

Membrane fouling control through aggregate design and trans-membrane pressure selection

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Abstract Treatment of waters and wastewaters by microfiltration (MF) requires the addition of chemical coagulants to enhance the removal of dissolved substances. Under these conditions the feed to the MF contains flocculated particulates which must be retained by the membrane. While an extensive knowledge base on the effect of dispersed particles on membrane cake formation and fouling exists, much less information is available on the impact of aggregates on cake characteristics. Results of impact of the size and structure (as characterized by the fractal dimension) of particulate aggregates on microfiltration membrane fouling are in qualitative agreement with a simple model based on the Carman–Kozeny equation. Larger flocs form a cake with large inter-floc porosity which results in a significantly higher permeate flux than achieved for smaller flocs. Concomitantly, looser flocs (of low fractal dimension) are likely to form a cake that has higher intra-floc voidage thus flux is higher than a cake made of compact flocs of similar size. Analysis of cake compression indicates that compressibility is strongly influenced by trans-membrane pressure (TMP). The placement of highly porous aggregates onto the membrane results in formation of a highly porous cake layer provided a low TMP is maintained. Rapid compression of the cake occurs at higher TMPs as shown by the significantly lower porosity of the cake. Under high TMP conditions, the cake porosity exhibits a strong size dependence with larger floc sizes yielding higher porosities. This result possibly indicates formation of relatively impermeable assemblages (as a result of significant compaction) with flux controlled by inter-aggregate flow, i.e. flow around compressed flocs. In comparison, the marked lack of size dependence of porosity at low TMP suggests that permeate flux is dominated by flow through (rather than around) the highly permeable flocs. These results suggest that it should be possible to control both operating conditions (such as TMP) and floc characteristics such that high permeate flux at a given TMP or low cake resistance at a fixed flux is achievable.

Keywords Compression; flocculation; floc structure; fouling; membrane technology

Introduction

Treatment of waters and wastewaters by microfiltration (MF) requires the addition of chemical coagulants to enhance the removal of dissolved substances (Crespo and Bøddeker, 1994; Wiesner and Laine, 1996). Under these conditions, the feed to the MF contains flocculated particulates which must be retained by the membrane. While an extensive knowledge base on the effect of dispersed particles on cake formation exists (Brinkman, 1948), much less information is available on the impact of aggregates on cake characteristics. We are now able to control the size and structure (as characterized by the fractal dimension) of particulate aggregates and here report on the impact of well characterized hematite aggregates of defined size and structure on microfiltration cake formation over a range of trans-membrane pressures (Zhou and Chu, 1991; Waite *et al.*, 1999). Preliminary results of studies are presented in this paper with more detailed consideration of the results given elsewhere (Lee *et al.*, 2002).

Experimental

Sample preparation

Hematite ($\alpha\text{-Fe}_2\text{O}_3$) particles were prepared by hydrolysis of FeCl_3 at 100°C (Matijevic and Scheiner, 1978, Amal *et al.*, 1991). The particles obtained were thoroughly washed then redispersed in MilliQ water and the concentration measured using atomic absorption spectrometry. The suspension was stored at pH 4 in a refrigerator. Analytical reagent grade potassium chloride was used for particle destabilization and 0.1 N HCl and NaOH solutions were used to control solution pH. Aqueous salt solutions were made using MilliQ water ($>18\text{ M}\Omega/\text{cm}$) and filtered using GVWP membrane before use.

Flocculation

Aggregation of hematite particles (particle size $d_p \sim 70\text{ nm}$) was performed in KCl solution under the presence of shear forces provided by an overhead stirrer. The KCl concentration used ranged from 50 mM to 150 mM which covered both reaction-limited cluster–cluster aggregation (RLCA) and diffusion-limited cluster–cluster aggregation (DLCA) mechanisms (Waite *et al.*, 1999). To prepare a 200 mL hematite floc suspension, 100 mL of KCl solution with double the desired concentration of KCl was prepared first and pH adjusted to 4. 100 mL of hematite suspension of known hematite concentration (20 ppm Fe) and of pH 4 was prepared and sonified for at least 10 minutes to disaggregate any spontaneously flocculated particles. This suspension was then slowly added to the KCl solution in a 500 mL glass beaker. Hematite particle size was measured and then mixing applied at a controlled rate using an overhead stirrer with blade size of 1 cm in height and 5 cm in width. Flocculation was performed under the same pH and ionic strength but at different mixing speeds and for different flocculation times.

Small-angle laser light scattering (SALLS)

A Malvern Mastersizer/E (Malvern Instruments, UK) was used to measure the floc size and structure. The Mastersizer is a static small-angle laser light scattering (SALLS) instrument designed to characterize particles of sizes ranging from submicron to $600\ \mu\text{m}$ (using three different lens). The 100 mm lens that covers $0.5\text{--}180\ \mu\text{m}$ was used in this study. By measuring the scattered intensity (I) at a series of scattering angles (θ), particle size distribution could be estimated. The light scattering data obtained in this manner were also used to obtain a qualitative measure of floc compactness by measuring the slope of $\log I$ versus $\log q$ plots (where $q = (4\pi n/\lambda)\sin \theta/2$) in the fractal scattering regime (Bushell and Amal, 2000).

Dead-end microfiltration (DEMF)

Dead-end microfiltration was used to determine the specific cake resistance and the compressibility of the filter cake. Hydrophilic Millipore GVWP membranes (PVDF, pore size $0.22\ \mu\text{m}$) of filterable area either $15.2\ \text{cm}^2$ or $0.8\ \text{cm}^2$ were used for all the filtration experiments. Membranes were washed thoroughly after placing in the membrane housing. Nitrogen gas was used to apply pressure and feed suspension was not stirred in the membrane filtration housing.

The specific resistance of cakes formed from hematite flocs was obtained by measuring the permeate volume as a function of filtration time for various suspension and operating conditions (particularly TMP). The specific cake resistance (α) was obtained from Eq. (1) by measuring the slope of t/V versus V plots.

$$\frac{t}{V} = \frac{\mu\alpha C}{2A^2\Delta P}V + \frac{R_m\mu}{A\Delta P} \quad (1)$$

where μ is viscosity of the medium, C is the particle concentration, A is the filter area, ΔP corresponds to the trans-membrane pressure (TMP) and R_m is the membrane resistance.

In order to measure cake compressibility, dead-end MF was performed in two steps. A reservoir that contained flocculated hematite suspension was connected to the membrane cell and hematite suspension was filtered through the GVWP membrane under low TMP. Driving force of the hematite suspension filtration was either gravity (for the 15.2 cm² membrane) or pumping (for the 0.8 cm² membrane). The flux was nearly constant and similar to that of the virgin membrane at the low TMPs used (gravity: 7 kPa; pumping: 20 kPa). When the reservoir became empty and the membrane cell was still full of solution, the reservoir was removed and a new reservoir, which contained a large amount of KCl solution of the same concentration and pH as that of the hematite suspension was connected to the filtration cell. Filtration of the salt solution followed with nitrogen gas pressure increased step by step. The flux increased and then declined at each step increase of TMP enabling determination of the compressibility of the hematite cake using Eq. (2)

$$\alpha = \alpha_0 \Delta P^n \quad (2)$$

where ΔP is the TMP, n is a cake compressibility factor and α_0 is an empirical constant that represents specific cake resistance in the absence of TMP (Tiller and Kwon, 1998).

Results and discussion

Flocculation and floc structure

Floc size distribution and floc structure were measured using SALLS before the particles were filtered. While primary particles could not be detected using SALLS, flocs became evident, depending on salt concentration and mixing speed, after 5 to 20 minutes. When the floc size reached a steady state or approached the desired size, cessation of flocculation was achieved by stopping mixing. Both salt concentration and mixing speed were used to influence the nature of flocs produced. Typical results obtained for various process conditions are shown in Table 1.

Effect of floc size on cake resistance

According to the Carman–Kozeny equation (Eq. (3)), specific cake resistance of filtration can be described as follows (Carman, 1938):

$$\alpha = \frac{36K''(1 - \varepsilon)}{d_p^2 \rho_p \varepsilon^3} \quad (3)$$

where d_p is the mean diameter of particles, ρ_p is the density of particles, K'' is the Kozeny constant and ε is the porosity of the cake deposited on the membrane surface. While this expression has been found to describe specific cake resistance as a function of particle and

Table 1 Example of flocs of specified median size (D_{50}) and compactness obtained for particular conditions of mixing speed and salt concentration

Sample no.	Mixing speed (rpm)	KCl (mM)	D_{50} (μm)	Compactness
30a	30	100	10.27	Low
30b	30	100	13.89	Low
30c	30	100	46.85	Low
90a	90	100	8.28	Medium
180a	180	100	9.93	High
180b	180	100	8.05	High
180c	180	100	48.54	High
180d	180	50	40.60	Very high

cake properties for hard spheres (where cake permeability will be determined principally by inter-particle porosity), it may also be of use for aggregates if account is taken of any additional (intra-particle) porosity.

The results shown in Figure 1a, which were obtained at a low TMP of 6–7 kPa, illustrates that larger flocs have small α values in accordance with expectation from the Carman–Kozeny equation. It should be noted, however, that intra-particle porosity of flocs exhibiting fractal character will also increase with floc size (Veerapaneni and Wiesner, 1996). If this porosity is maintained to greater or lesser extent on incorporation into the filter cake, the behavior shown in Figure 1a may be attributable to both inter- and intra-floc porosity effects. For example, α values at floc sizes of 10 and 50 μm differ by a factor of about five, whereas Eq. (3) predicts a factor of 25. The effect may also be apparent when comparing the results shown in Figure 1b (50 kPa), where higher values of α are observed than in Figure 1a (< 10 kPa). Some restructuring of flocs would also be expected at this higher pressure with a likely reduction in intra-floc porosity, as discussed below.

Effect of floc structure on cake resistance

Figures 2a and 2b show influences of floc structure upon specific cake resistance. The diameter of each circle is indicative of the measured diameter of each floc (from SALLS). The results in Figure 2a were obtained for TMPs of 50 kPa in all cases while for Figure 2b resistances were obtained over a range of TMPs and the α at 50 kPa obtained by interpolation.

The effect of floc structure appears to be significant for cakes made of small flocs (8.0–10.3 μm) (with α increasing as floc compactness increases), but it is negligible for cakes made of large flocs (40.6–48.5 μm). This phenomenon can be rationalized by recognizing that floc size has a strong influence on floc porosity when flocs are small, but a much

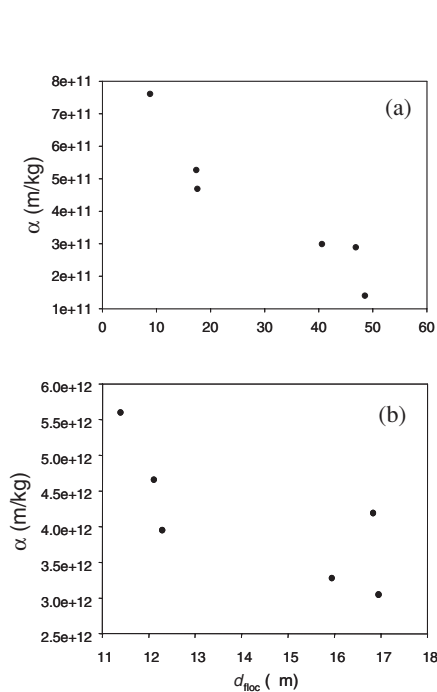


Figure 1 Variation in α as a function of mean floc size for studies with: (a) TMP of 6–7 kPa, and (b) TMP of 50 kPa (from Lee *et al.*, 2002)

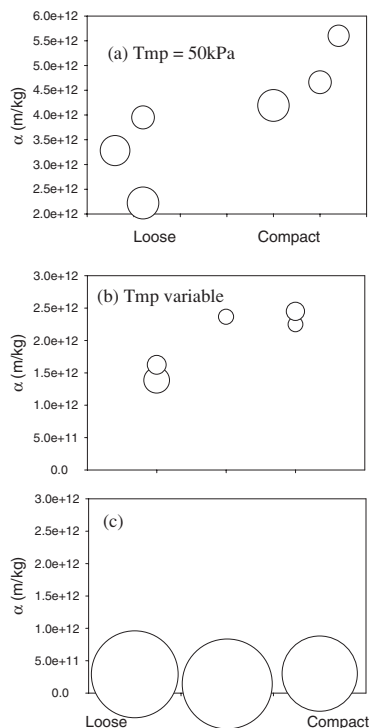


Figure 2 Variation in α as a function of structure of hematite flocs of various sizes (from Lee *et al.*, 2002)

less dramatic effect for large flocs where porosity is relatively high whether the flocs are compact or loose (Veerapaneni and Wiesner, 1996; Waite *et al.*, 1999). Note that no consideration to compaction effects has been given in this discussion.

Effect of floc size on cake compressibility

It is to be expected that as TMP is increased, the filter cake will compress and porosity will decrease. This is confirmed in Figure 3 where “cake-average” porosity (calculated using the Carman–Kozeny equation with the size of the primary particles (d_p) used in the calculation) is seen to decrease markedly on increase in TMP, presumably as a result of compaction effects. This “cake-average” porosity can be considered to be a composite of both inter- and intra-floc porosity and would appear to be maintained at a high level provided a low TMP is used.

The effect of floc size on cake compressibility is shown in Figure 4. Under high TMP conditions, the cake porosity exhibits a strong size dependence with higher floc sizes yielding higher porosities. This result possibly indicates formation of relatively impermeable assemblages (as a result of significant compaction) with flux controlled by inter-aggregate flow, i.e. flow around compressed flocs. In comparison, the marked lack of size dependence of porosity at low TMP suggests that permeate flux is dominated by flow through (rather than around) the highly permeable flocs.

Effect of floc structure on cake compressibility

The results presented above suggest that filter cakes developed from fractal aggregates can be compressed with their compressibility dependent on both floc structure and size. It might be expected that looser flocs will result in less compact filter cakes with higher flux and/or lower resistance than filter cakes formed from compact flocs. It should be borne in mind, however, that cakes generated from very loose aggregates may be more susceptible to compression effects as at higher TMPs. This issue is explored in Figure 5 where the effect of TMP on filtration flux of cakes formed from flocs of various size and structure is reported.

In general, cakes made of small, loose flocs (Figure 5a) exhibit high compressibility, whereas cakes made of small, compact flocs (Figure 5b) are less compressible. Interestingly, it would appear from Figure 5a that a certain TMP must be reached before the cake formed from the small, loose flocs actually undergoes significant compression. Once the TMP is sufficiently high, it would appear that the cakes formed from the small, loose flocs are almost twice as compressible as those formed from small, compact flocs ($n = 1.0$ for runs 30a and b, compared to $n = 0.5$ for runs 180a and b).

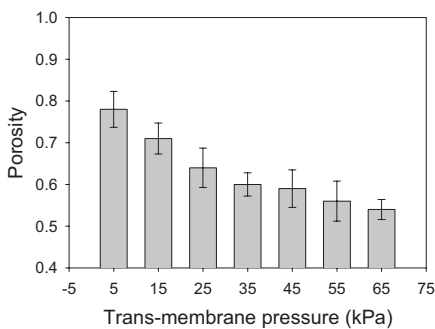


Figure 3 Effect of trans-membrane pressure on cake porosity calculated using the Carman–Kozeny equation (adapted from Lee *et al.*, 2002)

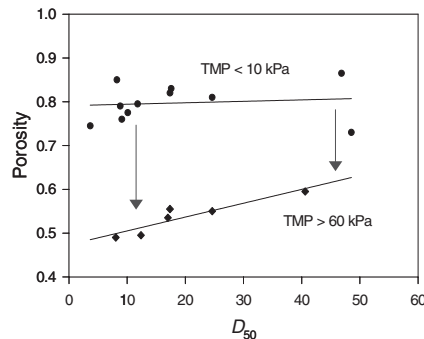


Figure 4 Calculated cake porosity as a function of median floc size (adapted from Lee *et al.*, 2002)

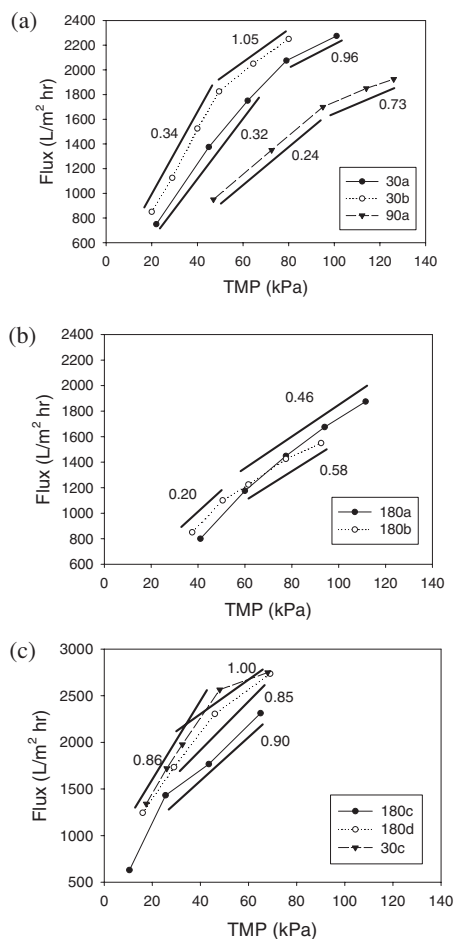


Figure 5 Filtration flux as a function of trans-membrane pressure (TMP). Also shown are the compressibility values (n) for each set of data points (obtained using Eq. (2)). Cakes in (a) were formed from small, loose flocs, while those in (b) were formed from small, compact flocs. Large flocs of varying structure (see Table 1) were used in (c) (adapted from Lee *et al.*, 2002)

The results in Figure 5c show high flux for cakes made of large flocs. As discussed earlier, this high flux might be expected as a result of both high inter-floc and intra-floc porosity for large flocs. Compressibility of these “large floc” cakes is high for both loose (30c) and more compact (180c and d) flocs but a high flux is maintained. These results confirm that cakes made from large flocs are porous irrespective of whether the flocs are loose or compact. That is, large floc size ensures the formation of a high porosity cake.

Conclusions

Results of impact of the size and structure (as characterized by the fractal dimension) of particulate aggregates on microfiltration cake formation are in qualitative agreement with a simple model based on the Carman–Kozeny equation. Larger flocs form a cake with large inter-floc porosity which results in a significantly higher permeate flux than achieved for smaller flocs. Concomitantly, looser flocs (of low fractal dimension) are likely to form a cake that has higher intra-floc voidage, thus the flux is higher than a cake made of compact flocs of similar size.

Analysis of cake compression indicates that compressibility is strongly influenced by trans-membrane pressure (TMP). The placement of highly porous aggregates onto the

membrane results in the formation of a highly porous cake layer provided a low TMP is maintained. Rapid compression of the cake occurs at higher TMPs as shown by the significantly lower porosity of the cake. Under high TMP conditions, the cake porosity exhibits a strong size dependence with higher floc sizes yielding higher porosities. This result possibly indicates formation of relatively impermeable assemblages (as a result of significant compaction) with flux controlled by inter-aggregate flow, i.e. flow around compressed flocs. In comparison, the marked lack of size dependence of porosity at low TMP suggests that permeate flux is dominated by flow through (rather than around) the highly permeable flocs.

These results suggest that it should be possible to control operating conditions (such as TMP) and floc characteristics such that high flux and/or low cake resistance is maintained.

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