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Bio-inspired, fouling resistant, tannic acid functionalized halloysite nanotube reinforced polysulfone loose nanofiltration hollow fiber membranes for efficient dye and salt separation

G.P. Syed Ibrahim[a,c], Arun M. Isloor[a,c,*], A. Moslehyani[b,c], A.F. Ismail[b,c]

[a] Membrane Technology Laboratory, Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Mangalore 575 025, India
[b] Department of Chemical and Biological Engineering, University of Ottawa,161 Louis Pasteur St., Ottawa, ON K1N 6N5, Canada
[c] Advanced Membrane Technology Research Center (AMTEC), Universiti Teknologi Malaysia, 81310 Skudai, Johor Bahru, Malaysia

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ABSTRACT

Superficial functionalization of the hollow fiber membrane with progressive nanomaterials exhibits increased hydrophilicity, outstanding selectivity, and permeability. In the present study, a simple and novel loose nanofiltration (NF) membranes were prepared by the addition of tannic acid functionalized halloysite nanotubes (THNTs) in polysulfone (PSf) membrane matrix via phase inversion method. The successful modification of halloysite (HNTs) was confirmed by FT-IR, zeta potential measurement, TGA, TEM and EDX analysis. The membrane permeation studies were carried out with a sequence of salts (NaCl and Na_2SO_4) and dyes (reactive black 5 and reactive orange 16). The resulted membranes exhibited increased hydrophilicity, porosity, water uptake, antifouling performance, along with higher dye rejection (> 99% for reactive black 5 and > 90% of reactive orange 16) and low salt rejection (2.5% of NaCl and 7.5% of Na_2SO_4) properties. The nanocomposite membrane also exhibited the highest pure water flux of 92 L/m^2 h compared to the pristine membrane of 18 L/m^2 h made it a worthy candidate for the wastewater purification.

1. Introduction

The increased concentration of pollutants is inflowing water provisions through anthropogenic sources, affecting in the insufficient entry to clean water for the rising worldwide inhabitants [1]. The wastewater from the industries such as a dye, paper, paint, and tanneries are needed to treat appropriately before discarding or recycling. The direct discharge of organic dyes into water stream lead to severe environmental imbalance, as most of them are non-biodegradable, toxic and consume dissolved oxygen [2–4]. More complex structure, high molecular weight and synthetic origin of reactive dyes make them more stable, particularly even just 1.0 mg/L concentration in drinking water possibly will impart color [5,6]. In dye industry, water is employed primarily as steam for heat treatment of the bath and then for transferring dyes to the fibers. The dyeing of about 1 kg of cotton needs around 152 L of water, ~0.8 kg of NaCl and somewhere around 60 g of dyestuff [7]. Therefore, reclamation of dye from wastewater has excessive importance. Furthermore, inorganic salts such as NaCl (~6 wt %) and Na_2SO_4 (~5.7 wt%) were incorporated to improve dye pickup ability of the cotton and during synthesis of dye, quite large amount of low molecular weight intermediates are produced [8]. The occurrence of inorganic salts not only restraining the biodegradation of dyes but complicates the treatment processes as well [9,10]. In the thought of sustainability, the recovery of dyes and salts from the wastewater needs a new technique which is cost effective, less time consuming and environmental friendly. Conventional methods, such as electrochemical [11,12], oxidation [13], coagulation by polymeric aluminum species [14] are having the similar disadvantages that, the resources are not recycled adequately [15].

The employment of loose nanofiltration (NF) membrane has been recognized as the complementary nominee for the wastewater management as it has advantages like low cost, low operating pressure, environmentally friendly, less energy consumption, high dye rejection and high salt permeability [16–18]. Even though NF has the capacity to reject more than 99% of dyes, it has a high rejection of inorganic salts (> 30% NaCl), membrane fouling, concentration polarization and molecular weight cut-off (MWCO) of 100–1000 Da signifying the near pore size of 1 nm. Unavoidably, NF requires a high frequency of chemical cleaning, which would affect the lifespan of membranes. The above shortcomings make the NF as the insignificant candidate for the separation of dye/salt mixture [19–22]. Therefore, it is of prime importance to study the loose NF membranes. Lin et al. reported the

* Corresponding author at: Membrane Technology Laboratory, Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Mangalore 575 025, India.
E-mail address: isloor@yahoo.com (A.M. Isloor).

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separation of direct dye and salt in aqueous solution. The results exhibited that, 99.0% of dye retention with 95% of NaCl permeation [23]. According to Yu et al. the poly (ionic liquid) functionalized SiO_2 loose NF membrane showed the increased permeation of salts with high rejection of dyes [24]. Lixin et al. prepared negatively charged PSS-SiO_2 incorporated PES membranes for the high rejection of dyes with less than 11% of salt rejection [6]. Liang et al. reported the positively charged hydrotalcite nanosheets modified by poly (ionic liquid). The loose NF membrane could reject 95% of reactive black 5 and around 90% of reactive red 49 with non-zero salt rejection properties [25]. Junyong et al. investigated the effect of adding chitosan-montmorillonite nanosheets to loose NF membranes and the modified membrane exhibited high rejection of reactive red 49 and reactive black 5 along with high salts permeation [26].

Polysulfone (PSf) is one of the perfect polymeric material for the preparation of membranes, mostly because of its high thermal stability, long range of pH and chlorine tolerance along with outstanding chemical resistance [27–29]. However, the pristine PSf membranes are suffering from severe fouling. The fouling of membrane can be ascribed mainly due to the lesser hydrophilicity of the membrane. Since PSf membrane is less hydrophilic, it would foul very fast and the lifespan of the membrane would be reduced to a great extent. Consequently, the maintenance cost of the membrane would be enhanced. Of late, significant extent of efforts has been taken to improve the innovative composite polymeric membranes for obtaining better surface hydrophilicity and antifouling performances [30–33]. Sharma et al. prepared PSf ultrafiltration membranes using racemic and enantiomeric tartaric acid as an additive. It is reported that the as-prepared membrane exhibited the enhanced removal of crystal violet dye [34]. Chai et al. demonstrated the preparation of PSf-Fe_3O_4/GO mixed matrix membranes for humic acid rejection [35]. In 1966, Mahon prepared the first hollow fiber (HF) membranes [36]. Related to flat sheet membranes, the HF membrane is the superior of membrane since it has the following advantages: (i) the increased surface area per unit volume of membrane module, which renders enhanced efficiency; (ii) easy cleaning, handling, and preparation; (iii) consistent results; (iv) it does not need any mechanical support [37,38]. In recent days, HF membranes are also used in gas separation, reverse osmosis (RO), ultrafiltration (UF), dialysis and pervaporation.

Over the past decades, Halloysite nanotubes (HNTs) has received greater attention by the researchers due to its efficacy in the different fields. Fig. 1 denotes the increased attention paid towards the HNTs for the past few years. These data are attained based on Scopus database. Moreover, HNTs is very cheap, non-toxic and extensively found in soils worldwide. On the other hand, the foremost morphology of HNTs is elongated tubule with the diameter of 50–100 nm and length of 100–2000 nm [39]. Fig. 2 represents the structure of HNTs. Moreover,

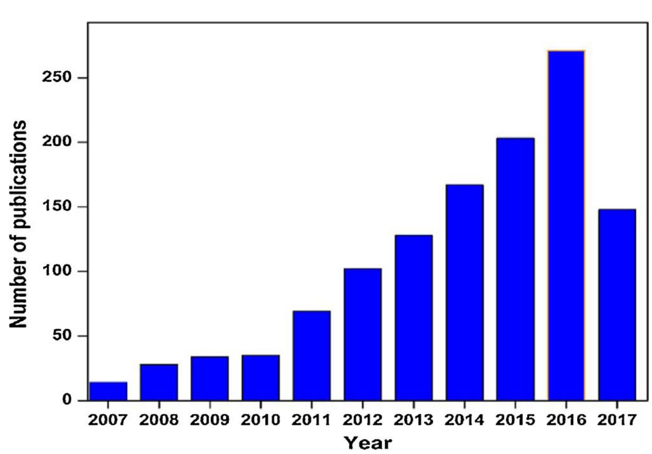

Fig. 1. The number of publications based on the keyword "Halloysite nanotube" (Scopus; as on 06th July 2017).

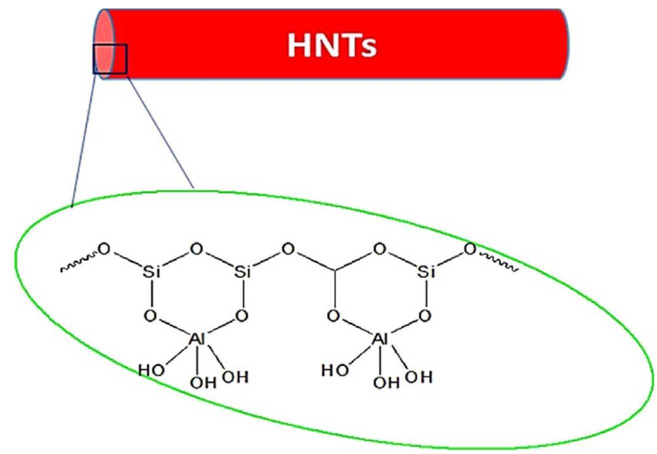

Fig. 2. The structure of HNTs.

the lumen surface of HNTs is covered with alumina and the outer surface is covered with silica predominantly, as a result it is having the net negative charge on the outer surface [40,41]. The presence of plenty of hydroxyl groups on the surface of HNTs makes the nanomaterial more hydrophilic and easy for further modifications. Nevertheless, to reject the anionic dyes based on the electrostatic repulsion, the HNTs must be functionalized with selected worthy materials.

Messersmith et al. reported facile and one step modification using polydopamine (pDA) as an effective modifier [42]. According to Hebbar et al. the pDA coated HNTs enhanced the flux, porosity, antifouling, and antibiofouling properties of the as-prepared membranes [43]. Although pDA is unsophisticated to use on any substrate and offers many potential applications, the cost of dopamine and typical dark color of pDA coating would impairment some hands-on applications [44,45]. Tadas et al. described the usage of polyphenols as an active alternative to pDA for the surface coatings [45]. Inspired by the phenomenon of staining of teacups by the tea water, the plant-based polyphenol such as tannic acid (TA) was identified as the universal coating. These type of biomolecules consist of dense gallol functional groups and thus exhibit strong solid-liquid interfacial properties [46]. TA is the low-cost, environmental friendly polyphenol. The commercial slight yellowish amorphous TA powder is straight away extracted from the plants. In tanneries, TA is used for the tanning of leathers. TA holds numerous advantages similar to pDA and deposits under similar conditions. Moreover, it is hundredfold cheaper and delivers colorless multifunctional coatings. The presence of plenty of hydroxyl groups in TA make the coating more hydrophilic and enhance the surface charge. In addition, it has excellent resistant towards the fouling by bacterial and mammalian cells [47]. Kunping et al. studied the effect of adding TA coated graphene. The results indicated that the functionalized graphene showed excellent adsorption capacity towards the Rhodamine B from the aqueous solution [48]. According to Li et al. the maleimido-containing TA coated stainless steel surface exhibited outstanding antifouling character [49]. Xi et al. stated the co-deposition of TA and diethylenetriamine (DETA) on the commercially available polypropylene and poly (vinylidene fluoride). The modified membranes displayed high water flux, hydrophilicity and more surface wettability [50]. Yan et al. examined the performance of NF membrane via interfacial polymerization of TA and trimesoyl chloride. The thin film composite membrane exhibited the enhanced permeation and antifouling performances along with excellent chemical stability [51]. Lin et al. demonstrated the use of TA coating on iron ions via coordination. The results showed that, the increased ratios of dye and salt rejection with the antioxidant ability [52]. Xi et al. reported that the as-formed interlayer using TA and diethylenetriamine in the thin-film composite membrane, enhanced the flux and rejection capacity as the interlayer assisted in the formation of defect-free polyamide layer [53].