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Original scientific paper

Construction of Environment-Friendly PVA/Chitin Composite Foams via Supercritical Carbon Dioxide Foaming for Wastewater Treatment

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Abstract: Water pollution, particularly from heavy metal ions, remains a major environmental challenge, necessitating the development of cost-effective and sustainable adsorbents. This study presents a novel polyvinyl alcohol (PVA)/chitin composite foam synthesized via solid-state shearing milling (S^3M) and supercritical carbon dioxide ($scCO_2$) foaming technologies. The composite foams with high cell density exhibited improved structural integrity, mechanical strength, and adsorption capacity. The composite foam with 10% chitin loading demonstrated a 193% increase in copper ion adsorption and a 56% improvement for lead ions compared to pure PVA foam. The results indicate that the synergistic effect of PVA and chitin enhances the comprehensive performance of the foams parts.

Keywords: chitin, heavy metal removal; PVA; sustainable adsorbent, wastewater treatment

1 INTRODUCTION

With the acceleration of industrialization, the wastewater discharged from various industrial processes has resulted in the serious ecological pollution [1]. Especially the presence of heavy metal ions, such as lead ion, copper ion, and chromium ion, in wastewater poses a huge threat to human health and ecological environment, which accordingly garnered considerable attention on the dispose of wastewater in both industry and academia. Nowadays, the general approaches for wastewater treatment encompass flocculation, ion exchange, solvent extraction, chemical precipitation, and adsorption [2-8]. Among these, adsorption strategy is considered as a favored avenue attributed to its simplicity, high efficiency and low cost. Commonly used adsorbers, such as attapulgite, activated carbon, and zeolite, possess abundant functional groups like amino, hydroxyl, and carboxyl groups, which can combine with heavy metals and further enhance the adsorption capacity through surface modification [9]. For instance, M. Danish et al. [10] prepared activated carbon from date palm pits via pyrolysis at 300 °C, achieving a good adsorption capacity of for Pb^{2+} in aqueous solutions. However, it was usually fabricated by high-temperature pyrolysis, which could consume much energy and time. It is urgent to develop novel materials with easier preparation process and lower consumption [11, 12]. An alternative solution to this problem is to utilize the polymer foams as the absorber, which can be fabricated via facile foaming strategy to construct the adjustable porous structure and high specific surface areas. However, conventional polymer foam, such as polyethylene foam and polystyrene foam, possesses the weak hydrophilicity and limited active group, making it unsuitable for the adsorption of heavy metal ion in the wastewater [13, 14].

Polyvinyl alcohol (PVA), as a typical polar hydrophilic polymer with good mechanical properties, stable chemical performance and environmental friendliness, can be produced through the non-petroleum routes on large scale that bypasses the traditional fossil fuel dependency [15]. More importantly, the abundant hydroxy groups of PVA molecules endow it with certain capacity to adsorb the heavy metal ions and organic matters, which can be significantly improved by constructing the porous structure in the matrix [16, 17]. However, PVA-based porous materials are commonly prepared through the solution method, and it is quite difficult to realize the thermal processing because of its close decomposition temperature and melting temperature, which constrain the large production on scale [18, 19]. Our group realized the thermal foaming of PVA foams through utilizing the water and other small molecules as the plasticizer and foaming agent [20, 21], while the cell structure of the foam part was hard to control and the adsorption capacity of the single foam was still required to improve. Supercritical carbon dioxide ($scCO_2$) has been considered as the green and efficient physical blowing agent due to its good solvating capacity, mild supercritical condition and superior affinity with polymer matrix, which can more facilely construct the uniform and dense cell structure.

Nowadays, biomass adsorbent has attracted more and more attention due to the environmental friendliness, making it a promising approach with broad application in the wastewater treatment. Li et al. [22] synthesized a ZIF-8/BC/chitosan composite aerogel through mixing, freeze drying, soaking and further freeze drying, which was used for the efficient adsorption of heavy metal ions in wastewater. The specific surface area of the aerogel was 268.7 m^2/g. Yuan et al. [23] prepared the bio-based adsorption foam composed of metal-organic frameworks and polyethyleneimine-modified cellulose through a three-step process, which exhibited the high adsorption capacity for anionic dye, with recyclability and reusability while the complex preparation process might limit the further application.

Chitin, as a naturally occurring organic compound second only to cellulose in abundance on Earth, is mainly derived from the shells of crustaceans. The unique chemical structure and superior performance of chitin endows it with the broad application prospects [24-26]. For example, the rich hydroxyl groups enable chitin to adsorb the heavy metal ions, which is of great significance in the wastewater treatment. However, the dense crystalline structure, insolubility in most solvents, and limited

compatibility with other materials, have increased the processing challenges and further constrained the applications of chitin. Nowadays, chitin is usually treated through the solvent strategy, which inevitably increased the preparation steps and time and money consumption. Developing mechanical approach to realize the solid-state utilization of chitin seems to be an economical and efficient route. But conventional crushing method, such as ball milling, cannot achieve the efficient pulverization and blending [27-29]. In previous work, we have realized the pulverization and exfoliation of chitin through the solid state shear milling (S^3M) and achieved the PVA-based composite film with good comprehensive performance based on the in-situ compatibilization [30, 31]. However, the film was fabricated through the twice milling process and the feasibility of foaming and application prospect in the wastewater treatment have not been investigated [32].

In this work, the pre-treated chitin sheets were directly co-milled with PVA via S^3M technology to realize the efficient dispersion and compatibilization. And the composite foam was fabricated through the thermal molding and $scCO_2$ foaming technologies. The influence of chitin on the melting behavior and foaming performance was investigated, and the mechanical performance and ion adsorption capacity of the composite foam were measured. Chitin could effectively improve the cell structure and compressive strength of the foam, as well as the adsorption capacity of heavy metal ions, which provided a novel strategy fabricating the environment-friendly polymers foams to realize the efficient utilization of biomass resource and treatment of wastewater.

2 EXPERIMENTAL SECTION

2.1 Materials

PVA1799 (polymerization degree: 1700 ± 50, alcoholysis degree: 99%), was purchased from Sinopec Sichuan VinylonWorks. Chitin was purchased from Zhejiang Golden-shell Co., Ltd. Anhydrous Copper Sulfate, Tianjin Bodi Chemical Co., Ltd. Lead Nitrate and Deionized Water was supplied by Chron Chemical Co., Ltd. Carbon dioxide with 99.5% purity was provided by Chengdu Xuyuan Chemical Gas Co., Ltd.

2.2 Preparation of PVA/Chitin Composites

Initially, pre-treated chitin fragments were mixed with dried PVA particles in a predetermined ratio and introduced into the S^3M equipment together. The mixture was co-milled at the ambient temperature, and after a series of 10 milling cycles, the desired PVA/chitin composite powders were successfully achieved. To systematically evaluate the influence of varying composition ratios on the comprehensive performance of the composite and foams, the PVA/Chitin composites were designated as PVA/Chitin-n, where n represented the ratio of chitin. For example, PVA/Chitin-1 represented the PVA/Chitin composite with 1% chitin content. The obtained PVA/Chitin composite powders were mixed with water, which served as the plasticizer, and then the mixture was swollen at 60 °C for 48 hours. The plasticized powders were then hot-pressed and molded via using flat vulcanizing machine (TY-7006A, Tian Yuan Test Instrument). The hot-pressing process was conducted at a temperature of 170 °C and a pressure of 10 MPa, achieving the PVA/Chitin composite sheets.

2.3 Preparation of PVA/Chitin Composite Foams

$ScCO_2$ was used as the physical foaming agent to prepare PVA/Chitin composite foams. The molded PVA/Chitin composites were placed in the high-pressure autoclave (SLM-250, Beijing Century SenLong experimental apparatus Co., Ltd), introducing the carbon dioxide to exhaust the air inside the autoclave. Then the autoclave was maintained at 35 ℃ and 7 MPa for 30 minutes. The autoclave was heated to the foaming temperature of 90 °C, with the foaming pressure over 10 MPa. Consequently, the required PVA/Chitin composite foams were achieved through the rapid pressure release.

2.4 Ion Adsorption Tests

The color-developing solutions were initially prepared via dissolving the color developers in the deionized water. The specific metal salts were dissolved in deionized water to prepare the ion standard solution with the concentration of 1 g/L. The buffer solution, color-developing solution, and ion solution were mixed in a certain ratio and diluted, yielding standard solutions with concentration gradients of 10, 20, 30, 40, and 50 mg/L. A UV-3600 ultraviolet-visible-near-infrared spectrophoto-meter (Shimadzu Corporation, Japan) was employed to measure the different absorbance of solutions with varying ion concentration, and a fitted curve was established through fitting the absorbance and the concentration of heavy metal ions in the solution. Therefore, the ion concentration after the adsorption of the foam could be calculated via the fitted curve and measured absorbance. Consequently, the adsorption capacity of the foam could be achieved. During the adsorption tests, the ion solution was mixed with foam sample and subjected to static adsorption at room temperature for 48 hours. Then the supernatant was collected to determine the ion concentration of the solution after adsorption.

2.5 Characterization

The morphology of the PVA/chitin composite powders and the cell structure of the fabricated foams were collected using scanning electron microscopy (SEM, FEI Company). The samples were all coated golden before test. The images of fractured surface of the samples were processed using Nano Measure software to calculate the average cell size, cell density, and cell size distribution. Subsequently, the cell density (N) was calculated using the following formula:

$$N = \left(\frac{nM^2}{A} \right)^{\left(\frac{3}{2}\right)} \quad (1)$$

where n was the number of cells in the SEM image, M was the magnification, and A was the SEM image area.

To elucidate the interactions between PVA and chitin and the melting point of the composite, differential scanning calorimetry (DSC) measurement of the composite was performed on a TAQ20 thermal analyzer (TA Instruments, USA) from 40 to 250 °C with the heating rate of 10 °C/min.

The mechanical performance of the composite foams was assessed using a DWD-10KN universal testing machine (Sichuan DexiangKechuang Instrument Co., Ltd.). The compression tests were conducted in the 200 N mode to obtain the cyclic compression curves, and each sample was compressed from 0 to 10% strain.

The ion adsorption capacity of the foam was measured and calculated through the measured absorbance and fitted curve as mentioned above. During the adsorption testing, certain concentration of the ion solution was adopted and the composite foams with various chitin loadings were applied to investigate the ion adsorption capacity. According to the fitted curve, the ion concentration of the solution after adsorption by foams could be calculated. The adsorption capacity of heavy metal ions, Qe (mg/g), was calculated based on the following formula:

$$Qe = \frac{C_0 - C_e}{M} V \tag{2}$$

where Q_e represented the adsorption capacity / mg/g, C_0 was the initial solution concentration / mg/ml, C_e was the solution concentration after adsorption / mg/ml, M was the mass of the adsorbent / mg, and V was the volume of the solution / ml.

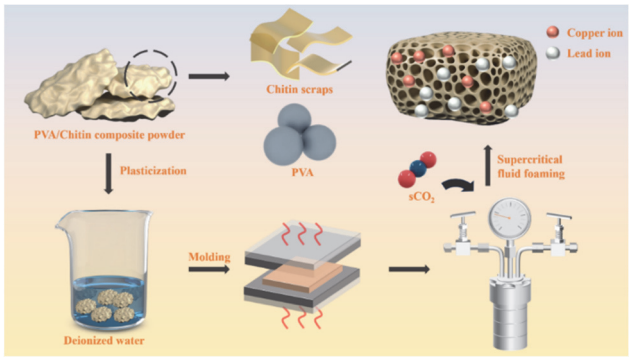

Figure 1 Schematic illustration of the production process of PVA/Chitin composite foams

3 RESULTS AND DISCUSSION

3.1 Morphology and Structure of Co-Milling Composite Powders

In order to reflect the co-milling effects of PVA and chitin, the morphologies of the fabricated composite powders were investigated through the SEM measurement. Fig. 2 presents the SEM images of the co-milling PVA/chitin composite powders with various chitin loadings after 10-cycle milling. The composite powders appeared with no obvious difference even mixed with various chitin loadings. Nearly no distinct chitin particles were observable on the surface of the composite powder, which indicated the efficient blending of PVA and chitin. As the schematic illustration depicted in Fig. 2i, under the effect of strong shearing and squeezing force provided by S^3M equipment, the large flaky chitins were pulverized and further mixed with PVA particles, resulting in the in-situ compatibilization and good dispersion, which improved the compatibility between chitin and PVA.

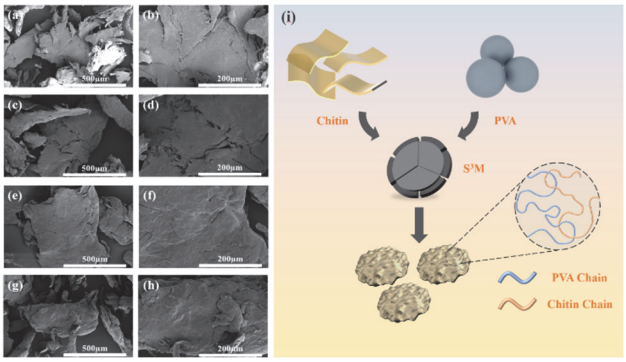

Figure 2 SEM images of PVA/Chitin composite powders with various chitin loadings after S^3M (a, b: PVA/Chitin-1, c, d: PVA/Chitin-3, e, f: PVA/Chitin-5, g, h: PVA/Chitin-10) and the mechanism of milling and mixing (i)

3.2 Morphology and Property of Composites

The well-mixed composite powders were plasticized and molded through thermal compression molding, which were prepared for the following $scCO_2$ foaming process. The morphology of the fractured surface of PVA/Chitin composites was observed by SEM equipment in Fig. 3a, Fig. 3b and Fig. 3c. When the chitin content was low (1%), the fractured surface of the composite appeared smooth with the uniform dispersion of the chitin particles. Even when the chitin content was increased to 10%, the fractured surface still remained smooth and the chitin particles were homogeneously dispersed and tightly embedded in the PVA matrix, confirming the efficient pulverization and compatibilization effect of S^3M technology. To further investigate the interactions between PVA and chitin after co-milling, DSC analysis was performed on the composite materials.

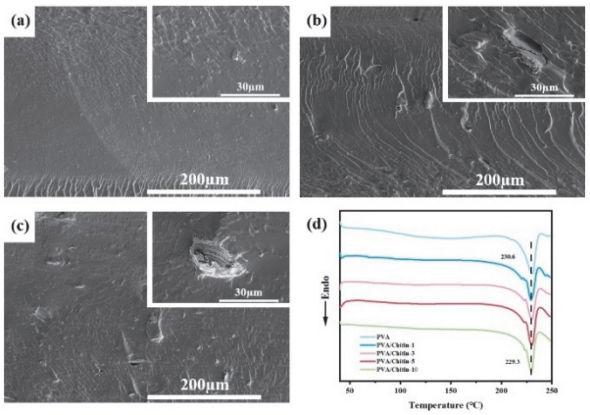

Figure 3 The morphology of the fractured surface of the PVA/Chitin composites (a: PVA/Chitin-1, b: PVA/Chitin-5, c: PVA/Chitin-10), and the DSC curves of the PVA/Chitin composites with various chitin loadings (d)

Fig. 3c showed the DSC curves of the PVA/chitin composite with various chitin loadings. As illustrated, both pure PVA and the composites exhibited a melting endothermic peak around 230 °C. With the incorporation of Chitin, the melting point of the composites decreased a little, from 230.6 °C of pure PVA to 229.3 °C of PVA/chitin-10, probably attributed to the formation of novel hydrogen bonding between chitin and PVA molecules, which disrupted the original hydrogen bonding between PVA molecules, reduced the crystallinity of PVA, and consequently lowered the melting point.

3.3 Cell Structure of Foams

Cell structure containing cell size and cell density is of great significance to the comprehensive performance of the foams, which could be influenced and controlled via the incorporation of chitin. Therefore, in order to investigate the effect of chitin content on the foaming behaviors of the composite materials, Fig. 4 presents the SEM images of the fractured surface of the foam, along with the cell size distribution, with different chitin loadings. Incorporating chitin could effectively decrease the cell size and increase the cell density. In addition, the more chitin was incorporated, the smaller the average cell size and the highest the cell density were achieved of the composite foam.

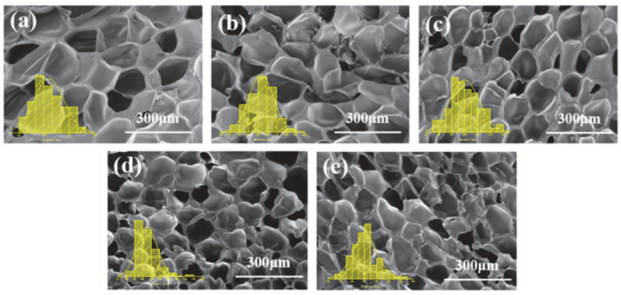

Figure 4 SEM images of the cell structure of composite foams with various chitin loadings and corresponding cell size distribution (a: pure PVA foam, b: PVA/Chitin-1 foam, c: PVA/Chitin-3 foam, d: PVA/Chitin-5 foam, e: PVA/Chitin-10 foam)

The average cell size and cell density of the composite foam were calculated and depicted in Fig. 5 Chitin could serve as the heterogeneous nucleation agent, which provided more nucleation sites, thus resulting in the smaller cell size, higher cell density, and more uniform cell structure. For example, the cell density rose from 5.0×10^5 cells/cm³ of pure PVA foam to 1.2×10^6 cells/cm³ of PVA composite foam with 5% chitin loadings, while the average cell size decreased from 131.3 μm of pure PVA foam to 89.5 μm of PVA composite foam with 5% chitin loadings. When chitin loadings reached 10%, the achieved foam possessed the highest cell density with the smallest average cell size of around 80.4 μm, which might contribute to the improvement of comprehensive performance of the composite foam.

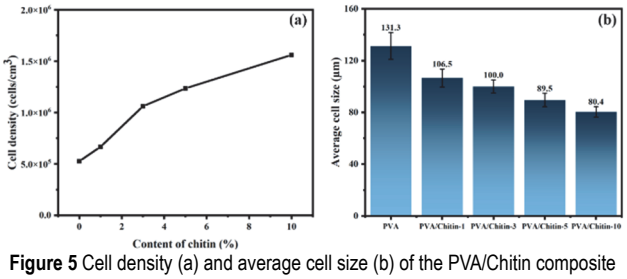

Figure 5 Cell density (a) and average cell size (b) of the PVA/Chitin composite foams with various chitin loadings

3.4 Mechanical Property of Foams

Compression performance is the key indicator to evaluate the practical usability of the polymer foam. To further investigate the effect of chitin loadings on the mechanical properties of the composite foam, compression testing was conducted. Fig. 6a and Fig. 6b, depicted the compression curves and the compressive stress at 10% strain of the composite foam parts with various chitin loadings. As seen from the curve, the compressive stress increased with the increase of the compressive strain, attributed to the gradual densification of the foam part and improvement of resistance to deformation ability. Besides, incorporating chitin could effectively increase the compressive strength of the composite foam, which continuously increased with the elevation of the chitin content. When adding 10% chitin, the PVA/chitin foam exhibited the highest compressive stress of 42.3 kPa at 10% compressive strain. It was because the well dispersed and mixed chitins could serve as the enhancing fillers to improve the strength of the cell wall, thus improving the compressive strength of the composite foam. To more clearly reflect the enhancing mechanism, the fractured morphology of the composite foam (PVA/Chitin-5 foam) was exhibited in Fig. 6c. It was observed that chitins were embedded in the cell walls, exhibiting the good compatibility with PVA and functioning as a reinforcing component. In addition, with the incorporation of chitins, the cell density was increased, which also contributed to the enhancement of the capacity to resist compressive external force as well.

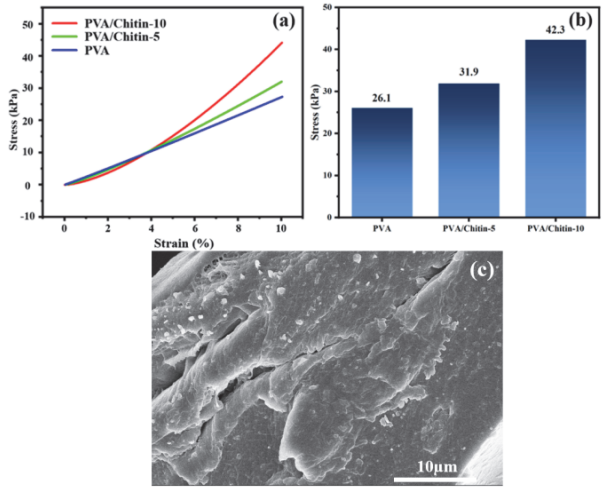

Figure 6 Compressive stress-strain curves of the PVA/Chitin composite foam (a), and the compressive stress of PVA/Chitin at 10% compressive strain composite foam (b), the morphology of chitin in PVA/Chitin-5 foam (c)

3.5 Adsorption Performance of Foams

The adsorption capacity of the composite foam was investigated. The relationship between ion concentration of lead ions and copper ions and the corresponding absorbance was fitted, as depicted in Fig. 7a and Fig. 7b, respectively, which was utilized to measure the changing of the ion concentration and further assess the adsorption capacity of the composite foam. Fig.7c illustrated the adsorption capacity of PVA/Chitin composite foam for lead and copper ions, respectively. The results indicated that pure PVA foam possessed certain ion adsorption capacity, whose adsorption capacity for lead ions and copper ions was 1.04 mg/g and 0.97 mg/g, respectively. Because of that the porous structure and rich hydroxyl groups of the PVA foam endowed it with high specific surface area and complexation capacity to adsorb the heavy metal ions.

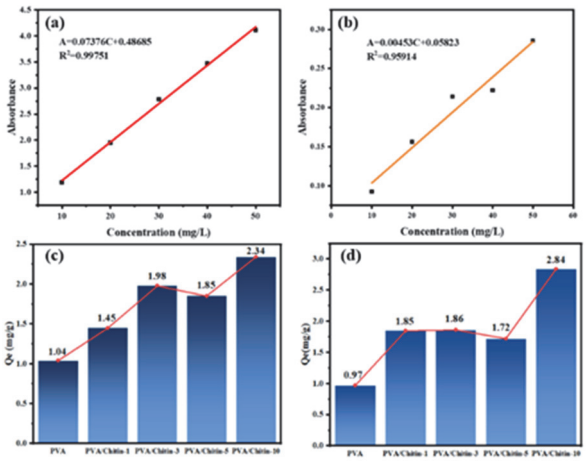

Figure 7 The fitted curves of absorbance and ion concentration (a: lead ions, b: copper ions), and the lead ions (c) and copper ions (d) adsorption capacity of the composite foams with various chitin loadings

With the incorporation of chitin, the adsorption capacity of the foam was further improved. When 1% chitin was introduced, the adsorption capacity of lead ions was increased to 1.45 mg/g, along with the copper ions reaching 1.85 mg/g. The adsorption capacity of lead ions and copper ions exhibited an upward trend. The chitins were pulverized and activated under the strong shearing and squeezing effect of S^3M. The activated hydroxyl group could bind with heavy metal ions in the water, as well as the nitrogen atoms in the chitin molecule, which improved the adsorption capacity of the composite foam. Furthermore, the cell density of the composite foam was also increased with the more incorporated chitin, serving as the heterogeneous nucleating agent, which endowed the material with more opportunities to contact heavy metal ions in solution, thus synergistically improving the adsorption capacity. Eventually, the PVA/Chitin-10 foam exhibited the best adsorption capacity for heavy metal ions, whose adsorption capacity reached 2.34 mg/g and 2.84 mg/g for lead ions and copper ions, respectively, nearly 2 times and 3 times of that in pure PVA foam.

Fig. 8 vividly illustrated the adsorption mechanism of the composite foam. The activated functional groups in chitin molecules could form weak interactions with ions in the solution. Additionally, metal ions might also be embedded in the layered structure of chitin with a high specific surface area [33]. PVA, as the polyhydroxy polymer, provided the hydrophilic matrix and carrier. When prepared into composite foams, both the porous structure and chitin played the significant roles in the adsorption of heavy metal ions, which contributed to the improvement of the composite foam. This novel environmental-friendly composite foam holds significant value for the resource utilization of biomass and exhibits promising applications in the field of wastewater treatment.

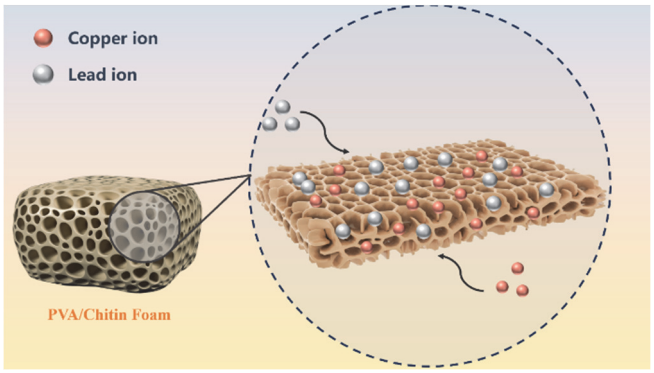

Figure 8 The schematic illustration of the PVA/Chitin composite foam adsorbing the heavy metal ions

4 CONCLUSIONS

In this study, an environment-friendly PVA/chitin composite foam was successfully fabricated using a combination of solid-state shearing milling (S^3M) and supercritical carbon dioxide ($scCO_2$) foaming technologies. The addition of chitin significantly improved the adsorption capacity, mechanical properties, and structural stability of the foams. The optimized composite with 10% chitin exhibited a 193% and a 56% enhancement for copper and lead adsorption, respectively, demonstrating its strong potential for environmental remediation. The results suggest that environment-friendly composite foams could serve as cost-effective alternatives for wastewater treatment. It realizes the efficient utilization of biomass materials, which is of great significance.

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