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Preparation of polyethersulfone/plant-waste-particles mixed matrix membranes for adsorptive removal of cationic dyes from water

Chia-Hao Lin [a], Chin-Hau Gung [a], Jia-Jun Sun [a], Shing-Yi Suen [a,b,*]

[a] Department of Chemical Engineering, National Chung Hsing University, Taichung 402, Taiwan, ROC
[b] Center of Nanoscience and Nanotechnology, National Chung Hsing University, Taichung 402, Taiwan, ROC

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ABSTRACT

This paper focuses on the preparation of porous mixed matrix membranes (MMMs) by filling plant waste particles in polyethersulfone (PES), specifically for adsorptive removal of cationic dyes from water. Three kinds of plant wastes, including banana peel, tea waste, and shaddock peel, were adopted as fillers to fabricate the MMMs via water-vapor-induced phase inversion. The prepared particles and MMMs were characterized by BET, FTIR, SEM, TGA, zeta potential, porosity, and ion-exchange capacity (IEC). In batch process, the saturated dye adsorption capacities of plant waste particles were found to be 1055–1173 mg/g particles for methylene blue and 1085–1244 mg/g particles for methyl violet 2B, which are larger than the corresponding results of biosorbents reported in the literature. The adsorptivities of the MMMs were essentially contributed from the filled plant waste particles. Desorption greater than 95% could be achieved with the use of 1 M KSCN in 80% methanol, indicating that the cationic dyes were bound with the MMMs through a combination of electrostatic interaction, hydrophobic interaction, and hydrogen bonding. In the dead-end (flow-through) operation with one piece of 25 mm MMM disc at 1 mL/min, the original dye removal and recovery efficiencies could be successfully retained after three adsorption/desorption cycles no matter the feed was dilute solution (5 mg/L, pH 4) or synthetic dye wastewater (200 mg/L methylene blue, 100 g/L Na_2SO_4, pH 10). The dynamic adsorption capacity for a 10 cm × 10 cm membrane module was also investigated in both the cross-flow and dead-end modes. The MMM performance could be effectively repeated at a larger membrane area scale in the dead-end operation.

1. Introduction

With the increasing public concerns on environmental protection, removal of colorful dye stuffs from wastewater effluents has become an especially important issue. Among numerous separation techniques attempted for dye removal, the adsorption process is commonly favored owing to its simplicity and effectiveness [1–5]. The applied adsorbents include natural and synthetic materials with adsorption efficiencies varying from one to another.

In recent years, research studies have particularly focused on the adsorbents made from plant wastes (e.g. fruit peels, tea leaves, plant seeds, hulls, etc.) due to their advantages of low cost (or even free of expense), accessibility, and eco-friendliness [5]. In general, plant wastes contain COOH, OH, or phenolic groups that could provide charge interaction, hydrogen bonding, or hydrophobic interaction with contaminant species [5,6]. Based on this nature, it has been demonstrated in several previous works [3–28] that plant wastes can serve as economical and effective adsorbents for removal of heavy metals, dyes, phenolic compounds, etc. In those studies, particles of millimeter-to-micrometer size were prepared from raw plant waste materials by a series of procedures (chopping, decoloration, grinding, etc.) to achieve suitable pore size and sufficient surface area.

Nevertheless, the effective application of particulate adsorbents is still severely challenged by a few crucial problems. In batch process, there may be difficulties in uniform particle suspension at a large tank and additional cost for final solid–liquid separation by filtration or centrifugation. In packed-bed operation, slow mass transfer, high pressure drop, long process time, clogging, bed compression, etc. usually occur for low bed porosity and long bed height. On the other hand, non-uniform packing such as channeling and dead volume may happen for the cases with a wide and short bed. To circumvent these limitations, a more appropriate design would be making the adsorbent in the form of membrane, i.e. so-called adsorptive membrane, membrane adsorber, or membrane chromatography. For adsorptive membrane, packing is not necessary. Channeling, bed compression, and intraparticle diffusion can also be avoided [29–32]. Most importantly, the membrane structure could provide shorter bed height,

* Corresponding author at: Department of Chemical Engineering, National Chung Hsing University, Taichung 402, Taiwan, ROC. Tel.: +886 4 22852590; fax: +886 4 22854734.
E-mail address: sysuen@nchu.edu.tw (S.-Y. Suen).

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higher bed porosity, and larger pores for convective flow, which leads to the operation at lower pressure drop, higher flow velocity, and shorter residence time [29–36]. Furthermore, the adoption of membrane adsorber could offer a further advantage of simple scale up by either stacking more pieces of membranes together, or using a spiral-wound configuration, or developing a bundle of fiber membranes [29–35].

Porous mixed matrix membrane (MMM) is one kind of adsorptive membrane, which could be prepared via filling the adsorbent particles in polymeric matrix. In the previous MMM studies, commercial ion-exchange resins, clays, chitosan beads, functionalized silica particles, and metal ion charged beads were taken as the fillers for adsorption of biomolecules or pollutants [29–31,33–42]. The separations were proven to be successful and the processes were simple.

In this study, various plant waste particles (banana peel, tea waste, and shaddock peel) were blended with polyethersulfone (PES) to form the PES/plant-waste-particles MMMs. Banana, shaddock, and green tea are popular agricultural products in Taiwan and their peels or wastes can be easily collected without any cost. Since the raw materials were obtained from cheap polymer and free agricultural wastes, the direct material cost of these MMMs was extremely low. The prepared MMMs were applied in the adsorption process of cationic dyes (methylene blue and methyl violet 2B). In batch process, adsorption isotherms and rate curves were evaluated. Moreover, desorption was conducted in order to recover the bound dyes and regenerate the MMMs for repeated use. Such an effort would prevent the environment from secondary pollution by the dumping of dye-loaded adsorbents. In flow process, the adsorption/desorption cycles were carried out and the related process efficiencies (breakthrough curve, dye recovery, membrane reusability, synthetic dye wastewater, two operation modes (dead-end and cross-flow), scale up, etc.) were systematically investigated.

2. Experimental

2.1. Materials

Polyethersulfone (PES, RADEL A-300A, density = 1.37 g/cm^3) was purchased from Solvay Advanced Polymer (USA). Banana, green tea, and shaddock were from the local markets in Taiwan. Two cationic dyes adopted in this study, methylene blue trihydrate (80% purity, MW = 374.2, λ_{max} = 668 nm) and methyl violet 2B (75% purity, MW = 379.5, λ_{max} = 575 nm), were bought from ICN Biomedicals (USA) and Sigma-Aldrich (USA), respectively. Their molecular structures are illustrated in Fig. 1. These dyes were used as received.

2.2. Preparation and characterization of plant waste particles

Banana peels, tea wastes, and shaddock peels were adopted for preparing the adsorbent particles. In the beginning, the plant waste sample was cut into small pieces (about 1-cm square), washed with deionized water, and then dried in an oven at 60 °C for 24 h. These chopped plant wastes were then ground into powders using an industrial grinder (RT-02A, Rong Tsong Precision Technology, Taiwan) at 30,000 rpm (940 W) for 3 min. The obtained powders were further sieved using a 450-mesh sieve (Retsch, Germany). For decoloration, the particles were immersed in deionized water at 50 °C and shaken for 24 h. Finally, the filtered particles were dried in an oven at 60 °C for 24 h.

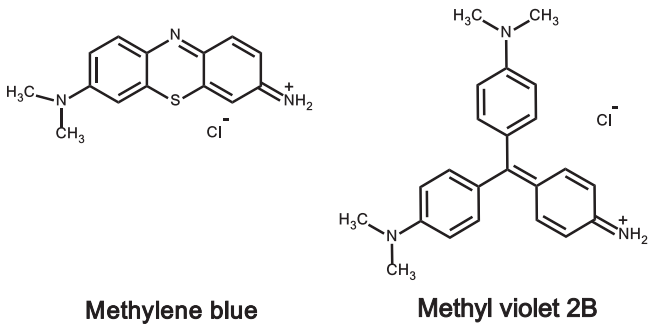

Fig. 1. Cationic dye structures.

The 90Plus Particle Size Analyzer of Brookhoven Instruments (USA) was employed to analyze the particle size range for plant waste powders. The average pore diameter and surface area of plant waste particles were measured by a Micromeritics BET (ASAP 2010, USA). Prior to BET measurement, the particles were degassed at 120 °C, under vacuum for 24 h. To characterize their functional groups, the plant waste particles were mixed with KBr to make a pellet and its spectrum was recorded by FTIR spectroscopy (FT-720, Horiba, Japan) at a resolution of 4 cm^{-1} in the range of 500–4000 cm^{-1}. The pH at zero point of charge (pH_{zpc}) for each kind of plant waste particles (2 mg in 10 mL of water for 10 min) was determined with a zeta potential meter (Zetasizer Nano-ZS, Malvern, USA).

As for the measurement of ion-exchange capacity (IEC), 0.05 g of plant waste particles were immersed in 20 mL of 0.1 N HCl, and shaken for 24 h at room temperature. The particles were then continuously washed with deionized water for 24 h to remove the acid trace. Subsequently, the particles were equilibrated with 20 mL of 0.01 N NaOH solution for 24 h. The cation-exchange capacity (CEC) was determined from the alkalinity reduction in NaOH solution by back titration using 0.01 N HCl and calculated with ($M_{O,NaOH}$–$M_{E,NaOH}$)/weight of particles, where $M_{O,NaOH}$ and $M_{E,NaOH}$ are the moles of NaOH before and after the equilibration, respectively.

2.3. Preparation and characterization of PES/plant-waste-particles MMMs

3.605 g of PES were dissolved and mixed in 12 g of NMP at 80 °C for 24 h. 1.545 g of plant waste particles (30 wt%) were then added in PES solution and stirred uniformly for 24 h at room temperature. The above casting solution was spread over a smooth glass plate using a doctor blade (200 μm) to form a film. The film was exposed to an air of > 90% relative humidity for 10 min at room temperature. Next, the film with glass plate was immersed in deionized water bath at room temperature until the membrane was detached from the glass plate. Prior to use, the prepared membrane was dried at room temperature for 24 h. It may be worthy to note that the MMMs with 40 wt% particle content were also examined in our study under two different conditions. When the polymer amount remained the same, the addition of 40 wt% plant waste particles led to a high viscosity in the casting solution and failed for a proper casting. This phenomenon has also been observed in other MMM literature [31,37]. When the whole amount of polymer and particles was kept constant, the membranes resulted from a 40 wt% particle loading became brittle and was partially cracked as water passed through. Subsequently, 30 wt% can be considered as the optimal loading content.

A thickness gauge (543-251-70, Mitutoyo, Japan) was utilized to measure the membrane thickness. The membrane morphology was characterized by FE-SEM (JSM-6700F, Jeol, Japan). Thermogravimetric analysis (TGA) for the particles and membrane samples was performed by the instrument Thermo Cahn HS/Versa Therm (Thermo Fisher Scientific, USA) from 100 to 800 °C at a rate 10 °C/min in nitrogen atmosphere. The IEC measurement for membranes was the same as that for plant waste particles.