

# Selective Separation and Concentration of Pd(II) from Fe(III), Co(II), Ni(II), and Cu(II) Ions Using Thiourea-Formaldehyde Resin

Nazan Muslu, Mustafa Gülfen

Department of Chemistry, Faculty of Arts and Sciences, Sakarya University, TR54187-Sakarya Turkey

Received 22 June 2010; accepted 3 October 2010

DOI 10.1002/app.33509

Published online 11 February 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Thiourea-formaldehyde (TUF), a well-known chelating resin, has been synthesized and it was used in the adsorption, selective separation, and concentration of Pd(II) ions from Fe(III), Co(II), Ni(II), and Cu(II) base metal ions. The composition of the synthesized resin was determined by elemental analysis. The effect of initial acidity/pH and the adsorption capacity for Pd(II) ions were studied by batch technique. The adsorption and separation of Pd(II) were then examined by column technique. FTIR spectra and SEM/EDS analysis were also recorded before and after the adsorption of Pd(II). The optimum pH was

found to be 4 for the adsorption. The adsorption data fitted well to the Langmuir isotherm. The maximum adsorption capacity of the TUF resin for Pd(II) ions was found to be  $31.85 \text{ mg g}^{-1}$  ( $0.300 \text{ mmol g}^{-1}$ ). Chelating mechanism was effective in the adsorption. Pd(II) ions could be separated efficiently from Fe(III), Cu(II), Ni(II), and Co(II) ions using TUF resin. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 3316–3324, 2011

**Key words:** palladium; thiourea-formaldehyde resin; chelating resin; adsorption; separation

## INTRODUCTION

Platinum group metals (PGMs) are widely used in different industries because of their specific physical and chemical properties. Palladium, a platinum group metal or a precious metal, is used extensively in jewelry, electronics, electroplating, medicine, converters, and some chemical reactions. Increasing demand and limited resources have encouraged palladium recovery from secondary metal-containing sources like electronic, industrial wastes, and separation from base metal ion solutions.<sup>1,2</sup> Solvents for extraction, ion exchangers, membrane separation, activated carbon, and chelating resins can be used to separate Pd(II) ions. Comparatively, chelating resins or ion exchangers with chelating functional groups are more preferable due to reusability and more selectivity. Based on hard-soft acid-base theory (HSAB) by Pearson,<sup>3</sup> chelating resins or ion exchangers with functional groups containing S or N donor atoms interact strongly with soft acids like precious metal ions. This condition is satisfied by Pd(II) ions. A wide range of chelating resins selective toward Pd(II) ions is known.<sup>4–11</sup>

Thiourea functional group containing N and S donor atoms or soft ligand atoms has been studied by many researchers to separate or adsorb a lot of soft metals or Pd(II) ions.<sup>6,11–20</sup> Thiourea-formaldehyde (TUF) resin can be synthesized easily with less starting material in an aqueous solution. This resin has not been focused on only the separation of palladium ions from base metal ions although there is collective metal ion sorption study.<sup>21</sup>

In the present study, thiourea-formaldehyde resin has been synthesized and it has been used in the selective separation and concentration of Pd(II) ions from a solution including Fe(III), Co(II), Ni(II), and Cu(II) base metal ions.

## EXPERIMENTAL

### Chemical reagents

All the reagents used in the experimental studies were of analytical grade and used as received. Formaldehyde (37%,  $1.09 \text{ g mL}^{-1}$ , solution) and thiourea used in the synthesis of TUF resin were purchased from Merck (Germany). A stock solution of  $1000 \text{ g mL}^{-1}$  Pd (II) was prepared by dissolving  $1.0000 \text{ g}$  of pure palladium (Merck, Germany) in  $1000 \text{ mL}$  of aqua solution including  $1 \text{ M HNO}_3$  and  $3 \text{ M HCl}$ . Fe(III), Co(II), Ni(II), and Cu(II) stock solutions were prepared from  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (Merck, Germany), respectively. The thiourea eluent

Correspondence to: Dr. M. Gülfen (mgulfen@sakarya.edu.tr).

Contract grant sponsor: Scientific Research Commission at Sakarya University; contract grant number: FBYLTEZ 2009-50-01-016.

solution was made up by dissolving 0.5 mol of thiourea in 1000 mL of 0.5M HCl. Distilled water was used in the synthesis of the resin and the preparation of the metal ion solutions.

### Apparatus

A Shimadzu AA-6701 model flame atomic absorption spectrophotometer (FAAS) (Japan) was used in the determination of the metal ion concentrations. The measurements of Pd(II) were carried out with a hollow cathode lamp (Koto, Japan) at a wavelength of 244.8 nm using an air-acetylene flame. The column studies were performed with a column of length 10 cm and inner diameter of 0.8 cm. A constant flow rate during the adsorption or elution by column technique was provided with a peristaltic pump (Masterplex, Cole-Polmer, UK). FT-IR spectra were recorded on a Shimadzu-IRPrestige-21 spectrophotometer (Japan). The elemental analysis of the TUF resin was performed with the use of a LECO CHNS 932 elemental analyzer (Leco, USA) at Tubitak in Ankara, Turkey. SEM/EDS analyses were carried out using a JEOL JSM 6060-LV type (Jeol, Japan), scanning electron microscope (SEM) equipped with an energy-dispersive spectrometer (EDS).

### Synthesis of TUF resin

The TUF resin used in the experimental studies was synthesized by well-known amine-formaldehyde reactions (Cannizzaro reaction), composed of hydroxymethylation and condensation steps.<sup>21–29</sup> The synthesis of TUF resin may result in different chemical composition and physical properties according to initial mole ratio of thiourea to formaldehyde and drying conditions.

The molar ratio of thiourea to formaldehyde was chosen as 1 : 1 in this study. It was aimed to more linear or less branched copolymer for the adsorption. In a 600-mL beaker on a magnetic stirrer, 15.2 g (0.2 mol) of thiourea, 50 mL of distilled water and 15 mL of formaldehyde (37% aqueous solution, containing 0.2 mol formaldehyde) were mixed and dissolved. pH was adjusted to between 8 and 10 by adding 1M NaOH solution. The solution was heated at 80°C for 60 min to carry out hydroxymethylation. Then, pH was adjusted to 2 by adding 1M HCl for the condensation, while the mixture was stirring and heating at 80°C. The obtained condensates were filtered and washed with distilled water and then dried at 80°C. The resin was powdered and washed with distilled water and dried again. This powdered resin was used in the all experimental studies.<sup>25–29</sup>

### Batch method adsorption studies

#### Effect of initial acidity/pH

The effect of initial acidity/pH on the adsorption of Pd(II) ions was studied in the pH range of 1–6 and at

1M and 3M HCl concentrations by stirring 0.2 g resin in 100 mL of 50 mg L<sup>-1</sup> Pd(II) solution. The adsorption studies were carried out at 25°C for 90 min. Three milliliters of the samples were taken at time intervals for the analysis of residual Pd(II) concentration in the solution. The adsorption densities ( $q_e$ , mg g<sup>-1</sup>) were calculated from the concentrations of Pd(II) in the solutions after the correction of volume [eq. (1)]

$$q_e = \frac{(C_0 - C_e)}{m} \cdot V \quad (1)$$

where  $C_0$  and  $C_e$  are initial and equilibrium concentrations of Pd(II) (mg L<sup>-1</sup>), respectively;  $m$  is the quantity of the resin (g) and  $V$  is the volume of the solution (L).

### Adsorption isotherms

To examine the Langmuir and the Freundlich adsorption isotherms, different initial concentrations were studied by placing 0.1 g TUF resin into a series of flasks containing 100 mL solutions at 30, 50, 70, and 90 mg L<sup>-1</sup> Pd(II) concentrations and at the optimized pH of 4.0. The adsorption data obtained were correlated to the Langmuir [eq. (2)] and the Freundlich isotherms [eq. (3)].<sup>30–33</sup>

$$\frac{C_e}{q_e} = \frac{1}{bQ_{\max}} + \frac{C_e}{Q_{\max}} \quad (2)$$

where  $C_e$  is the concentration of Pd(II) at equilibrium in the solution (mg L<sup>-1</sup>);  $q_e$  is the amount of Pd(II) ions adsorbed per unit weight of the adsorbent (mg g<sup>-1</sup>); the constant  $Q_{\max}$  is the theoretical saturation adsorption capacity of the monolayer (mg g<sup>-1</sup>); and  $b$  is related to the energy of adsorption (L mg<sup>-1</sup>).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

where  $C_e$  is the equilibrium concentration (mg L<sup>-1</sup>);  $q_e$  the amount of Pd(II) ions adsorbed by per gram of the resin, and  $K_F$  and  $n$  are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity, respectively. The Langmuir and the Freundlich isotherm coefficients were calculated from the graphics of the isotherms.

### Column experiments

#### Adsorption

The fixed-bed column system mainly consisted of a peristaltic pump and a glass column of length 10 cm

and inner diameter of 0.8 cm. A schematic diagram was shown in Figure 1. A 0.5 g portion of the TUF resin was packed into the column, plugged with glass wool at the bottom. A Pd(II) solution at 150 mg L<sup>-1</sup> concentration and at pH 4 was passed through the column at the flow rate of 0.5 mL min<sup>-1</sup>. Each 10 mL of the effluent solution was collected separately and Pd(II) concentrations in this effluents were determined by FAAS.

### Elution

The elution studies were also performed with same system in Figure 1. The adsorbed Pd(II) ions onto the TUF resin were eluted by 0.5M thiourea and 0.5M HCl solution. The concentrations of thiourea and HCl in the elution solution were predetermined. Through the elution, each 10 mL of the effluent solution was collected separately and Pd(II) concentrations in this effluents were determined by FAAS, again.

### Separation of Pd(II) ions from Fe(III), Ni(II), Co(II), and Cu(II)

The selective separation of Pd(II) ions from Fe(III), Co(II), Ni(II), and Cu(II) ions using the TUF resin was also studied by column technique. After 0.5 g of the TUF resin was placed into the column, a solution including 150 mg L<sup>-1</sup> concentrations for each metal ions of Pd(II), Fe(III), Co(II), Ni(II), and Cu(II) ions was passed through the column to examine the competitive adsorption. Afterwards the adsorbed metal ions were eluted by 0.5M thiourea and 0.5M HCl solution. In the adsorption or elution studies, each 10 mL

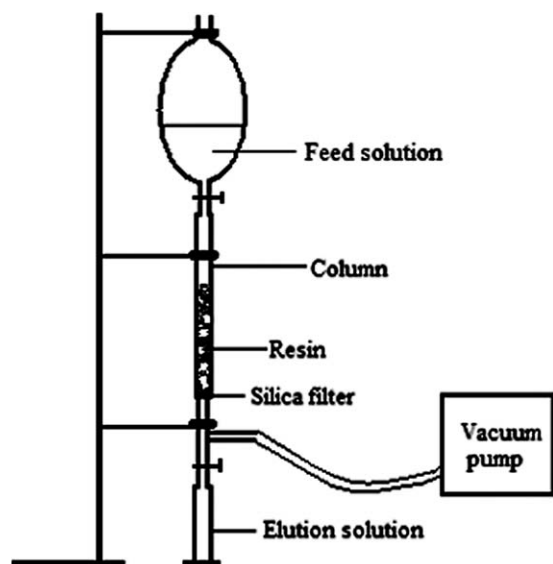


Figure 1 Schematic diagram of column study.

TABLE I  
Elemental Composition of TUF Resin

Component	C	N	H	S	O
% (w/w)	25.32	27.92	4.41	32.21	10.15

of the effluent solution was collected separately and then the metal ions were analyzed by FAAS.

Moreover the separation factors of Pd(II) ions from Fe(III), Co(II), Ni(II), and Cu(II) ions for some bed volumes were also calculated using eq. (4) from the experimental data in the column studies.<sup>21,25</sup>

$$\text{Separation factor; } K_{A/B} = \frac{(C_{A1} - C_{A2})C_{B2}}{(C_{B1} - C_{B2})C_{A2}} \quad (4)$$

where  $C_{A1}$  is the concentration of A metal ions before adsorption,  $C_{A2}$  is the concentration of A metal ions after adsorption,  $C_{B1}$  is the concentration of B metal ions before adsorption,  $C_{B2}$  is the concentration of B metal ions after adsorption.

## RESULTS AND DISCUSSION

### Characterization of TUF resin

#### Elemental analysis

The elemental analysis was carried out on the synthesized TUF resin to determine C, N, H, and S contents. The obtained results are given in Table I. N and S ligand concentrations in the resin were found as 27.92 and 32.21%(w/w), respectively. In addition, oxygen content was calculated from the difference of all the other composition. In addition oxygen content shows —C—O—C structure in the resin. It was found that the expected composition of TUF resin was obtained, nearly.

#### FT-IR analysis

The FT-IR spectra of the resin before and after the adsorption of Pd(II) ions were recorded and the obtained results are given in Figure 2. The peaks could

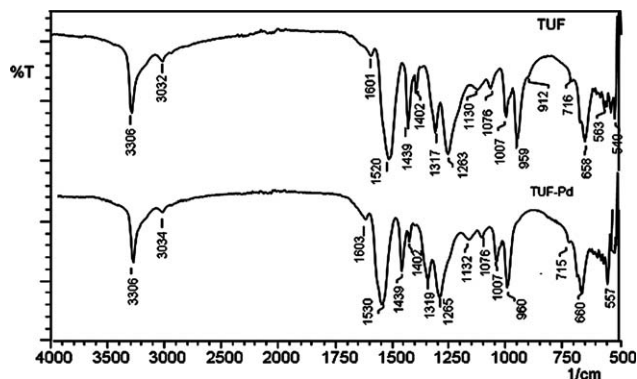


Figure 2 FT-IR spectra (Resolution: 4 cm<sup>-1</sup>, powder sample).

be analyzed as follows: the adsorption at  $3306\text{ cm}^{-1}$  shows  $>\text{N}-\text{H}$  in secondary amino,  $1603$  and  $1132\text{ cm}^{-1}$  are the peaks of  $-\text{N}-(\text{C}=\text{S})-$  group,  $1520\text{ cm}^{-1}$  is  $>\text{C}=\text{NH}$ , and  $959$  and  $540\text{ cm}^{-1}$  are  $>\text{C}-\text{S}-$ .<sup>21,23,28,29</sup> It was found that TUF resin included  $-\text{C}-\text{O}-\text{C}-$ ,  $-\text{N}-(\text{C}=\text{S})-$ ,  $>\text{C}=\text{NH}$ , and  $>\text{C}-\text{S}-$  groups. These groups show that TUF resin has complex chemical composition. Two peaks in FT-IR spectrum after Pd(II) adsorption showed changes at  $557\text{ cm}^{-1}$  as a stronger peak and at  $1530\text{ cm}^{-1}$  as the peak at higher frequency. These changes may be due to fact

that Pd(II) ions bind to  $>\text{C}=\text{NH}$  and  $>\text{C}-\text{S}-$  groups via coordinative covalent bonding. This is the indicator of the chelation of Pd(II) ions with N and S ligand atoms on the surface of the TUF resin.

#### SEM/EDS analysis

The SEM/EDS analyses of the resin before and after Pd(II) adsorption were also examined and the obtained results are given in Figures 3 and 4. It was found that the TUF resin included C, N, S, and O

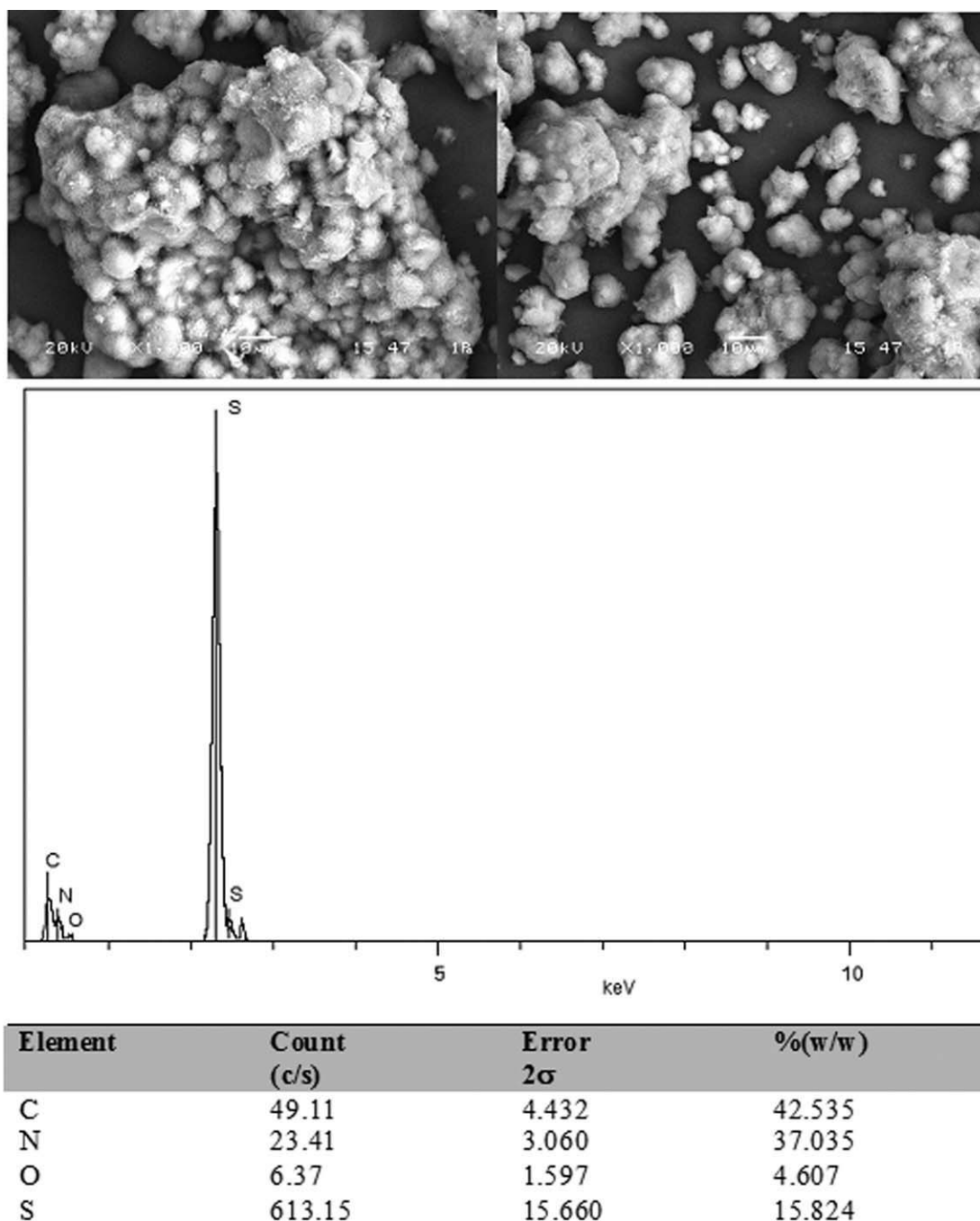
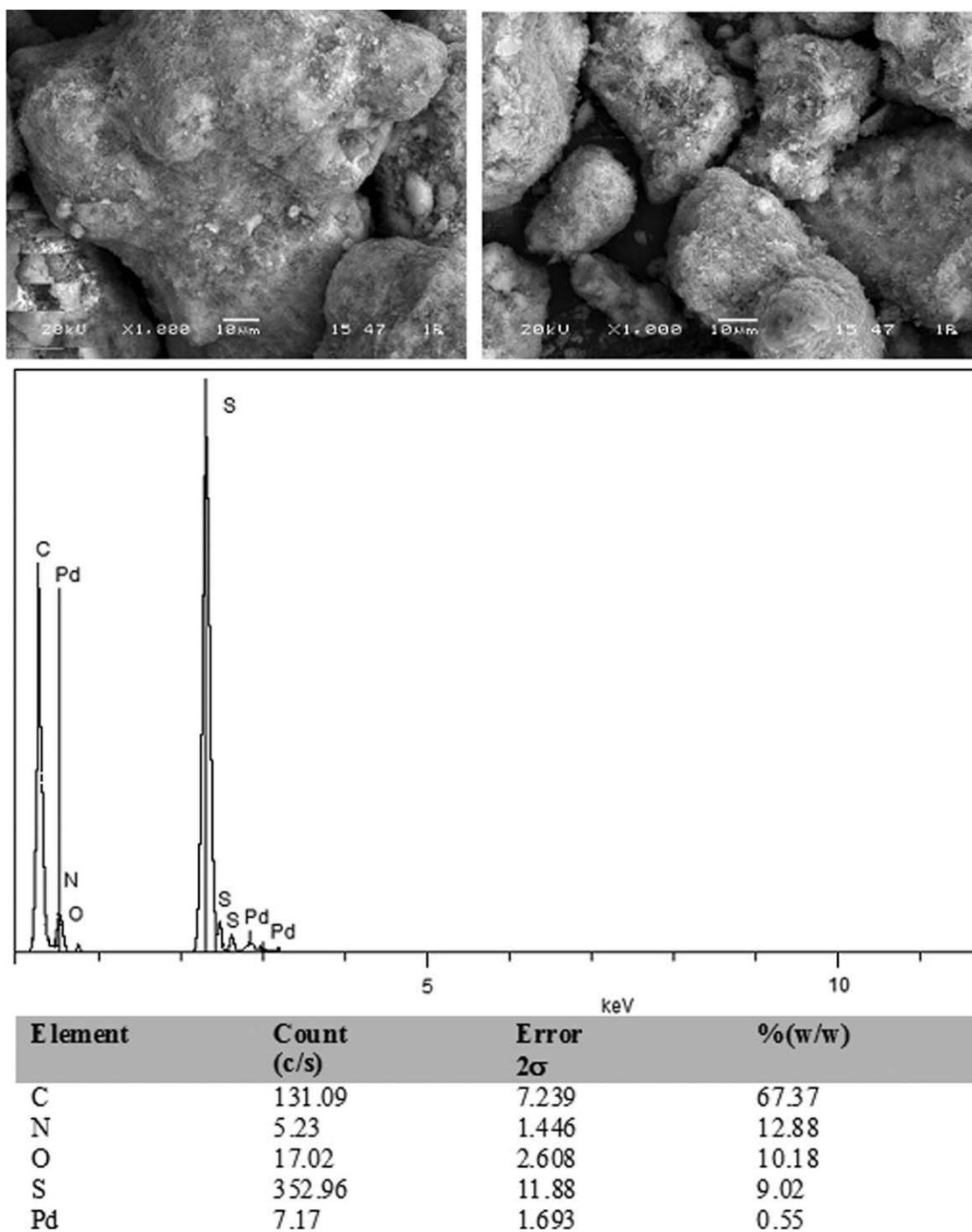


Figure 3 SEM/EDS analysis of TUF resin (20 kV,  $\times 1000$ ).





**Figure 4** SEM/EDS analysis of TUF resin after Pd(II) adsorption (20 kV,  $\times 1000$ ).

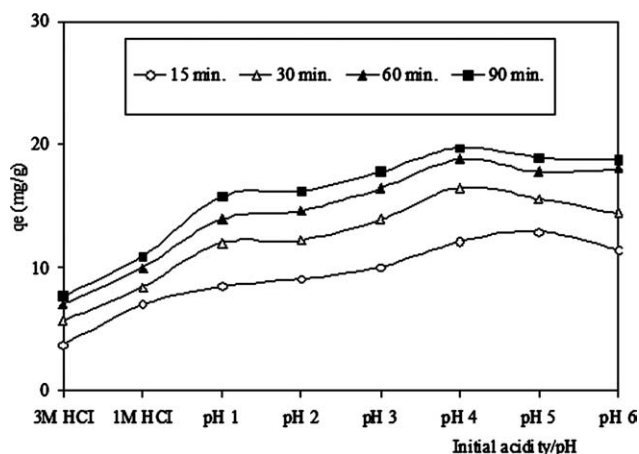
atoms before the adsorption and Pd atoms after the adsorption. SEM micrographs showed that the particles in the resin converted to bigger flocculated particles after the Pd(II) adsorption. This may be expressed by crosslinking via Pd(II) bridges during the adsorption. The EDS surface analysis was not a true chemical analysis because of the measurements on a carbon paper. It was found that the carbon content obtained by the EDS analysis was higher than the content by the elemental analysis. In addition, a

chemical analysis on the surface of TUF resin may be different according to total chemical analysis. Therefore, the EDS analyses were considered as a qualitative or semi quantitative chemical analysis.

#### Batch method adsorption studies

##### Effect of initial acidity/pH

The effect of initial acidity/pH on the adsorption of Pd(II) by TUF resin was studied in the pH range of

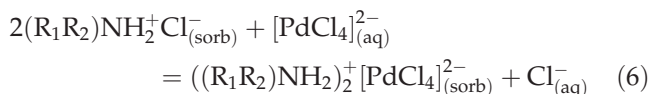
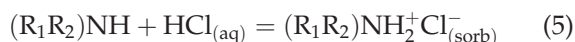


**Figure 5** Effect of initial acidity/pH on Pd(II) adsorption (0.2 g resin; 100 mL solution, 50 mg L<sup>-1</sup> Pd(II), 25°C).

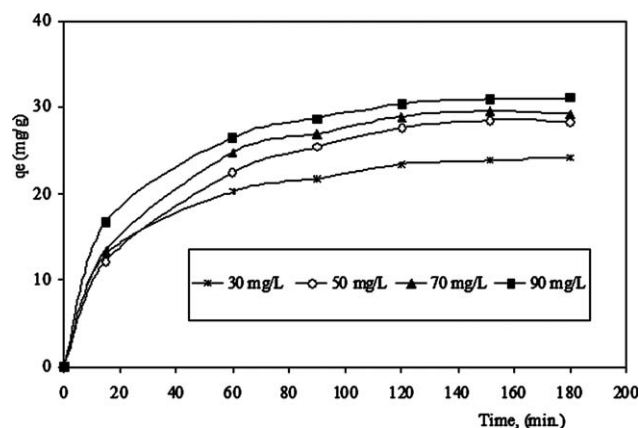
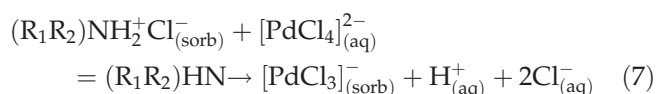
1–6 and at 1M and 3M HCl concentrations. The adsorption quantity per gram TUF resin ( $q_e$ , mg g<sup>-1</sup>) was calculated by eq. (1) for time intervals and different acidities. The results obtained are given in Figure 5. It was seen from the results that the adsorption led to equilibrium in 60 min, and in general, the pH values between 1 and 6 were effective in the adsorption. The optimum pH of 4 was selected for the later experimental studies.

Cruywagen and Kriek<sup>34</sup> studied the complexation of Pd(II) ions with chloride and hydroxide, and calculated the  $\log \beta_n$  values of  $\text{PdCl}_4^{2-}$ ,  $\text{PdCl}_3(\text{OH})^{2-}$ ,  $\text{PdCl}_2(\text{OH})_2^{2-}$ ,  $\text{PdCl}(\text{OH})_3^{2-}$ , and  $\text{Pd}(\text{OH})_4^{2-}$  as 11.51, 16.48, 20.63, 24.02, 26.23, respectively. The major fraction of the Pd-complexes in an acidic solution at 0.1M or higher chloride concentration is  $\text{PdCl}_4^{2-}$ . Above pH of 8, the other hydroxide-chloride or hydroxide complexes form.<sup>34</sup> Pd(II) adsorption onto TUF resin may be governed by ionic interaction mechanism between protonated amines  $>\text{NH}_2^+$  and chloro-palladate complexes, chelation mechanism between Pd(II) and N or S donor atoms on the resin or both two mechanism. The possible reactions are given by eqs. (5–8).<sup>6,16,33,35,36,37</sup>

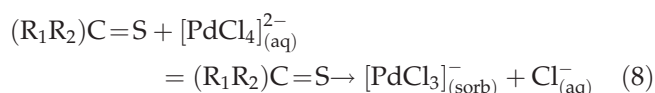
#### Ionic interaction



#### Chelation



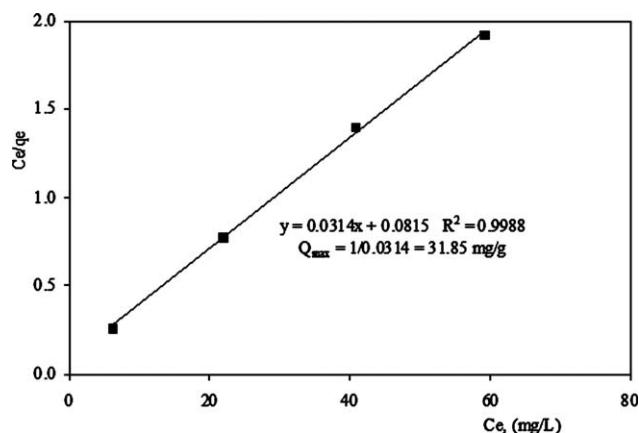
**Figure 6** Effect of concentration on Pd(II) adsorption (0.1 g resin; pH 4, 100 mL Pd(II) solution, 25°C).



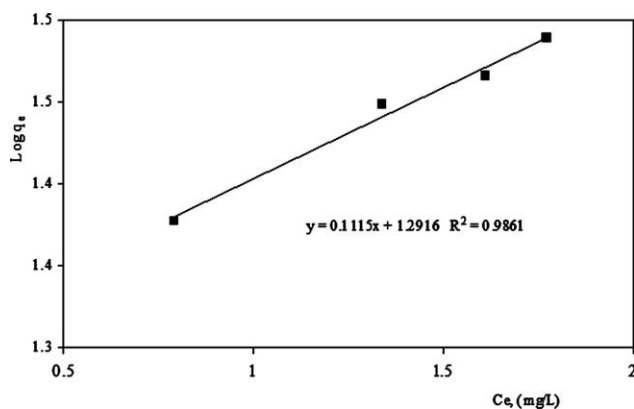
Ionic interaction mechanism occurs in the adsorption at high HCl concentrations. However, chelating mechanism is effective mechanism at high pH values. In this study, it may be suggested that chelating mechanism is effective.

#### Adsorption isotherms

For interpretation of the adsorption data, the Langmuir [eq. (2)] and the Freundlich [eq. (3)] isotherm models were used. Pd(II) solutions at different concentrations were shaken for 180 min with the TUF resin. The experimental results are given in Figure 6. The Langmuir and the Freundlich adsorption isotherms were plotted using the experimental data in Figures 7 and 8, respectively. Moreover, the Langmuir and the Freundlich constants were calculated from Figures 7 and 8 and they are given in Table II.



**Figure 7** The Langmuir isotherm (0.1 g resin; pH 4, 100 mL Pd(II) solution, 25°C).



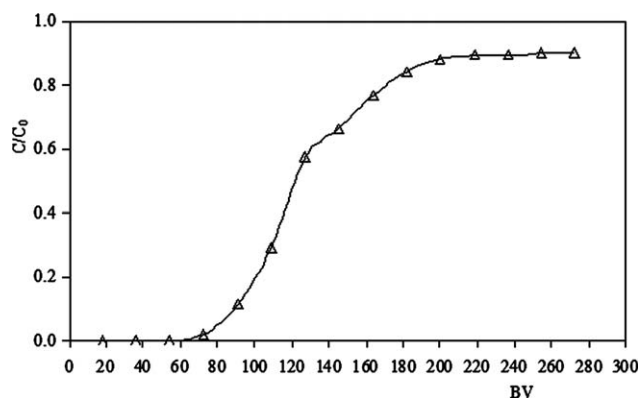
**Figure 8** The Freundlich isotherm (0.1 g resin; pH 4, 100 mL Pd(II) solution, 25°C).

As seen from Figures 7 and 8, and Table II, the  $R^2$  values (regression coefficients) indicate that the experimental data fits better to the Langmuir isotherm than the Freundlich isotherm. The theoretical saturation adsorption capacity of the TUF resin for Pd(II) ions was calculated as  $31.85 \text{ mg g}^{-1}$  ( $0.300 \text{ mmol g}^{-1}$ ). In the previous our study with melamine-formaldehyde-thiourea resin,<sup>13</sup> the adsorption capacity had been found as  $15.29 \text{ mg g}^{-1}$  ( $0.144 \text{ mmol g}^{-1}$ ). The TUF resin has more adsorption capacity for Pd(II) ions than melamine-formaldehyde-thiourea (MFT) resin. In the literature, there are many adsorbents with higher adsorption capacities for Pd(II) ions. However, TUF resin can be prepared easily from the less and cheap reagents by controlling the acidity of the synthesis reactions.

## Column studies

### Adsorption

The performance of the TUF resin under dynamic adsorption conditions was studied. Figure 9 gives the breakthrough curve for the adsorption of Pd(II) ions ( $150 \text{ mg L}^{-1}$ ; pH:4; flow rate:  $0.5 \text{ mL min}^{-1}$ ). The initial and the down flow Pd(II) concentrations were indicated by  $C_0$  and  $C$ , respectively. The breakthrough curve was obtained by plotting of  $C/C_0$  versus BV (Bed volume). It was seen that all the concentration of Pd(II) was adsorbed onto the resin, up to 60 BV and the resin began to saturate after



**Figure 9** Breakthrough curve for the adsorption of Pd(II) ions (0.5 g resin,  $150 \text{ mg L}^{-1}$  Pd(II), pH 4,  $0.5 \text{ mL min}^{-1}$  flow rate, 25°C).

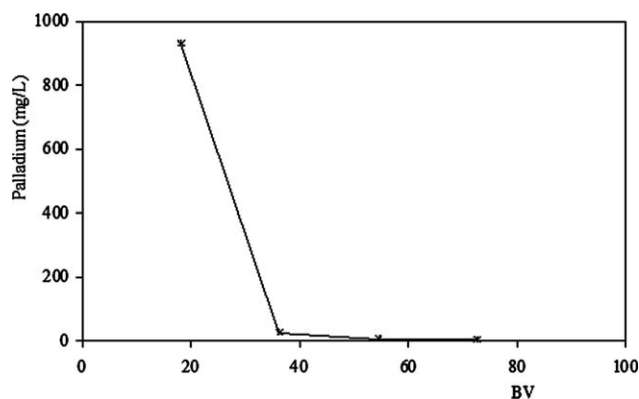
this point. This curve will continue to higher BV values in case of less Pd(II) concentration.

### Elution

After the column adsorption, the loaded Pd(II) ions were eluted by 0.5M thiourea and 0.5M HCl solution at  $0.5 \text{ mL min}^{-1}$ . The elution solution was predetermined and the optimum elution concentrations were selected. The results of the elution study are given in Figure 10. It was found that the first effluent volume of 10 mL (18.18 BV) contained about  $930 \text{ mg L}^{-1}$  Pd(II) concentration. Pd(II) ions could be concentrated from 150 to  $930 \text{ mg L}^{-1}$ . This shows that TUF resin can be used in the concentration of Pd(II) ions for analytical or hydrometallurgical processes.

### Separation of Pd(II) ions from Fe(III), Ni(II), Co(II) and Cu(II)

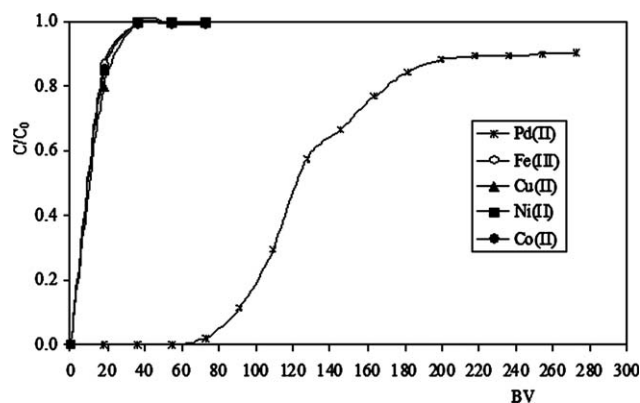
The separation of Pd(II) ions from Fe(III), Ni(II), Co(II), and Cu(II) base metal ions is important for analytical preconcentration or hydrometallurgical



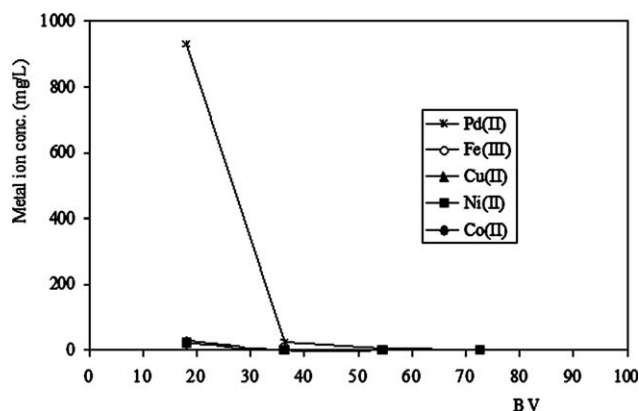
**Figure 10** Elution of Pd(II) ions (Elution solution: 0.5M thiourea and 0.5M HCl,  $0.5 \text{ mL min}^{-1}$  flow rate, 25°C).

**TABLE II**  
Coefficients of the Langmuir and Freundlich Isotherms

The Langmuir isotherm			The Freundlich isotherm		
$Q_{\max}$ ( $\text{mg g}^{-1}$ )	$b$ ( $\text{L mg}^{-1}$ )	$R^2$	$k_F$ ( $\text{mg g}^{-1}$ )	$n$	$R^2$
31.85	2.60	0.9988	19.57	8.968	0.9861



**Figure 11** Breakthrough curves of metal ions mixture (0.5 g resin, 150 mg L<sup>-1</sup> conc. for each metal ion, pH 2, 0.5 mL min<sup>-1</sup> flow rate, 25°C).



**Figure 12** Elution profiles of adsorbed metal ions (Elution solution: 0.5M thiourea and 0.5M HCl, 0.5 mL min<sup>-1</sup> flow rate, 25°C).

separation. Because palladium may occur in the matrices including iron, nickel, cobalt, and copper etc. In addition, the chloride, nitrate, and sulfate salts of these metals were also used. Especially, chloride salts was selected to compare the adsorption results of PdCl<sub>4</sub><sup>2-</sup> and FeCl<sub>4</sub><sup>-</sup> complex anions in a competitive conditions. A palladium solution may contain nitrate and sulphate anions. At the same time, this study shows whether palladium can be recovered from chloride-nitrate-sulfate media, or not. Any precipitation did not form after the mixture solution was prepared. A solution including each metal ion concentration of 150 mg L<sup>-1</sup> for Pd(II), Fe(III), Ni(II), Co(II), and Cu(II) was passed through the column. Then the adsorbed metal ions were eluted by same acidified thiourea solution (0.5M thiourea and 0.5M HCl). The adsorption and elution profiles for the separation of Pd(II) ions are given in Figures 11 and 12, respectively.

After one adsorption-elution cycle, Pd(II) ions were concentrated from 150 to 930 mg L<sup>-1</sup>, whereas the other base metal ions were diluted from 150 to 20–40 mg L<sup>-1</sup>. In addition, the column capacities of Pd(II), Fe(III), Cu(II), Ni(II), and Co(II) were calculated as 19.35, 0.406, 0.606, 0.466, and 0.466 mg g<sup>-1</sup> in the competitive conditions, respectively.

In addition the separation factors of Pd(II) ions from Fe(III), Co(II), Ni(II), and Cu(II) ions were also calculated using eq. (4)<sup>21,25</sup> and the obtained results are given in Table III.

According to the column results, it was found that TUF resin could be used effectively in the separation of Pd(II) ions from Fe(III), Ni(II), Cu(II), and Co(II) ions and chloride-nitrate-sulfate media. It was also found that PdCl<sub>4</sub><sup>-</sup> anions were more adsorbed than FeCl<sub>4</sub><sup>-</sup> anions. Both anionic complexes may bind via >NH<sub>2</sub><sup>+</sup>MCl<sub>4</sub><sup>n-</sup> ionic interaction. However, the results showed that PdCl<sub>4</sub><sup>2-</sup> was more and more adsorbed because of the chelation of Pd(II). On the other hand, Fe(III) ions did not show an important difference from Cu(II), Ni(II), and Co(II) divalent ions. This result may be due to the fact that Fe(III), Cu(II), Ni(II), or Co(II) hard acid metal ions show less chelation effect toward to N and S soft ligand atoms on the surface of TUF resin.

Moreover palladium separation by TUF resin can be applicable to other solutions including other base metal ions or other hard/borderline acid metal ions suggested by Pearson,<sup>3</sup> i.e., Al(III), Ca(II) and Zn(II) etc. However, soft metal ions such as Ag(I) and Hg(II) ions may be competitive with Pd(II) ions.

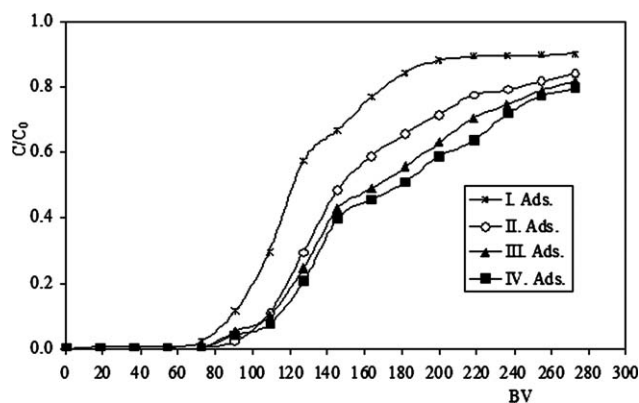
#### Reusability of TUF resin

The stability of the TUF resin was also examined at similar column conditions. The concentration profiles for the adsorption-elution cycles with Pd(II) ions are presented in Figures 13 and 14, respectively. In general, similar adsorption and elution values were obtained in the re-usage of the resin. TUF resin

**TABLE III**  
Separation Factors of Pd(II) from Fe(III), Co(II), Ni(II), and Cu(II)

BV	18	36	55	73	91	109	127	145	164	182	200	218	236	255	273
K <sub>Pd/Fe</sub>	10858	164,901	164,901	4851	775	239	74	50	30	19	14	12	12	11	11
K <sub>Pd/Cu</sub>	6663	248,184	248,184	7301	1166	359	111	75	45	28	20	18	18	17	17
K <sub>Pd/Ni</sub>	9197	248,184	248,184	7301	1166	359	111	75	45	28	20	18	18	17	17
K <sub>Pd/Co</sub>	9691	248,184	248,184	7301	1166	359	111	75	45	28	20	18	18	17	17





**Figure 13** Adsorption in the cycling tests (0.5 g resin, 150 mg L<sup>-1</sup> Pd(II), pH 4, 0.5 mL min<sup>-1</sup> flow rate, 25°C).

can be re-used or regenerated efficiently in the selective separation of Pd(II) ions.

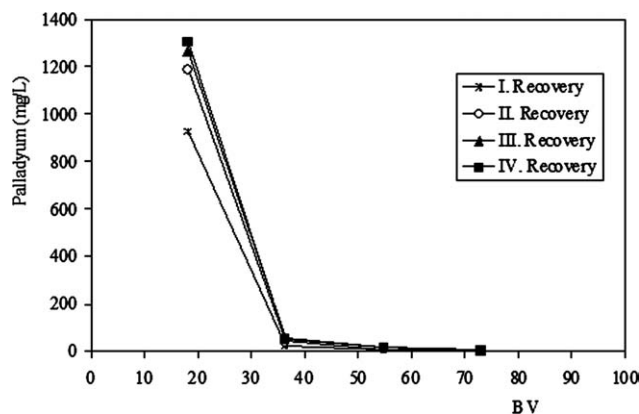
### CONCLUSIONS

TUF resin was synthesized and examined in the selective separation and concentration of Pd(II) ions from Fe(III), Co(II), Ni(II), and Cu(II) base metal ions. Some important results were summarized following; The optimum pH of 4 was found for the adsorption of Pd(II) ions. The adsorption of Pd(II) ions can be studied in the pH range of 1–6. SEM micrographs showed that bigger particles occurred during the adsorption via palladium Pd(II) coordination. The adsorption data were found to fit well to the Langmuir isotherm. Palladium adsorption capacity of 31.85 mg g<sup>-1</sup> (0.300 mmol g<sup>-1</sup>) was achieved using the TUF resin. Chelating mechanism is effective in the adsorption of Pd(II) ions. In conclusion, Pd(II) ions can be concentrated and sep-

arated efficiently from Fe(III), Cu(II), Ni(II), and Co(II) using TUF resin.

### References

1. Rao C. R. M.; Reddi, G. S. *Trends Anal Chem* 2000, 19, 565.
2. Wołowicz, A. Z.; Hubicki, Z. *Hydrometallurgy* 2009, 98, 206.
3. Pearson, G. R. *J Am Chem Soc* 1963, 85, 3533.
4. Hubicki, Z.; Wawrzekiewicz, M.; Wołowicz, A. *Chem Anal (Warsaw)* 2008, 53, 759.
5. Shah, R.; Devi, S. *Anal Chim Acta* 1997, 341, 217.
6. Hubicki, Z.; Wołowicz, A. *J Hazard Mater* 2009, 164, 1414.
7. Huang, Z. J.; Wang, X. G.; Yang, Z. Q. *Anal Lett* 2010, 43, 876.
8. Huang, Z. J.; Chang, J.; Feng, S. P.; Yang, Z. Q. *Asian J Chem* 2010, 22, 2018.
9. Hassanien, M. M. *Microchim Acta* 2009, 167, 81.
10. Wołowicz, A.; Hubicki, Z. *Chem Eng J* 2009, 152, 72.
11. Zhou, L. M.; Liu, J. H.; Liu, Z. R. *J Hazard Mater* 2009, 172, 439.
12. Zhou, L. M.; Wang, Y. P.; Liu, Z. R.; Huang, Q. W. *J Hazard Mater* 2009, 161, 995.
13. Birinci, E.; Gülfen, M.; Aydın, A. O. *Hydrometallurgy* 2009, 95, 15.
14. Turanov, A. N.; Karandashev, V. K.; Proshin, A. N. *Solvent Extr Ion Exc* 2008, 26, 360.
15. Tikhomirova, V. I.; Desyatova, T. A.; Suvorova, V. A. *Russ J Appl Chem* 2007, 80, 1636.
16. Hubicki, Z.; Leszczynska, M.; Lodyga B.; Lodyga, A. *Desalination* 2007, 207, 80.
17. Guibal, E.; Sweeney, N. V.; Vincent, T.; Tobin, J. M. *React Funct Polym* 2002, 50, 149.
18. Guibal, E.; Sweeney, N. V.; Zikan, M. C.; Vincent, T.; Tobin, J. M. *Int J Biol Macromol* 2001, 28, 401.
19. Liu, P.; Pu, Q.; Su, Z. *Analyst* 2000, 125, 147.
20. Zuo, G.; Muhammad, M. *React Polym* 1995, 24, 165.
21. Ni, C. H.; Yi, C. H.; Feng, Z. Y. *J Appl Polym Sci* 2001, 82, 3127.
22. Christjanson, P.; Pehk, T.; Siimer, K. *J Appl Polym Sci* 2006, 100, 1673.
23. Nalwa, H. S.; Vasudevan, P. *Mater Res Bull* 1983, 18, 897.
24. Aydın, A.; Imamoglu, M.; Gülfen, M. *J Appl Polym Sci* 2008, 107, 1201.
25. Yirikoglu, H.; Gülfen, M. *Sep Sci Technol* 2008, 43, 376.
26. Ertan, E.; Gülfen, M. *J Appl Polym Sci* 2009, 111, 2798.
27. Kırıcı, S.; Gülfen, M.; Aydın, A. O. *Sep Sci Technol* 2009, 44, 1869.
28. Çelik, Z.; Gülfen, M.; Aydın, A. O. *J Hazard Mater* 2010, 174, 556.
29. Ahamad, T.; Kumar, V.; Nishat, N. *Polym Int* 2006, 55, 1398.
30. Farag, B.; Soliman, M. H.; Abdel-Rasoul, O. S.; El-Shahawi, M. S. *Anal Chim Acta* 2007, 601, 218.
31. Moawed, E. A. *Anal Chim Acta* 2006, 580, 263.
32. Daniel, S.; Rao, P. P.; Rao, T. P. *Anal Chim Acta* 2005, 536, 197.
33. Wołowicz, A.; Hubicki, Z. *Solvent Extract Ion Exc* 2010, 28, 124.
34. Cruywagen, J. J.; Kriek, R. J. *J Coord Chem* 2007, 60, 439.
35. Guibal, E.; Ruiz, M.; Vincent, T.; Sastre, A.; Navarro-Mendoza, R.; *Sep Sci Technol* 2001, 36, 1017.
36. Ramesh, H.; Hasegawa, W.; Sugimoto, T. M.; Ueda, K. *Biore-source Technol* 2008, 99, 3801.
37. van Middlesworth, J. M.; Wood, S. A. *Geochim Cosmochim Acta* 1999, 63, 1751.



**Figure 14** Elution in the cycling tests (Elution solution: 0.5M thiourea and 0.5M HCl, 0.5 mL min<sup>-1</sup> flow rate, 25°C).