Journal of Water Process Engineering 4 (2014) 6–11

Contents lists available at ScienceDirect

Journal of Water Process Engineering

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

Electro-separation of synthetic azo dyes from a simulated wastewater using polypyrrole/polyacrylonitrile conductive membranes

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ARTICLE INFO

Article history:
Received 30 January 2014
Received in revised form 17 July 2014
Accepted 25 August 2014
Available online 20 September 2014

Keywords:
Electro-separation
Conducting electroactive polymers
Wastewater
Dye transport
Diffusion coefficient

ABSTRACT

Polypyrrole/polyacrylonitrile (PPy/PAN) conducting electroactive polymer membranes (CEPMs) were fabricated and evaluated for their potential use as electro-separation of synthetic azo dyes from simulated wastewaters. The PAN substrate films were prepared from a N,N-dimethylformamide (DMF) solution at 25 °C. The PPy/PAN CEPMs were fabricated by synthesizing of PPy layer on both sides of the PAN substrate films from an ethanol solution containing 5 wt% pyrrole monomer using aqueous $FeCl_3$ solution as a strong oxidant. The structure and morphology of the prepared PPy/PAN membranes were investigated using Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM). The electrical conductivity of PPy/PAN CEPMs was measured at room temperature. The PPy/PAN CEPMs were installed in a designed electrochemical cell including two separate compartments, each with a capacity of 750 cm^3. The effect of applying electrical current across the prepared PPy/PAN CEPMs on the transport flux of synthetic azo dyes, i.e. Basacryl Red GL, Basacryl Blue GL and Direct Yellow 12 from the simulated wastewater was investigated. Electrochemically controlled transport of the dyes was monitored by measuring the dye concentrations in the permeate solution. The diffusion coefficients of the dyes in the PPy/PAN membranes were determined by the concentration profile of pseudo-steady state data points.

1. Introduction

Conducting electroactive polymers (CEPs) such as polyacetylene (PAc), polypyrrole (PPy), polyaniline (PANi) and polythiophene (PTh) have recently received a lot of attention due to their remarkable physical properties for potential applications in a variety of areas, including electrochemically controlled transport [1–3], ion separation [4], waste water treatment [5], rechargeable batteries [6,7], sensors [8] and gas separation [9]. These polymers are deeply investigated for their good conductivity and light in weight [10]. Among the various applications of CEPs, they have attracted an enormous interest for fabrication of conducting electroactive polymers membranes (CEPMs). Because of their different and unusual properties arising from combining the electrical conductivity of metals with the strength and processability of synthetic polymers, CEPs have shown a particular interest in the development of the CEPMs in the recent years [11]. The electrodynamic nature or redox switching of CEPMs consisting of/or coated with the CEPs can be stimulated in situ using small electrical pulses or stimuli to trigger the transport of electroactive ions, transition metal ions, small organic molecules and even large macromolecular species such as proteins. The flux and selectivity attainable of CEPMs are dependent on several factors, i.e. the composition of membrane, the porosity as determined by CEPs and/or a more porous support onto which the polymer may be coated and the electrochemical conditions used during operation, e.g. potential, pulse height and pulse width [12].

Recently, much effort has been directed toward making synthetic CEPMs with a view to preventing fouling and extending their lifetime by using CEPs and respective nanocomposites. Among CEPs, PPy with high electrical conductivity and environmental stability is widely used material for a lot of potential applications, such as sensors [13], solid electrolytes, electrodes for capacitors and solid-state batteries [14]. In recent years, several researchers have been interested in the development and utilization of CEPMs based on PPy [15].

A free-standing membrane with strong mechanical stability, flexibility and desirable permeability properties can be used for a selective separation of species form the mixtures in the industrial separation processes. Initial studies were performed using free-standing PPy membranes for the transport of metal ions and

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http://dx.doi.org/10.1016/j.jwpe.2014.08.008
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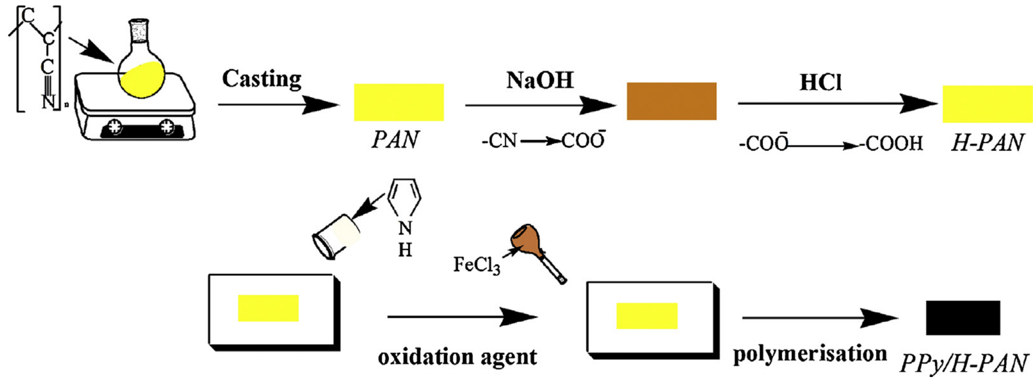

Fig. 1. Schematic diagram of PPy/PAN membrane synthesis.

charged organic molecules. However, due to the limited strength and porosity of the free-standing CEPMs, new PPy based composite, new composite membranes using some non-conductive polymer supports were developed [1,16]. During the last decade, membrane separation processes have gained enhanced interest and today they are frequently used as an efficient and economical procedure for many industrial wastewater treatments and water purification processes [17,18]. Dye released to the wastewater streams could exert great impact to the environment. These materials can be considered as one of the most dangerous contaminants [19]. For the reason of their reactivity to form covalent bonds with OH, NH and SH groups in fibers, the majority (60–70%) of industrially synthesized dyes are azo compounds which can be reduced and decolorized not only by bacteria under anaerobic conditions, but also by reduction agents such as sodium dithionite and sodium sulfide [20]. These dyes with different charges and concentrations, i.e. Basacryl Red GL, Basacryl Blue GL, Chrysophenine GX are found to be the brightest class of the soluble dyes, which cause serious environmental and health problems [19]. Hence, many researchers try to find an economical and effective method of dye-containing wastewater treatment. Many studies have been performed on the chemical, physical, and biological methods to remove dyes from the dye-containing wastewaters. Among them, the membrane separation processes play a crucial role in the wastewater treatments especially in the textile industries.

In the electro-separation method, the CEPMs can be used to transfer species from one side of the membrane to the other with some control over selectivity and flux. This control was achieved by applying an electrical field across both sides of the used CEPM.

The present work is concerned with the development of electro-separation process for removal of azo dyes from a simulated wastewater using polypyrrole/polyacrylonitrile (PPy/PAN) membranes as CEPM. The special electrical properties of PPy will be used to enhance the separation performance of the fabricated CEPM. The fabricated PPy/PAN CEPM is capable of responding to electrical stimuli. The application of electrical potential to the CEPM causes the movement of ions in and out of the membrane to affect the ion transport and separation process. The effect of applying electrical current across membranes on the separation flux of azo dyes from the simulated wastewaters is investigated.

2. Experiments

2.1. Materials and methods

Polyacrylonitrile fibers (PAN, Isfahan Petrochemical Company, Iran), and N,N-dimethylformamide (DMF, Merck) were used in the synthesis of support membranes. Pyrrole monomer (Py, Merck) and iron chloride (III) ($FeCl_3$, Merck) were used in the synthesis of polypyrrole layer. Azo dyes (Basacryl Red GL, Basacryl Blue GL,

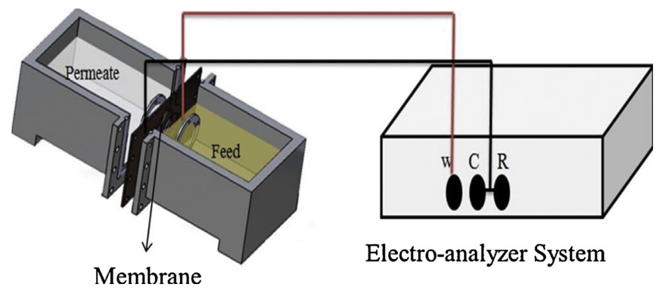

Fig. 2. Schematic diagram of the designed membrane transport cell.

Direct Yellow 12) were also obtained from local dye suppliers for investigation of the fabricated PPy/PAN CEPMs performance. Pyrrole was distilled prior to use and all the other chemicals were used as received.

2.2. PPy/PAN CEPMs preparation

PPy/PAN CEPMs were fabricated from PAN as a substrate film using a two-step procedure [21]. The substrate films play a crucial role in providing mechanical strength to the CEPMs. At the first step, the PAN substrate films were prepared from PAN, 14 wt% solution in N,N-dimethylformamide (DMF), cast on a glass plate support using a casting knife. The solution was stirred for 3 h at temperature of 80 ± 2 °C. The cast films were immersed into a coagulant bath of distilled water to form the porous support film. Temperature and relative humidity of casting environment were 24 ± 2 °C and 23%, respectively. The PAN substrate films were hydrolyzed (H-PAN) in 10 wt% NaOH at 25 °C for 60 min. Before preparing PPy/PAN CEPMs, the H-PAN films were first immersed in HCl for 2 h to convert —COONa groups into —COOH groups. The prepared PAN films were stored in water.

At the second step, before synthesizing of PPy layer on the H-PAN substrate films, the residual water was quickly removed from the H-PAN surface with tissue paper. The schematic of the preparation method is shown in Fig. 1. Hence, PPy monomer (5 wt%) from an ethanol solution was poured on the both sides of H-PAN substrate films. After which the membranes were kept in air for 1 min to evaporate the ethanol, immersed in a strong oxidant (0.25 M aqueous $FeCl_3$) for 1.5 h to form the PPy layer. The polymerization process can be controlled by the $FeCl_3$ concentration. The prepared PPy/PAN CEPMs were immersed in water for minimum 12 h to remove all $FeCl_3$.

2.3. Transport experiments (Electrochemically transport of dyes)

The electrochemically controlled transport of dyes across the prepared PPy/PAN CEPMs was carried out using the transport cell depicted in Fig. 2. The cell used in this work consisted of two