

Fouling Mechanism of Microfiltration/Ultrafiltration by Macromolecules and a Suppression Strategy from the Viewpoint of the Hydration Structure at the Membrane Surface

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Abstract: This short review focuses on fouling by proteins and macromolecules in microfiltration/ultrafiltration. First, an experimental system that enables investigation of how the extent of the adsorption of proteins and macromolecules on membrane surfaces contributes to a decrease in filtrate flux in microfiltration/ultrafiltration is described. Using this system, a causal relationship - not a correlation - indicating that adsorption results in a decrease in filtrate flux could be clearly demonstrated in some cases. Second, a hydration structure at the membrane surface that can suppress adsorption is discussed, inspired by biomaterial research. In their hydrated states, polymers with low-fouling properties have water molecules with a particular structure. Finally, some successful examples of the development of low-fouling membranes via surface modification using low-fouling polymers are discussed.

Keywords: *fouling, adsorption, filtrate flux, hydration structure, surface modification*

1. Introduction

Microfiltration/ultrafiltration is widely used in various industrial fields, including water purification and wastewater treatment. However, the problem of fouling remains a considerable issue, which can result in the reduction of the filtrate flux in constant pressure microfiltration/ultrafiltration and an increase in the transmembrane pressure in constant flux microfiltration/ultrafiltration. A number of factors, such as the membrane materials, pore structures, surface roughness, and hydrophilicity/hydrophobicity, can affect the fouling phenomena[1-3]. Additionally, it is almost impossible to quantitatively determine the fouling substances because the feed solution generally contains various kinds of solutes[4,5]. Furthermore, the chemical structures of almost all of these solutes cannot be identified exactly

[6,7]. Because of these complexities, a fundamental solution for fouling, based on an understanding of the fouling mechanisms, has not yet been achieved, despite a large number of publications on fouling.

Extensive research has been carried out into the development of low-fouling membranes. Most of the research has focused on the hydrophilicity/hydrophobicity of the membrane surfaces based on the assumption that membranes having a hydrophobic surface tend to suffer nonspecific adsorption of fouling substances because of the hydrophobic interaction. There are many reports indicating that surface modification methods using hydrophilic polymers are effective in achieving low-fouling properties[8,9]. However, to the best of our knowledge, there are no quantitative data showing systematically a relationship between hydrophilicity and low-fouling properties. The development of low-fouling membranes

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to date has just been based on empirical knowledge.

In this short review, evidence that the adsorption of proteins and polysaccharides, which has been assumed to be a dominant factor in fouling, is actually the dominant factor in constant pressure cross-flow microfiltration/ultrafiltration is discussed. This evidence indicates that there is a need to develop membranes having non-adsorptive surfaces. Research on surfaces having non-adsorptive properties toward proteins is then reviewed. These studies focused on the water structures in the vicinity of the membrane surfaces, inspired by the fact that one of the most important factors in biomaterial development is the acquisition of anti-thrombogenic properties. Finally, some surface modification methods for commercially available membranes to achieve such ideal surfaces and their filtration performances are summarized to demonstrate their low-fouling properties.

2. Fouling by Proteins and Macromolecules in Microfiltration/Ultrafiltration

2.1. A simple experimental system for quantitatively determining the effect of adsorption on the decline in filtrate flux in microfiltration/ultrafiltration

There have been many reports stating that adsorption is the dominant factor contributing to the decline in the filtrate flux in microfiltration/ultrafiltration. This assumption is based on conventional filtration tests demonstrating a relationship between the concentration of fouling substances in feed and the steady-state flux, together with conventional adsorption tests demonstrating a relationship between the concentration of fouling substances in feed and the adsorption on the membrane. However, other types of fouling, such as pore clogging and cake layer formation, may occur independently or simultaneously. To date, there have been no publications demonstrating conclusive evidence that the adsorption of fouling substances on a membrane surface actually results in flux decline. To address this issue, Akamatsu *et al.* have developed a novel and simple experimental system[10]. This system consists of (1)

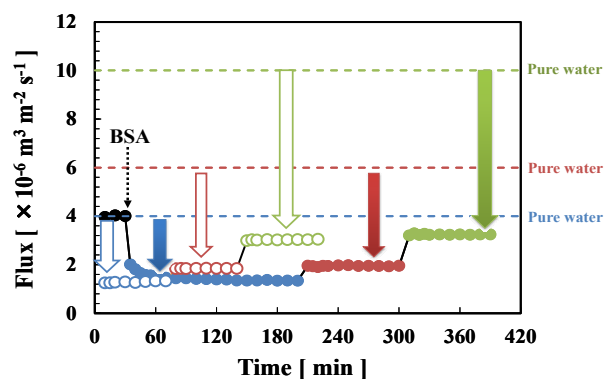


Fig. 1. Comparison of (1) filtrate flux in the closed-loop, cross-flow filtration test (closed circles) and (2) pure water flux with immersed membrane (open circles) (Reproduced with permission from Akamatsu *et al.*, [10], Elsevier).

closed-loop, cross-flow filtration tests to determine the effect of the concentration of fouling substances in the feed on the steady-state flux, and (2) pure water flux tests with membranes which are immersed in solutions of the same fouling substances before carrying out the tests to show the effect of the adsorption on the increase in the filtration resistance. When the filtrate flux obtained in experiment (1) and the pure water flux obtained in experiment (2) are equal under the conditions where the concentration of the fouling substances in the solution and the applied pressure are equal, we can conclude that the adsorption is the dominant factor in the flux decline.

Fig. 1 shows an example when 500 ppm bovine serum albumin (BSA) and polyethylene microfiltration membranes with 60 nm pores were used as the solution and the membrane, respectively. In experiment (1), for the first 30 min pure water was supplied and the applied pressure was controlled to achieve a flux of $4.0 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$. The feed was then changed to the BSA solution at the same pressure, and the filtrate flux decreased drastically. The filtrate flux became almost constant at a value of $1.3 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$. When this constant flux was observed, the applied pressure was then increased to 1.5 times the initial pressure to achieve a flux of $6.0 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ in case the membrane was not fouled at all. At this pressure, we also observed a constant flux ($2.0 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$). Again,

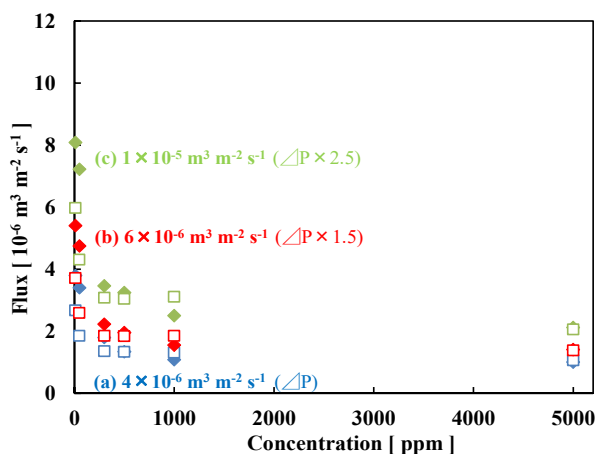


Fig. 2. Relationships between (1) the concentration of BSA and the filtrate flux in the closed-loop, cross-flow microfiltration test (closed symbols), and (2) the concentration of BSA in the immersed solution and pure water flux (open symbols) under flux conditions of (a) 4.0×10^{-6} , (b) 6.0×10^{-6} , and (c) $1.0 \times 10^{-5} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ if the membrane was not fouled (Reproduced with permission from Akamatsu *et al.*, [10], Elsevier).

the applied pressure was increased, to 2.5 times the initial pressure, to achieve a flux of $1.0 \times 10^{-5} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ in case the membrane was not fouled at all, and a constant flux was observed ($3.2 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$) at this pressure. In experiment (2), a virgin membrane was first immersed into 500 ppm BSA solution in a shaking bath for 5 h. The pure water flux was measured at the same applied-pressure profile. At the lowest pressure where the pure water flux should be $4.0 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ in the case of no adsorption of BSA, the pure water flux was $1.3 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$. Under the second and the third applied-pressure conditions, the pure water fluxes were 1.8×10^{-6} and $3.0 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$. The filtrate flux in experiment (1) and the pure water flux in experiment (2) were comparable with each other when the applied pressures were equal. These results indicated that the adsorption of BSA is the dominant factor causing the decrease in the filtrate flux in cross-flow microfiltration. The results for these experiments using different BSA concentrations are shown in Fig. 2. Both the fluxes were comparable, even when the BSA concentration ranged from 10 to 5000 ppm, meaning that the adsorption was the domi-

nant factor causing the decrease in the filtrate flux. Additionally, it should be noted that both the fluxes decreased drastically with increasing BSA concentrations and then became constant. This trend can be explained by considering the Langmuir-adsorption model. In this model, monolayer coverage of the membrane surface and pore walls by the foulant is assumed. The total amount of adsorption increases linearly over a low concentration range and then becomes independent of the concentration. If the increase in the permeation resistance is only because of the adsorption, the flux should decrease linearly over the lower concentration range and become independent of the concentration. This trend can be observed in Fig. 2 indicating that adsorption was the dominant factor for the decrease in the filtrate flux. A similar trend was also observed when sodium alginate was used in place of BSA, which indicated that the adsorption of sodium alginate was the dominant factor for the decrease in the filtrate flux[10].

This experimental system can be used to determine the extent that the adsorption contributes to the flux decline because the second pure water flux test with the immersed membrane focuses only on the effect of the adsorption. Clear evidence that adsorption was the dominant factor was provided in some cases, as discussed above. In such cases, the flux decline should be able to be alleviated by developing membranes that prevent the adsorption of foulants.

2.2. Characteristics of membrane surfaces having low-fouling properties from the viewpoint of the hydration structures

On the basis of the findings in the previous section, a strategy to construct membrane surfaces with less adsorptive properties can be a promising one. One such strategy is to render the membrane surface hydrophilic, which is based on the concept that hydrophobic membranes generally suffer nonspecific adsorption. In biomaterial research, there has been extensive investigation of the mechanism of anti-thrombogenic properties from the viewpoint of the hydration structures near the surface of the biomaterials. An analogy can be drawn be-

tween the biomaterial research and the membrane research because the membranes need to have low-fouling properties toward various types of organic substances. For example, Ishihara *et al.*, who first developed poly(2-methacryloyloxyethyl phosphorylcholine) (polyMPC) as a biomaterial polymer[11], determined that surfaces with anti-thrombogenic properties are mainly covered with free water. Tanaka *et al.*, who first developed poly(2-methoxyethylacrylate) (polyMEA), another biomaterial polymer, have demonstrated the presence of some water molecules showing cold crystallization phenomena that may prevent the adsorption of organic substances on the surface of the polymers [12]. Hatakeyama *et al.* have demonstrated that polyMPC also has water molecules showing cold crystallization [13]. Akamatsu *et al.* have demonstrated that a carboxybetaine polymer (polyCMB)[14], which is also a well-known biomaterial polymer, has water molecules showing cold crystallization[15]. In general, this behavior is not observed for water molecules in the vicinity of conventional synthetic polymers. However, several biomaterial polymers have been shown to have water molecules showing cold crystallization. The hydration structures near the material surfaces are thus believed to determine their adsorptive properties.

Molecular dynamics (MD) simulations have also provided thermodynamic insights into the adsorptive properties enabling the development of low-fouling membranes. Nagumo *et al.* carried out a series of MD simulations to estimate the free energy profiles in the situation where biomolecules approach polymeric material surfaces in the presence of water molecules[16-18]. A simplified approach using amino acid residues in place of proteins, and monomer units in place of polymeric materials, was employed in these studies, and the accuracy of this convenient way to predict antifouling properties was investigated. Fig. 3 shows the free energy profiles as a function of the intermolecular distances between a phenylalanine residue and (a) a polyethylene terephthalate (PET) monomer and (b) CMB monomer [16]. An energy minimum is clearly observed in the free energy profile for PET. This deep and wide energy

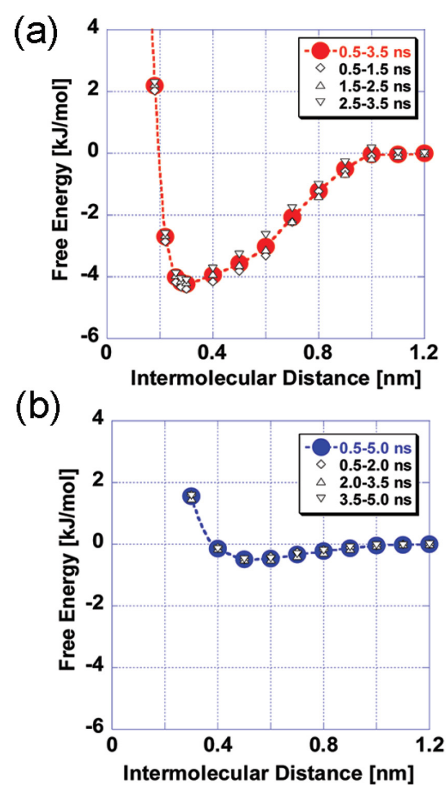


Fig. 3. Free energy profiles as a function of the intermolecular distances between a phenylalanine residue and (a) a polyethylene terephthalate monomer and (b) CMB monomer (Reproduced with permission from Nagumo *et al.*, [16], American Chemical Society).

minimum indicates that the adsorption of biomolecules on the PET surface would occur. In contrast, the free energy profile for CMB is almost flat, no energy minimum is observed, thermodynamically indicating that adsorption on the CMB surface would not occur. Similar trends were also observed in combinations of amino acid residues and MEA monomers[17]. That is, nearly flat profiles were observed for amino acid residues approaching the repeating units of polymer materials in their hydrated states that have water molecules showing cold crystallization.

Nagumo *et al.* have also investigated the mobility and orientation of such water molecules in the vicinity of self-assembled monolayers using MD simulations[19]. Their results suggested that a particular dynamic/static behavior of water molecules exists in the vicinity of phospholylcholine, carboxybetaine, and sulfobetaine SAM

surfaces. Nevertheless, the influence of the microscopic behavior of water molecules showing the cold crystallization phenomena on the free energy profiles remains unknown. It is important to clarify the microscopic mechanism of fouling from the viewpoint of the hydration structures in the vicinity of the membrane surfaces.

2.3. Surface modification using polyCMB and poly-MEA to prevent adsorption

As discussed above, in some cases adsorption is the dominant factor that causes a decrease in the filtrate flux, and some polymers with particular hydration structures in aqueous solution show anti-adsorptive properties. Thus, it should be effective to modify commercially available membrane surfaces with these polymers. The dynamically-forming method, which was first developed in 1966 by a group at the Oak Ridge National Laboratory[20], is one of the simplest surface modification methods, even though it was not developed for preparing low-fouling membranes. In this method, polymers or colloidal materials are filtered with porous supports, and the dynamically-formed layers on the supports are defined as membranes. When an aqueous solution containing the polymers with the desired hydration structures are filtered with microfiltration or ultrafiltration membranes, the physically deposited polymers will work as low-fouling layers. There are a few reports on the development of low-fouling ultrafiltration membranes using copolymers of CMB and *n*-butyl methacrylate (BMA) as the surface modifiers in the dynamically-forming method[21]. However, there is a concern regarding the durability of such dynamically-formed layers because the polymers are just deposited physically on the supports.

Immobilization via chemical bonds is thus preferable to carry out the surface modification. UV-initiated grafting[22,23], plasma-initiated grafting[24], and surface-initiated atom transfer radical polymerization [25,26] have been employed for modifying membrane surfaces with polymers. For example, Akamatsu *et al.* carried out the surface modification of a microfiltration membrane via the plasma-graft polymerization of poly-

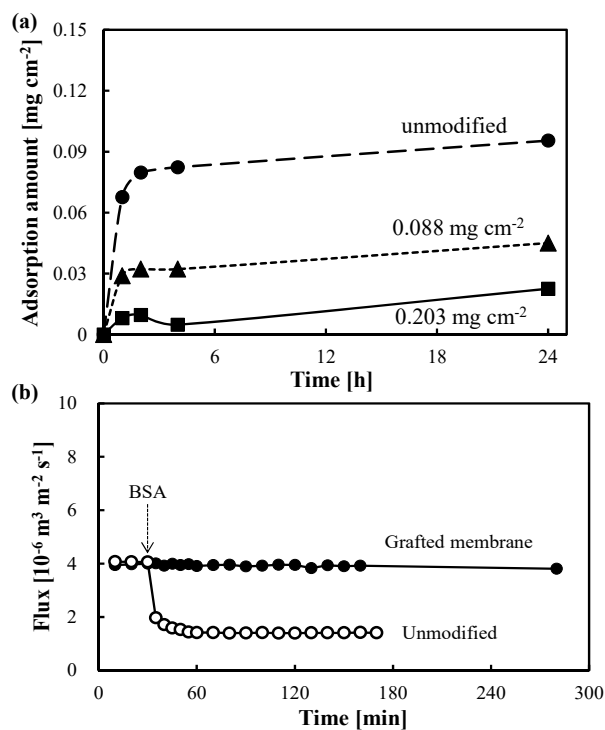


Fig. 4. (a) Time courses of the adsorption of BSA in the unmodified substrate and membranes with grafting amounts of 0.088 and 0.203 mg cm^{-2} . (b) Time courses of the fluxes in an unmodified substrate and a membrane with a grafting amount of 0.121 mg cm^{-2} in response to 1000 ppm of BSA (Reproduced with permission from Akamatsu *et al.*, [27], Elsevier).

CMB[27]. Fig. 4(a) shows the time courses of the adsorption of BSA per area of membrane when an unmodified polyethylene microfiltration membrane and two membranes modified with polyCMB, with grafting amounts of 0.088 and 0.203 mg cm^{-2} , were immersed into aqueous solution containing 1000 ppm BSA. The surface modification resulted in the drastic suppression of BSA adsorption. Fig. 4(b) shows the time courses of the filtrate fluxes when an aqueous solution containing 1000 ppm BSA was filtered in the constant-pressure, cross-flow mode with an unmodified polyethylene microfiltration membrane and a membrane modified with polyCMB with a grafting amount of 0.121 mg cm^{-2} . Pure water was supplied for the first 30 min, and then the feed solution was changed to the BSA solution. When an unmodified membrane was used, a drastic decrease in the flux was observed just after the change

of the feed. In contrast, when the membrane modified with polyCMB was used, no decrease in flux was observed even after the change of the feed. These results indicate that the modification using polyCMB suppressed the adsorption of BSA and accordingly the filtrate flux was maintained. This is a simple and clear demonstration of the development of low-fouling membranes from the viewpoint of the hydration structures.

Surface modification using polyMEA via plasma-graft polymerization has also been demonstrated to be effective for developing low-fouling membranes[28]. Because the grafted polymers increased the filtration resistance of the membranes, it will be necessary to graft short-length polymers with high grafting density to achieve high pure water permeability as well as low-fouling properties. This increased resistance is one of the important issues in membrane design to be tackled in the future.

3. Conclusion

Fouling occurs in most membrane processes, including wastewater treatment, water purification, and seawater desalination. No two feed solutions are exactly alike and many factors of the membranes, such as material, pore size, surface roughness, and hydrophilicity/hydrophobicity, can affect the fouling phenomena. There are also no unified operating conditions, namely the pressures and flow rates. Thus, despite much research, a solution to the problem of membrane fouling has not yet been found. In this short review, we present some insights into membrane fouling, in particular, from the viewpoint of hydration structures. Some polymers in their hydrated states have water molecules that show the phenomenon called cold crystallization, and these types of polymers are regarded as having non-adsorptive properties. Some betaine polymers, such as polyMPC, polysulfobetaine, polycarboxybetaine, and some nonionic polymers, such as polyMEA, can have such properties. Surface modification using these polymers successfully suppressed fouling by adsorption. Even

though the process of fouling is complicated, this fundamental research will help the understanding and accordingly the development of low-fouling membranes.

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