



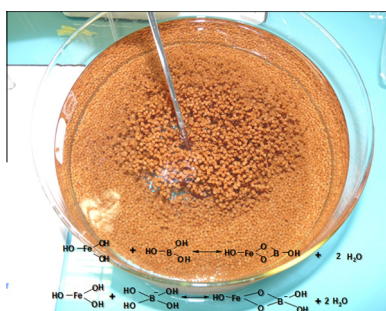
Boron recovery from seawater with a new low-cost adsorbent material

H. Demey^{a,b,*}, T. Vincent^b, M. Ruiz^a, M. Nogueras^a, A.M. Sastre^c, E. Guibal^b^a Universitat Politècnica de Catalunya, Department of Chemical Engineering, EPSEVG, Av. Víctor Balaguer, s/n, 08800 Vilanova i la Geltrú, Spain^b École des Mines d'Alès, Centre des Matériaux des Mines d'Alès, 6 Avenue de Clavières, F-30319 Alès CEDEX, France^c Universitat Politècnica de Catalunya, Department of Chemical Engineering, ETSEIB, Diagonal 647, 08028 Barcelona, Spain

HIGHLIGHTS

- A new composite containing chitosan and iron(III) hydroxide has been manufactured.
- SEM-EDX analysis revealed a homogenous distribution of Fe(OH)₃ in whole material.
- An adsorption column system was used for boron recovery from seawater.
- Adsorption–desorption cycles were performed and desorption uptake remained >40%.
- Elution was efficiently eluted with water at pH 12.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 17 March 2014

Received in revised form 13 May 2014

Accepted 14 May 2014

Available online 3 June 2014

Keywords:

Chitosan

Iron(III)

Boron

Seawater

New sorbent

ABSTRACT

A new adsorbent [chiFer(III)] for boron recovery from seawater was prepared using chitosan and iron(III) hydroxide. Experiments were carried out in a column system. Seawater samples were collected from the Mediterranean Sea off the coast of Vilanova i la Geltru, Spain (coordinates: 41.18; 1.75). Several adsorption–desorption cycles were performed to evaluate the efficiency of the adsorbent, and a desorption step was carried out using MilliQ-water of pH 12 (0.01 M NaOH solution). The molar ratio between the mass of adsorbed boron in the five consecutive cycles and the mass of iron(III) hydroxide present in the adsorbent beads was $10.7 \text{ mmol}_B \cdot (\text{mol}_{\text{Fe}(\text{OH})_3})^{-1}$. The experimental results were evaluated using the Thomas, Yoon and Nelson, and Bohart–Adams models, which fitted the experimental data adequately. The adsorbent was characterized by SEM-EDX analyses and BET surface; porosity studies confirmed that the chiFer(III) composite is a mesoporous material.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Water is essential to the survival of humans, animals and plants and has played a major role in human behavior throughout the history of mankind; scarcity of water in particular regions led to forced migrations and, in the most extreme cases, is thought to

have been responsible for the disappearance of ancient cultures. The increasing demand for potable water is a pressing concern, and although Earth is composed mainly of water, only 1% of this is consumable fresh water. Therefore, the search for advanced seawater treatment mechanisms is very important for human survival.

Boron is a mineral present in seawater. It belongs to group 13 of the Periodic Table and has two stable isotopes, B₁₀ and B₁₁. This study considers boron in terms of the health risks highlighted by the World Health Organization (WHO), on the basis of a study in which short- and long-term oral exposure to boric acid or borax

* Corresponding author at: Universitat Politècnica de Catalunya, Department of Chemical Engineering, EPSEVG, Av. Víctor Balaguer, s/n, 08800 Vilanova i la Geltrú, Spain. Tel.: +34 938937778; fax: +34 934017700.

E-mail address: hary.demey@upc.edu (H. Demey).

in laboratory animals was found to cause toxicity that consistently targeted the male reproductive tract. Testicular lesions have been observed in rats, mice and dogs given boric acid or borax in food or drinking-water, and a guide level of 2.4 mg L^{-1} has been recommended in drinking water [1].

According to Östürk et al. [2], the ingestion of large amounts of boron can affect the central nervous system and the reproductive system in humans. Although small quantities of boron are important for plant growth, high levels are harmful to most species [3]. The maximum recommended boron concentration in irrigation waters varies considerably according to the type of plant: lemon and blackberry plants cannot tolerate boron concentrations greater than 0.5 mg L^{-1} (extremely sensitive plants); orange, peach, cherry, plum, onion, and grape can only tolerate boron concentrations of up to 0.75 mg L^{-1} (very sensitive plants); but sorghum, cotton, celery and asparagus can tolerate boron concentrations of up to 10 mg L^{-1} (very tolerant plants) [3].

Currently there is no simple method for removing boron from seawater. Nevertheless, several methodologies have been used for boron removal from aqueous solutions, such as adsorption with clays [4], fly ash [5], ion exchange with boron-specific resins [6,7], reverse osmosis [8–10], electrodialysis [11], precipitation [12], chemical coagulation and electrocoagulation [13].

Reverse osmosis (RO) technology has been widely used over the last decade to desalinate water [3]. However, a specific problem is encountered in the removal of boron compounds: the use of a multi-pass reverse osmosis membrane and the modification of pH are needed for better boron separation, which increase the cost of desalination plants. RO is usually combined with ion-exchange to effectively separate boron from seawater [3]; effective ion-exchange resins (with N-methyl-D-glucamine as functional groups) have been used in a second purification stage, but these resins are also costly to regenerate.

Different materials have been reported in the literature as inexpensive sorbents for boron removal; for example, calcium alginate beads have been found by Demey et al. [14] and Ruiz et al. [15,16] to be effective for boron recovery from aqueous solutions (biosorption) at high pH ($\text{pH} > 9$). Layered double hydroxide (LDH) materials synthesized by co-precipitation have been evaluated by Ferreira et al. [17]: Mg/Al and Mg/Fe-LDHs. It was found that the mechanism governing boron removal on Mg/Fe-LDH was basically adsorption rather than a combination of anion exchange and adsorption on external surface (on Mg/Al-LDH); maximum boron removal was 92% for Mg/Al-LDH and 33% for Mg/Fe-LDH.

Despite the good boron uptake of LDHs (as demonstrated by Koilraj and Srinivasan [18]), some drawbacks were detected by Ferreira et al. [17]: metal ion release was greater into the solution using Mg/Al-LDH than the solution using Mg/Fe-LDH. Studies by Yoshioka et al. [19] also confirmed a partial dissolution of Mg/Al-LDH (prepared by co-precipitation and thermally activated at $500 \text{ }^\circ\text{C}$) upon removal of tetrafluoroborate ions; 10% of the initial magnesium content in the material (4:1, Mg/Al) was found to dissolve into the solution (until 3.6:1), apparently due to the formation of a soluble complex with F^- and boron species. Similar conclusions were reported by Koilraj and Srinivasan [18] using $\text{Zn}_2\text{Al}-\text{Cl}-\text{CLDH}$: below pH 4 and above pH 11, the sorbent was very unstable owing to leaching of Zn^{+2} and Al^{+3} ions into the solution [18].

Zhang and Reardon [20], using hydrocalumite ($\text{Ca}_4\text{Al}_2(\text{OH})_{12}(\text{OH})_2\text{6H}_2\text{O}$) and ettringite ($\text{Ca}_6\text{Al}_2(\text{OH})_{12}(\text{SO}_4)_3\text{26H}_2\text{O}$) for the removal of oxyanions (including tetrahydroxy-borate $\text{B}(\text{OH})_4^-$ ions) from aqueous solution, found that neutral boric acid is not easily adsorbed by LDHs in acidic conditions; the best results are generally achieved in basic conditions because of the high pH-buffering capacity, which strongly increases the final pH of the solutions [21]. This is an obvious constraint on the use of these materials in certain applications, especially for boron recovery from

seawater. As such, further research is needed to improve the stability of these materials in order to optimize the benefits of their adsorption uptake at neutral pH. Theiss et al. [21] also note that there are few studies on boron desorption (regeneration of LDH-sorbents) and few studies carried out in continuous system applications (rather than small-scale batch systems) [21].

Therefore, in this study a new low-cost adsorbent has been manufactured for boron recovery from seawater. The adsorbent is a composite of chitosan and iron(III) hydroxide [chiFer(III)], in which chitosan acts as a matrix (hybrid polymeric/inorganic material). Previous studies have reported the use of hydroxides to remove boron from aqueous solutions: Turek et al. [22] used $\text{Ni}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, $\text{Co}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ for the adsorption/co-precipitation of boron from aqueous solutions.

A good sorbent, especially for large-scale application, must be recyclable in order to be competitive. Turek et al. [22] reported a boron removal percentage (from aqueous solutions) greater than 40% using $\text{Fe}(\text{OH})_3$, but no desorption data were presented; standard chitosan-based spherical beads can improve the handling of the active material [$\text{Fe}(\text{OH})_3$] and improve the adsorption-desorption process. This study reports the preparation of a new chitosan-based composite to improve the handling of $\text{Fe}(\text{OH})_3$ as an adsorbent to recover boron from seawater in a continuous system. Reuse of the adsorbent was evaluated in several adsorption-desorption cycles, and the Thomas [23], Yoon and Nelson [24,25], and Bohart-Adams [26] models were used to fit the experimental results.

2. Experimental

2.1. Materials

Boron solutions were prepared using boric acid ($\text{B}(\text{OH})_3$) provided by Merck AG (Germany). Iron(III) chloride hexahydrate used for sorbent preparation was provided by Panreac (France). Chitosan was supplied by Aber Technologies (France), and its molecular weight ($125,000 \text{ g mol}^{-1}$) was previously reported by Ruiz et al. [27] using Size Exclusion Chromatography (SEC) coupled with light scattering and refractometry. The degree of deacetylation determined by Fourier Transform Infrared (FTIR) spectroscopy was found to be 87% [28].

2.2. Preparation of chiFer(III) composite microspheres

A chitosan solution was prepared by dissolving 1 g of chitosan in 1% w/w acetic acid solution and stirring for at least 3 h. Twenty grams of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ powder were mixed in 60 mL of HCl solution (1 M) until complete dissolution. The chitosan solution (640 g, 1% w/w) was then mixed with iron(III) solution under vigorous stirring (600 rpm) for 120 min.

The chitosan-iron(III) solution was added drop-by-drop with a peristaltic pump through a thin nozzle ($\text{Ø} 1.6 \text{ mm}$) into an aqueous solution of 1 M sodium hydroxide under magnetic stirring to produce microspheres of the composite chitosan/iron(III) hydroxide [chiFer(III)].

The composite particles were kept under stirring for 6 h at room temperature ($25 \text{ }^\circ\text{C}$) and then filtered and washed intensively with distilled water to remove the excess iron on the surface of the composite beads. The standard wet beads used in this study had an average diameter of 2.0 mm and are shown in Fig. 1.

2.3. Characterization of sorbents

2.3.1. BET surface area and porosity of chiFer(III)

Nitrogen adsorption apparatus (Micrometrics, TriStar 3000) was used to determine the porosity and specific surface area. In order to

Download English Version:

<https://daneshyari.com/en/article/147274>

Download Persian Version:

<https://daneshyari.com/article/147274>

[Daneshyari.com](https://daneshyari.com)