



A novel chitosan based adsorbent for boron separation

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ABSTRACT

A new type of adsorbent was synthesized by grafting N-methyl-D-glucamine (MG) onto the surface of chitosan beads to separate boron element. The physicochemical properties of modified chitosan beads (CTS-MG) were examined by FT-IR and SEM analyses. The results indicated that MG had grafted on chitosan beads (CTS) successfully. Compared to surface of pure CTS, CTS-MG had a rougher surface. While the pH value ranged 3–8, CTS-MG would have a high efficiency of adsorption to boron. The characteristics of the adsorption process were evaluated by Langmuir and Freundlich adsorption isotherms, and the maximum adsorption capacity of CTS-MG was $20.36 \text{ mg} \cdot \text{g}^{-1}$. When mass of adsorbent was not lower than 0.1 g, the concentration of 10 ml boron solution would decrease from 50 to 0.5 mg/L. This adsorption process fit to the pseudo-second-order kinetic model. CTS-MG had a comparatively high selectivity because general competing ions had little influence on the adsorptive ability of CTS-MG. After 5 times adsorption-desorption cycles, adsorptive capacity of CTS-MG did not decrease obviously. CTS-MG was hopefully used in the process of boron desorption in salt lake brine.

1. Introduction

The salt lake brine contains many useful chemical elements, such as potassium, magnesium, boron etc., which could be extracted from the salt lake brine. Most boron element is precipitated in the form of boric acid from the residual solution, from which potassium element firstly extracted as potash fertilizer, in order to further produce magnesium salt. The remaining solution with low boron content (about B_2O_3 10 g/L) and high magnesium content is called as the acidified brine after the boron deposition. The brine solution has been widely used to produce magnesium chloride, magnesium hydroxide and magnesium carbonate. However, the presence of low content boron would affect the quality of subsequent magnesium products seriously. Thus proper deep removal of limited boron element from old brine could not only improve the quality of subsequent magnesium and related products, but also make full use of boron resources in salt lake brine. Boron extracted from salt lake brine has become an effective method to solve boric resource shortage [1].

The methods of extracting boron from the salt lake old brine include chemical precipitation, flotation, acidification, solvent extraction, ion exchange and adsorption [2–4]. Among them, the adsorption offer advantages over the low content of boron extraction. Referring to these acidified and precipitated brines, the recycle rate would be improved

through adsorption. The adsorbed boric acid could be recycled through elution, evaporation, crystallization, filtration and drying. The effect of boric acid on the purity of magnesium and lithium would be efficiently avoided in subsequent processes.

The adsorption method is considered to be one of the most promising methods because of its advantages of simple operation, easy design and low cost. Therefore, many boron adsorbent materials have been developed, including double layer hydroxide [5], nano-materials [6] and boron selective adsorption resin [7–10], etc. Qiu et al. [11] synthesized a novel layered double hydroxide (LDH) intercalated gluconate based on traditional Mg/Al LDH, and the maximum sorption capacity of the material reached to 13.73 mg/g , calculated by Langmuir adsorption isotherms. The material could be obtained easily and its cost is very low, however its adsorption efficiency is poor. Mine Özdemir et al. [12] has obtained boron adsorbent with a diameter of $6 \mu\text{m}$ and a maximum boron adsorption capacity of 65.9 mg/g by calcining magnesite at 600°C . Ping Li et al. [6] used ultrasonic method to prepare MgO nanosheets with a lateral diameter of about 200–600 nm and a thickness of 10 nm. The maximum boron adsorption capacity is 87 mg/g . Both of them manifested excellent adsorption capacities due to their larger surface area at the nanometer or micron scale. However, it is difficult to separate and recycle, which brings great difficulties to the reuse of adsorbent and industrial applications. Therefore, it is urgent to

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develop new adsorbents with the advantages of suitable particle size, easy separation, and large adsorption capacity.

In recent years, the polymer resins with the vicinal polyalcohol function groups have been widely used in the separation of boron element. In the process of boron-specific removal, Amberlite IRA-743 is one of commercial resin. However, it is not satisfying in boron uptake. Due to the regeneration, resin would have a high cost and capacity loss [13]. The property of copolymers or strong hydrophobic group limit most polymer based resin efficiencies. Samatya et al. [14] prepared a monodisperse porous boron adsorbent with Vinylbenzene Bismuth (VBC) copolymer and divinylbenzene (DVB) as backbone and MG as functional group, the static equilibrium adsorption capacity of which was 14.05 mg/g. This kind of boron adsorption resin with styrene and divinylbenzene copolymers as the carrier, is not easy to be infiltrated in water molecular solution because of its strong hydrophobicity, resulting in the adsorption rate is limited [15]. Therefore, it is necessary to develop boron resin with both fast high capacity and adsorption rate.

Chitosan is wide source of materials, low prices, friendly environment polymer, which is one of the excellent basic substances for the synthesis of new resins. Chitosan has the advantages of polystyrene-divinylbenzene, polyethylene and polyurethane and other synthetic polymer materials due to amino inside itself [16,17]. Besides, it is beneficial to enhance the adsorption rate with good hydrophilicity. M. Oshima et al. [18] grafted N-methyl-D-glucamine onto the surface of cross-linked chitosan resin with ethylene glycol diglycidyl ether as crosslinking agent, a new boron adsorbent with adsorption capacity up to 22.7 mg/g and high adsorption rate was synthesized. But its particle size was 100–300 μm , which was also easy to lose and was difficult to separate and recovered. Paul Chen et al. [9] grafted N-methyl-D-glucamine onto the surface of cross-linked chitosan resin with glycidyl ether as crosslinking agent by atom transfer radical polymerization (ATRP). The particle size was 1 μm , and adsorption capacity reached to 35.13 mg/g, but the synthesis process was complex and the cost was high, which was not good for industrial application.

In this study, a low-cost and environmental-friendly chitosan was used as the substrate and epichlorohydrin (ECH) as the crosslinking agent, in order to develop a novel adsorbent with high content of vicinal hydroxyls for enhancing boron removal. The 3-chlorine-2-hydroxypropyl chitosan beads (CCTS) was synthesized through the reaction of ECH and chitosan beads (CTS). A novel chitosan based adsorbent was synthesized by grafted N-methyl-D-glucamine (MG) onto the surface of CCTS. The structure and morphology of MG modified chitosan beads (CTS-MG) were characterized by FT-IR and SEM analyses. Langmuir and Freundlich adsorption isotherms models were used to simulate the adsorption process in this experiment. And the adsorption capacity of CTS-MG is high to 20.36 mg/g. In the range of boron concentration from 20 to 2000 mg/L, the boron adsorption action of CTS-MG in water base solution was tested and studied. Meanwhile, we investigate the effect of polyanionic species formation on boron adsorption behavior of CTS-MG.

2. Experiment

2.1. Reagents and apparatus

Chemical reagents sodium hydroxide, boric acid, hydrochloric acid, acetic acid, ethyl alcohol, disodium ethylenediaminetetraacetate (EDTA-2Na), ammonium acetate, ascorbic acid, dioxane, isopropanol, and epichlorohydrin (ECH) purchased from Yuanli Chemical Technology Co. Ltd. (Tianjin, China) are all analytically pure. Chitosan (CTS, 90% and deacetylated) was purchased from Shanghai Yuanye Biotechnology Co. Ltd. (Beijing, China). N-methyl-D-glucamine (MG, 99%) and Azomethine-H acid were obtained from Aladdin Co. (Shanghai, China).

Fourier transform infrared (FT-IR) were tested by Nicolet 6700 Fourier transform infrared spectrophotometer (Thermo Scientific Co.,

USA), using KBr pellets in the 4000–400 cm^{-1} region with a resolution of 2 cm^{-1} . The morphologies of the CTS and CTS-MG were carried out by scanning electron microscope (SEM, Su8020, Hitachi, Japan). The boron concentration was analyzed by UV spectrophotometer (UV, L5S, Shanghai Jingke Co., China) after SEM. The pH values of boron solutions were measured by a Mettler Toledo FE20 digital pH meter (Mettler Toledo Shanghai Co., China).

2.2. Synthesis of CTS-MG beads

2.2.1. Preparation of chitosan beads (CTS)

Chitosan (2.5 g) was dissolved in the acetic acid solution (50 ml, 8% v/v), then the solution was dropwise added into 3.75 mol/L NaOH solution through the peristaltic pump by a stainless steel needle following the formation of saccharoid particles. The saccharoid particles were hardened for 12 h followed by washing with distilled water till neutral.

2.2.2. Synthesis of 3-chlorine-2-hydroxypropyl chitosan beads (CCTS)

2.5 g CTS was dispersed in the mixture of 40 ml water and 60 ml isopropanol solution, then pH was adjusted to 10 by alkali. 12 ml ECH was added to the solution with refluxing for 4 h at 60 °C. Finally, the CCTS was obtained by filtration with water and ethanol for three times to remove ECH, respectively.

2.2.3. Synthesis of MG modified 3-chlorine-2-hydroxypropyl chitosan beads (CTS-MG)

CCTS was suspended in aqueous solution of 100 ml dioxane and 40 ml NaOH (0.8 M), and 30.3 g MG was added and refluxed at 60 °C for 3.5 h. After reaction, CTS-MG was obtained by filtration with water and ethanol respectively three times to remove MG left in reaction. Then CTS-MG was stored in deionized water.

2.3. Adsorption experiments

Experiment was carried out by a batch-type operation. 0.1 g CTS-MG and 10 ml boric acid solution with concentration of boric acid of 100 mg/L were added into the centrifuge tube, which was shaken continuously for 10 h at room temperature (293 ± 1 K) via a thermostatic shaker. After the adsorption, the concentration of boron in the solution was measured.

2.3.1. The effect of pH value on adsorption process

0.1 g CTS-MG was added into the centrifuge tube with 10 ml boric acid solution (100 mg/L). The pH of boric acid solution was adjusted by 0.5 M HCl and 0.5 M NaOH, ranging from 2 to 12. The concentration of boron in the solution was measured after the centrifuge tube was oscillated by the thermostatic oscillator for 10 h.

2.3.2. Adsorption isotherms

In the investigation of adsorption isotherm, the initial concentration of B ranged from 50 to 2000 mg/L. In the experiment, 0.1 g CTS-MG was added into the centrifuge tube which contained 10 ml boric acid solution with different concentration. The initial pH value of boric acid solution was 7, then the concentration of boron in the centrifuge tube was measured after shaking for 10 h.

2.3.3. Adsorption kinetics

0.1 g CTS-MG was added into 10 ml boric acid solution (100 mg/L), of which the initial pH value was 7. The adsorption time ranged from 15 to 600 min. In order to study the effect of contact time during the adsorption process, the concentration of boron in the solution was measured at different intervals.

2.3.4. Effects of other competitive ions

The six common anions and cations, such as Na^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- and SO_4^{2-} , effected on the adsorption capacity of adsorbents,

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