Removal of Fe(III) Ions from Dilute Aqueous Solutions by Alginic Acid-Enhanced Ultrafiltration

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ABSTRACT: The removal of Fe(III) ions from aqueous solutions was studied using membrane filtration. A water-soluble polymer alginic acid (AA) was used to bind the metal ions, which was followed by batch ultrafiltration using poly(methyl methacrylate-methacrylic acid) membranes modified with poly(ethylene glycol) (PMMA-MA-PEG). The complexation behavior of AA and the effect pH on the rejection of iron were investigated. Maximum recovery of 87.13% was obtained when the filtration was carried out in the presence of AA at pH 3.1. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1096–1101, 2000

Key words: ultrafiltration; metal ion concentration; preconcentration; polymer membrane; poly(methyl methacrylate-methacrylic acid) copolymer

INTRODUCTION

The removal and separation of hazardous substances from aqueous systems such as industrial waste fluids, natural waters, and radionuclides are a technological challenge with respect to industrial and environmental applications.

Conventional methods include the use of water-insoluble polymers for the quantitative and selective removal of substances. However these heterogeneous methods require additional steps, such as back extraction, elution, and so on. Recently membrane processes have become a routine technique for the removal of toxic materials from aqueous systems.[1–3] The advantages of these methods are the low energy requirement and the high selectivity. By far the most important membrane processes used are ultrafiltration (UF), reverse osmosis, microfiltration, and electrodialysis.[1] The main element of these processes is the semipermiable membrane. Certain solution components will pass through the membrane forming the permeate whereas others will be retained by the membrane forming the retantate or the concentrate.

Retention of a component by the membrane depends on many parameters, including solute type, solution composition, pH, membrane material, and membrane pore size. In many cases, however, the size of the component to be separated is the main factor for the retention. One way to improve the separation is enlarging the molecular dimensions by binding the component to macromolecules. The method that can meet this requirement is polymer-enhanced ultrafiltration (PUF). PUF is the combination of two phenomena: binding of the component to be separated to a water-soluble polymer and UF. This large molecule having a larger molecular size than that of membranes pores will be retained whereas the noncomplexed components pass through the membrane.
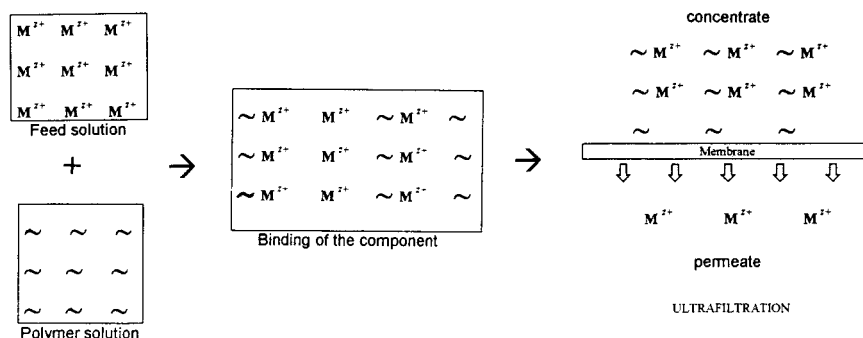
Generally low-molecular-weight species can be bound to macromolecules by all intermolecular forces, mainly ionic, complex bond, or the combination of both.

Majority of the studies that were published in the literature are related to the separation of

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Figure 1 Diagrammatic representation of PUF.

metal ions.[1–14] An example of a case where the species to be separated are bound to polymers by ionic interactions is the removal of iron, manganese, and calcium from ground water. According to the work of Volcheck and coworkers,[4] these metals present in the feed solution could be removed depending on pH.

Complex bonds are significantly more selective than ionic attractions. The formation of complexes with water-soluble polymers occurs in the same manner as in the case of chelating resins. For this reason synthetic polyelectrolytes containing carboxylic, imino, and sulfonic groups were used as the macromolecular binding agents.[4,6–10,11–16]

Sarzanini et al.[5] used 1,2-dihydroxybenzene-3,5-disulfonic acid with metal ions for developing preconcentration techniques. *N,N*-dimethylacrylate-co-acrylic acid,[6] poly(vinyl alcohol) (PVA),[7,8] and dextran[9] have also been used as polymeric supporting material in the UF of metal ion solutions.

Studies of Geckeler et al.[10] based on the investigation of metal-complexing properties of five different polyaziridines in an aqueous solution with regard to the side-chain effects using membrane filtration.

Poly(ethylene imine) (PEI) and its derivatives are most commonly used binding agents in UF experiments for the removal of metal ions.[4,11–14] Although PEI's demonstrates a good selectivity toward transition metals, their use is restricted because these polymers are considered to be fairly toxic.

UF membranes have been made from numerous materials such as cellulose derivatives, acrylics, polysulfones, polycarbonates, fluoropolymers, and polyamides. Polyacid-based membranes, because of their hydrophilicity, are of special interest in UF studies. Poly(methyl metacrylate-co-metacrylic acid) copolymer (PMMA-MA) is also a

suitable hydrophilic polymer to be used in membrane processes.[8,17,18] In our previous study we have modified PMMA-MA membranes using poly-(ethylene glycol) (PEG) to obtain additional hydrophilicity and elasticity[8] and used the modified membranes to concentrate Fe(III) solutions using PVA as the binding macromolecule.

In this study we have aimed to use these membranes in Fe(III) UF using AA as polymeric binding agent, because AA is a nontoxic, hydrophilic polyuronic acid with complexable functional groups.[19,20] Effect of pH on the retention was also investigated.
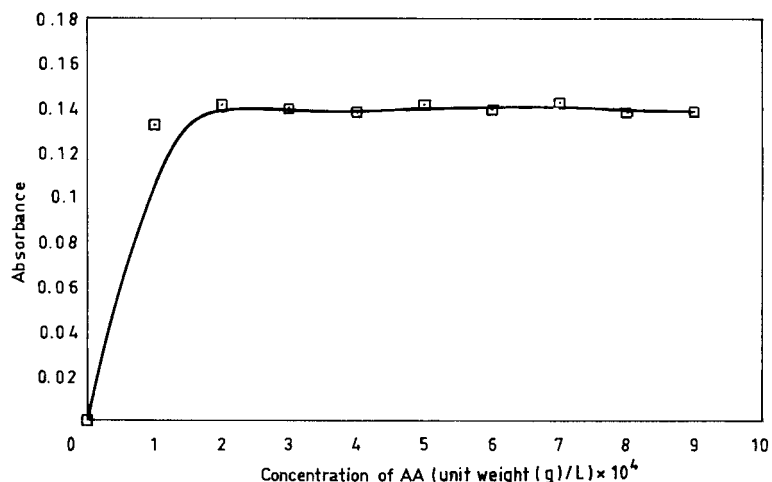
EXPERIMENTAL

Materials

P(MMA-MA) copolymer (random) was kindly provided by Rhom Pharma as Eudragid L-100 with
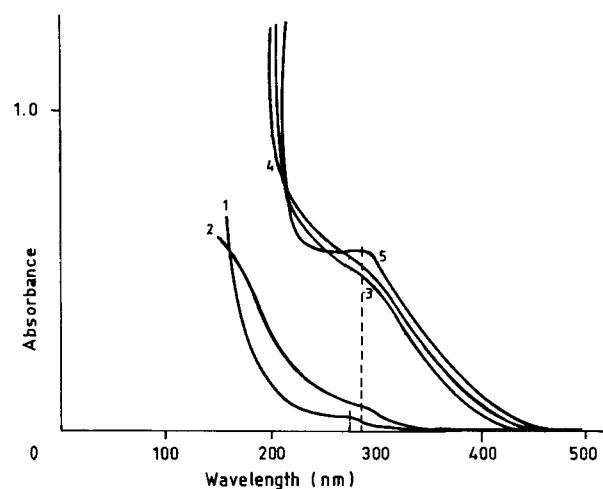
Figure 2 Complexing of Fe(III) with AA. 1-AA; 2-(4 mL AA + 1 mL Fe); 3-(3 mL AA + 2 mL Fe); 4-(2 mL AA + 3 mL Fe); and 5-(1 mL AA + 4 mL Fe).

Figure 3   Evaluation of the necessary amount of AA for complex formation.

48.3% (unit/g) methacrylic acid groups [$\eta = 1.2$]. AA was supplied from Sigma as sodium salt (medium viscosity). PEG (MW: 20 000), KSCN, HCI, NH$_3$, FeCI$_3 \cdot$ 6H$_2$O were all Merck products.

Preparation of Membranes

Membranes were prepared by casting[8] P(MMA-MA) solution (8% w/v) in ethanol that contains 60% (w/v) PEG. Casting solution (1.5 mL) was poured onto glass petri dishes (49 cm^2) and solvent was allowed to evaporate for a period of 13.5 min at 30°C. Then the petri dishes were immersed in a bath of deionized water and membranes were removed. They were preserved in deionized water at least 9 days to remove unbonded PEG and to obtain additional pores. The thickness of the membranes were measured as 25 μm with a precision micrometer (Aldrich), by taking the arithmetic average of numerous readings.

UF Experiments

UF experiments were carried out using a batch-scale, mechanically stirred vacuum filtration apparatus with effective membrane area of 17.5 cm^2 (Sartorius).

Filtration of Fe(III) solutions in the presence of AA

Membranes were mounted to the two compartment permeation cell (each 250 mL). The upper compartment was filled with distilled water and filtration was carried out until a steady-state flow
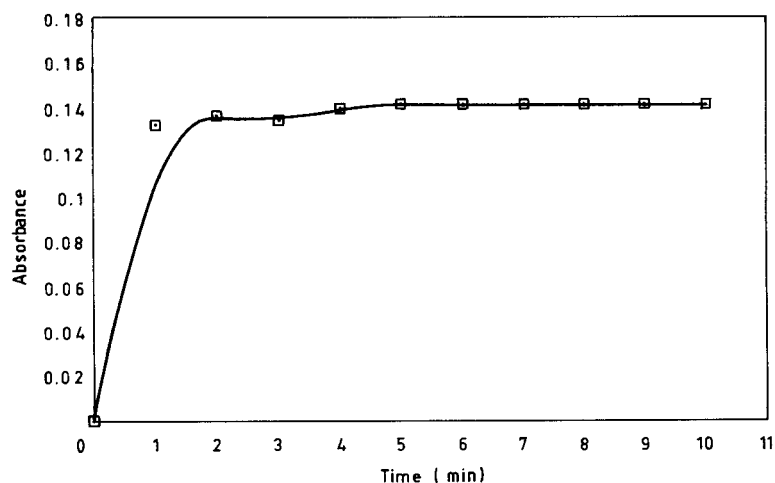
Figure 4   Determination of the time necessary for complex formation (Fe(III)-AA).
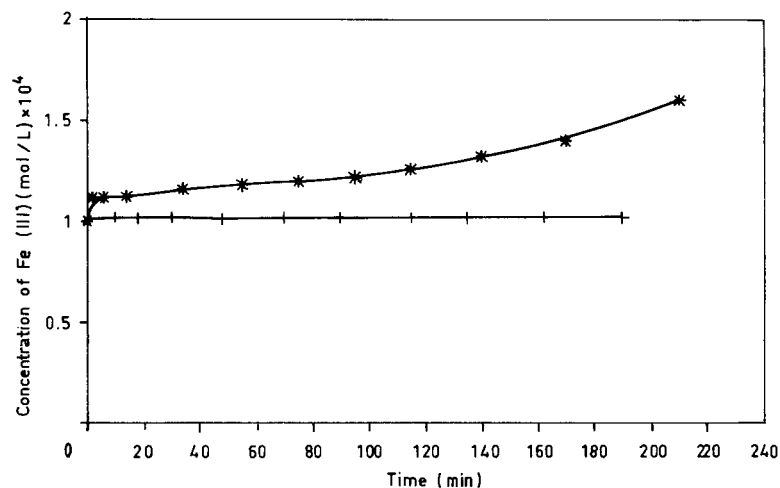
Figure 5 pH dependence of iron rejection. +-pH 2.0; *-pH 3.1.

condition was reached. One hundred and twenty-five milliliters of $(1.0–9.0) \times 10^{-4}$ repeating unit weight/L AA was added to 125 mL of 1.0×10^{-4} M Fe(III) solution, and then the mixture was supplied to the upper compartment of the cell. The pH of the filtration solution was adjusted to predetermined pH (2.0–3.1) using 0.1 M NH_3 and 0.1 M HCl solutions.

Filtration was carried out at room temperature (23–25°C) taking five samples up to 10 mL solution retained in the upper compartment. The quantity of Fe(III) retained in the membrane was determined by soaking the membrane in concentrated HCl then washing with deionized water.

Analysis

Fe(III) concentrations were determined spectrophotometrically.[8] Formation of Fe(III)-AA com-

Table I   Percentage Recovery of Fe(III) in Filtration of Fe(III) Solutions In the Presence of AA

Filtrate	Fe(III) μmol	Fe(III) (%)
F_1	0.99	7.90
F_2	0.43	3.44
F_3	0.08	0.64
F_4	0.06	0.48
F_5	0.05	0.40
R	10.94	87.13

F is filtrate samples; R is retantate (membrane + upper compartment).

plex was investigated by using UV spectrometer (Baush Lamp Spectronic 2000).

RESULTS AND DISCUSSION

Hydrophilic, noncross-linked polymers allow the application of membrane filtration by virtue of the great difference in their molecular mass compared with the other interacting species. Thus, the retention of ions by a membrane that separates macromolecules from low-molecular compounds can be investigated and applied to ion concentration (Fig. 1).

A soluble polymer reagent with chelating groups is characterized by two main components: the polymer backbone, which provides the solubility and stability of the reagent, and the functional groups, which are necessary for the selective reactivity of the polymer.

AA is a linear polysaccharide consisting of two uronic acids, namely D-mannuronic acid(M) and L-guluronic acid(G). The product utilized in this study was a polyuronic acid composed of primarily of anhydrous mannuronic acid with 1–4 linkages.

A series of experiments was performed to evaluate the complex formation of AA with Fe(III). Complexes are characterized by absorption patterns. Wavelength was shifted from 274 nm to 290 nm for AA with the addition of Fe(III) solutions, which is the indicator of the structural changes that occur on the molecules (Fig. 2). Fe(III) form strong carbonyl complex as a result of the interaction of Fe(III) with the nonbonding

electrons in the carbonyl group of the alginic acid so a shift in the wavelength maxima takes place. This might be due to the $\pi - \pi^*$ transitions.[9]

To determine the required amount of AA for complex formation solution of different concentrations $(1.0 - 9.0) \times 10^{-4}$ repeating unit weight/L of AA were added to 1.0×10^{-4} M Fe(III) solutions. Results are presented in Figure 3. As it is reflected from Figure 2–3, repeating unit weight of AA is necessary for each mole of Fe(III).

Water-soluble polymers tend to be adsorbed on both hydrophilic and hydrophobic surfaces because these polymers have polar and nonpolar moieties. Polymer adsorption leads to the formation of a layer on the surface and inside the pores of the membrane. This results in an increase of the retaining characteristics of the membrane and a decrease in the permeate flux.[4] However, the high permeate flux could be sacrificed in order to obtain a satisfactory retention. Taking this point into account polymer concentration was taken as four repeating units of AA per mole of Fe(III), which is some what higher than that required for the binding.

Time necessary for the complex formation is shown in Figure 4. As can be seen from the figure, 5 min will be required for the complex formation.

The pH value is a very important factor in most cases of polymeric binding because either protons or hydroxyl anions can compete with the component to be bound to the polymer.[7,12,13,21]

A set of experiments were carried out to investigate the effect of pH on the rejection. Selected pH values were 2.0 and 3.1 (Fig. 5). One can see from Figure 5 that as the pH of the solution increases, retention of metal cation also increases in the acidic region. However, it should be noted that increasing pH reinforces not only the binding of metals to polymer, but also causes the formation of metal hydroxides that are unable to interact with the polyacid.[4] Fe(III) ions form hydroxides with very low solubility at pH values higher than 3.1. Similar results concerning the effect of pH were reported in the literature[5,7,8,9] on the retention of various metal ions.

Retention of iron determined as described previously[8] and results are shown in Table I. As Table I shows, flux decline toward the end of the filtration. The large particles tend to leak on to the membrane surface irreversibly. Because the diffusion coefficient of large particles is very small, this macromolecular layer results in decrease in flux. However, the layer formed on the membrane surface can be said as a concentrated
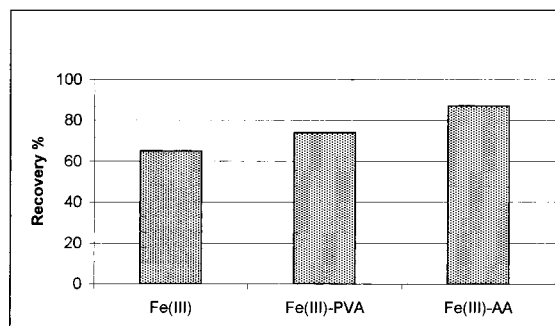
Figure 6   Retention of Fe(III) the presence of AA, PVA[8] and without any complexable polymer.[8]

macromolecular layer.[22] For this reason, at the end of the filtration the amount present in this layer was added to the retention value. Retention of 87.13% was obtained when the filtration was carried out in the presence of AA.

As a result it can be said that retention in the presence of AA (87.13%) is greater than retention in the presence of PVA (74%) and in the case without any complexable polymer (65%)[8] (Fig. 6).

CONCLUSIONS

From the results of our study we conclude that concentration and separation of Fe(III) from dilute aqueous solutions by complexing with AA and using PMMA-MA-PEG membranes can be proposed as a suitable method with the recovery of 87.13% at pH 3.1. We found that an increase in the concentration of complexing polymer first facilitates the complex formation, then remains constant. In addition, an increase in pH causes an increase in Fe(III) rejection.

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