



A spherical *N*-methyl-D-glucamine-based hybrid adsorbent for highly efficient adsorption of boric acid from water



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ABSTRACT

Preparation of a novel hybrid boron-selective adsorbent with *N*-methyl-D-glucamine functional groups was reported. The adsorbent was synthesized by inverse suspension polymerization method based on chemistry of sol-gel reaction. The structure and morphology of the hybrid adsorbent were characterized by MS, FTIR, XPS, BET analysis and PXRD, etc. The perfectly spherical hybrid adsorbent exhibits exceptionally efficient adsorption of boric acid from the aqueous solution. The boron adsorption behavior on the adsorbent was investigated by varying the dosages of the adsorbent, pH, and competitive ions. The adsorption isotherm was in better accordance with the Langmuir model, exhibiting a theoretical maximum adsorption capacity of 2.02 mmol/g. The adsorption capacity peaks at pH ~ 9 due to the vast formation of stable tetrahedral structure between dominant $B(OH)_4^-$ and the adsorbent. The presence of Na^+ ions has slight effect on boron adsorption while Mg^{2+} cations significantly enhanced the adsorption capacity because of the simultaneous adsorption attributed by $Mg(OH)_2$.

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1. Introduction

Boron is widely distributed in the natural waters, especially in seawater and wastewater. As an essential micronutrient for plants, trace amount of boron is favorable for plant growth as it is not only a structure component of cell wall [1], but also an influencing factor for enzyme reaction, synthesis of nucleic acid and pollen germination [2]. Boron is also important for animals and human beings in metabolism of nutrients, but the gap between deficiency and excess is rather narrow [3,4]. The World Health Organization (WHO) has set the tolerance limit in drinking water to 2.4 mg/L [5]. Although the new standard becomes more relaxed for the drinking water, irrigation water is still limited in the level of 0.5 mg/L due to the herbicidal effect of boron [6,7]. In the past decades, a significant increase of the concentration of boron in drinking water (even up to 1000 mg B/mL), has been observed due to natural and anthropogenic factors, such as leaching of salt deposits and industrial activities [8]. Thus, the problem of removing boron from water is persistent and intractable. There are many methods available to effectively remove boron from water including precipitation-coagulation [9], reverse osmosis [10], electro dialysis [11], solvent extraction [12], membrane filtration [6,13],

and adsorption [14–18]. Among these methods, adsorption is probably a more efficient and acceptable technique for treating the solution with broad boron concentration.

As reported previously, molecules containing three or more hydroxyl groups tend to form stable complex with boric acid in acidic and alkaline conditions [18,19]. Especially, hydroxyl groups are reactionless with common metal ions and other species in the natural waters, accordingly, it could be a promising approach for selectively removing boric acid from the natural waters by employing polyhydroxyl groups as chelating agent. Based on this principle, polymer or silica supported resins with polyhydroxyl molecules, such as *N*-methyl-D-glucamine [20], sorbitol [21], and mannitol [22], have been widely used as boron-specific adsorbent. Amberlite IRA-743 has possibly been one of few commercial resins for the boron-specific removal. However, it exhibits less satisfactory performance for the boron uptake (usually less than 1 mmol B/g). The operational cost and capacity loss during the regeneration make the resin less economically attractive [23]. Furthermore, most polymer-supported resins are based on the copolymers of styrene and divinylbenzene, which limit their efficiencies due to their strong hydrophobic properties [24]. The low mechanical strength of polymer-support also will sharply shorten the resin's lifetime, and restrict its application. Therefore, it is highly desired to develop an adsorbent that is highly selective for boron species while possessing efficient adsorption capability in addition to

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being commercially affordable. In this work, we reported a novel spherical organic-inorganic hybrid adsorbent of high efficiency for boron removal from water via inverse suspension polymerization using *N*-methyl-*D*-glucamine-based organosiloxane. The structure and morphology of the synthesized hybrid adsorbent were comprehensively characterized. The adsorption isotherm of boric acid on the hybrid adsorbent was reported, and the effect of pH and competitive ions including Na^+ and Mg^{2+} on the boron adsorption were also investigated.

2. Experimental

2.1. Materials and reagents

N-methyl-*D*-glucamine (NMDG), (3-glycidoxypropyl)-trimethoxysilane (GPTMS), sorbitan monooleate (Span 80), and Amberlite 743 resin were purchased from Sigma-Aldrich Co. (USA). Tetramethoxysilane (TMOS), and boric acid were obtained from Aladdin Co. (Shanghai, China). MgCl_2 , NaCl, *N,N*-dimethylformamide (DMF), methanol, *n*-hexane, hydrochloric acid, and liquid paraffin (all were AR grade) were obtained from Sinopharm Co. (Shanghai, China), and used without further purification.

2.2. Synthesis of precursor Si-NMDG

The organosiloxane precursor (denoted as Si-NMDG) was synthesized following a similar reported method (Scheme 1) [25]. 20 g NMDG was dissolved in 100 mL anhydrous DMF in a 250 mL three-necked flask. Then 24 mL GPTMS was added to the mixture with stirring. The stirring was continued at 80 °C until ivory monolith formed after 6 h. The as-synthesized monolith was ground, further purified by Soxhlet extraction with methanol, and dried under vacuum at 30 °C for 24 h.

2.3. Preparation of Si-NMDG sol

In the preparation of Si-NMDG sol, 8 g Si-NMDG and 40 mL methanol aqueous solution (1:1, *v/v*) were added to a 100 mL Teflon-lined autoclave, and then 2 mL TMOS was added with continuous stirring. The pH of mixture was adjusted to 2 by dropwise addition of hydrochloric acid (1 mol/L) for facilitating hydrolysis. The mixture further underwent the hydrolysis and subsequent condensation reactions in the Teflon-lined autoclave at 80 °C for 12 h until the solution transformed into viscous transparent sol.

2.4. Preparation of spherical hybrid adsorbent

To get the hybrid adsorbent with uniform spherical morphology, inverse suspension polymerization technique was employed. 20 mg Span 80 was homogeneously dispersed in 500 mL liquid paraffin at 80 °C with stirring, subsequently, 50 mL

as-synthesized Si-NMDG sol was gradually transfused into the mixture, and reacted at 80 °C for 72 h with a continuous stirring at speed of 350 rpm (IKA Ultra Turrax® blender). The transparent beads were obtained by filtration, and washed with *n*-hexane, ethanol and deionized water successively. Then the product was dried at 25 °C under vacuum.

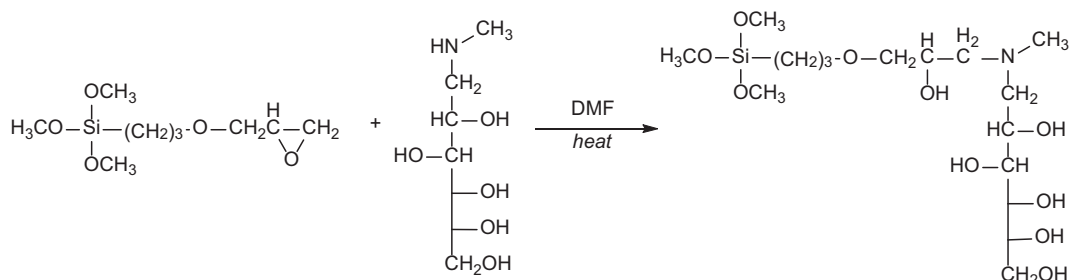
2.5. Characterization

Mass spectra of the precursor Si-NMDG, the sol, and the complex between NMDG and boric acid were obtained on a Varian 4000 MS-500 using D_2O as solvent. The element compositions were measured by a combined VG ESCALAB MARK II X-ray photoelectron spectrometer (XPS) with a non-monochromatized $\text{MgK}\alpha$ radiation (1253.6 eV). The vacuum in the analysis chamber was at a base pressure of 7.1×10^{-10} mbar during analysis. The morphology of the hybrid adsorbent was observed on CX22 Biological Microscope (Olympus Co., Japan). Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 Fourier transform infrared spectrophotometer (Thermo Scientific Co., USA) with usual KBr pellet technique, using a resolution of 4 cm^{-1} and 16 scans in the range of 400 and 4000 cm^{-1} . Nitrogen adsorption isotherms were obtained at 77 K on an Autosorp-IQ-MP Specific Surface Area Analyzer (Quantachrome Instruments, USA). Powder X-ray diffraction (PXRD) patterns of the samples were recorded with an XPert diffractometer (Panalytical Corp., Netherlands) using $\text{Cu K}\alpha$ ($\lambda = 0.1543 \text{ nm}$) radiation at 40 kV from 3° to 70° (2θ angle range) with a step size of 0.02°.

2.6. Adsorption experiments

To evaluate the performance of hybrid spherical adsorbent, batch adsorption studies were carried out to examine its adsorption capacity for boric acid in water. To benchmark the performance of the hybrid adsorbent, the boron adsorption capacity of the commercial resin Amberlite-743 was also investigated in the same condition. The adsorption isotherm experiments for each adsorbent were conducted by varying dosages of the adsorbent with a fixed 50 mL 1.0 mg/mL boric acid aqueous solution (at initial pH of 9) in the flasks. The dosages were 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, and 1.5 g, respectively. All flasks were tightly sealed and shaken in a thermostatic shaker (Zhichu Instruments, China) at 30 °C for 72 h, which has been checked long enough to reach equilibrium. Once equilibrium established, boric acid concentration in supernatant was determined by Azomethine-H spectrophotometric method on a UV-vis spectrophotometer (UV-2550, Shimadzu Corp., Japan) with detection wavelength set at 415 nm [26]. The adsorbed amount was calculated according to the following equation:

$$q_e = \frac{(C_0 - C_e)}{W \times m} \quad (1)$$



Scheme 1. Synthesis pathway of organosiloxane Si-NMDG.

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