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Use of Poly(methyl methacrylate-co-methacrylic acid) Membranes in the Ultrafiltration of Aqueous Fe^{3+} Solutions by Complexing with Poly(vinyl pyrrolidone) and Dextran

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Abstract: In this study water soluble complexible polymers, poly(vinyl pyrrolidone) (PVP) and dextran, were used for the ultrafiltration (UF) of aqueous Fe^{+3} solutions by using poly(methyl methacrylate-co-methacrylic acid) (PMMA-co-MA) membranes. Effects of polymer concentration and pH on the volume collected in the filtration of Fe^{+3} solutions and percent retentions (R%) were examined. It was determined that increase in polymer concentration decreased the permeability of PMMA-co-MA membrane and pH increased the retention of Fe^{3+} solutions. R% for Fe^{3+} solutions were obtained as 62% and 48% with PVP and dextran respectively at pH 3.0, for a filtration period of 80 minutes and retention for Fe^{3+} solution without using any complex forming polymer was found as 14%. Membranes were characterized by AFM analysis and contact angle measurements.

Keywords: Membranes, poly(methyl methacrylate-co-methacrylic acid), retention metal ions, ultrafiltration, water soluble polymers

INTRODUCTION

According to United Nations estimations, by 2025 two-thirds of the world population will not have enough drinking water (1). In view of the

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projected world wide shortage of water in most regions of the world, improvement in the efficiency of currently used technologies can have a tremendous impact on the quality of human life in many regions of the world (2). For this reason, removal, separation, and enrichment of hazardous metal ions in aqueous solutions play an important role for the environmental remediation of municipal and industrial wastewater (3). Since the late sixties, membrane filtration processes have found industrial applications and started to compete with processes like distillation, evaporation, or extraction. UF is a relatively low-pressure membrane process and its use in water treatment has increased rapidly in the last decade due to stricter regulations for finished water quality, low cost, simplicity of installation, and improved reliability when compared with conventional treatment processes such as sedimentation and rapid filtration (4). UF is generally used for concentration of solutions and size-selective separation of large molecules from low molecular weight species (5). The efficient retention of trace metals and their enrichment and removal from dilute aqueous solutions can be achieved by using water-soluble, polymeric reagents in combination with membrane filtration (6–24). The unbound metals and low molecular mass compounds pass through the membrane; therefore, the polymers and their macromolecular complexes are retained (Fig. 1). The advantages of this method are high removal efficiency because of effective binding (9).

Juang and Shiau (9) studied the removal of divalent metals, Cu(II), Co(II), Ni(II), and Zn(II) from aqueous solutions by chitosan enhanced UF with using regenerated cellulose membranes. They have concluded that the removal of Cu(II) is more efficient than other metals due to its higher coordination ability with chitosan.

Şolpan and Şahan studied the concentration and separation of $[Cu^{2+}]$, $[Ni^{2+}]$ and $[Fe^{3+}]$ in the presence of dextran (10), alginic acid (AA) (12) and poly(vinyl alcohol) (PVA) (11) by using ethylene cellulose-poly(ethylene glycol) (EC-PEG 4000) alloy membranes. They obtained greater retention percentage in the presence of water soluble polymers.

Pizarro et al. (25) studied the metal ion (Cu(II), Cr(III), Co(II), Zn(II), Pb(II), Cd(II), and Fe(III)) interaction of water soluble copolymers containing carboxylic acid groups in aqueous phase by membrane filtration technique. Rivas et al. (21) have studied the retention profiles of metal ions; they used water-soluble polymer materials as complexing reagents for the separation of metal ions using membrane filtration.

Asman and Şanlı studied the UF of aqueous Fe^{3+} solutions in the presence of PVA (7) and alginic acid (AA) (6) by using PMMA-co-MA membranes. They have obtained a recovery of 74% and 87.3% for Fe^{3+} solutions with PVA and AA respectively.

PVP and dextran are also water soluble polymers and can form complex with Fe^{3+} (10, 26–29). In this study, asymmetric porous membranes

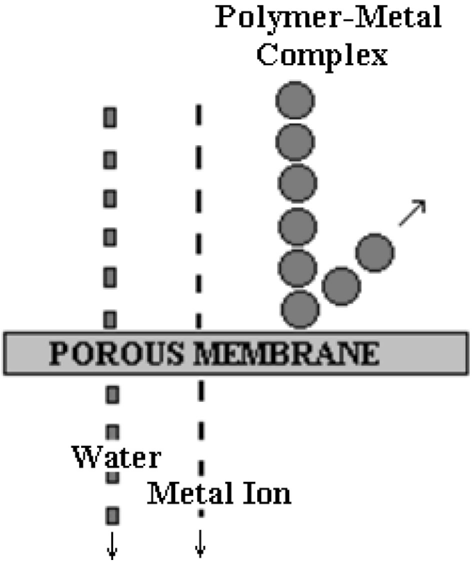

Figure 1. Schematic diagram for the permeation of aqueous metal solutions and polymer-metal complex solutions through porous membrane.

were prepared as filters by using PMMA-co-MA and PEG was used to increase the porous structure of the membranes. The aim of the study to filtrate aqueous Fe^{3+} solutions in the presence of macromolecular complexing agents PVP and dextran to form macromolecular complexes of Fe^{3+} to increase the performance of PMMA-co-MA membranes for retention of Fe^{3+}. In the study UF method in which pressure is the driving force and the rejection mainly based on the size and shape of the solutes relative to the pore size of the membrane was used. The effect of the pH of the feed solution and concentration of polymeric reagent on the filtration performance were investigated. Outer layer interactions of the membranes with filtrate solutions were examined by using contact angle (CA) measurements and the characterization of the PMMA-co-MA membranes was done by using AFM analysis in non contact mode.

EXPERIMENTAL

Materials

PMMA-co-MA copolymer (random) was kindly provided by Röhm Pharma (GMBH Co., KG, Lauda-Königshofen) as Eudragid L-100 with

48.3% (unit/g) methacrylic acid groups. PVP ($M_{wt} = 40000$ g/mol) and dextran ($M_{wt} = 200000$ g/mol) was Fluka (Steinheim, Germany) product, poly(ethylene glycol) (PEG) ($M_{wt} = 20000$ g/mol), KSCN, HCl, NH_3, $FeCl_3 \cdot 6H_2O$ were all Merck (Hohenbrunn, Germany) products.

Preparation of Membranes

PMMA-co-MA membranes were prepared by phase inversion method and PEG was used to obtain additional pores in the membrane as in our previous study (6–7). Membranes were casted from 8% (w/v) solutions of PMMA-co-MA in ethanol, which contains 60% (w/w) PEG. Casting solution (1.5 mL) was poured onto glass petri dishes (49 cm^2) and the solvent was allowed to evaporate for a predetermined period of 13.5 min at 30°C. Then the petri dishes were immersed in a distilled water bath. Since the solvent (ethanol), used for the preparation of copolymer solution is miscible with water and water is a nonsolvent for PMMA-co-MA, copolymer precipitated in water, then removed from the water bath. In order to obtain additional pores in the membrane, un-bonded PEG was removed from the membrane by sorting them in distilled water till they get constant weight and found that the membranes include 3.4% (w/w) PEG at the end of a period of 9 days. The prepared membranes were preserved in distilled water. The thickness of the membranes was measured as (25 ± 10) μm with a precision micrometer (Aldrich) (Milwaukae, USA).

Preparation of Filtration Solution of Fe^{3+} in the Presence of PVP

125 mL 1.0×10^{-4} M Fe^{3+} solution was mixed with 125 mL of aqueous PVP solution in the concentration range of 1.0×10^{-4}–3.0×10^{-4} repeating unit weight/L. pH of the solution was adjusted to 2.0–3.0 by using 0.1 M NH_3 and 0.1 M HCl solutions. A microprocessor pH-meter (Hanna Inst.-pH 211) was used for the pH measurements.

Preparation of Filtration Solution of Fe^{3+} in the Presence of Dextran

125 mL 1.0×10^{-4} M Fe^{3+} solution was mixed with 125 mL of aqueous dextran solution in a concentration range of 1.0×10^{-4}–3.0×10^{-4} repeating unit weight/L. pH of the solution was adjusted to 2.0–3.0 as explained above.

UF Experiments

UF experiments were carried out by using a batch scale, mechanically stirred vacuum filtration apparatus with an effective membrane area of 17.5 cm^2 (Sartorius). The permeation cell contains two compartments (each 250 mL) and the membrane was placed on a polypropylene support between the two parts of the cell. Filtrates were removed from the lower compartment with the aid of the vacuum pump (Vacuu Brand RD15, GMBH & Co., Germany) at 1.5 mbar and the upper part was allowed to reach atmospheric pressure. Experiments were carried out at room temperature (23–25°C). In order to get a constant flux, distilled water was permeated through the membranes just before the filtration process till it reached a constant permeation rate. In the filtration process, the first 10 mL of filtrate was discarded and the filtrate samples were taken and analyzed at 5 min, 10 min, 20 min, 40 min, 60 min, and 80 min time intervals in order to follow-up the evolution of the permeability throughout the filtration process. Composition of the retentate was also determined at the end of the filtration period of 80 min and the quantity of Fe^{3+} retained in the membrane was found by soaking the membrane in conc. HCl and then washing with distilled water and the determined amount of retained Fe^{3+} in the membrane was also conceded as retented metal ion at the end of a filtration period of 80 min. The analysis of Fe^{3+} in the filtrate and the retentate solutions were determined spectrophotometrically.

Analysis

Spectrophotometric Measurements

Concentration of Fe^{3+} was determined from the spectrophotometric analysis of Fe^{3+}-PVP and Fe^{3+}-dextran complexes at 293 nm and 287 nm respectively. The complexation of polymers with Fe^{3+} has been proved by the wavelength maxima shift from 265 nm to 293 nm for PVP and shift from 266 nm to 287 nm for dextran. The quantity of the Fe^{3+} was determined by using 0.5 M HCl and 0.1 M KSCN and the absorbance of the red complexes were measures at 456 nm.

Contact Angle Measurements

Interaction of the outer layer of membrane surface with the aqueous polymer solutions was analyzed by using contact angle measurements. The measured contact angles were the average values of the angles taken at both sides of the drop. Measurements were done by using a Contact Angle Micrometer (Surface Electro Optics PHX 150 model, S.E.O. Co., Ltd. Korea).

AFM Analysis

AFM analysis was done in non contact mode by using AFM (Omicron-VF STM-AFM).

RESULT AND DISCUSSION

Effect of Presence PVP and Dextran on Volume of Permeate Collected in the Filtration of Fe^{3+} Solutions

To determine the effect of the presence of PVP and dextran solutions on the permeation performance of PMMA-co-MA membranes for the filtration of Fe^{3+} solutions, PVP and dextran solutions were prepared at a concentration of 1.0×10^{-4} repeating unit weight/L and were mixed with an equal volume of 1.0×10^{-4} M Fe^{3+} solution (each 125 mL) at pH 2.0, in order to get a mixing ratio of (1:1). Results of the permeations were given in Fig. 2. As it is seen from the figure, the presence of the water soluble-complexing polymer decreased the filtration volume and lowered the amount of permeate collected in the presence of PVP than the presence of dextran although dextrans with molecular weight greater than 10000 behave in a highly branched manner (30).

To investigate the tendency of PMMA-co-MA toward the aqueous solutions of PVP and dextran a series of static contact angle measurements were carried out. Contact angle measurement is one of the most sensitive techniques used to analyze the outer layer of polymer surfaces (31). In the study static measurements of contact angles, in which the measurement take place on the solid/liquid interface was done by using the tangent line method. The CA values determined for PVP and dextran solutions (for a concentration range of $1.0 \times 10^{-4} - 3.0 \times 10^{-4}$ repeating unit weight/L) at pH 2.0 were given in Table 1. As it is seen from the table, the lower contact angle values were obtained with PVP than dextran. Lower contact angle value represents higher interaction between two phases, i.e. membrane and aqueous polymer solution. So it can be stated that the interaction of PMMA-co-MA membrane with PVP solution is more effective than for the dextran solutions. This might be possibly due to the hydrogen bond interaction between the $-COOH$ groups of PMMA-co-MA and the $-C=O$ group (lactam carbonyl) of PVP. PVP is capable of forming a high degree of hydrogen bonding with

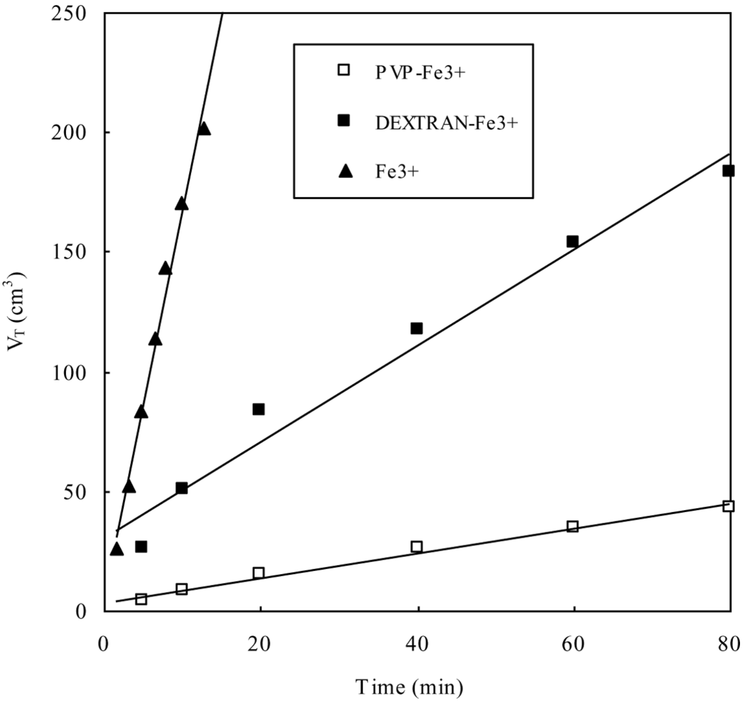

Figure 2. Effect of the presence of PVP and dextran on the volume of permeate collected at pH 2.0; Fe^{3+}/polymer ratio is 1:1. (V_T is the total amount of permeate collected at time t).

aqueous and non-aqueous solvent systems in the absence or presence of cosolutes (32, 33). Whenever there exist greater interactions between the permeating species with the membrane material this causes more resistance toward permeation through the membrane and this leads to a decrease in volume of permeate collected by filtration.

Table 1. Contact angle (CA) measurements for PMMA-MA membranes and polymer solutions at pH = 2.0

Conc. of Polym. Soln's (Rep. unit wt/L) $\times 10^4$	CA (degree) (PMMA-co-MA/PVP)	CA (degree) (PMMA-co-MA/ Dextran)
1.0	57.8 ± 0.9	61.4 ± 0.2
2.0	44.8 ± 0.2	58.7 ± 0.4
3.0	43.4 ± 0.2	53.2 ± 0.2

Effect of Fe^{3+}/PVP and Fe^{3+}/dextran Ratio on the Filtration Performance of PMMA-co-MA Membranes

In order to determine the effect of Fe^{3+}/polymer ratio on the filtration performance of PMMA-co-MA membranes, 1.0×10^{-4} M Fe^{3+} solution at a pH of 2.0, were mixed with equal volume of PVP and dextran solutions in a concentration range of 1.0×10^{-4} – 3.0×10^{-4} repeating unit weight/L to get mixing ratio of (1:1), (1:2), and (1:3) and the amount of permeate collected in the filtration of Fe^{3+}/PVP and Fe^{3+}/dextran solutions were given in Figs. 3 and 4 respectively. As it is seen from both the figures there was a good linear relation between the volume of permeate collected and the filtration period. Increase in the concentration of polymer solution decreased the collected amount of permeate.

Even though UF has a wide range of advantages, there are several factors affecting the membrane performance such as pore size and the surface characteristics of the membrane, shape of the permeant, physical and chemical interaction of permeants with the membrane material etc. It is evident that the fouling is one of the most important effects that can cause a limiting performance of the membrane overtime in the filtration

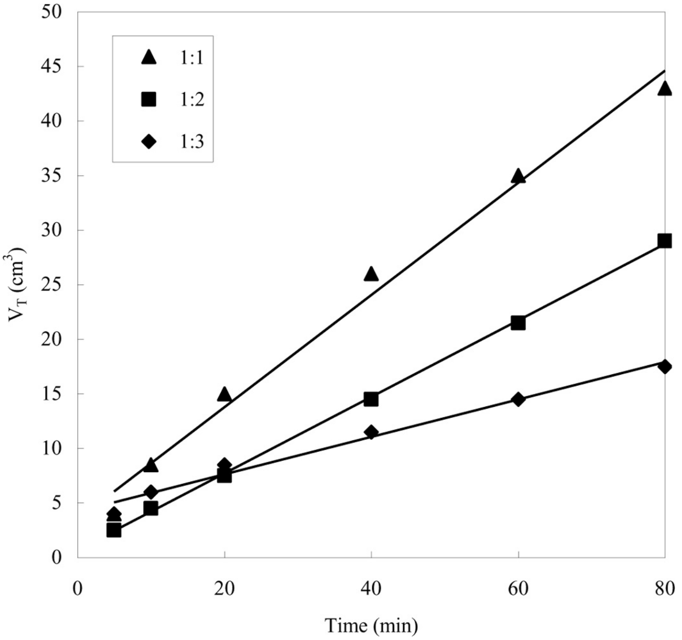

Figure 3. Effect of Fe^{3+}/PVP ratio on volume of permeate collected at pH 2.0.

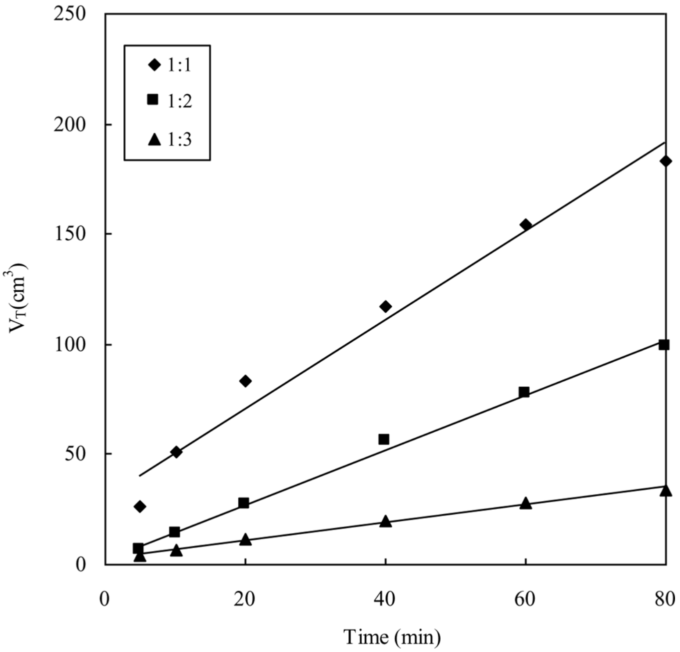

Figure 4. Effect of Fe^{3+}/Dextran ratio on volume of permeate collected at pH 2.0.

processes. This is most likely caused from the cake or gel formation of the polymer solution on the surface of the membrane material which is likely caused from the concentration polarization. The separation of the solute and the solvent takes place at the membrane surface where the solvent passes through the membrane and the retained solute causes the concentration at the membrane surface to increase. In Fig. 5 AFM micrographs of PMMA-co-MA membranes were given. The light regions are supposed to be the highest points and the dark regions are the depressions (pores) (34). As it is seen from the micrographs, PMMA-co-MA membranes have porous structure and their surface is not smooth, therefore they are so suitable for the accumulation of permeating molecules.

Macromolecular solute retained by the membrane (physically or chemically) accumulates at the surface or in the pores of the membrane and results in concentration build-up that causes flux to decrease. This effect is known as concentration polarization which accounts for both the gel layer and solute rich layer at the membrane surface (35) and it leads the membrane to show resistance to filtration. To determine the

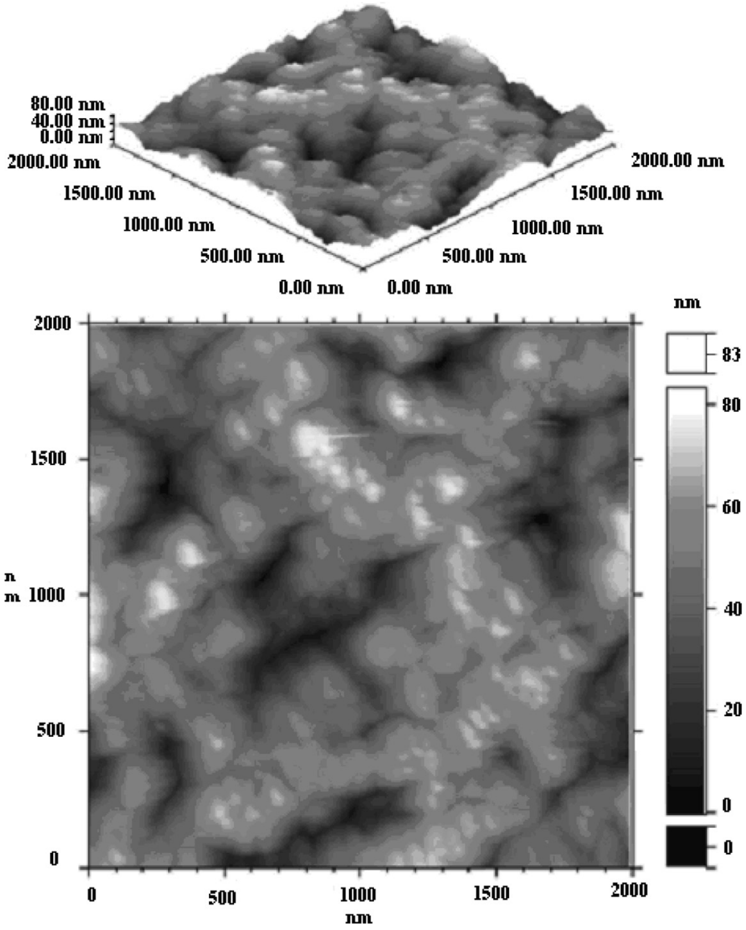

Figure 5. AFM micrographs of PMMA-co-MA membranes.

resistance of cake or gel on the surface of the membrane toward permeation, Equation 1 can be used (9).

$$\frac{dt}{dV} = \left(\frac{\eta \alpha_{av} c}{\Delta P A^2}\right) V + \left(\frac{R_M}{\Delta P A}\right) \tag{1}$$

Where t is the filtration time, V is the filtrate volume, A is the membrane cross-sectional area, R_M is the resistance of the membrane, α_{av} is the average resistance, c is the concentration, ΔP is the pressure drop across the membrane, and η is the viscosity of solution. The slope of (dt/dV) vs. V gives a straight line and the slope $(\eta \alpha_{av} c/\Delta P A^2)$ is commonly called the

Table 2. AFR values for the UF of Fe^{3+} in the presence of PVP and Dextran

Fe^{3+}/ polymer ratio	Fe^{3+}/PVP		Fe^{3+}/Dextran	
	AFR (min/cm^6) × 10^2	M_R (min/cm^3) × 10	AFR (min/cm^6) × 10^2	M_R (min/cm^3) × 10
1:1	3.9	8.5	0.3	0.1
1:2	26.8	13.2	0.4	6.2
1:3	71.6	17.7	6.2	10.0

average filtration resistance (AFR) of the gel or cake which has a unit of min/cm^6 and the intercept, M_R that is simply ($R_M/\Delta PA$), gives information about the membrane resistance because it includes the term R_M. AFR and M_R values of the PMMA-co-MA membranes for the filtration were determined from the slope and intercept of dt/dV vs. V lines for PVP and dextran at the studied concentrations and they were given in Table 2. As it is seen from the table both AFR and M_R values that were obtained for the filtration of Fe^{3+} solution in the presence of PVP were found to be greater than that obtained with dextran solutions for all Fe^{3+}/polymer ratios which means that PMMA-co-MA membranes show greater resistance for the filtration of Fe^{3+}/PVP solutions than that for the Fe^{3+}/dextran solutions. From Table 2 it can also be seen clearly that as the amount of PVP or dextran in the feed solution increased both the AFR and M_R values increased too. The higher the concentration, the higher the particles in the solution and therefore a greater chance for the deposition layer on the surface or pores of the membrane form. So increasing the macromolecule concentration increases the resistance of the membrane. When the resistance increases this indicates that a gel layer forms and the permeating species have difficulties to cross the membrane as well as water molecules. Therefore the amount of permeate collected in the filtration decreases.

Effect of pH on the Filtration of Fe^{3+} Solutions Through PMMA-co-MA Membranes

In order to determine the effect of pH on the filtration of aqueous Fe^{3+} in the presence of PVP and dextran, 125 mL of 1.0×10^{-4} M Fe^{3+} were mixed with 3.0×10^{-4} repeating unit weight/L of polymer solution to get a metal ion/polymer ratio as (1:3). Because of the solubility of PMMA-co-MA membranes at pH values equal to or greater than 4, filtration studies were carried out at pH 2.0 and 3.0. Retention % values

(R%) were calculated by using Equation 2, where C_t is the concentration at time t and C_o is the initial concentrations. Results of the permeations were presented in Fig. 6 as R% values vs. time.

$$R\% = \frac{C_t - C_o}{C_o} \times 100 \tag{2}$$

as it seen from the figure, greater R% were found for both Fe^{3+}/PVP and Fe^{3+}/dextran solutions at pH 3.0 than pH 2.0 and furthermore complexing with PVP increased the R% of Fe^{3+}; A retention percentage of 62% and 48% were obtained in the presence of PVP and dextran at pH 3.0 for a filtration period of 80 minutes, although the retentions that were obtained for Fe^{3+} solutions without using any complexing polymer is only 14% at pH 3.0 by using PMMA-co-MA membranes.

Increase in the R% with pH is most possibly due to the relaxation behavior of the polymer chains. Dextran and PVP has –OH and –C = O groups respectively which can be affected by pH changes. pH is also an important parameter for the viscosity of the polymer chains.

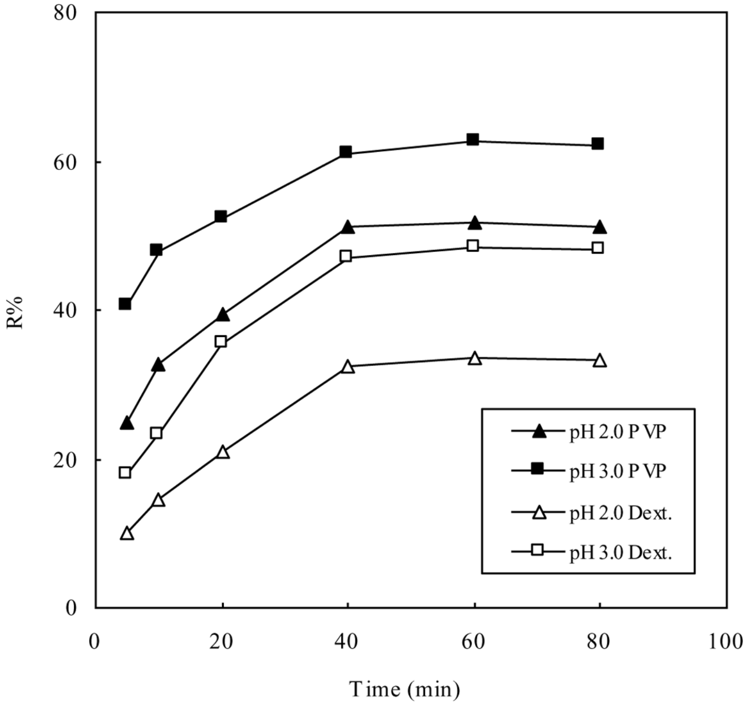

Figure 6. Effect of pH on R% (Fe^{3+}/polymer ratio is 1:3).

Table 3. Contact angle (CA) measurements for PMMA-MA membranes and polymer solutions at constant polymer solution concentration (3.0 x10^{-4} repeating unit weight/L)

pH	CA (degree) (Buffer solution)	CA (degree) (PVP)	CA (degree) (Dextran)
2.0	46.9 ± 0.7	43.3 ± 0.4	53.2 ± 0.2
2.5	48.4 ± 0.9	41.2 ± 0.9	51.5 ± 0.9
3.0	48.0 ± 0.7	38.4 ± 0.6	47.7 ± 0.5

Increase in pH, increases the ionic charge density on the polymer chain, thus the polymeric chain opens due to ionic repulsion that results in an increase in the viscosity of polymer solution therefore the retention increase with an increase in pH (12).

Rivas et al. (21) studied the separation of metal ions using membrane filtration in the presence of water-soluble polymer materials and they have stated that as the pH increases, the metal ion retention increases. Rivas et al. (20) have reported that at pH 1.0 where the concentration of the monovalent H^+ ions is high, low interaction rates are always found and the interaction rates increase rapidly with an increase in pH. They have also stated that the metal ion retention ability of water-soluble polymer depends strongly on the pH; increase in pH increases the metal ion retention.

A higher R% in the presence of PVP can be explained by the interaction of PVP with membrane material since PVP has a high hydrogen bonding ability (32, 33), as stated above. In Table 3 the contact angle values of PVP and dextran at different pH values were given. As it is seen from the table, smaller contact angle values were obtained at pH 3.0 for both PVP and dextran containing solutions. Additionally for each pH value, CA values for PVP are smaller than CA for dextran, which indicates greater interaction with the membrane material. Although the presence of water soluble polymers increase the retention of metal ions, greater interactions of polymers with the membrane material causes membrane fouling which leads to flux decline. Flux (J) ($mL/s \cdot cm^2$), the volume (V) of filtrate permeated in unit time (t) per unit area (A) is one of the parameter to investigate the performance of a membrane in a filtration process.

$$J = \frac{1}{A}\frac{V}{t} \tag{3}$$

fluxes of the permeations of aqueous Fe^{3+} solutions in the presence of PVP and dextran for each sampling period were calculated by using Equation 3 and the results were given in Fig. 7.

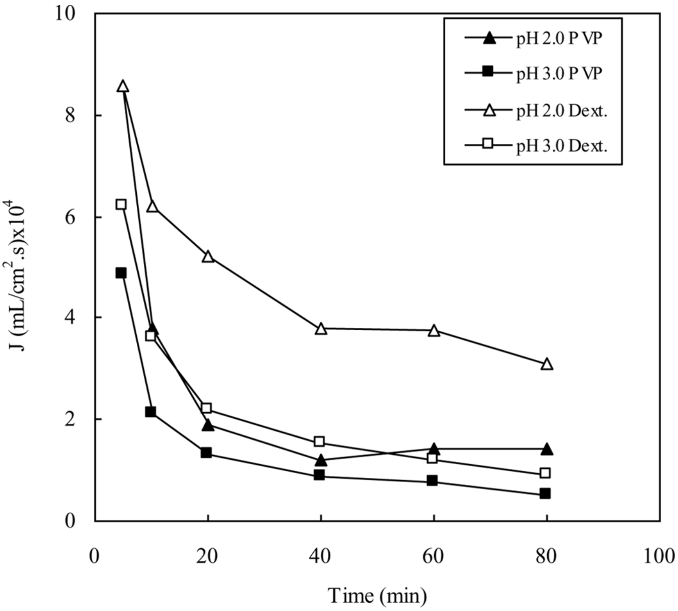

Figure 7. Effect of the presence of PVP and dextran on flux (Fe^{3+}/polymer ratio is 1:3).

As it is seen from the figure flux values for PVP and dextran are very low for both pH values, especially for PVP. After a filtration period of 80 minutes it becomes almost impossible to complete the filtration because of this low flux, therefore carrying on the filtration after 80 minutes is not practical and energetically economical. This was the reason for giving the retentions for a period of 80 minutes and to accept the solutions as concentrated Fe^{3+} solutions with a retention percentage of 62% and 48% for PVP and dextran respectively, at pH 3.0.

CONCLUSION

In this study filtration performance of asymmetric porous PMMA-co-MA membranes toward aqueous Fe^{3+} solutions was examined by UF method in the presence of water soluble polymers, with dextran and PVP as macromolecular-complexing agents. The following conclusions were drawn from the study:

1. Complexing Fe^{3+} with PVP was found to be more effective than that of dextran for getting greater retention percentage of Fe^{3+}.

2. Increasing the polymer/metal ion ratio decreased the permeated amount of filtrate.
3. pH affected the retention percentage; increase in pH increased the R% of Fe^{3+}.
4. Retention percentages for 1.0×10^{-4} M Fe^{3+} solutions mixed at equal volume of 3.0×10^{-4} repeating unit weight/L PVP and dextran were found to be as 62% and 48% at pH 3.0, respectively for a filtration period of 80 minutes by using PMMA-co-MA membranes.

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