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# Preparation, characterization and performance of poly(*m*-phenylene isophthalamide)/organically modified montmorillonite nanocomposite membranes in removal of perfluorooctane sulfonate

*Qin Luo*[1,2], *Yanxia Liu*[1], *Guixia Liu*[1,*], *Changwei Zhao*[2,*]

1. *Key Laboratory of Applied Chemistry and Nanotechnology at Universities of Jilin Province, Changchun University of Science and Technology, Changchun 130022, China*
2. *State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China*

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ABSTRACT

Nanocomposite membranes containing poly(*m*-phenylene isophthalamide) (PMIA) and organically modified montmorillonite (OMMT) were prepared by a combination of solution dispersion and wet-phase inversion methods, and the effects of OMMT addition on the properties and performance of fabricated nanofiltration membranes were investigated. The membranes were characterized by contact angle measurements, scanning electron microscopy (SEM), atomic force microscopy (AFM), thermogravimetric analysis, and zeta potential. The performance of the membranes was elucidated by the removal of perfluorooctane sulfonate (PFOS) at neutral pH. Increasing OMMT concentration improved the thermal stability and hydrophilicity of the membranes. The permeation and rejection of PFOS were significantly improved. The performance of fabricated nanofiltration membranes in removal of PFOS varied depending on the solute and membrane properties as well as solution conditions. Finally, a comparison between fabricated membranes and a commercial NF membrane (ESNA1-K1, Hydecanme) proved that the OMMT addition is a convenient procedure for producing nanocomposite membranes with superior properties and performance.


## Introduction

In recent years, there has been increasing concern about the global contamination of water environments caused by the widespread use of perfluorinated compounds (PFCs). Potassium perfluorooctane sulfonate (PFOS) is a typical PFC and has a range of applications, *e.g.*, in surfactants, fire retardants, lubricants, and polymer additives (Moody et al., 2001; Giesy and Kannan, 2001; Moody and Field, 2000). Although PFOS was listed as a persistent organic pollutant (Tang et al., 2006), its use is still allowed in some industries, *e.g.*, chrome plating in China. It has been reported that the concentrations of PFOS in surface waters near industrial zones were as high as 5.7 μg/L (Rattanaoudom et al., 2012). It is important to remove PFOS from such point sources before discharge into the environment. However, PFOS is very stable, and it is difficult to decompose in ambient environments using conventional techniques, such as biological degradation, oxidation, and reduction (Vecitis et al., 2009). Conventional

* *Corresponding authors.* E-mail address: liuguixia22@163.com (Guixia Liu).

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treatment methods are inadequate and may even produce toxic byproducts. The performance required of removal processes is also becoming increasingly stringent. Membranes provide an alternative method for effectively removing PFOS from wastewater; they are cheap, simple to operate, and use less chemicals (Baker, 2004).

Nanofiltration membranes are one of the most important types of membrane for the removal of multivalent ions and organic compounds (100–1000 Da), especially persistent organic pollutants, from water and wastewater sources. Research on improving nanofiltration properties has focused on modification of membrane materials, in order to increase the strength, heat resistance and so forth. Among various inorganic fillers, *e.g.*, zeolites (Gevers et al., 2005), inorganic compounds (Rajesh et al., 2012; Fang and Duranceau, 2013; Romanos et al., 2012; Pourjafar et al., 2012; Namvar-Mahboub and Pakizeh, 2013; Gholami et al., 2014; Chen et al., 2014), and ceramic oxides (Schmidt et al., 2014; Zhang et al., 2014; Pages et al., 2013), layered silicates are of particular interest, because they can be dispersed in polymeric matrices at the nanoscale. The most-used clays in polymer-clay nanocomposites (PCNs) are those containing smectite clay minerals, particularly organomontmorillonite (OMMT). OMMT is a hydrophilic clay, and its addition at low contents (<10 wt.%) can be useful for producing PCNs with improved properties, and for enhancing the hydrophilicity of the material (Rajesh et al., 2012; Gevers et al., 2005; Schafer et al., 2004; Anadão et al., 2010).

Despite nanocomposite membranes' potential for application in the field of nanofiltration, only a few studies have been devoted to these membranes (Anadão et al., 2010; Monticelli et al., 2007). Poly(*m*-phenylene isophthalamide) (PMIA) is widely used in membranes for various applications (Cheng et al., 2000; Wang et al., 2013; Ren et al., 2010; Yu et al., 2013). In this work, we prepared and characterized PMIA-based nanocomposite membranes containing various concentrations of commercially available OMMT, using a combination of solution dispersion and wet-phase inversion methods. The performance of fabricated membranes was evaluated in terms of the permeation and rejection of solutions containing the selected perfluorooctane sulfonate (PFOS) under different solution conditions. Finally, the ability of these nanocomposite membranes in the removal of PFOS was compared with a commercial nanofiltration membrane, ESNA1-K1.

## 1. Experimental

### 1.1. Materials

Fibrous PMIA was obtained from the Yantai Spandex Co., Ltd. (China); its chemical structure is shown in Fig. 1. The polymer

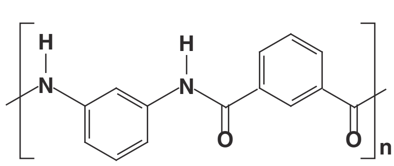

**Fig. 1 – Chemical structure of poly(m-phenylene isophthalamide.**

was dried for at least 5 hr at 80°C and then used to prepare a polymer solution. Analytical grade *N*, *N′*-dimethylacetamide (DMAc) and LiCl, used as the solvent and cosolvent, respectively, were purchased from the Tianjin Fuchen Chemicals Reagent Factory (China). OMMT clays were purchased from the Beijing Eastwest Specialty Chemicals Co.; schematic drawings are shown in Fig. 2. PFOS (99%) was purchased from AccuStandard, Inc. (USA). A commercial composite polyamide nanofiltration membrane, ESNA1-K1, was kindly supplied by Hydecanme, as a flat sheet. Each experiment was carried out twice and double-distilled water was used in all the experiments.

### 1.2. Feed

Nanofiltration was carried out with a solution containing PFOS with a concentration of 100 μg/L and at solution pH value of 7.0. Due to their p$K_a$, perfluorooctane sulfonate (PFOS) molecules are ionized and therefore negatively charged at both neutral and acid solution pH values.

### 1.3. Preparation of pristine PMIA membrane

A casting solution containing PMIA (20 wt.%) dissolved in DMAc was prepared by stirring for 8 hr at 5.0 Hz (300 r/min) and 50°C. The solution was cast by spreading on a glass plate substrate, using a laboratory-made casting knife, at a thickness of 250 μm. The substrate then was moved to a non-solvent (water) bath for immersion precipitation at room temperature. After primary phase separation and formation of the membrane, it was stored in water for 24 hr to guarantee complete phase separation. This allowed the water-soluble components in the membrane to leach out. The rejection of NaCl and $MgSO_4$ by the PMIA membrane were respectively about 27% and 48%, with a feed concentration of 500 mg/L under $5.5 \times 10^5$ Pa. According to the parameters provided for the commercial NF membrane, under the same conditions, the rejection values of the commercial membrane were greater than 92%.

### 1.4. Preparation of nanocomposite membranes

Nanocomposite membranes were prepared using a combination of wet-phase inversion and solution dispersion techniques. Dispersions with various OMMT contents (0.5%–5%) and 20 wt.% PMIA in DMAc were prepared under vigorous mechanical stirring for 8 hr at 50°C. First, one-quarter of the 20 wt.% PMIA was added, and after solubilization, one-quarter of the total amount of OMMT was added. This procedure was continued until both additions were complete, as previously reported by Anadão et al. The casting and immersion of the nanocomposite membranes were performed using the same method as for the pristine PMIA membrane.

### 1.5. Membrane characterization

The surface morphologies and thicknesses of the synthesized membranes were examined using scanning electron microscopy (SEM; SU8000, HITACHI) and atomic force microscopy (AFM; Digital Instruments, USA). The arithmetic average ($R_a$) roughness of the membranes was estimated from topographic images of area 5 μm × 5 μm. The static water contact angles of the