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To cite this Article Chang, Dong-Jang and Hwang, Shyh-Jye(1996) 'Removal of Metal Ions from Liquid Solutions by Crossflow Microfiltration', Separation Science and Technology, 31: 13, 1831 — 1842
To link to this Article: DOI: 10.1080/01496399608001013
URL: http://dx.doi.org/10.1080/01496399608001013

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SEPARATION SCIENCE AND TECHNOLOGY, **31**(13), pp. 1831–1842, 1996

Removal of Metal Ions from Liquid Solutions by Crossflow Microfiltration

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ABSTRACT

The applicability of crossflow microfiltration (CFMF) to the removal of metal ions from liquid solutions was studied. Three treatment processes were employed in this study. The first process was filtration of liquid solutions containing metal ions by CFMF. The second process was CFMF with membranes precoated by $CaCO_3$ cake. The third process used suspension flocculation as a pretreatment step before CFMF. It was found that CFMF or CFMF with precoated membranes could not remove the metal ions (Cu^{2+}, Mn^{2+} and Fe^{2+}) from water efficiently. On the contrary, CFMF with suspension flocculation as a pretreatment could remove the metal ions from water completely under suitable pH values. The unsteady-state permeate flux for CFMF with suspension flocculation increased with an increase in temperature but decreased with an increase in pH of the liquid solutions. In addition, an optimal permeate flux existed in the relationship among the permeate flux, crossflow velocity, membrane pore size, and pressure drop. Furthermore, the unsteady-state permeate flux obtained experimentally for CFMF with suspension flocculation could be predicted by a mathematical model developed previously if an equivalent diameter of the flocs in the suspension was used in the model.

INTRODUCTION

Metal ions removal has always been a perplexing problem in conventional water and wastewater treatment processes. For example, alkali precipitation followed by sedimentation and sand filtration generates a large

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amount of sludge that is difficult or expensive to dispose of. Another example is ion exchange. The concentration of metal ions in the effluent of an ion exchanger is sometimes at a level higher than acceptable due to breakthrough or leakage. In addition, the spent ion exchange resins must be carefully disposed of. Recently, membrane filtration processes have been replacing conventional treatment processes for the removal of metal ions from water (1–6) due to their advantages of improving the effluent quality, savings on water purification chemicals and operation costs, easier operation and maintenance, and savings in space, time, and the cost of construction of water purification plants.

Crossflow microfiltration (CFMF) is a membrane process which operates at a lower pressure drop and yields a higher permeate flux rate compared to other membrane processes. However, depending on the specifications of the membrane used in crossflow microfiltration for metal ions removal from water and wastewater, some pretreatment processes may be necessary.

This paper describes two pretreatment processes for improving the efficiency of metal ions removal and for enhancing the permeate flux by minimizing fouling during crossflow microfiltration. The first process involves precoating membranes with a $CaCO_3$ cake. The metal ions in water are expected to be separated by or adsorbed on the $CaCO_3$ cake layer. The second process involves suspension flocculation by polyaluminum chloride (PAC). The adsorption and binding effects of the resultant flocs can remove metal ions. These flocs are then removed by crossflow microfiltration. A previously developed mathematical model based on hydrodynamic theory and mass balance (7) is used to predict the unsteady-state permeate flux of crossflow microfiltration when suspension flocculation is used as a pretreatment step.

EXPERIMENTAL APPARATUS AND METHODS

A schematic diagram of the experimental setup is shown in Fig. 1. The dimensions of the filtration channel in the CFMF cell were 6 × 0.6 × 0.036 cm, and the filters used were Durapore membranes made by Millipore. The nominal membrane pore diameters were 0.1, 0.2, 0.45, and 0.65 μm. The aqueous solutions used in the experiments contained Cu^{2+}, Mn^{2+}, and Fe^{2+} ions. In all experiments the solutions or suspensions flowed under the membrane of the CFMF cell, and the flow rate and inlet and outlet pressures of the solutions or suspensions were measured by a rotameter and pressure gauges, respectively. The permeate flux through the membrane was measured by an electronic balance and recorded by a recorder. The concentrations of the metal ions in the permeate flux were

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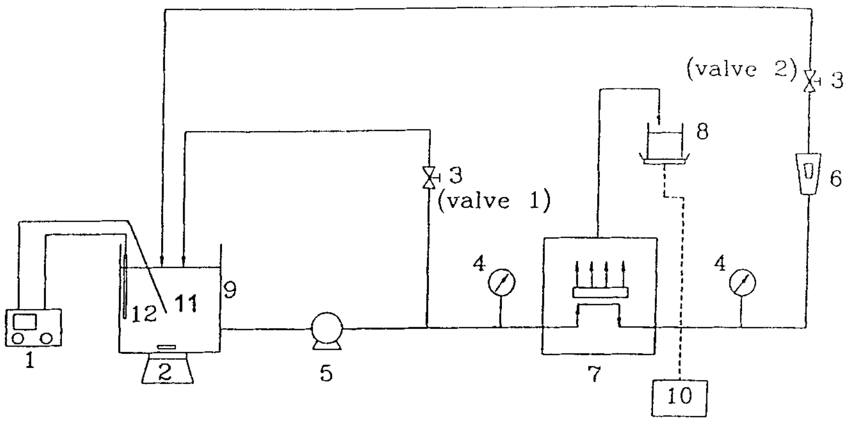

1. temp controller | 2. stirrer
3. valves | 4. pressure gauge
5. squeezing pump | 6. rotameter
7. filtration cell | 8. electronic balance
9. stock tank | 10. recorder
11. temp sensor | 12. heater

FIG. 1 Schematic diagram of experimental set-up.

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measured by atomic absorption spectrometry. The solutions or suspensions flowing out of the CFMF cell were recycled to the stock tank.

The unsteady-state permeate flux and the concentrations of the metal ions in the permeate were investigated in this study by 1) CFMF, 2) CFMF with precoated membranes, and 3) CFMF with suspension flocculation. The two pretreatment procedures are described as follows.

1. Precoating Membranes with $CaCO_3$. A suspension of $CaCO_3$ (10 wt%) was delivered from a stock tank equipped with a temperature controller to the CFMF cell by a squeezing pump under the same operating conditions used in the CFMF experiments for metal ions removal. The duration of the precoating process was about 30 minutes to ensure a uniform $CaCO_3$ cake layer on the membrane surface.

2. Suspension Flocculation. The liquid solution containing metal ions in the stock tank was controlled under optimum pH (by 1 M NaOH or 1 M H_2SO_4 solution), PAC (polyaluminum chloride) dosage, and alkalinity (1 M NaOH solution was used as the alkalizing agent). The optimum pH, PAC dosage, and alkalinity were determined by the jar test. The formation of flocs in the solution occurred when suitable mixing rates were used for the solution. The floc suspension was then used in the CFMF experiments.

For CFMF with suspension flocculation, the effects of various operating conditions, including crossflow velocity, membrane pore size, pressure drop, pH, and suspension temperature, on the unsteady-state permeate flux and the rejection ratios of the metal ions were investigated. In addition, dead-end filtration experiments were also carried out in the CFMF with suspension flocculation to obtain the specific resistance of the cake formed in the CFMF.

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RESULTS AND DISCUSSION

CFMF

A liquid solution containing Cu^{2+}, Mn^{2+}, and Fe^{2+} was treated by CFMF with a 0.2-μm membrane. The concentration of each metal ion in the solution was 5 mg/L. The results are shown in Fig. 2. The permeate flux reduced slightly in the first 20 minutes and then dropped rapidly. This was due to oxidation of Fe^{2+} and Mn^{2+} ions to Fe_2O_3 and MnO, which resulted in membrane fouling. In addition, the rejection ratios of the metal ions were low, i.e., the permeate contained rather high concentrations of the metal ions. Note that the rejection ratio, R, is defined as

$$R = 1 - C_p/C$$

where C and C_p are the concentrations of individual metal ions in the feed and permeate, respectively. Therefore, the metal ions could not be removed efficiently by CFMF alone.

CFMF with Precoated Membranes

A liquid solution containing Cu^{2+}, Mn^{2+}, and Fe^{2+} was treated by CFMF with a 0.2-μm membrane precoated with a uniform $CaCO_3$ cake layer. The concentration of each metal ions in the solution was 5 mg/L. Figure 3 indicates that low rejection ratios of the metal ions are obtained, i.e., the permeate still contains very high concentrations of the metal ions. Similar results were obtained when a precoated 0.1 μm membrane was used. Therefore, CFMF with precoated membranes was also unable to remove the metal ions from the solution efficiently.

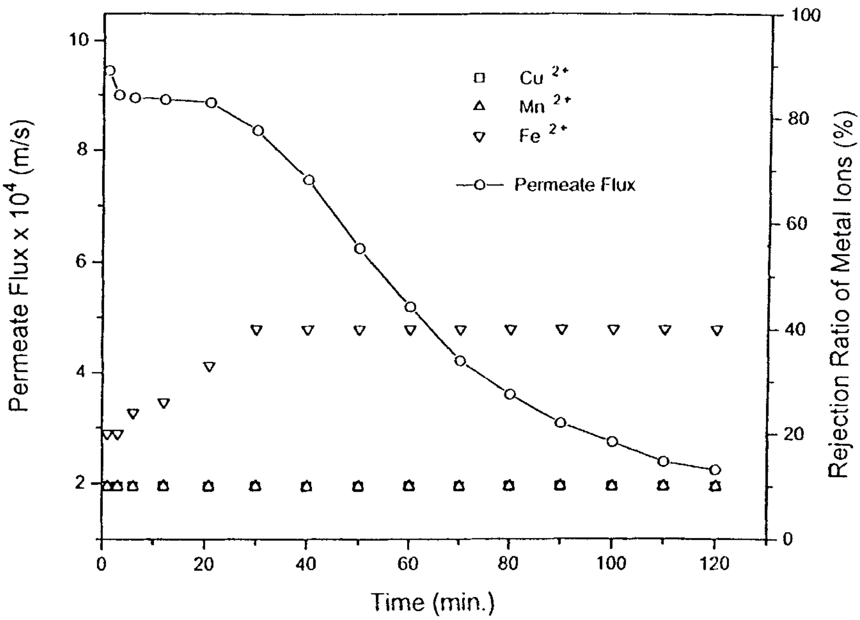

FIG. 2 The performance of CFMF (d_m = 0.2 μm, ΔP = 3.8 × 10^4 N/m^2, T = 30°C, pH 7.5, u_o = 1.8 m/s, $C_{Cu^{2+}} = C_{Mn^{2+}} = C_{Fe^{2+}}$ = 5 mg/L).

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CFMF with Suspension Flocculation

As mentioned earlier, during the experiments Fe^{2+} and Mn^{2+} were oxidized by O_2 to form precipitates of metal oxides. As a result, it was difficult to determine exactly the metal ions removal efficiency of the CFMF systems. Therefore, a liquid solution containing only Cu^{2+} was used in CFMF with suspension flocculation. It should be noted that the pH and PAC dosage were kept at optimum conditions (pH 7.5, PAC = 20 mg/L) except when the effect of pH was investigated. The effects of various operating conditions on the permeate flux and the rejection ratio of Cu^{2+} are described as follows.

Effect of Crossflow Velocity

The effect of crossflow velocity on the permeate flux and rejection ratio is shown in Fig. 4. Crossflow velocities used were 2.5, 1.8, and 1.0 m/s. As shown in this figure, the permeate flux first increases and then de-

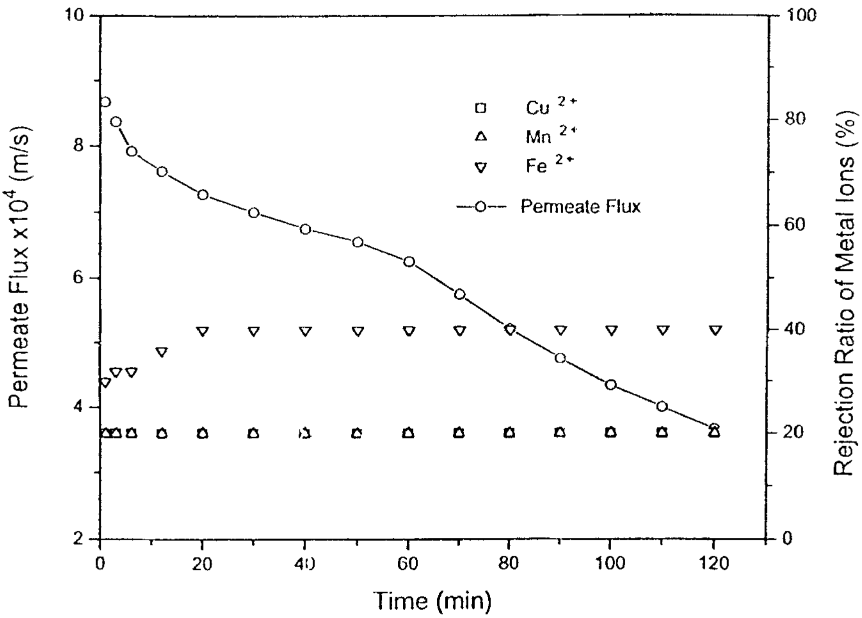

FIG. 3 The performance of CFMF with a precoated membrane (d_m = 0.2 μm, ΔP = 3.8 × 10^4 N/m², T = 30°C, pH 7.5, u_o = 1.8 m/s, $C_{Cu^{2+}} = C_{Mn^{2+}} = C_{Fe^{2+}}$ = 5 mg/L).

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creases with crossflow velocity. At a low crossflow velocity, the cake is thick, which leads to a low permeate flux (7). At higher crossflow velocities, the backtransport velocity is higher (7). In addition, the backtransport velocity of a floc increases with its size (7). Consequently, at a higher crossflow velocity the average size of the flocs in the suspension should be higher and that in the cake should be lower. On the other hand, the shear force at a higher crossflow velocity is higher, which should lead to smaller flocs in the suspension and cake. These two counteracting effects result in a higher permeate flux at a crossflow velocity of 1.8 m/s than at 2.5 m/s. Also shown in Fig. 4 is that the rejection ratio of Cu^{2+} ions is 100% under various crossflow velocities. Thus, CFMF with suspension flocculation can remove Cu^{2+} ions from the liquid solution completely. Finally, the equivalent diameters of the flocs in the suspension obtained by the model proposed by Chang and Hwang (7) are 4.2, 5.2, and 3.7 μm, respectively, for crossflow velocities of 2.5, 1.8, and 1.0 m/s. Thus, smaller flocs in the suspension result in lower permeate flux. This is consistent

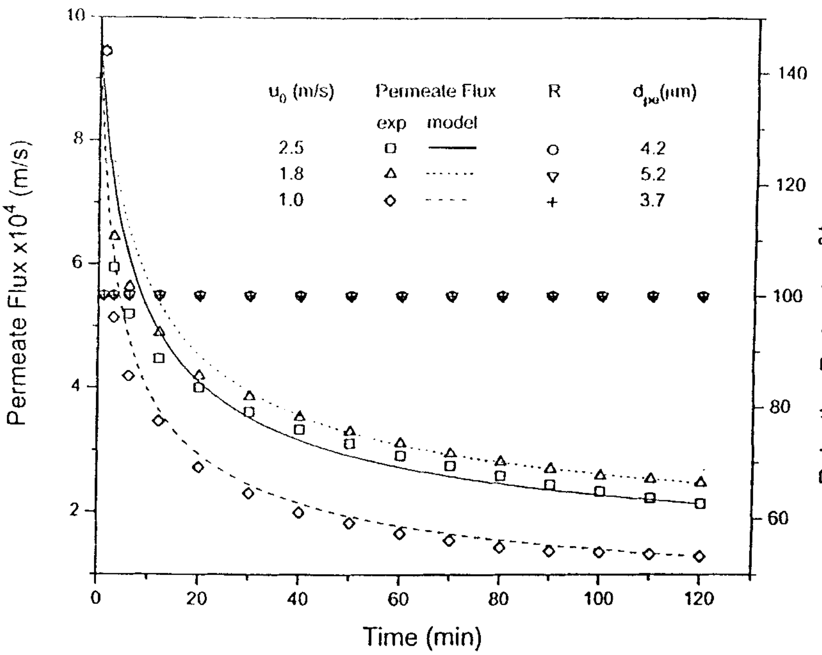

FIG. 4 Effect of crossflow velocity on the performance of CFMF with suspension flocculation (d_m = 0.2 μm, ΔP = 3.8 × 10^4 N/m^2, T = 30°C, pH 7.5, $C_{Cu^{2+}}$ = 5 mg/L, PAC = 20 mg/L).

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with the relationship between the permeate flux and the particle size observed by Chang and Hwang (7).

Effect of Membrane Pore Size

Membranes with pore size of 0.1, 0.2, 0.45, and 0.65 μm were used to study the effect of membrane pore size on the rejection ratio of Cu^{2+} and permeate flux. The results are shown in Fig. 5. As shown in this figure, the rejection ratio of Cu^{2+} ion is 100% under various membrane pore sizes. In addition, a membrane with larger pores has a lower membrane resistance, and thus a higher permeate flux is obtained during the initial filtration period. However, as the filtration proceeds, a membrane with larger pores has a larger amount of flocs depositing on its surface and pores, which leads to a higher filtration resistance. The combination of these two opposite effects (membrane resistance and cake resistance) re-

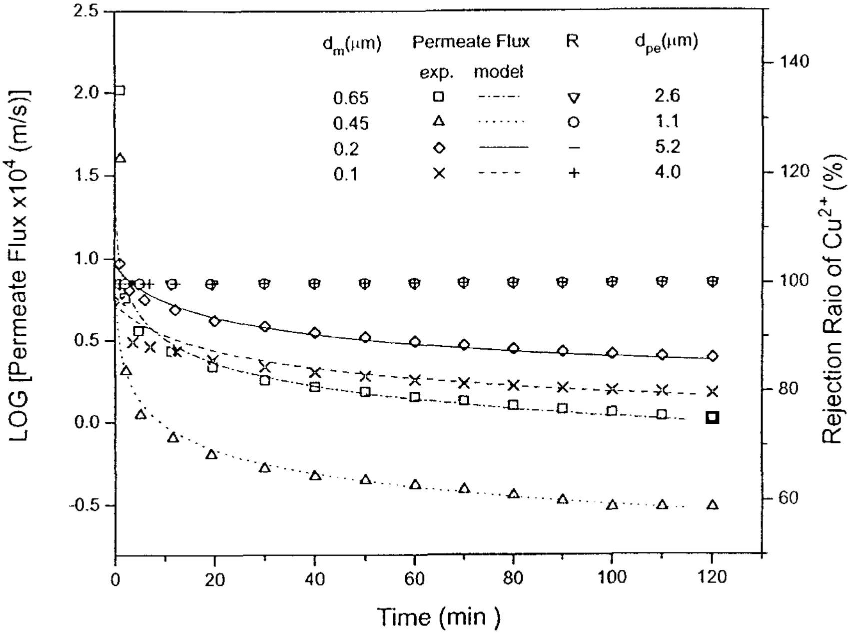

FIG. 5 Effect of membrane pore size on the performance of CFMF with suspension flocculation (ΔP = 3.8 × 10^4 N/m^2, T = 30°C, pH 7.5, u_o = 1.8 m/s, $C_{Cu^{2+}}$ = 5 mg/L, PAC = 20 mg/L).

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sults in a maximum permeate flux, which occurs when the membrane with a pore size of 0.2 μm is used. Finally, the equivalent diameters of the flocs in the suspension obtained by the model (7) are 2.6, 1.1, 5.2, and 4.0 μm, respectively, for membrane pore sizes of 0.65, 0.45, 0.2, and 0.1 μm.

Effect of Pressure Drop

The effect of pressure drop across the membrane on the rejection ratio of Cu^{2+} and the permeate flux was studied using three different pressure drops: 1.7 × 10^4, 3.8 × 10^4, and 5.2 × 10^4 Nt/m^2. Figure 6 indicates that the rejection ratio of Cu^{2+} ion is 100% under various pressure drops. In addition, the permeate flux first increases and then decreases with increasing pressure drop. This is similar to that observed in the filtration of monodispersed suspensions (7). According to Darcy's equation, the permeate flux increases with increasing pressure drop. However, the voidage of the

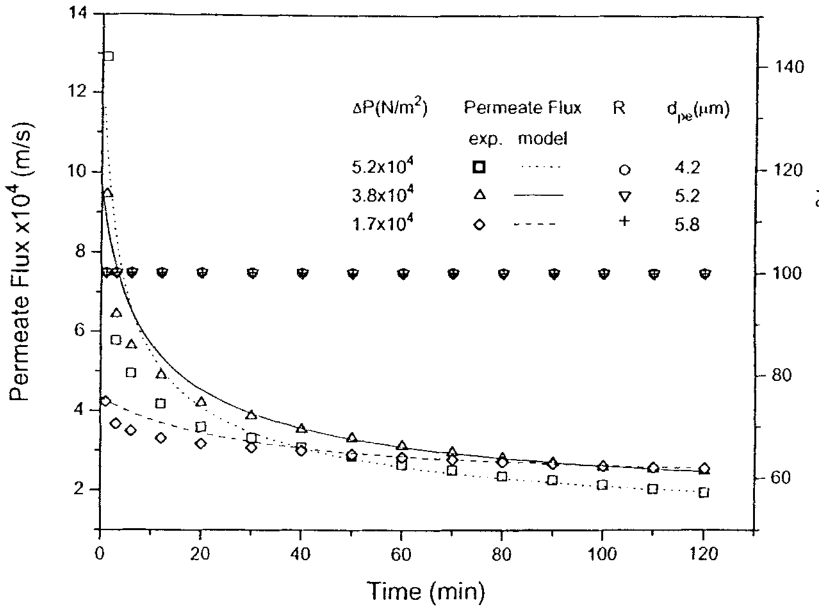

FIG. 6 Effect of pressure drop on the performance of CFMF with suspension flocculation (d_m = 0.2 μm, T = 30°C, pH 7.5, u_o = 1.8 m/s, $C_{Cu^{2+}}$ = 5 mg/L, PAC = 20 mg/L).

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cake is low at a high pressure drop. As a result, the permeate flux is reduced at a high pressure drop due to high cake resistance. Therefore, a maximum permeate flux exists due to these two counteracting effects. Finally, the equivalent diameters of the flocs are 4.2, 5.2, and 5.8 μm, respectively, for pressure drops of 5.2×10^4, 3.8×10^4, and 1.7×10^4 Nt/m^2.

Effect of pH

The effect of pH was studied using three different pH values: 11.0, 7.5, and 4.0. Solutions of 1 M HCl and 1 M NaOH were used to adjust the pH of the liquid solution, and a 1 M NaCl solution was used to keep the ionic strength of the liquid at the same value in all experiments. Figure 7 shows that the rejection ratio of Cu^{2+} ion is 100% at a pH of 7.5 and 11.0; however, it is very low at a pH of 4.0. This is due to the fact that it is out of the range of PAC flocculation at a pH of 4.0, thus only a small number of fluffy flocs are formed in the suspension. As a consequence, the rejection ratio of Cu^{2+} is very low. In addition, at pH 4.0 the permeate

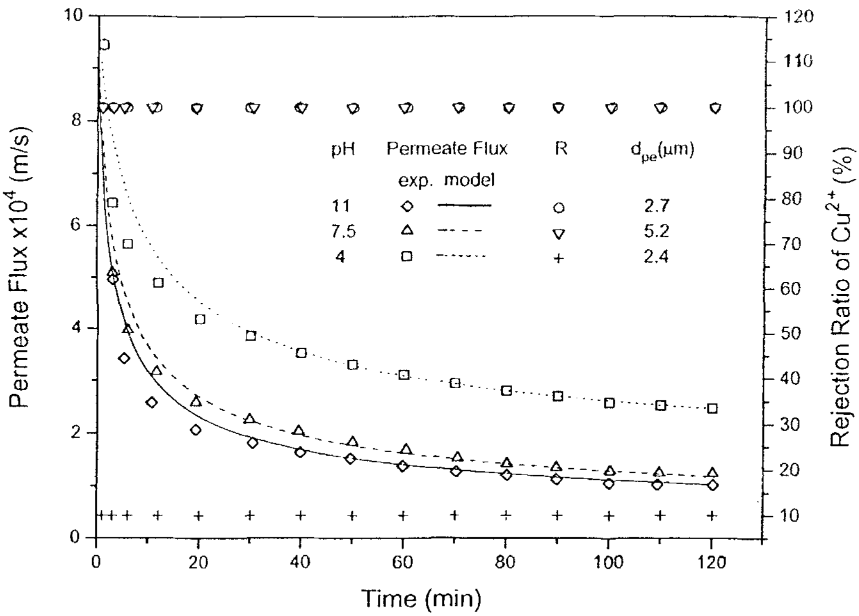

FIG. 7 Effect of pH on the performance of CFMF with suspension flocculation (d_m = 0.2 μm, ΔP = 3.8 × 10^4 N/m^2, T = 30°C, u_o = 1.8 m/s, $C_{Cu^{2+}}$ = 5 mg/L, PAC = 20 mg/L).

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flux is at its highest due to low cake resistance. Furthermore, the permeate flux at pH 7.5 is higher than that at pH 11.0. This is due to a better flocculation condition for PAC at pH 7.5 than at pH 11.0. As a result, larger flocs are formed at pH 7.5, which leads to a higher permeate flux. Finally, the equivalent diameters of the flocs in the suspension obtained by the model (7) are 2.7, 5.2, and 2.4 μm, respectively, for pH 11.0, 7.5, and 4.0.

Effect of Temperature

The effect of temperature of the liquid solution on the rejection ratio of Cu^{2+} and permeate flux was studied using three different temperatures: 45, 30, and 15°C. Figure 8 indicates that the rejection ratio of Cu^{2+} ions is 100% at various temperatures. In addition, the permeate flux increases with increasing temperature because the viscosity of the suspension is lower at higher temperatures. Furthermore, the size of the flocs is larger when the viscosity is lower, which leads to lower filtration resistance. Therefore, the permeate flux increases as the temperature is increased.

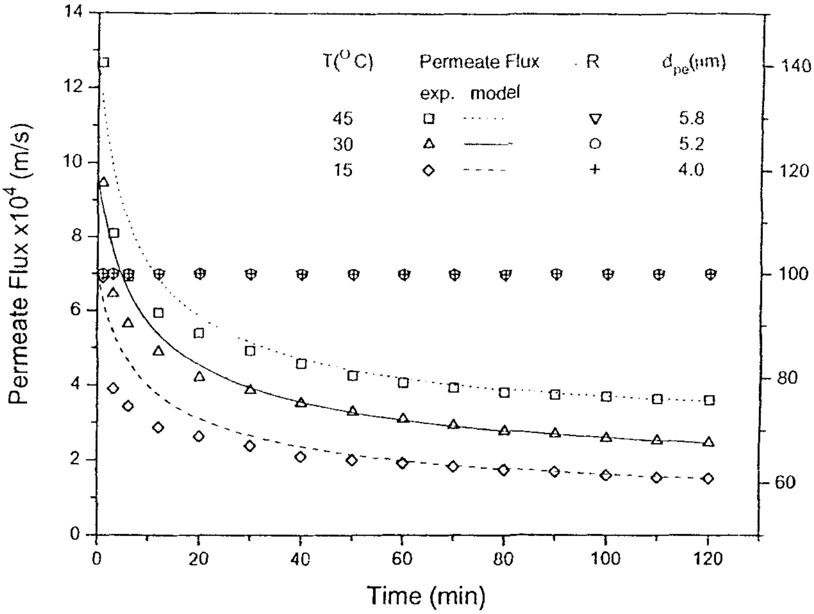

FIG. 8 Effect of temperature on the performance of CFMF with suspension flocculation (d_m = 0.2 μm, ΔP = 3.8 × 10^4 N/m^2, pH 7.5, u_o = 1.8 m/s, $C_{Cu^{2+}}$ = 5 mg/L, PAC = 20 mg/L).

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Finally, the equivalent diameters of the flocs in the suspension are 5.8, 5.2, and 4.0 μm, respectively, for temperatures of 45, 30, and 15°C.

CONCLUSIONS

Experiments were conducted to study the crossflow microfiltration of liquid solutions containing metal ions of Cu^{2+}, Mn^{2+}, and Fe^{2+}. It was found that CFMF or CFMF with precoated membranes cannot remove the metal ions from the liquid efficiently. However, CFMF with suspension flocculation can completely remove the metal ions from the liquid under a suitable pH range. In addition, the unsteady-state permeate flux for CFMF with suspension flocculation increases with an increase in temperature or a decrease in pH. Furthermore, there are optimal crossflow velocity, membrane pore size, and pressure drop values under which the permeate flux is the highest.

The experimental results of the permeate flux for CFMF with suspension flocculation can be predicted by a mathematical model developed by

Chang and Hwang (7) if an equivalent diameter of the flocs in the suspension is employed. This is helpful in understanding the filtration mechanism of the floc suspension.

ACKNOWLEDGMENT

This work was supported by the National Science Council under Grant NSC 84-2214-E-007-023.

NOTATIONS

C	concentration of metal ions in the feed (mg/L)
C_p	concentration of metal ions in the permeate (mg/L)
d_m	membrane pore size (μm)
d_{pe}	equivalent diameter of flocs (μm)
ΔP	pressure drop across membrane (N/m^2)
R	rejection ratio
T	temperature (°C)
u_o	crossflow velocity (m/s)

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Received by editor September 29, 1995