



A novel membrane showing both hydrophilic and oleophobic surface properties and its non-fouling performances for potential water treatment applications

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ABSTRACT

Membrane organic and biological fouling has been one of the major problems for membrane technology applications in water and wastewater treatment. In this study, a novel membrane showing both hydrophilic and oleophobic surface properties was developed and evaluated for its resistance against organic and biological fouling. The membranes in flat sheet configuration were prepared from PVDF as the base matrix polymer, blended with an additive polymer that was synthesized to contain both hydrophilic and oleophobic segments. The prepared novel membranes displayed high affinity to water but low affinity to oil. Experimental results from the filtration of protein solution, humic acid solution and oil/water emulsion confirmed that the developed membranes had greatly enhanced water flux and reduced organic fouling performance (shown as slow flux decay and high flux recovery after membrane cleaning). In the biofouling tests with the developed membranes being immersed in bacteria suspension or used for the filtration of bacteria suspension, it was found that the novel membranes effectively prevented bacteria adhesion on the membrane and the flux decay incurred during the filtration can be fully recovered after a simple cleaning with water under the experimental conditions. This study also demonstrated that a membrane surface showing both hydrophilic and oleophobic surface properties provided an effective and better way to reduce the effect of membrane fouling by organic as well as biological foulants than a membrane surface showing the hydrophilic property only. The developed membrane has a great potential for water and wastewater treatment applications.

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1. Introduction

Membrane separation is an emerging technology that offers great potential for applications in effective water and wastewater treatment. However, one of the major obstacles in the application of membrane technology is the adverse effect of membrane fouling. Various types of foulants, including inorganic (clays and mineral particles), biological (bacteria, fungi) and organic (oils and humics) ones, in the feed can cause membrane fouling [1]. According to the interaction nature and strength between foulants and membrane surfaces, membrane fouling may be broadly divided into reversible and irreversible fouling [2]. Inorganic fouling can often be considered to be reversible fouling because the foulants may be effectively removed by a simple physical or chemical cleaning method, including those such as water flushing or backwashing. In contrast, biological and organic foulants often

result in irreversible fouling of membranes and the fouled membranes become very difficult, if not impossible, to be fully recovered by usual physical or chemical cleaning methods. Because irreversible fouling of a membrane can cause permanent loss of the membrane's permeate flux and thus significantly increase the cost of membrane applications, a lot of research efforts have been made to develop membranes that can prevent organic and biological fouling through membrane formulations or surface modifications.

In general, it is commonly accepted that a hydrophilic membrane surface provides better performance than a hydrophobic membrane surface against organic and biological fouling caused by substances such as proteins, natural organic matters (NOM) and bacteria [3]. Since most membranes available in the market are often hydrophobic, various methods have therefore been developed to enhance the surface hydrophilicity of the membranes for water treatment applications. For example, hydrophilic substances have been immobilized onto hydrophobic membranes via adsorption and surface coating [4–6]; chemical reactions induced by high energy substances (UV, plasma) or strong acids

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were applied to produce hydrophilic groups on a hydrophobic membrane surface [7,8]; and surface grafting of a functional monomer or polymer on a base membrane was carried out to increase its surface hydrophilicity [9–11]. In addition, incorporation or blending of hydrophilic polymers in base membrane materials was also used as a method to enhance the hydrophilicity of the prepared membrane products [12,13]. The possible antifouling mechanism of a hydrophilic membrane surface has been attributed to the formation of a compact hydration layer on the surface that may reduce the possibility of foulants in direct contact with or adhesion on the membrane surfaces [14].

However, a hydrophilic surface usually has a relatively high surface free energy, as compared to those of organic and biological foulants in water. It has been demonstrated that, if a membrane's surface free energy is higher than the surface tension of oils (which are usually super-hydrophobic), the oils will spread on the membrane surface and exhibit very small contact angle [15,16]. This can lead to the difficulty of effectively cleaning a fouled membrane by organic components and, particularly, by oils. To reduce the adhesion strength of organic foulants and facilitate membrane cleaning, membranes of low surface free energy may have advantage. In the literature, ultrafiltration membranes with low surface free energy (very hydrophobic) have been tested for oil/water emulsion separation to enhance membrane cleaning [17]. The tested membranes indeed showed good resistance to the fouling of oils under dynamic stirring (this may be possibly attributed to the weaker adhesion), but these membranes also unavoidably showed poor affinity with water and hence had very low water permeability or water flux [17]. Besides, highly hydrophobic membranes were indeed commonly observed to be easily fouled by biological and organic foulants such as microorganisms [18,19] and humic substances [20], etc.

Fouling of a water filtration membrane will largely depend on the relative interactions among water and the membrane surface and foulants in water. The surface tension of water and the interfacial free energy of the membrane surface and foulants in water all play a role. Most organic and biological foulants in water are often completely or partly hydrophobic, with much lower interfacial free energy than the surface tension of water. Because of the natural repulsion by the water medium, the foulants brought to the membrane surface during membrane filtration would preferentially accumulate at the membrane interface, serving as a plausible surfactant, especially when the membrane surface is hydrophobic. This may explain the reason that a hydrophobic membrane is often observed for organic and biological fouling in water filtration. When a hydrophilic membrane is used, a hydration layer already on the membrane surface may reduce the adhesion of the foulants brought to the vicinity of the membrane surface due to both the convective flow and the water-foulants interaction effect. It is however arguable that the hydration layer may be broken through or replaced by the foulants due to the large drag force exerted on them by the filtration pressure and the greater interaction strength between membrane surface with the foulants than membrane surface with the water medium. This may explain the phenomenon that a hydrophilic surface, if fouled, is more difficult to be cleaned than a hydrophobic surface. There are also the cases or occasions where a membrane surface, even hydrophilic, may be exposed to the air medium or air/water interface during a filtration operation (such as during system installation, start-up, in preparing for cleaning, and system breakdown or maintenance, etc.), which increases the risk for the surface to be even more easily fouled by the foulants at the interface. In other words, even though the hydrophilic approach for water filtration membranes may be able to reduce membrane organic and biological fouling to some extents, the approach may not be expected to completely prevent the fouling effect.

Ideally, a membrane surface for water treatment may need to display both hydrophilic as well as oleophobic properties, with the former helping to achieve high water permeability and the latter to realize low adhesion rate as well as low interaction strength between the membrane surface and the concerned foulants. It may be worth to point out here that an oleophobic surface is not simply a hydrophobic surface but a surface with very low surface free energy, less than those of oils. Thus, an oleophobic surface can be expected to be even more effective in preventing the adhesion of most other organic foulants (whose surface free energy is usually greater than that of oils). Since hydrophilicity and oleophobicity are usually two distinctively opposite surface properties, a membrane surface with such two properties cannot be obtained by a homopolymer. In this line, only very limited research work has been reported in the literature. General Electric Company reported an asymmetric membrane system containing oleophobic and hydrophilic layers, prepared through a layer-by-layer coating method [21]. However, the outer surface of the developed membrane will still be predominated by either the oleophobicity or hydrophilicity but most probably not both. Surfactants containing perfluorinated end (oleophobic) and polyethylene glycol chain (hydrophilic) were reported to be covalently grafted onto glass membranes for oil/water emulsion separation [10]. Even though improved performance was observed in such approach, glass membranes are relative expensive and more difficult to be prepared in comparison with commonly used polymeric membranes. Another work reported the construction of a ternary amphiphilic block copolymers consisting of hydrophilic block (polyethylene oxide) and fluorine-containing hydrophobic blocks (oleophobic) as an additive to prepare modified PVDF membranes [14]. The obtained composite PVDF membrane however was shown to have water contact angles at above 80°, suggesting that the obtained membrane surface remained to be highly hydrophobic but not very hydrophilic yet.

In this study, a synthesized additive polymer was blended with PVDF (the base polymer) to obtain a novel polymeric membrane with both hydrophilic and oleophobic surface properties. The prepared membranes were characterized and the performance of the developed membrane for resisting both organic and biological fouling was evaluated through a series of comprehensive sets of experiments. The results reported in this paper are new and similar results have not been reported in the literature so far.

2. Materials and methods

2.1. Materials

The additive polymers were synthesized in our group. First, *tert*-butyl methacrylate (tBMA) monomers were graft-copolymerized from poly(vinylidene fluoride-co-chlorotrifluoroethylene) or (P(VDF-co-CTFE)) via atom transfer radical polymerization (ATRP). Second, the grafted PtBMA chain was hydrolyzed to poly(-methacrylic acid) (PMAA). Finally, P(VDF-co-CTFE-g-PMAA) was esterified with perfluoroalkyl PEG surfactant or PEG to produce the respective additive polymers desired (AP1 or AP2). The structures of the additive polymers are shown in Fig. 1. In particular, AP1 has a PVDF backbone with side chains containing hydrophilic internal segment and oleophobic terminal segment, and AP2 however containing hydrophilic segment only. The detailed synthesis procedures of the additive polymers can be found elsewhere [22].

Polyvinylidene fluoride (PVDF, Mw ca. 534,000), bovine serum albumin (BSA, Mw ca. 66,000), humic acid (HA), sodium chloride, hexadecane and polyethylene glycol (PEG, Mw ca. 600 and 1000)

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