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European Polymer Journal 42 (2006) 254–258

EUROPEAN POLYMER JOURNAL

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The sorption mechanism of Au(III) on sulfur-containing chelating resin poly[4-vinylbenzyl (2-hydroxyethyl) sulfide]

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Received 23 June 2005; accepted 1 July 2005
Available online 22 August 2005

Abstract

The sorption mechanism of sulfur-containing chelating resin, poly[4-vinylbenzyl (2-hydroxyethyl) sulfide], towards Au(III) was investigated by Fourier transform infrared spectra (FTIR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), energy dispersive X-ray microanalysis (EDX), and X-ray diffraction (XRD). It was showed that the sulfide bond in the resin was oxidized into sulfoxide and sulfone bond, and Au(III) was deoxidized into Au(0).

Keywords: Poly[4-vinylbenzyl (2-hydroxyethyl) sulfide]; Sorption mechanism; Au(III); Redox

1. Introduction

Commonly, sulfur-containing chelating resins interact with most noble metals to form coordinative bonds. Over the last several years, a number of sulfur-containing chelating resins were synthesized [1–4] and used widely in preconcentration, separation, purification, recovery of noble metals [5–11]. However, it is difficult to soak most sulfur-containing chelating resins in aqueous solution because of their hydrophilic groups, which further affect the diffusion of metal ions into the matrix of chelating resins. Recently, we synthesized a novel hydrophilic chelating resin containing both sulfur and oxygen atoms, poly[4-vinylbenzyl (2-hydroxyethyl) sulfide] (PVBS), by introducing a hydrophilic group –OH into a sulfur-containing chelating resin [12]. This resin exhibited both hydrophilic nature and excellent sorption property for noble and heavy metal ions such as Ag(I), Au(III), Pt(IV), Pd(II), and Hg(II) etc. In the sorption process of Ag(I), Au(III) and Hg(II) on PVBS resin, an interesting phenomenon, seriously redox, was found. The sorption mechanism of Au(III) on chelating resins has recently been reported [13–17], most of which focus on the changes of metal ions rather than the changes of resin structure. In order to figure out what happened to both chelating resin and metal ions during the sorption process, in this study, the sorption mechanism of PVBS for Au(III) was investigated by Fourier transform infrared spectra (FTIR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and

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doi:10.1016/j.eurpolymj.2005.07.001

X-ray diffraction (XRD). In order to justify the structure of PVBS resin after sorption, two kinds of control resins poly[4-vinylbenzyl (2-hydroxyethyl) sulfoxide] (PVBSO) and poly[4-vinylbenzyl (2-hydroxyethyl) sulfone] ($PVBSO_2$) were synthesized by oxidizing PVBS in the present study.

2. Experimental

2.1. Materials and methods

PVBS, PVBSO and $PVBSO_2$ resins were synthesized according to our previous work [18]. $HAuCl_4 \cdot 4H_2O$ and other reagents, analytical grade, were purchased from No.1 Reagent Factory of Shanghai and used without any further purification.

2.2. Determination of static sorption kinetics

A known amount of resin (about 0.05 g) was suspended in definite volume (in general 50 mL) of Au(III) solution in an iodometric flask, which was placed in the thermostatic vibrator, and 0.2 mL of Au(III) solution was taken out to determine the amount of Au(III) adsorbed by a resin in different time interval at room temperature. Sorption amount (Q) was calculated as follows:

$$Q(\text{mmol g}^{-1}) = \frac{(C_0 - C)V}{W}$$

where C_0 and C are the concentrations of Au(III) solution before and after sorption (mmol L^{-1}), respectively; V is the volume of the solution used for sorption (L); and W is the mass of the dry resin (g).

2.3. Instruments

The concentrations of Au(III) solution were determined on a GBC-932 atomic absorption spectrophotometer made in Australia. The infrared spectra were recorded on a Nicolet MAGNA IR-550 (Series II) spectrophotometer, OMNIC32 software, version 6.0a, and test conditions were listed as follows: potassium bromide, scanning 32 times, resolution 4 cm^{-1}. XPS spectra were collected on PHI 1600ESCA system, Perkin–Elmer Co., USA, test conditions were listed as follows: MgKα (1253.6 eV), power 200.0 W, resolution 187.85 eV. Quantitative and qualitative analysis were carried out using special data treatment software offered with the instrument. The shapes and surface morphology of the resins were measured on a scanning electron microscope (SEM), JSF5600LV, JEOL. Energy dispersive X-ray microanalysis (EDX) was performed by a EDX analytical instrument (Quest Level 2) made by Thermo Noran Co.

3. Results and discussion

3.1. FTIR characterization of PVBS, PVBSO and $PVBSO_2$ resins and their sorption properties for Au(III)

In Fig. 1, the PVBSO peaks at 1010–1044 cm^{-1} enhanced and widened evidently compared with those of PVBS, indicating that the –S– bond had been probably oxidized into –SO– after reacting with hydrogen peroxide. Besides, although the XPS demonstrated the existence of partial $–SO_2–$ groups in PVBSO resin (see Table 2), the characteristic absorption peak of $–SO_2–$ in its FTIR spectrum was not obvious due to its lower content.

$PVBSO_2$ could be prepared through oxidizing PVBSO or PVBS. The FTIR spectra of $PVBSO_2$ prepared from PVBSO and PVBS did not show evident differences in their characteristic peaks. Compared with PVBS and PVBSO (Fig. 1), $PVBSO_2$ showed novel absorption peaks at 1289, 1119, and 1064 cm^{-1}, which revealing the –S– or –SO– bonds had been oxidized into $–SO_2–$.

As shown in Table 1, the saturated sorption capacity of PVBS slightly increased when it was oxidized into PVBSO, but greatly decreased when oxidized into $PVBSO_2$, indicating that the chelating capacity of –SO– was higher than that of –S– bond and greatly higher than $–SO_2–$ bond.

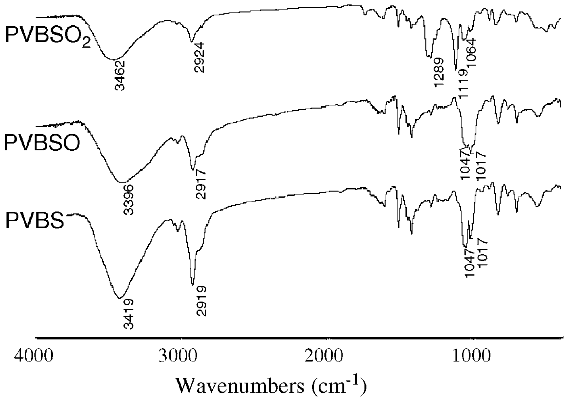


Fig. 1. The FTIR Spectra of PVBS, PVBSO and $PVBSO_2$.

Table 1
The saturated sorption capacities of PVBS, PVBSO, and $PVBSO_2$ for Au(III) at 25 °C (mmol g^{-1})

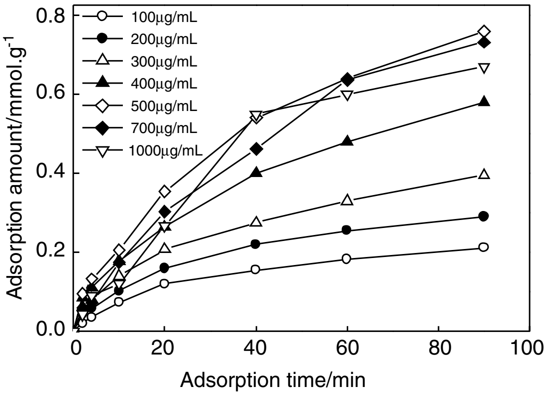
Metal ions	PVBS	PVBSO	$PVBSO_2$
Au(III) (pH = 4.0)	1.4800	1.5270	0.0300

3.2. The effect of Au(III) concentration on the sorption of PVBS for Au(III)

The effect of Au(III) concentration on the sorption of PVBS was investigated at room temperature (Fig. 2). The sorption rate and sorption amounts of PVBS for Au(III) increased with the concentration of Au(III) when it was lower than 500 μg/mL. However, when the concentration of Au(III) was higher than 700 μg/mL, the sorption curves became abnormal. After 60 min in 700 μg/mL Au(III) solution or 40 min in 1000 μg/mL Au(III) solution, the sorption amounts of PVBS for Au(III) were both less than in 500 μg/mL Au(III) solution, and the decreased value of sorption amounts increased with the increasing of the Au(III) solution concentration. This phenomenon suggests the possible existence of other reactions in the sorption process except chelating reaction.

In the sorption experiment some phenomena were found as follows: (1) under the condition of a low concentration solution (e.g. less than 10 μg/mL) or the total amount of Au(III) ions in solution was much less than the saturated sorption capacity of the resin, the color of PVBS resin maintained white or primrose yellow or yellow during the whole period of sorption; (2) under the condition of a high concentration of solution (e.g. more than 100 μg/mL) or the total amount of Au(III) ions in solution was more than the saturated sorption capacity of the resin, the color of the resin changed slowly from white to primrose yellow, yellow, red, ruby red orderly with the proceeding of sorption; (3) the changing rate of color increased with the increasing of Au(III) solution concentration.

The facts above could be explained by the following three-steps adsorption mechanism: (1) the Au(III) ions in the solution were firstly adsorbed on the resin to form chelate complexes, then the resin appeared slightly primrose yellow; (2) the Au(III) ions adsorbed on the resin were reduced into Au(I) by the resin, which made the resin yellow [19]; (3) the Au(I) ions adsorbed on the resin were replaced by other free Au(III) ions from the solution. The Au(I) ions replaced by Au(III) entered the solution, and were converted into Au(0) and Au(III) ions. The color change of resin from white to ruby red probably indicated the formation of nano-sized Au(0) particles [20].



sorption condition: 298K, pH=4, 0.05g of resin, 25mL Au(III) solution.

Fig. 2. Sorption kinetics of PVBS resin for Au(III).

3.3. SEM analysis

The SEM images of resins after sorption (Fig. 3) distinctly showed there were great deals of grains of elemental gold distributing on the surface and interior of polymeric microspheres; and the size of Au particles on the surface of resin microspheres was bigger than that in the outer layer or the interior of resin. A probable explanation for this was that the content of functional groups on the surface was higher than that in the interior of resin, which resulted in the formation of more Au(0). It could be observed that most of Au particles in the outer layer and inner of chelating resin were nano-sized, which was in agreement on the deduction in Section 3.2.

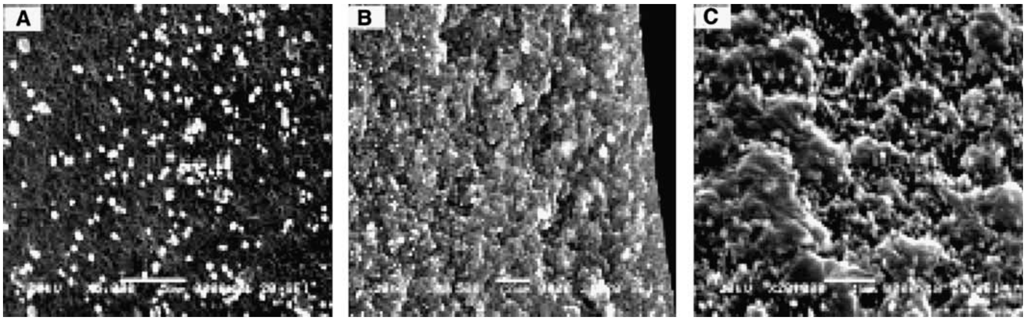


Fig. 3. The SEM images of Au(III)-loading PVBS (A: the surface of the resin; B: the outer section of the resin; C: the interior section of the resin).

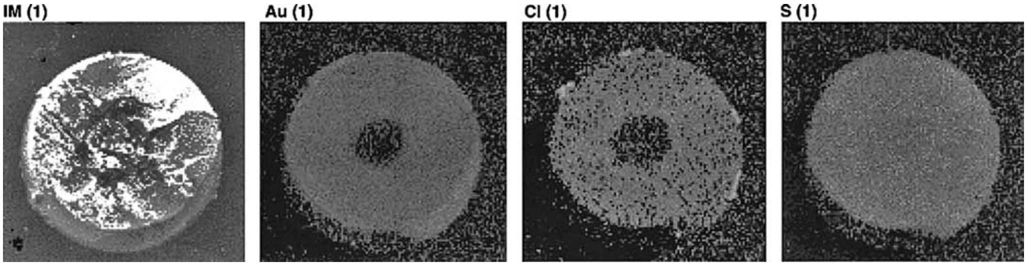


Fig. 4. The EDX graphs of PVBS resin.

3.4. EDX analysis

The results of EDX analysis of Au(III)-loading PVBS were shown in Fig. 4. S element distributed homogeneously from the center to the outer layer of the resin, however, Au element mainly distributed on the surface and outer layer of the resin, implying that Au(III) ions could hardly enter the center of the resin because of the obstruction of the Au(0) particles formed during the sorption. The distribution of Cl element was similar to that of Au element, demonstrating that Au(III) was sorbed by PVBS resin in a form of chloro-coordinated anion.

3.5. XRD analysis

The XRD graphs of PVBS (Fig. 5) demonstrated that there were five characteristic diffraction peaks of crystal faces of elemental gold appeared at $2\theta = 37.5°$, 44.05°, 64.05°, 77.35°, and 81.5° after sorption Au(III), which also proved that there was elemental gold in the resin after sorption.

3.6. XPS analysis

Three kinds of resins were characterized by XPS (Table 2). There was only one kind of binding energy peak of S_{2p} in both PVBS and $PVBSO_2$. The peaks at 163.79 eV in PVBS and 168.36 eV in $PVBSO_2$ belonged to S_{2p} of –S– and $–SO_2–$respectively. The single peak of S_{2p} demonstrated that there was only one type of sulfur atom in $PVBSO_2$, implying that the –S– in PVBS resin or –SO– in PVBSO resin were thoroughly oxidized into $–SO_2–$. It is safe to say the reaction of oxidizing –S– or –SO– into $–SO_2–$ could be carried out completely. The XPS spectrum of PVBSO showed that the proportion of the three types of sulfur in PVBSO resin was 30.3:55.0:14.7. The conversion percentage of $–SO_2–$ was 14.7% which took only small part in the total amount of sulfur, so the characteristic absorption of $–SO_2–$ in FTIR spectra of $PVBSO_2$ was undistinguishable. This result accorded with that of FTIR.

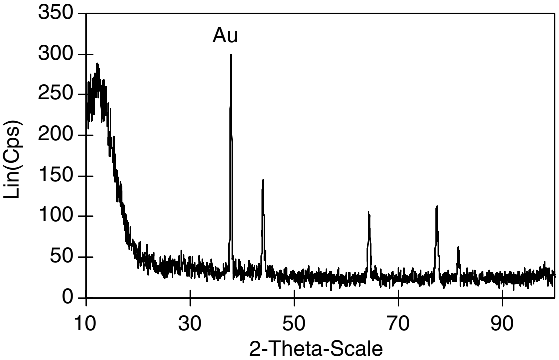


Fig. 5. The XRD graph of Au(III)-loading PVBS.

Table 2
The binding energy (eV) of S_{2p} in PVBS, PVBSO, $PVBSO_2$ and Au(III)-loading PVBS

PVBS	PVBSO	$PVBSO_2$	PVBS–Au(III)
163.79	163.50 166.21 168.78	168.36	163.69 166.33 169.16

The three kinds of binding energy peaks of S_{2p} in the XPS of Au(III)-loading PVBS at 163.69, 166.33, and 169.16 eV, could be assigned to S_{2p} of –S–, –SO–, and $–SO_2–$ respectively. This proved that Au(III) did oxidize part of the sulfide bonds into sulfoxide and sulfone. The proportion of –S–, –SO–, and $–SO_2–$ in the resin after sorption determined by XPS was 20.8:65.5:13.7.

Compared the XPS spectra of PVBSO with that of PVBS after sorption, the shifts of binding energy of S_{2p} in –S–, –SO–, and $–SO_2–$ were 0.19, 0.11, and 0.38 eV respectively, implying that chelation still existed between –S–, –SO–, $–SO_2–$ and gold ion or gold atom after redox reaction. This conclusion was approved by the sorption experimental results showed in Table 1.

In summary, the whole sorption process of PVBS resin for Au(III) can be described as the following chemical equations:

$$\mathrm{Au(III)Cl_4 + PS\text{-}CH_2SC_2H_4OH + H_2O}$$
$$\mathrm{\rightarrow Au(I)Cl_2 + PS\text{-}CH_2SOC_2H_4OH + 2Cl^- + 2H^+}$$

$$\begin{aligned}&\mathrm{Au(III)Cl_4} + \mathrm{PS\text{-}CH_2SOC_2H_4OH} + \mathrm{H_2O}\\&\quad\rightarrow \mathrm{Au(I)Cl_2} + \mathrm{PS\text{-}CH_2SO_2C_2H_4OH} + 2\mathrm{Cl}^- + 2\mathrm{H}^+\end{aligned}$$

$$\mathrm{Au(I)} \underset{\text{aq.}}{\overset{\text{disproportionate}}{\rightleftharpoons}} \mathrm{Au(III)} + \mathrm{Au(0)}$$

Acknowledgements

The authors are grateful for the financial support from the Postdoctoral Science Foundation of China (No. 2003034330), the Science Foundation for mid-youth elite of Shandong Province, the Nature Science Foundation of Shandong Province (No. Q99B15) and the Science Foundation of Yantai Normal University (No. 032912).

References

[1] Dong SH, Hu YH, Zhao YM, Zhang WH, Xu YW. J Wuhan Univ (Nat Sci Edi) 1995;41:161.
[2] Xu YW, Li HP, Dong SH. J Wuhan Univ (Nat Sci Edi) 1995;41:401.
[3] Ni CH, Xu YW. Huaxue Shijie 1992;14:153.
[4] Sánchez JM, Hidalgo M, Valiente M, Salvadó V. J Polym Sci A Polym Chem 2000;38:269.
[5] Chen YY, Chao L, Yan C. React Funct Polym 1998;36:51.
[6] Shah R, Devi S. Analyst 1996;121:807.
[7] Schilling T, Scgramel P, Milckake B, Knapp G. Mikrochim Acta 1996;124:235.
[8] Xu YW, Li J, Dong SH. Acta Polym Sin 1993;5:576.
[9] Chang XJ, Luo XY, Su ZX, Zhao B, Lu YH. Chem J Chin Univ 1988;9:574.
[10] Chen YY, Cai GP, Wang ND. J Macromol Sci Chem 1990;A27:1321.
[11] Grote M, Schumacher U. React Funct Polym 1997;35:179.
[12] Qu RJ, Cheng GX, Ji CN, Wang CH. Environ Chem 2003;22:284.
[13] Liu RX, Li Y, Tang HX. J Appl Polym Sci 2002;83:1608.
[14] Tang SQ, Lu Y, Zeng HM. J Appl Polym Sci 2001;81:1985.
[15] Tang SQ, Tang XP, Lu Y, Zeng HM. J Appl Polym Sci 1999;73:47.
[16] Gao F, Xu Y. J Appl Polym Sci 1997;65:931.
[17] Lin WP, Lu Y, Zeng HM. J Appl Polym Sci 1993;49:1635.
[18] Qu RJ, Sun CM, Wang CH, Ji CN, Sun YZ, Guan LX, et al. Eur Polym J 2005;41:1525.
[19] Saul P. The chemistry of organic derivatives of gold and silver. John Wiley & Sons, Ltd; 1999. p. 645.
[20] Williams JA, Rindone GE, McKinstry HA. J Am Ceram Soc 1981;64:709.