

# Study on the Redox Adsorptive Properties of Fiber Containing Iso-Thiourea Group toward Au(III)

SHUNQING TANG,<sup>1</sup> YUN LU,<sup>2</sup> HANMIN ZENG<sup>2</sup>

<sup>1</sup> Biomedical Engineering Institute of Jinan University, Guangzhou, China 510632

<sup>2</sup> Materials Science Institute of Zhongshan University, Guangzhou, China 510275

Received 21 March 2000; accepted 17 October 2000

**ABSTRACT:** Functional fiber containing iso-thiourea group was prepared by reactive chloromethylated poly(vinyl acetate)-*graft*-polystyrene-divinylbenzene (PVA-*g*-PS-DVB) being reacted with thiourea. The functional group content of the fiber was 2.90 mmol/g. The chloromethylated PVA-*g*-PS-DVB reacted with sulfur atoms in the thiourea molecules; this made the fiber containing iso-thiourea group. The results of static adsorption experiments showed that the adsorption amount of the fiber toward Au(III) reached a maximum amount, 1000 mg/g, at pH 1.5. It reduced the adsorbed Au(III) into Au(0), and the maximum reduction percentage was 90% at pH 2.0. The amount of Au(III) adsorbed by the fiber increased with increasing solution temperature but decreased with the increasing ionic strength of the solution. It was proven by electron spectroscopy for chemical analysis that some of the sulfur atoms in the fiber were oxidized into sulfone groups or sulfate ions. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1985–1990, 2001

**Key words:** redox fiber; fiber containing iso-thiourea group; gold; redox adsorption

## INTRODUCTION

It is well known that thiourea has a high complex constant with Au ion, and it is expected that thiourea would substitute cyanic acid for the recovery of gold ion, which would play a good role in environmental protection. Warshowsky's group<sup>1</sup> studied a resin containing iso-thiourea group to recover Au ion and Ag ion substituting for cyanic acid, and it was proven that the resin had a high adsorption toward Au ion. We were studying some fibrous adsorbents. They had fast adsorption and desorption speeds and could be used in various forms such as yarn, fabrics, and nonwoven fabrics for satisfying the

need of different exchange adsorption processes. In particular, we found that some fibrous adsorbents such as activated carbon fibers, the organic fibers containing amidoxime or hydroxy-alkyl amino groups, could reduce Au(III) into elemental gold<sup>2–4</sup> and might be used for simplifying the recovery process of Au ion. In this article, the fiber containing iso-thiourea group was prepared, and its redox adsorptive properties toward Au(III) were studied. It was expected that the fiber would have a higher adsorption toward Au(III) and be able to reduce Au(III) into Au(0) for the economical recovery of Au(III). In addition, the fiber containing iso-thiourea group was easy to hydrolyze into a fiber containing mercapto group that has been used widely in trace analysis and the separation of poisonous heavy metallic ions from wastewater.<sup>5</sup>

---

Correspondence to: S. Tang.

*Journal of Applied Polymer Science*, Vol. 81, 1985–1990 (2001)  
© 2001 John Wiley & Sons, Inc.

## EXPERIMENTAL

### Preparation of the Redox Fiber

Poly(vinyl acetate) (PVA) fiber was grafted with polystyrene-divinylbenzene (PS-DVB) to produce PVA-g-PS-DVB, and the grafting ratio was 445% (w/w). Then, the graft was chloromethylated, and the chloromethylated grafting fiber was reacted with thiourea in ethanol as a solvent at different temperatures for a certain time to search for the most favorable reaction condition. The increasing weight percentage ( $W\%$ ) of the chloromethylated fiber reacting with thiourea under different conditions was determined as follows:

$$W\% = \frac{W_1 - W_0}{W_0} \quad (1)$$

where  $W_1$  is the weight of the chloromethylated fiber after the reaction with thiourea and  $W_0$  is the original weight of the fiber. The N content of the fiber containing iso-thiourea group was analyzed with a PerkinElmer 240C elemental analyzer (American PE Co.).

### Properties of the Fiber Containing Iso-Thiourea Group in Adsorbing Au(III)

1. In static adsorption experiments, about 0.02 g of the fiber was added to 25 mL of a 2 mmol L<sup>-1</sup> Au(III) solution in an iodometric flask, which was placed in a thermostatic vibrator. The flask was shaken for 24 h at the required temperature under different adsorption conditions (e.g., different ionic strengths of the solution and different temperatures). The concentration of the Au(III) solution before and after adsorption was determined with a WFC-1C atomic absorption spectrometer (Beijing Third Analytical Instrument Co.). The adsorption amount ( $E_a$ ) toward Au ion was calculated:

$$E_a(\text{g g}^{-1}) = (M_o - M) * V * 197/W \quad (2)$$

where  $M_o$  and  $M$  are the concentrations (mmol L<sup>-1</sup>) of the Au(III) solution before and after adsorption, respectively;  $V$  is the volume (mL) of the solution used for ad-

sorption, and  $W$  is the weight (g) of the fiber used.

2. Au ion ( $E_d$  is the amount of Au ion adsorbed on or in the fiber) adsorbed on the fiber was desorbed with a mixture of 90% (v/v) acetone, 5% hydrochloride acid, and 5% distilled water, and the reduction adsorption amount of the fiber toward Au(III) ( $E_r$ ) was calculated:

$$E_r = E_a - E_d \quad (3)$$

The reduction percentage ( $R_p$ ) of Au(III) on the fiber was equal to  $E_r$  over  $E_a$ .

3. Sulfate ions in the remaining Au(III) solution were tested with a barium chloride-nitric acid solution.

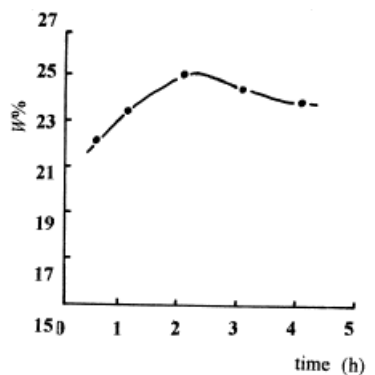
### Instrument Analyses

1. The chloromethylated fibers before and after the reaction with thiourea were cut into fine pieces and dried *in vacuo* and then pressed into pellets with KBr. The IR absorption spectra of the fibers were recorded on a Nicolet 170SX Fourier transform infrared spectrometer.
2. Elemental gold on the fiber was verified with a Rigaku D/max IIIA X-ray diffractometer with nickel-filtered Cu K $\alpha$  radiation generated at 40 kV and 30 mA. The diffraction spectra with diffraction angles of 30–80° were obtained.
3. The binding energy data of carbon, nitrogen, sulfur, and gold atoms in or on the fiber before and after adsorbing Au(III) at pH 2.0 were obtained with an ESCALAB MKII spectrometer (British Vacuum Generators Co.).

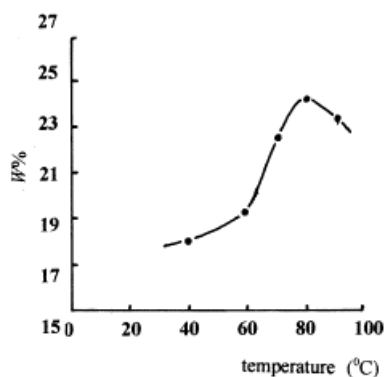
## RESULTS AND DISCUSSION

### Preparation of the Functional Fiber

Figure 1(a, b) provides the results of the increasing weight percentage of the chloromethylated fiber for different reaction times and temperatures. In Figure 1(a), the weight percentage reaches a maximum value, 25.2%, when the reaction is performed at 80°C for 2 h. It is easy to understand that the weight percentage increases with reaction time between 0 and 2 h. Weight percentage decreases a little when the reaction



(a)

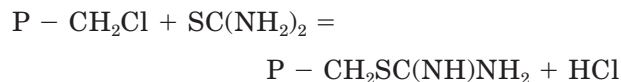


(b)

**Figure 1** (a) Relationship between the weight percentage and reaction time (reaction temperature = 80°C) and (b) relationship between the weight percentage and reaction temperature (reaction time = 4 h).

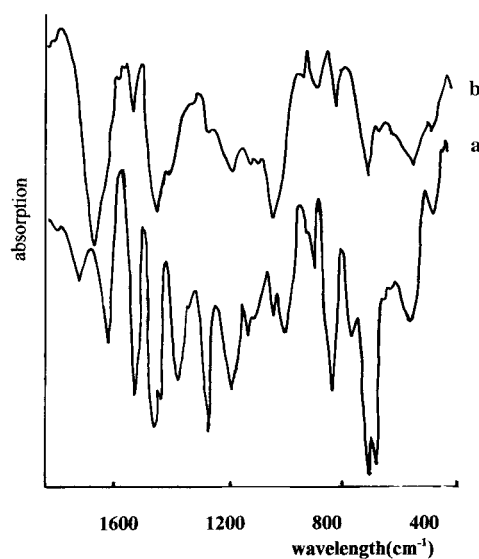
time is longer than 2 h because of polymer chain breaking at a higher temperature (80°C) for a longer reaction time. In fact, most of the raw fibers break during the reaction performed at 80°C for 4 h. In Figure 1(b), the weight percentage has a maximum, 24%, when the reaction temperature is 80°C. The weight percentage decreases obviously over 80°C. This may be related to the polymer chain breaking at a higher reaction temperature too. These results show that the weight percentage reaches a maximum value when the reaction is performed at 80°C for 2 h in ethanol as a medium. Because the weight percentage changes linearly with the reaction ratio in this no-additional-crosslinking reaction system, this reaction condition, that the reactive fiber has a maximum weight percentage, must be the most favorable one. According to ref. 6, it was a sulfur atom in a thiourea molecule reacting with the

chloromethyl group connecting with the benzene ring in PS; there was no additional crosslinking in this reaction system, and the reaction condition was similar to the previous one. The chloromethylated PVA-*g*-PS-DVB fiber reacts with a sulfur atom in a thiourea molecule in the same way and makes the fiber containing iso-thiourea group. The reaction is



where P stands for the polymer chain.

The elemental analysis results show that the content of iso-thiourea group in the functional fiber is 2.90 mmol g<sup>-1</sup>. The calculated total reaction ratio of the chloromethylated fiber is 64% (molar ratio of the functional group over the chloromethylated group) for this reaction condition. This indicates that the reaction ratio is high in this macromolecular reaction system because of some chloromethyl groups in the internal layer of the fiber being difficult to react with thiourea. The IR spectra (Fig. 2) show that the stretching vibration (670 cm<sup>-1</sup>) of the C—Cl bond in the chloromethylated fiber weakens obviously or disappears after reacting; an absorption peak at 1640 cm<sup>-1</sup> for the IR absorption of amino group appears, and IR absorption peaks about benzene rings in the fiber at 1540, 940, and 830 cm<sup>-1</sup> do not change. This means that most of the chloromethyl groups



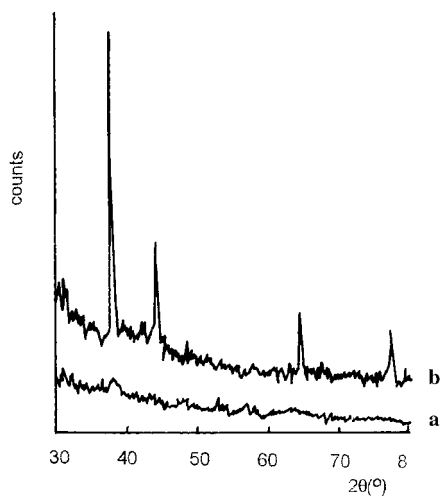
**Figure 2** IR spectra of the chloromethylated fibers (a) before and (b) after reacting with thiourea.

in the fiber react with thiourea, and the benzene ring does not join the reaction. In addition, the fiber containing iso-thiourea group is easy to hydrolyze into mercapto group containing fiber in a 2N NaOH solution and can be used conveniently and effectively in the analysis of laboratory wastewater containing Hg ion.<sup>5</sup>

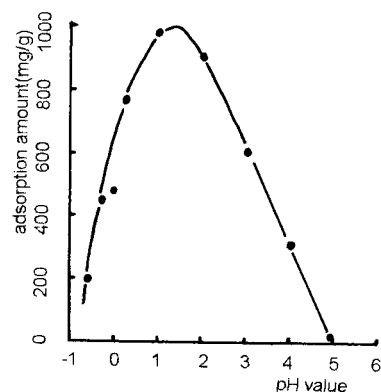
### Properties of the Functional Fiber in Adsorbing Au(III)

The wide-angle X-ray diffraction (WAXD) graphs (Fig. 3) of the fibers demonstrate that there are four diffraction peaks of crystal faces at 38, 45, 65, and 78° after the adsorption of Au(III), but there is no peak (only noise signals) for the raw fiber under the same adsorbing condition. These peaks correspond to four diffraction main peaks of crystal faces of elemental gold: 111, 200, 220 and 311. This proves that there is elemental gold in the fiber after adsorbing. This means that the functional fiber can reduce Au(III) into Au(0) at pH 2.0.

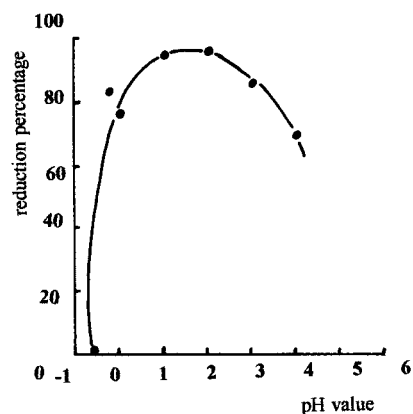
Figure 4(a,b) shows the relationship between the adsorption amount and the reduction percentage of the fiber containing iso-thiourea group toward Au(III) and the pH value of the solution. In Figure 4(a), the adsorption amount for Au(III) reaches a maximum amount, 1000 mg/g, at pH 1.5, and higher or lower acidity has a great effect on the adsorption amount. When the pH is lower than -1 or higher than 5.0, the adsorption amount is near zero. Figure 4(b) shows that the maximum reduction percentage of the fiber con-



**Figure 3** WAXD graphs of the fiber (a) before and (b) after adsorbing Au(III).



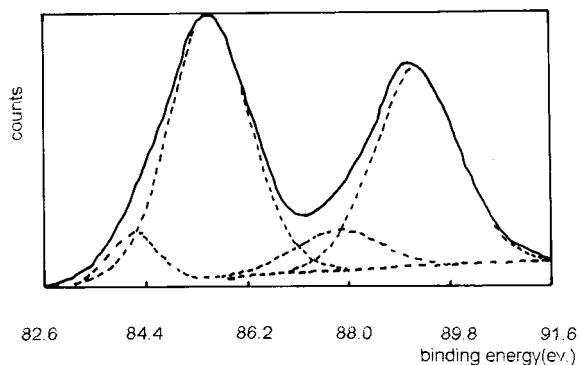
(a)



(b)

**Figure 4** (a) Relationship between the adsorption amount of the fiber containing iso-thiourea group and the pH value of the solution and (b) relationship between the reduction percentage of the fiber containing iso-thiourea group and the pH value of the solution.

taining iso-thiourea group toward Au(III) is 90% at pH 2.0, and the pH has an effect on the reduction percentage as well. When the pH is lower than -0.6, the reduction percentage is zero; that is, the fiber cannot reduce Au(III). However, when the pH is higher than 4, the reduction percentage of the fiber is higher, although the adsorption amount is low. The Au<sub>4f</sub> spectrum of Au adsorbed on the fiber (Fig. 5) demonstrates that the peak area at 84 eV is very small and is only 20% of the total peak area (the peak area at 84 eV and 85.6 eV). The binding energy (peak position) of elemental gold is 84 eV, and the energy of Au ion (III) is 85.6 eV. It is concluded that there is only 20% elemental gold on the fiber containing iso-thiourea group. The result is different from what Figure 4(b) shows, that the reduction percentage of iso-thiourea containing fiber toward Au(III) is



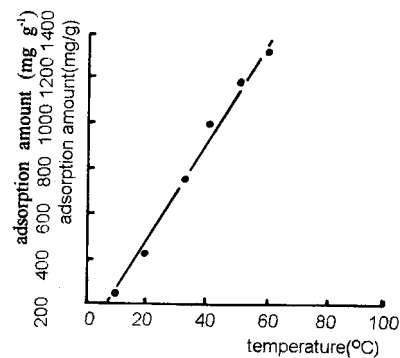
**Figure 5**  $Au_{4f}$  spectrum of the adsorbed Au(III) on the fiber (the dotted line is a result of the computer simulation).

90%, and the reason is that some grains of elemental gold drop off from the surface of the fiber and precipitate in the bottom of an iodometric flask during the adsorption process. Elemental gold pieces are easy to drop off from the surface of the fiber because it contains much fewer hydrophilic groups.

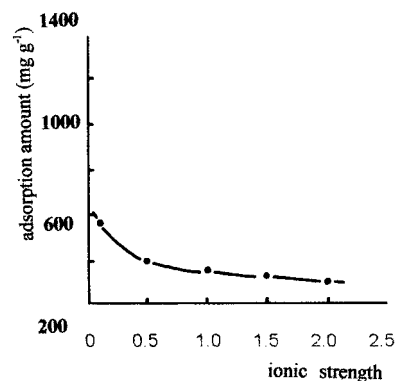
Figure 6(a,b) shows the effect of the temperature and ionic strength of the solution on the amount of Au(III) adsorbed by the fiber. Figure 6(a) indicates that the amount of Au(III) adsorbed by the fiber increases linearly with the increasing solution temperature at pH 2.0. A higher temperature may be favorable to the redox adsorption process, an endothermic reaction. Figure 6(b) shows that the adsorption amount of the fiber toward Au(III) decreases with the increasing ionic strength of the solution (adjusted by sulfate of magnesium). Because there are more  $HAuCl_4$  molecules formed in a higher ionic strength solution,<sup>7</sup> there are fewer  $AuCl_4^-$  ions left for ion-exchange adsorption by the fiber.

#### Reaction Between Au(III) and the Functional Fiber

Sulfate ions are found in the remaining adsorption solution with a barium chloride–nitric acid solution. There is a white precipitate in the solution when the barium chloride–nitric acid solution is added. The precipitate should be barite because it is unsolvable in a nitric acid solution. This proves that some of the sulfur atoms in the fiber are oxidized into sulfate ions by Au(III) at pH 2.0. In the meantime, the  $S_{2p}$  spectra (Fig. 7) of the fiber before and after adsorption show that there appear some peaks at a higher binding energy. In the  $S_{2p}$  spectrum of the fiber after adsorb-



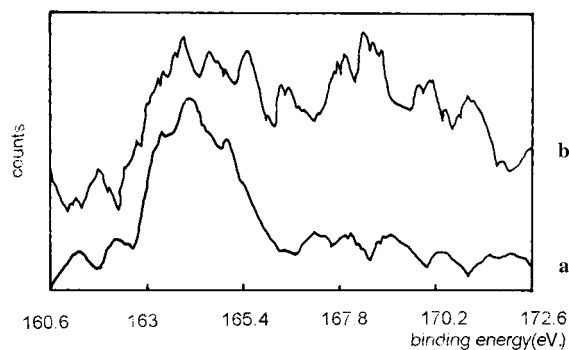
(a)



(b)

**Figure 6** (a) Effects of the temperature on the amount of the fiber adsorbing Au(III) and (b) effects of the ionic strength of the solution on the amount of the fiber adsorbing Au(III).

ing, there is a peak at 168 eV about the binding energy of sulfone groups. This proves that some of the sulfur atoms in the fiber are oxidized into sulfone groups after adsorbing Au(III). These results indicate that sulfur atoms in the fiber con-



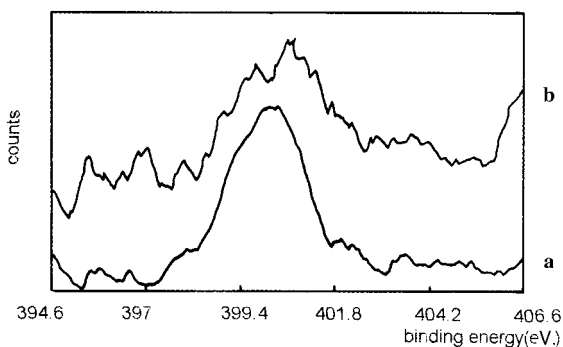
**Figure 7**  $S_{2p}$  spectra of the fiber (a) before and (b) after adsorbing Au(III).



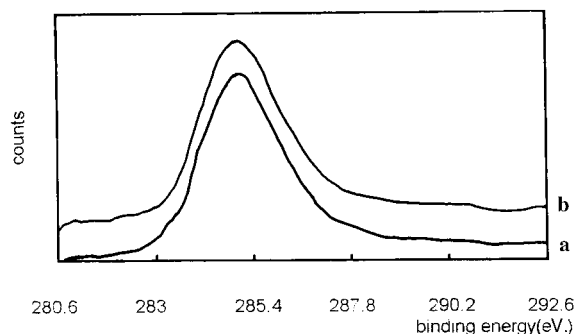
taining iso-thiourea groups are oxidized into sulfone groups and then into sulfate ions. The  $N_{1s}$  spectra (Fig. 8) of the fiber before and after adsorption show that nitrogen atoms in the fiber are not oxidized, and many nitrogen atoms drop off from the fiber with the oxidization of the sulfur atoms oxidized into sulfate ions; we can conclude from this that the strength of the  $N_{1s}$  peak at 399 eV is weakened obviously after adsorbing, and there is no  $N_{1s}$  peak above 403 eV around the N—O bond peak. The  $C_{1s}$  spectra (Fig. 9) of the fiber containing iso-thiourea group show that the peaks are unchanged before and after adsorption. This means that the carbon atoms in the fiber are not oxidized or join other adsorption reaction after adsorbing Au(III).

## CONCLUSIONS

1. The fiber containing iso-thiourea group can reduce Au(III) into Au(0), and the maximum reduction percentage of the fiber reaches 90% at pH 2.0. The adsorption amount of the fiber toward Au(III) reaches a maximum amount, 1000 mg g<sup>-1</sup>, at pH 2. The amount of Au(III) adsorbed by the fi-



**Figure 8**  $N_{1s}$  spectra of the fiber (a) before and (b) after adsorbing Au(III).



**Figure 9**  $C_{1s}$  spectra of the fiber (a) before and (b) after adsorbing Au(III).

ber increases with the increasing solution temperature but decreases with the increasing ionic strength of the solution.

2. The sulfur atoms in the fiber are oxidized into sulfone groups or sulfate ions, and they disappear from the fiber partly after adsorbing Au(III). The carbon atoms in the fiber containing iso-thiourea group are not oxidized.

## REFERENCES

1. Warshowsky, A.; Pit Mihalik, M. M. B.; Murphy, T. G. *Sep Purif Methods* 1980, 9, 209–265.
2. Lin, W.; Lu, Y.; Zeng, H. *React Polym* 1992, 17, 255–261.
3. Lin, W.; Tang, L.; Fu, R.; Lu, Y.; Zeng, H. *Proceedings of the 34th IUPAC, Beijing, China, Peking University Press, 1993; T4311.*
4. Tang, S.; Tang, X.; Lu, Y.; Zeng, H. *J Appl Polym Sci* 1999, 73, 47–54.
5. Tang, S.; Lu, Y.; Zeng, H. *Proceedings of the Second Water Treatment Technology (in Chinese), Shanghai, China, East China University of Science and Technology Press, 1993; p 131.*
6. Xu, R.; Li, N. *Chin J Ion Exch Adsorption* 1990, 6, 16–19.
7. Fu, X.; Chen, R. *Physical Chemistry; People Education: Beijing, 1978; Part 1, Chapter 6, p 265.*