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Boron removal from seawater using date palm (*Phoenix dactylifera*) seed ash

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ABSTRACT

The feasibility of date seed ash, a low-cost agricultural by-product in Oman, for the removal of boron from aqueous solution was investigated. The aim of this study was to understand the mechanism that governs boron removal from seawater using date seed ash as an adsorbent in batch adsorption experiments. The effects of adsorbent dose, contact time, and temperature on boron removal were tested. A surface study of the date seed ash was investigated using scanning electron microscope, energy-dispersive X-ray spectroscopy, and Fourier transform infrared. Thermogravimetric-analysis, specific area using Brunauer, Emmett and Teller method, and particle density were also obtained. The maximum removal efficiency of boron was around 47% at neutral pH. The application of date seed ash is a promising adsorbent for boron removal where it can be used as pretreatment before reverse osmosis desalination process. This will increase the stability of membranes, minimize the membrane scaling, and ultimately reduce the operating cost.

Keywords: Boron; Date seed ash; Adsorbent

1. Introduction

Boron is a naturally occurring element throughout the environment. It was found that boron induces male reproductive impediments in laboratory animals [1]. WHO guidelines for drinking water proposed a 0.3 mg boron/L based on the NOEL (no-observed-adverse-effect level). Later, the standard was set to 0.5 mg/L because it was very difficult to achieve [2]. In 2011, a new WHO guideline was issued relaxing the limit to 2.4 mg/L. Unlike most of the elements in seawater, boron is not ionized (i.e. it has no charge). Boron is present in water as boric acid H_3BO_3 and borate $H_3BO_2^-$. The form of boron present depends mainly on the pH of the water. In seawater which has a typical pH of near 8, the H_3BO_3 will dominate. Many countries that suffer from a shortage of fresh

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water supply have developed desalination plants (mainly RO) using seawater or brackish water.

Desalination of seawater by reverse osmosis and other standard wastewater treatment methods are not effectively active for the removal of boron from raw water [3]. RO is much better at removing charged ions. Hence, it was found that boron rejection by RO ranged from 43 to 78% [4] which results in permeate that does not comply with boron concentration for drinking water purposes as per WHO standards. The rejection of boron by RO membranes is a function of pH, closely following the dissociation ratio of boric acid. The dissociation ratio increases with the feed salinity (ionic strength) and a relatively minor increase of pH of seawater feed will result in a significant reduction of boron passage [5]. At pH above the pk_a (acid dissociation constant) of boric acid (9.25 at 25°C), the ionic borate species predominates and its removal by RO and NF (Nanofiltration) membranes is relatively high [6,7]. However, at the pH of natural waters and wastewaters, boron occurs as boric acid and, consequently, the rejection of this uncharged species by RO and NF membranes is relatively low [8,9].

Additional treatment steps are employed in desalination plants to reach drinking water standards, including pH adjustment of feed water or permeate from initial stages, ion-exchange and passing the desalinated water through another RO stages. Many process configurations were proposed to reach lower concentrations of boron [5,9–19]. One of them is using adsorption process. Many authors have reported the application of different adsorbents for boron removal such as fly ash, zeolite, demineralized lignite, mannitol, activated alumina, activated carbon, and tartaric acid [20–27]. There is a great need and interest to look for adsorbents made from natural materials. Some studies have shown that dates contain boron up to 63 mg/100 g in the flesh and the date seed [28].

Date (*Phoenix dactylifera*) is considered as a valuable crop in arid and semiarid regions. It plays an important part in the social and economic lives of the people living in these regions [2,29]. The date fruit consists of fleshy pericarp which forms around 85–95% of date fruit weight [30]. Dates can be an excellent source of energy because of the high content of carbohydrates (70–80%), while the date seeds are considered as a waste by-product and form around 10% of the fruit weight [31]. Date seeds are used as feed for cattle, sheep, camel and poultry [32]. Recently, Al. Ithari et al. [28] found that the date seed ash has high boron removal efficiency (71%). The chemical composition of date seeds explains the natural affinity for boron. Table 1 represents the chemical composition, physical and chemical properties of different date seeds [33]. In this study, the effects of different adsorbent doses, contact time, and temperature were investigated.

2. Experimental work

2.1. Materials

Seawater was collected from the gulf of Oman. The boron concentration in the seawater was found to be 7.0 mg/L. Seeds of date fruits were collected from a farm in Oman, dried and burnt at 500°C for 1 h in a furnace, then crushed into very fine particles (53–200 μm in size).

2.2. Scanning electron microscope

A scanning electron microscope (SEM) was used to study the morphological structure of date seed ash before and after adsorption of boron. A small amount of date seed ash was placed on a 10 mm diameter aluminum stub. Each sample was supported with a double-side carbon adhesive on the stub. Samples were coated with a thin layer of gold using a sputter coating machine then screened using JEOL JSM-5600LV scanning electron microscope and micrographs were revealed. Energy-dispersive X-ray spectroscopy (EDS) signals were detected using an oxford detector and analyzer attached to the SEM machine.

2.3. Fourier transform infrared

The date seed ash was analyzed using the Perkin–Elmer spectrum one Fourier transform infrared (FTIR) spectrometer. A small portion of the date seed ash was mixed with potassium bromide (KBr). The concentration of the sample in the KBr should in the range of 0.2–1%. The mixture was ground in a mortar to a fine powder. A film was prepared using hydraulic press. The film should be homogenous and transparent in appearance.

2.4. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed to investigate the thermal degradation characteristics of date seed ash. TGA is widely used to study the thermal degradation properties of agricultural waste and other materials [34]. TGA was performed using Perkin Elmer (STA 6000) analyzer under inert atmosphere using N_2 gas. The experiments were conducted at heating rate of 5°C/min and a gas flow of 20 ml/min from 25 to 900°C. At the start of the experiment, 30 min of N_2 purging was applied.

Table 1
Chemical composition, physical and chemical properties from date seeds (33)

Component	Concentration
Chemical composition of seeds	
Moisture contents (%)	10.20 ± 0.25
Oil—dry matter (%) (oil = weight of extracted oil × 100/weight of seed)	10.36 ± 0.29
Ash—dry matter (%)	1.18 ± 0.02
Protein (protein = (N (%) × 6.25))	5.67 ± 0.15
Carbohydrates (carbohydrate obtained by difference)	72.59 ± 0.28
Potassium (in mg/100 g of dry matter)	255.43 ± 0.02
Magnesium (in mg/100 g of dry matter)	62.78 ± 0.18
Calcium (in mg/100 g of dry matter)	48.56 ± 0.56
Phosphorus (in mg/100 g of dry matter)	41.33 ± 0.66
Sodium (in mg/100 g of dry matter)	8.77 ± 0.22
Iron (in mg/100 g of dry matter)	3.21 ± 0.34

2.5. Boron concentration

Boron concentration was measured using inductively coupled plasma optical emission spectrophotometry ICP-OES (Perkin Elmer).

2.6. Specific surface area

The specific surface area of date seed ash was determined using the multi-point BET method. Nitrogen gas adsorption at 77.3 K was obtained using different values for relative vapor pressure (P/P_o).

2.7. X-ray diffraction

The structure of date seeds was analyzed by using Rigaku Miniflex 600 X-ray Diffractometer.

2.8. Particle density

Date seed particle density was measured using the pycnometer method.

2.9. pH measurements

The pH measurements were performed using Jenway pH meter.

2.10. Experimental procedures

The use of date seeds ash to remove boron from seawater was conducted in batch adsorption experiments. One liter water samples were used. In the beginning, the removal of boron as a function of adsorbent concentration and pH was tested. 1.0, 3.0, and 5.0 g/L of date seed ash were used with and without pH adjustment. The samples were first placed under high-speed mixing (150 rpm) for 2 min and then for 30 min under low-speed (20 rpm) mixing. The samples were left for 24 h at room temperature to allow the sedimentation of flocs. Samples were taken from the supernatant after 24 h and passed through 0.45 μm filter. The concentration of boron present in the samples was measured using ICP-OES.

The effects of adsorbent dose, contact time, temperature, and pH were tested (Table 2). Adsorbent doses of 0.1, 0.2, 0.3, and 0.4 g/L were used. The contact time was set to be 2 and 24 h without adjusting the pH, since the pH has no effect on the boron removal by date seed ash as reported in previous trials. The aliquot was filtered through 0.45 μm filter and boron concentration was measured.

In the third experiment the effect of temperature on boron removal was investigated. The temperature was set to 25 and 50°C. The contact time was set to 2 and 24 h. The agitation speed was set to 150 rpm. The samples were allowed to settle for 24 h after the mixing, and then, the aliquot from the supernatant were collected and tested for boron removal.

Table 2
Experimental test conditions for boron adsorption by date seed ash

Parameter	Range
Boron concentration (mg/L)	7.0
Date seed ash dosage (g/L)	0.1, 0.2, 0.3, 0.4, 1.0, 3.0, and 5.0
Contact time (h)	2 and 24
Temperature (°C)	25 and 50
pH	7 and 10

3. Results and discussion

3.1. Physical and chemical characteristic

Table 3 illustrates the physical and chemical properties of seed ash. The size of the ash was in the range between 53 and 200 μm with 2.83 g/cm^3 bulk density and 104 m^2/g surface area. The dominant mineral is SiO_2.

3.2. SEM and EDS analysis

SEM and EDS analysis of date seed ash before and after adsorption are shown in Figs. 1 and 2. The internal surface and availability of pores can be clearly seen in the SEM pictures before adsorption in Fig. 1. The dominant elements present in date seed ash were potassium (K), calcium (Ca), and carbon (C).

The samples were coated with gold as part of the analysis procedure; this explains why Au appears in the structure of date seed ash. We can notice from Fig. 2 that less pores were available as sodium and chloride have been adsorbed on the surface of the date seed ash. The adsorption mechanism of boron onto date seeds has been a matter of considerable debate. The mechanism of adsorption of boron onto date seed ash can be classified as surface adsorption or/and chemisorption. The process starts with a mass transfer of boron into the external surfaces of date seeds ash and might be followed by diffusion of boron into date seed ash through the pores. The presence of many molecules in the aqueous solution (seawater) will compete with the uptake of boron onto the surfaces of date seed ash.

3.3. Fourier transform infrared

Date palm seeds are composed mainly of protein, oil, and carbohydrates. The most abundant fatty acids in date seeds are oleic, lauric, palmitic, capric, myristic, and stearic [29,33,35,36]. Date seeds contain different functional groups that form active sites for sorption on the surface of the material. The FTIR spectra patterns for date seed raw and ash are shown in Fig. 3. The date seed raw is composed of a mixture of functional groups. The O–H stretch functional group can be seen by the band at 3,342.7, while the C–H stretch (alkane) is indicated by 2,928.3 and the C–H stretch appears at 2,845. The rest of the functional groups ranges between C=O, C=C, C–N, P=O, and =C–H bend, while the date seed ash has less intensity compared with the raw. The main functional groups are O–H stretch, S–H, C–N stretch, N=O, and P=O.

Table 3
Physical and chemical composition of date seed ash

Parameter	Value	Reference
Particle density (g/cm^3)	2.83	This study
Surface area (m^2/g)	104	This study
Size (μm)	53–200	This study
XRD	SiO_2	This study

3.4. Primary trials to study the effect of adsorbents dosages and pH

Fig. 4 shows the effect of adsorbent dosages on boron removal at pH 7 and pH 10. The removal efficiency was very close for the three doses used. It was clear that date seed ash concentrations above 1.0 g/L will not change much in the boron removal efficiency. It would be more appropriate to use concentrations less than 1.0 g/L from an economical point of view and to investigate the removal efficiency as well. The date seed ash was found to work well at neutral pH. Further increase in the pH to 10 causes a slight increase in the boron removal efficiency. Similar results were found by Yüksel and Yürüm [21] in his study on boron uptake by fly ash, zeolite, and demineralized lignite. The results revealed that higher pH enhanced the uptake of boron although the uptake of boron was not significant with zeolite and demineralized lignite compared to fly ash. Whereas Cengeloglu et al. [26] in his study, found that pH above 8.3 will reduce the adsorption of boron on neutralized red mud as the surface of the adsorber particles is negative charged and as a result repulsive forces between the $B(OH)_4^-$ and negative charged surface leading to decrease in adsorption. Polowczyk et al. [27] also investigated the effect of pH in the range of 5–10 on the uptake of boron onto fly ash agglomerates. The amount of boron adsorbed varies from 0.15 to 0.2 mg/g.

3.5. Thermogravimetric analysis

The thermal decomposition of date seeds was obtained by the thermogravimetric analysis. The initial mass loss region occurred between 30 and 240˚C. The major loss in mass reaches it maximum around 430˚C. From Fig. 5, we found that the glass transition point is at 370˚C. After this temperature, there was gradual decrease in the weight loss. This can be attributed to the decomposition process of the remaining solid residues or char, which continued until 900˚C.

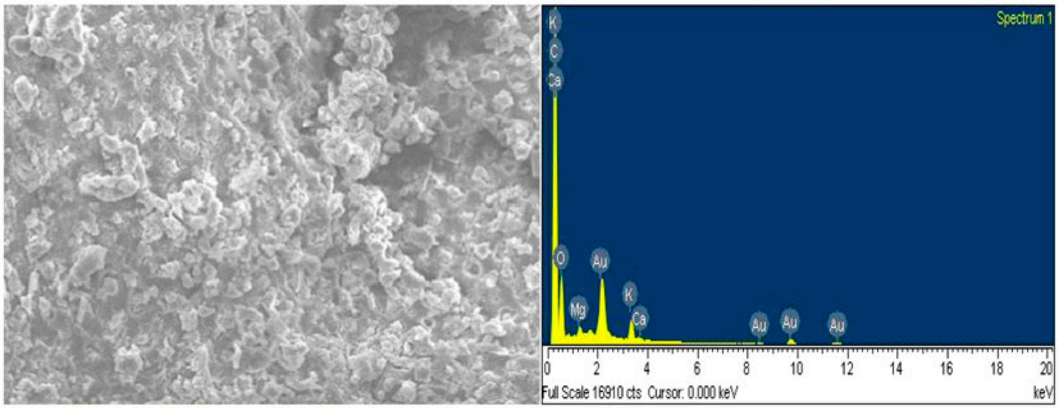

Fig. 1. SEM and EDS of date seed ash before adsorption.

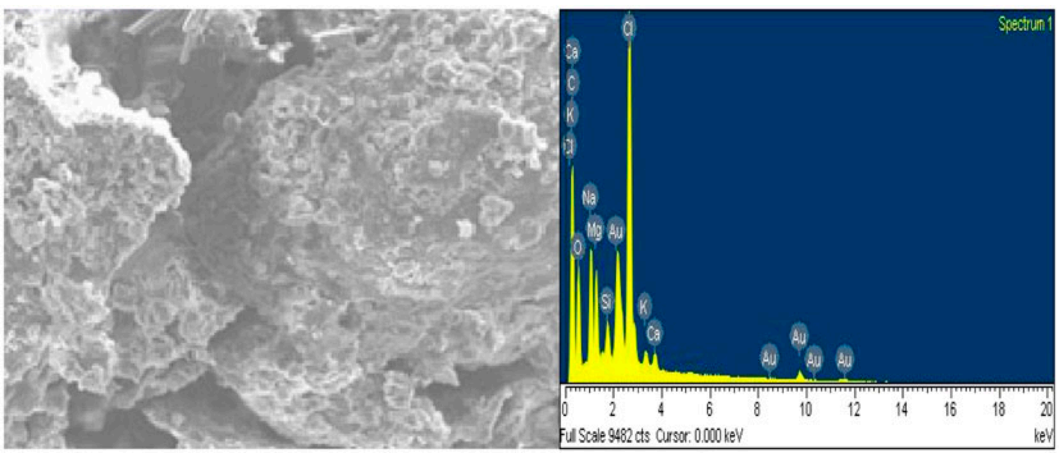

Fig. 2. SEM and EDS of date seed ash after adsorption.

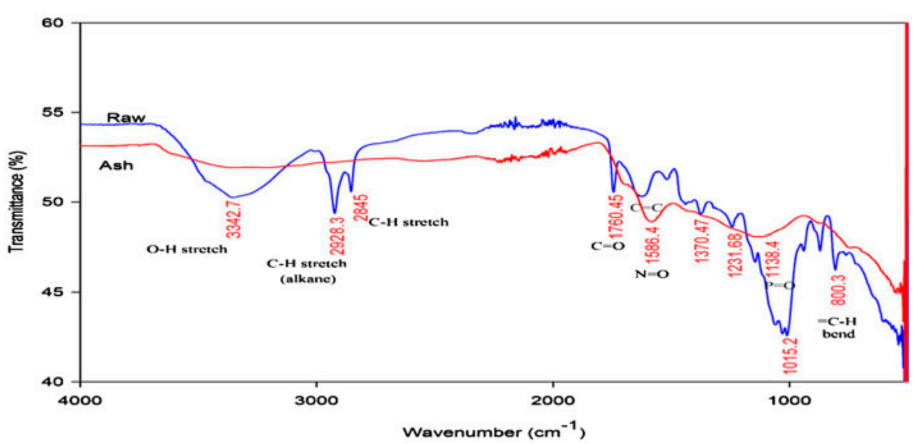

Fig. 3. FTIR spectra's of raw and ash date seed.

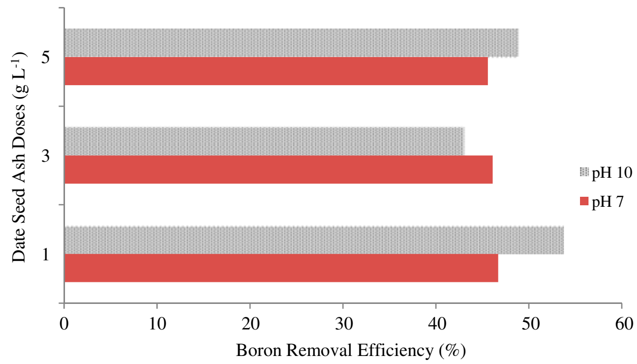

Fig. 4. Effect of pH on the removal efficiency of boron.

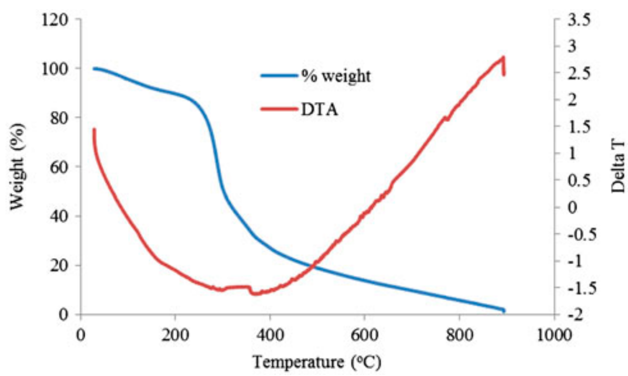

Fig. 5. TGA and DTA of date seeds.

3.6. Effects of date seed ash dose and contact time

Doses of 0.1, 0.2, 0.3, and 0.4 g/L were used, and the contact time was set to 2 and 24 h. It was found that there is no significant difference between 2 and 24 h in boron removal efficiency. As the date seeds ash dose increases, the removal efficiency increased. The increase in the percentage of boron removal with the elevation of the date seeds dose can be attributed to the increase in the active adsorptive sites.

It is clear from Fig. 6 that 2 h is the optimum reaction time from an economical point of view. Higher adsorption efficiencies of boron were achieved after 2 h.

As the date seeds dose increases from 0.1 g to 0.3 g, the removal efficiency increased from 45% to 47% and the equilibrium adsorption capacity decreased from 31.7 to 11.04 mg/g (Figs. 6 and 7). The increase in the percentage of boron removal with the elevation of the date seeds dose can be attributed to the increase in the active adsorptive sites. While the decrease in the equilibrium adsorption capacity can be due to the fact that date seeds would tend to aggregate as the date seeds increase resulting in lower

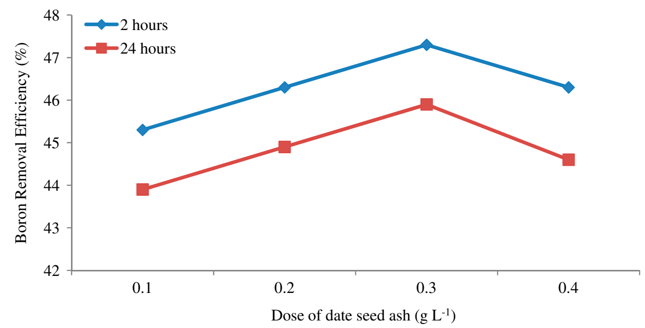

Fig. 6. The effect of contact time on boron removal.

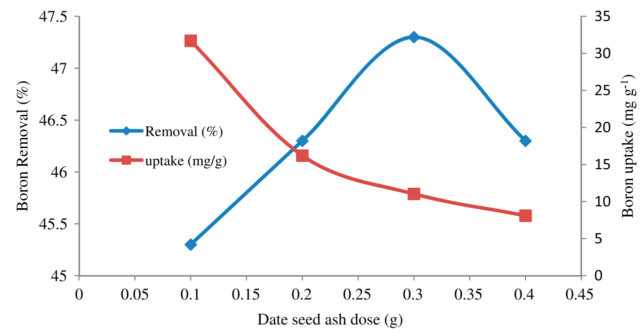

Fig. 7. The effect of date seed dose on boron uptake.

surface area availability for adsorption and causing an increase in the diffusion path length of boron.

3.7. Effect of temperature

The temperature was set to 25 and 50°C. It was found that temperature has a slight effect on the boron removal efficiency. It seems that temperature enhances the adsorption of boron to a certain extent probably due to the dissociation of salts present in seawater and eventually increases the ability of date seed ash to adsorb boron. The same results were reported by Polowczyk et al. [27] indicating that the boron uptake

Table 4
The effect of temperature on boron removal

	Removal efficiency (%)	
Dose of date seed ash (g/L)	25°C	50°C
0.1	43.9	46.3
0.2	44.9	47
0.3	45.9	47
0.4	44.6	47.3

onto fly ash agglomerates increases with increasing temperature. While Yüksel and Yürüm [21] reported opposite results indicating that the adsorption of boron on fly ash is inversely proportional to the temperature. Table 4 shows the data obtained.

4. Conclusions

Adsorption of boron from seawater with date seed ash has been examined using static (batch) tests. It was found that date seed ash works well at neutral pH. The date seed ash has a unique capacity for boron removal at neutral pH, while most of the methods to remove boron such as reverse osmosis work better in an alkaline pH in the range of 9–10. This indicates that date seed ash works well in removing the neutral boric acid while the other methods which depend on elevated pH (9–10) works better in removing negatively charged borate ions. The optimum boron removal efficiency was around 46%. Temperature and reaction time were found to have very minor effect on the adsorption process.

Date seeds have natural affinity for boron. It contains organic matters that adsorb high amounts of boron. Although the exact reason behind why date seed ash is so effective in boron removal could not be fully explained, it was found that the calcium in seed ash helps in the physical adsorption process.

An advantage of applying date seed ash is the fact that it is natural, nontoxic, abundantly found and works at neutral pH which makes it an excellent adsorbent for boron. Due to the effectiveness of the date seed ash in removing boron from seawater, it can be proposed as a pretreatment in desalination plants.

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