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Superiority of date seed ash as an adsorbent over other ashes and ferric chloride in removing boron from seawater

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ABSTRACT

Many desalination plants, especially those utilising seawater as feed water, have trouble in reducing boron levels to the drinking water standards. The objective of this study is to investigate the removal of boron from seawater using low cost methods: three fly ashes as adsorbents and ferric chloride. Parameters which could affect boron removal efficiency were investigated, including pH, reaction time, and liquid/solid (l/s) ratio. The results suggested that fruit (date seed) based ash had remarkably higher efficiency of boron removal (71%) than power plants fly ash, pine tree fly ash, and coagulants. The optimum removal efficiency was achieved with the date seeds ash at pH 7 and l/s of 5. The results from the study are of practical significance as the date seed ash is showing highest removal efficiency at neutral pH. In particular, the considerable capability of date seed ash to remove boron at a neutral pH is important in reverse osmosis (RO) process, as it enables better membrane stability and minimal membrane scaling and subsequently renders low operating costs.

Keywords: Adsorbent; Boron; Date seed; Fly ash; Pre- treatment; Seawater

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1. Introduction

Boron is an important micronutrient for plants, animals and humans, although the range between deficiency and excess is narrow (e.g. 0.3–0.5 mg/L in citrus) [1–3]. As one of the dilute elements in water and a minor element in nature, boron appears in concentration usually less than 1 mg-B/L in most of the natural waters and its concentration seldom exceeds 4.4–4.6 mg in seawater. Drinking water does not commonly contain boron, having typical concentrations of 0.1–0.2 mg-B/L [1–3].

The main boron sources, whose presence is detected in surface waters, are urban wastes rich in detergents and cleaning products; industrial wastes, which can come from a wide range of different activities as well as several chemical products used in agriculture [4]. From the wide range of boron-derived compounds, only oxianions appear in waters since they are soluble. Moreover, the different uses that can cause liquid spillages directly involve orthoboric acid or borax, or transformation reactions of the by-products towards these more soluble, oxidised and stable states. In most aqueous environments, boron is mainly present as borate and borate ions, of which the dominating form is based on a Lewis acid reaction [5]:

$$B(OH)_3 + H_2O \leftrightarrow B(OH)_4^- + H^+ \quad (1)$$

$$(K_a = 5.8\times10^{-10}\ \text{mol/l};\ pK_a = 9.24)$$

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The boron problem is magnified by the fact that neither standard wastewater treatment nor desalination of seawater by reverse osmosis (RO) can bring about its successful elimination from the raw water [6]. Moreover, owing to the predominance of the non-charged boric acid in the solution, only a fraction of the boron (≈ 60%) is removed during reverse osmosis (RO) desalination [7–11]. Thus, even RO desalted seawater contains high level of boron (≈ 1.7 mg/L) above the maximum admissible international values. Since boric acid has no ionic charge, it diffuses in a similar way to that of carbonic acid or water itself [11]. The possible increase of the pH in the second pass for shifting the equilibrium to the side of the borate and to obtain high rejection (99.0–99.5% at pH 11) [8,12], the cost associated with the injection of large amounts of caustic soda required and associated corrosion. The stability of the membrane and the service life in real operating condition has not yet been examined [8]. In addition, future management scenarios in water-stress areas consider recycling of RO-desalination, wastewater treatment, and irrigation with treated wastewater as a way to overcome the water shortage, as cited in [14].

So far, the use of ion exchange resins and composite reverse osmosis (RO) membrane systems, as well as their combination with or without pH increase, are the only used technologies considered effective for the removal of boron. For selective ion exchange resins, the problems are high regeneration costs [15], expensive resins and low capacity with scale up problems [9,16,17]. Extensive research is being carried out today aimed at the development of new technologies as well as the reduction of costs in existing ones. The boron specific ion-exchange resin (Amberlite IRA-743) has the capacity of almost 100% removal of boron under high pH conditions but it also has very high regeneration cost and is used to remove boron from high-boron effluents in Turkey [14]. Therefore, a both practically effective and economical method to remove boron is yet to be discovered.

There is a growing interest in employing low cost adsorbents in water treatment process. The use of adsorbents made from naturally (untreated) and abundantly existing materials has hence become a potential strategy in boron removal. Boron is a rare and important element in dates, especially for the growth of some organisms. The studies have shown that dates contain boron up to 63 mg/100 g in the flesh and the date seed [18]. Some varieties of palm trees show great sensitivity to boron deficiency, which leads to the failure of the contract micronutrients. So date tree or palm tree (*Phoenix dactylifera*) usually tends to absorb boron from soil [19].

In this study, a novel method is proposed to use date seed ash to remove boron from seawater. In addition, the other three easily procurable and popular materials, ferric chloride as coagulant, fly ash from power plant and fly ash from part of pine plant, were also employed to remove boron in batch studies. The effectiveness of boron removal by the four different materials was compared. The possible controlling factors (pH, liquid to solid ratio (l/s) and contact time) in batch experiment were also investigated.

2. Experimental

2.1. Material and analytical method

Seawater collected from the Indian Ocean at Perth was used for all the experiments. The boron concentration in the seawater was 4.5 ± 0.2 mg/L. Fly ash was collected from a local power plant in Western Australia. The seeds and pine plant were burnt at 500°C for 1 h in a furnace, then crushed into fine particles.

$FeCl_3$ stock solution (1 g-Fe(III)/L) was prepared by dissolving 1.66 g $FeCl_3 \cdot 6H_2O$ crystals in 500 mL deionsed water and dilute it to 1 L in a volumetric flask.

The pH measurements were performed using HACH30d potable pH meter, with an error of ± 0.1. Total aqueous boron concentration was measured spectrophotometrically by Aquakem200 analyzer at wavelength of 405nm obeying Azomethine-H method, with measurement error of ± 0.2 mg-B/L.

Stock Boron Standard — 1000 mg/L B: Standard boron stock solution (1000 mg/L) was prepared by dissolving 5.719 g of Boric acid in 500 mL of deionised water and diluting to 1 L in a volumetric flask. The solution was stored in a polyethylene bottle at 4°C.

2.2. Experimental procedures

2.2.1. Boron removal by coagulation

$FeCl_3$ coagulation to remove boron in the seawater was conducted through a series of jar tests, with each jar containing 0.5 L water sample. The effectiveness of boron removal was assessed as a function of coagulant concentration and coagulating pH. The former was achieved by varying the dosage of $FeCl_3$ stock solution to make ferric concentrations at 20, 40 and 60 mg/L in bulk water. The pH was maintained at 5 ± 0.1 in bulk water with each ferric concentration. To assess the impact of coagulating pH, the jar test with 60 mg-Fe(III)/L coagulant concentration was duplicated and so different coagulating pH could be practiced in the duplicate samples. The pH adjustment was done by titrating with HCl (1 N) or NaOH (1 N) at the initial stage of coagulation until the target pH values were reached.

Jar testing was conducted at 180 rpm for the initial 2 min after ferric salt addition, followed by a slow (20 rpm) stirring period of 30 min. Then, bulk water was left intact for 30 min at room temperature to allow the sedimentation of flocs. Two aliquots were withdrawn from the supernatant immediately after the sedimentation, with one being filtered through 0.45 μm filter and the other remaining unfiltered. The solutions were then left intact for further 30 min and more aliquots were withdrawn without filtration. Total boron concentration in all aliquots was measured.

2.2.2. Boron removal by fly ash, pine tree ash and date seed ash

The capacity of each type of ash was tested through a series of batch experiments following the similar procedure illustrated below:

Bulk water of 50 mL was employed in each batch experiment. Different amounts of ash were weighed and added into duplicate bulk water samples to achieve various liquid to solid ratio (l/s) of 5, 10 and 20 in order to investigate the optimum concentration of ash, for boron removal. Following the same method of pH adjustment, pH of 7, 8 and 10 were investigated in each duplicate sample.

An aliquot of each sample was withdrawn at 3–4-h time interval over two days of the batch experiments. The aliquot was filtered through 0.45 µm filter and total boron concentration in the filtrate was measured.

3. Results and discussion

3.1. Coagulation by ferric chloride

Fig. 1 shows the effect of coagulant concentration on aqueous boron removal at pH 5. The removal was enhanced by increased coagulant concentration from 20 mg/L to 60 mg/L and it recorded maximum removal efficiency of 7% with 60 mg/L coagulant dose after filtration. However, a slight increase in removal efficiency was observed when the post-coagulation sample was filtered. This can be attributed to boron attached to particles or colloids which were removed by the filtration. Comparing the results of 30 min and 60 min settling time, it appears that no further removal occurred within the additional settling time.

Fig. 2 shows the effect of pH on boron removal by $FeCl_3$. It has been reported that pH can have significant effect on boron removal efficiency by shifting the direction of reaction [Eq. (1)] and hence changing the dominating boron species [14,20,21]. It is usually expected that the increased proportion of negatively charged borate ions would lead to enhanced boron removal due to the positively charged iron hydroxide flocs. According to Fig. 2, boron removal after filtration was increased by 12% when pH was increased from 5 to 8. However, a further pH increase from 8 to 10 led to a decreased in B removal efficiency. This may be due to the diminishing adsorption capacity of iron hydroxide flocs at high pHs, due to increased floc size which outweighed the advantage of borate ions formation.

3.2. Power plant fly ash

Fig. 3 shows the boron removal by power plant ash as a function of pH, l/s ratio and reaction time. The batch experiment were conducted up to 72 h.

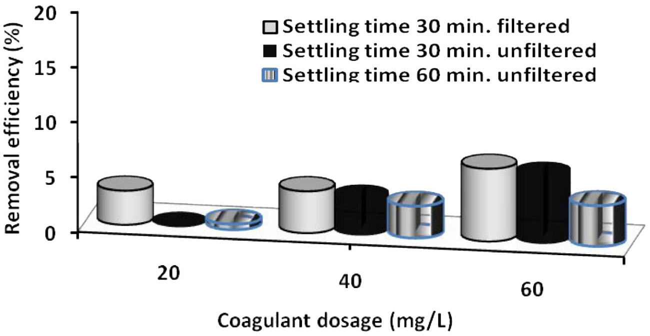

Fig. 1. Effect of coagulant concentration on boron removal from seawater (pH was maintained constant at 5).

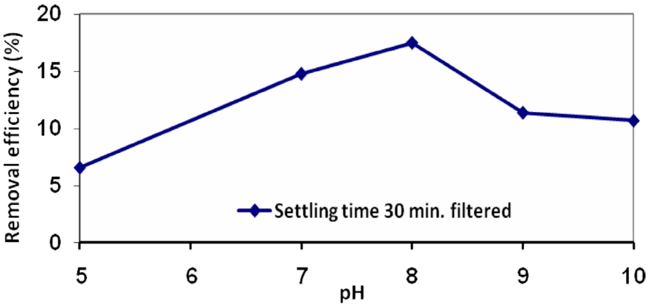

Fig. 2. Effect of pH on coagulation efficiency to remove boron ($FeCl_3$ concentration: 60 mg/L).

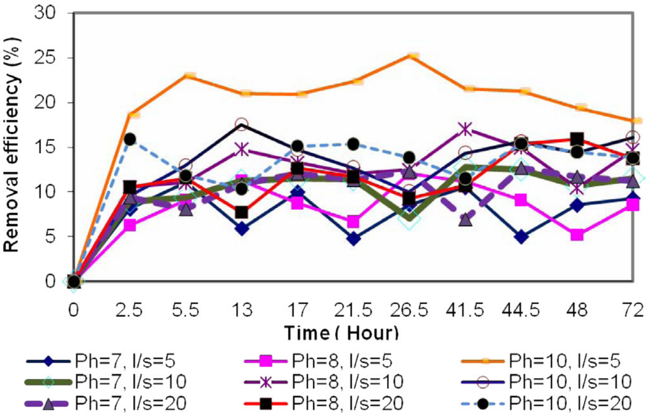

Fig. 3. Effect of reaction time on boron removal efficiency (power plan fly ash).

The results from the test were inconclusive with no clear trends with time, L/s or pH. Removal of boron efficiency varied between 5 and 25% over the 3 day period. Maximum removal efficiency recorded with pH = 10 and

L/s = 5 was about 25% after 26.5 h contact time. To achieve more conclusive results, it is recommended to use a continuously stirred mixer or column tests.

3.3. Pine tree ash

Fig. 4 shows the results of boron removal by pine tree ash. With each l/s ratio, different pHs (7, 8 and 10) were investigated in batch experiments. No apparent trends can be found between boron removal efficiency, l/s and pH. In most cases a value 22% was registered.

3.4. Date seed ash

According to Fig. 5, boron removal was generally enhanced with increased reaction time, irrespective of pH and l/s ratio with maximum removal recorded after 24 h reaction. The results also showed a positive effect of adsorbent dosage on boron removal. Generally, boron removal was enhanced by increasing the date seed ash concentration. The maximum boron removal of 71% was recorded with L/s value of 5 at pH 7 after 24 h reaction time.

The effect of varying pH on boron removal showed strikingly different results from those using the other three materials. Removal efficiency was decreased with increasing pH when date seed was used. The highest removal of 71.1% was achieved at pH 7. It indicates that boron removal by date seed ash is not related to the proportion of negatively charged borate ions. In contrast, date seed ash demonstrated its optimum capacity to remove neutral boric acid. This finding revealed a unique character of date seeds when most of other methods such as RO and coagulation to remove boron require an alkaline pH in the range of 9–10 [21] which can increase scaling propensities. In addition, without being saturated after 24 h reaction time, date seed showed enormous capacity to remove boron. It rendered the advantages to date seed ash over many known adsorbents [9,13,14,21–23]. Furthermore, this seed ash is a low cost material.

4. Comparison of four materials and methods

Fig. 6 summarizes the optimum efficiency of boron removal by each material after 24 h reaction time under similar batch experimental conditions (pH:7; l/s: 5; and initial boron concentration: 5 mg/L). According to Fig. 6, the date seed showed the highest capacity to remove boron from seawater in which 71.1% of boron was removed while the other three materials were far from comparable with date seeds in their ability to remove boron, with the second highest removal efficiency of 21.5% achieved with pine tree ash.

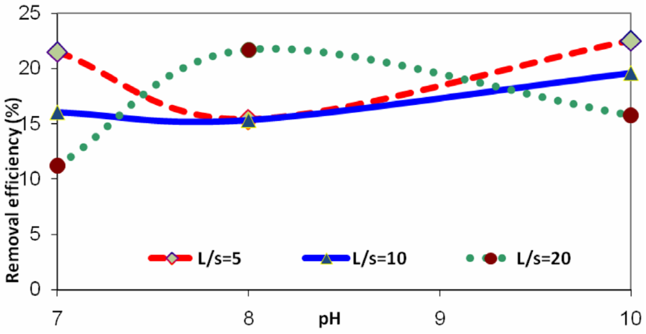

Fig. 4. Effect of adsorbent dosage (l/s) on boron removal efficiency for different pH values at 24 h, pine tree ash with seawater.

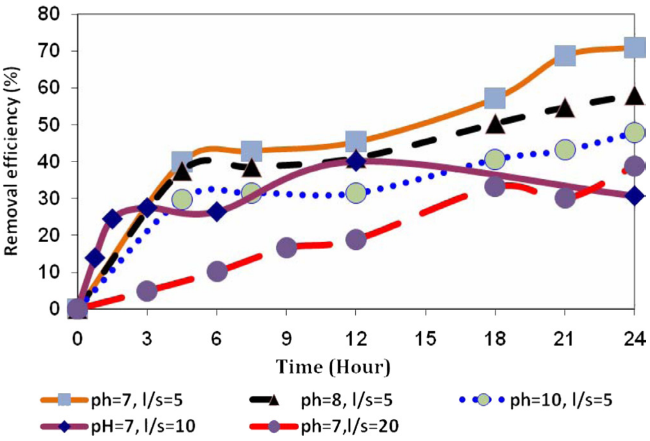

Fig. 5. Boron removal efficiency for 1-d reaction time date seed with seawater.

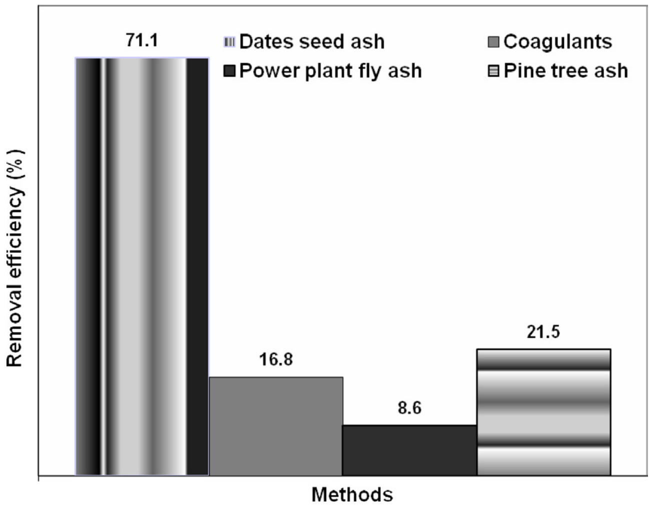

Fig. 6. Removal of boron by various materials (5 mg/L boron solution; pH = 7 and l/s = 5 at 24 h) as performed by batch experiments. Best removal efficiency with pH = 7 was selected for coagulation by ferric chloride.

5. Conclusions

Out of all materials employed in the study to remove boron from seawater, date seed performed with the highest effectiveness of 71.1% boron removal, which is significantly superior to the performance of other methods. More importantly, date seed shows its optimum capacity at pH 7 when the other materials require basic pH values. This discovery offers date seed the advantage over the other materials being integrated into reverse osmosis (RO) processes which enables better membrane stability and minimum scaling on membrane and consequently renders lower operating costs of RO systems.

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