International Journal of Biological Macromolecules 86 (2016) 562–569

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: www.elsevier.com/locate/ijbiomac

Biosorption of lead from aqueous solutions by ion-imprinted tetraethylenepentamine modified chitosan beads

Bingjie Liu [a,*], Wei Chen [a], Xiaoning Peng [a], Qiqi Cao [a], Qianrui Wang [b], Dongfeng Wang [a], Xianghong Meng [a], Guangli Yu [c]

[a] College of Food Science and Engineering, Ocean University of China, Qingdao 266003, China
[b] Faculty of Science, The University of Hong Kong, Hong Kong, China
[c] School of Medicine and Pharmacy, Ocean University of China, Qingdao 266003, China

ARTICLE INFO

Article history:
Received 14 October 2015
Received in revised form 12 January 2016
Accepted 27 January 2016
Available online 2 February 2016

Keywords:
Chitosan
Cross-linking
Ion-imprinting
Lead
Selective adsorption

ABSTRACT

In this paper, the bio-based ion-imprinted tetraethylenepentamine (TEPA) modified chitosan beads using Pb(II) as imprinted ions (Pb–ITMCB) were chemically synthesized, characterized and applied to selectively adsorb Pb(II) ions from aqueous solutions containing other metal ions, which has the same concentration as that of Pb(II) ions. Batch adsorption experiments were performed to evaluate the adsorption conditions, selectivity and reusability. FTIR, SEM and TEM technologies were used to elucidate the mechanism of Pb–ITMCB adsorbing Pb(II) ions. The results showed that the adsorption capacity of Pb–ITMCB for Pb(II) ions reached 259.68 mg/g at pH 6, 40 °C. The adsorption data could be fitted well with pseudo-second order kinetics model and Langmuir isotherm model. Compared with other metal cations, Pb(II) ions showed an overall affinity of being adsorbed by Pb–ITMCB. With the participation of active groups including $—NH_2$, —NH— and —OH, the adsorption reaction took place both inside and on the surface of Pb–ITMCB. It indicated that Pb–ITMCB is a comparatively promising biosorbent for selective removal of Pb(II) ions from aqueous solutions.

1. Introduction

As an important compound, lead (Pb(II)) is widely used as an inter-media in processing industries including plating, paint, dyes and lead batteries [1]. However, the existence of Pb(II) ions in soil and water can lead to contaminated food and water being taken up by animals and human being through gastrointestinal tract, which poses a great threat to human health. In order to purify the water contaminated by hazardous metal ions [2,3], numerous adsorbents such as synthetic chitosan resin [4–6], activated carbon [7,8], wheat bran [9,10], carbon nanotubes [11–13], activated tea waste [14], natural and synthetic zeolite [15,16], modified and unmodified clay minerals [17,18] have been tested to remove hazardous metal ions from water and wastewater. Among them, natural and modified chitosan resin was a promising adsorbent. Because of some unique properties including physiochemical combination and reusability, natural as well as modified chitosan resin was chosen as the most prospective adsorbent from all alternatives, adsorbing hazardous metal ions with high efficiencies and low costs.

The presence of amine ($—NH_2$) and hydroxyl (—OH) groups, which may serve as coordination sites to form complexes with various heavy metal ions in neutral solutions, makes chitosan as an excellent natural adsorbent. Moreover, chitosan, with high content of amino groups, can also be chemically modified to promote selectivity and adsorption capacity. However, poor acidic resistance and mechanical strength determine that further treatments are necessary to be implemented to improve its chemical resistance and particular adsorption conditions [19]. As cross-linking agents like glutaraldehyde [20], epichlorohydrin [21,22] and ethylene glycol diglycidyl ether [23] could weaken the adsorption efficiency of chitosan, inserting active agents with functional groups is an effective way to promote the adsorption capacity of beads. Many literatures have been reported on the removal of metal ions and dyes by chitosan derivative, such as Mo(VI) [24], Cr(VI) [25], Fe(III) [26], UO_2^{2+} [27], Reactive Black 5 [28], eosin Y [29] and anionic dye [30]. Recently, we have attempted not only to enhance the adsorption ability, but also to improve the selectivity of ion-imprinted chitosan by modifying with TEPA. In that case, TEPA modified chitosan beads with Pb(II) as imprinted ions were synthesized to selectively adsorb Pb(II) from aqueous solutions.

With the ability of recognizing a specific chemical substance, molecular imprinted technology makes selective adsorption as a feasible idea for the removal of heavy metal ions from aqueous

* Corresponding author. Fax: +86 532 82032093.
E-mail address: liubj@ouc.edu.cn (B. Liu).

http://dx.doi.org/10.1016/j.ijbiomac.2016.01.100
0141-8130/

solutions [31]. Metal ion-imprinting, which uses metal coordination as a bond between templates and functional monomers, is one of the most important methods of molecular imprinted technology [32,33].

The aim of this work was to prepare Pb(II) ions imprinted TEPA modified chitosan beads and to investigate its adsorption behavior and mechanism through FT-IR, SEM and TEM methods. Effects of various parameters, such as pH, temperature, contact time and initial concentration, were evaluated in selective adsorption studies of Pb–ITMCB. Additionally, adsorption isotherm and kinetics models were used to fit with experimental data.

2. Materials and methods

2.1. Materials

Chitosan (degree of deacetylation, 92.2%, molecular weight, 5.0×10^5 Da) was purchased from Shandong Hecreat Marine Biotech Co., Ltd. (Qingdao, China). All metal ions standard solutions were obtained from national steel material test center of China (Beijing, China). Acetic acid, lead nitrate, liquid paraffin, ethyl acetate, glutaraldehyde, tetraethylenepentamine and all the other reagents used in this experiment were of analytical grade or better, and used as received without further purification. All of aqueous solutions were prepared with Millipore (18.4 MΩ) deionized–distilled water.

2.2. Preparation of Pb–ITMCB

(I) Pb–ITMCB was prepared according to the patent of Wang et al. [34]. Briefly, 10.0 g chitosan was dissolved in 200 mL acetic acid solution for 24 h. And then, it was removed to a 1000 mL beaker flask, which contained 200 mL liquid paraffin. After the mixture being continuously stirred at 300 rpm, 40 °C for 20 min, the temperature was raised to 60 °C and glutaraldehyde was added as cross-linking agent. The polymeric beads were generated in an afterwards continuously stir at 175 rpm for 3 h, and were thoroughly washed with petroleum ether, ethanol and deionized distilled water in sequence later, with all unreacted compounds removed completely.

(II) 0.5 g chitosan beads were dissolved in 25 mL of 0.5 mol/L NaOH aqueous solution, with 4 mL epichlorohydrin dropwise into it. This was continuously stirred at 150 rpm, 55 °C for 5 h. The product was washed with ethanol, aether and deionized distilled water in sequence to remove the unreacted fraction, and then dried at 60 °C.

(III) 0.5 g of above beads were swelled into 25 mL 0.1 mol/L NaOH aqueous solution, 5 mL of TEPA was drop-wise added into the solution, continuously stirred at 150 rpm, 55 °C for 5 h. After completion of reaction, the beads were extensively washed with ethanol, aether and deionized distilled water in sequence to remove any unreacted fraction, dried at 60 °C.

(IV) The TEPA modified chitosan beads were swelled into 1 mol/L Pb(II) aqueous solution, continuously stirring at 30 °C for 12 h, Pb(II) was removed by 0.5 mol/L HNO_3. The obtained product, Pb(II) imprinted TEPA modified chitosan beads, was collected, abbreviated as Pb–ITMCB. As a control, non imprinted TEPA modified chitosan beads were also prepared, abbreviated as NITMCB.

2.3. Characterization of Pb–ITMCB

The FT-IR spectra of Pb–ITMCB were recorded before and after Pb(II) adsorption, using Nexus 470 FT-IR spectrometer with a resolution of 4 cm^{-1}. The dried sorbents, Pb–ITMCB before and after adsorption of Pb(II), were ground into powder. For each type of powder, 1 mg chitosan beads powder was blended with 100 mg IR-grade KBr in an agate mortar and pressed into a tablet. The tablets were scanned by FT-IR spectrometer, within the spectra range from 400 to 4000 cm^{-1}.

The microscopic observation of Pb–ITMCB was carried out by a scanning electron microscope (S-4800, Hitachi, Japan) and a transmission electron microscope (H-7650, Hitachi, Japan).

2.4. Batch adsorption experiments

Batch adsorption experiments were carried out in 50 mL Erlenmeyer flasks, with 0.1 g adsorbent and 25.0 mL aqueous solution. The pH of aqueous solution was adjusted by 1.0 mol/L NaOH or 1.0 mol/L HCl aqueous solution and measured with a pH meter (Delta 320, Mettler-Toledo). Batch adsorption experiments were carried out at a constant temperature of 40 °C for 24 h. After reaching adsorption equilibration, the adsorbent was separated by filtration. The Pb(II) and other metal ions concentration of the filtrate were measured by a flame atomic absorption spectrophotometer (FAAS) (AA-6800, Shimadzu, Japan) at 283.3 nm wavelength.

The adsorption capacity of Pb–ITMCB for Pb(II) ions was calculated according to Eq. (1):

$$q_e = \left(\frac{C_i - C_e}{W}\right) V \tag{1}$$

where q_e is the adsorption capacity of the beads (mg/g); C_i and C_e are the concentrations of Pb(II) in the initial and equilibrium solution (mg/L), respectively; V is the volume of the aqueous solution (L) and W is the mass of dry beads (g).

2.5. Selective adsorption study

The selectivity of Pb–ITMCB and NITMCB for Pb(II) ions compared with other metal ions were evaluated from the selectivity coefficient ($\beta_{Pb^{2+}/M^{n+}}$), which was obtained by incubating 0.1 g adsorbent with 25 mL of 0.02 mol/L each heavy metal ion solution under the identical condition. The selectivity coefficient is defined as Eq. (2) [35]:

$$\beta_{Pb^{2+}/M^{n+}} = \frac{D_{Pb^{2+}}}{D_{M^{n+}}} \tag{2}$$

where $D_{Pb}{}^{2+}$ and $D_M{}^{n+}$ are distribution ratios of Pb(II) and other coexistent metal ions, respectively. Distribution ratio (D) was calculated by Eq. (3):

$$D = \frac{C_i - C_e}{C_e} \times \frac{V}{W} \tag{3}$$

where C_i and C_e are the initial and equilibrium concentrations of metal ions (mg/L), respectively; V is the volume of aqueous solution (L) and W is the mass of dry beads (g).

The effect of imprinting on selective adsorption was evaluated by the relative selectivity coefficient, β_r, which can be defined as Eq. (4):

$$\beta_r = \frac{\beta_{imprinted}}{\beta_{non\text{-}imprinted}} \tag{4}$$

2.6. Desorption and reuse studies

Desorption studies are very important since the regeneration of adsorbents can contribute to economic benefits. In the present study, several solvents/solutions have been tried to regenerate the biosorbents. Out of these solvents/solutions, 0.5 mol/L HNO_3 aqueous solution was found to be effective in desorbing Pb(II) ions from loaded Pb–ITMCB. Thus, Pb–ITMCB was repeatedly regenerated by