Journal of the Taiwan Institute of Chemical Engineers 70 (2017) 352–358

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Cyclodextrin functionalized cellulose nanofiber composites for the faster adsorption of toluene from aqueous solution

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ARTICLE INFO

Article history:
Received 20 January 2016
Revised 28 September 2016
Accepted 17 October 2016
Available online 1 November 2016

Keywords:
Cellulose
Nanofibers
Cyclodextrin
Toluene
Adsorbent

ABSTRACT

Herein, we report cyclodextrins (CDs)-modified regenerated cellulose nanofibers (CDs/RCNFs) as green adsorbents for the removal of toluene from wastewater. Two different methods, namely, physical mixing and chemical grafting, were opted to combine the CDs with RCNFs. The CDs with three different kinds such as α-, β-, and γ were employed. Initially, various electrospinning parameters were optimized to obtain the better morphology of CDs/RCNFs. Scanning electron microscopy (SEM) results confirmed the good surface morphology of CDs/RCNFs. The effective dispersion and successful chemical modification of RCNFs with CDs were acknowledged by SEM, X-ray photoemission spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR) analyses. The usefulness of the prepared materials was realized from the higher adsorption rate of toluene. It was found that the chemically modified RCNFs with γ-CDs have a better toluene adsorption rate of 82% after only 180 min.

1. Introduction

Owing to the rapid population growth, several industries including small factories are newly opened to fulfill people's requirements and to improve their life style. On the other hand, the hazardous wastes from the industries and factories have also started creating huge environmental issues [1]. The hazardous industrial wastes, which may be in solid, liquid or gaseous form, may cause risk to health and environment. It is presumed that about 10–15% of wastes produced by industries are hazardous. Particularly, in the last few years, it has raised much and the generation of hazardous wastes is increasing at the rate of 2–5% per year, especially in the developing countries [2]. The contamination of wastewater is also one of the highly problematic environmental issues since the common industrial processes require organic solvents such as toluene, methanol, ethanol, nitromethane, benzene, and dichloromethane [3, 4]. There are several methods such as coagulation, filtration with coagulation, precipitation, ozonation, adsorption, ion exchange, reverse osmosis and advanced oxidation processes are developed to remove the organic solvents from wastewater [2]. However, these methods are limited since they often involve relatively high investment and operational cost.

Adsorbents are often used as key materials to remove the organic substances from wastewater. The most important properties of the adsorbents are the surface area, wettability, and pore properties [5]. The higher surface area can provide more adsorption sites and therefore enhance the adsorption nature of the materials. Activated carbons (ACs) are the most commonly used materials for the removal of organic solvents [6]. However, the powder form of ACs is difficult to handle and inhaling of ACs may cause health problems. Cyclodextrins (CDs), a family of macrocyclic oligosaccharides linked by $\alpha-1,4$-glycosidic bonds, have been extensively studied in diverse fields. CDs have toroid-shaped molecular structure in which the inner side is composed of hydrophobic groups and the outside is full of hydrophilic groups, which provides the CDs to adsorb hydrophobic molecules [7]. Therefore, the CDs have been widely applied as an adsorbent for the removal of organic solvents from wastewater.

Electrospun nanofibers are demonstrated as enormous potential applications in water filtration, due to its higher surface area, better porous properties, easy handling and lower production cost

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http://dx.doi.org/10.1016/j.jtice.2016.10.028
1876-1070/

[8]. Particularly, owing to the simple and unique surface modification, cellulose and its composites are often employed for various applications such as energy, catalysis, biomedical, separators and filters [9]. In addition, the solubility of cellulose in various aqueous and organic solvents is nearly zero due to the existence of multiple hydrogen bonds [10]. Very recently Kayaci et al. [11] prepared cyclodextrin modified electrospun polyester nanofibers for the removal of phenanthrene from aqueous solution. They found that the nanofiber composite is effective and easy to handle. Alike, Celebioglu et al. [12] prepared cyclodextrin-grafted electrospun cellulose acetate nanofibers via “Click” reaction for removal of phenanthrene. In our recent course of investigation, we developed a new Prussian blue nanoparticle incorporated polyvinyl alcohol composite nanofiber (*c*-PBNPs/PVA) [13]. The *c*-PBNPs/PVA showed nearly 100% adsorption of cesium (Cs) from radioactive wastewater. However, most of the electrospun nanofibers and their composites are physically as well as chemically unstable. Particularly, during the adsorption of organic solvents, the nanofibers are soluble either completely or partially. To overcome this issue, chemical modification or cross-linking methods are often required for electrospun mats. We presumed that the surface modification of cellulose nanofibers with cyclodextrin would show higher adsorption rate toward removal of toluene from wastewater. Moreover, tuning the cellulose acetate electrospun mat to cellulose nanofibers by simple method would assist to obtain a stable adsorbent. Herein, we prepared CDs modified cellulose nanofiber composites (CNFs) by a simple chemical treatment. The prepared materials were completely characterized and tested as an adsorbent for the removal of toluene from wastewater.

2. Materials and methods

2.1. Materials

Cellulose acetate (CA, Mw = 30,000) was purchased from Sigma-Aldrich. *N, N*-dimethylformamide (DMF), acetone, sodium hydroxide (NaOH), cyclodextrin (α-CD, β-CD and γ-CD), citric acid, sodium hypophosphite hydrate (SHPI), and toluene, were purchased from Wako Pure Chemicals. All chemicals were used without further purification.

2.2. Preparation of CDs/RCNFs by physical mixing method

At first, 19 wt% of CA solution was prepared by dissolving 2.345 g of CA in 10 mL of DMF/acetone [6/4 (w/w)] binary solvent mixture. Subsequently, different weight percentages of CDs/CA solutions were prepared by simply adding CDs (α-CDs, β-CDs and γ-CDs) to the above prepared CA solution under vigorous stirring condition at room temperature. The obtained CDs/CA solutions were electrospun under an electric field of 12 kV at a tip-to-collector distance of 15 cm. A metallic Cu wire was used as an anode and a cathode was attached to a rotating metallic collector (RMC). The RMC was wrapped with aluminum foil and used as a collector for the nanofibers. The electrospun CDs/CANFs were dried in air and then dipped in 0.05 M NaOH solution for 48 h. Finally, the nanofibers were washed with distilled water and thoroughly dried [Fig. 1(a)].

2.3. Preparation of CDs/RCNFs by grafting method

The CANFs with 19 wt% was prepared according to our previously reported procedure [14]. The electrospinning condition was same for the both mixing and grafting methods. After preparing CANFs, the electrospun CANFs was dipped in 0.05 M of aqueous NaOH solution for 48 h to obtain RCNFs. For the grafting of CDs on the RCNFs, citric acid was used as a cross-linker [15]. Graft solution was prepared by mixing particular amounts of CDs (α-CDs, β-CDs or γ-CDs), citric acid and SHPI in distilled water under vigorous stirring at 60 °C. Then, the regenerated RCNFs were dipped into the above prepared solution at 60 °C for 4 h. Finally, the samples were washed with distilled water and dried in air for 24 h [Fig. 1(b)].

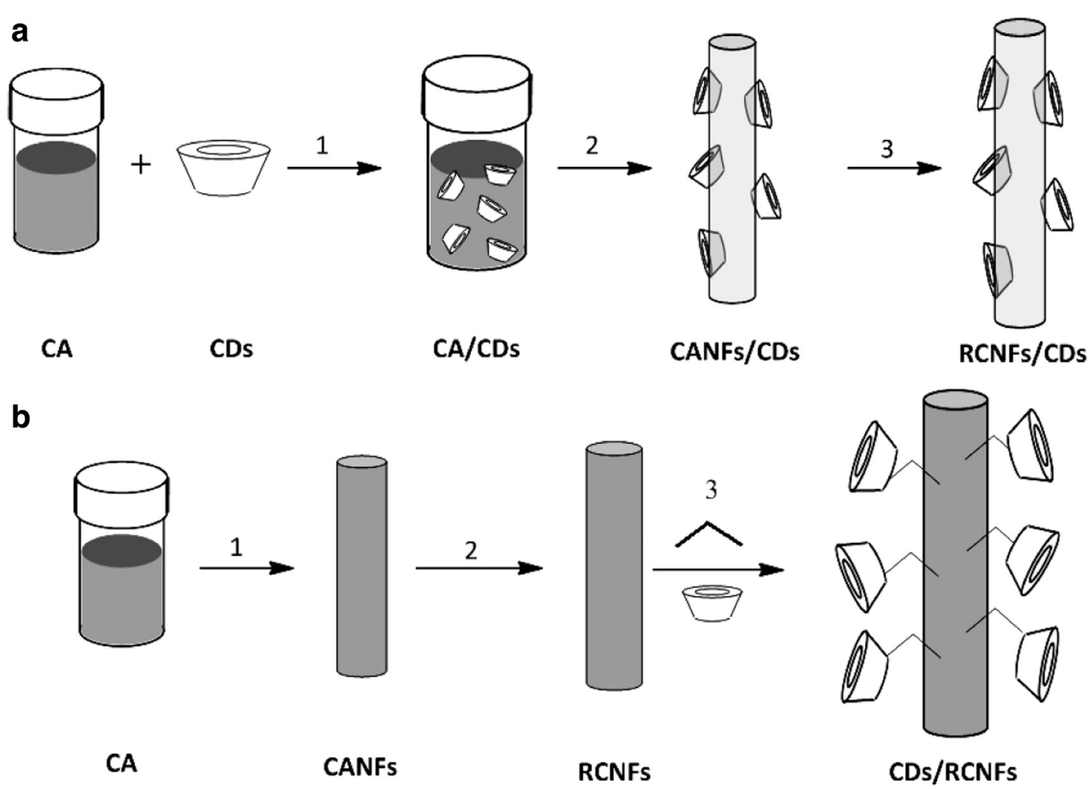

Fig. 1. Schematic illustration of the preparation of CDs/RCNFs composites; (a) physical mixing method and (b) grafted method.