Retention Properties of Efficient Adsorbent to Silver(I)

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ABSTRACT: The binding capability of crosslinked poly(acrylic acid-*co*-2-acrylamide-2-methyl-1-propane sulfonic acid) for silver(I) ions by the batch equilibrium method is investigated. The effects of the pH, temperature, time of contact, and resin–metal ion molar ratio on the retention ability are studied. The retention for silver(I) increases from 21.7% at pH 1 to 94.6% at pH 5. The adsorption capacity at pH 5 is 1.18 meq/g dry resin. The maximum load capacity at the optimum pH is determined. In order to recover the resin, elution runs in acid and basic media are carried out. The best eluent is $4M$ HNO_3 (84.9%). Moreover, retention–elution cycles are performed. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1501–1506, 2002

Key words: crosslinked poly(acrylic acid-*co*-2-acrylamide-2-methyl-1-propane sulfonic acid); resin; retention properties; silver ions

INTRODUCTION

Polymers with ligands capable of coordinating or ion exchange with metal ions have attracted great interest for cleaning up wastewater and the recovery of metal ions. Current efforts are at the stage of developing selective separation of any desired metal ion from binary or ternary mixtures, which can be achieved to some extent by controlling the pH. In this regard, the chelate-forming polymeric ligands have been extensively studied and many reviews are available in the field.[1–5] These resins have been used for the preconcentration and separation of trace elements from seawater, and their analytical use in conjunction with atomic absorption spectroscopy has been well established.

For practical applications, strong and selective binding of the target metal ions, rapid complexation of the metal ion, and recovery of the resin are required. Moreover, minimal loss of the metal–ion binding capability after many cycles of application is needed. The chemical nature of the functional groups containing atoms able to form donor–acceptor bonds, which represent the basis of the polymer–metal complexes, is very different and generally complicated. The primary, secondary, and tertiary amine groups are probably the simplest.[6–10] In general, the sorption selectivity of chelating resins has been reported to be dependent mainly on the chelate-forming properties of functional groups that are chemically bonded on the supports, such as macroporous copolymers, at appropriate pH values. The selectivity in the metal–ion uptake of the polymers can be well explained by the Pearson principle.[11] It is well known that ligands with soft-type donors prefer interactions with soft (i.e., large and more polarizable) acceptors such as silver, gold, and mercury. However, the success of the selectivity strongly depends on the crosslinking density[12–14]; and, in this case, diffusion of metal ions into the polymer matrix becomes slower as the crosslink-

ing density increases. For this reason, this method seems to be applicable or suitable for large-scale separations. Therefore, the best method of achieving selective separations is to use a metal-specific ligand, but it proved impossible to find specific ligands for each metal ion.

Silver(I) ions are of interest for recovery from environmental, geological, and medicinal samples[15] and for the potential applications of the resin–Ag(I) material as a catalyst reagent.

Accordingly, this article describes the silver(I) retention properties of crosslinked poly(acrylic acid-co-2-acrylamido-2-methyl-1-propane sulfonic acid) [P(AA-co-APSA)] under different experimental conditions that contain strong and weak acid moieties.

EXPERIMENTAL

Reagents

The AA and APSA were purchased from Merck and Aldrich, respectively. The AA was purified by distillation and APSA was used without further purification. Ammonium peroxydisulfate (APS, Merck) and N,N-methylene-bisacrylamide (MBA, Merck) were used as received, and $AgNO_3$ (Merck) was analytical grade.

Resins

The resins were synthesized by radical polymerization using APS as an initiator and MBA as a crosslinking reagent. For the crosslinked P(AA-co-APSA) a feed molar ratio of 1 : 1 AA/APSA was used. The resins were completely insoluble in water.[16]

Swelling Percentage

A weighed amount of dry resin (0.5 g) was immersed in 250 mL of water (1.0 μS cm^{-1}, pH 5.62, 25°C) in a beaker for 36 h. The percentage of swelling (S) was determined gravimetrically by the following equation:

$$S\ (\%) = [(M_t - M_0)/M_0] \times 100$$

where M_0 is the initial weight and M_t is the weight of the swollen gel at time t.

Batch Equilibrium

A weighed amount of the resin was added to the metal–ion solution at the desired pH, and the mixture was shaken for 1 h at 20°C. The mixture was adjusted to the required pH by the addition of dilute HNO_3 or NaOH. The mixture was filtered off and the amount of the metal–ion remaining in the filtrate was determined by atomic absoption spectrometry. To investigate the effect of the temperature and time of contact on the retention at pH 5, 100 mg of the resin were put in contact with the silver(I) solution at the desired time and temperature. The amount of the silver(I) ions sorbed into the resin was calculated from the difference between the amounts of the metal ion in the filtrate and in the starting solution.

Maximum Load Capacity for Ag(I)

To obtain the maximum load capacity for Ag(I), 50 mL of an aqueous solution containing 1 g/L of silver(I) was added to 1 g of the resin. The mixture was shaken for 1 h at 20°C and pH 5.0. The process was repeated 3 times, and a new solution with the same concentration was used each time. The silver(I) ions were determined as above.

Desorption of Silver Ions

The silver(I)–resin (100 mg) was added to 10 mL of an aqueous solution of 1 and 4M HNO_3, 1 and 4M $HClO_4$, 1 and 4M H_2SO_4, and 0.25 and 1M Na_2CO_3 and stirred for 1 h at 20°C. Then the resin was filtered and washed with water. Silver(I) ions were determined in the filtrates by atomic absorption spectrometry.

Loading–Stripping Cycles

Batches of 100 mg of the Ag(I)-loaded resin were stripped with 10 mL of an aqueous solution of 1M HNO_3. This procedure of loading and stripping was repeated 4 times with fresh metal solution [0.621 and 0.835 g/L for P(AA-co-APSA) and P(APSA), respectively] and a solution of the most effective stripping reagents.

Measurements

The pH was measured with a H. Jürgens & Co. pH meter. The IR spectra were obtained on a Nicolet FTIR 550 Magna spectrophotometer. The determination of metal ions was performed with a Unicam Solaar M5 spectrometer. The thermal

Table I   Effect of Particle Size and pH on Retention Properties

Resin	Particle Size (μm)	pH	Retention of Ag(I)		
			%	mmol/g	mg/g
P(APSA)	180–250	1	7.5	0.04	4.3
P(APSA)	250–500	1	4.0	0.02	2.2
P(APSA)	180–250	3	78.1	0.35	37.8
P(APSA)	250–500	3	81.5	0.36	38.8
P(APSA)	250–500	5	85.4	0.40	43.1
P(AA-*co*-APSA)	180–250	1	21.7	0.08	8.6
P(AA-*co*-APSA)	250–500	1	21.7	0.08	8.6
P(AA-*co*-APSA)	180–250	3	72.4	0.26	28.0
P(AA-*co*-APSA)	250–500	3	73.1	0.26	28.0
P(AA-*co*-APSA)	250–500	5	94.6	0.34	36.7

The resin : Ag(I) molar ratio is 10 : 1 for 1 h at 20°C.

stability of the resins and resins–silver(I) ions under N_2 was evaluated by thermogravimetric analysis with a Polymer Laboratories STA 625 thermogravimetric analyzer with a heating rate of 10°C/min.

RESULTS AND DISCUSSION

The P(AA-*co*-APSA) was synthesized by radical polymerization by using APS (0.5 mol %) and MBA (4 mol %) as an initiator and crosslinking reagent, respectively. The yield was 95%. An equimolar feed molar ratio of AA:APSA was used.[16] The P(APSA) was synthesized by radical polymerization with similar conditions[17] to compare the retention properties with the copolymer. Hence, the matrix does not dissolve in aqueous media due to its 3-dimensional network structure, but the chains do expand. In this case, the transport of the silver ions into the polymer network is diffusion controlled. In the complexation of polymeric ligands with silver ions, the polymer matrix contracts or expands by intrachain or interchain complexation. The particle size of the resin immediately after the polymerization was higher than 500 μm. Subsequently, the resin was crushed to yield materials with particle sizes of 180–250 and 100–180 μm. These fractions were used to study the metal–ion binding capacity.

The FTIR spectra show the most characteristic absorption signals at 1645 cm^{-1}, which are attributed to the stretching C=O (from the amide group), for P(APSA), and 1720 cm^{-1}, which are

due to the stretching C=O (from the carboxylic acid group), for P(AA-*co*-APSA).

A fundamental relationship exists between the swelling of a crosslinked polymer in a solvent and the nature of the polymer, and the solvent also has a strong effect on the availability of the ligand or ion exchange site to interact with the metal ions. The crosslinked P(AA-*co*-APSA) shows a high swelling percentage value of 693%.

As in the protonation and deprotonation properties of the acidic and basic groups of the ion exchanger, its sorption behavior for metal ions is influenced by the pH value, which influences the surface structure of sorbents, speciation of the metal ions, and the interactions between sorbents and the metal ions. Therefore, the pH dependence of the adsorption for the metal ions was examined.

Because of the interest in concentrating silver(I) from aqueous solutions, the following runs were carried out on the single metal ion.

The sorption characteristics of the sorbent toward silver(I) were investigated in an aqueous solution at pH 1–5 using the batch equilibrium procedure. The sorption affinity of the sorbent as a function of the pH and particle size (180 and 250 μm) are summarized in Table I. The particle size has no important effect, but the resins show a high affinity for the silver ions. The silver ion retention increases as the pH is increased, and the highest values are achieved at pH 5: 94.6% (0.34 mmol/g) for P(AA-*co*-APSA) and 85.4% (0.40 mg/g) for P(APSA). The low retention at low pH should be explained by the low charge density of the monovalent silver ions, which does not favor
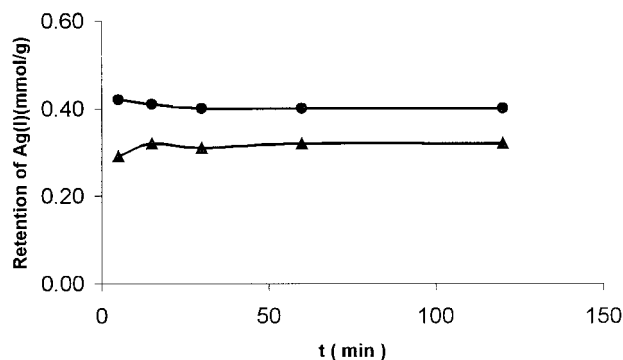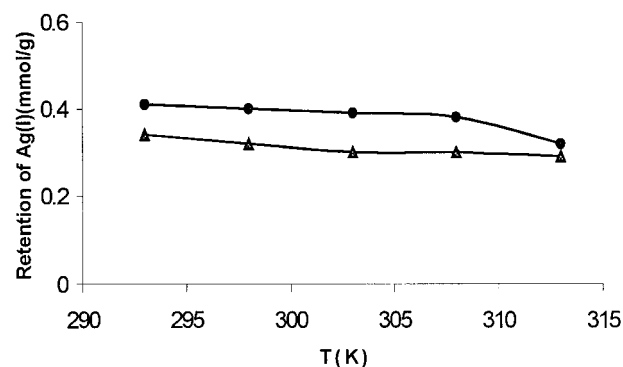
Figure 1 The effect of time on the silver(I) ion retention of the (●) P(APSA) and (▲) P(AA-*co*-APSA) resins at pH 5.0.

the electrostatic interaction type, particularly with the strong acid groups. The deprotonation of the carboxylic acid groups at pH 5.0 should also be responsible for the higher values of the silver(I) ion retention, indicating that it is retained by the coordination mechanism.

Taking into account that there is no significant effect on the Ag(I) retention, the following studies were carried out with only the 250-μm particle size.

The time required for 90% (0.3 mmol/g) and 80% (0.4 mmol/g) uptakes for P(AA-*co*-APSA) and P(APSA), respectively, was found to be 5 min. That meant that the equilibrium was achieved relatively fast considering that the resin–metal ion interaction is occurring in a heterogenous medium. Moreover, the resin should be suitable for column operation a low flow rate (Fig. 1).

In addition, there is also no important effect of the temperature on the retention of silver ions in the 20–40°C range (Fig. 2).

Figure 2 The effect of the temperature on the silver(I) ion retention of the (●) P(APSA) and (▲) P(AA-*co*-APSA) resins at pH 5.0 for 1 h.
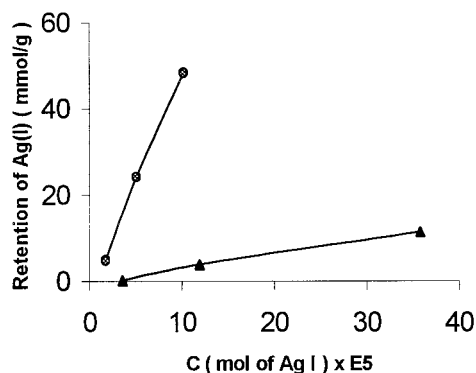
Figure 3 The effect of the resin–silver(I) ions molar ratio on the retention of the (●) P(APSA) and (▲) P(AA-*co*-APSA) resins at pH 3.0 for 1 h.

To explore the applications of the sorbent, it is relevant to obtain knowledge on the sorption capacity of the resin toward Ag(I) ions (Fig. 3). Accordingly, with these data the maximum load capacity was determined for both resins at pH 5 for 1 h at 20°C. The values obtained are 1.19 meq/g (128.4 mg/g) for P(AA-*co*-APSA) and 1.19 meq/g (128.4 mg/g) for P(APSA).

The sulfonic acid and carboxylic groups have a different involvement in the retention of the silver ions. Thus, the sulfonic groups could interact electrostatically with the ions but the carboxylate groups could interact through a complexation. Both mechanisms should be occurring in a different magnitude, depending on the pH. At low pH the contribution of the electrostatic effect is stronger than at higher pH where the complex formation should be more important.

To be useful in the ion-recycling process, the metal ion adsorbed by the resin should be easily released under appropriate conditions. The effect of the different eluents on the desorption of the silver(I) ions is given in Table II. Sodium carbonate up to 1M was not an effective eluent reagent. With 4M H$_2$SO$_4$ it was possible to elute about 60% of the sorbed Ag(I) ions. Nitric acid (1 and 4M) and HClO$_4$ (1 and 4M) emerged as the most effective eluents for the recovery of the Ag(I) ions from the resin. At 1M the elution was close to 80% with a treatment for 1 h. Moreover, the sorbent was able to withstand the strong acidic conditions and its metal ion-binding ability was retained after repeated acid treatment. Hence, to obtain the reusability of P(AA-*co*-APSA), the sorption–desorption cycle was repeated 4 times using the same sorbent. Initial amounts of 0.835 and 0.621 g/dL

Table II   Effect of Eluent on Recovery of Resin

Resin	Eluent	Elution (%)
P(APSA)	H_2SO_4 (1*M*)	51.6
P(APSA)	H_2SO_4 (4*M*)	60.3
P(APSA)	$HClO_4$ (1*M*)	63.9
P(APSA)	$HClO_4$ (4*M*)	66.2
P(APSA)	HNO_3 (1*M*)	70.5
P(APSA)	HNO_3 (4*M*)	72.1
P(APSA)	Na_2CO_3 (0.25*M*)	2.3
P(APSA)	Na_2CO_3 (1*M*)	8.4
P(AA-*co*-APSA)	H_2SO_4 (1*M*)	60.3
P(AA-*co*-APSA)	H_2SO_4 (4*M*)	60.3
P(AA-*co*-APSA)	$HClO_4$ (1*M*)	80.9
P(AA-*co*-APSA)	$HClO_4$ (4*M*)	79.4
P(AA-*co*-APSA)	HNO_3 (1*M*)	83.3
P(AA-*co*-APSA)	HNO_3 (4*M*)	84.9
P(AA-*co*-APSA)	Na_2CO_3 (0.25*M*)	5.7
P(AA-*co*-APSA)	Na_2CO_3 (1*M*)	10.9

Table III   Thermal Stability of Unloaded and Ag(I) Loaded P(APSA) and P(AA-*co*-APSA)

Resin	Weight Loss at Different Temperatures (°C)				
	100	200	300	400	500
P(APSA)	0.87	7.82	35.90	68.49	78.11
P(APSA)–Ag(I)	1.28	9.56	31.72	65.80	74.10
P(AA-*co*-APSA)	2.23	9.38	37.37	58.36	83.28
P(AA-*co*-APSA) –Ag(I)	2.15	4.62	33.82	54.66	74.67

The heating rate is 20°C/min under N_2.

temperatures under dynamic conditions (Table III). The unloaded resins are very stable up to 200°C with a weight loss lower than 10%. Then it increases up to values close to 80%. The silver(I)-loaded resins show similar thermal behavior without an important effect of the silver(I) ions on the thermal stability.

CONCLUSIONS

The crosslinked P(AA-*co*-APSA) that was synthesized by solution radical polymerization shows great promise in the removal of silver(I) ions from aqueous media, particularly at pH 5.0. The silver(I) ions adsorption was rapid, and adsorption equilibrium was reached in about 15 min. The adsorption capacity at pH 5.0 was 1.18 meq/g of dry resin. Adsorbed silver(I) ions were relatively easily desorbed by using 1*M* HNO_3 and 1*M* $HClO_4$. Consecutive adsorption and desorption showed the feasibility of this resin for silver(I) ion adsorption.

of Ag(I) were employed to load the P(APSA) and P(AA-*co*-APSA) resins, respectively. In each cycle the adsorption was performed at pH 5.0 for 1 h using 1*M* HNO_3. Figure 4 shows the results of these studies. The carboxylic acid moiety increases the loading capacity in the P(AA-*co*-APSA) with respect to P(APSA). As seen here, the resorption ability of the resin decreases around 20–25% during repeated sorption–desorption cycling. It can be attributed to probable destruction (partial hydrolysis) of the sorbent sites.

To determine the effect of the Ag(I) ions adsorbed into the resin on the thermal stability, thermogravimetric analysis was carried out. The resin was saturated with Ag(I) at pH 5.0. The weight loss was measured under N_2 at different
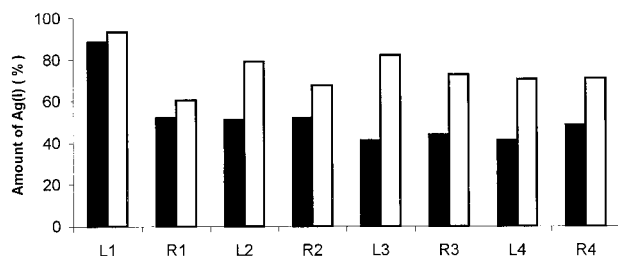
Figure 4   The amounts of Ag(I) ions on the (□) P(AA-*co*-APSA) and (■) P(APSA) resins after four cycles of loading (L) and regeneration (R) with 1*M* HNO_3. The initial amounts of Ag(I) for P(APSA) and P(AA-*co*-APSA) are 8.35 and 6.21 mg/L, respectively.

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