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Mitigation of membrane biofouling through surface modification with different forms of nanosilver

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HIGHLIGHTS

- PES UF membranes were modified through silver nanoparticles by three techniques.
- Membrane modifications resulted in mitigation of biofouling.
- Modified membranes displayed strong antimicrobial properties.
- Membranes modified through diffusion and PEI method showed improved permeability.

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ABSTRACT

Membrane biofouling is a serious problem limiting widespread application of membrane technology. Modification of membranes using silver nanoparticles appears to be a promising option for mitigating biofouling.

NADIR® UP150 ultrafiltration membranes made of polyethersulfone were modified with different forms of nanosilver through (i) diffusion of silver ions with subsequent reduction, (ii) addition of polyethyleneimine-capped silver nanoparticles, and (iii) thermal-pressure fixation of silver-modified nanofibres. The modified membranes for any changes in permeability, antimicrobial properties, silver leaching and contact angle were examined.

All modified membranes displayed antimicrobial properties. Both membranes modified through diffusion of silver and polyethyleneimine-capped silver nanoparticles method mitigated biofouling. These membranes also showed slightly higher permeability than the unmodified control, while silver-modified nanofibre membranes had the lowest permeability of all the membranes tested. Filtration results corresponded well with contact angle measurements. All modified membranes exhibited low levels of silver leaching over time.

1. Introduction

Despite the numerous advantages of membrane technology in the field of water and wastewater treatment, including excellent effluent quality and a reduced footprint due to the high concentration of activated sludge in membrane bioreactors (MBR), there are still some drawbacks limiting its widespread application. One of the most serious problems of this technology is fouling of the membrane surface [1,2]. Membrane fouling, which leads to a decrease in system hydraulic performance and an increase in operational costs, is a complex problem affected by a number of different factors and their combination [3,4]. As a result, a wide range of issues related to MBR membrane fouling has been intensively studied, including operational conditions, wastewater characteristics or membrane material [5–8].

There are several ways to minimise membrane fouling and improve long-term membrane performance. In general, two approaches are considered efficient. The first requires changes in MBR operational conditions, such as changes to sludge and hydraulic retention time [4], the food to microorganisms ration [4,9] or oxygen supply [10]. All of which affect biomass characteristics or production of extracellular polymeric substances and, subsequently, interaction with the membrane surface and biofouling.

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Changes to the filtration cycle, e.g. filtration time and flux and time of backpulse/backwashing (including flux applied or relaxation), can also influence membrane fouling [1]. Severe membrane fouling can be avoided by operating the system under critical flux as well; however, under actual operational conditions, problems occur with unstable conditions and, notably, low hydraulic system performance [4].

A second option for mitigating membrane biofouling and enhancing system hydraulic performance requires modification of the original membrane surface or preparation of new membranes. This approach usually leads to an increase in hydrophilic surface character and additional membrane features. Such surface modification reduces mutual hydrophobic interactions between the membrane surface, microorganisms and compounds present in the feed, thereby reducing membrane biofouling [11].

A number of modification techniques and procedures for mitigating membrane biofouling have now been developed and tested. In general, modification procedures can be divided into two basic groups, i.e. physical and chemical techniques. Physical methods include e.g. plasmatic surface modification, such as that undertaken by Yu et al. [12,13], who subjected polypropylene hollow fibre membranes to ammonia (NH_3) and carbon dioxide (CO_2) plasma treatment. Nitrogen and air have also been used for plasmatic modification of the membrane surface [14,15]. Due to the plasmatic exposure, new primary amine (—NH_2) and carboxylic (—COOH) groups were grafted onto the surface [12–15]. A further option is that of employing UV or gamma irradiation [16], which generally results in increased surface hydrophilicity and a decreased tendency toward membrane fouling. These techniques have a number of drawbacks, however, including a significant increase in final membrane production costs due to the employment of such high-energy methods [17].

Of the chemical techniques available, covalent bonding or the 'self-assembly' method enables the preparation of a thin film on the membrane surface (e.g. [17–19]). Various compounds, including polyethylene oxide, polyvinyl alcohol, zirconium compounds, magnesium or titanium oxide, and silver have been used for this technique [11,17,20,21]. The thin film produced is hydrophilic, which significantly reduces any hydrophobic interactions. In addition, deposited foulants are readily removed from the membrane's surface through cross-flow effect [11,20], thereby improving the membrane's operational characteristics and maintaining its hydraulic performance for longer period.

Modification of membranes using silver nanoparticles is a promising option for mitigating membrane biofouling. Application of silver nanoparticles has the potential to achieve the required long-term membrane permeability, together with antimicrobial properties limiting the mutual interaction of microorganisms with the membrane surface. Both silver ions and silver nanoparticles have proven antibacterial properties; hence membranes containing silver nanoparticles could prove a great asset in wastewater treatment [22,23]. Indeed, according to Meng et al. [4], nanotechnology in general has great potential for the development of strong hydrophilic membranes.

The main goal of this study, therefore, was to modify a commercially available ultrafiltration membrane, and to determine changes in membrane characteristics caused by different modification procedures. Different techniques involving silver nanoparticles were used to achieve the surface modification, i.e. functionalization through diffusion of silver ions, followed by their reduction; addition of polyethyleneimine-capped silver nanoparticles; and fixation of silver-modified nanofibres. Following modification, changes in filtration performance under different conditions as well as surface properties, silver leaching and antimicrobial properties were assessed.

2. Materials and methods

2.1. Membrane modification

2.1.1. Diffusion method

The first modification method was based on the diffusion and entrapment of silver in a polymer matrix of membrane. Individual reagent concentrations and processing conditions of this method are based on own results of a number of previously performed experiments using polyethersulfone (PES) membranes.

In short, a commercial PES NADIR® UP150 membrane was soaked in 3.5% (wt.) silver nitrate ($AgNO_3$; Sigma–Aldrich) solution and leached for 4 h at room temperature while stirring on a shaker at 50 rpm. The membrane was then intensively rinsed with demineralised water and the silver reduced by soaking in a 2% (wt.) ascorbic acid ($C_6H_8O_6$; Sigma–Aldrich) solution for 2 h. Following reduction, the membrane was again rinsed intensively with demineralised water, and then heated for 2 h at 70 °C while mixing the sample on a shaker at 50 rpm. Modified membrane was stored in demineralised water for later use.

2.1.2. Polyethyleneimine method

The second modification procedure made use of polyethyleneimine-capped silver nanoparticles (PEI-Ag). This procedure was derived from Czech patent No. 2011-549 (A3) [24]. A NADIR® UP150 membrane was first soaked in polyethyleneimine solution (5% wt. PEI in water; MW ~2000 Da, Sigma–Aldrich) and placed on a stirrer for 2 h at 50 rpm. PEI with a molecular weight of 2000 Da was chosen to provide a compromise between sufficient PEI fixation to the membrane surface and to restrict ultrafiltration membrane pore blockage (Molecular Weight Cut-Off 150 kDa). Fixation of PEI was followed by a thorough rinse with demineralised water. Subsequently, the silver precursor $AgNO_3$ (Sigma–Aldrich) in 3.5% (wt.) solution was added to the membrane and heated for 2 h at 70 °C while mixing the sample on a shaker at 50 rpm. After heating, the membrane was left for 24 h in this solution, after which it was rinsed intensively with demineralised water. The silver ions remaining on the membrane surface was reduced using a 2% (wt.) solution of ascorbic acid (Sigma–Aldrich). The membrane was then rinsed with demineralised water and stored in demineralised water for later use.

2.1.3. Nanofibre method

The third modification method was based on the use of polyurethane nanofibres doped with silver nanoparticles. The nanofibres were prepared according to the procedure described in Dolina et al. [25] i.e. nanofibres were produced on a free surface electrospinning device assembled according to Czech patent No. 294274 (B6) [26]. Heat-pressure lamination of the nanofibres onto the original NADIR® UP150 membrane surface was performed using an Oshima Mini Press (OP-450GS) device (Oshima, China). During lamination, the pressure was set at 0.02 bar and the temperature kept within a range of 95–100 °C in order to avoid significant structural changes to the nanofibres.

2.2. Filtration tests

Following modification, the filtration performance of each membrane was assessed using a LabUnit M10 laboratory-scale cross-flow filtration unit provided by Alfa Laval (Sweden), which allows for the testing of two membranes (each 84 cm^2) in parallel. Three different filtration tests were carried out. Prior to the start of each test, the membranes were rinsed intensively with demineralised water.