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A facile synthesis of core-shell/bead-like poly (vinyl alcohol)/alginate@PAM with good adsorption capacity, high adaptability and stability towards Cu(II) removal

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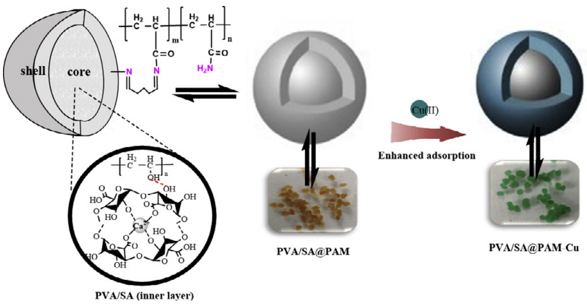
HIGHLIGHTS

- Core-shell/bead-like PVA/SA@PAM biosorbent was firstly prepared by a facile route.
- It was factionalized by introducing amino groups and achieved better Cu (II) removal.
- A better adsorption capacity than most of reported similar alginate-based biosorbent.
- It exhibits excellent adaptability and high mechanical and chemical stability.

GRAPHICAL ABSTRACT



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ABSTRACT

A facile route of poly (vinyl alcohol)/alginate@ polyacrylamide (PVA/SA@PAM) for heavy metal adsorption was prepared by crosslinking with PAM onto PVA/SA, which complemented both benefits of natural and synthetic polymers, resulting from the design of core–shell/bead-like structure and polymer blending. Fourier transform infrared (FT-IR), scanning electron microscopy and energy-dispersive X-ray spectrometry (SEM-EDS) and X-ray photoelectron spectroscopy (XPS) etc. were applied to characterize as-synthesized beads. The results showed the optimal pH value was 5.0. The adsorption process of Cu(II) fitted well with the Freundlich isotherm model and the pseudo-second-order model in batch system. The experimental maximum adsorption capacity was 79.5 ± 1.6 mg/g under the optimal condition, which is approximately 2.3 and 2 times higher than that of plain SA beads and PVA/SA beads, respectively. Thermodynamic studies revealed the adsorption process was spontaneous and endothermic in nature. Thomas model was fitted better than Bohart-Adams model with breakthrough curves under different initial Cu(II) concentration in a column system. More importantly, the PVA/SA@PAM showed excellent mechanical stability and resistance for interference of co-existing ions. Besides, its removal ability only decreased slightly even after eleven cycles in reusability tests. Overall, PVA/SA@PAM exhibits attractive characteristics of simple production process, low cost, good adsorption capacity, excellent adaptability and chemical and mechanical stability.

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1. Introduction

Recently, emerging utilization of natural polymers (e.g., SA, chitosan and cellulose) for the design of biosorbent has attracted great attention from acknowledging costs and security concerns. SA is a natural polysaccharide with abundant carboxyl (–COOH) and hydroxyl (–OH) functional groups. Strikingly, SA can react with multivalent metal ions to form a three-dimensional network structure and just make up for the limitation of separation and regeneration of the adsorbent [1]. Besides, its excellent properties such as better metal ions binding ability, biocompatibility, biodegradability and easily available in natural resources, further make it an ideal material for potential heavy metal adsorption. However, it still restricted by disintegration and weak mechanical strength [2]. Naturally, these make people explore some physicochemical modifications to improve it. Among various methods, polymer blending provides an idea for developing adsorbents with desirable properties. Successful attempts also involved with one or more kinds of polymers, such as chitosan [2], gelatin [3] and cellulose [4]. Among them, synthetic polymers such as PVA have attracted extensive attention due to its excellent mechanical and chemical properties [5]. For instance, Jiang et al. [6] prepared PVA/SA hydrogels to combine the benefits of both polymers with high toughness. However, it is still limited by the small quantities of binding sites themselves. To enhance adsorption capacity, Mahdavinia et al. [7] developed magnetic hydrogel beads by initially mixing of SA, PVA and magnetic laponite and then physically crosslinking by Ca^{2+}. Considering these, developing adsorbents with high adsorption capacity is always the key area in basic and applied research.

Based on the theory hard and soft acid and base (HSAB), functional groups containing elements such as O, N and S are conducive to the formation of complex with specific adsorbate [8,9]. For instance, Wu et al. [10] employed cyclodextrin modified PVA hydrogel beads for benzene ions removal. The cyclodextrin addition has positive effects on both the removal efficiency and rate. Yan et al. [1] synthesized a polyethyleneimine-modified alginate beads with abundant amino groups for hexavalent chromium removal. Additionally, Song et al. [11] prepared a xanthated carboxymethyl chitosan for the uptake of lead ions from aqueous solution. As we can see, the introducing of functional groups facilitates adsorption. Strikingly, PAM is a well-known cheap and easily available synthetic polymer with abundant of acyl amino groups and it has been widely used as an adsorbent material [12–14]. Accordingly, it is simple to blend PAM with other polymers and further form bead-like structure, while some of PAM will be embedded inside rather than exposed to the outside of the adsorbent. Thus, some of PAM could not be utilized for direct adsorption, resulting in lower removal rate and even adsorption capacity. Considering with these concerns, we discussed the design and prepared with a core-shell-like hydrogel beads for adsorption.

In the present work, a novel bio-sorbent with core-shell/bead-like structure was prepared to remove copper (Cu(II)) from aqueous solution. The bio-sorbent was synthesized by using PVA/SA hydrogel beads as supporting materials to graft PAM onto the surface through physicochemical crosslinking reaction. Intermolecular hydrogen bonding could be formed between the hydroxyl groups of PVA/SA and amino groups (–NH_2) of PAM after physical stirring. Besides, a one-step conjugation method was used through simply adding glutaraldehyde to the mixture, where glutaraldehyde may easily react with some polar groups in nucleophilic reactions. In the first option, a glutaraldehyde molecule may react with two amino groups (to form a Schiff base linkage) of intra-or intermolecular of PAM branched chain [15]. Herein, the final product could complement both benefits of natural and synthetic polymers. The physicochemical characterization of the synthesized beads was conducted by FT-IR, SEM-EDS, FESEM-EDS, XPS and other conventional methods. Batch experiments were carried out for pH, adsorption isotherms, kinetics behaviors, adsorption thermodynamic and interference ions studying. Further, column studies under different Cu(II) concentration and adsorption-desorption experiments were also investigated to demonstrate the potentiality of this novel bio-sorbent.

2. Materials and methods

2.1. Materials

All chemicals and reagents were of analytical grade or higher and directly used without any purification. All solutions were prepared with deionized water unless otherwise stated throughout this study. SA [$(C_6H_7NaO_6)_m$] was purchased from Qiangsong Fine Chemicals Co., Ltd (Wuhan, China). In addition, other reagents such as PVA [$(C_2H_4O)_n$], PAM [MW ≥ 3000000, $(CH_2CH(CONH_2))_x$], calcium chloride ($CaCl_2$), glutaraldehyde aqueous solution (25%, $C_5H_8O_2$), cupric nitrate [$(Cu(NO_3)_2\cdot 3H_2O)$] hydrochloric acid (HCl), sodium hydroxide (NaOH), and sodium chloride (NaCl) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). A stock Cu(II) solution of 1000 mg/L was prepared and further diluted to the desired levels for later use.

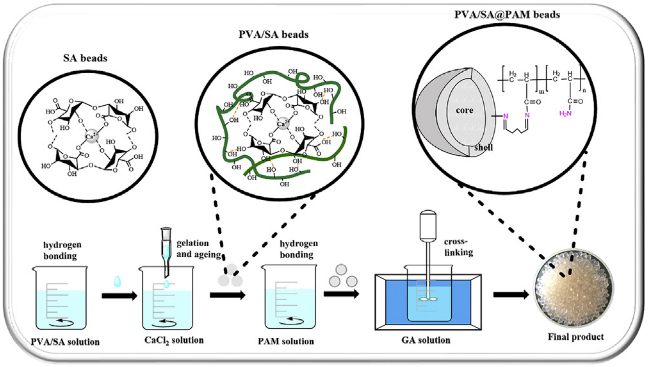
2.2. Preparation of PVA/SA@PAM hydrogel beads

The facile synthesis route of PVA/SA@PAM was depicted in Scheme 1. Initially, 2.0 g of sodium alginate was added into 100 mL of polyvinyl alcohol solution (1%, w/v) under continuously stirring for 24 h. Then the mixture was dropped carefully into a 400 mL of $CaCl_2$ solution (5%, w/v) and further aged for 24 h. The PVA/SA hydrogel beads were collected by filtration and repeatedly washed with deionized water. In the control trials, plain SA hydrogel beads were fabricated only without the addition of PVA. Then, the PVA/SA beads were mixed in 200 mL of polyacrylamide solution, and the mixture was stirred at room temperature for 12 h to allow the formation of intermolecular hydrogen bonding among the aforementioned substances. After that, the mixture was immediately transferred into 200 mL glutaraldehyde reaction solution (1%, w/v) while stirring gently for 1 h under 50 °C water-bath condition to allow cross-linking reaction [1]. Finally, the PVA/SA@PAM hydrogel beads were collected, washed and stored for further use in experiments.

Corresponding to the different contents of functional reagent PAM (0.5, 1.0, 1.5 and 2.0 g), the as-synthesized PAM modified PVA/SA were named as PVA/SA@PAM-0.5, PVA/SA@PAM-1.0, PVA/SA@PAM-1.5 AND PVA/SA@PAM-2.0 respectively. In the control trials, blending PAM into form PVA/SA/PAM bead-like adsorbent was also prepared.

2.3. Batch adsorption experiments

Batch experiments were performed to determine the optimal conditions for Cu(II) adsorption process from aqueous solution. Typically, 0.05 g of dried bio-sorbent was added into a 50 mL covered tube with given concentration (20–500 mg/L) of Cu(II) solution at desired pH values (26). The tubes were incubated at different temperature



Scheme 1. Schematic presentation for synthesis of PVA/SA@PAM beads.