Reduction of cake layer by re-aggregation in coagulation-crossflow microfiltration process

S. Kim, S.-H. Cho and H. Park

Department of Civil and Environmental Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, South Korea (E-mail: *hkpark@kaist.ac.kr*)

Abstract Cake layer in crossflow microfiltration(CFMF) can be reduced by coagulation, enhancing membrane flux. This is because enlarging particle size by coagulation increases shear-induced diffusivity and the back-transport of rejected particles. However, it is known that the enlarged particles are disaggregated by the shear force of the pump while passing through it. This study looks at the disaggregation in relation to cake layer reduction. Kaolin and polysulfon hollow fiber microfilters are used for experiments. The reduction of cake resistance by coagulation is observed in a range of 17% to 53% at the various coagulation conditions. Particle size analysis results of the experiments show that aggregated particles in feed are completely disaggregated by the pump but re-aggregation of particles occurs in the membrane. This suggests that the re-aggregation of particles is critical to cake reduction and flux enhancement, since the aggregated particles are completely broken. The mechanisms for re-aggregation in the membrane are the same as those for coagulation in the feed tank. Charge neutralization is better for CCFMF than sweep flocculation although it has two drawbacks in operation.

Keywords Cake layer; coagulation-crossflow microfiltration; charge neutralization; re-aggregation; sweep flocculation

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Introduction

Suspended particles are transported to the membrane surface, forming cake layer, by permeate flow due to the imposed pressure drop in crossflow microfiltration (CFMF). The cake layer in turn induces membrane permeate flux to decline. This is one of the major problems in pressure-driven membrane processes. The most important factor affecting cake formation is known to be the back-transport mechanisms of particles which include Brownian diffusion, shear-induced diffusion, turbulent transport, axial transport (or particle rolling), inertial-lift forces, and particle–particle interaction force. It is known that shear-induced diffusion is a main backtransport mechanism in CFMF, since the particles filtered are mainly larger than 0.1 µm (refer to Figure 1; Wiesner *et al*., 1989). The shear-induced diffusivity is given by an empirical relationship, independent of concentration, which is proposed by Eckstein *et al*. (1977).

$$D_s = 0.03\gamma a^2 \quad (1)$$

where D_s is shear-induced diffusion coefficient, γ shear rate, and a particle radius. The equation tells that enlarging particle size enhances back transport from membrane surface to bulk flow and decreases particle deposition on the membrane surface. As a result, increasing particle size has been suggested as an effective way for reducing cake formation (Kim *et al*., 2001a). Particle–particle interaction by surface charge of particle is also an important mechanism because it can affect shear-induced diffusivity. Bacchin *et al*. (1996) found that particles aggregated and effective sizes of particles increased when their zeta potentials were in a range of –20mV to near 0mV (refer to Figure 2). The increased sizes of particles enlarge the shear-induced diffusivity (refer to Eq. (1)). Therefore, it can be said

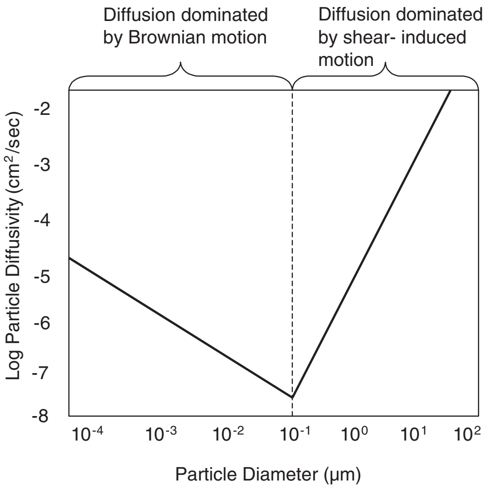


Figure 1 Diffusivity vs particle size (Wiesner *et al.*, 1989)

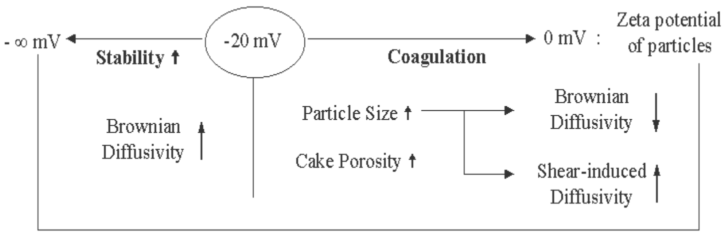


Figure 2 The effect of particle charge in CFMF

that the cake resistance in CFMF can be reduced by coagulation processes of which the main purpose is to aggregate particles using surface charge and others.

Among several mechanisms of coagulation, two are frequently referred to for colloid particles: charge neutralization by chemical reaction between positively charged coagulant and negatively charged particles, and sweep flocculation by rapid formation of amorphous precipitate (solid-phase $Al(OH)_3$ in the case of alum as a coagulant). As shown in Figure 3, alum is changed to positive aluminium ion when hydrated and it is also changed to $Al(OH)_3$. Forming positive aluminum ion is dominant in low pH and forming $Al(OH)_3$ is dominant in high pH. Therefore, it is known that coagulation by charge neutralization is dominant in a range of pH smaller than 4.5 and sweep flocculation is so in a range of pH 6–8 (Lee *et al.*, 2000).

Several previous studies on coagulation-crossflow microfiltration (CCFMF) reported the following results (Peuchot and Aim, 1992; Wiesner *et al.*, 1989; Soffer *et al.*, 2000; Lee *et al.*, 2000; Kim *et al.*, 2001b). (1) Enhancement of permeate flux by coagulation was found in all the works. (2) The optimal coagulation condition in which fouling is minimized

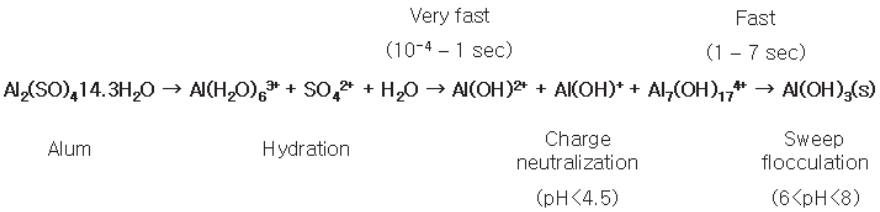


Figure 3 Charge neutralization and Sweep flocculation

is the same as the optimal condition determined by jar test, or the condition in which the zeta potential of particles reaches zero, or the condition in which the average size of aggregated particles is largest. (3) At the charge neutralization condition, fouling is less severe than at the sweep flocculation condition.

However, in all these studies, it is overlooked that the aggregated particles by coagulation can be disaggregated when they pass through the pump, as van der Graaf *et al.* (2001) discussed that the feed pump broke larger flocs into smaller ones. But, all the previous works had observed flux enhancement by coagulation. We think that there are two different hypotheses to explain this flux enhancement in CCFMF under the "floc breaking phenomenon". One is that the degree of disaggregation is not that high. That means that flocs break partially and thus "unbroken or partially broken flocs" flow into the membrane. The other is that the degree of disaggregation is high and "completely broken flocs" re-aggregate in the membrane. The purpose of this study is to verify which hypothesis describes cake reduction in CCFMF (i.e., flux enhancement) better and to discuss a more comprehensible mechanism of cake reduction in CCFMF in relation to increase of particle size.

Methods

Materials

MF membrane used in this study is a hollow fiber of polysulfone membrane (SKM-103 model, SK Chemical Co., Korea) whose pore size is 0.01–0.1 μm and effective surface area is 0.06 m^2. Kaolin (Junsei Chemical Co., Japan) is used for making suspensions and all particles in kaolin are over 1um in diameter and they just deposit to membrane surface without internal clogging. Alum[$Al_2(SO_4)_3 \cdot 14\text{–}18H_2O$, Junsei Chemical Co., Japan] is used as a coagulant.

Experiments

A schematic diagram of the experimental setup for crossflow microfiltration is shown in Figure 4. A centrifugal pump feeds flow into a membrane from a 70 litre feed tank. The membrane is 36 cm in length, and 0.8 mm in diameter. Transmembrane pressure (TMP) and crossflow velocity are controlled by a pump and valves. To maintain the characteristics of feed, both the retentate and permeate are discarded as shown in Figure 4.

TMP is fixed at 1.15 kgf/cm^2 to maintain the same initial flux condition (about 300 L/m^2h), crossflow velocity and feed concentration are fixed at 0.66 m/s and 0.1 g/L respectively. The permeate flux is measured by gauging volumetric permeate flow after

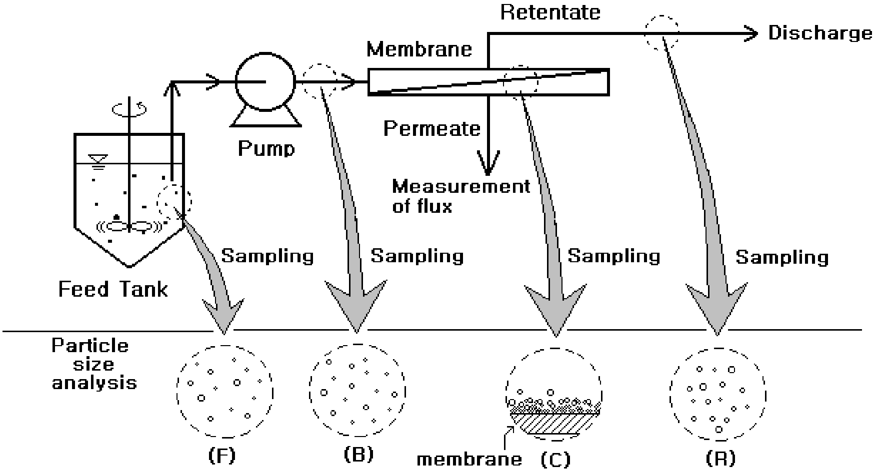


Figure 4 Schematic of experimental setup

30 to 100 min since the start of the operation. After that time, the flux decline is hardly observed. This proves that the time period used in the experiment is a required time to reach a steady state. Also, the cake resistance is calculated by Eq. (2).

$$J = \Delta P/\mu(R_m + R_c) \tag{2}$$

where, J is the permeate flux(m/s), ΔP TMP(N/m^2), μ viscosity of feed(0.009N·s/m^2 in 20°C), R_m membrane resistance(1.53×10^{11}/m), which is calculated by measuring pure water flux, and R_c cake resistance(/m). Kaolin particles used in this study is much larger than the pore size of membrane. So, inner fouling resistance term is neglected in Eq. (2).

The samples for particle size distribution are taken from four different points, as shown in Figure 4. They are at the feed tank (F) for observation of particle aggregation, a point before the membrane inlet (B) for observation of floc breaking, membrane surface (C) (in fact, the samples are taken from the backwashed water) for observation of cake constitution, and retentate line (R) for observation of re-aggregation. For particle size analysis, PAMAS-2120 (PAMAS, Germany) has been used, which uses laser scattering method. It analyses correctly the size distribution of rigid particle, but it cannot measure the exact size of the aggregated floc because of floc breaking during the measuring process. So the floc size measured with PAMAS-2120 can be said to be smaller than "real" floc size. Most particle size analysers have this kind of drawback in measuring the floc size. Nevertheless, we think the degree of aggregation can be relatively compared in this way. As a token of that, we found that the optimal condition of jar test is identical with the condition of the largest particle size detected by PAMAS-2120 (Cho *et al.*, 2001).

For coagulation, alum is dosed at concentrations of 10, 20, 30, 50, 80, 100, 150 mg/L at pH 4 and 8, respectively. The aluminium solubility diagram shown in Figure 5 indicates that coagulation would be mainly accomplished by positive aluminium ions at pH 4 and by $Al(OH)_3$ precipitate at pH 8 in these range of alum dosage. The rotation rate of the stirrer is fixed at 120 rpm.

Results and discussions

The degree of aggregation in feed

The mean diameter of aggregated particles can describe the degree of aggregation of particles. The degree of aggregation is high when the mean diameter of aggregated particles

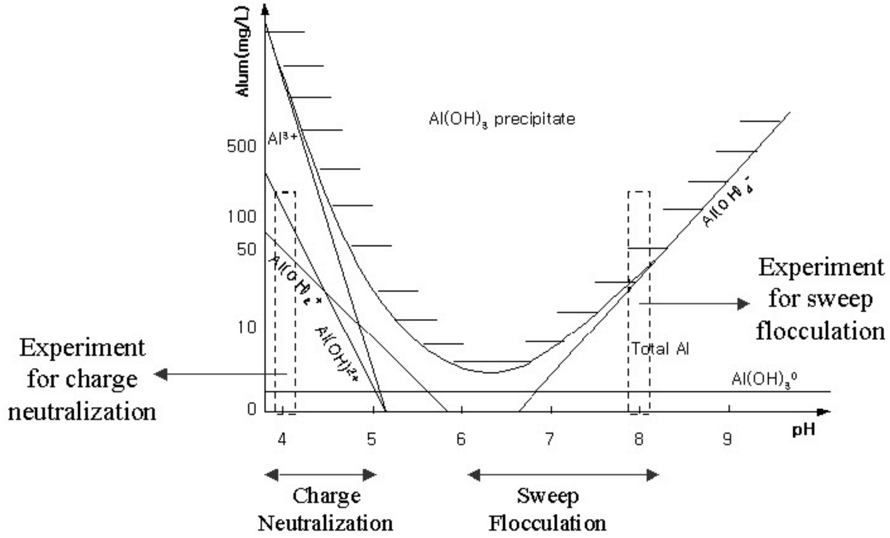


Figure 5 Aluminium solubility diagram (Dentel and Gosset, 1988)

is large. The optimum dosages of alum at which the degree of aggregation is highest, are 30 mg/L at pH 4 and 80 mg/L at pH 8 (refer to Figure 6). When alum is used more than the optimum dosage, the degree of aggregation decreases sharply at pH 4 and slowly at pH 8, as shown in Figure 6. Positive aluminium ions stick on the surface of particle which has negative charge, and make the surface charge of particles increase to zero. The closer to zero the surface charge gets, the degree of aggregation gets higher, too. But, the overdosing of alum makes the surface charge positive, which induces the degree of aggregation to decrease. This confirms that aggregation of particles largely depends on the amount of aluminium ion at pH 4 while it largely depends on the amount of $Al(OH)_3$ precipitate at pH 8. Furthermore, this leads to a conclusion that coagulation at pH 4 is accomplished by charge neutralization and coagulation at pH 8 by sweep flocculation.

Cake resistance at the steady state

Figure 7 shows that the reduction of cake resistance by coagulation is 17% to 53% at the various coagulation conditions and that the lowest cake resistances occur at 30 mg/L and 80 mg/L when pH is 4 and 8, respectively. Comparing with the results discussed just above, this further tells that the condition in which the cake resistance is lowest (i.e., fouling is minimized) is the same as the condition in which the degree of aggregation in feed is highest. It confirms that the cake reduction mechanism in CCFMF is closely related with the degree of aggregation in feed. As shown in Figure 7, the slopes near the optimal point are steeper at the charge neutralization condition than at the sweep flocculation condition. This rather tells that the degree of aggregation in feed is a more important factor affecting cake

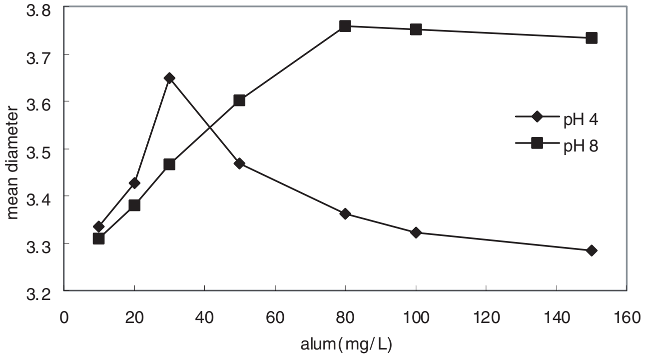


Figure 6 Mean diameters of aggregated particles in various coagulation conditions

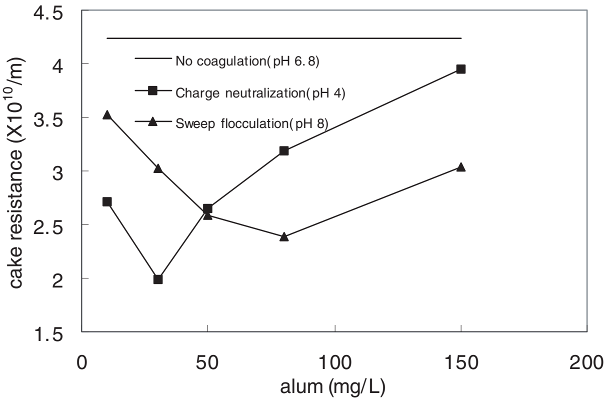


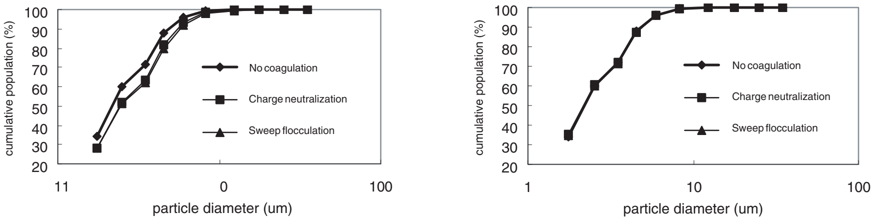
Figure 7 Cake resistances at steady state in various coagulation conditions

reduction in CCFMF at the charge neutralization condition than at the sweep flocculation condition. Also, the cake resistance at the optimal charge neutralization condition is smaller than at the optimal sweep flocculation condition and thus the degree of flux enhancement is higher at the former.

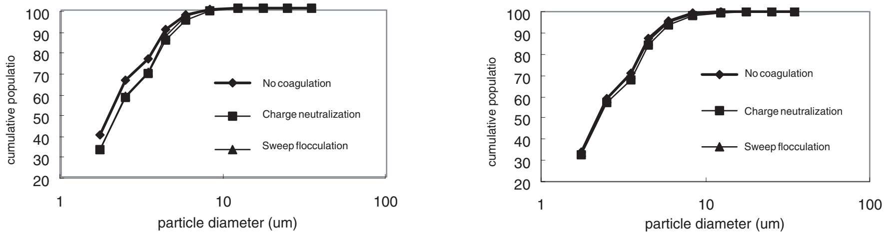
Re-aggregation in the membrane

As clearly shown in Figure 8(e), in the case of no coagulation, the retentate contains larger particles than the raw water and the cake contains smaller particles than the raw water. This is because smaller particles are more subjected to deposition than larger particles because of shear-induced diffusion. In the two coagulation conditions, aggregated particles in feed are wholly disaggregated before flowing into the membrane inlet and the particle size distribution is almost identical with that of no coagulation (refer to Figures 8(b) and 8(e)). This indicates that the size distribution of particles which flow into membrane inlet is almost same whether coagulation is accomplished or not. In our case, the hypothesis of "completely broken flocs" is right, not "unbroken or partially broken flocs". But, we also think that the degree of disaggregation may be different according to the kind of pump and the constitution of aggregate.

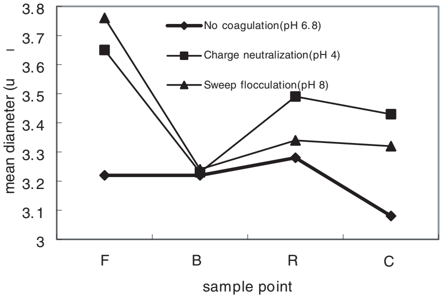
Nevertheless, the cake reduction is clearly observed with the cases of coagulation, as shown in Figure 7, which is only possible with the increased sizes of particle. Figures 8(c) and 8(d) indicate that the portion of smaller particles is less in the coagulation conditions



(a) F samples (b) B samples



(c) C samples (d) R samples



(e) Mean diameter of each samples

Figure 8 Results of the particle size analysis (charge neutralization: alum 30 mg/L and pH 4 sweep flocculation: alum 80 mg/L and pH 8 F: sample from feed, B: before the membrane inlet, C: cake, R: retentate) than the no-coagulation condition. That explains why their mean diameters in the retentate and the cake are larger than those in the latter condition. This result gives an important clue to re-aggregation of particles in the membrane module and also to flux enhancement in CCFMF. Considering the complete disaggregation by pump, this increase of particle size is only possible by re-aggregation in the membrane module and also enhance shear-induced diffusivity. In turn, the porosity of the cake layer increases and the cake resistance decreases and eventually the flux increases. According to Figures 6 and 7, optimal aggregation condition results in the lowest degree of fouling, which is from highest degree of aggregation. This means that the optimal re-aggregation condition occurs at the optimal coagulation condition. Therefore, the mechanisms for re-aggregation in membrane are said to be the same with those for coagulation in feed tank.

All these results explain that aggregated particles by coagulation are disaggregated due to the shear force of the pump. Then, the disaggregated ones are somehow re-aggregated while passing across the membrane surface. This re-aggregation increases particle size, reduces cake resistance and enhances the flux. As a result, we think the hypothesis of particle re-aggregation is highly plausible.

Charge neutralization and sweep flocculation

As shown in Figure 8(e), the mean diameters of the retentate and the cake are larger at the charge neutralization condition than at the sweep flocculation. This indicates that the degree of re-aggregation and the porosity of cake are higher in the former. This again explains why the cake resistance at the optimal charge neutralization condition is smaller than at the optimal sweep flocculation condition in Figure 7. It is also thought that the deposition of the residual $Al(OH)_3$ in cake layer at the sweep flocculation condition, resulting in the increase of cake resistance, may contribute to the difference. Also, we can confirm that re-aggregation by sweeping by $Al(OH)_3$ precipitate is lower than the degree of re-aggregation by charge-neutralized particles from the results of this study. This is because the degree of re-aggregation at pH 8 is lower than the degree of re-aggregation at pH 4 (refer to Figure 8(e)).

Despite the advantage in re-aggregation, there are two shortfalls in the charge-neutralization condition. One is low pH in charge neutralization condition. As shown in Figure 5, the solubility of aluminium is rapidly changed with the change of pH in the low pH condition. So, it is difficult to maintain the optimal charge neutralization condition. The other is the sensitivity of aggregation and re-aggregation near the optimal charge neutralization condition. As shown in Figure 6, a sharp peak exists near the optimal point of 30 mg/L as alum dosage and a slight change in alum dosage near the point can sharply change the degree of aggregation. The same thing is applied to the degree of re-aggregation. The sharp valley with charge neutralization condition in Figure 7 also indicates the same sensitivity near the optimal point because the cake resistance mainly depends on the degree of re-aggregation. These two shortages can degrade the performance of the CCFMF process operated with the charge neutralization condition.

Conclusions

In summary, this study concludes as follows.

1. In our experiment, the pump breaks down all the flocs to their original sizes before coagulation. But, the degree of disaggregation may be different according to the kind of pump and the constitution of aggregate.
2. Disaggregated particles (broken flocs) re-aggregate in the membrane. And, the re-aggregation of particles is a main cause for reducing fouling in coagulation-crossflow microfiltration (CCFMF).

3. Mechanisms for re-aggregation are the same as those for coagulation. This suggests that the current methods for determining optimum coagulation condition in CCFMF, such as those with jar-test and zeta-potential measurement, are good for determining optimal condition for re-aggregation.
4. Charge neutralization is better for CCFMF than sweep flocculation, since the former creates larger flocs with no $Al(OH)_3$ precipitate. But, it is difficult to maintain the optimal charge neutralization condition and the degree of aggregation and re-aggregation near the optimal charge neutralization condition vary sensitively.

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