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An in-situ integrated system of carbon nanotubes nanocomposite membrane for oil sands process-affected water treatment

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ABSTRACT

This study evaluates membrane systems for the removal of the extractable organic fraction (EOF) from oil sands process-affected water (OSPW). Experiments were performed using in-situ integrated membrane units that consisted of low pressure-driven membrane (LPM) and high pressure-driven membrane (HPM) modules. LPM was prepared with a polysulfone (PSU) phase inversion casting process and HPM was fabricated by polyamide (PA) thin-film composite (TFC) interfacial polymerization. To change membrane physicochemical properties, each membrane was developed with and without multiwalled carbon nanotubes (MWNTs). The MWNTs were modified with strong acid to enhance dispersion in an organic solvent. Dispersion of the MWNTs and physicochemical properties of the membranes were characterized by microscopic and spectroscopic methods. The results showed that acid-modified MWNTs developed surface functional groups that increased their hydrophilicity, increasing the rejection of hydrophobic pollutants, increasing OSPW permeate flux, and significantly reducing membrane fouling. The LPM and HPM combinations with MWNTs were tested for the optimal organic pollutants removal from OSPW.

1. Introduction

The oil sands industry consumes large amounts of fresh water to extract bitumen from oil deposits in Alberta, Canada. The extraction process generates large volumes of oil sands process-affected water (OSPW) containing 2000 to 2500 mg/L inorganic and organic dissolved solids [1] that include toxic substances such as naphthenic acids (NAs) which is a fraction of the extractable organic fraction (EOF) in OSPW [2,3]. NAs are alkyl substituted cyclic and noncyclic carboxylic acids with the general formula $C_nH_{2n+Z}O_x$, where n is the carbon number and Z is zero or a negative even integer related to the number of rings in the molecule, and x is 2 (NAs), and 3 to 5 (oxidized NAs) [2,4]. NAs concentrations account for nearly 50% of the entire EOF in OSPW [3]. EOF is one of most critical components in OSPW because the toxicity of OSPW to organisms is believed to be caused by the polar organic carboxylic acids [3,5], among other components of EOF [6]. Therefore, research efforts focused on OSPW remediation are concerned with the cost-effective removal of the EOF from OSPW as well as ionic species so that the water can be reused in the bitumen extraction process or safely discharged to the receiving environment.

Coagulation, flocculation and sedimentation (CFS) [2], adsorption [7], advanced oxidation [6,8], bioreactors [3,9], and membrane filtration [10] have been introduced to treat OSPW. To reduce the total dissolved solids (TDS) level in OSPW, membrane filtration can be applied because membrane is one of the best technologies to remove dissolved solids and ionic species from the water phase [11,12]. However, pretreatment of OSPW is required because OSPW contains high concentrations of solids and particulates (total suspended solids (TSS)) and organics. It is important to remove TSS before applying the membrane to reduce membrane fouling. For instance, CFS pretreatments [11] or low pressure-driven membrane prefiltration [13] can be used to remove TSS, and ozonation [14] or advanced oxidation processes can be applied to reduce organic species before applying nanofiltration (NF) and reverse osmosis (RO) treatments.

Among these technologies, the membrane prefiltration by low pressure-driven membranes (LPM), such as microfiltration (MF) and ultrafiltration (UF) membranes, are commonly selected to remove particles, colloids, and turbidity during municipal and industrial wastewater treatment [15,16], biopharmaceutical industry for wastewater treatment [17], distillation plant for water desalination [18] and food industries for water purification and wastewater treatment [19,20]. However, those case studies have shown that membrane fouling on LPM, which reduces permeate flux and increases trans membrane pressure (TMP), resulting in an increases in operating and maintenance costs. Therefore, it is necessary to reduce the membrane fouling on the LPM in the membrane prefiltration process.

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The applications of nanomaterials in polymeric membranes have received wide attention due to their ability to enhance permeate flux and reduce membrane fouling [21,22]. By altering the nanomaterials in membranes (i.e., nanofiller), the physicochemical properties of the membrane can be manipulated. Titanium dioxide [21,23,24], zeolites [25,26], silver [27,28], and carbon nanomaterials [22,29,30] are commonly used for fabrication of nanocomposite membranes. The carbon nanotubes (CNTs) are the most widely used in membrane applications for water and wastewater treatment, because they have excellent mechanical, electrical, thermal, and antibacterial properties [31,32] and are also efficient adsorbents of solids in water and wastewater treatment processes [33]. Membrane roughness, surface functional groups, hydrophilicity, and fouling can influence permeate fluxes of CNT composite membranes [31,34,35]. Two types of nanocomposite membranes, mixed matrix membranes (MMM) and thin-film nanocomposites (TFN), have been developed to optimize the advantages of nanomaterialsin water and wastewater treatment [36–38].

This study evaluated LPM with and without acid-modified multiwalled CNTs (MWNTs) for in-situ pretreatment of OSPW before final treatment with high pressure-driven membranes (HPM) with and without acid-modified MWNTs. Raw OSPW was applied to the integrated membrane system (i.e., combinations of LPM and HPM), and pressurized to reject EOF and ionic species from feed water. A flow diagram of the experimental setup is shown in Fig. 1; N denotes the presence of MWNTs: pretreatment of OSPW with LPM and subsequent treatment with HPM (Fig. 1a), pretreatment of OSPW with MWNTs embedded LPM (NLPM) and subsequent treatment with HPM (Fig. 1b), and pretreatment of OSPW with NLPM and subsequent treatment with MWNTs embedded HPM (NHPM) (Fig. 1c). Membrane permeate flux, rejection ratios of EOF and ionic species, and fouling index and recovery of membranes were examined to evaluate the performance of the integrated system. Several physicochemical properties such as hydrophobicity, morphology, roughness and surface functional groups of membranes were investigated in regard to their impacts on the OSPW treatment efficiency.

2. Materials and methods

2.1. Chemicals and source water

Certified ACS grade polysulfone (PSU) ($MW=16{,}000$, transparent pellets), polyvinylpyrrolidone (PVP) ($MW=10{,}000$), 1,3,5-benzenetricarbonyl trichloride (TMC) ($>98\%$), and 1,3-phenylenediamine (MPD) ($\geq 99\%$) were purchased from Sigma-Aldrich, St. Louis, MO, USA; *n*-hexane (95%, Sigma-Aldrich, St. Louis MO, USA) and anhydrous *N*,*N*-dimethylformamide (DMF) (99.8%, Sigma-Aldrich, St. Louis MO, USA) were used to solvate the polymers. MWNTs (average diameter 5–10 nm, length 10–30 μm, specific surface area $>200\ \mathrm{m^2/g}$) were purchased from Sun Innovations Inc., Fremont, CA, USA.

OSPW was obtained from the West in Pit, Syncrude Canada Ltd., Fort McMurray, AB, Canada; OSPW characteristics are listed in Table 1. Tested OSPW contained high TDS and TSS concentrations that can develop severe membrane fouling [11,12], and high EOF of OSPW increased the OSPW toxicity [3,6]. The concentration range of salts (e.g., sodium and chloride) makes OSPW considered to be slightly brackish water [1]. OSPW was stored in a container at 4 °C and was well mixed before being treated. The in-situ integrated membrane treatment system was configured to be operated in a batch mode in which retentate was directed back to the feed tank (Fig. 1).

2.2. Modification of MWNTs and membrane preparations

MWNTs are naturally hydrophobic and have low solubility in all solvents [39], thus, surface modification is necessary to fabricate a homogeneous nanocomposite membrane. MWNTs

Table 1
Physicochemical properties and composition of fresh OSPW.

Parameters	Concentration
Physicochemical property	
Turbidity, NTU	71.6 ± 0.2
Conductivity, μS/cm	3459 ± 7.9
Total suspended solids (TSS), mg/L	97.0 ± 0.2
Total dissolved solids (TDS), mg/L	2477 ± 2.2
Chemical oxygen demand (COD), mg/L	243.1 ± 0.8
Extractable organic fraction (EOF), mg/L	64.2 ± 2.4
Cations	
Lithium, mg/L	0.23 ± 0.01
Sodium, mg/L	846.7 ± 6.1
Potassium, mg/L	17.0 ± 0.2
Magnesium, mg/L	15.1 ± 0.4
Calcium, mg/L	25.3 ± 0.9
Anions	
Fluoride, mg/L	2.63 ± 0.08
Chloride, mg/L	715.7 ± 17.0
Nitrite, mg/L	5.81 ± 0.12
Nitrate, mg/L	34.0 ± 0.3
Sulphate, mg/L	602.6 ± 14.2

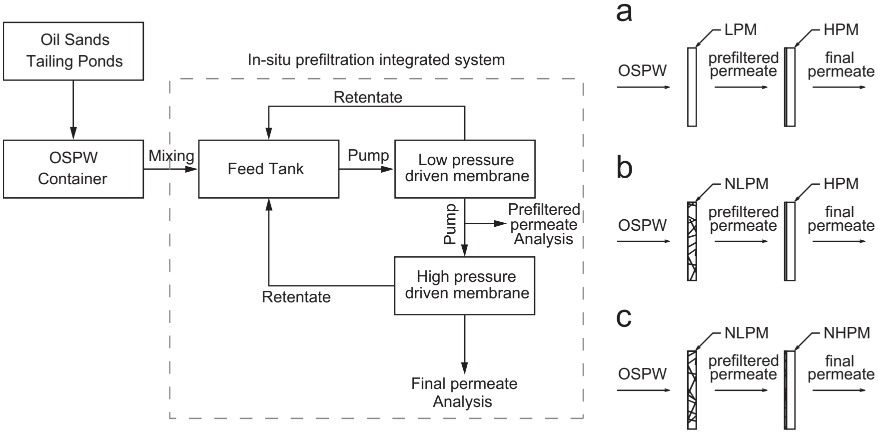

Fig. 1. The schematic diagram of proposed system.