

# Ultrafiltration of Fe(III) Solutions in the Presence of Poly(vinyl alcohol) Using Modified Poly(methyl methacrylate-co-methacrylic acid) Membranes

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**ABSTRACT:** Poly(methyl methacrylate-methacrylic acid) P(MMA-MA) copolymer membranes were used in the filtration process to concentrate Fe(III) solutions. Suitable gelation period and thickness were determined, and transport properties of the membranes were modified using poly(ethylene glycol) (PEG) in the casting solution. The effects of pH and a complexable polymer [poly(vinyl alcohol) (PVA)] on the rejection of iron were investigated. Maximum recovery of 74% was obtained when the filtration was carried out in the presence of PVA at pH 3.1. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1115–1121, 1997

**Key words:** membrane preparation; filtration; preconcentration; poly(methyl methacrylate-methacrylic acid) membranes

## INTRODUCTION

The continuous increase of world needs for most of the known metals, and the decrease in grade of the available ores, make it interesting to find effective and efficient methods for processing waste solutions containing metal ions, even at very low concentrations.<sup>1–12</sup>

Ultrafiltration is fast-emerging, a new and versatile unit operation in separation technology, in concentration, purification, and separation processes. This technique can also be used for the reduction of the detection limits and matrix interferences in instrumental determinations. R. W. Baker and H. Strathman<sup>11</sup> used ultrafiltration technique to study the properties of high flux membranes with macromolecular solutions. Tsuneda et al.<sup>12</sup> used commercial hollow fiber membranes for concentration of cobalt solutions. Since the time of Benchold,<sup>13</sup> who coined the term "Ultrafiltration," all the research work reported

was mainly associated with colloidon membranes and cellophane films. With the development of asymmetric membranes, other polymeric materials have become the subject of investigation by research workers.<sup>14–17</sup> The study of different polymeric materials for use in membrane filtration involves selection of suitable polymers, membrane morphology in relation to its use as an ultrafilter and effect of fabrication, operational, and hydraulic variables.

Polyacrylic acid-based membranes are of particular interest because of their hydrophilicity and because of the fact that carboxylic groups can dissociate to give a charged character to the membrane material. Ovsapian and Yampol'skii<sup>15</sup> studied the diffusion of chloromethanes in copolymers of chloroprenes with methylmethacrylate and methacrylic acid. Şanlı and Aras<sup>16</sup> and Bdair, Aras, and Şanlı<sup>17</sup> have used P(MMA-MA) copolymer to prepare dialysis membranes. For this purpose several membranes prepared from the copolymer and its Li<sup>+</sup>, Zn<sup>2+</sup>, Na<sup>+</sup>, Ba<sup>2+</sup>, Cs<sup>+</sup>, Al<sup>3+</sup> ionomers were tested for NaCl, creatinine, and urea permeability.

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**Table I** Variation of Water Flux with the Thicknesses of the Membranes

Membrane	Volume of Casting Solution (mL)	Thickness ( $\mu\text{m}$ )	Flux (J) ( $\text{kg/s} \cdot \text{m}^2$ )
I	1.0	10	83.03
II	1.5	25	18.05
III	2.0	35	3.61
IV	2.5	65	3.60
V	3.0	75	—

As a part of a broader study on the P(MMA-MA) membranes, in this study useability of these membranes to concentrate the Fe(III) solutions with filtration technique was investigated. Experimental study was performed in two parts. In the first part, the effects of membrane thickness, gelation period, addition of water soluble and complexable polymer to the casting solution were investigated. In the second part, membranes were used in filtration and the effects of pH of the solution and addition of a complexable polymer (PVA) to the feed solution were examined.

## EXPERIMENTAL

### Materials

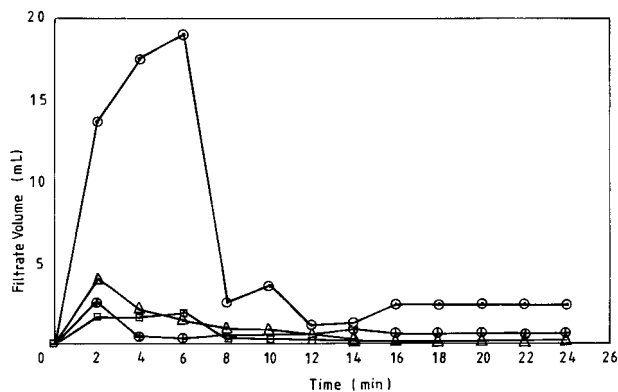
P(MMA-MA) copolymer (random) was kindly provided by Rohm Pharma as Eudragit L-100 with 48.3% (unit/g) methacrylic acid groups. PEG (MW: 20000), PVA (MW: 72000), KSCN, HCl,  $\text{NH}_3$ ,  $\text{FeCl}_3$ , 6  $\text{H}_2\text{O}$  were all Merck products.

### Preparation of Membranes

Membranes were cast from 8% (w/v) solutions of P(MMA-MA) copolymer in ethanol. Casting solutions (1–3 mL) were poured onto glass Petri

**Table II** The Dependence of Water Content on the Thicknesses of the Membranes

Membrane	Thickness ( $\mu\text{m}$ )	Water Content (%)
I	10	75.0
II	25	33.0
III	35	26.7
IV	65	6.2
V	75	6.1

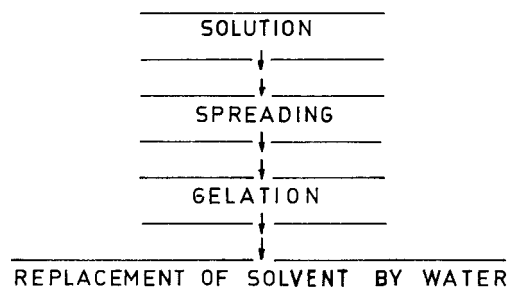
**Figure 1** Change of filtrate volume with time. ○, 10  $\mu\text{m}$ ; △, 25  $\mu\text{m}$ ; ⊕, 35  $\mu\text{m}$ ; □, 65  $\mu\text{m}$ .

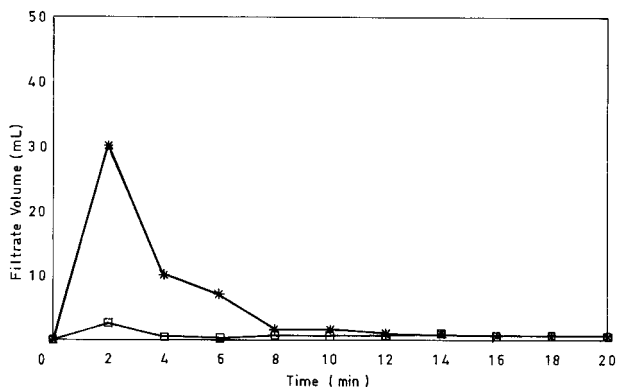
dishes ( $49 \text{ cm}^2$ ) and solvent was allowed to evaporate at  $30^\circ\text{C}$  to dryness (membranes I–V) or a predetermined gelation period. Then the Petri dishes were immersed in a bath of deionized water at room temperature for  $\sim 1$  h, and membranes were separated and preserved in distilled water until they were used. The thicknesses of the membranes were measured with a precision micrometer (Aldrich) ( $10$ – $65 \mu\text{m}$ ).

The water content of the membranes was determined gravimetrically; samples were preequilibrated in deionized water at room temperature and quickly blotted dry and weighed. They were then transferred to a vacuum oven until constant weight was maintained. Results were expressed in weight percent based on the dry film weight.

### Ultrafiltration Experiments

A batch, mechanically stirred filtration apparatus (Sartorius) was used for filtration experiments.

**Figure 2** Diagrammatic representation of membrane preparation.

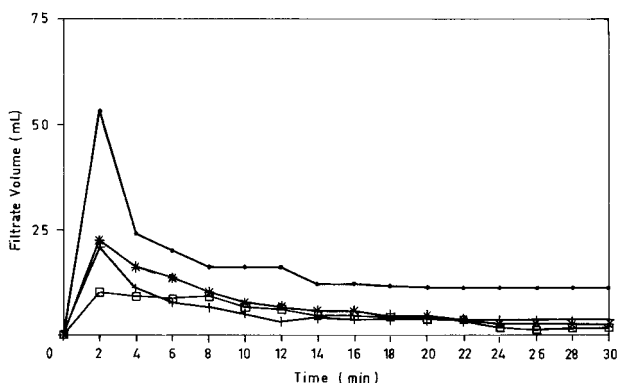


**Figure 3** Water flux of the membranes. Solution is evaporated. \*, 20 min. □, Dryness.

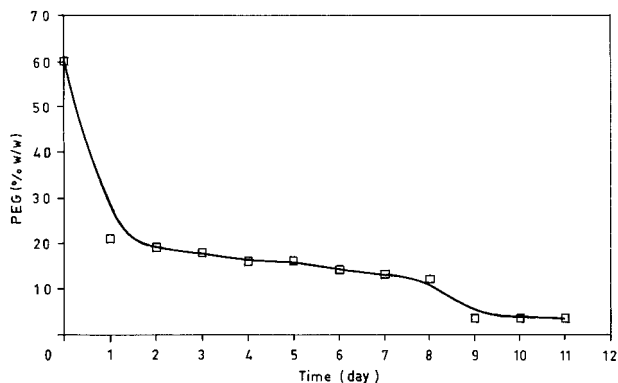
It was a two-compartment (each 250 mL) cell with an effective membrane area of 17 cm<sup>2</sup>. A polypropylene film was used to support the membranes. The filtrate was removed from the membrane with the aid of a vacuum pump. Experiments were carried out at room temperature (23–25°C).

#### Filtration of Fe(III) Solutions

Membranes were mounted in the permeation cell, the upper compartment was filled with distilled water, and filtration was carried out up to a steady-state flow condition. The cell was dried and filled with 250 mL 1 × 10<sup>-4</sup> M Fe(III) solution at different pH values (2.0–4.0). Seven-mL samples were taken at 2-min intervals. Filtration was carried out until 10 mL feed solution was retained in the upper compartment. pH adjustments were made by using 0.1 M NH<sub>3</sub> and 0.1 M HCl solutions.



**Figure 4** Variation of water flux with time for L100+PEG membranes prepared with different gelation periods. ●, 13.5 min; \*, 15.0 min; +, 20.0 min; □, 25.0 min.



**Figure 5** Change of PEG content of the membranes with time.

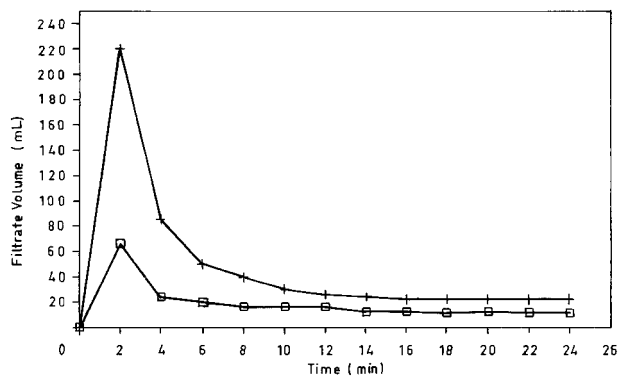
The quantity of Fe(III) retained in the membranes was determined by soaking the membrane in concentrated HCl, then washing with deionized water.

#### Filtration of Fe(III) in the Presence of PVA

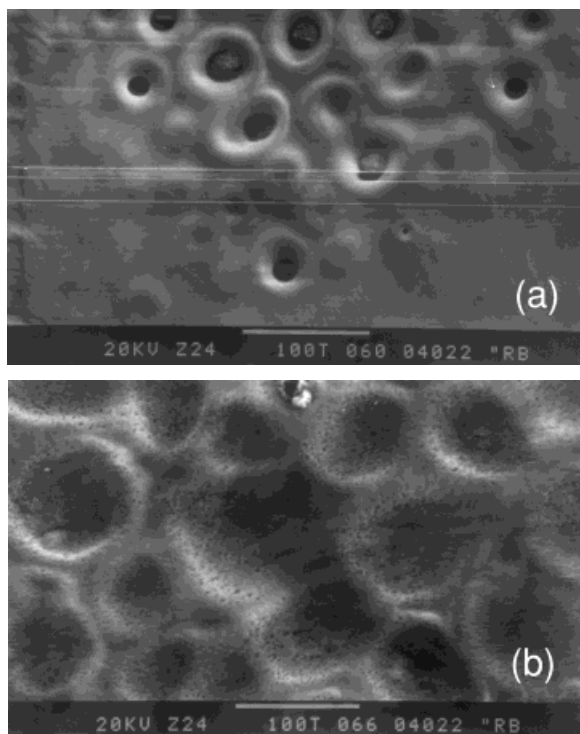
125 mL 1.0 × 10<sup>-4</sup> repeating unit weight/L PVA was added to the 1.0 × 10<sup>-4</sup> M Fe(III) solution, then the mixture was supplied to the upper compartment of the cell; pH of the solution was adjusted to the predetermined pH (2.0–3.1), and filtration was carried out as stated previously.

#### Analysis

Fe(III) concentrations were determined spectrophotometrically. Four drops of 0.5 M HCl and 2 drops of 0.1 M KSCN were added to the 7 mL of



**Figure 6** Water flux of the membranes. +, PEG is removed; □, PEG is not removed.

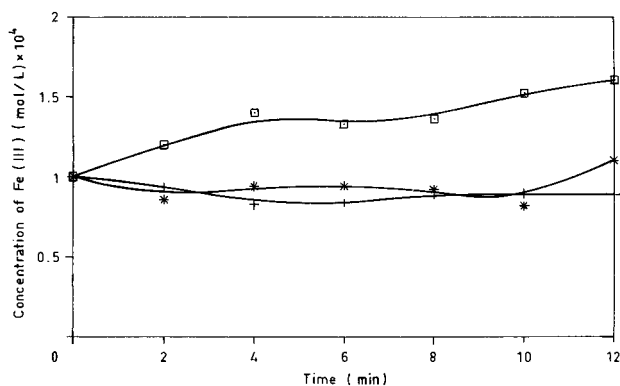


**Figure 7** SEM micrograph of the membranes at  $\times 500$  magnification. (a) L-100; (b) L-100 + PEG (PEG is removed partially).

filtrate samples, and absorbance of the red complexes were measured at 456 nm.

Formation of Fe(III)-PVA complex was investigated by using UV-spectrometer (Baush Lamb Spectronik 2000).

The scanning electron micrographs (Laitz AMR 1000) of the membranes were taken after sticking the membranes on stubs, followed by freeze-drying and coating with gold (Polaron



**Figure 8** pH dependence of iron rejection in filtration of Fe(III) solutions.  $\square$ , pH: 4.0; \*, pH: 3.1; +, pH: 2.0.

**Table III** Percentage Recovery of Fe (III) in Filtration Fe (III) Solution F: Filtrate, R: Retantate (membrane + upper compartment)

Filtrate	Fe (III) $\mu\text{mol}$	Fe (III) %
F <sub>1</sub>	1.32	6.24
F <sub>2</sub>	1.26	5.95
F <sub>3</sub>	1.32	6.38
F <sub>4</sub>	0.9	4.25
F <sub>5</sub>	0.60	2.83
F <sub>6</sub>	0.60	2.83
F <sub>7</sub>	0.80	3.78
F <sub>8</sub>	0.60	2.83
F <sub>9</sub>	0	0
R	13.74	65.00

100). The magnification was in the range of 200–500.

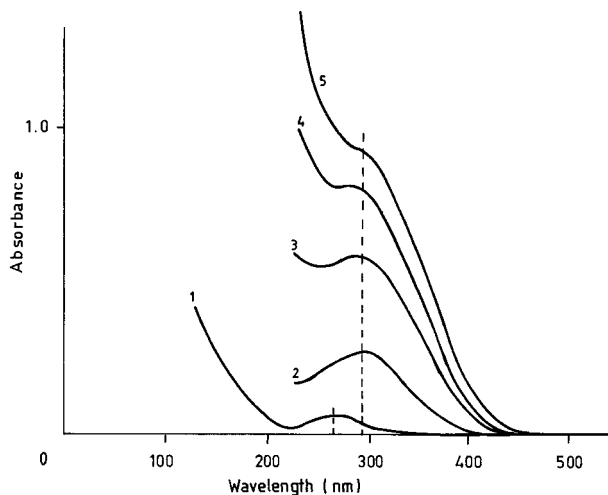
## RESULTS AND DISCUSSION

In filtration experiments it is desirable to prepare membranes with high solvent flux for the rejection of the solute and permeation of the solvent. The dependence of water flux and water content of P(MMA-MA) membranes on the thicknesses of the membranes were shown in Tables I and II. It is clear from the tables that when the thickness of the membrane increases, the membrane resistance increases as expected. Although the water flux of the membrane I is higher than membrane II, due to the weak mechanical strength of the membrane I, membranes with the thickness of 25  $\mu\text{m}$  (II) were used in the rest of the study.

In Figure 1, change of filtrate volume with filtration time is presented. As it is seen from the figure, filtrate volume first increases, passes through maximum, then decreases, and levels off. Initial increase in the filtrate volume can be attributed to the release of the water absorbed by the membranes.

Water permeability of the membrane II was improved by preparing the membrane with the phase inversion method (Fig. 2), that is, after a gelation period of 20 min (the minimum period for the membrane to be removable from the Petri dishes) it was immersed in deionized water.

Change of filtrate volume with time is shown in Figure 3. As it is seen from the figure, permeation is increased when the membrane is prepared by the phase-inversion method. Two pro-



**Figure 9** Complexing of Fe(III) with PVA. 1. PVA. 2. (4 mL PVA + 1 mL Fe(III)) 3. (3 mL PVA + 2 mL Fe(III)) 4. (2 mL PVA + 3 mL Fe(III)) 5. (1 mL PVA + 4 mL Fe(III)).

cesses probably occur during the evaporation: a gradual aggregation as the proportions of the solvent and nonsolvent change, and a sudden gelling when the concentration of polymer becomes sufficiently high for the aggregates to lock into a rigid structure. The extent to which the aggregation has proceeded by the time gelation occurs largely determines the membrane porosity. Further evaporation from the set gel, accompanied by shrinkage of the gel when it is immersed in water, will decrease the eventual porosity.

A further increase in water permeability can be obtained with the addition of particular polymer capable of interaction with the copolymer to form a polymer-polymer complex. PEG is a suitable polymer for this purpose.<sup>18-24</sup> It is added to the casting solution (60%) (w/v) to increase the water permeability. The interaction of the polymer used occurs through cooperative hydrogen bonding between oxyethylene and undissociated carboxyl units.<sup>18,22</sup> Figure 4 presents the change of filtrate volume with filtration time for different gelation periods for PMMA+PEG membranes. As the gelation period decreases, permeation increases. In the rest of the study membranes were prepared with 13.5 min of gelation period.

PEG is a water-soluble polymer. Removal of the unbounded PEG in the membrane structure will produce additional porosity. For this purpose membranes were immersed in deionized water 1-11 days, and their weight decrease were followed to constant weight (Fig. 5). At the end of 9 days,

only 3.4% PEG was found to be retained in the membranes as complexed.

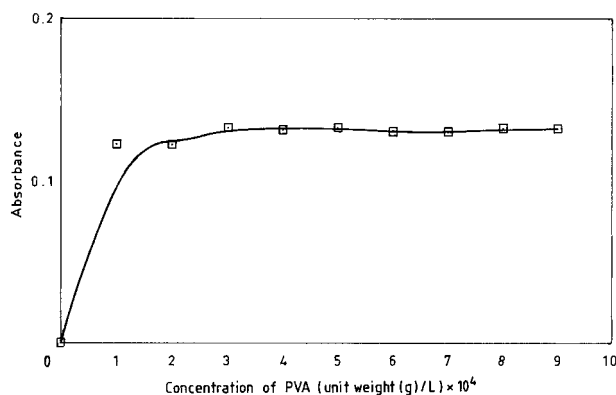
Permeability of the membranes increased two-fold when PEG was removed from the membrane (Fig. 6).

SEM micrographs also verify the increase in permeability due to the additional porosity (Fig. 7). Similar results were obtained in the filtration of macromolecules: on treatment with PEG, the performance in protein separation of crosslinked polymethacrylic acid (PMA) membranes treated with PEG was improved  $\sim 240$ -fold for albumin, and 55-fold for hemoglobin, when compared with an untreated PMA membrane.<sup>23,24</sup>

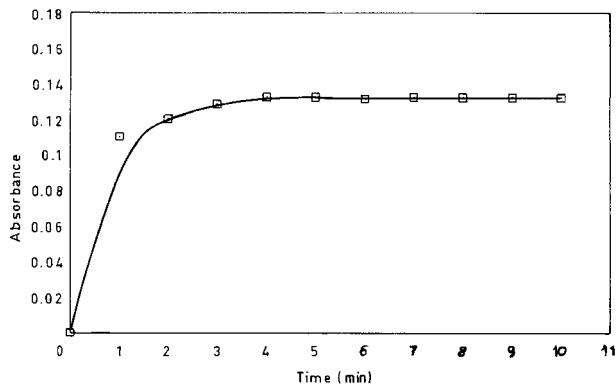
### Filtration of Fe(III) Solutions

A series of experiments were carried out using  $1.0 \times 10^{-4} M$  Fe(III) solutions. pH dependence of iron rejection in filtration is shown in Figure 8. At pH 2 and 3.1, concentration of iron first decreased, then increased. However, at pH 4.0, concentration increased steadily in the upper compartment. The initial decrease at pH 2 and 3.1 can be attributed to the interaction of metallic ion with the carboxyl group in the copolymer,<sup>3,5</sup> and retention of iron at high pH values is probably due to the hydrolyzed species. Also, at low pH values, PMA units will be mostly un-ionized, resulting in a compact conformation, and the membrane will exhibit high permeability and low retention. At high pH, PMA will be mostly ionized in an extended conformation; apparent permeability will be low, leading to high retention.

To evaluate the efficiency of filtration, samples of 250 mL were introduced to the filtration cell. Fractions of 25 mL (F) are collected and the per-



**Figure 10** Evaluation of the necessary amount of PVA for complex formation.



**Figure 11** Determination of the time necessary for complex formation (Fe(III)-PVA).

cent recovery of 65.00% was obtained at pH 4 (Table III).

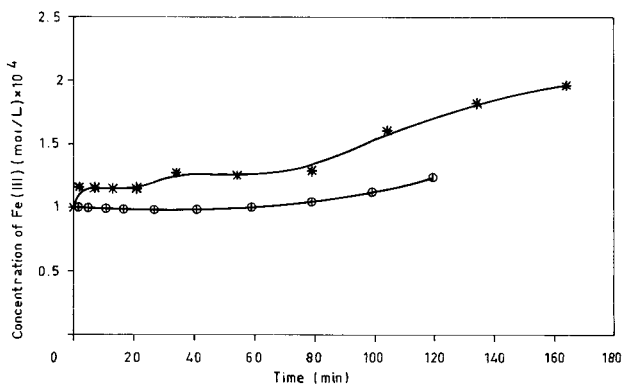
### Complex Formation with PVA

The complexing of Fe(III) with PVA was investigated spectrophotometrically. Wavelength was shifted from 270 to 293 nm for PVA with Fe(III) addition (Fig. 9). To evaluate the necessary amount of PVA for complex formation, solutions with different concentrations of PVA were added to the  $1.0 \times 10^{-4} M$  Fe(III) solutions. As reflected from Figure 10, three repeating unit weights of PVA were found necessary for each mol of  $Fe^{+3}$ .

The time necessary for complex formation is presented in Figure 11. As it is seen from the figure, 4 min were found necessary for PVA.

### Retentions of Iron in the Presence of PVA

Experiments were carried out to investigate the effect of pH on iron rejection in the presence of PVA (Fig. 12). The increase in rejection with increasing pH was observed.



**Figure 12** pH dependence of iron rejection in filtration of Fe(III)-PVA solution. \*, pH: 3.1; ⊕, pH: 2.0.

**Table IV** Percentage Recovery of Fe (III) in Filtration of Fe (III)-PVA Solution F: Filtrate, R: Retantate (membrane + upper compartment)

Filtrate	Fe (III) $\mu\text{mol}$	Fe (III) %
F <sub>1</sub>	1.15	9.44
F <sub>2</sub>	0.90	7.40
F <sub>3</sub>	0.65	5.34
F <sub>4</sub>	0.35	2.89
F <sub>5</sub>	0.10	0.86
F <sub>6</sub>	0.04	0.32
F <sub>7</sub>	0.01	0.08
F <sub>8</sub>	0	0
F <sub>9</sub>	0	0
R	8.97	74.00

Retention of iron is determined as previously, and results are shown in Table IV. Complexing with PVA apparently increased iron rejection, and this increase was most likely a consequence of the increased size of the resulting metal complex compared to the size of unbound hydrated metal ion.

### CONCLUSIONS

1. Membranes with the thickness of 25  $\mu\text{m}$  were found to be suitable to obtain high permeability and good mechanical strength.
2. Addition of PEG to the casting solution and the removal of the unbound PEG improves the permeability.
3. Presence of complexing polymer (PVA) enhances iron rejection.

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