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Response of zeta potential to cake formation and pore blocking during the microfiltration of latex particles

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ABSTRACT

The responses of zeta potential of membrane, ζ_{obs}, to the pore blocking and cake formation during microfiltration of latex particle suspension were studied by monitoring both the filtration resistance and streaming potential during the filtration. The pattern of the change in ζ_{obs} during the filtration was quite different between the cake filtration and the pore blocking filtration. In the cake filtration ζ_{obs} changed from the intrinsic zeta potential of membrane, ζ_m, to the zeta potential of cake layer, ζ_c, depending on the proportion of the hydraulic resistance of the cake layer to the total filtration resistance. In the pore blocking filtration followed by the cake filtration ζ_{obs} jumped from ζ_m to a certain value between ζ_m and ζ_c just after the start of the filtration and became almost stable. The zeta potential at the blocked pore, ζ_b, depended on the gap between surfaces of the blocked pore and the blocking particle and indicated the extent of pore blocking. It was confirmed that the change in ζ_{obs} during filtration will reflect both the location of pressure drop and the local zeta potential.

1. Introduction

The membrane fouling is one of the major problems in the application of microporous membranes and is caused by specific physical and/or chemical interactions between the membrane and various components in feed stream. The membrane fouling is observed as the flux decline and alteration in retention during the filtration.

The fouling phenomenon in microfiltration (MF) membrane can be qualitatively evaluated by analyzing the flux decline with filtration models [1]. The flux decline in dead-end filtration can be explained by the pore constriction, pore blocking, and cake formation models. Pore constriction model is used to explain for the fouling caused by smaller foulant compared to pore size for instance the protein adsorption onto MF membranes [2–4]. The pore blocking (pore plugging) filtration depends on mainly the pore morphology. The membranes with cylindrical pore structure such as track-etched polycarbonate (PC) MF membranes will be highly affected by the pore blocking caused by particles while the membranes with a highly inter connected pore structure will be weakly affected by the pore blocking [5]. In the cake filtration model the flux decline can be explained by the building-up of cake layer which provides hydraulic resistance. The combination of these filtration models have been applied to fouling mechanism in MF and ultrafiltration membranes by bovine serum albumin (BSA), humic acid, or national organic matter [2,6–9]. The analyzing of the flux decline with these classical filtration models are useful as a simple method for prediction of the fouling mechanism although the actual fouling mechanism will be more complex than the hypothesises of these models. In order to understand the detail of fouling status during filtration online monitoring methods for more qualitative information, such as optical image, cake layer thickness, hydrophilicity, charge, or pore size, are desired in addition to flux decline measurement [10].

The surface charge condition of membrane is a monitoring property of interest because the electrostatic interaction between membrane and foulant is considered as a major interaction causing fouling. Electrokinetic techniques such as streaming potential (SP) measurements have been applied to the characterization of the surface charge condition of membranes and the SP can be monitored during filtration. The zeta potential estimated using Helmholtz–Smoluchowski (H–S) equation from SP has been used as an index of the surface charge and applied for the characterization of membrane material [11], surface modification of membrane[12–14], effect of cleaning [15–18].

The relationship between fouling status and the zeta potential is not fully understood. In the standard blocking filtration such as the MF of proteins the zeta potential will reflect the surface charge condition of pore. In the fouling of MF membranes caused by BSA

Abbreviations: MF, microfiltration; PC, polycarbonate; BSA, bovine serum albumin; SP, streaming potential; H-S, Helmholtz–Smoluchowski; MCE, mixed cellulose ester; NY, nylon; PMMA, polymethyl methacrylate.

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adsorption the surface charge properties such as isoelectric point of the fouled membranes showed almost same properties as that of BSA [19,20,21,22]. The extent of the change in zeta potential in the BSA adsorption depended on the surface coverage of the pore surface adsorbed by BSA [3]. These observations show that the change in zeta potential in the standard blocking filtration will reflect the adsorption status of pore surface during the filtration. In the cake filtration the zeta potential will reflect the charge condition of both membrane and cake layer [23–26]. In the pore blocking filtration the response of the zeta potential to the pore blocking status have not been clear.

In this study we focused on the response of zeta potential during the pore blocking filtration and the cake filtration in the dead-end filtration of latex particles with MF membranes. The purposes of this study was (1) to confirm the relationship among the zeta potential, the location of pressure drop, and local charge condition, (2) to study the response of zeta potential to the cake filtration, and (3) to study the response of zeta potential to the pore blocking filtration.

2. Theory

The hydraulic resistance is usually used as an index of hydraulic permeability of membrane and fouling layer.

$$J_v = \frac{1}{R_{\text{total}}}\frac{P}{\mu} \tag{1}$$

where J_v is permeate flux, R_{total} is filtration resistance, P is filtration pressure, μ is viscosity of filtrate. The filtration resistance can be divided into three local resistances in series, which are hydraulic resistance of clean membrane R_m, hydraulic resistance at the pore entrance blocked by particles R_b, and hydraulic resistance of cake layer R_c. R_{total} is the sum of these local filtration resistances.

$$R_{\text{total}} = R_{\text{m}} + R_{\text{b}} + R_{\text{c}} \tag{2}$$

Fig. 1 shows the location of these resistances. The local pressure drop can be written as following,

$$P_{\text{m}} = \frac{R_{\text{m}}}{R_{\text{total}}}P, \quad P_{\text{b}} = \frac{R_{\text{b}}}{R_{\text{total}}}P, \quad P_{\text{c}} = \frac{R_{\text{c}}}{R_{\text{total}}}P \tag{3}$$

$$P = P_{\text{m}} + P_{\text{b}} + P_{\text{c}} \tag{4}$$

where P_{m} is pressure drop in membrane, P_{b} is pressure drop at blocked pore, and P_{c} is pressure drop in cake layer.

The pore blocking filtration will only occur at the early stage of filtration and be followed by the cake filtration. The smooth transitions from the pore blockage to cake filtration were observed in protein fouling [27], humic acid fouling [7] and they were elucidated by a combined pore blockage and cake filtration model.

In order to elucidate the dependence of the filtration resistances on filtration volume a simple model was developed based on the combined pore blocking and cake filtration models. In the pore blocking filtration the pores on the filtration surface are directly blocked by particles. R_{b} depends on the surface coverage of particles and the hydraulic resistance at the gap between the blocked pore and the blocking particle. The filtration area A_0 can be expressed as the sum of A_{open}, which is area of unblocked membrane, and A_{blocked}, which is area of membrane blocked by particles.

$$A_0 = A_{\text{open}} + A_{\text{blocked}} \tag{5}$$

The decreasing rate of A_{open} to filtration volume is assumed to be directly proportional to A_{open},

$$\frac{dA_{\text{open}}}{dv} = -kA_{\text{open}} \tag{6}$$

where k is a constant and v is the filtration volume per unit filtration area, V/A_0. A_{open} can be evaluated by integrating Eq. (6).

$$A_{\text{open}} = A_0 e^{-kv} \tag{7}$$

The resistance provided by the pore blocking R_{b} is proportional to the ratio of A_{blocked} to A_0,

$$R_{\text{b}} = \frac{A_{\text{blocked}}}{A_0}R_{\text{b},\infty} = (1 - e^{-kv})R_{\text{b},\infty} \tag{8}$$

where $R_{\text{b},\infty}$ is the hydraulic resistance at the end of the pore blocking filtration, which means $A_{\text{blocked}} = A_0$, and it can be an index of the extent of the pore blocking.

In the cake filtration model, the filtration resistance provided by the cake layer is proportional to the cake mass per unit filtration area, $C_0 v$,

$$R_{\text{c}} = (1 - e^{-kv})\alpha C_0 v \tag{9}$$

where α is specific cake resistance.

The total filtration resistance R_{total} can be expressed as a function of v using Eqs. (2), (8) and (9).

$$R_{\text{total}} = R_{\text{m}} + R_{\text{b}} + R_{\text{c}} = R_{\text{m}} + (1 - e^{-kv})R_{\text{b},\infty} + (1 - e^{-kv})\alpha C_0 v \tag{10}$$

Fig. 2 shows a typical patterns of the $R_{\text{total}}/R_{\text{m}}$ versus v plot calculated using Eq. (10). When the pore blocking filtration and the cake filtration occur successively, the initial increase in the filtration resistance is due to the pore blocking and then the filtration resistance increases linearly due to the cake formation. When $R_{\text{b},\infty}$ is too small, the filtration resistance will increase linearly from the start of the filtration. In other words, when the filtration resistance increases linearly from the start of the filtration, the effect of the pore blocking on R_{total} can be negligible.

The zeta potential is usually used for the characterization of surface charge condition of porous membrane or particles. The zeta potential of membrane can be measured by the SP method. The SP

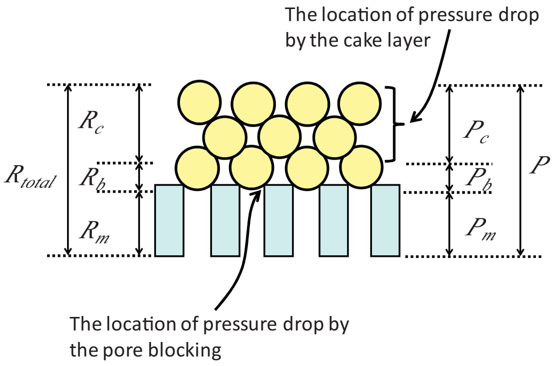

Fig. 1. The filtration resistance and the location of pressure drop in the pore blocking filtration and the cake filtration.

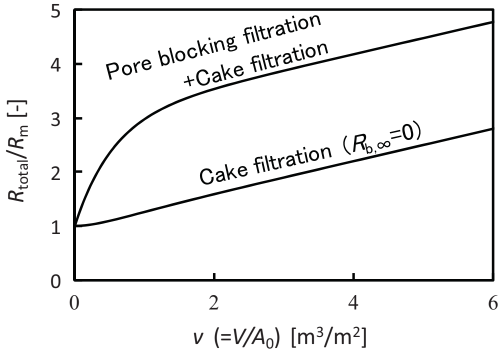

Fig. 2. Changes in the total filtration resistance during the pore blocking filtration and the cake filtration predicted by Eq. (10).