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Electrospun core-shell polyamide 6/chitosan-Fe^{3+} composite fibers: An efficient and recyclable adsorbent for removal of antibiotic

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ABSTRACT

A novel core-shell polyamide 6 (PA6)/ chitosan (CS) – Fe^{3+} composite fibers with PA6 core and CS shell was fabricated by coaxial electrospinning and chelating with ferric iron. The transmission electron microscope (TEM) indicated that CS was uniformly distributed on the surface of PA6. The energy dispersion spectroscopy (EDS) and X-ray photoelectron spectroscopic (XPS) demonstrated the existence of Fe^{3+} and complexing between Fe^{3+} and CS. In addition, the core-shell PA6/CS-Fe^{3+} composite fibers exhibited high tetracycline removal rate, and could retain its high efficiency after desorption and regeneration. The prepared materials have excellent potential as adsorbents for wastewater treatment.

1. Introduction

The electrospun fibers have extraordinary high surface area-to-volume ratio and high porosity with excellent pore interconnection, and have been widely used in a range of hi-tech fields, such as filters, biomaterials and adsorbing materials [1,2]. Lately, increasing interest has been drawn to the application of fibers for removal of organic pollutants from water [3]. Compared with traditional adsorbents (activated carbon, silica and montmorillonite *etc.*), the electrospun fibers can be easily separated from a liquid medium.

PA6 has been used to produce fibers to apply in the field of wastewater treatment owing to its good mechanical and physical properties and non-toxic in nature [4,5]. In addition, cheap and environmentally friendly CS is one of the widely used polymer materials to adsorb pollutants due to the presence of active amino and hydroxyl functional groups [6,7]. It has been reported that chitosan-Fe^{3+} was applied to remove alkaline dyeing from aqueous solution [8]. However, CS fibers are difficult to be fabricated by the conventional electrospinning because of the polyelectrolytic nature and strong hydrogen bonding of CS. So CS has been electrospun by blending with other polymers [9]. Therefore, we want to take the advantage from both PA6 and CS by coaxial electrospinning to combine them into fibers with core-shell structures.

To obtain a basic understanding of adsorption ability of the fibers towards organic pollutants for developing the high-performance adsorbent, we have selected tetracycline (TC) as the removal objective in this study. As well known, the organic pollutants contain many species, such as antibiotics, hormones, dyes, phenols, *etc.* TC is the mostly important broad spectrum antibiotics, which pose great hazards to human and animal health [10]. The current work is aimed at the preparation of the novel core-shell PA6/CS composite fibers with PA6 core and CS shell by coaxial electrospinning. Moreover, Fe^{3+} was introduced into the composite fibers to increase the removal efficiency of TC. Their morphology and adsorption performance were investigated.

2. Experimental

PA6 solution with a concentration of 27 wt% was prepared by dissolving PA6 in formic acid as core component. As a shell component, chitosan solution (4 wt%) was obtained by dissolving chitosan in formic acid. To produce the core-shell PA6/CS composite fibers, we used the coaxial electrospinning technology. The electrospinning parameters were as follows: shell flow rate was constant at 0.3 mL/h, the core flow rate was constant at 0.20 mL/h,

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applied voltage was 21 kV, distance between the spinneret and the collector wheel was 15 cm. Incorporation of Fe^{3+} into the core-shell PA6/CS composite fibers was carried out by the reaction of the PA6/CS composite fibers with a 0.2 mol/L isopropanol solution of ferric chloride for 24 h at 25 °C. The mixture was then filtered, washed with isopropanol and water. Finally the obtained product was dried for 12 h at 60 °C under vacuum.

The microstructure of PA6/CTS composite fibers was examined by a Tecnai G220 transmission electron microscope (TEM) (FEI, Netherlands). The morphology of the electrospun fiber coated with a thin layer of platinum was observed by field emission scanning electron microscope (FE-SEM) (FEI Sirion 200, Netherlands) equipped with energy dispersion spectroscopy (EDS). The core-shell PA6/CTS-Fe^{3+} composite fibers was analyzed by X-ray photoelectron spectroscopic (XPS) (Vacuum Generator Mutilab2000).

All the TC adsorption experiments were performed in 100 mL conical flasks, which were sealed and agitated at 160 rpm in a thermostatic shaker maintained at 25 °C. The typical reaction mixture was initiated with 20 mL TC solution with the concentration of 20 mg/L and 15 mg fibers at the condition of pH = 7. On the adsorption procedure, solution were collected every 12 h to measure the TC concentration by using a Puxi TU-1901 UV–vis spectrometer. After the adsorption for 48 h, the TC-loaded fibers could be easily separated from water. For desorption experiments, the TC-loaded PA6/CS-Fe^{3+} fibers was then stirred in 50 mL of 1 mol/L NaOH solution at room temperature to strip the TC. In the regeneration process, the deionized water containing 0.1 mol/L HCl was used. And the cleaned fibers was then dried in a vacuum oven at 60 °C. The first adsorption-desorption cycle was followed by five other cycles using the same adsorbent batch.

3. Results and discussion

To corroborate the core-shell structure of the fibers, TEM image is shown in Fig. 1A. It can be seen that CS shell layer with uniform thickness is distributed onto the surface of PA6 fibers. The diameters of the core and shell are approximately 127 nm, 230 nm, respectively. As shown in Fig. 1B, the core-shell PA6/CS composites fibers with average fiber diameter of 180 ± 50 nm are fabricated. Fig. 1C shows the morphology of Fe^{3+} modified PA6/CS composite fibers. Obviously, the incorporation of Fe^{3+} do not retain the smooth surface of PA6/CS fibers, and increase mildly the diameter of the PA6/CTS fibers due to the swell and conglutinate with the adjacent fibers. The element analysis of the PA6/CS-Fe^{3+} composite fibers by EDS is shown in Fig. 1D. The Fe elements were detected with sharp peaks showing the existence of Fe^{3+} in the electrospun fibers.

Fig. 2A gives the wide survey scan of XPS spectra in the range 200–800 eV, which reveals carbon, oxygen, nitrogen, and iron are the predominant elements observed on the surface of fibers. The high resolution Fe 2p XPS spectra of PA6/CS-Fe^{3+} is shown in Fig. 2B. The peak positions of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ are 710.9 and 724.3 eV, respectively, which suggest the presence of Fe^{3+} on the core-shell PA6/CS composite fibers [11]. The high resolution N 1s

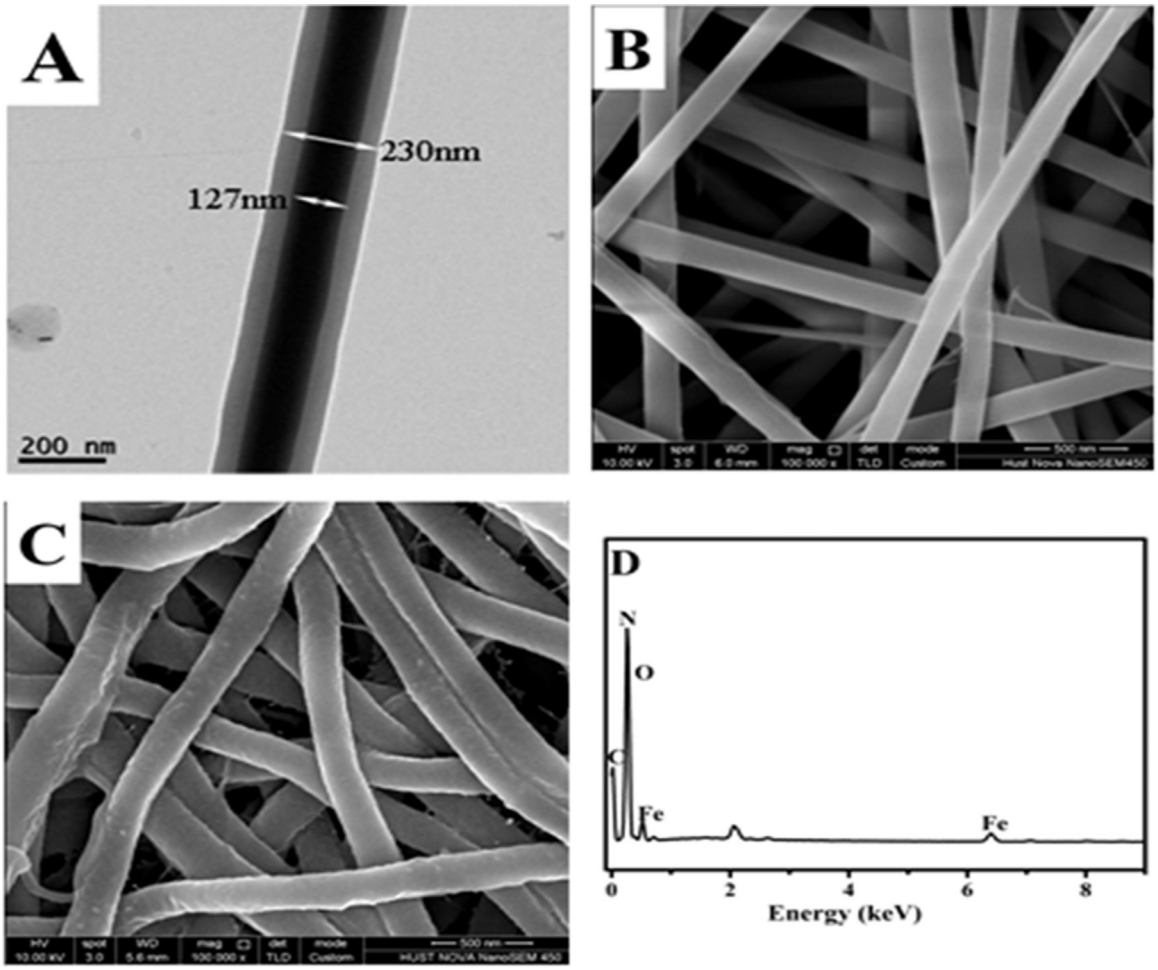

Fig. 1. TEM images of the core-shell PA6/CTS composite fibers (A); SEM images of fibers: PA6/CTS (B), PA6/CTS-Fe^{3+} (C) EDS of PA6/CTS-Fe^{3+} (D).