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Recovery of nickel from mixed solution containing light metals by PSt/MA resin

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Abstract: The construction procedure and structure of Ni^{2+} macromolecular complexes with series of poly styrene and maleic anhydride (PSt/MA) were studied. Both the copolymers and the complexes (Ni-PSt/MA) were characterized by means of FTIR, elemental analysis, gel permeation chromatography (GPC) and atomic adsorption spectrometer (AAS). A further study using PSt/MA as chelating resin to recover Ni^{2+} was performed. The adsorption behavior for Ni^{2+} and various relating parameters of PSt/MA in the separation process were determined. The results indicate that the adsorption capability varies with pH values and the PSt/MA can recover Ni^{2+} in higher adsorption rate and higher selective coefficient from a mixed solution containing light metals such as Ca^{2+} and Mg^{2+} impurities.

Key words: nickel; macromolecular complexes; recovery; separation; adsorption

1 Introduction

Nickel is one of the most valuable metals and plays an important role in many fields such as steel making, electroplating and ceramic industry, battery and accumulator manufacturing[1]. However, it always exists as mixture rather than an individual mineral in nature. New and cost-effective methods for metal recovery are currently developed [2-4]. The recovery of Ni²⁺ from aqueous solution includes membrane filtration, adsorption, precipitation or ion exchange[5-7]. With recent rapid developments in technology, a great deal of attention has been paid to polymer materials[8-11], which can be used repeatedly as chelating resin and liquid membrane extractant for recovery of metals from impurities contained system. These polymers are capable of coordinating to different metal ions through reactive functional groups containing O, N, S, and P as donor atoms[12–13] to form metal macromolecular complexes (MMC). While synthesizing chelating resin, the choice of ligands always plays an important role in achieving selectivity. Among the ligands, the synthetic poly styrene and maleic anhydride (PSt/MA) has attracted special attention due to the advantage of its convenient preparation and solubility of alkali salt in water, as well as it is a spaghetti-shaped linear polymer with varying lengths (that is to say that the distribution of relative

molecular mass can be adjusted).

In previous work, the synthesis of MMC containing rare earth metals with polymeric ligands and their applications as florescent materials were reported[14–15]. As part of our continuing investigation into the development of MMC involving nickel, herein the procedure to form Ni-PSt/MA with series polymeric ligands of PSt/MA was presented, and a detailed research on the structure and property characterization for both the copolymers and Ni-PSt/MA complexes was performed. The results indicate that the PSt/MA resin can be used as a potential chelating adsorbent to recover nickel from complicated system. For the purpose of developing practical approach for recovery of nickel in industry, the adsorption behavior of PSt/MA for Ni²⁺ was investigated. In addition, the adsorption isotherm and parameters in the procedure were determined.

2 Experimental

2.1 Instruments

Vibration spectra from 4 000 to 400 cm⁻¹ were recorded on Thermo Nicolect Mattson 2110 FTIR spectrometer (KBr discs). Element analyses for C and H were carried out on Elemental Vario-El elemental analyzer. Metal contents were determined on Hitachi 180-80 polarized Zeeman atomic adsorption spectrometer (AAS). The average relative molecular

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mass of PSt/MA was estimated by SN-01A Gel permeation chromatography (GPC), using THF as fluent.

2.2 Materials

All the chemicals used in this work were of analytical reagent grade. Styrene was washed with 10% aqueous sodium hydroxide to remove the inhibitor, and followed by washing with water until it was neutral. The solution of Ni²⁺ containing light metal ions such as Ca²⁺ and Mg²⁺ were prepared by dissolving the appropriate amount of analytical grade sulfates in water.

2.3 Preparation of PSt/MA resin

A mixture of different molar ratio of styrene and maleic anhydride (about 15 g) was added dropwise to 100 mL toluene at (75 ± 1) under stirring for 6 h with benzoyl peroxide(1% of monomer) as an initiator. The precipitate generated was washed repeatedly with toluene and acetone respectively to remove the unreacted monomers and initiator, and then dried in a vacuum oven at 40 to a constant mass. The resulting resin is white, amorphous solid and the average relative molecular mass evaluated by GPC method is about 20 000. The synthetic route of the PSt/MA resin and the Ni-PSt/MA are described in Fig.1 and Fig.2.



Fig.1 Synthetic route of PSt/MA resin



Fig.2 Structure unit of complexes Ni-PSt/MA

2.4 Adsorption experiments

2.4.1 Adsorption capacity

About 1 g dry PSt/MA resin was put into dilute NaOH (0.1 mol/L) solution; the mixture was stirred at room temperature to dissolve completely. The resulting polymeric sodium carboxylates (Na-PSt/MA) solution

was adjusted to the pH range of 6-7, and then a sulfate solution containing 1.02 g/L Ni²⁺ was added. The mixtures were stirred continuously and the concentration of metals was determined by atomic adsorption spectrometry. The formed precipitates (Ni-PSt/MA) were isolated from the solution by centrifugation, then washed with water to remove Ni²⁺ and any another impurities, and finally washed with ethanol and dried in a vacuum desiccator. The Ni-PSt/MA precipitates cannot be dissolved in water, alcohol and other normal organic solvents, but can be easily dissolved by inorganic acid to release Ni2+, and the protonated insoluble resin of PSt/MA is regenerated. The adsorption capability Q(mg/g) is calculated according to:

$$Q = \frac{(c_0 - c)V}{W} \tag{1}$$

Where c_0 and c are the initial concentration of Ni²⁺ and the equilibrium one of Ni²⁺ in supernatant after sorption; V is the volume of solution used for sorption; and W is the mass of the resin.

2.4.2 Adsorption selectivity

To determine the adsorption selectivity of PSt/MA under competitive condition, the resin was contacted with a binary mixture, in which the concentration of each metal ion was approximately equal. Thus, accurate amount of sodium PSt/MA solution was stirred with a solution of binary mixture. Then, the resin was separated by filtration and the concentrations of the metal ions in the binary mixture were determined by AAS.

2.4.3 Adsorption isotherm

The adsorption isotherm studies were carried out by different volume of sodium PSt/MA solution stirred with 30 mL metal-ion solutions of Ni²⁺. Then the solutions were filtered, and the concentrations of the metals were determined by AAS. The adsorption data for Ni²⁺ were analyzed by a regression analysis to fit the Freundlich isotherm model. These data were plotted as a function of the amount of Ni²⁺ bonded to the resin at equilibrium versus the Ni²⁺ valuable metal concentration of the solution at equilibrium. The coefficients of this model were computed with linear least-square fitting.

3 Results and discussion

Ni²⁺ 3.1 Characterization of macromolecular complexes (Ni-PSt/MA)

3.1.1 Elemental analysis

The elemental analysis results of the PSt/MA resin and Ni-PSt/MA are shown in Tables 1 and 2.

It could be seen that the composition of the resin is slightly different from that of two monomers as starting materials. This may be caused by the different reactivity

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Table 1 Elemental analysis results of PSt/MA resin						
Complay	Feed ratio of	f Element content/%				
Complex	PSt to MA	C(calc.)	H(calc.)	n		
L1	0.33	61.64(61.66)	5.99(6.09)	0.34		
L2	0.11	53.20(53.21)	5.42(5.51)	0.13		
<i>n</i> is the mole ratio of PSt/MA in the resin						

 Table 2 Elemental analyses results of complexes Ni-PSt/MA

Commlan	Element content/%					
Complex	C(calc.)	H(calc.)	Ni(calc.)	m		
NiL1	37.86(37.89)	5.51(5.95)	12.64(12.63)	0.54		
NiL2	29.09(29.13)	4.83(5.29)	15.46(15.47)	0.28		
is the mount	an of the mite th	est is mot home	lad to control Ni	2+ in the		

m is the number of the units that is not bonded to central Ni^{2+} in the structure unit of Ni-PSt/MA.

ratio of two monomers[16]. According to the results of composition determination, the structural unit of Ni-PSt/MA was shown in Fig.2, in which each Ni²⁺ is bonded to two carboxylates in the chain of the polymer (not necessarily in only one chain), forming stable and repeatable building blocks.

3.1.2 Infrared spectra analysis

The FTIR spectra of the Ni-PSt/MA are obviously different from that of the PSt/MA resin, but they resemble each other. The FTIR spectra data of PSt/MA and the Ni-PSt/MA are listed in Table 3 and the FTIR spectra of the L1 resin and the corresponding Ni-L1 are shown in Fig.3.



Table 3	FTIR	spectra	data	of	PSt/MA	resin	and	complexes
Ni-PSt/M	A						cm ⁻¹	
Comple	ex 1	Vo u	v_{c-o}		V	<i>v</i>	00-	Δv_{aa}

Complex	v_{O-H}	$v_{C=0}$	v_{asCOO^-}	$v_{\rm sCOO^-}$	$\Delta v_{\text{as-s}}$
PSt/MA	3 4 3 1	1 704	-	-	-
K-PSt/MA	3 422	-	1 563	1 404	159
NiL1	3 4 2 6	1 705	1 562	1 410	152
NiL2	3 4 3 0	1 706	1 560	1 408	154

The results show that all the Ni-PSt/MA still have a weaker absorption band at 1 700-1 706 cm⁻¹ ascribed to $v_{C=0}$ of the uncoordinated carboxylic group; the absorption intensity is apparently lower than that of the PSt/MA resin. Two strong absorption bands at 1 408-1 414 cm^{-1} and 1 560-1 563 cm^{-1} are observed in Ni-PSt/MA, which are assigned to the symmetric vibration absorption $(v_{sCOO^{-}})$ and asymmetric vibration absorption (v_{asCOOT}) of the carboxylic group, respectively. The $v_{C=0}$ absorption band at about 1 700 cm⁻¹ in Ni-PSt/MA does not disappear completely. This is due to a higher hindrance in polymer chains of PSt/MA, which makes the complexes Ni-PSt/MA exist in non-stoichiometric form. The determined Δv ($\Delta v =$ $v_{asCOO^{-}(A)} - v_{sCOO^{-}(A)}$) for the Ni-PSt/MA is far smaller than that for K-PSt/MA (159 cm⁻¹), which shows that the symmetry of the carboxylic group in the resin is C_{2v} , the same as the free ion. This clearly shows that the carboxylate acting as a bidentate chelate coordinates to the Ni^{2+} in the resins[17]

3.2 Results of adsorption experiments

3.2.1 Dependence of pH values

The chelating of Ni^{2+} with the resin is highly dependent on pH. The effect of pH values on the chelation of Ni^{2+} is illustrated in Fig.4.

At lower pH values, carboxylates (COO⁻) in PSt/MA are in the form of protonation, which induces an electrostatic repulsion of Ni²⁺. Therefore, competition



Fig.4 Relationship between adsorption capability and pH values

exists between protons and metal ions for adsorption sites and decreases the adsorption capacity. Thus, the adsorption capability cannot reach the maximum. These results indicate that metal ions can compete with hydrogen ions in adsorption by the carboxylate ions of PSt/MA[18]. On the contrary, under the circumstances of existing excessive chelating resin, especially at higher pH values, the adsorption capability decreases. This phenomenon can be illustrated as the strong tendency that Ni²⁺ form coordinated anion with carboxylate, which causes the Ni-PSt/MA dissolving in water. The results indicate that the maximum adsorption capability is 338.12 mg/g for L2 resin in the pH value of 8. 3.2.2 Adsorption selectivity of PSt/MA

The ability to selectively remove some particular metal ions from aqueous solution under competitive conditions is of utmost importance in designing chelating resins. The adsorption selectivity of PSt/MA for Ni²⁺ in a binary component system was investigated. The selective coefficient (K) is calculated as:

$$K = \frac{c_{\rm AI}c_{\rm B2}}{c_{\rm A2}c_{\rm B1}} \tag{3}$$

where c_{A1} and c_{B1} stand for molar fraction of the metal in the solution after adsorption, c_{A2} and c_{B2} stand for molar fraction of the metal in the phase of the resin[19] (A=Ni²⁺1.02 g/L, B=Ca²⁺0.92 g/L and Mg²⁺ 1.10 g/L). The experimental results are listed in Table 4.

Table 4 Selective coefficient (K) of PSt/MA resin

Resin	$K(Ni^{2+}-Ca^{2+})$	$K(Ni^{2+}-Mg^{2+})$
L1	180.6	2.9×10^{3}
L2	208.9	3.2×10^3

It can be seen that Ni^{2+} is prior to be adsorbed, and Ca^{2+} , Mg^{2+} is not adsorbed completely by PSt/MA. All the data imply that the PSt/MA resin can recover Ni^{2+} in industry.

3.2.3 Adsorption isotherm

A well known model for the adsorption process, particularly for chemisorption process, is presented by Freundlich equation:

$$\lg Q_e = \lg K + 1/n \lg c_e \tag{4}$$

where $Q_e(mg/g)$ is the amount of metal adsorbed at equilibrium; *n* is the constant; *K* is the binding energy constant which reflects the affinity of chelating material to metal ions. A linear plot of lg Q_e vs lg C_e shows the applicability of the Freundlich model (Fig.5). The Freundlich constant *K* and *n* are calculated and presented in Table 5, in which R^2 represents the linear correlation coefficient.

The values 1 < n < 10 indicate the favorable adsorption of metal ions onto the chelating material.

Table 5 Freundlich model for Ni ²⁺					
Resin	Freundlich equation	n	R^2		
L1	$\log Q_{\rm e} = 1.82 + 0.59 \log c_{\rm e}$	1.69	0.96		
L2	$\lg Q_{\rm e} = 1.73 + 0.72 \lg c_{\rm e}$	1.39	0.98		



Fig.5 Freundlich isotherms for adsorption of Ni²⁺

3.2.4 Determination of coordination ratio

The coordination reaction of Ni²⁺ with PSt/MA resin can be illustrated as follows[20]:

$$pR + Ni^{2+} RpNi$$
 (5)

When the coordination reaction reaches equilibrium,

$$K_{\rm e} = \frac{c_{\rm RpNi}}{c_R^P C_{\rm Ni^{2+}}} = \frac{D}{c_R^P} \tag{6}$$

where K_e is the equilibrium constant, D is the distribution coefficient ($D=Q_e/c_e$), p is the coordination ratio, R is the carboxylic content in the PSt/MA resin (mmol). The above formula can be changed as the following equation:

$$lg D = lg K_e + plg R$$
(7)

The equilibrium data are analyzed with the above linearized equation, and Fig.6 shows that the slope is the



Fig.6 Relationship between lg D and lg R of L1

coordination ratio.

The slope 2.08 is consistent with the Ni-PSt/MA structure units we discussed before.

4 Conclusions

1) The PSt/MA resin has rather strong coordination ability to Ni²⁺ to form Ni-PSt/MA, which possess three-dimensional network structure and can't dissolve in water and normal organic solvents.

2) Adsorption experiments reveal that the maximum adsorbing capability of PSt/MA resin is 338.12 mg/g. The isothermal adsorbing study illuminates that the adsorption is consistent with the Freundlich equation. The PSt/MA resin has good adsorption selectivity for Ni²⁺ and has promising use in recovering of nickel.

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