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Separation of chromium (VI) using modified ultrafiltration charged carbon membrane and its mathematical modeling

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Abstract

Supported non-interpenetrating modified ultrafiltration carbon membrane has been prepared by gas phase nitration using NO_x (mixture of NO and NO_2) at 250 °C and subsequently aminated in the second step using hydrazine hydrate at 60 °C. Separation experiments on the chromic acid solution have been carried out using unmodified (giving 96% rejection), nitrated (giving 84% rejection) and aminated (giving 88% rejection) carbon membrane. The water flux of the modified membrane however, has been found to increase by two times compared to that for the unmodified membrane with only 12% loss in rejection. This work presents a transport mathematical model through cylindrical charged capillaries of the membrane based on two-dimensional space charge model consisting of Nernst–Planck equation for ion transport and non-linear Poisson–Boltzmann equation for the radial distribution of potential. The solutions of these non-linear equations are computationally intensive and the difficulty has been overcome by a series solution of the Poisson–Boltzmann equation for the charge distribution. The effective pore size and non-dimensional pore wall potential of the membranes have been determined using this model by fitting the experimental data of the separation. The effective pore radius of the unmodified, nitrated and aminated carbon membranes are found to be 2.0, 2.8 and 3.3 nm respectively, which are less than the average pore size value determined from the molecular weight cut-off experiment and indicates the partial blocking of the pores by chromate ions.

Keywords: Carbon membrane; Phenol–formaldehyde; Raman spectra; Separation of chromium (VI); Space charge model

1. Introduction

Membrane-based technology has been presently used at several industrial processes and applications. The development of new membrane materials could play a significant role in the future of membranes in separations. Among the various types of membrane materials, carbonaceous materials are widely utilized for applications such as water and air purification, gas separation, catalysis, and energy storage. In recent studies, carbon membranes have shown that they can successfully compete with polymeric membranes and other porous inorganic membranes in separation processes [1]. Depending on the separation mechanism, two types of carbon membranes have been developed; these are molecular sieve carbon membranes (MSCMs) used to separate gas molecules with similar size (O_2–N_2, CO_2–N_2, CO_2–CH_4, etc.) and adsorption-selective carbon membranes (ASCMs) used to separate non-adsorbable or weakly adsorbable gases (H_2, N_2, air, etc.) from adsorbable gases (hydrocarbons). The former is used to separate effectively gas molecules and the latter is used for the selective adsorption of certain components of the gas mixture.

Normally, the supported carbon membranes are prepared using coating methods such as dipping, spraying, spinning and ultrasonic deposition. Microporous carbon membranes have been prepared by carbonization and activation of an asymmetric phenolic resin structure and are used for CO_2 separation by supercritical liquefaction [2]. Kita et al. [3] coated thin layers of phenolic resin on the outer surface of

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a porous alumina substrate and then carbonized the polymer under N_2 at 600 °C. Phenolic resin-derived carbon membranes [4] have been obtained by repeating two to three times of the coating–pyrolysis cycle which showed higher performance for CO_2–N_2 separation. The separation property of carbon membrane depends on the polymeric precursors and the pyrolysis conditions. In recent works, some authors reported on the use of a phenolic resin as suitable precursor to obtain MSCMs with good capabilities towards the separation of O_2–N_2 and CO_2–CH_4 mixtures [5,6]. Flat and capillary MSCMs having microstructure (pore size, pore volume, etc.) have been prepared by controlling the pyrolysis conditions and post treatment [7]. The phenolic resin has also been used to prepare ASCMs which are used to recover the non-adsorbable or weakly adsorbable gases (He, H_2, air, O_2, CH_4, CO_2, etc.) from strongly adsorbable gases (hydrocarbons (C^{2+}), NH_3, SO_2, H_2S, etc.) [8–10]. Zhou et al. [11] prepared MSCMs derived from phenolic resin with a pendant sulfonic acid group that showed higher separation of O_2 compared to that of the other phenolic resins. More recently, Novolak resin-derived-carbon membranes obtained by two time coating which is applied for separation of H_2–N_2 and H_2–CH_4 [12].

The discharge of wastewater polluted with toxic metal into the environment is strictly controlled by legislation. Therefore, the development and application of effective treatment process is very important. Several methods have been reported for the control of metal toxicants. Chromium salts are used in many industries such as leather, electroplating, dye and textile industries and these industries produce effluent containing large amount of chromium (high toxic) in different salt forms (Cr(III), Cr(VI)). The most widely used techniques for removing Cr(VI) from waste water are precipitation as hydroxides, carbonates or sulfides, adsorption using activated carbon, electrolytic recovery, evaporation and liquid–liquid extraction. However, these are highly expensive and the membrane separation process is an attractive and suitable technique and the separation can be carried out at room temperature. Polysulfone (MWCO as 10–60 kDa) [13] and polyvinyldene fluoride (MWCO 15–25 kDa) [14] membranes have been used for the recovery of Cr(VI) and Cr(III) respectively by ultrafiltration with the maximum rejection of 20 and 30.5% respectively.

The charges on the membrane are known to greatly affect their separation properties and fouling tendency due to the electrical interaction between membrane wall charge and ionic solutes [15]. For neutral solutes, the electrical interaction occurs due to non-zero average induced instantaneous dipole moment and polar–polar interaction. The fixed charge model proposed by Teorell [16] and Meyer and Sievers [17] (TMS model) has been used to describe the rejection of charged ultrafiltration membranes [18]. It assumes a fixed wall charge density and a uniform radial distribution of potential and ion concentration and is independent of the pore structure. A more realistic two-dimensional (in cylindrical coordinates) model known as space charge model (SCM) was originally developed by Osterle and co-workers [19,20]. According to this, the membrane is visualized as a bundle of cylindrical capillaries in which variation of the potential and concentrations in the radial direction occurs. The basic equations of the SCM are the non-linear Poisson–Boltzmann equation for the radial distribution of potential and ion concentration, the Nernst–Planck equation for ion transport and the Navier–Stokes equation for volumetric flow. The model involves coupled non-linear differential equations and is highly computationally intensive [21–26].

This paper reports the preparation of modified ultrafiltration carbon membrane on a macroporous clay support. The unmodified carbon membrane (reported in our earlier work [27]) has been nitrated using NO_x at 250 °C, followed by aminating it using hydrazine hydrate at 60 °C. We have carried out the separation of chromic acid solution (1000 ppm) using unmodified (giving 96% rejection), nitrated (giving 84% rejection) and aminated (giving 88% rejection) carbon membranes. We have compared the pure water flux, permeate flux and rejection obtained for the modified membranes with those for the unmodified membrane. In describing the separation characteristics by SCM, it was observed that in the curve fitting the experimental data of separation, the numerical solution of the non-linear Poisson–Boltzmann equation (PB equation) had to be obtained several times. On adopting the numerical procedure suggested in the literatures, we found that the computations had to be carried out in several batches with total time of computation as 15 h. In order to overcome this difficulty, we developed a series solution for the PB equation [28,29] which reduced this computation time to 15 min. We have subsequently determined the effective pore diameter and the wall charge of the membranes.

2. Theory

The basic equations used for the space charge model to analyze the separation of ionic solutes by membrane as given below. The flux of ions are given by the Nernst–Planck equation as [28–30]

$$j_{i,x} = u_x c_i - D_i \frac{\partial c_i}{\partial x} - \frac{D_i}{\Re T} z_i c_i F \frac{\partial \Phi}{\partial x} \tag{1a}$$

$$j_{i,r} = u_r c_i - D_i \frac{\partial c_i}{\partial r} - \frac{D_i}{\Re T} z_i c_i F \frac{\partial \Phi}{\partial r} \tag{1b}$$

where u_x and u_r are the fluid velocity component in the x and the r directions respectively, z_i the valency, D_i the diffusion coefficient, c_i the concentration of ith ion, F the Faraday constant and Φ the electrical potential.

The steady state fluid velocities u_x and u_r are given by the Navier–Stokes equation and are given as [28–30]

$$0 \cong -\frac{\partial P}{\partial x} - \left(\sum_i F z_i c_i\right) \frac{\partial \Phi}{\partial x} + \mu \left(\frac{1}{r}\frac{\partial}{\partial r}\left(r \frac{\partial u_x}{\partial r}\right) + \frac{\partial^2 u_x}{\partial x^2}\right) \tag{2a}$$