Hydrometallurgy 100 (2009) 82–86

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Enrichment and separation of silver from waste solutions by metal ion imprinted membrane

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ARTICLE INFO

Article history:
Received 12 July 2009
Received in revised form 9 October 2009
Accepted 13 October 2009
Available online 22 October 2009

Keywords:
Silver
Enrichment and separation
Metal ion imprinted membrane
Adsorption properties

ABSTRACT

Using blends of chitosan and polyvinyl alcohol as film-forming materials, the metal ion imprinted membrane was prepared with silver ions as template (Ag(I)-IIM). The DSC curve shows that the membrane does not exhibit the heat resistance very well but the favorable compatibility. FT-IR analysis implies that the coordinating atoms may be N atom of –NH_2 in chitosan and O atom of –OH in polyvinyl alcohol. The results on the experiment of competitive adsorption indicate that Ag(I)-IIM has the ability of specificity and recognition to Ag(I). The large adsorption capacity for Ag(I) indicates that Ag(I)-IIM can be used in silver enrichment and separation from waste solutions as an effective material.

1. Introduction

Selective enrichment and separation of metal ions is an important research field. These metallic ions mainly include toxic heavy metal ions in water (Chen et al., 2009; Li et al., 2008), low content of rare metal ions in the earth crust as well as some precious metals. Owing to its excellent properties of electrical and thermal conductivity and ductility, silver has been widely applied in fields of aerospace, communications, chemical industry, medical equipment, electroplating, photographic materials, electronic industries, *etc*. As known, however, silver resources in the world are extremely scant and mainly associated with lead, copper and antimony deposits. In addition, there are considerable waste solutions, containing silver ions, produced by electroplating wastewater, waste fixative as well as the Ag-containing wastewater in laboratory. Therefore, silver recovery from waste solutions becomes more and more important with developing society. However, due to the low concentration, it is necessary to enrich and separate silver ions before recovery.

There are some traditional techniques to recover silver from waste solutions such as electrolysis, replacement, precipitation and ion exchange in industry. Recently, Donia et al. (2007) have studied a chemically modified chitosan with magnetic properties, which can be used in silver recovery from aqueous solutions. Silver from thiosulfate and thiocyanate leach solutions can be recovered by anion exchange resins and activated carbon (Kononova et al., 2007). Instead of columns filled with particles, membranes have become increasingly attractive for efficient separation due to their promising properties of ease and low energy of operation (Zhai et al., 2008). The membrane has wide application in metal enrichment and separation, and membrane technology is an established part of several industrial processes (Nunes and Peinemann, 2001). While, the common membrane does not perform very well on selective enrichment and separation of the target metal ions, and the problem can be effectively solved by the technique of molecular imprinting, which is a convenient and powerful technique recognizing the imprinted molecule selectively by preparing polymeric materials with artificial receptor-like binding sites for various substances (Xu et al., 2004; Yin et al., 2005; Liu et al., 2005; Guo et al., 2005). As a branch of molecular imprinting, ion imprinting has the character as well. Furthermore, ion imprinted polymers have been applied in solid phase extraction, sensors and membrane separations of inorganics (Rao et al., 2006), and there are a few reports on ion imprinted membrane used for recover silver in waste solutions (Shawky, 2009). Overall, combining the technique of ion imprinting with membrane, metal ion imprinted membrane has extensive prospect in metal ion recovery.

This study is to prepare metal ion imprinted membrane with selective enrichment and separation for silver ions. Complexing mechanism between imprinted ions and membrane was analyzed by infrared spectrogram; pH, adsorption capacity and selective recognition were investigated in this work. The membrane could be applied in field of silver enrichment and separation in waste solutions.

2. Experimental

2.1. Chemicals and materials

Chitosan–acetate solution was prepared by dissolving chitosan (CTS, 90.0% deacetylation degree, loss on drying ≦8.0%, Sinopharm

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doi:10.1016/j.hydromet.2009.10.006

Group Chemical Reagent Co., Ltd. China) in acetate solution (2% volume fraction). Polyvinyl alcohol solution was prepared by dissolving polyvinyl alcohol (PVA, 1750 ± 50 polymerization degrees bought from Xiangzhong Chemical Reagent Development Center, Hunan, China) in deionized water. Glutaraldehyde was used as main composition to prepare mixed cross linker. Silver nitrate ($AgNO_3$, standard) supplied by Chemical Factory in Beijing was used to provide imprinted ions. NaOH solution was used to strip the membrane and 0.04 mol/L $Na_2S_2O_3 \cdot 5H_2O$ was to elute the imprinted ions. Mixed solutions of lead, copper, potassium were prepared by dissolving $Cu(NO_3)_2 \cdot 3H_2O$, KNO_3, and $Pb(NO_3)_2$ in deionized water to carry out competitive adsorption test. All above are analytical reagents.

2.2. Instruments and apparatus

IRPrestige-21/FT-IR-8400S Fourier transform infrared spectrometer (FT-IR, Shimadzu.co., Japan) was used to characterize and analyze the complex mechanism between imprinted ions and blend membrane. 910S differential scanning calorimeter (DSC, TA instruments, USA) was used to detect the compatibility and heat resistance of the blends. The absorbance of Ag(I) after adsorption was detected by GFS97 graphite furnace atomic absorption spectrophotometer (GFAAS, Thermo co., USA) in 328.1 nm.

2.3. Preparation of Ag(I) imprinted membrane

Certain amounts of 2% acetate solution of CTS and 5% aqueous solution of PVA were stirred at room temperature until forming homogeneous phase. 0.01 mol/L $AgNO_3$ solution (avoided light) and mixed cross linker were added in sequence. Additives above were reacted for several hours till the homogeneous casting solutions were obtained. Then, the casting solutions were coated on the glass at a certain thickness, and placed in hot blast drying oven at 60 °C for thermal crosslinking and air-dried at room temperature. CTS/PVA blend membrane containing Ag(I) was obtained by stripping membrane with NaOH solution, and labeled as Ag(I)-CTS/PVA.

Ag(I)-CTS/PVA was cleaned by deionized water repeatedly and eluted by 0.04 mol/L $Na_2S_2O_3$ solution until Ag(I) in eluent could not be detected by GFAAS. After washing and drying, CTS/PVA blend Ag(I) imprinted membrane was prepared, and labeled as Ag(I)-IIM.

Non-imprinted membrane was prepared under the same condition in the absence of Ag(I), and labeled as NIIM.

2.4. Adsorption isotherm test

Ag(I) solutions in the range 1 mmol/L–10 mmol/L were prepared and the experiment of oscillation adsorption was carried out at 25 °C. The relationship between adsorption capacity (Q, mmol/g) and concentration (c, mmol/L) was studied by using GFAAS to detect the absorbance of Ag(I). Adsorption capacity could be calculated by Eq. (1).

$$Q = (c_0 - c) \cdot V / m \tag{1}$$

where Q represents the adsorption capacity of Ag(I)-IIM, c_0 and c are the initial and equilibrium concentrations of Ag(I), m (mg) is the quality of membrane, and V (mL) is the volume of solution.

The blank experiment was carried out by NIIM under the same condition.

2.5. Competitive adsorption experiments

Ag(I)-IIM was immersed into the mixed solutions (50 mL) containing Ag(I), Cu(II), Pb(II), and K(I) (0.5 mM for each) to perform the competitive adsorption test in the condition of oscillation by the oscillator. The adsorption capacities of Ag(I)-IIM for these interfering ions were investigated by detecting each ion's residual concentration with GFAAS.

Distribution coefficients (K_d, mL/g) of Cu(II), Pb(II), and K(I) with respect to Ag(I) were calculated by Eq. (2) (Andac et al., 2004).

$$K_d = \frac{c_0 - c}{c} \frac{V}{m} \tag{2}$$

where K_d represents the distribution coefficient, c_0 and c are the initial and equilibrium concentrations of metal ions, m (g) is the quality of Ag (I)-IIM, and V (mL) is the volume of solution.

Selectivity coefficient (k) for the binding of Ag(I) in the presence of competitor species can be calculated by Eq. (3) (Dai et al., 1999).

$$k = \frac{K_{\text{template metal}}}{K_{\text{interferent metal}}}. \tag{3}$$

Relative selectivity coefficient (k') can be defined as

$$k' = \frac{k_{\text{imprinted}}}{k_{\text{control}}}. \tag{4}$$

All coefficients above provide an estimation of the effect of imprinting on selectivity, and the blank experiment was carried out by NIIM under the same condition.

3. Results and discussion

3.1. Optimization of Ag (I)-IIM adsorption capacity by orthogonal experiment

The factors of blending ratio of CTS and PVA (A), concentrations of imprinted ions (B), cross linker (C) and alkali (D) were investigated by orthogonal experiment of four factors and three levels. The preparing conditions of Ag (I)-IIM with the larger adsorption capacity were optimized by investigating the adsorption capacity of membrane as an evaluation index.

The optimum combination program was found to be $A_1B_3C_2D_1$, viz. $V(CTS):V(PVA) = 4:6$, $\varphi(AgNO_3) = 1.2\%$, $\varphi(\text{cross linker}) = 0.8\%$, $w(NaOH) = 1.0\%$, by evaluating the $K(k)$ values of each factor in Table 1. In order to prove the optimized result with the largest adsorption capacity in Table 1, verification tests using Ag (I)-IIM were performed three times. The results show that the optimum combination program is $A_1B_3C_2D_1$ with 21.411 mmol/g of the adsorption capacity. It is in agreement with the results from orthogonal experiment.

Table 1
Orthogonal design experiment of Ag(I)-IIM.

	$V(CTS)/V(PVA)$ A	$\varphi(AgNO_3)$/% B	φ (cross linker)/% C	$w(NaOH)$/% D	Q /mmol/g
1	1(4:6)	1(0.8)	1(0.6)	1(1.0)	19.682
2	1(4:6)	2(1.0)	2(0.8)	2(3.0)	20.854
3	1(4:6)	3(1.2)	3(1.0)	3(5.0)	21.086
4	2(5:5)	1(0.8)	2(0.8)	3(5.0)	16.771
5	2(5:5)	2(1.0)	3(1.0)	1(1.0)	14.721
6	2(5:5)	3(1.2)	1(0.6)	2(3.0)	12.693
7	3(6:4)	1(0.8)	3(1.0)	2(3.0)	12.107
8	3(6:4)	2(1.0)	1(0.6)	3(5.0)	12.982
9	3(6:4)	3(1.2)	2(0.8)	1(1.0)	18.229
$K1$	61.622	48.560	45.357	52.632	
$K2$	44.185	48.557	55.854	45.654	
$K3$	43.318	52.008	47.914	50.839	
$k1$	20.541	16.187	15.119	17.544	
$k2$	14.728	16.186	18.618	15.218	
$k3$	14.439	17.336	15.971	16.946	
R	6.102	1.150	3.499	2.326	
Optimal scheme	$A_1B_3C_2D_1$				