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Extraction and recovery of precious metal ions in wastewater by polystyrene-coated magnetic particles functionalized with 2-(3-(2-aminoethylthio)propylthio)ethanamine

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ABSTRACT

Cobalt ferrite magnetic particles were coated with polystyrene through atom transfer radical polymerization (ATRP), followed by surface functionalization with 2-(3-(2-aminoethylthio)propylthio)ethanamine. The obtained products (AEPE-PS-MPs) were employed in the extraction of Ag(I) and Au(III) ions in solution. The modified magnetic particles showed a good affinity toward Ag(I) and Au(III) ions and the stability of the particles in acidic solutions was also improved by the coating. The optimal pH for Ag(I) and Au(III) extraction was pH 5.0 and pH 4.0, respectively. The adsorption of the metal ions onto AEPE-PS-MPs followed Langmuir isotherm model with the maximum adsorption capacity of 0.44 mmol Ag(I) g^{-1} and 0.19 mmol Au(III) g^{-1}. The recovery of Ag and Au from the adsorbents could be achieved by using 1.0 M thiourea in 1% HNO_3 and 1.0 M thiourea in 2% HCl, respectively. The reuse of the adsorbents is possible. The products were shown to have potential in the extraction of Ag and Au in real wastewater.

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1. Introduction

Precious metals such as silver and gold are applied in many industrial activities including the electronic, pulp and jewelry industries. These industries generate wastewater containing significant amount of Ag and Au. The recovery of these metals from wastewater has drawn much attention. The one widely studied method is the extraction with various adsorbents such as natural zeolite [1], resins [2–4], molecular-imprinted biosorbent [5], chitosan resin modified with magnetite [6], and modified magnetic particles [7].

Recently, magnetic particles (MPs) have been widely studied for various applications including separation and extraction of target molecules or ions. The advantage of the MPs is that they can be separated by external magnetic field and the magnetic particles surface can be modified to suit the application. In metal ions extraction, the magnetic particles extract metal ions by surface hydroxyl groups via ion exchange mechanism [8]. However, the drawbacks of using magnetic particles in metal extraction are the low selectivity toward target metal ions and low stability of the particles in strong acidic aqueous media. To improve the selectivity and the adsorption efficiency, the surface of magnetic particles can be modified with complexing molecules. Kraus et al. reported the modification of $CoFe_2O_4$ magnetic particles with (3-mercaptopropyl)trimethoxysilane and demonstrated that the obtained products had higher efficiency in Au(III) extraction [7]. The particle stability in strong acidic solutions was also improved when coated.

Polymer coating is one of the alternatives to improve the stability of the particles and allows the modification of surface with functionalities. The polymer coated magnetic particles could be prepared by different methods including encapsulation of the particles in polymer coating by seeded emulsion polymerization [8] and formation of polymer shell on particles surface via atom transfer radical polymerization (ATRP) [9–12]. The ATRP offers several advantages including the presence of a variety of the functional groups on the end-polymer grafted on the particles surface. These active sites allow the further functionalization of the desired molecules on the polymer shell. In ATRP process, the initiators molecules attach on the inorganic surface through different processes i.e. physisorption [10], ligand exchange with previously attached initiators [9,12] or a combination of ligand exchange and chemical bonding [11]. In this study, $CoFe_2O_4$ particles were coated with polystyrene via ATRP and the initiator molecules were directly covalently bonded to the surface of MPs without adding any ligands before, hence there was no ligand exchange step. The polystyrene was grafted from the initiator sites on surface, and then the polymer coating was subsequently functionalized with the ligand 2-(3-(2-aminoethylthio)propylthio)ethanamine (AEPE) to improve the extraction efficiency and selectivity toward gold,

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silver and soft Lewis acid metal ions [13]. The preparation of the adsorbents is described and the obtained products were characterized and used in the extraction of Ag(I) and Au(III) ions from solution. The adsorption isotherms and adsorption kinetics were also investigated. The recovery of the metal ions was performed using different eluents.

2. Materials and methods

2.1. Synthesis of $CoFe_2O_4$ magnetic particles

$CoFe_2O_4$ magnetic particles were synthesized via co-precipitation of ferric chloride with cobalt nitrate hexahydrate. Ferric chloride ($FeCl_3$; 3.52 g, 21.70 mmol) and cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$; 3.16 g, 10.86 mmol) were dissolved in 0.2 M nitric acid (250 mL). The solution was stirred for several minutes and 6 M NaOH (29 mL) was added into the solution leading to the formation of a black precipitate [6]. These particles were separated by centrifugation, washed with de-ionized water (3 × 100 mL) and dried at 110 °C overnight. Finally, the magnetic particles were grinded with a mortar and pestle, calcined at 500 °C for 6 h and finally grinded once again. The yield of 2.5 g of magnetic particles was obtained.

2.2. Preparation of polystyrene-coated $CoFe_2O_4$ magnetic particles

The polystyrene-coated $CoFe_2O_4$ magnetic particles (PS-MPs) were prepared as schematically shown in Fig. 1. First, the initiator-coated magnetic particles (Ini-MPs) were prepared. 3-Aminopropyltriethoxysilane (1.52 mL, 6.4 mmol) and ethyl-2-bromopropionate (0.96 mL, 6.4 mmol) were added into dry acetonitrile (40 mL). The solution was stirred for 2 h at 60 °C under nitrogen atmosphere. Then $CoFe_2O_4$ magnetic particles (1.0 g) were added into the solution and the mixture was stirred for an additional 24 h under the same conditions. The particles were subsequently washed with ethanol (3 × 30 mL) and dichloromethane (3 × 30 mL) and dried at room temperature under vacuum.

The obtained Ini-MPs were further used to prepare PS-MPs. Cu(I)Br (57.6 mg, 0.4 mmol) and PMDETA (0.084 mL, 0.4 mmol) were added to DMF (2 mL) and the mixture was stirred under nitrogen atmosphere until a blue color was observed. Then styrene monomer (4 mL, 34.80 mmol) and Ini-MPs (1.0 g) were added. The mixture was further stirred at 110 °C for 16 h under nitrogen atmosphere. After the polymerization was complete, the solution was transferred to methanol. The final product, PS-MPs, was washed with methanol (3 × 30 mL) and dried at room temperature under vacuum.

2.3. Preparation of AEPE-modified $CoFe_2O_4$ magnetic particles

The ligand 2-(3-(2-aminoethylthio)propylthio)ethanamine (AEPE) was synthesized as described previously [14,15]. The polystyrene-coated magnetic particles (3 g) were dispersed in dry acetonitrile (100 mL) and AEPE (1 g) was added. The mixture was stirred at 60 °C for 24 h under nitrogen atmosphere. The final product, AEPE-PS-MPs, was separated by external magnetic field, washed with ethanol (3 × 50 mL) and dried at room temperature under vacuum. All synthesized $CoFe_2O_4$ magnetic particles were characterized by X-ray diffraction (XRD; Rigaku Dmax2200/Ultima+), Fourier transform infrared spectrometry (FTIR; Nicolet FT-IR Impact 410), thermogravimetric analysis (TGA; PerkinElmer, Pyris 1), surface area analysis (BEL Japan, BELSORP-mini) and scanning electron microscope (SEM; JEOL, JSM-5410 LV).

2.4. Extraction experiments

A batch method was used to study the extraction of metal ions (Ag(I) or Au(III)) from aqueous solutions. The adsorbent (5.0 mg) was added to 5 mL of metal solution and the mixture was stirred for 60 min to ensure adsorption equilibration. The adsorbents were separated by external magnetic field and the residual concentration of Ag(I) or Au(III) in solution was determined using flame atomic absorption spectroscopy (FAAS; PerkinElmer, Analyst 100). The initial concentration was 50 mg L^{-1} and 40 mg L^{-1} for Ag(I) and Au(III), respectively. The metal ion solutions were prepared by dilution of the standard solution of Au(III) (1000 mg L^{-1} in 0.1 M HCl) or Ag(I) (1000 mg L^{-1} in 0.5 M HNO_3) with de-ionized water. The pH and the ionic strength of the solutions were controlled using 0.05 M sodium acetate. The effect of pH, contact time, ionic strength and foreign ions was investigated.

2.5. Recovery of metal ions and reuse of adsorbents

The desorption of Ag(I) or Au(III) ions from the adsorbents was studied using different eluents (HNO_3, HCl or thiourea in HNO_3 or in HCl). The adsorbents were first used in adsorption experiments. Five millilitre of metal ion solution (50 mg L^{-1} Ag(I) or 40 mg L^{-1} Au(III)) was stirred with 5 mg adsorbent for 60 min. The used adsorbents were separated from solution and washed thoroughly with de-ionized water. Subsequently, 5 mL of the eluent was added and the mixture was stirred for 60 min. The desorption time was studied and it was found that 60 min is sufficient for metal recovery. The amount of desorbed metal ion was determined using FAAS. To evaluate the reusability of the adsorbents, at least five consecutive adsorption/desorption cycles were performed. The adsorbents were washed with de-ionized water before use in subsequent adsorption/desorption cycles.

3. Result and discussion

3.1. Synthesis and characterization of AEPE-modified $CoFe_2O_4$ magnetic particle adsorbents

The synthesized $CoFe_2O_4$ magnetic particles were characterized by XRD. The XRD pattern showed six peaks with d-spacing values of 2.94 Å, 2.52 Å, 2.08 Å, 1.70 Å, 1.61 Å and 1.48 Å, respectively. These values correspond to the characteristic peaks of $CoFe_2O_4$ reported previously [16,17]. The PS-MPs and AEPE-PS-MPs also gave the same XRD pattern, indicating that the modification did not affect the internal structure of the particles.

FT-IR analysis was performed to characterize the surface composition of modified magnetic particles. The FT-IR spectra are shown in Fig. 2. The FT-IR spectra of bare $CoFe_3O_4$ particles (Fig. 2a) shows the characteristic peak at 587 cm^{-1} which corresponds to the Fe–O and Co–O vibration related to magnetite phase [18]. Furthermore, the broad peak centered at 3400 cm^{-1} was attributed from the hydroxyl groups. The oxide preparation method via precipitation by NaOH would bare the hydroxyl groups on its surface. After initiator modification (Fig. 2b), the characteristic peaks of the Si–O–Si stretching vibration are present at 1035 cm^{-1} and 1127 cm^{-1}. The small peak at 1226 cm^{-1} corresponds to C–N bond stretching and the peaks at 1614 cm^{-1} and 1742 cm^{-1} correspond to amide bond (N–CO) stretching. When modified with polystyrene (Fig. 2c), the signal for aliphatic C–H bond stretching appears at 2929 cm^{-1} and the C=C bond stretching of the conjugated ring at 1642 cm^{-1} and 1458 cm^{-1}. A new small peak for N–H bond bending is observed at 1378 cm^{-1} after surface modification with AEPE (Fig. 2d).

The thermal stability of the particles obtained from each modification step was investigated. The results from thermogravimetric

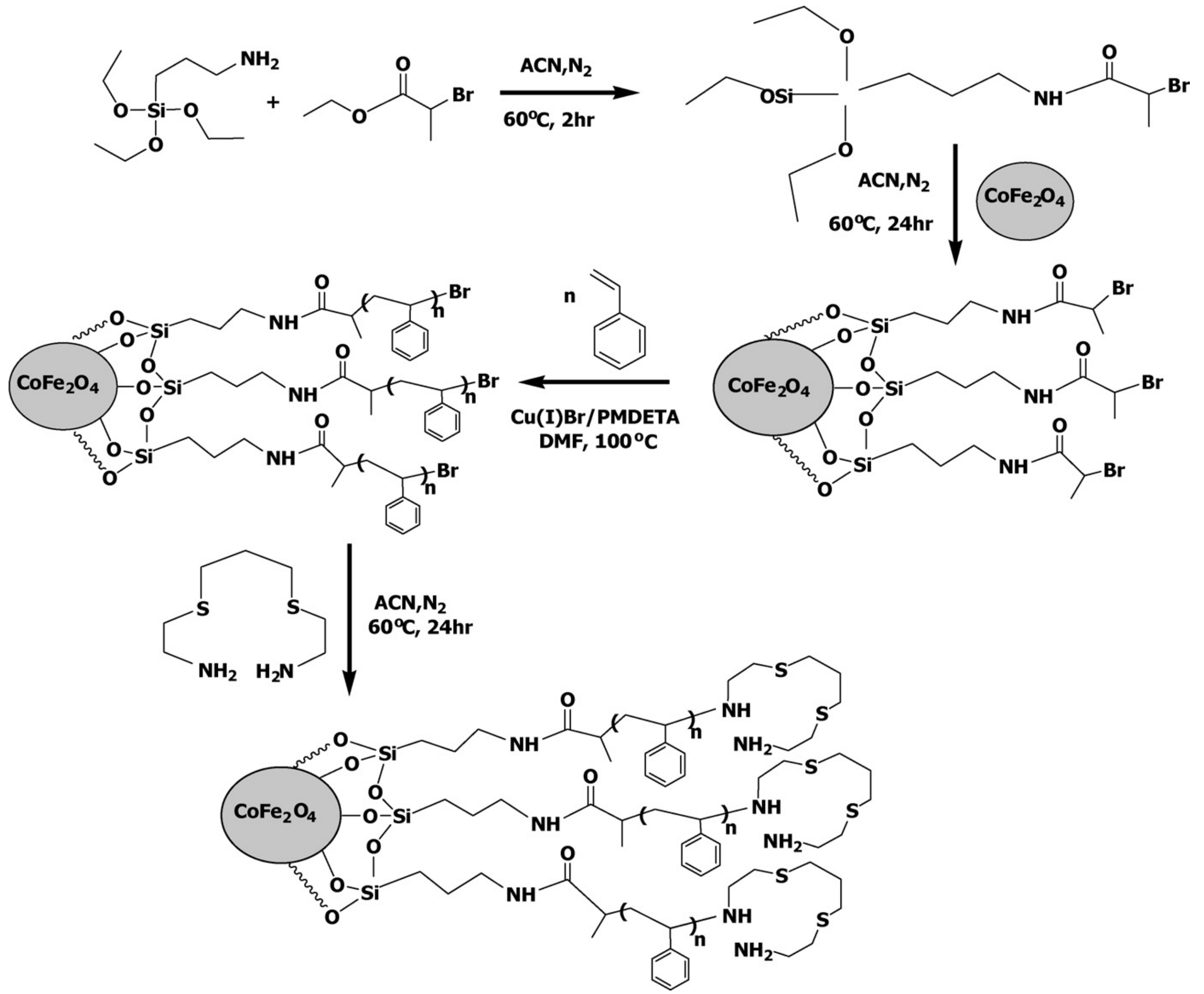

Fig. 1. Synthetic route for polystyrene-coated magnetic particles modified with AEPE.

analysis (TGA) are shown in Fig. 3. All TGA curves show the weight loss at the temperature below 200 °C due to the vaporization of moisture and residual organic solvent. The TGA curve of Ini-MPs (Fig. 3b) shows the weight loss of 6.6% at the temperature range of 250–550 °C, corresponding to the loss of initiator molecules. When further modified the surface with polystyrene (PS-MPs), the weight loss increased to 12.8% at the temperature range of 175–550 °C (Fig. 3c) due to the organic contents in initiator and polymer-modified chains. The TGA curve of AEPE-PS-MPs (Fig. 3d) shows the total weight loss of 13.8% at temperature range of 175–550 °C. An additional weight loss of 1.0% at the temperature range of 175–280 °C was observed, indicating the successful modification by AEPE ligand. However the exact amount of AEPE ligand could not be calculated because of the multi-step modification process with various organic reactants and solvents and the complicated decomposition of a long organic chain. In addition, it could be noticed that the decomposition peak of polystyrene parts shift to the higher temperature due to the modification with AEPE ligand at the chain ends.

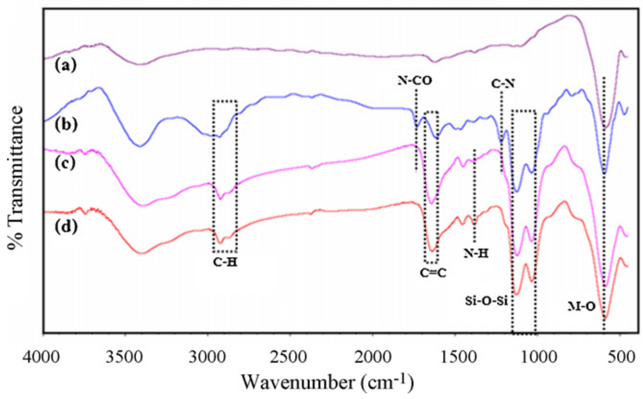

Fig. 2. FT-IR spectra of: (a) bare magnetic particles, (b) initiator-coated magnetic particles, (c) polystyrene-coated magnetic particles and (d) AEPE-modified magnetic particles.

The SEM image of bare magnetic particles and AEPE-PS-MPs show the agglomerate particles in various sizes (Fig. 4). The particle size of MPs appears to be smaller than a micron; however, the agglomeration in various degrees is observed (Fig. 4a). Upon the polymer coating (Fig. 4b), the appearance of agglomerate particles is similar to that of the bare MPs, but the outer surface of AEPE-PS-MPs appears to be smoother than the bare MPs. Moreover, the bulb polymer phase is not found. These

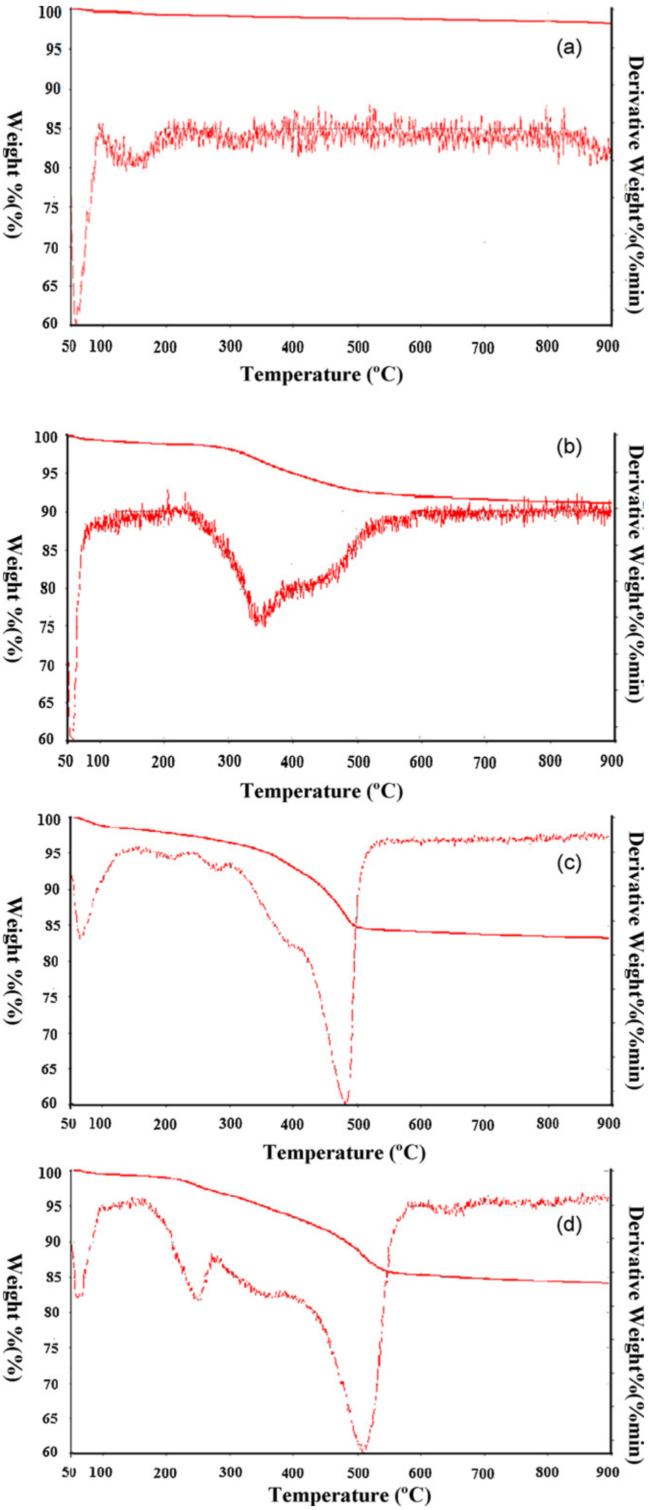

Fig. 3. TGA profiles of (a) MPs, (b) Ini-MPs, (c) PS-MPs and (d) AEPE-PS-MPs.

SEM images indicate the success of trapping the magnetic particles.

The surface area of MPs, Ini-MPs, PS-MPs and AEPE-PS-MPs was determined by surface area analyzer using BET model (Table 1). The results show a significant decrease in surface area of Ini-MPs compared to MPs due to the grafting of initiator molecules on MPs surface. Moreover, PS-MPs and AEPE-PS-MPs show the very low surface area compared to MPs and Ini-MPs because of the non porous polystyrene coating on the agglomerates of MPs. Thus, these results indicate that the polystyrene was coated on the surface after initiator grafting.

Table 1
Surface area analysis.

Phase	Surface area ($m^2\ g^{-1}$)[a]
MPs	47.5 ± 4.3
Ini-MPs	23.7 ± 1.9
PS-MPs	1.0 ± 0.3
AEPE-PS-MPs	0.7 ± 0.2

[a] Mean ± SD ($n = 3$).

3.2. Extraction of metal ions

3.2.1. Effect of pH on metal extraction

The pH value is one of the parameters that influence the extraction of metal ions on adsorbents. The adsorption efficiency of bare magnetic particles and AEPE-modified polystyrene-coated $CoFe_2O_4$ magnetic particles (AEPE-PS-MPs) were evaluated and presented as adsorption capacity at various pH values. The adsorption capacity of bare magnetic particles increased slightly from 1.0 $mg\ g^{-1}$ to 12.6 $mg\ g^{-1}$ for Ag(I) extraction and from 0.7 $mg\ g^{-1}$ to 7.1 $mg\ g^{-1}$ for Au(III) extraction when the pH of metal solutions was increased from 1.0 to 8.0. The effect of pH on Ag(I) and Au(III) ion adsorption on AEPE-PS-MPs is shown in Fig. 5. The extraction of metal ions by the particles is greatly enhanced when modified with AEPE. In strong acidic solutions, the adsorbents show low adsorption capacities, probably due to the surface protonation of the bare magnetic particles and the amine group of AEPE on the modified particles. The resulting positively charged surface seems to have low binding ability toward Ag(I) and Au(III) ions. The extraction efficiency improved by increasing the pH of solution to pH 4 and are relatively constant for Ag(I) extraction at higher pH values. Hence, the optimum pH value for Ag(I) extraction ranged from 5 to 8. On the other hand, the extraction of Au(III) ions from solution having pH values higher than 4 decreased. Therefore, the suitable pH for extraction of Au(III) ions is 4.

The dissolution of magnetic particles could limit the use of the particles as adsorbents. Therefore the leaching of Co and Fe from the particles was studied. The solutions of Ag(I) or Au(III) ions were analyzed by FAAS to determine the amount of dissolved Co and Fe. A significant dissolution of the particles was found in strong acidic solutions ($pH < 3$). At pH 1.0, the leaching extent (%, w/w) of Co and Fe increased up to 1.4% and 2.2% from bare magnetic particles while less than 1.0% leaching extent from AEPE-PS-MPs was observed. The coating resulted in a better acid resistance property of the particles. Nevertheless, the observed leaching of Fe and Co from the coated particles in strong acid solution indicates that the surface of the adsorbents was not completely protected.

3.2.2. Adsorption kinetics

The adsorption kinetics of Ag(I) and Au(III) were studied (Fig. 6). Two widely used kinetic models were adopted. The pseudo-first order [19] and pseudo-second order kinetic models [20] are shown in Eqs. (1) and (2), respectively. The variables q_t and q_e represent adsorption capacity ($mg\ g^{-1}$) at contact time t and at equilibrium, respectively. The first order kinetic constant (k_1) and second order kinetic constant (k_2) can be determined from the slope of the linear plot of $\log(q_e - q_t)$ versus t and from the intercept of the linear plot of t/q_t versus t, respectively.

$$\log(q_e - q_t) = \log\ q_e - \frac{k_1}{2.303}t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

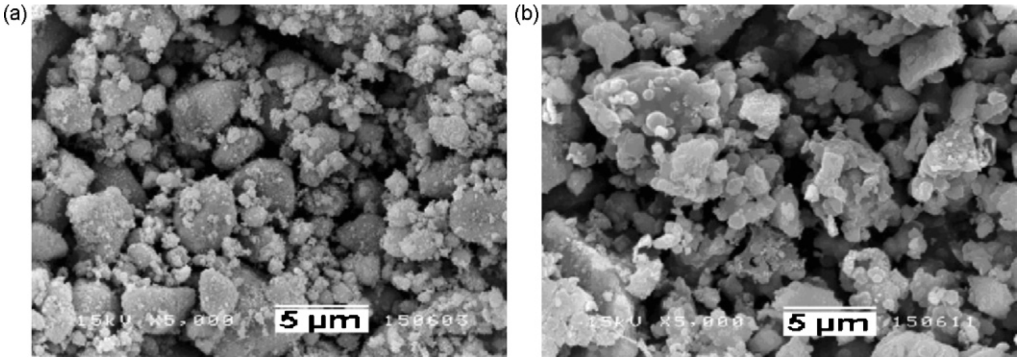

Fig. 4. SEM images of (a) MPs and (b) AEPE-PS-MPs. (5000×)

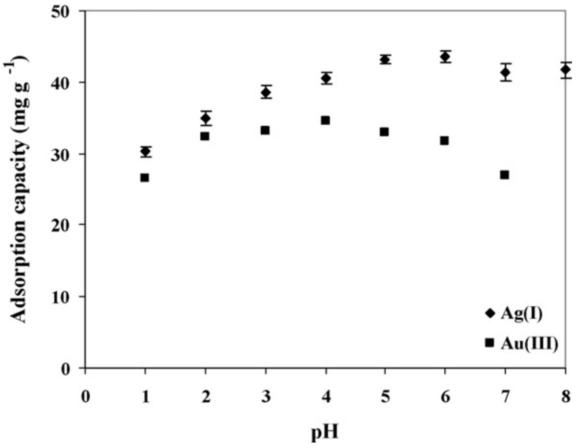

Fig. 5. Effect of pH on the adsorption of Au(III) and Ag(I) from solution using AEPE-PS-MPs. (Ag(I) 50 mg L^{-1}, Au(III) 40 mg L^{-1}, adsorbent dose 1 g L^{-1}.)

Table 2
Pseudo-second order kinetic parameters of Au(III) and Ag(I) adsorption on AEPE-PS-MPs.

Metal	$q_{e,exp}$ (mg g^{-1})	$q_{e,cal}$ (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2
Au(III)	35.8	35.5	0.011	0.998
Ag(I)	44.9	45.2	0.015	0.999

Under the experimental condition used, the adsorption of metal ions on AEPE-PS-MPs occurs rapidly and the adsorption equilibrium could be reached within 60 min. The pseudo-first order kinetic plots were not linear for the adsorption of Ag(I) and Au(III). The experimental data fit well to the pseudo-second order kinetic model. The kinetic parameters are shown in Table 2. The adsorption capacities at equilibrium calculated from the kinetic equations ($q_{e,cal}$) are in agreement with the experimental values ($q_{e,exp}$), indicating a good fit of the experimental data to the kinetic model. The kinetic constants of the adsorption of Ag(I) and Au(III) are high and close to one another, indicating that the adsorption of these metal ions on the adsorbent occurs rapidly.

3.2.3. Adsorption isotherms

The adsorption equilibrium of metal ions between aqueous solution and the adsorbent can be described by an adsorption isotherm. The adsorption experiments were performed using different initial concentrations of metal ions at 25 °C. The results are shown in Fig. 7a. The capacity of the adsorbent increased upon increasing the initial concentration of metal ions and reached a constant value in the high initial concentration range. In an attempt to describe the adsorption behavior, the Langmuir and Freundlich model were adopted. The Langmuir isotherm (Eq. (3)) assumes monolayer adsorption onto the homogeneous surface with specific sites [21]. The Freundlich isotherm assumes multilayer adsorption onto heterogeneous surface and can be calculated using Eq. (4) [22].

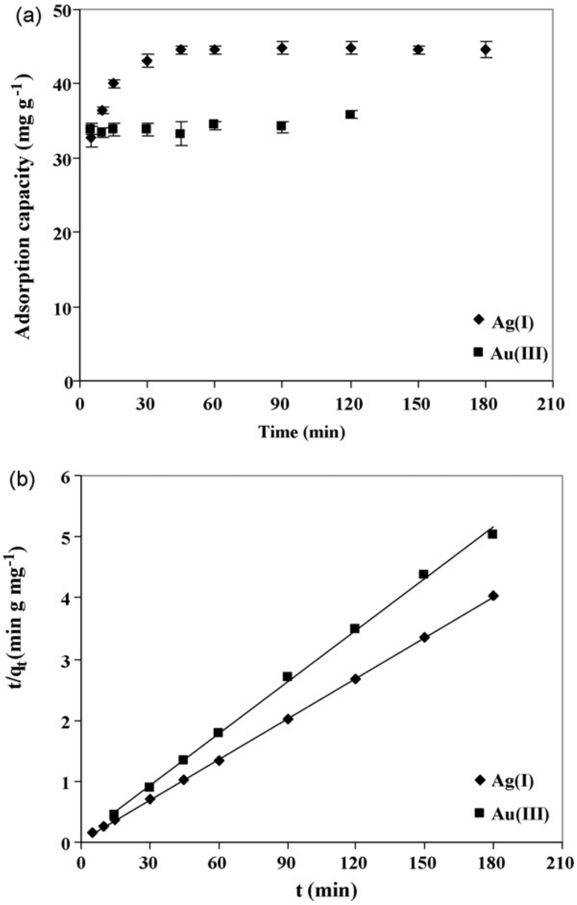

Fig. 6. The adsorption capacity of AEPE-PS-MPs toward Ag(I) and Au(III) ions as a function of: (a) contact time and (b) adsorption kinetics. (Ag(I) 50 mg L^{-1} (pH 5), Au(III) 40 mg L^{-1} (pH 4), adsorbent dose 1 g L^{-1}.)

$$\frac{C_e}{q} = \frac{C_e}{q_m} + \frac{1}{bq_m} \tag{3}$$

$$\log q = \log K_f + \frac{1}{n}\log C_e \tag{4}$$

q and C_e are the adsorption capacity (mg g^{-1}) and metal concentration (mg L^{-1}) at equilibrium. b and q_m are the Langmuir constant (L mg^{-1}) and maximum adsorption capacity (mg g^{-1}) determined by the intercept and slope of the linear plot of C_e/q versus C_e, while n and K_f are Freundlich constants, obtained from

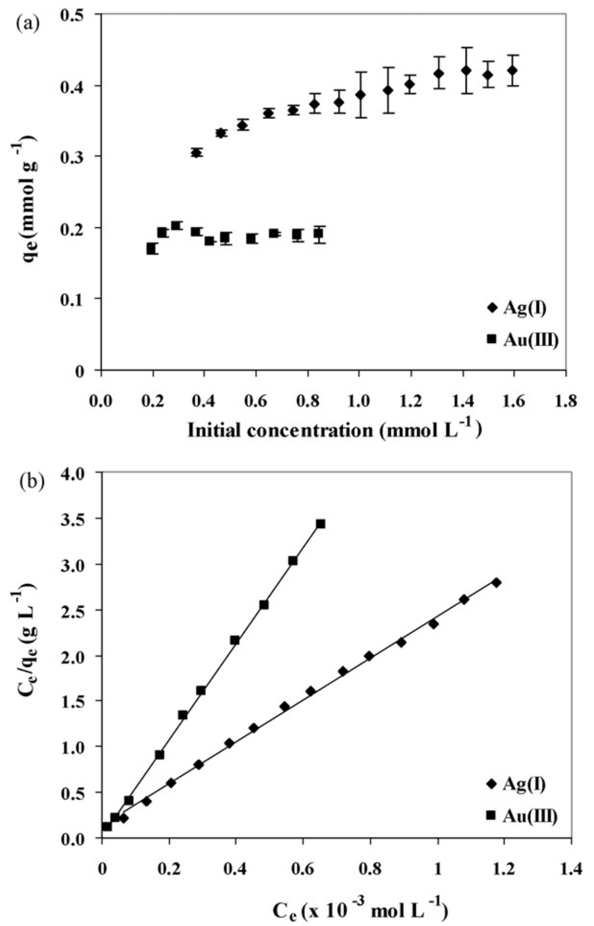

Fig. 7. (a) Adsorption isotherms and (b) Langmuir plot for the adsorption of Ag(I) and Au(III) onto AEPE-PS-MPs.

the slope and the intercept of the linear plot of log q versus log C_e.

A non-linear relation for the adsorption of the metal ions ($R^2 < 0.97$) was obtained when the experimental data was used to construct the Freundlich plot. On the other hand, the experimental data fit to the Langmuir model better ($R^2 > 0.99$) for adsorption of Ag(I) and Au(III) (Fig. 7b). The Langmuir constant (b) calculated from the linear equation is 1.69×10^4 L mol^{-1} and 6.87×10^5 L mol^{-1} for adsorption of Ag(I) and Au(III), respectively. The high values of the Langmuir constants indicate the high affinity of the adsorbent toward Ag(I) and Au(III) ions and the adsorption mechanisms of the metal ions onto the adsorbent are likely to be chemisorption via coordination with the donor site of the AEPE ligands. The maximum adsorption capacity (q_m) from the calculation is 0.44 mmol g^{-1} for Ag(I) and 0.19 mmol g^{-1} for Au(III) with monolayer coverage of metal ions onto the adsorbent.

3.2.4. *Effect of foreign ions*

In general, water contains ions other than Ag(I) and Au(III) with different concentrations depending on the source. These ions may affect the extraction efficiency of AEPE-PS-MPs due to the competition for the binding sites between Ag(I) or Au(III) ions and other ions. Certain ions can also form complex with Ag(I) or Au(III) resulting in insoluble compounds. The extraction efficiency of AEPE-PS-MPs was evaluated in the presence of foreign ions (Table 3). There was no change in the efficiency of the extraction of Ag(I) and Au(III) ions in the presence of alkali metal ions (Na^+ or K^+). On the other hand, there was a slight decrease in extraction efficiency when alkali earth metal ions (Mg^{2+} or Ca^{2+}) were present. This slight decrease is likely due to the high ionic strength of the solution containing alkali earth metal ions which could lead to a change in adsorption equilibrium. Nevertheless, the results indicate that the extraction of Ag(I) or Au(III) ions onto the AEPE-PS-MPs occurs via complex formation between the AEPE ligand and Ag(I) ions or Au(III) ions according to hard/soft- acid/base theory. The results also show that NO_3^- and SO_4^{2-} did not affect the extraction of Ag(I) and Au(III) ions. When the solutions contained Ni^{2+} and Cd^{2+}, the extraction efficiency for Ag(I) or Au(III) ions was slightly affected. The AEPE ligand shows higher selectivity toward Ag(I) and Au(III) over Cd^{2+} and Ni^{2+}.

Table 3
Extraction efficiency of AEPE-PS-MPs for Ag(I) or Au(III) in the presence of different salts in solution.

Salt	Concentration (M)	% Extraction[a]	
		Ag(I)	Au(III)
$NaNO_3$	0.1	78.5 ± 2.1	63.0 ± 1.2
	1.0	78.6 ± 3.9	54.7 ± 1.3
Na_2SO_4	0.1	77.2 ± 2.3	59.7 ± 1.5
	1.0	75.3 ± 1.2	68.6 ± 0.8
KNO_3	0.1	80.0 ± 0.7	61.1 ± 0.5
	1.0	78.2 ± 3.5	51.4 ± 1.5
$Mg(NO_3)_2$	0.1	78.8 ± 2.1	62.7 ± 1.3
	1.0	78.5 ± 2.6	64.0 ± 0.7
$Ca(NO_3)_2$	0.1	80.3 ± 0.6	60.3 ± 1.5
	1.0	78.1 ± 3.2	48.4 ± 0.9
$Cd(NO_3)_2$	5×10^{-4}	71.0 ± 4.4	68.1 ± 0.6
	5×10^{-3}	69.6 ± 0.4	63.3 ± 1.2
$Ni(NO_3)_2$	5×10^{-4}	72.9 ± 1.5	69.0 ± 1.0
	5×10^{-3}	69.4 ± 0.6	60.9 ± 0.3

Initial concentration: 0.47 mM Ag(I) and 0.20 mM Au(III).

[a] Mean ± SD ($n = 3$).

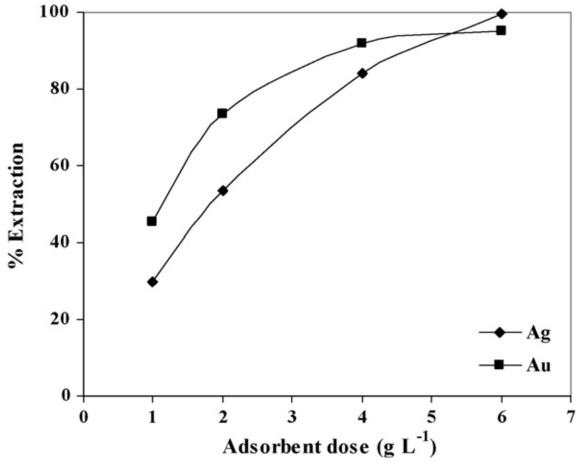

Fig. 8. Efficiency of AEPE-PS-MPs in metal ion extraction from real wastewater using different adsorbent doses. (initial concentration in wastewater: Ag(I) 145 mg L^{-1} (pH 5), Au(III) 75 mg L^{-1} (pH 4).)

3.3. *Extraction of metal ions in wastewater*

Two batches of wastewater were collected from the Gem and Jewelry Institute of Thailand (Public organization). The first batch of wastewater contained 4642 mg L^{-1} Ag, 0.2 mg L^{-1} Au, 31 mg L^{-1} Cu, 24 mg L^{-1} Zn and 12 mg L^{-1} Ni, while the second batch contained 5 mg L^{-1} Ag, 141 mg L^{-1} Au, 205 mg L^{-1} Cu, 35 mg L^{-1} Zn and 8 mg L^{-1} Ni. The first batch of wastewater was diluted 30 times and the pH was adjusted to pH 5.0 for Ag extraction. The second batch of wastewater was used for Au extraction after 2 times dilution and pH adjustment to pH 4.0. The extraction efficiency was determined as a function of adsorbent dose (Fig. 8).

Table 4
Recovery of Ag(I) from the used adsorbents using various eluent conditions.

Eluent	% Recovery
1% HNO_3	6.6 ± 0.4
5% HNO_3	9.1 ± 1.0
0.1 M thiourea in 1% HNO_3	83.6 ± 1.0
0.5 M thiourea in 1% HNO_3	85.2 ± 1.8
1.0 M thiourea in 1% HNO_3	87.3 ± 0.3
0.1 M thiourea in 5% HNO_3	84.8 ± 0.9
0.5 M thiourea in 5% HNO_3	86.7 ± 1.5
1.0 M thiourea in 5% HNO_3	90.0 ± 2.0

[a] Mean ± SD (n = 3).

Table 5
Recovery of Au(III) from the used adsorbents using various eluent conditions.

Eluent	% Recovery[a]
2% HCl	14.0 ± 0.2
10% HCl	93.0 ± 1.2
0.1 M thiourea in 2% HCl	90.9 ± 1.3
0.5 M thiourea in 2% HCl	95.4 ± 1.0
1.0 M thiourea in 2% HCl	27.7 ± 0.6
0.1 M thiourea in 10% HCl	81.3 ± 2.0
0.5 M thiourea in 10% HCl	86.1 ± 2.2
1.0 M thiourea in 10% HCl	87.0 ± 0.9

[a] Mean ± SD (n = 3).

The extraction efficiency increased with increasing adsorbent dose. The other metals in the wastewater were also simultaneously extracted by the adsorbents, but to a much smaller extent. In the first batch of wastewater, the extraction of Cu, Zn and Ni reached 17%, 3% and 26%, respectively when used the highest adsorbent dose. In the second batch, the extraction of Ag, Cu, Zn and Ni was 46%, 11%, 12% and 12%, respectively. The results indicate that AEPE-PS-MPs has higher affinity toward Ag(I) and Au(III) ions than the other metal ions under competitive conditions.

In addition, larger scale adsorption experiments were performed using 1 g of AEPE-PS-MPs in 1 L of wastewater containing 45 mg L^{-1} Ag(I). The adsorbents could extract 90% of Ag(I) from wastewater with the adsorption capacity of 40 mg g^{-1}. The capacity was in agreement with the values observed in smaller scale experiments (39–43 mg g^{-1}), indicating that the sorbents could be used in large scale treatment.

3.4. Recovery of metal ions and reuse of adsorbents

Nitric acid, hydrochloric acid and thiourea were chosen as reagents to recover the metal ions from the adsorbents. The suitable concentration for the recovery was investigated and the results are shown in Tables 4–5. The leaching of Fe and Co from the particles was also monitored. An increase in acid concentration led to an increasing amount of Fe and Co leached from the adsorbents. The leaching of Fe and Co from the adsorbents was within the range of 0.3–3.0% (w/w) and 0.2–0.8% (w/w), respectively. From the results, 1.0 M thiourea in 1% HNO_3 and 1.0 M thiourea in 2% HCl were chosen as eluents for the recovery of Ag(I) and Au(III), respectively, in respect to high recovery efficiency and low dissolution of the particles. The metal ions could also be recovered and concentrated in small volume eluent. Under the lab scale experiment, the desorption efficiency was as high as 83% when used a reduced eluent volume (3 mL) to recover Ag(I) from adsorbents. Nevertheless, the total recovery of the metals from AEPE-PS-MPs could not be achieved due to the high affinity of the AEPE ligand toward Ag(I) and Au(III).

Finally, several consecutive adsorption/desorption cycles were performed (Fig. 9). The extraction efficiency of the adsorbents decreased gradually when reused. The reduction in adsorption efficiency is attributed to the incomplete elution of the sorbed metal on the adsorbents. Therefore, the efficiency decreased each time the adsorbents were reused. After five cycles of use, the extraction efficiency decreased to 60% of the first cycle. To regenerate the adsorbents more efficiently, higher concentration of acid is recommended after several cycles of use.

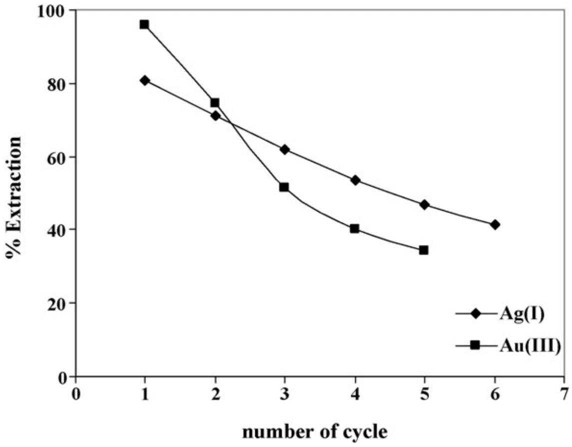

Fig. 9. Reuse of the adsorbents in metal ion extraction. (Ag(I) 50 mg L^{-1} (pH 5), Au(III) 40 mg L^{-1} (pH 4), adsorbent dose 1 g L^{-1}.)

4. Conclusion

The synthesis of magnetic particles coated by polystyrene shell and further modified with AEPE was proposed. The obtained adsorbents were characterized and used in the extraction of Ag(I) and Au(III) in solutions. The adsorbents showed a good efficiency in Ag(I) and Au(III) extraction and a high selectivity toward the target metal ions. The effects of pH and foreign ions on the extraction efficiency were studied. The adsorption of Ag(I) and Au(III) ions on the adsorbents followed Langmuir isotherm and pseudo-second order kinetics. The adsorbents showed a good potential in the extraction of Ag(I) and Au(III) from real wastewater. The recovery of Ag(I) and Au(III) could be achieved and the reuse of the adsorbents is possible.

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