (HETP). Thus, aqueous solution (1.0 L) containing bismuth (III) at concentration of 100 μg L^{-1} at the optimum experimental conditions was percolated through the PUFs packed columns (1.0 ±0.001 g) at 5 mL min^{-1} flow rate. Complete retention of [BiI$_4$]$^-$ was achieved as indicated from the analysis of bismuth in the effluent solution using ICP-MS. The retained bismuth (III) species were then eluted with HNO$_3$ (10 mL, 3 mol L^{-1}) and a series of fractions (2.0 mL) of eluent solution at 2.0 mL min^{-1} were then collected and analyzed by ICP –OES. The calculated values of N and HETP values from the chromatogram method (Fig. 14) using Gluenkauf equation [14] were equal to 90 ± 3.02 and 0.11± 0.02mm, respectively. The values of N and HETP were also computed from the breakthrough capacity curve (Fig. 15) by percolating aqueous solution (2.0 L) containing bismuth (III) at 100 μgL^{-1} under the experimental conditions through PQ$^+$.Cl$^-$ loaded PUFs column at 5 mL min^{-1} flow rate of. The critical and breakthrough capacities [42, 45] calculated from Fig.15 were 1.95 ± 0.1 and 31.25 ± 1.02 mg g^{-1}, respectively. These HETP (97 ± 4) and N (0.13 ± 0.02 mm) values are in good agreement with the values obtained from the chromatogram method.
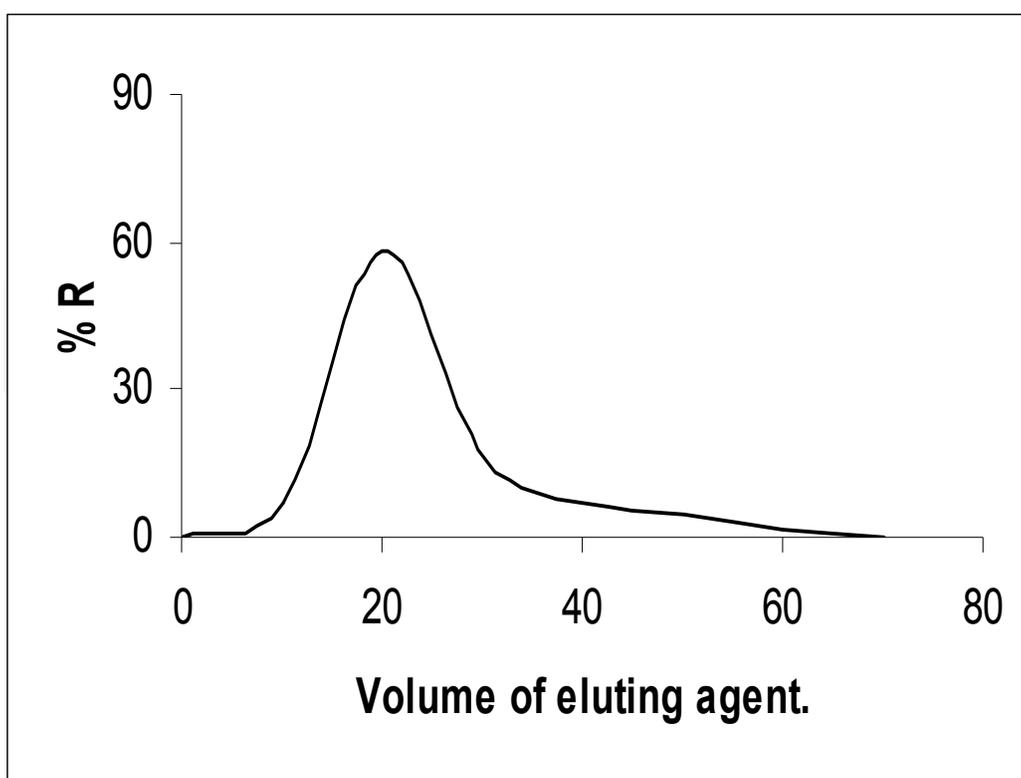
Figure 14. Chromatogram of bismuth (III) recovery from PQ+.Cl⁻ loaded PUFs packed column using
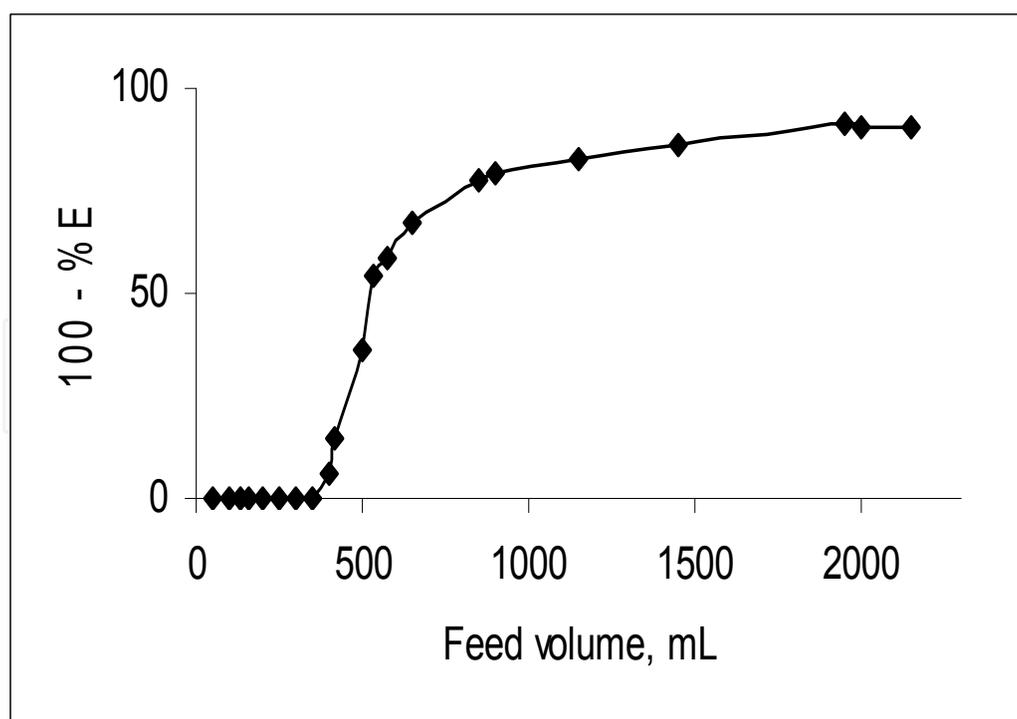nitric acid (5 mol L⁻¹) as eluting agent at flow rate of 2.5 mL min⁻¹.

Figure 15. Breakthrough capacity curve for bismuth retention onto PQ+.Cl⁻ loaded packed column at
the optimum conditions.

3.8. Figure of merits of the PQ⁺.Cl⁻ immobilize PUFs packed column

The LOD, LOQ, enrichment and sensitivity factors and relative standard deviation, (RSD) under the optimized conditions were determined. The plot of signal intensity of ICP- OES (I) versus bismuth (III) concentration (C) has the regression equation:

$$I= 4.19 \times 10^3 C \text{ (ng L}^{-1}) + 12.96 \text{ (r=0.9995)} \tag{21}$$

According to IUPAC [46, 47], the LOD = $3S_{y/x}/b$ and LOD = $10S_{y/x}/b$ were 0.9 and 3.01 ngL^{-1}, respectively (V $_{sample}$ = 100 mL) where, $S_{y/x}$ is the standard deviation of y- residual and b is the slope of the calibration plot [46]. The LOD of the developed method is much better than direct measurement by ICP – OES (5.0 µg mL^{-1}). The enrichment factor (F_c = $V_{s,b}$ /$V_{e,v}$) was defined as the ratio between the volume of analyte sample ($V_{s,b}$ = 1000 mL) before preconcentration and the eluent volume ($V_{e,v}$) after retention and recovery. An average value of F_c of 100 was achieved. The sensitivity factor (the ratio of the slope of the preconcentrated samples to that obtained without preconcentration) was 33.3. The RSD of the method for the determination of standard bismuth (III) solution (50 µg L^{-1}) was ± 2.5% (n= 5) confirming the precision of the method. The figure of merits of the developed method were compared satisfactorily to the reported methods e.g. ICP-OES [45], spectrophotometric [47] and electrochemical [49 -51] (Table 5) in water confirming the sensitivity and applicability of the proposed method. The LOD of the method could be improved to lower values by prior pre concentration of bismuth (III) species from large sample volumes of water (>1.0L). Thus, the method is simple and reliable compared to other methods [50 -52].

SPE	Technique	Linear range, µgL^{-1}	LOD, µgL^{-1}	Reference
Microcrystalline benzophenone	UV – Vis	0 – 2 X10^4	—	34
Microcrystalline naphthalene	DPP	180 – 135x10^2	55	35
Octylsilane (RP-8) cartridge	ASV	10.5 – 1000	0.73	36
Amberlite XAD-7 resin	HG-ICP-OES	Up to 100	0.02	6
Modified Chitosan	ICP-MS		0.1*	15
PQ⁺ .Cl⁻ loaded PUFs	ICP – OES	0.01 – 100	2.7*	Present work

ng L^{-1}

Table 5. Figure of merits of the developed and some of the reported SPE coupled with spectrochemcal and electrochemical techniques for bismuth determination in water

3.9. Interference study

The influence of diverse ions relevant to wastewater e.g. alkali and alkali earth metal ions Ca^{2+}, Mg^{2+}, Cl^-, Zn^{2+}, Mn^{2+}, $Cu2^+$, Hg^{2+}, Fe^{2+}, Fe^{3+}, Pb^{2+}, Al^{3+}, Ni^{2+}, $Co2^+$ and nitrate at various concentrations (0.5 -1.0 mg/ 100 mL sample solution) on the sorption of 10 µg bismuth (III)

from a sample volume of 100 mL at the optimum conditions was studied. The tolerance limits (w/w) less than ± 5% change in percentage uptake of bismuth was taken as free from interference. The tested ions except Pb^{2+} did not cause any significant reduction on the percentage (96 -102 ± 2%) of bismuth (III) sorption. Lead ions were found to interfere at higher concentrations (> 0.5 mg/ 100 mL sample solution). Thus, it can be concluded that, the method could applied for the separation and / or determination of bismuth (III) and bismuth (V) after reduction of the latter to trivalence.

3.10. Analytical applications

The validation of the developed method was performed using the certified reference materials (CRM-TMDW). Good agreement between the concentration measured by the proposed method (8.9 ± 0.9 μgL^{-1}) and the certified value (10.0 ± 0.1 μgL^{-1}) of the total bismuth was achieved confirming the accuracy of the method for trace analysis of bismuth in complex matrices.

The method was also applied for the determination of bismuth in wastewater samples (1.0 L) after digestion and percolation through the PUFs packed columns as described. Complete retention of bismuth was achieved as indicated from the ICP-MS analysis of bismuth in the effluent. The retained $[BiI_4]^-$ species were recovered with HNO_3 (10 mL, 3.0 mol L^{-1}) and analyzed by ICP-OES. Various concentrations of bismuth (III) were spiked also onto the tested wastewater samples and analyzed (Table 6). Bismuth (III) determined by the method and that expected (Table 6) in the tested water samples revealed good recovery percentage (98.4± 2.3 – 104 .3 ± 2.8 %) confirming the accuracy and validation of the method.

Bismuth (III) added, (μgL^{-1})	Bismuth (III) found, ($\mu g\ L^{-1}$)	Recovery, %*
–	22	–
50	75	104.3 ±2.8
100	120.5	98.4±2.3

* Average recovery of five replicates ± relative standard deviation.

Table 6. Recovery study applied to the analysis of bismuth in wastewater by the developed method

The selectivity of the procedure was further tested for the analysis of bismuth in Red sea water at the coastal area of Jeddah City, Saudi Arabia following the standard addition. as described..The results are summarized in Table 7. An acceptable recovery percentage of 107.01 ±3.5 -108.1 ±2.7 was achieved confirming the selectivity, accuracy and validation of the method.

Bismuth (III) added, ($\mu g\ L^{-1}$)	Bismuth (III) found, ($\mu g\ L^{-1}$)	Recovery, %*
–	0.07	–
0.30	0.40 ± 0.01	108.1 ±2.7
0.5	0.61 ±0.02	107.01 ±3.5

* Average recovery of five replicates ± relative standard deviation

Table 7. Recovery test for bismuth in sea water by the developed method

4. Conclusion

PQ$^+$.Cl$^-$ treated PUFs solid sorbent was successfully used for the pre concentration/separation procedures of bismuth (III) and bismuth (V) after reduction of the latter species to bismuth (III). The developed method minimizes the limitations related to sensitivity and selectivity for bismuth determination in various matrices. The intra-particle diffusion and the first order model of bismuth (III) retention onto the tested PQ$^+$.Cl$^-$ PUFs sorbent are confirmed from the kinetic data. PUFs packed column has shown itself to be a very useful and precise for the analysis of total bismuth (III) & (V) species in water at trace concentrations in water. The PUFs packed column can be reused many times without decrease in its efficiency. Work is continuing for calculating ligation capacity, influence of competitive agents and organic material present in water samples. The LOD of the method is quite close to the concentration of bismuth species reported in marine water. Work is still continuing on developing PQ$^+$.Cl$^-$ treated PUFs packed column mode for on line determination of bismuth (III) and/ or (V) species at ultra concentrations in aqueous media.

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