

# Preparation of Adsorbent for Palladium Ions by Amination of Acrylonitrile Grafted Polypropylene Nonwoven Fabrics

Jianhua Zu,<sup>1</sup> Shiqiang He,<sup>1</sup> Young Chang Nho,<sup>2</sup> Jeun Joon Pyo,<sup>2</sup> Feng Yan<sup>1</sup>

<sup>1</sup>Shanghai Applied Radiation Institute, Shanghai University, Shanghai 201800, China

<sup>2</sup>Korea Atomic Energy Research Institute, Daejeon 305-600, South Korea

Received 13 September 2008; accepted 18 May 2009

DOI 10.1002/app.30795

Published online 4 January 2010 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A new chelating fabrics are synthesized by radiation induced grafting of acrylonitrile (AN) onto polypropylene nonwoven fabrics (PP fabrics) and subsequent conversion of cyano to an imine by reaction with ethylene diimine (EDA). Influence of various parameters such as initial concentration, pH and adsorption time on the adsorption amount for palladium ions was investigated. It was found that adsorbent achieved excellent adsorption performance in

palladium ion removal in the pH range of 1.88–5.70. The adsorption amount of ions increased with shaking time and initial concentration of palladium ions. The grafted and aminated fabrics were characterized by FT-IR, TGA and SEM. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1414–1421, 2010

**Key words:** polypropylene; radiation grafting; acrylonitrile; ethylene diimine; palladium ions

## INTRODUCTION

The recovery of palladium is a concern work because of its rareness and usefulness. As a matter fact, many chemists have carried out a great deal of work in this domain and have used many separation methods including chemical precipitation,<sup>1</sup> extraction,<sup>2</sup> ion exchange,<sup>3</sup> ultra filtration<sup>4</sup> and adsorption<sup>5</sup> to treat palladium ion solutions. Comparably, chelating adsorbents have been widely applied owing to their effective and low cost cleaning processes. Although adsorbent developed from natural polymers may be cost-effective, they are generally less physically and chemically stable than adsorbents prepared from synthetic polymers.<sup>6</sup> Synthetic chelating adsorbents with immobilized functional groups have flexibility to be prepared by selecting ligand-containing compounds as functional groups and polymer substrate as the carrier for functional groups. Primary imine and ethylenediimine<sup>7</sup> 3-aminopropyl imidazol,<sup>8</sup> carboxymethylchitin and carboxymethylchitosan,<sup>9</sup> sulfuric acid,<sup>10</sup> etc have been selected as functional compounds to prepare the adsorbent for recovery of trace of palladium ions in aqueous solution. The high content of nitrogen, oxygen, or sulfur atoms in these adsorbents allowed

uptake of palladium ions through chelation mechanism.

Radiation-induced grafting is an improving approach to synthesize chelating polymer adsorbents because of its uniform creation of radical sites on the polymer matrix and its moderate reaction condition. As acrylonitrile (AN) contains a nitrile group which can be easily converted to imine chelating functional group, AN has been extensively investigated in grafting copolymer field by means of chemical,<sup>8</sup> microwave,<sup>11</sup> gamma-rays<sup>12</sup> or electron beam<sup>13</sup> initiator. For instance, Kumar et al.<sup>13</sup> synthesized grafted adsorbent by post irradiation grafting of AN onto a nonwoven thermally bonded polypropylene (PP) sheet using 2 MeV electron beam accelerator and chemically modifying a nitrile group to an amidoxime group. This adsorbent was tested for its suitability as an adsorbent for removal of heavy metal ions such as Co<sup>2+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>, Cd<sup>2+</sup> and various experimental variables on the grafting extent was investigated; Nalan et al.<sup>14</sup> synthesized fibrous adsorbents by radiation-induced graft polymerization of AN onto PP fibers and followed by functionalization of nitrile groups to amidoxime groups with hydroxylimine. The adsorbents exhibited a high grafting rate and the adsorption tests proved the performance of these fibrous adsorbents as a promising material for uranium recovery from seawater; A chelating membrane<sup>15</sup> has been synthesized by direct radiation grafting of AN and vinyl acetate in a binary monomers mixture onto low density polyethylene. Its sorption capacity and selectivity towards different metal ions such as Cu<sup>2+</sup>, Co<sup>2+</sup>,

Correspondence to: Y. C. Nho (ycnho@kaeri.re.kr).

Contract grant sponsor: Shanghai Leading Academic Disciplines; contract grant number: S30109.

Fe<sup>3+</sup>, Pb<sup>2+</sup>, Sr<sup>2+</sup>, Cd<sup>2+</sup>, and Li<sup>+</sup> were investigated. But there was not a precedent article narrating functional PP-g-AN adsorbent to recovery of palladium ions from aqueous solution.

Therefore, in this present work, chelating fabrics were synthesized by radiation-induced grafting of AN onto PP nonwoven fabrics and subsequent conversion of nitrile groups in grafted AN to an imine by reaction with EDA. In succession this chelating fabrics adsorbent was used for the recovery of the palladium ions from aqueous solution for the first time. Influence of adsorption time, pH, initial concentration and functionalized PP fabrics concentration in solution on the adsorption features for palladium ions was investigated.

EXPERIMENTAL

Materials and reagents

PP fabrics were supplied by Nonwoven, Korea. AN was obtained from Shaowha Chemical Reagent Co. Ltd., Japan. PdCl<sub>2</sub> was obtained from Merck. Other chemicals, such as *N,N*-dimethylformamide (DMF) and ethylene diimine (EDA) and acid were analysis grade and used as received.

Equipments and method of characterization

Accelerator (ELV-4, Samsung Company) was used to irradiate PP fabrics. The ungrafted, grafted and aminated grafted fabrics were characterized by studying their FTIR spectroscopy (Nicolet IR 200). The thermograms were obtained under a nitrogen atmosphere at a uniform heating rate of 10°C /min from

ambient temperature to 800°C with STA-409PC (NETZSCH). The concentration of metal ion was measured by ICP (Plasma-400, Thermo Elemental). The pH value of the solution was determined with pH meter (PHB-4, Shanghai Leici Instrument Scientific Co. Ltd.).

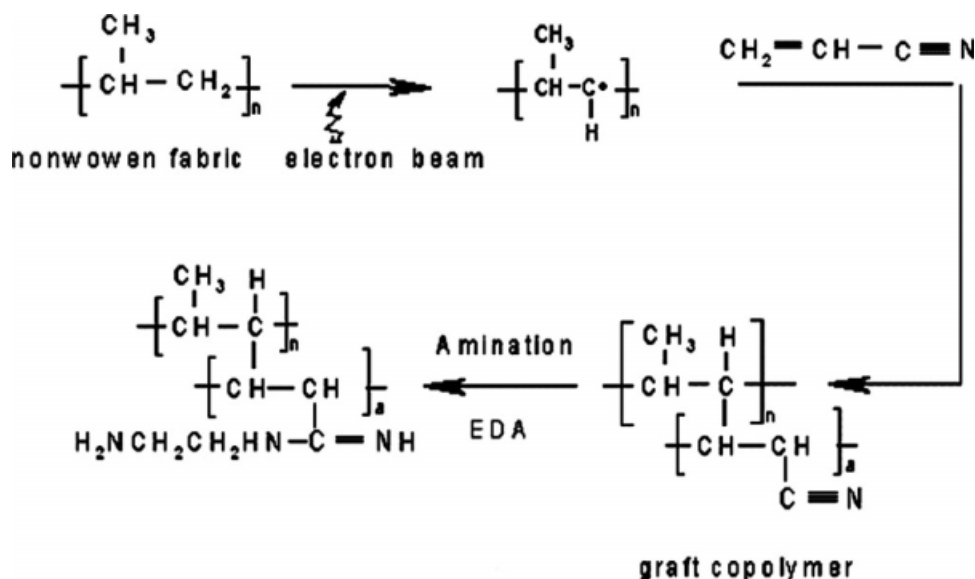
Preparation of chelating fabrics

The preparation of chelating fabrics involved two steps: (1) preparation of graft copolymer by radiation-induced polymerization, (2) subsequent amination of graft copolymer by reacting with EDA. The preparation process is illustrated in Scheme 1. The PP fabrics were filled with pure nitrogen, sealed and irradiated in electron beam source at ambient temperature. Then the irradiated fabrics were immediately reacted with AN in DMF solvent. The grafted fabrics were taken out and washed with DMF and then immersed in DMF for 24 h at 80°C for several times to eliminate the unreacted monomer and the homopolymer on the surface of fabrics. The grafting products were dried in a vacuum oven at 40°C for 12 h. The grafting yield could be obtained using the following formula:

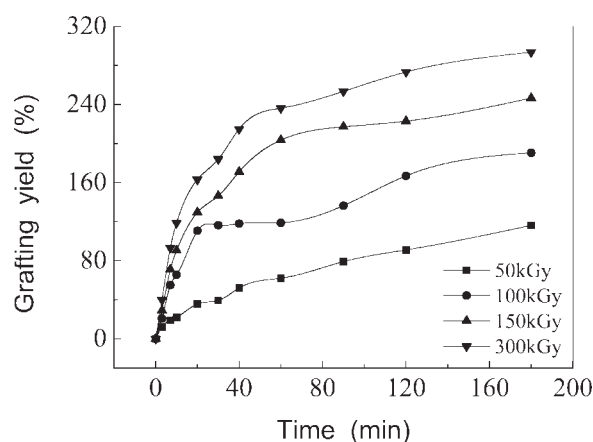
$$\text{Grafting yield} = \frac{W_g - W_0}{W_0} \times 100 \quad (1)$$

where  $W_g$  and  $W_0$  are the weights of PP-g-AN and ungrafted PP fabrics, respectively.

The resultant nitrile groups were converted into an imine groups by immersing the AN-grafted PP fabrics in 100% EDA solutions at a constant temperature for some hours. Subsequently, the PP fabrics were repeatedly washed with deionized water. The



Scheme 1 Preparation of grafting fabrics and modified with EDA.



**Figure 1** Influence of reaction time at different irradiation dose on grafting yield. Grafting conditions: AN concentration in DMF, 60% (v/v); grafting temperature, 60°C; reaction time, 3 h.

conversion ratio is determined by:

$$\text{Conversion ratio \%} = \frac{W_a - W_g}{W_g - W_0} \times \frac{53.06}{60.11} \times 100 \quad (2)$$

where  $W_a$  is the weight of amination PP-g-AN fabrics, 53.06 and 60.11 are the molecular weight of AN and EDA, respectively.

### Adsorption experiments

30 mg dried chelating fabrics were added in 100 ml palladium ion solution adjusted to the desired pH. The mixture was stirred throughout the experiment. The initial and final palladium ion concentration in solution was analyzed with an inductively coupled plasma-optical emission spectrometer (ICP). The adsorption amount is calculated as follows:

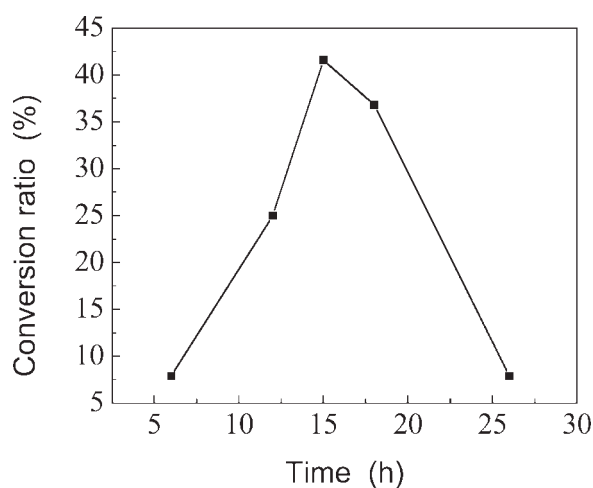
$$Q = \frac{(C_0 - C_e) \cdot V}{W} \quad (3)$$

where  $Q$  is the adsorption amount (mg/g),  $W$  is the weight of the chelating adsorbent fabrics (g),  $V$  is the volume of solution (l), and  $C_0$  and  $C_e$  are the initial and equilibrium palladium ions concentrations (mg/L), respectively.

## RESULTS AND DISCUSSIONS

### Influence of grafting time at different irradiation dose on grafting yield

As revealed in Figure 1, in the whole range of grafting reaction time, the grafting yield increased with the increase in the irradiation dose with the range of 50–300 kGy. In the initial reaction stage, the grafting rate increased with the increase of irradiation dose. This was due to the higher formation of free radicals



**Figure 2** Influence of amination time on conversion ratio when PP-g-AN fabrics react with 100% EDA. Temperature: 110°C; grafting yield of PP-g-AN fabrics: 86%.

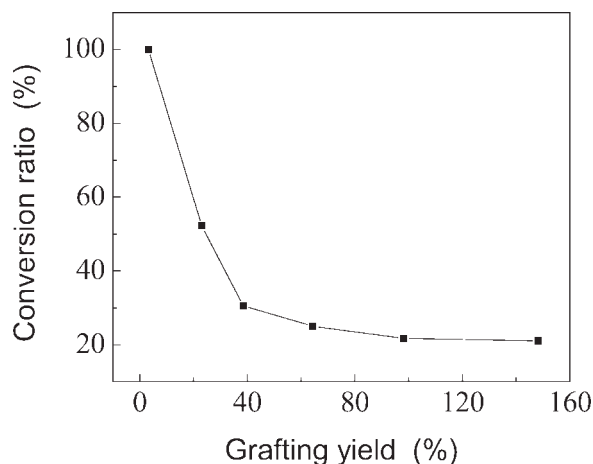
in the PP substrate with the irradiation dose, which subsequently led to a higher grafting yield.

### Influence of amination time on conversion ratio

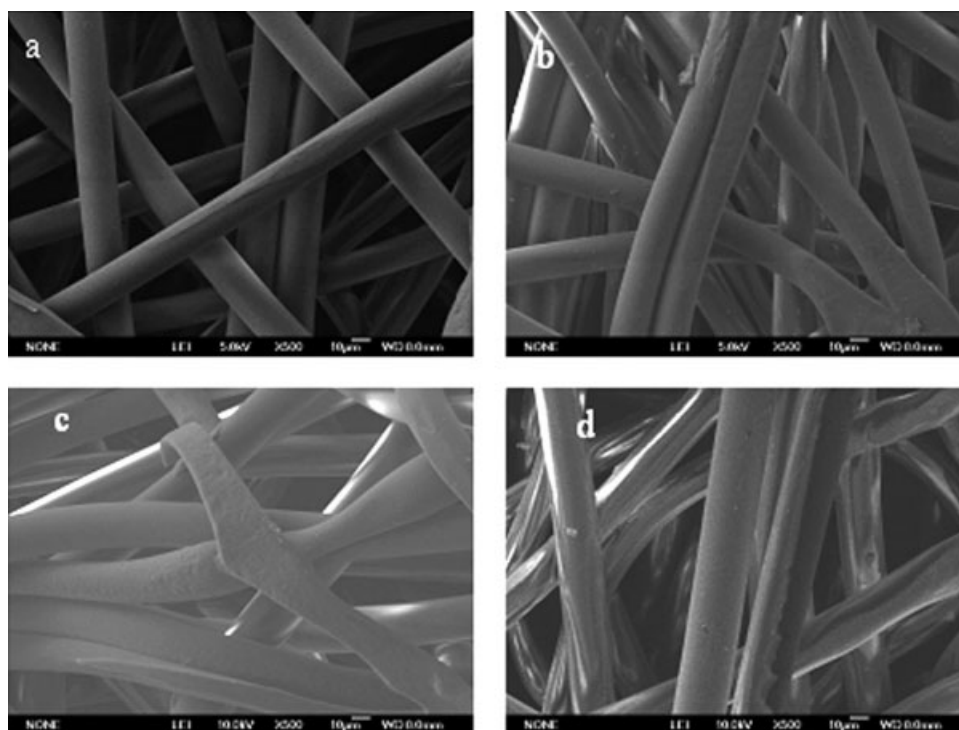
It could be seen in Figure 2, the conversion ratio increased with amination time reaching the maximum value at about 15 h and then decreased with prolonging of the time. The highest conversion ratio was 41.6%. It was assumed that this decrease might be attributed to the dissolution of the grafted PP-g-AN fabrics into EDA solvent.

### Influence of grafting yield on conversion ratio

The curve of the conversion ratio versus the grafting yield was exhibited in Figure 3. It was obvious that the conversion ratio decreased with increasing



**Figure 3** Influence of grafting yield on conversion ratio when PP-g-AN fabrics react with EDA. Temperature: 90°C; concentration of EDA: 100%; reaction time: 12 h.



**Figure 4** SEM images of ungrafted PP (a), PP-g-AN (b, c), and amination of PP-g-AN (d). (b) grafting yield: 21.96%; (c) grafting yield: 91.1%; (d) conversion ratio: 30%. Grafting conditions: monomer concentration: 40% (solvent, DMF); temperature: 60°C; reaction time: 40 min. Amination conditions: concentration of EDA: 100%; temperature: 80°C; reaction time: 12 h.

grafting yield, then leveled off after 64.4% grafting yield. This decrease was likely to the reason that the grafted chains on the surface of PP-g-AN fabrics become more dense with increasing grafting yield, which reduce the diffusion rate of EDA molecules inside the substrate matrix.

### Characterization of the samples

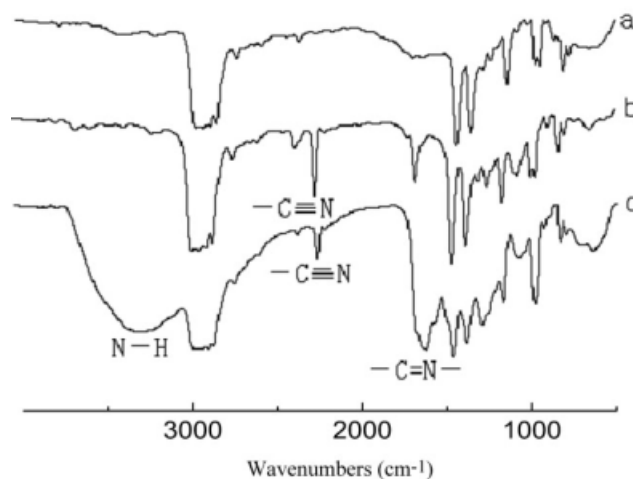
#### SEM

Figure 4 exhibited the surface morphology of a ungrafted PP fabric (a), a 22.0% AN-grafted PP fabric (b), a 91.1% AN-grafted PP fabric (c) and amination of PP-g-AN (d). The diameter of fabrics increased as a result of the grafting of AN onto PP and subsequent amination of grafted AN with EDA. This increase was attributed to the growth of graft chains on the surface of fabrics. And it was obvious that the surface of the grafted and amination samples became rougher.

#### FTIR

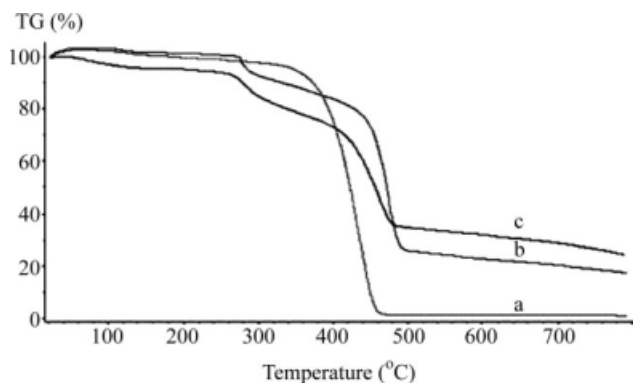
Figure 5 illustrated the FTIR spectra of the ungrafted PP, PP-g-AN, and amination of PP-g-AN. In the IR spectrum of the PP-g-AN fabric, a characteristic peak at 2230  $\text{cm}^{-1}$  due to  $-\text{C}\equiv\text{N}$  group stretching of poly-AN was observed. On the other hand, no such peak was observed in IR spectrum of the ungrafted

PP fabric. This result clearly indicated that the introduction of poly-AN onto PP fabric produced a grafted fabric. In the IR spectrum of the amination of PP-g-AN fabric, a characteristic peak at 3450  $\text{cm}^{-1}$  and 1598  $\text{cm}^{-1}$  due to  $\text{N}-\text{H}$  and  $-\text{C}=\text{N}-$  group



**Figure 5** FTIR spectra of ungrafted PP (a), PP-g-AN (b), and amination of PP-g-AN (c). (b) grafting yield: 76.7%; (c) conversion ratio: 30%. Grafting conditions: monomer concentration: 40% (solvent, DMF); temperature: 60°C; reaction time: 40 min. Amination conditions: concentration of EDA: 100%; temperature: 80°C; reaction time: 12 h.





**Figure 6** TGA curves of ungrafted PP (a), PP-g-AN (b), and amination of PP-g-AN (c). (b) grafting yield: 113%; (c) conversion ratio: 42%. Grafting conditions: monomer concentration: 60% (solvent, DMF); temperature: 60°C; reaction time: 3 h. Amination conditions: concentration of EDA: 100%; temperature: 80°C; reaction time: 12 h.

stretching was observed, respectively; Moreover, the peak at  $2230\text{ cm}^{-1}$  due to  $\text{—C}\equiv\text{N}$  group stretching became weaker. These results also clearly indicated the introduction of imine group into the PP-g-AN fabric chains.

#### TGA

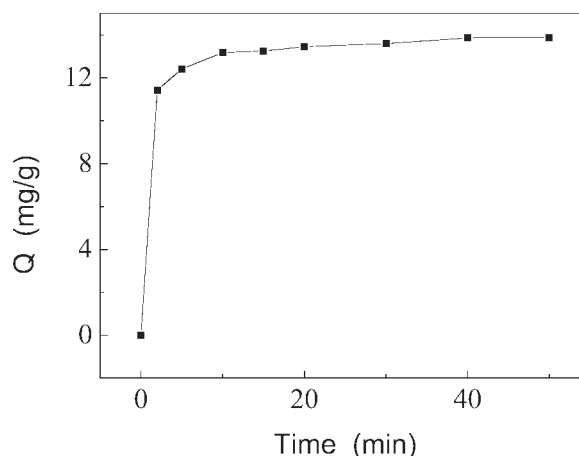
Figure 6 illustrated TGA curves of the (a) ungrafted PP, (b) 113% PP-g-AN, (c) amination of PP-g-AN. A considerable change in the thermal behavior of the PP fabrics occurred upon grafting and subsequent amination. In Figure 6(c), weight loss was observed at three different temperature regions. The first weight loss at 44°C could be interpreted as the loss of moisture on the surface; the second weight loss at 244°C, as the deimine of adsorbent fabrics; and the third weight loss at 317°C for all TGA curves attributes to the loss of PP substrate. Furthermore, in Figure 6(b), the weight loss at 262°C could be aroused from the loss of nitrile groups. These results clearly suggested that the ungrafted PP fabrics took the highest thermal stability among these materials, moreover, the amination of PP-g-AN had excellent thermal stability up to 240°C.

#### Studies on adsorption features of chelating fabrics

The selection of appropriate adsorption conditions for adsorbent is very important to the adsorption process. In this study, some factors affecting the treatment process for palladium ions were investigated.

#### Influence of adsorption time

The capacity of the chelating fabrics is decided by amount of imine groups on the fabrics which pro-



**Figure 7** Influence of adsorption time on adsorption amount of the  $\text{Pd}^{2+}$  by PP-g-AN functionalized fabrics. Initial concentration of palladium ions: 48 ppm; temperature: 35°C; pH: 3.3 grafting yield: 113%; conversion ratio: 42%.

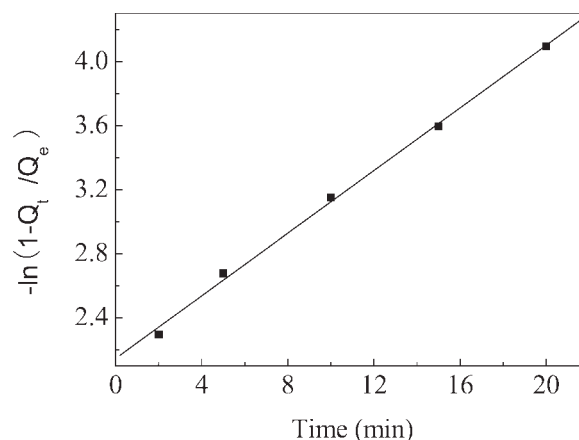
vide additional binding sites for the palladium ions<sup>16</sup> and adsorption conditions. Figure 7 indicated the adsorption capacity of palladium ions increased with the adsorption time during the first 15 min, and then leveled off toward the equilibrium adsorption capacity.

According to the adsorption equation<sup>17</sup>

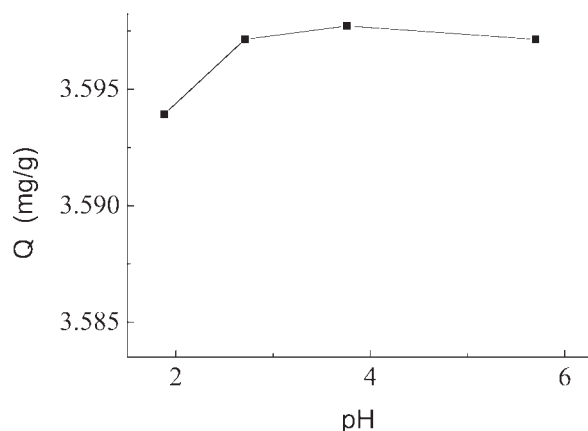
$$-\ln\left(1 - \frac{Q_t}{Q_e}\right) = kt + c \quad (4)$$

where,  $Q_t$  and  $Q_e$  are the adsorption amount at time  $t$  and equilibrium, respectively;  $t$  is the adsorption time,  $k$  is the adsorption rate constant, and  $c$  is a constant.

Figure 8 unfolded the drawing of  $-\ln(1 - Q_t/Q_e)$  versus  $t$ . The curve is linear, and indicates the adsorption behavior fits Langmuir isotherm. From the slope of the line, it was shown that the



**Figure 8** Drawing of  $-\ln(1 - Q_t/Q_e)$  versus  $t$ . Initial concentration of palladium ions: 48 ppm; temperature: 35°C; pH: 3.3 grafting yield: 113%; conversion ratio: 42%.



**Figure 9** Influence of pH on adsorption amount of the Pd<sup>2+</sup> by amination of PP-g-AN fabrics. Initial concentration of palladium ions: 12 ppm; temperature: 35°C; adsorption time: 3 h; grafting yield: 113%; conversion ratio: 42%.

adsorption rate constant of the palladium ions was  $9.79 \times 10^{-2} \text{ min}^{-1}$ .

**Influence of pH of feed solution**

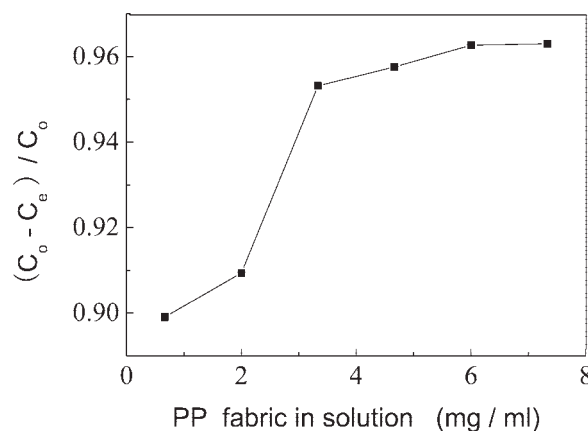
Adsorption amount of chelating fabrics for Pd<sup>2+</sup> was measured under different pH of feed solution ranged from 2.0 to 6.0, and the results were given in Figure 9. It could be seen that the palladium uptake was almost steady-going with the increasing pH. The result might be ascribed that the imine groups on the surface of chelating fabrics were protonated and deprotonated gently along with the variety of pH, and the palladium ionic valency was low, then the effective cationic repulsion could not occur between the palladium ions and the chelating fabrics.

**Influence of chelating fabrics concentration in solution on adsorption efficiency**

The adsorption efficiency is defined as the ratio of the initial palladium and equilibrium concentration difference ( $C_0 - C_e$ ) to the initial concentration ( $C_0$ ) in the aqueous phase. The effect of chelating fabrics concentration in solution on the adsorption efficiency was given in Figure 10. The results unfolded that the values of the adsorption efficiency increased with the increase of the adsorbent concentration and then leveled off toward 96.3%. Apparently, there was an optimum chelating fabric concentration for a fixed palladium ions initial concentration.

**Influence of initial concentration of palladium ions on adsorption amount**

From Figure 11, it was observed that increasing the concentration of palladium ions also resulted in an



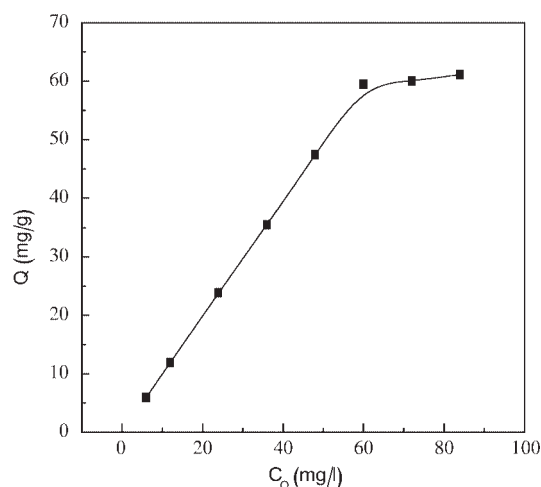
**Figure 10** Influence of amination of PP-g-AN fabrics content in solution on adsorption efficiency. Initial concentration of palladium ions: 12 ppm; temperature: 35°C; pH: 3.31; adsorption time: 3 h; grafting yield: 113%; conversion ratio: 42%.

increase in the palladium ions uptake, which then reached a plateau value at higher levels of concentration. This means that a maximum amount of metal ion was removed from the solution when the chelating sites were saturated. The chelating sites of adsorbent are considered to be saturated when the palladium concentration reaches 60 ppm within a fixed amount of adsorbent (30 mg/100 ml).

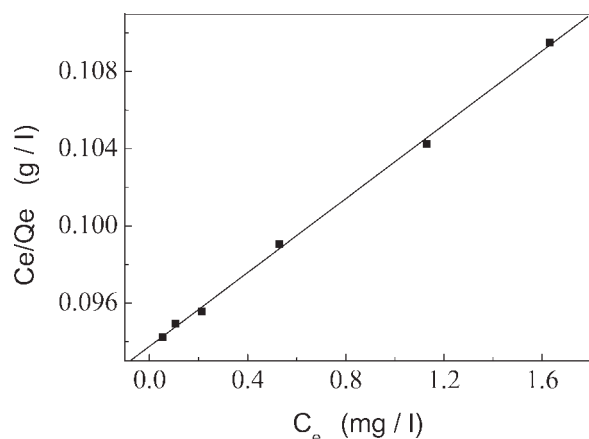
According to the Langmuir equation

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_s} + \frac{1}{Q_s b} \tag{5}$$

where,  $C_e$  and  $Q_e$  are the equilibrium palladium ions concentration in solution and the equilibrium adsorption amount, respectively;  $Q_s$  is the saturated adsorption capacity, and  $b$  is a constant. The relation curve of  $C_e/Q_e$  versus  $C_e$  was drawn in Figure 12.



**Figure 11** Influence of initial concentration of palladium ions on adsorption amount. Temperature: 35°C; pH: 3.3; adsorption time: 3 h; grafting yield: 113%; conversion ratio: 42%.



**Figure 12** Drawing of  $C_e/Q_e$  versus  $C_e$ . Temperature: 35°C; pH: 3.3; adsorption time: 3 h; grafting yield: 113%; conversion ratio: 42%.

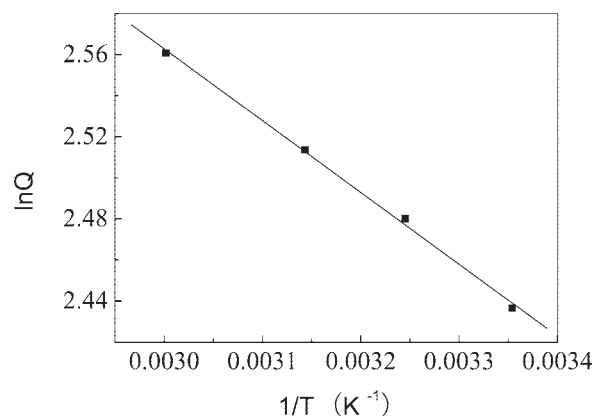
The saturated adsorption capacity was calculated as 104.49 mg/g from the slope.

#### Influence of temperature on adsorption amount

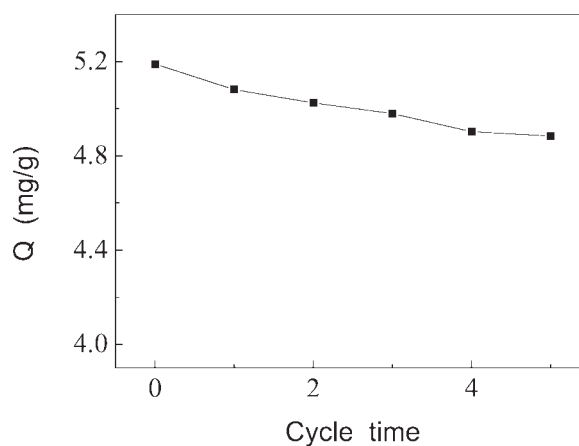
The influence of the temperature on the adsorption amount of palladium ions was studied in a temperature range of 25–60°C. According to the Arrhenius equation, from the slope of Figure 13 the activation energy of the adsorption process was calculated as 2.9 kJ/mol. This low value of activation energy hinted that adsorption of the functionalized PP-g-AN fabrics for palladium ions was an easy process.

#### Reusability of chelating adsorbent

The adsorbed palladium ions were easily desorbed with 0.1 mol/L nitric acid at room temperature for 2 h with stirring. To evaluate the reusability of the chelating adsorbent, the adsorption–desorption cycle



**Figure 13** Drawing of  $\ln Q$  versus  $1/T$ . Initial concentration: 48 ppm; pH: 3.3; adsorption time: 1 h; grafting yield: 113%; conversion ratio: 42%.



**Figure 14** Influence of cycle time on adsorption amount. Desorption temperature: 25°C; nitric acid: 0.1 mol/L; desorption time: 2 h; adsorption temperature: 35°C; pH: 3.3; adsorption time: 3 h; grafting yield: 113%; conversion ratio: 42%.

was repeated five times. As shown in Figure 14, the adsorption capacity of chelating fabrics showed a slight decrease after five times adsorption–desorption cycle. About 5% adsorption capacity lost after five cycle times.

## CONCLUSIONS

The chelating adsorbent with imine groups was synthesized by grafting of AN onto PP fabrics using preirradiation and subsequently modified by reacting with EDA. The grafting yield increased with increasing of irradiation dose and grafting reaction time. Results showed that the highest conversion ratio was obtained at 110°C when amination reaction was carried out for 15 h. FTIR and TGA test indicated that nitrile and imine groups were introduced into functionalized PP-g-AN fabrics respectively.

The chelating adsorbent showed high adsorption rate and great adsorption amount toward palladium ions. At 35°C, the highest equilibrium adsorption amount could reach 59.5 mg/g within 30 min. The adsorption rate constant, the saturated adsorption amount, and the activation energy were calculated as  $9.79 \times 10^{-2} \text{ min}^{-1}$ , 104.49 mg/g, 2.90 kJ/mol, respectively. At experimental range of the pH and the temperature, the adsorption performance of the chelating fabrics was excellent and varied within a narrow range. The adsorbed palladium ions were easily desorbed with 0.1 mol/L nitric acid at room temperature.

## References

1. Vincent, T.; Guibal, E.; Chiarizia, R. *Sep Sci Technol* 2007, 42, 3517.
2. Hirokazu, N.; Mikiya, T.; Kazuko, M. *Miner Eng* 2008, 21, 483.

3. Pokhitonov, Y.; Korolev, V. In Proceedings of the International Conference on Environmental Remediation Radioactive Waste Management 2005, September 4–8, Glasgow, Scotland.
4. Lisa, G.; Brian, H. R.; Fernando, S.; Maria, R. T.; Marcella, V. *Colloids Surf A* 2008, 329, 12.
5. Gentsheva, G.; Vassileva, P.; Tzvetkova, P.; Lakov, L.; Peshev, O.; Ivanova, E. *J Porous Mater* 2008, 15, 331.
6. Yantasee, W.; Lin, Y.; Fryxell, G. E. *Eng Chem Res* 2004, 43, 2759.
7. Kawakita, H.; Inoue, K.; Ohto, K.; Shimada, S.; Itayama, K. *Solvent Extr Ion Exch* 2007, 25, 845.
8. Aurély, P.; Thierry, V.; Magdalena, P.; Andrzej, W. T.; Eric, G. *Hydrometallurgy* 2008, 92, 1.
9. Wasikiewicz, J. M.; Mitomo, H.; Seko, N.; Tamada, M.; Yoshii, F. *J Appl Polym Sci* 2007, 104, 4015.
10. Cox, M.; Pichugin, A. A.; El-Shafey, E. I.; Appleton, Q. *Hydrometallurgy* 2005, 78, 137.
11. Mishra, A.; Clark, J. H.; Vij, A.; Daswal, S. *Polym Adv Technol* 2008, 19, 99.
12. Meligi, G. A. *Polym Plast Technol Eng* 2008, 47, 106.
13. Kumar, V.; Bhardwaj, Y. K.; Dubey, K. A.; Chaudhari, C.V.; Goel, N. K.; Biswal, J.; Sabharwal, S.; Tirumalesh, K. *Sep Sci Technol* 2006, 41, 3123.
14. Nalan, K.; Akio, K.; Takanobu, S. *Radiat Phys Chem* 1995, 46, 833.
15. Hegazy, A.; Kamal, H.; Khalifa, N. A.; Mahmoud, G.A. *Iranian Polym J* 1999, 8, 223.
16. Okieimen, F. E.; Sogbaike, C. E.; Ebhoaye, J. E. *Sep Purif Technol* 2005, 44, 85.
17. Ramazan, C.; Cengiz, S.; Mehmet, S. *React Funct Polym* 2006, 66, 599.