



Vapor deposition of blanket polymeric nanocoatings on porous substrates for the facile preparation of thin film composite membranes



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ABSTRACT

In this study a thin film composite (TFC) membrane was fabricated using initiated chemical vapor deposition (iCVD) of poly(glycidyl methacrylate-diethylamino ethyl methacrylate) thin films on porous fabric membrane supports. iCVD allowed very high deposition rates (50 nm min^{-1}) at low substrate temperatures. SEM analysis confirmed that iCVD forms a defect-free blanket type coating over the support surface. The resultant TFC membrane was used for the selectively facilitated transport of Cr(VI) with a maximum transport amount of 81.25% in aqueous medium. The transport efficiency of the TFC membrane was reproducible and it could be efficiently used in the long-term separation processes.

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1. Introduction

A membrane is a thin barrier or film through which solvents and solutes are selectively transported. In the past decades, membranes have gained an important place in industry due to their broad range of applications. Among many applications are; purification, concentrating products, desalination, sterilizing, demineralization, clarification, drug delivery, etc. In separation applications, the goal is to allow one component of a mixture to permeate the membrane freely, while hindering permeation of other components. Membrane materials can be categorised as either dense or porous, and by the mechanism by which separation is actually achieved. Separation by dense membranes relies to some extent on physico-chemical interactions between the permeating components and the membrane material, and relate to separation processes having the highest selectivity. Porous membranes, on the other hand, achieve separation mechanically by size exclusion, where the

rejected material may be either dissolved or suspended depending on its size relative to that of the pore.

Chromium is a naturally occurring heavy metal that is commonly used in industrial processes. There exist two common oxidation states of chromium that have become widely distributed in the environment. Cr(III) is an essential trace element, while Cr(VI) compounds are considered highly toxic because of their carcinogenic, teratogenic, and mutagenic effects on humans and other living organisms [1,2]. Cr(VI) is widely present in the effluents of electroplating, metal finishing, leather tanning and pigment industries. Therefore, the removal of Cr(VI) from industrial effluents is important before discharging it into aquatic environments or onto land. A variety of techniques, such as ion-exchange [3,4], adsorption [5,6], solvent extraction [7], non-dispersive solvent extraction [8], reduction [9], chemical precipitation [10], and membrane-based technologies have been developed to recover or remove of Cr(VI) contaminants from wastewater. However, many of these processes are not widely practiced because of disadvantages including incomplete metal removal, high cost, and generation of toxic sludge or other waste products that require disposal. The membrane-based methods (i.e., nanofiltration [11], micellar

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enhanced ultrafiltration [12,13], Donnan dialysis [14], electro-dialysis [15,16], facilitated transport through bulk liquid membrane (BLM) [17], and supported liquid membrane (SLM) [18], polymer inclusion membrane (PIM) [19,20], emulsion liquid membrane (ELM) [21] and activated composite membrane (ACM) [22,23], etc.) have been used for the separation of Cr(VI) from aqueous phase.

An alternative separation technology is transport across polymeric thin film composite membrane consisting of an ultra-thin selective top layer on a highly porous substrate. The ultra-thin active layer is the key component, which controls mainly the separation properties of the membrane, while the porous substrate gives the necessary mechanical strength. At present, it is an ambitious challenge to develop ultra-thin coatings (<1000) nm with controlled nanostructures on large scale at competitive costs. Defect-free thin films in the nanometer range are produced by various thin film coating methodology and developed to obtain simple, fast, practical and effective separation devices. The most common processes of manufacturing thin films as membranes are dip-coating [24,25] and interfacial polymerization [26–28] grafting [29], spin coating [30], electron beam irradiation [31], surface initiated atom transfer radical polymerization [32], plasma-initiated polymerization and chemical vapor deposition [33,34]. A simpler, faster, and cleaner method of forming TFC membranes with controlled surface chemistry is necessary for the future use of such structures in a much wider range of applications and in larger scales.

The aim of this study is to demonstrate the manufacture of TFC membranes by using initiated chemical vapor deposition (iCVD) process. iCVD shares the similar hardware with the well-known PECVD process, except that the energy required to start polymerization reactions is supplied by the heated filaments inside the reactor, other than plasma activation [35,36]. The polymerization mechanism is believed to follow a radical polymerization pathway and the use of an initiator allowed polymerization at very low filament temperatures [37]. Due to the low temperatures applied during the depositions and the lack of the harmful plasma environment, very high retention of the functional groups of the monomers was observed in previous studies [38,39]. The coating process is not subject to surface tension limitations, and pinhole-free, conformal coatings can be obtained on essentially any substrate, including porous ones [40–42]. In recent years, various applications of iCVD deposited thin polymeric films as membrane materials were demonstrated [43,44].

Previously, liquid membranes containing tertiary amine groups were used for efficient Cr(VI) transport [45,46]. A basic problem for such membranes is the loss of membrane solvent and poor durability. In this study, a polymer thin film containing functional epoxide and tertiary amine groups was deposited on a porous support material using iCVD technique to prepare a TFC membrane. As-deposited poly(glycidyl methacrylate-diethylamino ethyl methacrylate) copolymer has tertiary amine functionality, which take part in the complexation process for Cr(VI) transport, whereas the epoxide functionality is responsible for mechanical durability and insolubility. The resultant TFC membrane was characterized by contact angle measurements, FTIR and SEM analyses. The effects of some important parameters, i.e., initial pH and Cr(VI) concentration of the feed phase, film thickness, concentration of the stripping phase and other ionic species on the transport of Cr(VI) were investigated.

2. Materials and methods

2.1. Materials

The monomers glycidyl methacrylate (GMA, 97%, Aldrich) and

2-(Diethylamino)ethylmethacrylate (DEAEMA, 99%, Aldrich), and the initiator tert-butyl peroxide (TBPO, 98%, Aldrich) were used as received. The chemical reagents used for the transport experiments are potassium dichromate (99.5%) and hydrochloric acid (37%, HCl), which were purchased from Sigma–Aldrich. Hollytex 3329, which was purchased from Kavon Filter Products Co, was used as porous support material. Hollytex 3329 is a non-woven fabric polyester material with a porosity of 47.15 ± 4.8 .

2.2. Preparation of P(GMA-co-DEAEMA) TFC membranes by iCVD

P(GMA-DEAEMA) thin films were deposited on silicon wafer and non-woven fabric membrane support material (Hollytex 3329) by initiated chemical vapor deposition method in a custom-built vacuum reactor. The reactor contains a resistively heated tungsten (Alfa Aesar) filament array which is placed 20 mm above the substrate surface. All depositions were carried out at substrate and filament temperatures of 25 and 280 °C, respectively. Monomers GMA and DEAEMA were vaporized in separate stainless steel jars, which were heated to 65 and 80 °C, respectively. The initiator TBPO was vaporized in a different jar at room temperature and fed to the reactor by using a mass flow controller (MKS). The flowrates of TBPO, GMA and DEAEMA were kept constants at 1.0 sccm, 0.50 sccm and 0.25 sccm, respectively during the experiments. Reactor pressure was kept at 350 millitorrs, which was measured and controlled by a capacitance manometer (MKS Baratron) and a downstream butterfly valve operated by a PID pressure controller (MKS), respectively. The reactor was equipped by a laser interferometry system for real time monitoring of the deposition thickness. During the depositions, silicon wafers (100, p-type) were also placed next to the Hollytex 3329 support membrane materials, for characterization purposes, and for interferometric thickness determination. The chemical structures of the monomers and the resultant polymer are given in Fig. 1. The post-deposition annealing of the thin films was performed in a vacuum oven at 60 °C for 60 min. The resultant TFC membrane sheet was cut into 3.3 cm diameter circular discs to be used in the further transport experiments.

2.3. Transport studies

The transport studies were carried out by using a two-compartment cell (Fig. 2) described in literature [47]. The TFC membrane, which has an effective membrane area of 7 cm², was placed tightly between two compartments of 40 mL (equal volumes of feed and stirring phases) capacity. In each experiment, the stirring rates of both phases were kept constant at 300 rpm and all experiments were carried out at 25 °C.

The effects of Cr(VI) concentration (in feed phase), HCl concentration (in stripping phase), P(DEAEMA-GMA) film thickness, pH of feed phase, the effect of other metal ions (As, Cd, Se and Sb) on the transport and the stability of the TFM were investigated. The experimental parameters studied were Cr(VI) concentration of the feed phase (1×10^{-2} – 1×10^{-4} mol L⁻¹), initial pH (1.0–5.0), thickness of TFM (0.2–2.0 μm), and the HCl concentration of stripping phase (0.5–4.0 mol L⁻¹). A pH-meter (Orion) equipped with a combined glass-Ag/AgCl was used for pH measurements. Furthermore, the effects of the various metal ions (i.e., Cd, As, Se and Sb, etc.) on the transport of Cr(VI) were investigated.

The influence of the studied parameters on the transport of Cr(VI) was evaluated by means of the transport percentage, which can be defined according to Equation (1):

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