Chemical Engineering Journal 290 (2016) 263–272

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Electrospun zein nanoribbons for treatment of lead-contained wastewater

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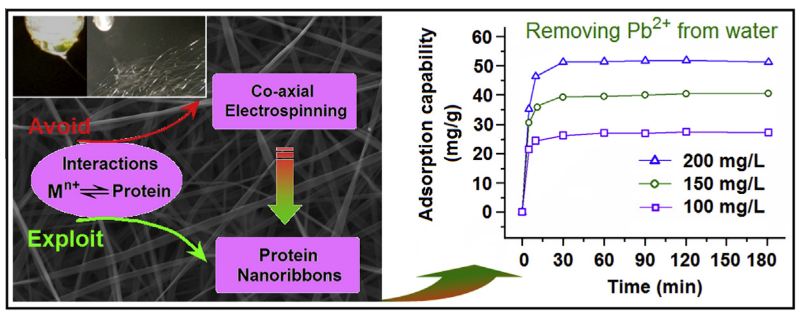
HIGHLIGHTS

- A protein ribbon mat for treating Pb(II)-contained water is introduced.
- Zein ribbons are fabricated continuously using a modified coaxial electrospinning.
- A surfactant solution is used as sheath fluid to thin and flatten the nanoribbons.
- The nanoribbons show fine performance with a maximum adsorption of 89.37 mg/g.
- A new method for SEM observation of the nanoribbons' cross-sections.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 October 2015
Received in revised form 8 January 2016
Accepted 10 January 2016
Available online 28 January 2016

Keywords:
Nanoribbon
Zein
Coaxial electrospinning
Adsorption
Pb(II)

ABSTRACT

This paper reports the preparation of zein nanoribbons and their application in the removal of Pb(II) from polluted water. A modified coaxial electrospinning process was conducted permitting the smooth and continuous generation of zein nanoribbons. The process utilized sodium lauryl sulfate ethanol aqueous solution as the sheath fluid to overcome protein–metal interactions and the corresponding spinneret clogging. Scanning electron microscopic images demonstrated that the zein nanoribbons created using the modified processes had a flatter and narrower morphology than the analogous materials from a single-fluid process. By exploiting the favorable interactions between metal and protein, these zein nanoribbon mats were used to treat Pb(II)-polluted water. Adsorption results indicated that equilibrium was obtained in 60 min for Pb(II) solutions with initial concentrations of 100, 150 and 200 mg/L. The process can be described using the pseudo-second-order model. Isotherm data fitted well to the Langmuir isotherm model, with a maximum adsorption of 89.37 mg/g. Desorption results showed that the adsorption capacity can remain up to 82.3% even after 5 cycles of re-use. Mechanisms underlying both the preparation and application of the zein nanoribbons were proposed.

1. Introduction

Heavy metals result in damage to public health and environmental systems, and such damage has become a global problem. Heavy metal exposure is linked to conditions such as genetic cell alteration, bladder cancer, neurotoxicity, and embryogenesis [1]. Among the heavy metals, Pb(II) is a highly toxic and common water pollutant that easily accumulates in living systems. Pb(II) can cause a series of adverse effects on humans, such as retardation of mental and physical development, irreversible brain damage, and poor muscle coordination [2]. A wide variety of technologies, such as chemical precipitation, filtration, biological treatment, adsorption, and ion exchange, have been developed to effectively

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http://dx.doi.org/10.1016/j.cej.2016.01.055
1385-8947/

remove heavy metal contamination from water [3]. Adsorption, which is also broadly used in practical industrial applications, is a convenient and easy approach to be applied for water decontamination [4]. Many types of adsorbents that can be used for the removal of heavy metals (such as graphene, carbon nanotube, nanofibrous membrane and ion exchanger) have been investigated [5,6]. Among these adsorbents, electrospun nanofiber mats have been found to be highly effective adsorbents during the past two decades [7,8].

Electrospun nonwoven mats have been broadly investigated for filtration, separation, and desalination to treat wastewater and waste vapor [9]. These potential applications are closely related to the advantages conferred by their randomly self-assembled nonwoven mats, in terms of high surface area and permeability to water [10–12]. To date, electrospun nanofiber mats have been used in several strategies for the development of advanced adsorbent nanomaterials, as follows: (I) surface modification of the fibers with functional groups or molecules for adsorption [7,13]; (II) incorporation of guest adsorbents, such as graphene oxide and β-cyclodextrin, in the host filament-forming polymer matrix during the electrospinning processes [8,14]; and (III) development of new types of electrospun fiber mats for direct usage as adsorption [15,16]. The third strategy is highly valued because of its facile and direct application and because it further allows the incorporation of other types of adsorbents for higher functional performance through synergistic action.

Biomacromolecules (such as polysaccharides and proteins) have the potential to become excellent adsorbents for the removal of heavy metals [17,18]. Particularly, protein molecules contain numerous groups with lone pairs of electrons and partial negative charges, and these groups allow protein molecules to absorb metal ions through electrostatic interaction and/or chelation. Proteins are naturally abundant and eco-friendly. Their "positive" interactions with heavy metal ions can further exert their actions in treating wastewater provided they can be converted into electrospun nanofiber mats. The mats can provide huge porosity and large surface areas for the contact of heavy metal ions with the functional groups on the nanofibers' surface, thereby resulting in higher levels of functional performance (Fig. 1).

However, the proteins are very difficult to be treated using a single-fluid electrospinning, such as zein, which is a mixture of proteins from corn gluten meal [19]. During preparation, the "negative" interactions between zein and the metal of the spinneret nozzle result in rapid clogging of the spinneret and finally a failure electrospinning process. Kanjanapongkul et al. reported a method for preventing clogging by introducing additional solvent to the spinneret nozzle [20], which is not easy to be manipulated. Subsequently a modified coaxial process is reported for the preparation of zein-based nano products for bio-medical applications, where only organic solvents were exploited as sheath fluids [21,22]. The unspinnable sheath organic solvent can lubricate the spinneret to effectively eliminate the interactions between the zein fluid and the metal nozzle. Thus the clogging can be completely prevented to ensure a stable, smooth, and continuous fiber preparation process with size and shape controllable nano-products (Fig. 1).

Coaxial and side-by-side electrospinning are both types of double-fluid electrospinning processes [23–25]. Based on the electrospinnability of the sheath fluids, coaxial electrospinning can be divided into two categories: traditional coaxial electrospinning and the modified coaxial process [22]. In the traditional coaxial electrospinning, the sheath working fluid must be electrospinnable [26]. Its capability of creating structural nanofibers is very limited because of only a few polymeric solutions possessing fine electrospinnability. In contrast, the modified coaxial electrospinning, which is characterized by the unspinnable sheath liquids, can exploit numerous different types of liquids (such as solvent, solution containing little molecules, dilute polymer solution, suspension and emulsion) as a sheath working fluid [21]. Thus the modified coaxial process can greatly expand the capability of electrospinning in generating nano products.

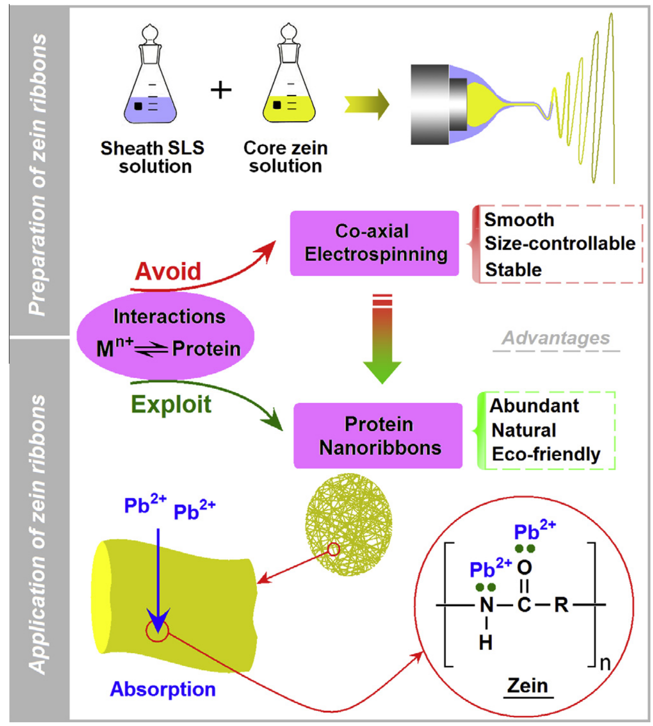

Fig. 1. A diagram explaining the rationale behind the preparation of zein nanoribbons using coaxial electrospinning and their application in removing heavy metal ions from water.

No matter what types of electrospinning, a stable and robust process is a result of the balance between electrical force and working fluids' surface tension and viscoelasticity [27–30]. In the single-fluid electrospinning, surfactants are often added into polymeric solutions or emulsions to enhance their electrospinnability or to ensure the generation of nanofibers with high quality [31–33]. In this study, we investigated the preparation of zein nanoribbons using a modified coaxial electrospinning process and the potential application of these ribbons in the treatment of water containing heavy metals. A pure surfactant solution containing sodium lauryl sulfate (SLS) was exploited as the sheath fluid to ensure a continuous nanofabrication process, and meanwhile to downsize and to flatten the zein ribbons. The prepared nanoribbons exhibited fine functional performance of removing Pb(II) from water.

2. Experimental

2.1. Materials

Zein was obtained from Aldrich (98% purity; Milwaukee, WI, USA). Lead(II) nitrate [$Pb(NO_3)_2$, 99.99%], 4,4′-diaminodiphenymethane (DDM), SLS, anhydrous ethanol, and Na_2EDTA were provided by the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Epikote-828 (EP) was supplied by Royal Dutch Shell (Shanghai, China). Water was double distilled just before use. All other chemicals and reagents were of analytical grade.

2.2. Electrospinning

Core fluids were prepared by dissolving 30 g zein in 100 mL of a 75%/25% (v/v) ethanol/water mixture. These had a dark yellow