Research Article



Application of a high-efficient surface-modified ultrafiltration membrane for activated sludge filtration

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The present study compared the potential performance of a pristine polyacrylonitrile (PAN) ultrafiltration membrane and a surface-modified PAN ultrafiltration membrane in rejecting sludge from an industrial wastewater treatment plant. It should be mentioned that the modified membrane was fabricated based on the optimal surface-modified membrane from a previous investigation in which a mixture of lipase and protease enzymes were immobilized on the PAN membrane surface via a proper linker (a dopamine layer on the membrane surface). Industrial sludge with mixed liquor-suspended solids (MLSS) of 8000 mg/l was passed through a dead-end setup to test and compare the performance of both mentioned membranes. The results show that the hydrophilicity and pure water flux (PWF) of the pristine PAN membrane has been glaringly increased by immobilizing the aforesaid enzymes on the membrane surface. In addition, after 6 cycles of sludge filtration, the surface-modified membrane showed outstanding performance so that the permeate flux did not decrease over filtration time, while the pristine one showed a descending trend in permeate flux after cycle 4. Overall, the reported data from this research corroborates that integrating a mixture of enzymes on membrane surfaces could be considered a proper approach to enhance the antifouling property and permeate flux.

Keywords: Biofouling, surface modification, sludge filtration, ultrafiltration

Introduction

. Cost-effective wastewater treatment has been one of the big concerns of industrial owners in the contemporary world due to strict discharge regulations and water source alleviation. This means that across different wastewater treatment methods, biological treatment has been considered an effective and economical technique applied all over the world. Researchers have assessed various high-rate bioreactors to promote treatment efficiency in carbon and nutrient removal. As a fact, single and coupled bioreactors showed higher performance and lower energy consumption than conventional biological systems[1, 2]. Asadi and her coworkers have published obtained data from operating an airlift bioreactor for treating soft drink wastewater. An outstanding result for carbon and nutrients removal has

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been reported that 98, 72, and 65% of carbon, nitrogen, and phosphorus removal, respectively, under optimum experimental conditions were achieved [3].

Membrane bioreactor (MBR) presents a category of high-rate bioreactors that couple biological and membrane technology to enhance treatment yield [4, 5]. To the best of our knowledge, MBR provides high biomass concentration without concern about sludge sedimentation. Higher biomass concentration and higher treatment capacity will be obtained. Therefore, applying MBR increases effluent quality and decreases energy consumption by reducing treating time [6]. Nevertheless, membrane biofouling is a bottleneck of this technology to widespread use, and great efforts have been dedicated by researchers to solve this drawback [7, 8]. Membrane modification has been implemented to improve the fouling resistance of commercialized membranes categorized into two main categories, including mixed matrix and surface modification methods [5, 9, 10]. Surface modification techniques have been considered for maintaining mechanical and thermal characterization of support membranes, while surface features like hydrophilicity could be improved. Different surface modification methods have been developed, such as plasma treatment, interfacial polymerization, grafting, and surface coating [11]. Each modification approach shows some pores and cones, however; the coating is a simple and effective method to amend the membrane surface[12].

A new strategy could incorporate biomolecules into the membrane surface to boost its hydrophilicity and antifouling features. Enzymes are famous biomolecules that were applied as modifying agents for membrane technology. Enzymes like lipase and protease on the membrane surface could act as destructive agents for lipids and proteins, the main molecules responsible for biofouling [13]. In the previous study by our research team[14], lipase and protease were immobilized onto **Materials and methods**

Membrane preparation and surface modification

As mentioned, the optimal surface-modified membrane from the previously published work has been utilized for faltering sludge from an ordinary activated sludge system. The preparation methodology in detail has been provided in the aforesaid research paper [14]. In this research, the PAN ultrafiltration membrane was prepared as a pristine membrane using the phase inversion method. The casting solution is composed of 16%, 1%, and 83% of PAN, polyvinylpyrrolidone (PVP), and dimethylformamide (DMF), respectively. The casting solution was poured on a glass support, and a casting knife was used to obtain a film of the polymer was used. The glass support was then immersed in the deionized water bath. After getting a sheet of membrane, it was dried between two filter papers for a night, and then a pristine sheet was used for surface modification. To integrate both lipase and protease enzymes onto the pristine surface, it was immersed in NaOH solution with a concentration of 3 M, and then it was submerged into 0.03 M of dopamine Tris-HCl solution (pH 8.5) to get a layer of dopamine on the membrane surface. Dopamine acts as a proper linker to attach enzymes to the membrane surface. Finally, a solution containing 1 g/l of each enzyme was prepared, and the activated membrane was immersed into the solution to obtain an integrated layer of enzymes on the membrane's surface.

Membrane filtration

Sludge was taken from a working industrial wastewater treatment plant with mixed liquor-suspended solids (MLSS) of 8000 mg/l. A dead-end setup was used to filter the aforesaid sludge, as shown in Figure 1. The applied dead-end setup was filled with sludge and nitrogen gas was utilized to provide 3 bar of pressure in the vessel. The pristine and optimal membranes were inserted in distilled water before being used for an hour. At first, pure water flux was attained by passing through distilled water for an hour. After that, the sludge was filtered, and permeate flux was calculated. Then the used membrane was cleansed and immersed in distilled water for a half-hour. The mentioned cycle was repeated 8 times for both membranes. Pure water flux (PWF) and permeate flux were calculated according to the following equation:

$$J_{w.1} = \frac{M}{A\Delta t} \tag{1}$$

Where M, A, and Δt were the weight of permeate (kg), the operative membrane surface area (m2), and the permeation time (h), respectively.WCA was determined using the sessile drop method (25 °C) with a goniometer (G10, KRUSS, Germany) to evaluate the membrane surface hydrophilicity.



Figure.1. A picture of the used dead-end setup.

Results and discussion

The water contact angle (WCA) and PWF of both membranes were displayed in Figure. 2. From the presented data, a significant enhancement in hydrophilicity of the surface-modified membrane could be found as WCA decreased from 62.940 to 39.80

As an explanation, the hydrophilic nature of dopamine and enzymes caused a remarkable reduction in WCA. On the other hand, the integration of dopamine on the membrane surface not only decreased WCA but also caused a boost in PWF, so that PWF increased from 46.31 to 78.9 kg/m2.h. As a fact, the introduction of dopamine and a mixture of enzymes on the membrane surface creates a hydrated layer near the surface which draws water molecules to the membrane surface and creates channels for passing water molecules [15]. Overall, the water affinity of the optimal surfacemodified membrane was significantly enhanced by the presence of hydrophilic groups on the membrane surface, so it could be expected to attain higher filtering performance in rejecting biomass from biological systems. Therefore, sludge with an MLSS of 8000 mg/l was passed through the pristine and optimally modified membranes to present the effect of the modification on the membrane performance.

trend of flux over time was achieved for the enzymeimmobilized membrane, demonstrating a remarkable effect of enzyme immobilization on the membrane performance. This outcome corroborates that immobilized enzymes on the membrane surface showed good functionality on the membrane surface in confronting the microorganism's cell. Lipase and protease enzymes derelict lipids and proteins in the microorganism cell walls; therefore, the adhesion of biomass to the membrane surface was decreased significantly. On the other hand, the hydrophilic nature of the optimally surfacemodified membrane creates a hydrated layer near the surface, inhibiting the adhering hydrophobic molecules on the surface and making water molecules' passage easier.

Conclusion

The performance of the pristine PAN ultrafiltration membrane and the surface—modified membrane in rejecting sludge taken from an industrial treatment plant

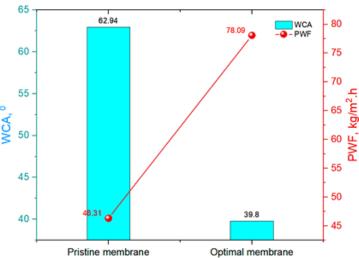


Figure 2. WCA and PWF of the pristine and optimum surfacemodified membrane.

Figure 3 demonstrated permeate flux versus time over 6 filtration cycles. As observed in the Figure, the optimally modified membrane presented a higher flux in rejecting biomass than the unmodified membrane. The pristine membrane's flux was diminished gradually over time after cycle 4, the PWF could not be recovered after cleansing, and a descending trend in PWF could be observed. This reduction was also shown in permeate flux over sludge filtration for the pristine membrane. Despite the pristine membrane, a substantial ascending

was compared. Qaq2 and protease enzymes were immobilized on the membrane surface using a linker (a dopamine layer on the membrane surface) to promote immobilization. As a result, the optimum surface-modified membrane showed higher hydrophilicity (WCA of 390) and higher PWF (78 kg/m2.h) than the pristine membrane. Likewise, it showed higher antifouling performance in rejection sludge filtration, so its permeate flux did not decrease over filtration cycles.

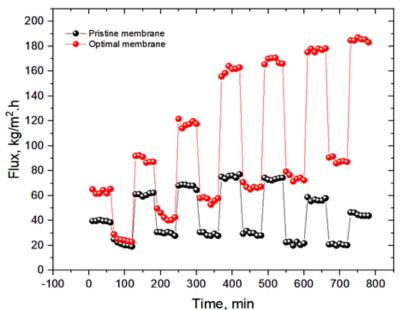


Figure. 3. Flux versus time over 6 cycles of sludge filtration for both the pristine and optimum surface-modified membrane.

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