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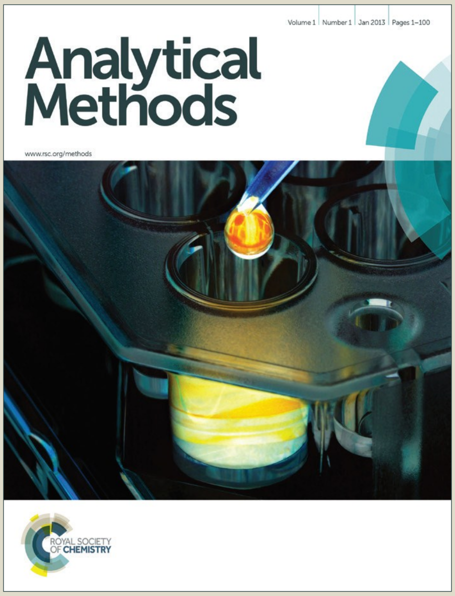

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Cytosine-functionalized polyurethane foam and its use as a sorbent for the determination of gold in geological samples

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A solid phase extraction procedure was developed for the separation and preconcentration of trace amounts of Au(III) in geological samples by using a polyurethane foam column modified with cytosine. The influence of flow rate of sample solution, the pH effect, eluent type, sorption capacity, and presence of matrix ions on the solid phase extraction procedure were investigated. The analytical results for international gold reference materials measured by this new method were in close agreement with those obtained by other well-established methods and values. Under the optimum conditions, the detection limit (3σ, $n = 6$) for the analyte was 6 ng L^{-1}, with an enrichment factor of 480. The equilibrium data were best represented by the Langmuir isotherm model, showing pseudo-first-order kinetics. The maximum adsorption capacity of Au(III) on the adsorbent was 98.9 mg g^{-1}.

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Introduction

Gold is one of the most important noble metals in the modern world due to its wide variety of applications in the industry, medicine, and global economy.[1] Demand for gold and other noble metals is growing with modernization. However, gold occurs in very low concentrations in the Earth's crust.[2] Even though the sensitivity of modern instrumentation has increased enormously over the decades, direct analysis of gold in real samples is still very difficult owing to its very low abundance and instrumental interferences caused by matrix elements. Gold is chalcophile element, which is distributed heterogeneous in silicate and tend to concentrate in sulfide and alloy phases in the mantle. It is usually called "nugget effect". Preconcentration is an important step in the determination of traces of gold in geological materials.[3]

Different techniques are available for the preconcentration of gold, including the classical fire assay method using various collectors,[4] precipitation and coprecipitation techniques,[5] extraction processes,[6] and sorption approach.[7] The classical fire assay method is used for routine laboratory analyses that can accommodate a large sample mass (15–30 g) that reduces the nugget effect, but in general procedural blanks are relatively high. In addition, the fire assay procedure is quite tedious and time-consuming.[8] Compared to liquid–liquid extraction and coprecipitation, the use of solid phase extraction (SPE) is more advantageous due to its high enrichment capability, ease of separation, and ability to sync with different instrumental techniques.

In recent years, complexing sorbents and ion exchangers have been widely used for noble metal preconcentration.[9] Some newly designed materials such as bonded-phase silica sorbents,[10] polymeric sorbents,[11] biosorbents,[12] and carbon-based sorbents have been proposed and are of interest.[13] In terms of gold mineral analysis, activated carbon and polyurethane foam (PUF) are the most practical and commonly used adsorbing materials. AC has a large specific surface area and good selectivity to Au, but small size of AC cause high pressure in the SPE cartridge, while PUF combines the advantages of high efficiency, low cost, easy handling, and easy storage.

Bowen first used PUF as an absorbent material for the sorption and recovery of inorganic and organic compounds from aqueous solutions.[14] Then, PUF was used to separate and recover gold by Braun.[15, 16] These studies aroused wide interested, and PUF have been extensively studied.[17, 18] However, two main problems have necessitated the need for the preparation of a functionalized PUF: (1) lack of selectivity of PUFs, and (2) low sorption capacity. To date, modified PUFs have exhibited higher adsorption capacities and selectivity capacities than those of untreated PUFs, thus allowing wider application of modified PUFs.[19] Functionalized PUFs have been used as excellent sorbents with good stability, high capacity, and good flexibility.[20, 21] Also, functionalized PUFs have been shown to facilitate

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relatively fast separations with good enrichment capacities.[22, 23]

In the present work, PUF was acid hydrolyzed to produce PUF-NH_2, and it was then further modified with the chelating ligand cytosine (Cyt) through a linking arm to form the Cyt-functionalized PUF (PUF-Cyt). Cytosine is a kind of natural product obtained easily and satisfied immobilization on PUF as a good ligand for metal ions due to the presence of heteroatoms (N, O). PUF-Cyt was used as the sorbent for the separation and preconcentration of gold in geological samples. The new sorbent showed high selectivity, sensitivity, and adsorption capacity for the solid phase extraction of Au(III). Several factors influenced the performance of PUF-Cyt. These factors, including the solution acidity, adsorption capacity of the adsorbent, effect of other metal ions, and recovery behavior, were systematically studied and optimized. The proposed method was applied to the determination of trace amounts of gold in geological samples.

Experimental

Reagents and materials

All solvents were reagent grade or better. Ultrapure water with a resistivity of 18.2 MΩ cm^{-1} was obtained from a Milli-Q water purification system. Concentrated HNO_3 (65%–68%, w/w), HCl (36%–38%, w/w), and HF (40%, w/w) were ultrapure grade (BV-III, Beijing Institute of Chemical Reagent, Beijing, China). Suprapure H_2O_2 (30%, m/m; Merck, Darmstadt, Germany) was used for acid digestion. Glutaraldehyde (25 wt%, Sigma–Aldrich, Germany) and cytosine (Sinopharm, China) were used to prepare PUF-Cyt. The standard stock solution for Au(III) was obtained from Merck (Darmstadt, Germany). Working standard solutions were prepared by appropriate dilution of the commercial stock solution. Commercial PUF (a polyether of open-cell type, ca. 100% open cell, JX-1) was purchased from Jixiang sponge co., LTD in Yangzhou, China.

Instrumentation

iCAP 7400 ICP-OES (Thermo, USA) with a concentric nebulizer and a cinnabar spray chamber was employed for the determination of all metal ions. The wavelength of Au was selected 242.795 nm and the optimum operation conditions were summarized in Table S1. Infrared spectra were recorded on a Nicolet Nexus 6700 FTIR apparatus (Thermo Scientific, USA), and were used to confirm the structure of PUF and PUF-Cyt. Elemental analysis was carried out using a universal CHNOS elemental analyzer Vario EL III (Elementar Analysensysteme GmbH, Germany). The column process was performed using a BT101F peristaltic pump (Lead Fluid Technology Co., Ltd., Baoding, China). A THZ-C-1 horizontal shaking bath (Taicang Instrument Factory, Jiangsu, China) was used in batch procedures. The pH value was measured using a pHS-3G digital pH meter (Lei Ci Device Works, Shanghai, China). A model L550 centrifuge (Xiangyi Centrifugal Machine Equipment Co., Ltd., Changsha, China) and Milli-Q-purified water apparatus (Millipore Co., Bedford, MA, USA) were used in a variety of tests. A muffle furnace (SX2-4-10) was obtained from Great Wall Furnace Company, China. Round-bottom Savillex PFA screw-cap capsules (180 mL; Savillex Corporation, Eden Prairie, MN, USA) were used for sample digestion experiments.

Synthesis of PUF-Cyt

Commercial PUF (2.0 g) was crushed using a mincing machine, and then boiled in a 2 mol L^{-1} HCl solution for 2 h to generate the maximum number of free amino groups. Amine derivatives of PUF (PUF-NH_2) were obtained, and then washed with water four times. The product was collected and dried under vacuum at 25 °C. Finally, 1.9 g of dry PUF-NH_2 was achieved. Cyt was immobilized on PUF-NH_2 using the bifunctional reagent glutaraldehyde as a linking arm to form imine. Then, 2 mL of 25% aqueous glutaraldehyde solution was diluted to 100 mL with a phosphate buffer (pH 7). Purified PUF-NH_2 (1.0 g) was immersed in this solution and stirred at room temperature in an argon atmosphere for 1 h. Finally, 0.1 g of Cyt dissolved in 60 mL of phosphate buffer (pH 7) was added to the reaction system under an argon flow. The reaction was allowed to continue with stirring for about 5 h at room temperature under an argon atmosphere. The solution was then stored for 2 days at room temperature. Finally, the product was filtered and washed with water, and then dried under vacuum at 25 °C. Subsequently, PUF-Cyt was smashed by a food-processing blender and sieved. Particles between 100 and 200 μm were used for adsorption studies. The scheme for the synthesis of PUF-Cyt used in this study is shown in Fig. 1. The estimated mass fraction of Cyt in the PUF-Cyt was 8.7% (please see details in Supporting Information).

Fig. 1 Scheme for the synthesis of PUF-Cyt.

Sample preparation

Ten gram samples were used to reduce the risk of erratic results due to the presence of native gold particles, known as the nugget effect. The digestion was carried out using a slightly modified aqua regia procedure described in the literature.[24] Approximately 10 g of finely powdered sample (200 mesh) was placed in a porcelain crucible (100 mL) and heated at 650 °C for 1 h in a muffle furnace with the door half open. The sample was then transferred into a 180 mL Savillex PFA vessel. Next, 40 mL of 50% aqua regia was added to the Savillex PFA vessel and the mixture was heated on an electric hot plate (150 °C) until the mixture evaporated to a moist residue. This procedure was repeated again with 20 mL of 50% aqua regia. After digestion with aqua regia, 15 mL of HF + 10 mL of HNO_3 was added slowly to avoid violent boiling due to the exothermic reaction. The solutions were then evaporated to dryness on a hot plate to remove silicates. After diluting with the desired concentration of HCl for the extraction of the analyte, the sample was transferred to a 100-mL volumetric flask and diluted up to the mark with the same concentration of HCl. After ~30 min, the solids settled to the bottom of the flask. Then, 25 mL of the resulting clear solution was used for the sorption and preconcentration of gold in geological samples. Above sample treating is a general procedure which would be slightly different from each rock types. For example, the sample mass can reduce to 5 g for soil and ultramafic rocks; For Ni–Cu sulphide samples, it would be reduce to 2 g, which have relatively low nugget effects. The corresponding acid consumption should reduce in proportion to the sample mass. But for ultramafic rocks contain refractory minerals (olivine, spinel, etc.), further processing is required. After the dissolution of silicate minerals in mixtures of hydrofluoric acid and nitric acid, 10 mL of HCl and additional H_2O_2 (3 mL) were added. Then, the vessel was capped and heated at 180 °C in an electric oven for 2 h. The vessel was opened and evaporated to a moist residue on an electric hot plate. Finally, the sample was diluted to the volume with the procedures above mentioned.

Batch procedure

A series of standards or sample solutions containing Au(III) were transferred into a 50 mL grinding mouth Erlenmeyer flask with a matching stopper. The pH of each solution was adjusted to 1 with 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} $NH_3 \cdot H_2O$. The volume was then adjusted to 10 mL with ultrapure water. PUF-Cyt (0.05 g) was added, and the mixture was shaken vigorously for 30 min using a mechanical reciprocating shaker to attain equilibrium. The adsorbent was then separated. The amount of the metal ions remaining in the aqueous solution was measured by inductively coupled plasma optical emission spectrometry (ICP-OES). The amount of the metal ions extracted with the foam was calculated by difference. The amount of Au(III) retained at equilibrium (capacity of adsorbent, Q_e, mg g^{-1}) on the tested solid adsorbent was calculated using Eq. (1).

$$Q_e = {(C_0 - C)V}/{m} \qquad (1)$$

where C_0 and C are the before and after extraction concentrations of Au(III) in solution, respectively; and V and m are the volume (mL) and mass (g) of the solution and adsorbent, respectively.

Column procedure

PUF-Cyt (0.25 g) was packed in a PP column (83 mm×15.6 mm ID) blocked with frits at the inlet and outlet of the column. The bottom of the column was connected via a pump tubing to a peristaltic pump to control the flow rate. Before use, 0.25 mol L^{-1} HCl and deionized water were successively passed through the column in order to clean and neutralize it. Portions of aqueous standard or sample solutions of Au(III) (25 mL) adjusted pH to 1 with 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} $NH_3 \cdot H_2O$ were passed through the column at a flow rate of 4 mL min^{-1}. Afterwards, the analyte retained on the column were eluted with 5.0 mL of 1% (m/v) thiourea in 0.1 mol L^{-1} HCl. The effluent or eluted solution containing the target analyte was analyzed by ICP-OES. Blank samples were subjected to the same procedure. All values obtained were corrected by subtracting the values of the procedural blank.

Results and discussion

Characterization of PUF-Cyt

FTIR spectra were obtained for PUF, PUF-NH_2 and PUF-Cyt to determine the presence of Cyt on PUF. The FTIR spectra for these samples are illustrated in Fig. 2. Comparing the IR spectrum of PUF, PUF-NH_2 and PUF-Cyt, the broad band at 3300.5 cm^{-1} assigned to $\nu_{N\text{-}H}$ and $\nu_{O\text{-}H}$ for PUF was shifted to 3376.5 cm^{-1} for PUF-NH_2 and 3415.4 cm^{-1} for PUF-Cyt, with significant increase in the peak areas. Because the amino increased significantly for PUF-NH_2 and the number of secondary amine (N-H bond) in Cyt increased for PUF-Cyt. The spectrum for PUF-Cyt shows additional peaks at 1685 cm^{-1} for the C=N bond and 1725 cm^{-1} for C=O bond of cytosine moiety. The peak at ≈1450^{-1} in the FTIR-spectrum of the PUF-Cyt is the vibration of -CH- bond in cytosine moiety.

Fig. 2 FTIR spectra of PUF and PUF-Cyt.

Scanning electron microscopy (SEM) imaging was performed on AURIGA Compact FIB-SEM. The SEM image (Fig. S1a and Fig. S1b) at magnification 117 showed a ruptured structure of PUF-Cyt formed by the breakage of chemical bonds during hydrolysis.

The pH of the zero point-of-charge (pH_{ZPC}) was measured according to the method proposed by Noh.[25] A series of flasks containing 25 mL of the sample solution were adjusted to pH values ranging from 1 to 13 by adding HCl or NaOH. PUF-Cyt (0.1 g) was added to each of these pH-adjusted solutions. After 24 h, the final pH (pH_f) of each solution was measured. The difference between the initial and final pH values ($\Delta pH = pH_f - pH_i$) was plotted against pH_i. pH_{ZPC} is the pH at which $pH_i = pH_f$. The pH_{ZPC} value for PUF and PUF-Cyt were determined from these plots and found to be 7.2 and 7.5, respectively (Fig. S2). Using this data, it was determined that the surfaces sites of PUF-Cyt are positively charged at pH values lower than 7.5, and become negatively charged at pH values greater than 7.5.

Elemental analysis of PUF-Cyt showed that the hydrogen (8.7%) and nitrogen (7.6%) contents of the samples increased, whereas the amounts of carbon (64.3%) decreased compared with that of PUF (Table 2). This result likely occurred because Cyt contains more nitrogen. The amount of cytosine modified on the PUF was calculated by difference, details are at Supporting Information. Consequently, these experimental results suggest that PUF was successfully modified by Cyt.

Table 2 Properties of PUF and PUF-Cyt.

Effect of pH on adsorption of Au(III)

The acidity of a solution is one of the most important factors affecting the adsorption process, and has two effects on metal adsorption. First, protons in acid solutions can protonate the binding sites of chelating molecules. Second, hydroxide in basic solutions may complex and precipitate metals.[26] Therefore, the pH of a sample solution is a vital parameter for quantitative adsorption and recovery of analyte using the SPE technique. In this experiment, the effect of pH and sample acidity on the degree of sorption of Au(III) and base metals was evaluated through the batch procedure. The effect of solution acidity on the degree of sorption was investigated over the pH range of 0.6–5 (Fig. 3). Maximum Au(III) recoveries occurred in the pH range of 0.6–2. In HCl, the main chemical form of the Au(III) ion in aqueous solution is $AuCl_4^-$, which has a high formation constant (logβ_4 = 31.05).[27] The chloro-anionic species can be adsorbed by protonated –CH=N– (imine) groups on PUF-Cyt, forming ion-pair complexes. Therefore, electrostatic interactions are very effective in the adsorption of $AuCl_4^-$ (Fig. S3). According to the hard/soft acid/base theory,[28] a chelating sorbent with N or O donor atoms can strongly bind noble metals. In acidic solutions, according to the results obtained in this work, the mechanism for adsorbing gold on PUF-Cyt involves ion chelation process with the aid of electrostatic interactions. In addition, 10 mL of 1.0 μg mL^{-1} of base metal cation solutions, such as Fe(III), Co(II), Ni(II), Cu(II), Pb(II), Zn(II), Cr(III), Cd(II), and Ru(IV), were also investigated by equilibrating with 50 mg of sorbent, as was done for the experiments at pH 1. The degree of sorption for the base metal cations was generally low at high acidity and increased with increasing pH. Therefore, we selected pH 1 as the enrichment acidity for subsequent studies in order to eliminate the adsorption of other base metal ions that may be present in the samples.

Fig. 3 Effect of pH on the adsorption of 1.0 μg mL^{-1} Au(III). Other conditions: 50 mg PUF-Cyt, shaking time 30 min, temperature 25 °C (n = 3).

Effect of shaking time and adsorption kinetics

The effect of shaking time on the adsorption of Au(III) was studied by the batch procedure. Different shaking times ranging from 0.2 to 30 min were tested to determine the percent extraction of Au(III) by PUF-Cyt (Fig. 4).

Fig. 4 Effect of shaking time on the adsorption of 1.0 μg mL^{-1} Au(III). Other conditions: 50 mg PUF-Cyt, pH 1.0, temperature 25 °C (n = 3).

From the graph shown in Fig. 4, it is evident that the adsorption of Au(III) was greater than 95% during the first min. After 1 min, however, the rate of adsorption of Au(III) reduced considerably. The amount of the adsorbed Au(III) increased with increasing contact time and reached a maximum at 30 min. Therefore, 30 min was selected as the adsorption equilibrium time. This fast initial sorption is probably due to the high affinity between gold ions and amino groups on the sorbent.

In order to investigate the mechanism of the adsorption process and obtain characteristic constants of adsorption, kinetic models were exploited to analyze the experimental data. Models for pseudo-first-order, pseudo-second-order, and intraparticle diffusion were used to test the experimental data. The data was fitted into each of these three models (Fig. S4). Eqs. (2)-(4) show the equations of the three kinetic models.

Pseudo-first-order kinetic model:

$$\log(Q_e - Q_t) = logQ_e - \frac{k_1 t}{2.303} \qquad (2)$$

Pseudo-second-order kinetic model:

$$t/_{Q_t} = 1/_{k_2 Q_e^2} + t/_{Q_e} \qquad (3)$$

Intraparticle diffusion kinetic model:

$$Q_t = k_i\sqrt{t} \qquad (4)$$

where Q_e and Q_t (mg g^{-1}) are the amounts of gold ions adsorbed at equilibrium and at time t, respectively; k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}); k_2 is the pseudo-second-order adsorption rata constant (g mg^{-1} min^{-1}); and k_i is the intraparticle diffusion rate constant (mg g^{-1} min$^{-0.5}$).

The regression coefficients and rate constants k_1, k_2, and k_i for these three kinetic models are listed in Table 2. As can be seen in Table 2, the values of the regression coefficients (R^2, 0.988) for the pseudo-first-order rate equation are higher than those of the pseudo-second-order rate equation (R^2, 0.970), suggesting that the pseudo-first-order rate equation best represents the adsorption system. It is clear from Fig. S4c that the linear portion of the plot did not pass through the origin. Such a situation may suggest that the reaction is multilinear, indicating that two or more steps took place during adsorption.[29] Recall that the adsorption of Au(III) was found to be rapid initially, but then became slow and stagnate with time and Au(III) was slowly transported into the pores and retained in the micropores.

Table 2 Kinetic parameters for the adsorption of Au(III) on the experimental adsorbent.

Effect of the initial concentration of Au(III) ions on the adsorption isotherm

The influence of the initial Au(III) concentration on the adsorption capacity of PUF-Cyt was investigated.

Fig. 5 Effect of the initial concentration of Au(III) ions on PUF-Cyt at various temperatures. Other conditions: 50 mg PUF-Cyt, pH 1.0, shaking time 30 min (n = 3).

As shown in Fig. 5, the amount of Au(III) ions adsorbed per unit mass of PUF-Cyt increased initially, and then reached a plateau. This result showed that the initial Au(III) concentration provided a driving force to overcome the mass transfer resistance between the adsorption medium and the adsorbent. Higher ion concentrations increase the mass transfer driving force and enhance the collision probability between metal ions and adsorbent.[30] The capacity study was adopted from the report of Maquieira et al.[31] A breakthrough curve was obtained by plotting the concentration (µg mL^{-1}) versus the micrograms of Au(III) adsorbed per gram of PUF-Cyt. From the breakthrough curve, the maximum adsorption capacity of PUF-Cyt for Au(III) was determined to be 98.8 mg g^{-1} at 298 K. The adsorption isotherm is critical in optimizing the use of the adsorbent, since it can be used to assess the adsorption capacity of the adsorbent and describe how the adsorbate interacts with the adsorbent. For interpreting the adsorption experimental data, the Langmuir[32], Freundlich[33], and Dubinin–Radushkevich (D–R)[34] isotherm models were applied. Eq. (5) gives the expression of the Langmuir model.

$$ {}^{C_e}/_{Q_e} = {}^{C_e}/_{Q_{max}} + {}^{1}/_{KQ_{max}} \qquad (5)$$

where C_e is the equilibrium concentration of gold ions in the solution (mg g^{-1}), Q_e is the adsorption capacity of the metal ions adsorbed at equilibrium (mg g^{-1}), Q_{max} is the theoretical maximum adsorption capacity (mg g^{-1}), and K is the Langmuir constant related to the affinity of the binding sites (L mg^{-1}). Q_{max} and K are calculated from the slopes and intercepts of the straight lines of plot of $C_\mathrm{e}/q_\mathrm{e}$ versus C_e. The Freundlich equation was also employed to assess the adsorption of Au(III) on the adsorbents. The linear form of the Freundlich isotherm model is represented as:

$$logQ_e = logK_f + \tfrac{1}{n}logC_e \qquad (6)$$

where Q_e and C_e have the same definitions as in Eq. (5), K_f (mg g^{-1}) (L mg^{-1})$^{1/n}$ and n are constants incorporating all factors affecting the adsorption capacity and intensity of adsorption.

The values of n and K_f were calculated from the slope and intercept of the plot of $log\ Q_e$ versus $log\ C_e$. The calculated values of the Langmuir and Freundlich equations' parameters are given in Table 3. As can be seen, the Langmuir model (Fig. S5a) exhibited higher values of the regression coefficients than those obtained from the Freundlich model (Fig. S5b). The theoretical Q_{max} value (96.90 mg g^{-1}, 298 K) obtained from the Langmuir model was close to the experimental values (98.8 mg g^{-1}). The R^2 values for the Langmuir isotherm model are greater than 0.988. Thus, the Langmuir model is better to describe the adsorption isotherm and the sorption behavior of Au(III) onto PUF-Cyt is considered to be representative of sorption onto a monolayer. Additionally, both Q_{max} and k decreased with increasing temperature, indicating that the bonding between heavy metals and the active sites of the adsorbent weakened at higher temperatures, and that the adsorption process is exothermic.

Table 3 Parameters of the Langmuir, Freundlich, and Dubinin–Radushkevich isotherms for the adsorption of Au(III).

The dimensionless constant, R_L, was used to evaluate the influence of adsorption isotherm favorable or unfavorable, which referred to as separation factor, defined by following equation:

$$R_L = \frac{1}{1+KC_0} \qquad (7)$$

where K is the Langmuir constant (L mol^{-1}) and C_0 is the initial concentration (mol L^{-1}).

The R_L values (illustrated in Table 3) were between 0 and 1, suggesting that the adsorption was favorable. The Langmuir and Freundlich isotherms could not be used to evaluate the physical and chemical characteristics of adsorption. Therefore, the equilibrium data were also analyzed by the Dubinin–Radushkevich isotherm (D–R isotherm) to determine whether the adsorption processes were physical or chemical. The linearized D–R equation has the following form:

$$lnQ_e = lnQ_{D-R} - \beta\varepsilon^2 \qquad (8)$$

where Q_e is the adsorption capacity at equilibrium (mg g^{-1}), $Q_{D\text{-}R}$ is the maximum monolayer adsorption capacity (mg g^{-1}), β is the activity coefficient related to adsorption mean free energy (mol^2 J^{-2}), and ε is the Polanyi potential as represented by Eq. (9).

$$\varepsilon = RTln(1 + \frac{1}{C_e}) \qquad (9)$$

where R is the gas constant (J mol^{-1} K^{-1}), T is the absolute temperature (K), and C_e is the equilibrium concentration of the adsorbate in aqueous solution (mg L^{-1}).

Sorption energy E (kJ mol^{-1}) gives information about the adsorption mechanism, whether it is physical or chemical. If the magnitude of E is between 8 and 16 kJ mol^{-1}, the sorption process follows chemical ion exchange. The sorption mechanism is physical when $E < 8$ kJ mol^{-1}. This relationship is represented by Eq. (10).

$$E = \frac{1}{\sqrt{-2\beta}} \qquad (10)$$

All the parameters calculated are presented in Table 3. The value of the correlation coefficient (0.557) indicated that the D–R isotherm (Fig. S5c) is a poor fit to the adsorption process. The values of $Q_{D\text{-}R}$ are not high enough to indicate the adsorption capacity, whereas the values of the apparent energy of adsorption depict the physical adsorption process. Therefore, the D-R isotherm did not give a good fit to the adsorption process.

A comparison of the maximum adsorption capacities of PUF-Cyt for Au(III) plus other adsorbents reported in the literatures is given in Table 4. Compared with other alternative adsorbents, it was apparent that the adsorption capacities of PUF-Cyt had higher adsorption capacities than other types of PUF adsorbents and most of the other adsorbents. The results indicated that PUF-Cyt exhibited good adsorption efficiency and it is a promising adsorption material for the analysis of Au(III).

Table 4 Comparative data from some recent studies on the preconcentration of Au(III).

Adsorption thermodynamics

The thermodynamic parameters for the sorption of Au(III) were calculated using Van't Hoff equations (Eq. (11) and Eq. (12)).

$$ln\, K = {}^{\Delta S^0}/_{R} - {}^{\Delta H^0}/_{RT} \qquad (11)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (12)$$

where K is the Langmuir constant ($K = Q_e/C_e$), R is the gas constant (8.314 J mol^{-1} K^{-1}), and T is the temperature (K). The values of ΔH and ΔS^0 can be calculated from the slope and intercept of the plot of ln K versus $1/T$, respectively (Fig. S6). The thermodynamic parameters are summarized in Table 5. The negative value of ΔH^0 (−8.59 kJ mol^{-1}) indicates that the sorption process of Au(III) is an exothermic chemisorption. Hence, the amount of Au(III) adsorbed at equilibrium must decrease with increasing temperature. The negative ΔS^0 (−3.30 J mol^{-1} K^{-1}) indicates a decreased randomness at the solid–liquid interface during the sorption of Au(III). The negative values of ΔG^0 indicate the adsorption process is feasible and spontaneous with a high preference for Au(III) on PUF-Cyt.

Table 5 Thermodynamic parameters for the adsorption of Au(III) on the adsorbent.

Effect of sample flow rate, sample volume, and enrichment factor

The effect of the sample flow rate on the recovery of Au(III) was investigated by passing 25 mL of the sample solution through the column at a rate of 1.0–8.0 mL min^{-1}. Flow rates in the range of 1.0–4.0 mL min^{-1} exerted no significant effect on the recovery of Au(III), whereas flow rates greater than 4.0 mL min^{-1} decreased the recovery percentage (Fig. 6). Hence, all subsequent experiments were conducted at a flow rate of 4.0 mL min^{-1}.

Fig. 6 Effect of sample flow rate on the recovery (%) of Au. Other conditions: 0.25 g PUF-Cyt; pH 1.0; concentration of Au(III): 1.0 μg mL^{-1}.

In order to obtain reliable analytical results and a high concentration factor, it is important to get satisfactory recovery of the analyte from large volumes of sample solutions. Hence, the effect of sample volume on the retention of analyte was investigated by passing 100–3200 mL of sample solutions containing 20.0 μg of Au(III) through the PUF-Cyt column, and subjecting them to the procedure discussed in this paper. The results indicated that Au(III) ions were recovered in high quantities when the sample volume was less than 2400 mL. After elution with 5 mL of the eluent, an enrichment factor of 480 was achieved. These results were excellent when compared with those obtained by using other materials for the preconcentration of gold.

Fig. 7 Effect of sample volume on the recovery of Au(III). Effect of sample volume on the recovery of Au(III). Other conditions: Au, 20.0 μg; sample flow rate, 4.0 mL min^{-1}; 0.25 g PUF-Cyt; pH 1.0 (n = 3).

Optimization of elution conditions

Quantitative desorption of gold can be done if an eluent is used to decompose the ion-pair complexes formed on the sorbent surface. The effects of various eluting agents such as HCl and H_2NCSNH_2 were examined. It was found that adding small amounts of thiourea as a chelating reagent in 0.1 mol L^{-1} HCl helped elute gold from the adsorbent. Hence, thiourea combined with 0.1 mol L^{-1} HCl was employed and the effect of different concentrations of thiourea was investigated for the elution of Au. The experimental results (Fig. 8) indicated that high recovery (>95%) was obtained with 1% (m/v) thiourea. The eluent solution consisting of 1% (m/v) thiourea in 0.1 mol L^{-1} HCl was able to completely remove the analyte. Thiourea develops a positive charge in hydrochloric acid, thus favoring complex formation with gold-chloro complexes. In addition, gold has a higher affinity for S than N. Therefore, thiourea with 0.1 mol L^{-1} HCl was used in the experiment. It was found that 5.0 mL of this elution solution was sufficient to quantitatively recover the analyte. Hence, 5.0 mL was selected as the eluent volume for subsequent experiments. Effluents were collected separately and analyzed by ICP-OES. Higher concentrations of thiourea (5% (m/v)) were also effective for desorbing the analysts; however, high concentrations of thiourea interfere with analyses done using ICP-OES.

Fig. 8 Elution recovery of Au(III) adsorbed on PUF-Cyt.

Effect of matrix ions

Matrix effects are important in the analysis of gold in real samples. A binary mixture (25 mL) containing 25 μg of Au(III) and interfering cations such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Mn^{2+}, Cr^{3+}, Cl^-, and NO_3^{2-} was investigated to assess method selectivity under the optimal conditions described previously. Solutions for testing anions were prepared by dissolving their corresponding sodium salts in water, whereas cation interferences were prepared using their nitrates. The results showed that none of these ions induced a remarkable influence on the assay. The tolerance limit of coexisting ions causing recoveries of the examined elements was set to <90%, which is shown in Table 6.

Table 6 Effect of potentially interfering ions on the percent recovery of 1.0 μg mL^{-1} Au(III) on the sorbent followed by elution with 1% (m/v) thiourea in 0.1 mol L^{-1} HCl. Other conditions: sample volume: 25 mL; sample flow rate, 4.0 mL min^{-1}; 0.25 g PUF-Cyt; pH 1.0 (n = 3).

Analytical performance

In order to assess the applicability of this method to real samples, separation and recovery of gold in geological samples were attempted. The accuracy of the method was verified by determining Au in WMS-1a, MA-2c

(International Standard Reference Materials; CANMET, Hamilton, Canada), and GAu-14, GAu-16, GAu-18 (certified reference material;, Beijing, China), which were either developed especially for the task of gold analysis or are well known and commonly used reference materials for major and trace element analysis. Certified values and standard deviations of reference values were obtained from the database available at the CANMET internet website, http://www.nrcan.gc.ca/mining-materials/certified-reference-materials/8001/. The proposed values for GAu-14, GAu-16, and GAu-18 are obtained from Yan et al.[46] The results, listed in Table 7, are in good agreement with the certified values. The details on the certified reference materials of WMS-1a, MA-2c, GAu 14, GAu 16, GAu 18 are listed in the Table S2.

Table 7 Analytical results of the determination of Au in geological samples (n = 3).

The reliability of our method was checked by spiking experiments with tap water, sea water, and GAu-18. The results are shown in Table 8. The recovery of the spiked samples was satisfactory, and, hence, the presented procedure indicates that the reliability of PUF-Cyt for the determination of Au in geological samples is acceptable.

Under optimized conditions, calibration curve (Fig. S7) was constructed in the linear range of 0.05–10 μg mL^{-1} with the correlation factor of 0.9998 ($Y = 10.6684X + 0.2762$). Based on the definition of the International Union of Pure and Applied Chemistry, the detection limit was calculated as the concentration of analyte that corresponds to three times the standard deviation of eight replicate measurements of the procedural blank sample using the entire sample treatment process (LOD=3σ, where σ is the standard deviation of blank determination).[47] Using this procedure, the detection limit for gold was determined to be 0.006 μg L^{-1} and the limit of quantitation (LOQ=10σ) for gold was 0.02 μg L^{-1}.

Table 8 Added/found method for Au(III) determination in water and ore samples. Other conditions: sample volume: 25 mL; sample flow rate, 4.0 mL min^{-1}; 0.25 g PUF-Cyt; pH 1.0 (n = 5).

Conclusions

A novel adsorbent was prepared based on the modification of PUF with a Cyt ligand. The kinetic and thermodynamic of the gold ions sorption on PUF-Cyt was studied. A negative ΔS value and exothermic enthalpy value indicated moderately strong affinity of Au(III) for the modified sorbent. The sorption mechanism of gold ions on PUF-Cyt may proceed via the chelation and ion association. The selectivity and recovery of PUF-Cyt for the extraction and preconcentration of gold ions from geological samples were also investigated. The procedure offers a useful and reliable enrichment technique for the preconcentration of Au(III) with acceptable accuracy and precision. The optimal conditions for preconcentration were investigated systematically. This method represents high tolerance limits for potential matrix ions, satisfactory reproducibility, and relatively high sorption capacity. The detection limit and enrichment factor were better than most of the previously reported methods (Table 4).

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Table 1 Properties of PUF, PUF-NH_2 and PUF-Cyt.

Property	PUF	PUF-NH_2	PUF-Cyt
Elemental analysis C, H, N, S and O (%)	65.3, 8.4, 6.7, 0.5 and 19.1	64.6, 8.6, 7.8, 0.5 and 18.5	64.3, 8.7, 7.6, 0.5 and 18.9
Color	white	faint yellow	brown
pHzpc	7.2	3.0	7.5
Density (kg m^{-3})	13.8	18.3	21.5

Table 2 Kinetic parameters for the adsorption of Au(III) on the experimental adsorbent.

Pseudo-first-order model	k_1 (min^{-1})	R^2
	3.162	0.988
Pseudo-second-order model	k_2 (g $mg^{-1}min^{-1}$)	R^2
	0.642	0.970
Intraparticle diffusion model	K_i (mg g^{-1} $min^{-0.5}$)	R^2
	2.029	0.941

Table 3 Parameters of the Langmuir, Freundlich, and Dubinin–Radushkevich isotherms for the adsorption of Au(III).

Adsorption isotherms	Isotherm constants	Temperature (K)			
		280	298	310	323
Langmuir isotherm constants	Q_{max} (mg g^{-1})	101.94	96.90	90.25	80.45
	K (L mg^{-1})	0.05810	0.05562	0.03865	0.03321
	R^2	0.9884	0.9908	0.9908	0.9898
	R_L	0.0211–0.6325	0.0220–0.6426	0.0313–0.7212	0.0363–0.7507
Freundlich isotherm constants	K_f (mg g^{-1}) (L $mg^{-1})^{1/n}$	7.810	7.107	5.542	4.754
	n	2.028	2.003	1.958	1.960
	R^2	0.9799	0.9723	0.9777	0.9693
Dubinin–Radushkevich isotherm constants	Q_{D-R} (mg g^{-1})	3.458	3.469	3.300	3.211
	$\beta \times 10^{-2}$ (mol^2 J^{-2})	-8.709	-10.498	-10.12	-7.729
	E	2.396	2.182	2.223	2.543
	R^2	0.5208	0.5565	0.4231	0.3711

Table 4 Comparative data from some recent studies on the preconcentration of Au(III).

Sorbent	Reagent used	EF	Capacity (mg g^{-1})	LOD (μg L^{-1})	LQD (μg L^{-1})	Ref.
IEPUF	Polysiloxane	—	5.29	0.01 (FAAS)	0.033	35
PUF-NH_2	HCl	125	41.4	—	—	36
LPPF	HCl, $NaNO_2$	450	70.5	0.0033 (UV-vis)	0.011	37
Attapulgite	Triocarbohydrazide	150	66.7	0.32 (ICP-OES)	—	38
Amberlite XAD-200	Diethyldithiocarbamate	200	12.3	16.6 (FAAS)	36.5	39
Activated carbon	1-amino-2-naphthol-4-sulfonate	200	32.3	0.26 (ICP-OES)	—	40
Silica gel	Nanometer TiO_2	50	3.56	0.21 (FAAS)	—	41
Carbon nanotubes	*N*,*N′*-bis(2-hydroxybenzylidene)-2,2′(aminophenylthio)ethane	250	75	0.03 (FAAS)	—	42
Cellulose fiber	Taurine	–	34.5	–	—	43
Chitosan	4-amino-4′-nitroazobenzene	–	69.93	0.01 (FAAS)	—	44
Alumina	Polyethylenimine ion-exchange polymer	460	6	0.0262 (FAAS)	—	45
PUF-Cyt	Cytosine	480	98.8	0.006 (ICP-OES)	0.02	Present work

EF: Enrichment factor

Table 5 Thermodynamic parameters for the adsorption of Au(III) on the adsorbent.

Temperature (K)	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})
280	-7.66	−8.59	−3.30
298	-7.60		
310	-7.56		
323	-7.52		

Table 6 Effect of potentially interfering ions on percent recovery of 1.0 µg mL^{-1} Au(III) on the sorbent followed by elution with 1% (m/v) thiourea in 0.1 mol L^{-1} HCl. Other conditions: sample volume: 25 mL; sample flow rate, 4.0 mL min^{-1}; 0.25 g PUF-Cyt; pH 1.0 (n = 3).

Coexisting ions	Concentration (µg mL^{-1})	Recovery of gold (%)
Na^+,	1000	96.40
K^+	1000	97.92
Cl^-	1000	99.03
Ca^{2+}	600	96.41
Mg^{2+}	600	97.12
NO_3^{2-}	600	97.58
Al^{3+}	300	96.33
Fe^{3+}	300	95.24
Co^{2+}	100	95.98
Ni^{2+}	100	96.46
Cu^{2+}	100	97.66
Pb^{2+}	100	95.65
Zn^{2+}	100	95.72
Mn^{2+}	100	94.93
Cr^{3+}	100	98.27
Sn^{2+}	100	98.64
Tl^+	100	97.22
Pt^{4+}	100	95.76
Pd^{2+}	100	96.11
Te^{4+}	100	95.87
Sb^{3+}	100	95.14

Table 7 Analytical results of the determination of Au in geological samples (n = 3)

Sample	Found (µg g^{-1})	Certified value (µg g^{-1})
GAu-14 (ng g^{-1})	104 ± 6.0	100.0 ± 3.0
GAu-16	1.11 ± 0.06	1.09 ± 0.03
WMS-1a	0.32 ± 0.02	0.30 ± 0.02
MA-2c	3.00 ± 0.11	3.02 ± 0.06

Table 8 Added/found method for Au(III) determination in water and ore samples. Other conditions: sample volume: 25 mL; sample flow rate, 4.0 mL min^{-1}; 0.25 g PUF-Cyt; pH 1.0 (n = 5).

Sample	Added (μg mL^{-1})	Found (μg mL^{-1})	Recovery (%)	RSD (%)
Tap water	–	ND [a]	–	–
	10	10.20	102 ± 1.3	2.65
Sea water	–	ND	–	–
	10	9.75	97.5 ± 1.6	3.13
GAu-18 [b]	–	19.16	–	3.80
(Certified : 10.00 ± 0.20 μg g^{-1})	20	37.84	96.6 ± 2	4.24

a ND: no detected; b 10.0 g sample was used in spiking experiment.

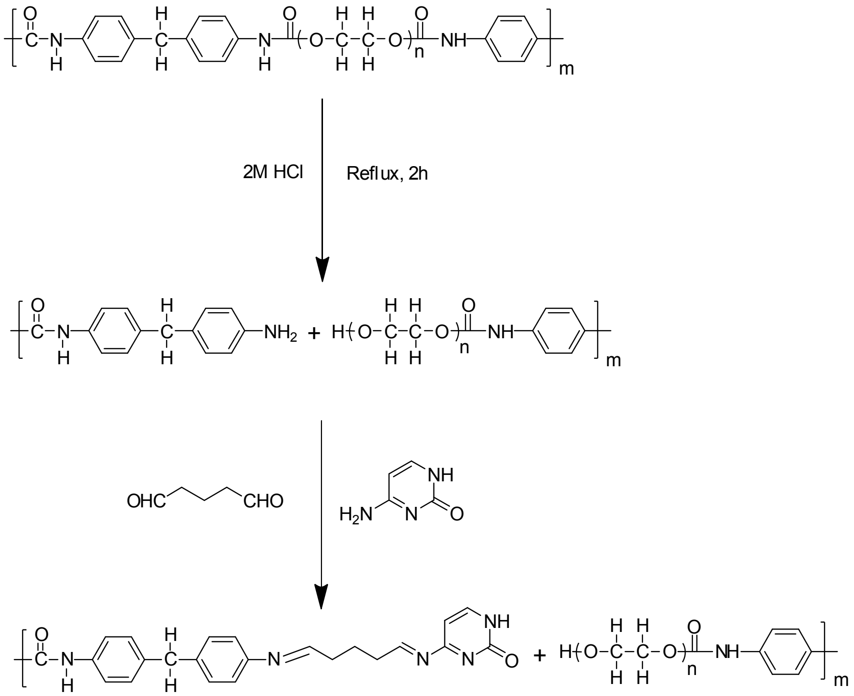

Fig. 1 Scheme for the synthesis of PUF-Cyt.

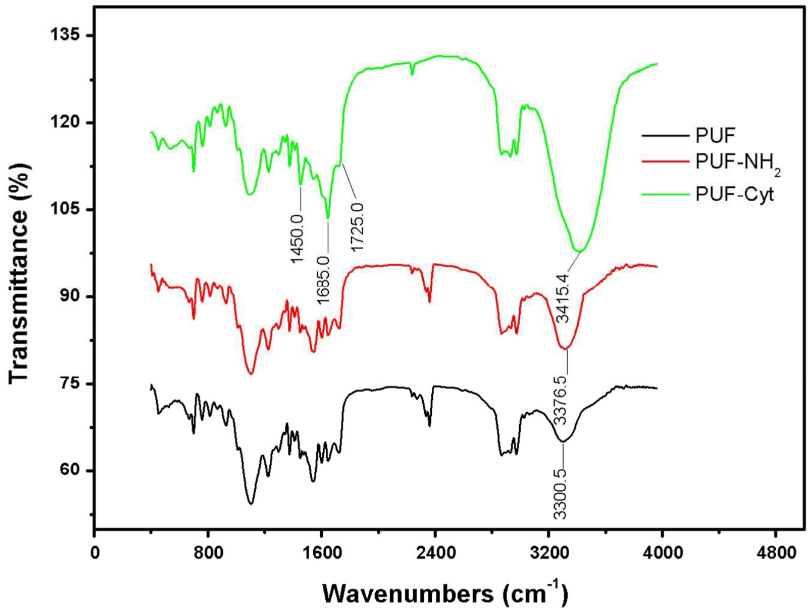

Fig. 2 FTIR spectra of PUF, PUF-NH_2 and PUF-Cyt.

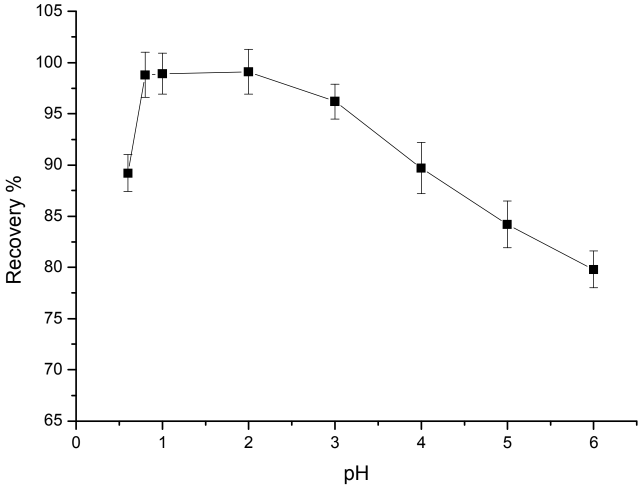

Fig. 3 Effect of pH on the adsorption of 1.0 μg mL^{-1} Au(III). Other conditions: 50 mg PUF-Cyt, shaking time 30 min, temperature 25 °C (n = 3).

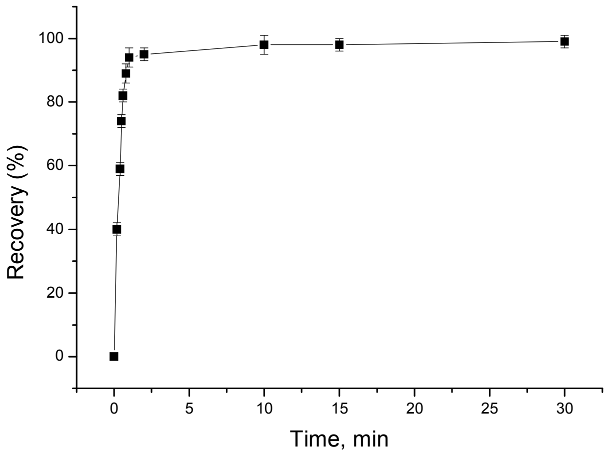

Fig. 4 Effect of shaking time on the adsorption of 1.0 μg mL^{-1} Au(III). Other conditions: 50 mg PUF-Cyt, pH 1.0, temperature 25 °C (n = 3).

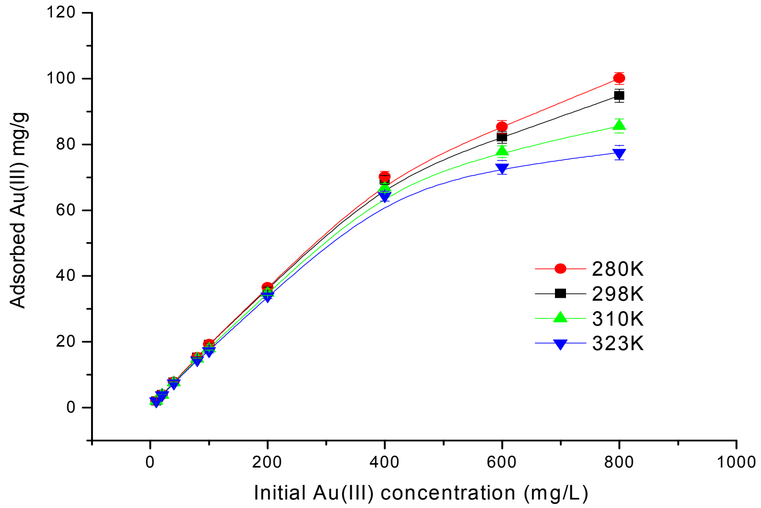

Fig. 5 Effect of the initial concentration of Au(III) ions on PUF-Cyt at various temperatures. Other conditions: 50 mg PUF-Cyt, pH 1.0, shaking time 30 min (n = 3).

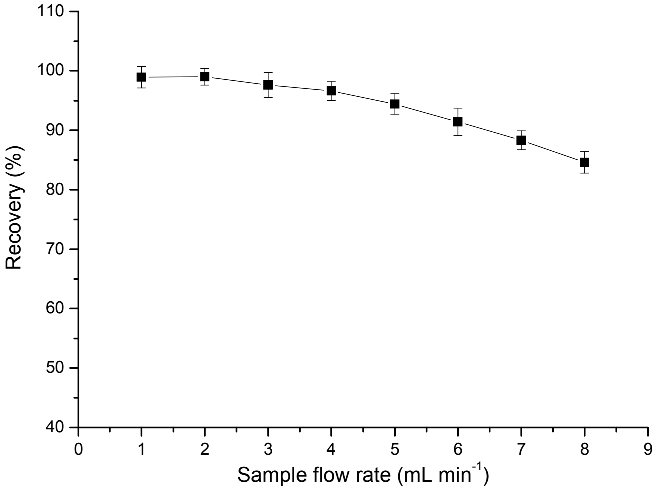

Fig. 6 Effect of sample flow rate on the recovery (%) of Au. Other conditions: 0.25 g PUF-Cyt; pH 1.0; concentration of Au(III): 0.10 μg mL^{-1}.

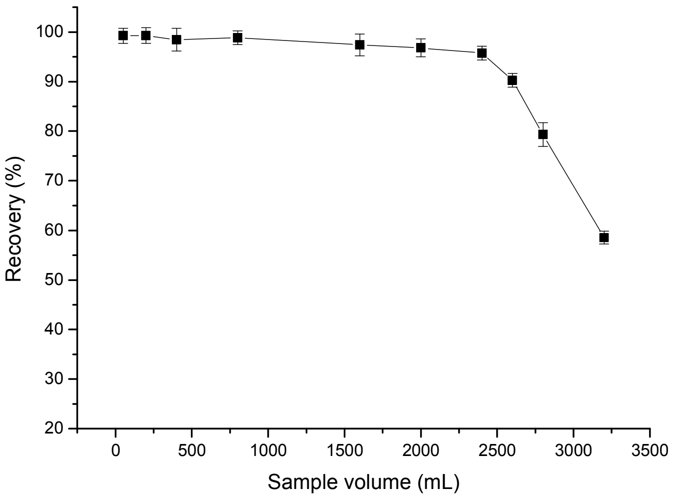

Fig. 7 Effect of sample volume on the recovery of Au(III). Other conditions: Au, 20.0 µg; sample flow rate, 4.0 mL min^{-1}; 0.25 g PUF-Cyt; pH 1.0 (n = 3).

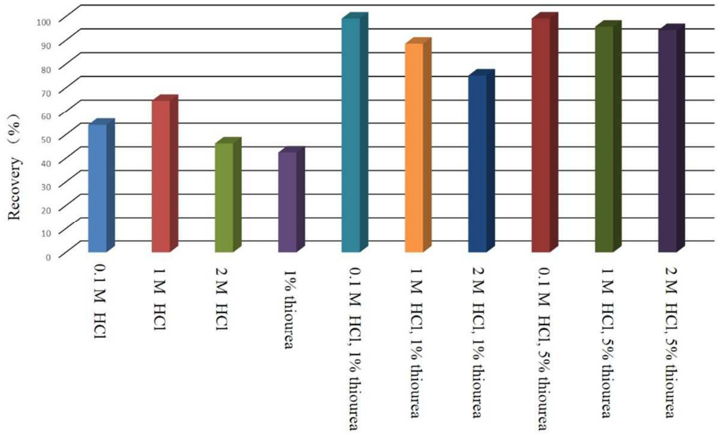

Fig. 8 Elution recovery of Au(III) adsorbed on PUF-Cyt.