Separation and Purification Technology 118 (2013) 226–233

Contents lists available at SciVerse ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Polydopamine coating – Surface modification of polyester filter and fouling reduction

Lifen Liu *, Bing Shao, Fenglin Yang

Key Laboratory of Industrial Ecology and Environmental Engineering, Ministry of Education, School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China

ARTICLE INFO

Article history:
Received 16 March 2013
Received in revised form 30 June 2013
Accepted 2 July 2013
Available online 11 July 2013

Keywords:
Polydopamine
Surface modification
Hydrophilicity
Membrane bioreactor
Dynamic membrane

ABSTRACT

To develop a high flux and antifouling membrane to be used in membrane bioreactor for water pretreatment, a low cost polyester filter cloth was modified by coating with polydopamine (PDA), based on the easy self-polymerization and strong adhesion characteristics of dopamine (DA) under mild conditions. The apertures and surface morphological changes were characterized using SEM. The influence of the modifying conditions such as coating time and DA concentration on the membrane properties was investigated. It was found that the most reasonable modification conditions to obtain the best antifouling performance are 1.5 g/L DA concentration and 24 h coating time. There was 142.67% increment of the stable flux during filtrating yeast suspension for the PDA modified membrane under the best conditions compared with that of the original membrane. The result showed that the PDA modified filter membrane has higher flux, excellent antifouling properties and good stability. The stable flux increase in the short-term test in MBR was ~36% after PDA coating. The results of the relatively longer term experiments in MBR indicate that the membrane modified by PDA reduced the membrane fouling in active sludge, especially the irreversible fouling. This work provides a simple method of modifying low cost filter membrane for better antifouling properties and potential application in MBR.

1. Introduction

Membrane bioreactor (MBR) has been widely applied in wastewater treatment and water purification due to the advantages of smaller footprint, better effluent qualities and higher sludge concentration [1]. Unfortunately, the high cost of the membrane materials and membrane fouling are critical challenges and barriers to the improvement of MBR systems [2,3]. To reduce membrane costs, low cost non-woven and mesh filters, had been tested in submerged MBR [4–6]. These textile materials are composed of a network of overlapping fibers, which create multiple connected pores. Though the large apertures materials themselves cannot adequately fulfill the solid–liquid separation functions, MF or UF equivalent separation result can be achieved due to the self-forming dynamic membrane (SFDM) [7,8]. Polyester and nylon mesh filters have been used as filtration materials in MBR to reduce manufacturing and operating cost, which could also provide high removal ratio of COD (chemical oxygen demand), TSS (total soluble solid) and TKN (total kjeldahl nitrogen) [9]. Fuchs et al. [10] had studied the effect of different pore sizes and different mesh module configurations on the effluent quality, which resembled the quality of activated sludge process treatment system. Excellent effluent quality were achieved and also compared to those of conventional activated sludge systems. However, similar to the MF membrane fouling, the fouling of mesh filter membrane caused by pore blocking is the main problem limiting its application, especially when the membrane was relatively hydrophobic [11,12]. Membrane fouling occurred is more serious on hydrophobic membranes than hydrophilic ones. As a result, much attention has been paid to reduce membrane fouling by modifying hydrophobic membranes to increase their hydrophilicity. There are some research papers about modifying the non-woven fabric for higher flux and better antifouling performance [13,14]. For the polyester filter, we have used it in studying a new helical membrane module for better antifouling properties [15] and have coated it with polypyrrole to make it hydrophilic as well as electrically conductive [16]. We have also modified the polyester filter cloth using TiO_2/PVA to inhibit the irreversible fouling, and the results showed a remarkable improvement of hydrophilicity and low resistance compared with the commercial PVDF membrane [17]. Compared to other modification methods, the coating technique is simple and easy to use in large-scale industrial applications. A major issue with coating based method is to achieve permanent modification and increase

* Corresponding author.
E-mail addresses: yuzhe25521@yahoo.com.cn, lifenliu@dlut.edu.cn (L. Liu).

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http://dx.doi.org/10.1016/j.seppur.2013.07.003

the stability of modifying substance on membrane surface. Hence, the development of novel methods overcoming this issue is desirable for surface modification of the membrane. Polydopamine (PDA) is a novel polymer sharing similar properties to the adhesive proteins in mussels. The adhesive mechanisms and outstanding adhesive behaviors of PDA have been reported [18]. DA (3,4-dihydroxy-phenylala-nine) is able to self-polymerize in aqueous solution and form a PDA layer, which can firmly attach to a wide range of substrates such as rocks, metals, polymers and wood [19]. The polar groups in PDA layer, such as hydroxyl and amine groups, endow the substrates with improved hydrophilicity and anti-fouling ability [20]. Additionally, PDA has been successfully applied in modifying PVDF, PE and PS polymer membranes for higher membrane fouling resistance [21–23]. However, so far, only limited information on the application of PDA modification is available.

In this research, PDA is used for filter membrane modification because of its highly hydrophilic nature and the stable polymerization of simple ingredients under mild reaction condition. We choose the low cost polyester cloth as a cheap membrane and expect the firm PDA modification to reduce the irreversible fouling. The application performance of PDA coated membranes in MBR is also reported. We tried to demonstrate that the PDA modification can reduce fouling of the large aperture filter materials and prolong the membrane life in MBR. The effects of different coating conditions, such as coating time, solution concentration on membrane properties are also investigated in detail.

2. Methods

2.1. Materials

Polyester filter cloth (Shanghai Suita Filter Material Co. Ltd.) and its specifications: the fiber weight per unit area is 275 g/m^2, the thickness is 0.5 mm, and in 10 cm length. The number of fiber was 295 and the stretch rate was 30.87% in latitude directions. And in longitude direction, the number of the fiber was 200 and the stretch rate was 14.6%. Because of the irregularity of the pore shape and size, the real pore size is hard to define. Its pore size is not as equally accurate or important as the pore size of the UF or NF membrane. The average pore size value was ~100 μm, measured using a bubble point method. 3,4-Dihydroxyphenethylamine (dopamine or DA) was purchased from J&K China Chemical Ltd. and used as received. The water used in the following experiments was deionized water. Ethanol, hydrochloric acid (Melonepharma Chemical Reagent Co. Ltd.) and hydroxymethyl aminomethane (Tris, Sinopharm Chemical Reagent Co. Ltd.) are all analytical reagents and used without further purification.

2.2. Preparation of PDA modified membrane

Polyester filter cloth was dipped in deionized water and set in ultrasonic cleaner for 30 min at 30 kHz. After that, the cloth was dipped in ethanol for another 30 min, then washed by deionized water. Different amount of dopamine was dissolved in 200 ml deionized water to make a dilute aqueous solution, buffered to a pH typical of marine environments (10 mM Tris, pH = 8.5) to obtain a DA solution. The concentration of DA solution was set at 0.5, 1.0, 1.5 and 2.0 g/L respectively. After that, the polyester cloth was immersed into the DA solution immediately and shaken for a designed time at 30 °C and 150 rpm/min. After modification the membranes were taken out followed by a thorough washing with ethanol and deionized water. The filter membrane before and after PDA modification was compared by characterization with SEM (JEOL JSM-5600LV).

2.3. The filtration experiments

The filtration set-up used was shown in Fig. 1. A flat sheet membrane module (filtration area 0.0072 m^2) was installed into a cylindrical container vertically, which had an effective volume of 3.925 L. Aeration was supplied by an air pump through air diffusers at the bottom of the cell, and the aeration intensity was 0.15 m^3/h. In all experiments, the permeation was operated in a gravitational filtration mode, at constant trans-membrane pressure (TMP) 7.6 kPa.

Before the filtration tests, the membrane was dipped into the deionized water for 30 min to be wetted. The pure water flux was examined first, after that the fresh bakers yeast suspension was used as foulant particles to test antifouling properties. The size of the particle suspension is ~7 μm and the concentration of the yeast was 5 g/L in all experiments. Furthermore, to ensure the accuracy of the tests and verify the stability of the dopamine coated membrane, the filtration test was repeated for three cycles, in each cycle, the filtration lasted 1.5 h. At the end of each cycle, the membrane was only physically cleaned by washing with tap water.

In the filtration test, the influence of the coating time and the DA concentration on the membrane flux and antifouling properties was studied. We chose 0.5 g/L DA concentration, when the influence of the coating time was studied. Then we changed the DA concentration and studied its influence, at the best coating time derived from our experiments results.

2.4. Antifouling properties in MBR

To gain more information on filtration performance of the modified membranes under practical conditions, both relatively short-term and long-term tests in the laboratory-scale MBR were designed to characterize their antifouling properties. The diagram of the test-rig MBR was shown in Fig. 2. The reactor had an effective volume of 10 L and the membrane area of each membrane module was 0.04 m^2 (0.1 m × 0.2 m × 2). Constant aeration was maintained at 0.3 m^3/h. A synthetic wastewater was used in the experiments, and the composition of the water was sucrose 5, NH_4Cl 0.07, KH_2PO_4 0.003 and $CaCl_2$ 0.002 (g/L). The influent was controlled by a liquid level balance tank. There are only two types of membranes, which were original polyester cloth and PDA coated polyester cloth. Here we had chosen membrane modified at PDA concentration 1.5 g/L and coating time 24 h. The above operation conditions were adapted in both short-term and long-term test if there was no further explanation.

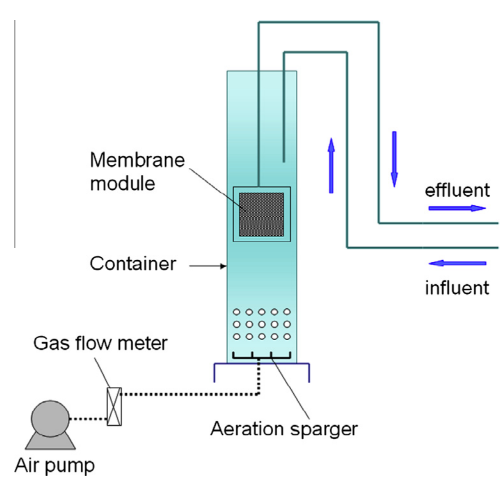

Fig. 1. The filtration test set-up.