



Magnetic nanoparticles augmented composite membranes in removal of organic foulant through magnetic actuation



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ABSTRACT

Exploring ways to remove foulants is of great importance for sustainable membrane operation in wastewater treatment. This study investigates the efficiency of humic acid removal by a magnetic responsive Fe_3O_4 -PES nano-composite membrane. Magnetic responsive iron oxides (Fe_3O_4) were first end-capped onto the surface of a polyethersulfone (PES) membrane using a polyelectrolyte modification method. The amount of end-capped Fe_3O_4 was varied by adjusting the concentration of suspended magnetite nanoparticles from 100 ppm to 2500 ppm. A quartz crystal microbalance with dissipation (QCM-D), atomic force microscopy (AFM), field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS), contact angle measurement and X-ray photoelectron spectroscopy (XPS) were used to determine the adsorption kinetics and the morphology of Fe_3O_4 deposited on PES membranes. The combined results of frequency shifts (Δf) and changes in the dissipation factor (ΔD) from QCM-D demonstrated an increased deposition rate of Fe_3O_4 as the concentration of suspended magnetite nanoparticles was increased. As for filtration studies, when the Fe_3O_4 -PES nano-composite membranes were exposed to an alternatively switching oscillating external magnetic field, torque effects on the nanoparticles were generated and twisted the deposited Fe_3O_4 nano-colloids. This magnetic nanoparticles augmented nano-composite membrane was able to retain a normalized flux of 0.96 ($J=32.8 \text{ L m}^{-2} \text{ h}^{-1}$) with rejection of $99.4 \pm 0.14\%$. This was due to the twisting effect of the Fe_3O_4 nanoparticles that reduces concentration polarization near the top surface of the membrane and consequently reduces the potential for membrane fouling.

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1. Introduction

Over the past few decades, water quality standards have become more stringent and have opened up a plethora of new applications for wastewater treatment. The use of membranes for water and wastewater treatment has progressed to more advanced membrane materials employed in various configurations. In this context, the development of a nano-composite membrane has become an area of intense research. Membranes are now challenged to continuously perform at a high level. The most critical limitation of current membranes is that they can be fouled easily. Membrane fouling will cause a severe decline in flux over time, affecting the quality of the water produced. Severe fouling may require intense chemical cleaning or membrane replacement which will increase the operating costs. Indeed, organic fouling is common in membrane filtration, as the source water often has

relatively high natural organic matter (NOM) content. Humic acid is one of the NOM components. The humic substances are commonly found in the wastewater, surface and ground waters [1–4], which is an inevitable obstacle to further developments in membrane technology.

A common strategy to control membrane fouling is to modify the membrane surface by altering its hydrophilicity, surface roughness and/or surface charge [5–9]. This strategy is effective because initial fouling usually occurs when strong interactions take place between the membrane surface and the foulants. It is well known that the hydrophilic character of a membrane could influence the adsorption rate of organic matter present in the feed water [5]. For example, an ultrafiltration composite membrane based on the poly(vinyl alcohol) hydrogel produced by Wang and co-workers [10] exhibited markedly higher water throughput with similar rejection efficiency relative to an uncoated membrane. Good fouling control was achieved by applying a very thin coating of hydrogel to the membrane, demonstrating the advantages of such hydrophilic coating layers for mitigating membrane fouling [10,11].

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In particular, the beneficial effects of nanoparticle-based membranes on the mitigation of membrane fouling have been reported recently by many research communities [7,12–17]. Nanomaterials have been identified as the newest material expected to have a critical impact in water quality engineering. Newly available nanomaterial and nanotechnology tools enable the synthesis of polymer–inorganic composites to manufacture higher performance membranes with increased permeability, selectivity, and resistance to fouling. The nano-composite membrane not only provides better membrane filtration performance and higher resistance to fouling but can also be engineered to be antibacterial [7] and photodegradable [18]. For example, Diagne et al. [7] designed a polyelectrolyte and silver nanoparticle microfiltration membrane which reduced bacterial growth and organic fouling due to the existence of silver nanoparticles and hydrophilic polyelectrolytes on the membrane surface.

Several techniques have been explored to incorporate nanoparticles onto the membrane surface, including radical grafting [19,20], hydrogel coating [15], self-polymerization [18], and polyelectrolyte multilayer modification (PEM) [7]. Himstedt et al. [19] and Yang et al. [20] demonstrated the integration of magnetite nanoparticles on surface of polyamide nanofiltration (NF) membrane through surface-radical polymerization. In the studies, the hydrophilic polymer chains, poly(2-hydroxyethyl methacrylate), were first grafted on surface of polyamide NF membrane via controlled surface-initiated atom transfer radical polymerization. The superparamagnetic (Fe_3O_4) nanoparticles were then attached to the polymer chain ends. As for membrane filtration, the modified magnetic responsive membranes operated under presence of an oscillating magnetic field manifested improvement of permeation (30% higher flux) and salt rejection (15% higher rejection of CaCl_2) than the membrane operated in the absence of an oscillating magnetic field [19].

In the present work, a relatively simple and direct polyelectrolyte multilayers (PEM) modification method was adopted, to end-cap the magnetite nanoparticles (Fe_3O_4) on surface of a polyethersulfone (PES) microfiltration membrane. PEM is an attractive method for preparing an ultrathin layer on top surface of the nano-composite membrane. With this technique, the ultrathin layers are formed by alternating electrostatic deposition of oppositely charged polyelectrolytes on the membrane surface. The advantages of PEM include control over surface charge, hydrophilicity, and film thickness [21–23]. In previous published work [24], we have demonstrated the effectiveness of the PEM method to end-capping the strong negatively charged PSS functionalized Fe_3O_4 nanoparticles on the membrane surface. The nanoparticles experience a magnetic force as well as a torque under an oscillating external magnetic field, which successfully demonstrated the suppression of fouling for organic separation applications. Here we build upon our previous work to study the extent of magnetophoretic actuation for different concentrations of attached nanoparticles and to investigate the membrane longevity anti-fouling behavior.

Quartz crystal microbalance with dissipation (QCM-D) is utilized to study the deposition kinetics and mass uptake of the magnetite nanoparticles onto the membrane surfaces. Specifically, QCM-D is a surface-sensitive instrument that gives real time information of mass changes in thin layers on any surface. It has been used to study the deposition kinetics and mass uptake of the nanoparticles onto various surfaces as demonstrated by numerous researchers [25–29]. For example, Park and co-workers [28] used QCM-D to study the adsorption kinetics and to determine the equivalent Langmuir adsorption isotherms of nanoparticles adsorbed on an aminosilane layer for a range of nanoparticle concentration. Based on the QCM-D analysis, the deposition rate and mass of CdSe/ZnS nanoparticles adsorbed onto the aminosilane

layer was found to increase with increasing nanoparticles concentration [28].

The present work proposes to integrate the magnetically responsive magnetite nanoparticles onto the surface of a PES membrane, in order to improve the membrane's resistance to fouling. Oppositely charged polyelectrolyte layers (polyanion poly sodium 4-styrenesulfonate, PSS and polycation poly diallyldimethylammonium chloride, PDDA) were added to the membrane; to increase the amount of magnetite nanoparticles that can be deposited onto the PES membrane surface. Overall adsorption kinetics and the mass of Fe_3O_4 adsorbed onto the PSS/PDDA–PES membrane surfaces were interpreted using QCM-D for different concentrations of magnetite nanoparticles. The morphologies and surface properties of the newly formed Fe_3O_4 –PES nano-composite membranes were evaluated using atomic force microscopy (AFM), field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS), contact angle measurement and X-ray photoelectron spectroscopy (XPS). All findings from the measurements of adsorption kinetics and surface properties were then correlated to the membrane filtration performances, which was determined based on the permeation flux and humic acid rejection in the absence or presence of an external oscillating magnetic field.

2. Materials and methods

2.1. Chemicals and materials

Neat microfiltration (MF) PES flat-sheet membranes with 0.1 μm pore size were obtained from Koch (Wilmington, Massachusetts, USA). Neat ultrafiltration (UF) PES membranes with molecular weight cut-off 20,000 were obtained from GE Osmonics (Minnetonka, MN, USA). Before use, membranes were washed with 2-propanol (99.8%, Merck, Darmstadt, Hessen, Germany) followed by deionized (DI) water to remove any protective coating layer that may have been present. Iron oxide magnetite nanoparticles Fe_3O_4 were purchased from NanoAmor (Houston, Texas, USA). PDDA (MW 100,000–200,000 Da, 20% aqueous solution) and PSS (average MW approximately 70,000 Da) were supplied by Sigma-Aldrich (St. Louis, MO, USA). PES polymer (Ultrason E6020P with MW 58,000 Da) was obtained from BASF (Ludwigshafen, Germany), and N-methyl-2-pyrrolidone (NMP) was purchased from Merck (Darmstadt, Hessen, Germany). In the present study, PES polymers were spin coated onto the surface of quartz crystal cells to act as the model membrane for QCM-D experiments. Humic acid (HA) obtained from Sigma-Aldrich (53680, CAS no. 1415-93-6, St. Louis, MO, USA) was used as the organic foulant for membrane filtration tests. 1 M of NaOH (Merck, Darmstadt, Hessen, Germany) and 1 M of HCl (analytical reagent grade obtained from Fisher Scientific) were used for pH adjustment. All chemicals were used as received without further purification.

2.2. Surface functionalization of magnetite nanoparticles

Bare Fe_3O_4 nanoparticles were first functionalized using negatively charged PSS polyelectrolytes for better nano-colloid dispersion to aid in forming a composite thin film on PES membranes [30]. The procedure started with dissolving PSS polymer in DI water (0.02 mol L^{-1}) and adjusting the solution pH to 3.5. Similarly, a 2500 mg L^{-1} suspension of Fe_3O_4 nano-colloids was prepared in DI water at pH 3.5. The Fe_3O_4 suspension was added dropwise to the PSS solution under ultrasonication. Physisorption of PSS onto Fe_3O_4 via electrostatic attraction was allowed to occur for 1 day on an end-to-end rotating mixer (Stuart, UK). Finally, the functionalized Fe_3O_4 (F-MNPs) were separated from the bulk solution using a permanent magnet and pre-washed to remove excess PSS before final dispersion in DI water.

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