

Poly(propylene carbonate)/exfoliated graphite nanocomposites: selective adsorbent for the extraction and detection of gold(III)

SHER BAHADAR KHAN^{1,2,*}, HADI M MARWANI^{1,2}, JONGCHUL SEO³, ESRAA M BAKHSH², KALSOOM AKHTAR⁴, DOWAN KIM³ and ABDULLAH M ASIRI^{1,2}

¹Center of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia

²Department of Chemistry, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia

³Department of Packaging, Yonsei University, Wonju-si, Kangwon-do 720-221, South Korea

⁴Division of Nano Sciences and Department of Chemistry, Ewha Womans University, Seoul 120-750, South Korea

MS received 18 May 2014; revised 15 September 2014

Abstract. In this study, poly(propylene carbonate) (PPC) and exfoliated graphite (PPC-EG) composites were prepared by the solution blending method and their selective extraction and detection of gold(III) were investigated. Specifically, a new effective adsorbent was developed for a selective extraction and determination of gold(III) by use of inductively coupled plasma optical emission spectrometry. The selectivity of PPC (PPC-EG 0.5, PPC-EG 1, PPC-EG 2, PPC-EG 3 and PPC-EG 5) was investigated toward several metal ions, including Au(III), Cd(II), Co(II), Cu(II), Hg(II), Pb(II), Pd(II) and Zn(II). Based on selectivity and pH studies, Au(III) was the most quantitatively adsorbed on PPC-EG 0.5 phase at pH 2, indicating that PPC-EG 0.5 was the most selective toward Au(III) among other metal ions. The adsorption isotherm followed the Langmuir model with adsorption capacity of 157.61 mg g⁻¹ of PPC-EG 0.5 for Au(III), which was in agreement with experimental data of adsorption isotherm study. The kinetic of adsorption for Au(III) was investigated by a pseudo-first- and second-order models. Results of kinetic models displayed that the adsorption of Au(III) on the PPC-EG 0.5 phase obeyed a pseudo-second-order kinetic model. In addition, results of thermodynamic investigation demonstrated that the adsorption mechanism of PPC-EG 0.5 toward Au(III) was a general spontaneous process and favourable.

Keywords. Polymer-matrix nanocomposite; exfoliated graphite; Au(III); adsorption; batch method; ICP-OES.

1. Introduction

Global warming and environmental pollution are primarily caused by the massive release of carbon dioxide into the atmosphere. Nowadays, the incorporation of carbon dioxide into polymers has attracted a great deal of interests in academic and industrial fields to reduce greenhouse gas pollution and has been considered an alternative to overcome shortages in conventional petroleum fuel supplies.¹ Among the polymeric materials that use carbon dioxide, poly(propylene carbonate) (PPC) was first synthesized by Inoue *et al*² via the copolymerization of carbon dioxide and propylene oxide. It is a biodegradable aliphatic polycarbonate that can be degraded to H₂O and carbon dioxide in natural environment. PPC synthesis recycles carbon dioxide from the environment and has interesting chemical and physical properties such as compatibility with other materials, impact resistance, translucence and innocuousness. Such specific properties are advantageous in adhesives, solid electrolytes, barrier materials, plasticizers and new materials for biomedical and packaging applications.

However, to expand the application of PPC, works should be devoted to improving the thermal, mechanical and sensing properties by blending it with other polymers,³ introducing inorganic fillers⁴ or chemically modifying the end groups.⁵ To improve the mechanical and gas barrier properties of PPC, it was combined with exfoliated graphite (EG) via a solution blending method, and resulting in highly enhanced barrier properties.⁶ PPC-silica hybrid films showed proficient aqueous ethanol sensing properties.⁷

In general, it is very important to find appropriate methods that meet a quality control for determination of metal ions. However, direct determination of metal ions using analytical methods is insufficient owing to their low concentrations and the high concentration of interfering matrix components in most real samples. Thus, an effective separation procedure is usually required prior to the determination of metal ions for sensitive, accurate and interference-free determination of metal ions. There are a wide range of treatment techniques for separation of metal ions, for example, precipitation,⁸ liquid-liquid extraction,⁹ ion-exchange,¹⁰ cloud point extraction¹¹ and solid phase extraction (SPE).^{12,13} Although the solvent extraction has been widely used due to the effective extraction ability and separation selectivity, the large amount of organic solution

* Author for correspondence (sbkhan@kau.edu.sa)

strongly destroys the environment and harms human health. Among various methods, adsorption technique is doubtless the most frequently used method. As an economical and efficient method, adsorption technique has found its extensive applications to this field, in which many kinds of adsorbents are used as adsorption materials, including inorganic oxides,^{14–16} zeolites,¹⁷ silica,^{18–21} various resins,^{22–25} biological adsorbents,²⁶ activated carbon^{27–29} and carbon nanotubes.³⁰

In accordance, the aim of this study was to explore the analytical potential of newly synthesized PPC–EG 0.5 phase toward a selective extraction and determination of Au(III) prior to its determination by inductively coupled plasma-optical emission spectrometry. The selectivity of PPC (PPC–EG 0.5, PPC–EG 1, PPC–EG 2, PPC–EG 3 or PPC–EG 5) toward several metal ions, including Au(III), Cd(II), Co(II), Cu(II), Hg(II), Pb(II), Pd(II) and Zn(II), was studied. In addition, the effect of pH on the selectivity and effectiveness of PPC–EG 0.5 for adsorption of Au(III) was investigated. Other parameters, such as concentration and contact time effects, influencing the maximum uptake of Au(III) on the PPC–EG 0.5 phase were studied under batch techniques. Adsorption isotherm data of Au(III) adsorption on PPC–EG 0.5 followed the classical adsorption isotherm of Langmuir. The kinetic analysis for adsorption process suggested that the adsorption isotherm data obeyed the pseudo-second-order kinetic model. Finally, the thermodynamic behaviour of Au(III) adsorption on the PPC–EG 0.5 phase was investigated.

2. Experimental

2.1 Chemicals and reagents

PPC with an average molecular weight (M_n) of 180,000 g mol⁻¹ was provided by SK Innovation Co., Ltd. (Chunan, Korea). Expandable graphite powders (EXP-527, purity >99%) were purchased from Hyundai Coma Co., Ltd. (Youngju, Korea). Dimethyl formamide (DMF) was purchased from Dusan Chemical Co., Ltd. (Ansan, Korea). All materials in this study were used as received, without further purification. Stock standard solutions of 1000 mg l⁻¹ Au(III), Cd(II), Co(II), Cu(II), Pb(II) and Zn(II) were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Mercuric nitrate [Hg(NO₃)₂] and palladium nitrate [Pd(NO₃)₂] were also obtained from Sigma-Aldrich. All reagents used were of analytical and spectral purity grade. Doubly distilled deionized water was used throughout experimental studies.

2.2 Preparation of the new solid phase extractor

In this study, exfoliated graphite (EG) was prepared by rapid heating of powder expandable graphite at 1050°C and subsequent ultrasonication and centrifugation, as described in our previous study.⁶ The PPC–EG nanocomposite films with EG loadings of 0.5–5 wt% were prepared as follows: PPC

(2 g) was dissolved in 30 ml of DMF at 50°C. EG powder were dispersed in DMF and dissolved by ultrasonication for 20 min. To investigate the effect of EG content on the properties of the nanocomposite films, formulations with several different EG contents were prepared; 0.5, 1, 2, 3 and 5 wt% with respect to the PPC content. These samples depending on the PPC content were coded as PPC–EG 0.5, PPC–EG 1, PPC–EG 2, PPC–EG 3 and PPC–EG 5, respectively. The obtained homogeneous solutions were slowly dropped onto a glass plate and vacuum dried to a constant weight at 60°C. The films were approximately 30 µm thick and were peeled from the plate for additional testing.

2.3 Adsorption method procedure

All stock standard solutions of Au(III), Cd(II), Co(II), Cu(II), Hg(II), Pb(II), Pd(II) and Zn(II) were prepared in 18.2 MΩ cm distilled deionized water and stored in the dark at 4°C. For selectivity study, standard solutions of 1 mg l⁻¹ of Au(III) (or other metal ions) were prepared and individually mixed with 20 mg PPC (PPC–EG 0.5, PPC–EG 1, PPC–EG 2, PPC–EG 3 or PPC–EG 5). In addition, standard solutions of 1 mg l⁻¹ Au(III) ion were prepared, adjusted to pH values ranging 1.0–9.0 with appropriate buffer solutions, 0.2 mol l⁻¹ HCl/KCl for pH 1.0 and 2.0, 0.1 mol l⁻¹ CH₃COOH/CH₃COONa for pH 3.0–6.0 and 0.1 mol l⁻¹ Na₂HPO₄/HCl for pH 7.0–9.0. Then, all standard solutions were individually mixed with 20 mg PPC–EG 0.5 in order to study the effect of pH on the selectivity of PPC–EG 0.5 adsorption toward Au(III). All mixtures were mechanically shaken for 1 h using a mechanical shaker at 150 rpm and room temperature. The PPC–EG 0.5 phase was then removed by filtration, and the concentration of Au(III) in the aqueous solution was determined by inductively coupled plasma-optical emission spectrometer. For the study of adsorption capacity of Au(III) under batch conditions, standard solutions of 5, 10, 15, 20, 30, 50, 75, 100, 125, 150, 200 and 250 mg l⁻¹ Au(III) were prepared as above, adjusted to the optimum pH value of 2.0 and individually mixed with 20 mg PPC–EG 0.5. In addition, the effect of contact time on Au(III) uptake capacity was performed under the same batch conditions but at different equilibrium periods (2.5, 5, 10, 20, 30, 40, 50 and 60 min). For thermodynamic investigation, standard solutions of 5 mg l⁻¹ Au(III) were prepared, adjusted to the pH value of 2.0 as above and individually mixed with 20 mg PPC–EG 0.5. Thermodynamic study of the adsorption of PPC–EG 0.5 toward Au(III) was also performed under the same batch conditions at different temperatures (273, 298, 313, 338 and 353 K).

2.4 Instrumentation

A pH meter (InoLab® pH 7200, IL, USA) was employed for the pH measurements with absolute accuracy limits at pH measurements being defined by NIST buffers. A Perkin

Elmer inductively coupled plasma-optical emission spectrometer (ICP-OES) model Optima 4100 DV, USA was used for the determination of metal ions. The ICP-OES instrument was optimized daily before measurement and operated as recommended by the manufacturers. The ICP-OES spectrometer was used with following parameters: FR power, 1300 kW; frequency, 27.12 MHz; demountable quartz torch, Ar/Ar/Ar; plasma gas (Ar) flow, 15.0 l min⁻¹; auxiliary gas (Ar) flow, 0.2 l min⁻¹; nebulizer gas (Ar) flow, 0.8 l min⁻¹; nebulizer pressure, 2.4 bar; glass spray chamber according to Scott (Ryton), sample pump flow rate, 1.5 ml min⁻¹; integration time, 3 s; replicates, 3; wavelength range of monochromator 165–460 nm. Concentrations of selected metal ions were determined at wavelengths of 267.60 nm for Au(III), 228.80 nm for Cd(II), 230.79 nm for Co(II), 327.39 nm for Cu(II), 253.65 nm for Hg(II), 220.35 nm for Pb(II), 340.46 nm for Pd(II) and 206.20 nm for Zn(II).

3. Results and discussion

3.1 Selectivity study

The preparation of EG and PPC-EG nanocomposite films and their physical properties were described in our previous

Table 1. Selectivity study of different phases (20 mg) adsorption toward different metal ions at ($N = 3$).

Phase	Metal ion	q_e (mg g ⁻¹)	K_d (ml g ⁻¹)
PPC	Au(III)	0.74	1.80×10^3
PPC-EG 0.5	Au(III)	1.24	2.49×10^5
	Cd(II)	1.22	4.88×10^4
	Hg(II)	1.17	1.89×10^4
	Zn(II)	1.05	6.66×10^3
	Pd(II)	0.98	4.46×10^3
	Cu(II)	0.82	2.38×10^3
	Pb(II)	0.77	2.01×10^3
	Co(II)	0.76	1.95×10^3
PPC-EG 1	Au(III)	0.78	2.09×10^3
PPC-EG 2	Au(III)	1.22	5.31×10^4
PPC-EG 3	Au(III)	0.69	1.56×10^3
PPC-EG 5	Au(III)	0.96	4.16×10^3

study.⁶ Selectivity of PPC (PPC-EG 0.5, PPC-EG 1, PPC-EG 2, PPC-EG 3 or PPC-EG 5) toward different metal ions was investigated based on determination of the distribution coefficient. The distribution coefficient (K_d) can be obtained from the following equation:³¹

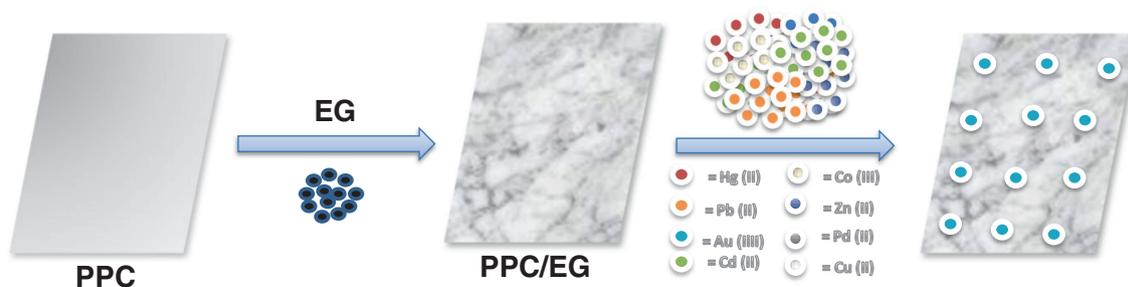
$$K_d = \frac{(C_o - C_e)}{C_e} \times \frac{V}{m}, \quad (1)$$

where C_o and C_e are the initial and final concentrations before and after filtration with the adsorbent, respectively, V refers to the volume (ml) and m the weight of adsorbent (g). Distribution coefficient values of all metal ions investigated in this study are illustrated in table 1. As shown in table 1, it can be clearly observed that PPC-EG 0.5 phase has the greatest distribution coefficient value (2.49×10^5 ml g⁻¹) toward Au(III) among all metal ions. These results indicated that the selectivity of newly synthesized PPC-EG 0.5 phase toward Au(III) was the most as compared to other metal ions investigated in this study (scheme 1). However, it can also be noted that the trend in the uptake capacity of Au(III) is not followed for PPC-EG 1 and PPC-EG 2 in table 1. This behaviour is in agreement with the saturation of binding sites of PPC-EG nanocomposite film with EG loading of 0.5 wt%. When EG loading of nanocomposite film increased from 0.5 to 5 wt%, fluctuations in the maximum uptake capacity of Au(III) can be expected after the saturation process.

3.2 Effect of pH

Extraction of metal ions from aqueous media by adsorption is usually pH dependent because pH affects the surface charge of adsorbent, the degree of ionization and species of adsorbate.³² In this study, the effect of pH on the adsorption of Au(III) by newly synthesized PPC-EG 0.5 phase was investigated. A concentration of 1 mg l⁻¹ Au(III) was chosen, and pH values of sample solutions were adjusted to a range from 1.0 to 9.0 with corresponding buffer solutions. All standard solutions were individually mixed with 20 mg PPC-EG 0.5.

It can be clearly observed from figure 1 that the % extraction is strongly dependent on the pH value of solution. Figure 1 depicts that there is an increase followed by a subsequent decrease in the % extraction of Au(III) with an increase



Scheme 1. Schematic view of adsorption process.

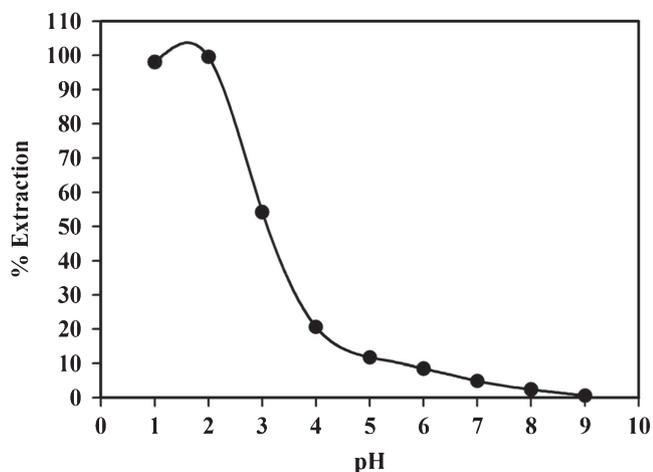


Figure 1. Effect of pH on the adsorption of 1 mg l^{-1} Au(III) on 20 mg PPC-EG 0.5 phase at 25°C .

of the pH value from 1.0 up to 9.0. However, it is motivating to notice that the % extraction of Au(III) was reached to the highest (99.52%) at pH 2.0, providing that the PPC-EG 0.5 phase was most selective toward Au(III) at this pH value.

The highest percentage of Au(III) extraction and selectivity with PPC-EG 0.5 phase can be attributed to the electrostatic interaction between protonated sites, presented on carbonyl groups and their two flanked alkoxy groups of PPC-EG 0.5 at pH 2.0, and negatively charged species (AuCl_4^-), the primary form of Au(III) in HCl solution. Thus, it makes possible to selectively separate Au(III) from the matrix. On the basis of the above results, the optimum pH value of 2.0 was selected to be the optimum for the study of other parameters controlling its maximum uptake on PPC-EG 0.5 under static conditions.

3.3 Determination of adsorption capacity

Adsorption capacity is the maximum metal quantity taken up by 1 g of solid phase and given by mg metal g^{-1} . In this study, the uptake capacity of Au(III) was investigated by varying amounts of Au(III) and individually mixing them with 20 mg PPC-EG 0.5 at pH 2.0 under batch procedure.

From adsorption isotherm study, the adsorption capacity of PPC-EG 0.5 for Au(III) was determined to be 155.71 mg g^{-1} (figure 2), which is higher than those previously reported the adsorption capacity of Au(III) with other adsorbents (12.30 ,³³ 14.80 ,³⁴ 33.57 ,³⁵ 33.57 ,³⁵ 57.0 ,^{36,37} and 72.01 ,^{38,39} mg g^{-1}). From figure 2, it can also be observed that there is a minimal decrease in the uptake capacity of PPC-EG 0.5 for Au(III) after saturation. This behaviour is consistent with the saturation of binding sites of PPC-EG 0.5 with AuCl_4^- species, in particular at the highest concentration of Au(III), 250 mg l^{-1} . Thus, minimal to no effect of concentration may be noted in the maximum uptake capacity of PPC-EG 0.5 for Au(III) after this saturation process.

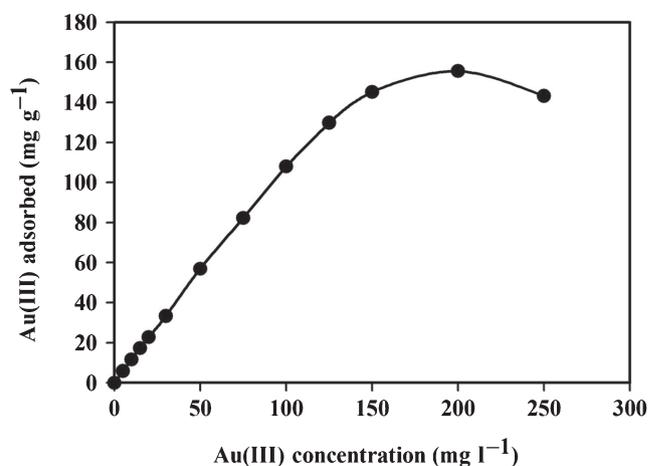


Figure 2. Adsorption profile of Au(III) on 20 mg PPC-EG 0.5 in relation to the concentration at pH 2.0 and 25°C .

3.4 Adsorption isotherm models

It is very important to study adsorption isotherm models in order to develop an equation that accurately represents the results. Both Langmuir and Freundlich adsorption isotherm models^{37,38} were used to interpret equilibrium isotherm data. In this study, experimental data were well correlated to Langmuir equation. The Langmuir isotherm model is based upon an assumption of monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform energies of adsorption with no transmigration of adsorbate in the plane of the surface. The Langmuir classical adsorption isotherm can be expressed as follows:³⁹

$$C_e/q_e = (C_e/Q_o) + 1/Q_o b, \quad (2)$$

where C_e is the concentration of metal ion in solution at equilibrium (mg ml^{-1}), and q_e represents the amount of metal ion per gram of the adsorbent at equilibrium (mg g^{-1}). The symbols Q_o and b refer to Langmuir constants for PPC-EG 0.5 and are related to the maximum Au(III) adsorption capacity (mg g^{-1}) and affinity parameter (l mg^{-1}), 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. Moreover, essential characteristics of the Langmuir adsorption isotherm model can be obtained in terms of a dimensionless constant separation factor or equilibrium parameter, R_L , which is defined as follows:

$$R_L = \frac{1}{(1 + bC_o)}, \quad (3)$$

where b is the Langmuir constant, indicating the nature of adsorption and shape of isotherm, and C_o denotes the initial concentration of Au(III). The value of R_L describes the nature of the adsorption isotherm, and R_L values between 0 and 1 represent a favourable adsorption.⁴⁰

A linear plot was obtained from Langmuir isotherm equation based on the least-squares fit, confirming the validity

of the Langmuir adsorption isotherm model for the adsorption process (figure 3). On the basis of the above results, one can conclude that the adsorption process was mainly monolayer on a homogeneous PPC-EG 0.5 surface. Calculated Langmuir constants Q_0 and b are determined to be 157.61 mg g^{-1} and 0.13 l mg^{-1} , respectively. The correlation coefficient (R^2) obtained from the Langmuir model is found to be 0.99 for adsorption of Au(III) on PPC-EG 0.5, further providing that the data were well fit with the Langmuir model. The R_L value of Au(III) adsorption on PPC-EG 0.5 is 0.04, supporting a highly favourable adsorption process based on the Langmuir model. It is also of interest to observe that the Au(III) adsorption capacity (157.61 mg g^{-1}) calculated from Langmuir equation was strongly in agreement with that (155.71 mg g^{-1}) experimentally obtained from the adsorption isotherm study.

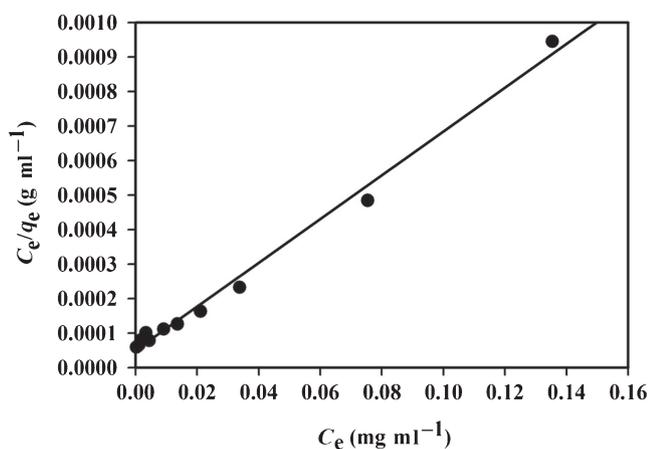


Figure 3. Langmuir adsorption isotherm model of Au(III) adsorption on 20 mg PPC-EG 0.5 at pH 2.0 and 25°C . Adsorption experiments were obtained at different concentrations ($5\text{--}250 \text{ mg l}^{-1}$) of Au(III) under batch conditions.

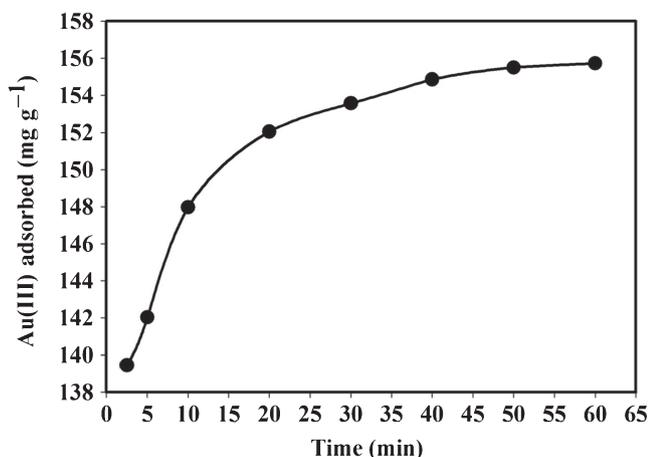


Figure 4. Effect of contact time on the adsorption of 200 mg l^{-1} Au(III) on 20 mg PPC-EG 0.5 at pH 2.0 and 25°C .

3.5 Effect of contact time

The effect of shaking time on the % extraction of Au(III) is a significant factor for determining the possible discrimination order in the behaviour of PPC-EG 0.5 adsorption toward Au(III) and estimating the time required to attain equilibrium. In this study, different contact times ranging from 2.5 to 60.0 min were investigated at the concentration of 200 mg l^{-1} Au(III) (figure 4). As displayed in figure 4, the amount of Au(III) adsorbed onto PPC-EG 0.5 phase dramatically increased with an increase of the contact time, indicating that PPC-EG 0.5 had rapid adsorption kinetics for Au(III). It can be clearly observed from figure 4 that over 147 mg g^{-1} Au(III) was adsorbed on the PPC-EG 0.5 phase after only 10 min of the equilibrium periods. The amount of Au(III) adsorbed was also raised up to more than 153 mg g^{-1} after 30 min until the maximum adsorption of PPC-EG 0.5 for Au(III) was reached to 155.71 mg g^{-1} after 60 min.

3.6 Kinetic study

The effect of concentration on reaction rates is very essential in understanding the reaction mechanism. The adsorption kinetic data of Au(III) adsorption on PPC-EG 0.5 were investigated in terms of different kinetic models⁴¹ in order to quantify changes in adsorption with time and evaluate kinetic parameters. Kinetic models were used for goodness of fit for the experimental data using the correlation coefficient (R^2) as a measure of agreement between the experimental data.

The pseudo-second order model is based on the assumption that the rate limiting step may be chemical adsorption involving valence forces through sharing or exchanging of electrons between the adsorbent and adsorbate.⁴² The pseudo-second-order equation can be written as follows:

$$t/q_t = 1/v_0 + (1/q_e)t, \quad (4)$$

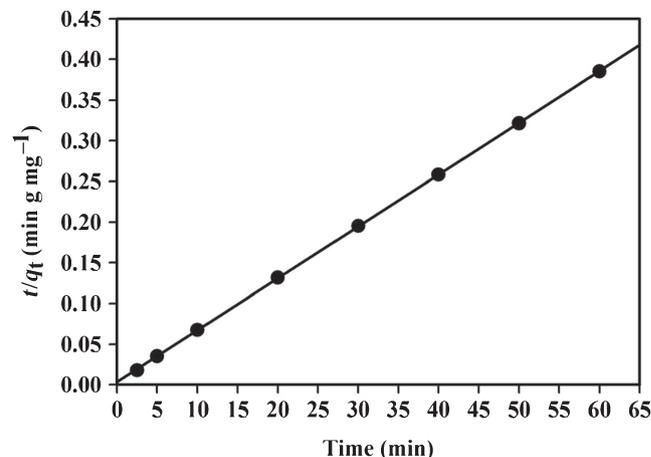


Figure 5. Pseudo-second-order adsorption kinetic model of Au(III) uptake on 20 mg PPC-EG 0.5 at pH 2.0 and 25°C .

Table 2. Calculated thermodynamic parameters of 5 mg l⁻¹ Au(III) adsorption on 20 mg PPC-EG 0.5 (*N* = 3).

ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)				
		<i>T</i> = 273 K	<i>T</i> = 298 K	<i>T</i> = 313 K	<i>T</i> = 338 K	<i>T</i> = 353 K
-12.66	38.58	-23.22	-24.14	-24.64	-25.86	-26.20

where $\nu_0 = k_2 q_e^2$ denotes the initial adsorption rate (mg g⁻¹ min⁻¹), and k_2 (g mg⁻¹ min⁻¹) corresponds to the rate constant of adsorption, q_e (mg g⁻¹) refers to the amount of metal ion adsorbed at equilibrium, and q_t (mg g⁻¹) is to the amount of metal ion on the surface of adsorbent at any time *t* (min). The parameters q_e and ν_0 can be easily obtained from the slope and intercept, respectively, of a plot of t/q_t vs. *t* (figure 5). It is interesting to note that adsorption kinetics data were well fit with the second-order kinetic model. The correlation coefficient (*R*²) factor was found to be 0.99, indicating the reliability and accuracy of the pseudo-second-order adsorption. The parameters q_e , ν_0 and k_2 were determined to be 156.92 mg g⁻¹, 299.09 mg g⁻¹ min⁻¹ and 0.01 g mg⁻¹ min⁻¹. The adsorption capacity of Au(III) on PPC-EG 0.5 estimated from the pseudo-second-order kinetic model (156.92 mg g⁻¹) was also in good agreement with adsorption capacities obtained from both adsorption isotherm experiments (155.71 mg g⁻¹) and Langmuir isotherm model (157.61 mg g⁻¹), confirming the highest applicability of the pseudo-second-order nature of the adsorption of Au(III) on PPC-EG 0.5.

3.7 Thermodynamic study

The study of thermodynamic parameters provides a deeper mechanistic understanding of the adsorption of Au(III) on PPC-EG 0.5. Therefore, the effect of temperature on the adsorption of 20 mg PPC-EG 0.5 for 5 mg l⁻¹ Au(III) was investigated at different temperatures (273, 298, 313, 338 and 353 K). The distribution adsorption coefficient (K_d) corresponding to the character of a metal ion adsorbed by an adsorbent (ml g⁻¹) can be obtained from equation (1). In addition, thermodynamic parameters of the standard enthalpy change (ΔH° , kJ mol⁻¹) and standard entropy change (ΔS° , J mol⁻¹ K⁻¹) were determined, as summarized in table 2, from the slope and intercept, respectively, of the linear variation of $\ln K_d$ with the reciprocal of temperature ($1/T$) as follows:

$$\ln K_d = \Delta S^\circ/R - (\Delta H^\circ/RT), \quad (5)$$

where *R* denotes the universal gas constant (8.314 J mol⁻¹ K⁻¹), and *T* represents the temperature in Kelvin. The standard Gibbs free energy change (ΔG° , kJ mol⁻¹) reported in table 2 was calculated from the following equation:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ. \quad (6)$$

As can be depicted from table 2, calculated values of standard enthalpy change ΔH° and Gibbs free energy change

ΔG° are negative, while that of the standard entropy change ΔS° is positive. The observed negative ΔH° value suggested an exothermic adsorption of Au(III) on PPC-EG 0.5. In addition, the adsorption mechanism of PPC-EG 0.5 toward Au(III) is considered to be a general spontaneous process and thermodynamically favourable because of the negative ΔG° together with positive ΔS° . The positive value of ΔS° also provides that the degree of freedom increases at the solid-liquid interface during the adsorption of Au(III) on PPC-EG 0.5. These results strongly supported the data obtained from adsorption isotherm experiments, Langmuir and kinetic adsorption isotherm models.

4. Conclusion

To investigate the feasibility of PPC to apply for the selective extraction and detection of Gold(III), a series of PPC-EG nanocomposite films were prepared by solution blending PPC and EG prepared by rapid thermal heating. The proposed method based on the newly synthesized PPC-EG 0.5 phase not only had the efficiency toward a selective adsorption of Au(III) but also provided high uptake capacity of Au(III). Results obtained from adsorption isotherm models displayed that the Langmuir adsorption isotherm model was best described the Au(III) adsorption on PPC-EG 0.5. Kinetic isotherm results demonstrated that the adsorption of PPC-EG 0.5 toward Au(III) obeyed a pseudo-second-order kinetic reaction. Based on thermodynamic study, the adsorption mechanism of Au(III) adsorption on PPC-EG 0.5 was a general spontaneous process and thermodynamically favourable. Moreover, the adsorption process is found to be exothermic in nature. This method can be an effective approach in providing a selective separation and determination of Au(III) from the complex matrices.

Acknowledgements

This project was funded by the Center of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz University, Jeddah, under Grant no. CEAMR-SG-7-435.

References

1. Wang S J, Du L C, Zhao X S and Tjong S C 2002 *J. Appl. Polym. Sci.* **85** 2327
2. Inoue S and Tsuruta T 1975 *Appl. Polym. Symp.* **26** 257
3. Ma X, Chang P R, Yu J and Wang N 2008 *Carbohydr. Polym.* **71** 229

4. Shi X and Gan Z 2007 *Eur. Polym. J.* **43** 4852
5. Peng S, An Y, Chen C, Fei B, Zhuang Y and Dong L 2003 *Polym. Degrad. Stab.* **80** 141
6. Lee Y, Kim D, Seo J, Han H and Khan S B 2013 *Polym. Int.* **62** 1386
7. Khan S B, Rahman M M, Akhtar K, Asiri A M, Seo J, Han H and Alamry K 2012 *Int. J. Electrochem. Sci.* **7** 4030
8. Souza A L, Lemos S G and Oliveira P V 2011 *Spectrochim. Acta Part B* **66** 383
9. Nasu A, Yamaguchi S and Sekine T 1997 *Anal. Sci.* **13** 903
10. Hershey J W and Keliher P N 1989 *Spectrochim. Acta Part B* **44** 329
11. Manzoori J L, Abdolmohammad-Zadeh H and Amjadi M 2007 *Microchim. Acta* **159** 71
12. Ahmed S A 2008 *J. Hazard. Mater.* **156** 521
13. Alvarez A M, Alvarez J R E and Alvarez R P 2007 *J. Radioanal. Nucl. Chem.* **273** 427
14. Rauf M A, Hussain M T and Hasany S M 1993 *Sep. Sci. Technol.* **28** 2237
15. Hang Y, Qin Y, Jiang Z and Hu B 2003 *Chem. J. Chin. Univ.* **24** 1980
16. Liang P, Cao J, Liu R and Liu Y 2007 *Microchim. Acta* **159** 35
17. Pasinli T, Eroglu A E and Shahwan T 2005 *Anal. Chim. Acta* **547** 42
18. Mashhadizadeh M H, Pesteh M, Talakesh M, Sheikhshoaie I and Mazloum M 2008 *Spectrochim. Acta Part B* **63** 885
19. Zhang A, Wei Y and Kumagai M 2007 *Sep. Sci. Technol.* **42** 2235
20. Liang P and Fa W 2005 *Microchim. Acta* **150** 15
21. Jia Q, Kong X, Zhou W and Bi L 2008 *Microchem. J.* **89** 82
22. Kim J S, Han C, Wee J H and Kim J S 2006 *Talanta* **68** 963
23. Jain V K, Handa A, Sait S S, Shrivastav P and Agrawal Y K 2001 *Anal. Chim. Acta* **429** 237
24. Jelinek L, Wei Y, Arai T and Kumagai M 2007 *Solvent Extr. Ion Exch.* **25** 503
25. Dave S R, Kaur H and Menon S K 2010 *React. Funct. Polym.* **70** 692
26. Diniz V and Volesky B 2005 *Water Res.* **39** 239
27. Jankowski K, Yao J, Kasiura K, Jackowska A and Sieradzka A 2005 *Spectrochim. Acta Part B* **60** 369
28. Marwani H M, Albishri H M, Soliman E M and Jalal T A 2012 *J. Disp. Sci. Technol.* **33** 549
29. Marwani H M, Albishri H M, Jalal T A and Soliman E M 2012 *Desalin. Water Treat.* **45** 128
30. Biparva P and Hadjmohammadi M R 2011 *Clean: Soil, Air, Water* **39** 1081
31. Han D M, Fang G Z and Yan X P 2005 *J. Chromatogr. A* **1100** 131
32. Zhang L, Chang X, Zhai Y, He Q, Huang X, Hu Z and Jiang N 2008 *Anal. Chim. Acta* **629** 84
33. Senturk H B, Gundogdua A, Bulut V N, Duran C, Soylak M, Elci L and Tufekci M 2007 *J. Hazard. Mater.* **149** 317
34. Liang P, Zhao E, Ding Q and Du D 2008 *Spectrochim. Acta Part B* **63** 714
35. Albishri H M and Marwani H M 2011 *Arab. J. Chem.*, doi: 10.1016/j.arabjc.2011.03.017, in press
36. Rahman M M, Khan S B, Marwani H M, Asiri A M, Alamry K A and Al-Youbi A O 2013 *Talanta* **104** 75
37. Mckay G 1984 *Chem. Eng. Sci.* **39** 129
38. Ho Y S, Wase D A J and Forster C F 1996 *Environ. Technol.* **17** 171
39. Langmuir I 1916 *J. Am. Chem. Soc.* **38** 2221
40. Mckay G, Blair H S and Gardener J R 1982 *J. Appl. Polym. Sci.* **27** 3043
41. Rao M M, Kumar Reddy D H K, Venkateswarlu P and Seshiah K J 2009 *Environ. Manag.* **90** 634
42. Ho Y S and Mckay G 2000 *Water Res.* **34** 735