Boron Removal Through Precipitation Process in Produced Water

by

Jivendra A/L Vadiveloo

17005668

Dissertation submitted in partial fulfilment of the requirements for the

Bachelor of Engineering (Hons)

(Civil and Environmental Engineering)

JANUARY 2022

Universiti Teknologi PETRONAS,

32610, Bandar Seri Iskandar,

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Automated Defects Detection Model for IBS Elements considering IR 4.0 Application Environment

by

Jivendra A/L Vadiveloo

17005668

A project dissertation submitted to the

Civil Engineering Programme

Universiti Teknologi PETRONAS

in partial fulfilment of the requirement for the

BACHELOR OF CIVIL ENGINEERING WITH HONOURS

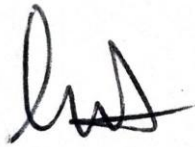Approved by,

_____

(Dr Ho Yeek Chia)

UNIVERSITI TEKNOLOGI PETRONAS

SERI ISKANDAR, PERAK

January 2022

I

Certificate of Originality

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

_____

JIVENDRA A/L VADIVELOO

ABSTRACT

The amount of boron in the water generated is quite high. When oil and gas are drilled, they bring water with them, which is known as "produced water." As a result, it comprises both the formation's characteristics and the hydrocarbon itself. Simply put, if the boron content in the generated water is not appropriately eliminated, the water will be useless. Potable water must have a boron content of 0.5 mg/L to meet World Health Organization (WHO) recommendations for its release into the environment. There are a variety of ways to remove boron from the water that is generated. Boreal molecular weight and its ionic dissociation constant have been observed to hinder its use. Because boron compounds are considered to be of second-class toxicological threat by medico-biological studies, the health consequences of boron ingestion are substantial. There are several applications for the toxic metal, including as health supplements and industrial items, that are useful to human life and the economy. As a part of this study, researchers want to not only remove, but also recover, boron from the water that is created by the precipitation process of calcium hydroxide, calcium carbonate and oxalic acid in general.

Table of Contents

List of Figures

List of Tables

CHAPTER 1

INTRODUCTION

1.1 Background

Water that is extracted in conjunction with oil and gas production is known as "produced water." Submarine forces sculpted the geology of the world's oil and natural gas reserves. The common formation type are sand stones by sand settling from vast streams and rivers and limestones from by settling shells and marine life. These sedimentary rock formations are porous, and the porous phases are filled with water from which the solid particle precipitated. The porous rock layer alternate with non-porous rock formed form very fine particles of silt and clay that settle from slow flowing waters (Zelmanov & Semiat, 2014). Organic materials from plant and animal life also precipitates from the water. Over very long periods of time and under the effect of bacteria, great pressure and temperature this organic material is converted into oil and natural gas inside the porous sandstone and limestone reservoirs. The oil and gas are less dense than the water in the formation and migrate upward in the reservoir.

During oil and gas extraction, water rises to fill up the void left by the removal of oil and gas from the reservoir, ultimately bringing both to the surface. Produced water refers to the water extracted from the reservoir. Enhanced Oil Recovery (EOR) operations typically reintroduce produced water from onshore wells back into the producing reservoir (Ezechi et al., 2015).

1

Many substances from the manufacturing process end up in produced water, including soluble and non-soluble organics, suspended particles, and dissolved solids. A high level of boron is present in this water because it has been in touch with hydrocarbon deposits for such an extended period of time. As a result, the water generated is unfit for human consumption as shown in Figure 1 below of the process of produced water in production of oil and gas.
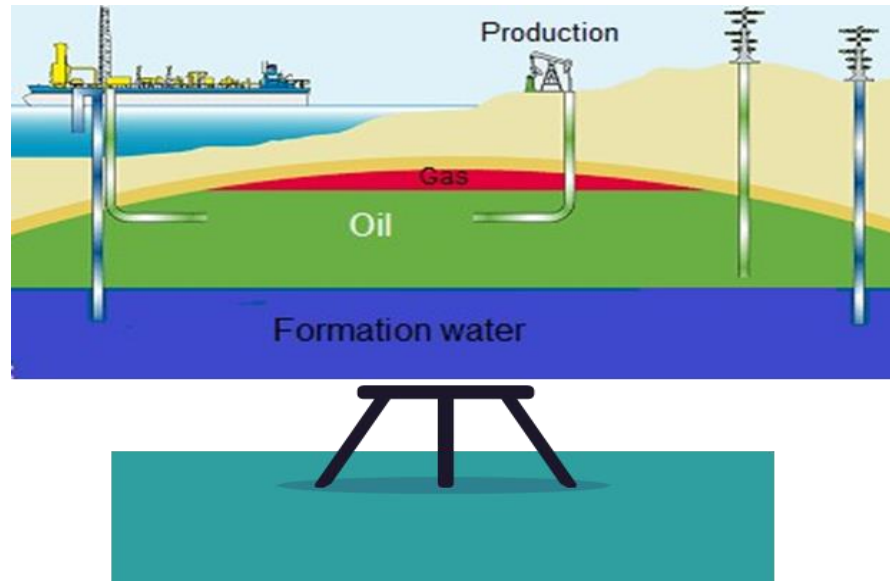
FIGURE 1: BORON FROM PRODUCED WATER

1.2 Problem statement

A boron content of 0.5 mg/L has been specified by the World Health Organization (WHO) as a guideline for potable water outflow. Because large concentrations of boron in water may be hazardous to aquatic creatures, animals, and people, we must remove it from generated water. Boron is not considered as a dietary requirement even though the human body contains about 0.7 ppm of boron. There is boron present in food, yet the amount present in fruits and vegetables are below the toxicity boundary (Wang et al.,

2016). It became dangerous if the intake of boric acid is more than 5g at a rate of daily intake which will cause nausea, vomiting, diarrhoea, and blood clotting.

Even though there are bad adverse effects of boron as shown in Figure 2, there are many applications of boron in human life. For example, Pyrex, ceramics, agriculture, detergents, bleaches, manufacturing of bullet proof vest, as a nutrients factor for plants. Borax which is a mixture of chemical composition which contains boron is also used in making enamels and paints. On the other hand, orthoboric acid made from boron is also used as mild antiseptic. Boron-10 isotopes could also be used in nuclear industry as a protective shield in form of metal borides (Zhang et al., 2016).

Since it can benefit us and at the same time could harm us in by giving adverse effects to our health, it is best to remove the element from produced water to benefit from both the water and the element boron for the environment and human life. With the use of calcium hydroxide and the other precipitation agents mentioned above, the
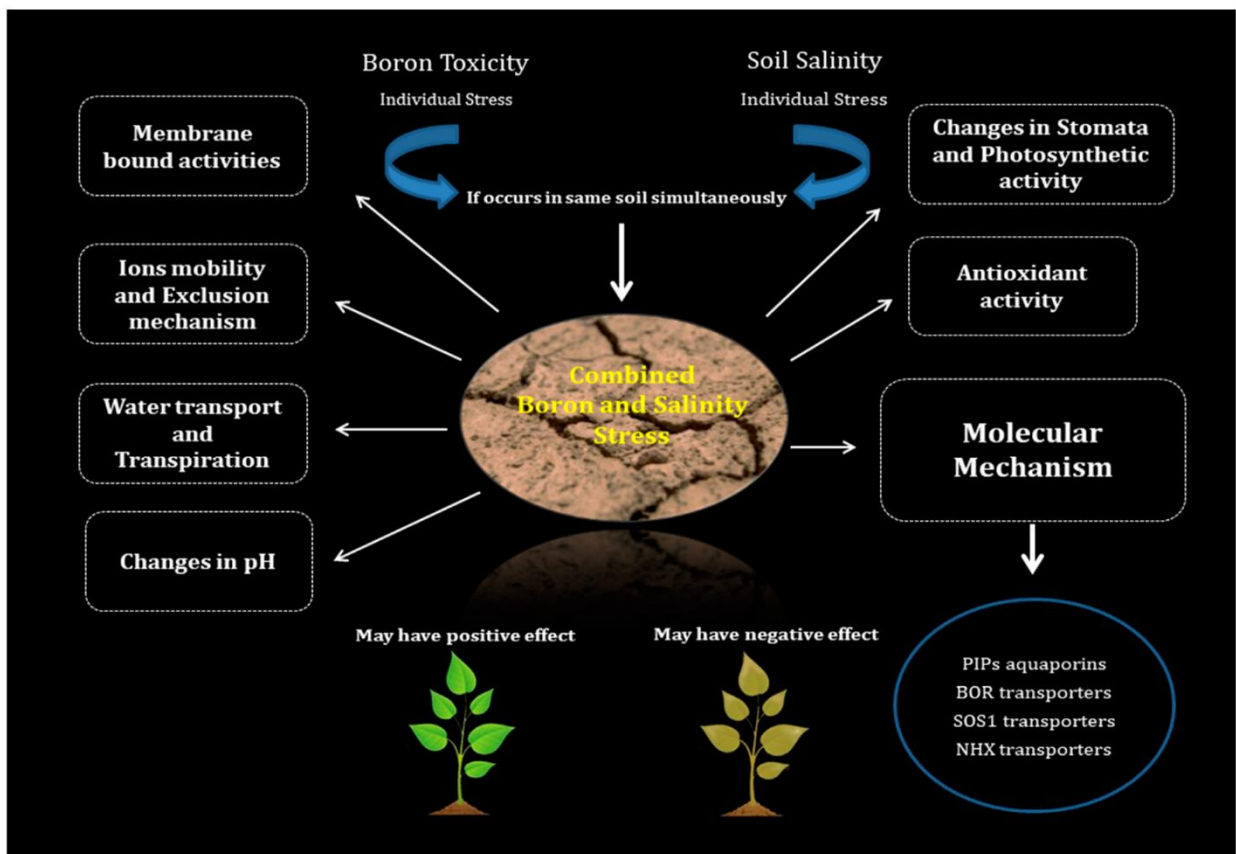

FIGURE 2: BORON TOXICITY

of the generated water may be greatly reduced and boron can also be recovered (Kürklüet al., 2017). For this experiment, we need to know the pH value, temperature, boron concentration at the start, precipitant concentration at the end, and time.

1.3   Objectives

1. To assess boron recovery from produced water via precipitation method.
2. To evaluate the cost analysis for boron recovery from produced water.

1.4   Scope

This study focusses on recovering boron from produced water through precipitation by using calcium hydroxide, calcium carbonate, and oxalic acid. This produced water which naturally occur during the oil and gas extraction contains various amount of chemicals composition. The chemical or element that were prioritized in this project is to extract the boron for its beneficial uses. Thus, the condition is that best chemicals and precipitation method should be used to extract the most out of it with the most cost and time efficient way (Lyu et al., 2017). This process should also give less negative impact to the environment, best if it does not. Hence the purpose of this project is to study the method and chemicals needed to extract boron from produced water with the condition mentioned above. Boron removal was researched using calcium hydroxide, calcium carbonate and oxalic acid to chemically precipitate boron from aqueous solutions. In a batch system, operational parameters such as pH, beginning boron concentration, molarity of precipitation, stirring speed, and solution temperature were chosen. Scope of work that will be done in this experiment also include jar test. A jar test for assessing coagulant dose in water treatment can be characterised as a test in which the results of two or more

samples are compared and a multiple stirring device is used to vary the time, type, and velocity of stirring. Yet this study will not include the experiment of the after product of jar test. Only stated below will be explored in this study.

- Presence of boron in produced water
- Effects of boron to environment
- Using synthetic water to replace produced water
- Running test to determine boron concentration
- Studying effects of all manipulated
- Running Jar Test
- Calculating percentage of removal

CHAPTER 2

LITERATURE REVIEW

2.1   Boron in produced water

Other types of produced water include water that has been sucked up from the ground or pumped into the well to force crude oil to the surface. Oil and water are separated using an oil/water separator. In the early stages of oil production, water content is normally low, but may rise to as much as 80% in the latter years of the well. According to estimates, oil and gas exploration produces over 250 million barrels of produced water per day, compared to around 80 million barrels of oil per day. Aquifer-generated water has a different chemical composition and behaviour than surface water because of this restriction (Bunani et al., 2017). Produced water has qualities due to the presence of organic and inorganic waste, excessive salinity, BTEX, PAH, and other environmental contaminants.
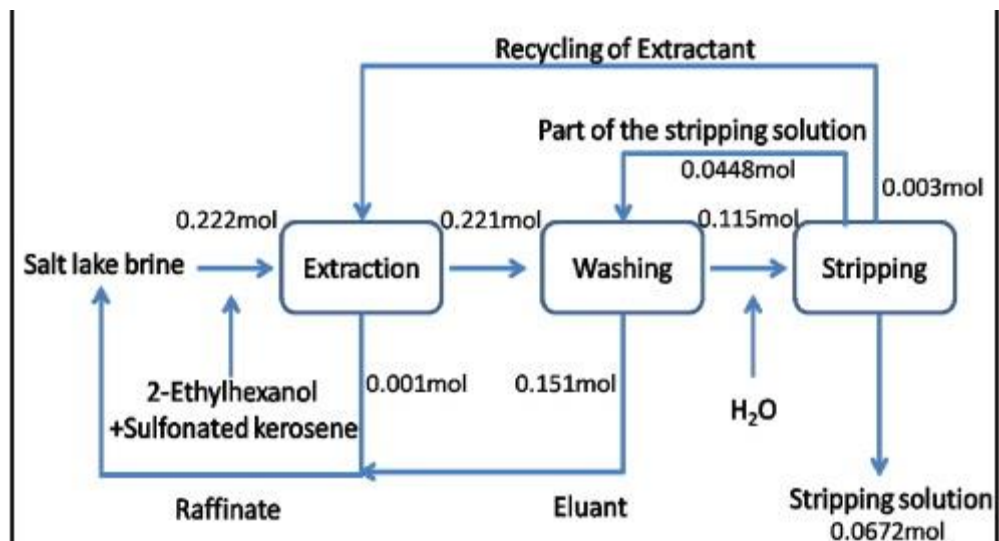
FIGURE 3 PROCESS OF BORON RECOVERY

Bacteria naturally present in the water supply may induce microbial corrosion of pipes and other water conveyance systems, which can lead to leaks and other problems. Microbial corrosion is caused by the build-up of biofilms on metal surfaces. The composition of the water produced by each well varies and might be different. Boron concentrations in generated water range from 26 to 28 parts per million (ppm), while the pH of the water is between 6 and 8 (Noguchi et al., 2018). When it comes to replenishing limited freshwater supplies in many parts of the United States and other countries, generated water is becoming more popular. As a consequence, in arid regions where farmers experience water constraint, proper therapeutic approaches for treating this crucial water should be applied.

It is well-known that boron, a common contaminant found in drinking water, hinders the reproduction of living creatures. Boric acid and borax are the most common natural forms of boric ion. Dissociated boric acid and borate ions are the most common forms in aquatic environments. It is mostly found in detergents, cleaning chemicals, industrial effluents, and agricultural chemical products found in surface water. Heavy metals including Pb, Cu, Co, Ni, cd, and other heavy metals may become more harmful when

7

boron compounds form complexes with them when boron-rich water is used for irrigation (Guo et al., 2020). These chemicals pose substantial health and environmental risks if they are absorbed into ground water. Carbon beats boron in a broad variety of applications. boron compound production has increased significantly in recent years as a result of the increased demand for boron compounds in nuclear technology, rocket engines as fuels, heat resistant materials such as refractories and ceramics, high quality steel, heat-resistant polymers, catalysts, glass industrial production, pharmaceuticals, corrosion inhibitors in anti-freeze active ingredients for motor vehicle and other cooling systems, dyestuff production, cosmetics, and flame retardants (Almustafa et al., 2020).

Soil boric acid, which roots absorb and transfer, provides boric acid as a source of boric to plants. Additionally, Boron is necessary for plant carbohydrate metabolism and sugar transport as well hormonal activity in plants as well as biological membrane development and functioning, neutron capture treatment as well as other commercial products. Depending on the degree of the boron deficit, plants may face a reduction in growth, a decrease in yield, or even death. Plant growth and development are affected by the amount of anions that may be taken up by plants in the narrow range between boron shortage and toxicity (Chruszcz-Lipska et al., 2021). In order to prevent the loss of boron via rainfall, it is necessary to provide the mineral on a regular basis. Toxic effects on the human reproductive system have been linked to the presence of boron, which is suspected of being teratogenic. Boron was discovered to impair male reproduction in studies conducted in the lab. Rats, mice, and rabbits have all shown a variety of developmental and teratogenic consequences. In recent years, boron toxicity has received a lot of attention because of the rising demand for desalination water, where boron concentrations may be too high for safe irrigation (Peng et al., 2021).
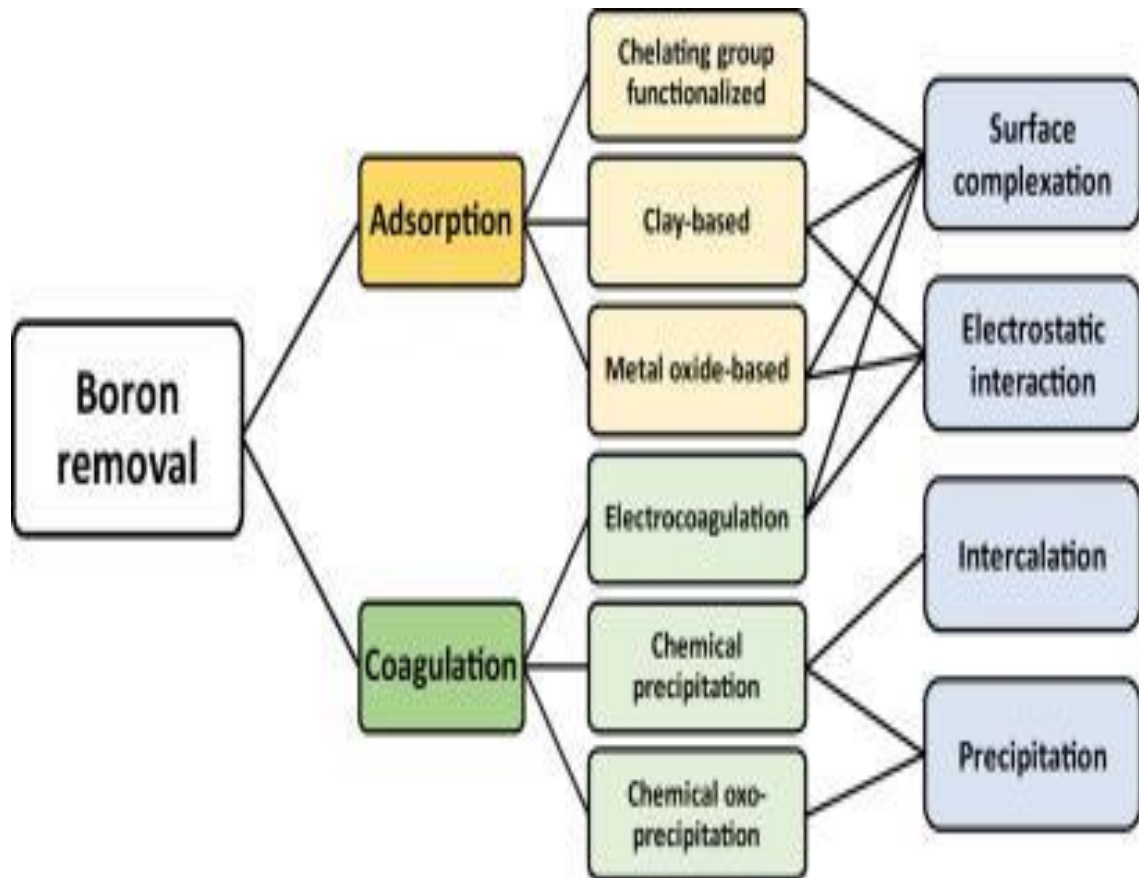
FIGURE 4: BORON REMOVAL PROCESS

Several authors have investigated the influence of salinity on the toxicity of boron in plants. However, one study indicated that increased salinity lowers boron toxicity in several vegetables and rootstocks, wheat, and chickpeas, but when both occur concurrently, salinity may reduce or exacerbate boron toxicity. Irrigation water must have a very low boron content for some metabolic activities (Xu et al., 2021). However, it becomes toxic when present in higher concentrations than necessary. Several variables impact the availability of boron to plants. boron availability to plants is influenced by the soil pH, soil texture, temperature/moisture, soil calcium carbonate, and soil organic matter. A wide range of soil components and ions, notably cations, have an impact on boron's solubility and retention in soil. Because of the limited range between toxicity and deficiency, careful control of this essential element in plants is necessary. Plants' tolerance for boron varies. Boron could be remove as shown in Figure 4.

2.2 Boron

Boron is a metalloid that has a Lewis acid behaviour (Arias et al., 2011). At higher pH, the borate monovalent anion B(OH)2 dominates, but at lower pH, non-ionized boric acid B(OH), dominates.

The following is a description of how boric acid dissociates in water:

$$H_3BO_3 \rightarrow HBO_2 + H_2O \ pKa = 9.3 \ at \ 170°C \qquad (1)$$
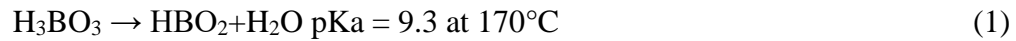
Dissociation of boric acid in water occurs at higher temperature below:

$$4HBO_2 \rightarrow H_2B_4O_7 + H_2O \ (300°C) \qquad (2)$$

$$H_2B_4O_7 \rightarrow 2B_2O_3 + H_2O \qquad (3)$$
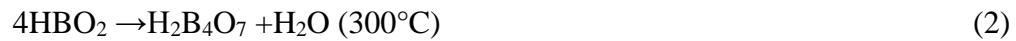
Boric acid does not dissociate as a Bronsted acid in aqueous solution, but rather as a Lewis acid that interacts with water molecules to create tetrahydroxyborate on (Arias et al., 2011):

$$B(OH)_3 \ H_2O \rightarrow B(OH)^-_4 + H + (pKa \ 9.15) \qquad (4)$$
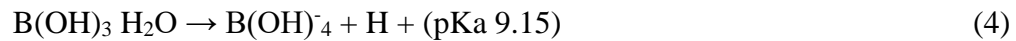
In the range of pH 7 and 10 with high concentration (>0.025 mol L-1), polyborate anions are formed:

$$4B(OH)^-_4 + 2H + B_4O_7^{2-} + 9H_2O \qquad (5)$$

Boric acid is the dominating boron species at lower pH, whereas borate compounds has proven a stumbling block for several treatment methods at higher pH. The properties of boron are shown in Figure 5 below.
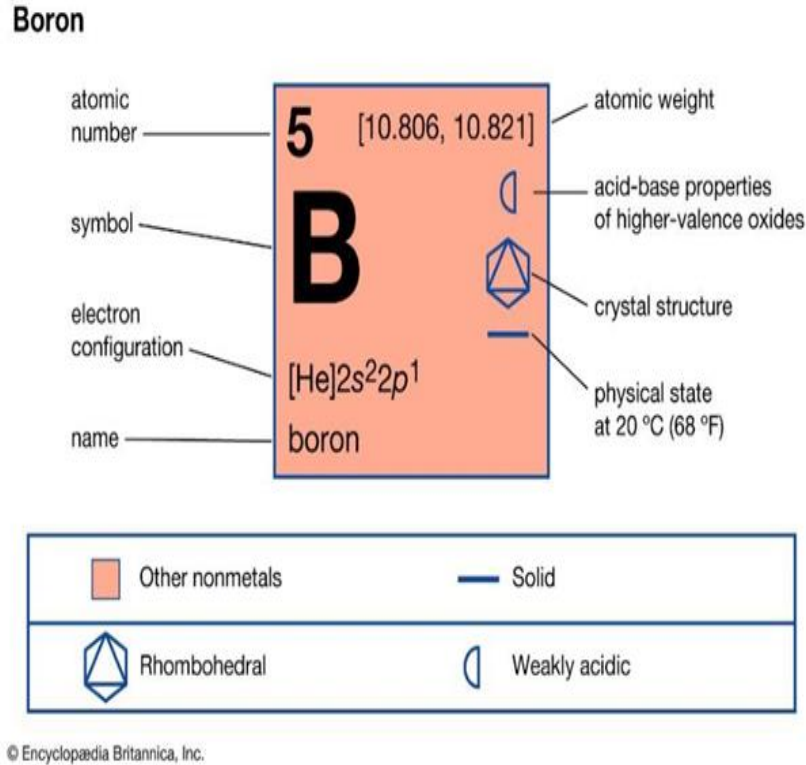
Boron

FIGURE 5: PROPERTIES OF BORON

2.3 Types of natural coagulants for Boron

They have properties that make them non-toxic to aquatic environments. Microbial polysaccharides, bio-waste, alginate, gelatine, cellulose-based polymers, and Chitosan are among the ingredients. Natural coagulants can be separated into three types based on their origin. Carbohydrates, protein, and lipids make up natural coagulants. Polymers comprising polysaccharides and amino acids are the primary building blocks. Charge neutralisation and polymer bridging are the major mechanisms determining coagulation activity, according to earlier research (Seval et al., 2021).

11

2.3.1 Animal based natural coagulants

Deacetylate chitin is the starting material for Chitosan, a linear copolymer. Chitosan provides a number of benefits over traditional chemicals. To name a few advantages, it's widely available, non-toxic, biodegradable, soluble in mild acidity, pH-sensitive and improved bio sorbent; no secondary contamination; sludge may be utilised as agricultural fertiliser; and so on. Chitosan may also reduce the amount of suspended particles, turbidity, and chemical oxygen demand in water (Peng et al., 2021).

2.3.2 Plant based natural coagulants

From about 2000 BC, Egyptians carved traces of plants used for water purification, and the practise has continued ever since. Although it is not known for certain whether these nuts were utilised in Sudan, Egypt, or India; it is certain that they are. There is evidence that these nuts may aid the coagulation of murky water. Polyelectrolytes and polymers derived from plants have been researched as coagulants since the 1970s. An organic, water-soluble polymer that is ionic or non-absorbable is a plant-based coagulant, which may be created from various plant parts (Xu et al., 2021). By creating micro- or macro-flocs by charge neutralisation in the colloid-free aqueous state and colloidal particle solution consisting of limited irreversible loop arrangements, they maintain random configurations and help in destabilisation. Flocculants, which are plant-based substances that aid in the formation of flocs, may be found in several foods. In a number of research, plant-based coagulants have been utilised to treat water and wastewater. As a result, the majority of coagulants investigated come from plants in the Fabaceae family. Plant coagulant Moringa oleifera, which belongs to the Moringaceae family, is extensively utilised and studied. Turbidity has been reduced by nirmali seeds, Tannins, Roselle seeds, Hyacinth bean, and other common coagulants. They're inexpensive, non-toxic, readily accessible, and simple to execute.

2.4   Calcium hydroxide

Calcium hydroxide is a white, odourless powder having a molecular weight of 74.08. (OH). It has a high pH and is insoluble in alcohol despite its poor water solubility, which decreases with increasing temperature. Since it takes a long time for it to dissolve in tissue fluids when it comes into direct touch with critical tissues, its limited solubility makes it an excellent therapeutic agent. Ca^{2+} and OH-ion ionic dissociation and their influence on vital tissues, resulting in hard tissue deposition and antibacterial activity, are the primary effects of the substance (Lee et al., 2021). When calcium hydroxide comes into touch with water, it breaks down into calcium and hydroxyl ions. hydroxyl ions are assumed to be responsible for calcium hydroxide's antibacterial high alkalinity.

2.5   Calcium Carbonate

In its purest form, calcium carbonate is a white, tasteless powder or crystal. Largely insoluble in water. All across the world, it may be found in a variety of rocks. Limestone mining produces a by-product called ground calcium carbonate (Almustafa et al., 2020). The finely powdered product may be utilised either dry or in a slurry, and the extraction procedure ensures that the carbonate is as pure as possible. Sodium carbonate is a by-product of the Solvay process, which produces precipitated calcium carbonate as a by-product of decomposing limestone to calcium oxide and then decarbonizing it. There are distinct advantages to working with precipitated calcium carbonate over crushed calcium carbonate.

2.5   Oxalic Acid

Oxalic acid is an odourless white solid. Sinks and mixes with water. Oxalic acid has the chemical formula $C_2H_2O_4$ and is a dicarboxylic acid. The potassium and calcium salts of oxalic acid can be found in the cell sap of Oxalis and Rumex species of plants. Oxalic acid is a weak acid that will only partially ionise in an aqueous solution. Oxalic acid has two protons that are acidic. The first ionisation produces $HC_2O_4^-$, a weak acid that will also ionise. Oxalic acid is one of the strongest organic acids, capable of removing carbonic acid and a variety of other acids from their salts. Most organic substances in nature form oxalic acid when they are exposed to either potash hydrate or nitric acid. It's also known as diprotic acid (Guo et al., 2020).

2.6   Jar Test

Jar test is very crucial I water plant operation. When the jar test is required in correlational research, however, the necessity for an objective and quantitative evaluation of the test's outcomes quickly emerges. A method was created in combination with coagulation research at the Robert A. Taft Sanitary Engineering Centre, which has largely addressed this need. It has been determined a floe's settling rate by evaluating for iron in a series of samples taken at measured time intervals from six jars during the settling phase. From these data, a curve was constructed by plotting percentage \s of iron remaining against settling time \s in minutes. From a depth. above the jars' bottoms, samples were syphoned out sequentially from each jar through copper sampling tubes. The effect of specific variables on the quality of coagulation is widely observed in coagulation research. In general, the impacts created by these variables are so subtle that they are difficult to detect, necessitating more precise measurements than judgement alone. The method described has provided the required objective type of data to allow for the discovery of tiny coagulation variations. Furthermore, over the course of a week or more, a long series

of coagulations studying possibly a single variable could be run, with judgements on the quality of postponed until the data collection was completed. As a result, permanent records exist that explain coagulation in clear terms. The time it takes to conduct a sequence of six coagulations could be a disincentive to more widespread use of this approach. While it is standard practise to make a visual assessment of a series of coagulations during the coagulation and settling period, followed by a single determination of ultimate turbidity, the present approach necessitates more time to determine turbidity on four or five samples from each jar. The settling rate curves are then calculated and plotted using these data. This procedure takes roughly one hour to complete. The extra time necessary for each set of coagulations, on the other hand, has enabled work that would not have been possible without this technology.

CHAPTER 3

METHODOLOGY

3.1 Boron detection in Synthetic Produced Water

Boric acid is used as a substitute for the generated water (BCl_3). Oil and gas field water will be tested for boron using the carmine technique, which is following standard. DR6000 spectrophotometer will be used to measure boron concentrations in synthetic water ranging from 1 mg/L to 40 mg/L. BoroVer 3 Reagent Powder Pillow is the reagent to be utilised. Carminic acid and sulphuric acid will react to generate a reddish to blue colour when boron is present. The wavelength measurement will be 605 nm since the quantity of colour is exactly proportional to the boron content in the solution.

3.2 Boron recovery from Produced Water

Precipitation method and process will be experimented to recover boron in the form of boron compound. Calcium Hydroxide, Calcium Carbonate and Oxalic Acid will be used as a precipitant agent to precipitate boron from the solution. Efficiencies of gaining the product will be observe during the experiment with adjusting different types of parameters to gain maximum outcome from each precipitant. Parameter's factor and range that was expected for this experiment are as follows.

- Time: 10 minutes to 30 minutes
- Temperature: 30ºC to 90°C (work in fume chamber)

- pH: 3 to 9
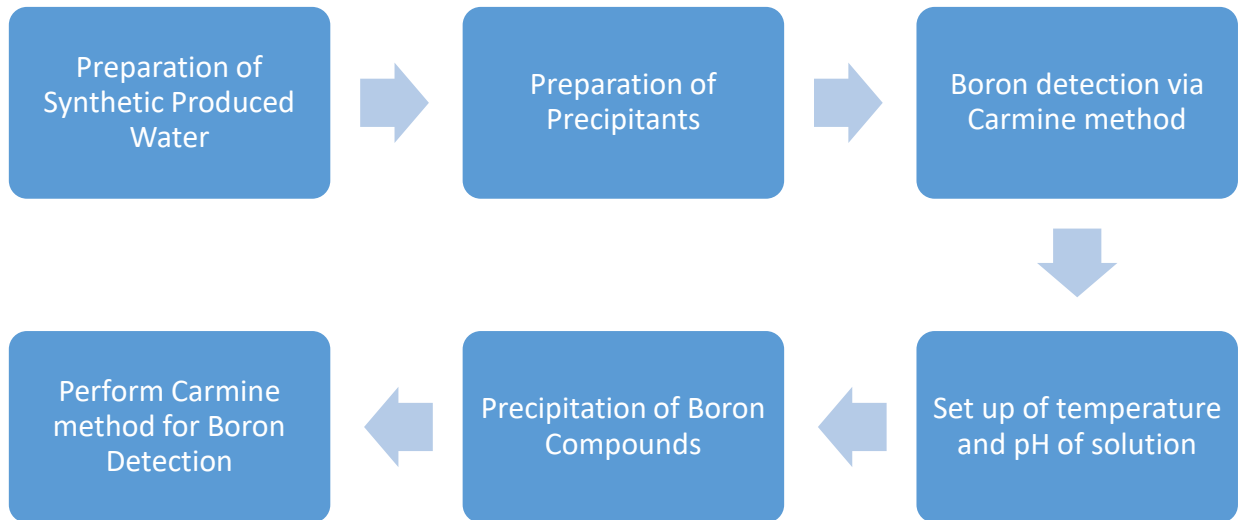
FIGURE 6: EXPERIMENTAL METHODOLOGY

Variables above will play a vital role in recovering boron at a highest percentage possible. It is expected to gain more than 90% of boron compared to its initial concentration. The chemical reaction above will give an expected result as:

- Calcium Hydroxide: $3\,Ca\,(OH)_2 + 2\,H_3BO_3 = Ca_3(BO_3)_2 + 6\,H_2O$
- Oxalic Acid: $H_3BO_3 + H_2C_2O_4 = B_2(C_2O_4)_3 + HCl$
- Calcium Carbonate: $CaCO_3 + 2\,H_3BO_3 = Ca\,(BO_2)_2 + 3\,H_2O + CO_2$

3.3 Procedure for Boric Acid Preparation

Experimental procedure for preparation of Boric Acid.

Materials and Apparatus:

- 1000 ml of distilled water
- 1000 ml beaker

17

- Glass Rod
- 0.205g of Boric Acid
- Micro weight balancer
- Petri dish

Procedure

First, Clean the beaker with distilled water to remove any impurities. Use the micro weight balancer to and measure 0.205g of Boric Acid and add it into 1000ml of distilled water to reach 36 mg/L of Boron. Then, stir the solution with glass rod to dissolve the Boric Acid powder.

3.4   Procedure to measure concentration of Boron in solution

Materials and Apparatus:

- DR 6000 spectrophotometer
- Borover 3 Reagent Powder Pillow
- Sulfuric Acid (Concentrated >90%)
- Tubes glass with caps 16mm x 100mm
- Cylinder 100ml
- Pipet TenSette, 0.1 – 1.0 ml
- Pipet tip for 0.1 – 1.0 ml
- Pipet TenSette, 1ml – 5ml
- Pipet tip for 1ml – 5ml
- 250ml Erlenmeyer flask

Procedure.

Use a 100ml cylinder to measure 75 mL of concentrated sulfuric acid under a fume hood. Pour the acid into a plastic 250-mL Erlenmeyer flask. In a well-ventilated area or fume hood, add the contents of one BoroVer 3 Reagent Powder Pillow to the flask.Swirl the flask immediately to mix. Swirl for up to 5 minutes to dissolve the powder completely.

To prepare the blank remove the cap from a clean 16-mm tube. Add 0.2 mL of deionized water. To prepare the sample remove the cap from a clean 16-mm tube. Add 0.2 mL of sample. Add 3.5 mL of the BoroVer 3 Solution from step 3 to the prepared sample tube. Put the cap on the prepared sample and invert to mix. The solution in the tube will get warm. Add 3.5 mL of the BoroVer 3 Solution from step 3 to the blank sample tube. Put the cap on the blank. Invert to mix. The solution in the tube will get warm. Let the solution to react for 30 minutes. Start program 41 Boron HR on the DR 6000 spectrophotometer. After 30 minutes, clean the blank sample cell. Insert the blank into the cell holder. Push ZERO. The display shows 0.0 mg/L B HR. Clean the prepared sample cell. Insert the prepared sample into the cell holder. Push READ. Results show in mg/L B. Observe and record the readings.

3.5 Procedure of Precipitation of Boron from Boric Acid with temperature variable.

Materials and Apparatus

- 1 mol of Calcium Hydroxide. (90 mg/L)
- 1 mol of Calcium Carbonate. (66 mg/L)
- 1 mol of Oxalic Acid. (74 mg /L)
- Distilled water.
- Synthetic produced water. (Boric Acid, 36 mg/L)
- Thermometer.
- Heating pan.
- Micro Weight Balancer.
- Jar test apparatus.

Procedure

Weight Calcium Hydroxide to 90mg/L using micro weight balancer. Add the measured chemical powder into the 500 ml of synthetic produced water. Repeat step 1 and 2 for two more times to prepare 3 samples of solution. Stir the solution using the jar test apparatus

at 100rpm for 1 minute. Heat up the solution using heating pan until each solution reaches temperature of 30°C, 60°C, 90°C. Measure the temperature using thermometer to identify the temperature. Stir the solution using the jar test apparatus with 25 rpm for 20 minutes. Let the solution settle for 15 minutes. Observe for any precipitants visible. Take the sample solution to test the boron concentration using DR 6000 spectrophotometer stated in boron detection procedure. Record the findings. Repeat step 1 to 11 with 66mg/L Calcium Carbonate and 74mg/L of Oxalic acid.

3.6   Procedure of Precipitation of Boron from Boric Acid with time variable

Materials and Apparatus

- 1 mol of Calcium Hydroxide. (90 mg/L)
- 1 mol of Calcium Carbonate. (66 mg/L)
- 1 mol of Oxalic Acid. (74 mg /L)
- Distilled water.
- Synthetic produced water. (Boric Acid, 36 mg/L)
- Micro Weight Balancer.
- Jar test apparatus.

Procedure

Weight Calcium Hydroxide to 90mg/L using micro weight balancer. Add the measured chemical powder into the 500 ml of synthetic produced water. Repeat step 1 and 2 for two more times to prepare 3 samples of solution. Stir the solution using the jar test apparatus at 100rpm for 1 minute. Stir each of the solution using the jar test apparatus with 25 rpm for 10minutes, 20 minutes and 30 minutes respectively. Let the solution settle for 15 minutes. Observe for any precipitants visible. Take the sample solution to test the boron concentration using DR 6000 spectrophotometer stated in boron detection procedure. Record the findings. Repeat step 1 to 9 with 66mg/L Calcium Carbonate and 74mg/L of Oxalic acid.

3.7   Procedure of Precipitation of Boron from Boric Acid with pH variable

Materials and Apparatus

- 1 mol of Calcium Hydroxide. (90 mg/L)
- 1 mol of Calcium Carbonate. (66 mg/L)
- 1 mol of Oxalic Acid. (74 mg /L)
- Distilled water.
- Synthetic produced water. (Boric Acid, 36 mg/L)
- Micro Weight Balancer.
- Jar test apparatus.
- pH meter
- Sodium hydroxide (diluted)
- Sulfuric Acid (diluted)
- Glass rod

Procedure

Weight Calcium Hydroxide to 90mg/L using micro weight balancer. Add the measured chemical powder into the 500 ml of synthetic produced water. Repeat step 1 and 2 for two more times to prepare 3 samples of solution. Stir the solution using the jar test apparatus at 100rpm for 1 minute. Record the pH of each of the solution and set it to 3, 6 and 9 pH respectively by adding few drops of Sodium Carbonate to increase the pH and Sulfuric Acid to reduce the pH. Stir the solution with glass rod after every drop of Sodium Carbonate or Sulfuric Acid. Stir the solution using the jar test apparatus with 25 rpm for 20 minutes. Let the solution settle for 15 minutes. Observe for any precipitants visible. Take the sample solution to test the boron concentration using DR 6000 spectrophotometer stated in boron detection procedure. Record the findings. Repeat step 1 to 11 with 66mg/L Calcium Carbonate and 74mg/L of Oxalic acid.

After obtaining the results from all the procedure, compare and select each value of parameter that gives the best efficacy of boron removal. Then repeat the procedure of setting up the parameters following by setting the pH of the solution, then heating up to desired temperature and finally flocculate it using the jar test equipment with the best stirring time for each precipitant. Test the final boron concentration of each sample. The result should be equal or less than 36 mg/L of boron which is 95% removal of boron.
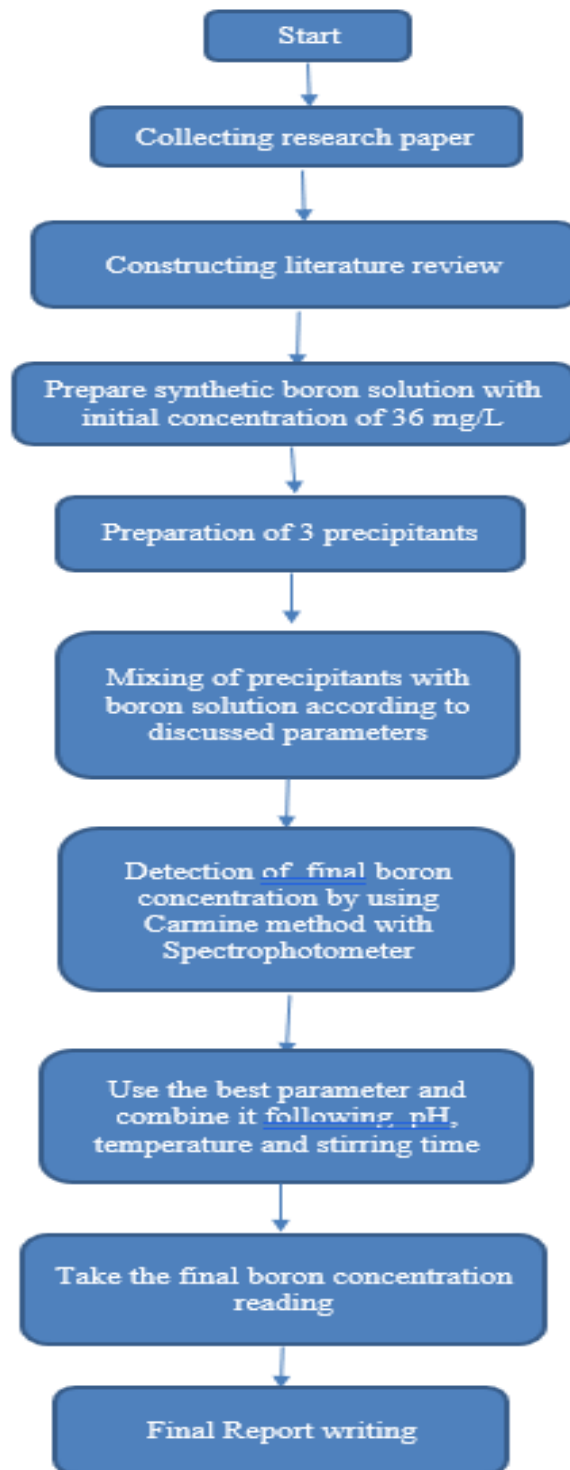
3.8 Project flow chart

FIGURE 7: PROJECT FLOW CHART

CHAPTER 4

RESULTS AND ANALYSIS

2.1 Experimental results

Initial concentration of Boron to be set as 36 mg/L in boric acid solution.

Chemical Precipitant	Parameters		Final Boron concentration (mg/L)	Percentage of Boron Removed (%)
Calcium Carbonate ($CaCO_3$)	Stirring time	10 minutes	18.7	48.06
		20 minutes	15.8	56.11
		30 minutes	15.7	56.39
	Temperature	30°C	16.3	54.72
		60°C	14.1	60.83
		90°C	11.5	68.05
	pH	9	16.9	53.05
		6	15.1	58.05
		3	20.5	43.05
Calcium Hydroxide ($Ca[OH]_2$)	Stirring time	10 minutes	22.6	37.22
		20 minutes	21.9	39.16
		30 minutes	21.1	41.39

	Temperature	30°C	20.9	41.94
		60°C	16	55.55
		90°C	15.3	57.50
	pH	9	22.4	37.78
		6	20.8	42.22
		3	22.2	38.33
Oxalic Acid ($C_2H_2O_4$)	Stirring time	10 minutes	18.7	48.05
		20 minutes	15.8	56.11
		30 minutes	15.1	58.05
	Temperature	30°C	15.3	57.50
		60°C	12.8	64.44
		90°C	11.2	68.89
	pH	9	22.2	38.33
		6	14.3	60.28
		3	15.90	55.83

TABLE 1: RESULTS 1

2.2 Role of parameters

In this experiment, investigation of the parameters' influence such as pH, temperature and stirring time on the precipitation of boron was studied.

2.3 Influence of pH

It is proved that pH has significant number of effects on chemical precipitation process. The effects of pH on the removal of boron were observed and measured at 3, 6 and 9 pH for all three precipitants.

Values of constant are the molarity of Calcium Carbonate, Calcium Hydroxide and Oxalic Acid of 1 mol, initial concentration of Boric Acid 36 mg/L of boron concentration, room temperature, stirring speed of 100 rpm for 1 minute and 25 rpm for 20 minutes. The pH of the solution was manipulated using sodium hydroxide to increase the pH and sulphuric acid to reduce the pH of the solution. The solution is then mixed after adding few drops and a pH meter was used to read the pH of the solution. The graphical results were shown in the figure below.
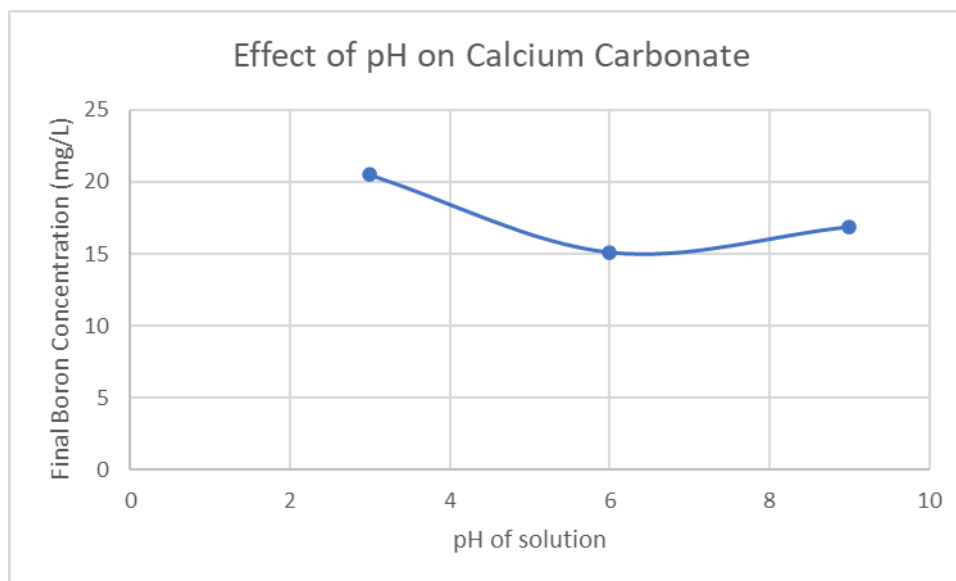

FIGURE 8: pH ON CALCIUM CARBONATE

From the result above in Figure 8 it is noticed that parameters for pH of 6 removes the most boron from the solution in this experiment using Calcium Carbonate. pH value

less than 6 shows that the removal efficiency drops drastically than the alkaline pH of this solution.

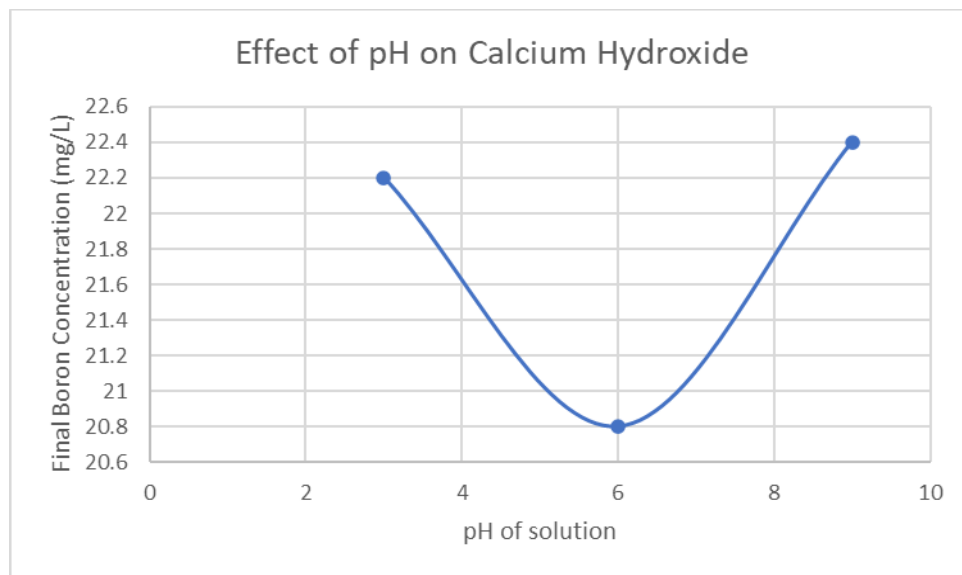## Effect of pH on Calcium Hydroxide

FIGURE 9: pH ON CALCIUM HYDROXIDE

From the result above in Figure 9 is it noticed that the removal efficacy of boron is at the highest at pH 6 from the solution. pH 3 and 9 has the least amount of boron removed from the solution, thus higher acidic or alkaline pH is not effective in removing boron as the removal efficacy drops drastically
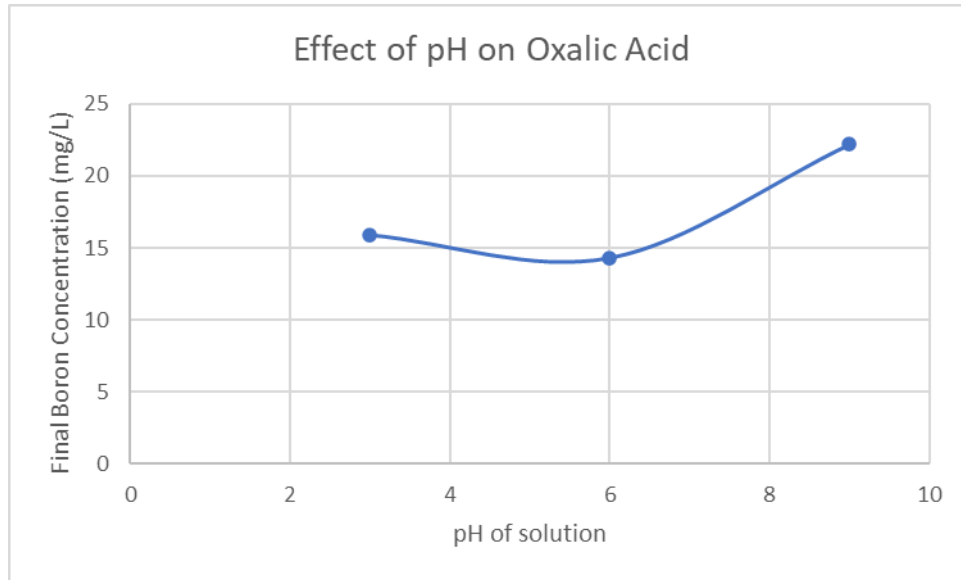
FIGURE 10: pH ON OXALIC ACID

From the graphical result above in Figure 10, the graphs shows that the removal efficacy of boron is at highest at pH 6 compared to pH 3 and 9. In this case, the pH value higher than 6 has the least efficacy in removing boron compared to the pH lower than 6. This study here proves that for Oxalic Acid as a precipitant the removal efficacy works the best as acidic rather than alkaline.

2.4 Influence of Temperature

In this study, the temperature effects on boron precipitation were observed and measured. The temperature parameters were set at 30°C, 60°C, 90°C for all three precipitants.

Values of constant are the molarity of Calcium Carbonate, Calcium Hydroxide and Oxalic Acid of 1 mol, initial concentration of Boric Acid 36 mg/L of boron concentration, natural pH value of 1 mol of precipitants stirring speed of 100 rpm for 1 minute and 25 rpm for 20 minutes. The temperature of the solution if manipulated by heating up the solution to desired temperature using a heating pan in fume chamber.
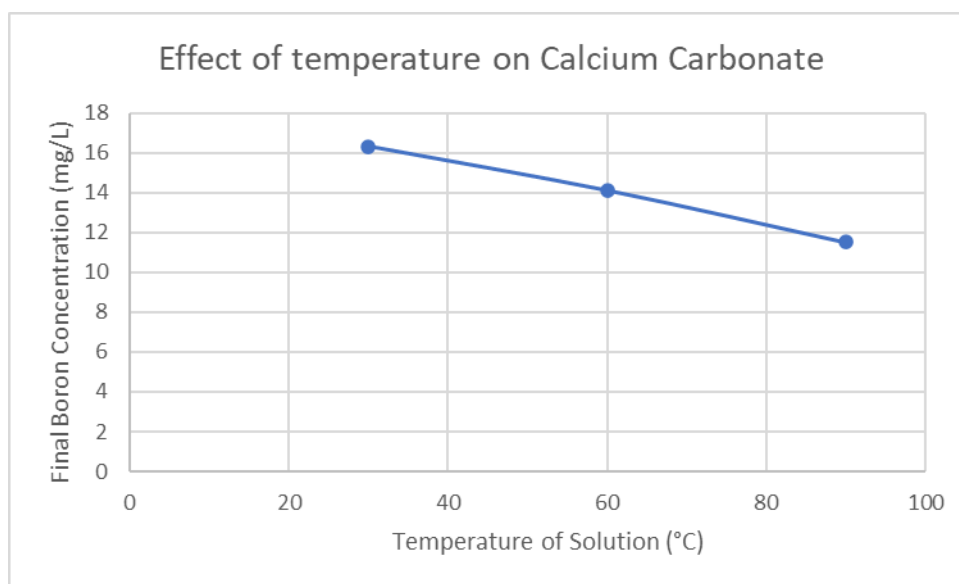

FIGURE 11: TEMPERATURE ON CALCIUM CARBONATE

The graphical result above for Calcium Carbonate shows that the most effective temperature among the chosen parameter to remove boron is 90°C. From this result, it is known that the temperature of the solution and final boron concentration is inversely proportional as higher the temperature, the lower the final boron concentration. In other words, the higher the temperature of the solution the higher the percentage of boron

removal which say result of temperature vs efficacy of boron removal is directly proportional for Calcium Carbonate as a precipitant.
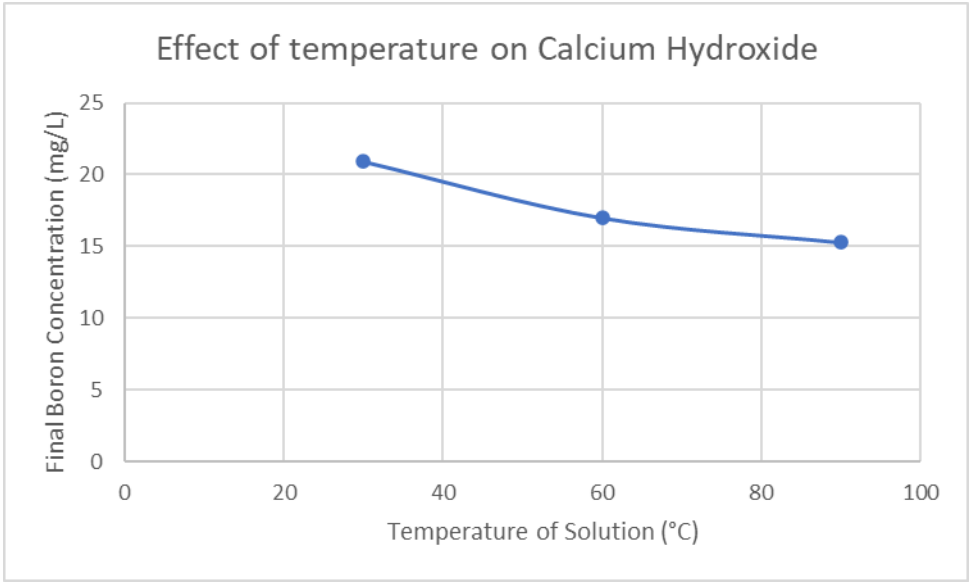

FIGURE 12: TEMPERATURE ON CALCIUM HYDROXIDE

From the result above it shown in Figure 12 that the higher efficacy of boron removal is achieved at 90°C of solution temperature. However, after 60°C the drop in boron final concentration has dropped drastically which shows that efficacy of boron removal dropped after 60°C. Although the difference of final boron concentration in

solution at 60°C and 90°C is 2.7 mg/L, this study shows that if a higher removal efficacy needed to be achieved then temperature solution of 90°C should be consider.
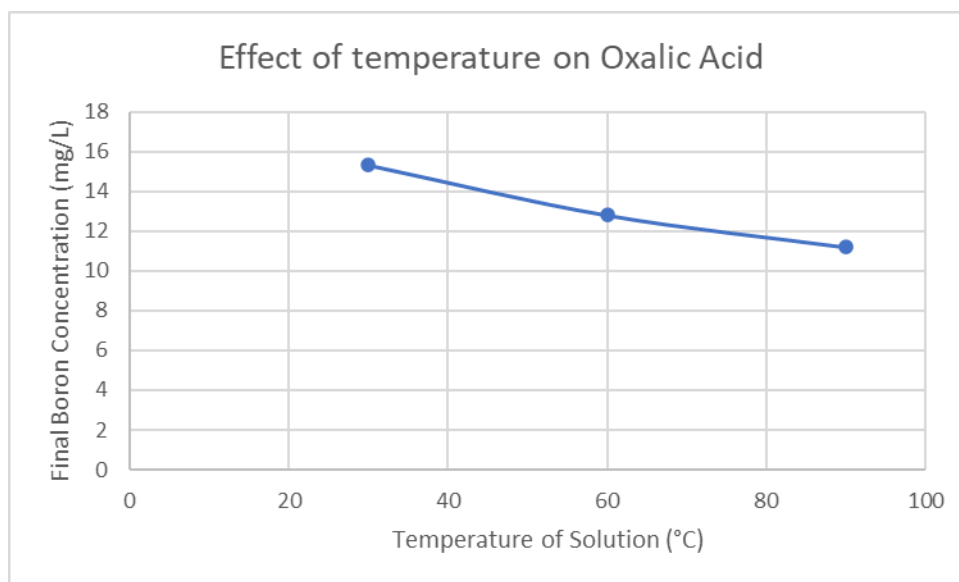

FIGURE 13: TEMPERATURE ON OXALIC

The graphical result Figure 13 above shows that the higher efficacy of boron removal is achieved at 90°C of solution temperature. The difference between solution temperature of 60°C and 90°C in removing boron is 1.6 mg/L. However, if the initial concentration of boron in solution is increased, hypothetically the difference between those two parameters will increase. Thus, it is better to proceed with the higher efficacy of removal to achieve the objective.

2.5   Influence of Stirring time

The effect of stirring time was studied in this experiment. The parameters are 10 minutes, 20 minutes, and 30 minutes of stirring time at 25 rpm.

Values of constant are the molarity of Calcium Carbonate, Calcium Hydroxide and Oxalic Acid of 1 mol, initial concentration of Boric Acid 36 mg/L of boron concentration, natural pH value of 1 mol of precipitants, stirring speed of 100 rpm for 1 minute at room temperature.
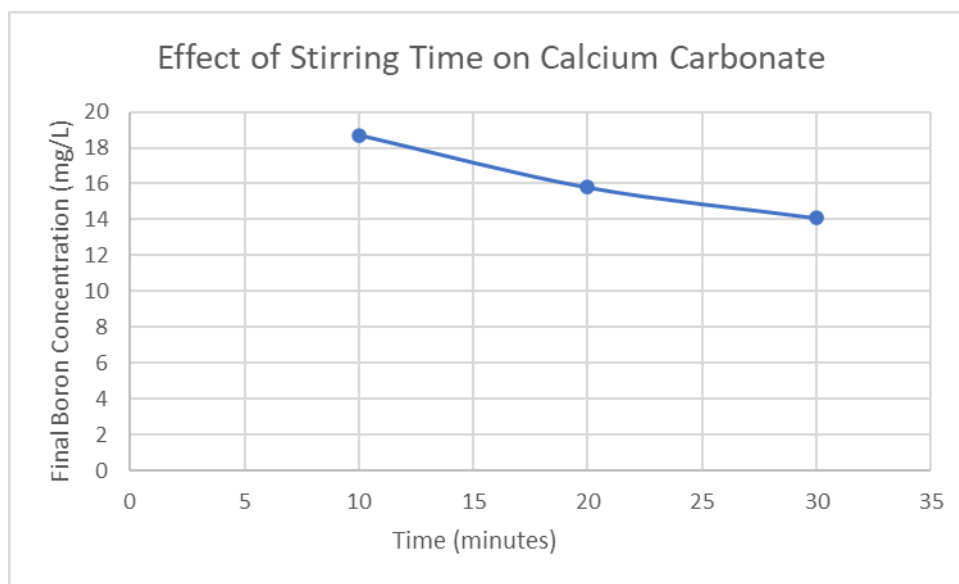

FIGURE 14: TIME ON CALCIUM CARBONATE

The graphical result Figure 14 above shows that the stirring time 30 minutes has the highest efficacy in removing boron compared to the other two stirring time parameters. Hence it is proven that the higher the stirring time the lower the final boron concentration

in the solution. Which concludes that more stirring time can give higher efficacies in boron removal.
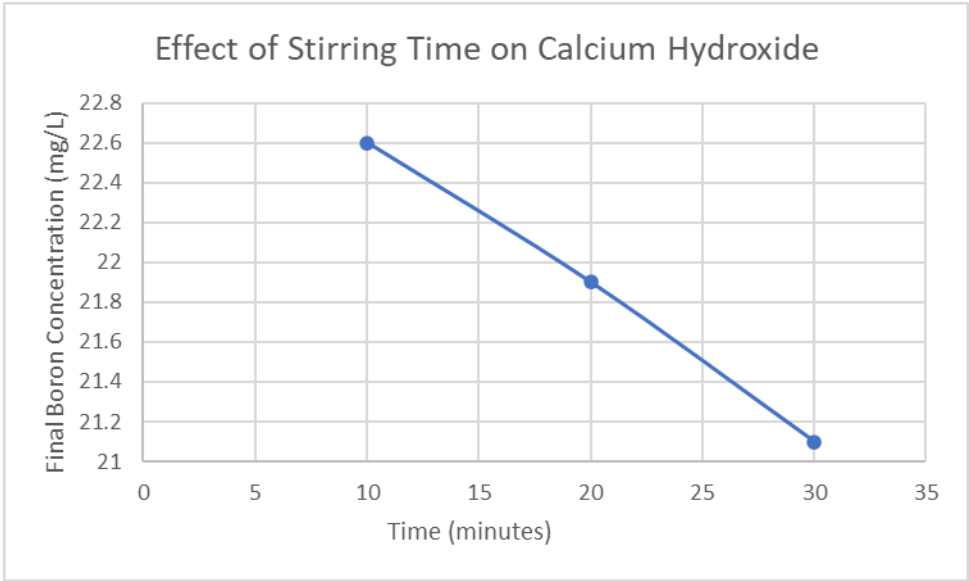
FIGURE 15: TIME ON CALCIUM HYDROXIDE

The graphical result Figure 15 above shows that the stirring time 30 minutes has the highest efficacy in removing boron compared to the other two stirring time parameters. Hence it is proven that the higher the stirring time the lower the final boron concentration in the solution. Which concludes that more stirring time can give higher efficacies in boron removal.

FIGURE 16: TIME ON OXALIC ACID

The graphical result above shows that the stirring time 30 minutes has the highest efficacy in removing boron compared to the other two stirring time parameters. Hence it is proven that the higher the stirring time the lower the final boron concentration in the solution. Which concludes that more stirring time can give higher efficacies in boron removal.
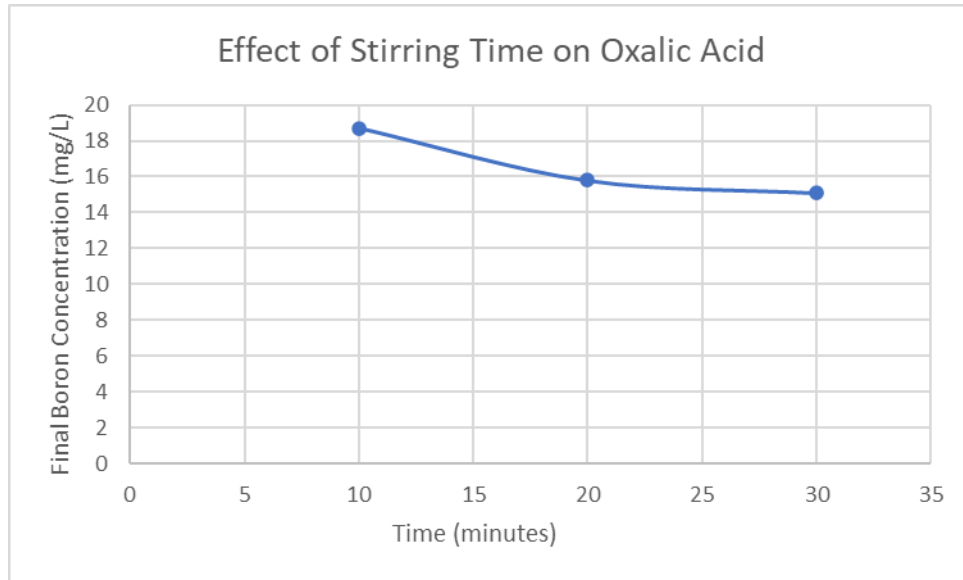
To achieve the boron removal percentage of more than 90% the best result from the three parameters for all the precipitants are chosen as shown in the table below.

	pH	Temperature (°C)	Stirring Time (minutes)
Calcium Carbonate (CaCO₃)	6	90°C	30
Calcium Hydroxide (Ca [OH]₂)	6	90°C	30
Oxalic Acid (C₂H₂O₄)	6	90°C	30

TABLE 2: RESULTS 2

First, the pH of the solution will be adjusted according to the choose value in the table with sulphuric acid and sodium hydroxide. Secondly the temperature will be adjusted to 90°C by using a heating pan in fume chamber. Finally, the solution will be stirred under 25rpm for 30 minutes before letting it to settle down to observe any precipitants and boron testing by using Carmine method for Oil and Gas wastewater boron detection procedure. The results are shown in the table below.

Chemical Precipitant	Initial Boron Concentration (mg/L)	Final Boron Concentration (mg/L)	Percentage of boron recovered (%)
Calcium Carbonate (CaCO$_3$)	36	1.1	96.4
Calcium Hydroxide (Ca [OH]$_2$)	36	0.9	97.5
Oxalic Acid (C$_2$H$_2$O$_4$)	36	1	97.2

TABLE 3: RESULTS 3

FIGURE 17: PIE CHART

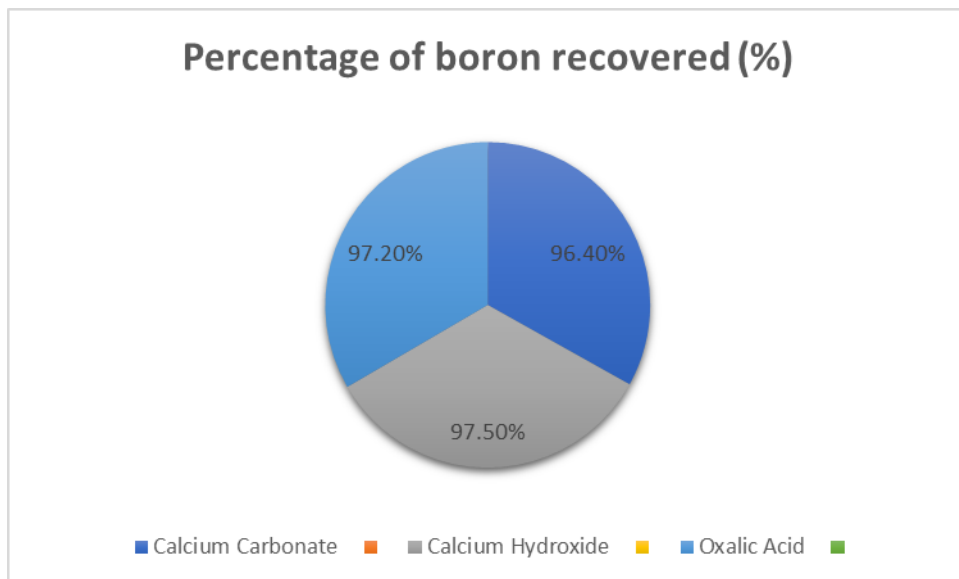From the table and pie chart above in Table and Figure 17, respectively, the chemical precipitant with the highest efficacy in removing boron is Calcium Hydroxide with a percentage of 97.5% and the least amount of efficacy in removing boron is Oxalic Acid with a percentage of 96.4%.

2.6   Cost Analysis

The cost analysis for boron precipitation in this experiment is shown in the table below

Materials	Estimated Price (RM)
Boron Powder Pillow (100 pcs)	726.00
Boric Acid Powder (500 g)	51.25
Calcium Carbonate Powder (500 g)	42.05
Calcium Hydroxide Powder (500 g)	46.28
Oxalic Acid Powder (500 g)	58.96
Sulfuric Acid (2.5L)	194.00
TOTAL ESTIMATED COST =	RM 1118.54

TABLE 4: ESTIMATED COST RESULT

CHAPTER 5

CONCLUSION, RECOMMENDATIONS, AND IMPLICATIONS

3.1 Conclusions

Through this project, the precipitation agents will be compared to each other to observe its efficiencies to recover boron as well as the workability of the product. Boron pollution is an important problem in the world, especially in the countries where boron deposits are high. Boron removal from the environment using efficient and economical methods is still a challenging problem. Our effort is to contribute to solving this problem. To achieve the circular economic purposes which is aimed by all the industries around the globe, the recovery should be at the highest percentage with lower cost and workability of the product as possible. The uses of boron could benefit many areas in medical and sustainable materials manufacturing. it is expected to recover 95% of Boron.

3.2   Recommendations

I recommend that a brand-new boron powder is used, specific spatula and petri dish is used for each chemical. To tackle parallax error, I would recommend making sure the eye position is straight to the reading on the beaker. Also, I recommend working in place free of other people working and to close the glass panel on the micro weight balancer to prevent air flow disturbance in it. Finally, I would recommend using any coagulant agent to precipitate the solution to get a quick result and to get a final product that is easy to change into other compound without requiring heat or specific solvent to save cost and time while moving towards the circular economic motive that is being implemented in most of the industries around world.

3.3   Implications

This experiment that was conducted has some flaws such as impurities that caused the initial concentration of boron to not be tally throughout the entire experiment. This caused extra time to check the initial boron concentration to make sure the concentration is set at 36 mg/L. Also, there some errors such as parallax error when the volume of solution. When measuring weight of the chemical powder there is some disturbance such as air flow and others doing their work nearby the micro weight balancer which might influence the reading of the balancer.

References

Almustafa, G., Sulaiman, R., Kumar, M., Adeyemi, I., Arafat, H. A., & AlNashef, I. (2020). Boron extraction from aqueous medium using novel hydrophobic deep eutectic solvents. *AIChE Annual Meeting, Conference Proceedings*. https://doi.org/10.1016/j.cej.2020.125173

Bunani, S., Kabay, N., Bunani, S., Arda, M., Yoshizuka, K., Nishihama, S., & Bunani, S. (2017). Effect of process conditions on recovery of lithium and boron from water using bipolar membrane electrodialysis (BMED). *Desalination*. https://doi.org/10.1016/j.desal.2017.04.017

Chruszcz-Lipska, K., Winid, B., Madalska, G. A., Macuda, J., & Łukańko, Ł. (2021). High content of boron in curative water: From the spa to industrial recovery of borates? (Poland as a case study). *Minerals*. https://doi.org/10.3390/min11010008

C. Irawan, Y. L. Kuo and J. C. Liu, Desalination, 280, 1-3, 280 (2011). Treatment of boron-containing optoelectronic wastewater by precipitation process". https://agris.fao.org/agris-search/search.do?recordID=US201500090372

Ezechi, E. H., Hasnain Isa, M., Kutty, S. R. B. M., & Ahmed, Z. (2015). Electrochemical removal of boron from produced water and recovery. *Journal of Environmental Chemical Engineering*. https://doi.org/10.1016/j.jece.2015.05.015

R. Boncukcuo lu, A. E. Y lmaz, M. M. Kocakerim and M. Copur, Desalination, 160, 159 (2004)

Guo, J., Yang, Y., Gao, X., & Yu, J. (2020). Boron extraction from lithium-rich brine using mixed alcohols. *Hydrometallurgy*. https://doi.org/10.1016/j.hydromet.2020.105477

Kürklü, S., Velioğlu, S., Ahunbay, M. G., Tantekin-Ersolmaz, S. B., & Krantz, W. B.

(2017). A novel energy-efficient concurrent desalination and boron removal (CDBR) process. *Desalination*. https://doi.org/10.1016/j.desal.2017.09.005

Lee, C., Kang, Y., Kim, D. H., & Kim, I. S. (2021). Practical considerations of wastewater–seawater integrated reverse osmosis: Design constraint by boron removal. *Membranes*. https://doi.org/10.3390/membranes11040240

C.E. Cao, Y.J. Wang, X.Y. Su, H.R. Shen, C.H. Xiong and N.Z. Zheng: China Ceramic Industry Vol.10 No.6(2003), pp.50.

Lyu, J., Zeng, Z., Zhang, N., Liu, H., Bai, P., & Guo, X. (2017). Pyrocatechol-modified resins for boron recovery from water: Synthesis, adsorption and isotopic separation studies. *Reactive and Functional Polymers*. https://doi.org/10.1016/j.reactfunctpolym.2016.12.016

Noguchi, M., Nakamura, Y., Shoji, T., Iizuka, A., & Yamasaki, A. (2018). Simultaneous removal and recovery of boron from waste water by multi-step bipolar membrane electrodialysis. *Journal of Water Process Engineering*. https://doi.org/10.1016/j.jwpe.2018.04.010

Peng, X., Shi, D., Zhang, Y., Zhang, L., Ji, L., & Li, L. (2021). Recovery of boron from unacidified salt lake brine by solvent extraction with 2,2,4-trimethyl-1,3-pentanediol. *Journal of Molecular Liquids*. https://doi.org/10.1016/j.molliq.2021.115301

L.Y. Tao and X.J. Zheng: Production and Application of Boron Compounds (Chengdu Science & Technology University Publications, Sichuan, China 1992).

Seval, K., Onac, C., Kaya, A., & Akdogan, A. (2021). Separation of boron from geothermal waters with membrane system. *Membranes*. https://doi.org/10.3390/membranes11040291

Wang, G., Wang, J. song, Yu, X. yun, Shen, Y. feng, Zuo, H. bin, & Xue, Q. guo. (2016). Innovative method for boron extraction from iron ore containing boron. *International*

Journal of Minerals, Metallurgy and Materials. https://doi.org/10.1007/s12613-016-1233-0

Xu, Z., Su, H., Zhang, J., Liu, W., Zhu, Z., Wang, J., Chen, J., & Qi, T. (2021). Recovery of boron from brines with high magnesium content by solvent extraction using aliphatic alcohol. *RSC Advances*. https://doi.org/10.1039/d1ra01906f

Zelmanov, G., & Semiat, R. (2014). Boron removal from water and its recovery using iron (Fe+3) oxide/hydroxide-based nanoparticles (NanoFe) and NanoFe-impregnated granular activated carbon as adsorbent. *Desalination*. https://doi.org/10.1016/j.desal.2013.11.027

. Camp, T. R.; Root, D. A.; & Bhoota, B. V. Effects of Temperature on Rate of Floe Formation. Jour. AWWA, 32:1913 (Nov. 1940).

Zhang, R., Xie, Y., Song, J., Xing, L., Kong, D., Li, X. M., & He, T. (2016). Extraction of boron from salt lake brine using 2-ethylhexanol. *Hydrometallurgy*. https://doi.org/10.1016/j.hydromet.2016.01.001