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Research article

Eggshell membrane as a novel bio sorbent for remediation of boron from desalinated water

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A B S T R A C T

This study investigated the use of eggshell membrane (ESM) as a bio-sorbent and the effect of temperature, pH, and initial concentration on its efficiency. Furthermore, by altering the chemical composition, modified eggshell membrane (MESM) was prepared, and its efficiency was compared with the ESM. Results showed that the adsorption of boron preferred an acidic condition; pH 6 at 35 °C. In addition, the positive value of ΔH° suggested that the reaction favored endothermic pathway, while the negative value for ΔG° further suggested that the adsorption process was spontaneous. Furthermore, the ESM could adsorb 97% of boron, while MESM was able to adsorb 95%. From the Fourier transform infrared (FTIR), different functional groups were recorded on the surface of the ESM and MESM, and they played key role in the boron adsorption mechanisms. Linear Freundlich model was suggested to best describe the experimental data with 99.4% correlation coefficient.

1. Introduction

Water crisis has gradually become one of the major global concerns in scientific community. Dramatic increase in population, industrialization, agricultural activities, increase supply and water demand, inappropriate use and degradation of natural resources are some of the reasons that can be held accountable for such crisis. In the 20th century alone, the population has been recorded to increase fourfold while the demand of water has increased up to nine-fold, and by the year 2025, several countries are expected to face water crisis (Shenvi et al., 2015). To cater the problem, water industry has started greatly depending on desalination of seawater or treatment of highly saline water. By doing so, some trace contaminants could appear in the final product, including boron (Güler et al., 2011). Furthermore, this process requires great amount of financial and natural resources. Therefore, investigators have been researching for alternative technology that might be environmental friendly and effective in delivering potable water with acceptable and permissible boron and other trace metals concentration without degrading natural resources (Qasim et al., 2015; Kabay, 2015).

Boron occurs widely in the environment in various mixtures of its isotopes (^{10}B and ^{11}B) rather than its elemental form. According to Tu (2010), boron in aquatic condition is primarily found as boric acid, which appears as a waxy solid that it soluble in water, and consequently forming a weak acid. Usually the concentration of boron in freshwater is less than 0.1 mg/L, while in groundwater it is a site specific. In seawater, however, the concentration of boron is nearly 4.6 mg/L (Hilal et al., 2015).

Boron is one of the essential micronutrients for plants, animal, and human for their growth and development (Hilal et al., 2015). However, if plants are supplied with excess boron, it has been reported to have an adverse effect. These include reduction of root cell division, retarded shoot and root growth, inhibition of photosynthesis and disposition of lignin (Hilal et al., 2011; Shaaban, 2010). High consumption of water containing boron can be hazardous for living organisms (Shaaban, 2010). The acceptable amount of boron that is considered non-toxic is 13 mg/day according to World Health Organization (WHO) (1996). Since the impact of boron on human health is not been completely studied; therefore there are no set guideline for permissible concentration of boron in drinking water. For instance, in 1990, WHO set up a limit of 0.3 mg/L standard for the acceptable concentration of boron, which was revised in 1998 and again in 2011 to 2.4 mg/L.

For the boron remediation purposes, various adsorbents including activated carbon (Cana et al., 2012; Çelik et al., 2008; Köse et al., 2011), alginate gel beads (Demey-Cedeño et al., 2014), polyamide thin film composite (Güler et al., 2011), polystyrene-based

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resin (Kluczka et al., 2015), fly ash (Guan et al., 2016), and ion exchange resin (Alharati et al., 2017) have been utilized and reported to be effective for the removal of boron from water. Moreover, adsorption method has gained great attention and is considered as one of the main innovative methods of treating many pollutants from water (Hawari et al., 2014; Al-Ghouti et al., 2017, 2013, 2010). However, the quest to develop efficient adsorbent with high sorption capacity for the removal of micro-pollutant in water remains a challenge (Wang et al., 2017). Various studies have shown incredible efficiency, especially using granulated activated carbon (Hegazi, 2013). As a result, due to advancement in adsorption, many low-cost adsorbents are being investigated and experimented such as eggshells and coconut husks to remove heavy metals and other elements from water (Salam et al., 2011).

The value of eggshell membrane (ESM) has long been underestimated because it was considered as a waste by-product. However, immense researches have proven the usefulness ESM as a potential sorbent for various substance including metals (Daraei et al., 2012; Chen et al., 2013; Liu et al., 2013), phenol (Daraei et al., 2012), and dyes (Abdel-Khalek et al., 2017; Lazar, 2014; Arami et al., 2006; Pramanpol and Netayapat, 2006). A typical hen eggshell consists of ceramic materials, which comprise three-layered structures namely, the cuticle (on the outer surface), a spongy (calcareous) layer and the inner lamellar (or mammillary) layer (Baláž, 2014; Maxwell, 2012). The spongy and the inner lamellar layers form a matrix, which consists of protein fibers that are bonded to calcite (calcium carbonate) crystal (Wei et al., 2009; Nakano et al., 2003; Ahmed et al., 2017).

For adsorption to be efficient, it is essential to establish the most appropriate equilibrium correlation conditions. These equilibrium correlation conditions are known as adsorption isotherms. They illustrate how the adsorbed molecules are distributed between the liquid and solid phase when the process reaches equilibrium (Hamdaoui and Naffrechoux, 2007).

In this paper, eggshell membrane (ESM) was used as an adsorbent for remediation of boron from water, and the effect of initial concentration, temperature and pH were investigated and compared with the modified esterified eggshell membrane (MESM). In the project, different experimental parameters were proposed; namely pH, optimal temperature and comparison between modified and non-modified eggshell membrane. The purposes of this study can be summarized as: (i) prepare chemically modified form from the eggshell membrane by esterification (MESM), (ii) study the physical and chemical characterizations of the ESM and MESM, and (iii) study the boron remediation characteristics using ESM and MESM by taking into accounts the initial pH of the boron solution, initial boron concentration, and solution temperature. The result of this study is expected to indicate whether the eggshell membrane can be a novel bio-sorbent for effective removal of boron from water.

2. Materials and methods

2.1. Preparation of ESM

A hole from the top and the bottom of fresh eggs was made using a clean knife, and then the raw egg was blown out by blowing from one of the holes. This was done with 210 raw eggs. Afterwards, those eggshells were washed with distilled water, and then placed in a container containing 15% of hydrochloric acid (HCl, Merck grade) overnight in order to dissolve the outer layer of the eggshell leaving behind the eggshell membranes (ESMs) only. Next, the ESMs were extracted from the eggshells and were washed three times using distilled water in order to make sure that the excess acid was removed. After being washed, the membranes were placed in a beaker inside an oven at 50 °C overnight to completely dry. The membranes were then crushed using a chopper in order to achieve powder form, and after that they were transferred to Breville coffee grinder in order to obtain fine particles. The samples were then sieved using mechanical siever (Retsch, 5657 HAAN W Germany). Four different mesh sizes were obtained, namely 0.500–0.250 mm, 0.250–0.125 mm, 0.125–0.063 mm and <0.063 mm. The 0.250–0.125 mm particle size was used throughout the experiment because it had the greatest sample size. In this study, three experimental factors were investigated; effect of pH, effect of initial concentration and effect of temperature.

2.2. Modification of ESM

A 6.00 g of the ESM was placed in a mixture containing 50 mL of methanol (Merck grade) and 2% of HCl (Merck grade); the membrane powder was then kept in this solution for 20 h at 80 °C. This was essential in order to make sure that all the carboxylic groups on the eggshell membrane surface were esterified. After the esterification, the ESM was referred to as methyl esterification eggshell membrane (MESM). The MESM was again rinsed thoroughly three times using distilled water in order to remove the excess methanol solution. After that, the modified egg membranes were dried overnight at 50 °C. Afterwards, the MESM was crushed using a chopper in order to achieve a powder form. The MESM was then sieved using mechanical siever (Retsch, 5657 HAAN W Germany). Four different particle sizes were obtained namely 0.500–0.250 mm, 0.250–0.125 mm, 0.125–0.063 mm and <0.063 mm. The 0.250–0.125 mm particle size was used throughout the experiments because it had the greatest sample size.

2.3. Adsorption isotherm of boron onto ESM and MESM

The boron concentration in the desalinated water used was 0.45 mg/L. A fixed amount (0.05 g) of ESM or MESM and 50 mL of H_3BO_3 solution were placed in a capped volumetric plastic flask, and was shaken at 150 rpm using a temperature controlled water bath for 48 h. The samples were then filtered, and the boron concentration was determined using the inductively coupled plasma – optical emission spectroscopy (ICP-OES). To investigate the effect of solution pH on the boron adsorption, the initial pH values of the H_3BO_3 solution were adjusted using NaOH (0.05 mol/L) and HCl (0.05 mol/L) solutions. Anhydrous boric acid (H_3BO_3), obtained from Reidel-de Haen Company (Germany), was utilized in this project. Hydrochloric acid, nitric acid and sulfuric acid (Merck grade), and sodium hydroxide (Merck grade) were used.

2.3.1. The effect of pH on the adsorption capacity of boron onto ESM and MESM

Studying the effect of pH is one of the significant parameters in adsorption process. A 50 mg/L stock solution of anhydrous boric acid was prepared. The samples were then adjusted to different pH values (2, 4, 6, 8, and 10) using Jenway 370 pH meter and three replications were prepared following the same protocols. The experiment was conducted at an adsorbent dosage of 0.05 g at constant boric acid solution (50 mg/L) in plastic bottles. Moreover, the pH was adjusted using NaOH (0.05 mol/L) and HCl (0.05 mol/L). All samples were placed in a mechanical shaker at 150 rpm for 48 h at room temperature (25 °C).

2.3.2. Effect of concentration on the adsorption capacity of boron onto ESM and MESM

The experiments were carried out by preparing a 100 mg/L boric acid stock solution. Different initial concentrations of boric acid