Electrospun zein/polyvinyl alcohol nanofabrics incorporated with nanosized hydroxyapatite for efficient heavy metal ion adsorption

Na Ma  
Beijing Technology and Business University

Ke Li  
Beijing Technology and Business University

Bo Xu  
Beijing Technology and Business University

Huafeng Tian (✉️ tianhuafeng@th.btbu.edu.cn)  
Beijing Technology and Business University

Songbai Ma  
Beijing Technology and Business University

Jinlong Li  
Beijing Technology and Business University

Yuge Ouyang  
Beijing Technology and Business University

Qian Liu  
Beijing Technology and Business University

Dagang Liu  
Nanjing University of Information Science and Technology

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Abstract

In order to solve the problem of heavy metal treatment in water pollution, the biodegradable film based on zein/polyvinyl alcohol (PVA) with incorporation of nano-hydroxyapatite (nHAP) were fabricated through electrospinning in this study, and the copper ion was taken as the representative of heavy metal ions. The result showed that the fiber morphology, hydrophobicity and thermal performance were influenced by the contents of nHAP. The incorporated nHAP nanoparticles were dispersed within the zein/PVA matrix and strong hydrogen bonding interactions were formed between the filler and matrix. The adsorption capacities of nanofibrous films for Cu$^{2+}$ were greatly increased after the addition of nHAP. When the nHAP content was 20% (based on the weight of the solid content), the adsorption capacity could reach up to 23.86 mg/g, and the adsorption efficiency was 13.94% higher than that of neat zein/PVA nanofibers. In the system of copper ion adsorption, based on the electrostatic interaction and complexation of zein/PVA, the ion exchange effect, electrostatic interaction and complexation of nHAP significantly increased the adsorption capacity of the whole system. This work suggests the potentials of the electrospun zein/PVA/nHAP nanofibrous films as desirable ecofriendly materials in metal removal applications.

1. Introduction

Industrial, agricultural wastewater and domestic sewage discharge has result in great damage to ecological environment, social environment and human health, and water pollution has become a global concern (Yap et al. 2021). Heavy metals in water pollution continue to accumulate and enter the food supply chain through rice, vegetables and other agricultural products (Li et al. 2022). After biomagnification in the food chain, it can cause teratogenicity and cancer, and ultimately pose a serious threat to human health.

Over the past few decades, great efforts have been made to remove heavy metals from wastewater, such as extraction, redox, adsorption and separation, and biochar repair technology (Kong et al. 2021), etc. Among them, adsorption and separation technology has the characteristics of low cost, easy operation, flexibility and simple design (Carolin et al. 2017), which has been recognized as an effective way in wastewater treatment (Luo et al. 2019). While due to the significantly higher surface area to volume with larger porosity, reliable filtration and adsorption capabilities, nanofibers have been used in water treatment (Saleem et al. 2020). Among the various preparation methods of nanofibrous films, electrospinning is considered to be the most advantageous and effective method for its advantages of simple operation, high production efficiency and low cost (des Ligneris et al. 2020; Lyu et al. 2021).

For the increased concern of white pollution caused by synthetic nonbiodegradable polymers, natural polymers including cellulose, polysaccharose and protein, etc. have reached quick development in recent years (Deeksha et al. 2021; He et al. 2022; Oyeoka et al. 2021). Proteins have been widely explored as natural biomaterials on account of the sustainable, biocompatible, renewable ability and adjustable structure (Rani et al. 2021), and zein is one of the most widely applied proteins. Zein is a kind of gliadin
extracted from maize endosperm, which is abundant in nature (Shukla and Cheryan 2001). On account of high proportion of non-polar hydrophobic amino acid residues (50%) (Wang and Padua 2010), zein exhibits high hydrophobicity. Zein is easily soluble in ethanol solution and acetic acid solution, and its solubility in ethanol increases with the increase of ethanol concentration (Bisharat et al. 2018). Coupled with flexibility, toughness, glossiness (Amjadi et al. 2022), non-toxicity, renewability, biodegradability, high availability, excellent biocompatibility and active groups which have strong interactions with pollutants and can trap pollutants (Yu et al. 2020), zein not only has a wide range of applications as food packaging (Altan et al. 2018), wound dressings (Fiorentini et al. 2021), drug delivery (Marin et al. 2018; Yang et al. 2021), but also is a desirable natural material for promising adsorbent for mental or dye adsorption (Deng et al. 2019). Compared with zein films, zein-based nanofibers would show better adsorption performance against pollutants for the large surface areas (Deng et al. 2020; Wen et al. 2016).

As illustrated in our previous studies, neat zein based nanofibers exhibited poor electrospinning ability (Li et al. 2020). Cospinning polymers, including polyvinyl alcohol (PVA), poly(ethylene oxide) (PEO) (Tian et al. 2018), etc. were often incorporated into zein matrix to facilitate the electrospinning process. In this regard, bioplastics make up for the spinning properties while reducing the environmental pollution (Han et al. 2022). PVA is a polyhydroxy environment-friendly polymer, which is easily soluble in water and possessed excellent film-forming properties (Guo et al. 2015; Niu et al. 2020). In addition, due to the large number of hydroxyl groups in the PVA molecular chain, heavy metal ions can be adsorbed through cross-linking and hydrogen bonding, thus removed from the wastewater (He et al. 2021). Owing to the distinguished properties, PVA nanofiber has wide application for water treatment (Siddiqui and Khan 2020; Tian et al. 2019; Ullah et al. 2020).

Hydroxyapatite (HAP) is a natural mineralization of calcium apatite with the molecular formula \( \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \). Due to the superior adsorption capacity, acid-base tunability, ion exchange capacity and thermal stability, HAP is widely used as a non-polar adsorbent in the treatment of polluted air, water and soil. Noteworthy, HAP possesses anionic sites, endowing the nanofibers with electrostatic adsorption properties and further improving the trapping ability of metal ion (Deng et al. 2022). In addition, the flexible lattice enables HAP to have a strong ability to tolerate defects and vacancies (Ibrahim et al. 2020), so that metal ions can replace calcium ions on HAP and fix metal ions, thereby achieving excellent adsorption effect on metal ions. Nano hydroxyapatite (nHAP) has a larger specific surface area based on the special lattice and excellent adsorption properties of hydroxyapatite (Koliyabandara et al. 2022; Pai et al. 2020), which makes it widely used in water treatment. Hogarthian et al. (Googerdcchian et al. 2012) incorporated natural nano-hydroxyapatite (nHAP) into alginate polymer to prepare bio-composite adsorbents. It is found that nHAP-alginate film can remove ions from aqueous solution and has a good application prospect in water treatment as a composite adsorbent. nHAP was also prepared as a composite adsorbent and gas gel for adsorption of \( \text{Cd}^{2+} \) and uranium from wastewater (Wang et al. 2022).

Building on the aforementioned research progress, the current research presented a novel biodegradable nanofibrous film prepared with zein/PVA/nHAP. To investigate the internal mechanism of
zein/PVA/nHAP nanobrous films and the influence of nHAP on adsorption capacity of zein/PVA films, the structures and adsorption performance were characterized in detail. The results showed that the addition of nHAP greatly improved the adsorption performance of the nanofibrous films, which suggested this novel biodegradable nanofibrous film could play an important role in the environmental behavior of heavy metals.

2. Materials And Methods

2.1 Materials

Zein (92%) was supplied by Yuanye Bio-technology Co., Ltd (Shanghai, China). PVA (117) was provided by Kuraray Co., Ltd. Acetic acid was obtained from Aladdin Biochemical Technology Co., Ltd (Shanghai, China). Nano-hydroxyapatite (nHAP, 95%) was supplied by Mindray Technology Co., Ltd (Beijing, China).

2.2 Preparation of zein/PVA/nHAP nanobrous film

Zein powder was dissolved in 80%(v/v) acetic acid solution to form a homogeneous solution with a solid content of 10 wt.% under magnetically stirring for 1 h at room temperature. Meanwhile, preparation of 10 wt.% PVA solution was in a similar way, stirring for 1 h at 95°C. Then solution with the mass ratios of zein and PVA of 1:1 was mixed to obtain a precursor solution. After that, different concentration of nHAP (4.7 wt.%, 11.1 wt.%, 15.8 wt.% and 20 wt.%, based on the weight of solid content) was adding into the zein/PVA solution, stirring for 1 h at room temperature until the bubble was discharged.

The well-mixed solution was injected into a syringe pump with a voltage of 20 kV applied to the spinneret and pumped by a monoinject syringe pump. The spinning solution was spun into nanofibers under the action of electrostatic field, and the paper towel substrate fixed on a grounded copper mesh was to collect the nanofibers. The distance from the spinneret to collector was 12 cm, and an average flow rate of 1.0 mL·h⁻¹ was utilized. Then zein/PVA/nHAP nanofibrous films of ca. 0.12mm thickness were prepared after 10h.

2.3 Characterization

The morphology and microstructures of the nanofibrous films were observed by scanning electron microscopy (SEM, Quanta FEG-250, FEI Nanoports, USA), operated at 10 kV. The samples were pasted on the sample stage with conductive adhesive, sprayed with gold spraying treatment and then tested under high vacuum. The average fiber diameter and the size distribution were determined by measuring sizes in the SEM images and statistically analyzed by image-Pro Plus software. The average diameter was calculated by the Eq. (1):

\[
d = \frac{\sum_{i=1}^{n} d_i}{n}
\]
Where $\bar{d}$ is the average fiber diameter; $d_i$ is the diameter of the $i^{th}$ fiber; $n$ is the number of fibers in the SEM images.

The functional groups and their interactions of samples were analyzed by Fourier transform infrared spectroscopy (FTIR, Nicolet iN10MX, USA), scanned in adsorption mode at 4 cm$^{-1}$ resolution with the wavenumber of 4000 – 400 cm$^{-1}$. The FTIR spectra were analyzed by OMNIC (version 9.0).

The water contact angle (WCA) of all films was evaluated by contact shape analyzer OCA 35 (Dataphysics Instruments GmbH, Germany). The samples were dried at 60 °C for 1h in an oven, then fixed on the platform. The deionized water (2 µL) was dropped and deposited on the film surface. The static water contact angle and drop shape with the different positions of the film were recorded by CCD video camera and image analysis, calculated by using Ellipse Fitting method. Each film was measured at least five times.

The thermodynamic properties of nanofibrous films were analyzed by the differential scanning calorimetry (DSC) instrument (Q2500, TA Instruments, United States) in the N$_2$ atmosphere. The sample weight was about 5–10 mg.

The copper adsorption performance of the films was tested by inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Optima 8000). First, standard Cu$^{2+}$ solutions with a concentration of 0, 20, 40, 60, 80 and 100mg/g with different gradients were prepared, and a standard curve of Cu$^{2+}$ concentration could be obtained by testing them successively. Then, appropriate amount of the heavy metal solution to be measured before and after adsorption was put into the centrifugal tube. Each sample reported were averaged over three consecutive times.

50 mg of nanofibrous films with different nHAP contents were weighed, immersed in 50 ml of 50 mg/L copper standard solution, and oscillated at 200 rpm/min at 25°C for a period of time. The concentration of the liquid to be tested was used to calculate the adsorption capacity. After the Cu$^{2+}$ concentration was measured, the adsorption capacity of the film could be calculated according to the following equation:

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

$q_t$ (mg/g) indicates the amount of adsorption at any time, $C_0$ (mg/L) is the initial ion concentration of sample, $C_t$ (mg/L) indicates the measured ion concentration of each sample, $V$ (L) is the solution volume and $m$ (mg) is the quantity of the nanofibrous film.

The conductivity was tested by DDS-307 conductivity meter (Shanghai Yueping Scientific Instrument Company). Took an appropriate amount of adsorbed copper solution in the centrifuge tube, immersed the
probe in the liquid until the solution passed the probe, waited for the indicator to be stable, and then took the average value after consecutive measurements for three times.

3. Results And Discussion

Figure 1 illustrated the schematic preparation and design of the multifunctional nanofibrous film for water treatment based on zein/PVA incorporated with different contents of nHAP. Zein possesses favorable fiber-forming and adsorption ability, which facilitates the formation of nanofibers by electrospun from the zein solution. To overcome the extremely poor mechanical properties of zein nanofibers and further improve the electrospinning properties of zein, PVA was introduced. As one of the most common materials employed in electrospinning, PVA is featured to be biodegradable, processable, spinnable, and eco-friendly.

Besides, nano-hydroxyapatite with remarkable biocompatibility and biological performance, has high specific surface area and excellent ability of adsorption(Elango et al. 2016). In this work, we focused on the preparation of composite nanofibrous materials by electrostatic spinning based on the mixed system of zein and PVA, adding different contents of nHAP to improve the copper ions adsorption performance of nanofibrous films and explored the influence of different factors on the adsorption effect of copper ions. The successful preparation of modified nanofibrous films showed that these composite nanofibrous materials had broad application prospects in the field of water treatment.

3.1 Morphology of nanofibers

Figure 2a showed the SEM images and diameter distribution of nanofibrous films with varying nHAP content. Only representative pictures (0%, 4.7%, 11.1%) were shown in this paper, and the electron micrographs and diameter distribution of all nanofibrous films incorporating different levels of nHAP were shown in Figure S1 and S2. It can be obviously observed that without the addition of nHAP, the nanofibers of zein/PVA had smooth surface and uniform diameter distribution. With the addition of nHAP, the surface of the fibers became rough and the diameter distribution was no longer uniform which from 450 nm turned to 394 nm, 620 nm, 588 nm and 491 nm, respectively. At higher magnifications, it could be observed that nHAP was encapsulated in the nanofibers and formed agglomeration. The agglomeration was attributed to the characteristics of small particle size and high activity of nHAP, which made it prefer to cause mutual attraction due to the increase of the interaction force among particles. With the content of nHAP increased, the agglomeration on the nanofibers gradually become apparent. Significantly, with the agglomeration and nodules of nHAP, the diameter of nanofiber continuously increased. As the content of nHAP was 11.1%, the diameter reached up to the maximum. This because the addition of nanoparticles increased the viscosity of the solution, thus enlarging the nanofiber diameter. Then the diameter of nanofiber decreased with the continuous addition of nHAP. It has been reported the incorporated nHAP could generate more charge on the surface of ejected jet, thus enhancing the charge density and facilitating the increase of the mass flow of the ejected jet from the spinneret tip to the collector, which resulted in the decrease of average diameter(Ni et al. 2019). The addition of nHAP significantly changed the morphology and microstructures of the nanofibers.
3.2 Structure and interaction

The FTIR spectra was employed to analyze the functional groups vibration and intermolecular interactions of the zein/PVA/nHAP nanofibrous films. As shown in Fig. 2b, the peak at 3440 cm$^{-1}$ of pure PVA film spectrum could be assigned to O-H stretching vibration. The C-H from alkyls groups could be observed at 2922 cm$^{-1}$. Absorption peaks at 1734 cm$^{-1}$ and 1084 cm$^{-1}$ were corresponding to carboxyl groups (C = O) and stretching C–O groups, respectively. In the spectrum of pure zein, amide bond at 1651 was assigned to the C = O stretching, and amide II band at 1538 cm$^{-1}$ was attributed to the N-H deformation of the. In the spectrum of the zein/PVA nanofibrous film, the 1453 cm$^{-1}$ band referred to the -CH$_2$ bending vibration, and the band at 1080 cm$^{-1}$ could be assigned to the C-O stretching vibration. The large and broad peak shifted from 3340 to 3340 cm$^{-1}$. Based on this, we could suggest that interactions, such as hydrogen bonds, had established between zein and PVA. With the addition of nHAP, several new bands appeared on the basis of original spectrum. The peaks at 1022 cm$^{-1}$, 602 cm$^{-1}$ and 562 cm$^{-1}$ were assigned to the characteristic vibrations of PO$_4^{3-}$ (P-O: 1022 cm$^{-1}$, O-P-O: 602 cm$^{-1}$, 562 cm$^{-1}$).

Significantly, the typical band intensity of PO$_4^{3-}$ displayed changes with the addition of nHAP. The peaks corresponding to the O-H and N-H vibrations range from 3340 cm$^{-1}$ to 3416 cm$^{-1}$, 3596 cm$^{-1}$ and 3605 cm$^{-1}$ when the nHAP was 4.7%, 11.1% and 15.8% respectively. When 20% nHAP was added, the peak transferred to 3487 cm$^{-1}$. Thus, the peak shifts at 3340 cm$^{-1}$ and 1022 cm$^{-1}$ could be assigned to the intermolecular hydrogen bonding of nHAP with zein and PVA.

As the Fig. 2d showed, zein and PVA were crosslinked with nHAP by electrostatic attraction, hydrogen bonding and surface complexation. nHAP was enriched with positively charged calcium ions and negatively charged phosphate ions on the crystal surface, providing ample ion binding sites (Chahkandi 2017). Due to the positive charge of calcium ions on nHAP, it could interact with carboxyl and hydroxyl groups on zein and PVA, while the phosphate group on nHAP can interact with amino groups on zein due to its positive charge. Besides, during the adsorption process of copper ions solution, PO$_4^{3-}$ was considered to be involved through surface complexation between ≡POH and copper ions on the HAP surface (Wei et al. 2021). The surface complexation also formed from Ca with -OH groups of zein and PVA. Above all effects made nHAP immobilized well inside the nanofibers. Thus, during metal absorption, the nHAP particles would not easily be dispersed into the solutions from the nanofabrics.

3.3 Surface wettability

The time-dependent water contact angles of nanofibrous film with varying nHAP contents were shown in the Fig. 3a. With the extension of time, the water contact angle of all films decreased in varying degrees. More visual photograph of the water contact angle of nanofibrous films with different content of nHAP over time were shown in Figure S3. Obviously, it could be observed that when the water droplets contacted with the nanofibrous film, the water droplet could not keep a certain shape all the time.

Figure 3b showed the variation of water contact angle of nanofibrous films at 10s. With the increase of nHAP, the contact angle first increased and then decreased, reaching a maximum when the nHAP content...
was 37.5%, which might be caused by the agglomeration of nHAP. The contact angle between the water droplet and the nanofibrous film gradually decreased, and the contact surface became larger until it was completely absorbed by the film. Comparing the graphs of the water contact angle under different nHAP contents, it was obviously that with the addition of nHAP, the wettability of the material decreased and the hydrophobicity increased. The hydrophobicity of zein/PVA nanofibrous film was mainly attributed to the abundant hydrophobic groups in zein and PVA. After adding nHAP, the polar groups were occupied and faced to inside on account of the hydrogen bonding, resulting in the more stable matrix. In addition, water-insoluble inorganic nHAP nanoparticles dispersing on the surface of nanofiber, contributing to the increased hydrophobicity (Xu et al. 2013). However, with the extension of time, the nanofibrous film gradually became hydrophilic, and the contact angle gradually decreased to 0°, which mainly due to the abundant hydrophilic group -OH in the matrix.

### 3.4 Thermal analysis

Figure 3c and 3d showed the thermodynamic properties of the nanofibrous films with different contents of nHAP. Table 1 summarized the detailed thermal data. The nanofibrous films showed crystallization peak and melting peak at ca. 146 °C and 150 °C, respectively, indicating the successful cross-linking of PVA and Zein. It could be seen that the melting point ($T_m$) and crystallization temperature ($T_c$) of the nanofibers exhibited a slight decrease with the addition of nHAP. It showed that the nHAP had good thermal stability which could keep stability and the addition of nHAP rarely changed the melting point and crystallization temperature of neat zein/PVA nanofibers. In the melting curve, the nanofibers all showed an endothermic peak around 200°C, which was mainly caused by the degradation of PVA.

<table>
<thead>
<tr>
<th>nHAP content (%)</th>
<th>$T_m$ (°C)</th>
<th>$T_c$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>150.13</td>
<td>146.56</td>
</tr>
<tr>
<td>4.7</td>
<td>149.12</td>
<td>146.57</td>
</tr>
<tr>
<td>11.1</td>
<td>149.41</td>
<td>145.90</td>
</tr>
<tr>
<td>15.8</td>
<td>149.40</td>
<td>145.69</td>
</tr>
<tr>
<td>20</td>
<td>149.19</td>
<td>146.30</td>
</tr>
</tbody>
</table>

### 3.5 Adsorption performance

The physical photo of copper ion solution before and after adsorption were depicted in Fig. 4a. As shown in the photo taken by the digital camera, the copper ion solution before adsorption was blue, and after adsorption, the color of the solution became lighter. The color change was because copper ions were adsorbed by the nanofibrous film, and the concentration of free copper ions in the solution decreased. With the extension of time, the nanofibers were partially decomposed, copper ions were adsorbed on the
fibers and precipitated to the bottom of the bottle, and the whole solution reappeared in a clear and transparent color. The composite nanofibers were originally white, and after the adsorption of copper ions, copper ions were attached to the film and forming a layer of blue precipitate.

Figure 4b showed the change of the adsorption capacity of copper ions with time, and they exhibited the similar adsorption trend. The copper adsorption capacity did not have a linear relationship with time. At first, the adsorption capacity increased rapidly, and then the curve gradually stabilized and reached a plateau after 12 h adsorption. After that, the adsorption amount exhibited small change with the extension of time. It was obviously that for each adsorption curve, with the extension of the adsorption time, the nanofibrous films initially had a great effect on copper ions.

At the same time, the conductivity of the copper ions solution was tested. The level of conductivity reflected the ability of the solution to conduct current in the water, and was often used to infer the concentration of ions in the water. As the concentration of copper ions increased, the conductivity of the solution was enhanced. When the concentration of copper ions in the solution decreased, the conductivity would decrease. With the adsorption of the nanofibrous film, the copper ion concentration decreased, and the conductivity curve showed a rapid decrease and then slightly decreased until it was flat. It could be seen from Fig. 4c that the curve obtained from the conductivity test was basically corresponded to the adsorption results obtained in Fig. 4b, the adsorption capacity first rises rapidly, then slowly until it is flat.

Figure 4d was a comparison chart of the adsorption performance of nanofibrous films with different nHAP contents after 12 h adsorption when the adsorption had reached the equilibrium. The copper adsorption rate was calculated by dividing the capacity of copper ions adsorbed by the nanofibrous film by the capacity of copper ions in the original solution. Compared with the zein/PVA nanofibrous film, the nHAP nanofibrous films showed higher copper adsorption rates. The curves of adsorption capacity and adsorption rate of the nanofibrous films were shown in the Fig. 4b and 4d, and the specific data of adsorption capacity and rate for each time period were shown in Table S1 in the supporting. Since PVA and zein had the ability to adsorb copper ions, the zein/PVA nanofibrous film exhibited certain adsorption ability of 20.94 mg/g for copper ions. The addition of nHAP further improved the adsorption capacity of the composite film. With the increase of nHAP content, the adsorption capacity of the nanofibrous films enhanced. When the nHAP content was 20%, the adsorption capacity could reach up to 23.86 mg/g, and the copper adsorption rates was 13.94% higher than that of neat zein/PVA nanofibers.

Adsorption kinetics was often used to predict the adsorption efficiency and the control mechanism of the desorption process (Huang et al. 2021; Teng et al. 2022). In this study, the Pseudo-first-order model and the Pseudo-second-order model were used to analyze the mechanism of copper ions adsorption by nanofibrous films. These two models did not follow the ideal kinetic model, but were updated models obtained after correction. The compliance with the Pseudo-first-order kinetic equation means that the physical adsorption play the main role during the adsorption process (Al Ketife et al. 2021). The hydrogen bonding, van der Waals and electrostatic forces are usually supposed to be the main driving forces of adsorption process. The adsorption process conforms to the pseudo-second-order kinetic equation,
indicating that the chemisorption of electron sharing or electron gain and loss play the main role in the adsorption process. The two kinds of calculating models are shown in Eq. (3) and Eq. (4), respectively (Li et al. 2022).

The Pseudo-first-order model can be calculated as follow:

\[ \ln(q_e - q_t) = \ln q_e - k_1 t \]

The Pseudo-second-order model can be calculated as follow:

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]

Figure 4 (e) and 4 (f) were the curves fitted by the pseudo-first-order and pseudo-second-order equations for the adsorption of copper ions on nanofibrous films with different nHAP contents. The fitting data were shown in Table 2. The \( R^2 \) in the table indicated the correlation coefficient of the model. The \( R^2 \) in the Pseudo-first-order model and the Pseudo-second-order model were both larger than 0.9, reflecting that both models could perfectly simulate the adsorption process of copper ions by zein/PVA/nHAP nanofibrous films process, and also showed that physical adsorption and chemical adsorption coexisted in the copper adsorption process of nanofibrous films. It could be seen from Table 2 that \( R_1^2 \) were higher than \( R_2^2 \), result showed that Pseudo-first-order model was more reliable (Yang et al. 2021). Besides, the similarity of calculated adsorption capacity to the experimental data further testified Pseudo-first-order model was valid to interpret the kinetic adsorption, indicating that physical adsorption played the major role. From the of the Pseudo-first-order model, it could be found that the \( k_1 \) of the nHAP composite nanofibrous films were larger than that of the pure zein/PVA nanofibrous film, indicating that the physical adsorption rate was accelerated after the addition of nHAP, and the adsorption capacity was increased due to the electrostatic interaction and van der Waals force between nHAP and the adsorbed ions. In the Pseudo-second-order model, \( k_2 \) increased with the addition of nHAP, indicating the chemical adsorption enhanced, which was mainly due to the ion exchange and complexation of nHAP in copper ion adsorption. Through the above analysis, it could be seen that in the process of zein/PVA/nHAP nanofibrous film adsorption of copper ions, the physical adsorption played the main role due to the electrostatic interaction. At the same time, chemical adsorption such as complexation and ion exchange assisted the adsorption. Overall, due to the capture of copper ion by electrostatic action, complexation and ion exchange, the addition of nHAP could enhance the physical and chemical adsorption of the nanofibrous films, thus the ability of removing copper ion of the composite films were significantly enhanced.
The nanober structure changes of nanocomposite films before and after adsorption of copper ions could be seen more intuitively by scanning electron microscope. After freeze-drying the nanofibrous film after adsorption tests, it could be seen from the SEM image in Fig. 5 that the nanofiber swelled with water after adsorption, the diameter became larger, and the space between the fibers was greatly reduced. The binding between the nanofibers and the solvent caused the fibers to swell. The SEM images of zein/PVA/nHAP nanofibrous films after adsorption at different magnifications could be seen in Figure S4. With the increase of nHAP content, copper ions attached to the bers, and the ber morphology gradually disappeared and formed stacked morphology.

In Fig. 5, the reasonable copper adsorption mechanism of the zein/PVA/nHAP nanofibrous film was depicted. There were three main adsorption mechanisms for copper ions in this system, electrostatic interaction, complexation and ion exchange. In neutral solutions, the zein molecular chain contains a large number of groups with lone pair electrons and some negatively charged groups, which enable zein molecules to absorb copper ions through electrostatic interaction and complexation. PVA molecular chain contains a good deal of hydroxyl groups, which can adsorb copper ions in wastewater by electrostatic interaction and complexation. The flexible lattice made nHAP have a strong ability to tolerate defects and vacancies, so that metal ions can replace calcium ions on nHAP and x metal ions, thereby achieving excellent adsorption effect on metal ions. Taking copper ions as a representative, the substitution of calcium ions in the nHAP lattice is transformed into the following equation(Huang et al. 2021; Stoetzel et al. 2009)

\[
Ca_{10}(PO_4)_6(OH)_2 + xCu^{2+} \rightarrow Ca_{10-x}Cu_x(PO_4)_6(OH)_2 + xCa^{2+}
\]

The nHAP adsorbs copper ions through electrostatic interaction due to the $PO_4^{3-}$ (Zhu et al. 2022). Besides, copper ions can deposit on the surface of nHAP to form an amorphous layer through surface complexation(Casado et al. 2022).
Accordingly, in the process of zein/PVA/nHAP nanofibrous film for copper ion adsorption, the physical adsorption played the main role due to the electrostatic interaction with copper ions, and chemical adsorption played a supporting role by complexation and ion exchange. Through the joint action of physical adsorption and chemical adsorption, the composite nanofibrous films had excellent adsorption effect for copper ion.

4. Conclusion

In the study, with the increase of nHAP, hydrogen bonds were formed between the nHAP molecules, and the morphology of the nanofibers formed agglomeration, the hydrophobicity also increased, and the melting point and crystallinity did not change significantly. The adsorption effect in the nanofibrous film was mainly controlled by three mechanisms: electrostatic interaction, complexation and ion exchange. The zein/PVA nanofibrous film with the addition of nHAP showed the improved adsorption performance in the copper ion adsorption, and the adsorption process could be described by the Pseudo-first-order model and the Pseudo-second-order model. Meanwhile, the adsorption process was dominated by physical adsorption. Therefore, with excellent adsorption performance and environmentally friendly material, the zein/PVA/nHAP-based nanofibrous films have a good potential as biodegradable film for multifunctional and high-efficiency water-adsorption materials and pave a new path for reducing water pollution in industrial applications.

Declarations

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Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

Ethical approval and consent to participate

This article does not contain any studies with human participants or animals performed by any of the authors. All authors contributed to the study conception and design. All authors read and consent to the final manuscript before submission.

Author contribution

Consent for publication

All authors agreed with the content and that all gave explicit consent to submit and that they obtained consent from the responsible authorities at the institute/organization where the work has been carried out, before the work is submitted.

Availability of data and materials

All data and materials are available.

Author information

Authors and Affiliations

Beijing Advanced Innovation Center for Food Nutrition and Human, Beijing Technology and Business University, Beijing, China

Na Ma, Bo Xu & Jinlong Li

Beijing Key Laboratory of Quality Evaluation Technology for Hygiene and Safety of Plastics, School of Chemistry and Materials Engineering, Beijing Technology and Business University, Beijing, China

Ke Li, Bo Xu, Huafeng Tian, Yuge Ouyang & Qian Liu

School of E-Business and Logistics, Beijing Technology and Business University, Beijing, China

Songbai Ma

School of Environment Science & Engineering, Nanjing University of Information Science &Technology, Nanjing, China

Dagang Liu

Corresponding authors

Correspondence to Huafeng Tian or Bo Xu or Dagang Liu.

Compliance with Ethical Standards

This article does not contain any studies with human participants or animals performed by any of the authors, and the authors have no relevant financial or non-financial interests to disclose and informed
References


Figures

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Schematic preparation and design of the multi-functional zein/PVA nanofibers incorporated with nHAP.
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Schematic illustration of the copper adsorption mechanism for the zein/PVA/nHAP nanofibrous films.

Supplementary Files

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