Fouling-resistant membranes prepared via fully biobased layer-by-layer self-assembly

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Abstract
A fully biobased layer-by-layer deposition method, containing kraft lignin and chitosan as the polyelectrolytes, was employed to improve the anti-fouling properties of polyethersulfone membrane. Results revealed that the water in air contact angle decreased from 70° ± 2° for the pristine membrane to 34° ± 1° for the modified double-bilayer membrane, indicating enhanced hydrophilicity. The synthesized film was ultrathin and caused a slight decrease in permeation flux of the modified membrane compared to the pristine membrane. Additionally, the deposited film showed excellent stability after 6 hours running water test using a dead-end filtration cell. Keywords: Lignin, chitosan, layer-by-layer deposition, polyethersulfone

1. Introduction
Accumulation of agro-industrial waste in large scale results not only in economic problems for companies but also causes environmental deterioration. Among this biomass, lignin is the main waste of paper and pulp industry and commercially available mainly in the form of lignosulfonate and kraft lignin (Aro and Fatehi, 2017; Davis et al., 2016).

Chitosan is also a natural biopolymer that commercially is manufactured on a large scale from chitin (Rampino et al., 2013). Chitin is an abundant biopolymer resulted from the exoskeleton of crustaceans (Rampino et al., 2013).

On the other hand, nowadays, the oil sands industry faces several problems related to produced water treatment (Allen, 2008). Hence, it is imperative to develop new efficient methods for treatment and recycling oil sands produced water. Membrane separation is an emerging water treatment technique that has been turned into a vital part of the oily water treatment (Dickhout et al., 2017). However, fouling has been the obstacle of membrane separation since the birth of this technology (Dickhout et al., 2017; Ding et al., 2016). Engineering the physiochemical characteristics of the membranes to have hydrophilic surfaces can address the fouling problem.

Recently, considerable efforts have been made to effectively use lignin in the modification of membranes to improve properties such as thermomechanical properties, porosity, fouling resistance, etc. Chitosan, also with excellent film-forming properties, has been recently widely employed in membrane modification (Kaner et al., 2015).

This work aimed to prepare layer-by-layer (LbL) assembled polyelectrolyte composite membranes based on chitosan and lignin. To the best of our knowledge, this is the first work reporting the development of chitosan/lignin layer-by-layer membranes supported by polyethersulfone substrate for treatment of oily wastewater.

2. Materials and Methods
Chitosan polycation solution is obtained by dissolving 1 gr of chitosan powder in 5% (v/v) acetic acid solution and lignin polyanion solution is prepared by dissolving 2 gr of lignin in DI water. A clean polyethersulfone substrate is placed in a holder, and chitosan polycation solution is poured over the active surface of the membrane. Then, the membrane is washed with DI water before exposing to the lignin polyanion solution. The cycle is repeated to achieve the desired number of bilayers. To enhance the stability of the layer-by-layer self-assembled film, modified membranes are heat treated using an air circulating oven.

3. Results
To investigate the effect of chitosan/lignin bilayers on the performance of the resulting membranes, pure water flux of membranes with 1 and 2 bilayers was tested using a dead end cell filtration. The results are presented in Figure 1. It can be observed that the permeability (A) of the modified membrane slightly decreased by increasing the number of bilayers, which indicates the formation of an ultrathin film over the surface of membranes.
Figure 1. Flux test performed on pristine, and coated membranes.

To evaluate the hydrophilicity, static water in the air contact angle of the modified and pristine membranes was evaluated (see Figure 2). The results showed that layer-by-layer deposition decreased the contact angle from 70° ± 2° for the pristine membrane to 37° ± 1° and 34° ± 1° for the membrane modified with 1 and 2 bilayers of chitosan/lignin, respectively. This significant increase in the surface hydrophilicity of membrane can be related to the existence of the hydrophilic functional groups in the lignin as the outermost layer of the modified membrane.

Figure 2. The contact angle of (a) pristine (b) single-bilayer and (c) double-bilayer membranes

The surface morphology of the single bilayer membranes was evaluated using FESEM test. Figure 3 presents the FESEM surface images of the pristine (panel a) and the coated membrane with 1 bilayer of chitosan/lignin (panel b). The pristine membrane has a porous structure. The pores were partially covered by the bilayer of chitosan/lignin.

Figure 3. FESEM top surface images of (a) pristine PES support and (b) membrane coated with a bilayer of chitosan/lignin

References