Separation and Purification Technology 157 (2016) 229–240

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Novel carbon-nanoparticle polysulfone hollow fiber mixed matrix ultrafiltration membrane: Adsorptive removal of benzene, phenol and toluene from aqueous solution

Raka Mukherjee, Sirshendu De *

Department of Chemical Engineering, Indian Institute of Technology Kharagpur, Kharagpur 721302, India

ARTICLE INFO

Article history:
Received 29 June 2015
Received in revised form 7 November 2015
Accepted 12 November 2015
Available online 14 November 2015

Keywords:
Activated carbon nanoparticle
Hollow fiber
Mixed matrix membrane
Benzene adsorption
Breakthrough

ABSTRACT

Novel mixed matrix (MMM) hollow fiber membranes were prepared and characterized with varying concentration of super adsorbent carbon nanoparticle and polysulfone. Nanoparticles accumulated on the membrane surface, enhancing surface roughness, improving hydrophilicity and mechanical strength but reducing porosity and permeability. The hollow fibers had positively charged surface at pH 7, with point of zero charge at 8 and had high adsorption capacity (q_{max}) for benzene, toluene and phenol. MMM with 4 wt% of carbon nanoparticle showed q_{max} = 67 mg/g for benzene at pH 4. Performance of the membranes was tested in terms of removal of benzene, toluene and phenol from aqueous solution. MMM with 2 wt% of nanoparticle was selected as optimum membrane having a trade-off between permeate flux and rejection values. Desired condition for filtration of benzene was found as 69 kPa trans-membrane pressure and 10 l/h cross flow rate, with more than 97% rejection of benzene. Around 15 h of breakthrough time was obtained with 0.028 m^2 area for all three solutes. Developed membrane can offer one stage filtration combining adsorption and filtration, making it a potential medium for treatment of industrial effluent.

1. Introduction

Presence of organic contaminants in aqueous streams, particularly from the pesticides, petrochemicals, printing and pharmaceutical discharges, causes risk to human health and ecological system [1,2]. Major pollutants from these industries are volatile organic compounds, particularly benzene and its derivatives. Benzene is carcinogenic to human and it features in the list of top ten most hazardous chemicals of United States Environmental Protection Agency [3]. In the last decade, attempts have been made to remove organic contaminants from water using various technologies such as advanced oxidation [4], coagulation [5], adsorption by activated carbon [6], chemical treatment [7] and biosorption [8]. Among these techniques, adsorption by activated carbon is widely employed, as it is useful for removing variety of organic materials with high capacity. However, being a physical and rate governed process, membrane separation is faster and more efficient compared to the equilibrium driven processes, like adsorption. Since, conventional membrane separation is based on molecular sieving, dense membranes are required for separation of organic compounds, resulting in an energy intensive process. There are very few reports of removal of organic contaminants using reverse osmosis [9], nanofiltration [10] and pervaporation membranes [11]. Disadvantages of such processes are high energy requirement and ineffectiveness for solute removal in trace amounts. A few researchers have used hybrid process schemes using activated carbon followed by membrane filtration [12,13]. These hybrid schemes require more than one stage applications and hence, are complex, time consuming and their operation and maintenance become critical. However, the present state of the art in membrane science involves combining two features, namely, adsorption of smaller solutes and filtration of larger solutes in one step in the form of mixed matrix membrane (MMM). Highly selective removal using more open membrane is possible through this process. Hence, MMM has found immense application in selective solute removal with high throughput at lower operating pressure [14,15]. Balta et al., have shown that MMM with zinc oxide nanoparticle can be applied in purification of dye solution by excellent tuning of hydrophilic properties [16]. Adsorption of bovine serum albumin on a composite membrane can lead to good rejection of the protein [17]. Poly ether sulfone/Fe–Mn binary oxide ultrafiltration mixed matrix membrane can remove As (III) from contaminated water [18]. Campbell et al., have demonstrated that

---

* Corresponding author.
E-mail address: sde@che.iitkgp.ernet.in (S. De).

http://dx.doi.org/10.1016/j.seppur.2015.11.015

Nomenclature

A_T	Temkin isotherm equilibrium binding constant (l/g)
b_T	Temkin isotherm constant
C_e	equilibrium concentration (mg/l)
K_F	Freundlich isotherm constant (mg/g)(l/g)^n
K	Langmuir isotherm constant (l/mg)
N	adsorption intensity
q_e	amount of adsorbate in the adsorbent at equilibrium (mg/g)
R	universal gas constant (8.314 J/mol K)
T	temperature (K)
v_m	maximum monolayer coverage capacity (mg/g)

MMM with metal organic framework can be used efficiently for filtration of polystyrene solution [19].

In this context, applicability of carbon nanoparticle embedded MMM is relevant. These nanoparticles are well known for their good adsorption capacity but a fixed bed of these in an adsorption column results in extremely high pressure drop rendering the process difficult to operate. On the other hand, MMM can work at much lower operating pressure drop leading to less energy consumption. Secondly, the separation of pollutant loaded toxic nanoparticles from the filtrate becomes a limitation in a fixed bed of these particles. In case of MMM, the immobilization of carbon nanoparticle in the membrane matrix precludes the mixing with filtrate. Also, removal of suspended solids by sieving mechanism from effluent by the membrane is an added advantage. This makes specific removal of lower molecular weight toxic solutes in an effluent by MMM superior to a conventional adsorption column [20].

Choice of polymer is also important for extended life and application of the membrane. Polysulfone (PSF) has high affinity toward water, good thermal and chemical resistance, and low fouling tendency and is stable in wide pH range and it is selected as base polymer in many studies [21].

For real life cost effective application of membrane separation, low pressure membrane modules in continuous mode are essential. Hollow fibers are important in this regard providing high filtration area in low volume. However, preparation of mixed matrix hollow fibers is not attempted extensively due to challenges associated in demixing stability of polymer–inorganic solution and controlling the rheological characteristics for spinning the fibers. Often the hollow fibers are surface modified by chemical treatment, graft polymerization and interfacial polymerization to improve their efficiency. However, all the surface modifications are aimed at constricting the pore size (reduction in molecular weight cut off) of the membrane resulting to decrease in its permeability [22]. A recent study by de Grooth et al., reported salt removal with nanofiltration hollow fiber membrane, coated with charged polyelectrolytes [23]. However, low permeability leads to low throughput, restricting real life application. As the surface charge of MMM can be tailor made, it is effective for removal of charged solutes as well. Removal of nitrate is reported using microfiltration hollow fiber membrane doped with activated alumina nanoparticles [24]. However, in this case, activated alumina nanoparticles have specific adsorption property to nitrate.

The present study is focused on removal of benzene and its derivatives from water using novel ultrafiltration mixed matrix membrane prepared by dispersing activated carbon nanoparticles in polysulfone matrix. As per the authors' knowledge, this is the first study on removal of organic compounds using mixed matrix polymeric hollow fibers. Having high adsorption capacity, carbon nanoparticles cannot be used in adsorption bed owing to large pressure drop and difficulty in separation from the filtrate as discussed earlier. Thus, it is envisaged to immobilize carbon nanoparticles in polymeric membrane matrix offering one stage filtration for carcinogenic organic compounds at minimal pressure drop, making it highly potential separation device. The interaction between the polymer chains with carbon nanoparticle was investigated in this work. Performance in terms of throughput and removal efficiency of aromatics was evaluated for different nanoparticle concentration and an optimum membrane composition was selected. The hollow fibers were characterized in terms of their molecular weight cut-off, permeability, porosity, morphology, hydrophilicity, fourier transform infrared spectroscopy (FTIR) analysis, mechanical strength, surface charge and adsorption properties. Effects of solution pH, cross flow rate and transmembrane pressure on the performance were studied. Long duration experiments were performed to estimate the breakthrough capacity.

2. Materials and methods

2.1. Materials

Polysulfone (average molecular weight 22,400 Da) was supplied by Solvay Chemicals, Mumbai, India. N,N-dimethyl formamide (DMF), polyethylene glycol (molecular weight 400, 600 Da and 4, 6, 10, and 20 kDa), benzene, toluene and phenol were procured from Merck (India) Ltd., Mumbai, India. The carbon nanoparticles were obtained from US Research Nanomaterials Inc. Houston, USA. For preparation of phosphate buffer, di-potassium hydrogen phosphate and potassium di-hydrogen phosphate, hydrochloric acid and sodium hydroxide were purchased from Merck (India) Ltd., Mumbai, India.

2.2. Hollow fiber module preparation

2.2.1. Preparation of casting solution

The casting solution for MMM consisted of PSF, as base polymer, DMF as solvent and carbon nanoparticle as additive. Concentration of PSF was kept constant at 20 wt% for uniform membrane matrix and good mechanical strength [25]. Concentration of nanoparticles was varied from 0.5 to 4 wt% and the rest was DMF. First, PSF was mixed with DMF completely, using magnetic stirrer at 60 °C for 6 h. Required amount of nanoparticles was then added in the solution under continuous magnetic stirring at the same temperature. After one hour of stirring, the mixture was sonicated using probe type sonicator for one hour to obtain homogeneous dispersion of nanoparticles [26,27]. Sonication was performed at 50 Hz, with 10:4 s on off pulse and with 250 W power. The sonicator was manufactured by Optic Invymen System, model CY-500, Las Rozas de Madrid, Spain. This method of preparation of casting solution was reported by Mukherjee and De [24].

2.2.2. Fiber spinning and module preparation

The hollow fiber was spun by wet-spinning method, using a two-needle assembly. Details of the spinning conditions and module preparation are supplied in the supporting document (section S.1). The membranes with 0, 0.5, 1, 2 and 4 wt% carbon nanoparticles are named as M0, M0.5, M1, M2 and M4, respectively.