



# Synthesis, characterization of low density polyhydroxy polyurethane foam and its application for separation and determination of gold in water and ores samples



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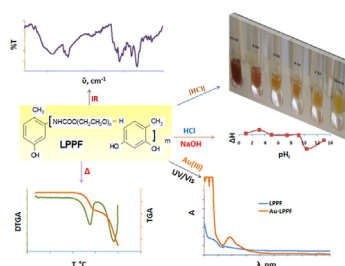
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## HIGHLIGHTS

- A new inexpensive polymeric adsorbent was prepared from polyurethane foam (LPPF).
- The character of LPPF makes it suitable to recovery gold from real sample.
- It has low density, high sorption capacity and very fast gold extraction.
- The LPPF was regenerated and reused cycles without decreasing their capacities.
- A simple and sensitive detection for nano-determination of gold has been developed.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this work, a new type of sorbent (low density polyhydroxy polyurethane Foam, LPPF) was synthesis by using water hydrolysis of polyurethanediazonium chloride salt. LPPF was characterized using different tools e.g. elemental analysis, UV–vis and IR spectra, TGA, SEM, density and  $\text{pH}_{\text{ZPC}}$ . It was tested for separation, preconcentration and determination of gold in environmental samples using batch and dynamic techniques. The sorption experimental data was fitted by the pseudo-first kinetic mathematical equation ( $R^2 = 0.991$ ). The sorption rate of the Au (III) ions is very fast, the half-life ( $t_{1/2}$ )  $\approx 34$  s. The equilibrium process is well described by the Freundlich isotherm model, the  $R^2$  value is 0.967, which attributed to the heterogeneous surface structure of the LPPF. The breakthrough capacity of LPPF and the recovery of gold ions were  $0.36 \text{ mmol g}^{-1}$  ( $70.5 \text{ mg g}^{-1}$ ) and 99–100%, respectively. The lower detection limit of gold by using spectrophotometric method is  $3.3 \text{ ng L}^{-1}$  with preconcentration factors  $\approx 450$  ( $\text{RSD} \sim 1.66\%$ ,  $n = 4$ ). The values of  $\Delta G$  and  $\Delta H$  for the sorption of gold onto LPPF were  $-12.5$  and  $-103.5 \text{ kJ mol}^{-1}$ , respectively, which indicate that the sorption of Au (III) onto LPPF is spontaneous and exothermic reaction. The obtained results indicate that the ion chelation and ion association might be the most probable mechanism of gold sorption onto LPPF. The study shows LPPF has the potential of application as an efficient sorbent for the extraction and determination of gold in water, gold alloys pharmaceutical and granite samples.

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## 1. Introduction

Gold metal is one of the most important noble metals due to its wide applications as well as economic activity [1]. Gold have many applications in industry, jewelry and medicine. It is one of the precious metals and extensively used in various areas and is now heavily utilized in chemistry, biology and medicine [2]. Many methods to determine gold have been reported, such as flame atomic absorption spectrometry (FAAS), graphite furnace (GFAAS) or electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma mass spectrometry and spectrophotometry [3]. The direct determination of gold is to some extent a problem because the high concentration of interfering matrix components in most real samples. The importance of the sensitive and selective methods for gold determination is due to the economic value of gold. The pretreatment step (preconcentration/separation) of the sample before analysis is led to facilitate the desired sensitivity and selectivity of the measurement [4]. Various techniques have been used for separation and preconcentration of gold such as ion exchange [5], coprecipitation [6], solvent extraction [7], dispersive liquid–liquid microextraction [8], cloud point extraction [9], electrodeposition [10] and adsorption on a solid phase [11–13]. Among them, solid-phase extraction has attracted more attention as it is more capable and conventional in preconcentration [14]. Different sorbents such as carbon nanotube [15], nanoclay [16], silica gel [17], cotton fiber/chitosan [18] and polyurethane foam [19] have been used for preconcentration of Au (III) ions from various media.

Polyurethane foam (PUF) is copolymer-containing blocks of low molecular weight polyether covalently bonded by urethane group (–NHCOO–). The importance of PUF has been increased as a collector material due to their efficiency, low cost, easily handling and storage. Many reports studied the uses of the PUF with reagent immobilization [20], incorporation of the chelating ligands onto a matrix [21] and coupling of the ligand with PUF backbone [22]. The high density of reagent-PUF is inconvenience, which they cause to decrease sorption capacity of PUF and decrease the extraction rate of metal ions. This problem demand preparation of low density PUF has high sorption capacity. The methodology is developed for synthesis PUF that contains polyhydroxyl functional group as silica or sol gel [23,24]. The low density polyhydroxy polyurethane foam (LPPF) was prepared from commercial PUF by replacing the primary amine with hydroxyl group. We used new was steps for this purposing (i) PUF was washed by boiling 2 M HCl and (ii) LPPF was blended in a food-processing blender into small size. The new type of PUF (LPPF) is found to be very suitable for the separation and preconcentration of gold from environment. Also, the importance of developing PUF non containing washable reagent with the ability to be recycled many times without significantly decrease in their capacities.

## 2. Experimental

### 2.1. Apparatus

All spectrophotometric measurements were performed on a Shimadzu Model UV-1800 (Shimadzu Corporation, Japan). IR spectra were recorded on a Shimadzu FTIR-8400 Fourier transform infrared spectrophotometer. A TGA-50H (Shimadzu Thermogravimetric Analyzer, Japan) was used for the TGA analysis. The pH measurements were carried out using a pH meter from Microprocessor pH Meter (HANNA Instruments).

### 2.2. Reagents and materials

#### 2.2.1. Preparation of LPPF

The low density polyhydroxy polyurethane foam (LPPF) was prepared by cutting the PUF (open cell polyether type) into similar cubes (~0.125 cm<sup>3</sup>). Five-gram PUF cubes were boiled in a 2 mol L<sup>-1</sup> HCl for 2 hours to liberate the maximum number of free amino groups. PUF washed with water, placed in a 0.1 mol L<sup>-1</sup> HCl solution and then cooled in an ice bath. The PUF is diazotized by adding of 50 mL of NaNO<sub>2</sub> (2 mol L<sup>-1</sup>) solution to the cold solution containing the PUF, and stirred vigorously until the pale yellow color appeared due to the formation of diazonium chloride. Then, it was boiling for 6 h in distilled water. The yellow LPPF material is washed with distilled water followed by acetone and the air-dried. LPPF was blended in a food-processing blender. The PUF was sieved from <45 to >250 μm size. The particles between 90 and 250 μm were used for adsorption studies.

#### 2.2.2. Gold standard solution and calibration curve

A 0.1 g portion of pure gold metal was dissolved in 20 mL of aqua regia; evaporate the solution nearly to dryness. The residue was dissolved in 2 mL conc. HCl and diluted with deionized water to 100 mL in a measuring flask. A series of 25 mL for gold standard solutions (0–75.0 μg mL<sup>-1</sup> Au in 0.16 mol mL<sup>-1</sup> KBr) were used for calibration curve. The absorption spectrum is shown in Fig. S1 (λ<sub>max</sub> = 381). The linear regression equation obtained was  $A = 26.62C - 0.005$  ( $R^2 = 0.999$ , Fig. S2).

### 2.3. Recommended procedures

Extraction of Au (III) was carried out by a batch technique at 25 °C. Adsorption experiments were carried out by agitating 0.1 g of LPPF with 25 mL of Au (III) solutions (5 μg mL<sup>-1</sup>) in a shaker adjusted to the desired shaking speed. After shaking for 30 min, the flasks were removed from the shaker. The gold concentration remaining in the supernatant solution (as effluente) was determined by using UV–vis spectrophotometer at λ = 381 nm [25]. The following equations were used to calculate the uptake percentage of gold (%E), capacity of sorbents (Q, mg g<sup>-1</sup>) and distribution coefficient (K):

$$\%E = \left( \frac{C_0 - C}{C_0} \right) \times 100 \quad (1)$$

$$Q = \frac{(C_0 - C)V}{m} \quad (2)$$

$$K = \frac{((C_0 - C)/C)V}{m} \quad (3)$$

where  $C_0$  and  $C$  are the initial and remain concentrations of Au (III) in solution, respectively.  $V$  is the volume of solution and  $m$  is the mass of PPF.

pH<sub>ZPC</sub> is the pH when the charge on the LPPF surface is zero (zero point charge). To determine the pH<sub>ZPC</sub> of the LPPF surface, we take 25 mL of solution in a series of 100 mL flasks whose pH in the range 1–13. The initial pH (pH<sub>i</sub>) of the solutions was determined and 0.1 g of the LPPF was added to each flasks. After completion of 24 h, the final pH (pH<sub>f</sub>) of the solutions was measured. The difference between the initial and final pH values (ΔpH = pH<sub>f</sub> – pH<sub>i</sub>) was plotted against the pH<sub>i</sub>. The pH<sub>ZPC</sub> was noted at the pH in which the initial pH equals the final pH.

In the dynamic experiments, 1.0 g portion of LPPF was packed into a column (25-cm long and 1.5 cm in diameter). 50 mL of Au (III) solution (1 μg mL<sup>-1</sup>) were passed through the LPPF column ( $L = 12$  cm) at flow rate 2 mL min<sup>-1</sup>. Effluates were collected and were analyzed spectrophotometrically at λ = 381 nm. The elution of

the gold from the LPPF column was carried out using (1:1)  $\text{NH}_4\text{OH}$ . The eluates were collected then added 1 mL of HCl (1:1) and the amount of the Au (III) was determined spectrophotometrically at  $\lambda = 381 \text{ nm}$ .

### 3. Results and discussion

#### 3.1. Characterization of PPF

To make sure about the proposed formula and structure for LPPF, analysis using infrared and ultra violet/visible spectra, thermogravimetric analysis, elemental analysis and scanning electronic microscope were carried.

The elemental analysis of PUF and LPPF was studied. The nitrogen percentage in LPPF (6.6%) is less than in PUF (7.2%). The percentage of oxygen in LPPF (20.0%) is more than in PUF (18.8%). This result shows that the hydroxyl group was replaced the primary amine group.

For UV–vis spectrophotometric measurements, a thin film of LPPF and PUF ( $3.5 \times 0.8 \times 0.2 \text{ cm}$ ) was used. There are placed in the path of light in a cell filled with  $\text{H}_2\text{O}$ . The spectrum of LPPF thin film (solid phase) compared with that of PUF. The results showed that the new two peaks at 257 and 342 nm that appear in LPPF (Table 1), which shifted to 244 and 384 nm after gold sorbed (Fig. S3).

The detection of phenolic group in LPPF was tested by using  $\text{FeCl}_3$  using UV–vis spectrophotometer. The color of LPPF is changed from yellow to violet ( $\lambda_{\text{max}} = 638 \text{ nm}$ ) by the addition of  $\text{FeCl}_3$  solution indicates that the LPPF contain phenolic group.

The surface acid sites of LPPF matching the phenolic sites were determined. The phenolic sites were back titrated with a  $0.05 \text{ mol L}^{-1}$  NaOH solution. The LPPF was shown to contain  $0.175 \text{ mmol g}^{-1}$  of phenolic group. This result indicates that the surface of LPPF is acidic and good adsorbent for extraction of organic and inorganic species like as silica gel.

The infrared spectra of PUF and LPPF were tested using thin film technique. The results showed that the broad band at  $3461.6\text{--}3137.6 \text{ cm}^{-1}$  characteristic of O–H and N–H groups was shifted to  $3708.4\text{--}3048.9 \text{ cm}^{-1}$  due to addition of phenolic groups (Fig. S4). In addition, LPPF spectrum showed new absorption band have appeared at  $1411.6 \text{ cm}^{-1}$  assigned for the O–H (def.) aromatic groups.

The color of LPPF changed from yellow to red after addition of HCl solution (Fig. S5) while the color of LPPF not changed in NaOH solution. The color intensity is increased with the increasing of the HCl concentration due to protonated of ether and urethane groups. The result indicates that the LPPF exists as a resonance structure.

The protonated group loses the hydrogen ion at about 1 M HCl. The loss of the proton changes the electronic structure of the compound, resulting in a change of color from red to yellow. This result indicates that the LPPF can be used as acid indicator from 2 M to 10 M HCl.

The  $\text{pH}_{\text{ZPC}}$  value is determined to be approximately 4.8 for the LPPF (Fig. S6). At pH lower than of  $\text{pH}_{\text{ZPC}}$  ( $\text{pH} < 4.8$ ), the surface of the LPPF is positively charged while at pH greater than pH 4.8, the surface of the LPPF becomes negatively charged. The  $\text{pH}_{\text{ZPC}}$  value is based on membrane-like structure of the LPPF such as urethane  $\text{NHCOO}$ , ether  $\text{CH}_2\text{--O--CH}_2$  and terminal OH groups [26].

The densities of the PUF and LPPF were measured. The values of densities of PUF and PPF are  $13.5$  and  $18.7 \text{ kg m}^{-3}$ , respectively (Table 1). This result indicates that the LPPF is denser than the PUF. The higher density of the LPPF may be attributed to the formation of hydroxyl groups and the inter bonding between them. In addition the result indicates that the LPPF is less dense than reagent-PUF [20–22]. The low density LPPF is led to increasing of the extraction rate of metal ions and also increasing of capacity of sorbent.

Thermal properties of LPPF and PUF were evaluated using thermogravimetric analysis (TGA) under nitrogen atmosphere. TGA curves of LPPF and PUF showed a smooth stepwise manner containing three steps of thermal degradation (Fig. S7). The TGA curve of LPPF showed that the thermal decomposition begins at  $175.8^\circ\text{C}$  and the weight loss are 28.9, 60.7 and 10.7% in the ranges  $176\text{--}290$ ,  $290\text{--}400$  and  $>400^\circ\text{C}$ , respectively. On the other hand TGA curve of PUF showed that the thermal decomposition begins at  $207.1^\circ\text{C}$  and the weight loss are 34.1, 55.7 and 10.0% in the ranges  $207\text{--}302$ ,  $302\text{--}400$  and  $>400^\circ\text{C}$ , respectively (Fig. S5). From the results obtained show that the first step of TGA curves showed that the LPPF has low thermal stability due to its high oxygen content than PUF. The second and third steps of TGA curves showed that the LPPF was higher thermal stability more than PUF due to interbonding between the OH groups. The differential thermogravimetric curve (DTGA) of LPPF showed two endothermic peaks at  $275.1$  and  $380.6^\circ\text{C}$  while; DTGA curve of PUF showed two endothermic peaks at  $288.5$  and  $356.8^\circ\text{C}$  (Fig. S8). The maximum endothermic peak of the LPPF (at  $380.6^\circ\text{C}$ ) is bigger than that of PUF ( $356.8^\circ\text{C}$ ). This is due the thermal decomposition of interbonding between the OH groups.

Surface morphology of LPPF and PUF investigated using scanning electron microscopy (SEM). Fig. S9 represents electron scanning microscopic images of LPPF at magnification of 800. The microstructure of LPPF image showed that the cells are nearly spherical and irregular in size and distribution. The cell size of LPPF is bigger than PUF due to the rupture of some crosslinking bonds during hydrolysis process.

**Table 1**  
Comparison between the characterization of PUF and LPPF.

Property	PUF	LPPF
Elemental analysis C, H, N, S and O (%)	64.0, 9.5, 7.2, 0.5 and 18.8	63.0, 9.9, 6.6, 0.5 and 20.0
UV–vis spectra $\lambda_{\text{max}}$ (nm)	Nil	257, 342
After sorbed $\text{FeCl}_3$	Nil	638
Phenolic ( $\text{mmol g}^{-1}$ )	Nil	0.175
IR spectra $\nu\text{--OH}$ , NH aromatic ( $\text{cm}^{-1}$ )	Broad band at $3461.6\text{--}3137.6$	Broad band at $3708.4\text{--}3048.9$
$\nu\text{--OH}$ (def.) aromatic ( $\text{cm}^{-1}$ )	Nil	1411.6
Color	White	Yellow-orange
$\text{pH}_{\text{ZPC}}$	8.8	4.8
Density ( $\text{kg m}^{-3}$ )	13.5	18.7
TGA and DTG Weight losses (%)	34.1, 55.7 and 10.0	28.9, 60.7 and 10.7
Endothermic peak ( $^\circ\text{C}$ )	288.5 and 356.8	275.1 and 380.6

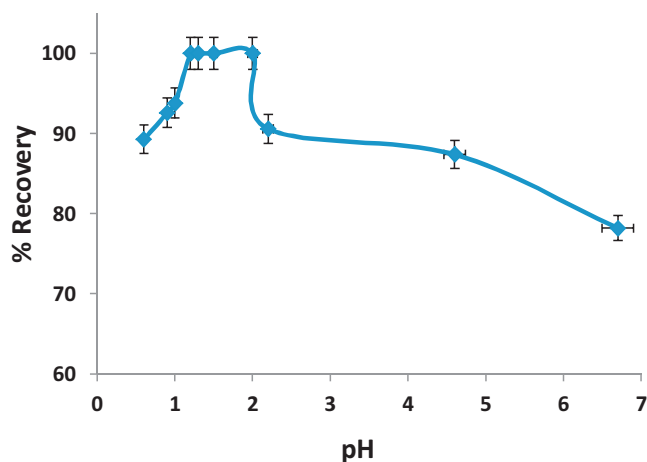


Fig. 1. Effect of pH on the sorption of gold (III) onto LPPF.

The chemical stability of LPPF studied with different solvents in batch mode. According to the forgoing results, LPPF showed a good chemical stability in the presence of 6M H<sub>2</sub>SO<sub>4</sub>, conc. HCl, conc. acetic acid, methanol, ethanol, isopropanol, acetone, benzene, toluene, p-xylene, formaldehyde, benzyl alcohol and benzyl chloride. The expected scheme for preparing LPPF represented in scheme (Fig. S10).

### 3.2. Optimum condition for sorption of gold onto LPPF

#### 3.2.1. Batch technique

The effect of pH and acidity on the extraction of gold (III) ions from bromide solution using LPPF has been examined by batch technique. The pH of the Au (III) solution was adjusted before equilibration with pH over a range of 0.5–6.7. The percentage extraction of Au (III) was plotted against the pH value and acidity. It is noted that LPPF extracted Au (III) as bromide complex from aqueous solution at pH 1.2–2 (Fig. 1) or having acidity ranging between 0.01 and 0.12 mol L<sup>-1</sup> HCl (Fig. S11). The maximum gold recovery (100% Au) was in pH 1–2 then decreased to ~90% in pH 2–4.6. The result obtained is good agreement with gold extracted as its bromo complex with tri-n-octylamine [27], ferrioin [28] and methyl violet [29] in pH 1–1.3. The result shows that the extraction process mainly depends on the ion association complex formed between the LPPF cation in acidic medium (pH<sub>ZPC</sub> = 4.8) and the anion complex of the gold (III) bromide (LPPF<sup>+</sup>: [AuBr<sub>4</sub>]<sup>-</sup>) or chelation process.

The effect of initial gold concentration on the sorption capacity of LPPF was studied. Fig. S12 shows that relation between the amount of sorbed gold per unit mass of LPPF (capacity, Q<sub>c</sub>) and the initial gold concentration. A perfect linear curve with zero intercept ( $9 \times 10^{-6}$ ) and good correlation ( $R^2 = 1$ ) has been obtained. It is clear that the capacity was increased with increasing the initial concentration and reached a plateau (maximum uptake capacity values) were obtained. The sorption capacities of LPPF for gold from bromide and aqueous solutions were estimated to be 0.338 and 0.103 mmol g<sup>-1</sup>, respectively (66.6 and 20.3 mg g<sup>-1</sup>). It is evident from the achieved results the developed sorbent exhibits greater capacity toward gold in bromide solution (anion gold bromide complex) than gold in aqueous solution (without ligand). The LPPF is more efficient than other type of PUF [19,30,31] and other sorbents [13,32–39] (Table 2).

The detection limit (LOD) was established by analyzing four blank solutions (LOD = 3σ, where σ is the standard deviation of blank determination). The value of LOD of Au (III) was 3.3 ng L<sup>-1</sup>. Also, the limit of quantitation (LOQ = 10σ) was 11.0 ng L<sup>-1</sup>. The LOD and LOQ value for the studied ions with the LPPF would be enable

Table 2

Comparison of maximum sorption capacities of various sorbents for gold.

Sorbent	Q <sub>max</sub> (mg g <sup>-1</sup> )	Reference
Polyurethane foam	5.29	[31]
Tetraheptyl amm. bromide immobilized PUF	19.5	[19]
HCl treated polyurethane foam	41.4	[30]
Ion exchange polyurethane foam	11.21	[31]
Triocarbonylhydrazide modified attapulgite	66.7	[13]
Chelating resin Dowex M 4195	8.1	[32]
Single granular activated carbon	16.5	[33]
Carbon nanotubes	10	[34]
Polymer coated multiwalled carbon nanotubes	67	[35]
CuO microspheres	57	[36]
Mesoporous silica functionalized with 3-aminopropyl	3.98	[37]
Nanometer TiO <sub>2</sub> immobilized on silica gel	3.56	[38]
Amberlite XAD-2000	12.3	[39]
Polyhydroxy polyurethane foam	70.5	This work

the use of this material in collection of gold ions at a trace concentration prior to their determination with high accuracy. The values of LOD and RSD due to the application of LPPF method for the determination of Au (III) indicate that the LPPF sorption method is more efficient than other methods [1,4,11,13,40].

The accuracy and precision for the different fortification levels of the sample were estimated. The recoveries percentage values ranged from 97.9% to 99.6% with the low relative standard deviation values (RSD = 0.77%, n = 4) for the analysis of four samples replicates of Au (III) indicate a good precision and accuracy of the proposed method. This result shows that the LPPF is suitable for the determination of tested metal ions in water samples.

A simple and sensitive spectrophotometric method for the nano-determination of gold (III) has been developed. This method is based on the sorption of Au (III) onto LPPF. The color formed on the surface of the LPPF material is used for the determination of nano-gram amounts of Au (III) spectrophotometrically. The electronic absorption spectra of [AuBr<sub>4</sub>]<sup>-</sup> sorbed onto PPF was studied. The UV–vis spectrum of LPPF after absorbing the Au (III) was compared with thin film (0.1 cm) of LPPF in distilled water. The suitable wavelength of spectrophotometric measurement for the absorption spectra of the LPPF after absorbing Au (III) was 384 nm (Fig. S3). The value of molar absorptivity (ε) for PPF–[AuBr<sub>4</sub>]<sup>-</sup> complex was  $3.4 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>. The value of the lower detection limit (LDL) of Sandell's sensitivity (S) is 5.9 ng cm<sup>-2</sup>,  $S = 0.001/a$  where "a" is specific absorptivity. The results obtained show that the LPPF method is more sensitive than the direct spectrophotometric method for the determination of Au (III) in bromide solution ( $\epsilon = 4.8 \times 10^3$  L mol<sup>-1</sup> cm<sup>-1</sup>) [25]. Finally, from the result obtained, the proposed method is one of the simple and rapid spectrophotometric methods for the determination of gold ions compared to direct spectrophotometric method.

The extraction of gold ions with LPPF were found to be strongly dependent on the ligand concentration, therefore the concentration of bromide in the extraction medium was examined at concentration range from 0.01 up to 1.0 mol L<sup>-1</sup> KBr (Fig. S13). A 0.08 mol L<sup>-1</sup> is the minimum concentration of KBr necessary for the maximum extraction (99–100%) of Au (III). Also, the uptake of gold ions sorption from bromide solution is larger than those from aqueous solution. This confirms that the LPPF is more efficient for extraction of gold ions in bromide solution than that from aqueous solution due to the ion-pairs formation between LPPF with anion gold complex.

The effect of different ligand (Cl<sup>-</sup>, I<sup>-</sup> and SCN<sup>-</sup>) on the sorption percentage of gold onto LPPF was also studied. From the results obtained the uptake percentage of [AuCl<sub>4</sub>]<sup>-</sup>, [AuI<sub>4</sub>]<sup>-</sup> and [Au(SCN)<sub>4</sub>]<sup>-</sup> onto LPPF have been estimated to be 96%, 97% and 92%, respectively. The uptake sequence is in the order

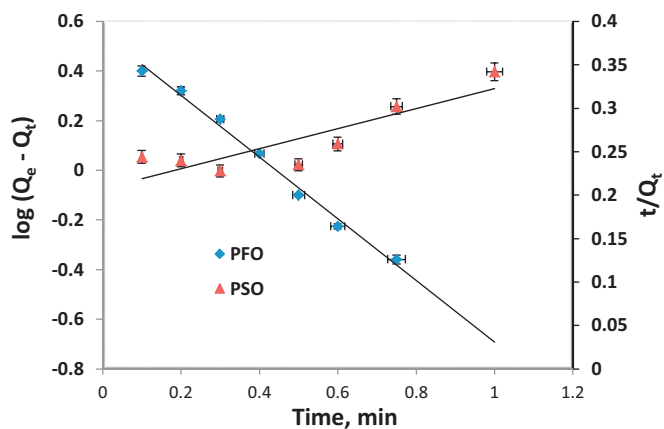


Fig. 2. The plots of pseudo first order and pseudo second order models for the sorption of gold ions onto LPPF.

$[\text{AuBr}_4]^- > [\text{Au}_4]^- > [\text{Au}(\text{SCN})_4]^- > [\text{AuCl}_4]^-$ . The difference in sorption uptake of the gold complexes may be attributed to their different ionic sizes and the nature of complexes. Chloride, bromide and thiocyanate ions are effect on the intensely colored of gold (III) bromide complex which formation of mixed complexes [25]. But there are no effects on the recovery percentage Au.

The rate of extraction of  $[\text{AuBr}_4]^-$  onto LPPF has been measured using batch extraction mode at different time intervals (1–30 min). The result obtained shows that the time required for extraction of (III) is 60 s (Fig. S14a). This indicated that the rate of sorption of the gold ions onto LPPF was rapid. The pseudo first order  $[\log(Q_e - Q_t) = (\log Q_e) - (k_1 t/2.303)]$  and pseudo second order  $[t/Q_t = (1/k_2 Q_e^2) + (t/Q_e)]$  kinetic models are tested to fit the experimental data for the sorption of gold ions onto LPPF (Fig. 2). The  $R^2$  value for pseudo first order sorption model (0.991, Fig. 14b) is higher than the value of  $R^2$  (0.734) for pseudo second order kinetic (Fig. S14c). This suggests that the pseudo first order adsorption mechanism is predominant. The value of the rate constant of the sorption ( $k_1$ ) calculated from the slope is  $1.24 \text{ min}^{-1}$ . The values of half-life ( $t_{1/2}$ ), rate constant of desorption ( $k_{-1}$ ) and the overall rate constant ( $k'$ ) of the sorption of gold ions are 34 s, 0.01 and  $1.25 \text{ min}^{-1}$ , respectively.

The dependence of extraction of Au (III) onto LPPF with temperature has been studied. The result shows that the maximum sorption of gold (III) occurs at low temperature and the uptake of gold ions decreases with the increasing of the temperature. Thermodynamic parameters for the sorption of Au (III) were calculated using the equations:  $\ln K = -\Delta H/RT + \Delta S/R$ ,  $K = ((C_0 - C)/C)$  and  $\Delta G = \Delta H - T\Delta S$  where  $K$  is the distribution coefficient for sorption. The plot of  $\ln K$  vs.  $1/T$  gives the numerical values of  $\Delta H$  and  $\Delta S$  from slope and intercept of the plot ( $R^2 = 0.985$ , Fig. S15). The negative value of  $\Delta H$  ( $-103.5 \text{ kJ mol}^{-1}$ ) interpret that the sorption process of gold is exothermic chemisorptions. While the average value of entropy ( $-215.4 \text{ J K}^{-1} \text{ mol}^{-1}$ ) is an indication of the faster sorption of Au (III) onto LPPF. The  $\Delta G$  have been evaluated using the equation:  $\Delta G = \Delta H - T\Delta S$ . The negative values of  $\Delta G$  ( $-12.5 \text{ kJ mol}^{-1}$ ) indicate that the feasibility of the process and its spontaneous nature without induction period.

The effect of batch factor (sample volume to the 0.05 g of LPPF,  $V/m$ ) on the uptake of Au (III) has been studied (Fig. S16). The result indicated that the maximum uptake of gold ions in batch factor ( $V/m$ ) 200–500. Also, the uptake of gold ions decreases with the increasing of the batch factor, recovery percentage becomes 92.2 in  $V/m$  value 2000.

The influences of some foreign ions which may interfere with sorption of the gold ions onto LPPF were investigated in order to identify the method selectivity. For this purpose, 10 mL model

solution containing 10  $\mu\text{g}$  of Au (III) was mixed with the interfering species (200  $\mu\text{g}$ ) and adjusted to optimum pH and shacked for 15 min. The obtained data reveal that the strongest interference was occurred by  $\text{Fe}^{2+}$  and  $\text{Pt}^{4+}$  ions while  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Bi}^{3+}$  ions reduce the sorption of  $\text{Au}^{3+}$  (Fig. S17). Besides controlling the pH of the sorption medium, masking agent e.g., tartaric acid, citrate or phosphate ions masks several common ions and minimizes their interfering effect.  $\text{Ni}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mo}^{6+}$  and  $\text{Ag}^+$  ions did not interfere. Silver bromide precipitate was formed on the addition of bromide solution, but it had no effect on the sorption of Au. Generally, the majority of the examined foreign ions were not found interfere, that is confirm the adequate selectivity of LPPF material and feasibility for quantitative determinations in natural samples with relevant accuracy. Furthermore, the added concentrations of foreign ions were higher than those exist in most natural samples which predict the validity of the developed procedure. The results also extended the use of the LPPF for extraction of gold species from the industrial effluent.

### 3.2.2. Dynamic technique

The sample flow rate through the LPPF column is a very important parameter since it controls the time of analysis. The dependence of the uptake of the gold (III) on the flow rate has been studied, the sample flow rate being varied from 1 to  $40 \text{ mL min}^{-1}$  and the retention percentage of the gold ion into the column was determined. The maximum recovery observed in the range  $1\text{--}25 \text{ mL min}^{-1}$ . Faster flow rates than  $25 \text{ mL min}^{-1}$  led to decrease the recovery percentage. This confirms the relation between the retention sensitivity and the contact time of Au (III) with LPPF.

The effect of various eluting agents like HCl, NaOH,  $\text{NH}_4\text{OH}$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{H}_2\text{NCSNH}_2$  and  $\text{CH}_3\text{COCH}_3$  on the stripping of  $[\text{AuBr}_4]^-$  from LPPF have been studied. It is observed that  $[\text{AuBr}_4]^-$  was completely eluted from LPPF with (1:1)  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{NCSNH}_2$ .

The elution of 2 mg of Au (III) from the LPPF column by using  $\text{NH}_4\text{OH}$  (1:1) has been examined at various flow rates ( $1\text{--}20 \text{ mL min}^{-1}$ ). The chromatograms indicate that Au (III) was completely eluted within the first 4–20 mL (Fig. S18). The height equivalent to a theoretical plate (HETP) is calculated from the elution curves using Glueckauf equation ( $\text{HETP} = LW^2/16V_R^2$ ) and Van Deemeter equation ( $\text{HETP} = A + (B/U) + CU$ ), where  $V_R$  is the volume of elute at peak maximum,  $W$  is the width of the peak,  $L$  is the length of the PPF bed,  $U$  is the flow rate and  $A$ ,  $B$ ,  $C$  are constants. The values of HETP and  $N$  found to be equal 0.057 cm and 227, respectively at a flow rate  $4.1 \text{ mL min}^{-1}$ . The HETP value is slightly increases with increasing of the flow rate, which indicate that the column performance is slightly affected with flow rate. The value of the standard deviation of LPPF column efficiency calculated from the equation:  $H = \sigma^2/L$  is 0.6.

The dynamic capacity of the LPPF column has been computed by percolating it with gold solution ( $7.5 \mu\text{g mL}^{-1}$ ) at flow rate  $2 \text{ mL min}^{-1}$ . Breakthrough curves were obtained by measuring the content of gold ion in 100 mL collected fractions from the effluent as shown in Fig. 3. Evidently, the breakthrough point was found to be at 9400 mL. The breakthrough capacity could be calculated by the equation:  $C_W = (V_b \cdot C_0)/m$  where  $C_W$  is the column capacity ( $\text{mmol g}^{-1}$ ),  $V_b$  is the collected volume of effluent between the first fraction and the breakthrough point (mL),  $C_0$  is the initial concentration of Au (III) and  $m$  is the weight of sorbent (g). The capacity values were found to be  $0.358 \text{ mmol g}^{-1}$  ( $70.5 \text{ mg g}^{-1}$ ).

## 4. Analytical applications

For assaying the gold in gold alloys (Gold grad 18, Au/Cu  $\approx$  3:1) was separated and determined. A set solution (25 mL) containing 2 mg of gold was passed through LPPF column. Cu

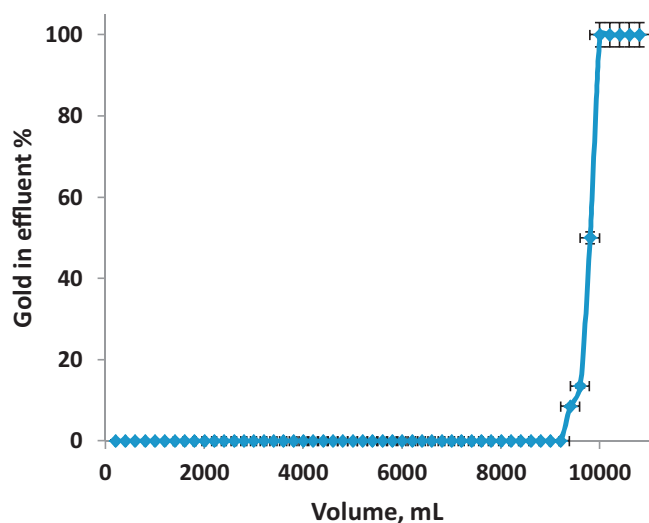


Fig. 3. Breakthrough curve for extraction of gold (III) from bromide solution.

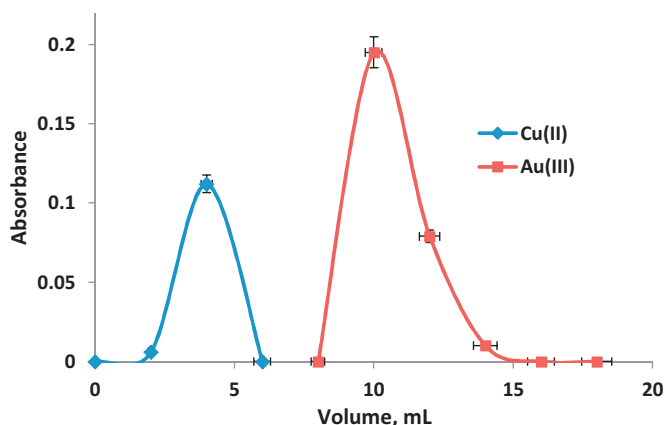


Fig. 4. Separation of gold from gold alloy using LPPF column with  $\text{NH}_4\text{OH}$  (1:1).

**Table 3**  
Extraction of gold from Makkah underground water using LPPF.

Concentration ( $\mu\text{g L}^{-1}$ )	Found		
	$\mu\text{g}$	%	RSD%
5	5.0	100	2.43
10	9.54	95.4	
20	9.6	96	
40	9.48	94.8	

(II) and Au (III) have been eluted using  $\text{NH}_4\text{OH}$  (1:1) at flow rate of  $3 \text{ mL min}^{-1}$ . The eluates were collected then determined spectrophotometrically as thiocyanate complexes at  $\lambda_{317 \text{ nm}}$  and  $\lambda_{360 \text{ nm}}$ , respectively (Fig. S19). The chromatograms resolution factor ( $R_s$ ) of gold and copper was calculated by using equation:  $R_s = 2(V_{R-\text{Au}} - V_{R-\text{Cu}})/(W_{\text{Au}} + W_{\text{Cu}})$ . The value of the resolution factor is 1.4, which gives complete separation of copper from gold (Fig. 4).

**Table 4**  
Preconcentration of gold from sea water of Arabian Gulf using LPPF column.

Initial volume (mL)	Desorption volume (mL)	Recovery (%)	Preconcentration factor	RSD%
1000	20	100	50	1.67
2500	20	100	125	
5000	20	100	250	
9000	20	96.7	450	

**Table 5**  
Recovery of gold from different type of water using batch technique.

Sample	Add ( $\mu\text{g}$ )	Found ( $\mu\text{g}$ )	Recovery (%)	RSD%
Wastewater	10	9.0	90	3.6
Spring water	10	9.5	95	4.2
Sea water	10	9.68	96.8	0.3

This technique allows the separation and determination of gold in gold alloys.

The tests of addition/recovery of different amounts of gold were performed for the underground water of Makkah city (water composition: Na:  $19 \text{ mg L}^{-1}$ ; K:  $1.8 \text{ mg L}^{-1}$ ; Ca:  $19 \text{ mg L}^{-1}$ ; Mg:  $3 \text{ mg L}^{-1}$ ; Fe:  $0.0 \text{ mg L}^{-1}$ ; TDS:  $127 \text{ mg L}^{-1}$ ;  $\text{HCO}_3$ :  $29 \text{ mg L}^{-1}$ ; Cl:  $33 \text{ mg L}^{-1}$ ;  $\text{SO}_4$ :  $27 \text{ mg L}^{-1}$ ,  $\text{NO}_3$ :  $2.8 \text{ mg L}^{-1}$ , F:  $1.0 \text{ mg L}^{-1}$ , Au: 0.0 and pH: 7.6) in order to estimate the accuracy of the presented procedure. A 0.1 g portion of the LPPF was mixed with 25 mL of water sample which spiked with 5–20  $\mu\text{g}$  of gold (III) and add 0.5 mL of  $4 \text{ mol L}^{-1}$  KBr then the batch procedure applied. The results are given in Table 3. The recovery percentage of gold ions from the water samples onto LPPF were 95.4–100%. Good agreement between the added and found gold content using the batch procedure have been obtained. The standard deviation values for the spiked samples were in the average of 3.9%. It shows that the presented method could be applied for the extraction of gold in the real environmental samples.

Preconcentration of Au (III) from different volume of sea water of Arabian Gulf in Dammam city (water composition: Na:  $3511 \text{ mg L}^{-1}$ ; K:  $177 \text{ mg L}^{-1}$ ; Ca:  $160 \text{ mg L}^{-1}$ ; Mg:  $468 \text{ mg L}^{-1}$ ; TDS:  $12,721 \text{ mg L}^{-1}$  Au: 0.0 and pH: 7.5) has been investigated. Using 1 mg of Au (III) in different volume (250–10,000 mL) of sea water samples (adjusted to the optimum pH) has been allowed to pass through the LPPF columns at flow rate of  $20 \text{ mL min}^{-1}$ . The elution of the gold from the LPPF columns was carried out by 20 mL of  $\text{NH}_4\text{OH}$  (1:1) solution and the amount of Au (III) in the eluate was determined by the recommended method. The results were given in Table 4; which shows that the recovery percentages of 97–100% with preconcentration factors  $\approx 450$  (RSD  $\sim 1.66\%$ ,  $n=4$ ). These results show that the gold can be concentrated effectively from the large volumes of dilute solutions using LPPF columns.

The recovery of the gold from different water samples of spring water of Aljouf city, sea water of Arabian Gulf in Dammam city and industrial wastewater from El-Dammam industrial city (Au is not detected) have been studied using batch technique. A 25 mL aliquot of water sample is spiked with 10  $\mu\text{g}$  of Au (III), and then the solution shacked for 15 minutes. The recovery percentage of gold ions from the water samples onto LPPF were 90–97% (Table 5). The RSD% values are found to be in the range 0.3–4.2% which is considered relevant for real samples. The results show that LPPF is suitable sorbent for extracting of the gold ions from spring, sea and waste water.

LPPF sorbent has been also used for determining gold in multi-vitamin capsules (Au = 0) using batch technique. A capsule of AZINC (mass 0.4196 g) which containing Ca: 10.7 mg; Cu: 1 mg; Cr: 25  $\mu\text{g}$ ; Fe: 4.9 mg; Mg: 19.2 mg; Mn: 1.9 mg; P: 8.0 mg; Se: 25  $\mu\text{g}$ ; Zn: 7.6 mg (Arkopharma, Carros, France) was digested in a beaker with 2 mL of concentrated  $\text{HNO}_3$  by slowly increasing the temperature to  $150^\circ\text{C}$  until a solid residue remained. After cooling, the residue was dissolved in 20 mL of concentrated  $\text{HNO}_3$ . The solution was gently

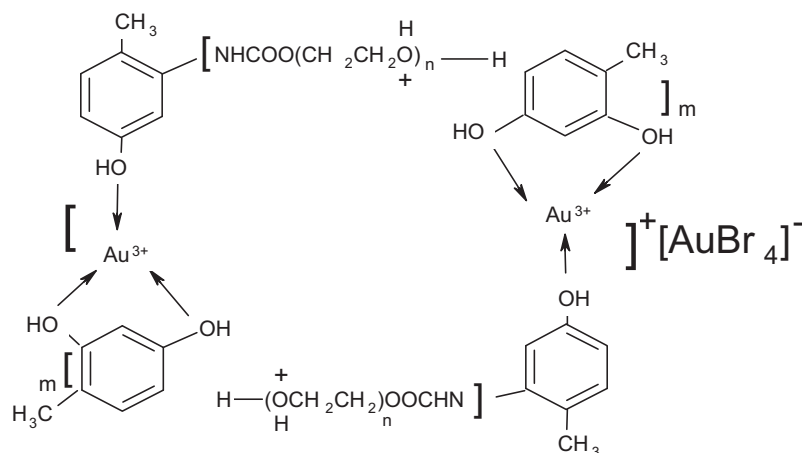


Fig. 5. The expected sorption of gold (III) onto polyhydroxy-polyurethane foam.

**Table 6**  
Determination of gold from real samples using batch technique.

Sample	Add ( $\mu\text{g}$ )	Found ( $\mu\text{g}$ )	Recovery (%)	RSD%
Pharmaceutical	10	9.33	92.3	0.67
Granite	10	9.43	94.3	0.86
Sand beach	10	9.27	88.6	0.84

evaporated on a steam bath till a residue was again left. The residue is mixed with 50 mL of distilled water, and concentrated  $\text{HNO}_3$  is added dropwise until a clear solution was obtained. The sample is spiked with 10  $\mu\text{g}$  of Au (III), the pH of solution is adjusted to 1.0 and add 0.5 mL of 4 mol  $\text{L}^{-1}$  KBr then the recommended procedure applied. The recovery percentage of Au (III) is 92.3% (RSD 0.67%,  $n=3$ , Table 6). These results showed the suitability of the LPPF for determination of gold in pharmaceutical samples.

The applicability of the LPPF was evaluated by analysis of the several real samples. The Granite reference sample (G2, US Geological Survey Certificate of Analysis, USGS) and Sand beach (Dammam city) were analyzed. The obtained results are shown in Table 6. Adequate recovery values were obtained to be in the range 88.6–94.3% with the average value of RSD 0.85%. The obtained data conferred susceptible accuracy of the developed method based on the satisfactory values of RSD in addition to the reasonably high sensitivity and validity of the proposed method for determination in environmental samples.

Analysis of gold in 0.02 g of  $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$  (Fluka AG, Chem, 49.5% Au) was studied by using bromide method. The average gold concentration was found to 49.45% using proposed method with average value of RSD 1.21% ( $n=5$ ). This result is compared with data obtained by using flame atomic absorption spectrometry (Analytical lab of KFUPM). The result obtained is in good agreement with value of obtained by FAAS measurements (48.36%, RSD = 2.38%).

## 5. Sorption mechanism

The LPPF surface becomes positively charged at pH lower than 4.8 and the positively charged surface groups decrease as pH increases. Accordingly, an electrostatic attraction between the anion gold bromide complex and surface groups took place in  $\text{pH} < 4.8$ . Lowering the pH tends to protonate the oxygen atoms of the LPPF and increases gold sorption. As the pH increases, the positive charge density of the LPPF decreases, so that electrostatic attraction between the negatively charged gold bromide complex and the surface of the PPF is decreased, which results in a decrease in the sorption of the gold. Based on the behavior of gold ions

extraction on the LPPF, it has been speculated that ion association ( $\text{LPPF}^+ : [\text{AuBr}_4]^-$ ) may be the principal mechanism for the sorption of gold.

In strong acidic medium, the color of LPPF was changed from yellow to red. The red color of LPPF can be attributed from the formation of six member ring (Fig. S20) and resonance in aromatic ring. Moreover, the maximum sorption of gold occurs in 0.01–0.12 mol  $\text{L}^{-1}$  HCl (Fig. S11) then decreased with increasing of HCl concentration, the decreased of gold sorption is due to the steric hindrance effect.

The batch sorption capacity of LPPF for gold (III) ions from aqueous solution is 0.1 mmol  $\text{g}^{-1}$ , which represents 30.5% from the total LPPF capacity (0.34 mmol  $\text{g}^{-1}$ ) by using bromide solution. This result indicates that the reaction between  $\text{Au}^{3+}$  and the function group of LPPF has been occurred and the sorption mechanism of Au (III) onto LPPF is also ion chelation process. These results indicate that the ion chelation and ion association might be the most probable mechanism of gold sorption onto LPPF (Fig. 5).

The amount of hydroxyl group on the LPPF matrix is 0.18 mmol  $\text{g}^{-1}$  whereas the amounts of gold (III) ions sorbed on LPPF are 0.10 mmol  $\text{g}^{-1}$ . The corresponding molar ratio of gold ions against hydroxyl groups of LPPF is 1:1.8.

The sorption of gold ions on LPPF may involve three steps: bulk transport of solute in solution, film transfer involving diffusion of solute through a hypothetical film boundary layer, and diffusion of the solute within the pore volumes of the adsorbent and along pore-wall surfaces to active adsorption sites. In order to study the particle diffusion mechanism of the sorption of Au (III) onto LPPF, the Morris–Weber ( $q_t = k_M \sqrt{t}$ ) equation was applied (Fig. S14d). Where  $q_t$  is the amount of metal ions sorbed at time  $t$  and  $k_M$  is the rate constant of interparticle transport. The obtained data show that the plot of  $q_t$  vs.  $\sqrt{t}$  is linear and the value of  $k_M$  is 3.77  $\mu\text{mol g}^{-1} \text{min}^{-1/2}$ . According to the foregoing results, the diffusion rate is rapid.

The experimental data for the sorption isotherm was analyzed using Langmuir [ $C_e/Q_c = (1/K_L b) + (C_e/K_L)$ ] and Freundlich ( $\log Q_c = \log K_F + (1/n) \log C_e$ ) equations (Fig. 6). Where  $C_e$  is the amount of gold sorbed at equilibrium,  $K_F$ ,  $n$ ,  $K_L$  and  $b$  are constants. The plot of  $Q_c/C_e$  vs.  $C_e$  for the data according to Langmuir model give a bad linear relationship ( $R^2 = 0.128$ ) for the sorption of gold onto LPPF (Fig. S21a). This model suggested that the sorption of dye from aqueous solution to the solid is monolayer coverage. The plot of  $\log q_c$  vs.  $\log q_e$  (Freundlich model) was shown in Fig. S21b. The results demonstrated that the Freundlich equation provides an accurate description of the experimental data, which is confirmed by the high value of the correlation coefficient ( $R^2 = 0.999$ ). This

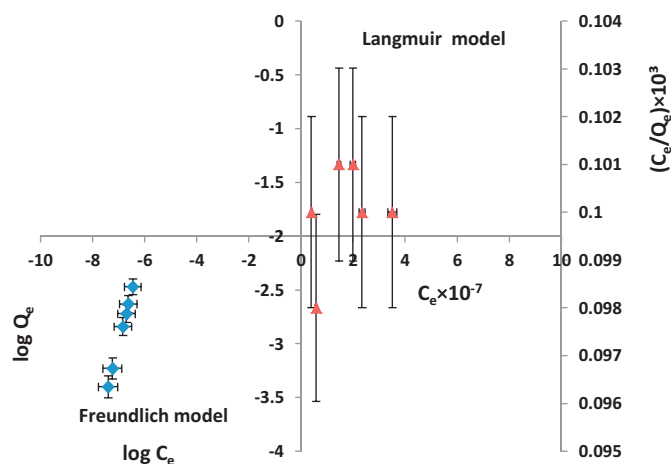


Fig. 6. Freundlich and Langmuir isotherm models for sorption of Au (III) onto LPPF.

may suggest that the LPPF has heterogeneous surface structure. The slope ( $1/n$ ) of the plot of Freundlich model is 0.98 for sorbed gold ions. Value of  $1/n$  ranging between 0 and 1 represent a favorable adsorption condition.

The results of the gold concentration on LPPF were analyzed using Dubinin Radushkevich ( $\ln Q_c = \ln k_{DR} - \beta \varepsilon^2$  and  $\varepsilon = RT \ln[1 + (1/Q_c)]$ ) equations where  $k_{DR}$  is the maximum amount of gold retained onto the solid sorbent;  $\beta$  is a constant related to the energy of transfer of the solute from the bulk aqueous solution onto the solid sorbent and  $\varepsilon$  is Polanyi potential. The value of  $\beta$  for sorption of gold onto LPPF is  $-0.005$  (Fig. S22). The value of sorption energy (activation energy,  $\Delta E$ ), were correlated to  $\beta$  ( $E = 1/\sqrt{-2\beta}$ ). The value of ( $E$ ) evaluated is  $10.0 \text{ kJ mol}^{-1}$ . Thus, a dual sorption mechanism involving "ion association" and/or an "anion exchange" and an added component for "surface adsorption" are most probable model for gold uptake by LPPF. The low activation energy of the gold sorption as compared to the enthalpy indicates the strong attraction operation during sorption and the uptake process occurs even under normal conditions.

## 6. Conclusion

The present work is concerned with the preparation of new sorbent (LPPF) containing hydroxyl groups. The LPPF was used for extraction and determination of Au (III) traces. The kinetic and thermodynamic of the gold ions sorption onto LPPF was studied. The negative values of  $\Delta G$  and  $\Delta H$  indicated that the spontaneous and exothermic nature of the sorption of Au (III). The sorption of anionic gold bromide complex occurs in acidic medium. The sorption mechanism of gold ions onto LPPF may proceed via the chelation and ion association. This study could conclude that LPPF has the ability to separate and determine gold in water and gold alloys. Finally, the LPPF was used as an excellent sorbent, which processes good

stability in different solvents and high sorption capacity for metal ions. LPPF has the interesting property of relatively fast separation and preconcentration of gold ions compared to other solid sorbents.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.aca.2013.05.064>.

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