Boron Recovery by Precipitation Process

by

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22009549

A Research Project Dissertation

Submitted to Universiti Teknologi PETRONAS

In Partial Fulfilment of the Requirement for the Degree of

MSc. in INDUSTRIAL ENVIRONMENTAL ENGINEERING

APRIL 2024

Universiti Teknologi PETRONAS,

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Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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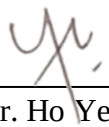

(Dr. Ho Yeek Chia)

UNIVERSITI TEKNOLOGI PETRONAS

SERI ISKANDAR, PERAK

April 2024

CERTIFICATION 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.

SYED ABDUR RAHMAN

ABSTRACT

This project discusses chemical oxo-precipitation (COP) as a method to recover boron from a synthetic produced water solution prepared using boric acid with boron concentration similar to that of produced water (40 mg/L-B), using hydrogen peroxide as the oxidant and zirconium chloride as the precipitant. Produced water is the main waste stream from oil and gas exploration and is produced when oil and gas are extracted. Here, zirconium is used as the precipitant in order to recover boron. Its use is expected to increase boron removal from the synthetic solution via COP. Different factors such as pH, mole ratio of hydrogen peroxide to boron, mole ratio of zirconium chloride to boron, reaction time, settling time and speed of the stirrer, and their ranges were taken into consideration in the experimental design which was developed using Design Expert software. Their effect on boron removal was determined by performing analysis of variance (ANOVA) for the results obtained from factorial design and Box-Behnken design runs using Design Expert software. It was found that the boron removal improved when the pH was maintained throughout the precipitation process. The removal percentage was highest at pH 8 and lowest at pH 12. The elemental composition of the precipitate obtained at pH 12 which had the lowest boron removal was analyzed using X-ray fluorescence spectroscopy (XRF) to check for the presence of boron and other elements, zirconium concentration was found to be the highest (87.6%) and no boron was detected. Based on the cost analysis of zirconium chloride and calcium hydroxide as precipitants in boron removal, calcium hydroxide was found to be more economical.

TABLE OF CONTENT

CERTIFICATION OF APPROVAL i

CERTIFICATION OF ORIGINALITY ii

ABSTRACT iii

LIST OF FIGURES vi

LIST OF TABLES vii

CHAPTER 1 INTRODUCTION 8

1.1 Background 8

1.2 Problem Statement 9

1.3 Research Aim and Objectives 9

1.4 Significance and Contribution of Research 10

1.5 Scope of Study 10

CHAPTER 2 LITERATURE REVIEW 11

2.1 Introduction 11

2.2 Chemical oxo-precipitation 12

2.3 Zirconium chloride 12

2.4 Zirconium in wastewater treatment 13

2.5 Research gap 13

CHAPTER 3 MATERIALS AND METHODS 14

3.1 Research flowchart 14

3.2 Materials 15

3.3 Methodology 15

3.3.1 Jar Test Experimental Procedure 15
3.4 Tools 19
3.4.1 Preparation of boric acid solution 19
3.4.2 Preparation of BoroVer 3/sulfuric acid solution 19
3.4.3 Measuring the boron concentration 19
3.4.4 Adjusting the pH 19
3.4.5 Jar test 19
3.4.6 Batch test 20
3.4.7 Collecting and filtering the supernatant 20
3.4.8 Drying the filtered precipitate 20
3.4.9 For Elemental analysis of the precipitate using XRF 20
3.5 Key Milestones 21
3.6 Gantt Chart 22
CHAPTER 4 RESULTS AND DISCUSSION 23
4.1 Introduction 23
4.2 Jar test results 23
4.3 Batch test results 25
4.4 X-ray fluorescence spectroscopy (XRF) Result 30
4.5 Cost Analysis 31
CHAPTER 5 CONCLUSION AND RECOMMENDATION 33
5.1 Conclusion 33
5.2 Recommendation 33
REFERENCES 34
APPENDICES 36

LIST OF FIGURES

Figure 1: Research Flowchart 14
Figure 2: Methodology Flowchart for Jar test 16
Figure 3: Methodology Flowchart for Batch test 18
Figure 4: AB vs Boron removal % 29
Figure 5: BC vs Boron removal % 29
Figure 6: AC vs Boron removal % 30

LIST OF TABLES

Table 1: Gantt Chart 22
Table 2: Jar test results for the Factorial design. 23
Table 3: ANOVA for the Factorial design developed using Design Expert 24
Table 4: Fit statistics of the Factorial model 25
Table 5: Batch test results for the Factorial design 25
Table 6: ANOVA for the Factorial design developed using Design Expert 26
Table 7: Fit statistics of the Factorial model 27
Table 8: Batch test results for Box – Behnken design 27
Table 9: ANOVA for Box – Behnken design developed using Design Expert 28
Table 10: Fit statistics of the Box - Behnken model 28
Table 11: XRF result 30
Table 12: Boron removal results using $ZrCl_4$ as the precipitant. 31
Table 13: Boron removal results using $Ca(OH)_2$ as the precipitant. 31
Table 14: Amount of precipitant for which highest boron removal was achieved 32
Table 15: Amount of precipitant used and cost to remove 100 mg/L 32

CHAPTER 1

INTRODUCTION

1.1 Background

Produced water according to Emmons et al. (2022) consists of a complex mixture of several organic solubles and elemental species, ranging from naturally occurring radioactive compounds to polycyclic aromatic hydrocarbons. With the development of hydraulic fracturing technology, oil and gas production has emerged as a significant worldwide energy resource, resulting in a lot of drilling-related wastewater (Emmons et al., 2022). It is the main waste stream from oil and gas exploration and is produced in large quantities, its global ratio to oil production is approximately 3:1 (Fakhru'l-Razi et al., 2009). In order to maintain pressure and achieve higher recovery levels during oil and gas production activities, more water is pumped into the reservoir leading to both formation and injected water creation along with hydrocarbon mixture. At the surface hydrocarbons are removed from produced fluid or produced water using different processes (Fakhru'l-Razi et al., 2009).

The source of boron in produced water could be natural or anthropogenic, or both. Produced water has high boron concentrations, rendering it useless unless treated as boron compounds fall under second class of toxicology danger according to medico-biological assessment making its consumption a significant threat to health (Ezerie Henry Ezechi, 2012).

In the field of wastewater treatment, boron removal is a significant challenge. Various technologies have been developed for boron removal, including adsorption, precipitation, reverse osmosis, ion exchange, and adsorption membrane filtration. Chemical precipitation methods, such as coagulation and chemical oxo-precipitation (COP), have shown promise in boron recovery (Zeytuncu et al., 2023). COP is a modified precipitation method that has been developed for boron removal.

COP utilizes hydrogen peroxide to promote the precipitation of metal perborate salts

from boric acid solutions. This method has shown high efficiency in removing boron from solution at room temperature and relatively neutral pH (Lin et al., 2016).

1.2 Problem Statement

Produced water has high concentrations of boron which is not desirable and has a negative impact on the environment, therefore it must be removed before the wastewater is discharged into the water bodies. Excessive levels of boron can be toxic to the environment, especially for plants. A 0.5 mg/L limit for boron concentration in drinkable water had been established by the World Health Organization (WHO) (Shih et al., 2014). However, in light of boron's beneficial impacts on human health, this number was revised in 2011 to 2.4 mg/L by WHO. Although 2.4 mg/L is below the level of human tolerance, this value is higher than required for a number of plant types that are sensitive to boron (Kim et al., 2023). In order to reduce the negative effects of boron exposure on aquatic life and plants, several nations have implemented boron effluent standards, which vary from 1.5 to 10 mg-B/L (Mahasti et al., 2022). Using COP to recover boron is effective but the precipitant used in the recovery process could result in harmful sludge production. Barium based COP is the most effective so far in boron recovery using COP but it produces sludge that is considered hazardous (Mahasti et al., 2022). Therefore, requiring further treatment.

1.3 Research Aim and Objectives

The aim of this research is to recover boron using an environmentally friendly, low energy and cost process which is efficient. COP using hydrogen peroxide as an oxidant and zirconium chloride as the precipitant is anticipated to achieve this aim.

The measurable objectives of this study are as follows:

1. To assess and optimize COP utilizing hydrogen peroxide as an oxidant and zirconium chloride as the precipitant to recover boron from synthetic produced water.
2. Application of XRF to analyze the elemental composition of the precipitate obtained from synthetic produced water solution after performing COP.
3. To conduct cost analysis of zirconium hydroxide and calcium hydroxide as

4. precipitants based on boron removal achieved employing batch tests to deter which of the two is more economical.

1.4 Significance and Contribution of Research

The significance of this study is to promote environmental health by finding a suitable precipitant to reduce boron concentration in produced water to safe levels.

1.5 Scope of Study

The scope of this project is to evaluate boron removal through COP using zirconium chloride as the precipitant and hydrogen peroxide as the oxidant from synthetic produced water with a boron concentration of 40 mg/L. Jar tests and batch tests will be carried out to determine the optimal pH, mole ratio of hydrogen peroxide to boron and zirconium chloride to boron based on boron removal percentage. From the different batch test runs carried out, the precipitate of the batch test run with the lowest boron removal will be analyzed using XRF to identify its elemental composition.

Cost analysis of zirconium hydroxide and calcium hydroxide as precipitants based on boron removal achieved employing batch tests will be carried out to deter which of the two is more economical.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Natural sources of elemental boron are uncommon due to its formation of complex compounds, like boric acid, borate, perborate, and other such compounds (Lin et al., 2016). Being one of the seven necessary trace elements found in nature, boron is intimately linked to the survival and well- being of living things. Consuming small amounts of boron helps humans and animals grow and develop; it also prevents diseases (Liu et al., 2022). The usage of boron and its compounds is spread across more than 300 different industries, these include those that produce glass, energy, electronics, ceramics, porcelain, cosmetics, semiconductors, leather, pharmaceuticals, pesticides, catalysts, fuels, fertilizers, cancer treatments, and cleaning goods. Over half of the world's production of boron compounds is consumed by the glass sector, which is the largest consumer (Kim et al., 2023). Manufacturing and mining processes can produce wastewater with boron concentration as high as 1000 mg/L (Mahasti et al., 2022).

Boron in water can exist in multiple chemical configurations and varying quantities, which makes it challenging to find an easy and affordable treatment solution (Lin et al., 2016). Boron at concentrations less than 216 mg/L is usually found in $B(OH)_3$ and $B(OH)^-_4$ forms (Zeytuncu et al., 2023). The maximum boron concentration in natural gas produced water according to Fakhru'l-Razi et al. (2009) is 56 mg/L. At a pH of less than 9, the predominant species is the uncharged $B(OH)_3$ molecule while at a pH of greater than 9, the fully hydrated form, $B(OH)_4$ appears (Shih et al., 2014).

Removing boron from wastewater employs various methods such as electro-coagulation, chemical precipitation, membrane filtering systems, forward osmosis, reverse osmosis, adsorption and exchange of ions. Electro-coagulation has been shown as an effective method for removing boric acids. When dealing with high

concentrations, chemical oxo-precipitation and reverse osmosis are the most suitable method for removing boric acid in wastewaters (Mahasti et al., 2022).

2.2 Chemical oxo-precipitation

COP has emerged as a promising technique for the recovery of boron, utilizing hydrogen peroxide as an oxidant and various precipitants. It involves using precipitants such as barium, strontium, magnesium and calcium-based precipitants. The precipitants are added to pretreated boric acid solution to form insoluble compounds which can be easily removed from water. Pretreatment is majorly performed by hydrogen peroxide or any other suitable oxidant (Shih et al., 2014).

Shih et al. (2014) optimized the COP process for boron removal at room temperature and found that the addition of hydrogen peroxide substantially improved the precipitation of boric acid, with 98.5% of boron being recovered as a borate salt using barium ions at pH 10. Lin et al. (2016) demonstrated that COP with H_2O_2 as the oxidant and barium hydroxide ($Ba(OH)_2$) as the precipitant achieved 99.7 % recovery of boron as barium perborate salts at room temperature.

COP using different precipitants, such as poly aluminum chloride (PACl), lime, calcium chloride($CaCl_2$), and barium chloride ($BaCl_2$), along with hydrogen peroxide as an oxidant, achieved significant boron removal (Zeytuncu et al., 2023). The authors, Zeytuncu et al. (2023) found that the addition of hydrogen peroxide improved boron removal due to perborate formation which can be removed more easily highlighting the potential of COP for the recovery of boron from aqueous solutions.

2.3 Zirconium chloride

Zirconium chloride dissolves in water to give zirconyl chloride and hydrochloric acid (Williams, 2013). According to Rijnten (1971) zirconyl solutions prepared using zirconium chloride are identical in behaviour to zirconyl solutions prepared using Zirconium (IV) oxychloride octahydrate ($ZrOCl_2.8H_2O$), dissolving one mole of $ZrOCl_2.8H_2O$ in water results in the formation of at least one mole HCl and addition of NaOH to neutralize this acid increases the degree of polymerization. Continuing the neutralization to a pH of 3 led to the start of precipitate formation which was completed at equivalence point (pH 9) and a gelatinous precipitate of hydrous zirconia

$Zr(OH)_4$) was obtained (Rijnten, 1971). Under alkaline conditions, as pH increases, solubility of $Zr(OH)_4$ increases (KOBAYASHI et al., 2007).

2.4 Zirconium in wastewater treatment

As an element or in compounds, zirconium (Zr) is typically considered to be nontoxic. Zirconium – based coagulants such as zirconium tetrachloride ($ZrCl_4$) and zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$), have rarely been included in water quality guidelines due to reports of their low toxicity (Uysal and Boyacioglu, 2021). This suggests that zirconium-based coagulants are a safer choice for treating wastewater as opposed to other coagulants that can pose health and environmental risks. Zirconium tetrachloride and zirconium oxychloride have been studied and compared to other coagulants by Uysal and Boyacioglu (2021), both demonstrated good pollution elimination and were effective in removal of a wide range of contaminants, including chemical oxygen demand (COD), total suspended solids (TSS), total phosphorus (TP), metals (including copper and zinc), and colour, with notable water purification. According to Uysal and Boyacioglu (2021), zirconium based coagulants out performed conventional coagulants such as ferric chloride and aluminum sulfate in terms of TP, copper and zinc removal. They also had good settling properties as per the sludge volume index (SVI) and settled sludge volume measurements.

2.5 Research gap

Recovery of boron especially from wastewater, has become a topic of interest in the field of research due to its use in different industries and impact on the environment. Many treatment and recovery methods have been investigated so far for this purpose, one of which is COP. Zirconium chloride has been used as a coagulant in wastewater treatment previously. However, these studies are very limited and its use as a precipitant in COP is yet to be explored.

CHAPTER 3

MATERIALS AND METHODS

3.1 Research flowchart

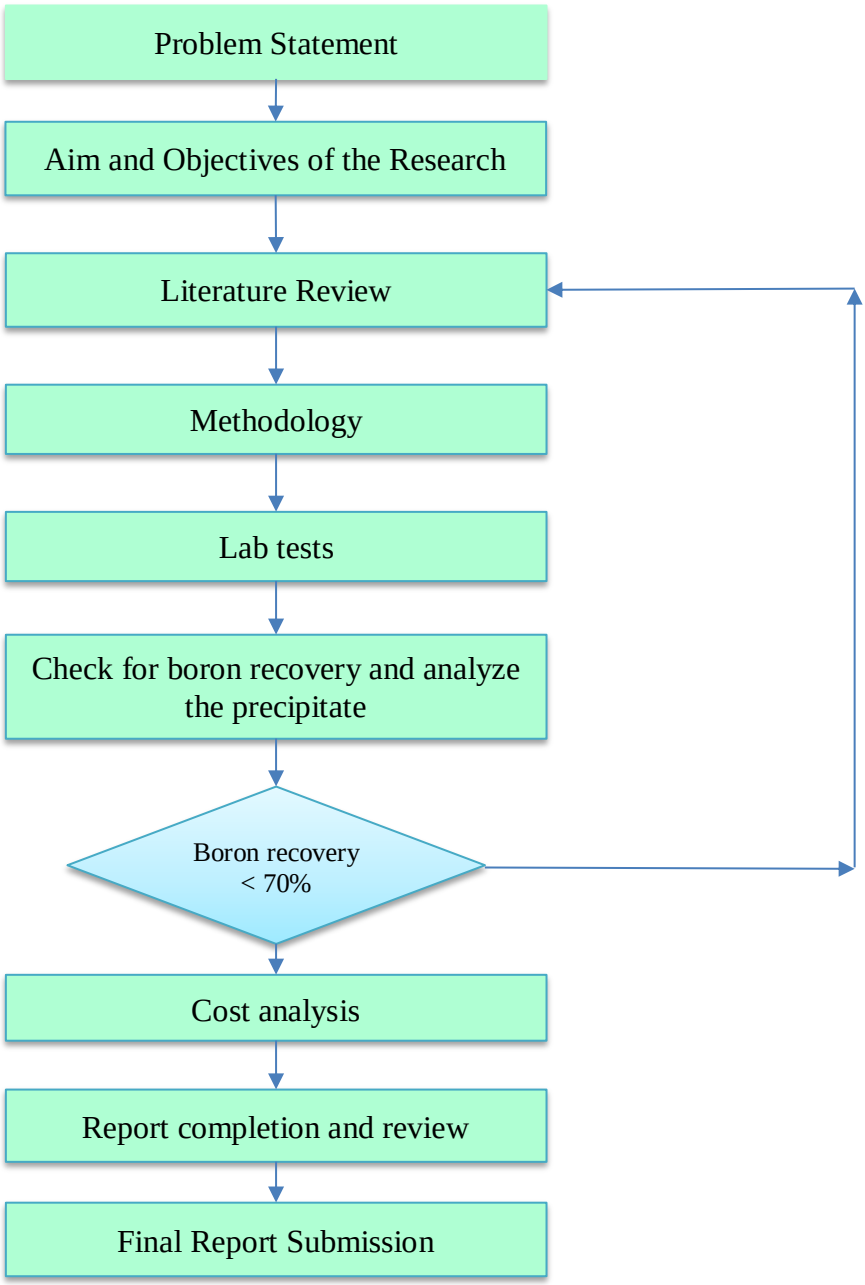

Figure 1: Research Flowchart

3.2 Materials

Analytical grade hydrogen peroxide (H_2O_2), zirconium chloride ($ZrCl_4$), boric acid (H_3BO_3), hydrochloric acid (HCl), sodium hydroxide (NaOH), BoroVer 3 reagent powder pillow, concentrated sulfuric acid and distilled water to prepare synthetic produced water using boric acid.

3.3 Methodology

3.3.1 Jar Test Experimental Procedure

A factorial design is developed using Design Expert, a software. Based on the number of factors an appropriate factorial design is selected, which in this case is a Regular Two-Level Factorial Design with one block and 5 center points per block as 6 factors are taken into consideration (pH, mole ratio of H_2O_2/B, mole ratio of $ZrCl_4$/B, reaction time, settling time and speed of the stirrer). Regular Two-Level Factorial Design can be used for 2 to 21 factors where every factor is set to 2 levels. The factors and their ranges are given as input to come up with the design.

Analytical grade boric acid is used to prepare a synthetic boron solution with desired concentration (40 mg/L - B) of which 400 mL is transferred into each 0.5 L beaker and adjusted to the desired pH value based on the experiment design using NaOH or HCl.

Employing Jar test, H_2O_2 and $ZrCl_4$ are added in a specific mole ratio of H_2O_2/B and $ZrCl_4$/B to the boric acid solution. The mixture is stirred for a fixed duration at a specific speed and then let to settle, all based on the experiment design developed using Design Expert software.

Once the mixture has settled, the supernatant is withdrawn, a 0.45 μm PVDF membrane is used to filter the extracted supernatant and remove any suspended particles (Shih et al., 2014). Using the Carmine method and DR3900 spectrometer determine the concentration of boron. The degree of boron removal can be determined by comparing the initial and final concentrations.

Rinse the collected precipitates multiple times and let the precipitates to dry for a full day at 110°C (Shih et al., 2014). Using X-ray fluorescence spectroscopy verify the elemental composition of the precipitates.

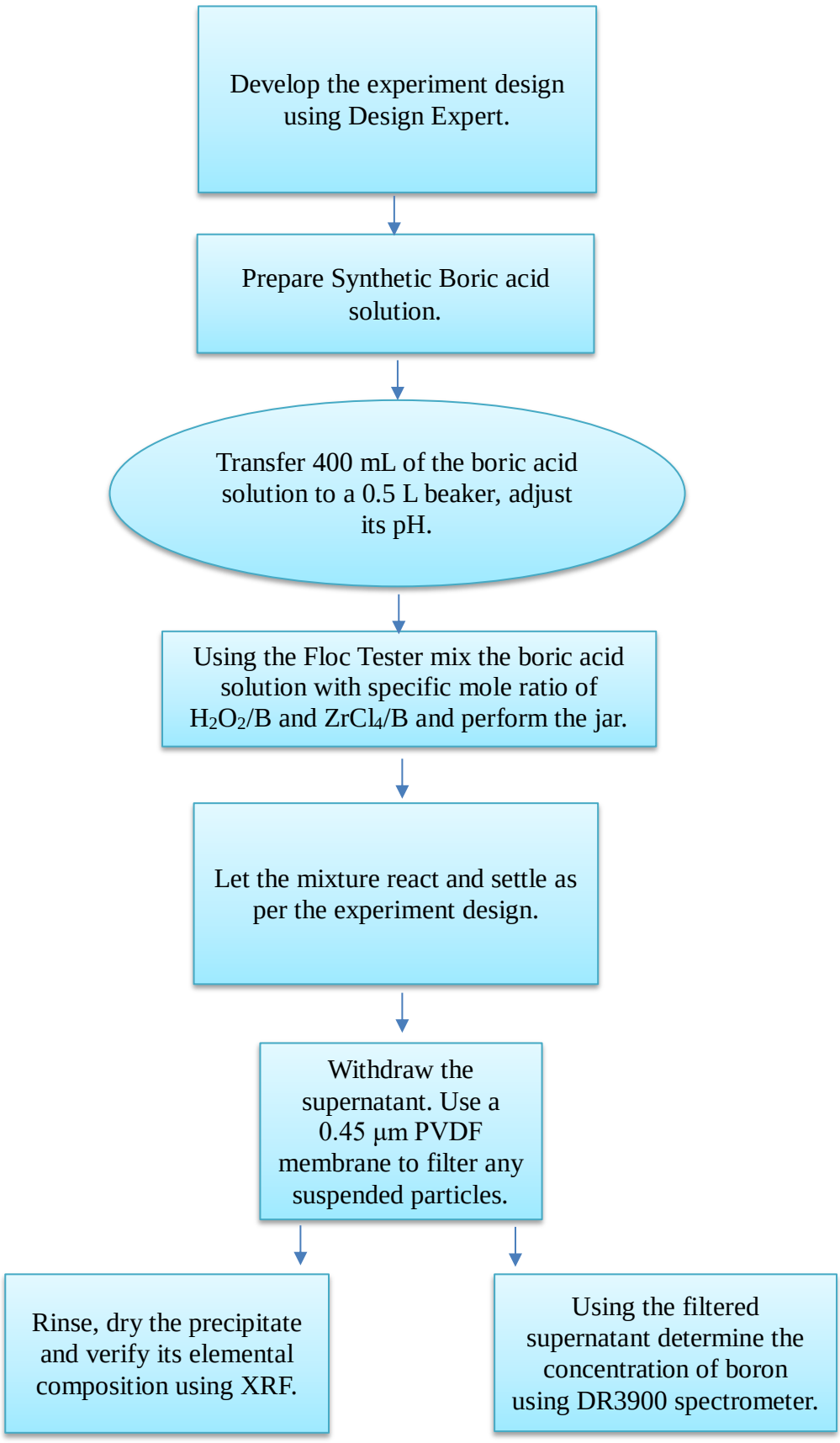

Figure 2: Methodology Flowchart for Jar test

3.3.2 Batch Test Experimental Procedure

The Factorial design and Box – Behnken design for batch test are developed using Design Expert. Based on the number of factors an appropriate factorial design is selected, which in this case is a Regular Two-Level Factorial Design with one block and 5 center points per block as 3 factors are taken into consideration (pH, mole ratio of H_2O_2/B, mole ratio of $ZrCl_4$/B). Regular Two-Level Factorial Design can be used for 2 to 21 factors where every factor is set to 2 levels. For Response Surface Methodology (RSM), Box – Behnken design was selected. Box – Behnken design can be used for 3 to 21 factors where each factor is set to 3 levels. Here, since 3 factors are taken into consideration, Box – Behnken Design with one block and 5 center points per block was selected. The factors and their ranges are given as input to come up with the Factorial and Box- Behnken design.

Analytical grade boric acid is used to prepare a synthetic boron solution with desired concentration (40 mg/L - B) of which 400 mL is transferred into each 0.5 L beaker and adjusted to the desired pH value based on the experiment design and maintained at that specific pH throughout each run using NaOH or HCl.

Batch tests are carried out using a hot plate stirrer, H_2O_2 and $ZrCl_4$ are added in a specific mole ratio of H_2O_2/B and $ZrCl_4$/B to the boric acid solution. The mixture is stirred for a fixed duration of 30 minutes at 120 rpm. The mixture is allowed to settle for an hour and its Supernatant is withdrawn. A 0.45 μm PVDF membrane is used to filter the extracted supernatant and remove any suspended particles (Shih et al., 2014). Using DR3900 spectrometer and Carmine method determine the concentration of boron. The degree of boron removal can be determined by comparing the initial and final concentrations.

Rinse the collected precipitates multiple times and let the precipitates to dry for a full day at 110°C (Shih et al., 2014). Using an X-ray fluorescence spectroscopy verify the elemental composition of the precipitates.

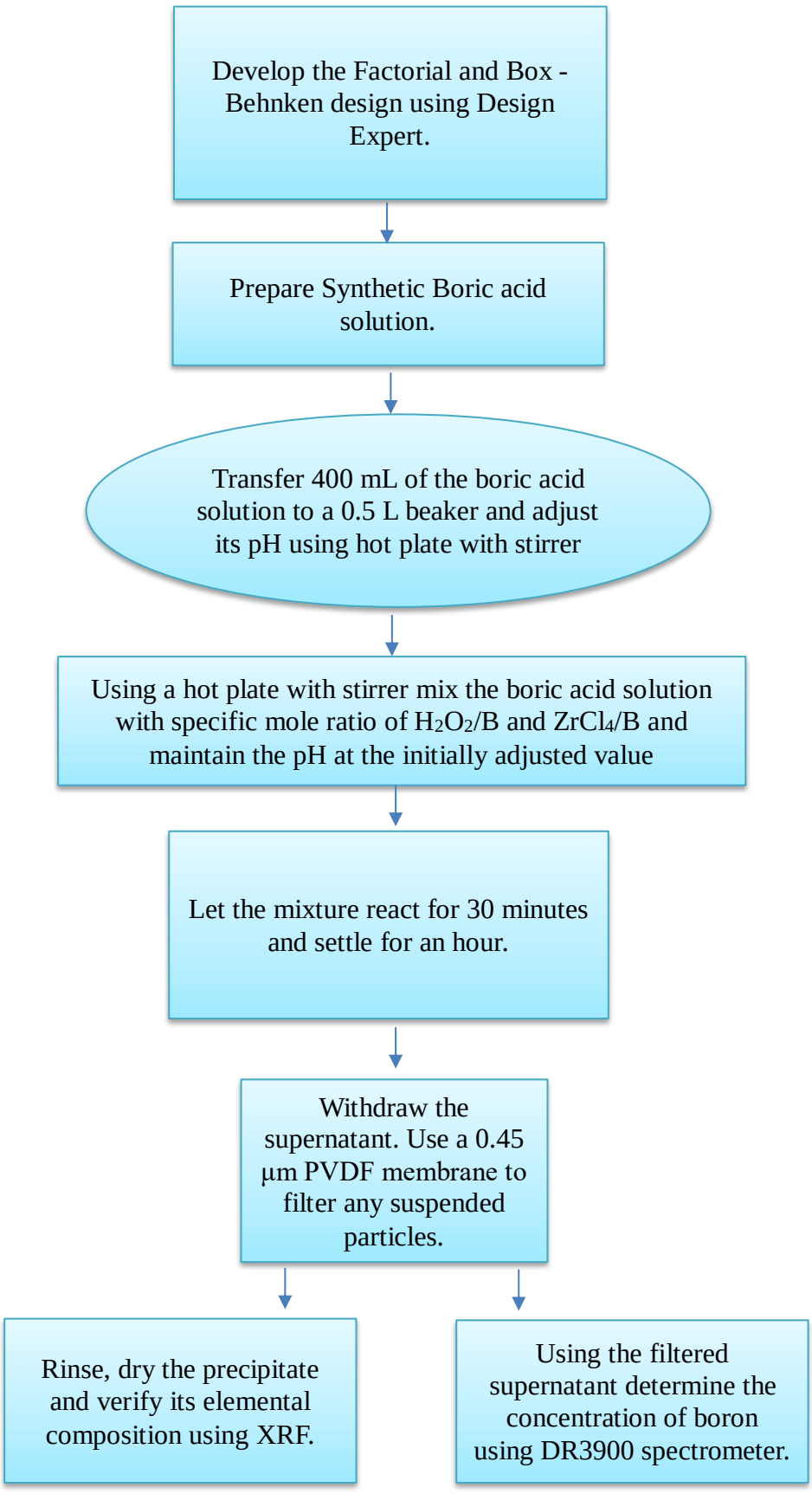

Figure 3: Methodology Flowchart for Batch test

3.4 Tools

3.4.1 Preparation of boric acid solution

Equipment and apparatus required:

I. Conical flask
II. Glass plate
III. Spatula
IV. Analytical balance
V. Funnel
VI. Glass rod
VII. 2-liter volumetric flask

3.4.2 Preparation of BoroVer 3/sulfuric acid solution

Apparatus required:

I. 100 mL measuring cylinder
II. 250 mL conical flask

3.4.3 Measuring the boron concentration

Equipment and apparatus required:

I. Micro-pipette (1 mL and 5mL)
II. Mirco-pipette tips
III. Glass tubes 16mm x 100 mm
IV. DR3900 Spectrometer

3.4.4 Adjusting the pH

Equipment and apparatus required:

I. 0.5 L beakers
II. Hot plate with stirrer
III. 3 mL disposable pipettes
IV. pH meter

3.4.5 Jar test

Equipment and apparatus required:

I. 0.5 L beakers
II. Weighing boat

III. Analytical balance
IV. micro-pipette (0.1 mL and 1 mL)
V. micro-pipette tips
VI. Floc Tester

3.4.6 Batch test

Equipment and apparatus required:

I. 0.5 L beakers
II. Hot plate with stirrer
III. Weighing boat
IV. 3 mL disposable pipettes
V. pH meter
VI. micro-pipette (0.1 mL and 1 mL)
VII. micro-pipette tips

3.4.7 Collecting and filtering the supernatant

Equipment and apparatus required:

I. Pipette
II. Filter paper
III. Glass tube

3.4.8 Drying the filtered precipitate

Equipment and apparatus required:

I. Aluminum dish
II. Metal tray
III. Drying oven

3.4.9 For Elemental analysis of the precipitate using XRF

Equipment:

I. Bruker S-8 Tiger

3.5 Key Milestones

1. Research project commencement: formal initiation of the project, after research topic selection and supervisor's approval.
2. Problem statement and Research objectives: this includes finding the effects of boron on the environment when it exceeds regulation limits, identifying problems in boron recovery using precipitation based on literature review and coming up with objectives to address the problem.
3. Formulation of methodology: this stage marks the end of the process of designing the experiment.
4. Completion of Research Proposal Defense VIVA: this milestone is marked by the completion of a power point presentation before the internal examiners and the supervisor.
5. Completion of lab: completion of all the experimental design runs marks the end of lab work, it also includes elemental analysis of the precipitate using XRF and batch tests to compare zirconium chloride and calcium hydroxide as precipitants in boron removal.
6. Completion of Data and Cost analysis: this milestone marks the completion of data and cost analysis, the collected data will be analyzed to determine COP's effectiveness, effect of different factors such as pH, mole ratio of zirconium chloride to boron and hydrogen peroxide to boron, on boron removal and to evaluate which of the two precipitants either zirconium chloride or calcium hydroxide is more economic.
7. Final report submission: this stage marks the end of the process of reviewing and modifying the final report. The final report is submitted for assessment.
8. Completion of Power Point preparation: this milestone is marked by the completion of power point slides and VIVA preparation
9. Completion of Project 2 VIVA: completion of a presentation before the internal, external examiner and the supervisor defending the project marks the end of this milestone.

3.6 Gantt Chart

Table 1: Gantt Chart

Semester	Semester 3 (Research Project 1)					Semester 4 (Research Project 2)		
Activities/Week	3	4	5	6-9	10-11	2-10	11	12
Problem statement and Research objectives								
Literature Review								
Methodology								
Power point preparation								
Lab work								
Data, cost analysis and report Writing								
Final report submission								
Power point preparation								

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

Based on the experimental design jar tests and batch tests were carried out to determine boron removal % and the effect of different factors on boron removal.

4.2 Jar test results

Table 2: Jar test results for the Factorial design.

		Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Response 1
Std	Run	A: pH	B:mole ratio (H_2O_2/B)	C:mole ratio ($ZrCl_4$/B)	D: reaction time	E: settling time	F: speed	Boron removal
					min	min	rpm	%
20	1	9	3	1.5	30	45	90	8
14	2	12	2	2	40	30	30	5.25
16	3	12	4	2	40	60	150	4.25
15	4	6	4	2	40	30	150	4.75
8	5	12	4	2	20	60	30	6
1	6	6	2	1	20	30	30	4.25
2	7	12	2	1	20	60	30	5
9	8	6	2	1	40	30	150	3.75
13	9	6	2	2	40	60	30	7.75
5	10	6	2	2	20	60	150	6
21	11	9	3	1.5	30	45	90	8
12	12	12	4	1	40	30	30	5.75
7	13	6	4	2	20	30	30	5.75
10	14	12	2	1	40	60	150	3.75
18	15	9	3	1.5	30	45	90	7.75
11	16	6	4	1	40	60	30	8.75
3	17	6	4	1	20	60	150	6.75
19	18	9	3	1.5	30	45	90	7.5
17	19	9	3	1.5	30	45	90	7.75
4	20	12	4	1	20	30	150	4.75
6	21	12	2	2	20	30	150	5

A total of 21 runs were carried out and boron removal percentage was calculated for each run by comparing the initial (40 mg/L boron) and final boron concentration. Boron removal was highest in run 16 as observed in Table 2 and lowest in run 8 and 14.

The pH of the solution after adding zirconium chloride to the jar in the mole ratio of $ZrCl_4$/B equivalent to 1, 1.5 and 2 resulted in the pH of the solution dropping to around 2 which is very low. At this pH the dominant species in the solution is boric acid which is a weak Lewis acid and does not readily form complexes with zirconium, this could be a reason for the low boron removal percentage.

Analysis of variance (ANOVA) was carried out for the Factorial design results which is shown in Table 3.

Table 3: ANOVA for the Factorial design developed using Design Expert

Source	Sum of Squares	df	Mean Square	F-value	p-value	Significance
Model	4.60	15	0.3065	43.79	0.0011	Significant
A-pH	0.6400	1	0.6400	91.43	0.0007	Significant
B-mole ratio (H2O2/B)	0.3600	1	0.3600	51.43	0.0020	Significant
C-mole ratio (ZrCl4/B)	0.0400	1	0.0400	5.71	0.0751	
D-reaction time	0.0025	1	0.0025	0.3571	0.5823	
E-settling time	0.8100	1	0.8100	115.71	0.0004	Significant
F-speed	0.9025	1	0.9025	128.93	0.0003	Significant
AB	0.0625	1	0.0625	8.93	0.0404	Significant
AC	0.0025	1	0.0025	0.3571	0.5823	
AD	0.1600	1	0.1600	22.86	0.0088	Significant
AE	1.56	1	1.56	223.21	0.0001	Significant
AF	0.0100	1	0.0100	1.43	0.2980	
BD	0.0000	1	0.0000	0.0000	1.0000	
BF	0.0400	1	0.0400	5.71	0.0751	
ABD	0.0025	1	0.0025	0.3571	0.5823	
ABF	0.0025	1	0.0025	0.3571	0.5823	
Curvature	3.31	1	3.31	473.23	< 0.0001	
Pure Error	0.0280	4	0.0070			
Cor Total	7.94	20				

The model is significant as its p-value in the above table is 0.0011 which is less than 0.0500. Using the p-values from the table significance of different factors on boron removal can be determined. Factors with a p-value less than 0.0500 are considered significant whereas factors with a p-value greater than 0.1000 are considered not significant.

Therefore, based on the p-values factors A (pH), B (mole ratio of (H_2O_2/B), E (settling time), F (speed), AB, AD and AE are significant.

Table 4: Fit statistics of the Factorial model

Std. Dev.	0.2092	**R^2**	0.9939
Mean	6.02	**Adjusted R^2**	0.9712
C.V. %	3.47	**Predicted R^2**	NA(1)
		Adeq Precision	26.5684

The model is valid as its R2 value is greater than 0.95 as shown in Table 4.

4.3 Batch test results

Table 5: Batch test results for the Factorial design

		Factor 1	Factor 2	Factor 3	Response 1
Std	Run	A: pH	B:mole ratio (H_2O_2/B)	C:mole ratio ($ZrCl_4$/B)	Boron removal %
1	1	4	0.4	0.2	1.75
11	2	8	1.2	0.6	8.3
10	3	8	1.2	0.6	8.1
6	4	12	0.4	1	3
8	5	12	2	1	3.5
9	6	8	1.2	0.6	7.9
5	7	4	0.4	1	1.9
12	8	8	1.2	0.6	8
4	9	12	2	0.2	0.9
13	10	8	1.2	0.6	8.2
3	11	4	2	0.2	2.8
7	12	4	2	1	3
2	13	12	0.4	0.2	0.3

A series of batch tests were performed where the pH was maintained at a specific value based on the experimental design throughout the run. Boron removal was highest in run 2 with 8.3 % as observed in Table 5.

When the pH was adjusted and maintained at 8 a gelatinous precipitate was observed which is a physical characteristic of zirconium hydroxide. At this pH the concentration of borate ions is also higher compared to lower pH values (pH > 7), but is still less compared to boric acid. The presence of more borate ions could have led to an increase in perborate formation by reacting with the added hydrogen peroxide. The gelatinous precipitate generated could have trapped the boron species in the solution and removed them from the solution by settling.

As the pH was increased the white gelatinous precipitate generated around pH 7-8 gradually decreased in size, which could be due to it dissolving back into the solution. The boron removal percentage was the least at pH 12 with just 0.3%.

Table 6: ANOVA for the Factorial design developed using Design Expert

Source	Sum of Squares	df	Mean Square	F-value	p-value	Significance
Model	8.90	7	1.27	50.84	0.0010	Significant
A-pH	0.3828	1	0.3828	15.31	0.0173	Significant
B-mole ratio (H2O2/B)	1.32	1	1.32	52.81	0.0019	Significant
C-mole ratio (ZrCl4/B)	3.99	1	3.99	159.61	0.0002	Significant
AB	0.1378	1	0.1378	5.51	0.0787	
AC	3.06	1	3.06	122.51	0.0004	Significant
BC	0.0003	1	0.0003	0.0125	0.9164	
ABC	0.0028	1	0.0028	0.1125	0.7542	
Curvature	109.16	1	109.16	4366.39	< 0.0001	
Pure Error	0.1000	4	0.0250			
Cor Total	118.16	12				

The model is significant as its p-value in the above Table 6 is 0.0010 which is less than 0.0500. Using the p-values from the table significance of different factors on boron removal can be determined. Factors with a p-value less than 0.0500 are considered significant whereas factors with a p-value greater than 0.1000 are considered not significant.

Therefore, based on the p-values factors A (pH), B (mole ratio of H_2O_2/B), C (mole ratio of $ZrCl_4$/B), and AC are significant.

Table 7: Fit statistics of the Factorial model

Std. Dev.	0.1581	**R^2**	0.9889
Mean	4.43	**Adjusted R^2**	0.9694
C.V. %	3.57	**Predicted R^2**	NA(1)
		Adeq Precision	59.2891

The value of R2 as shown in Table 7 is greater than 0.95, indicating the model is valid.

Table 8: Batch test results for Box – Behnken design

		Factor 1	Factor 2	Factor 3	Response 1
Std	Run	A: pH	B:mole ratio (H_2O_2/B)	C:mole ratio ($ZrCl_4$/B)	Boron removal %
6	1	12	1.2	0.2	0.3
8	2	12	1.2	1	3.9
10	3	8	2	0.2	6.8
7	4	4	1.2	1	3.1
3	5	4	2	0.6	2.6
1	6	4	0.4	0.6	2.2
15	7	8	1.2	0.6	8.6
14	8	8	1.2	0.6	8.5
5	9	4	1.2	0.2	1.5
12	10	8	2	1	9.8
16	11	8	1.2	0.6	8.3
11	12	8	0.4	1	9
4	13	12	2	0.6	2.9
13	14	8	1.2	0.6	8.5
2	15	12	0.4	0.6	1.7
17	16	8	1.2	0.6	8.4
9	17	8	0.4	0.2	5.5

Boron removal was highest in run 10 with 9.8 % as observed in Table 8 and lowest in run 1 with 3.75 %.

Table 9: ANOVA for Box – Behnken design developed using Design Expert

Source	Sum of Squares	df	Mean Square	F-value	p-value	Significance
Model	167.64	9	18.63	435.34	< 0.0001	Significant
A-pH	0.0450	1	0.0450	1.05	0.3392	
B-mole ratio (H2O2/B)	1.71	1	1.71	40.00	0.0004	Significant
C-mole ratio (ZrCl4/B)	17.11	1	17.11	399.93	< 0.0001	Significant
AB	0.1600	1	0.1600	3.74	0.0944	
AC	1.0000	1	1.0000	23.37	0.0019	Significant
BC	0.0625	1	0.0625	1.46	0.2660	
A^2	143.73	1	143.73	3359.19	< 0.0001	Significant
B^2	0.3013	1	0.3013	7.04	0.0328	Significant
C^2	0.7339	1	0.7339	17.15	0.0043	Significant
Residual	0.2995	7	0.0428			
Lack of Fit	0.2475	3	0.0825	6.35	0.0531	Not significant
Pure Error	0.0520	4	0.0130			
Cor Total	167.94	16				

The model is significant as its p-value in Table 9 is 0.0001 which is less than 0.0500. Using the p-values from the table significance of different factors on boron recovery can be determined. Factors with a p-value less than 0.0500 are considered significant whereas factors with a p-value greater than 0.1000 are considered not significant.

Therefore, based on the p-values factors B (mole ratio of H_2O_2/B), C (mole ratio of $ZrCl_4$/B), AC, A^2, B^2, and C^2 are significant. The lack of fit however is not significant which shows the model fits.

Table 10: Fit statistics of the Box - Behnken model

Std. Dev.	0.2068	**R^2**	0.9982
Mean	5.39	**Adjusted R^2**	0.9959
C.V. %	3.84	**Predicted R^2**	0.9759
		Adeq Precision	59.3308

The difference between the adjusted R2 and the predicted R2 is less than 0.2, this indicates a good fit.

Figures 4, 5 and 6 show the 3D surface model graphs for AB vs Boron removal %, BC vs Boron removal % and AC vs Boron removal %. Using these 3D models boron

removal percentage for respective AB, BC and AC values can be determined.

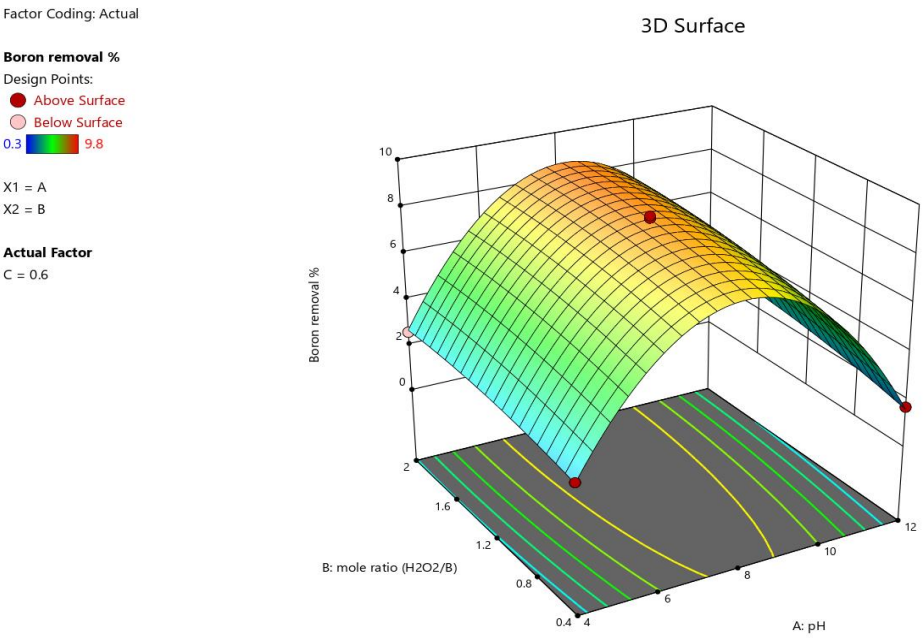

Figure 4: AB vs Boron removal %

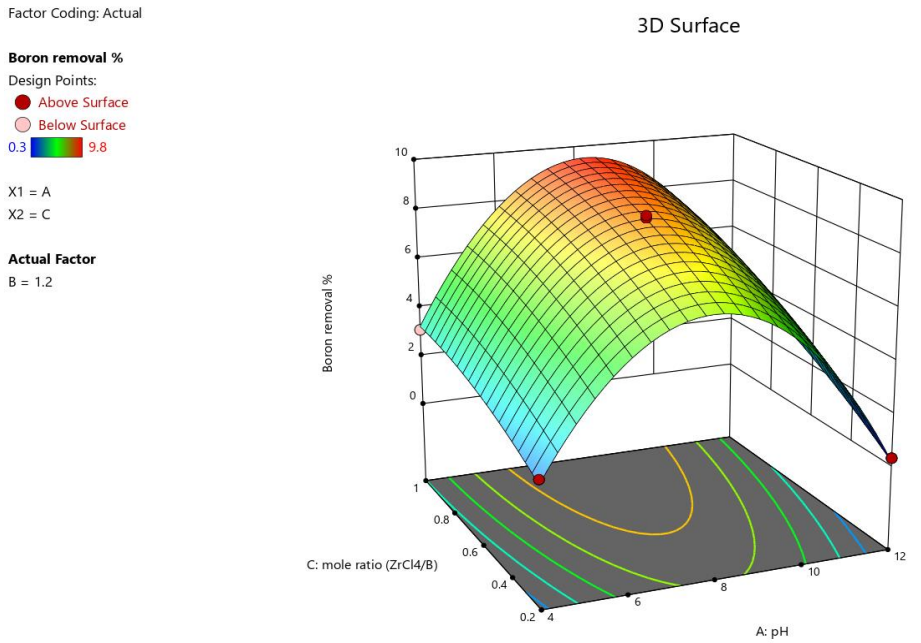

Figure 5: BC vs Boron removal %

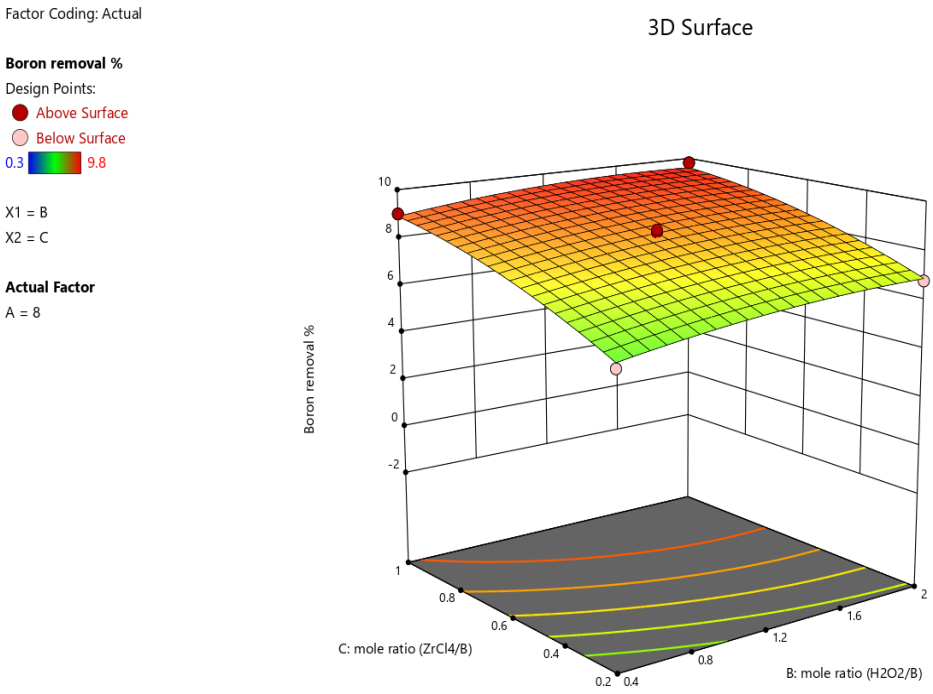

Figure 6: AC vs Boron removal %

4.4 X-ray fluorescence spectroscopy (XRF) Result

Table 11: XRF result

Formula	Concentration	Status	Analyzed Layer	XRF %
Zr	87.6 %	XRF 1	145 µm	87.57
Na	5.02 %	XRF 1	0.77 µm	5.02
Cl	2.62 %	XRF 1	1.23 µm	2.62

Table 11 shows the elemental composition of the precipitate obtained when the pH was maintained at 12 and the mole ratio of H_2O_2/B added was 0.4 and that of $ZrCl_4$/B was 0.2.

The results show that no boron was found, which is in agreement with the results obtained employing batch test where the boron removal for the same factor values was 0.3% which is not zero but very small and therefore can be neglected.

4.5 Cost Analysis

Chemical precipitation requires precipitants, in addition to their effectiveness in precipitating the metal of concern and environmental effects, their cost and availability plays a crucial role in deciding whether or not the precipitant is used.

To compare zirconium chloride with calcium hydroxide ($Ca(OH)_2$), one of the most widely used precipitant, three runs with randomized values were carried out.

Table 12: Boron removal results using $ZrCl_4$ as the precipitant.

pH	mole ratio (H_2O_2/B)	mole ratio ($ZrCl_4$/B)	Boron removal %
9.981	0.980	0.255	4.76
11.968	0.430	0.534	1.1
10.281	0.775	0.215	3.8

Table 13: Boron removal results using $Ca(OH)_2$ as the precipitant.

pH	mole ratio ($Ca(OH)_2$/B)	Boron removal %
9.981	0.255	1.2
11.968	0.534	5.4
10.281	0.215	2.3

Tables 12 and 13 show that using zirconium hydroxide as the precipitant gave better results compared to calcium hydroxide for the same amount of precipitant except at pH 11.968. Though the runs were all at a high pH which favor $Ca(OH)_2$ according to Remy et al. (2004) compared to zirconium hydroxide which is more effective at a slightly acidic to basic pH of 8 as seen from previous results the difference isn't much. The boron removal percentage for 0.534 mole ratio of calcium hydroxide to boron was 5.4%, this compared to the highest boron removal percentage (9.8%) achieved using zirconium chloride which was at a pH of 8 and 1 mole ratio of $ZrCl_4$/B based on the batch test results gives a difference of 4.4%, which is low.

The cost of 1 kg of analytical grade calcium hydroxide by Sigma-Aldrich is MYR 630 (INR 10,980) whereas the cost of 1 kg of zirconium chloride by Sigma-Aldrich is MYR 2340.5 (INR 40,790), which is quite high. According to the above pricing each gram of $Ca(OH)_2$ will cost you MYR 0.63 in comparison to zirconium chloride which will set you back MYR 2.340 every gram. Since the difference in boron removal %

between $Ca(OH)_2$ and $ZrCl_4$ is just 4.4% paying MYR 1.71 more for every gram doesn't seem economical.

Table 14: Amount of precipitant for which highest boron removal was achieved

Precipitant	Amount used in grams	Boron removal in mg/L
$ZrCl_4$	0.3448	3.92
$Ca(OH)_2$	0.1044	2.16

Table 15: Amount of precipitant used and cost to remove 100 mg/L

Precipitant	Amount used in grams	Cost in RM
$ZrCl_4$	8.79	20.56
$Ca(OH)_2$	4.83	3.042

The highest boron removal (3.92 mg/L) achieved using zirconium chloride was at 0.3448 g as shown in Table 14 compared to calcium hydroxide which was 2.16 mg/L at 0.1044 g.

Based on the amount of precipitant used and boron removal achieved, the amount of precipitant used and its associated cost to remove 100 mg/L of boron is calculated and shown in Table 15. The cost associated with removing 100 mg/L of boron using zirconium chloride is 85 % higher than that of calcium hydroxide which doesn't seem economical.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This project was carried out to investigate an innovative approach for recovering boron from produced water using COP method. This method involves the use of an oxidant and a precipitant. Laboratory experiments were carried out to determine the effects of different factors such as boron pH, mole ratio of hydrogen peroxide to boron, mole ratio of zirconium chloride to boron, settling time, and speed of the stirrer on boron removal. Based on the jar tests in which the pH was adjusted initially, factors A (pH), B (mole ratio of (H_2O_2/B), E (settling time) and F (speed) were found to be significant. From the batch tests in which the pH was maintained throughout the precipitation process, factors A (pH), B (mole ratio of H_2O_2/B) and C (mole ratio of $ZrCl_4$/B) were found to be significant. Maintaining the pH throughout the precipitation process led to an increase in boron removal percentage, which was highest at pH 8 for mole ratio of H_2O_2/B and $ZrCl_4$/B equal to 2 and 1, respectively. The elemental composition of the precipitate obtained at pH 12 which had the lowest boron removal was analyzed using X-ray fluorescence spectroscopy (XRF) to check for the presence of boron and other elements, zirconium concentration was found to be the highest (87.6%) and no boron was detected. Cost analysis comparing calcium hydroxide and zirconium chloride based on boron removal was carried out, and calcium hydroxide was determined to be the better precipitant in terms of cost.

5.2 Recommendation

Tests should be carried out at pH 6 and 7 to better understand precipitation using zirconium chloride. The chemical sludge formed as a result of chemical precipitation in most cases is waste and requires further treatment before it is disposed. This adds to the overall cost. Precipitants that form less sludge or sludge that has use should be explored.

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APPENDICES

Calculations:

1) To prepare a 2-liter boric acid solution with boron concentration equal to 40 mg/L:

1 mol of Boron = 10.81 g

How many moles of boron (?) = 40 mg (0.040 g)

40 mg of Boron in moles = $\frac{0.040\ g}{10.81\ g}$ * mol = 0.0037 mol

Moles of boron = moles of boric acid (H_3BO_3)

Molarity = $\frac{moles}{volume\ (L)} = \frac{0.0037\ mol}{1\ L}$ = 0.0037 mol/L

Mass of boric acid (g) = Concentration (mol/L) * Volume (L) * Formula Weight (g/mol)

Mass of boric acid (g) = 0.0037 mol/L * 2 L * 61.83 g/mol

Mass of boric acid (g) = 0.4575 g

2) Moles of boron in 400 mL (each jar = 400 mL):

Moles of boron = 0.4 L * 0.0037 mol/L

Moles of boron = 0.00148 mol

3) Calculating for mole ratio of H_2O_2/B = 2:

Since number of moles of boron in every jar (400 mL) = 0.00148 mol

Moles of hydrogen peroxide required = 0.00148 * 2 = 0.00296 mol

Molarity of H_2O_2 = 9.8 M

Volume of H_2O_2 required = $\frac{moles}{Molarity\ (M)} = \frac{0.00296\ mol}{9.8\ mol/L}$ = 0.0003020 L = 0.3020 mL

Similarly Calculate for mole ratio of H_2O_2/B as required.

4) Calculating for mole ratio of $ZrCl_4$/B = 2:

Since number of moles of boron in every jar (400 mL) = 0.00148 mol

Moles of zirconium chloride required = 0.00148 * 2 = 0.00296 mol

1 mol of zirconium chloride = 233.03 g

0.00296 mol = how many grams of zirconium chloride (?)

Required grams of zirconium chloride = $\frac{0.00296\ mol * \ 233.03\ g}{1\ mol}$ = 0.6897 g

Similarly Calculate for mole ratio of $ZrCl_4$/B as required.