



Selective removal of mercury ions using a chitosan–poly(vinyl alcohol) hydrogel adsorbent with three-dimensional network structure

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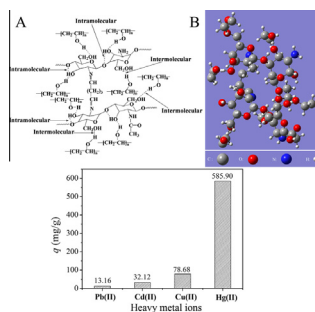
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HIGHLIGHTS

- The CTS–PVA hydrogel adsorbent with three-dimensional network structure was prepared.
- The hydrogel showed superior adsorption capacity and selectivity for Hg(II) ions.
- Three-dimensional network structure of the hydrogel was characterized and modeled.
- The selective adsorption mechanism of the hydrogel for Hg(II) ions was proposed.
- The hydrogel holds great promise in Hg(II) removal from aqueous environment.

GRAPHICAL ABSTRACT



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ABSTRACT

The chitosan–poly(vinyl alcohol) (CTS–PVA) hydrogel with three-dimensional network structure was developed via a glutaraldehyde cross-linking method in combination with an alternate freeze–thawed process. The formation of the three-dimensional network structure was confirmed by SEM and parallel FT-IR measurements. According to the analysis of parallel FT-IR measurements and MM+ molecular mechanics theoretical simulation, the three-dimensional network architecture is built mainly by inter- and intra-molecular hydrogen bonds as well as C=N bonds formed by the reaction of –NH₂ groups of CTS and –CHO groups of glutaraldehyde. Parallel adsorption experiments and comparative studies showed that the hydrogel adsorbent has superior adsorption capacity and selectivity for Hg(II) ions. Its adsorption capacity for Hg(II) ions reaches 585.90 mg/g. Its selectivity coefficient of the hydrogel for Hg(II) ions is 487.7, 36642.5, 284298.5 times higher than that for Cu(II) ions, Pb(II) ions, and Cd(II) ions, respectively. Its selective adsorption mechanism for Hg(II) ions was proposed based on FT-IR and XPS spectral analysis before and after Hg(II) adsorption. All nitrogen-containing functional groups are involved in Hg(II) adsorption, especially, –NHCOCH₃ and C=N groups are the main selective functional groups responsible for Hg(II) adsorption. The existing form of the adsorbed Hg(II) may be in mercury acetate.

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1. Introduction

Mercury (Hg) is one of the most toxic heavy metals commonly found in the global environment. Hg contamination is much more widespread and difficult to be removed than other metals [1]. Among mercury species, the highly reactive Hg(II) is the most toxic

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form because it can be methylated by reducing bacteria in anoxic habitats and transformed into methylmercury (MeHg^+ or Me_2Hg). Methylmercury can be uptaken by aquatic organisms and accumulated in the food web, resulting in the bio-magnification of Hg contamination through the food chain [2]. Therefore, removal of Hg(II) ions from water and wastewater becomes very important.

By far, the most efficient method for the Hg(II) removal from aqueous effluents is adsorption. The most commonly used adsorbent is activated carbon, due to its high adsorption capacity and cost effectivity [3]. However, Hg(II) ions often coexist with other heavy metals in wastewater. The presence of large amount of other heavy metals will reduce the removal efficiency of mercury by a non-selective adsorbent and result in the recovery of mercury very difficult due to the interference of other heavy metals on the adsorbent [4]. From this prospect, developing selective adsorbent for Hg(II) ions to effectively remove mercury is very significant.

Recently, hydrogels with three-dimensional network structure as well as functional groups are well documented to be used for the removal of heavy metals from aqueous solutions [5–7]. Hydrogels can swell considerably in aqueous medium without dissolution, which is helpful for adsorbing and trapping of metal ions. The unique swelling property of hydrogels and the porous network structure make heavy metal ions more easily access to functional groups on hydrogels. Meanwhile, it was found that nitrogen-containing functional groups, e.g., amino, amide, and C=N groups, possess superior adsorption capacity and selectivity for Hg(II) ions and are often utilized in designing polymer sorbents for binding Hg(II) ions selectively [8–10]. This is because that the nitrogen atom has a lone pair of electrons, which can bind with a metal ion through donating the lone pair of electrons to form a metal complex. Among nitrogen-containing functional groups, amino group contribute a high adsorption capacity but bad adsorption selectivity for different metal ions [11]. Amide groups show excellent adsorption selectivity for Hg(II) ions because of the electron-withdrawing effect by carbonyl groups where makes amide groups show slight tendency for coordination with transition-metal ions. On the other hand, amide is a soft basic, which has a good affinity with Hg(II) ions (a soft acid) [12]. In addition, the C=N group is a softer basic ligand than the amino group, and researches have shown that it can also interact with a very soft acid such as Hg(II) ions [13,14].

In this study, we designed and synthesized a crosslinked hydrogel adsorbent with special Hg(II) adsorption properties using chitosan (CTS) as the base material. CTS is a nitrogen-containing biopolymer which contains plenty of amino and amide groups and shows excellent metal-binding capability and special adsorption selectivity for Hg(II) ions [15–17]. The as-prepared hydrogel adsorbent possesses a three-dimensional network structure with plenty of $-\text{NH}_2$ groups, $-\text{NHCOCH}_3$ groups and C=N groups. This study focused on the three-dimensional network architectures of the hydrogel adsorbent and the high adsorption selectivity for Hg(II) ions. This study would contribute to an in-depth understanding of the adsorption phenomena and develop a special biosorbent possessing high adsorption capacity and selectivity for Hg(II) ions from aqueous solutions.

2. Materials and methods

2.1. Materials

CTS (industrial grade, the degree of deacetylation was 75%, and the average molecular weight was 3×10^5 g/mol) was supplied by Zhejiang Golden-Shell Biochemical Co. Ltd. (Zhejiang, China). Poly(vinyl alcohol) (PVA, industrial grade, the degree of hydrolysis was 99% and the average degree of polymerization was 1700) was

supplied by Lanzhou Xinxibu Vinylon Company Ltd. (Gansu, China). Glutaraldehyde with a concentration of 25%, mercury(II) acetate, cadmium(II) acetate dehydrate, lead(II) acetate trihydrate, copper(II) acetate monohydrate and all other chemicals were of analytical grade and commercially obtained from Tianjin Kermel Chemical Reagent Co., Ltd. (Tianjin, China). Aqueous solutions were all prepared with Millipore water ($\sim 18.25 \text{ M}\Omega/\text{cm}$).

2.2. Preparation

The CTS–PVA hydrogel was prepared via a glutaraldehyde cross-linking method in combination with an alternate freeze–thawed process. 490 mL of 2% CTS solution was mixed mechanically with 42 mL of 10% PVA aqueous solution at room temperature for 2 h to obtain a homogeneous solution. 4 mL of glutaraldehyde aqueous solution (25%) was added dropwise into the above mixture and continuously stirred at room temperature for another 4 h to obtain homogeneously blended gel. The gel was froze in a refrigerator at -18°C for 24 h, and then thawed at room temperature for 6 h. After three freeze–thawed cycles, the hydrogel was obtained. The obtained hydrogel was immersed in a diluted sodium hydroxide solution overnight to neutralize the excess acetic acid, and then washed with Millipore water several times until pH of the suspension is close to 7.0. The neutralized product was dehydrated using ethanol as a dewatering agent for three times. For adsorption studies, the dehydrated product was dried in an oven at 80°C overnight and then milled and sieved through an 80-mesh screen.

An interesting characteristic of the CTS–PVA hydrogel adsorbent is its swelling properties. Before drying, the hydrogel swells very well in distilled water with a swell ratio of about 200 g/g (see Fig. 1B). However, once dried, it can only swell slightly with a swell ratio in distilled water of 4.66 g/g (see Fig. 1C). The digital photos and the SEM image of as-prepared CTS–PVA hydrogel adsorbent before and after drying were shown in Fig. 1. From the SEM image (Fig. 1D), it can be seen that the as-prepared CTS–PVA hydrogel adsorbent indeed has a three-dimensional network structure.

2.3. Adsorption experiments

A preliminary kinetic test indicates that the adsorption equilibrium of heavy metal ions on the CTS–PVA hydrogel adsorbent can be achieved within 24 h. Therefore, an equilibrium time of 24 h was adopted for all the adsorption processes. All batch adsorption experiments were performed by adding the dried adsorbent into a simulated wastewater containing the object metal ions, and then the mixture was shaken in a thermostatic shaker bath (THZ-98A) at 30°C until the equilibrium to be established. The pH of solution was adjusted by adding diluted acetic acid or sodium hydroxide solution. To investigate the effect of the initial pH (pH_0) of Hg(II) solution on adsorption, a pH range from 2.00 to 5.85 was selected to avoid precipitation of Hg(II) ions, and the initial Hg(II) concentration was 2239.39 mg/L. The adsorption selectivity of the hydrogel adsorbent for Hg(II) ions was investigated by parallel adsorption experiments and comparative studies. The selective adsorption experiment conditions carried out in single- and multi-component heavy metal solutions were shown in Table 1.

The concentrations of Cu(II), Cd(II) and Pb(II) ions were determined by an inductively coupled plasma atomic emission spectrometer (ICP, VISTA-PRO, Varian, USA). The concentration of Hg(II) ions was determined by an atomic fluorescence spectrophotometer (AF-640, Beijing Beifengruili Analytical Instrument Co., China). The adsorption capacity of the hydrogel adsorbent for heavy metal ions at a given time t or at equilibrium can be derived using the following equation:

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