Electrospun zein nanoribbons for treatment of

lead-contained wastewater

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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.

Keywords: Nanoribbon; Zein; Coaxial electrospinning; Adsorption; Pb(II)

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 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

93 strategies for the development of advanced adsorbent nanomaterials, as follows: I)
94 surface modification of the fibers with functional groups or molecules for adsorption
95 [7,13]; II) incorporation of guest adsorbents, such as graphene oxide and
96 β -cyclodextrin, in the host filament-forming polymer matrix during the
97 electrospinning processes [8,14]; and III) development of new types of electrospun
98 fiber mats for direct usage as adsorption [15,16]. The third strategy is highly valued
99 because of its facile and direct application and because it further allows the
100 incorporation of other types of adsorbents for higher functional performance through
101 synergistic action.

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

112 However, the proteins are very difficult to be treated using a single-fluid
113 electrospinning, such as zein, which is a mixture of proteins from corn gluten meal
114 [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 of the 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).

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.

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.

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(NO₃)₂, 99.99%], 4,4'-diaminodiphenylmethane (DDM), SLS, anhydrous ethanol, and Na₂EDTA 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 color. The sheath fluid consisted of 0.5% (w/v) SLS in 75%/25% (v/v) ethanol/water.

Two KDS 100 syringe pumps (Cole-Parmer, Vernon Hills, IL, USA) and a ZGF200 high-power supply (60 kV/2 mA, Shanghai Sute Corp., Shanghai, China) were used in single-fluid and coaxial electrospinning. All experiments were conducted under ambient conditions at 22 ± 5 °C with a relative humidity of $58 \pm 6\%$. A homemade concentric spinneret was used to implement both single-fluid (with the sheath fluid adjusted to 0 mL/h) and coaxial electrospinning. The electrospinning processes were recorded using a digital camera (PowerShot A490; Canon, Tokyo, Japan). Following optimization, the applied voltage and the spinneret to collector distance were fixed at 15 kV and 20 cm, respectively.

2.3. Morphology

The morphology of the nanoribbons was examined using an S-4800 field-emission scanning electron microscope (FESEM, Hitachi, Tokyo, Japan). The average ribbon width was determined by measuring their sizes in FESEM images at more than 100

different places using the NIH Image J software (National Institutes of Health, Bethesda, MD, USA). The elemental composition of the samples was analyzed by an Energy Dispersive Spectrometer (EDS, IE300X, Oxford, U.K.) attached to the FESEM.

Cross-sections of the zein nanoribbons were prepared using the following procedures. First, the EP was outgassed using a vacuum pump for 30 min at 80 °C. DDM was then added at a ratio of 28:100 by weight. Subsequently, the mixture was outgassed and stirred using a mechanical agitator at 80 °C for 15 min, after which it was poured onto a piece of pre-cut zein mat. The zein mats covered with EP/DDM were solidified in an oven at a fixed temperature of 100 °C for 4 h. Finally, the resultant compact could be manually broken for platinum coating and SEM observation.

2.4. Physiochemical property of the zein nanoribbon mats

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) analysis was conducted using a Nicolet–Nexus 670 FTIR spectrometer (Nicolet Instrument Corporation, Madison, USA). A DSA100 drop shape analysis instrument (Krüss GmbH, Hamburg, Germany) was used to measure water contact angles on the zein nanoribbons.

2.5. Pb(II) adsorption experiments

Pb(NO₃)₂ was used as the Pb(II) source. An ICP OES (PerkinElmer, Optima 7000DV, Waltham, MA, USA) was used for Pb(II) quantification. Data acquisition and processing were performed using the WinLab 32 software (PerkinElmer). All

adsorption experiments were conducted in a thermostatic shaker bath operating at 25 °C and 100 rpm. The removal percentage of Pb(II) can be calculated using the following equation:

$$\%removal = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_0 is the initial concentration of Pb(II) in solution (mg/L) and C_e is the equilibrium concentration (mg/L).

For comparison of the two nanoribbons (R1 and R2), 100 mg of the mats were directly added into beakers containing 30 mL of 100, 150, and 200 mg/L Pb(II) solutions with a pH value of 7 for 12 h.

For investigation of the influence of pH value, 100 mg pieces of the R2 sample were added into beakers containing 30 mL of 200 mg/L Pb(II) solutions at a series of pH values of 1, 3, 5, and 7, and shaken for 12 h. To further study the influence of pH value on the performance of the mats, a Raman Station 400F Raman Spectrometer (PerkinElmer) was used to record the Raman spectra of the recovered and dried zein ribbon mats after immersion in solutions of different pH values for 12 h. Spectra were obtained using a 785 nm wavelength near infrared excitation laser light.

The adsorption isotherms for Pb(II) were established by batch adsorption experiments. A 100 mg zein nanoribbon mat was immersed into 30 mL of Pb(II) solutions with different concentrations. The pH value was fixed at 7. The adsorption experiment was run for 12 h to establish adsorption equilibrium. The equilibrium adsorption capability was calculated using the following equation:

$$q_e = \frac{C_0 - C_e}{m} V \quad (2)$$

where C_0 is the initial concentration of Pb(II) in solution (mg/L), C_e is the equilibrium concentration (mg/L), q_e is the equilibrium adsorption capability (mg/g), m is the mass of adsorbent (g), and V is the volume of solution (L).

The kinetic adsorption performance was investigated by placing 100 mg zein nanoribbon mats into Pb(II) solutions with different initial concentrations and at a pH value of 7. Samples (0.1 mL) were obtained from the solution at different times. The adsorption capability was calculated using the following equation:

$$q_t = \frac{C_0 - C_t}{m} V \quad (3)$$

where q_t is the adsorption capability at time t (mg/g), C_0 is the initial concentration of Pb(II) in solution ($\mu\text{g/mL}$), C_t is the Pb(II) concentration at time t (mg/L), m is the mass of adsorbent (g), and V is the volume of solution (L).

2.6. Desorption investigation

For desorption studies, 100 mg of a zein nanoribbon mat was immersed in 30 mL of a 200 mg/L Pb^{2+} solution for 12 h. Then, the zein ribbon adsorbent loaded with Pb(II) was immersed into 50 mL of 0.02 M Na_2EDTA solution for 30 min. The above procedure was repeated five times to determine the reusability of the zein ribbon mats.

3. Results and discussion

3.1. Modified coaxial electrospinning

Visual observations of the modified coaxial processes performed in this work are shown in Fig. 2. The electrospinning system (Fig. 2a) comprised two syringe pumps, which were used to drive the core and sheath fluids. The high voltage power supply

was connected to the spinneret using an alligator clip (Fig. 2b). The fibers were collected on an earthed collector comprising aluminum foil wrapped around a flat piece of cardboard. The homemade concentric spinneret used is depicted in the upper-right inset of Fig. 2a.

Initially, the sheath fluid was switched off, resulting in single-fluid electrospinning of the core fluid. A semi-solid yellow substance was observed to appear and grow up on the nozzle of spinneret, rapidly leading to clogging (Fig. 2c). Manual removal of the blockage was frequently required for continuous fiber preparation. In addition, the zein ribbons were scattered across the whole collector, as indicated by the left inset of Fig. 2a. In sharp contrast, the collection of nanoribbons from the coaxial process is able to be concentrated in a small circular region. When the flow rates of the sheath/core fluids were adjusted to 0.2/0.8, a stable and robust process could be observed (Figs. 2b and 2d). The modified coaxial process started from a compound core-sheath Taylor cone (the upper-right inset of Fig. 2d), which was converted from a core-sheath droplet (the upper-right inset of Fig. 2c) after a high voltage of 15 kV was applied. Subsequently, a straight fluid jet was emitted, followed by an unstable region. However, when the sheath/core fluid flow rate ratio was changed to 0.5/0.5 mL/h, division of the sheath fluid from the core fluid jet was occasionally observed, as shown in the lower-right inset of Fig. 2d. Four types of zein nanoproducs were fabricated under different conditions, and their preparation parameters are detailed in Table 1.

Fig. 2. Implementation of modified coaxial electrospinning for the preparation of zein nanoribbons. (a) the arrangement of the apparatus (left inset: the collection of ribbons from single-fluid electrospinning; upper-right inset: the homemade concentric spinneret); (b) a digital picture of the connection between the spinneret, working fluids and power supply (inset: a core-sheath droplet before applying voltage); (c) the spinneret clogging when electrospinning was performed without the sheath solution; (d) a digital picture of modified coaxial electrospinning; (upper-right inset: the compound Taylor cone with a sheath-to-core fluid flow rate ratio of 0.2/0.8; bottom-right inset: the partial separation of the sheath fluid from the core fluid under an excessive sheath-to-core fluid flow rate ratio of 0.5/0.5).

Table 1 Parameters of the electrospinning processes and their products

No.	Process	F_c^a (mL/h)	F_s^b (mL/h)	Fiber Morphology	Width ^c (μm)
R1	Single	1.0	0.0	Linear ribbon	1.31 ± 0.42
R2		0.8	0.2	Linear ribbon	0.89 ± 0.31
R3	Coaxial	0.7	0.3	Linear ribbon with few nanoparticles	0.57 ± 0.34
R4		0.5	0.5	Hybrids of ribbons & particles	--

^a F_c is the flow rate of the core zein solution.

^b F_s is the flow rate of the sheath SLS solution.

^c Expressed as the mean $\pm$ SD of over 100 fiber width measurements.

3.2. Morphologies of the nanoribbons

Figs. 3a to 3d show FESEM images of the ribbons R1 to R4. The materials from the single-fluid electrospinning process have linear morphology with an average width of $1.31 \pm 0.42 \mu\text{m}$ (Fig. 3a and inset). Zein nanoribbon R2 from the modified coaxial process also showed a linear morphology with an average width of $0.89 \pm$

0.31 μm (Fig. 3b and inset). However, a further increase of sheath fluid flow rate to 0.3 mL/h to prepare ribbons R3 occasionally created a beads-on-a-string morphology, although they were further reduced to $0.57 \pm 0.34 \mu\text{m}$ (Fig. 3c and inset). Further increase of the sheath-to-core fluid flow rate ratio divided the Taylor cone, as well as resulted in a hybrid material with nanoribbons, beads-on-a-string morphologies, and some nanoparticles, as reflected in Fig. 3d and its inset.

Fig. 3. FESEM images of the prepared zein ribbons and their width distribution (a-R1; b-R2; c-R3; d-R4), and the cross-sections of R1(e) and R2 (f).

The cross-sections of the zein ribbons were observed using FESEM to further examine their morphologies. The traditional method for preparing nanofiber cross-sections requires the immersion of nanofibers in liquid nitrogen for a certain period of time before they can be manually broken for platinum coating [34]. However, this method failed in this experiment because the ribbons easily bent, thereby concealing the cross-sections. Thus, an epoxy resin embedding method was developed to prepare the samples of nanoribbon cross-sections for FESEM observations. This method is frequently utilized in preparing TEM samples [35,36] and is also occasionally used for AFM [37]. The cross-sections of the R1 and R2 ribbons are shown in Figs. 3e and 3f and their insets, respectively. Clearly, the R2

nanoribbons had a smaller width and were flatter than R1.

3.3. Zein nanoribbons' formation mechanism

The surface tension of the core solution and its conductivity are mainly responsible for initiating the Taylor cone formation in single-fluid electrospinning processes [38]. In the modified coaxial process, the formation of a compound core-sheath Taylor cone is mainly determined by the surface tension of the sheath working fluid and its conductivity (Fig. 4). The SLS solution had a smaller surface tension and a larger conductivity than the core fluid, which means that a smaller applied voltage was needed to initiate the coaxial electrospinning process than that was required in single-fluid spinning. Meanwhile, the sheath solution can keep the core fluid subject to electrical drawing for a longer time period before reaching the collector. Thus, under the same applied voltage of 15 kV, the R2 zein ribbons from the coaxial spinning had a smaller width than R1 from the single-fluid process. As the sheath-to-core fluid flow rate ratio increased, the ribbon widths decreased. This is expected to be because a greater flow of the sheath SLS solution led to further extended drawing processes. SLS is also expected to have influenced the proteins' conformations during the electrospinning processes, and thus promoted the formation of even flatter morphology. Similar investigations about the influence of surfactant on the behaviors of working fluids under an electrostatic field have been reported during the electrospraying processes [39]. Further investigations about the influence of selected surfactants and solvents on the nanofibers' morphology is being studied at present in our group.

During the electrospinning process, the following forces exerted their influences on the fluid jets (Fig. 4): the attractive forces between the two electrodes, i.e., the forces exerted on the fluid jets by the electrical field (f_1); the repulsion forces between the two unstable bending coils (f_2); and Coulombic repulsion forces within the fluid jets (f_3). Forces f_1 and f_3 are mainly responsible for reducing the diameter of the fluid jets through repulsion and drawing, whereas forces f_1 and f_2 allow the formation of nanofibers as the fluids travel from one electrode to another.

Fig. 4. Mechanisms by which the sheath SLS solution influences the formation of zein nanoribbons.

During the coaxial process, although the addition of SLS increased the Coulombic forces (f_3), which is favorable for drawing the core fluid and achieving finer nanoribbons, it will also cause an increase in the attractive forces between the two electrodes (f_1) and the repulsion forces between two unstable bending coils (f_2), and this will greatly shorten the traveling time from spinneret to collector. Correspondingly, in the coaxial process, the distance between two coils d_c should be larger than its counterpart d_s in the single-fluid process (Fig. 4). Thus, the area over which the zein ribbon R1 was collected had a larger diameter (D_s) than that of zein

nanoribbon R2 from the coaxial process (D_c). This can clearly be seen in Fig. 2a.

3.4. Properties of the zein nanoribbons

Although the SLS amount present was very small, it will influence the hydrophilic properties of the electrospun materials. The ATR-FTIR spectra and water contact angles of the nanoribbon mats were measured. Fig. 5a shows the characteristic bands of pure SDS at 1029 cm^{-1} and 1225 cm^{-1} , caused by symmetric (ν_s S–O) and asymmetric (ν_a S–O) stretching of the sulfate group. In the spectra of the nanoribbons, bands at 1031 and 1220 cm^{-1} were found, thereby reflecting the co-existence of SDS and zein in the nanoribbons.

Fig. 5. (a) ATR-FTIR spectra of zein, SLS, and the R2 nanoribbons; and (b) the contact angle of R1 to R3 nanoribbons.

Water contact angles of R1 to R3 were determined by placing 3 μL water droplets on the mats. The contact angles were measured 5 s after the droplets were stable. Fig. 5b shows that as the sheath fluid flow rate increased (leading to an increase of the amount of SDS on the surface of the ribbons), the contact angle gradually decreased from $138^\circ \pm 9^\circ$ for R1, $119^\circ \pm 12^\circ$ for R2, and $96^\circ \pm 15^\circ$ for R3.

The water droplets disappeared more rapidly on R3 than on the other two mats. These results, which agree with the FTIR spectra, suggest the presence of a small amount of SLS on the surfaces of the zein ribbons.

3.5. *Pb(II)* adsorption performance

The *Pb(II)* adsorption performance of R1 and R2 was first explored with different initial concentrations of *Pb(II)*; the results are shown in Fig. 6a. The R2 ribbons from the coaxial process always showed slightly greater adsorption than R1 from the single-fluid process. This finding is thought to be due to the larger surface area of ribbons R2 than R1.

The sizes, structures, shapes, and surface textures of nanomaterials have a profound influence on their functional performances [40]. Biomedical applications in drug delivery favor zein nanofibers with round morphology because this morphology can increase the distance through which the encapsulated active ingredient has to diffuse to leave the fiber, and thus is more likely to give a sustained-release profile [19]. However, for applications as adsorbents, a flat ribbon shape should be advantageous over a cylindrical shape because flat ribbons have a larger surface area than round fibers with the same weight or volume.

Fig. 6. (a) Effect of nanoribbons' morphology on the Pb(II) removal performance; and (b) the influence of nanoribbons' morphology on the surface area.

The cross-sections of the nanoribbons were treated as ellipses, and the macroaxis and brachyaxis were approximated at 1.3 and 0.5 μm for ribbon 1, and 0.9 and 0.2 μm for ribbon 2, respectively (Fig. 6a). Thus, the ratio of superficial area of the two ribbons can be calculated as follows:

The sectional area of ribbons 1:

$$A_1 = \pi m_1 b_1 = 3.1416 \times 1.3 \times 0.5 = 2.04 \mu\text{m}^2$$

The ellipse perimeter of cross-section of ribbons 1:

$$P_1 = 2\pi b_1 + 4(m_1 - b_1) = 2 \times 3.1416 \times 0.5 + 4(1.3 - 0.5) = 6.34 \mu\text{m}$$

The sectional area of ribbons 2:

$$A_2 = \pi m_2 b_2 = 3.1416 \times 0.9 \times 0.2 = 0.57 \mu\text{m}^2$$

The ellipse perimeter of cross-section of ribbons 2:

$$P_2 = 2\pi b_2 + 4(m_2 - b_2) = 2 \times 3.1416 \times 0.2 + 4(0.9 - 0.2) = 4.06 \mu\text{m}$$

Under the same volume, the length ratio of L_2/L_1 can be calculated according to $L_1 \times$

$$A_1 = L_2 \times A_2, \text{ i.e., } L_2/L_1 = A_1/A_2 = 2.04/0.57 = 3.58$$

Then the ratio of superficial area of the two ribbons is $S_2/S_1 = (P_2 \times L_2)/(P_1 \times L_1) =$

$$(4.06/6.34) \times 3.58 = 2.29$$

where m represents the macroaxis of ellipse, b represents the brachyaxis of ellipse, P represents perimeter, L represents length, A represents sectional area, S represents the surface area, and the subscripts "1" and "2" represent parameters of ribbons R1 or R2, respectively.

Although R1 and R2 nanoribbons have similar morphology, the surface area of

R2 ribbon from the modified coaxial process was more than double that of R1 ribbon from the single-fluid process. A larger surface area means increased number of functional groups on the surface of zein ribbons for adsorbing heavy metal ions. Thus, R2 exhibited a better adsorption performance than R1.

3.6. The influence of pH value on the adsorption

Proteins are sensitive to pH changes of aqueous solutions. The effect of the initial solution pH value on the Pb(II) adsorption was investigated. When the pH value of the initial solution changed from 7.0 to 5.0, 3.0, and 1.0, the adsorption efficiency correspondingly decreased from 86.7% to 57.1%, 46.3%, and 32.6% (Fig. 7a). This decrease was caused by the competitive interaction between H^+ and Pb(II), as well as the easy degradation of protein under acidic conditions, because both of which could weaken the interactions between Pb(II) and zein molecules. The following adsorption experiments were performed under an initial solution pH of 7.0.

To determine the possible changes of the zein nanoribbons after the adsorption experiments in different pH conditions for 12 h, the zein mats were dried naturally, and were later subjected to Raman spectroscopy. Fig. 7b shows the Raman spectra of the R2 zein nanoribbons (A) before and after the adsorption experiments. Lines B to E are Raman spectra of the nanoribbons after immersion in solutions with pH values of 7, 5, 3, and 1, respectively. These spectra demonstrate that the absorbance at approximately 1440 cm^{-1} (γ_{CH_2}) and 1672 cm^{-1} (Amide I) gradually increased with decreasing pH value. An acidic environment will accelerate the degradation of proteins, resulting in the formation of amino acids, which have give stronger Amide I

and $-\text{CH}_2$ group signal in Raman spectroscopy to the scattered light.

Fig. 7. (a) Effect of pH value on the removal of Pb(II) by R2 nanoribbons. (b) Raman spectra of A – R2 zein nanoribbons; B, C, D, and E – R2 after adsorption experiments in solutions with pH values of 7, 5, 3 and 1, respectively.

3.7. Adsorption kinetics and isotherm

The effects of adsorption time on the adsorption capability at different initial solution concentrations are shown in Fig. 8. The results obtained indicated that the adsorption capability for Pb(II) increased with increasing adsorption time until equilibrium was reached. The equilibrium times were all within 60 min. The equilibrium adsorption capacity increased from 27.3 to 39.2, and 51.7 mg/g for 100, 150, and 200 mg/L solutions, respectively.

Fig. 8. Effect of contact time and initial concentration on the adsorption of Pb(II) on the R2 zein nanoribbons. Temperature = 25 °C and initial solution pH = 7.0 (n = 3).

To further understand the adsorption behavior, kinetic data are often analyzed using two kinetic models, the pseudo-first-order equation and pseudo-second-order equations [41]. These models are used to describe the adsorption of solid/liquid

systems, and can be expressed in linear form as Eqs. (4) and (5), as follows:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where K_1 and K_2 are the pseudo-first-order and pseudo-second-order rate constants, respectively.

The adsorption kinetic plots for the adsorption of Pb(II) are shown in Fig. 9. The kinetic parameters obtained are summarized in Table 2. The values of the correlation coefficients demonstrated that the adsorption kinetics closely followed the pseudo-second-order model (Fig. 9b) rather than the pseudo-first-order model (Fig. 9a). The $q_{e,cal}$ values calculated from the pseudo-second-order kinetic model were closer to the experimental data $q_{e,exp}$ than those obtained from the pseudo-first-order kinetic model.

Table 2. Kinetics parameters for Pb(II) adsorption onto the zein nanoribbons

C_0 (mg/g)	^a $q_{e,exp}$ (mg/g)	Pseudo-first-order model			Pseudo-second-order model		
		K_1 (1/min)	^b $q_{e,cal}$ (mg/g)	R^2	K_2 (g/mg/min)	^b $q_{e,cal}$ (mg/g)	R^2
200	51.7	0.077	22.5	0.8213	0.019	52.1	0.9988
150	39.2	0.052	13.5	0.7288	0.022	39.4	0.9897
100	27.3	0.071	10.8	0.8926	0.039	27.1	0.9917

^a Equilibrium adsorption capability from the experiments.

^b Equilibrium adsorption capability calculated from the kinetic models.

Fig. 9. Fits of the pseudo-first-order kinetic model (a) and pseudo-second-order kinetic model (b) for adsorption of Pb(II) onto the R2 zein nanoribbons.

The linearized Langmuir isotherm model, given in Eq. (6) [42], was utilized to fit the equilibrium data.

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (6)$$

where q_m (mg/g) is the maximum adsorption capability, b (L/mg) is the Langmuir constant related to the energy of adsorption, and C_0 is the initial concentration of Pb(II) in solution (mg/L). Fig. 10 shows that the fitted Langmuir isotherm equation had a correlation coefficient R^2 of 0.9974, and hence this isotherm is appropriate for use here. The maximum adsorption capability calculated from the Langmuir model was 89.37 mg/g at a temperature of 25 °C.

Fig. 10. Langmuir isotherm model for adsorption of Pb(II) on R2 zein nanoribbons.

3.8. Desorption performance

For the reusability study, 50 mL of a 0.02 mM aqueous EDTA solution was used to regenerate zein nanoribbon mats loaded with Pb(II) ions. As shown in Fig. 11a, R2 zein nanoribbons exhibited good recyclability. The adsorption capability remained at 82.3% of the initial value after five cycles. However, the R2 nanoribbons became more fragile after each adsorption experiment. This is reflected in the SEM images of the nanoribbon mats after recycle experiments. Figs. 11b and 11c show that some

broken ends existed after fourth desorption experiments and numerous broken rods occurred on the surface of the mats after sixth adsorption experiments. EDS results demonstrated that Na₂EDTA could remove the Pb(II) from the zein ribbons well with only 0.34% (wt) residues after the 4th desorption (Fig. 11b), and that the recovered zein ribbons were still capable of effectively drawing Pb(II) from the contained water with a content of 5.09% (wt) Pb(II) on the zein ribbons after the 6th adsorption (Fig. 11b). The ribbons seemed also to become more cylindrical in shape after repeated adsorption/desorption cycles, likely to be a result of changes in the protein spatial conformation during the adsorption process. Further experiments about improving the mechanical performance of zein ribbons are under study, in which filament-forming polymers with fine mechanical properties are combined with zein in a core-shell or Janus nano-structural format through the coaxial or side-by-side electrospinning processes [43,44].

Fig. 11. (a) Adsorption–desorption cycles, and EDS results of zein ribbons R2 after (b) 4th

desorption experiment and (c) 6th adsorption experiments, the insets in (b) and (c) are the corresponding FESEM images zein ribbons.

4. Conclusions

A modified coaxial electrospinning was developed to fabricate zein nanoribbons. An unspinnable SLS solution was used as the sheath fluid. With selection of appropriate core and sheath working fluid flow rates, a smooth and continuous preparation process could be implemented, resulting in narrow and flat zein ribbons. The zein nanoribbon mats showed good functional performance in Pb(II) adsorption experiments. Adsorption equilibrium was reached within 60 min, and the uptake process can be described using the pseudo-second-order model. The adsorption data fitted well the Langmuir isotherm, with a maximum adsorption capability of 89.36 mg/g. In repeated cycles of absorption/desorption, the adsorption capacity remained at 82.3% of the initial value even after 5 cycles. This report pioneers a new approach to preparing one-dimensional nanomaterials from naturally recovered products and demonstrates the potential applications of these nanomaterials in the treatment of polluted water.

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figure 10

figure 11