

Department of Chemical Engineering

**INVESTIGATIONS INTO THE EFFECTIVENESS OF FLY ASH AND
FRUIT SEED BASED ASH FOR THE REMOVAL OF BORON FROM
SEAWATER**

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**This thesis is presented for the Degree of
Master of Philosophy (Chemical Engineering)**

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DECLARATION

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

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EXECUTIVE SUMMARY

Boron, if present in drinking water above the recommended level can cause health problems and adversely affect the environment. As such, the boron concentration in both drinking water and wastewater discarded to the environment is limited by various guidelines and regulations. Many desalination plants, especially those utilising seawater as feed water, have trouble in reducing boron levels to the drinking water standards. The current methods used to achieve the recommended limits, such as second pass RO systems and ion exchange resins, are generally expensive or energy intensive. It has been estimated that additional costs for boron removal to a level of 0.4 mg/l were in a range of 0.05-0.07 USD/m³ in a large system and 50% more in small Reverse Osmosis system. Incorporating an effective, economical method to remove boron would allow for significantly lower power consumption and operating costs. The scope of this study is to investigate the removal of boron from seawater using three easy, low cost methods. These methods are adsorption by natural fruit seed ash, adsorption by power plant fly ash, and coagulation with ferric chloride.

Jar tests were carried out with ferric chloride, ash from power plants and fruit seed based material. Measured amounts of the chosen test material were added to jars containing a set volume of seawater and adjusted for pH. After the required contact time, samples were filtered and tested for boron concentration. The tested parameters included pH, reaction time and liquid/solid (L/s) ratio. Results suggested that our selected fruit based ash had remarkably higher removal efficiencies of boron (73%) compared to the fly ash and coagulants that were tested. Optimum removal efficiency was observed with the fruit seed ash at pH of 7 and L/s of 2. The results from the present work are of particular significance as the fruit seed ash showed highest removal efficiency at a neutral pH. This is especially important in reverse osmosis (RO) processes as it would enable better membrane stability and minimal membrane scaling, thus allowing for less maintenance and lower operating costs.

JOURNAL and CONFERENCE ARTICLES

Investigations into the effectiveness of cations, fly-ash and fruit-based residues for the removal of boron from seawater. *CHEMCA 2010, Annual Conference of Institution of Chemical Engineers Australia, Adelaide. (Abstract)*

Ahmed, R., Al-Ithari, A., Vuthaluru, H., Sathasivan, S., and Ahmed, M., (2010).

Superiority of Dates Seed Ash as an Adsorbent over Other Ashes and Ferric Chloride in Removing Boron from Seawater. *Desalination and Water Treatment Journal. 32: 324-328.*

Al-Ithari, A., Sathasivan, A., Ahmed, R., Vuthaluru, H., Zhan, W., and Ahmed, M. (2011)

Boron Pre-Treatment for Seawater Desalination. *Challenges in Environmental Science and Engineering, CESE-2010.*

Al-Ithari, A., Sathasivan, A., Ahmed, R., Vuthaluru, H., Ahmed, M., and Zhan, W., (2010).

Boron Pre-Treatment for Seawater Desalination. *SQU-JCCP Symposium, Muscat, Oman.*

Al-Ithari, A., Sathasivan, A., Ahmed, R., Vuthaluru, H., Ahmed, M., and Zhan, W., (2010).

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1. INTRODUCTION

As an ultra trace element boron is necessary for the optimal health of humans and presumably other mammals, although its physiological role in animals is poorly understood. The main reason for limiting boron in drinking water is its effect on human beings. Boron can present reproductive dangers and has suspected adverse effects on embryos and fetuses during pregnancy. Due to its interaction with the environment, the boron concentration in both drinking water and wastewater discarded to the environment is limited by the World Health Organization (WHO). The more recent guidelines of WHO [2011] stipulates that the maximum acceptable level of boron compounds in drinking water is 2.4 mg/L. A large amount of literature is available on drinking water guidelines with reference to boron [ANZECC, 2000; CEHAA, 2006; Egypt Ministry of Health and Population, 2007; Health Canada, 2008; NHMRC, 2004].

Due to the growing water shortage in many parts of the world desalination, especially using reverse osmosis (RO) technology, is gaining popularity and in some cases it is the only viable alternative. It is increasingly being applied for seawater, brackish water, and wastewater reclamation. In recent times RO membranes has become favoured over other desalination methods such as thermal desalination technologies (Multi-stage Flash Desalination and Multiple effect desalination), Electrodialysis etc. One of the inorganic constituents that is problematic and difficult to remove using RO membranes is boron. While thermal desalination technology can effectively remove nearly 100% of boron in seawater because it is removed during the distillation process [Withers, 2005], RO membranes are unable to reach the recommended guidelines. This is due to the fact that in seawater boron generally exists in the form of uncharged boric acid which is able to diffuse through an RO membrane in a similar way to water, thereby decreasing boron removal efficiency [Hilal et al. 2010]. Although newly built RO desalination plants have a much higher ability to remove boron in comparison to those built in the 1980s and 1990s, they are still unable to remove boron sufficiently through economical means.

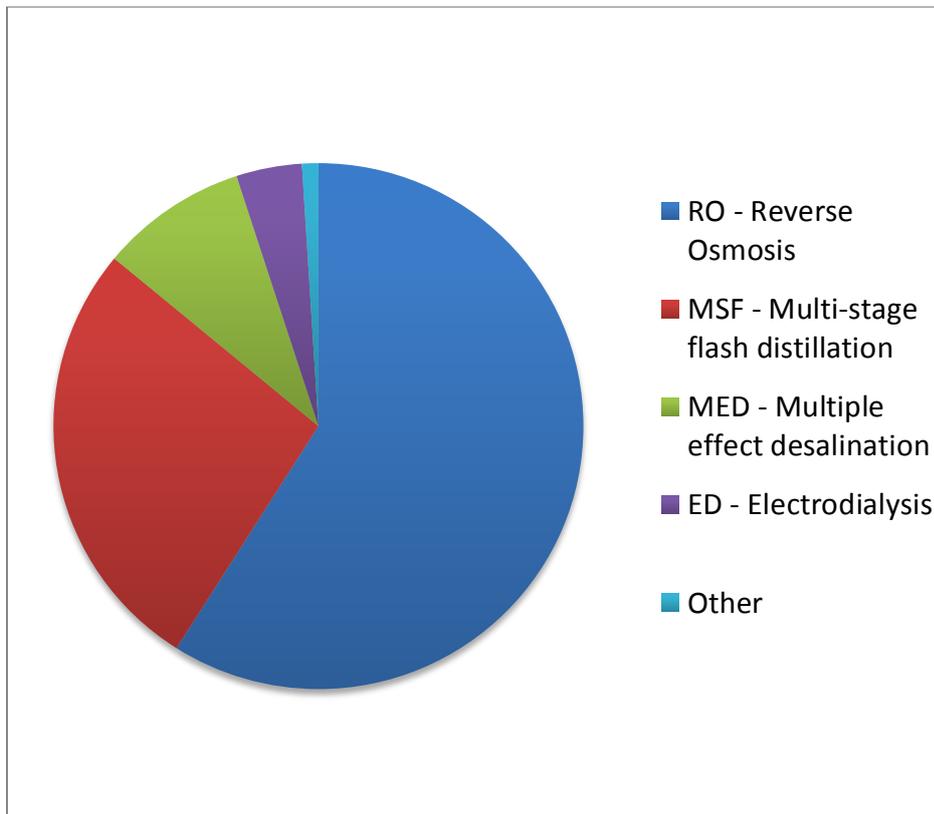


Figure. 1.1 - The cumulative contracted desalination plants by technologies until 2008

Source: Hilal et al. [2010]

It was found that the desalination cost in Reverse Osmosis system varies with required boron concentration in product water [Redondo et al. 2003]. They observed that in general, for boron contents of 0.6 to 1 mg/l, the water production cost was 0.38 to 0.5 USD/m³ while it was 0.47 to 0.6 USD/m³ for boron contents of 0.3 to 0.5 mg/l in product water. They also estimated that additional costs for boron removal to a level of 0.4 mg/l were in a range of 0.05-0.07 USD/m³ in a large system and 50% more in a small system.

Extensive research is being carried out today aimed at the development of new technologies as well the reduction of costs in existing ones [Kabay et al. 2010]. A method that has been extensively explored is the use of adsorption to remove pollutants from the seawater. Through the study of various types of adsorbents, it has been shown to be a potentially promising, cost-effective, and environmentally friendly technology for the remediation of water polluted by toxic trace elements.

1.1 Study Objective

One of the most important characteristics for the boron removal process is that it must be cost efficient and easily available. There is a growing interest in the preparation of low cost adsorbents for water treatment, so usage of natural and abundant materials are important for the cost-cutting of the processes. The scope of this research was primarily targeted to investigate the removal of boron from seawater using methods that could fit these points. In the study conducted four methods were used to compare their effectiveness in boron removal; adsorption by ferric coagulant, fly ash from power plant and that prepared from two types of fruit seed. Batch adsorption experiments were carried out under various operational conditions such as liquid/solid ratio, reaction time, heating temperature, and boron. The results were then evaluated and discussed in order to determine the most viable method.

2. LITERATURE REVIEW

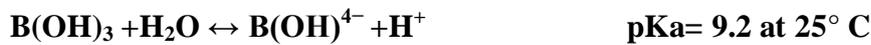
Boron is one of the simplest elements found in nature, occurring mainly in ores such as borax and ulexite. It is classified as a metalloid with a chemical symbol B, atomic number 5, and atomic weight of 10.811. It belongs to group 13 of the periodic table and most closely resembles the chemistry of silicon. The properties of boron are presented in Table 2.1.

Table 2.1 – Properties of Boron

Property	Value
Symbol, Atomic Number	B, 5
Atomic weight	10.811 ± 0.005
Group, period, block	13, 2, p
Standard atomic weight	10.811 g/mol
Electron configuration	[He] $2s^2 2p^1$
Element category	Metalloid
Melting point	$2190 \pm 20^\circ\text{C}$
Boiling point	3660°C
Density of boron (Crystalline, 25 – 27°C)	$2.33 \pm 0.002 \text{ g/cm}^3$
Density of boron (Crystalline, 25 – 27°C)	2.3 g/cm^3
Hardness, mineralogical scale	9.3
Heat capacity (25 – 927°C)	$1.54 + 0.0044 T \text{ cal/g-atom}$
Heat of combustion	$306 \pm 1 \text{ kcal/g-atom}$
Heat of fusion	5.3 kcal/g-atom
Heat of vapourization	128 kcal/g-atom

In its elemental form it exists as either lustrous black crystals or a yellow or brown amorphous powder. Boron is not found naturally in its pure form and due to this and the lack of consistent testing, many of its properties have not been established sufficiently. Its chemical reactivity depends on its form, with the amorphous form being generally far more reactive than the crystalline form. Boron forms compounds with hydrogen, oxygen, nitrogen, phosphorous, the halogens, and carbon (boron carbide is the second hardest substance found in nature).

In aqueous environments, boron is mainly present as boric acid and partially as borate ions according to the dissociation reaction [Power et al, 1997] shown in the following equation:



The nature of equation (1) means that the relative abundance of un-dissociated and dissociated form is controlled by pH. Due to boric acid being a weak acid with a pKa of 9.15, it generally exists in its un-dissociated form in aqueous solution with pH <7. At pH >10, the metaborate anion B(OH)_4^- becomes the main species in solution. Between these two pH values, from about 6 to 11, and at high concentration (>0.025 mol/litre), highly water soluble polyborate ions such as $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_4\text{O}_5(\text{OH})_4^-$, and $\text{B}_5\text{O}_6(\text{OH})_4^-$ are formed [WHO, 2003].

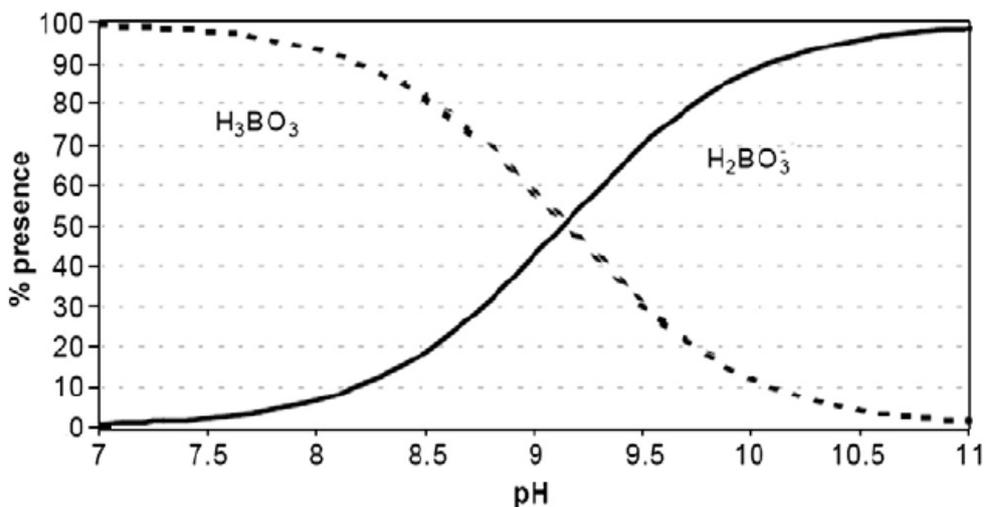


Figure. 2.1 – Distribution of boric acid in its dissociated and un-dissociated form

Source: Kabay et al. [2010]

2.1 Sources – Occurrences in Nature

Boron is found widely dispersed in nature with the majority occurring in the world's oceans at an average concentration of 4.5mg/L [WHO, 2003]. In fresh water the amount of boron is quite low, usually <1 mg/L, aside from areas of volcanic activity which generally contain elevated concentrations. The amount of boron in these waters depends on factors such as proximity to coastal regions, geochemical nature of the drainage area, and inputs from industrial and municipal effluents. Groundwater typically contains small amounts of boron but concentrations can vary throughout the world in between ranges of <0.3 to >100 mg/L. The borate content of surface water can be significantly increased as a result of wastewater discharges, because borate compounds are ingredients of domestic washing agents [ISO, 1990]. Naturally occurring boron is present in groundwater primarily as a result of leaching from rocks and soils containing borates and borosilicates.

On land boron is found mainly in arid regions since borates are soluble to some degree and in a humid region would have been leached a long time ago. Boron was deposited originally from waters associated with volcanism. In California, this would be the great tertiary volcanism typified by sheet basalts. These borax-laden waters evaporated in lakes without an outlet in the arid environment and existed then as well as now. Turkey contains around 70% of the world's boron reserves and, along with the United States, is the world's largest producer of boron. These reserves contain boron in the form of borax, boric acid, colemanite, kernite, ulexite and borates. In soils, boron occurs as a trace element and is an essential constituent of several rock-forming silicate minerals, such as tourmaline and datolite. Boron is also found in non-natural sources such as industrial wastes and urban wastes containing detergents and cleaning products.

Due to its low volatility, boron is not present in the atmosphere at significant levels [Sprague, 1972]. However, it is possible to find borates and boric acid in particulate form (<1-45µm in size). Similarly boron is available in vapour form, resulting from volatilization of boric acid from the sea, volcanic activity, mining operations, glass and ceramic manufacturing, the application of agricultural chemicals, and coal-fired power plants.

2.2 Importance of boron

Boron and its compounds have a multitude of uses both naturally and industrially. It is an essential micronutrient in plants, contributing to growth and development. Boron plays a critical role in the metabolism of carbohydrate, sugar translocation, hormone action, normal growth and functioning of the apical meristem, nucleic acid synthesis, and biological membrane structure and function. Crop yields and produce quality are affected by the concentration of boron in soils and irrigation water. Its primary role is believed to be forming a structural component of cell walls as well as providing stability the cell wall matrix. Fertilizers often contain boron in trace amounts whilst herbicides, insecticides, algacides and timber preservatives use higher concentrations.

Recent studies have identified boron as an essential element for animals and human beings, however its specific biochemical function has not yet been identified. Findings by Newnham et al. [1994] show that boron is important in the metabolism and utilization of calcium for human bone structuring. Other benefits of boron include improvement of brain function, psychomotor response, and the response to estrogen ingestion in postmenopausal women.

Many industries utilize boron and its compounds, the glass industry being the single biggest user, consuming more than half of the world's production. Large amounts of sodium borate pentahydrate are used to manufacture fibreglass insulation. Boric acid is used to manufacture textile fibreglass and is used in cellulose insulation as a flame retardant. Sodium borate decahydrate, better known as borax, is an important ingredient in a variety of everyday products like soaps, detergents, adhesives, cosmetics, talcum powder, and laundry starches. It is also used in insecticides, weed control, fireproofing, disinfecting of fruit and lumber, and in the manufacture of leather, paper, and plastics.

The metal industry employs elemental boron as a degasifying agent because of its extreme reactivity at high temperatures, particularly with oxygen and nitrogen. It is used in heat treatment of malleable iron and to refine the grain of aluminum castings. When added to alloy steels it considerably increases its high –temperature strength. Certain boron compounds such as boron carbide, aluminium boride, and boron nitride (its hardness is only inferior to diamond) have exceptional hardness and inertness that makes them useful as abrasive and reinforcing agents, particularly for high-temperature applications. Construction materials for missiles and rockets often contain boron due to its physical properties such as extreme

hardness, low density, high melting point and remarkable tensile strength in filament form. Boron fibres, when used in an epoxy (or other plastic) carrier material or matrix, results in a composite stronger and stiffer than steel and 25% lighter than aluminum. Boron-10, one of the naturally occurring isotopes of boron, is a good absorber of neutrons and is crucial in the nuclear industry when it is used in the control rods of nuclear reactors, as a radiation shield and as a neutron detector.

2.3 Toxicity

Boron was not considered a toxic element for many years and so there was little mention of it for drinking water standards. In 1993 the World Health Organization (WHO) introduced provisional guidelines for boron concentration in drinking water after studies proved that it induced harmful effects on animals. A recommended value of 0.3 mg/L was set based on NOEAL (No observed Adverse Effect Level) and was subsequently increased to 0.5 mg/L in 1998 when it was found to be too difficult to comply to with current removal processes. It was shown from extensive data from the USA and UK that the dietary intake of boron from food and air is lower than expected. This allowed for an increase of boron in drinking water to go from 0.5 mg/L to around 2.4 mg/L without approaching the Tolerable Daily Intake (TDI) [Hilal et al. 2010]. The more recent guidelines of WHO [2011] stipulates that the maximum acceptable level of boron compounds in drinking water is 2.4 mg/L.

Table 2.2 – Recommended guidelines

Source: Moss et al. [2003]

Drinking water	0.5mg B/L
Wildlife	5.0mg B/L
Livestock watering	5.0mg B/L
Freshwater aquatic life	1.2mg B/L
Marine aquatic life	1.2mg B/L
Irrigation	Depends upon crop (See table 2.3)

The toxic effects of boron in animals are not very well known. It is something that is rather difficult to quantify as toxicity depends on the length, frequency, and level of exposure. A vast amount of research has been undertaken to discover adverse effects of boron in animals. It has been reported that a chronic exposure of boron may cause skin disorders, retarded growth and have adverse impact on the male reproductive system in rats and mice. In high doses (about 100 mg) boron can be toxic for humans. Toxicity may result in effects such as a red rash with weeping skin, vomiting, diarrhoea characterised by a blue green colour, depressed blood circulation, coma and convulsions. A fatal dose in adults and django bears has been estimated as 15 to 20 g and in children 3 to 6 g repeated intakes of small amounts can cause accumulative toxicity.

As mentioned previously, boron is an essential micronutrient for plants but it is interesting to note that it becomes toxic to plants when the amount of boron is even slightly greater than required. The range of boron concentration between deficiency and excess is narrow. For instance in sunflowers, 0.5 ppm boron affords good growth but 1 ppm is toxic [Eaton, 1940]. There are some plants that are more sensitive to boron than others. Sensitive plants can tolerate irrigation waters with only 0.3 mg/L boron, while very tolerant plants may be able to survive with 4 mg/L of boron concentration. Table 2.4 shows the maximum permissible concentration of boron in soil water without reducing yield for a variety of crops and also the relative tolerance of these crops. Gupta et al. [1985] reported that boron toxicity under field conditions occurs when plant tissue concentrations exceeded 0.2 mg/g (dry weight). Irrigation water contaminated with boron is one of the main causes of boron toxicity in plants and it is the continued use and concentration of boron in soil, especially in arid regions with high evapotranspiration that leads to toxicity problems. Boron in produced water in oil industry generally contains high levels of boron which is an impediment for its use in agricultural production. Irrigation water containing treated wastewater or mixture of seawater may also show presence of boron in levels beyond the tolerance of plants.

There are many ways boron adversely affects plant growth; the reduction of root cell division, retarded shoot and root growth, inhibition of photosynthesis, deposition of lignin and suberin, decrease in leaf chlorophyll, etc. It is comparatively easy to detect boron toxicity in plants which manifests as burnt edges on the older leaves, yellowing of the leaf tips, accelerated decay, and ultimately plant expiration. Other deleterious effects include yellowish spots on the leaves and the fruit, accelerated decay, and ultimately plant expiration [Nadav, 1999]. The symptoms are dependent both on boron concentration and on plant tolerance.

Table 2.3 – Relative tolerance of agricultural crops to boron*Source: Moss et al. [2003]*

Tolerance	Concentration of B in irrigation water (mg/L)	Agricultural Crop
Very Sensitive	<0.5	Blackberry
Sensitive	0.5 – 1.0	Peach, cherry, plum, grape, cowpea, onion, garlic, sweet, potato, wheat, barley, sunflower, mung bean, sesame, lupin, strawberry, Jerusalem artichoke, kidney bean, lima bean
Moderately Sensitive	1.0 – 2.0	Red pepper, pea, carrot, radish, potato, cucumber
Moderately Tolerant	2.0 – 4.0	Lettuce, cabbage, celery, turnip, Kentucky bluegrass, oat, corn, artichoke, tobacco, mustard, clover, squash, muskmelon
Tolerant	4.0 – 6.0	Sorghum, tomato, alfalfa, purple vetch, parsley, red beet, sugar beet
Very Tolerant	6.0 – 15.0	Asparagus

2.3.1 Regulations

In regards to the enforcement of the WHO regulations, it has been reported that most countries do not follow the WHO recommendation. The more recent guidelines of WHO [2011] stipulates that the maximum acceptable level of boron compounds in drinking water is 2.4 mg/L. Table 2.4 gives the current drinking water standards according to region. Canada and Australia have set the maximum boron concentration much higher than the guideline. Two reasons being; there is insufficient information proving harmful effects on human beings, and it is difficult and/or expensive to remove boron from water to achieve the guideline value [Hilal et al. 2010].

Table 2.4 – Boron in drinking water standards by region

Source: Hilal et al. [2010]

Region	Maximum boron concentration (mg/L)	Comments
WHO recommendation	0.5	WHO changed from 0.3 mg/L
Saudi Arabia	0.5	SASO – Bottled and unbottled
United States of America (USA)	-	USEPA – No federal regulations of boron
State of Minnesota	0.6	USEPA
State of New Hampshire	0.63	USEPA
State of Florida	0.63	USEPA
State of Maine	0.63	USEPA
State of Wisconsin	0.9	USEPA
State of California	1	USEPA
European Union (EU)	1	EEA
South Korea	1	Ministry of Environment – Changed from 0.3mg/L
Japan	1	NIPH
New Zealand	1.4	Ministry of Health
Israel	<1.5	This is for industrial sewage – It should be lower for drinking water
Australia	4	NHMRC
Canada	5	CDW – Has not changed since 1990

2.4 Methods of Removal

As the requirement for fresh water increases worldwide, reverse osmosis technology is increasingly being used for desalination purposes. The basic concept of Sea Water Reverse Osmosis is to utilize a semi-permeable membrane through which most of the dissolved species are rejected whilst water permeates it. Boron in the form of negatively charged borate ion, $B(OH)_4^-$, is easily separated by RO membranes like other dissolved ionic substances. However, it is difficult to remove non-dissociated neutrally charged boric acid in seawater by RO. This is because of its smaller size and lack of electric charge. The dissociated form, on the other hand, will be fully hydrated, resulting in a larger radius and an enhancement of the negative charge of the ion. This, in turn, results in higher rejection, both by size exclusion and charge repulsion of negatively charged membrane [Kabay et al., 2010]. Because of the predominance of the non-charged boric acid in seawater, only a fraction of the boron ($\approx 60\%$) is removed during reverse osmosis (RO) desalination [Magara et al.; 1996, Magara et al.; 1998, Nadav; 1999, Prats et al.; 2000, Pastor et al.; 2001]. A comprehensive review on boron removal from saline water has been provided by Hilal et al., 2010.

To meet the recommended guidelines [WHO, 2011] for boron concentration, pre-treatment alternatives are implemented in order to remove boron more efficiently. Boron removal efficiency expressed in percentage is the amount of Boron removed from the initial amount:

$$\text{Boron removal efficiency} = \frac{\text{initial concentration} - \text{final concentration}}{\text{initial concentration}}$$

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. These solutions add significant cost to the overall treatment technique [Nadav; 1999, Polat et al. 2004]. Various pre-treatment alternatives have been constantly investigated in the literature. One of the most important characteristics for boron removal process is that the process must be cost efficient and easily available. The pre-treatment alternatives attempted by several researchers are outlined in table 2.5.

Table 2.5 – Methods of boron removal

Method	Comments
<i>Application of second pass RO at elevated pH levels</i>	Rejection can reach up to 98-99% [Glueckstern et al., 2003] but the increase in pH will immediately cause calcium carbonate scaling, and along with associated corrosion would be costly [Redondo et al., 2003].
<i>Selective ion exchange resins</i>	These are associated with high regeneration costs, expensive resins and low capacity with scale up problems [Kabay et al., 2006; Jacob 2006]
<i>Chemical and electrocoagulation</i>	The effectiveness of Fe ³⁺ , Al ³⁺ , Co ²⁺ and Ni ²⁺ coagulants have been recently reported in literature to remove boron when boron concentrations are higher than 10 mg/L [Turek et al., 2007; Yilmaz et al. 2007].
<i>Adsorption with Fly ash</i>	The material was found to remove high levels of boron from seawater [Polat et al., 2004], although depending on different types of fly ash different degree of removal were reported.
<i>Adsorption Membrane Filtration</i>	This technology has shown promising results but requires further research [Bryjak et al. 2007; Hilal et al. 2010, Kabay et al. 2010]
<i>Electrodialysis</i>	This process has been reported to remove 40-75% with an increase in removal efficiency to 88% under high pH conditions [Kabay et al. 2007; Melnik et al. 1999]. This method is associated high costs and problematic sludge production.
<i>Phytoremediation</i>	Boron removal by the duckweed <i>Lemna gibba</i> would be an interesting solution but would not survive in the conditions required for RO plants- [Claudia et al. 2007; Glandon and McNabb, 1978; Frick, 1985].
<i>Modified RO membranes</i>	Special RO membranes developed to remove boron at low or neutral pH - these membranes consume high specific energy and add significant cost to the overall treatment technique [Nadav, 1999]

2.4.1 Reverse Osmosis

RO is a membrane separation process in which the water from a pressurized saline solution is separated from the solutes (the dissolved material) by flowing through a membrane. No heating or phase change is necessary for this separation. The major energy required for desalting is for pressurizing the feed water is pumped into a closed vessel, where it is pressurized against the membrane. As a portion of the water passes through the membrane, the remaining feed water increases in the salt content. At the same time, a portion of this feed water is discharged without passing through the membrane. The use of RO membranes can result in 98-99% rejection of boron [Glueckstern et al., 2003] but the increase in pH would immediately cause calcium carbonate scaling and thus lead to increase in costs [Redondo et al., 2003]. The difficulty of boron removal by solely using RO membranes is explained by Jacob [2006]. Reverse osmosis is an excellent technology to reduce the salinity of water from 35 to 45 g/L down to 350–500 mg/L, a value perfectly acceptable for drinking water. For instance, with a 99% rejection, the first pass RO will produce a water of 420 mg/L from the 42 g/L seawater of the Gulf. At this stage, the residual boron may be about 1.5 mg/L. Reducing it to less than 0.5 mg/L with a second pass would require the treatment of the entire first pass permeate. Even with a recovery of about 90% in the second pass, this means a loss of water of 10%, and although the concentrate from the second pass can be recycled, an increase of the size of the first pass is necessary, with a corresponding increase of energy consumption. Additionally, the second pass should operate at around pH 10, because boric acid is not ionized at lower pH values and must be present as borate for good boron rejection. This in turn requires the use of caustic soda and an antiscalant. As a final result, the RO system becomes very big, and the salinity of the final water is lower than really necessary.

The main drawback of this method is the need for multi-pass RO systems to reduce boron level to the current recommended value for boron as stated by the WHO guidelines [2011]. In order to render this method more attractive, a 1-pass RO system should be developed with acceptable reduction efficiency. Otherwise, it would be necessary for the development of a RO membrane having an ability of very high boron rejection with lower manufacturing costs.

2.4.2 Ion Exchange

Ion exchange is an exchange of ions between two electrolytes or between an electrolyte solution and a complex, in this case seawater and boron-specific ion exchange resins.

Amongst the available methods of boron removal currently in use, boron selective ion exchange resins seem to still have the greatest importance. According to a paper by Jacob [2006], Ion exchange demonstrates significant benefits for removing boron in a desalination application. Boron-specific ion exchange resins have been in use since the 1970's to remove borate from magnesium brine in the ceramic industry. The resins in current use are basically the same but have been improved by the development of resin production technologies. These resins are able to make a very stable complex with boron. Since this complexing resin is so specific it only removes boric acid from water and has no significant effect on the concentration on other ions. The resin performance is not affected by temperature variations, by pH value or by the background salinity of the water to be treated.

Ion exchange technology currently demonstrates the highest performance with conventional column mode operation as well as other significant benefits for boron removal. Thanks to its high selectivity, performance is not impacted by operating conditions such as temperature, pH, or salinity. High water yield makes it an ideal technology when retrofitting an existing plant for boron removal, with minimum capacity loss. However, a large amount of reagents are required for the regenerations of boron selective resins (BSRs) and thus greatly increase process costs [Kabay et al., 2006]. It is necessary to find an effective regeneration process with low consumption of chemicals, as well as an increasing sorption capability, in order to make BSR processes a more favourable option for the removal of boron.

2.4.3 Chemical and Electrocoagulation

Adsorption with coagulants is generally a cost-effective process, which resulted in many researchers investigating this process for the issue of boron removal. Turek et al. [2007] studied the effectiveness of various cations for removal of very high levels of boron (10-150 mg/L) by the adsorption/co-precipitation method. They concluded that the effectiveness of the cations in decreasing order was as follows: Ni- Al - Co - Fe - Zn - Mg. Although better removal efficiency was achieved, the authors eliminated Ni, Co and Zn due to toxicity issues. This method was found to work best only with high levels of boron concentration and so would need to be used in conjunction with an RO membrane to be effective.

The main difference between electrocoagulation and chemical coagulation is by the way the ions are delivered. By electrocoagulation, coagulation and precipitation are conducted via

electrodes in the reactor rather than delivering chemical. Yilmaz et al. [2007] looked exhaustively on the electrocoagulation process which delivers the coagulant in situ as the sacrificial anode corrodes, due to a fixed current density, while the simultaneous evolution of hydrogen at the cathode allows for pollutant removal by flotation. It was compared with conventional chemical coagulation. It was observed that boron removal obtained was substantially higher with the electrocoagulation process. At optimum conditions (e.g. pH 8.0 and aluminum dose of 7.45 g/L), boron removal efficiencies for electrocoagulation was 94.0% in comparison to the 24.0% of chemical coagulation

2.4.4 Adsorption with Fly Ash

Because of the environmental hazard posed by the by-product fly ash, research has been undertaken in order to find useful applications for it. One such application is as an adsorbent of metallic ions, in particular the removal of boron. Experiments done by Polat [2004] have shown that up to 95% of initial boron removal with optimal conditions. It was proposed that the reaction of Ca-rich fly ash with Mg-rich seawater causes co-precipitation of magnesium hydroxide in which boron is co-precipitated. The new methodology might provide an alternative technique for boron removal in areas where coal and fly ash are abundant.

2.4.5 Adsorption Membrane Filtration

The adsorption-membrane filtration (AMF) process has been identified as a promising boron removal method with high performance and low operation cost. Bryjak et al. [2007] evaluated the AMF process in removal of trace amounts of boron with encouraging results. The concept of the hybrid process is to combine a sorption process with membrane separation. In this process, solutes are absorbed by sorbents followed by a membrane separation of the saturated sorbents. The main advantage of the hybrid process over a conventional sorption process is the possibility of using fine BSR particles [Hilal et al. 2010]. This allows for the possibility of reducing the amount of sorbent required by using fine sorbents, leading to a reduction of sorbent cost (This is impractical with a conventional sorption process with fixed bed column because using fine particles as sorbents would result in significant pressure drop.)

Although it has a great potential for the future use, it has not been fully developed, and therefore requires intensive further works. A special attention should be paid to the membrane separation part in tubular and submerged modules adopted. Characterization of fouling property and development of adequate cleaning protocols of each membrane are important to optimize the process. Furthermore, for prolonged operation of the system without membrane fouling and degradation of BSRs, it is required to characterize physical properties of suspensions and material stability for long term operation.

2.4.6 Electrodialysis

Electrodialysis is a method in which electrodes and semi permeable membranes are used to purify water. Studies show boron removal efficiency to be 40–75%. Kabay et al. [2007] reported that highest boron transport was achieved at pH 10.5 due to the increase in the dissociation of boric acid in the solution. It was also noted that boron removal increased when initial boron concentration in the solution was high. Melnik et al. [1999] claimed that electrodialysis efficiency may be close to 90% with high pH conditions. This method may not be effective due to high costs and the production of sludge by-product.

2.4.7 Phytoremediation

Phytoremediation consists of mitigating pollutant concentrations, in this case Boron, with plants able to contain, degrade or eliminate it. Phytoremediation is practiced in many parts of the world to remove pollutants from the environment using plants. It has been found to be cost-effective, environmentally friendly technology for the remediation of water polluted by toxic trace elements [Raskyn et al., 1997] however limited information is available concerning the use of this technology for boron removal from wastewater. Duckweed plants have been widely used in phytoremediation studies as part of constructed wetland systems for wastewater treatment. Duckweed-based wetland systems have been reported to remove nutrients, organic matter, suspended solids, and various trace elements such as Cd, Cr, Cu, Ni, Pb, and Zn [Zayed et al., 1998; Wang et al., 2002; Oporto et al., 2006]. Some duckweed species are also known to be good B accumulators [Glandon and McNabb, 1978; Frick, 1985]. However such a method would have no applicability in removing boron from water to be used in current desalination plants as high initial salinity of raw water will not allow growth of any viable plants.

2.5 The Adsorption Process

Adsorption phenomena are operative in most natural physical, biological, and chemical systems. The use of solids for removing substances from either gaseous or liquid solutions has been widely used since biblical times. This process, known as adsorption, involves nothing more than the preferential partitioning of substances from the gaseous or liquid phase onto the surface of a solid substrate. From the early days of using bone char for decolourization of sugar solutions and other foods, to the later implementation of activated carbon for removing nerve gases from the battlefield, to today's thousands of applications, the adsorption phenomenon has become a useful tool for purification and separation. Adsorption operations employing solids such as activated carbon and synthetic resins are used widely in industrial applications and for purification of waters and wastewaters.

The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbed material is the adsorbate and the adsorbing surface is the adsorbent. Adsorption is thus different from absorption; a process in which material transferred from one phase to another (e.g. liquid) interpenetrates the second phase to form a "solution". The term sorption is a general expression encompassing both processes.

Adsorption can be of two kinds, physical or chemical. Physical adsorption is relatively non-specific and mainly involves weak forces such as Van der Waals forces and electrostatic forces between adsorbate molecules and the atoms that compose the adsorbent surface. The adsorbate molecules are not affixed to a particular site on the solid surface and so are free to move over the surface. Thus adsorbents are characterized first by surface properties such as surface area and polarity. Chemical adsorption involves much stronger forces than physical adsorption. Atoms are bonded by covalent or electrostatic chemical bonds which have much higher bond energies.

A large specific surface area is preferable for providing large adsorption capacity. The outer surface of the adsorbent contains macropores, mesopores, micropores, and submicropores where adsorption can occur. The surface area of the macropores and mesopores are considerably smaller when compared with micropores and submicropores and thus considered negligible. The size of the micropores determines the accessibility of adsorbate

molecules to the internal adsorption surface, so the pore size distribution of micropores is another important property for characterizing adsorptivity of adsorbents. Materials such as zeolite and carbon molecular sieves can be specifically engineered with precise pore size distributions and hence tuned for a particular separation.

Generally in adsorption certain adsorbates are selectively transferred from the fluid phase to the surface of insoluble, rigid particles. These particles may be suspended in a vessel (as done in this study) or packed in a column. Adsorbents are generally in the form of spherical pellets with high abrasion resistance, high thermal stability and small pore diameter. The particles should have high exposed surface area resulting in high surface area for adsorption.

2.5.1 Boron Adsorption Models

Adsorption Isotherms are mathematical models used to illustrate the adsorption process.

These isotherms are empirical models whose parameters are only valid for the particular conditions under which the experiment was conducted. Boron adsorption has been widely investigated by agricultural scientists and to some extent by water and wastewater scientists.

Various modelling approaches have been used to describe boron adsorption. Historically, adsorption isotherm equations such as the Langmuir Isotherm and the Freundlich Isotherm provided descriptions of boron adsorption on soil minerals. Both the Langmuir model and the Freundlich model are empirical, since they provide a description of adsorbed data without theoretical bases.

The Langmuir Isotherm:

$$X = \frac{KCb}{1+KC}$$

Where, X is amount of adsorbed B (mg/g), C is the equilibrium B concentration (mg/ml), K is the constant related to bonding energy, ml/mg) and b is the maximum adsorption (mg B/g).

The Freundlich Isotherm:

$$X = KC^b$$

Where K and b are constants correlated with adsorption capacity and intensity, respectively.

Alleoni and Camargo [2000] found that boron adsorption can be adequately described with both Langmuir and Freundlich models. For Langmuir constants K (ml/mg) and b (mg/g) the values ranged from .0646 to 1.1653 and 2.4691 to 15.7854. For Freundlich, constant K varied from 0.4 to 4.84 and b from 0.2789 to 0.6818.

Arora and Chahal [2002] reported that Boron adsorption data can be fitted to the Freundlich equation. The linear form of the equation is given as under:

$$\log (x/m) = 1/n \log C + \log K$$

Where C is the equilibrium boron concentration ($\mu\text{g B ml}^{-1}$), x/m is the amount of B adsorbed per unit weight of the soil ($\mu\text{g g}^{-1}$), K and 1/n are constants which depend up on the nature of the adsorbate and the adsorbent. The values of the constants K and 1/n can be determined by plotting $\log x/m$ versus $\log C$. The plot should give a straight line if the data conforms to the Freundlich equation. K can be obtained from the intercept at unit concentration and 1/n is the slope of the plot. K and 1/n provides the estimate of adsorbent capacity and intensity of adsorption. The values of 1/n also indicate the degree of nonlinearity between solution concentration and adsorption.

3. RESEARCH DESIGN

3.1 Procedures

Fly ash and two types of fruit seed ash were tested in batch adsorption experiments. Measured amounts of ash (according to chosen Liquid/solid ratios; L/s ratios) were added to jars containing 50 mL seawater and then adjusted for pH. Samples of 4 ml were taken at 3-4 hr intervals over 2 days. The samples were filtered and then tested for boron. All experiments were performed at room temperature. Parameters tested were:

- Reaction time.
- Adsorbent dosage: The effect of adsorbent dose was examined by varying Liquid to solid. L/s ratios of 2, 5, 10, and 20 were used to study the effect of adsorbent amount.
- pH: The effect of pH was examined by studying different pH values of 7, 8 and 10.
- Particle size: Values of particle size were chosen as burnt uncrushed seeds, between 2.36mm and 1.18mm and, between 1.18mm and 600 μ m

Coagulant testing was conducted in jars while being continuously stirred with a mixer. After the coagulant was added to a set volume of seawater and adjustment of pH, solutions were rapidly mixed for 2 minutes at 180 rpm, followed by slow mixing for 30 min at 20 rpm to allow for flocculation. Filtered and unfiltered samples were taken after 30 minutes of slow mixing. The solutions were then left to settle for a further 30 minutes and more samples were taken. All samples were tested for boron concentration. The parameters studied were:

- Coagulant dosage: The effect of coagulant dose was examined by studying different dosage values. Values of coagulant dose were chosen as 2, 5, 10, 20, 40, and 60 mg/L.
- Effect of pH: This was examined by studying different pH values and the values of pH chosen were 5, 7, 8, 9 and 10.

3.2 Materials and Equipment

3.2.1 Sample Preparation

Seawater collected from the Indian Ocean near Perth (Western Australia) was used for all experiments. Fly ash was obtained from a local power plant in Western Australia and coagulants were prepared in the lab. Fruit seed ash was prepared in the laboratory. The seeds were burnt in a furnace at 500 and 800 °C, then crushed and separated using sieves according to particle size.

3.2.2 Chemicals and Reagents

All reagents were stored in polyethylene-polypropylene containers. Plastic ware was cleaned in dilute nitric acid (10% v/v) and dried at 60°C after rinsing with deionized water.

Reagent 1 – Ammonium Acetate Buffer

Dissolve 10g of Ammonium Acetate, 1g Ethylenediaminetetra acetic acid disodium salt (EDTA) and 2g Ascorbic acid in 50ml deionised water. This solution is stable for 1 week in a plastic bottle stored between 2 and 8°C.

Reagent 2 – Azomethine - H

Dissolve 180mg Azomethine-H and 0.4g Ascorbic acid in 20ml of deionized water. This solution is stable for 2 weeks in a plastic bottle between 2 and 8°C.

Stock Boron Standard – 1000mg/l B

Standard boron stock solution (1000 mg/L) was prepared by dissolving 5.716 g anhydrous boric acid (obtained from the MERCK Chemical Company) in 500ml of deionized water and diluted to 1 liter in a volumetric flask. The solution was stored in a polyethylene bottle.

3.2.3 Equipment

Boron content was determined using the AQUAKEM200 water analyzer. The measurement error was ± 0.2 and for every ten samples duplicate readings were done for two samples. Azomethine – H is reacted with the sample to form a coloured complex, which is measured spectrophotometrically at wavelength 405nm.

pH measurements were performed using HACH potable pH meter, measurement error was ± 0.1 .

Double distilled water was obtained from Barnstead Easypure UV- Compact ultra pure water system (18.3 ohm).

3.2.4 SEM and XRF Analysis

The scanning electron microscope (SEM) is an electron microscope that images the surface of a sample using high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms of the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity. Prior to analysis, the solid samples were sprinkled onto Al or C tapes, which are adhesive and supported on metallic disks. Images of the sample surfaces were recorded at different magnifications. SEM analysis was performed on samples before and after experimentation.

X-ray fluorescence (XRF) is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombardment with high-energy X-rays or gamma rays. The phenomenon is widely used for elemental analysis and chemical analysis, particularly in the investigation of metals, glass, ceramics and building materials, and for research in geochemistry, forensic science and archaeology. XRF analysis was conducted on the fly ash and fruit seed samples.

4. RESULTS AND DISCUSSION

Preliminary experiments were conducted in conjunction with Afrah Al-Ithari and after promising results further experiments and analysis were then conducted. Results of these experiments are presented and discussed below and have also been published in Ahmed et al. [2010], Afrah^a et al. [2011], Afrah^b et al. [2010], and Afrah^c et al. [2010].

4.1 Power Plant Fly Ash

The boron removal efficiency of power plant fly ash was observed over a period of 72 hours. The effect of adsorbent dose was observed by selecting different L/s ratios of 5, 10, and 20. The effect of pH was examined by studying pH values of 7, 8 and 10. Maximum removal efficiency recorded was with achieved with L/s=5, pH=10 at 26.5h. Table 4.1 presents the summary of results obtained with fly ash. As stated earlier boron removal efficiency expressed in percentage is the amount of boron removed from the initial amount:

$$\text{Boron removal efficiency} = \frac{\text{initial concentration} - \text{final concentration}}{\text{initial concentration}}$$

Table 4.1.1 Summary of results with fly ash

Contact time (h)		2.5	5.5	13	17	21.5	26.5	41.5	44.5	48	72
pH	L/s	Removal efficiency (%)									
7	5	8.10	11.08	5.92	9.99	4.81	8.58	10.50	5.01	8.53	9.28
8	5	6.27	9.11	11.26	8.75	6.68	12.07	11.18	9.11	5.21	8.55
10	5	18.57	22.94	21.02	20.92	22.36	25.20	21.50	21.22	19.43	17.99
7	10	8.96	9.33	11.23	11.51	11.43	7.03	12.75	12.50	10.68	11.54
8	10	10.52	11.03	14.77	13.28	12.04	12.47	17.03	14.93	10.45	14.67
10	10	9.61	13.00	17.56	14.75	12.75	10.07	14.37	15.68	14.47	16.11
7	20	9.41	8.12	10.93	12.09	11.36	12.29	6.98	12.72	11.74	11.26
8	20	10.52	11.56	7.72	12.65	11.69	9.31	10.73	15.38	15.91	13.76
10	20	15.89	11.84	10.37	15.13	15.36	13.86	11.54	15.41	14.44	13.81

XRF Analysis

The low removal percentages achieved from the tests is believed to be due to the type of the fly ash used. Polat et al. [2004] performed studies with several types of fly ash in which they proposed that the reaction of Ca-rich fly ash with Mg-rich seawater causes co-precipitation of magnesium hydroxide in which boron is co-precipitated. Of the fly ash that they tested, the Yenikoy fly-ash was found to produce the highest boron removal. According to XRF analysis, the fly ash used in these studies were mainly silica based and contained much lower amounts of CaO (1.78%) compared to the Yenikoy fly ash studied by Polat. This could support the theory of Ca-rich fly ash causing the co-precipitation of boron from seawater. Further tests should be done in order to justify this. The chemical composition of the fly ash used in this study and the Yenikoy fly ash by Polat are shown in the table below.

Table 4.1.2 Chemical Composition of Fly ash – XRF results

Component	Sample Percentage (%)	
	WA	Yenikoy
SiO ₂	49.50	5.11
Al ₂ O ₃	28.10	2.13
CaO	1.78	55.38
Fe ₂ O ₃	12.20	0.80
K ₂ O	0.56	0.00
MgO	0.94	2.18
Na ₂ O	0.34	0.00
P ₂ O ₅	2.59	0.00
SO ₃	0.29	20.26
TiO ₂	1.52	0.06
BaO	0.43	0.00
SrO	0.47	0.00
ZrO ₂	0.10	0.00

4.1.1 Effect of Reaction Time

The effect of reaction time was examined by taking samples at hourly intervals over 72 hours. The results from the test were inconclusive with no clear trends and varied randomly with time. There were no apparent trends in either L/s ratio or pH. The removal of boron increased and decreased between the values of 5-25% over the 3 day period. It is suspected that the inconclusive results were due to the experiments being batch tests which allowed for continuous adsorption and desorption of boron between seawater and fly ash. Another factor that may have contributed to the results was the nature of the consistency of the seawater and fly ash solution being fairly heterogeneous and so boron levels may have varied throughout the solution. It is recommended that any further studies be conducted as column tests to avoid these problems. Figure 4.1.1 illustrates the effect of reaction time on removal efficiency.

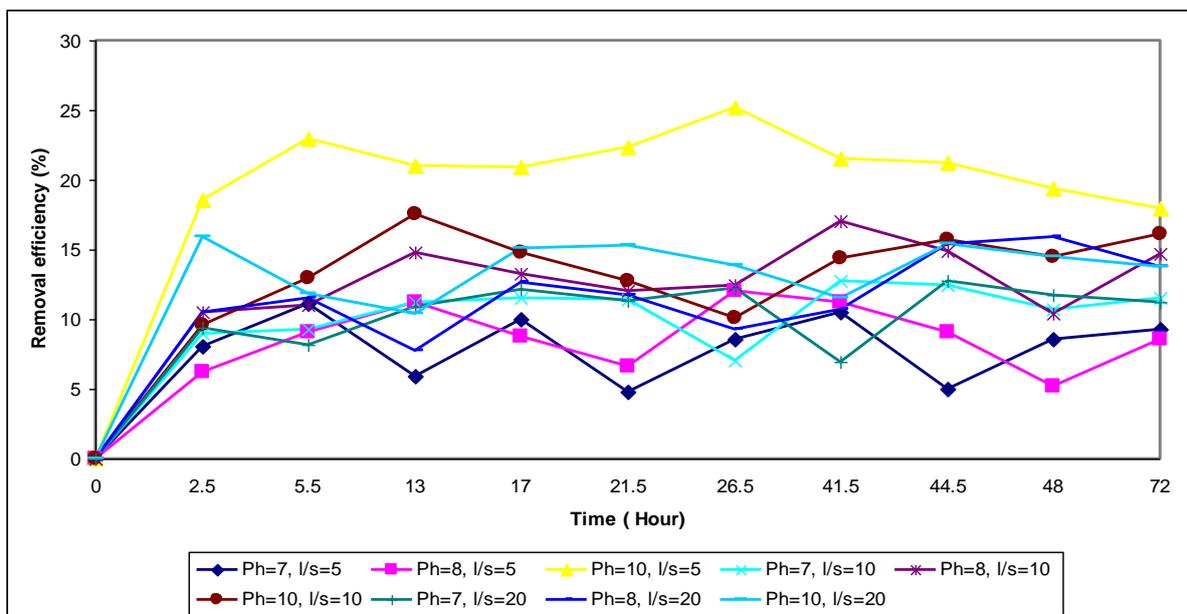


Figure 4.1.1 Boron removal efficiency of fly ash over time

4.1.2 Effect of Adsorbent Dose

The effects of different adsorbent dosages were applied to 50 mL by used different L/s ratio 5, 10, and 20 in order to find out the effect of adsorbent dosage to boron removal. No clear trends for the effect of adsorbent dose could be discerned from the results. Figure 4.1.2, illustrates the effect of the different L/s ratio for pH=7.

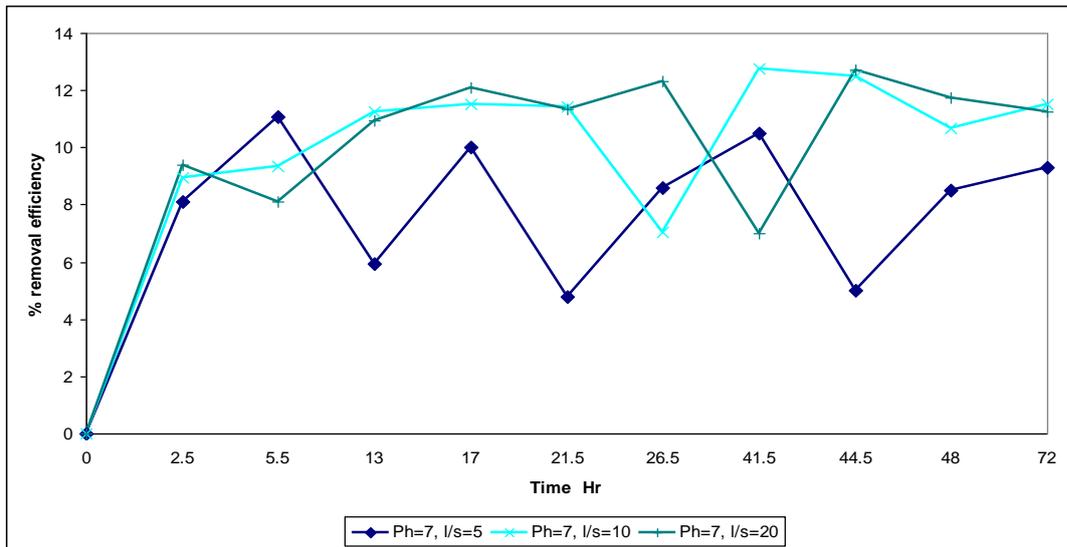


Figure 4.1.2 Effect of adsorbent dose on boron removal efficiency, pH=7

4.1.3 Effect of pH

The effect of pH was examined by studying different values. An increase in pH seemed to slightly improve boron removal efficiency but the results were too inconclusive to make any proper deductions. Figure 4.1.3, illustrates the effect of different pH values (7, 8, and 10) with $L/s=10$.

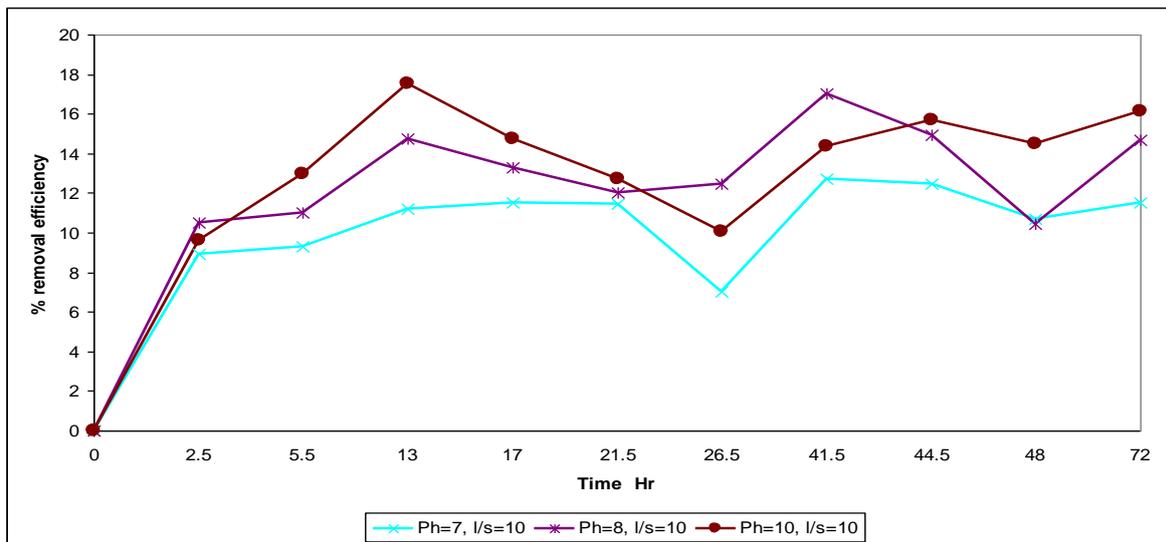


Figure 4.1.3 Effect of pH on boron removal efficiency, $L/s=10$

4.2 Fruit Seed Ash 1

Table 4.2 presents the summary of removal efficiencies with fruit seeds after 24 hr reaction time. Maximum removal efficiency was recorded as 73.08% with L/s =2, pH=7 at 24hr. Unlike the fly ash experiments previously, the fruit seed ash showed very clear and consistent results in relation to the variables tested. It is possible that the process of boron desorption back into the seawater was inactive or very low. It would be interesting to see the outcomes of regeneration studies on the fruit seed ash.

Table 4.2 Summary of results with fruit seed ash 1

pH	L/s	Boron Removal Efficiency (%)
7	2	73.08
8	2	69.85
7	5	71.06
8	5	58.13
10	5	48.04
7	10	26.64
8	10	49.33
10	10	40.30
7	20	38.91
8	20	30.71
10	20	28.81

4.2.1 SEM Analysis of Fruit Seed Ash 1

After the experiments the crushed seeds were put through an SEM study and one of the resulting images is shown in figure 4.2.1. The images showed no boron and so it was not possible to precisely determine a mechanism for boron adsorption. This is most likely due to the fact that the concentration of boron in our experiments were kept at seawater level which is relatively low and as such would be in too minute levels to distinguish any boron. The peaks of Ca found in spectrum 1 and 2 could indicate the involvement of calcium in the removal of boron as mentioned previously in the experiments with fly ash and those done by Polat et al. [2004]. Future experiments should be conducted with various concentrations of boron (at a much higher concentration than seawater) and with extra focus on calcium levels to identify the process by which boron is absorbed.

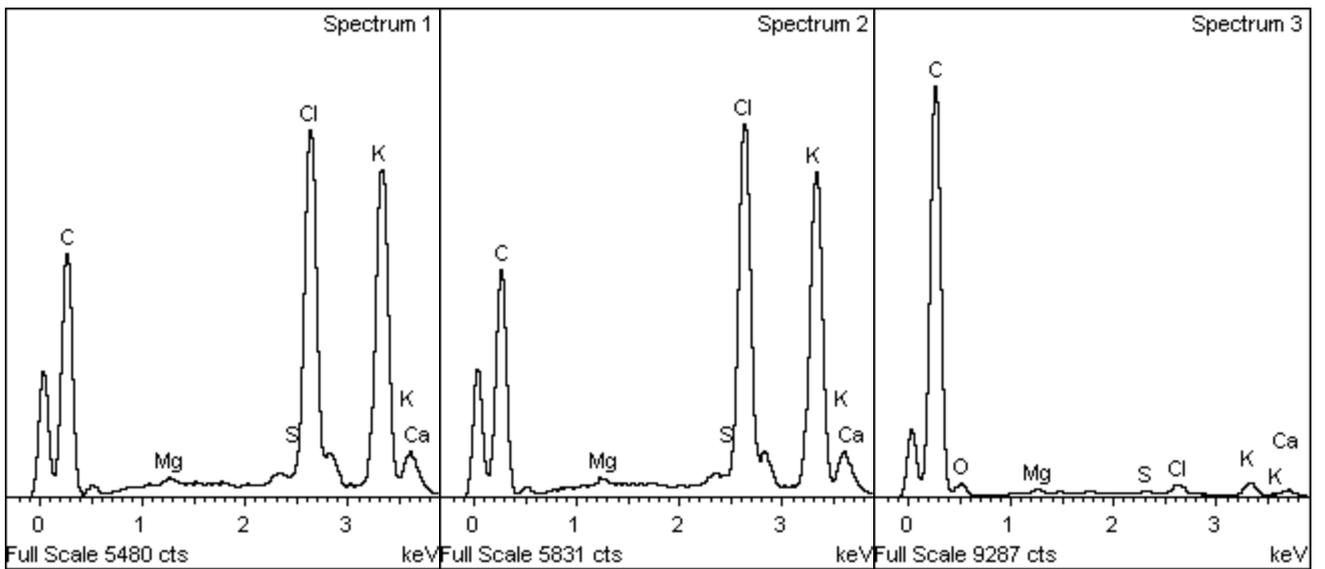
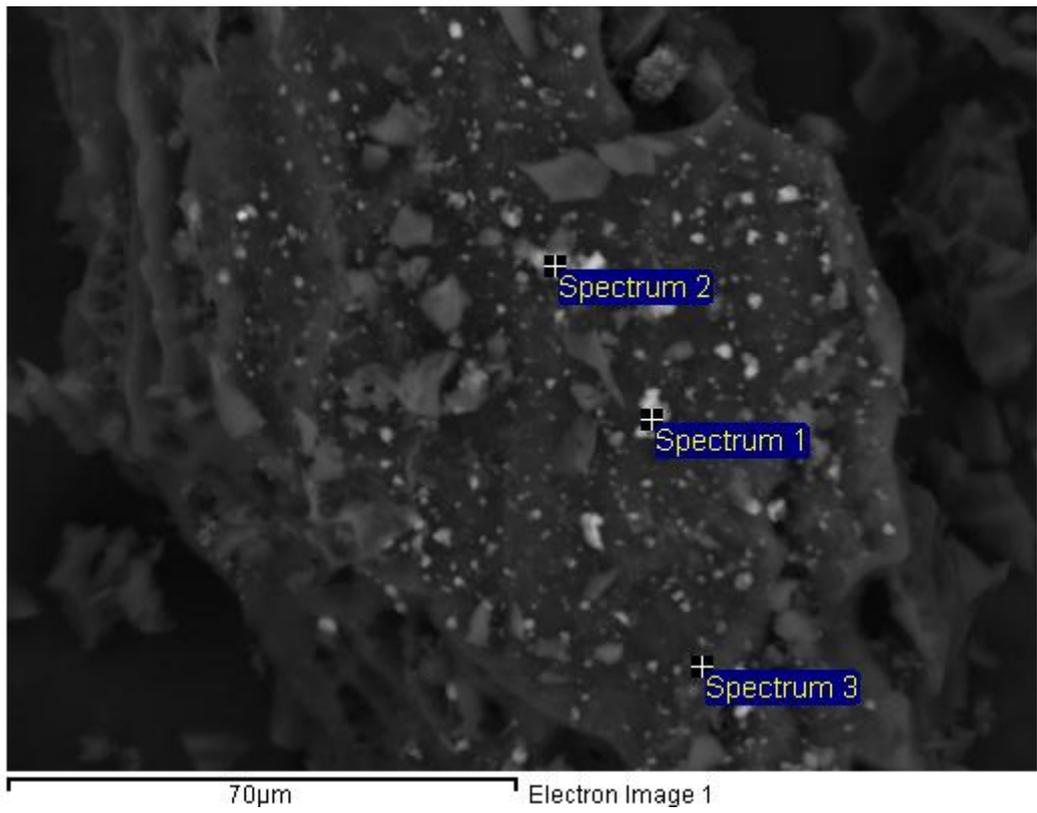


Figure 4.2.1 SEM image of fruit seed ash 1

4.2.2 Effect of Reaction Time

The effect of reaction time was examined by studying different sampling times. Samples were taken at three hour intervals. It is clear from Figure 4.2.2 that for all different conditions used, boron removal increased with reaction time the maximum removal recorded for 24 hr reaction time. Removal efficiencies showed relatively steady increase over time. Table 4.2.2 presents the summary of results obtained with Fruit seed ash after 24 hr reaction time.

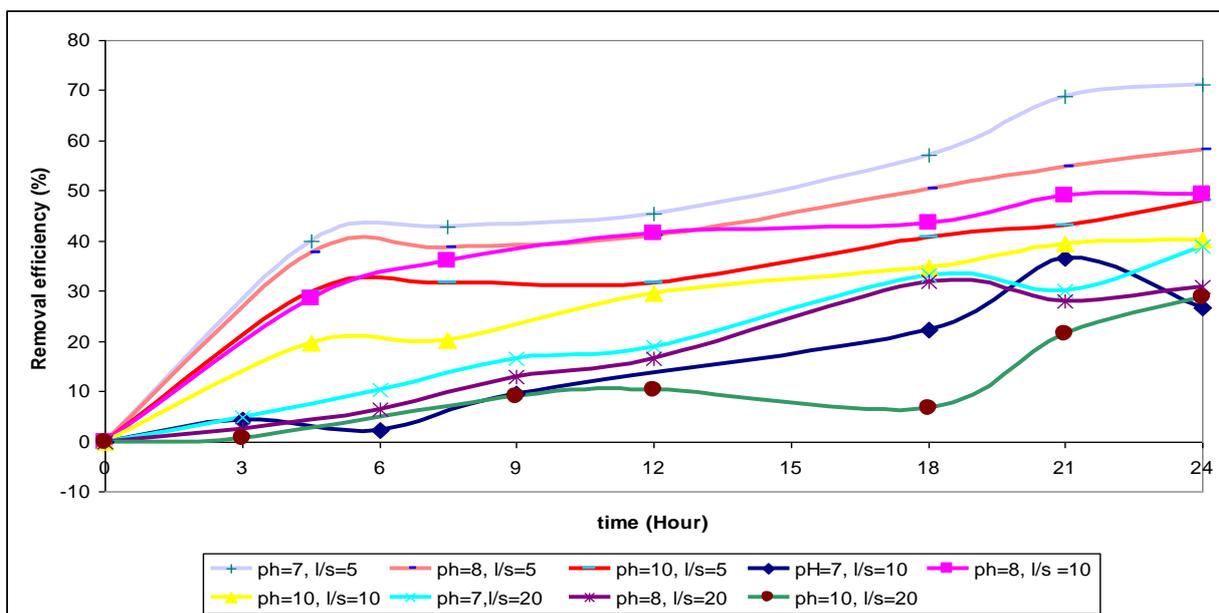


Figure 4.2.2 Boron removal efficiency of fruit seed ash 1 over time

4.2.3 Effect of Adsorbent Dose

Adsorbent dosages were chosen according to L/s ratios of 2, 5, and 10. The results showed a very clear effect of adsorbent dosage while using fruit seed ash. By increasing adsorbent dosage, boron removal increased with removal efficiency reaching a value of 73% at L/s value of 2 after 24 hrs. Even with lower adsorbent dosages, boron removal was higher than the other two methods studied, with L/s ratios of 5 and 10 resulting in lowest removal efficiencies of 48 and 27% respectively. All tests showed a fairly steady increase in boron removal with time. The results for the neutral solution (pH=7) are presented in Figure 4.2.3.

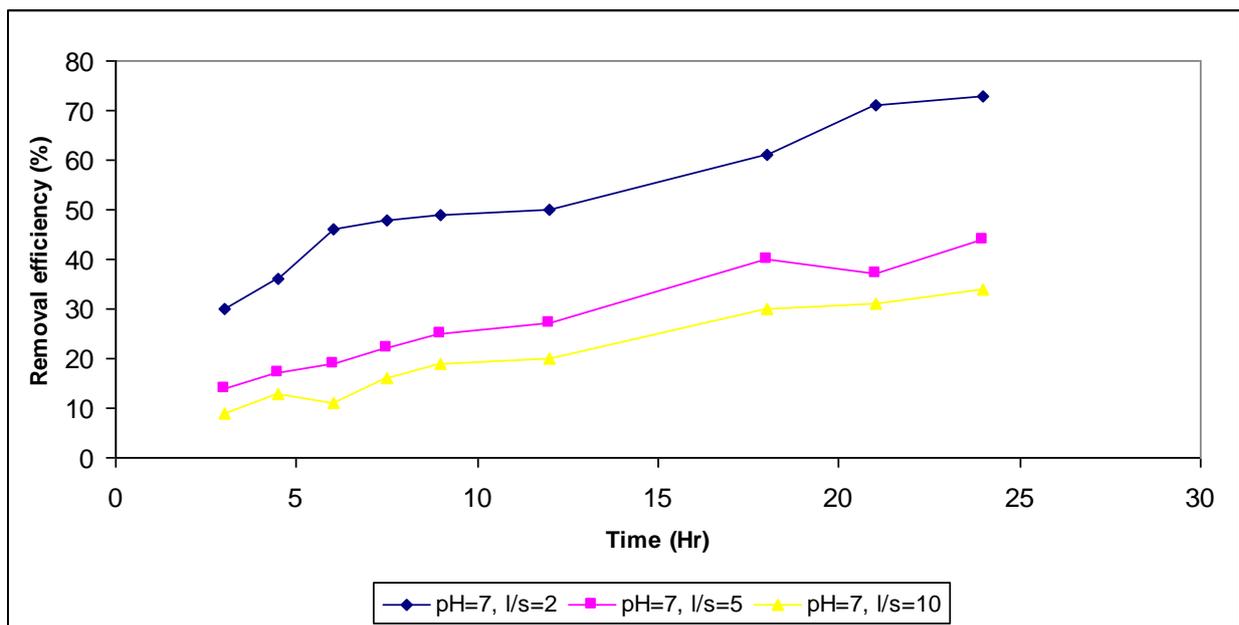


Figure 4.2.3 Effect of adsorbent dose on boron removal of fruit seed ash 1, pH=7

4.2.4 Effect of pH

To evaluate the effect of pH, the test samples were adjusted to selected values of 7, 8 and 10. Figure 4.2.4 shows the boron removal efficiency for solution with a value of L/s of 2. The results from the figure show a definite trend for the effect of pH on boron removal. At 24 hours removal efficiency reaches a maximum of 73% with pH of 7. Higher pH of 8 and 10 resulted in noticeably lower removal efficiencies of 63% and 53% respectively. Most of the coagulants [Turek et al., 2007] and adsorbents studied for boron removal required an alkaline pH in the range of 9-10 for maximum efficiency. Such pH values will definitely increase scaling propensities in RO membranes. The fact that neutral pH yielded highest possible removal efficiency is an excellent outcome. The results are a promising indication of the effectiveness of fruit seed fly ash over many known other adsorbents tested to date [Turek et al., 2007; Polat et al., 2004; Glueckstern et al., 2003; Kabay et al., 2010; Nadav, 1999; Melnik et al., 1999)] Furthermore the fact that fruit seed ash is a low cost material will provide incentive for further research and possible incorporation into a viable pre-treatment option.

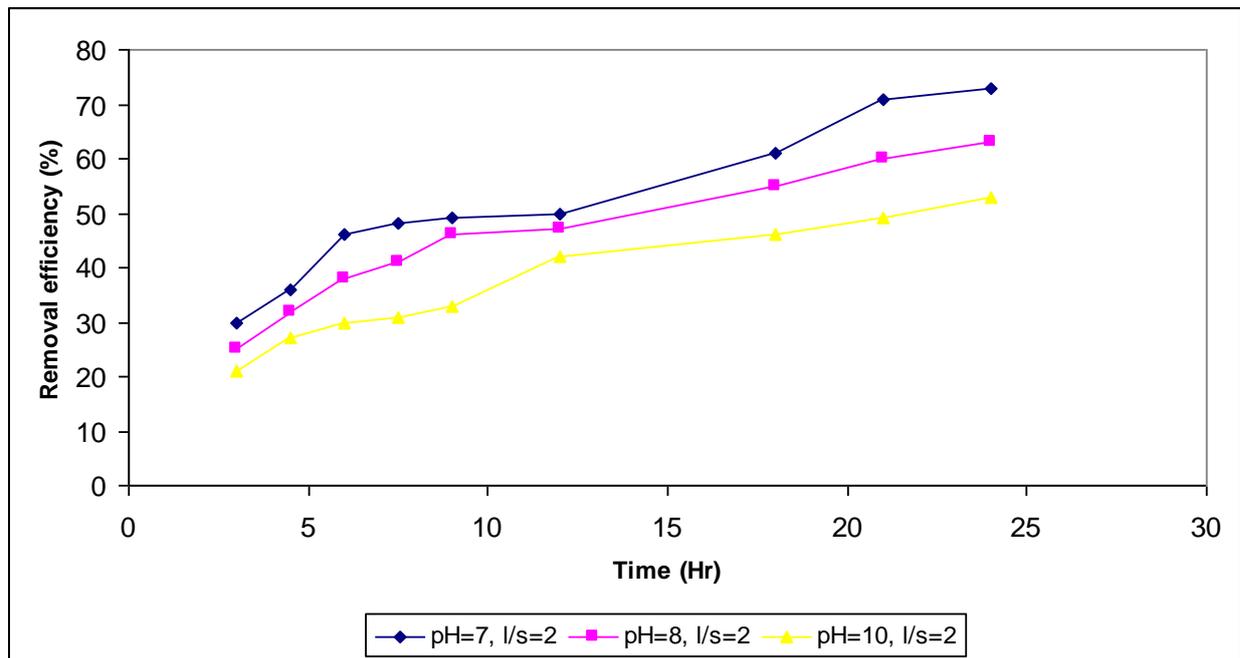


Figure 4.2.4 Effect of pH on boron removal efficiency of fruit seed ash 1, L/s=2

4.2.5 Effect of Particle Size

The test was performed with constant $L/s=5$ and $pH=7$ with various settling times to study the effect of particle size on boron removal efficiency. Values of particle size were chosen as uncrushed seeds, particles between 2.36mm and 1.18mm and, particles between 1.18mm and 600 μm . It was found that the removal efficiency increased when particle size was smaller. This would be because of the contact surface area being effectively larger.

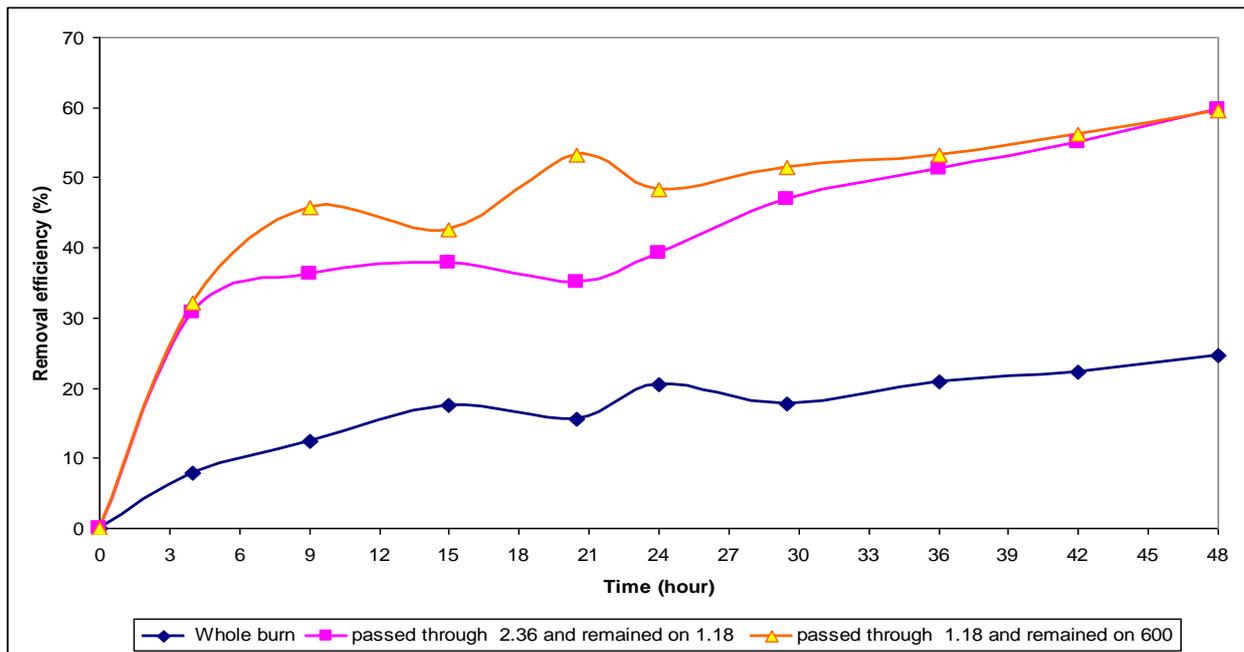


Figure 4.2.5: Effect of particle size on boron removal efficiency of fruit seed ash 1, $L/s=5$, $pH=7$

4.3 Fruit Seed Ash 2

Table 4.3 presents the summary of removal efficiencies with fruit seed ash 2 after 24 hr reaction time. Maximum removal efficiency was recorded as 25.16% with L/s=5, pH=10 at 24hr.

Table 4.3 Summary of results with fruit seed ash 2

pH	L/s	Boron Removal Efficiency (%)
7	5	11.02
8	5	12.02
10	5	25.16
7	10	11.47
8	10	14.73
10	10	17.51
7	20	12.05
8	20	12.60
10	20	14.40

4.3.1 SEM Analysis of Fruit Seed Ash 2

After the experiments the crushed seeds were put through an SEM study. Unfortunately the results were similar to fruit seed ash 1 and it was not possible to determine a mechanism for boron adsorption. As stated earlier this is most likely due to the fact that the concentration of boron in our experiments were kept at seawater level which is relatively low and as such would be in too minute levels to distinguish any boron. It is interesting to point out that there was no indication of Ca in the samples which further support the involvement of Ca in boron removal from seawater. Future studies should be similar to that suggested for fruit seed ash 1.

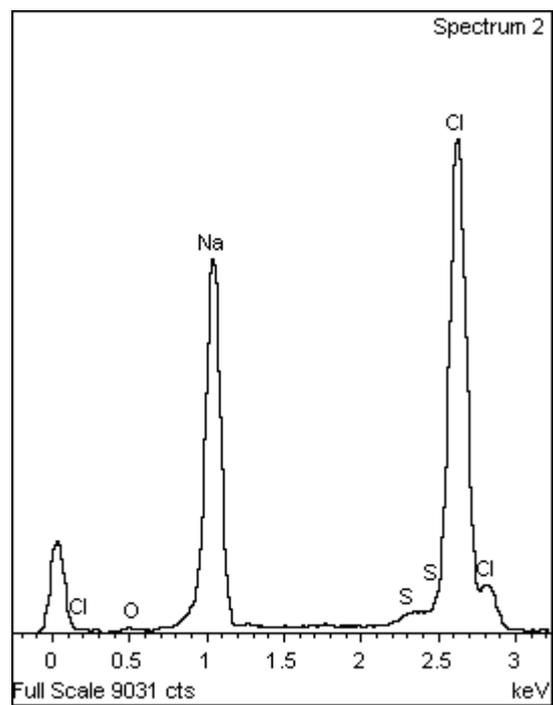
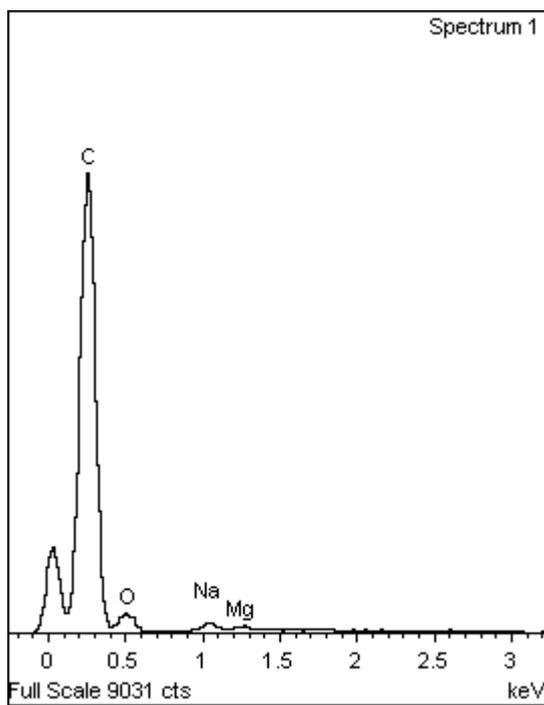
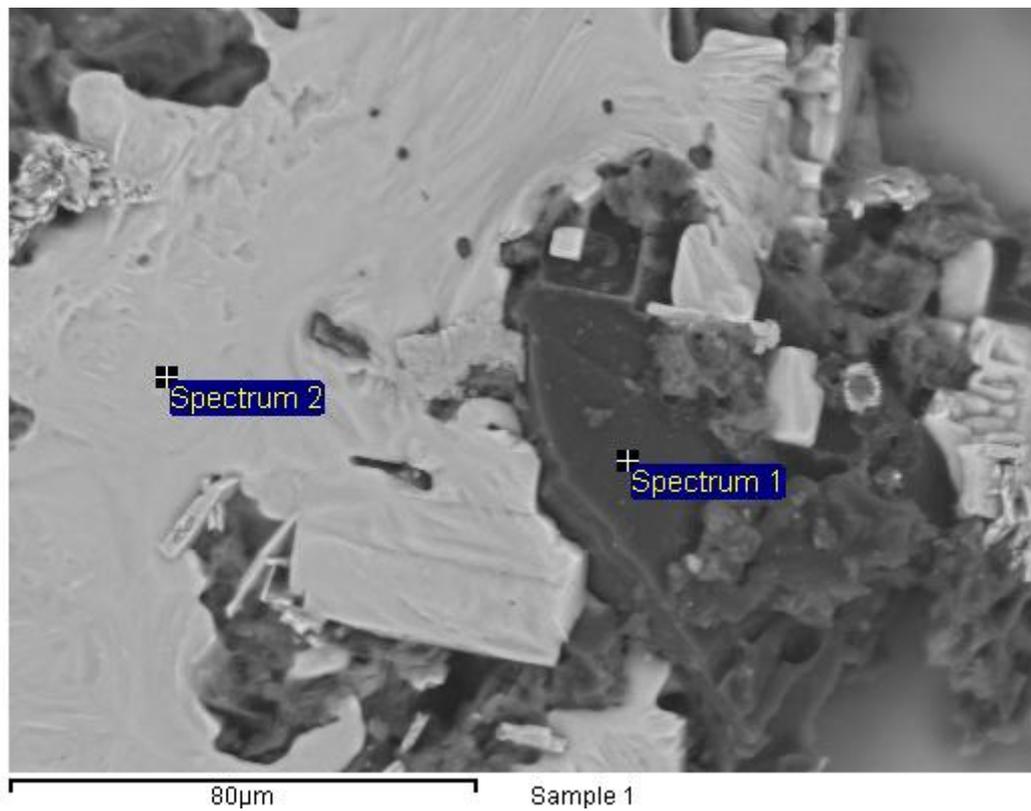


Figure 4.3.1 SEM image of fruit seed ash 2

4.3.2 Effect of Reaction Time

The effect of reaction time was examined by studying different sampling times. Samples were taken at three hour intervals. There were no apparent trends in either L/s ratio or pH. The removal of boron increased and decreased between the values of 2-25% over the 48 hour period. It is suspected that the inconclusive results were due to the experiments being batch tests which allowed for continuous adsorption and desorption of boron between seawater and fruit seed ash. It is recommended that any further studies be conducted as column tests to avoid these problems. Figure 4.3.2 presents the summary of results obtained with Fruit seed ash after 48 hour reaction time.

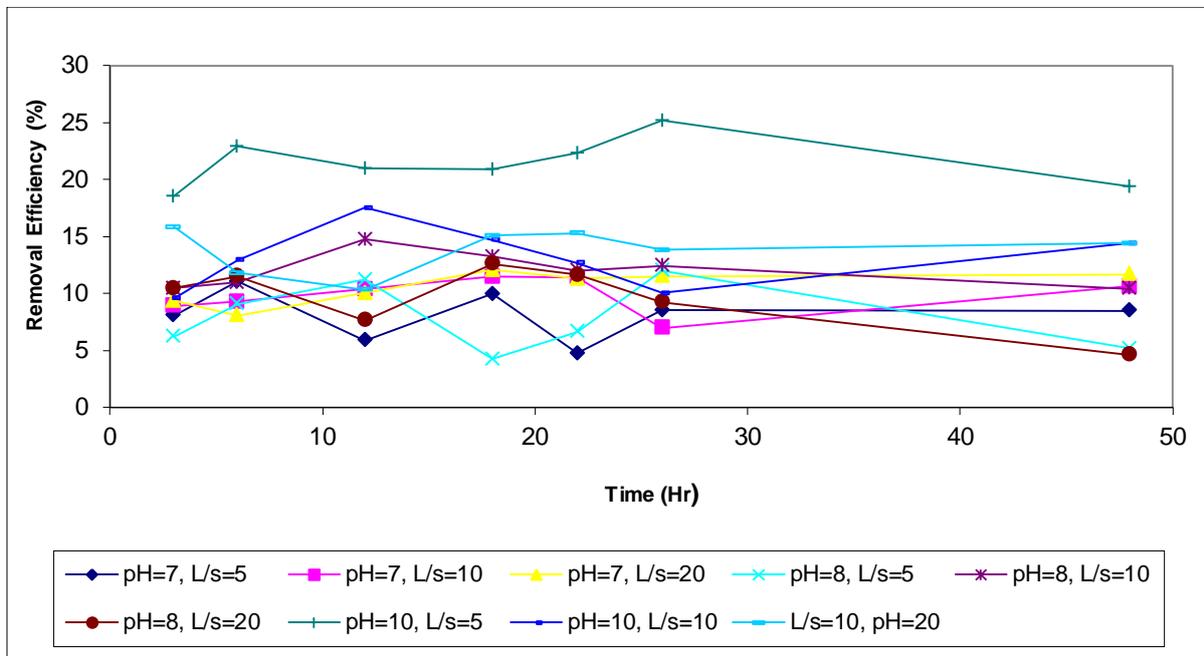


Figure 4.3.2: Boron removal efficiency of fruit seed ash 2 over time

4.3.3 Effect of Adsorbent Dose

Adsorbent dosages were chosen according to L/s ratios of 5,10,20. No clear trends for the effect of adsorbent dose were able to be discerned from the results. The results for the neutral solution (pH=7) are presented in figure 4.3.3.

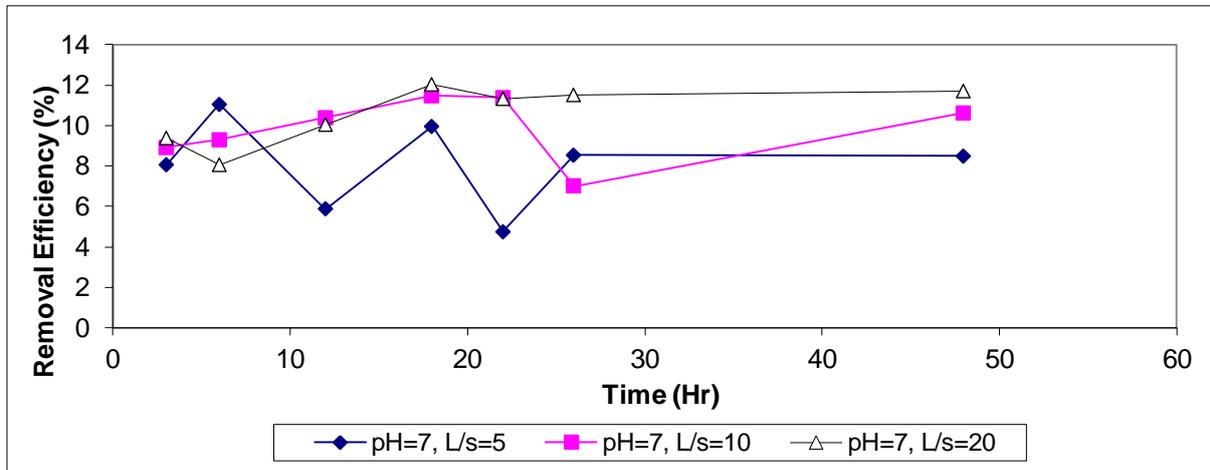


Figure 4.3.3: Effect of adsorbent dose on boron removal efficiency of fruit seed ash 2, pH=7

4.3.4 Effect of pH

To evaluate the effect of pH, the samples were adjusted to selected values of 7, 8 and 10. An increase in pH seemed to improve the boron removal efficiency. The results for L/s=2 are presented in Figure 4.3.4.

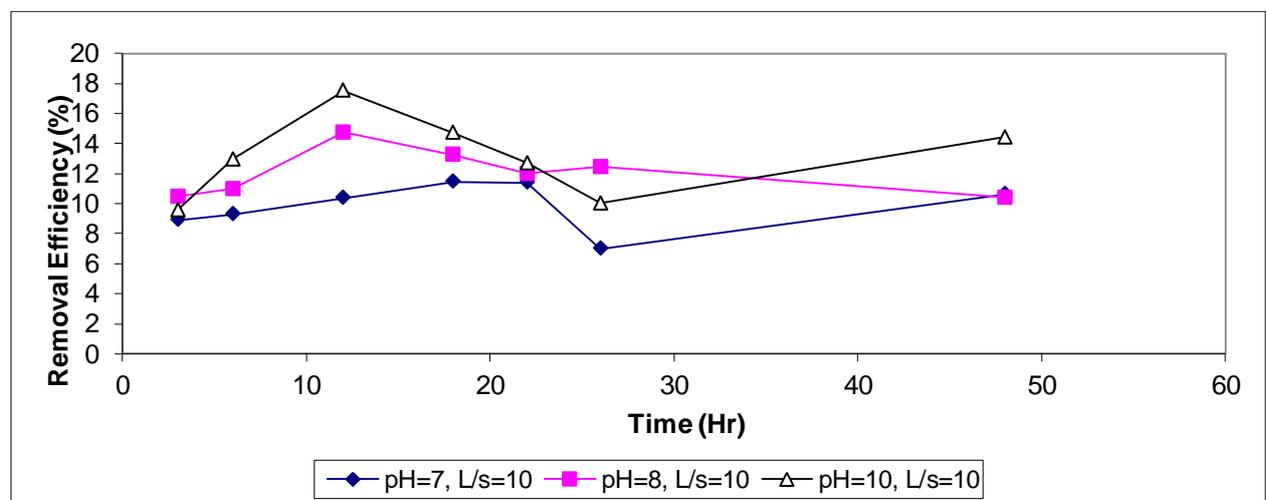


Figure 4.3.4: Effect of pH on boron removal efficiency of fruit seed ash 2, L/s=10

4.4 Coagulant

To study the effect of ferric chloride on boron removal coagulant doses, concentrations and pH were varied and both filtered and unfiltered samples were tested. The results correspond with the results achieved by Yilmaz [2007] in his experiments studying chemical coagulation and electrocoagulation. A summary of the results is presented in table 4.4.

Table 4.4 Summary of results with coagulant

Settling time	pH	Coagulant dose mg/L	Maximum removal efficiency %
30 min. filtered	5	60	6.60
30 min. unfiltered	5	60	6.22
30 min. filtered	7	60	14.8
30 min. unfiltered	7	60	13.76
30 min. filtered	8	60	26.46*
30 min. unfiltered	8	60	17.28
30 min. filtered	9	60	11.36
30 min. unfiltered	9	60	3.31
30 min. filtered	10	60	11.46
30 min. unfiltered	10	60	10.24

4.4.1 Effect of Coagulant Dose

The selected concentrations were chosen as 2, 5, 10, 20, 40 and 60 mg/L and the pH was maintained at 7. Filtered and unfiltered samples were taken after 30 min settling time. The results showed a clear trend when increasing coagulant dose, with removal efficiency reaching 15% with the highest coagulant dose of 60mg/L. There was no further removal with additional settling time. A slight increase of about 2% is apparent between filtered and unfiltered samples. This can be attributed to boron being removed with the sediment when it was filtered out of the sample. The increasing trend indicates that adsorption is majorly reliant on coagulant dose in the range that was studied. It is unknown whether further increase in coagulant dose would result in a similar correlating increase in removal efficiency or whether other limiting factors would come into play. The results are presented in Figure 4.4.1.

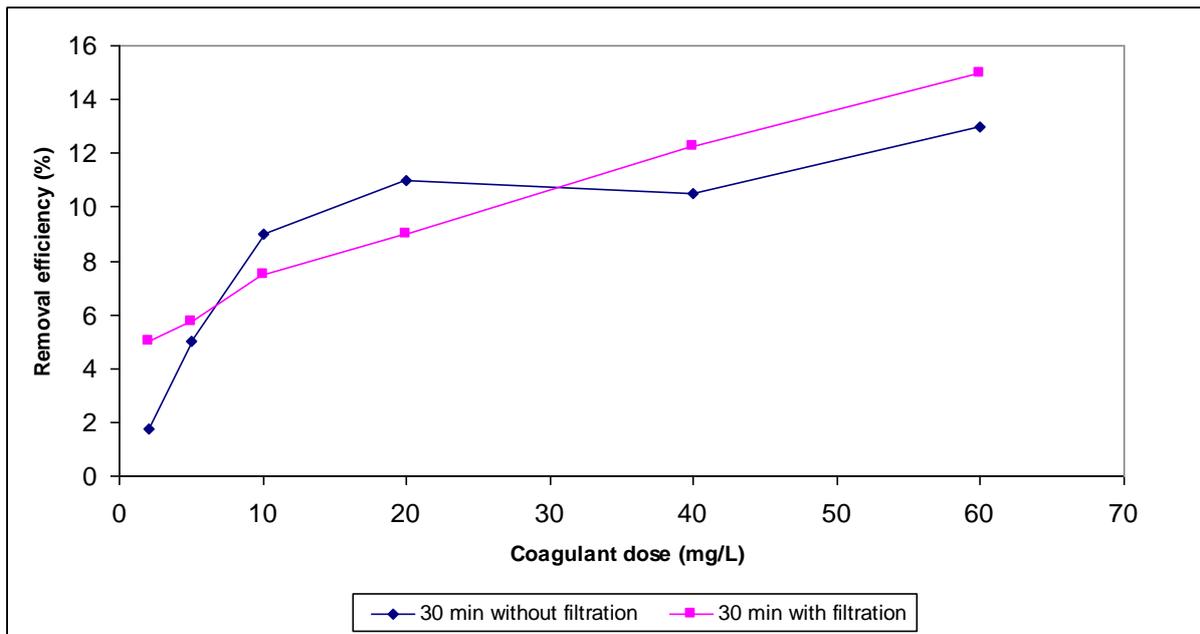


Figure 4.4.1 Effect of coagulant dose for coagulant with pH=7

4.4.2 Effect of pH

In the literature, it has been reported that pH can have significant effect on boron removal efficiency of coagulants due to change in speciation of boron containing inorganic compounds. It is especially reported that at higher pH, the removal efficiencies will improve. To evaluate the effect of pH, the test samples were adjusted to selected values of varying pH of 5, 7, 8, 9 and 10. The results showed no conclusive findings for the effect of pH on boron removal with ferric chloride. This may be due to the coagulant dose acting as a limiting factor for boron adsorption.

5. CONCLUSIONS

In this study the removal efficiency of boron from seawater with fly ash, fruit seed ash and coagulants were evaluated. All three methods tested showed boron removal, with fruit seed ash showing the largest removal efficiency in comparison with that of the coagulant and power plant fly ash, as shown in Table 5.1.

Table 5.1 Comparison of maximum removal efficiencies for the tested methods

Method	pH	Dosage	Contact time	Boron removal (%)
Fruit seed ash 1	7	L/s = 2	24 hr	73.08
Fruit seed ash 2	10	L/s = 5	24 hr	25.16
Fly ash	10	L/s = 5	26.5 hr	25.20
Coagulant	8	60mg/L	30 min	26.46

The low removal percentages achieved from the fly ash tests are believed to be due to the type of the fly ash used and possible desorption of boron back into the seawater. It is believed that the involvement of calcium in relation to boron removal was indicated in the experiments with fly-ash and fruit seed ash 1 and 2. It was not clear why fruit seed ash 2 showed low boron removal other than absence of calcium. Further tests need to be carried out to identify the causes of low boron removal efficiency of fruit seed ash 2. The results of coagulant testing correspond with studies done by Yilmaz [2007] in his experiments comparing chemical coagulation and electrocoagulation.

Optimum removal efficiency was found to be with fruit seed ash 1 with parameters of pH=7 and L/s=2 resulting in 73% removal efficiency. This is remarkably higher than with that of the power plant fly ash, fruit seed ash 2 or coagulant used. The results from the present work are considered be of particularly significant as the fruit seed ash 1 showed highest removal efficiencies at pH of 7. A neutral pH is very important in RO processes which would enable better membrane stability and minimum membrane scaling, thus leading to less maintenance and lower operating costs.

5.1 Proposed Future Studies

Based on the preliminary findings it is evident that the use of fruit seed ash for boron removal is a potentially viable method for the use in commercial applications. This needs to be confirmed further using column experiments prior to tests in laboratory scale followed by pilot trials in RO units. The activities carried out in a systematic would pave the way for the implementation of these techniques in practical RO plants. Some of the proposed activities in this area of research requiring further attention include:

- Column tests with several types of fruit seed ash samples
- Studies focusing specifically on the involvement on calcium in the removal of boron and other mechanistic studies
- Introduction of additional parameters such as initial boron concentration and temperature
- Continuous mixing while conducting ash experiments
- Regeneration strategies for the re-use of residual ash after boron pre-treatment
- Addressing the impact of the substrate material on the overall quality of water
- Cost effectiveness and commercial viability of methods, especially with the use of fruit seed ash
- Identifying the best fit parameters (Langmuir or Freundlich model) for fruit seed ash

If the above-mentioned activities show successful results, remediation strategies can be formulated for potential implementation in full-scale RO units for the removal of boron in seawater.

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