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Case Study

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TREATMENT OF OILY WASTERWATER USING ULTRAFILTRATION MEMBRANES MODIFIED BY NANO PARTICLES

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Abstract: The development of membrane filtration provides a promising alternative for oily produced water treatment. Membrane fouling is a critical issue that affects treatment efficiency and service life of membrane. Membrane surface modification is a viable approach to improve its antifouling ability. In this study, Polyvinylidene Fluoride (PVDF) membrane was grafted with poly(acrylic acid) (PAA) by cold plasma induced graft copolymerization. PAA provided sufficient carboxyl groups as anchor sites for further binding of nano-TiO_2. The nano-TiO_2 binding was achieved through an effective self-assembled technique. The results indicated that both the PAA layer and nano-TiO_2 were uniformly and strongly attached onto the membrane surface. The surface hydrophilicity of modified membrane was significantly improved, which was proved by the decreased water contact angle. The irreversibly binding of super hydrophilic nano-TiO_2 endows the membranes with strong antifouling performance.

Keywords: Membrane; Filtration; Modification; Nano particles

1 BACKGROUND

Oily produced wastewater comes as a bi-product during recovery of natural gas and crude oil from onshore and offshore production operations (Zhao et al., 2014). Over the economic life of a producing field, the volume of produced water can be more than 10 times the volume of hydrocarbon produced. This volume is expected to increase from maturing conventional oil and gas fields (Zhao et al., 2014). Treating produced water from enhanced oil recovery efficiently for beneficial recycle and/or reuse, such as irrigation, reinjection, can mitigate the cost of water disposal, potentially adverse environmental impact and have a significant impact on sustainable development in Canada.

Various studies have been carried out on oily produced water treatment (An et al., 2016), membrane filtration is an alternative technology, which is considered to be with the advantages of simple operation and high treatment efficiency. Many kinds of membranes have been developed and used in produced water treatment (Padaki et al., 2015), in particularly PVDF membrane, it has been widely used because it has excellent thermal stability and chemical resistance to aggressive reagents like organic solvents and acids (Tao et al., 2014). However, it suffers from fouling, the accumulation of contaminants on or within the membrane, which eventually leads to irreversible decline in permeate flux and treatment efficiency (Mondal 2016). To improve the performance of PVDF membranes, membrane modification have been considered as one of potential methods to improve the membrane hydrophilicity and fouling resistance. Recently, the innovative use of TiO_2 nanoparticles (NPs) has gained considerable attention as a means of membrane modification to alleviate fouling (Ong et al., 2015). The challenge to assemble TiO_2 is the need to have key functional groups on the surface of the membrane that can stably hold TiO_2.

Therefore, in this study, PAA will be plasma-grafted on PVDF to facilitate the self-assembly of TiO_2 NPs. PAA is hydrophilic in nature, and its functional groups could strongly bind TiO_2 via ion coordination or hydrogen bonding. To maximize the number of active binding sites, the grafting efficiencies under different conditions of plasma treatment and will be examined. Afterwards, membranes will be immersed in varying concentrations of TiO_2 suspension to evaluate the effect of TiO_2 loading. The surface hydrophilicity of modified PVDF membranes will then be studied.

2 METHODS

Poly(acrylic acid) (PAA), PVDF ultrafiltration membrane (0.1 um pore size), TiO_2 NPs (P25) were used. To stimulate the assembly of TiO_2, four different concentrations of TiO_2 suspension were prepared. The plasma-grafted membranes were dipped in the aqueous TiO_2 suspension to attach TiO_2 NPs. The compositions of modified membrane surface were analyzed using XPS and FTIR. The concentration distribution of nano-TiO_2 on membrane surface was investigated through synchrotron based X-ray fluorescence spectroscopy, which were carried out at the beamline 07B2-1 (VESPERS) at the Canadian Light Source (Saskatoon, Canada). The morphology of membrane surface was tested by SEM. Water contact angles of neat and modified PVDF membranes were measured.

3 RESULTS

The present study investigated the modification of PVDF ultrafiltration membrane for produced water treatment. The activated species of low energy plasma can trigger polymerization reaction of AA monomer on or near the membrane surface with short bursts of plasma exposure. Extreme thin and even PAA coatings without compromising the bulk structure were formed at the membrane surface through cold plasma induced graft copolymerization. The TiO_2 NPs were self-assembled and evenly distributed in the PAA layer. Both the PAA layer and nano-TiO_2 were strongly attached onto the membrane surface. The surface hydrophilicity of modified membrane was significantly improved, the contact angle dropped from 83° before modification to 20° after modification. The irreversibly binding of super hydrophilic nano-TiO_2 endows the membranes with strong antifouling performance.

4 CONCLUSION

This study presented the potential of membrane surface modification for produced water treatment. The results can help to demonstrate the effects of surface modification on antifouling properties of PVDF membranes, and thus help to improve treatment efficiency and maximize membrane life. Further studies are also needed to obtain more theoretical foundation for the mechanisms of membrane antifouling. Different modification approaches for different membrane types will be also investigated for other membrane separation applications.

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