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Removal of calcium and magnesium using polyaniline and derivatives modified PVDF cation-exchange membranes by Donnan dialysis

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ABSTRACT

In this work, polyaniline (PAni), poly-n-ethylaniline, poly-n-methylaniline and poly-o-anisidine were prepared by chemical polymerization. 1,3 (6 or 7)-napthalenetrisulfonic acid was used for the first time in the literature as a dopant to increase the solubility of the polymers in methanol solution. The structure and properties of these conducting polymers were characterized by FTIR, UV–Vis, elemental analysis and conductivity measurements. Poly(vinylidene fluoride) (PVDF) membranes were modified by PAni and its derivatives and used as cation-exchange membranes. Poly-n-ethylaniline, poly-n-methylaniline and poly-o-anisidine were also used for the first time for this purpose in the literature. Ion-exchange capacity, water uptake and fixed group concentration of the polymer modified PVDF membranes were investigated. The changes in the surface morphologies of non-modified and polymer modified PVDF membrane was investigated by AFM and SEM. The polymer modified membranes were used for the removal of calcium (II) and magnesium (II) ions from water samples with Donnan dialysis (DD) experiments. The modified membranes show excellent stability during 120 days.

1. Introduction

Recently, many applications of the ion-exchange membrane process based on the Donnan membrane equilibrium principle have been developed to solve two important environmental problems: recovery or enrichment of valuable ions and removal of undesirable ions from waste water [1], in particular, extraction of toxic metal ions [2,3]. Membrane processes such as reverse osmosis, nanofiltration, electrodialysis and Donnan dialysis (DD) were recently investigated to reduce fluoride concentrations in water [4]. DD is a potentially attractive membrane separation process for concentrating valuable materials in an ionic form from diluted solutions or removing undesirable ionic species from solutions [5].

Donnan dialysis is a membrane-based equilibrium process and is different from the classical dialysis technique. DD is used to exchange ions between two solutions, the feed (A) and receiver (R) solution, separated by an ion-exchange membrane. The difference in the electrochemical potential on both sides of the membrane acts as the driving force. Thus, fluxes of the two counter-ions moving through the membrane appear in opposite directions [6]. The main advantage of this process is that it is economical, simple and especially energy saving. In spite of these advantages, the process is not yet applied in the industry. However, some potential applications at a laboratory scale for treatment of metals have been conducted [7].

Different polymeric materials, poly(vinylidene fluoride) (PVDF), polysulfone (PS) etc. have been used as a membrane because of their good mechanical, chemical and heat resistance performances. To improve the hydrophilicity of these membranes, they can be easily modified with doped conducting polymers (CP) for ion exchange applications. CPs with functional groups can easily bind with the hydrophobic polymers or be firmly fixed on substrate membranes through different chemical reactions. In addition, special functional groups of organic nanomaterials might give substrate membrane novel performance [8]. CPs has recently attracted much attention from both fundamental and practical view points. Polyaniline (PAni) has been studied extensively as special member of the CP family because of its stability and potentially attractive economics. The associated difficulty of PAni for the application due to restricted solubility in common organic solvents has been tried to overcome by several researchers by different approaches. One of the methods employed to improve the solubility of PAni is the use of sulfonic acids as dopants. Introducing a —SO_3H group on the PAni chain affects the properties of parent PAni without substantially conductivity and is of specific interest for several reasons such as solubility, environmental stability, processibility, etc. [9–15].

The doping/undoping features of certain CPs could be advantageous as films for preconcentration and matrix separation of anio-

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nic [16,17], cationic [17–19] and neutral analytes [20,21]. The main advantage of using CPs in ion-exchange process is that the charge of the coatings can readily be controlled by oxidation and reduction of the polymers.

Hardness in water is mostly due to cations such as calcium and magnesium. The hardness of water is important parameter for industries. A number of studies were reported on the modification of CPs for water softening process. Weidlich et al. developed an electrochemically switchable ion exchanger based on CPs for water softening (i.e. removal of Ca^{2+} and Mg^{2+} ions). For that reason, they employed PPy modified with PSS^{-} counter ions [22–24].

Our group reported a new electrodes configuration for the use of electrochemical control of anion-exchange properties of polypyrrole and cation-exchange properties of overoxidized sulfonated polypyrrole film. The rapid extraction and selective determination of trace levels of chloride, nitrate, sulfate, calcium and magnesium ions were obtained by Ion Chromatographic system [25]. The developed method is straightforward and suitable for the in-situ extraction and analysis of anionic and cationic species in aqueous samples. PVDF membrane was modified with polyaniline, poly-n-etylaniline, poly-n-metylaniline and poly-o-anisidine doped with 1,3 (6 or 7)-napthalenetrisulfonic acid (NTSA). This organic acid was used as a dopant for the first time for these polymers in this work. The aim of this work is the removal of calcium and magnesium ions from water samples by PVDF/PAnis cationic membranes. This work also aims to develop an alternative novel modified membrane for water purification process for replacing commercial ion exchange membranes. The cation-exchange properties of PAnis provide an alternative way for future designing of water purification system.

2. Experimental

2.1. Chemicals and materials

Aniline, n-ethylaniline, n-methylaniline and o-anisidine were purchased from Aldrich and distilled repeatedly under vacuum until a colorless liquid was obtained, and kept under nitrogen atmosphere in darkness at 4 °C prior to use. All other reagents, HNO_3, HCl, NaOH, methanol, diethylether, DMSO, 1,3 (6 or 7)-napthalenetrisulfonic acid (NTSA) and ammonium peroxydisulfate (APS), are commercially available as analytical grade and used without further purification. PVDF membrane support sheets (0.22 μm) were obtained from Millipore.

2.2. Synthesis of PAni and its derivatives

Conducting polymer powders were prepared by a self-assembly method using an oxidizing system consisting of a dopant anion, NTSA (Aldrich) with APS (Aldrich). All solutions were prepared by using pre-distilled 18 $M\Omega\, cm^{-1}$ deionized water. The molar ratio of monomer to dopant was fixed at 1:1 and dissolved in 100 mL of distilled water, and then an aqueous solution of APS (0.57 g in 12.5 mL of distilled water) was added to the above mixture under stirring for 10 min. The polymerization was carried out in a stationary condition at room temperature during 24 h. Dark green–blue solid polymers were filtered and washed with water, methanol and diethylether until a colorless liquid passed through the filter and then dried under vacuum for 24 h.

2.3. Fourier transform infrared spectroscopy

The structures of the polymers were determined by Perkin Elmer Spectrum 100 FTIR spectrometer. Dry KBr powder was used to make a pellet of the polymer samples. The spectra were recorded in the spectral range of 400–4000 cm^{-1}.

2.4. UV–Vis spectroscopy

UV–Vis spectra of the polymer solutions in DMSO were recorded on a UV–3150 UV–VIS–NIR Spectrophotometer Shimadzu.

2.5. Elemental analysis

Elemental compositions of the polymers were determined by CHNO Elementar Vario EL III.

2.6. Conductivity measurements

The dry conductivity values were measured using a four-probe technique at room temperature. Gold plated probes were used to avoid any errors that might arise from ohmic contacts. At least, 10 different current values were used in the measurement of the potential drop.

2.7. Preparation of modified membrane

Membranes were modified with polymers by immersion method. Casting solutions were prepared by addition of 10 wt.% PAnis into methanol solution and sonicated for about 5 min at room temperature. Then, PVDF membranes were put into the polymer solutions and were kept for 24 h. Before use, the modified membranes were immersed in deionized water at 70 °C for 1 h to remove impurities and residual solvent [26]. Then they were conditioned in 1 M HCl solution for 24 h to ensure complete protonation of the PAnis. The polymer modified membranes were named as PVDF/PAni, PVDF/poly-n-ethylaniline, PVDF/ poly-n-methylaniline and PVDF/ poly-o-anisidine.

2.8. Donnan dialysis

Donnan dialysis experiments were carried out in a two-compartment cell made of Teflon. The volume of each cell was 40 mL and it was stirred at 700 rpm. The area of the exposed membrane was 4.91 cm^2. For the investigation of the transport properties of the polymer modified membranes, tap water (Anadolu University) and 0.1 M HCl solution were added in the feed and receiver compartments, respectively, while stirring at room temperature The samples were taken from the receiver compartment at certain time intervals and the amount of Ca^{2+} and Mg^{2+} ions transported across the membrane were determined by Flame Atomic Absorption Spectroscopy (Perkin Elmer Atomic Absorption Spectrometer A Analyst 800). All solutions were prepared by using pre-distilled 18 $M\Omega\, cm^{-1}$ deionized water. The measurements were carried out at 25 °C.

2.9. Properties of membranes

2.9.1. Ion-exchange capacity (IEC)

For ion-exchange capacity measurements, the membranes were remained in 0.1 M HCl solution for 24 h to ensure that the membranes were fully converted into the H^{+} form. These membranes were then washed with deionized water to remove excess of acidity. Then, the H^{+} forms of the membranes were converted to the OH^{-} form by leaching with a 0.1 M NaOH solution. The amount of OH^{-} ions released from the membranes were determined by an acid-base titration of 0.1 M HCl solution with phenolphtalein as an indicator and are given as mequiv/g dry membrane [27]. The ion-exchange capacity (E_c; mequiv/g) of the membrane was calculated by