Effect of the surface charge of monodisperse particulate foulants on cake formation

Han, Qi; Li, Weiyi; Trinh, Thien An; Fane, Anthony G.; Chew, Jia Wei

2018

Han, Q., Li, W., Trinh, T. A., Fane, A. G., & Chew, J. W. (2018). Effect of the surface charge of monodisperse particulate foulants on cake formation. *Journal of Membrane Science*, 548, 108-116. doi:10.1016/j.memsci.2017.11.017

<https://hdl.handle.net/10356/106855>

<https://doi.org/10.1016/j.memsci.2017.11.017>

© 2018 Elsevier. All rights reserved. This paper was published in *Journal of Membrane Science* and is made available with permission of Elsevier.

Downloaded on 26 Apr 2023 20:13:47 SGT

Effect of the Surface Charge of Monodispersed Particulate Foulants on Cake Formation

Qi Han^{a, b, c}, Weiyi Li^{a, b}, Thien An Trinh^{a, b}, Anthony G. Fane^b,

Jia Wei Chew^{a, b, *}

^a School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore

^b Singapore Membrane Technology Centre, Nanyang Environment and Water Research Institute, Nanyang Technological University, Singapore

^c Interdisciplinary Graduate School, Nanyang Technological University, Singapore

* Corresponding author: JChew@ntu.edu.sg; +65 6316 8916

Highlights

- Studied fouling mechanisms by latex particles of three different surface charges
- Positively charged particles surprisingly gave less fouling than negative ones
- Network model revealed different initial and specific cake resistances
- Monitoring of fouling in real time via OCT revealed different fouling patterns
- Different pore-blocking tendencies and cake morphologies hypothesized

Abstract

In microfiltration and ultrafiltration, particulate foulants are inevitably deposited on the membrane surface, forming a cake whose structure and behavior play crucial roles in the subsequent filterability of the suspensions. This study investigated the impact of fouling by three types of latex particulate foulants, which were of the same size (3 μm) but with different surface charges. Surprisingly, although the positively charged aminated latex was expected to perform the worst in the flux-decline experiments due to attractive electrostatic interaction with the negatively charged membrane, this latex displayed the best performance relative to the two negatively charged latex. To understand these counter-intuitive results, a novel network model

[1] and three-dimensional (3D) optical coherence tomography (OCT) image analysis [2] were employed to reveal the underlying reasons for the different fouling behaviors. Two mechanisms were found to contribute to the worse performance of the negatively charged latex. Firstly, these particles tended to deposit on the pore rather than non-pore region of the membrane due to the repulsive particle-membrane electrostatic interactions, which led to a more complete pore blockage and thereby greater initial cake resistance. Secondly, these particles had a greater tendency to cluster and deposit on other deposited latex due to similarly repulsive particle-membrane and particle-particle interactions, which led to a more inhomogeneous cake and thereby greater specific cake resistance.

Keywords: Membrane fouling, surface charge, network model, optical coherence tomography, microfiltration

1. Introduction

Membrane fouling is almost inevitable for all membrane filtration processes, but such filtration applications continue to grow because they offer key advantages like operation without a phase change, without the need for high temperatures or additives, and their potential for low energy consumption. In particular microfiltration is an attractive membrane filtration process due to its relatively lower operating pressures and higher permeation fluxes, which has motivated many studies dedicated to understanding and mitigating the fouling issue [3].

Experimentally, a variety of techniques have been used to study the onset and evolution of fouling [4-6] in order to shed light on the fouling mechanisms by different foulants. Examples of such techniques that allow for the monitoring of membrane fouling non-intrusively and in real time include electrical impedance spectroscopy (EIS) [7], direct observation through the membrane (DOTM) [8], confocal laser scanning microscopy (CLSM) [9] and optical coherence tomography (OCT) [2]. Many interesting observations and understandings have been obtained with the aid of these techniques. The evolution of fouling by colloidal particles and organic macromolecules has been characterized by the EIS [7], the effect of particle size and crossflow on critical flux has been revealed by DOTM [10], biofilm formation on a membrane in a membrane bioreactor has been studied by CLSM [11], and the velocity profile and changes in cake thickness have been observed using OCT [12]. In parallel with the experimental efforts, various models have been proposed to enhance the understanding of the fouling mechanisms during the filtration of colloids, as reviewed in Belfort et al. [3]. In addition to the hydrodynamic factors that account for particle size, particle concentration and shear rate, Bacchin et al. [13] factored into their model the contribution of the interfacial foulant-membrane interactions due to its non-negligible influence. Furthermore, based on the various pore-blocking phenomena proposed by Hermia [14], Ho and Zydney [15] extended such models by accounting for the various phenomena concurrently rather than each individually, which allowed for understanding the effect of foulant-membrane interactions through pore blockage parameters and initial cake resistances. Charfi et al. [16] proposed a mathematical model considering three fouling mechanisms to successfully assess the scouring effect of GAC particles on membrane fouling control. This continuum model subsequently led to discretized models with better spatial resolution to further improve the understanding of fouling particularly with respect to the topological aspects, such as the connectivity of the porous structure and the distribution of the deposits on the membrane [1, 17-19]. Such models,

coupled with the experimental results, are very useful for obtaining a more mechanistic understanding of the fouling mechanisms.

Although many studies have been carried out to investigate a variety of foulants during the membrane filtration process, a question that remains not fully answered is the effect of colloidal surface charge on membrane fouling. Colloidal particles are ubiquitous in natural waters which cover a wide size range from a few nanometers to a few micrometers. In the pH range of natural waters, most colloids carry a negative surface charge [20, 21]. Previous studies found that the negatively charged natural organic matter (NOM) would become positively charged when overdose a coagulant [22, 23]. Some of the industrial textile wastewater were found carrying positively charged in acid aquatic condition [24]. Since membrane filtration process is widely used to treat these kinds of wastewater, deep understanding of particle surface charge on membrane fouling formation is of great importance.

Some inroads have been made with regards to revealing the impact of the surface charges of particulate foulants. McDonogh et al. [25, 26] found that, regardless of dead-end or cross-flow filtration, as the zeta potential of monodisperse silica colloids increased beyond about 10 mV, the specific resistance of the cakes decreased monotonically; for potentials < 10 mV the trend was opposite due to colloid aggregation. The decreasing specific cake resistance trend was explained by a model of charged colloid interaction based on the classical DLVO theory. Similar trends, with more highly charged colloidal particles tending to give more porous cakes, were reported by other groups [27-29]. However, on the contrary, Huisman et al. [30] found that neither the zeta potential of the membrane nor the zeta potential of the particles influenced the observed critical flux. Since the zeta potential was changed by adjusting the pH, this may be explained by the results presented by Faibish et al. [29] in which solution pH had a negligible effect on flux decline. Recently [31], we have investigated two types of negatively charged particulate foulants and found significantly different fouling behaviors, which was attributed to the attractive and repulsive particle-membrane and particle-particle interactions quantified by Gibbs free energy [32]. However in this work the electrostatic component (which factors in zeta potential) of the Gibbs free energy was reported to be minor, relative to the other two components of Lewis acid-base and Lifshitz-van der Waals in the XDLVO theory, which agrees with previous reports [33, 34]. In summary, prior work have revealed both qualitative and quantitative differences in the observed effects of particle surface charge on membrane fouling, but the understanding remains incomplete because the zeta potential values have been limited to the negative range. As a result this study builds on the knowledge base to date and

applies deadend flow (to minimise tangential shear effects) to the filtration of particles that are identical except for their surface charges which span positive and negative zeta potentials. The evaluation is made using a novel non-continuum model and noninvasive observation using OCT.

Thus, the objective of this work is twofold: (i) investigate the effect of surface charges of particulate foulants on flux-decline trends; and (ii) understand the differences in the fouling mechanisms via a network model [1] and OCT image analysis [2]. Latex particles of the same size but of different surface charge (namely, one positively charged and two with different negative charges) were investigated. The flux decline data were obtained under deadend filtration, and fitted to the network model to obtain the fouling parameters (namely, probability to deposit on non-pore regions of the membrane, initial cake resistance and specific cake resistance). The OCT technique allowed for 3D imaging of the fouling process non-intrusively and in real-time, which provided an understanding not only of the progress of fouling on the membrane surface but also the cake growth.

2. Experimental Procedure

2.1 Membrane fouling experiments

In the current study, dead-end filtration was employed to investigate the effect of three different surface charges of particulate foulants on membrane fouling. The membrane used was a polycarbonate track-etched (PCTE) membrane (catalog number WH-111111, Whatman, USA), with relatively uniform cylindrical pores each with a diameter (d_{mp}) of 2 μm and relatively low porosity (ε_m) of 0.05. The zeta potential (Malvern Zetasizer nano-zs, UK) of the PCTE membrane was measured in the presence of 1mM KCl at pH 6.2 using 300 nm latex particles as the tracer particles, indicating that the membrane had a negative surface charge of -35.3 mV. A new membrane was used in each experiment. The three particle types were all latex particles with uniform particle diameters (d_p) of 3 μm : one was non-modified (catalog number 79166, Sigma, Aldrich, USA), and two had surfaces modified with functional groups, namely, aminated (catalog number AM003UM, Magsphere, USA) and carboxylated (CA003UM, Magsphere, USA). The zeta potentials (Malvern Zetasizer nano-zs, UK) of the three particle types, as listed in Table 1, indicated that the surface charges span -31.0 to 10.5 mV, and two were negatively charged while one was positively charged. The concentration of the latex particles was constant for every experiment at 0.005 g/L.

Table 1. Zeta potential values of the PCTE membrane ($d_{mp} = 2 \mu\text{m}$ and $\varepsilon_m \approx 0.05$) and the three particulate latex foulants with uniform particle diameters of $3 \mu\text{m}$.

	Zeta potential (mV)	Standard deviation (mV)	Feed medium
PCTE Membrane	-35.3	0.75	1 mM KCl
Aminated Latex	10.5	2.38	DI water
Non-modified Latex	-20.8	0.88	DI water
Carboxylated Latex	-31.0	0.53	DI water

The dead-end filtration cell was made of acrylic, and consisted of a top feed chamber ($70 \text{ mm} \times 70 \text{ mm} \times 24 \text{ mm}$) and a bottom permeate chamber ($70 \text{ mm} \times 70 \text{ mm} \times 24 \text{ mm}$) separated by the membrane, which has an effective filtration area of 9.62 cm^2 . Gravity was used as the driving force across the membrane, which provided a constant trans-membrane pressure (TMP) to result in the permeate flux. The TMP was fixed at different values around 6 kPa in order to maintain the permeation flow rate of DI water at a value of 80 ml/min. Similar to our previous study [1], in order to minimize the entrance effects, the feed stream entered the upper chamber via four sub-streams through the four holes (each with a diameter of 6 mm) uniformly distributed on the lateral walls. A porous stainless steel plate was also positioned under the membrane to provide mechanical support. The permeation flow rate (Q_m) was measured by the change in the permeation volume over 30 s. For each experiment, 0.005 g/L (5 ppm) of latex particles of a particular charge was used and each test for each condition was repeated at least three times.

2.2 Network model

In order to obtain a mechanistic understanding of the complex interactions involved during fouling, a novel network model [1] was employed to extract the fouling parameters (namely, probabilistic factor accounting for dead zone deposition β , initial cake resistance R_{c0} and specific cake resistance R'_c) by best-fitting the experimental flux-decline data via regression analysis. Specifically, the network model was constructed by generating a two-dimensional (2D) network of pores to represent the membrane in terms of the key characteristic

of membrane porosity and mean pore diameter. Then, a series of probabilistic criteria was employed to describe the fate of each individual particle, namely, deposit in the dead zone, deposit on the cake, deposit on the pore, or passes through the pore. Lastly, a protocol for evaluating the fouling was established during constant-TMP filtrations to obtain the three fouling parameters. More details about the development of network modeling could be found in previous study [1]. In the current study, the network model comprised 631×631 unit cells corresponding to a membrane area of 25 mm^2 . The application of the network model allowed for the accounting of the topological and stochastic aspects of the fouling process, and provided a more in-depth understanding of the effect of particle surface charge on the complex interactions between the fluid flow, membrane, and foulant particles.

2.3 Optical coherence tomography (OCT)

The optical coherence tomography (OCT; GANYMEDE-SP5, Thorlabs, USA) technique was used to carry out three-dimensional (3D) scans of the membrane filtration cell during fouling. The light beam had a central wavelength of 905 nm and a bandwidth of 200 nm, giving a depth resolution of $2 \text{ }\mu\text{m}$ in water. An overview of the OCT technique is illustrated in Fig. 1(a). Part of the light beam emitted from a broadband light source reached the membrane filtration cell, and the light backscattered was combined with the light reflected from a reference mirror and collected by a spectrometer, which generated the intensity versus depth profiles that were transformed into three-dimensional (3D) images of the sample. More details of the principles of OCT can be found in previous reports [1, 2]. For each experiment, the 3D OCT scan was initially performed for 5 minutes with DI water, after which 0.005 g/L of latex particles of a particular charge was added and the scans continued for another 35 minutes. In this study, the OCT scans were continuously performed via an A-scan, which provides a depth profile [35], at the rate of 30 kHz and the time interval between two consecutive scans was 1.5 s.

Figure 1. (a) Schematic depicting the principle of the 3D scan of dead-end membrane cell using the low-coherence Fourier-domain OCT; (b) side view of the virgin membrane via 3D OCT scanning, with the red line denoting the membrane-fluid interface obtained via resolving the OCT data; and (c) side view of the used membrane showing the deposition of the non-modified latex particles ($t = 35$ min, TMP ≈ 6 kPa, foulant concentration = 0.005 g/L) via 3D OCT scanning.

The analysis of the OCT signals relied on the method first proposed by Li et al. [2], whereby the coordinate surface of the feed-membrane interface was determined by comparing the intensity gradients with a pre-determined threshold gradient value, and the positions at which the OCT intensity gradients were greater than the threshold value were designated as the surface of the feed-membrane interface. As representative examples, Figs. 1b and c display the side views of the virgin and used membranes (after filtering the non-modified latex particles), respectively, with the red lines denoting the feed-membrane interfaces determined. The Li et al. [2] method then was further developed to analyze the topological aspects of particle deposition on the membrane. Specifically, a new coordinate system (namely, x_m - y_m - z_m) was established based on the determined feed-membrane interface, after which a series of coordinate surfaces parallel to the feed-membrane interface was defined in order to monitor the progressive growth of the cake layer. The coordinate surfaces were uniformly spaced apart by

2 μm in vacuum, which was approximately the depth resolution of the OCT system. Because the distances in the OCT images are the optical path lengths measured using the refractive index of vacuum, the real physical distance in pure water is approximately equal to 1.5 μm , as indicated in Fig 2a. Fig. 2a shows that the layer corresponding to the feed-membrane interface was indexed as layer 0, and each layer above was progressively numbered.

Figure 2. (a) Schematic indicating the layers identified from the analysis method for interpreting the OCT data; and (b) snapshots showing the evolution of fouled voxels during membrane filtration.

After the layers were identified, the evolution of the cake layer could be monitored by distinguishing the voxels that reflect that particles have deposited (i.e., fouled), as reported in an earlier study [2]. Specifically, the means and standard deviations of the OCT intensities were first calculated for each layer at $t = 0$, then a voxel in that layer was determined as a fouled voxel if its intensity was greater than the mean plus twice the standard deviation (i.e., 95% confidence interval [36, 37]). The fouled voxels determined at the 95% confidence level were determined for each layer at each time point, and marked in red in the projected area of 0.9 mm by 0.15 mm, which was chosen to be large enough to be representative (about 2200 pores in the area captured) and yet small enough to allow for reasonable scan rates (1.5 s per image; a larger image requires more time per scan), as depicted in Fig.2b. To quantify the extent of fouling, the number fraction of fouled voxels with respect to the total number of voxels were

quantified for each layer at each time step. Furthermore, to have a qualitative understanding of the topology of the deposits, the deposit patterns at each layer were also analyzed.

3. Results and discussion

3.1 Evolution of permeate flux for latex particles of three different surface charges

Because the membrane was negatively charged (Table 1), it was expected that the positively charged aminated latex would lead to the worst fouling due to attractive foulant-membrane interactions. Surprisingly, Fig. 3, which displays the evolution of the permeate flow rate normalized with respect to the initial permeate flow rate (Q_m/Q_{m0}) for feeds containing the latex particle with three different surface charges, indicates instead that the more negatively charged carboxylated latex gave the worst performance, whereas the positively charged aminated latex gave the best performance. The same trends were observed for repeated tests. This counter-intuitive behaviour was further probed by the network model and OCT.

Figure 3. Evolution of the permeate flow rate normalized with respect to the initial permeate flow rate (Q_m/Q_{m0}) for feeds containing the latex particle with three different surface charges investigated, with the discrete points denoting the experimental data and the solid lines being the results of the regression analysis for obtaining the fouling parameters defined in the network model. R_a^2 , R_n^2 and R_c^2 represents the coefficient of determination for experiment-model fitting of aminated latex, non-modified latex and carboxylated latex, respectively.

3.2 Interpreting the fouling process based on the best-fit parameters via network modeling

The non-linear curve-fitting associated with the network model [1] was implemented on all three experimental permeate flux trends, as denoted by the solid lines in Fig. 3. Satisfactory coefficient of determination for aminated latex (0.9935), non-modified latex (0.9879) and carboxylated latex (0.9902) implies good agreement was obtained between all three regression trendlines (solid lines) and the corresponding experimental data (discrete points). The fitting results indicates that the network model was able to account for the variation in the surface charges of particulate foulants, and thereby that the best-fit fouling parameters obtained from the network model could be harnessed to understand the fouling mechanisms reliably.

The variations of the best-fit fouling parameters, β , R_{c0} and R'_c , are presented in Figs. 4a, b and c, respectively, for the three particle types. The error bars represent 95% confidence intervals from the t-test [38]. Fig. 4a clearly shows that the aminated latex particle exhibited the greatest β value, which indicates the highest probability of depositing on the dead zone (i.e., area of the membrane not occupied by pores). The probably reason is the attractive electrostatic interactions between the negatively charged membrane and the positively charged aminated latex. Analogously, the least value of β for negatively charged carboxylated latex may possibly be due to the repulsive electrostatic interactions between the particle with the membrane. In terms of probability of blocking the open pores ($P_b = 1 - \beta(1 - \varepsilon_m)$), the carboxylated particles exhibited a significantly higher P_b value ($P_b = 0.94$) compared to that of the non-modified latex ($P_b \approx 0.52$) and aminated latex ($P_b \approx 0.43$). Since the membrane used in the current study had symmetric straight-thorough pore structures and low porosity ($\varepsilon_m \approx 0.05$), the highest P_b value of the carboxylated latex led to the severe flux decline seen in Fig. 3.

Figure 4. Comparison of the fouling parameters obtained by best-fitting of the experimental flux data via regression analysis to obtain the fouling parameters in the network model: (a) the probabilistic factor for deposition in the non-pore regions of the membrane (β), (b) the initial cake resistance R_{c0} , and (c) the specific cake resistance R'_c .

Regarding cake resistance, Figs. 4b and c indicate respectively that R_{c0} and R'_c values increased as the zeta potential values decreased, which agrees with a previous crossflow study [39]. Since hydrodynamics effects were similar in view of all three particulate foulants being of the same sizes ($d_p = 3 \mu\text{m}$), the variations were presumably related to the foulant-membrane

and/or foulant-foulant interfacial interactions. With respect to R_{c0} (Fig. 4b), the different foulant-membrane interactions among the three particulate foulants would have played a key role. Figure 5 depicts hypothesized pore interactions and cake morphologies for a range of scenarios. For the positively charged aminated latex, because of the attractive interactions with the negatively charged membrane, the preferential deposition on the dead zone (i.e., membrane surface without pores; Fig. 4a) may lead to lesser alignment of the particle to the pore, as depicted in Fig. 5a. For the more negatively charged carboxylated latex, due to the lesser affinity to the membrane, the alignment of the particle to the pore could be more complete, as illustrated in Fig. 5b. Correspondingly, the incomplete pore blockage by the aminated latex would give a lower R_{c0} value than the more complete pore blockage by the carboxylated latex. Regarding R'_c (Fig. 4c), the aminated and carboxylated latex gave respectively the least and greatest cake resistance as the cake developed because of the nature of the cake layer. Figs. 5c and d illustrate the hypothesized cake morphologies for the different cakes. Because the positively charged aminated latex had greater affinity to the negatively charged membrane, they preferentially deposited on the membrane rather than other deposited aminated latex, thereby forming a more uniform cake layer (Fig. 5c) with relatively less resistance (R'_c). On the other hand, because the negatively charged carboxylated latex particles were approximately equally deposited either on the negatively charged membrane or other negatively charged carboxylated particles deposited, an inhomogeneous cake (Fig. 5d) was likely formed, which conferred greater cake resistance (R'_c) partly due to the thicker cake. Such differences in the distribution of the particulate foulants constituting the cake layers and the corresponding differences in the resistances have been proposed by Ethier et al. [40].

Figure 5. Schematic of the hypothesized cake morphology based on the fouling parameters (namely, R_{c0} and R'_c) of the network model: (a) the ‘incomplete pore blockage’ refers to initial particle deposition when particle-membrane electrostatic interactions are attractive, resulting in a low R_{c0} ; (b) the ‘complete pore blockage’ refers to initial particle deposition when particle-membrane electrostatic interactions are repulsive, resulting in a high R_{c0} ; (c) the ‘uniform cake’ refers to a uniform deposition of foulants due to attractive particle-membrane electrostatic interactions, resulting in a smooth cake layer on the membrane surface and a low R'_c ; and (d) the ‘inhomogeneous cake’ refers to clusters of foulants due to repulsive particle-membrane electrostatic interactions, resulting in localized uneven cake layers on the membrane surface and a high R'_c .

3.3 Analyzing the fouling phenomenon using OCT

Armed with the understanding from the network model, the OCT was used to provide further evidence of the mechanistic picture given by the network model of the different fouling phenomena by the latex particles of different surface charges. Fig. 6 illustrate the evolution

with respect to filtration volume of the fraction of fouled voxels of four different layers (namely, 1, 3, 5 and 7) above the feed-membrane interface, which reflect the extents of fouling at different distances from the membrane. Regardless of surface charge, Fig. 6 indicates that the fraction of fouled voxels increased as filtration progressed, which reflect the extent of fouling increasing with the filtration volume, with the layers closer to the membrane generally increasing more. Three observations are worth highlighting. Firstly, the fractions of fouled voxels were the greatest for the carboxylated latex, which corresponds to the most severe flux decline (Fig. 3), followed by the non-modified latex and lastly the aminated latex. The evolution of the fraction of fouled voxels with respect to time is displayed in Fig. A1 in the appendix; these plots have more data points because the OCT data were taken every 1.5 s while the filtration volume was taken every 30 s. Secondly, among the three surface charges, the trends of the four layers were most distinctive from one another for the positively charged aminated latex (Fig. 6a), whereas the trends for Layers 1 and 3 were closer to each other for the non-modified latex (Fig. 6b) and carboxylated latex (Fig. 6c). This agrees with the mechanistic picture of the different cake layers in Figs. 5c and d, and thereby the R'_c trends in Fig. 4c. The distinctive trends of the four layers for the aminated latex (Fig. 6a) suggests the sequential build-up of the cake layers, which suggests uniform cake layers (Fig. 5c). On the other hand, the less distinctive trends between Layers 1 and 3 for the other latex imply the deposition of the particulate foulants at the same rates in both layers, which indicates inhomogeneous cakes (Fig. 5d). Thirdly, the significantly greater fraction of fouled voxels in Layers 5 and 7 for the carboxylated latex particles relative to that of the aminated was likely due the growth of the clusters (Fig. 5d), which became rapidly taller than the uniform cake (Fig. 5c). In particular for Layer 7 (which was 10.5 μm above the feed-membrane interface), the final fractional blockage for the carboxylated latex was more than 10%, whereas that for the non-modified latex and aminated latex were approximately 5% and 0%, respectively. This provides affirmation of the hypothesis proposed in Fig. 5.

Figure 6. Comparison of the evolution of the cake layer with filtration volume when the feed contained 0.005 g/L of (a) aminated latex particles, (b) non-modified latex particles, and (c) carboxylated latex particles. Each error bar represents the 95% confidence interval based on a t-test; note that error bars are included in Fig. 6(c), but too small to be clearly visible.

3.4 Topology of the deposits

The OCT data also provided more information on the topology of the deposits. The patterns of the fouled voxels in each layer (Fig. 2b) were further analyzed based on the techniques described by Dixmier [41]. Specifically, the fouled voxels appeared either as individual voxels (i.e., no adjacent fouled voxel) or as groups (i.e., a few adjacent fouled

voxels). To study the topology, these patterns were classified into four categories using Matlab: Category A represents individual fouled voxels; Category B represents groups of 2 to 5 adjoining fouled voxels; Category C represents groups of 6 to 10 adjoining fouled voxels; and Category D represents groups of more than 10 adjoining fouled voxels. For each layer, the fractions of fouled voxels in each category with respect to the total number of fouled voxels were analyzed. Figs. 7 and Fig. 8 illustrate this fraction at various filtration volumes for respectively Layer 1 (i.e., $\sim 1.5 \mu\text{m}$ above the feed-membrane interface) and Layer 3 (i.e., $\sim 3 \mu\text{m}$ above the feed-membrane interface).

Regarding Layer 1 (Fig. 7), the change in the deposit patterns as the filtration volume increased is clear. At the filtration volume (V_f) of 200 mL (Fig. 7a), the deposits were more dispersed and thereby largely classified as Categories A and B. The difference among the three particle types was negligible, which indicates that the effect of surface charge was insignificant in dictating the fouling patterns at this initial phase of fouling. As the filtration volume (V_f) increased to 500 mL (Fig. 7b), larger clusters of deposits corresponding to Categories C and D appeared as fouling became more extensive and the effect of the different surface charges became significant. The positively charged aminated latex had the greatest fractions in Categories A and B, whereas the more negatively charged carboxylated latex had the greatest fraction in Category D. This indicates that the positively charged aminated latex preferentially deposited individually or in smaller clusters compared to the negatively charged latex. The tendency of the non-modified latex to cluster rather than form a more dispersed layer of deposits agrees with our previous study, and was attributed to the attractive Gibbs free energy of interaction [31]. As the filtration volume (V_f) further increased to 800 mL (Fig. 7c), the fractions in Category D increased while those in Categories A and B decreased, signaling the worsening of the fouling. The effect of the different surface charges was consistent in that the positively charged aminated latex displayed the most dispersed deposits, as evident in the highest fractions in Categories A – C and lowest fraction in Category D. Conversely, the more negatively charged carboxylated latex had the lowest fractions in Categories A – C and highest in Category D, which indicates the most clustered deposits. Therefore, Fig. 7 shows that, for the first layer of deposition on the membrane, the positively charged aminated latex tended to deposit as individual particles or as small clusters of particles due to foulant-membrane attraction but foulant-foulant repulsion, whereas the negatively charged carboxylated latex exhibited greater tendency to form larger deposited clusters due to more similar foulant-membrane and foulant-foulant affinities and the drag force by permeate flow. With respect to

Layer 3 (Fig. 8), similar trends as Layer 1 (Fig. 7) were observed. Collectively, the results in Figs. 7 and 8 are consistent with the hypothesized cake morphology resulting from the network model results, in that the aminated latex tended to form a more uniform cake (Fig. 5c) while the carboxylated latex a more inhomogeneous cake (Fig. 5d).

The results obtained show clear effects of particle charge on fouling evolution. However it is recognized that the membranes used are idealized and further work is planned to assess the effect of membrane type on fouling by charged foulants using the Network Model and OCT analysis.

Figure 7. Comparison of the contribution of each category of deposition on Layer 1 for the three particle types with different surface charges at filtration volumes of (a) 200 mL, (b) 500 mL, and (c) 800 mL. Category A represents individual fouled voxels, while Categories B, C

and D represent groups of fouled voxels consisting of 2 – 5 adjoining fouled voxels, 6 – 10 adjoining fouled voxels and greater than 10 adjoining fouled voxels, respectively. Each error bar represents the 95% confidence interval based on a t-test.

Figure 8. Comparison of the contribution of each category of deposition on Layer 3 for the three particle types with different surface charges at filtration volumes of (a) 200 mL, (b) 500 mL, and (c) 800 mL. Category A represents individual fouled voxels, while Categories B, C and D represent groups of fouled voxels consisting of 2 – 5 adjoining fouled voxels, 6 – 10 adjoining fouled voxels and greater than 10 adjoining fouled voxels, respectively. Each error bar represents the 95% confidence interval based on a t-test.

4. Conclusions

The current study employed a network model [1] and 3D OCT image analysis [2] to understand the impact of the surface charge of particulate foulants on cake formation. Low-porosity PCTE membranes were used, and the model particulate foulants used were latex, which were of the same sizes (3 μm) but had different surface charges (namely, positively charged aminated, and negatively charged non-modified and carboxylated).

Surprisingly, although the positively charged aminated latex was expected to perform the worst in the flux-decline experiments due to attractive electrostatic interactions with the negatively charged membrane, this latex displayed the best performance relative to the two negatively charged latex. This counter-intuitive behaviour was examined by the network model and OCT image analysis to understand the underlying reasons for the different fouling behaviors.

The network model indicated that the positively charged aminated latex exhibited the greatest probability for deposition in the dead zones (i.e., non-pore membrane region; β), and the lowest initial cake resistance (R_{c0}) and specific cake resistance (R'_c). The initial pore-blocking phenomenon and subsequent cake morphologies were then hypothesized. Regarding pore-blocking, the ‘incomplete pore blockage’ results from attractive particle-membrane electrostatic interactions and leads to a lower R_{c0} value, while the ‘complete pore blockage’ results from repulsive particle-membrane electrostatic interactions and leads to a higher R_{c0} value. As for cake morphology, the ‘uniform cake’ results from attractive particle-membrane electrostatic interactions leading to a smooth cake layer on the membrane surface and a lower R'_c value, while the ‘inhomogeneous cake’ refers to clusters of foulants above pores due to repulsive particle-membrane electrostatic interactions, resulting in uneven cake layers on the membrane surface and a higher R'_c value.

3D OCT characterization further affirms the hypotheses on the different fouling behaviors by the particulate latex foulants of different surface charges. Specifically, the progressive cake buildup on the feed-membrane interface was analyzed in terms of the fraction of fouled voxels at each incremental layer. Three observations were obtained. Firstly, the fractions of fouled voxels were the greatest for the carboxylated latex, which corresponds to the most severe flux decline, followed by the non-modified latex and lastly the aminated latex. Secondly, the trends of the four layers were most distinctive from one another for the positively

charged aminated latex, which suggests the progressive growth of the uniform cake layer; on the other hand, the trends for Layers 1 (i.e., 1.5 μm above the feed-membrane interface) and 3 (i.e., 3 μm above the feed-membrane interface)) were closer to each other for the non-modified latex and carboxylated latex, which suggests the growth of an inhomogeneous cake. Thirdly, the significantly greater fraction of fouled voxels in Layers 5 and 7 for the carboxylated latex particles relative to that of the aminated was likely due the growth of an inhomogeneous cake, which became locally taller more rapidly than the uniform cake.

The coupling of the network model and OCT characterization affirmed the counter-intuitive filtration performance of the three particulate latex foulants (3 μm) of different surface charges. It should be noted that membrane porosity[40], different operating mode and different initial permeate flux [42] would also have significant effects on charged particle deposition which needs to further investigate.

5. Acknowledgements

We acknowledge funding from the Singapore Ministry of Education Academic Research Funds Tier 2 (MOE2014-T2-2-074; ARC16/15) and Tier 1 (2015-T1-001-023; RG7/15), and the GlaxoSmithKline (GSK) - Singapore Economic Development Board (EDB) Trust Fund.

The Singapore Membrane Technology Center (SMTC) acknowledges support from the Singapore Economic Development Board (EDB).

References

- [1] Q. Han, W. Li, T.A. Trinh, X. Liu, J.W. Chew, A network-based approach to interpreting pore blockage and cake filtration during membrane fouling, *Journal of Membrane Science*, 528 (2017) 112-125.
- [2] W. Li, X. Liu, Y.N. Wang, T.H. Chong, C.Y. Tang, A.G. Fane, Analyzing the Evolution of Membrane Fouling via a Novel Method Based on 3D Optical Coherence Tomography Imaging, *Environ Sci Technol*, 50 (2016) 6930-6939.
- [3] G. Belfort, R.H. Davis, A.L. Zydney, The behavior of suspensions and macromolecular solutions in crossflow microfiltration, *Journal of Membrane Science*, 96 (1994) 1-58.
- [4] S. Suwal, A. Doyen, L. Bazinet, Characterization of protein, peptide and amino acid fouling on ion-exchange and filtration membranes: Review of current and recently developed methods, *Journal of Membrane Science*, 496 (2015) 267-283.
- [5] X. Li, Y. Mo, J. Li, W. Guo, H.H. Ngo, In-situ monitoring techniques for membrane fouling and local filtration characteristics in hollow fiber membrane processes: A critical review, *Journal of Membrane Science*, 528 (2017) 187-200.

- [6] V. Chen, Non-invasive observation of synthetic membrane processes ? a review of methods, *Journal of Membrane Science*, 241 (2004) 23-44.
- [7] L. Sim, Z. Wang, J. Gu, H. Coster, A. Fane, Detection of reverse osmosis membrane fouling with silica, bovine serum albumin and their mixture using in-situ electrical impedance spectroscopy, *Journal of membrane science*, 443 (2013) 45-53.
- [8] H. Li, A.G. Fane, H.G.L. Coster, S. Vigneswaran, Direct observation of particle deposition on the membrane surface during crossflow microfiltration, *Journal of Membrane Science*, 149 (1998) 83-97.
- [9] B.-K. Hwang, C.-H. Lee, I.-S. Chang, A. Drews, R. Field, Membrane bioreactor: TMP rise and characterization of bio-cake structure using CLSM-image analysis, *Journal of membrane science*, 419 (2012) 33-41.
- [10] H. Li, A.G. Fane, H.G.L. Coster, S. Vigneswaran, An assessment of depolarisation models of crossflow microfiltration by direct observation through the membrane, *Journal of Membrane Science*, 172 (2000) 135-147.
- [11] Y. Yu, Z. Yang, Y. Duan, Structure and flow calculation of cake layer on microfiltration membranes, *Journal of Environmental Sciences*, 56 (2017) 95-101.
- [12] Y. Gao, S. Haavisto, W. Li, C.Y. Tang, J. Salmela, A.G. Fane, Novel approach to characterizing the growth of a fouling layer during membrane filtration via optical coherence tomography, *Environ Sci Technol*, 48 (2014) 14273-14281.
- [13] P. Bacchin, P. Aimar, V. Sanchez, Model for colloidal fouling of membranes, *AIChE Journal*, 41 (1995) 368-376.
- [14] J. Hermia, Constant Pressure Blocking Filtration Laws - Application to Power-Law Non-Newtonian Fluids, *T I Chem Eng-Lond*, 60 (1982) 183-187.
- [15] C.-C. Ho, A.L. Zydney, A combined pore blockage and cake filtration model for protein fouling during microfiltration, *Journal of Colloid and Interface Science*, 232 (2000) 389-399.
- [16] A. Charfi, M. Aslam, G. Lesage, M. Heran, J. Kim, Macroscopic approach to develop fouling model under GAC fluidization in anaerobic fluidized bed membrane bioreactor, *Journal of Industrial and Engineering Chemistry*, 49 (2017) 219-229.
- [17] W. Li, Fouling models for optimizing asymmetry of microfiltration membranes, Diss., University of Cincinnati (2009).
- [18] W. Li, Y. Gao, C.Y. Tang, Network modeling for studying the effect of support structure on internal concentration polarization during forward osmosis: model development and theoretical analysis with FEM, *Journal of membrane science*, 379 (2011) 307-321.
- [19] I.M. Griffiths, A. Kumar, P.S. Stewart, A combined network model for membrane fouling, *J Colloid Interface Sci*, 432 (2014) 10-18.
- [20] X. Zhu, M. Elimelech, Colloidal Fouling of Reverse Osmosis Membranes: Measurements and Fouling Mechanisms, *Environmental Science & Technology*, 31 (1997) 3654-3662.
- [21] M. Zhang, W. Peng, J. Chen, Y. He, L. Ding, A. Wang, H. Lin, H. Hong, Y. Zhang, H. Yu, A new insight into membrane fouling mechanism in submerged membrane bioreactor: osmotic pressure during cake layer filtration, *Water research*, 47 (2013) 2777-2786.
- [22] M. Yan, D. Wang, J. Yu, J. Ni, M. Edwards, J. Qu, Enhanced coagulation with polyaluminum chlorides: Role of pH/Alkalinity and speciation, *Chemosphere*, 71 (2008) 1665-1673.
- [23] A. Matilainen, M. Vepsäläinen, M. Sillanpää, Natural organic matter removal by coagulation during drinking water treatment: A review, *Advances in Colloid and Interface Science*, 159 (2010) 189-197.
- [24] M.A. Al-Ghouti, M.A.M. Khraisheh, S.J. Allen, M.N. Ahmad, The removal of dyes from textile wastewater: a study of the physical characteristics and adsorption mechanisms of diatomaceous earth, *Journal of Environmental Management*, 69 (2003) 229-238.
- [25] R.M. McDonogh, C.J.D. Fell, A.G. Fane, Surface charge and permeability in the ultrafiltration of non-flocculating colloids, *Journal of Membrane Science*, 21 (1984) 285-294.
- [26] R.M. McDonogh, A.G. Fane, C.J.D. Fell, Charge effects in the cross-flow filtration of colloids and particulates, *Journal of Membrane Science*, 43 (1989) 69-85.

- [27] M.S. Chun, G.Y. Chung, J.J. Kim, On the behavior of the electrostatic colloidal interaction in the membrane filtration of latex suspensions, *Journal of Membrane Science*, 193 (2001) 97-109.
- [28] D. Elzo, I. Huisman, E. Middelink, V. Gekas, Charge effects on inorganic membrane performance in a cross-flow microfiltration process, *Colloid Surface A*, 138 (1998) 145-159.
- [29] R.S. Faibish, M. Elimelech, Y. Cohen, Effect of interparticle electrostatic double layer interactions on permeate flux decline in crossflow membrane filtration of colloidal suspensions: An experimental investigation, *Journal of Colloid and Interface Science*, 204 (1998) 77-86.
- [30] I.H. Huisman, E. Vellenga, G. Trägårdh, C. Trägårdh, The influence of the membrane zeta potential on the critical flux for crossflow microfiltration of particle suspensions, *Journal of Membrane Science*, 156 (1999) 153-158.
- [31] F. Zamani, A. Ullah, E. Akhondi, H.J. Tanudjaja, E.R. Cornelissen, A. Honciuc, A.G. Fane, J.W. Chew, Impact of the surface energy of particulate foulants on membrane fouling, *Journal of Membrane Science*, 510 (2016) 101-111.
- [32] C.J. Van Oss, Chapters 2 - 5, in: *Interfacial forces in aqueous media* (2nd ed.), CRC Press, Boca Raton, FL, 2006.
- [33] J.A. Brant, A.E. Childress, Assessing short-range membrane-colloid interactions using surface energetics, *Journal of Membrane Science*, 203 (2002) 257-273.
- [34] J.A. Brant, A.E. Childress, Colloidal adhesion to hydrophilic membrane surfaces, *Journal of Membrane Science*, 241 (2004) 235-248.
- [35] R.A. Leitgeb, R.M. Werkmeister, C. Blatter, L. Schmetterer, Doppler optical coherence tomography, *Progress in retinal and eye research*, 41 (2014) 26-43.
- [36] D.G. Rees, Continuous probability distributions, in: D.G. Rees (Ed.) *Essential Statistics*, Springer US, Boston, MA, 1989, pp. 65-76.
- [37] D.G. Rees, Confidence interval estimation, in: D.G. Rees (Ed.) *Essential Statistics*, Springer US, Boston, MA, 1989, pp. 85-99.
- [38] H. Hotelling, *A GENERALIZED T TEST AND MEASURE OF MULTIVARIATE*, (1951).
- [39] S. Lorenzen, Y. Ye, V. Chen, M.L. Christensen, Direct observation of fouling phenomena during cross-flow filtration: Influence of particle surface charge, *Journal of Membrane Science*, 510 (2016) 546-558.
- [40] C.R. Ethier, R.D. Kamm, The hydrodynamic resistance of filter cakes, *Journal of membrane science*, 43 (1989) 19-30.
- [41] J. Dixmier, *General Topology* (Chapter VIII to Chapter X), in: *Undergraduate Texts in Mathematics*, New York, Springer 1984.
- [42] W. Xu, S. Chellam, Initial Stages of Bacterial Fouling during Dead-End Microfiltration†, *Environmental Science & Technology*, 39 (2005) 6470-6476.

Appendix

Figure A1. Comparison of the evolution of the cake layer with time when the feed contained 0.005 g/L of (a) aminated latex particles, (b) non-modified latex particles, and (c) carboxylated latex particles. The dead-end filtration was carried out at $TMP = 6$ kPa and membranes used were PCTE membranes ($d_{mp} = 2$ μm and $\varepsilon_m \approx 0.05$). Each error bar represents the 95% confidence interval based on a t-test.