



Preparation of nanoporous composite carbon membrane for separation of rhodamine B dye

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ABSTRACT

In this work, a clay-supported carbon membrane has been synthesized by carbonizing a blend of polyethylene glycol and resole-type phenol formaldehyde resin at 500 °C. The membrane thus prepared was characterized with respect to its pore structure and surface morphology. The hydraulic permeability was found to be considerably higher than that reported in literature. The thickness of the carbon membrane was determined to be 30 μm and the molecular weight cutoff experiments gave the average pore size of 1.8 nm. Experiments show that the real rejection of the dye is in the range of 90–100% and depends on the pressure and concentration of the dye. In the pH range of 6–8, the dye tends to dimerize and forms greater aggregations due to attractive electrostatic interaction, suggesting separation of the dye from its solution due to sieving by the membrane. In addition, since the membrane has charge opposite to that of the dye, it is likely that the latter may have adsorbed on the pore mouth as well as pore wall, this way offering much lower pore diameter than 1.8 nm to the flow of dye solution.

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1. Introduction

Industries such as textile, paper, plastics etc. release color to water bodies and even the presence of very small quantities (less than 1 ppm) is noticeable and unacceptable. Dye separation from industrial effluents is one of the most important environmental concerns [1] and the widely used methods for dye removal are chemical, physical and biological methods. The chemical methods include oxidative processes like using Fenton's reagent [2], sodium hypochlorite [3], ozonation [4] and photochemical methods [5]. Various physical treatments include membrane separation processes, adsorption (activated carbon, peat, wood chips, silica gel and fly ash and coal mixture), ion exchange, irradiation and electrokinetic coagulation that have been reviewed recently [6]. The biological methods include decolorization by white-rot fungi [7] and many more microorganisms reviewed by Forgacs et al. [8].

There are certain advantages and limitations of each method and cannot be used to separate all classes of dyes. Membrane separation processes allow the removal and recovery of dyes, chemicals and water without the degradation of the components or the addition of chemicals, acting purely as a physical barrier. However, most of the commercial nanofiltration membranes are made of polyamide which has a tendency to adsorb dyes. As a result of this, the permeate flux decreases drastically, fouling the membrane irreversibly [9].

In view of this, in this work, a carbon membrane of well-defined pore structure has been synthesized for the separation of dyes.

Dyes have been classified on the basis of their chemical structure as acidic or basic. Their molecules consist of functional groups responsible for the dye color, called chromophores and electron-withdrawing or electron-donating substituents that intensify the color of chromophores, called auxochromes [10]. Some of the important chromophores are azo (–N=N–), carbonyl (–C=O), methine (–CH=), nitro (NO₂) and quinoid groups and the auxochromes are amine (–NH₃), carboxyl (–COOH), sulfonate (SO₃H) and hydroxyl (–OH) groups [10].

Basic dyes are cationic due to the positive charge delocalized throughout the chromophoric system and have affinity towards textile materials having negatively charged functional groups [11]. Since these are recalcitrant organic molecules, resistant to aerobic digestion and are stable to heat, light and oxidizing agents, waste water containing dyes is difficult to purify. Rhodamine B is a basic dye which is widely used as a colorant in textiles and food materials and as biological stains in biochemical laboratories at high concentrations. It causes irritation to skin, eyes and respiratory tract if ingested by animals and human beings [12]. The carcinogenicity, reproductive and developmental toxicity, neurotoxicity and chronic toxicity towards humans and animals have been experimentally proven.

Carbon membranes have been mainly used for gas separation but there lies a large potential for these membranes to be used for

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aqueous and solvent based applications due to their high temperature and chemical resistance. Only a few works have been reported [13–22] that have explored carbon membranes for microfiltration and ultrafiltration applications. The characteristics of carbon microfiltration membranes are mainly determined by the pore structure and therefore, it is very important to closely control it. A unique way of controlling the pore structure is by preparing the membrane using polymer blends, with one component as thermally labile polymer and the second, a thermally stable polymer. The decomposition of the thermally labile polymer creates mesopores (2–50 nm), while the thermally stable polymer leads to the formation of micropores (<2 nm) during pyrolysis. The pyrolysis of the blended polymer precursors leads to the formation of porous structure since the thermally labile polymer is completely decomposed at a lower temperature than the thermally stable polymer [14,15]. The most commonly used thermally labile polymers are poly (ethylene glycol), poly (vinyl butyral) and poly (vinylpyrrolidone) [15].

Strano et al. [16] have prepared carbon ultrafiltration membranes using spray deposition and pyrolysis (stream of flowing N₂, heating at the rate of 5 °C/min and held at 600 °C for 2 h) of poly (furfuryl alcohol)/poly (ethylene glycol) mixtures on macroporous stainless steel supports. They used polyethylene glycols of different molecular weights (1000, 2000, 3400 and 8000 Da) as a non-carbonizing template molecule to control porosity of the carbon film. Permeation of a polydisperse dextran solution has been used to quantify the retention properties of the membranes as a function of template size. Although nanoporous membranes have been prepared that had dextran sieving curves comparable to conventional ultrafiltration membranes, the water permeability for the nanoporous carbon was less than 10 lm⁻² h⁻¹ bar⁻¹, which is an order of magnitude lower than that of commercial inorganic and polymeric ultrafiltration membranes. This low permeability was a direct result of the large thickness of the selective layer (up to 15 μm) produced by the multiple pyrolysis steps required to make an integral membrane [16].

Further, it was possible to get a four-fold increase (41 lm⁻² h⁻¹ bar⁻¹) in the membrane permeability by reducing the thickness of the membranes to 7 μm [17]. The authors have slip-cast the stainless steel supports by silica particles to block the macropores to reduce the defects of the supports. They have carried out protein (Bovine serum albumin, BSA) separation from these membranes.

Pugazhenthii et al. [22] have prepared non-interpenetrating ultrafiltration carbon membranes having pore size of 4.8 nm (determined from MWCO experiments). They used resole-type phenolic resin and their studies consisted of functionalizing these by two-stage modification. In the first one, the membranes were nitrated using NO_x at 220 °C and in the second, aminated using hydrazine hydrate at 60 °C. On doing this, the pore size increased to 7.0 and 8.0 nm for the nitrated and aminated membrane. Experiments on the removal of Cr (VI) from its aqueous solution were carried out using the unmodified, nitrated and aminated membranes, respectively. The unmodified membrane gave a rejection of 96%, while nitrated gave 84% and aminated 88%. The pure water permeability obtained for the carbon membrane synthesized in this work is almost two orders of magnitude more than that reported in our earlier work [22].

In this work, we have developed a composite nanoporous carbon membrane using blend polymers that consist of a thermally labile polymer (polyethylene glycol, 400 Da) and a thermally stable polymer (phenol/formaldehyde resole) prepared at much lower temperature (500 °C as opposed to 900 °C reported in literature). The carbon membrane reported in this work has higher pure water flux and permeability (1.8 times) than the membranes reported in literature [17]. Basic dye, rhodamine B has been separated and the real rejection calculated by including the concentration polariza-

tion effect. The effect of pressure and feed concentration on the rejection has been determined which is found to be in the range of 90–100%.

2. Experimental

2.1. Materials

Analytical grade phenol crystals (99.5%), formaldehyde (37–41%, w/v), xylene, polyethylene glycol (PEG), rhodamine B dye, ethanol, toluene, sodium hydroxide pellets were procured from SD Fine Chemicals Ltd., Mumbai, India.

2.2. Composite carbon membrane preparation

The preparation of composite carbon membrane constitutes three main steps. Firstly, the ceramic support is prepared from a mixture of clays. This is followed by the preparation of polymer precursor mixture of resole type phenol formaldehyde resin with PEG (molecular weight 400 Da) in ethanol. Finally, the polymer solution was spin coated on the clay support, cross-linked by further heating and carbonized to get a porous carbon membrane. In the following sections, each of these steps is described in detail.

2.2.1. Preparation of clay supports

An integral part of the supported membranes is the support itself which provides mechanical and chemical strength to it. Clay supports were prepared using different clays (kaolin, ball clay, pyrophyllite, calcium carbonate, feldspar and quartz) following a procedure already reported in our previous work [23]. The materials were mixed well in the given composition with distilled water to obtain a homogeneous paste and then cast in the form of circular disc on a gypsum surface. The supports were first dried at room temperature overnight, then at 100 °C for about 24 h and finally at 250 °C for another 24 h. After the complete drying of the supports, they were calcined at 900 °C in the furnace for 12 h. These were further dipped in a solution of tetraethyl orthosilicate (TEOS) and calcined at 1000 °C for a period of 5 h in a furnace.

2.2.2. Polymer synthesis

The low molecular weight (300–700 Da) resole-type phenolic resin was prepared by condensation polymerization of phenol (94 g, 1.0 gmol) and 37% aqueous formaldehyde (123 g, 1.5 gmol) in presence of basic catalyst (sodium hydroxide, 5 g, 0.125 gmol). The reaction mixture was refluxed in a 1-l reactor at 95 °C under continuous stirring for 5 h to obtain a dark red colored viscous mass of the polymer. The polymer syrup, thus prepared, was cooled immediately and stored at –5 °C to arrest the polymerization. A mixture of PEG (molecular weight 400 g/mol) and the resole-type polymer (PF) in 1:1 weight ratio was prepared in ethanol and stirred properly to make a homogeneous solution.

2.2.3. Preparation of carbon membrane

The polished clay support was dipped in xylene, a nonsolvent for the polymer solution, to displace the air present inside the pores. Since, xylene is a volatile solvent, the clay support was kept on polyurethane foam completely soaked in xylene. Approximately, 2 g of a 60 wt. % solution of polymer mixture (PF + PEG) in ethanol was spin-coated on the clay support (wet with xylene) at 1200 rpm. The polymer coated clay support was allowed to dry in air for 1 h at room temperature and then for 2 h at 60 °C. The membrane was then cross-linked by heating it at 120 °C for 12 h. A second coat of the polymer blend was applied on the membrane and again crosslinked at 120 °C. The clay composite membrane was finally carbonized in N₂ atmosphere at a heating rate of 2.5–3 °C/min and kept at 500 °C

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