

# Selective extraction and detection of noble metal based on ionic liquid immobilized silica gel surface using ICP-OES

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**Abstract.** In this study, an efficiently employed ionic liquid combined with commercially available silica gel (SG-CIPrNTf<sub>2</sub>) was developed for selective detection of gold(III) by use of inductively coupled plasma–optical emission spectrometry (ICP-OES). The selectivity of SG-CIPrNTf<sub>2</sub> was evaluated towards seven metal ions, including Y(III), Mn(II), Zr(IV), Pb(II), Mg(II), Pd(II) and Au(III). Based on pH study and distribution coefficient values, the SG-CIPrNTf<sub>2</sub> phase was found to be the most selective towards Au(III) at pH 2 as compared to other metal ions. The adsorption isotherm of Au(III) on the SG-CIPrNTf<sub>2</sub> phase followed the Langmuir model with adsorption capacity of 59.48 mg g<sup>-1</sup>, which was highly in agreement with experimental data of adsorption isotherm study. The kinetics study indicated that Au(III) adsorption kinetics data were well fit with the pseudo-second-order kinetic model on the basis of correlation coefficient fitting (0.996) and adsorption capacity agreement (62.26 mg g<sup>-1</sup>). Furthermore, SG-CIPrNTf<sub>2</sub> phase was effectively performed for the determination of Au(III) in real water samples with satisfactory results.

**Keywords.** Au(III); ionic liquid; silica gel; adsorption; kinetic model; batch mode.

## 1. Introduction

With the dramatic increase in economic growth, noble metals have been extensively utilized for wide range of industries and economic activities. Gold is one of the noble metals, which used in various applications because of its unique properties. However, various reports have mentioned that gold species may cause an allergic eczematous dermatitis and several nephrotoxic effects, although it is not one of the essential toxic elements [1]. The importance to develop precise and reliable analytical approaches for gold determination arises from the fact that presence of huge amount of gold species in the environment and related effects on human health [2,3].

Several analytical techniques have been employed for determination of Au(III), such as flame atomic absorption spectrometry [1], graphite furnace atomic absorption spectrometry [4], neutron activation analysis [5], inductively coupled plasma-mass spectrometry [6] and inductively coupled plasma–optical emission spectrometry (ICP-OES) [7]. It has been also established that ICP-OES is one of the most powerful techniques for analysis of metal ions, particularly at ultra-level concentration. However, direct determination of gold at ultra-trace concentration level in complex matrices by use of

these analytical methods is insufficient due to its low concentrations and system interferences proportional to the detection limits of the used instruments [8,9]. This drawback can be overcome by selective extraction procedure for Au(III) prior to its detection by analytical techniques.

Solid-phase extraction (SPE) is one of the commonly used methods for separation, concentration and clean-up of selected analyte in samples pretreatment [10–12]. The popularity of SPE technique is due to its direct application in microlitre volume without any sample loss, simple to use, minimal cost, and it is also considered to be environmentally benign [13–15]. Moreover, elasticity to select the suitable solid phase material for optimum results is one of SPE advantages [16]. According to this point, different solid phase extractors were studied and applied to environmental samples [16–21]. For example, silica gel (SG) is one of the significant materials due to its large surface area, high porosity and ease of sample handling, and it does not swell or strain and has excellent chemical stability [22–26]. Nevertheless, the lack of selectivity and efficiency of SG to act as an adsorbent for extraction and preconcentration of heavy metal ions lead to low adsorption capacity of metal ions. This can be attributed to the weak interaction between such metal ions and silanol groups presented on the surface [27]. As a consequence, modification of SG is very essential to improve its selectivity towards the analyte of interest. The efficiency and selectivity of SG

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considerably rely on the structure of compound functionalized on SG, nature of donor atoms (O, N, P and S), functional groups position along the surface of solid phase and the steric requirements of the formed complex after uptake of the metal ion of interest [28,29]. Based on those factors, there are several recent research studies concerning the use of functionalized SG for metal ions separation prior to their determination. Different types of organic complexing agents were immobilized on SG, such as 2-mercaptobenzothiazole [30], aminothioamidoanthraquinone [31], 4-amino-2-mercaptopyrimidine [32] and 5-nitro-2-furaldehyde [33].

However, applications of room temperature ionic liquids, including additive in mobile phases for liquid chromatography (LC) [34], background electrolyte [35] and physically supported solid adsorbents [23] for extraction and preconcentration of metal ions, have been received much attention. Ionic liquids (ILs) immobilized onto SG have been successfully applied as solid phase adsorbents for speciation of metal ions in environmental samples. Immobilization of ILs could be achieved by either covalently attached or electrostatic interaction onto SG surface. To best of our knowledge, a few studies addressing functionalizing SG by IL compounds have been reported. For instance, 1-hexylpyridinium hexafluorophosphate [Hpy][PF<sub>6</sub>] IL was immobilized onto SG for removal of trace levels of Fe(III) ion from aqueous samples by acid-catalysed sol-gel processing [36]. In addition, 3-methylimidazolium hexafluorophosphate [C<sub>3</sub>mim][PF<sub>6</sub>] IL and trialkyl phosphine oxides (Cyanex 923) were immobilized onto SG via a sol-gel method for Y(III) uptake [37]. Liang and Peng [38] reported the modification of SG with 1-butyl-3-methylimidazolium hexafluorophosphate [C<sub>4</sub>mim][PF<sub>6</sub>] IL as a solid phase extractor for Cd(II) ion.

In the current study, a new hydrophobic IL (CIPrNTf<sub>2</sub>) immobilized on SG was successfully developed. The formation of newly modified SG-CIPrNTf<sub>2</sub> phase was confirmed by thermal desorption method as well as Fourier transform infrared (FTIR) spectroscopy and scanning electron microscope (SEM). The adsorption behaviour of the newly synthesized SG-CIPrNTf<sub>2</sub> adsorbent towards Au(III) was studied under static conditions. Various parameters such as pH, concentration and contact time effects on the adsorption capacity of Au(III) onto SG-CIPrNTf<sub>2</sub> phase were evaluated. Adsorption isotherm and kinetic models for Au(III) uptake onto SG-CIPrNTf<sub>2</sub> phase were also investigated. The effect of coexisting metal ions on the efficiency of Au(III) adsorption over SG-CIPrNTf<sub>2</sub> was also studied. Finally, the newly developed SG-CIPrNTf<sub>2</sub> phase was applied to the determination of Au(III) in real water samples with acceptable results.

## 2. Experimental

### 2.1 Chemicals and reagents

Chlorpromazine hydrochloride (CIPrCl), bis(trifluoromethane)sulphonamide lithium (LiNTf<sub>2</sub>), toluene, ethyl alcohol (Et-OH),

diethyl ether and SG (SiO<sub>2</sub>, particle size 10–20 nm) with purity of 99.5% were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Metal ion salts of magnesium nitrate (Mg(NO<sub>3</sub>)<sub>2</sub>), palladium nitrate (Pd(NO<sub>3</sub>)<sub>2</sub>) and yttrium nitrate (Y(NO<sub>3</sub>)<sub>3</sub>), as well as stock standard solutions of 1000 mg l<sup>-1</sup> Mn(II), Zr(IV), Pb(II) and Au(III), were also obtained from Sigma-Aldrich. All chemicals and reagents used were of analytical and spectral purity grade. In addition, double-distilled deionized water (18.2 MΩ·cm) was used throughout experiments.

### 2.2 Synthesis of new SG-based solid phase extractor

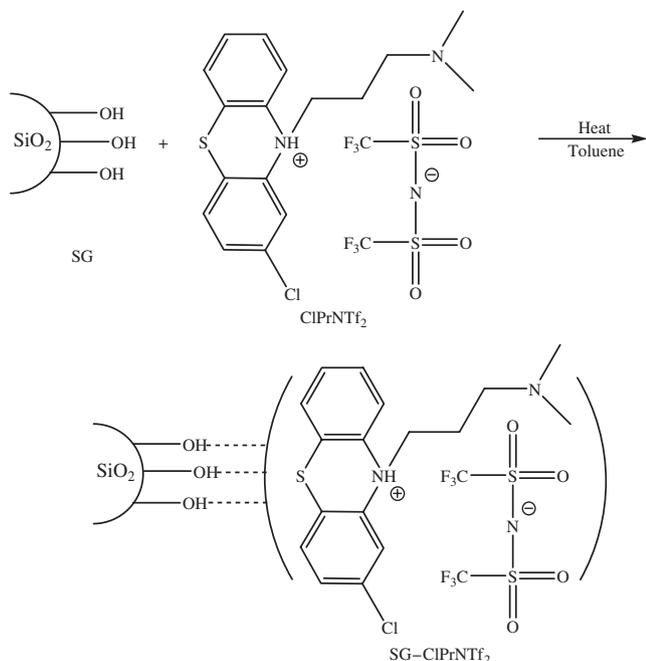
**2.2a Preparation of CIPrNTf<sub>2</sub> IL:** The IL (CIPrNTf<sub>2</sub>) was prepared as previously reported by Marwani [39,40]. Specifically, 1 g CIPrCl was weighed and dissolved in double-distilled deionized water. Then, a mixture was made with dissolved CIPrCl and an equimolar amount of LiNTf<sub>2</sub>. The mixture was stirred for 2 h at 25°C, and the reaction resulted in two layers. The lower layer was isolated and dried under vacuum overnight. The purification was accomplished by vacuum drying at a drying temperature of 353 K and vacuum of 0.4 kPa.

**2.2b Activation of SG:** Activation process of SG was performed by refluxing and stirring 25 g of SG powder with 200 ml of 50% (v/v) concentrated hydrochloric acid solution for 8 h, for eliminating metal oxides as well nitrogenous impurities and enhancing silanol groups content on the surface of SG. The activated SG powder was then filtered, repeatedly washed with double-distilled deionized water until acid free and oven dried for 5 h at 120°C.

**2.2c Synthesis of SG-CIPrNTf<sub>2</sub>:** The SG-CIPrNTf<sub>2</sub> phase was prepared based on the functionalization of hydrophobic IL (CIPrNTf<sub>2</sub>) on the surface of activated SG. A suspension was formed between 5 g activated SG and 100 ml toluene. In addition, an amount of 2 g CIPrNTf<sub>2</sub> was completely dissolved by warming in 50 ml toluene. Then, CIPrNTf<sub>2</sub>-toluene mixture was added to the activated SG suspension. The reaction mixture was stirred at 60°C for 12 h. The resultant SG-CIPrNTf<sub>2</sub> phase was filtered and washed with 50 ml toluene in three portions followed by double-distilled deionized water and diethyl ether. The SG-CIPrNTf<sub>2</sub> adsorbent was then dried in an oven at 80°C for 5 h and kept in a desiccator for further use. The synthetic route of SG-CIPrNTf<sub>2</sub> is presented in scheme 1.

### 2.3 Static method procedure

The uptake capacity of SG-CIPrNTf<sub>2</sub> towards Y(III), Mn(II), Zr(IV), Pb(II), Mg(II), Pd(II) and Au(III) ions was determined under static (batch) techniques. Each metal ion at a fixed concentration of 2 mg l<sup>-1</sup> in a 25 ml volumetric flask was added to 20.0 mg SG-CIPrNTf<sub>2</sub> phase at pH values



**Scheme 1.** Synthetic route of the SG-CIPrNTf<sub>2</sub> phase.

of 1.0–9.0, 0.2 mol l<sup>-1</sup> HCl/KCl for pH 1.0 and 2.0, 0.1 mol l<sup>-1</sup> CH<sub>3</sub>COOH/CH<sub>3</sub>COONa for pH 3.0–6.0 and 0.1 mol l<sup>-1</sup> Na<sub>2</sub>HPO<sub>4</sub>/HCl for pH 7.0–9.0. The mixture was then thoroughly shaken for 1 h at room temperature. The resultant supernatant concentration of metal ion was directly determined by ICP-OES after filtration. For the study of Au(III) uptake capacity under batch conditions, desired concentrations of 0, 5, 10, 20, 30, 40, 50, 60, 80, 100, 125, 150 and 200 mg l<sup>-1</sup> Au(III) were prepared as above, under the same batch conditions, but at the optimum pH of 2.0. Furthermore, the effect of shaking time on the Au(III) uptake capacity was evaluated under equilibrium periods of 2.5, 5, 10, 20, 30, 40, 50 and 60 min at the same batch conditions.

#### 2.4 Sampling

Lake water and seawater samples were gathered from forty lake and Red sea coastal regions at Jeddah in Saudi Arabia, respectively. Tap water samples were obtained from our research laboratory (King Abdulaziz University, Jeddah, Saudi Arabia). Drinking water samples were purchased from several local markets. After sampling, all water samples were immediately filtered through a 0.45 μm polytetrafluoroethylene millipore filters. The pH of selected water samples was adjusted to 2.0 with an appropriate buffer solution.

#### 2.5 Apparatus

Different instruments were employed in the current study, including Perkin Elmer spectrum 100 series FTIR spectrometer (Beaconsfield, Bucks, UK), field emission-scanning

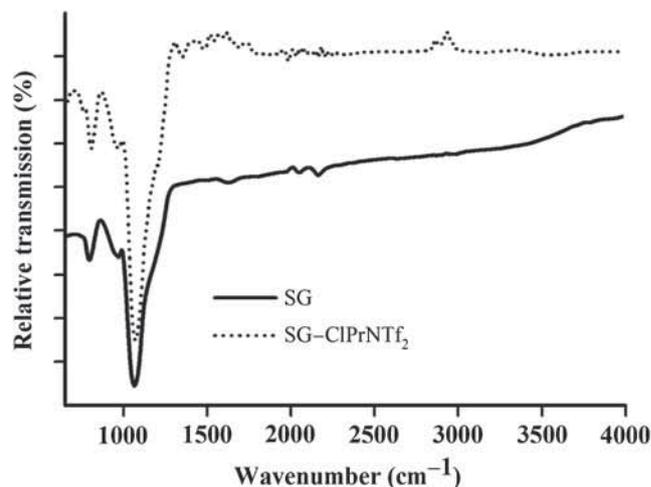
electron microscope (FESEM, QUANT FEG 450, Amsterdam, The Netherlands), Thermolyne 47900 furnace, Jenway model 3505 laboratory pH meter (CamLab, UK) and Perkin Elmer ICP-OES model Optima 4100 DV, USA. Instrumental parameters used in this study were similar to those applied in our previous study [41]. However, selected wavelengths for determination of Y(III), Mn(II), Zr(IV), Pb(II), Mg(II), Pd(II) and Au(III) by ICP-OES were 361.104, 257.610, 343.823, 220.353, 285.213, 340.458 and 267.595 nm, respectively.

### 3. Results and discussion

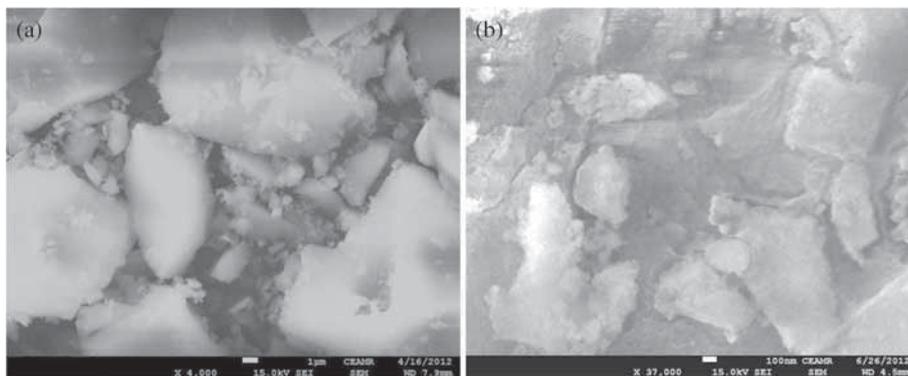
#### 3.1 Characterization of SG-CIPrNTf<sub>2</sub>

**3.1a Surface coverage determination:** A dry porcelain crucible contained an amount of 100 mg SG-CIPrNTf<sub>2</sub> was gradually heated into a furnace from 50 to 700°C, and the ignited phase was kept at this temperature for 1 h. The remaining SG-CIPrNTf<sub>2</sub> phase was left to cool in a desiccator and weighed to determine the mass of desorbed CIPrNTf<sub>2</sub>. The weight loss of CIPrNTf<sub>2</sub> IL was calculated by the difference in sample masses before and after thermal desorption process. The concentration of CIPrNTf<sub>2</sub> was estimated to be 0.34 mmol g<sup>-1</sup> on the activated SG surface based on thermal desorption method.

**3.1b FTIR analysis:** For confirming the structural formation of newly modified adsorbent, activated SG and SG-CIPrNTf<sub>2</sub> were identified by use of FTIR spectroscopy. Figure 1 shows FTIR spectra of activated SG and newly modified SG-CIPrNTf<sub>2</sub> adsorbent. In the FTIR spectrum of SG-CIPrNTf<sub>2</sub>, it can be noticed that new bands appeared at the positions of about 1347, 1478 and 1557 cm<sup>-1</sup> for (NSO<sub>2</sub>), (C-S) and (C=C) bonds, respectively. Also, characteristic stretching vibrations bands for (NH) bond were observed at the positions of about 2917 and 3569 cm<sup>-1</sup>. These spectral



**Figure 1.** FTIR of activated SG and SG-CIPrNTf<sub>2</sub> phases.



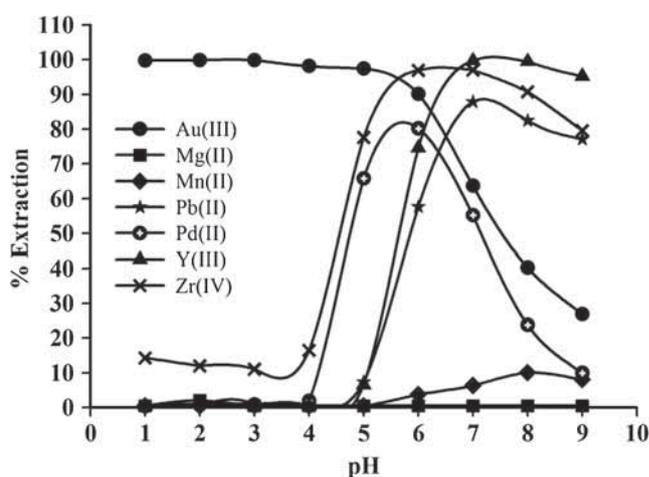
**Figure 2.** SEM images of (a) activated SG and (b) SG-CIPrNTf<sub>2</sub> phases.

changes on the FTIR spectrum of SG-CIPrNTf<sub>2</sub> phase are associated with both CIPrNTf<sub>2</sub> and activated SG phase and confirm the formation of the newly modified SG-CIPrNTf<sub>2</sub> phase as a result of immobilization of CIPrNTf<sub>2</sub> IL onto activated SG surface. Other new peaks appeared in the FTIR spectrum of SG-CIPrNTf<sub>2</sub> can be attributed by their characteristic absorbance  $\nu$  (cm<sup>-1</sup>) as follows: 2846 (–C–H) and 3018 (=C–H).

**3.1c Morphological structure:** SEM images were recorded to explore the changes in surface morphology of activated SG and SG-CIPrNTf<sub>2</sub> and confirm the CIPrNTf<sub>2</sub> immobilization on the surface of activated SG, as displayed in figure 2a and b. From figure 2b, it can be obviously remarked that the homogeneity and pronounced change in the surface morphology of activated SG as a result of its modification with the CIPrNTf<sub>2</sub> IL. It is of interest to note that the activated SG particles were collected in aggregate forms and completely covered with CIPrNTf<sub>2</sub>. It can be also observed that the particles of SG-CIPrNTf<sub>2</sub> (figure 2b) are individually distributed in uniform and homogeneous arrangement in comparison to activated SG (figure 2a).

### 3.2 Batch method

**3.2a Effect of pH and selectivity study:** The most significant factor to be initially optimized is the pH of aqueous solutions. Therefore, the influence of pH on adsorption behaviour of SG-CIPrNTf<sub>2</sub> towards different metal ions including Y(III), Mn(II), Zr(IV), Pb(II), Mg(II), Pd(II) and Au(III) was investigated in the range of 1.0–9.0. In this study, an amount of 20.0 mg SG-CIPrNTf<sub>2</sub> phase was individually mixed with 25 ml sample solution of 2 mg l<sup>-1</sup> for each selected metal ion. Figure 3 clearly displays the dependency of % extraction on the pH of sample solutions. Figure 3 shows an increase followed by a subsequent decrease in the % extraction of all metal ions, except Mg(II), with an increase in the pH. For Mg(II) ion, there is no remarkable change on its % extraction of Mg(II) when increasing the pH. Disparity in this behaviour may be



**Figure 3.** Effect of pH on the adsorption of 2 mg l<sup>-1</sup> Y(III), Mn(II), Zr(IV), Pb(II), Mg(II), Pd(II) and Au(III) on 20 mg SG-CIPrNTf<sub>2</sub> at 25°C.

ascribed to different binding affinities of the binding sites for the SG-CIPrNTf<sub>2</sub> phase towards metal ions included in this study. However, it is motivating to remark that the % extraction of Au(III) was reached to the highest (99.85%) among all metal ions at pH 2.0, providing that the SG-CIPrNTf<sub>2</sub> phase was most selective towards Au(III).

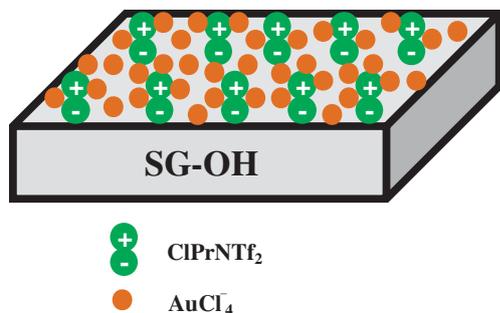
The highest selectivity of SG-CIPrNTf<sub>2</sub> phase towards Au(III) was also supported by calculating the distribution coefficient ( $K_d$ ) for all metal ions at pH 2.0 (table 1). The distribution coefficient ( $K_d$ ) is defined as follows [42].

$$K_d = \frac{(C_i - C_e)}{C_e} \times \frac{V}{m},$$

where  $C_i$  and  $C_e$  represent the initial and final concentrations (mg l<sup>-1</sup>), respectively,  $V$  donates the volume of solution (ml) and  $m$  refers to the mass of adsorbent (g). From table 1, it can be obviously noticed that the highest  $K_d$  value was obtained for Au(III),  $8.32 \times 10^5$  ml g<sup>-1</sup>, corroborating the high incorporated selectivity of SG-CIPrNTf<sub>2</sub> phase towards Au(III).

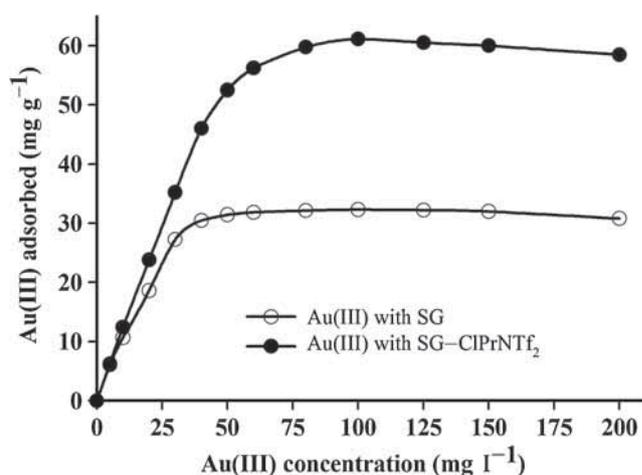
**Table 1.** Selectivity study of 20 mg SG–CIPrNTf<sub>2</sub> towards different metal ions.

Metal ion	Concentration (mg l <sup>-1</sup> )	q <sub>e</sub> (mg g <sup>-1</sup> )	K <sub>d</sub> (ml g <sup>-1</sup> )
Au(III)	2.00	2.496	8.32 × 10 <sup>5</sup>
Zr(IV)	2.00	0.300	170.45
Mg(II)	2.00	0.050	25.51
Y(III)	2.00	0.025	12.63
Pb(II)	2.00	0.021	10.72
Pd(II)	2.00	0.019	9.45
Mn(II)	2.00	0.013	6.28


**Figure 4.** Interaction mechanism between SG–CIPrNTf<sub>2</sub> and Au(III).

The highest percentage of Au(III) extraction and selectivity at pH 2.0 with SG–CIPrNTf<sub>2</sub> phase can be attributed to the electrostatic interaction of the protonated silanols of SG–CIPrNTf<sub>2</sub> and the negatively charged species (AuCl<sub>4</sub><sup>-</sup>). Moreover, CIPrNTf<sub>2</sub> immobilized on the activated SG possesses donor atoms such as N, O and S (scheme 1 and figure 4) that strongly enhance the selectivity of SG–CIPrNTf<sub>2</sub> towards Au(III) adsorption. At high pH values, the % extraction of Au(III) was gradually decreased as shown in figure 3, probably due to the chloroaurate ion hydrolysis to form many species, such as AuOHCl<sub>3</sub><sup>-</sup> and Au(OH)<sub>2</sub>Cl<sub>2</sub><sup>-</sup>. Based on the above results, Au(III) was selected for studying other parameters governing its maximum uptake on SG–CIPrNTf<sub>2</sub> at pH 2.0.

**3.2b Au(III) uptake capacity:** To estimate the adsorption capacity of Au(III), a series of 25 ml samples for Au(III) in concentration ranges of 0–200 mg l<sup>-1</sup> were prepared at pH 2.0 with 0.2 mol l<sup>-1</sup> HCl and 0.2 mol l<sup>-1</sup> KCl and mixed with 20 mg SG–CIPrNTf<sub>2</sub>. All mixtures were mechanically shaken for 1 h at 25°C, and the unadsorbed fractions of Au(III) in the supernatant was determined by ICP-OES after filtration. A breakthrough curve was acquired by plotting the Au(III) concentration (mg l<sup>-1</sup>) against milligrams of Au(III) adsorbed per gram SG–CIPrNTf<sub>2</sub> as presented in figure 5. From the breakthrough curve, 61.10 mg g<sup>-1</sup> Au(III) was experimentally obtained as a maximum adsorption capacity of SG–CIPrNTf<sub>2</sub> phase, which is comparable to those reported previously for Au(III) with other adsorbents (12.3 [43], 14.8 [44], 33.57 [45], 57.0 [46] and


**Figure 5.** Adsorption profile of Au(III) on 20 mg activated SG and SG–CIPrNTf<sub>2</sub> in relation to the concentration at pH 2.0 and 25°C.

70.34 [47] mg g<sup>-1</sup>). The adsorption capacity of activated SG for Au(III) was found to be 32.28 mg g<sup>-1</sup> under the same static conditions (figure 5). These results clearly clarified that the uptake capacity of Au(III) was improved by 89.28% with the newly modified SG–CIPrNTf<sub>2</sub> phase.

### 3.3 Adsorption isotherm models

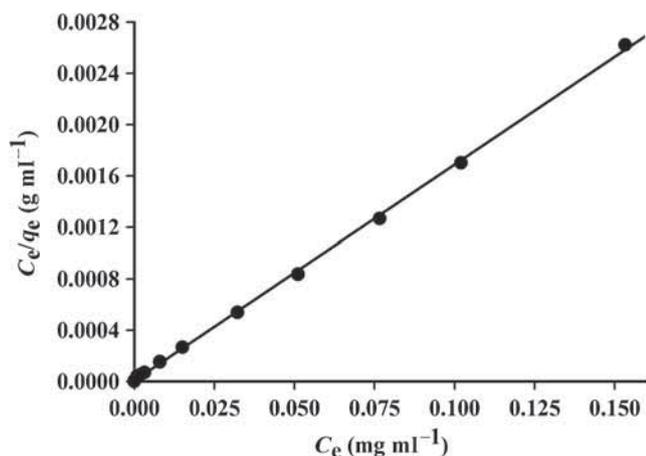
Adsorption isotherm models are important for finding an equation that accurately represents the results. In this study, Langmuir and Freundlich isotherm models were investigated for describing the adsorption isotherm process of SG–CIPrNTf<sub>2</sub> towards Au(III). Langmuir equation follows a monolayer adsorption onto a completely homogeneous surface and can be presented by the following equation [48]:

$$C_e/q_e = (C_e/Q_o) + 1/Q_o b,$$

where  $C_e$  refers to metal ions concentration in solution at equilibrium (mg ml<sup>-1</sup>), and  $q_e$  is the amount of metal ion per gram of the adsorbent at equilibrium (mg g<sup>-1</sup>).  $Q_o$  and  $b$  correspond to Langmuir constants for SG–CIPrNTf<sub>2</sub> and are related to the maximum Au(III) adsorption capacity (mg g<sup>-1</sup>) and affinity parameter (l mg<sup>-1</sup>), respectively. Langmuir constants  $Q_o$  and  $b$  can be calculated from a linear plot of  $C_e/q_e$  against  $C_e$  with a slope and intercept equal to  $1/Q_o$  and  $1/Q_o b$ , respectively. In addition, the essential characteristics of the Langmuir model can be displayed in terms of a dimensionless constant separation factor,  $R_L$ , which can be expressed as follows:

$$R_L = 1/(1 + bC_i),$$

where  $b$  denotes the Langmuir constant indicating the nature of adsorption and the shape of the isotherm and  $C_i$  refers to the initial concentration of Au(III). The value of  $R_L$  describes the nature of the adsorption isotherm, and  $R_L$  values usually range between 0 and 1, thus indicating that the adsorption process is favourable [49]. Figure 6 clearly shows that the adsorption isotherm data were well fit with the Langmuir



**Figure 6.** Langmuir adsorption isotherm model of Au(III) adsorption on 20 mg SG-CIPrNTf<sub>2</sub> at pH 2.0 and 25°C. Adsorption experiments were obtained at different concentrations (0–200 mg l<sup>-1</sup>) of Au(III) under batch conditions.

model based on the least square fit, giving a linear relationship between  $C_e/q_e$  against  $C_e$  with correlation coefficient ( $R^2$ ) value of 0.999. This finding confirmed that the adsorption process follows Langmuir classical model.

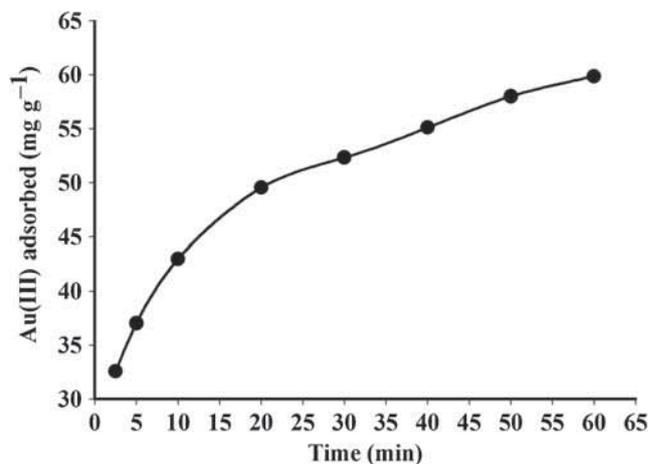
In context, Langmuir constants  $Q_o$  and  $b$  were also estimated to be 59.48 mg g<sup>-1</sup> and 2.41 l mg<sup>-1</sup>, respectively. The  $R_L$  value of Au(III) adsorption on SG-CIPrNTf<sub>2</sub> was found to be 0.004, emphasizing a highly favourable adsorption process. It is also interesting to observe that the Au(III) uptake capacity (59.48 mg g<sup>-1</sup>) calculated from Langmuir model was strongly in agreement with that (61.10 mg g<sup>-1</sup>) of experimentally obtained.

### 3.4 Effect of contact time

Contact time is an another significant parameter for confirming applications possibilities of the newly modified SG-CIPrNTf<sub>2</sub> to selectively bind Au(III) ion and obtaining the time needed to reach equilibrium. The recommended batch procedure was carried out at different shaking times (2.5–60.0 min) for the concentration of 100 mg l<sup>-1</sup> Au(III), as shown in figure 7. The amount of Au(III) adsorbed onto SG-CIPrNTf<sub>2</sub> phase was remarkably increased when increasing the contact time. After 60 min, the equilibrium was achieved and the maximum adsorption capacity of SG-CIPrNTf<sub>2</sub> phase towards Au(III) was reached to 59.85 mg of Au(III) adsorbed per gram solid phase. Thus, it can be easily perceived that equilibrium kinetics for Au(III) were very rapid.

**3.4a Kinetic models:** In this study, kinetic models were also evaluated to interpret the kinetic mechanism of the adsorption process. Both pseudo-first- and second-order kinetic equations were applied to analyse the experimental data. The pseudo-first-order equation can be obtained as follows [50]:

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t,$$



**Figure 7.** Effect of contact time on the adsorption of 100 mg l<sup>-1</sup> Au(III) by 20 mg SG-CIPrNTf<sub>2</sub> at pH 2.0 and 25°C.

where  $q_e$  (mg g<sup>-1</sup>) and  $q_t$  (mg g<sup>-1</sup>) correspond to the amount of Au(III) adsorbed at equilibrium and at time  $t$  (min), respectively. The symbol  $k_1$  is the adsorption rate constant of pseudo-first-order adsorption (min<sup>-1</sup>). By plotting  $\log(q_e - q_t)$  vs.  $t$ , the adsorption rate constant ( $k_1$ ) and adsorption capacity ( $q_e$ ) can be estimated from the slope and intercept, respectively. The pseudo-second-order equation can be given as follows [51]:

$$t/q_t = 1/v_o + (1/q_e)t,$$

where  $v_o = k_2q_e^2$  denotes the initial adsorption rate (mg g<sup>-1</sup> min<sup>-1</sup>) and  $k_2$  is the rate constant of the pseudo-second-order adsorption (g mg<sup>-1</sup> min<sup>-1</sup>),  $q_e$  (mg g<sup>-1</sup>) refers to the amount of Au(III) adsorbed at equilibrium and  $q_t$  (mg g<sup>-1</sup>) represents the amount of Au(III) on the SG-CIPrNTf<sub>2</sub> surface at any time (min). From a linear plot of  $t/q_t$  vs.  $t$ , parameters  $q_e$  and  $v_o$  can be determined.

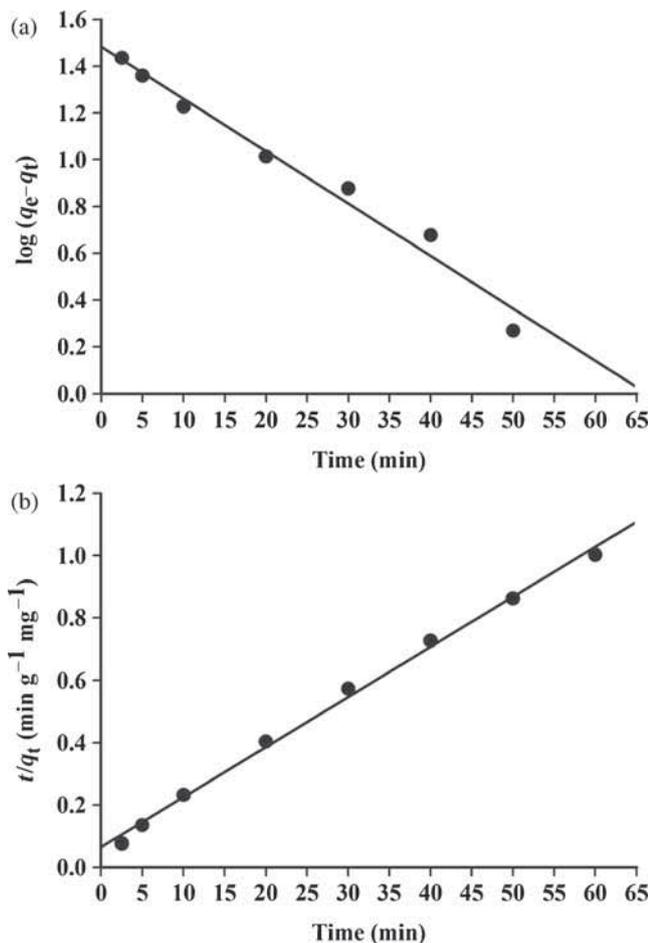
The pseudo-first- and second-order kinetics constants for Au(III) adsorption on SG-CIPrNTf<sub>2</sub> are displayed in table 2. Data of adsorption kinetics were well fit with both pseudo-first- and second-order kinetic models (figure 8a and b). However, the Au(III) uptake capacity on SG-CIPrNTf<sub>2</sub> calculated from pseudo-second-order equation was found to be 62.26 mg g<sup>-1</sup>, which is relatively related to those acquired from the experiments (61.10 mg g<sup>-1</sup>) and the Langmuir model (59.48 mg g<sup>-1</sup>). Thus, the pseudo-second-order kinetic model supported the validity of Langmuir adsorption isotherm model. According to the pseudo-second-order kinetic model, the value of correlation coefficient ( $R^2$ ) factor and  $v_o$  were determined to be 0.996 and 15.41 mg g<sup>-1</sup> min<sup>-1</sup>. These results indicated that the pseudo-second-order adsorption is more precise and reliable in comparison to those achieved from the pseudo-first-order kinetic model.

### 3.5 Performance of method in analytical applications

**3.5a Effect of interfering ions:** Coexisting ions may interfere through the detection of Au(III) in different real water

**Table 2.** Calculated kinetic parameters of the pseudo-first- and second-order kinetic models for Au(III) adsorption on SG-CIPrNTf<sub>2</sub> phase at pH 2.0 and 25°C.

Metal ion	Pseudo-first-order			Pseudo-second-order		
	$q_e$ (mg g <sup>-1</sup> )	$k_1$ (min <sup>-1</sup> )	$R^2$	$q_e$ (mg g <sup>-1</sup> )	$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	$R^2$
Au(III)	30.47	0.051	0.977	62.26	0.004	0.996



**Figure 8.** (a) Pseudo-first- and (b) second-order adsorption kinetic models of Au(III) uptake on 20 mg SG-CIPrNTf<sub>2</sub> at pH 2.0 and 25°C.

samples. Therefore, the effect of interfering ions was investigated according to recommended procedure under the optimized conditions. It can be inferred from the results presented in table 3 that 5000 mg l<sup>-1</sup> of Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup> and Ba<sup>2+</sup>; 1000 mg l<sup>-1</sup> of Cd<sup>2+</sup>, Co<sup>2+</sup>, Hg<sup>2+</sup>, Ni<sup>2+</sup> and Pb<sup>2+</sup>; 500 mg l<sup>-1</sup> of La<sup>3+</sup> and Cr<sup>3+</sup>; 4000 mg l<sup>-1</sup> of Cl<sup>-</sup>, F<sup>-</sup> and NO<sub>3</sub><sup>-</sup>; and 3000 mg l<sup>-1</sup> of CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> did not interfere with the extraction and detection of Au(III) by SG-CIPrNTf<sub>2</sub> phase. Thus, the newly modified SG-CIPrNTf<sub>2</sub> phase is very selective towards Au(III), and the proposed method is applicable for the determination of Au(III) in real environmental samples.

**Table 3.** Effect of matrix interferences on the extraction of 1 mg l<sup>-1</sup> Au(III) by 20 mg SG-CIPrNTf<sub>2</sub> (N = 3).

Coexisting ions	Concentration (mg l <sup>-1</sup> )	% Extraction of Au(III)
Na <sup>+</sup> , K <sup>+</sup> , NH <sub>4</sub> <sup>+</sup>	5000	98.55
Ca <sup>2+</sup> , Ba <sup>2+</sup>	5000	99.11
Cd <sup>2+</sup>	1000	97.12
Co <sup>2+</sup>	1000	98.01
Hg <sup>2+</sup>	1000	96.88
Ni <sup>2+</sup>	1000	97.54
Pb <sup>2+</sup>	1000	98.63
La <sup>3+</sup>	500	97.89
Cr <sup>3+</sup>	500	97.55
Cl <sup>-</sup> , F <sup>-</sup> , NO <sub>3</sub> <sup>-</sup>	4000	98.74
CO <sub>3</sub> <sup>2-</sup> , SO <sub>4</sub> <sup>2-</sup>	3000	97.15
PO <sub>4</sub> <sup>3-</sup>	3000	98.39

**Table 4.** Determination of Au(III) at different concentrations in real water samples using 20 mg SG-CIPrNTf<sub>2</sub> (N = 3).

Samples	Added (mg l <sup>-1</sup> )	Unadsorbed (mg l <sup>-1</sup> )	Extraction (%)
Tap water	1	0.008	99.20
	25	0.328	98.69
	75	1.832	97.56
Lake water	1	0.002	99.81
	25	0.699	97.20
	75	2.290	96.95
Seawater	1	0.012	98.78
	25	0.731	97.08
	75	3.284	95.62
Drinking water	1	0.001	99.90
	25	0.151	99.40
	75	0.936	98.75

**3.5b Application of the proposed method:** For emphasizing the validity and accuracy of the analytical method, the proposed methodology was implemented to the detection of Au(III) in different real water samples. In this study, standard addition method was used under the same static conditions as above (table 4).

Evidently, results reported in table 4 showed that the extraction of Au(III) was feasible for trace analysis in the range of 95.62–99.90%. Thus, the applied analytical method was highly confirmed the possibility of the SG–ClPrNTf<sub>2</sub> phase for the separation and detection of Au(III) in real environmental samples prior to ICP-OES analysis.

#### 4. Conclusions

In the present study, a new solid-phase extraction method was developed by immobilization of hydrophobic ClPrNTf<sub>2</sub> IL on activated SG surface for selective extraction of Au(III) from aqueous samples. Data of Au(III) adsorption isotherm followed Langmuir isotherm model. In addition, kinetics of Au(III) adsorption on SG–ClPrNTf<sub>2</sub> obeyed the pseudo-second-order model. The newly modified SG–ClPrNTf<sub>2</sub> phase provided great selectivity for Au(III) even in the presence of several interfering ions. Further, the proposed methodology was effectively applied to the detection of Au(III) in environmental water samples with reliable and reasonable results.

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