Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Study on the Treatment of Industrial Wastewater Containing Pb2 Ion Using a Coupling Process of Polymer Complexation-Ultrafiltration

Yong-Feng Zhang[a]; Zhen-Liang Xu[a]
[a] Chemical Engineering Research Center, East China University of Science and Technology, Shanghai, P.R. China

To cite this Article Zhang, Yong-Feng and Xu, Zhen-Liang(2003) 'Study on the Treatment of Industrial Wastewater Containing Pb2 Ion Using a Coupling Process of Polymer Complexation-Ultrafiltration', Separation Science and Technology, 38: 7, 1585 — 1596
To link to this Article: DOI: 10.1081/SS-120019094
URL: http://dx.doi.org/10.1081/SS-120019094

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, No. 7, pp. 1585–1596, 2003

Study on the Treatment of Industrial Wastewater Containing Pb^{2+} Ion Using a Coupling Process of Polymer Complexation-Ultrafiltration

Yong-Feng Zhang and Zhen-Liang Xu*

Chemical Engineering Research Center, East China University
of Science and Technology, Shanghai, P.R. China

ABSTRACT

A batch complexation-ultrafiltration coupling process was studied at the laboratory level for pollutant removal and wastewater reuse from industrial wastewater containing lead (Pb^{2+}) ion. This process was used to concentrate and recover lead from acetate solution and to reuse the wastewater. Pb^{2+} ion was so small that it could not be retained by ultrafiltration membrane, which was a polyvinyl chloride (PVC) hollow fiber membrane with the molecular weight cut-off of 50,000. Therefore, Pb^{2+} ion was first complexed with a water-soluble macroligand (polyacrylic acid) and then it was removed. Effects of loading ratio (L), pH value, operating pressure (ΔP), volume concentration factor (VCF), and tangential linear velocity (V_L) across the membranes on the rejection (R) and permeate flux (J) were investigated. At better operating

---

*Correspondence: Zhen-Liang Xu, Chemical Engineering Research Center, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P.R. China; E-mail: chemxuzl@ecust.edu.cn.

DOI: 10.1081/SS-120019094 0149-6395 (Print); 1520-5754 (Online)

www.dekker.com

conditions (pH = 7.15, $L = 1$, $\Delta P = 200\,\mathrm{Kpa}$ and $V_L = 0.6\,\mathrm{m \cdot s^{-1}}$), the rejection of $\mathrm{Pb^{2+}}$ ion was more than 99.98%, whereas the smallest permeate flux was 38 $\mathrm{L/m^2hr}$. Besides, the permeate water could be reused under better operating conditions.

Key Words: Ultrafiltration membrane; Polyacrylic acid; Lead ion; Pollutant removal; Wastewater reuse.

INTRODUCTION

Lead is recognized as one of the serious environment contaminants because of its high toxicity, accumulation, and retention in the human body. It is a cumulative toxicant causing chronic poisoning. The pollution sources of lead are industrial activities such as battery industry, pigments, and metallurgical industries. For these reasons, the environmental regulation is becoming increasingly strict. For instance, the maximum permissible level in treated wastewater is 1.0 mg/L in China. In addition to stricter standards, there is an increasing emphasis by industry to stop storing its waste in certified discharges. There are currently numerous effective processes for the purification of small volumes of solution without forming metallic hydroxide sludge. The primary objective of these processes is to obtain a waste product with a content that will be lower than the maximum limit imposed by the current standard. Among these processes, they are electrolysis, ion exchange resins, cementation, and others. Each of these techniques can used only be within a given concentration range, and thus far none can treat large volumes of effluents containing low concentrations of metal ions to recover and upgrade the metal. The coupling process described in this article should allow this objective to be reached. Ultrafiltration (UF), which is a membrane technology used to separate and concentrate species of high molecular weight present in the solution, is not able to removal ionic species such as metallic ions. In this coupling process, a fixation of these ions on macromolecular species is performed to increase their molecular weight. These compounds, which then become bigger than the pore sizes of the selected membrane, can be retained and flow out in the retentate, whereas water of permeate is then purified from heavy metals. Consequently, the process is consisted of two steps: (1) complexation of a metal ion by a macroligand and (2) ultrafiltration of the complex.

Some attempts at these processes had already been undertaken.[1–3] Ruey-Shin and Chwei-Huamm demonstrated that it was possible to fix $\mathrm{Cu^{2+}}$

and Zn^{2+} using ultrafiltration by complexing them with weakly basic water-soluble polymers.[4] Sanli and Asman tried also to remove Fe^{3+} by using polymer alginic acid.[5] It had also been demonstrated by Juang and Liang that copper and zinc solution could be concentrated using polyacrylic acid (PAA).[6] But all membranes used in these processes were flat modules.

The goal of this case was to treat the wastewater containing Pb^{2+} to reuse the wastewater and recovery the heavy metal. Using phase inversion, hollow fiber membranes were spun from polyvinyl chloride (PVC).[7] The physicochemical and operation conditions, such as the concentration of the macroligand, pH value of the aqueous solution, operating pressure, volume concentration factor, and tangential linear velocity across the membranes, were determined. Simulated wastewater containing Pb^{2+} was prepared by placing a predetermined amount of its metal salts in the solution. Their concentrations were 100 mg/L, which set a typical effluent concentration for the production of lead-acid secondary battery wastewater.

THEORY AND DEFINITION

In this process, the first step was to find the best physicochemical conditions of complexation by macroligand of species to be captured by membrane.[8] The formation of a metallic complex, ML_x, is as follows:

$$M + xL \Leftrightarrow ML_x \tag{1}$$

Where M is metal ion and L is a macroligand. The stability constant (K_x) is:

$$K_x = \frac{[ML_x]}{[M][L]^x} \tag{2}$$

Eq. (2) is dependent on pH, because M acts as a weak acid, macroligand L acts as a weak base, and ML_x is sometimes amphoteric. The efficiency of UF process to retain a specific component is mainly characterized by the rejection (R), defined as:

$$R = 1 - \frac{C_p}{C_f} \tag{3}$$

Where C_p is the concentration of the components in the permeate and C_f is the concentration of the components in the retentate. The rejection (R) depends on the macroligand-membrane pair (i.e., molecular weight of macroligand and molecular weight cut-off of PVC hollow fiber membrane) and physicochemical conditions. With fixed conditions, rejection is bound to permeate and retentate concentrations.

An index called volumetric concentration factor (*VCF*) is used to determine how many times the feed concentration has been concentrated. *VCF* is defined as

$$VCF = \frac{V_0}{V_r} \tag{4}$$

Where V_0 and V_r are the volume of initial and retentate, respectively.

EXPERIMENTAL

Materials

Polyacrylic acid, with an average molecular weight of 100 000 Da, and lead acetate ($Pb(CH_3COO)_2$) were chemical reagents used in the experiments. Besides, the polyacrylic acid must be prefiltered before use to eliminate from the solution the smaller molecular weight macromolecules, which can go through the membrane. This pretreatment of polymer solution was carried out by the cycle of operations comprising a filtration step followed by a dilution of the retentate obtain a polymer rejection level stabilized at approximately 98%. The UF membrane was a PVC hollow fiber membrane type having an effective area of 0.0042 m^2 and molecular weight cut-off of 50 000 Da.[7]

Apparatus

A laboratory-scale membrane apparatus shown in Fig. 1 was employed.[9] Flow rates of the feed-solution and UF operating pressure were controlled by the means of back-pressure valve and other valves on the bypass line around a centrifugal pump. To determine the circulation rate of the feed solution, a flow meter was mounted on the feed line. The system was also equipped with a pH-meter for pH control.

UF Experiments

Feed solution at 100 mg/L Pb^{2+} ion concentration and desired PAA concentrations were prepared and stirred at about 200 rpm for 1 hour before the UF experiments. Experiments with longer mixing time demonstrated that

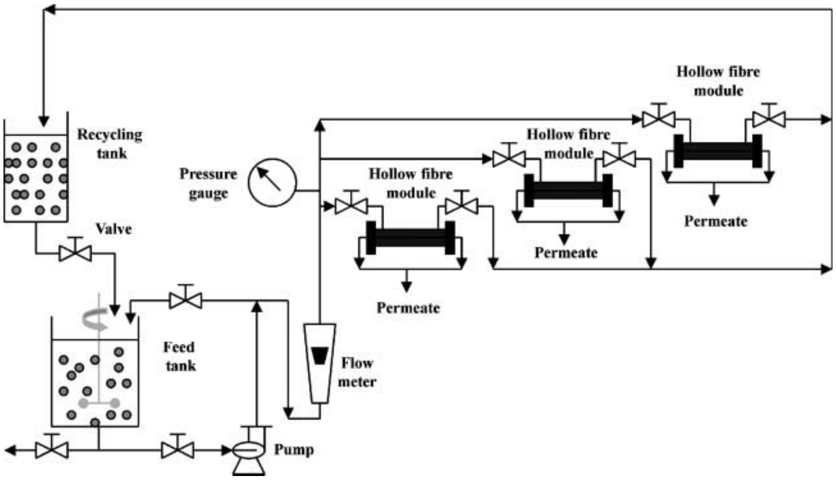

Figure 1. Schematic diagram of a batch complexation-ultrafiltration coupling process.

1 hour was sufficient to reach the complexation equilibrium. Deionlized water was circulated to wash the system before and after each run. Both retentate and permeate solutions were returned to the feed vessel to keep the concentration of the feed solution constant throughout the UF experiments. At certain time intervals, permeate flow rate was measured and samples from the permeate and feed were determined for their Pb^{2+} ion concentrations. And the pH was adjusted with HNO_3 and NaOH solutions and was continuously monitored during each run.

Analysis

Pb^{2+} ion concentration of the feed and permeate solution were determined by atomic absorption spectroscopy (Philips PU9200X).

RESULTS AND DISCUSSION

Effects of pH Values and Loading Rations on the Physicochemical Conditions

Generally, the formation of a metallic complex with a ligand is pH dependent. Therefore, the rejection coefficient of Pb^{2+} ions in the absence and presence of PAA as a function of pH is shown in Fig. 2. It is evident that the free Pb^{2+} ions can completely pass through the membrane at a pH below 5.0 but are almost completely retained at pH higher than 9.0 because of the precipitation of the metal hydroxide. In addition, a small rejection is observed between pH = 3 and 9, which may be the formation of soluble metal hydroxyl complexes in the aqueous phase.[10] Although the sizes of soluble metal hydroxy complexes are much smaller than those of the pore sizes of the PVC hollow fiber membranes, the non-zero rejection can presumably partly be attributed to the presence of some small-size pores in the PVC hollow fiber membranes. As seen in Fig. 2, the rejection coefficient is higher in the presence of PAA than in the absence of PAA. This may imply that the metal ions can be complexed with the negatively charged PAA in the presence of PAA.

To determine the binding capacity of PAA for lead and to increase our understanding of complexation and resultant separation, effect of metal loading L on rejection ratio was studied in detail. The R values obtained at different L values are plotted in Fig. 3. It is seen that R stays almost constant at a value very close to 100 until L becomes 1 kg of lead per kg of PAA. In other words, a flat plateau is observed between very low values and the critical value of L is 1. Hence, a capacity of 1 kg of PAA can be accepted as 1 kg of lead ion for practical purposes.

It is generally accepted that chemical binding between divalent metal ions and some well-defined groups on macromolecular chains, such as

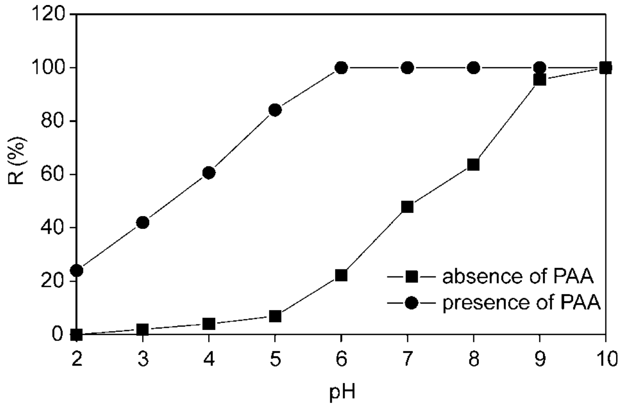

Figure 2. Effect of pH on the rejection rate in the absence and presence of PAA. $\Delta P = 200\,\mathrm{KPa}$; $V_L = 0.6\,\mathrm{m/s}$; $L = 1$.

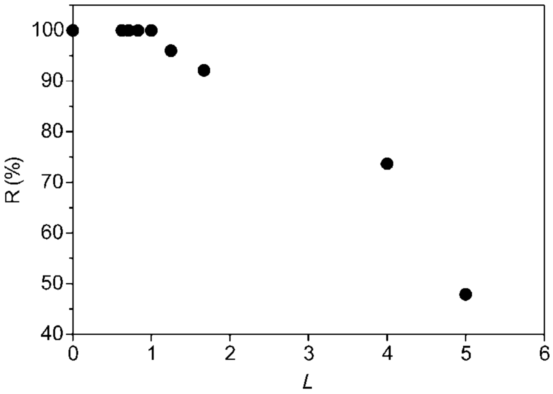

Figure 3. Effects of loading ratio on retention. $\Delta P = 200\,\mathrm{KPa}$; $V_L = 0.6\,\mathrm{m/s}$; pH = 7.15.

the carboxylate groups on PAA, does take place.[11−13] The number of PAA ligands participating in the complex formation has been suggested to be either two carboxylate groups,[14−16] or more than two, depending on the conditions. Constant R value, even at very low loading ratio (L) values obtained in this study, indicated that there was the equilibrium between free lead ions and PAA molecules and complexes formed. The addition of excess polymer did not increase the amount of lead complexed. Hence, it can be concluded that at low lead concentrations, lead ions almost completely bind to the PAA molecules. As the lead concentration is increased, a critical ratio is reached at which all the available sites of PAA are filled. Because the R value stays constant until the critical L, there is an opportunity of obtaining very high retention at polymer concentrations over a wide range of loading values.

When $L > 1$,excess lead ions cannot be complexed with PAA and they pass through the membrane. This brings a linear decrease in retention. At very high L values, R does not become zero but approaches a limiting value. This may be due to the membrane itself that also retains parts of the free lead ions.

Effects of Operating Pressures, PAA Concentrations, V_L, Time, and *VCF* on the Rejection and Permeate Flux

Variation of permeate fluxes are given in Fig. 4 as a function of operating pressure for pure water and for different concentrations of PAA. In all cases, an increase of operating pressure leads to an almost linear increase of

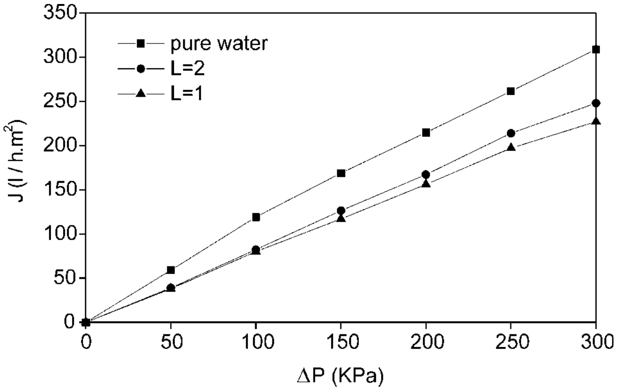

Figure 4. Effects of operating pressure on the permeate flux. $V_L = 0.6\,\mathrm{m/s}$; pH = 7.15.

the permeate flux. The comparison of the different curves shows that the permeate flux is strongly lowered from pure water to water with macroligand for a given pressure. But when water contains larger PAA concentration, the decrease of the permeate flux for a given pressure is not so important. It indicates that concentration polarization effects are not dominant for the polymer range studied.

The effect of the tangential linear velocity across the membrane on the permeate flux and rejection rate at a constant loading ratio ($L = 1$) is shown in Fig. 5. It is evident that the permeate flux and rejection rate is almost constant at different flow rates. It can be concluded that the Pb^{2+} complexed with the PAA is stable, so the rejection rate don't change with the tangential linear velocity across the membrane. On the other hand, it is illustrated that there is a linear relationship between the permeate flux and the operating pressure in Fig. 4. Based on the linear relationship between the permeate flux and the operating pressure, the permeate flux can be expressed as a product of the permeability constant and the operating pressure giving a permeability constant of $7.8 \times 10^{-4} m^3/m^2{\cdot}h{\cdot}kPa$, which demonstrate the superiority of the PVC hollow fiber membranes in the use of this coupling process.

Another factor influencing the permeate flux is time, especially as a consequence of membrane fouling. In the experimental conditions, the variation of permeate flux is measured during 6 hours (Fig. 6). It appears that after an important decrease at the beginning of the experiment, the permeate flux seems to be constant from 4 to 6 hours. It is concluded that there is no

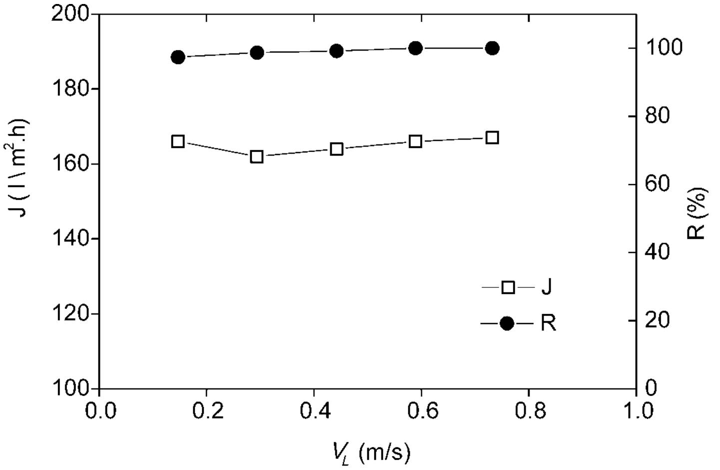

Figure 5. Effect of the tangential linear velocity on permeate flux and retention. $\Delta P = 200\,\text{KPa}$; $L = 1$; $\text{pH} = 7.15$.

increase of membrane fouling under the given experimental conditions after 4 hours.

To upgrade and concentrate the metal for recovery, the Pb^{2+} ion solution should be concentrated to a suitable degree. In this step, the permeate solution was extracted out. Experimental results are presented in Fig. 7, which shows

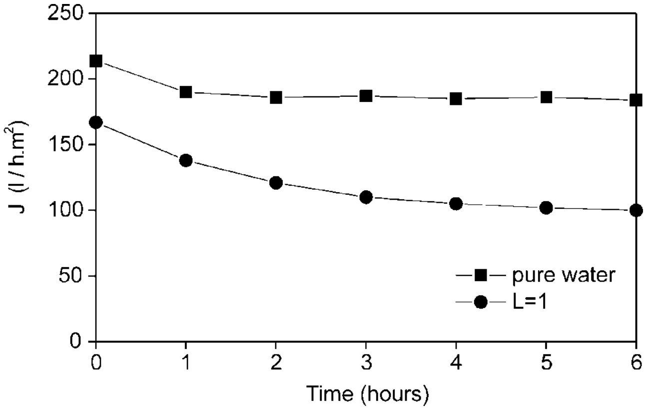

Figure 6. Effect of time on the permeate flux. $\Delta P = 200\,\text{KPa}$; $V_L = 0.6\,\text{m/s}$; $\text{pH} = 7.15$.

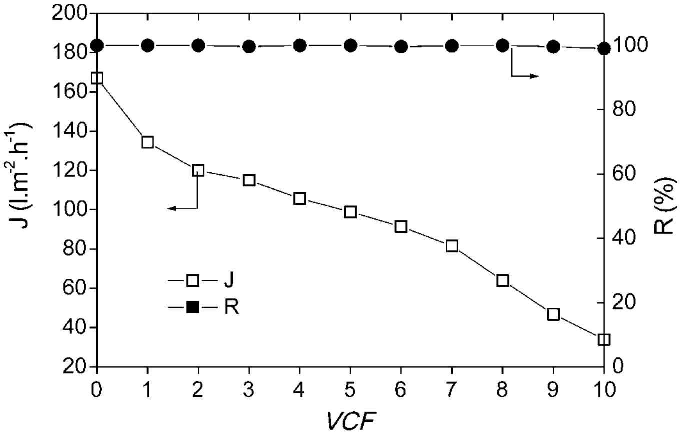

Figure 7. Effect of *VCF* on the permeate flux and *R*. $\Delta P = 200\,\text{KPa}$; $V_L = 0.6\,\text{m/s}$; $L = 1$; $\text{pH} = 7.15$.

a decrease in the flow rate of the permeate solution throughout the filtration, but the rejection rate is almost constant. During the filtration of the Pb^{2+} ion solution in the presence of PAA, the macromolecular species become more concentrated and the viscosity of the solution increases, which leads to the reducing of the flow rate of the permeate. Knowing the rejection of the Pb^{2+}-polymer complex by the membrane, the solute concentrates (C_o in the initial solution, C_r in the retentate, and C_p in the permeate), the rejection R and the volume concentration factor are related by:

$$C_r = \frac{C_0}{1 + R(1/VCF - 1)} \tag{5}$$

Under the given experimental conditions, C_0 is 100 mg/L. At the end of the concentration, the lead content of the retentate is 1000 mg/L, which corresponds to a volume concentration factor close to 10. Lead can be reclaimed using other method (for example, electrolysis) because it had also been concentrated. Corresponding, lead concentration in the permeate is only 0.2 mg/L, which is lower than the discharge content of the standard in China. And it can be reused in the process of the lead-acid battery production as the washing water. It also can be seen in Fig. 7 that the flow rate of the permeate become very low at the volume concentration factor of 10. Furthermore, the concentration in the permeate is then close to the maximum value fixed by the acceptable waste level standard. From a practical point of view, the volume concentration factor should not exceed 10. Under these condition, R and the permeate flux are 99.98% and 38 L/m^{2}h, respectively.

CONCLUSION

The complexation-UF coupling process was a promising technique applied to the treatment of effluents containing heavy metals such as lead. After fixing the better physicochemical conditions ($\mathrm{pH} = 7.15$, $L = 1$) and the best hydrodynamic conditions ($\Delta P = 200\,\mathrm{KPa}$, $V_L = 0.6\,\mathrm{ms}^{-1}$) a constant R of 99.98% was obtained until the VCF was up to 10. Rejection of lead was dependent on the lead-to-PAA ratio and pH value rather than other factors, such as VCF, V_L, and time. Under certain lead-to-PAA ratio, the pH value is the decisive phys-chemical condition on the rejection, whereas the $\mathrm{pH} > 6$, the rejection is almost 100%, but $\mathrm{pH} < 6$, the rejection is decreased strongly. The permeate flux increased linearly with UF operating pressure. Before developing a practical process, the heavy metal concentration in the retentate must be taken into account (i.e., first to separate heavy metal ions from the waste water; second to reuse the macroligand and to recovery the metals).

REFERENCES

1. Chaufer, B.; Deratani, A. Removal of metal ions by complexation ultrafiltration using water soluble macromolecules, perspective of application to wastewater treatment. Nucl. Chem. Waste Manag. **1988**, *8*, 175.
2. Renault, M.; Aulas, F.; Rumeau, M. Recovery of chromium from effluents using ultrafiltration. Chem. Eng. J. **1982**, *23*, 137.
3. Ennassef, K.; Persin, M.; Durand, G. Etude par ultrafiltration de la complexation des cations Ag(I) et Cu(II) par des macroligands oligomers d'acide polyacrylique. Analusis **1989**, *17*, 567.
4. Ruey-Shin, J.; Chwei-Huamm, C. Ultrafiltration rejection of dissolved ions using various weakly basic water-soluble polymers. J. Membr. Sci. **2000**, *177*, 207–214.
5. Sanli, O.; Asman, G. Removal of Fe(III) ions from dilute aqueous solutions by alginic acid-enhanced ultrafiltration. J. Appl. Polym. Sci. **2000**, *177*, 1096–1101.
6. Juang, R.S.; Liang, J.F. Removal of copper and zinc from aqueous sulfate solution with polyacrylic acid by a batch ultrafiltration process. J. Membr. Sci. **1993**, *82*, 175–183.

7. Xu J.; Xu, Z.L. Study on polyvinyl chloride (PVC) hollow fiber UF membrane, Proceedings of the third China–Korea conference on separation science and technology, Oct 31–Nov 2 2001, Hangzhao, China, 478–481
8. Kortly, S.; Sucha, L. *Handbook of chemical Equilibria in Analytical Chemistry*; Hellis Horweed, 1985.
9. Xu, Z.L.; Chung, T.S.; Loh, K.C.; Lim, B.C. Polymer asymmetric membrane made from polyetherimide/polybenzimidlazol/poly(ethyleneglycol) (PEI/PBI/PEG) for oil-surfactant-water separation. J. Membr. Sci. **1999**, *158*, 41–43.
10. Juang, R.S.; Liang, J.F. Equilibrium studies for the interaction of aqueous metal ions and polyacrylic acid by a batch ultrafiltration method. J. Membr. Sci. **1993**, *82*, 163–172.
11. Mandel, M.; Leyte, J.C. Interaction of polymethacrylic acid and bivalent counterions. I. J. Polym. Sci., Part A, **1964**, *2*, 2883.
12. Gregor, H.P.; Luttinger, L.B.; Loebl, E.M. Metal-polyelectrolyte complexes. I. The polyacrylic acid-copper complex. J. Phys. Chem. **1955**, *59*, 34.
13. Yamashita, F.; Komatsu, T.; Nakagawa, T. Study of metal-polycarboxylate complexes employing ion-selective electrode. II. Stability constants of copper (II) complexes with polyacrylic acid and polymethacrylic acid. Bull. Chem. Soc. Jpn **1979**, *52* (1), 30.
14. Mclaren, J.V.; Watts, J.D.; Gilbert, A. Interactions of nickel and copperwith polyacrylic acid. J. Polym. Sci., Part C, **1967**, (16), 1903.
15. Yamaoka, K.; Masujima, T. Spectroscopic and equilibrium dialysis studies of the polyacrylic acid-copper (II) copplex in the pH range 3.5–7. Bull. Chem. Soc. Jpn. **1979**, *52* (6), 1819.
16. Wall, F.T.; Gill, S.J. Interaction of cupric ions with polyacrylic acid. J. Phys. Chem. **1954**, *58*, 1128.

Received January 2002
Revised July 2002