The green, ultrafine cellulose-based porous nanofibrous membranes for efficient heavy metal ion removal through incorporation of chitosan by various electrospinning ways

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Research Article

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Abstract

The rapid global industrialization worsens the contamination of heavy metals in aquatic ecosystems on the earth. In this study, the green, ultrafine cellulose-based porous nanofibrous membranes for efficient heavy metal removal through incorporation of chitosan by the conventional and core-shell electrospinning ways were firstly obtained. The relations among parameters of electrospun solution, micro-morphology and porosity for nanofibers, the variation of chemical active sites and adsorption performance of biocomposite nanofibrous membranes for conventional and core-shell electrospinning as well as the adsorption effect factors of copper ions including initial concentration, pH of solution and interaction time were comprehensively investigated. The results show that the average diameter for conventional and core-shell ultrafine nanofibers at 50% chitosan and 30% chitosan loading can achieve 56.22 nm and 37.28 nm, respectively. The core-shell cellulose acetate/chitosan (CA/CS) biocomposite nanofibrous membranes induced the surface aggregation of copper ions to impede the further adsorption. The more uniform distribution for chemical adsorption sites can be obtained by the conventional single-nozzle electrospinning than by the core-shell one, which promotes the adsorption performance of copper ions and decreases the surface shrinkage of nanofibrous membranes during adsorption. The 30% CS conventional nanofibrous membranes at the pH=5 aqueous solution showed the optimum adsorption capacity of copper ions (86.4 mg/g). The smart combination of renewable biomass with effective chemical adsorptive sites, the electrospinning technology with interwoven porous structure and the adsorption method with low cost and facile operation shows a promising prospect for water treatment.

Introduction

The rapid development of modern global industrialization is leading to a worsening pollution crisis of aquatic ecosystems. The ever-elevated amounts of heavy metals in clean water resource on the earth by industrial and agricultural wastes as well as by natural weathering of crustal rocks and submarine volcanic eruptions cause serious health issues to living organisms and the ecosystem owing to their non-biodegradability, toxicity, and carcinogenicity, persistency, and bioaccumulation (Zou et al. 2016; Fan et al. 2019; Qasem et al. 2021). This also severely restricts human normal production, life and further sustainable development. Several methods like ion-exchange, precipitation and oxidation, photocatalysis, separation and adsorption have been attempted to eliminate heavy metal ions in polluted water environment (Liu et al. 2015; Ghafoor et al. 2018). The adsorption is considered as the outstanding technology due to its low cost of investment and operation, facile process, high efficiency and reversibility for the decontamination (Olivera et al. 2016).

Recently, green sustainable adsorbents derived from natural biomass resources have attracted great interest with the advantages of renewability, non-toxicity, biodegradation, and low cost (Kim et al. 2020). Cellulose composed of a linear homopolymer linked by β -D, 1, 4 glycosidic bond is the largest amount of biomass in the world, with excellent physical, mechanical properties, and stability as well as environmental-friendly property (Li et al. 2021). However, the lack of surface chemical activities, leading

to a poor chemical complex with heavy metal ions limits its use as an absorbent. To solve this problem, esterification (Yan et al. 2020), etherification (Hashem et al. 2010), oxidation (Zaccaron et al. 2020), and graft copolymerization (Hou et al. 2020) have been used to functionalize cellulose to promote its adsorption efficiency (Hashem et al. 2020). Chitosan (CS) mainly in exoskeleton of crustacean marine life is a promising natural adsorptive polymer composed of β -D, 1, 4, glucosamine (Xu et al. 2018). The special amino and hydroxyl groups existed in chitosan facilitate the formation of chelates with heavy metal ions (Lakhdhar et al. 2015; Habiba et al. 2017), providing excellent ion binding and adsorptive properties (Wang et al. 2018b). However, the original chitosan-based adsorbents like chitosan beads, powder or flakes generally appeared the low adsorption capacity because of the low porosity, covered inside functional groups as well as the poor mechanical strength and stability (Qasem et al. 2021; Upadhyay et al. 2021), which limits its huge potential and leads to inefficient regeneration. Hence, chemical modification by cross-linking or grafting have been proposed to alleviate these problems, but increasing the mechanical strength of CS by combining polymer chains with functional groups comes at the cost of reduced adsorption capacity and increasing consumption of chemicals and energy during modification (Vakili et al. 2018; Qasem et al. 2021).

The structure is another crucial factor for adsorption capacity of adsorbents. The porous membranes composed of nanofibers with high specific surface areas and potential controllable surface properties have gained considerable attention for efficient removing heavy metals (Awual et al. 2018). Electrospinning currently is the most straightforward and most efficient method to produce continuous nanofibers with diameters at micro or nanometers scales (Wang et al. 2017a), with a wide range of utilization due to their special nanofiber interwoven porous morphology, low carbon footprint, and zero contamination (Tian et al. 2019). Tian et al. (Tian et al. 2011) prepared cellulose acetate/acetone/N, N-dimethylacetamide nanofibers membrane by the way of electrospinning and modification of poly(methacrylic acid), which appeared an average diameter of 750 nm and a high adsorption selectivity for mercury ions. Liu et al. fabricated a ribbon-like porous cellulose acetate/acetone/dichloromethane composite micro-fibers using electrospinning with an average width of 940 nm and pore size of 52×98 nm for copper ion adsorption (Liu et al. 2015). Hamad et al. combined the nanocomposite fibers of pure cellulose acetate with hydroxyapatite by electrospinning with an excellent separation efficiency of 95.46% within 40 min (Hamad et al. 2020). Fan et al. reported an effective chitosan/ β -cyclodextrin/polyvinyl alcohol nanofibrous membrane prepared by electrospinning for the rapid adsorption of several heavy metal ions (Fan et al. 2019). Karim et al. reported poly(vinyl alcohol)/chitosan nanofibers membranes fabricated using an electrospinning technology for selective adsorption of cadmium and lead ions (Karim et al. 2019). Bates et al. designed and fabricated a “sandwich-like” TEMPO-oxidized cellulose/ chitosan-polyethylene oxide (TO-CE/CS-PEO) composite membrane for copper ion adsorption in which porous oxidized cellulose nanofibrils served as the core and an electrospun nanofibrous membrane of CS-PEO as the out-layer on both sides (Bates et al. 2021).

Cellulose and chitosan have an excellent biocompatibility together, which has been proved by many reports (Xu et al. 2018). Herein, to develop a new-generation green, porous nanofiber adsorption functional material with the lower diameter and the superior adsorption performance, we prepared a

cellulose acetate/chitosan (CA/CS) biocomposite ultrafine nanofibrous membrane by electrospinning and for the efficient removal of the aquatic copper ions. The relations among parameters of electrospun solution, micro-morphology and porosity for nanofibers, the variation of chemical active sites and adsorption capacity of biocomposite nanofibrous membranes for conventional and core-shell electrospinning were comprehensively investigated and characterized using tensiometer, conductometer, scanning electron microscopy equipped with energy dispersive X-ray spectrometry, transmission electron microscopy, atomic force microscopy, N₂ adsorption-desorption isotherms, Fourier transform infrared spectra, and X-ray photoelectron spectroscopy. In addition, the adsorption effect of copper ions, including the concentration of ions, interaction time, and pH of solution among the specimens, were comparatively analyzed and evaluated.

Experimental

Materials

Cellulose acetate (CA) was bought from Sinopharm Chemical Reagent Co., Ltd. Chitosan (CS) particles with 90% deacetylation were obtained from Qindao Huizhi Biological Engineering Co., Ltd. Anhydrous copper sulfate (CuSO₄) and bis(cyclohexanone) oxalyldihydrazone (BCO) were bought from Sinopharm Chemical Reagent Co., Ltd. Polyvinyl alcohol (PVA) (M_w=44000 g/mol) was provided by Shanghai Taitan Technology Co., Ltd. Glacial acetic acid was purchased from Guangdong Guanghua Technology Co., Ltd. All of them belong to the analytical grade. Deionized water can be obtained in our laboratory.

Fabrication of CA/CS biocomposite nonfibrous membrane

CA and CS were dissolved in acetic acid/deionized water at a 60:40 volume ratio with continuous stirring to obtain 3 wt% CA and 3 wt% CS solutions at ambient temperature. The mixed CA/CS solutions were prepared at various CA:CS mass ratios (10:0, 9:1, 7:3, 5:5, 3:7, 1:9 and 0:10), coded as CA, 10% CS, 30% CS, 50% CS, 70% CS, 90%CS, and CS. Then, 9 wt% PVA solution was added into the CA/CS solution and mixed by stirring. Subsequently, the solutions were directly used for electrospinning, which avoided the aging effects originating from conformational variation, aggregation, and partial chain scission of chitosan (Sorlier et al. 2002). The CA/CS biocomposite nanofibers with ordinary and core-shell composite structures were prepared by an electrospinning machine (Elite, Ucalery, China) respectively corresponding to the single and coaxial needles. The grounded negative electrode of the drum was covered with aluminum foil paper as a receiving device of nanofibers. The electrospinning parameters for the voltage, injection rate, and receiving distance were 15-17 kV, 14-18 cm, and 0.5 mL/min, respectively. The relative humidity in the electrospinning equipment was controlled at 35%. The collected CA/CS nanofiber membranes were heated to 240°C in an air atmosphere for pre-oxidation at a 2°C/min for 2 h prior to carbonization. The carbonized CA/CS nanofibrous membranes were obtained by heating to 800°C at a nitrogen atmosphere. The heating rate and holding time were 2°C/min and 2 h, respectively.

Characterization and measurement

Measurement of surface tension and conductivity of the electrospinning solution

The surface tension test by the method of a Wilhelmy plate were carried out on a tensiometer (HM301, Guodian, China). The electrical conductivity measurement was performed on a conductometer (DDSJ-318, Cilei, China) at room temperature. Three replicate samples were tested for average value and standard deviations.

Micro-morphology of nanofibrous membranes and distribution of copper ions

The micro-morphology of the CA/CS biocomposite membranes was observed by a scanning electron microscopy (SEM) (Hitachi S-3400, Philips, Japan) with an accelerating voltage of 10 kV. Prior to observation, the dried samples were sputter-coated with gold. Energy dispersive X-ray spectrometry (EDS) provided the distribution images of copper ions accompanying with a specific area before and after adsorption. The micro-morphology for core-shell structure nanofibers were observed using a transmission electron microscopy (TEM) (JEM 2100, JEOL, Japan) at 200 kV accelerating voltage.

Atomic force microscopy (AFM)

Atomic force microscopy (AFM, Bruker Multimode 8) was utilized to evaluate the surface roughness of the CA/CS biocomposite ultrafine nanofibrous membranes in tapping mode. Each sample was observed at a scan range of $6\text{ }\mu\text{m} \times 6\text{ }\mu\text{m}$. The roughness of surface was analyzed according to the root average arithmetic roughness (R_a).

N₂ adsorption-desorption isotherms

The N₂ adsorption-desorption isotherms of CA/CS biocomposite membranes were evaluated by an auto specific surface area analyzer (ASAP 2020, Micromeritics, USA) at a relative pressure of $P/P_0=0.99$ and a temperature of 77 K. The specific surface area of samples was calculated according to the Brunauer-Emmett-Teller (BET) method supported by a multilayer adsorption theory. The Barrett-Joyner-Halenda (BJH) model was selected to calculate the distribution of pore size.

Fourier transform infrared (FTIR) spectra

FTIR spectra of the CA/CS biocomposite membranes were collected in the region of $600\text{ to }4000\text{ cm}^{-1}$ by a Nicolet instrument (IS5, Thermo, USA) equipped with the attenuated total reflectance (ATR) Ge probe.

Evaluation of heavy metal adsorption

The copper sulfate particles were dissolved in deionized water with constant stirring at room temperature to obtain the copper ion (Cu^{2+}) solutions. The colored Cu^{2+} and BCO reactions were analyzed on a UV-visible spectrophotometer. To calculate the concentration of free Cu^{2+} solution, a calibration curve was established. The adsorption measurements were carried out on a conical flask by immersing a specific

number of specimens. The effects of adsorption parameters including Cu^{2+} initial concentration (10, 20, 30, 40 mg/L), pH value (2, 3, 4, 5, 6), and adsorption time (0-3000 min) on Cu^{2+} removal were also investigated. The adsorption properties of specimens were evaluated following Equation (1):

$$Q = (C_0 - C_t) V / m$$

1

Where Q is the adsorption capacity of specimens at any time in mg/g; C_0 indicates the initial concentration of heavy metal ions in mg/L; C_t represents the concentration of measured ions in mg/L; V is the solution volume in L; m is the mass of CA/CS biocomposite nanofibrous membranes in g.

X-ray photoelectron spectrometer (XPS)

The surface chemical compositions of CA/CS biocomposite membranes were analyzed by an Thermo Scientific XPS with monochromatic Al-K α . Its scanning step increment for samples was set at 0.1 eV.

Results And Discussion

Analysis of surface tension and conductivity

The surface tension and electrical conductivity of the spinning solution are the significant parameters that affect the micro-morphology of nanofibers. Fig. 1 displays the variation trend of the surface tension and electrical conductivity of the spinning solution at various CA and CS ratios. The conductivity of the electrospinning solution shows an ascending trend with the CS content increase. Specifically, the conductivity increased from 302 to 1370 $\mu\text{S}\cdot\text{cm}^{-1}$ with a CA to CS ratio varying from 10:0 to 0:10. This may be due to the chitosan dissolution in the acetic acid/water solvents forming ammonium salts, which act as polyelectrolytes, increasing the electrical conductivity of electrospinning solution (Qasim et al. 2018). The surface tension value just slightly dropped from 35.5 to 33.3 $\text{mN}\cdot\text{m}^{-1}$ as the CS content increased from 0–30% and then climbed back to 34.5 $\text{mN}\cdot\text{m}^{-1}$ with the further CS content increase to 90%. This demonstrated that the mixing of CA and CS with low concentration hardly affects the surface tension. Among the biocomposite membranes, the 50% CS group showed the optimum electrospinning performance. This is because, in addition to the interaction between CS and CA macromolecules, CA, CS, and PVA can form hydrogen bonds (Zhang et al. 2007) despite the solutions containing insufficient entanglement of molecular chains to achieve a critical level for producing fibers at low concentration (Du et al. 2007).

The morphology of CA/CS biocomposite nanofibers

The macro- and micro-morphologies and diameter distribution of CA/CS biocomposite membranes are shown in Fig. 2. The common composite nanofibrous membranes with CA and CS ratios appeared as porous web-like structures with average nanofibers diameters from 56.22 nm to 94.39 nm, which is smaller than the bio-based nanofibers in previous reports (Wang et al. 2017b; Yang et al. 2017; Wang et

al. 2018a; Xu et al. 2020). The average diameters initially decreased and then increased when the CS content varied from 10–90%. The lowest average diameter and narrowest distribution for the conventional composite structure were 56.22 nm at 50% CS loading, attributed to enhanced electrostatic forces and reduced surface tension of the resultant solution (Stefanescu et al. 2012). The surface of 30% CS and 50% CS membranes is smooth and bead-free. The excess CS conversely increased the surface tension of the spinning solution, leading to increased nanofiber diameters. Some mixed thinner nanofibers in Fig. 2(D and E) may be caused by partial deformation and splitting of the charged droplets at the electrospinning process. The physical adsorption capacity was mainly determined by porosity and specific surface area. Compared to our previous CE/CS biocomposite nanofibers, the current CA/CS nanofibers have smaller diameters, resulting in a better physical adsorption for copper ions. Additionally, the core-shell biocomposite nanofibrous membrane with CS as the “shell” and CA as the “core” at 30% CS loading can be clearly observed in Fig. 2G, which showed the lowest average diameter (37.28 nm) but a broader diameter distribution (Fig. 2F) compared to the 50% CS membrane (Fig. 2C).

The three-dimensional (3D) micro-morphology of the CA/CS biocomposite membranes was further examined by AFM. The nanofiber structure of the membrane shows different diameter distribution and smoothness, consistent with SEM images. The surface roughness of the nanofibrous membranes were evaluated by analyzing the AFM images with the WSXM software. The detailed pore depth and surface are shown in Fig. 3. A 3D web structure with various interstices was formed by the interconnected ultrafine nanofibers. The 30% CS (306 nm) has a relatively higher R_a than the 90% CS group (195 nm) and the 30% core-shell group (212 nm) because of its larger diameter, more uniform distribution, and smoother nanofibers. A beads and nanofibers mixture was also observed in 90% CS group. Some inhomogeneous regions of the core-shell membrane and the incorporation of interpenetrating nanofibers may lead to extremely small pore sizes.

BET analysis

The adsorption-desorption curves of N_2 as well as the distribution of pore width for CA/CS biocomposite membranes are displayed in Fig. 4. Fig. 4a shows that the curves display typical type-IV profiles with narrow hysteresis loops in the range of 0.8 to 0.99, especially for the core-shell and 50%CS groups, implying mesopores in the specimens in agreement with the pore width distribution in Fig. 4b. Table 1 lists the porosity parameters of the samples. The sample at 30% CS loading exhibits the lowest BET surface area ($6.65 \text{ m}^2/\text{g}$) but the largest average pore width (19.42 nm). Conversely, the samples with core-shell composite structure showed the highest surface area but smallest average pore width (11.91 nm). This analysis correlated well with the micro-morphology observation.

Table 1
Porous parameters of CA/CS biocomposite nanofibrous membranes

Samples	BET	Average pore	DFT cumulative
	surface area (m²/g)	width (nm)	pore volume (cm³/g)
30%CS	6.65	19.42	0.021
50%CS	8.66	19.03	0.038
90%CS	6.66	16.99	0.023
Core-shell	12.33	11.91	0.036

Analysis of FTIR

Figure 5 shows the FTIR spectra of the nanofiber membranes with ordinary composite structure at different CA and CS ratios and the core-shell composite nanofibrous membranes before and after adsorption. The adsorption bands at 2936 cm^{-1} and 2896 cm^{-1} are associated with the stretching vibration of CH_3 and CH_2 in both CA and CS, respectively. The 1740 cm^{-1} band is due to the stretching vibration of C=O derived from the residual vinyl acetate unit in PVA, the acetyl group in CS, and the carbonyl group in CA (Phan et al. 2019). The adsorption bands at 1370 cm^{-1} and 1230 cm^{-1} are ascribed to the CH_3 acetyl group (Wang et al. 2020). A shoulder peak at 1090 cm^{-1} can be explained as the stretching vibration of C-O in PVA (Koosha and Mirzadeh 2015). The bands at 1040 cm^{-1} and 1720 cm^{-1} are associated with the C-O-C and C=O stretching vibrations in CS. The band at 1620 cm^{-1} is related to the C-O stretching vibration due to the hydrogen bond between PVA and CS. There is a weaker N-H vibration at 1590 cm^{-1} , assigned to the mixed vibration of CS amide II and NH_2 (Li et al. 2012). The broad and strong peaks at 3360 cm^{-1} are $-\text{OH}$ and $-\text{NH}$ stretching vibrations. With the increase of chitosan content, the absorption band shifts from 3360 cm^{-1} to around 3650 cm^{-1} , indicating that many hydrogen bonds were formed in the nanocomposite (Koosha and Mirzadeh 2015). The band at 1260 cm^{-1} is related to the C-N bond (Yezer and Demirkol 2020). The amino group characteristic band for the 30% CS and core-shell biocomposite membrane shifted from 1590 cm^{-1} to 1620 cm^{-1} and an additional peak occurrence at 1640 cm^{-1} after adsorbing copper ion mainly due to the amino group chelation in CS with copper ions (Chen et al. 2019). Thus, both 30% CS and core-shell membranes have superior chemical adsorption for copper ions than other groups.

Micro-morphology before and after adsorption

The SEM-EDS images of CA/CS biocomposite nanofibrous membranes after copper ions adsorption are presented in Fig. 6. As observed in Fig. 6(A1-A4), many copper particles are evenly adsorbed onto the pure CS, 30% CS, and core-shell nanofibrous membranes, which was evidenced in the EDS images (Fig. 6(C1-C4)). The pores and gaps with various sizes and irregular shapes contribute to the physical adsorption of copper ions. Fig. 6B1 shows that some “cloud-like” thin layers were formed on the 30% CS membrane,

and the corresponding enlarged partial image shows that the surface is dense with a rough morphology. The chitosan nanofibers' excessive aggregation on the surface of the composite membrane after copper ions adsorption prevented the further entry of copper ions into the internal porous network of the membrane, leading to the lowest copper atomic content (0.49%). The many irregular pores on the surface of the 30% CS membrane in Fig. 6(A2 and B2) are attributed to hydrogen bonding and Van der Waals forces between CS and CA. It can be noticed from the magnified image that the nanofibers are interwoven and superimposed on each other. The stable porous nanofiber structure keeps the more chemically active sites for the removal of copper ions. The microscopic surface of the core-shell composite membrane is shown in Fig. 6(A3 and B3). Some lumps pieces are observed due to the existence of thin nanofibers and many cross-linking sites. After carbonization of 30% CS composite membrane in Fig. 6(A4 and B4), the surface fibers were twisted and irregular although the porous structure was not destroyed. The adsorption active sites with specific chemical groups were significantly reduced or disappeared during the carbonization process. Combined with the data in Table 2, the 30% CS composite membrane adsorbed the most copper content after adsorption corresponding to a relative atomic content of 1.85%. The relative atomic content of copper for core-shell composite membranes slightly decreased to 1.73%. The carbonized 30% CS composite film adsorption was only 0.11%, which can be explained by the NH_2 or NH_3^+ groups' destruction and transformation into C-N groups during the carbonization process (Wang et al. 2021).

Table 2
Elemental content of copper after adsorption in each different
proportion of composite membranes

Samples	Element	Weight(%)	Atomic(%)
CS	Cu k	2.20	0.49
30%CS	Cu k	7.93	1.85
Core-shell	Cu k	7.45	1.73
Carbonized 30%CS	Cu k	0.56	0.11

Adsorption performance and influencing factors

The adsorption performance of ultrafine CA/CS biocomposite nanofibrous membranes for copper ions (Cu^{2+}) is shown in Fig. 7. The absorption rate of nanofibrous membranes continuously increased with time for all groups (Fig. 7A). The absorption rate shows a sharp increase in the initial stage ($t < 30\text{min}$), which mainly attributed to the large specific surface area with many free adsorption sites on the composite nanofibrous membrane (Bock et al. 2012). The absorption rate slowed down and gradually reached a plateau, attributing to the Cu^{2+} concentration decrease in the solution and the consumption of adsorption sites. After equilibrium, the maximum and minimum adsorption rates corresponding to the 30% CS ordinary composite and core-shell composite membranes were 34.53 mg/g and 27.67 mg/g, respectively. Moreover, 52.8% of the total adsorption capacity was reached around 30 min for 30% CS

nanofibrous membranes. The total adsorption equilibrium time is longer, and the Cu^{2+} diffusion into the composite nanofiber membrane may take more time.

The variation of adsorption capacity of 30% CS ordinary composite membrane at different initial concentrations is displayed in Fig. 7B. The adsorption performance decreases with increasing initial concentration. Especially, there is a significant decline in the concentration range of 20 to 30 mg/L, corresponding to the reduction of adsorption capacity by 47.8%. This is because the total amount of Cu^{2+} in the solution increases with the initial Cu^{2+} concentration, but the number of available active sites on the composite membrane is constant. In addition, the high initial concentration promotes the efficient adsorption of the composite membrane with more Cu^{2+} congregating, hindering the diffusion of Cu^{2+} into the composite membrane.

The effect of pH values on the 30% CS ordinary composite membrane adsorption performance is illustrated in Fig. 7C. The adsorption performance of the composite membrane increased from 1.16 mg/g to 86.41 mg/g corresponding to the pH varying from 1 to 5. The adsorption performance can be achieved to the optimum level when the pH is equal to 5. This can be explained as the amine groups in chitosan can protonate either NH_3^+ or $(\text{NH}_2-\text{H}_3\text{O})^+$ groups under various pH of the solution. The copper species primarily were unhydrolyzed Cu^{2+} with partial $\text{Cu}(\text{OH})^+$, and $\text{Cu}(\text{OH})_2^{0-}$ in the pH range of 4–6. The protonated amine groups appear to be the predominant active sites for the copper ion adsorption. The coexistence of copper ions and hydrogen ions at low pH of 2–4 forms competitive adsorption, limiting the reaction of chitosan amino groups with Cu^{2+} (Yang et al. 2019). The amino group of chitosan formed an ammonium salt that is positively charged and repelled each other with the positively charged Cu^{2+} under acidic conditions, reducing its adsorption capacity (Bates et al. 2021). Conversely, the extent of protonation remarkably decreases as the pH is increased to 6 or higher, which leads to the decrease of adsorption capacity (Hasan et al. 2008).

XPS analysis

To reveal the mechanism of chemical adsorption on the CA/CS biocomposite nanofibrous membranes with conventional 30% CS and core-shell groups, XPS analysis was performed before and after adsorption, and its spectra are shown in Fig. 8. The surface atomic composition and states are listed in Table 3. However, there were no changes for the spectra of C1s and O1s in the binding energy position, indicating that the functional groups that contain carbon and oxygen hardly participate in copper ion binding reactions. The N1s spectra are seen in Fig. 8(A1 and A2, B1 and B2). Two peaks corresponding to the binding energy of 399.1 and 400.70 eV before copper ion adsorption was related with the $-\text{NH}_2$ and the $-\text{NH}-$ groups and their protonated $-\text{NH}_3^+$ groups in CS (Liu and Bai 2006; Yang et al. 2021). The two peaks show a significant shift to 399.7 and 401.7 eV after copper ion adsorption, respectively, agreeing with the previous report that chemical shifts are significant (Hasan et al. 2006). Therefore, it is verified that copper ions formed effective chemical coordination complexes with $-\text{NH}_2$, $-\text{NH}-$ and protonated $-\text{NH}_3^+$ groups in CS during adsorption probably due to surface bonding formation by sharing lone pair

electrons in N atoms with the copper ions. This promoted the states of oxidation and resultant elevated binding energy of the N atoms (Liu and Bai 2006). The area and width of the peak for -NH or -NH₂ after adsorption are larger and narrower than that before the adsorption, which is due to the formation of Cu[(-NH₂)]₂ through covalent bonds with [Cu-NH₃⁺]₂⁺ complex on the surface (Hasan et al. 2008), moreover, the more for core-shell samples compared to conventional samples. Nevertheless, the -NH₃⁺ lower binding energy intensity for the core-shell membrane may be attributed to the shrinkage of the composite membrane surface with an -NH₃⁺ enrichment, as seen in Fig. 6(B3), which leads to a space hindrance to react with the inner active sites, decreasing the adsorption capacity.

Table 3
The compositions of surface atomic elements and chemical groups of CA/CS biocomposite nanofibrous membranes

Composition	30%CS	30%CS	Core-shell	Core-shell
	after Cu (II)-loading		after Cu (II)-loading	
	Binding energy(eV)		Binding energy(eV)	
-NH- or -NH ₂	339.09	399.74	339.07	399.68
Atomic concentration (%)	0.67%	1.36%	0.56%	2.05%
-NH ₃ ⁺	400.70	401.75	400.70	401.68
Atomic concentration (%)	0.20%	0.13%	0.23%	0.24%
Total N1S	0.87%	1.49%	0.79%	2.29%
Cu 2p _{3/2}	—	933.47	—	933.42
Atomic concentration (%)	0%	0.35%	0%	0.37%
Cu 2p _{1/2}	—	953.27	—	953.27
Atomic concentration (%)	0%	0.1%	0%	0.1%
Total Cu 2p	0%	0.45%	0%	0.47%

The Cu2p spectrum is displayed in Fig. 6(C1 and C2). Two characteristic peaks corresponding to 932 eV and 952 eV are associated with Cu2p_{3/2} and Cu2p_{1/2}, respectively, which proves the effective adsorption of copper ions (Hasan et al. 2006). Although the atomic concentration of Cu2p_{3/2} for core-shell membranes was higher than that of conventional composite membranes, the corresponding adsorption performance was limited by the agglomeration of chitosan nanofibers on the surface with the blockage of porous network structures as seen in Fig. 6(B3). The two additional fluctuations in the 940–946 eV and 961–965 eV regions can be explained as the unsaturated state of electronic configuration (Hasan et al. 2008). The copper ions may have a coordinated bonding with the amine and hydroxyl groups in

chitosan, and the bonding ability varies with the pH of the solution, the concentration of metal ions, and the chitosan contents.

Table 4 compares the average diameter and adsorption capacity of copper ions in this study (ultrafine CA/CS nanofibers) with the previous reports using natural cellulose or chitosan to fabricate micro- or nano-fibrous membranes including cellulose acetate/chitosan (CA/CS) hollow microfibers, cellulose acetate/silicon dioxide (CA/SiO₂) nanofibers, TEMPO-oxidized cellulose/chitosan/polyethylene oxide (TOC/CS/PEO) sandwich-like nanofibers, cellulose nanocrystals/chitosan (CNC/CS) nanofibers, chitosan/polyethylene oxide (CS/PEO) nanofibers, phosphorylated cellulose/chitosan/polyethylene oxide (PCF/CS/PEO) bi-layer nanofibers, cellulose acetate/chitosan (CA/CS) nanofibers, cellulose/chitosan (CE/CS) nanofibers as well as the porous CE/CS hydrogel beads. The results obtained from our current study show the significantly thinner nanofibers (37-94 nm) as well as the superior adsorption capacity of copper ions (86.4 mg/g) than those from any other groups. This can be attributed to the ultrafine nanofiber porous and stable structure as well as the ideal distribution of chemical adsorptive sites. Additionally, the toxic chemical reagents or solvents used in previous cellulose- or chitosan-based nanofibers listed in Table 4 like acetone, dimethylacetamide, 2,2,6,6-tetramethylpiperidinoxy, trifluoroacetic acid, dichloromethane, sulfuric acid and sodium hydroxide would lead to the secondary pollution of ecosystem. The current ultrafine CA/CS nanofibrous membrane also has a greener solvent (polyvinyl alcohol) and a more facile preparation way without post-treatment, showing a promising prospect for water treatment.

Table 4

The average diameter and adsorption capacity of copper ions for various bio-based materials

Cellulose or chitosan-based adsorbents	Chemical reagents or solvents	Average diameter range (nm)	Adsorption capacity of copper ion (mg/g)	Reference
CA/CS hollow microfibers	Formic acid	600000-700000	4.1	(Liu et al. 2005)
CA/SiO ₂ nanofibers	Acetone, dimethylacetamide	> 500	23.0	(Gebru and Das 2017)
TOC/CS/PEO sandwich-like nanofibers	2,2,6,6-Tetramethylpiperidinoxy, acetic acid	159	36.8	(Bates et al. 2021)
CNC/CS nanofibers	Sulfuric acid, acetic acid, poly(vinyl alcohol)	262-498	45.0	(Wang et al. 2018a)
CE/CS hydrogel beads	Acetic acid, sodium hydroxide	—	53.2	(Li and Bai 2005)
PCF/CS/PEO bi-layer nanofibers	Urea, phosphate ester, acetic acid	372	74.5	(Brandes et al. 2020)
CA/CS nanofibers	Trifluoroacetic acid, dichloromethane	450-650	—	(Salihu et al. 2012)
CE/CS nanofibers	Trifluoroacetic acid, acetic acid	122-349	80.7	(Phan et al. 2018)
CA/CS ultrafine nanofibers	Acetic acid, poly(vinyl alcohol)	37-94	86.4	This study*

Conclusions

The green, ultrafine CA/CS nanofibrous membranes were successfully fabricated by facile electrospinning without post-treatment and used as the efficient removal of copper ions in polluted water. The average diameter for conventional and core-shell ultrafine nanofibers at 50% and 30% CS loading achieved 56.22 nm and 37.28 nm, respectively. The 30% CS conventional CA/CS biocomposite nanofibrous membranes at the pH=5 aqueous solution showed the optimum adsorption capacity of copper ions (86.4 mg/g). The core-shell CA/CS biocomposite nanofibrous membranes induced the surface aggregation of copper ions to impede the further adsorption. The more uniform distribution for -NH₂ or NH₃⁺ chemical adsorption sites can be obtained by the conventional electrospinning with single-nozzle needle than by the core-shell one with coaxial-nozzle needle, which promotes the adsorption performance of copper ions and decreases the surface shrinkage of nanofibrous membranes during adsorption. The smart combination of renewable biomass with effective chemical adsorptive sites, the electrospinning technology with interwoven porous structure and the adsorption method with low cost

and facile operation greatly contributes to the removal of heavy metals from polluted aqueous media to maintain the water sustainability and availability for human and other living organisms.

Declarations

Author contributions

Kaimeng Xu and Siqun Wang proposed the scientific target and designed the experiments. Qiushi Li, Ganmao Su, Ronggang Luo helped to complete the operations and data collection of tensiometer, conductometer and FTIR instruments. Linkun Xie and Jinsong Yan helped to do the analyses of curves in XPS and BET. Guanben Du and Juying Zhou and provided lots of help in discussing the relations among parameters of electrospun solution, micro-morphology and porosity for nanofibers, the variation of chemical active sites and adsorption performance of biocomposite nanofibrous membranes for conventional and core-shell electrospinning as well as the adsorption effect factors of copper ions. Jiayi Wu was responsible for completing all the other experiments and wrote the original draft. Zhengguan Tang polished the English grammar, and Siqun Wang further revised the manuscript. Kaimeng Xu, Siqun Wang and Linkun Xie provided the funds support.

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Figures

Figure 1

Surface tension and electrical conductivity of electrospinning solution at different CA/CS ratios

Figure 2

Macroscopic and microscopic morphologies of CA/CS biocomposite nanofibrous membranes and their diameters distribution: A. 10% CS, B. 30% CS, C. 50% CS, D. 70% CS, E. 90% CS, F. core-shell 30% CS, G. TEM image of core-shell structure

Figure 3

AFM of CA/CS biocomposite nanofibrous membranes: (A) 50% CS, (B) 90% CS, (C) core-shell

Figure 4

N_2 adsorption-desorption isotherms (A), and (B) pore width distribution of CA/CS biocomposite nanofibrous membranes

Figure 5

FTIR spectra of CA/CS biocomposite nanofibrous membranes

Figure 6

SEM-EDS after adsorption of heavy metal copper ions: A1-D1. CS, A2-D2. 30% CS, A3-D3. Core-shell, A4-D4 30%CS after carbonization

Figure 7

The adsorption performance of CA/CS biocomposite nanofibrous membranes: (A) the relation of time and Q_t , (B) the relation of initial concentration and Q_t , (C) the relation of pH and Q_t

Figure 8

Surface chemical compositions of CA/CS biocomposite nanofibrous membranes: (A1) and (A2) N1s spectra of 30%CS before and after adsorption; (B1) and (B2) N1s spectra of core-shell before and after adsorption; (C1) and (C2) Cu2p spectra of 30%CS and core-shell after adsorption

Figure 9

The adsorption mechanism of CA/CS biocomposite nanofibrous membranes