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TECHNICAL NOTE

The Separation of Cu^{2+} and Ni^{2+} from Fe^{3+} Ions by Complexation with Alginic Acid and Using a Suitable Membrane

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ABSTRACT

In this study the EC-PEG 4000 alloy membrane was used as a filter for the concentration and separation of metallic ions. Its permeability was first studied, and it was found that it is permeable to Cu^{2+} and Ni^{2+} but not to Fe^{3+} ions. This property of an EC-PEG 4000 alloy membrane was used to separate Fe^{3+} from Ni^{2+} and Cu^{2+} in aqueous solutions. Alginic acid was used as a complexing agent and the separation was carried out at different pH values for different concentrations of the complexing agent for Fe^{3+}/Ni^{2+} and Fe^{3+}/Cu^{2+} pairs separately.

Key Words. Alloy membranes; Metallic ions; Retention; Complexation; Concentration.

INTRODUCTION

The effects of water-soluble polymers on the concentration of aqueous solutions of metallic ions and their separation have been studied by various authors (1–7). The separation of metallic ions can be realized by an ultrafiltration-chelation process.

The concentration of the aqueous solutions of metallic ions and their separation can be achieved by using a semipermeable ultrafiltration membrane (8).

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The degree of separation is dependent on the type, size, and charge of the ion, the pressure, and also the polymer used (9). The semipermeable membrane used for this purpose must have high permeability for the solute and the solvent, and a certain molecular weight cutoff value (MWCO) (10). The complexation agent must have high selectivity for the ions studied and the capacity of interacting with metal ions. It also must easily dissolve in water and have a narrow molecular weight distribution. The weight and the type of metal, number of functional groups in the polymer, concentration, pH, ionic strength, applied pressure, temperature, and stirring speed are functions of complex formation.

EXPERIMENTAL

The alginic acid used in this study was supplied from Fluka. Cupric chloride, ferric chloride, and nickel chloride were obtained from Merck. Ethyl cellulose (EC) and polyethylene glycol (PEG 4000) used in the preparation of EC-PEG 4000 alloy membranes were obtained from Sigma and Merck, respectively.

EC-PEG 4000 alloy membranes are prepared by casting and are characterized by the method given in Ref. 11. Alloy membranes were obtained with PEG 4000 due to the fact that membranes without pores were only attained from ethyl cellulose. THF/CH_2CI_2 and lactic acid were used as solvent and nonsolvent, respectively. After a relaxation period, the membrane casting solution was cast on a glass surface with a doctor blade. The films, which were immersed and precipitated in an *n*-hexane quench medium, were kept in an alcohol/water bath. Membranes obtained from EC only were not porous, but the addition of PEG resulted in the formation of pores. The membrane containing 20% PEG was suitable for ultrafiltration due to its water permeability and molecular weight cutoff (MWCO). The so-called molecular weight cutoff is the pure water flux. The EC-20% PEG membrane exhibited the highest water permeability and a MWCO of 900.

The concentrations of Cu^{2+}, Ni^{2+}, and Fe^{3+} were determined spectrophotometrically using a Hitachi 100-60 double-beam UV spectrophotometer. Cu^{2+} was measured at 430 nm as a diethyldithiocarbamate complex extracted with carbon tetrachloride, Ni^{2+} as a dimethylglyoxime complex (λ = 327 nm) extracted with chloroform, and Fe^{3+} was determined in the form of a thiocyanate–Fe^{3+} complex (λ = 450 nm). The absorbances in the UV region of aqueous solutions of polymer and polymer ion complexes and the effect of pH on the complexation between polymer and metallic ions were determined.

The equimolar mixture of the two metallic ions in the presence of the complexing agent was ultrafiltered. The concentrations of the metallic ion and alginic acid were taken as 2×10^{-3} M and 2×10^{-3} g·L^{-1}, respectively.

The concentration of the retained metal ion was calculated by the following equation:

$$R = 1 - \frac{C}{C_0}$$

where C is the final metal ion concentration and C_0 is the initial feed concentration. The retention of metallic ion pairs at the same conditions was also determined.

RESULTS AND DISCUSSION

Methods of separation using membranes are important economic developments of the last few years. Among them, ultrafiltration is the most economic (12–15).

The water permeabilities of the EC-PEG 4000 alloy membranes were measured at different pressures. The retention of metallic ions at constant pressure but at different pH values was determined. It was found that the membrane is permeable to Cu^{2+} and Ni^{2+} but not to Fe^{3+}. Hydrolysis of Fe^{3+} takes place at acid pH values.

The variation of the retention of Fe^{3+} ions in the presence of alginic acid (complexing agent) versus time under constant pressure and temperature (100 mmHg, 25°C) for different pH values are shown in Fig. 1. The maximum retentions of the ions are summarized in Table 1.

The retention of complex molecules with a branched or spherical structure is expected to be higher than that of linear elastic molecules with the same molecular weight. But this study, and the previous one (11), have shown that functional groups on the polymer (complexing agent) have a dominant effect in retention.

As seen from the results, the retention of metallic ions increased with increasing pH. The removal of the acidic proton on alginic acid results in chelation of the metal ions by the anionic polymer. Alginic acid showed a definite selectivity toward the smaller Fe^{3+} ions due to their higher electrostatic potentials, with a retention value of 95.8% at pH 3.1. The retention of the metallic ions and complexation agent is a function of pH. The shape of the molecules can be changed by adjusting the pH or adding different ions to the medium. The ionic charge density on the polymer chain increases by increasing the pH of the solution, and thus the polymeric chain opens due to ionic repulsion. As a result it is not surprising that the viscosity of the polymer solution and the retention increase with an increase in pH.

The effect of pH on complexation between alginic acid and metallic ion is shown in Fig. 2. At pH values higher than the optimum retention pH,

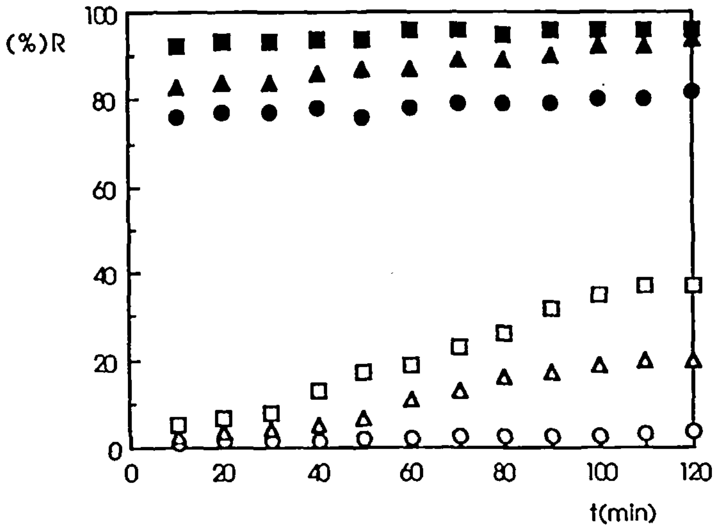

FIG. 1 Effect of pH on retentions for Fe^{3+}–alginic acid, $[Fe^{3+}] = 2 \times 10^{-3}$ M, [alginic acid] $= 2 \times 10^{-3}$ units g L^{-1}. The open and solid symbols are pH values in the absence and presence of alginic acid. The pH values are: (●, ○) 1.0, (▲, △) 2.0, and (■, □) 3.1.

decreases in the absorbances of the complexes were observed due to hydrolysis of the complexes.

The separation of Fe^{3+}/Cu^{2+} and Fe^{3+}/Ni^{2+} ion couples was studied by adding alginic acid at pH 3.0. Fe^{3+}/Cu^{2+} and Fe^{3+}/Ni^{2+} ion couples were studied for the separation of Fe^{3+} ions by adding alginic acid at pH 3.0. Alginic acid selectively forms more stable complexes with Fe^{3+} than with Ni^{2+} or Cu^{2+}. Retentions of Fe^{3+}/Cu^{2+} and Fe^{3+}/Ni^{2+} ion couples in the presence of alginic acid at pH 3.0 are 91.8, 6.5 and 96.0, 5.2 respectively. The retention

TABLE 1
Maximum Retentions for Cu^{2+}, Ni^{2+}, and Fe^{3+} Solutions at Different pH Values in the Presence of Alginic Acid (25°C)

pH	%*R* (Cu^{2+})	pH	%*R* (Ni^{2+})	pH	%*R* (Fe^{3+})
1.0	30.0	3.1	36.0	1.0	82.2
3.1	45.8	5.1	40.0	2.0	92.5
5.1	50.5	6.9	44.5	3.1	95.8
6.0	57.8				

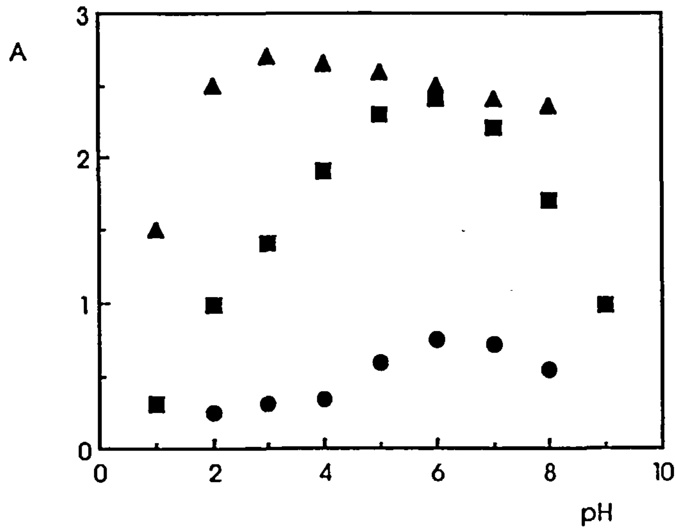

FIG. 2 Effect of pH on complex formation between alginic acid and Cu^{2+}, Ni^{2+}, and Fe^{3+} metal ions. [Alginic acid] = 2×10^{-3} units g·L^{-1}, [Cu^{2+}] = [Ni^{2+}] = [Fe^{3+}] = 2×10^{-3} M. (▲) Fe^{3+}–alginic acid, (■) Cu^{2+}–alginic acid, (●) Ni^{2+}–alginic acid.

values when the metal ions were used alone in complexation with alginic acid for Fe^{3+}, Ni^{2+}, and Cu^{2+} are 95.8, 36.0, and 45.8, respectively. The results show that an ion pair can be separated by a polymer selective for the Fe^{3+} ion.

The absorbance and wavelength maxima shift values for the alginic acid and alginic acid-metallic ion pairs are given in Table 2. As clearly seen, shifts in the wavelengths and absorbances are indicators of the structural changes that occur on the molecules. Fe^{3+}, Ni^{2+}, and Cu^{2+} form strong carbonyl complex. As a result of the interaction of Cu^{2+}, Ni^{2+}, and Fe^{3+} with the nonbonding

TABLE 2
Shifts in the Value of Wavelength Maxima (λ_{max}) of Alginic Acid and Alginic Acid–Metal Ion Couples

Polymer	A	λ_{max} (nm)	Polymer + metal ion	A	λ_{max} (nm)
Alginic acid	0.66	274	Alginic acid + Fe^{3+}	2.37	290
			Alginic acid + Cu^{2+}	0.27	281
			Alginic acid + Ni^{2+}	0.18	274

electrons in the carbonyl group of the alginic acid chain, a shift in the wavelength maxima takes place. This might be due to the n-π^* transition.

In conclusion, the concentration and separation of Fe^{3+} ion from the Fe^{3+}/Ni^{2+} couple and the Fe^{3+}/Cu^{2+} couple by complexing with alginic acid and ultrafiltration of EC-PEG 4000 alloy membranes is proposed as a suitable method.

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