Sorption characteristics and chromatographic separation of gold (I and III) from silver and base metal ions using polyurethane foams

A.B. Farag\(^a\),*, M.H. Soliman\(^a\), O.S. Abdel-Rasoul\(^a\), M.S. El-Shahawi\(^b,1\)

\(^a\) Chemistry Department, Faculty of Science, Helwan University, Helwan, Egypt
\(^b\) Chemistry Department, Faculty of Science at Damiatta, Mansoura University, Mansoura, Egypt

**Abstract**

The influence of different parameters on the sorption profiles of trace and ultra traces of gold (I) species from the aqueous cyanide media onto the solid sorbents ion exchange polyurethane foams (IEPUFs) and commercial unloaded polyurethane foams (PUFs) based polyether type has been investigated. The retention of gold (I) species onto the investigated solid sorbents followed a first-order rate equation with an overall rate constant \( k \) in the range 2.2–2.8 ± 0.2 s\(^{-1}\). The sorption data of gold (I) followed Freundlich and Langmuir isotherm models. Thus, the a dual-mode of sorption mechanism involving absorption related to “weak base anion exchanger” and an added component for “surface adsorption” seems the most likely proposed dual mechanism for retention profile of gold (I) by the IEPUFs and PUFs solid sorbents. The capacity of the IEPUFs and PUFs towards gold (I) sorption calculated from the sorption isotherms was found to be 11.21 ± 1.8 and 5.29 ± 0.9 mg g\(^{-1}\), respectively. The chromatographic separation of the spiked inorganic gold (I) from de ionized water at concentrations 5–15 \( \mu \)g mL\(^{-1}\) onto the developed IEPUFs and PUFs packed columns at 10 mL min\(^{-1}\) flow rate was successfully achieved. The retained gold (I) species were then recovered quantitatively from the IEPUFs (98.4 ± 2.4%, \( n = 5 \)) and PUFs (95.4 ± 3.4%, \( n = 5 \)) packed columns using perchloric acid (60 mL, 1.0 mol L\(^{-1}\)) as a proper eluting agent. Thiourea (1.0 mol L\(^{-1}\))–H\(_2\)SO\(_4\) (0.1 mol L\(^{-1}\)) system was also used as eluting agent for the recovery of gold (I) from IEPUFS (95.4 ± 5.4%, \( n = 3 \)) and also PUFs (93.4 ± 4.4%, \( n = 3 \)) packed columns. The performance of the IEPUFs and PUFs packed columns in terms of the height equivalent to the theoretical plates (HETP), number of plates (\( N \)), and critical and breakthrough capacities towards gold (I) species were evaluated. The developed IEPUFs packed column was applied successfully for complete retention and recovery (98.5 ± 2.7) of gold (III) species spiked onto tap-and industrial wastewater samples at <10 \( \mu \)g Au mL\(^{-1}\) after reduction to gold (I). The IEPUFs packed column was applied satisfactorily for complete retention and recovery (98.5 ± 2.7) of total inorganic gold (I) and/or gold (III) species spiked to tap- and industrial wastewater samples at <10 \( \mu \)g mL\(^{-1}\) gold. Chromatographic separation of gold (I) from silver (I) and base metal ions (Fe, Ni, Cu and Zn) using IEPUFS packed columns was satisfactorily achieved. The proposed method was applied successfully for the pre-concentration and separation from anodic slime and subsequent FAAS determination of analyte with satisfactory results (recoveries >95%, relative standard deviations <4.0%).

© 2007 Elsevier B.V. All rights reserved.

*Corresponding author.*
E-mail address: mohammad_el_shahawi@yahoo.co.uk (M.S. El-Shahawi).

\(^{1}\) Present address: Department of Chemistry, Faculty of Science, King Abduaziz University, Jeddah, Saudi Arabia.

0003-2670/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.aca.2007.08.049
1. Introduction

Gold is one of the most important noble metals due to its wide applications in industry and economic activity, yet it is not naturally abundant. Gold is the ultimate refuge from political, economic and financial calamity [1,2]. Gold and silver are commonly found associated with each other and have important applications, but a significant partition of their demand is found in jewelry, coinage and decorative arts [2]. The concentration level of gold in basic rocks and soil are about 4.0 ng g\(^{-1}\) and 1.0 ng g\(^{-1}\) [3], respectively. The values of 0.05 and 0.2 ng ml\(^{-1}\) were found in seawater and river water, respectively [3]. Due to the importance and low level of gold in the environmental samples, a simple, sensitive and selective method for gold separation and determination has been required. Several articles have been published on the pre-concentration of traces of gold in water and other matrices before their actual determination via solvent extraction, liquid solid and selective transport through liquid membrane [3-16].

Recent years have seen an upsurge in the application of a number of solid sorbents e.g. foamed plastics, chelating polymers and silica gel in the reversed phase extraction chromatography, gas-solid and gas-liquid partition chromatography for the pre concentration, separation and subsequent determination of a series of trace metal ions including gold [16-36]. The membrane structure and the available surface area of the polyurethane foams make it very suitable stationary phase and as a column filling material [21-26]. Ion exchange polyurethane foams (IEPUFs), unloaded PUFs and PUFs immobilizing specific reagents have been successfully employed for the separation and determination of metal ions [17-22,26-36] including gold [17,18,23-26] on domestic water; river water, raw sewage and secondary treated sewage.

In contrary to precious group metals (PGM), so far, no papers concerning inorganic gold (I) and gold (III) determination at ultra trace levels in the environmental samples employing polyurethane solid sorbents have been published. Therefore, the goals of the present article are aimed at developing simple, convenient and low cost procedures for the pre-concentration, selective separation and sequential determination of total inorganic gold (I) and gold (III) at ultra trace level in water after reduction of the latter to mono valence gold ions. The salient features regarding the selective separation of inorganic gold (I) and gold (III) in aqueous media from silver (I) and some other base metal ions (Fe, Ni, Cu and Zn) in anodic slime or fresh water samples using IEPUFs packed columns were critically examined.

2. Experimental

2.1. Reagents and materials

Analytical-reagent grade chemicals and solvents were provided by BDH (BDH Ltd., Poole, England), unless stated otherwise, and were used without further purification. Analytical grade potassium aurocyanide, KAu(CN)_2 (Fluka, AG, Buchs, Switzerland), HAuCl_4 (E. Merck, Darmstadt, Germany), silver nitrate and sodium hydroxide (BDH Ltd., Poole, England) were used for the preparation of stock solutions of gold (I), gold (III), silver (I) and NaOH in de ionized water, respectively. Other chemicals e.g. HNO_3, Na_2SO_3, H_2O_2, HCl, HClO_4, KCN and thiourea (Aldrich Chemical Company, Milwaukee, WC, USA) were used without further purification. Commercial polyurethane foam (PUFs) plugs (30 kg m\(^{-3}\)) were cut as cubes (10-15 mm), washed, dried at 80 + 0.1 °C in 250 mL beaker as described earlier [17,18] and were stored in low density polyethylene (LDPE) bottle, Nalgene in dark for further work. Stock solutions (1000 μg mL\(^{-1}\)) of iron(III), nickel (II), copper (II) and zinc (II) were obtained from BDH and were used for the preparation of more diluted solutions in de ionized water. A stock solution (1000 μg mL\(^{-1}\)) of gold (I) was prepared by dissolving the required weight of KAu(CN)_2 in alkaline NaOH (0.1 mol L\(^{-1}\)). A series of Britton–Robinson (B-R) buffer (2-11) was prepared by mixing equal proportions of acetic (0.04 mol L\(^{-1}\)), phosphoric (0.04 mol L\(^{-1}\)) and boric (0.04 mol L\(^{-1}\)) acids (BDH) in double distilled water and the pH of the solutions were then adjusted to the required pH by adding various volumes of NaOH (0.2 mol L\(^{-1}\)) solution as reported earlier [37].

2.2. Apparatus

A Perkin-Elmer (model A Analyst TM 800, Norwalk, Ct, USA) atomic absorption spectrometer (AAS) was used for measuring the concentration of Au, Ag, Fe, Ni, and Cu at the wavelengths 242.8, 328.1, 372.0, 232.0 and 324.7 nm, respectively at 0.7 nm slit width except for iron and nickel at 0.2 nm at oxidant (air) flow of 20.0 L min\(^{-1}\) and acetylene flow of 1.5 L min\(^{-1}\) before and after separation step from the aqueous phase under instrument's optimum settings. Flame emission atomic spectrometry (FES) was also used for the determination of ultra trace of gold at 267.6 nm, 0.2 nm slit width, oxidant flow of 16.0 L min\(^{-1}\) and 7.8 L min\(^{-1}\)-acetylene flow. De-ionized water was obtained from Milli-Q Plus system (Millipore, Bedford, MA, USA) and was used for the preparation of all solutions. A thermo Fisher Scientific, MA, USA) was employed for the pH measurements with absolute accuracy limits at the pH measurements being defined by NIST buffers. Glass columns (18 cm × 15 mm i.d.) and a variable GFL mechanical Shaker model 1063 (Gesellschaft Fur Laboratechnik, mbH, Burgwedel, Germany) with a shaking rate in the range 10-250 rpm were used for the retention experiments of gold (I) species at different pH.

2.3. Synthesis of the ion exchange polyurethane foam (IEPUFs)

IEPUFs sorbent was prepared by mixing the polyether (20 ± 0.1 g), de-ionized water (1.0 ± 0.1 g), dimethylen ethanolamine (0.04 ± 0.001 g), stannous octoate (0.04 ± 0.001 g) and polyether polysiloxane (0.25 ± 0.01 g). The mixture was stirred to complete homogeneity and an accurate weight of Amberlite IR 400 of pore diameter 9 nm and bead size 20-60 mesh was added with continuous stirring for 5 min and toluene di-isocyanate (13.0 ± 0.1 g) was then added gradually during stirring. The mixture was finally poured in a box for
24 h, dried and stored in polyethylene bottles. The prepared IEPUFs were cut into cubes (10–15 mm) washed and dried as reported earlier [17,18].

2.4 Batch experiments

In a thermostated mechanical shaker, an accurate weight (0.05 ± 0.001 g) of IEPUFs or PUFs sorbent was shaken at 200 rpm shaking rate with 25 mL of an aqueous solution containing gold (I) species (5 μg mL−1 Au) at different pH up to 2 h at 25 ± 0.1°C. After equilibrium, the amount of gold (I) retained on the foam sorbent, the extraction percentage, %E, the distribution coefficient, Kd and the sorption capacity, Q in mmol g−1 were then determined from the difference between the concentration of gold (I) determined in the aqueous phase before (C0) and after (Ce) shaking with the foam sorbent under instrument’s optimum settings. The concentration of the produced gold ions was then determined with the aid of calibration curve of gold (I) ions. Following these procedures, the effect of shaking time, potassium cyanide concentration (3.5 × 10−4–1.5 × 10−2 mol L−1), monovalent cation size (Na+, K+ and NH4+), analyte concentration (1.0 × 10−4–20 × 10−4 mol L−1) and sorbent dose on the gold (I) retention was carried out. The values of %E and Kd are the average of three independent measurements and the precision in most cases was ±2%.

2.5 Flow experiment

2.5.1 Retention and recovery of inorganic gold (I)

An aqueous solution (0.5 L) spiked with gold (I) at a concentration ≤15 μg Au mL−1 at pH 4–5 and in the presence of KCN (2%, w/v) was percolated through the IEPUFs or PUFs (1.0 ± 0.01 g) packed columns at 5 mL min−1 flow rate using the vacuum method of foam packing [17,18]. A blank experiment was also carried out in the absence of gold (I) ions. The sample and the blank foam packed columns were then washed with 100 mL of an aqueous solution containing potassium cyanide (2%, w/v). Complete retention of gold (I) ions took place as indicated from the determination of gold species in the effluent solution by AAS and/or FAAS as described before. Complete recovery of gold (I) content from the IEPUFs and PUFs packed columns was achieved by percolating HClO4 (80 mL, 1.0 mol L−1) or with an aqueous system (100–120.0 mL) containing thiourea (1.0 mol L−1)–H2SO4 (0.1 mol L−1) at 10 mL min−1 flow rate. Equal fractions of the eluate were then collected for gold determination with FAAS or AAS.

2.5.2 Separation and recovery of inorganic gold (II)

An aqueous solution (0.1 L) containing gold (III) species at concentration 1.0–5.0 μg mL−1 was first treated with sodium sulfite (1.0 mol L−1) in the presence of HCl (1.0 mol L−1) and heated for 10 min to reduce gold (III) to the mono valence gold (I) quantitatively. The test solution at the optimum conditions of gold (I) sorption described above was percolated through the IEPUFs (1.0 ± 0.01 g) packed columns at 5 mL min−1 flow rate using the vacuum method of foam packing [16,17]. Complete sorption and recovery of gold (I) ions with perchloric acid (80 mL, 1.0 mol L−1) was achieved as indicated from the analysis of gold species in the effluent of the test solution and after recovery by FAAS with the aid of AAS calibration curve for gold (I) and (III) constructed after reduction of gold (III) to gold (I) using the same reducing agent following the described procedures above.

2.5.3 Separation and recovery of total inorganic gold (I) and gold (III)

An aqueous solution of distilled-, tap- or industrial wastewater samples (0.1 L) containing the binary mixture of gold (I) and (III) species at a total concentration ≤10 μg mL−1 was first treated with sodium sulfite (1.0 mol L−1) in the presence of HCl (1.0 mol L−1) and heated for 15 min to reduce gold (III) to gold (I) quantitatively. The test solution at the optimum conditions of gold (I) sorption described above was percolated through the IEPUFs (1.0 ± 0.01 g) packed columns at 5 mL min−1 flow rate using the vacuum method of foam packing [16,17]. Complete sorption and recovery of gold (I) ions with perchloric acid (80 mL, 1.0 mol L−1) was achieved as indicated from the analysis of gold species in the effluent of the test solution and after recovery by FAAS with the aid of AAS calibration curve for gold (I) and (III) constructed after reduction of gold (III) to gold (I) using the same reducing agent following the described procedures above.

2.5.4 Separation of gold (I) from silver (I) ions

An aqueous solution (0.5 L) adjusted to pH 4–5 in LDPE bottle, Nalgene was spiked with gold (I) and silver (I) ions at a total concentration ≤5 μg mL−1 of each ion under the optimum conditions of gold (I) sorption was percolated through the IEPUFs (1.0 ± 0.01 g) packed columns at 5 mL min−1 flow rate using the vacuum method of foam packing [17,18]. A blank experiment was also carried out in the absence of gold (I) ions. The sample and the blank IEPUFs packed columns were then washed with 100 mL of an aqueous solution containing potassium cyanide (2%, w/v). Quantitative retention of gold (I) and silver (I) ions took place as indicated from their FAAS analysis in the effluent. The retained gold (I) and silver (I) species were then recovered quantitatively from the foam column with HClO4 (80 mL, 1.0 mol L−1) and an aqueous mixture of thiourea (120 mL, 1.0 mol L−1)–H2SO4 (0.1 mol L−1) at 5 mL min−1 flow rate, respectively.

2.5.5 Separation of gold (I) from silver (I) and other base metal (Fe3+, Ni2+, Cu2+, or Zn2+) ions

An aqueous solution (0.5 L) spiked with gold (I) and silver (I) and/or base metal (Fe3+, Ni2+, Cu2+ or Zn2+) ions at a total concentration of 5 μg mL−1 of each ion under the optimum conditions of gold (I) sorption was percolated through the IEPUFs columns at 5 mL min−1 flow rate as described in the experimental section. FAAS analysis of the effluent solutions revealed quantitative sorption of gold (I), silver (I) and other base metal ions. The retained base metal ions (Fe3+, Ni2+, Cu2+, or Zn2+) ions were then recovered quantitatively from the foam column by percolating H2SO4 (100 mL, 0.05 mol L−1), HClO4 (80 mL, 1.0 mol L−1), thiourea (1.0 mol L−1)–H2SO4 (0.1 mol L−1) mixture at 5 mL min−1 flow rate, respectively.
2.5.6. Separation and subsequent determination of gold in anodic slime

The surface of the metallurgical sample (anodic slime) directly after washing was dried at 110 °C for two hrs. An accurate weight (0.2–0.25 ± 0.01 g) of the sample was decomposed with aqua regia (10 mL) and the solution was evaporated to dryness and cooled. Ten milliliters of concentrated HNO₃ and 2.0 mL H₂O₂ (30%, v/v) were added to the residue and the suspension was filtered through filter paper. The insoluble residue was washed with a solution containing dilute nitric acid. The contents of the reaction vessel and the washing solutions were heated on a water bath for 20 min and diluted with distilled water in a 50 mL calibrated flask. The sample solution was first treated with sodium sulfite (1.0 mol L⁻¹) in the presence of HCl (1.0 mol L⁻¹) and heated for 15 min to reduce gold (III) to gold (I) in the sample. The test solution was then adjusted to pH 4–5 and percolated through the IEPUFs packed column at a reasonable flow rate 5–10 mL min⁻¹ then the general procedures were applied. A blank experiment was digested and analyzed following the same digestion and analytical procedures.

3. Results and discussion

3.1. Investigation of the various experimental variables

Preliminary experiments on the retention profile of gold (I) from the aqueous solutions onto the solid sorbents IEPUFs and the commercial unloaded PUFs have shown that the amount of gold (I) ions extracted depends on the solution pH. Therefore, the sorption profiles of gold (I) ions by the employed foam sorbents from the aqueous solutions containing B–R buffer (pH 2–12) were critically investigated after shaking for 2 h. The amount of gold (I) retained at equilibrium, qₑ, the extraction percentage, %E, and the distribution ratio, D, were then calculated employing the following equations [17,18]:

\[
q_e = \frac{(C_b - C_a) \times v}{w} \quad (1)
\]

\[
%E = \frac{(C_b - C_a) \times 100}{C_b} \quad (2)
\]

\[
D = \frac{\%E}{100 - \%E} \times \frac{v}{w} \quad (3)
\]

where C₀ and Cₐ are the gold (I) concentrations determined with AAS in the aqueous phase before and after shaking with the solid sorbents, v and w are the volume (mL) of the aqueous solution and the weight (g) of the foam cubes as solid sorbents, respectively. The data are summarized in Fig. 1. The results revealed that the gold (I) retention by the tested solid sorbents in aqueous acidic solution of pH <6, reached maximum. On the other hand, the retention of gold (I) onto the IEPUFs and PUFs decreased markedly on raising the solution pH higher than pH 6 (Fig. 1). This behavior is most likely attributed to the instability of the produced ternary complex ion associate of [Au(CN)₂]⁻ with the sorbent site of the IEPUFs or PUFs as reported earlier by El-Shahawi and Nassif [29] and Cordoba et al. [38] for [HgBr₃]⁻ complex species and subsequent hydrolysis. In acidic pH, the observed high retention of gold (I) species by the solid sorbents is most likely attributed to the protonation of the chelating sites (ether and/or urethane linkages) in the sorbents that enhanced the retention of the analyte via “solvent extraction and/or weak base anion exchange mechanism”. It has been shown that gold (I) and gold (III) can be extracted also by methyl isobutyl ketone and by solvents that posses ether linkages in their structures e.g. diethyl ether, isopropyl ether and polyurethane ether –type foams [16,22–28]. A similar retention profile for the extraction of auro cyanide ion-pairs with alkali metal ions into long chain poly ethers has been reported by Chow and co-workers [25,26]. Based on the results obtained and the data reported earlier [17,26,25–28], a possible “weak base anion ion exchanger” and a “solvent extraction” mechanism of the [Au(CN)₂]⁻ retention onto the protonated ether (–CH₂-OH–CH₂–) oxygen or urethane (–NH₂–COO–) nitrogen linkages of the IEPUFs or PUFs as ternary complex ion associates in acidic media is most likely proceeds, respectively as follows:

**Ether group, PUF:**

\[
(-CH₂-O-CH₂)_{foam} + H^+ \leftrightarrow (-CH₂=O-CH₂)_{foam}. \quad (4)
\]

\[
(-CH₂⁻O-CH₂)_{foam} + [Au(CN)₂]⁻_{aq} \rightarrow [Au(CN)₂]⁻_{foam}. \quad (5)
\]

**Urethane group, PUF:**

\[
(-NH-COO⁻)_{foam} + H^+ \leftrightarrow (⁻⁻⁻NH₂⁻⁻⁻COO⁻)_{foam}. \quad (6)
\]

\[
(⁻⁻⁻NH₂⁻⁻⁻COO⁻)_{foam} + [Au(CN)₂]⁻_{aq} \rightarrow [Au(CN)₂]⁻_{foam}. \quad (7)
\]

The pKₐ values of the protonation of the ether oxygen and/or urethane nitrogen (⁻⁻⁻NH₂⁻⁻⁻COO⁻) groups of the solid sorbents are 3 and 6 form [17,30,33], respectively. At pH higher

![Fig. 1 – Influence of pH on the uptake percentage, % of gold (I) at 5.0 µg mL⁻¹ from aqueous cyanide media (2%, w/v) onto IEPUFs (1) and PUFs (2) at 25 ± 0.1 °C.](image-url)
than pH 6, the sorption of the unloaded PUFs solid sorbent towards [Au(CN)2]− decreased markedly as compared to the IEPUFs sorbent (Fig. 1). This behavior is most likely attributed to the deprotonation of the ether oxygen (−CH2−OH−CH2−) and/or urethane nitrogen (−NH2−CO−) of the un-loaded PUFs. Such effect is most likely minimizes the formation of the complex ion associate between the complex anion [Au(CN)2]− and the unloaded PUFs sorbent. The diffusion of gold (I) as [Au(CN)2]− through the polyurethane film is most likely consistent with its solubility in the PUFs as reported earlier [39]. In this account, Gesser et al. [39] have suggested two alternative mechanisms for the sorption of the anionic metal complexes such as HMCl4 (e.g., HGaCl4) by the PUFs. Based on the close resemblance between the obtained sorption data onto the PUFs and the extraction with diethyl ether, PUFs material is most likely behaves as a polymeric sorbent for the anionic complex. The other mechanism results from protonation of the ether sites in the polymer when coming into contact with acids in aqueous media i.e. the protonated sites act as anion exchangers in the extraction of [Au(CN)2]−.

The influence of the competitive complexing anion (CN−) as potassium cyanide at various concentrations (3.5 × 10−4–1.5 × 10−2 mol L−1) on the sorption of gold (I) species (3.5 × 10−3 mol L−1) by the PUFs and IEPUFs from the aqueous media (pH 5–6) was carried out. The retention percentage (%E) of gold (I) species onto the solid sorbents increased on raising the cyanide ion concentration and reached maximum (E = 83%) at 1:2 Au+ :CN− molar ratio. At a molar ratio of cyanide ions to gold (I) species higher than 2:1 a leveling off and a slight decrease (E = 76%) of gold (I) retention onto the solid sorbents were noticed. The competitive extraction of CN− onto the solid sorbents may account for the observed behavior. On the other hand, the gold (I) sorption onto the IEPUFs sorbent was also higher than that of PUFs towards gold (I). The increased number of the available active sites on the IEPUFs compared to that of the unloaded PUFs and the possibility of the former sorbent to act as a “weak anion ion exchanger” may also account for the trend observed.

The influence of the cation size of the ions Li+, Na+, K+ and NH4+ as chloride salts at various concentrations (3.57 × 10−3–1.7 × 10−2 mol L−1) on the gold (I) retention by IEPUFs and PUFs was studied. On increasing the salt concentration, a significant decrease (∼10–21%) in the sorption percentage of [Au(CN)2]− onto the solid sorbents was noticed and the order of extraction followed the sequence:

\[
\text{Li}^+ (\log D = 3.3) > \text{Na}^+ (\log D = 3.24) > \text{NH}_4^+ (\log D = 3.19) > \text{K}^+ (\log D = 2.94)
\]

This trend is in accordance with the sequence of the hydrated radius of these mono valence ions: \(\text{NH}_4^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+\) [40]. This effect is most likely attributed to the reduction of the repulsive forces between adjacent sorbed gold (I) as complex anion [Au(CN)2]− [41]. The competitive extraction of the added anions may also be expected to be somewhat extractable as their neutral species like AuCl [23,26,38] and the ion-dipole interaction of NH4+ with the oxygen sites of the PUFs is not the only predominating factor in the extraction step of gold (I). Thus, “solvent extraction” mechanism with the salt acting as salting-out agent is not only the most probable mechanism. Other processes like specific sites on the sorbent are possibly involved simultaneously in the [Au(CN)2]− sorption from the bulk aqueous solution [17]. The added Li+, Na+, K+ and NH4+ ions may also reduce the number of water molecules available to solvate the gold (I) ions which would therefore, be forced out of the solvent phase onto the PUFs since some amount of the free water molecules are preferentially used to solvate the cations added. Therefore, it appears also that the water structure enforced ion-pairing (WSEIP) is some what the driving force for the extraction of [Au(CN)2]− [26,38]. These results are in good agreement with the data reported earlier [17,26].

The effect of the sorbent doze (w) and batch factor (u/w) on the gold (I) retention at 10 μg mL−1 onto the IEPUFs and PUFs was investigated. The gold (I) sorption increased on increasing the sorbent doze up to 0.2 g of the solid sorbent. Therefore, in the subsequent work, 0.2 g of the solid sorbent IEPUFs or PUFs was employed. The sorption percentage of gold (I) onto the IEPUFs and PUFs decreased up to 60 ± 3.5% and 45 ± 2.8%, respectively on increasing the sample volume from 50.0 mL to 500 mL.

3.2. Kinetic behavior of gold (I) sorption onto IEPUFs and PUFs

In batch experiments, the gold (I) ions sorption onto the IEPUFs and PUFs sorbents was quite fast and the equilibrium was attained more or less a constant value in about 30 min shaking and remained constant up to 2 h. This conclusion was supported by calculation of the half-life time \((t_{1/2})\) of gold (I) sorption from the aqueous solutions onto the solid sorbents IEPUFs and PUFs. The values of \(t_{1/2}\) calculated from the plots of \(\log C/C_0\) versus time (Fig. 2) for gold (I) sorption onto IEPUFs and PUFs where \(C_0 = C_0\) and \(C = C_0 - C_a\). The values of \(t_{1/2}\) were found to be 2.34–2.73 ± 0.05 min, for both PUFs and IEPUFs sorbents. Thus, gel diffusion is not the rate-controlling step for IEPUFs as in the case of common ion exchange resins [17].

![Fig. 2 – Rate of gold (I) sorption at 5.0 μg mL−1 gold (I) ions from aqueous cyanide media (2%, w/v) onto IEPUFs (1) and PUFs (2) at pH 4–5 and 25 ± 0.1 °C.](image-url)
Thus, a 60 min shaking time was adopted in the subsequent work.

The kinetic behavior of gold (I) sorption onto IEPUFs and PUFs sorbents depends on film diffusion and intraparticle diffusion, and the more rapid one will control the overall rate of transport. Thus, the retained gold (I) species onto the used sorbents were subjected to Weber–Morris model [42]:

\[
q_t = R_d(t)^{1/2}
\]

(8)

where \( R_d \) is the rate constant of intraparticle transport in mmol g\(^{-1}\) and \( q_t \) is the sorbed gold (I) concentration (mol g\(^{-1}\)) at time \( t \). The plots of \( q_t \) versus time were found linear (\( R^2 = 0.954-0.979 \)) up to 40.6 ± 1.1 min for both IEPUFs and PUFs and deviate on increasing the shaking time (Fig. 3). The diffusion rate was found high in the initial stages and decreased on passage of time indicating that the rate of the retention step can be a rate controlling step.

Moreover, the rate constant for the retention step was evaluated in the light of Lagergren rate equation [43]:

\[
\log(q_e - q_t) = \log q_e - \left( \frac{kt}{2.303} \right)
\]

(9)

where \( q_e \) is the amount of gold (I) sorbed at equilibrium, per unit mass of sorbent (mmol g\(^{-1}\)) and \( k \) is the first-order overall rate constant for the retention process, s\(^{-1}\) and \( t \) = time, s. The plots of \( \log(q_e - q_t) \) versus time were found linear as shown in Fig. 4. The values of \( k \) calculated from the slopes were found in the range 2.2–2.8 ± 0.2 s\(^{-1}\) and suggested first order kinetics for the gold (I) retention towards the two used sorbents. The influence of different sorbent dose and adsorbate concentration was investigated. The results also indicate that the value of \( k \) increases on increasing the sorbent dose and adsorbate concentration confirming the formation of monolayer of gold (I) species onto the surface of the used adsorbent as well as the first order kinetic nature of the process.

The value of \( B_t \), which is a mathematical function (F) of the ratio of the fraction sorbed (\( q_t \) in mmol g\(^{-1}\)) at time \( t \) and at equilibrium (\( q_e \) in mmol g\(^{-1}\)) i.e. \( F = q_t/q_e \) was calculated for each value of \( F \) employing Reichenburg equation [44]:

\[
B_t = -0.4977 - 2.303 \log(1 - F)
\]

(10)

Plots of \( B_t \) versus time at 25 °C for both sorbents towards gold (I) species were found linear (Fig. 5) up to 40 min. The straight lines do not pass through the origin indicating that particle diffusion mechanism is not only responsible for the kinetics of Au(CN)\(_2^–\) sorption onto the PUFs and IEPUFs sorbents. Thus, the uptake of Au(CN)\(_2^–\) onto the employed sorbents are most likely involved three steps: (i) bulk transport of Au(CN)\(_2^–\) in solution, (ii) film transfer involving diffusion of Au(CN)\(_2^–\) within the pore volume of IEPUFs or PUF and/or along the pore wall surface to the active sorption sites of the sorbent and finally (iii) formation of the ternary complex ion associate of the formula [–CH\(_2\)–OH–CH\(_3\)]–[Au(CN)\(_2^–\)]foam –. Therefore, the actual sorption of Au(CN)\(_2^–\) onto the interior surface is rapid and hence it is not the rate determining step in the sorption process. Thus, one may conclude that film and intraparticle transport might be the two main steps controlling the sorption step. Thus, “solvent extraction” or a “weak base anion exchanger” mechanism is not only the most probable participating mechanism and most likely, some other processes like specific sites on the PUFs are possibly involved simultaneously in the gold (I) retention from the bulk aqueous solution [16–19] on the solid sorbent.
3.3. Sorption isotherms of gold (I) species onto IEPUFs and PUFs sorbents

The retention profile of gold (I) over a wide range of equilibrium concentrations (1.0 × 10^{-4}–20 × 10^{-4} mol L^{-1}) from the aqueous solution onto the employed sorbents was determined at the optimum concentration of gold (I) retention. The plots of the amount of gold (I) ions retained on the IEPUFs and PUFs sorbents versus their equilibrium concentrations in the bulk aqueous solution revealed that at low or moderate analyte concentration, the amount of Au(CN)_{2}^{-} retained on the foam sorbent varied linearly with the amount remained in the bulk solution. The equilibrium was approached only from the direction that of gold (I) rich aqueous phase confirming the first-order sorption behavior. A relatively reasonable sorption capacity of gold (I) ions towards IEPUFs and PUFs sorbent as predicted from the sorption isotherm was found in the range 11.21 ± 1.8 and 5.29 ± 0.9 mg g^{-1}, respectively. The distribution ratio decreased on raising the gold (I) concentration where, the sorbent membranes became saturated with the retained species [Au(CN)_{2}^{-}] rapidly within 15 min of shaking. Therefore, diffusion of the solute through a hypothetical film or hydrodynamic boundary layer took place in the sorption step [45,46] and both intraparticle transport and the film diffusion may be the steps controlling the molecular diffusion at the macro pores of the sorbent.

The retention profile of gold (I) from the aqueous solution onto the used sorbents was subjected to Freundlich and Langmuir isotherm models [47] over a wide range of equilibrium concentration through linear regression in a condition of best fit. The Freundlich model [45] is expressed in the following form:

\[
\log C_{\text{ads}} = \log A + \frac{1}{n} \log C_{e}
\]

where \(A\) and \(1/n\) are Freundlich parameters related to the maximum sorption capacity of solute (mol g^{-1}) and \(C_{\text{ads}}\) is the sorbed gold (I) concentration onto the IEPUFs and PUFs PUF per unit mass (mol g^{-1}) at equilibrium. Plots of \(\log C_{\text{ads}}\) versus \(\log C_{e}\) (Fig. 6) was linear (\(R^2 = 0.96–0.97\)) over the entire concentration range of gold (I) indicating a better fit for the experimental data. The values of the Freundlich constants \(A\) and \(1/n\) computed from the intercepts and slopes of the plots for IEPUFs were found to be 0.42 ± 0.07 mol g^{-1} and 0.79 ± 0.01 for IEPUFs and 0.33 ± 0.053 mol g^{-1} and 0.617 ± 0.023 for PUFs sorbents, respectively. The values of \(1/n < 1\) indicate the favorable sorption of gold (I) onto the tested solid sorbents. The sorption capacity is slightly reduced at lower equilibrium concentration and the isotherm does not predict any saturation of the solid surface of the adsorbent by the adsorbate. Thus, infinite surface coverage is predicted mathematically and physico sorption on the surface is expected.

The Langmuir sorption isotherm is expressed in the following linear form [47]:

\[
\frac{C_{e}}{C_{\text{ads}}} = \frac{1}{Qb} + \frac{C_{e}}{Q}
\]

where \(C_{e}\) is the equilibrium concentration (mol L^{-1}) of gold (I) in solution and \(Q\) and \(b\) are Langmuir constants related to the maximum adsorption capacity of solute per unit mass of adsorbent required for monolayer coverage of the surface and \(b\) is an equilibrium constant related to the binding energy of solute sorption that is independent of temperature. The plots of \(C_{e}/C_{\text{ads}}\) versus \(C_{e}\) over the entire

---

**Fig. 5** – Freundlich sorption isotherms of [Au(CN)_{2}]^{-} from aqueous cyanide media (2%, w/v) onto IEPUFs (1) and PUFs (2) at pH 4–5 and 25 + 0.1 °C.

**Fig. 6** – Chromatographic separation of gold (I) from silver (I) ions from their aqueous media (100 mL) containing gold (I) ions at 5 μg Au mL^{-1} in the presence of KCN (2%, w/v) employing IEPUFs packed column at 10.0 mL min^{-1}, pH 4–5 and 25 + 0.1 °C.
concentration range of gold (I) were linear confirming that the adsorption characteristics of the analyte towards IEPUFs and PUFs obey the Langmuir model. The sorption parameters Q and b evaluated from the slopes and intercepts of the Langmuir plots were found to be $9.075 \pm 0.05 \text{mmol g}^{-1}$ and $20.34 \pm 0.05 \text{mmol L}^{-1}$ of the tested sorbent IEPUFs and $4.67 \pm 0.03 \text{mmol g}^{-1}$ and $5.9 \pm 0.01 \text{mmol L}^{-1}$ for PUFs sorbent towards gold (I) retention, respectively. These data confirm that an added component for "surface adsorption" participates in the gold (I) uptake.

Based on these results and the data reported earlier [30,33] a dual sorption mechanism involving absorption related to "weak-base anion exchange" and an added component for "surface adsorption" mechanism for gold (I) retention by unloaded PUFs and IEPUFs. Based on the data reported earlier by Chow et al. [23,24], this dual model can be expressed by the following equation:

$$C_r = C_{abs} + C_{ads} = \frac{D C_{aq} + S K_d C_{aq}}{1 + K_d C_{aq}}$$

where $C_r$ and $C_{aq}$ are the equilibrium concentrations of gold (I) ions onto the solid sorbent and in aqueous solution, respectively. $C_{abs}$ and $C_{ads}$ are the equilibrium concentrations of gold (I) ions retained onto the used solid sorbents as an absorbed species and adsorbed species, respectively and $S$ and $K_d$ are the saturation values for the Langmuir adsorption model [17].

### 3.4. Chromatographic behavior of gold (I) on IEPUFs and PUFs packed columns

The membrane structure, the good hydrodynamic and aerodynamic properties of the PUFs [17,18] suggested the use of the IEPUFs and unloaded PUFs in flow mode for the pre-concentration of gold (I) species from aqueous solutions. The kinetics and the sorption results of gold (I) onto the IEPUFs and PUFs also recommended the possible application of both sorbents IEPUFs and PUFs separately in packed columns for the chromatographic separation of gold (I) from aqueous solution and silver (I) and base metal ions. Percolation of an aqueous solution (0.1 L) at concentration levels 1.0–5.0 mmol L$^{-1}$ of gold (I) at concentration levels 1.0–5.0 mmol L$^{-1}$ was achieved from IEPUFs packed column even at high flow rate (>96%) of gold species was achieved. The extraction, recovery and subsequent determination of the total inorganic gold in the binary mixtures of gold (I) and (II) ions in the aqueous media (0.11 L) at a total concentration ≤10 μg mL$^{-1}$ by the developed IEPUFs packed columns were attempted as described in the experimental section. The results are summarized in Table 2. Satisfactory recovery percentage of total inorganic gold species was obtained in the range 96.5 ± 3.9 to 98.3 ± 2.2%.

The effect of flow rate (2–15 mL min$^{-1}$) on the uptake and recovery of gold (I) by the IEPUFs packed column was also examined by percolating 100 mL of distilled water spiked with gold (I). Complete retention of gold (I) was achieved (>96%) at flow rate <10 mL min$^{-1}$. At higher flow rate, the sorption performance has been decreased and the width of the elution peak increased on increasing the flow rate. On the other hand, the effect of the sample volume (0.1–1.0 L) on the gold (I) retention was also investigated at 10 mL min$^{-1}$ flow column was used more than one time without decrease in the column performance. Also, reproducible recovery percentages of gold (I) was achieved from IEPUFs packed column even at trace concentrations of gold (I) in the test solution. Therefore, IEPUFs packed columns and perchloric acid as a proper eluting agent were used for the pre-concentration, recovery and subsequent determination of gold (I) species at trace concentration were used in the subsequent work.

The proposed IEPUFs packed columns was employed for the collection and recovery of gold (III) species from aqueous solutions after reduction to gold (I) with Na$_2$SO$_3$ in acid medium as described earlier. The extraction and recovery of the produced gold (I) at concentration levels 1.0–5.0 μg mL$^{-1}$ (0.11 L) were determined as described earlier at pH 4–5 for gold (III). Satisfactory recovery percentage (96.0 ± 4.5%, n = 5) of gold species was achieved. The extraction, recovery and subsequent determination of the total inorganic gold in the binary mixtures of gold (I) and (III) ions in the aqueous media (0.11 L) at a total concentration ≤10 μg mL$^{-1}$ by the developed IEPUFs packed columns were attempted as described in the experimental section. The results are summarized in Table 2. Satisfactory recovery percentage of total inorganic gold species was obtained in the range 96.5 ± 3.9 to 98.3 ± 2.2%.

The effect of flow rate (2–15 mL min$^{-1}$) on the uptake and recovery of gold (I) by the IEPUFs packed column was also examined by percolating 100 mL of distilled water spiked with gold (I). Complete retention of gold (I) was achieved (>96%) at flow rate <10 mL min$^{-1}$. At higher flow rate, the sorption performance has been decreased and the width of the elution peak increased on increasing the flow rate. On the other hand, the effect of the sample volume (0.1–1.0 L) on the gold (I) retention was also investigated at 10 mL min$^{-1}$ flow

| Table 1 – Results of the collection and recovery of gold (I) spiked to distilled water by the proposed IEPUFs packed column at 5 mL min$^{-1}$ employing AAS |
|-----------------|------------------|
| Gold species (μg mL$^{-1}$) | Recovery (%)$^a$ |
| Gold (I) taken | Gold (I) found |
| 5.0 | 4.9 | 98.0 ± 3.4 |
| 10.0 | 9.75 | 97.5 ± 2.5 |
| 15.0 | 14.7 | 97.0 ± 2.1 |
| $^a$ Average recovery (n = 5) ± relative standard deviation. |

| Table 2 – The extraction and recovery of total inorganic gold (I) and gold (III) in the binary mixture in the aqueous media by the developed IEPUFs packed columns |
|-----------------|------------------|
| Gold species added | Average gold found, recovery (%) |
| Au$^+$ | Au$^{3+}$ |
| 1.0 | 5.0 | 5.9 | 98.3 ± 2.2 |
| 5.0 | 5.0 | 9.6 | 96.5 ± 3.9 |
| $^a$ Average recovery (n = 5) ± relative standard deviation. |
rate. Almost complete retention (96.0 ± 4.5%, n = 5) has been achieved successfully on the IEPUFs packed columns with good reproducibility.

3.5. Analytical performance of the developed foams packed columns

The performance (HETP & N) of the IEPUFs and PUFs packed columns (1.0 g) was determined by passing an aqueous solution (0.5 L) containing gold (I) at 5 μg mL⁻¹ concentration levels at the optimum condition through the packed column at 5 mL min⁻¹. Complete sorption of gold (I) took place on the IEPUFs packed column. The retained species of gold [Au(CN)₂]⁻ were then eluted with perchloric acid (80.0 mL, 1.0 mol L⁻¹). A series (8 × 10 mL) of fractions of the eluent solution at 5 mL min⁻¹ were then collected and analyzed for gold (I) species by FAAS. The HETP and the number of theoretical plates N calculated from the elution curves (Fig. 6) employing the equation [17]:

\[
N = \frac{8V_{\text{max}}^2}{W^2} = \frac{L}{\text{HETP}} \tag{14}
\]

where \( V_{\text{max}} \): volume of eluate at peak maximum, \( W \): width of the peak at 1/e times the maximum solute concentration and \( L \) is the length of the foam bed in mm were in the range to 0.96 ± 0.04 mm and 95 ± 3, respectively. The N and HETP of the foam packed columns were also calculated from the breakthrough capacity curves by percolating 0.5 dm³ of the spiked tap water samples with gold (I) at 5.0 μg mL⁻¹ through the column at 5.0 mL min⁻¹ flow rate. The results are displayed in Fig. 7. The rising portions of the S-shaped curve have large slopes indicating a high transfer rate of [Au(CN)₂]⁻ on/in the foam membranes and rapid attainment of equilibrium between the [Au(CN)₂]⁻ and the foams. The HETP and N values of the IEPUFs packed column were calculated employing the equation [17]:

\[
N = \frac{V_{50} \times V'}{(V_{50} - V')} = \frac{L}{\text{HETP}} \tag{15}
\]

where \( V_{50} \): volume of the effluent solution at the center of the breakthrough curve where the concentration is one-half the initial concentration and \( V' \): the volume at which the effluent solution has the concentration 0.1578 of the initial concentration. The HETP and N were in the range 1.1 ± 0.01 mm and 89 ± 3.2, respectively. These values are in good agreement with the results obtained from the chromatogram method. The critical and breakthrough capacities [17,46] of the gold (I) retained onto the IEPUFs and PUFs packed columns calculated from the breakthrough curve (Fig. 7) were found in the 1.75–2.1 and 0.27–0.29 mg gold (I) retention per gram of the solid sorbent.

The lower limits of detection (LOD) and limit of quantification (LOQ) of gold (I) retention, recovery and subsequent determination were calculated for the IEPUFs packed column using the equations [48]:

\[
\text{LOD} = \frac{3 \times \text{S.D.}}{b} \tag{16}
\]

and

\[
\text{LOQ} = \frac{10 \times \text{S.D.}}{b} \tag{17}
\]

where S.D. is the standard deviation (n = 3) of the blank and b is the slope of the calibration plot. Under the optimal experimental conditions of gold (I) retention and recovery using IEPUFs packed columns, linear calibration curve for gold (I) determination was obtained. For an aliquot sample (50 mL), the equation of the calibration curve obtained is as follows: sample volume, 100 mL, \( A = 0.0011 + 0.47C \) (n = 3; \( R^2 = 0.98 \) and \( C = 0.0–15 \mu g L^{-1} \) gold (I). The LOD and LOQ of 0.01 μg L⁻¹ and 0.033 μg L⁻¹ were achieved, respectively. Such limits could be improved to lower values by collection of gold (I) species from large sample volumes of the aqueous phase at the optimum experimental conditions. The precision of the IEPUFs packed column for the extraction and recovery of standard aqueous solutions (0.1 L) containing 1.0 and 5.0 μg L⁻¹ (n = 3) of gold (I) at 5.0 mL min⁻¹ flow rate were 1.98 and 2.9%, respectively, expressed as relative standard deviations.

3.6. Interference study

The influence of a relatively high excess (1 mg) of some diverse ions relevant to waste water e.g., alkali and alkaline earth metals, Cu²⁺, Al³⁺, Ni²⁺, Co²⁺, Cd²⁺, Hg²⁺, Fe³⁺, VO₃⁻, AsO₄²⁻, SO₄²⁻, and PO₄³⁻ ions on the pre-concentration of gold (I) at 5 μg mL⁻¹ concentration level from aqueous cyanide media (50 mL) by developed IEPUFs was investigated. The tolerance limit (w/w) less than ±3% change in the uptake of gold (I) is considered free from interference. The results showed that the presence of large amounts of foreign ions in the sample has no significant effect on the pre-concentration of gold (I). Good extraction efficiency (>98 ± 2%) for the gold (I) ions was achieved successfully in the presence of the investigated divers ions. In the presence of some other ions such as Fe³⁺ and VO₃⁻, 2 mL of NaF (1.0 mol L⁻¹) solution were introduced.

![Fig. 7 – Breakthrough curves of [Au(CN)₂]⁻ at 5.0 μg Au⁺ mL⁻¹ on the IEPUFs (1) and PUFs (2) packed column at 5 mL min⁻¹, pH 4–5 and 25 + 0.1°C and KCN (2%, w/v).](image-url)
to the aqueous solution to obtain unambiguous and selective pre-concentration of gold (I). The fact that NaF solution forms anionic complex species with both Fe³⁺ and VO₃⁻ anions. Also, in the presence of MnO₄⁻, sodium azide is added to reduce manganese (VII) to manganese (II) and to eliminate the interference of permanganate ions. After employing these modifications, the tolerance level of the interfering ions was improved to acceptable limit (98 ± 2%). These results extend the use of the proposed IEPUFs for the separation and sequential determination of gold (I) ions from the industrial effluent of electroplating industry of gold.

### 3.7. Analytical applications of IEPUFs packed columns

#### 3.7.1. Pre-concentration and separation of gold (I) and/or gold (III) in different water samples

The validation of the developed method was successfully assessed by performing the recovery tests for gold in tap- and industrial wastewater samples. The water samples were first acidified with phosphoric acid and filtered through a 0.45 µm cellulose membrane filter. An aqueous solution (100 mL) of the water sample was then spiked with gold (I) and/or gold (III) species at a total concentration in the range 6–10 µg L⁻¹ levels. The sample solution was first reduced and the solutions were percolated through the IEPUFs packed columns at 5–10 mL min⁻¹ flow rate as described earlier. The recovered gold species was subsequently determined by FAAS. The results are summarized given in Table 3.

#### 3.7.2. Separation of gold (I) from silver (I) and base metal ions

The analytical utility of the IEPUFs packed column for the chromatographic separation of gold (I) from silver (I) in aqueous solution was successfully achieved by the developed procedures. Complete sorption of both metal ions took place. The retained [Au(CN)₂⁻] and [Ag (CN)₂⁻] species in the column were then recovered quantitatively with 80 mL HClO₄ (1.0 mol L⁻¹) and 140 mL of thiourea (1.0 mol L⁻¹)–H₂SO₄ (0.1 mol L⁻¹), respectively. The results shown in Fig. 6 indicated the good performance of the proposed IEPUFs for the separation of both metal ions in their complex mixtures quantitatively.

#### 3.7.3. Separation of gold (I) from silver (I) and base metal ions in aqueous solution mixtures

The applicability of the IEPUFs packed column to separate gold (I) from silver (I) and base metal ions (Fe³⁺, Ni²⁺, Cu²⁺ or Zn²⁺) in their aqueous solution mixtures (100 mL) at 5.0 µg mL⁻¹ concentration level of each ion was critically investigated as described before. Complete retention of the tested metal ions

![Fig. 8 – Chromatographic separation of gold (I), silver (I) and nickel (II) from their aqueous mixtures (100 mL) at 5.0 µg mL⁻¹ of each metal ion in the presence of KCN (2%, w/v) employing IEPUFs packed column at 5 mL min⁻¹ flow rate at pH 4-5 and 25 ± 0.1 °C.](image-url)
was achieved as indicated from the analysis of effluent solutions. Quantitative recovery of the base metal ion was first achieved employing the eluting system H$_2$SO$_4$ (0.05 mol L$^{-1}$), gold (I) was then eluted by HClO$_4$ (1.0 mol L$^{-1}$) and finally silver (I) was recovered by the system thiourea (1 mol L$^{-1}$)-H$_2$SO$_4$ (0.1 mol L$^{-1}$). The results shown in Fig. 8 confirmed the accuracy of the developed IEPUFs column and suggested the analytical utility of the IEPUFs packed column for gold separation and recovery from dilute aqueous solutions samples.

3.7.3. Separation and determination of gold in gold slime

The IEPUFs packed column was applied to the anodic slime samples having a complex matrix for the pre concentration, separation and subsequent AAS determination of gold following the general recommended procedures. The validity of the method was tested by the analysis spiked gold to the anodic slime samples. The recovered gold species by the developed procedures was subsequently determined. Satisfactory results (recoveries >95%, relative standard deviations <4.0%) were obtained. Thus, the developed IEPUFs packed column can find applications for gold separation and/or pre-concentration, recovery from metallurgical samples and ultra diluted aqueous solutions followed by subsequent determination.

4. Conclusion

The developed IEPUFs and PUFs packed columns provides a simple, reliable, fairly rapid and low cost method were successfully used for the pre concentration, separation and subsequent determination of inorganic gold (I) and total inorganic gold (I) and gold (III) from metallurgical sample having a complex matrix such as anodic slime after reduction of the latter to the mono-valence gold. The developed procedures are able to minimize the limitations related to sensitivity and selectivity for gold determination in different kinds of matrices. The kinetic data confirmed that the intra-particle diffusion and the first order model for gold (I) retention onto the tested sorbents. The sorption of gold (I) ions onto the foam sorbents followed Langmuir and Freundlich adsorption isotherms. The IEPUFs packed column was reused many times without loss in the column performance (N, HPTP). The membrane-like structures of the PUFs is superior compared to the known rigid or granular solid sorbents and permit rapid separation at relatively high flow rate. Separation of gold (I) species from silver (I) and base metal ions e.g. Fe$^{3+}$, Ni$^{2+}$, Cu$^{2+}$, and Zn$^{2+}$ was achieved successfully using on IEPUFs packed column. However, work is still continuing for investigating the influence of memory effect, organic material present in the investigated fresh water samples, competitive complexing agents in addition to the on-line determination of inorganic gold (I) and total inorganic gold (I) and gold (III). The effects of some organic species e.g. citrate, oxalate, etc. are currently under investigation. Separation of gold (I) from silver (I) and other base metal ions on IEPUFs packed column followed by subsequent on-site analysis by cold vapor flame atomic absorption or other analytical techniques will be considered.

**REFERENCES**


