



MODELING OF ARSENIC REMOVAL FROM
AQUEOUS MEDIA USING SELECTED COAGULANTS

By

Avela Majavu

A dissertation submitted in fulfillment

of the requirements for the

Magister Technologia: Chemistry

Faculty of Applied Science

Nelson Mandela Metropolitan University

January 2010

Supervisor: Dr Gletwyn Rubidge

Co-Supervisor: Dr. Nicole Vorster

ACKNOWLEDGEMENTS

- My Lord and my Savoir for protection, love, hope, trust and for making me believe in myself in times of difficulties.
- Dr Gletwyn Rubidge for guidance as my supervisor.
- Mr Coos Bosma as my mentor in interpretation of ANOVA.
- Dr Eric Hosten for helping me with the ICP-MS runs.
- Nelson Mandela Metropolitan University scholarship for assistance.
- DAAD Scholarship for assistance.
- National Research Foundation for assistance.
- My family (Majavu Family) for their support, when I cry they pick me up (My father Boy, Christian, Mntwekhaya, my mother Nozuko, Junior, my brothers, Zama Coe, Ncedisa Obed and Mbiyozo Sikhona and only sister Kuhle)
- Mpepo Family (my grandmother Nonesi Alice and my aunties Mbuyie, Hlope, Sophakathi) for their support.
- Mr Gary Miller (Production Manager from Aspenpharmacare Ltd) as my language and communication assistant.

SUMMARY

The waste water from the industrial production of the herbicide monosodium methyl arsenate was treated using coagulation. The coagulation process as developed in this research proved to be suitable for arsenic removal in aqueous media using chromium (III), calcium (II), and combination of calcium (II) and chromium (III), and magnesium (II). The results obtained suggest that the coagulation process can be used for the treatment of the waste water from the monosodium methyl arsenate production. Response surface methodology was used to study the effects of the various parameters, namely pH, mole ratios (Cr:As, Ca:As, and Mg:As), concentration of flocculent and initial arsenic concentration. To optimize the process conditions for the maximum removal of arsenic. Central composite and factorial designs were used to study the effects of these variables and to predict the effect of each. ANOVA was used to identify those factors which had significant effects on model quality and performance. The initial arsenic concentration appeared to be the only significant factor. These models were statistically tested and verified by confirmation experiments.

CONTENTS	PAGE NUMBERS
TITLE	i
ACKNOWLEDGEMENTS	ii
SUMMARY	iii
CONTENTS	iv-xi
FOREWORD	1
CHAPTER 1: GENERAL BACKGROUND OF ARSENIC AND MOTIVATION FOR STUDY	2-33
1. Introduction	2
1.1 Motivation for proposed study	2
1.2 Objective	3
1.3 Significance of the research	3
1.4 History and properties of arsenic	3
1.4.1 Discovery	3
1.4.2 Occurrence	4
1.4.3 Properties of arsenic	4-6
1.4.3.1 The background of arsenic	4-5
1.4.3.2 Chemical properties	5
1.4.3.3 Physical properties	5
1.4.3.4 Production	6
1.4.3.5 Extraction	6
1.5 Chemistry of arsenic	6-8
1.6 Compounds of arsenic	8
1.7 Monosodium methyl arsenate (MSMA)	8-9
1.8 Uses of arsenic	10
1.9 Toxicology of arsenic and its compounds	10-15
1.9.1 The mechanism of arsenic	10
1.9.2 The fate of MSMA and its decomposition product in soil	11
1.9.3 The general principle of arsenic detoxification	12
1.9.4 Human exposure to arsenic	12

1.9.5 Arsenic poison symptoms	13-14
1.9.6 Detoxification and metabolization	15
1.10 Toxicology significant environmental occurred and effect of arsenic	15-16
1.11 Treatment of arsenic poisoning	16-17
1.12 Removal of arsenic removal from aqueous media	17-24
1.12.1 Coagulation / Precipitation / Flocculation / Sedimentation	17-18
1.12.2 Lime softening	18
1.12.3 Activated alumina	18-19
1.12.4 Iron adsorbents	19
1.12.5 Oxidation / Reduction	19
1.12.6 Adsorption	20
1.12.7 Ion exchange	20
1.12.8 Reverse osmosis	21
1.12.9 Nano-filtration	22
1.12.10 Micro-filtration (MF) and Ultra-filtration (UF)	22
1.12.11 Biological methods of arsenic removal	22
1.12.12 Solar distillation	22
1.12.13 Technologies available from arsenic treatment	23-24
1.13 Disposal of arsenic wastes	24
1.14 Leaching testing on sludge	25-26
1.17 References	27-33

CHAPTER 2: EXPERIMENTAL METHODOLOGY AND PROCEDURE	34-49
2.1 Materials	34
2.1.1 Chemicals used	34
2.2 Preparation of reagents	35
2.3 Arsenic analysis	35-36
2.3.1 Analytical instruments	35
2.3.1.1 Atomic Absorption Spectrometry (AAS)	36-38
2.3.1.2 Inductively Coupled Plasma Emission Spectroscopy (ICP-AES)	38-40
2.3.1.3 Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)	40-42
2.4 pH determination	42
2.5 MSMA Sample	42
2.6 Analytical procedure	42
2.6.1 Preparation of MSMA stock solution	42
2.6.2 Preparation of standards	43
2.7 Experimental Procedure	44-45
2.7.1 Coagulation procedure	44
2.7.2 Arsenic analysis	45
2.8 Modelling method	45-47
2.8.1 Analysis of variance (ANOVA)	45-46
2.8.2 Summary of criteria that model achieved	46-47
2.9 Experimental design	47-48
2.9.1 Selected theory of experiment design (Design)	47
2.9.1.1 Design Expert operating procedure (DOE)	47-48
2.10 References	49

CHAPTER 3: THE MODELLING OF ARSENIC (V) REMOVAL FROM AQUEOUS MEDIA USING CHROMIUM CHLORIDE (III)	50-70
3.1 Introduction	50
3.2 Experimental	50-53
3.2.1 Coagulation procedure	50
3.2.2 Mechanism of arsenate removal by chromium coagulation	50
3.2.3 Selection of the experimental domain	51
3.2.4 Design matrix for chromium (III)-based coagulation	52
3.2.5 The experimental design in coded values	52
3.2.6 The coded central composite design (CCD) used to investigate chromium (III)-based coagulation of arsenate	52-53
3.3 Results and discussion	54-57
3.3.1 Fitting a model to the experimental data	54
3.3.2. The actual values of the experimental design and responses	54-57
3.4 The model	57-59
3.4.1 Defining the polynomial equation describing the chromium (III)-based removal of arsenate	57
3.4.2 Final model describing the chromium (II)-based removal of arsenate	59
3.5. ANOVA	60-63
3.5.1 Definition of Anova terms	60-61
3.5.2 Interpretation of ANOVA	61
3.5.3 Summary of statically tests performed by Anova	62-63
3.6 Validation of the model	63-67
3.6.1 Graphic Model Validation	63
(I) Normal probability of studentized residuals	64-65
(II) Studenised residuals vs. predicted response	65-66
3.6.2 The final model representing chromium (III)-based coagulation of arsenate	67
3.6.3 Optimization of chromium (III)-based coagulation of	67

arsenate	
3.7 Experimental validation	68
3.7.1 Confirmation experiments	68-69
3.8 Conclusion	69
3.9 References	70-71
CHAPTER 4: THE MODELLING OF ARSENIC (VI) REMOVAL FROM AQUEOUS MEDIA USING CALCIUM CHLORIDE (II)	72-85
4.1 INTRODUCTION	72
4.2 Experimental	72
4.2.1 Coagulation procedure	72
4.2.2 Mechanism of arsenate removal by calcium coagulation	72
4.3 Experimental domain	73
4.4 The experimental domain	73
4.5 Results and discussion	74
4.5.1 ANOVA analysis	74-77
4.5.2 Defining the polynomial equation describing the calcium (II)-based removal of arsenate	75
4.5.3 Estimated coefficients for final models that described the calcium(II)-based removal of arsenate.	76-77
4.6 Validation of the model	78-83
4.6.1 Graphical model validation	78
(I) Full Normal probability plot of residuals	78-79
(II) Studentized residuals vs predicted response	80-81
(III) Half normal probability plot of residuals	81-82
4.6.2 The final model representing calcium (II)-based coagulation of arsenate	83
4.6.3 Optimization of calcium (II)-based coagulation of arsenate	83
4.7 Experimental validation	84
4.8 Conclusion	84
4.9 References	85

**CHAPTER 5: THE MODELLING OF ARSENIC (VI) REMOVAL FROM
AQUEOUS MEDIA USING A BINARY MIXTURE OF CHROMIUM CHLORIDE**

(III) AND CALCIUM CHLORIDE (II) AS COAGULANT	86-99
5.1 Introduction	86
5.2 Experimental	86-88
5.2.1 Coagulation procedure	86
5.2.2 Binary component studies	87
5.2.3 Coded values of the binary coagulation of arsenic	87-88
5.2.4 The results of factorial design	88
5.3 Results and discussion	89
5.3.1 ANOVA analysis	89-90
5.4 The model	90
5.4.1 Defining the polynomial equation describing the chromium (III) and calcium (II)-based removal of arsenate	90-91
5.4.2 Estimated coefficients for the final models that described the chromium (III) and calcium (II)-based removal of arsenate.	91-92
5.5 Validation of the model	92-94
5.5.1 Graphic validation	92
(I) Full Normal probability of studentized residuals	93-94
(II) Studentized residuals versus predicted response	94-95
(III) Half normal plot	96-97
5.5.2 The final model representing chromium (III) and calcium (II)-based coagulation of arsenate	97
5.5.3 Optimization of chromium (III) and calcium (II)-based coagulation of arsenate	97
5.6 Experimental validation	98
5.7 Conclusion	98
5.8 References	99

CHAPTER 6: THE MODELLING OF ARSENIC (VI) REMOVAL FROM AQUEOUS MEDIA USING MAGNESIUM CHLORIDE (II)	100-112
6.1. Introduction	100
6.2 Experimental	100
6.2.1 Coagulation procedure	100
6.2.2 Mechanism of arsenate removal by magnesium coagulation	100
6.3 Experimental design	101-102
6.3.1 Factorial design experiment for magnesium (II)-based coagulation of arsenic	101
6.3.2 Coded values of the magnesium (II)-based coagulation	101
6.3.3 Results of the half factorial design using magnesium (II) as coagulant	102
6.4 Results and discussion	102-105
6.4.1 Factorial design and ANOVA analysis	102-103
6.4.2 Defining the polynomial equation describing the magnesium (II)-based removal of arsenate.	104
6.4.3 Estimated coefficients for final models that described the magnesium (II)-based removal of arsenate.	105
6.5 Validation of the model	106-110
6.5.1 Graphic validation	106
(I) Full normal probability of studentized residuals	106-107
(II) Studentized residuals versus predicted response	107-118
(III) Half normal plot	109-110
6.5.2 Optimization of magnesium (II)-based coagulation of arsenate	110
6.6 Experimental validation	110
6.7 Conclusion	111
6.8 References	112

CHAPTER 7: CONCLUSION	113-119
7.1 Literature Review	113
7.2 Modelling studies	113-118
7.2.1 Introduction	113
7.2.2 Statistical Analysis	113
7.2.3 Chromium (III)-based coagulation	114-115
7.2.4 Calcium (II)-based coagulation	115-117
7.2.5 Combined calcium (II) and chromium (III)-based coagulation	117-119
7.2.6 Magnesium (II)-based coagulation	119-121
7.2.7 Comparisons of the coagulant systems	121-122
7.3 Model comparison with other research work	122-123
7.4 Cost consideration	124
7.5 Conclusion	125
7.6 Future research	125
7.7 References	126-127
Appendix 1- list of figures	128-129
Appendix 2- list of tables	130-134
Appendix 3- list of equations	134

FOREWORD

Arsenic has a sinister character and this is manifested in the old alchemist symbol which is a coiled serpent ready to strike. It is not surprising that there is a great deal of concern over its likely presence in drinking water because of its reputation as a preferred hazardous agent of popular detective novels. The objective of this study is to devise a method of coagulation using chromium, magnesium, calcium and binary mixtures that will be suitable for arsenic removal from bodies of water. This dissertation provides general information about arsenic; its occurrence, toxicology, health effects, the reagents, apparatus, as well as the methodology used during this research study. The preliminary investigation and examination of the factors which influence the removal of arsenic using chromium chloride, calcium chloride, magnesium chloride and binary mixture of calcium chloride and chromium chloride. The factors affecting arsenic removal by coagulation include coagulant type and dose, pH, arsenic oxidation state and concentration, presence of inorganic solutes.

I am an evil, poisonous smoke...
But when from poison I am freed
Through art and sleight of hand,
Then can I cure both man and beast
From dire disease ofttimes direct them,
But prepare me correctly, and take great care
That you faithfully keep watch over me,
For else I am poison, and poison remain
That pierces the heart of many a one
(Valentini 1694)¹

CHAPTER 1

GENERAL BACKGROUND OF ARSENIC AND MOTIVATION FOR THIS STUDY

This chapter provides an overview of the relevant chemistry of arsenic, the treatment of arsenic waste water, as well as the scope of this research work.

1.1 MOTIVATION FOR PROPOSED STUDY

Due to increasingly stringent environmental regulations, certain pesticide manufacturing industries are facing problems of disposal of arsenic-laden waste water generated during the production of arsenical herbicides. The motivation behind this study is to devise a method to improve the coagulation process for arsenic removal from aqueous media including effluents. Previously this topic was addressed by Rubidge² who suggested that investigations of other coagulants and their possible combinations would add value to the previous research. Coagulant systems that were proposed included Cr^{3+} , Ca^{2+} and Mg^{2+} . Trivalent chromium has also shown promise as a coagulant in experiments where chrome-containing liquid tannery waste was used to remove aqueous arsenate. Such an approach may permit co-disposal (or co-treatment) of effluents containing trivalent chromium and arsenate. Previously Rubidge performed binary coagulation experiments using iron (III) and alum and obtained improved arsenic removal relative to coagulation using alum.³

In this research it is envisaged that once the individual metal ions have been studied as coagulants then certain combinations will be tested for synergies and further modelling will be carried out, based on the results obtained from the preliminary studies.

1.2 OBJECTIVE

The primary objective of this study is to devise a coagulation method that will improve the coagulation process for removal of arsenic from industrial effluents.

The study has four sub-objectives:

- Investigation of various operational parameters that affect the removal of arsenic such as pH, initial arsenic concentration, metal (coagulant) ion: arsenic mole ratio, coagulant type (Cr^{3+} , Mg^{2+} , Ca^{2+}) and dose.
- Modelling studies of Cr^{3+} , Ca^{2+} and Mg^{2+} as single coagulants.
- Model validations.
- Study of the efficacy of mixtures of Cr^{3+} and Ca^{2+} when used as a binary coagulant.

1.3 SIGNIFICANCE OF RESEARCH

The knowledge gained from this study should contribute to coagulative arsenic effluent remediation. Should significant arsenic removal be attained through this research it can lead to a novel method of effluent treatment as well as holding possible beneficial application in drinking water treatment. This is of particular interest to geographical areas such as Bangladesh, South East India and the South Western United States of America where significant levels of arsenic occur naturally in ground water.²

1.4 HISTORY OF ARSENIC

1.4.1 Discovery

The word arsenic comes from the Greek word "arsenikon", which means yellow orpiment. Orpiment is a bright yellow mineral composed of arsenic sulphide (As_2S_3), and is the most highly-visible common arsenic mineral. In the mid 12th century (1250 A.D) arsenic was discovered by Albertus Magnus, a German monk who spent time studying and classifying natural materials. It is believed that Albertus Magnus heated soap and orpiment together and by doing so, isolated elemental arsenic.^{3, 4, 5}

1.4.2 Occurrence

Arsenic is the 52nd most common chemical element on the earth.⁶ Naturally, arsenic occurs in soils, rocks, water, plants and animals. It is classified as a metalloid which is widely distributed in the earth's crust and present at an average concentration of 2 mg/kg.⁶ Arsenic is introduced into water through the dissolving of minerals and ores. High concentrations of arsenic may be found in ground water due to anthropogenic activities including mining and the use of arsenical pesticides.⁷ Natural processes that may release arsenic include the oxidation of pyrite minerals, volcanic action, erosion of rocks and forest fires.⁸ Arsenic occurs in minerals as oxides, sulphides and arsenides: arsenolite (As_4O_6), realgar (As_2S_2), orpiment (As_2S_3), mispickel or arsenical pyrite (FeAsS), cobaltite or cobalt glance (CoAsS), a tin-white cobalt (CoAs_2), arsenical iron (AsFe and As_4Fe_3), nickel glance (NiAsS) and kupfernichel (NiAs).⁹ These compounds are obtained as by-products during the mining and purification of silver metal. Industries also contribute to arsenic in ground water in certain areas, caused by runoff, industrial dumping into rivers, groundwater wells and surface waters, resulting in contamination by arsenic. From a health viewpoint, employees working in the mining and herbicide industries may be exposed to large amounts of arsenic.¹⁰

1.4.3 Properties of arsenic

1.4.3.1 General properties

Arsenic has the chemical symbol As, it is found in group Vb of the periodic elemental table, and is classified as a semi-metallic chemical element. Arsenic has an atomic weight of 74.92160 g/mol, and its atomic number is 33. Grey arsenic is a very brittle semi-metallic solid. Its quantity in the crust of the earth is estimated as 5×10^{-4} %. Arsenic has 33 electrons in the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$. The same outer shell configuration (s^2p^3) is shared by nitrogen, phosphorus, antimony, and bismuth. There are two lighter elements above arsenic in the periodic table and two heavier elements below. Nitrogen and phosphorus are evident non-metals, while antimony and bismuth are

definitely metals, with metallic luster and conducting electricity. Arsenic falls between and is thus classified as a metalloid.¹¹

1.4.3.2 Chemical properties

Arsenic trioxide is an amphoteric oxide which shows a marked preponderance for its acidic properties and it dissolves readily in alkaline solutions to give arsenites. It is much less soluble in acids, but will dissolve in hydrochloric acid to give arsenic trichloride. It reacts with oxidizing agents such as ozone, hydrogen peroxide and nitric acid to give arsenic pentoxide As_2O_5 - the reaction with hydrogen peroxide can be vigorous. It is also readily reduced to arsenic and arsine (AsH_3) may also be formed.^{4, 6}

1.4.3.3 Physical properties

Of the two forms of arsenic, the abundant form in nature is a shiny, grey, brittle, metallic-looking solid, called gamma-arsenic. Synonyms: arsenic black, arsenicals, colloidal arsenic, grey arsenic, metallic arsenic, and arsenic -75.¹² The less common form is the yellow, crystalline solid, called alpha-arsenic. Synonyms: arsenic (III) sulphide, arsenic sulphide, arsenic trisulphide, diarsenic trisulphide. Gamma-arsenic which is also known as grey-arsenic form is produced when vapours of arsenic are cooled suddenly. When heated, arsenic sublimates. However, under high pressure, arsenic can be forced to melt at about $814^\circ C$ ($1,500^\circ F$). Arsenic has a density of 5.72 grams per cubic centimeter.^{9,12,24,19} Alpha-arsenic is formed when gamma-arsenic is heated in a stream of hydrogen and the yellow powder of alpha-arsenic is deposited in the cooler part of the tube. Alpha-arsenic is very sensitive to daylight and if exposed reverts to the gamma-arsenic form.⁹

1.4.3.4 Production

Arsenic is produced by heating arsenic-bearing minerals in the absence of air.⁹



Arsenic is prepared in the laboratory by reducing arsenious oxide, As_4O_6 , with carbon. $\text{As}_4\text{O}_6(\text{s}) + 3\text{C}(\text{s}) \xrightarrow{\Delta\text{H}} \text{As}_4(\text{s}) + 3\text{CO}_2(\text{g})$

1.4.3.5 Extraction

The process of recovering arsenic from its ores is a common one used with metals. The ore is first heated in air to chemically convert arsenic sulphide to arsenic oxide. The arsenic oxide is then heated with charcoal (pure carbon). The carbon reacts with the oxygen in arsenic oxide, leaving behind pure arsenic.¹³

1.5 Chemistry of arsenic

Arsenic exists in four valences: -3, 0, +3, and +5. Under reducing conditions arsenite (As^{3+}) is the leading form; arsenate (As^{5+}) is the generally stable form in oxygenated environments.⁶ In natural water arsenic occurs in both inorganic and organic forms where in natural water it is mostly found as trivalent arsenite (As^{3+}) and pentavalent arsenate (As^{5+}).¹⁴ Organic arsenic species are relatively abundant in seafood, but are less damaging to health and are readily eliminated by the body.³ The inorganic forms occur in soil and in rocks, which come mainly from the dissolution of the solid phases like arsenolite (As_2O_3), arsenic pentoxide (As_2O_5) and realgar (As_2S_2).¹³ In Figure 1.1 the acid-based chemistry of As^{5+} is represented. Arsenate is present in aqueous solution as: H_3AsO_4 , H_2AsO_4^- (predominates at $\text{pH} < 7$), HAsO_4^{2-} (predominates in the range of $\text{pH} 7$ to $\text{pH} 11.5$ so it is likely to exist in surface water) and AsO_4^{3-} (predominates in the range of $\text{pH} 12$ to $\text{pH} 14$). Figure 1.2 shows the acid-base chemistry of As^{3+} . Arsenite is present under reducing conditions, for example in anaerobic groundwater. It occurs mainly in aqueous solution as H_3AsO_3 , the associated weak acid being predominant from $\text{pH} 2$ to $\text{pH} 9$.¹⁵

Figure 1.1 Acid-base chemistry of As⁵⁺¹⁶

Chemical equilibrium diagram for As⁵⁺ in aqueous solution

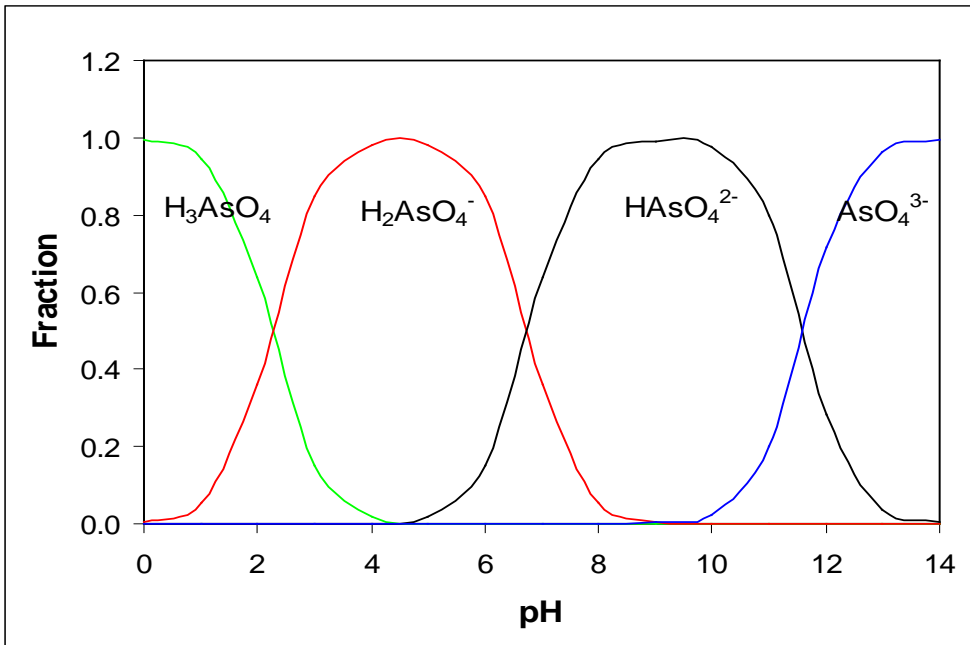
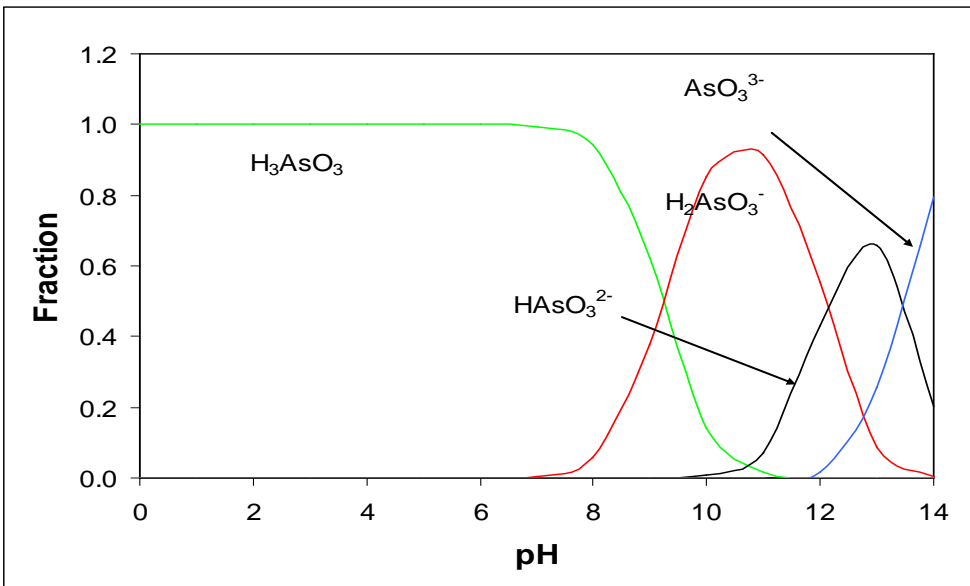


Figure 1.2 Acid-base chemistry of As³⁺¹⁶



In natural water, organic arsenic is present as a result of the use of organo-arsenical pesticides and due to the biomethylation mechanisms of micro organisms.¹⁷ Organic arsenic, namely dimethyl arsinic acid (cacodylic acid), disodium methyl arsonate (DSMA), monosodium methyl arsonate (MSMA) and

arsenic acids are still used as herbicides.¹⁷ The pKa values of the acids are helpful in determining the form that the acids manifest at various pH levels.

Table 1.1 lists pKa values for acids of arsenic: H_3AsO_3 , H_3AsO_4 , monomethyl arsonic acid (MMAA), and dimethylarsinic acid (DMAA).

Table 1.1: pKa values for arsenic acids.

	pK1	pK2	pK3
H_3AsO_3	9.2	12.2	13.4
H_3AsO_4	2.2	7.0	11.5
MMAA	3.6	8.2	-
DMAA	6.3	-	-

1.6 Compounds of arsenic

Arsenic compounds occur in crystalline, powder, amorphous or vitreous forms.³ These forms usually occur in trace quantities in rock, soil, water and in air. The trivalent arsenic trioxide, arsenic trichloride, arsenic trisulphide and sodium arsenite are typical inorganic forms of arsenic. Pentavalent forms include arsenic pentoxide, arsenic acid and sodium arsenate. Representative organic compounds are monomethyl-, dimethyl- and trimethylarsine, and arsenobetaine.¹⁸

1.7 Monosodium methyl arsenate (MSMA)

MSMA is an insecticide pesticide that is commonly used as an agricultural herbicide in the United States, but in nearby Canada MSMA is used only for forestry insect control.¹⁹ MSMA occurs in nature produced by many living organisms, including humans, from the inorganic arsenic that is a normal component of soil, water and foodstuffs.¹⁹

MSMA has the following chemical structure:¹⁹

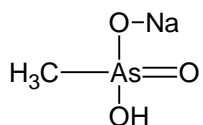


Table 1.2 shows the selected MSDS of MSMA.

Table 1.2: MSMA material safety data sheet ^{19, 20}

Product identification	
Synonyms	Monosodium methylarsonate
Hazardous ingredients	
Material or components %	72 %
Physical data	
Boiling Point	234 °C
Specific gravity	20
Percentage volatile by volume	1.580 %
Appearance and dour	Clear, colourless, odourless
Solubility in water by weight	Miscible
pH	6.6
Fire and explosion hazard data	
Flash point (test method)	Not flammable >200°C
Reactivity data	
Condition resulting to instability	Very stable
Condition contributing to hazardous polymerization	Will not occur
Incompatibility	Strong reducing agent Hazardous decomposition: methyl arsines.
Disposal, spill	
Waste disposal method	Bury in an approved landfill area away from water supplies.
Steps to be taken if material is release or spilled	Absorb on clay or vermiculite

1.8 Uses of arsenic

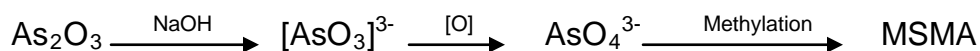
General uses of arsenic:

- In its elemental form, as with other metals, as hard, strong, and corrosion-resistant alloys with other metals.¹⁰
- Pigments, animal poisons, insecticides, paints, wallpaper, ceramics, and poisonous gases for chemical warfare (lewisite and adamsite).
- Glass making, in calico and indigo printing, and in pyrotechnics.
- Precursor in the manufacture of arsenic-based pesticides; (also As_2O_3) sodium arsenite, sodium arsenate, sodium cacodylate).⁹
- Precursor for the manufacture of certain arsenic-based pharmaceuticals and veterinary products, as a decolorizing agent for glasses and enamels, preservative for wood.⁹
- Cytostatic in the treatment of refractory promyelocytic subtype of acute myeloid leukemia.⁹

1.9 Toxicology of arsenic and its compounds

1.9.1 The mechanism of arsenic

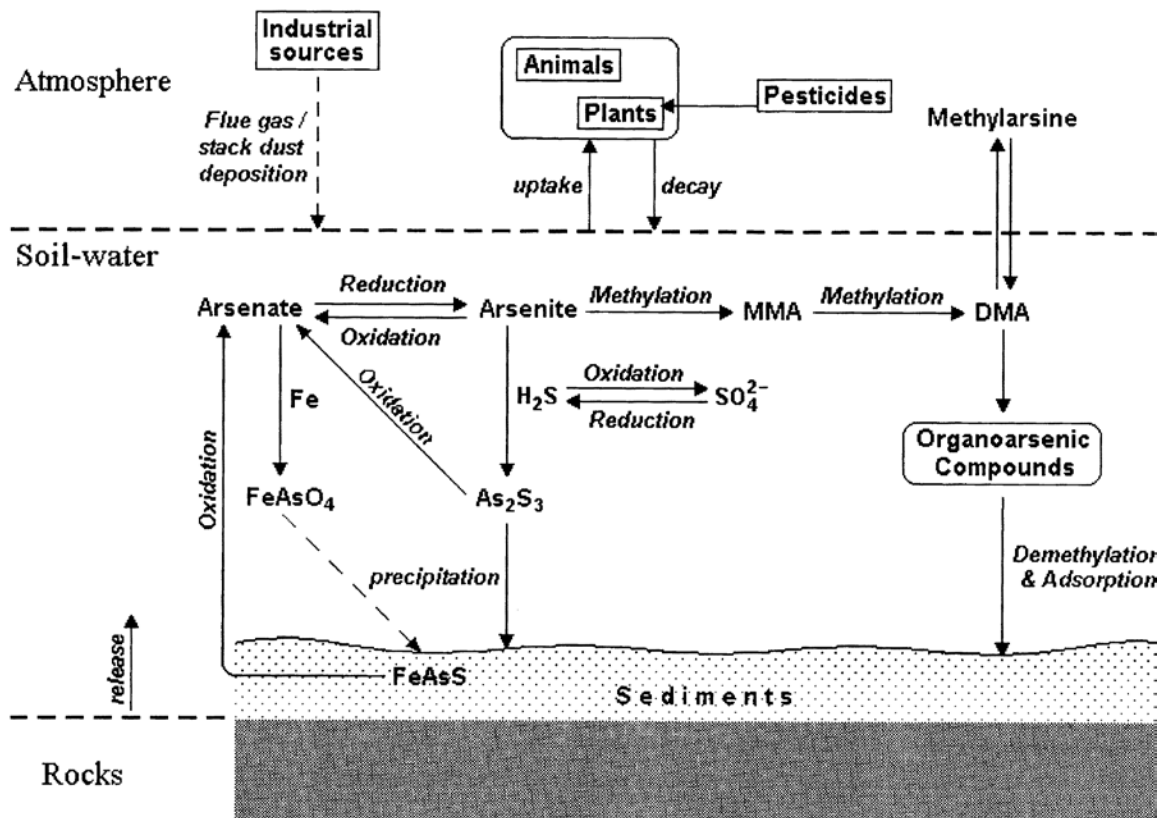
The mechanism of $\text{As}(\text{OH})_3$ involves a slow hydrolysis of arsenic trioxide in water and the addition of sodium hydroxide converts arsenous acid to the arsenite ions $[\text{AsO}_3]^{3-}$.²¹ Reduction of pentavalent to trivalent arsenic and oxidative methylation reactions in which trivalent forms of arsenic are sequentially methylated to form MSMA.²²



1.9.2 The fate of MSMA and its decomposition products in soil

Figure 1.3 shows the transformation and mobilization of arsenic in the environment.

Figure 1.3. Transformation and mobilization of arsenic in the environment.²³



This is a brief summary of transformation and mobilization of arsenic in the environment. Arsenic cycles in the environment and the major reactions occur in the soil–water and sediment–rock systems to influence the environmental transport, distribution and availability of arsenic. Arsenate–arsenite redox reactions are controlled by the availability of oxygen while adsorption and precipitation of arsenate and arsenite immobilize the soluble arsenic. Slow release of arsenic from rocks and sediments or oxidative dissolution of arsenopyrite (FeAsS) from sediments contributes to the flux of arsenic in the

environment. Methylation of arsenite to monomethylarsonic acid (MMA) or dimethylarsinic acid (DMA) followed by other organoarsenic compounds, constitute the major biological reactions in the arsenic cycle.²³

1.9.3 The general principle of arsenic detoxification

Toxicology is defined as the scientific study of the characteristics and effects of poisons. After absorbing arsenic trioxide, the toxic effects on the human digestive system are well known.¹⁰ Also, the effects occurring after inhalation of dust or fumes containing arsenic and even after direct skin contact are also documented.¹⁰ Arsenicosis is a result of chronic arsenic poisoning and this typically occurs after employee exposure (for example, in metal smelters), or where people or the local populations drink water containing high levels of arsenic (0.3–0.4 ppm). Patients being treated for long periods with arsenic-based pharmaceuticals also exhibit symptoms of arsenicosis.¹⁰ Arsenic trioxide has been shown to be a human carcinogen. There is a risk of lung cancer between 6–10 times higher for heavily exposed workers compared with the general population, this has been indicated in the studies on workers exposed in copper foundries in the United States, Japan and Sweden.¹⁰ Long-term ingestion of arsenic trioxide either in drinking water or as a medical treatment, can also lead to skin cancer.¹⁰ The study of women exposed to arsenic trioxide dust as employees or neighbours of a copper foundry has revealed that there are reproductive problems, for example low birth weight, high incidence of miscarriage, and certain congenital deformations which have also been indicated.¹⁰

1.9.4 Human exposure to arsenic

The first possible methods of human exposure to arsenic are through food, water, and air. As result of arsenic exposure humans can have both short and long term health effects.²¹ Acute effects can occur within hours or days of exposure and long term or chronic effects may occur over a longer period.¹⁰

1.9.5 Arsenic poisoning symptoms

The following symptoms can be developed within thirty minutes after the ingestion of arsenic:

- a metallic taste in the mouth,
- hypersalivation and
- dysphagia, (when it becomes difficult for people to swallow will be in serious pain when swallowing, and, for some people they will be completely unable to swallow liquids, foods, or saliva and this whole situation will make eating a challenge).¹⁰ Another difficulty resulting from dysphagia is that one cannot consume enough calories and fluids to nourish the body.¹⁰
- Focal hyperemia (a decrease of the blood flow to the body and veins).

Exposure to large concentrations of arsenic can lead to seizures, electrolyte disturbances and systemic shock; frequently death may occur. The inhalation of arsenic compounds can lead to inflammation of the mucous membranes of the nasal and oral pharyngeal passage-ways. This type of exposure may delay the process described above because the concentrations may be lower, but the results will show the same symptoms as arsenic poisoning by contact, and by ingestion.¹⁰

Exposure may also occur through skin contact with soil or water that contains arsenic.²⁴ Arsenic levels in food are fairly low, though, arsenic levels in fish and seafood may be high because fish and shellfish absorb arsenic from water they live in.²⁴ Exposure to arsenic may be higher for people who work with arsenic, people who drink significant quantities of wine, people who live in houses that contain chromium copper arsenate preserved wood of any kind, and for people who live on farming lands where arsenic containing pesticides have been used previously.

Various health effects, such as the irritation of stomach and intestines, decreased production of red and white blood cells, skin changes, and lung irritation can be caused by exposure to inorganic arsenic.²² Significant amounts of inorganic arsenic can increase the chances of cancer development, especially the chances of development of skin cancer, lung cancer, liver cancer and lymphatic cancer.²¹ Women who are exposed to high levels of inorganic arsenic may experience infertility and also miscarriages, and cause skin disturbances, declined resistance to infections, heart disruptions and brain damage. Finally, human DNA can be damaged by inorganic arsenic.²⁴

Arsenic poisoning can be characterized by the effects described above in humans and include: garlic odour to the breath and faeces, metallic taste in mouth, adverse gastro intestinal effect GI (GI is defined as an adverse gastro intestinal effect). Gastro intestinal effects may include inflammation, vesicle formation, and eventual sloughing of the mucosa in the mouth. Pancreatitis (an inflammation of the pancreas) can be acute, beginning suddenly, usually with the patient recovering fully. In a chronic case it may progress slowly with continued, permanent injury to the pancreas, bowel infarction (perforation), and acute cholecystitis (a painful inflammation of the gallbladder's wall).²⁵ This disorder can occur singly, or may recur many times. Effects that predominate include vomiting, abdominal pain, and diarrhea. Pharynx, esophagus and central nervous system effects are common. Headache, dizziness, drowsiness, and confusion occur. There may be muscular weakness and spasms, hypotension, lethargy, delirium, coma, and convulsions. Cardiovascular effects include shock, cyanosis, and cardiac arrhythmia (an arrhythmia is an abnormality in the heart's rhythm, or heartbeat pattern). Further, the patient's heartbeat becomes irregular. Liver damage may be manifested as elevated liver enzyme levels and jaundice. Injury to blood-forming tissues may cause anaemia, leucopenia and thrombocytopenia (thrombocytopenia is the bleeding disorders), cancer dehydration and death.²⁵

1.9.6 Detoxification and metabolism

It has been established that humans do have a biochemical mechanism for oxidizing As^{3+} to As^{5+} . This detoxification process has also been found to occur in other mammals such as cows and dogs.⁴ In 1973 Braman found that in humans, dimethylarsinic acid was the predominate form of arsenic in human urine, and in certain individuals on a normal diet.⁵ In humans arsenic is broken down in the liver. Ingested arsenic travels directly to the liver but this depends on the concentration that has been ingested; the liver is not always successful in converting it to a less harmful form. It can take up to two or three cycles at high levels, before the metabolic process is completed hence, the rapidity of the process reduces the possibility of chronic toxicity from As^{3+} and As^{5+} since neither can exist in the body for a long time.⁴

1.10 Toxicologically significant environmental occurrence and effects of arsenic

Arsenic is present in seawater at about 2-4 ppb, and in river fresh water systems at about 0.5-2 ppb. Half of the arsenic present in such water is bound to particles. Freshwater and sea algae contain about 1-250 ppm of arsenic; freshwater microphytes contain 2-1450 ppm, marine molluscs contain 1-70 ppm, marine crustaceans 0.5-69 ppm and fishes 0.2-320 ppm (all values are based on dry mass).¹⁸ The maximum legal limit for arsenic in drinking water applied by the World Health Organization (WHO) is 10 $\mu\text{g/L}$ as is the case in South Africa, while the US EPA limit is 50 $\mu\text{g/L}$.¹⁹ Naturally occurring arsenic is present in soils and minerals therefore may be present in the air, by means of wind-blown dust and in water through runoff and leaching.²⁶ Arsenic levels in air are lowest in remote and rural areas, and higher in urban areas, and highest close to industrial sources.²⁴ In water, levels of arsenic are lowest in seawater, higher in rivers and lakes and highest in water from underground areas containing volcanic rock or arsenic-rich mineral deposits.²⁴

Levels of arsenic in soil and sediment increase if there are natural and/or man-made sources of arsenic contamination present.²⁶ Copper, lead and zinc producing industries produce arsenic as by product. Arsenic cannot be destroyed in the environment because it is an element.⁷ Arsenic can be absorbed fairly easily by the plants which may cause high-ranking concentrations in certain foods. The concentrations of dangerous inorganic arsenics currently in surface water enhance the possibility of altering the genetic materials in certain species of fish. This is caused by the accumulation of arsenic in the bodies of these plant-eating freshwater organisms. Birds then eat the fish that contain the amounts of arsenic and will possibly expire as a result of arsenic poisoning as fish is digested.¹²

The quantities of arsenic inhaled in by non-smokers are minimal, except in industrially polluted areas. Smokers inhale more arsenic than non-smokers because arsenic is one of many hundreds of chemicals present in cigarette smoke.⁷ Exposure to arsenic in the workplace can be high, although the amounts present in the air in workplaces are effectively controlled in many countries.⁶ Volcanic eruptions and coal combustion are other sources of arsenic emission.⁷ Due to natural geological contamination, high levels of arsenic can be found in drinking water that has come from deep drilled wells. This is particularly true for Bangladesh.⁷

1.11 Treatment of arsenic poisoning

Arsenic poisoning can be effectively treated if detected early enough. Treatment may be through a series of injections into certain muscles. Every four hours, for the first two days, a patient requires 2.5-5.0 mg/kg of body weight of a drug called dimercaporal $C_3H_8OS_2$. This is followed by two injections on the third day and then one for each day the next five days.¹¹ Arsenic reacts with sulphur groups, thus it is recommended to eat foods with high sulphur content, such as eggs, onions, and garlic.²⁷ Sulphur supplements can also be obtained in tablet

form. Any other foods containing the amino acid cysteine are effective since cysteine contains sulphur.²⁷

If one suspects the possibility of arsenic poisoning, a course of charcoal tablets can be taken to prevent reduce arsenic from being absorbed by stomach and intestines.²⁷ Another method is chelation therapy involving the use of multidentate ligands to bind to arsenic (as well as other metals) to leach them out. Ethylene diaminetetra acetic acid, (EDTA) is one of the common molecules used in chelation therapy for arsenic.²⁷ Other methods of treating arsenic poisoning have been investigated using rats. Doses of vitamins C and E in conjunction with meso-2, 3-dimercaptosuccinic acid (or DMSA) or monoisoamyl DMSA significantly deplete concentrations of brain-arsenic in rats. Vitamins C and E play only a small role (when administered on their own having little effect on arsenic concentrations) in the depletion of the arsenic. The depletion is more a result of the thiol group in the chelate.²⁷

1.12 Removal of arsenic from aqueous media

Various technologies for removing arsenic have been proposed and the most commonly used technologies include, oxidation / reduction, coagulation / co-precipitation, sedimentation, filtration, adsorption, ion exchange, membranes / reverse osmosis, biological, nanofiltration, lime softening, iron and alum coagulation and coagulation-assisted microfiltration.³⁴ Since most of these methods rely on an ionic charge, As^{5+} will be easier to remove than As^{3+} in the normal working pH range of drinking water, and, therefore, if arsenite is present, pre-oxidation should be the first step.²⁸

1.12.1 Coagulation / precipitation / flocculation / sedimentation

Coagulation converts soluble arsenic into insoluble reaction products, allowing sedimentation and / or filtration. Factors affecting arsenic removal by coagulation include coagulant type and dose, mixing time, pH, arsenic oxidation state and concentration and presence of inorganic solutes.²⁹ Precipitation is the most

common method of removing soluble metals. In precipitation reactions, chemicals are added to convert dissolved constituents to form insoluble precipitates. Metals are precipitated as hydroxides, sulphides, and carbonates by adding an appropriate precipitant and adjusting the pH to favour insolubility. In many metals such as arsenic, cadmium, chromium (III), copper, iron (III), lead, mercury, nickel, zinc and many anionic species (phosphates, sulphates, and fluorides), precipitation can be used to effectively remove all.³² Improved removal efficiencies can be achieved with sulphide precipitation, but hydroxide precipitation, using lime or caustic, is more practiced. This is due to the fact that sulphide precipitation is more expensive and may produce the odorous and poisonous hydrogen sulphide.²⁸

1.12.2 Lime softening

Lime softening is not a favorable operating process as it only removes arsenic and it requires very expensive equipment. Lime softening removed arsenic more effectively through adsorption-co-precipitation combined with media filtration when lime was added to water to raise the alkalinity.³⁰ Lime softening operated at a pH of greater than 10.5 is likely to provide a high percentage of arsenic removal for an influent concentration of 50 µg/l.³¹

1.12.3 Activated alumina

In the 1970s Bellack³² discovered that activated alumina could remove arsenic from water. For both arsenate and arsenite, arsenic removal efficiency is typically > 95% and is controlled primarily by pH and influent arsenic concentration and speciation. According to Smedley and Kinniburgh³³ they revealed that arsenate removal capacity is the best in the narrow range from pH 5.5 to 6.0, where the alumina surfaces are protonated, but acid anions are not yet concentrated enough to compete with arsenic for sorption sites. Activated alumina has a negative charge, at pH 8.2 and below the surface it is positively charged, which it has a point of zero charge (PZC). Clifford³⁴ also stated that arsenic removal capacity drops sharply as the PZC is approached, and above pH 8.5, is reduced

to only 2-5% of capacity at the optimal pH of 5.5-6.0. pH adjustment may be necessary for effective arsenic removal for neutral and basic waters.^{32, 33}

1.12.4 Iron adsorbents

The successes of iron-based adsorbents; in removing arsenic are founded upon the adsorptive affinity of iron oxides for arsenic. Iron adsorbents show reduced capacity as the pH increases. The typical operation range is between pH 5.5 to 9. This wide pH window which simplifies treatment plants is a key advantage of iron adsorption media.³⁵

1.12.5 Oxidation / Reduction

Oxidation / reduction reactions render some inorganic constituents non-hazardous and more easily removed by subsequent treatment processes. Under controlled pH, the reaction involves the addition of a chemical oxidizing or reducing agent. Oxidizable inorganics such as cyanides, ammonia, and some metals (Fe, Mn, and Se) as well as reducible metals (Cr, Hg, Pb, Ag, Ni, Cu, and Zn) can be removed by oxidation / reduction.³⁶ Arsenic is best removed in the pentavalent state hence oxidation is applicable in the arsenic removal system. Oxidation / reduction is mostly used for cyanide destruction and the reduction of hexavalent chromium to trivalent chromium. These reactions are monitored by an oxidation / reduction potential probe which is carried out in closed reactors with rapid mix agitators. The reaction processes can be very violent because they are exothermic; therefore they are conducted with dilute concentrations and as batch processes.³⁶

1.12.6 Adsorption

Adsorption is the build up of material at an interface, typically a liquid / solid or even a gas / liquid or gas / solid boundary layer. Where a substance is transferred from the liquid phase to the surface of a solid and becomes bound by a chemical or physical force, it is known as a mass transfer process. As part of the process of coagulation / co-precipitation or on fixed media, adsorption can take place on suspended particles. Arsenic is adsorbed onto the surface of various substances, clay and cellulosic adsorbents, including: oxides (e.g. hydrated ferric oxide, titanium oxide, silicon oxide), iron oxide-coated or manganese dioxide-coated sand, clay minerals (e.g. kaolinite, bentonite,), synthetic anion exchange resins, chitin and chitosan, bone char and cellulose material (sawdust, newspaper pulp).³⁷ Chromium hydroxide is formed in situ hence offering a large potential surface area for adsorption of arsenic onto its surface and this is the one of the methods that forms part in this research.

1.12.7 Ion exchange

Ion exchange refers to the exchange of charged components that contact an ionic solid that is in contact with an electrolyte solution. The ion exchanger may undergo exchange either with positive or negative ions. The surface of solid carries either a net negative or positive charge depending on the nature of the surface and the pH.³⁶ Such exchange resins are made up of synthetic organic polymers or a natural zeolite. Weak electrostatic forces are used to attach ions such as H^+ , Na^+ , OH^- , and Cl^- to ion exchange. These ions are exchanged with ions in the contaminated solution that have a greater affinity for the agent. The ion exchange agent can be washed with a solution containing an excess of the original ions so that it can be regenerated.³⁶ This process occurs under pressure when the inflow enters the top of the column and penetrates through the resin, and also exits at the bottom of the column. When the ion exchange agent becomes exhausted the column is backwashed with regenerant solution. The use of ion exchange in tertiary treatment is limited to the lower concentrations; with the inflow contaminant concentrations not exceeding 2000 mg/L.^{36, 38}

1.12.8 Reverse osmosis

Reverse osmosis is primarily used to remove salt from brackish water. It has been applied where inorganic concentrations are very low in tertiary treatment. The separation of the two solutions with different concentrations in this process involves a semi-permeable membrane. The flow of water from one solution to the other would normally flow from the less concentrated salt solution to the more concentrated salt solution. Pressure is applied to the more concentrated solution, forcing the water to flow from the higher concentration to the lower concentration. This concentrates the contaminants. The membranes which are used in reverse osmosis are made of a thin but dense surface skin with a porous structure in between. The porous structures are typically made of cellulose acetate, aromatic polyamides, and thin-film composites. In order to withstand at high pressure these delicate membranes must be built into a support device. RO provides removal of arsenic efficiencies of greater than 95 percent when the operating pressure is at an ideal psi.^{36, 37}

1.12.9 Nano-filtration

Nanofilter membrane measured molecular weight cut off is 180-340 g/mole and is predictably constant with rejection due to the ionization of arsenic experiments. From 30% rejection at pH 4.5 to 80% at rejection pH 8.2 of As^{5+} increases with increasing pH and also percent rejection of As^{3+} was less than 10% across the same pH range. Non- ionic species, partial rejection of monovalent ions, and high rejection of divalent ions in nanofiltration results would be expected with the low rejection.²⁸

1.12.10 Micro-filtration (MF) and Ultra-filtration (UF)

These two membranes are not commonly used for separation processes of arsenic removal as their pore sizes are too large to exclude low molecular weight dissolved solids. MF and UF do not reject arsenic in solution.³³ They could, however, reject large species that contain adsorbed arsenic.

1.12.11 Biological methods of arsenic removal

Arsenic is removed or stabilized by means of microorganisms. These microorganisms are specific bacteria, which accomplish this by alteration of the form of arsenic by one of the following mechanism: oxidation / reduction, mineralization, detoxification, or methylation.³⁹ Critical factors include energy and carbon source, aerobic, anoxic, or anaerobic conditions, temperature and pH.²⁷ Bio-oxidation of organic matter by micro-organisms using bacteria include arsenic enzymes to break down polychlorinated biphenyls PCBs, pesticides, and other organic constituents into less toxic or innocuous compounds.³⁹

1.12.12 Solar distillation

The sun's energy used in solar distillation evaporates water, which then recondenses. This process of evaporation and recondensation separates water from all soluble chemicals, including arsenic.⁴⁰

1.12.13 Technologies available for arsenic treatment

Table 1.3 list the advantages and disadvantages of various technologies that are available for the treatment of arsenic.

Table 1.3 Technologies available for arsenic treatment.^{42, 43, 44}

Technologies	Advantage	Disadvantage	Removal (%)
Co-precipitation	No monitoring of a break through is required. Relatively low cost. Simple chemicals.	Serious short and long term problems with toxic sludge.	
Alum coagulation	Durable powder chemical normally available. Relatively low capital cost and simple in operation. Effective over a wide range of pH.	Produces toxic sludge. Low removal of trivalent arsenic. Pre-oxidation may be required. Sedimentation and filtration needed.	90
Iron coagulation	More efficient than alum on weight basis. Common chemicals are available.	Medium removal of As (III). Produces toxic sludge.	94
Lime softening	Most common chemicals are available commercially. Lime (Ca(OH) ₂ is much cheaper than Alum	Re-adjustment of pH is required.	91
Sorption techniques	No daily sludge problem.	Requires monitoring of break through or filter use. Requires periodical and disposal of desorbed toxic material or adsorbent and toxic material if both are disposed of together.	
Activated alumina	Relatively well known and commercially available.	Re-adjustment of pH is required.	88
Iron coated sand	Low cost. No regeneration is required. Removal both As (III) and As (V).	Yet to be standardized. Produces toxic solid waste.	93
Ion exchange resin	Exclusive ion specific resin to remove arsenic.	High cost medium. Require high tech operation and maintenance. Regeneration creates a sludge disposal problem.	87
Membrane Techniques	Low space requirement.	As ³⁺ is difficult to remove. High running costs. High investment costs. High tech operation and maintenance. Toxic wastewater. Re-adjustment water quality is required.	
Reverse Osmosis		Membrane does not withstand oxidizing agents. "High Tech" operation and	96

		maintenance. A toxic liquid is concentration is generated.	
Nanofiltration	Well-defined and high-removal efficiency.	Very high capital cost.	95
Electrodialysis	Capable of removing of other contaminants.	Toxic wastewater produced.	95
Oxidation / Precipitation	Relatively simple and low-cost. Chemical oxidation is rapid if strong oxidants are used. Oxidizes other impurities and kills microbes.	Relatively slow process (air oxidation). Removes only part of the arsenic.	
Air Oxidation	Relatively simple, low-cost, but slow process. "In situ" arsenic removal. Also oxidizes other inorganic and organic constituents in water.	Mainly removes arsenic ⁵ .	80
Chemical Oxidation	Oxidizes other impurities and kills microbes. Relatively simple and rapid process. Minimum residual mass.	Efficient control of pH and the oxidation step is needed.	90

1.13 Disposal of arsenic wastes

Water which contains arsenic is considered hazardous waste and its storage, treatment, and disposal are regulated by law. Since arsenic recovery poses little economic advantage, selection of one of the following options is the general trend in arsenic waste treatment:

- i) Concentration and containment.
- ii) Dilution and dispersion.
- iii) Encapsulation.²⁴

Sludge from industries has a large contamination potential because it contains all the suspended material removed from MSMA together with the chemicals used for coagulation. It must therefore be disposed of in a proper way in landfill to prevent contamination of water sources.

1.14 Leaching test on sludges

When the coagulation sludge is to be land-filled at a site identified for the disposal of hazardous organic and inorganic wastes the Toxicity Characteristic Leaching Procedure (TCLP) is used to test the waste for leaching of toxic material that may get into ground water.⁴⁵ The mobility of organic and inorganic analytes present in liquid, solid, and multiphase wastes is determined by this TCLP.⁴⁶ Legislation imposes leaching restrictions on potential secondary raw materials. This leaching test facilitates the prediction of the amount of heavy metals and other pollutants that will be released from a waste material when brought in contact with water. Environmental risks can be evaluated for treatment as a secondary raw material or for waste disposal. The impact of the material on the environment can be predicted by the results of the leaching tests. The selection of the leaching tests depends on the form of the material and the information required. Two types of tests are considered:

- (a) Grain-sized materials are tested in column leaching tests or agitation tests and
- (b) The diffusion leaching test is used for building materials and solid wastes.

Additional information can be obtained by means of pH-controlled tests or tests under reducing conditions.⁴⁶

To determine whether TCLP testing is necessary the following criteria are typically followed:

- TCLP tests need not be conducted if a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that the analytes are present at such low concentrations that the appropriate affected country's regulatory concentration level could not possibly be exceeded.
- According to the United States Environmental Protection Agency (USEPA) it is not necessary to analyze the remaining fractions of the extract, if an analysis of any one of the liquid fractions of the TCLP extract indicates that a regulated compound is present at such high concentrations that,

even after accounting for dilution from the other fractions of the extract, the concentration would be above the regulatory level for that compound. The waste is then considered to be hazardous.

- The extraction using the ZHE (Zero Headspace Extractor) is not necessary, if the analysis of the extract obtained by using a bottle extractor shows that the concentration of a USEPA regulated volatile analyte exceeds the regulatory level for that compound. Then the waste is considered to be hazardous. On the other hand an extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the stated United States regulatory level.⁴⁷

The waste generator has to consult environmental regulatory agencies for guidance on acceptable disposal practices prior to implementing land disposal of waste residue (including waste sludge). For possible reprocessing, elemental arsenic wastes should be placed in long term storage or returned to suppliers or manufacturers.⁴⁸ The solid waste generated by application of coagulation by Cr, Ca, Mg to real samples of industry must be subjected to leach testing to determine if it is suitable for disposal in a hazardous landfill or an ordinary general landfill.

Chapter 2 describes the experimental methodology and procedures, the experimental design used as well as instrumentation used.

1.15 REFERENCES

1. The removal of arsenic from potable water by pure flow filtration systems, Div. California Environmental Control, INC, Washington, CA 90608, Purveyors to the Water / Water waste Industry Since 1972.
2. Evaluation and optimization of selected methods of arsenic removal from industrial effluents by Dr Gletwyn Robert Rubidge. A dissertation submitted in fulfilment of the requirements for the Doctors Degree in Technology: Chemistry. In the faculty of Applied Science at the Port Elizabeth, Promoter Dr N. Vorster, Co-promoter: Prof B. Zeelie, 2004.
3. Arsenic Removal from Drinking Water by Coagulation/Filtration and Lime Softening Plants, by Keith A. Fields, Abraham Chen, Lili Wang, National Service Center for Environmental Publications, 2000.
4. Arsenic speciation in the environment, William R. Cullen , Kenneth J. Reimer Chemical Reviews, 1989, Volume 89, Issue 4, pp 713–764.
5. Physical properties of arsenic-doped tin oxide thin films, S.R. Vishwakarma, J.P. Upadhyay, H.C. Prasad, Department of Physics, University of Gorakhpur, Gorakhpur 273 009 India, 1989, Volume 176, Issue 1, pp 99-110.
6. Consumer perception versus scientific evidence about health benefits and safety risks from fish consumption, Wim Verbeke, Isabelle Sioen, Zuzanna Pieniak, John Van Camp and Stefaan De Henauw, Public Health Nutrition, 2005, Volume 8, Issue 4, pp422–429.
7. Removal of arsenic from water by zero valent iron, Sunback Bang, George P, Korfiatis and Xiaoguang Meng, Journal of hazardous material, 2005, Volume 121, Issue 1-3, pp 61-67.

8. Impact of safe water for drinking and cooking on five arsenic-affected families for 2 years in West Bengal, India, B.K. Mandal, T.R. Chowdhury, G. Samanta, D.P. Mukherjee, C.R. Chanda, K.C. Saha, D. Chakrabortiu, *The Science of the Total Environment* 218, 1998, pp 185-201.
9. Arsenic hyperaccumulator *Pteris Vittata* L. and its arsenic accumulation, Chen Tongbin, Wei Chaoyang, Huang Zechun, Huang Qifei, LU Quanguo & Fan Zilian, *Chinese Science Bulletin*, 2002, Volume 47, Issue 11, pp 902-905
10. Arsenic toxicity in Bangladesh and West Bengal, India - A review and commentary, *Journal of toxicology*, Rahman, 2001, Volume 39, Issue 7, pp 683 - 700.
11. Acute and chronic arsenic poisoning associated with treatment of acute promyelocytic leukaemia, Shang-Yi Huang, Cheng-Shyong, Chang Jih-Luh Tang, Hwei Fang Tien, Departments of Internal Medicine, *British Journal of Haematology*, 1998, Volume 103, pp 1092–1095.
12. Arsenic chemistry in municipal sewage sludge as affected by redox potential and pH, *Water research Carbonell Barrachina*, 2000, Volume 34, Issue1, pp 216.
13. Worldwide occurrence of arsenic in ground water, D. Kirk Nordstorm, *Science*, 2002, Volume 296, Issue 5576, pp 2143-2145
14. Arsenic removal from an aqueous solution by a modified fungal biomass, D.Pokhrel and T.Viraraghavan, 2006, Volume 40, Issue 3, pp 549-552.
15. Microbial methylation of metalloids: arsenic, antimony, and bismuth, *Microbiology and molecular biology*, 2002, Volume 66, Issue 2, pp 250.

16. Removal of Arsenic from Wastewater Using Chemical Precipitation Methods, Thomas R. Harper and Neville W. Kingham, Water Environment Research, 1992, Volume 64, Issue 3, pp 200-2003.

17. Arsenic removal from water using seawater neutralized red mud (Bauxon) by Hulya Gen, Fuhrman, PhD thesis, Enviromental, and resource DTU Technical University of Denmark Jan 2004.

18. Use of arsenic trioxide in the treatment of acute promyelocytic leukemia (APL): II. Shen, Z X, Clinical efficacy and pharmacokinetics in relapsed patients, 1997, Volume 89, Issue 9, pp 3354.

19., Public health, and environmental impacts of monosodium methane arsonate as used in beetle control in British Columbia, F.N. Dorst, Ministry of Forests Silviculture Practices Branch, 2007, pp 5-7.

20. Industries using arsenic and arsenic compounds, Saburo Ishiguro, Applied Organometallic Chemistry, 1992, Volume 6, Issue 4, pp 323-331.

21. Arsenic transport and transformation associated with MSMA Application on a golf course green by Min Feng, Jill E. Schrlau, Raymond Snyder, George H. Snyder, Ming Chen, John L. Cisar, and Yong Cai, Department of Chemistry and Biochemistry and Southeast Environmental Research Center, 2005, pp 3556-3562.

22. Arsenic and arsenic compounds, The first and second drafts of this monograph were prepared, under the coordination of Dr J. Ng, by the authors A. Gomez-Caminero, P. Howe, M. Hughes, E. Kenyon, D.R. Lewis, M. Moore, J. Ng, and by A. Aitio and G. Becking, Published under the joint sponsorship of the United Nations Environment Programme, the International Labour Organization,

and the World Health Organization, and produced within the framework of the Inter-Organization Programme for the Sound Management of Chemicals.

World Health Organization, Geneva, 2001.

23. Metabolism and toxicity of arsenic: A human carcinogen by Pradosh Roy and Anupama Saha, Department of Microbiology, Bose Institute, P-1/12, C.I.T. Scheme VII-M, Kolkata 700 054, India Current Science, 2002, Vol. 82, No. 1, pp 10.

24. Arsenic: occurrence, toxicity and speciation techniques, C. K. Jain, I Ali, Water Research, 2000, Volume 34, Issue 17, pp 4304-4312.

25. Arsenic poisoning, Schoolmeester WL, White DR, South Medical Journal, 1980, Volume 73, Issue 2, pp 198-208.

26. An overview of arsenic removal by pressure-driven membrane processes Ming-Cheng Shih, Desalination, Department of Biological Science and Technology, 2005, Volume 172, pp 85–97.

27. Treatment of arsenic in Bangladesh well water using a household co-precipitation and filtration system, Meng, X, Water research, 2001, Volume 35, Issue 12, pp 2805.

28. Role of iron in controlling speciation and mobilization of arsenic in subsurface environment, Bose, P, Water research, 2002, Volume 36, Issue 19, pp 4916.

29. Arsenic removal by coagulation and filtration: comparison of ground waters from the United States and Bangladesh, Wickramasinghe S. R., Desalination, 2004, Volume 169, Issue 3, pp 231.

30. Mobility of arsenic in soil from the Rocky Mountain Arsenal area, Corwin, D L
Journal of contaminant hydrology, 1999, Volume 39, Issue 1, pp 35.
31. Arsenic Removal by Adsorption, Shailendra K. Gupta and Kenneth Y. Chen
Shailendra K. Gupta and Kenneth Y. Chen, Journal of Water Pollution Control
Federate, 1978, Volume 50, Issue 3, pp 493-506.
32. Ensuring safe drinking water in Bangladesh, Ahmed, M. F., Science, 2006
Volume 314, Issue 5806, pp 1687.
33. Arsenic in Drinking-Water Water and Sanitation, Protection of the Human
Environment, Chapter 1. Source and behaviour of arsenic in natural waters by
Pauline L Smedley and David G Kinniburgh British Geological Survey,
Wallingford, Oxon OX10 8BB, U.K. Water Resources, 2001, pp 1-390.
34. Ion exchange and inorganic adsorption in water quality and treatment,
DA Clifford, Water quality and treatment, 1999, pp 1- 91.
35. Adsorption of arsenite and arsenate on amorphous iron hydroxide, Pierce, M.
L., Water research, 1982, Volume 16, Issue 7, pp 1247.
36. Treatment of hazardous organic and inorganic compounds through aqueous-
phase photocatalysis, Kabra K., Industrial & engineering chemistry research
2004, Volume 43, Issue 24, pp 7683.
37. Removal of arsenic from water by electrocoagulation, Ratna Kumar,
Chemosphere, 2004, Volume 55, Issue 9, pp 1245

38. Arsenic removal from drinking water during coagulation, Hering, J. G., Journal of environmental engineering, 1997, Volume 123, Issue 8, pp 800.
39. Arsenic removal via electrocoagulation from heavy metal contaminated groundwater in La Comarca Lagunera México Jose R. Parga, David L. Cocke, Jesus L. Valenzuela, Jewel A. Gomes, Mehmet Kesmez-George Irwin, Hector Moreno-and Michael Weir, Journal of hazardous materials, 2005, Volume 124, Issues 1-3, pp 247-254.
40. Appropriate remediation technologies for arsenic-contaminated wells in Bangladesh by Susan Murcott Massachusetts, Institute of technology murcott@mit.edu, presented at "Arsenic in Bangladesh Ground Water" in Wagner College, Staten Island, New York, 1999.
41. An Overview of Arsenic Removal Technologies in Bangladesh and India M. Feroze Ahmed, Technologies for Arsenic Removal from Drinking Water, pp 251-269.
42. Metal attraction: an ironclad solution to arsenic contamination, Frazer, Environmental health perspectives, 2005, Volume113, Issue 6, pp 398.
43. Chronic arsenic toxicity in Bangladesh and West Bengal, India-a review and commentary, Rahman, M M, Journal of toxicology, 2000, Volume 39, Issue 7, pp 683.
44. TCLP underestimates leaching of arsenic from solid residuals under landfill conditions, Ghosh A., Environmental science & technology, 2004, Volume 38 Issue 17, pp 4677.
45. Adsorption and desorption of arsenic on an oxisol and its constituents Ladeira, A. C. Q., Water Research, 2004, Volume 38, Issue 8, pp 2087.

46. The management of arsenic wastes: problems and prospects, M. Leist, R.J. Casey, D. Caridi, *Journal of Hazardous Materials*, 2000, pp 125–138.

47. Treatment of contaminated soils with organoclays to reduce leachable pentachlorophenol, J. M. Brixie and S. A. Boyd, *Journal of Environmental Quality*, 1994, Volume 23, No. 6, pp 1283-1290.

48. Hazardous waste information on How DOD and Federal and State Regulators Oversee the Off-Site Disposal of Waste from DOD Installations, 2007.

CHAPTER 2

EXPERIMENTAL METHODOLOGY AND PROCEDURE

In this chapter the experimental procedures as well as the methodology that was employed during the research are described. The key aspects of the coagulation are also explained.

2.1 MATERIALS

2.1.1 Chemicals used

An MSMA brine was obtained from Dow Agrosience. An arsenic stock solution was prepared from arsenic trioxide. The chromium solution was made from chromium chloride and solutions of magnesium chloride and calcium chloride were prepared from their salts.

Table 2.1 shows the list of chemicals and reagents used for experiments, their source and grade.

Table 2.1: List of chemicals used for experiments.

CHEMICAL NAME	FORMULA	SOURCE	GRADE
MSMA brine sample		Dow Agrosience	CP*
Coarse salt	Protea Chemicals	Saarchem	CP
Sodium hydroxide	NaOH	Aldrich	AR**
Hydrochloric acid (32%)	HCl	Saarchem	AR
Nitric acid (55%)	HNO ₃	Saarchem	AR
Chromium chloride (III) hexahydrate	CrCl ₃ .6H ₂ O	Saarchem	AR
Calcium chloride	CaCl ₂	Saarchem	AR
Magnesium chloride	MgCl ₂	Saarchem	AR
Potassium chloride	KCl	Saarchem	AR
Arsenic trioxide	As ₂ O ₃	Sanachem	AR
Buffers pH 7 and pH 4		Saarchem	AR
Flocculent (anionic polyacrylamide) KLARAIP AP1142		Betz Dearborn Johannesburg	AR

*CP: Chemically pure

**AR: Analytical reagent

2.2 PREPARATION OF REAGENTS

- 15 liters of saturated salt solution was prepared by adding 7500 grams (g) of coarse salt to distilled water in a 15 liters bottle.
- A 500 part per million (ppm) flocculent solution was freshly prepared by dissolving 0.500 g of the solid material anionic polyacrylamide-based flocculent (Trade name: KLARAIP AP1142, Betz Dearborn, Johannesburg) in 1 L of volumetric flask of distilled water.
- 50% chromium chloride solution was prepared by dissolving 50.00 g of chromium chloride in distilled water and making up to 100 ml in a volumetric flask.
- 50% magnesium chloride solution was prepared by dissolving 50.00 g of magnesium chloride in distilled water and making up to 100 ml in a volumetric flask.
- 50% calcium chloride solution was prepared by dissolving 50.00 g of calcium chloride in distilled water and making up to 100 ml in a volumetric flask.
- Sodium hydroxide solution was prepared by using laboratory grade pellets to make ~30 % and ~3% sodium hydroxide solutions.
- 32% concentrated hydrochloric and 3% hydrochloric acid were used for neutralizations.

2.3 ARSENIC ANALYSIS

2.3.1 Analytical Instruments

Arsenic can be determined by a variety of instrumental techniques. These include atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), molecular visible spectroscopy and voltammetry. Some of these techniques (e.g. ICP-MS) can serve as element-specific detectors when coupled to chromatographic separation techniques (e.g. HPLC and GC).¹ In this research the following techniques were used.

- Atomic Absorption Spectrometry (AAS).
- Inductively Coupled Plasma Mass Spectroscopy (ICP-MS).
- Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

The analytical technique of ICP-MS was used due to its high sensitivity and lower detection levels when compared to the technique of flame atomic absorption spectroscopy.² During the research period, the detection limit for flame atomic absorption spectroscopy was approximately 0.1 ppm thus limiting analyses to higher concentration. The ICP detection limit was approximately 0.05 ppm. However flame atomic absorption spectroscopy was well suited as a screening tool. The total dissolved salt content of the brine solution was kept low by diluting the brine solution twenty times because ICP and ICP-MS are adversely affected by salt solutions when salt levels exceed 1%.³

2.3.1.1 Atomic Absorption Spectrometry (AAS)

An element in its atomic form is introduced into a light beam of appropriate wavelength causing the atom to absorb light and enter an excited state. The absorption can be measured by the reduction in the intensity of the light beam which can be directly correlated with the concentration of the element. The absorbance of known calibration standards and an unknown sample can be carried out by comparing their light absorbance.

An atomic absorption spectrometer consists of an appropriate light source (usually a hollow cathode lamp containing the element to be measured), an absorption path (usually a flame but occasionally an absorption cell), a monochromator (to isolate the light of appropriate wavelength) and a detector. The flame temperature can be varied by using different fuel and oxidant combinations.⁴

The atomic absorption spectrometer was operated according to the manufacturer's instructions at the parameters specified in Table 2.2.

Table 2.2: The settings used on the Varian Spectra AA-10 atomic absorption spectrometer

Parameter	Settings
Hollow cathode lamp	Arsenic lamp
Wavelength	193.7nm
Slit width	0.5nm
Lamp current	10mA
D ₂ background correction	On
Flame	air and acetylene

The following procedure was used to optimize the atomic absorption spectrometer for arsenic analysis.

- The wavelength and slit width were set as per Table 2.2.
- The lamp position and wavelength were varied while observing the signal bar of the detector. The settings of lamp position and wavelength were adjusted to give the maximum transmittance.
- The burner position was optimized while having the flame lit and changing the vertical, horizontal and rotational settings to yield the maximum signal.
- The flame composition was adjusted by altering the acetylene flow to give the greatest possible signal.
- After a rinsing delay of 10 seconds, the absorbance of each solution was read three times.
- All the arsenic determinations were carried out in triplicate and average values were used.
- The absorbance of the instrument was adjusted to zero absorbance while aspirating distilled water.
- A set of calibration solutions (0.5, 10, 20, 30 and 50 ppm As³⁺) and a blank were aspirated in ascending order of concentration to generate a calibration curve.

Advantages of atomic absorption spectrometry (AAS)

- The principles of measurement are simple and well understood.
- The equipment is relatively simple to use and the technology is relatively inexpensive compare with ICP-MS.
- Sample throughput is high as each measurement takes only a few seconds.
- The technique is applicable over a wide range of concentrations for most elements.⁴

Disadvantages of atomic absorption spectrometry (AAS)

- All measurements are made following chemical dissolution of the element of interest. Therefore the measurement can only be as good as the quality of the sample digestion. In this research work ICP and ICPMS also suffer this disadvantage.
- AAS is a sequential analytical technique; hence the technique (that is, one element at a time) becomes time consuming when there are multi element analyses to be carried out.
- Interferences from other elements or chemical species can reduce atomisation and depress absorbance, thereby reducing sensitivity.
- Li, Na, K, Rb and Cs ionize rather easily, again reducing atomisation and complicating the measurement technique.⁴

ICP and ICP-MS contributed to this research by allowing analysis at As concentration that were below the detection limit of AAS, thereby permitting the use of higher levels of coagulation (higher metal: As mole ratio).

2.3.1.2 Inductively Coupled Plasma Emission Spectroscopy (ICP-AES)

In plasma emission spectroscopy, at a temperature of approximately 8000°C a sample solution is introduced into the core of inductively coupled argon plasma (ICP). All elements become thermally excited and emit light at their characteristic wavelengths at this temperature. This light is collected by the spectrometer and

passes through a diffraction grating that serves to resolve the light into a spectrum of its constituent wavelengths. Within the spectrometer, this diffracted light is then collected at characteristic wavelengths and amplified to yield an intensity measurement that can be converted to an elemental concentration by comparison with calibration standards.⁴

Table 2.3 show the settings used on the ICP-AES Spectrometer.

Table 2.3: Settings used on the ICP-AES Spectrometer

Parameters	Settings
Wavelength	193.696 nm
Calibration line	Argon line
Sample introduction settings	
Sample uptake delay	20s
Pump rate (rpm)	15s
Rinse time (s)	30s with calibration blank solution (0.15% HNO ₃)
Fast pump	Yes
Replicates	3
Peristaltic pump step (flow rate)	15 ml/min
Background correction mode	Fitted
Instrument	ICP Model Varian 715-ES

The following procedure was used to optimize the ICP-AES spectrometer for arsenic analysis:

- The instrument was calibrated by using 0.5, 10, 20, 30 and 50 ppm As³⁺ standard solutions and a blank was prepared in 0.15% HNO₃.
- Before the samples were read, a blank was read to check for baseline drift, and one standard was read to verify the calibration. After every five samples read, a standard solution was read to ensure instrument consistency.
- When the analysis was done, the system was rinsed with 10% HNO₃ for 10 minutes followed by distilled water for another 10 minutes to ensure that there were no traces of arsenic left in the sample introduction system.

Advantages of ICP-AES

- With the exception of argon, the technique has the ability to identify and quantify a vast majority of elements, since many wavelengths of varied sensitivity are available for determination of any one element.
- ICP is suitable for various concentrations from ultra trace levels to major components; detection limits are generally low for most elements with a typical range of 1 – 100 mg/L.
- When performing quantitative analysis multi-elemental analysis can be accomplished, and quite rapidly.⁴

Disadvantages of ICP-AES

- Certain unstable elements require special facilities for handling the radioactive fumes of the plasma, should such elements be determined.
- For handling halogens special optics for the transmission of very short wavelengths become necessary.⁴
- High cost of operation due to high argon consumption.

2.3.1.3 Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)

In plasma mass spectroscopy, the inductively coupled argon plasma (ICP) is used as an excitation source for the elements of interest. The plasma in ICP-MS is used to generate ions which are then introduced into the mass spectrometer. These ions are then separated and collected according to their mass to charge ratios. The constituents of an unknown sample can then be identified and measured. ICP-MS offers extremely high sensitivity to a wide range of elements including arsenic.⁴

Table 2.4 shows the setting used on the ICP-MS Spectrometer.

Table 2.4: Settings used on the ICP-MS

Parameter	Settings
Integration time	1000 ms
RF power	1100 W
Dual Detection Mode	Pulse
Arsenic mass weight	74.922 g/mol
Sample scan	10 times
Instrument	6100 ICP-MS and a Perkin-Elmer AS-90 auto sampler

The following procedure was used to optimize the ICP-MS spectrometer for arsenic analysis.

- Arsenic was analyzed at mass 74.922 grams per mole (g/mol).
- The sample was scanned ten times on the ICP-MS.
- The ion-lens voltage and nebuliser gas flow rate were optimized prior to each analysis.
- The arsenic standards were prepared from a *Spectra Scan* multi-element standard SS-028317.
- Standards were prepared in a 1% volume per volume (v/v) nitric acid medium with distilled water purified with a *Millipore Simplicity* 185 system.
- Standards used: 5, 10, 20, 50, 100, 300, 500 µg/l As.

Advantages of ICP-MS

- ICP-MS is capable of determining an extremely wide range of elements to very low detection limits (typically sub parts per billion).
- The analytical sensitivity is adequate to allow for the determination of isotopes.
- A large linear working range of several orders of magnitude is offered by ICP-MS.
- An element that is not easily measured by emission or absorption spectroscopy can be analyzed by this technique.⁴

Disadvantages of ICP-MS

- Instrument performance can be harmfully affected if the total dissolved salt content of the analyte solution is not kept low as high dilutions can result in less attractive detection limits for some elements.
- Some doubly charged ionic species create difficulties when using this technique.
- Ultra pure acids are required for leaches and digestions and increase the cost of measurements.⁴

2.4 pH DETERMINATION

In all experiments, pH measurements were performed using a Metrohm 654 digital pH meter with a WTW Sentix combined glass pH electrode (serial no. C000304091) calibrated daily using pH 4 and pH 7 buffers. Three molar solution of potassium chloride was prepared and added into the pH electrode when the internal electrode levels fell below the required level.

2.5 MSMA SAMPLE

The monosodium methyl arsenate (MSMA) used in this work was supplied by Dow–Agrosciences in Canelands, Durban, South Africa.

2.6 ANALYTICAL PROCEDURE

2.6.1 Preparation of MSMA stock solution

MSMA commercial product was analyzed for its arsenic content. MSMA stock was diluted 10 000 times and analyzed by ICP-AES. The arsenic concentration in MSMA stock was 25 000 ppm. After the determination of the arsenic content, a portion of pure MSMA stock was diluted to 2000 ppm and analyzed using AAS. The 2000 ppm MSMA was cross checked by analysis against arsenic standards using flame atomic absorption spectroscopy.

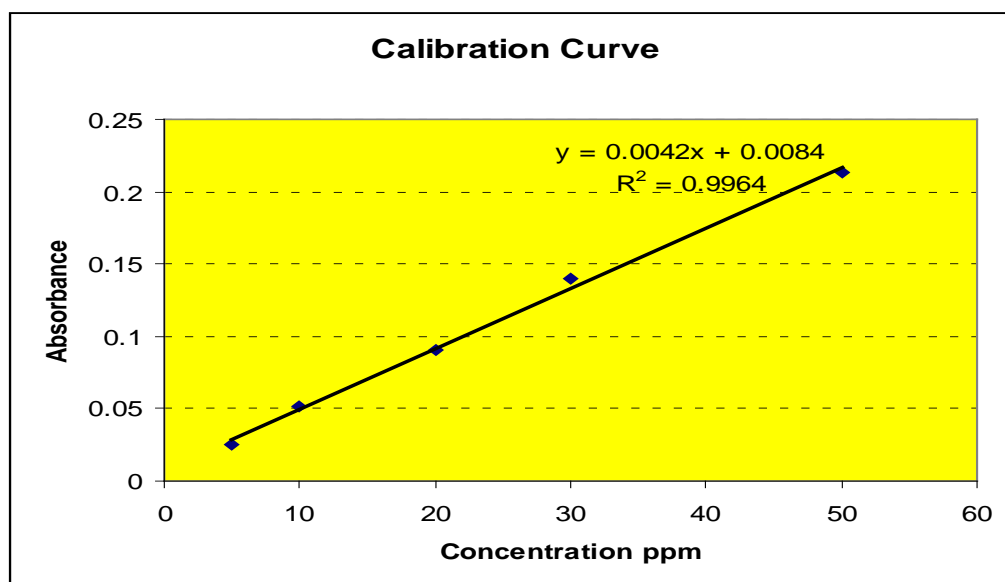
Table 2.5 shows initial concentration of MSMA.

Table 2.5: AAS results showing the determination of initial concentration of MSMA

As (ppm)	Absorbance	Concentration (ppm)
5	0.025	
10	0.052	
20	0.091	
30	0.140	
50	0.213	
MSMA	0.165	2000ppm (after 50Xdilution)

Figure 2.1 shows the calibration curve for the determination of the initial concentration of MSMA.

Figure 2.1: The calibration curve for the determination of the initial concentration of MSMA.



2.6.2 Preparation of standards

A 1 000 ppm arsenic trioxide stock solution was prepared by weighing 0.3303 g of As_2O_3 and adding 0.45 g of sodium hydroxide, dissolving in distilled water then lowering the pH to 7.0 using nitric acid. The solution was then made up to 250 ml with distilled water. Standards (1-100 ppm) were prepared from this stock solution.

2.7. EXPERIMENTAL PROCEDURE

Arsenic was removed from solution by coagulation in which the arsenic species adsorbs onto the surface of the precipitate that forms. The precipitates were the metal hydroxide of Cr^{3+} , Mg^{2+} , and Ca^{2+} .

2.7.1 Coagulation procedure

The following coagulation procedure was used for the different coagulation experiments:

- 600 ml glass beakers were washed with soap, rinsed with dilute nitric acid (20 ml nitric per liter) then rinsed with distilled water (DI) water and oven dried before use.
- The required amounts of MSMA stock (as 2000 ppm As^{5+}) and coagulant were added along with distilled water to achieve a final volume of 500 ml and the solutions were agitated.
- The pH was adjusted to near the required value with concentrated sodium hydroxide with dilute sodium hydroxide was used to provide the precise pH adjustment.
- A precipitate was formed, and once the pH was stable for 30 seconds, the required volume of anionic organic flocculent was added.
- The solution was agitated mildly for two minutes by stirring on a stirrer using magnetic follower and allowed to settle for an hour by standing.
- A portion of 20 ml of each of the decanted and subsequently filtered solutions were transferred into separate 100 ml volumetric flasks and acidified with 1 drop of concentrated nitric acid and made to volume with distilled water.
- The filtrates and decantates were analyzed for arsenic.

2.7.2 Arsenic analysis

The arsenic concentration in the filtrates and decantates were determined using atomic spectroscopy as described in section 2.4.

The arsenic removal (E) value was calculated by the following expression:

$$E = \frac{C_0 - C}{C_0} \times 100\% \dots \dots \dots \text{Eqn} \dots 2.1$$

where C_0 is the initial arsenic concentration from sample and C is the final arsenic concentration.

After the preliminary experiments were performed, experimental domains were selected from this data to be used in the modeling. *Design Expert Version 6.0 software* was used to generate the design (the actual experiments). The experiments were performed, arsenic analysis was done and the arsenic removals were determined. Predictive test experiments were done along with the modelling work. The statistical data was analysed using DE software and preliminary trends were observed. The models were then refined and validated. A summary of the criteria that the modelling achieved is stated in the next section.

2.8 MODELLING METHODOLOGY

2.8.1 Analysis of variance (ANOVA)

The ANOVA method includes tests for the linear and quadratic components of the effect of each variable on the response. If the design includes replication of experiments, then the estimate of pure error can be used for the ANOVA and significance testing; in that case an overall *Lack-of-Fit* test will also be performed.⁶ To aid in the interpretation of results, the *design expert* will compute the table of means (and confidence intervals) as well as insignificant means (and confidence intervals) for interactions. Graphical validations include plots of means with confidence intervals, normal and half-normal probability plots of effects, and response surface.⁶

The response surface model was determined by the *design expert*. The central composite design (CCD) is the most common experimental design used in response surface methods and has equal predictability in all directions from the center. CCD is an optimized design for fitting quadratic models. The CCD is sufficient to test statistical validity, the number of experimental points in the fitted model and lack-of-fit of the model. Due to experimental or random variability error the central point in CCD is estimated to replicate several times. Four independent variables were devised using the central composite design for investigation to obtain a quadratic predictive model. The different parameters that were chosen as main variables were designated as X_1 , X_2 , X_3 , and X_4 , respectively. The low, middle and high levels, of each variable were designated as -1 , 0 , and $+1$, respectively.

The response surface has the following mathematical form:

$$Y = B_0 + B_1X_1 + B_2X_2 + B_3X_3 + B_4X_4 + B_{12}X_1X_2 + B_{13}X_1X_3 + B_{14}X_1X_4 + B_{23}X_2X_3 + B_{24}X_2X_4 + B_{34}X_3X_4 + B_{11}X_1^2 + B_{22}X_2^2 + B_{33}X_3^2 + B_{44}X_4^2 \dots\dots\dots Eqn \dots 2.2$$

where X_1 , X_2 , X_3 and X_4 are input variables; B_0 is a constant; B_1 , B_2 , B_3 and B_4 are linear coefficients; B_{12} , B_{13} , B_{14} , B_{23} , B_{24} and B_{34} are cross-product coefficients; B_{11} , B_{22} , B_{33} and B_{44} are quadratic coefficients. Y is predicted response.⁷

2.8.2 Summary of criteria that suitable the models should achieve

- The "model F-value" was observed to be large and F- tests were used to evaluate the response surface model of decantation and filtration.
- Values of "*Prob>F*" of 0.0500 indicated model terms that were significant.
- A "p-value" was used to measure how much evidence there is against the null hypothesis. The smaller the "p-value", the more evidence there is against the null hypothesis to be rejected.

- “Lack of fit” values were greater than 0.1000 indicating that the model terms were not significant, which means that if “*Prob>F*” is significant and the “Lack of fit” was insignificant, then the models were good.
- Standard deviation and “R-Squared” values were approximately 1 which was desirable.
- "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable, indicating an adequate signal.
- All responses were explained by the model.
- The models were tested statistically and experimentally validated.
- Normal probability plots of the “studentized residuals” was used to check for normality of residuals and “studentized residuals” *versus* “predicted values” graphs were used to check for constant error, and also to check those influential values termed as outliers.

2.9 EXPERIMENTAL DESIGN

2.9.1 Selected theory of experiment design

The procedure that was used was taken from Design Expert operating (DOE) procedure which is as follows:

2.9.1.1 Design Expert operating (DOE) procedure

- The designs were created using Design *Expert* software and the selected designs were either -two levels factorial, or response surface, central composite.
- For each design the number of center points and replicates were selected and the software indicates the number of required experiments and the variable settings needed to be done. The variables, the units, and the high and low values were entered into the *Design Expert* table which described the experimental domain.
- Responses were selected, and then response names and units were entered.

- The full design is generated in a randomized order which is the only method of controlling all possible extraneous variables and this is the order in which the experiments were run.
- All the experiments were completed and the results were entered as the responses in the design table.
- The model was evaluated using ANOVA.

Chapters 3, 4, 5 and 6 describe experimental modelling of arsenic removal by coagulation using the following coagulants.

- Chromium (III) chloride,
- Calcium (II) chloride,
- Magnesium (II) chloride and
- Mixture of chromium (III) chloride and calcium (II) chloride as a binary coagulant.

Experiments were performed according to the experimental plan in Table 2.6. In chromium-based coagulation four factors were investigated using a central composition design which consists of a 2^4 factorial run and six centre point experiments. In the calcium, magnesium and binary coagulations three factors were investigated using a half design which consists of a 2^3 factorial run and three centre point experiments.

Table 2.6 presents an overview of the experimental designs used in the research.

Table 2.6 Overview of the experimental design used in the research

Model details	Design type	Number of factors	Form of Design	Variable
Chromium coagulation	Central composite design	4	Full design	pH, Cr:As,[As] , [Floculant]
Calcium coagulation	Factorial design	3	Half design	pH,Ca:As, [As]
Magnesium coagulation	Factorial design	3	Half design	pH, Mg:As,[As]
Binary coagulation using calcium and chromium	Factorial design	4	Half design	pH,Cr:As, Ca:As, [As]

2.10 REFERENCES

1. Arsenic Uptake in Plants, Abraham Regier, Natural Science Seminar, 2007
2. Optimization of process parameters for arsenic treatment with granular ferric hydroxide, Kashi Banerjee, Shokoufeh Nour, Mike Selbie, Miche, American Water Works Association, 2003.
3. Arsenate removal from water using sand–red mud columns, Genç Fuhrman, H Water Research, 2005, Volume 39, Issue 13, pp 2944.
4. Determination of mercury in environmental and biological samples using pyrolysis atomic absorption spectrometry with gold amalgamation, Costley, C T Analytica Chimica Acta, 2000, Volume 405, Issue 1, pp 179.
5. Simultaneous determination of As, Cd, Cr and Pb in *aqua regia* digests of soils and sediments using electrothermal atomic absorption spectrometry and fast furnace programs, Myöhänen T., Spectrochimica acta. Part B, Atomic spectroscopy, 2002, Volume 57, Issue 11, pp 1681.
6. Determination of arsenic removal efficiency by ferric ions using response surface methodology, Baskan M.B, Journal of hazardous materials, 2009 Volume 166, Issue 2, pp 796.
7. Use of response surface methodology to investigate the effect of food constituents on *Staphylococcus aureus* inactivation by high pressure and mild heat YL Gao, XR Ju, HH Jiang, Process Biochemistry, 2006

CHAPTER 3

THE MODELLING OF ARSENIC (V) REMOVAL FROM AQUEOUS MEDIA USING CHROMIUM (III) CHLORIDE

3.1 INTRODUCTION

This chapter discusses the modelling investigation of the factors which influence the arsenic (V) removal using chromium (III) chloride as coagulant. Other factors that are investigated include coagulant dose, pH, and initial arsenic concentration.

3.2 EXPERIMENTAL

3.2.1 Coagulation procedure

The coagulation was carried out as in section 2.7.1 and 50% CrCl₃ was used as coagulant. A greenish precipitate was formed and once the pH was stable for 30 seconds, the required volume of anionic organic flocculent concentration (500 ppm) was added, stirred for two minutes and allowed to settle by standing for an hour. Both decantates and filtrates were analyzed for arsenic using inductively coupled plasma mass spectrometry.

3.2.2 Mechanism of arsenate removal by chromium coagulation

The mechanism by which arsenic is removed by this procedure involved the formation of chromate oxyhydroxide. The removal is much more effective at low to neutral pH (pH 4-7), this behaviour could be due to the formation of different arsenic species in aqueous solution for instant at pH 4 the predominant arsenate species is H₂ASO₄⁻ and its concentration decrease when the pH increases, arsenate ion has mostly negative one charge and Cr(OH)₂ is very positive charge and a good removal of arsenic occurs than at higher pH >9 due to increased solubility of arsenic at high pH, arsenate ions have mostly negative two charge and Cr(OH)₃ is very negatively charge as well. Therefore a very poor arsenic removal performance would be expected because all the components have

negative charge surface and would thus repel each other as the theory behind is been described in section 1.5.

3.2.3 Selection of the experimental domain

The factors shown in Table 3.1 present the levels for the experimental design. This is a central composite design (CCD) wherein the factorial portion is a full factorial design. With all combinations of the factors at two levels high, (+1) and low, (-1) levels, the centre points (coded level 0), which is the midpoint between the high and low levels, is repeated seven times. The star points were set at high (+2) and low (-2) levels. The natural values used are shown in Table 3.1.

Table 3.1 shows the natural values of experimental domain:

Table 3.1 Natural values of experimental domain for chromium (III)-based coagulation.

Factor	Name	Units	Star low value	Low value	Middle value	High Value	Star high value
A	pH	-	4.5	5.5	6.5	7.5	8.5
B	[Flocculant]	ppm	1.5	2.0	2.5	3.0	3.5
C	Cr: As	-	1.0	2.0	2.5	4.0	5.0
D	Initial[As ⁵⁺]	ppm	50	250	450	650	850

The interpretations of the natural values in Table 3.1 are coded using the method of coding this value is given by the following formula.

$$\text{Coded Factor} = \frac{\text{Natural value} - \text{Midpoint}}{\text{Stepsize}} \dots\dots\dots \text{Eqn}\dots\dots 3.1$$

where midpoint = $\frac{\text{high value} - \text{low value}}{2} \dots\dots\dots \text{Eqn}\dots\dots 3.2$

stepsize = half the difference the and to obtain the star point = $2 \times \text{low coded}$.

The minimum and maximum range of variables investigated and the full experimental plan with respect to their actual and coded forms are listed in Table 3.2.

3.2.4 Design matrix for chromium (III)-based coagulation

Table 3.2 shows the coded design matrix for chromium (III)-based coagulation.

Table 3.2 The coded design matrix for chromium (III)-based coagulation.

Coded Factors	Variable	Units	Star low value	Low value	Middle value	High Value	Star high value
X ₁	pH	-	-2	-1	0	1	2
X ₂	[Flocculent]	ppm	-2	-1	0	1	2
X ₃	Cr:As	-	-2	-1	0	1	2
X ₄	[As]	ppm	-2	-1	0	1	2

3.2.5 The experimental design in coded values

The experimental plan generated using the *Design Expert Version 6.0 software* is shown in Table 3.2. A set of 31 experiments including six centre points was carried out. Each variable was studied at three different levels. All variables were taken at a central coded value of zero.² Table 3.3 depicts the coded experimental design.

3.2.6 The coded central composite design (CCD) using to investigate chromium (III) -based coagulation of arsenate

Table 3.3 present the coded CCD using to investigate chromium (III)-based coagulation of arsenate.

Table 3.3 The coded values of the experimental design used to investigate chromium (III)-based coagulation of arsenate solution.

Standard Order	Run Order	pH	B [Flocculent] ppm	C Cr: AS Mole ratio	D [As] Ppm	Type of point
1	20	-1	-1	-1	-1	F
2	28	1	-1	-1	-1	F
3	6	-1	-1	1	-1	F
4	25	1	-1	1	-1	F
5	3	-1	-1	-1	1	F
6	27	1	-1	-1	1	F
7	16	-1	-1	1	1	F
8	8	1	-1	1	1	F
9	31	-1	1	-1	-1	F
10	11	1	1	-1	-1	F
11	10	-1	1	1	-1	F
12	4	1	1	1	-1	F
13	14	-1	1	-1	1	F
14	21	1	1	-1	1	F
15	5	-1	1	1	1	F
16	17	1	1	1	1	F
17	1	-2	0	0	0	S
18	22	2	0	0	0	S
19	24	0	0	-2	0	S
20	19	0	0	2	0	S
21	2	0	-2	0	0	S
22	18	0	2	0	0	S
23	26	0	0	0	-2	S
24	29	0	0	0	2	S
25	12	0	0	0	0	Cp
26	23	0	0	0	0	Cp
27	7	0	0	0	0	Cp
28	15	0	0	0	0	Cp
29	13	0	0	0	0	Cp
30	30	0	0	0	0	Cp
31	9	0	0	0	0	Cp

F = factorial point

Cp = centre point

S = star point

3.3 RESULTS AND DISCUSSION

3.3.1 Fitting a model to the experimental data

The initial polynomial equation 3.3 model fitted to the data is given by:

$$\hat{Y}_1 = \hat{\beta}_0 + \hat{\beta}_1 A + \hat{\beta}_2 B + \hat{\beta}_3 C + \hat{\beta}_4 D + \hat{\beta}_5 AB + \hat{\beta}_6 AC + \hat{\beta}_7 AD + \hat{\beta}_8 BC + \hat{\beta}_9 BD + \hat{\beta}_{10} CD + \hat{\beta}_{11} A^2 + \hat{\beta}_{12} B^2 + \hat{\beta}_{13} C^2 + \hat{\beta}_{14} D^2 \dots \dots \dots \text{Eqn} \dots 3.3$$

where $\hat{Y}_1 = \text{predicted \% As removed (both decantation and filtration)}$

$A = pH$

$B = [\text{Flocculent}]$

$C = Cr : \text{As mole ratio}$

$D = \text{initial [As]}$

A partial t-test has been used to test the significance of the estimated coefficients ($\hat{\beta}_j$) where $j = 0, 1, 2, \dots, 14$ by using the aid of Excel version 2.3 2007. The null hypothesis for these tests is given by $H_0 : \beta_j = 0$, if the corresponding p-value for such a test is smaller than 0.05, the hypothesis is rejected and then we accept that the coefficient is significant which means that the corresponding factor has a significant effect on the response of percentage of arsenic removed for decantation and filtration.

3.3.2. The actual values of the experimental design and responses

Table 3.4 shows the design after converting the coded variables back to the original values, the following results were obtained.

Table 3.4 Results of the factorial design used to the model of the removal of aqueous arsenic (v) using chromium (III) as a coagulant.

Std Order	Run Order	pH	Vol Floculant	Cr : As	[As]	[As] Left Decantation	% As Removed Decatantion	[As] Left Filtration	% As Removed Filtration
		-	ppm	-	ppm	ppm	%	ppm	%
1	20	5.5	2	2	250	0.0822	99.9671	0.0806	99.9678
2	28	7.5	2	2	250	0.0683	99.9727	0.0778	99.9689
3	6	5.5	2	4	250	0.0558	99.9777	0.0577	99.9769
4	25	7.5	2	4	250	0.0660	99.9734	0.0579	99.9768
5	3	5.5	3	2	250	0.0566	99.9774	0.0501	99.9799
6	27	7.5	3	2	250	0.0787	99.9685	0.0598	99.9761
7	16	5.5	3	4	250	0.0855	99.9658	0.0744	99.9702
8	8	7.5	3	4	250	0.0855	99.9658	0.0652	99.9739
9	31	5.5	2	2	650	0.0881	99.9864	0.0594	99.9909
10	11	7.5	2	2	650	0.0666	99.9898	0.0460	99.9929
11	10	5.5	2	4	650	0.0937	99.9856	0.0623	99.9904
12	4	7.5	2	4	650	0.0765	99.9882	0.0772	99.9813
13	14	5.5	3	2	650	0.0665	99.9898	0.0768	99.9882
14	21	7.5	3	2	650	0.0664	99.9898	0.0521	99.9922
15	5	5.5	3	4	650	0.0859	99.9868	0.0572	99.9912
16	17	7.5	3	4	650	0.0833	99.9872	0.0617	99.9905
17	1	4.5	2.5	3	450	0.1056	99.9716	0.0790	99.9824
18	22	8.5	2.5	3	450	0.0830	99.9816	0.0649	99.9856
19	24	6.5	2.5	1	450	0.0179	99.9961	0.0732	99.9837
20	19	6.5	2.5	5	450	0.0767	99.9832	0.0687	99.9847
21	2	6.5	1.5	3	450	0.0549	99.9878	0.0531	99.9882
22	18	6.5	3.5	3	450	0.0788	99.9825	0.0885	99.9803
23	26	6.5	2.5	3	50	0.0736	99.8528	0.1156	99.7689
24	29	6.5	2.5	3	850	0.0515	99.9939	0.0667	99.9922
25	12	6.5	2.5	3	450	0.0715	99.9841	0.0998	99.9778
26	23	6.5	2.5	3	450	0.0756	99.9832	0.1056	99.9765
27	7	6.5	2.5	3	450	0.0471	99.9895	0.0544	99.9879
28	15	6.5	2.5	3	450	0.0690	99.9872	0.0774	99.9828
29	13	6.5	2.5	3	450	0.0686	99.9847	0.0763	99.9830
30	30	6.5	2.5	3	450	0.0686	99.9847	0.0763	99.9830
31	9	6.5	2.5	3	450	0.0686	99.9847	0.0763	99.9830

After some exploratory data analysis a single outlier was detected using Excel version 2.3 and *Design Expect*. An outlier is defined as a data point that derives from a different model than do the rest of the data.³ In Excel the data here appear to come from a linear model with a given slope and variation except for

the outlier which appears to have been generated from some other model. In *Design Expect* a residual plot amplifies the presence of an outlier thus it has a large residual value. The residual is an error in prediction from the model which is the difference between the predicted and observed values. Outlier detection was important for effective modeling and the outlier was excluded from the model fitting. Figure 3.1 is a scatter diagram showing the outlier for decantation.

Figure 3.1 Scatter diagram showing the outlier for the decantation.

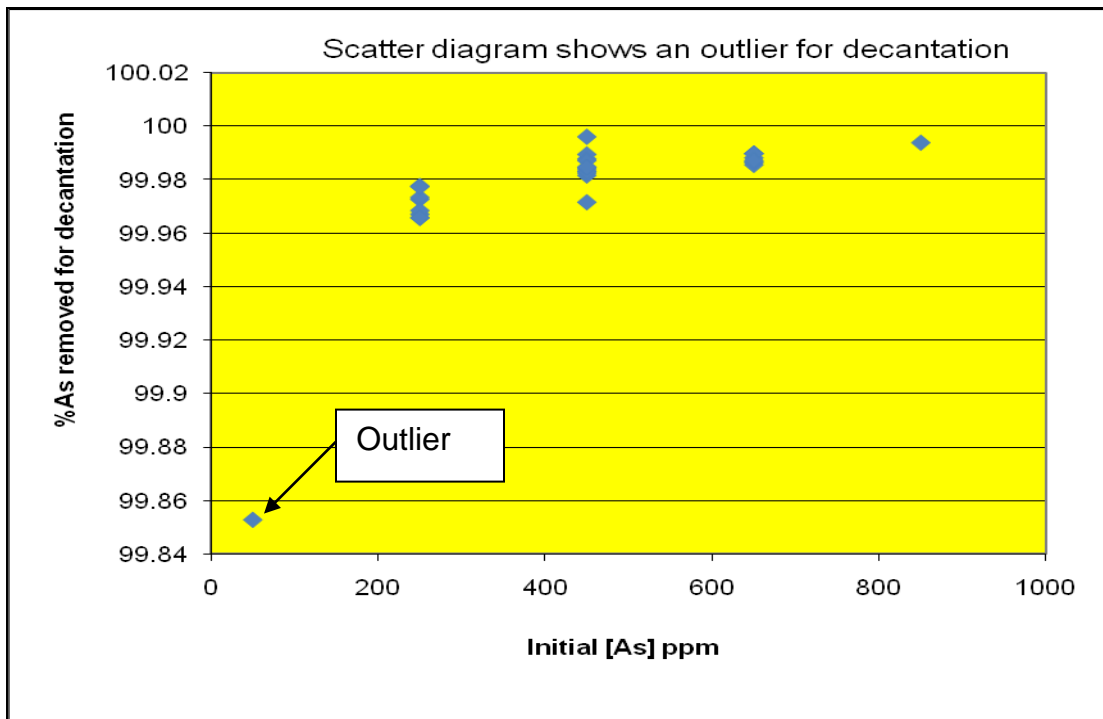
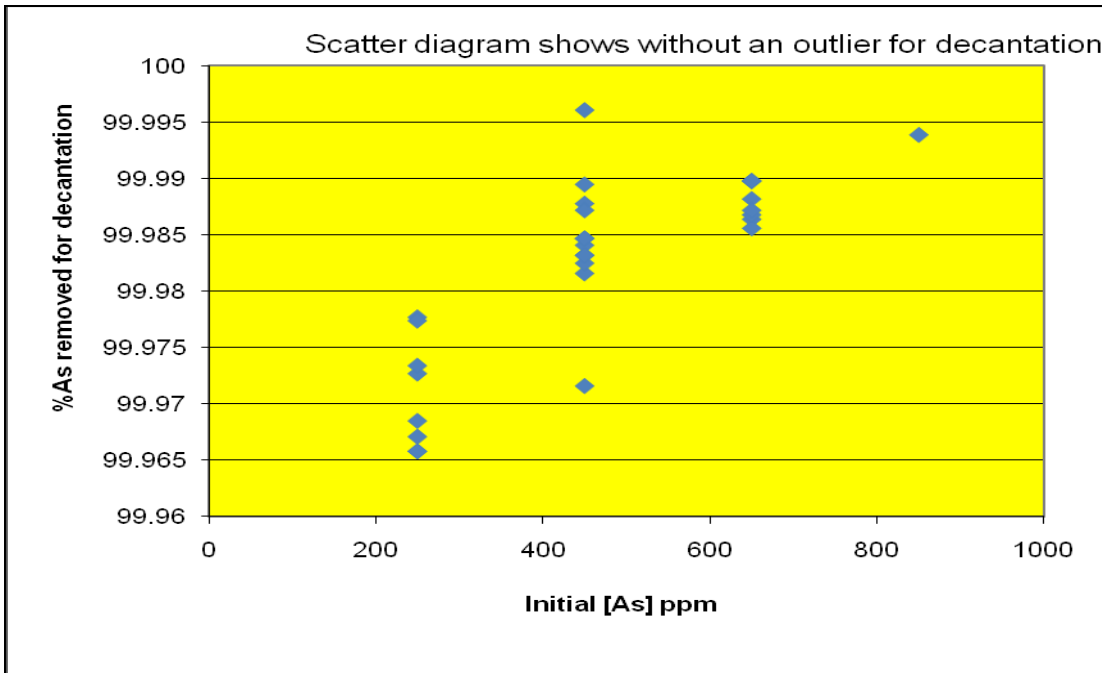


Figure 3.2 shows the scatter diagram after removal of the outlier. Experiment number 23 was found be an outlier.

Figure 3.2 Scatter diagram shown without the outlier for the filtration.



After removal of the outlier the decantation model was recalculated and is shown in Table 3.5 and further analysed in Tables 3.6 and 3.7. and Figures 3.3 and 3.4 will be based on the remaining 30 observations. Tables 3.5 and 3.6 show the initial polynomial equation that describes the chromium (III)-based removal of arsenate for decantation.

3.4 The model

3.4.1 Defining the polynomial equation describing the chromium (III)-based removal of arsenate

The first regression analysis shown in Tables 3.5 (a) and (b) included all the main effects as well as quadratic interactions.

Table 3.5 (a) The initial polynomial equation that describes the chromium (III)-based removal of arsenate for decantation.

Factor	Coefficient Estimate		Standard Error	t for H0	
		DF		Coeff=0	Prob > t
Intercept	99.99	1	6.437E-03		
pH	7.838E-04	1	7.518E-04	1.04	0.3136
[Floc]	-1.544E-03	1	7.518E-04	-2.05	0.0578
Cr:As	-8.526E-04	1	7.518E-04	-1.13	0.2746
[As]	8.795E-03	1	8.895E-04	9.89	< 0.0001
pH ²	-2.476E-03	1	6.989E-04	-3.54	0.0029
[Floc] ²	3.315E-04	1	6.989E-04	1.09	0.2950
(Cr:As) ²	-1.818E-03	1	6.989E-04	-0.47	0.6422
[As] ²	-2.872E-03	1	9.097E-04	-3.16	0.0065
pH*[Floc]	-8.427E-05	1	9.207E-04	-0.092	0.9283
pH*Cr:As	-9.808E-04	1	9.207E-04	-1.07	0.3036
pH*[As]	8.757E-04	1	9.207E-04	0.95	0.3567
[Floc]*Cr:As	-1.799E-03	1	9.207E-04	-1.95	0.0696
[Floc]*[As]	-3.056E-04	1	9.207E-04	-0.33	0.7446
Cr:As*[As]	1.057E-03	1	9.207E-04	1.15	0.2688

Table 3.6 (b) The initial polynomial equation that describe the chromium (III)-based removal of arsenate for filtration.

Factor	Coefficient Estimate		Standard Error	t for H0	
		DF		Coeff=0	Prob > t
Intercept	99.98	1	1.715E-03		
pH	1.295E-04	1	9.260E-04	0.14	0.8906
[Floc]	-1.385E-05	1	9.260E-04	-0.15	0.8831
Cr:As	1.816E-05	1	9.260E-04	0.020	0.9846
[As]	7.98003	1	1.096E-03	7.28	< 0.0001
pH ²	4.364E-04	1	8.609E-04	0.51	0.6195
[Floc] ²	4.929E-04	1	8.609E-04	0.58	0.5696
(Cr:As) ²	5.006E-04	1	8.609E-04	0.58	0.5696
[As] ²	-1.577E-03	1	1.121E-03	-1.41	0.1797
pH*[Floc]	-5.869E-04	1	1.134E-03	-0.52	0.6124
pH*Cr:As	5.654E-04	1	1.134E-03	0.50	0.6253
pH*[As]	-3.020E-04	1	1.134E-03	-0.27	0.7937
[Floc]*Cr:As	-9.600E-04	1	1.134E-03	-0.85	0.4106
[Floc]*[As]	-9.862E-04	1	1.134E-03	-0.87	0.3982
Cr:As*[As]	-2.083E-04	1	1.134E-03	-0.18	0.8567

Tables 3.5 (a) and (b) show initial models with significant and insignificant effects. The criterion for removing insignificant terms is rejection of terms with a p value greater than 0.05. The reduced models for the decantation and filtration are shown in Tables 3.6 (a) and (b) the final respective polynomial equation of models.

3.4.2 Final model describing the chromium (III)-based removal of arsenate.

Tables 3.6 (a) and (b) show the estimated coefficients for the final models after removal of the insignificant terms for decantation and filtration. The final model fitted to the data is given by following equation:

$$\hat{Y} = b_0 + b_1D + b_2D^2 \dots\dots\dots Eqn \dots 3.4$$

Table 3.6 (a) The final polynomial equation describing the response surface of chromium (III)-based coagulation of arsenate with decantation.

Factor	Coefficient Estimate		Standard Error	t for H0	
		DF		Coeff=0	Prob > t
Intercept	99.95	1	6.596E-03		
[As]	1.14E-04	1	2.88E-05	3.9476	0.00051
[As] ²	-7.6E-08	1	2.93E-08	-2.6069	0.01470

Table 3.6 (b) The final polynomial equation describing the response surface of chromium (III)-based coagulation of arsenate with filtration.

Factor	Coefficient Estimate		Standard Error	t for H0	
		DF		Coeff=0	Prob > t
Intercept	99.96	1	5.128E-03		
[As]	7.35E-05	1	2.24E-05	3.28470	0.00283
[As] ²	-3.8E-08	1	2.28E-08	-1.670	0.1065

3.5 ANOVA

In order to ensure a valid model, the following tests were performed:

- Significance of the regression model,
- Significance of individual model coefficients and
- Lack-of-fit.

The definitions of the terms used in ANOVA table are shown in Table 3.7.

3.5.1 Definition of ANOVA terms

Table 3.7 Definition of ANOVA terms.⁴

Terms	Abbreviation	Definition
Model		Terms estimating factor effects
Sum of squares	SS model	Total of the sum of squares for the model terms. A, B, C, A ² , B ² , C ² , A*B, A*C and B*C in the quadratic model
DF	DF model	Number of model coefficients, not including the intercept
Mean square		Estimate of model variance (SS model / DF model)
Residual		Combined estimate of experiment error
Sum of Squares	SS residual	SS lack of fit + SS pure error
DF	DF residual	DF lack of fit + DF pure error
Mean Square		Estimate of error variance (SS residual / DF residual)
Lack of Fit		The variation of mean responses about the fitted model
Sum of Squares	SS lack of fit	The sum of squares about the model
DF	DF lack of fit	Number of unique design points - 1 (for the intercept) - number of model coefficients
Mean Square		Estimate of lack of fit variance (SS lack of fit / D Lack of fit)
Pure Error		The variation obtained from genuine replicates.
Sum of Squares	SS pure error	The pooled sum of squares for all the genuine repeats
DF	DF pure error	Number of repeats of a unique design point - 1, summed over all design points with repeats.
Mean Square		Estimate of pure error variance (SS pure error / DF pure error)
Cor Total		Estimate of total variation, adjusted for the mean
Sum of Squares	SS total	Total SS for all cases about the mean.
DF	DF total	Number of experiments - 1.
F-Value		Tests the null hypothesis (H_0) that model terms are actually part of the error population, that is, EMS model = EMS residual. (EMS is the Expected Mean Square.) Large F values indicate the variation explained by the model is greater than would be expected by chance.
Prob > F		Probability of observing an F value this large if H_0 is true. P-values of 0.0001 include all values less than 0.0001.
Root MSE		Standard deviation (s) associated with the experimental error. SQRT (Mean

		Square Error).
Dep Mean		Dependent mean, the mean of the response over all cases.
Coefficient of variation	C.V.	The standard deviation as a percentage of the mean. = 100 x (Root MSE) / (Dep Mean)
R-Squared		The multiple correlation coefficient, sometimes called the coefficient of determination. Calculated after the effect of blocks has been removed $1 - [SS \text{ residual} / (SS \text{ residual} + SS \text{ model})]$
Adj R-Squared		R ² adjusted for the number of coefficients in the model relative to the number of points in the design. Measure of the amount of variation about the mean explained by The model. $1 - [(SS \text{ residual} / DF \text{ residual}) / ((SS \text{ residual} + SS \text{ model}) / (DF \text{ residual} + DF \text{ model}))]$
Predicted R-Squared		Measure the amount of variation in new data explained by the model. It is based upon the PRESS, see below = 1 - [SS press / (SS residual + SS model)]
Predicted Residual Sum of Squares	PRESS	A measure of how a particular model fits each point in the design. The coefficients for the model are calculated without the first point. This new model is then used to estimate the first point and calculate the residual for point one. This is done for each data point and the squared residuals are summed.

An ANOVA table is commonly used to summarize the tests performed.

3.5.2 Interpretation of ANOVA

The Design Expert Version 6.0 software was used to perform ANOVA on the experimental data. “Normal probability” and “residual versus predicted response” curves were plotted to evaluate selected model criteria. A good model must fit the observed data. “*Lack of Fit*” tests the overall fit of the model; the p-value associated with this test should exceed 0.1.¹ A general ANOVA will test whether the proposed model is significant in relation to the response of the model. The p-value for this test should be less than 0.05. The closeness of the fit is measured by the correlation squared (R^2) which should be approximately 1.¹

3.5.3 Summary of statistical test performed by ANOVA

Tables 3.8 (a) and (b), show the ANOVA table for the response surface.¹ *Design Expect* was used to calculate ANOVA.

Table 3.8 (a) ANOVA for the factorial model describing the chromium (III)-based coagulation of arsenate for the decantation model.

Source	Sum of Squares	DF	Mean	F Value	Prob > F
Model	1.800E-03	11	1.636E-04	14.15	<0.0001 significant
Residual	2.081E-04	18	1.156E-05		
<i>Lack of Fit</i>	<i>1.832E-05</i>	12	<i>1.527E-05</i>	3.68	<i>0.0602</i>
<i>Pure Error</i>	<i>2.488E-05</i>	6	<i>4.147E-06</i>		
Cor Total	2.008E-03	29			
Root MSE	3.400E-03		R-Squared	0.8964	
Dep Mean	99.98		Adj R-Squared	0.8330	
C.V.	3.401E-03		Pred R-Squared	0.5455	
PRESS	9.126E-04		Adeq Precision	13.122	Desire > 4

Table 3.8 (b) ANOVA for the factorial model describing the chromium (III)-based coagulation of arsenate for the filtration model.

Source	Sum of Squares	DF	Mean	F Value	Prob > F
Model	1.139E-03	7	1.627E-04	10.64	<0.0001 significant
Residual	3.365E-04	22	1.530E-05		
<i>Lack of Fit</i>	<i>2.505E-04</i>	6	<i>1.565E-05</i>	1.09	<i>0.4916</i>
<i>Pure Error</i>	<i>8.606E-05</i>		<i>1.434E-05</i>		
Cor Total	1.475E-03	29			
Root MSE	3.911E-03		R-Squared	0.7719	
Dep Mean	99.98		Adj R-Squared	0.6993	
C.V.	3.912E-03		Pred R-Squared	0.5624	
PRESS	6.457E-04		Adeq Precision	10.355	Desire > 4

There are no indications of outliers in the modified model when experiment number 23 has been excluded. The influence of the outlier affected the *Lack of Fit* since, for a valid model the *Lack of Fit* should be insignificant i.e. *Prob>0.1*. Since the pure error is very small and the precision is greater than 4, therefore

the “*Lack of Fit*” for decantation of 0.0602 is significant and P value of the model less than 0.1 has a significant effect on the response. After the single outlier was removed the model showed an acceptable fit ($p > 0.05$) and “*Lack of Fit*”. The “*Lack of Fit*” F value for decantation is 6.02% and for filtration is 49.16%. Insignificant “*Lack of Fit*” is desirable since the model should fit. The R^2 -value is 0.8964 for decantation and for filtration R^2 is 0.7719. These figures reasonably approach unity, which is acceptable. This implies that 89.64% and 77.19% of the variability in the data is explained by the model. The model “F-value” for decantation and filtration are significant i.e. < 0.0001 and therefore a null hypothesis stating that is rejected.

3.6 VALIDATION OF THE MODEL

Statically the model must be verified using graphical validation of the model. This mean that the residuals must be tested for normality and independence, to check the outliers. Once the model is validated, one of its functions is to predict a response for a given set of levels of the independent variables. It is highly desirable to also obtain a prediction interval in which the predicated response will lie with a given level of confidence.

3.6.1 Graphic model validation

Once the model fitting is complete, the next step is residual analysis to validate the assumptions used in the ANOVA. This analysis includes fitting a statistical model to identify outliers and examining diagnostic plots such as normal probability plots and residual plots. If these analyses are satisfactory, the model is considered adequate. Such graphic validations were generated on the Design Ease Version 5.09. These include:

- i) Normal probability plot of studentized residual to check for normality of residuals.
- ii) Residuals vs predicted responses - residuals to check for constant error.

(I) Normal probability of studentized residuals

The residual value is zero if it is assumed that none of the estimated effects have any influence on the experimental response, however, because of the pure experimental error, calculation of such effects will always give some or other value.² Since experimental error occurs randomly, it can be expected that such errors will be normally distributed and when points do not fall on the straight line, they represent significant points which have influence in the model. Figures 3.3 (a) and (b) show the plots of studentized residuals *versus* percentage normal probability for model chromium (III)-based coagulation of arsenate with decantation and filtration respectively. The outlier experiment number 23 has been omitted. The plots are both linear. After removal of the indicated outlier, the graphs are presented as follows.

Figure 3.3 (a) A plot of studentized residuals versus % normal probability for the model of chromium (III)-based coagulation of arsenate with decantation.

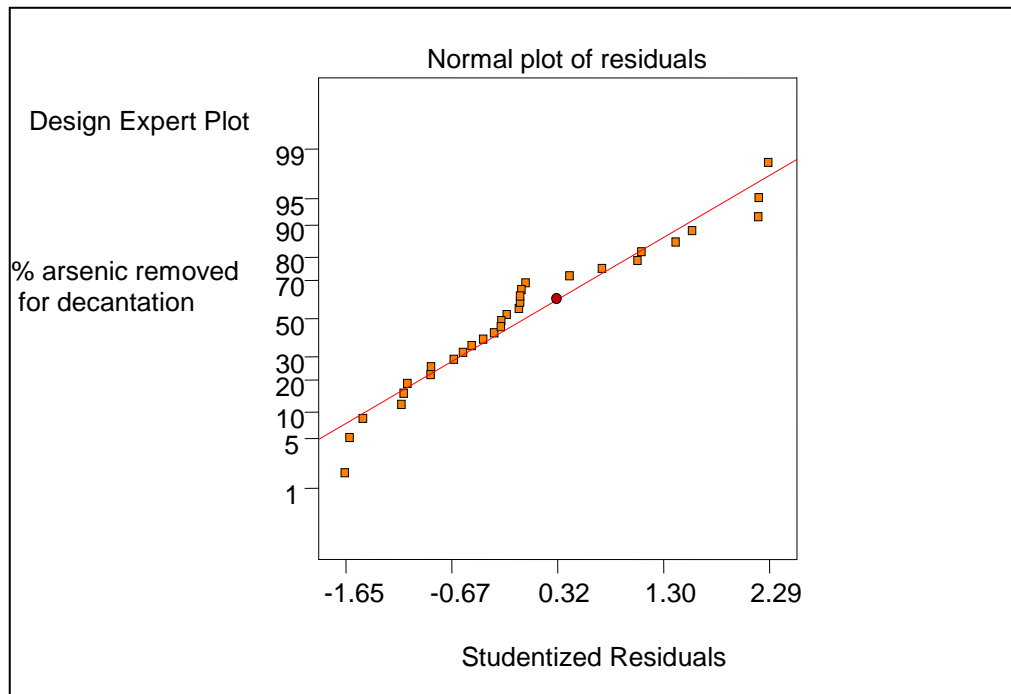
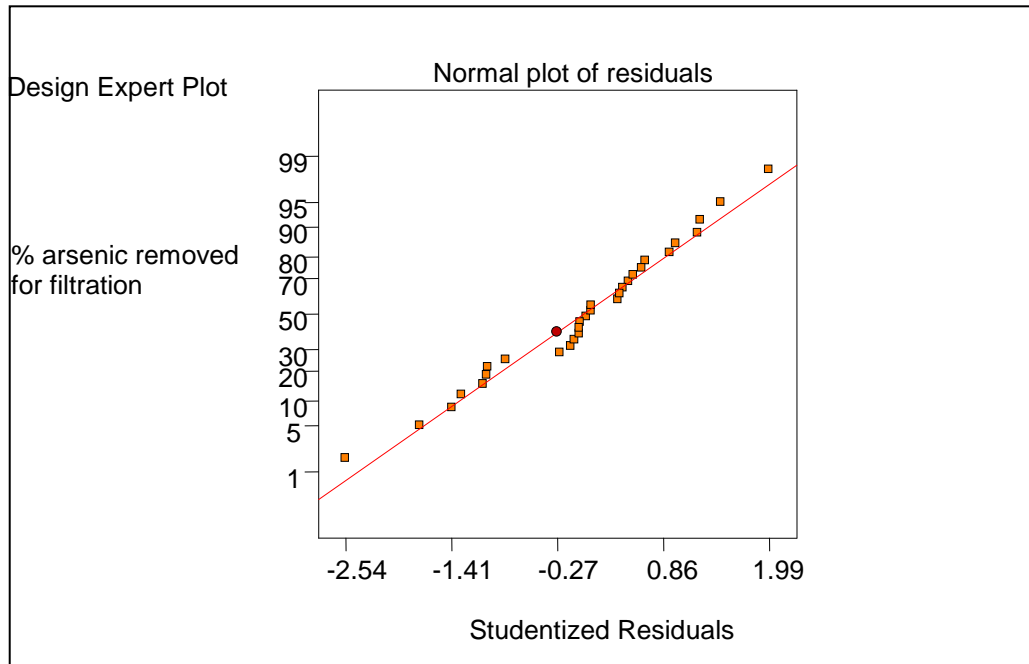


Figure 3.3 (b) A plot of studentized residuals versus % normal probability for the model of chromium (III)-based coagulation of arsenate with filtration.



(II) Studentized residuals versus predicted response

Figures 3.4 (a) and (b) show plots of residuals *versus* predicted responses for decantation and filtration respectively. A satisfactory model should give a plot in which the points show a random scatter about the zero residual level such as that the upper and the lower band of the pattern in the plot form two parallel horizontal lines at approximately equal distances from zero line.⁵ The experiment 23 was excluded and the plots were satisfactory. A standard ANOVA is permitted since the data was approximately normal, contained no outliers and the distribution of residuals lay randomly around the zero line for both decantation and filtration.⁶

Figure 3.4 (a) A plot of residuals *versus* predicted for the model of chromium (III)-based coagulation of arsenate for decantation.

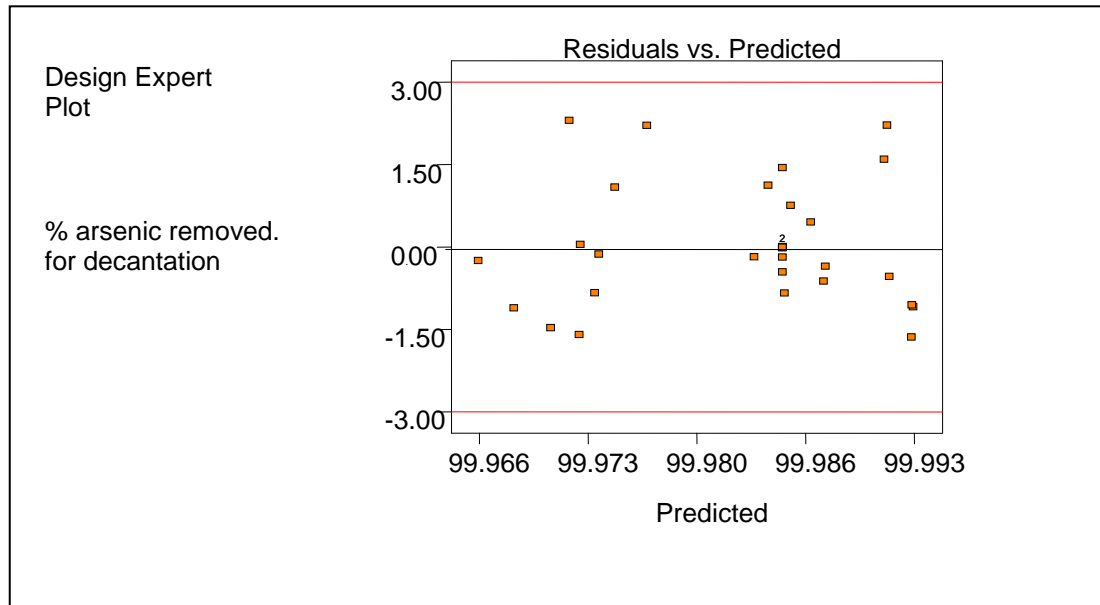
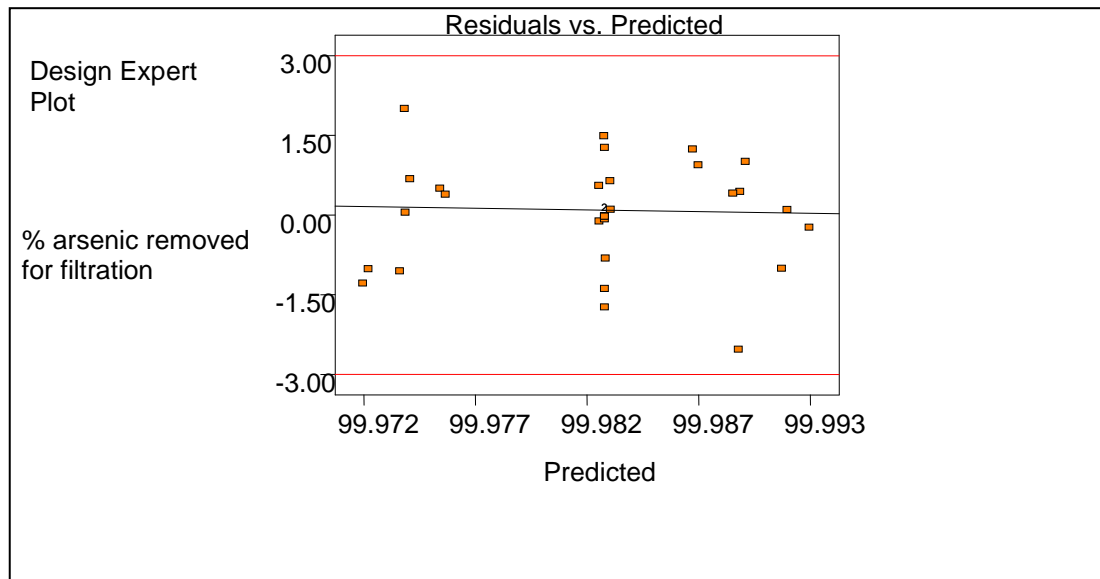


Figure 3.4 (b) A plot of residuals *versus* predicted for the model of chromium (III)-based coagulation of arsenate for filtration.



3.6.2 The final model presentation of chromium (III)-based coagulation of arsenate

The point for which the response \hat{Y} is optimized is the point at which the partial derivatives $\partial\hat{y}/\partial x_1, \partial\hat{y}/\partial x_2, \dots, \partial\hat{y}/\partial x_k$ are all equal to zero and this point is called the stationary point. The stationary point may be a point of maximum response or minimum response.⁷ The stationary point can be seen in Figures 3.5 (a) and (b) at their maximum response. This was performed using regression output as given by Excel version 2.3 2007 for model on experimental data. A regression model was primarily developed to predict the outcome of the process and to gain the insight in the relationship between variables.

Although it appears that the model $\hat{Y} = b_0 + b_1X + b_2X^2$ fits the data well and for

a polynomial model, a stationary point can easily be found by putting the derivative of the equation equal to zero, and then solving for X, where X refers to the initial concentration of arsenic at the stationary point.⁸

It appears that the relationship between initial concentration of arsenic and response of percentage of arsenic removed is not linear. Therefore, the main goal is to determine the optimum value of the variable such that the response is maximized. The optimization equation was used to predict the highest percentage of arsenic removed for this analysis.

3.6.3. Optimization of chromium (III)-based coagulation of arsenate

An appropriate model has been established, and responses were optimized simultaneously. Optimization was performed using a mathematical (numerical) model. Numerical optimization is called desirability or score function which requires defining an objective function that reflects the levels of each response in terms of minimum (zero) to maximum (one) desirability.⁹

Below is the final equation indicating the initial arsenic concentration at the maximum arsenic removal for decantation. Using data from Table 3.6 (a) which represents the final polynomial equation.

$$\hat{Y} = b_0 + b_1X + b_2X^2$$

$$\frac{\partial \hat{Y}}{\partial X} = b_1 - 2b_2X = 0 \dots \dots \dots \text{Eqn} \dots 3.5$$

$$X = \frac{b_1}{-2b_2}$$

$$X = \frac{0.0001}{-2 \times 8 \times 10^{-8}}$$

$$X = 625 \text{ ppm}$$

3.7 Experimental Validation

3.7.1 Confirmation experiments

In order to validate the adequacy of the model, four confirmation runs were performed. The conditions are depicted in Table 3.9. Utilizing the point prediction capability of the *Design Expert* software enables the prediction the final [As] and the percentage arsenic removed. The 95% prediction intervals are included. The predicted values and the associated prediction interval are based on the models. The experimental responses shown in Table 3.9 at three different setting values, were within the statistically predicted response at the 95% confidence limit hence confirming the validity of the model.

Table 3.9 Results of the confirmatory experiments used to validate the 2⁴⁻¹ model describing chromium (III)-based coagulation of arsenate.

Factors				Prediction 95% CL		Predicted Responses		Actual Responses	
A	B	C	D	CL Low	CL High	% As	% As	%As	%As
pH	[Flocculant] ppm	Cr:As Mole	[As] ppm	%As Removal (decant)	% As Removal (filtrated)	% As Removal Decant	% As Removal Filtrate	%As Removal (decant)	%As Removal (filtrated)
5.6	3.00	3.50	600.00	99.9700- 100.0100	99.9600- 100.0300	99.9700	100.0000	99.9788	99.9789
6.0	2.55	3.20	314.00	99.9500- 99.9800	99.9300- 99.9800	99.9700	99.9600	99.9789	99.9699
7.0	2.00	4.00	550.00	99.9800- 100.0200	99.9700- 100.03	100.0000	100.0000	99.9899	99.9899

3.7 CONCLUSION

A model predicting the arsenic (V) removed by Cr³⁺ coagulation was derived. The investigation included the following variables: pH, concentration of flocculent, initial arsenic concentration and chromium to arsenate mole ratio. Before the model was accepted as statistically valid, a residuals analysis was performed and *Lack of Fit* test was carried out. The result shows that filtration produced the higher arsenic removals. The only significant effect was the initial concentration of arsenate. The experimental models developed were accurate, for both decantation and filtration as all response values for the confirmation runs were within the 95% prediction interval.

3.9 REFERENCES

1. Factorial experimental design for recovering heavy metals from sludge with ion-exchange resin Hsien Lee, Yu-Chung Kuan and Jia-Ming Chern, *Journal of Hazardous Materials*, 2006, Volume 138, Issue 3, pp 549.
2. Application of statistical experimental design for optimization of alkaline protease production from *Bacillus* sp. RGR-14, Bhavna Chauhan and Rani, *Process Biochemistry*, Volume 39, 2004, pp 2115–212.
3. Outlier Detection for High Dimensional Data by Charu C. Aggarwal T. J. *Sigmod*, 2001, Volume 30, Issue 2, pp 37.
4. Statistical media optimization for cell growth and azadirachtin production in *Azadirachta indica* (A. Juss) suspension cultures, Gunjan Prakash, Ashok K. Srivastava, *Process Biochemistry*, Volume 40, 2005, pp 3795–3800.
5. Residuals in multiple regression analysis, Y. J. Jeng, A. Martin *Journal of pharmaceutical sciences*, 1985.
6. Plane Strain Fracture Behaviour of Fabric Reinforced Hybrid Composites under varied Notch Configurations, K. Mohamed Kaleemulla, B. Siddeswarappa, *Journal of Minerals & Materials Characterization & Engineering*, 2009, Volume 8, No.6, pp 495-508.
7. Experiment design and analysis by Box and Behnken, D. W., Some New Three Level Designs for the Study of Quantitative Variables, *Technometrics*, 1987, Volume 2, No. 4, pp 455-475.
8. A comparison of propensity score and linear regression analysis of complex survey data, Zanutto, E. L., *Journal of Data Science*, 2006, Volume 4, Issue 1, pp 67.

9. Comparison of Propensity Score and Linear Regression Analysis of Complex Survey Data, Elaine L. Zanutto, Journal of Data Science, Volume 4, 2006, 67-91.

CHAPTER 4

THE MODELLING OF ARSENIC (V) REMOVAL FROM AQUEOUS MEDIA USING CALCIUM CHLORIDE

INTRODUCTION

This chapter describes the modeling process for arsenic (V) removal using calcium chloride. Variables that were studied included initial arsenic (V) concentration, calcium chloride: arsenic (V) mole ratio, and pH. The motivation of the use of calcium (II) chloride is to study how effective Ca^{2+} is in the coagulation. Fuhrman reported that the presence of Ca^{2+} increased arsenate removal possibly due to a favourable electrostatic effect as Ca^{2+} increases the number of positively charge surface sites for the negative arsenate to bond with.¹

4.2 EXPERIMENTAL

4.2.1 Coagulation procedure

The coagulation was carried out as in section 2.7.1 and 50% CaCl_2 was used as coagulant. A white precipitate was formed and once the pH was stable for 30 seconds, 1 ml of anionic organic flocculent (500 ppm) was added, stirred for two minutes and allowed to settle for an hour. Both decantates and filtrates were analyzed using atomic absorption spectrometry.

4.2.2 Mechanism of arsenate removal by calcium coagulation

Calcium removes arsenic more effectively as the pH is raised (pH 10 – pH 12). At high pH values arsenate may be competing with the hydroxide ion for positively charged surface sites such that lower coagulation capacities found at higher pH values within this range are due to the decreasing availability of positively charged surface sites.² Calcium chloride forms complexes with arsenic in the form of $\text{CaH}_2\text{AsO}_4^+$, CaHAsO_4 , CaAsO_4^- , $\text{Ca}_3(\text{AsO}_4)_2$ which have higher affinity to the sorbent surface.² According to Wang the amount of adsorbed arsenic decreased when pH increased from 9 to 10.5. $\text{Ca}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ precipitation

started to occur at a pH of approximately 9.2 and became the predominant arsenic form at pH>10.³

4.3 EXPERIMENTAL DOMAIN

The natural values of experimental domain are presented in Table 4.1.

Table 4.1 The experimental domain used in the study of calcium (II)-based coagulation.

Factor	Name	Units	Low value	Middle Value	High Value
A	pH	-	10.0	11.5	12.50
B	Ca: As	-	0.5	1.75	3.00
C	Initial[As ^v]	ppm	250	550	850

4.4. THE EXPERIMENTAL DESIGN

The half factorial design involves three variables at two levels, type 3², and the coded values are shown in Table 4.2. The experimental results are shown in Table 4.3.

Table 4.2 The coded values of the experimental design used to optimise calcium (II)-based coagulation of arsenate.

Standard Order	Run Order	A pH	B [As] ppm	C Ca: As Mole ratio	Type of Point
1	5	-1	-1	1	F
2	6	1	-1	-1	F
3	7	-1	1	-1	F
4	4	1	1	1	F
5	2	0	0	0	Cp
6	3	0	0	0	Cp
7	1	0	0	0	Cp

F= factorial point

Cp= centre point

Table 4.3 Results of the half factorial design used to model the removal of aqueous arsenic (v) using calcium (II)-based as a coagulant.

Std Order	Run Order	pH	Ca: As	[As]	Conc As Left Decantation	% As Removed Decant	Conc As Left Filtration	% As Removed Filtrate
		-		ppm	ppm	%	ppm	%
1	5	10.00	3.00	250.00	12.9310	94.8278	12.0690	95.1724
2	6	12.50	0.50	250.00	15.5172	93.7931	12.9310	94.8276
3	7	10.00	0.50	850.00	16.3793	98.0730	12.0690	98.5801
4	4	12.50	3.00	850.00	12.9310	98.4787	13.7931	98.3773
5	2	11.25	1.75	550.00	12.9310	97.6489	12.9310	97.6489
6	3	11.25	1.75	550.00	14.6552	97.3354	12.0690	97.8056
7	1	11.25	1.75	550.00	12.0690	97.8056	12.0690	97.8056

4.5 RESULTS AND DISCUSSION

4.5.1 ANOVA analysis

Tables 4.4 (a) and (b) show the ANOVA the percentage arsenic removed for both decantates and filtrates. The R^2 value should be approximate unity. The predicted R^2 value was in agreement with the adjusted coefficient of determination R^2 . The significance of each factor was determined by the F-test method.⁵ As in Chapter 3, the fits of the regression equations with the responses were tested at the 95% confidence level.

Table 4.4(a) ANOVA for the factorial model describing the calcium (II)-based coagulation of arsenate for the decantation model.

Source	Sum of Squares	DF	Mean Squares	F Value	Prob > F
Model	18.74	3	6.35	29.59	0.0099 significant
Residual	0.63	3	0.21		
<i>Lack of Fit</i>	0.52	1	0.52	9.05	0.0950
<i>Pure Error</i>	0.11	2	0.057		
Cor Total	0.46	6			
Root MSE	0.46		R-Squared	0.9673	
Dep Mean	96.85		Adj R-Squared	0.9346	
C.V.	0.47		Pred R-Squared	0.5584	
PRESS	8.55		Adeq Precision	12.324	Desire > 4

Table 4.4(b) ANOVA for the factorial model describing the calcium (II)-based coagulation of arsenate for the filtration model.

Source	Sum of Squares	DF	Mean Squares	F Value	Prob > F
Model	13.94	3	4.65	651.02	<0.0001 significant
Residual	0.021	3	7.137E-03		
<i>Lack of Fit</i>	5.041E-03	1	5.041E-03	0.62	0.5148
<i>Pure Error</i>	0.016	2	8.185E-03		
Cor Total	13.96	6			
Root MSE	0.084		R-Squared	0.9985	
Dep Mean	97.17		Adj R-Squared	0.9969	
C.V.	0.087		Pred R-Squared	0.9916	
PRESS	0.12		Adeq Precision	58.760	Desire > 4

The model “F-values” of 29.59 for decantation and 651.02 for filtration implies the models are significant which means that they describe the effect of changing the variables producing the change in the response. For decantation there is only a 0.01% chance that a model “F-value” this large could occur due to noise. The value of “*Prob>F*” for decantation is 0.0099 and for filtration is 0.0001 which indicate the significances of the models. The “*Lack of Fit*” “F-value” of 0.0950 for decantation is significant and 0.5148 for filtration implies the “*Lack of Fit*” is not significant relative to the pure error. A non-significant “*Lack of Fit*” is desirable since the model should fit.

4.5.2 Defining the polynomial equation describing the calcium (II)-based removal of arsenate

The following equation is calculated using *Design Expert* software as in Chapter 3. The initial polynomial contains some main independent variables that are not significant and one that is significant in each case. The general equation describing the calcium (II)-based removal of arsenate.

$$\hat{Y} = b_0 + b_1A + b_2B + b_3C \dots \dots \dots \text{Eqn} \dots 4.1$$

Table 4.5 (a) The initial polynomial equation describing the calcium (II)-based removal of arsenate for decantation.

Factor	Coefficient Estimate		Standard Error	t for H0	
		DF		Coeff=0	Prob > t
Intercept	96.85	1	0.38		
pH	-0.16	1	0.50	-0.31	0.7748
As]	-0.16	1	0.50	3.95	0.0290
Ca:As	0.36	1	0.50	0.72	0.5253

Table 4.5 (b) The initial polynomial equation describing the calcium (II)-based removal of arsenate for filtration.

Factor	Coefficient Estimate		Standard Error	t for H0	
		DF		Coeff=0	Prob > t
Intercept	97.17	1	0.29		
pH	-0.14	1	0.39	-0.36	0.7457
[As]	1.74	1	0.39	4.52	0.0203
Ca:As	0.035	1	0.39	0.092	0.9324

Tables 4.6 (a) and (b) show the final equations of calcium (II)-based coagulation after insignificant factors have been eliminated form.

4.5.3 Estimated coefficients for final models that described the calcium (II)-based removal of arsenate.

The final polynomial equations which contain the main independent variable that is significant and the others that are not significant but which need to be included to make the model hierarchical, are included in the final response surface models. The hierachy refers to the ancestral relation flowing from the parent down succeeded by the next generation. In this statistical model it contains subsets of all possible main effects and generation of higher order interactions which are children.⁶

Table 4.6 (a) The final polynomial equation describing the response surface of the model of calcium (II)-based coagulation of arsenate for decantation.

Factor	Coefficient Estimate		Standard Error	t for H0	
		DF		Coeff=0	Prob > t
Intercept	97.60	1	0.27		
pH	-0.16	1	0.23	-0.68	0.5429
[As]	1.98	1	0.23	8.63	0.0033
pH ²	-1.30	1	0.35	-3.71	0.0339

Table 4.6 (b) The final polynomial equation describing the response surface of the model of calcium (II)-based coagulation of arsenate for filtration.

Factor	Coefficient Estimate		Standard Error	t for H0	
		DF		Coeff=0	Prob > t
Intercept	97.75	1	0.049		
pH	-0.14	1	0.042	-3.24	0.0478
[As]	1.74	1	0.042	41.18	<0.0001
pH ²	-1.01	1	0.065	-15.72	0.0006

As shown in Tables 4.6 (a) and (b), the concentration of arsenic does have more influence on arsenic removal than pH. The pH term present in the decantation model was not significant, but cannot be ignored because it has a small influence in arsenic removal whereas in the filtration model pH and initial concentration are significant. As presented in Table 4.6 arsenic concentration and pH² show a high significance (p<0.05) and pH² causes the curvature in the model, but pH should still remain in model in order to make a hierarchical model.

This shows that the relationship between (A, B, A²) and responses are not linear, therefore the following general model is proposed:

$$\hat{Y} = b_0 + b_1A + b_2B + b_3A^2 \dots \dots \dots Eqn \dots 4.2$$

4.6 VALIDATION OF THE MODEL

4.6.1 Graphic model validation

Different types of plots of the residuals from a fitted model were performed using normal probability and residuals vs predicted response plots and were described in chapter 3. Half-normal plots show the absolute value of the effect on the x-axis.

(I) Full normal probability plot of residuals

Figures 4.1 (a) and (b) are full normal probability plots of residuals shown for decantation and filtration respectively. The residuals are normally distributed along the straight line for decantation indicating that the hypothesis of normality holds. The normality plot for the filtration experiments is not normally distributed along a straight line. It appears to have too small a residual (to the left of the straight line in lower left hand side of the plot), and too large residual (to the right of the line in upper right hand side of the plot). Further study should be taken into consideration by considering a log-transformation and this will tend to symmetrize the distribution.⁷

Figure 4.1 (a) A plot of studentized residuals versus accumulative frequency for the model of calcium (II)-based coagulation of arsenate with decantation.

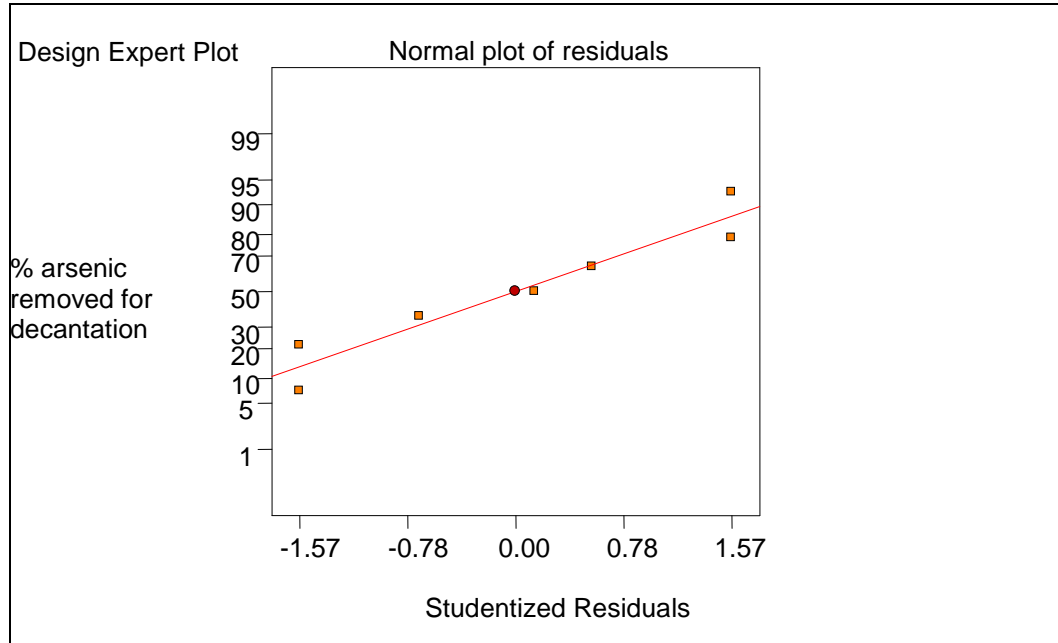
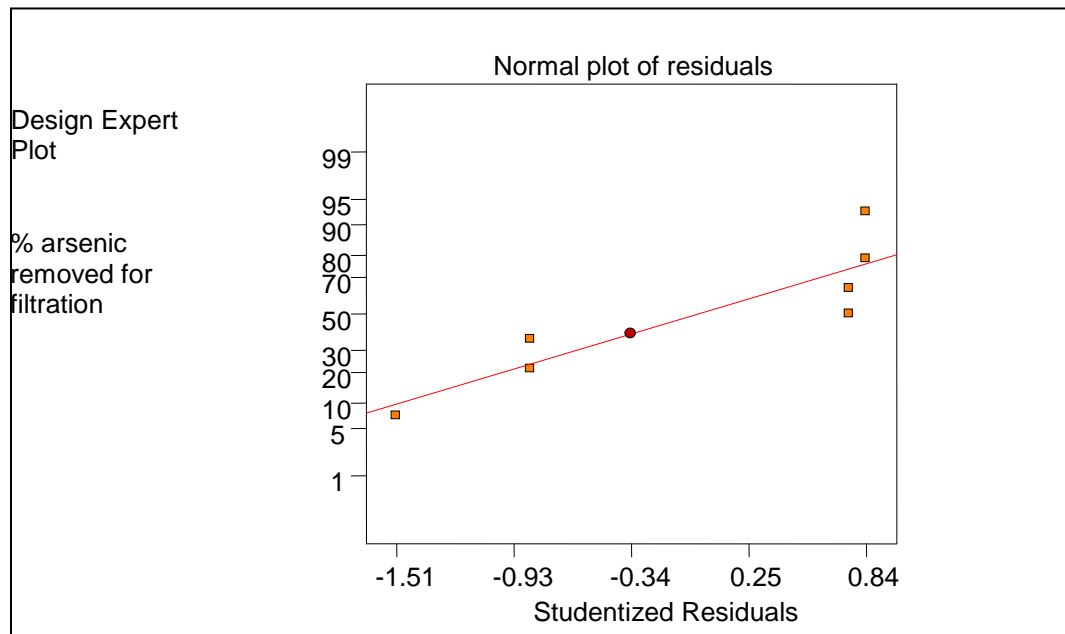


Figure 4.1 (b) A plot of studentized residual versus accumulative frequency for the model of calcium (II)-based coagulation of arsenate with filtration.



(II) Studentized residuals versus predicted response

Figures 4.2 (a) and (b) show the plot of studentized residuals *versus* predicted response decantation and filtration models respectively. These plots of studentized residuals *versus* the predicted values should give a plot in which the points show random scatter about the zero residual level such that the upper and the lower bands of the pattern in the plot form parallel and horizontal lines approximately equal distance from zero bands. Any points above 3.0 and -3.0 indicate outliers. By inspection the plots in Figure 4.2 (a) and (b) also show roughly equal scatter above and below no outliers.

Figure 4.2 (a) A plot of residuals *versus* predicted response for the model of calcium (II)-based coagulation of arsenate for decantation.

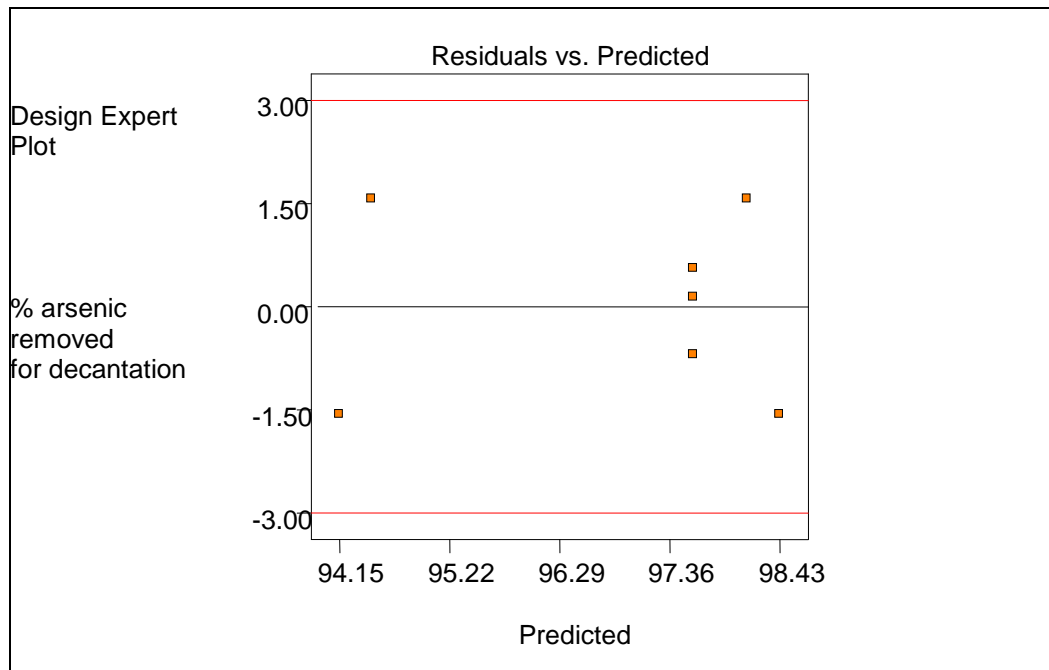
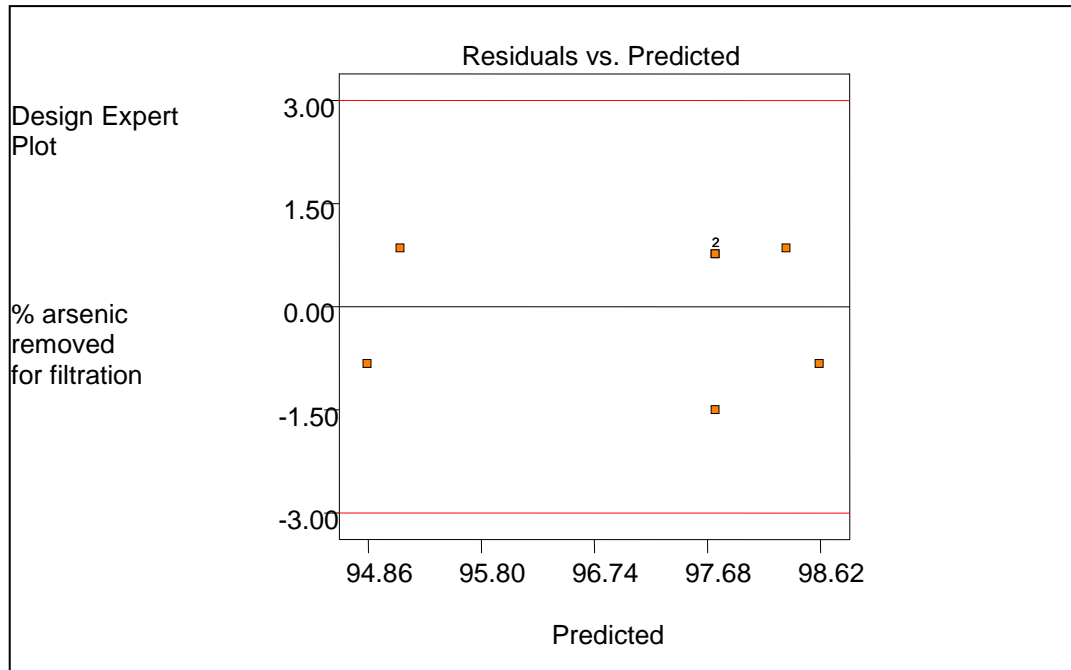


Figure 4.2 (b) A plot of residuals *versus* predicted response for the model of calcium (II)-based coagulation of arsenate for filtration.



(III) Half normal probability plot of residual

Figures 4.3 (a) and (b) show half normal plots for the models of calcium (II)-based coagulation of arsenate with decantation and filtration respectively. The factor that is located to the right of the regression line is significant, i.e. it has an effect on the response which is the final concentration of arsenic after coagulation. Those factors which fall approximately on the half normal lines are insignificant i.e., they have no effect on the response. Only factor B (initial concentration of arsenate) has an effect on the response.⁸

Figure 4.3 (a) A half normal plot for the model of calcium (II)-based coagulation of arsenate with decantation.

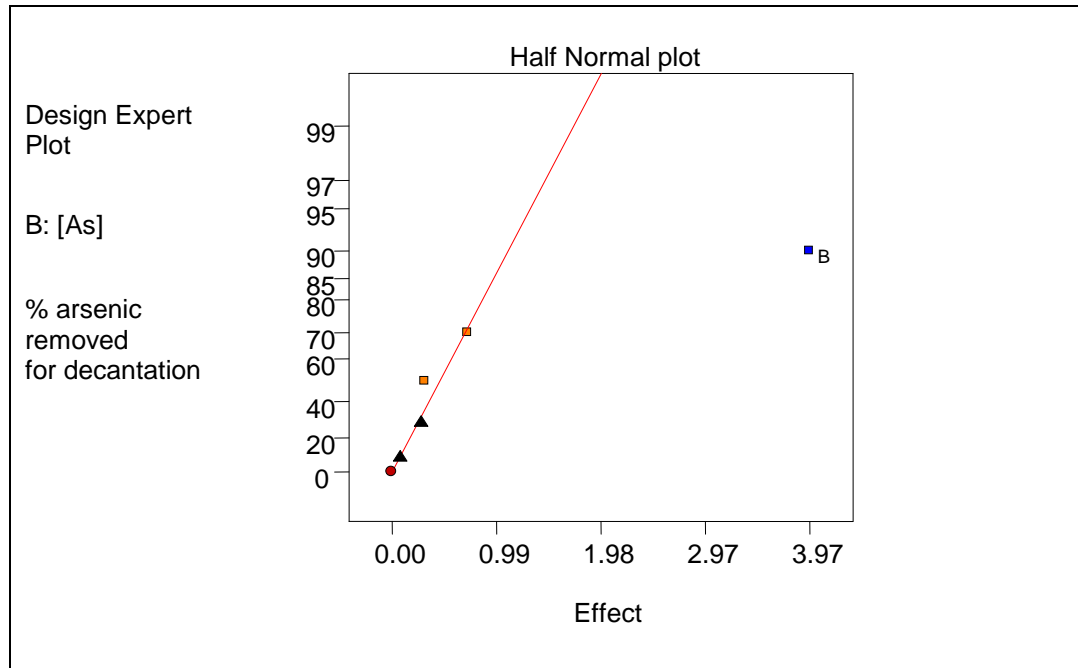
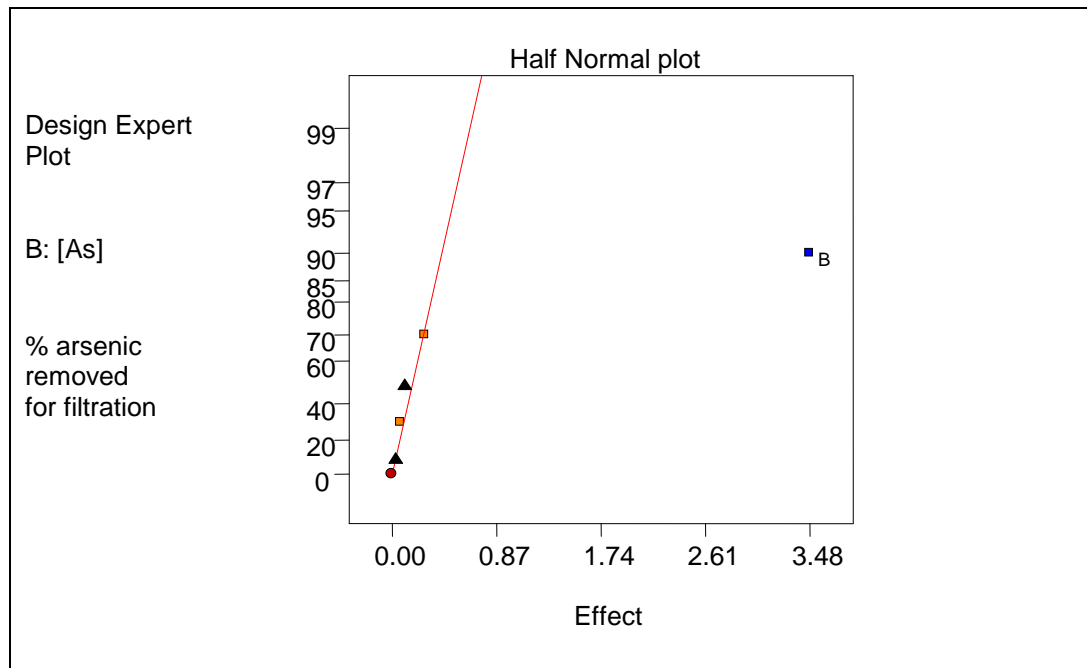


Figure 4.3 (b) A half normal plot for the model of calcium (II)-based coagulation of arsenate with filtration.



4.6.2 The final model presentation of calcium (II)-based coagulation of arsenate

As it has been described in chapter 3 page 67 the relationship between initial concentration of arsenic and response of percentage of arsenic removed is not linear. Therefore the second order model is utilized in response surface methodology by developing a mathematical model with the best fit finding the maximum value of response and finding an approximation of the true functional relationship between initial concentration of arsenic and percentage of arsenic removed.

4.6.3 Optimization of calcium (II)-based coagulation of arsenate

The maximum of arsenate removal was determined by the optimization process as described in chapter 3. The results obtained from the second order polynomial models were developed using Equation 3.5 in chapter 3.⁵

4.7 Experimental Validation

In order to test the model accuracy, confirmation experiments were carried out within the experimental domain. Table 4.7 shows the responses obtained from the confirmation experiments and the corresponding 95% confidence limits. There is a good agreement between the predicted values and experimental values. The actual responses fall within confidence limits.

Table 4.7 Results of the confirmatory experiments used to validate the model describing calcium (II)-based coagulation of arsenate.

Factors			Prediction 95% CL		Predicted Responses		Actual Responses	
			Cl Low	CL High	% As Removal (Decant)	% As Removal (Filtrate)	%As Removal (decant)	% As Removal (filtrated)
A pH	C Ca:As Mole	D [As] Ppm	%As Removal (decant)	% As Removal (filtrated)	% As Removal (Decant)	% As Removal (Filtrate)	%As Removal (decant)	% As Removal (filtrated)
10.50	2.00	600.00	96.0200- 97.2300	96.8100- 97.2500	96.6200	97.0300	96.9652	96.8732
11.00	3.00	700.00	96.6100- 97.9500	97.3700- 97.8500	96.6200	97.6100	97.4905	97.5302
12.00	2.50	750.00	96.9000- 98.3300	97.6400- 98.1600	97.6100	97.9000	97.4752	97.7852

4.8 CONCLUSION

The removal of arsenate by calcium (II) chloride was successfully investigated and modeled using a three factor half factorial design. On the basis of a quadratic polynomial equation of response surface methodology the effect of independent variables pH, initial concentration of arsenic and Ca:As were analyzed. The model was tested statistically and experimentally validated. Arsenic removals ranged from 93.8% to 97.8%. F-tests were used to evaluate the response surface model. Probability>F values for the models were considered acceptable because Prob > F was less than 0.05. The initial concentration of arsenic was the only significant effect which has influence on arsenic removal.

4.9 REFERENCES

1. Adsorption of arsenate from water using neutralized red mud, Hülya Genç, Jens Christian Tjell, David McConchie and Olaf, Journal of colloid and interface science, 2003, Volume 264, Issue 2, pp 327.
2. Evaluation of phyllosilicate clay catalyst as friedel-craft catalyst, Terence Nico Terblanche, Faculty of applied science at the Port Elizabeth technikon, pp 43,
3. Calcium effect on arsenic (v) adsorption onto coal fly ash, Tian Wang, Tingzhi Su, Jianmin Wang, Ken Ladwig, World of Coal Ash, 2007, pp 1-17.
4. Arsenic Mobility in iron hydroxide sludge stabilized with cement, C Jing, X Meng, GP Korfiatis, American Chemical Society, 2002, Volume 42, pp 107-111.
5. Concrete mixture optimization using statistical methods, Marcia J. Simon, International symposium on high performance concrete, 1997, pp 230-244.
6. Analysis of variance, Andrew Gelman, Annals of statistics, Volume 33, Number 1, 2005, pp 1-53.
7. Evaluation of goodness-of-fit indices for structural equation models. Mulaik Stanley A. James, Larry R. Van Alstine, Judith Bennett Nathan, Lind Sherri and Stilwell C. Dean, American psychological association, Volume 103, Issue 3, 1989, pp 430-445.
8. Colour and appearance of chilled mousse: a factorial study of ingredient and processing effects, Nazlin Imram, Nutrition and food science, Volume 99, Issue 1, 1999, pp 19-23.

CHAPTER 5

THE MODELLING OF ARSENIC (V) REMOVAL FROM AQUEOUS MEDIA USING BINARY MIXTURES OF CHROMIUM (III) CHLORIDE AND CALCIUM (II) CHLORIDE AS COAGULANTS.

5.1 INTRODUCTION

A literature survey, focusing on new developments with coagulation, did not reveal any investigations of the use of a binary coagulant consisting of calcium (II) chloride and chromium (III) chloride. This chapter discusses the modelling of arsenic removal from aqueous media using calcium chloride and chromium chloride as a binary coagulant. Calcium chloride is a very desirable electrolyte in that it is available, virtually free, in its high purity form as a waste product from the chemical industry.¹ The objective of the modelling was to evaluate the efficacy of mixtures of Cr^{3+} and Ca^{2+} to enable the removal of arsenate from aqueous media.

5.2 EXPERIMENTAL

5.2.1 Coagulation procedure

The coagulation was carried out as in section 2.7.1 and 50% CrCl_3 and 50% of CaCl_2 were used as binary coagulants. White to greenish precipitates were formed as the pH was adjusted. 1 ml of anionic organic flocculent concentration (500ppm) was added, stirred for two minutes and allowed to settle for an hour. Both decantates and filtrates were analyzed using inductively coupled plasma mass spectrometry.

5.2.2 Binary component studies

A single block, 2^4 factorial design was used for investigation of the removal of arsenate using the binary mixture. Table 5.1 shows the experimental domain used in this study.

Table 5.1 Experimental domain used in the study of chromium (III) and calcium (II)-based coagulation of arsenate.

Factor	Name	Units	Low value	Middle value	High Value
A	Cr :As	-	0.5	1.25	2.00
B	pH	-	5.5	6.5	7.5
C	Initial[As ^v]	ppm	250	450	650
D	Ca: As	-	0.5	1.25	2

5.2.3 Coded values of the binary coagulation

Table 5.2 presents the coded values for the binary coagulation of the factorial design used to optimize chromium (III) and calcium (II) coagulation of arsenate.

Table 5.2 The coded values of the experimental design used to optimise chromium (III) and calcium (II)-based coagulation of arsenate.

Standard Order	Run Order	pH	B Ca : As mole	C Cr : As mole	D [As] Ppm	Type of point
1	3	-1	-1	-1	-1	F
2	16	1	-1	-1	-1	F
3	1	-1	1	-1	-1	F
4	14	1	1	-1	-1	F
5	17	-1	-1	1	-1	F
6	2	1	-1	1	-1	F
7	15	-1	1	1	-1	F
8	8	1	1	1	-1	F
9	11	-1	-1	-1	1	F
10	13	1	-1	-1	1	F
11	18	-1	1	-1	1	F
12	19	1	1	-1	1	F
13	6	-1	-1	1	1	F
14	4	1	-1	1	1	F
15	7	-1	1	+1	1	F
16	10	1	1	1	1	F

17	5	0	0	0	0	Cp
18	12	0	0	0	0	Cp
19	9	0	0	0	0	Cp

F= factorial point

Cp= centre point

5.2.4 The results of factorial design

Table 5.3 presents results of the factorial design used to model the removal of aqueous arsenate using chromium (III) and calcium (II)-based as a combined coagulant.

Table 5.3 Results of the factorial design used to model the removal of aqueous arsenic (V) using binary mixtures of chromium (III) and calcium (II)-based as coagulants.

Std Order	Run Order	pH	Vol Floc	Ca : As	Cr : As	[As]	Conc As Left Decantate	% As Removed Decantate	Conc As Left Filtrate	% As Removed Filtrate
		-	ppm	-	-	ppm	ppm	%	ppm	%
1	3	6	1	0.5	0.5	250	0.0466	99.9814	0.0527	99.9789
2	6	12	1	0.5	0.5	250	0.0421	99.9831	0.0486	99.9805
3	1	6	1	2	2	250	0.0452	99.9805	0.0514	99.9794
4	14	12	1	2	2	250	0.0502	99.9819	0.0449	99.9820
5	17	6	1	0.5	0.5	250	0.0600	99.9799	0.0642	99.9743
6	13	12	1	0.5	0.5	250	0.0524	99.9798	0.0547	99.9781
7	15	6	1	2	2	250	0.0524	99.9790	0.0579	99.9768
8	8	12	1	2	2	250	0.0442	99.9823	0.0500	99.9800
9	19	6	1	0.5	0.5	850	0.0520	99.9939	0.0546	99.9936
10	16	12	1	0.5	0.5	850	0.0588	99.9931	0.0542	99.9936
11	9	6	1	2	2	850	0.0635	99.9925	0.0650	99.9923
12	18	12	1	2	2	850	0.0590	99.9931	0.0602	99.9929
13	10	6	1	0.5	0.5	850	0.0513	99.9940	0.0464	99.9942
14	4	12	1	0.5	0.5	850	0.0420	99.9946	0.0491	99.9941
15	7	6	1	2	2	850	0.0668	99.9921	0.0559	99.9934
16	2	12	1	2	2	850	0.0633	99.9926	0.0482	99.9943
17	5	9	1	1.25	1.25	550	0.0684	99.9876	0.0641	99.9988
18	11	9	1	1.25	1.25	550	0.0633	99.9885	0.0461	99.9917
19	12	9	1	1.25	1.25	550	0.0554	99.9899	0.0443	99.9919

5.3 RESULTS AND DISCUSSION

5.3.1 ANOVA analysis

Tables 5.4 (a) and (b) show the ANOVA for the decantated and filtered arsenic removals expressed as percentages. The ANOVA was obtained using *Design Expert*.

Table 5.4 (a) ANOVA for the factorial model describing the combined chromium (III) and calcium (II)-based coagulation of arsenate for decantation model.

Source	Sum of Squares	DF	Mean Squares	F Value	Prob > F
Model	6.103E-04	2	3.051E-04	225.40	<0.0001 significant
Residual	2.166E-05	16	1.354E-06		
<i>Lack of Fit</i>	<i>1.897E-05</i>	<i>14</i>	<i>1.355E-06</i>	<i>1.01</i>	<i>0.6043</i>
<i>Pure Error</i>	<i>2.687E-06</i>	<i>2</i>	<i>1.343E-06</i>		
Cor Total	6.319E-04	18			
Root MSE	1.164E-03		R-Squared	0.9657	
Dep Mean	99.99		Adj R-Squared	0.9614	
C.V.	1.164E-03		Pred R-Squared	0.9512	
PRESS	3.083E-05		Adeq Precision	26.577	Desire > 4

Table 5.4 (b) ANOVA for the factorial model describing the combined chromium (III) and calcium (II)-based coagulation of arsenate for filtration model.

Source	Sum of Squares	DF	Mean Squares	F Value	Prob > F
Model	1.037E-03	2	5.186E-04	109.69	<0.0001 significant
Residual	7.565E-05	16	4.728E-06		
<i>Lack of Fit</i>	<i>4.296E-05</i>	<i>14</i>	<i>4.728E-06</i>	<i>0.19</i>	<i>0.9809</i>
<i>Pure Error</i>	<i>3.269E-05</i>	<i>2</i>	<i>1.634E-05</i>		
Cor Total	1.113E-03	18			
Root MSE	2.174E-03		R-Squared	0.9320	
Dep Mean	99.99		Adj R-Squared	0.9235	
C.V.	2.175E-03		Pred R-Squared	0.8835	
PRESS	1.297E-04		Adeq Precision	17.805	Desire > 4

The regression equation obtained from ANOVA indicated that the R^2 values (multiple correlation coefficient) are 0.9657 for decantation and 0.9320 for filtration (a value 1.0 indicates suitability of the model). The models explained 96.75% of the variation of response for decantation and 93.20% of the variation of response for filtration.

The model has an adequate precision value of 26.577 for decantation and 17.805 for filtration. The signal to noise ratio is an index of the adequate precision value and these values exceed 4, which is an essential prerequisite for a model to be a good fit.² ANOVA analysis confirms a satisfactory adjustment of the reduced quadratic model to the experimental data which was indicated by a high “F-value” and non-significant lack of fit showing that the model is a good fit.²

5.4 THE MODEL

5.4.1 Defining the polynomial equation describing the chromium (III) and calcium (II)-based removal of arsenate

Tables 5.5 (a) and (b) show initial polynomial equations describing the chromium (III) and calcium (II)-based removal of arsenate. The general equation describing the chromium (III) and calcium (II)-based removal of arsenate is:

$$\hat{Y} = b_0 + b_1A + b_2B + b_3C + b_4D + b_5AB + b_6AC + b_7AD + b_8BC + b_9BD + b_{10}CD \dots \text{Eqn} \dots 5.1$$

Table 5.5 (a) The initial polynomial equation that describes the chromium (III) and calcium (II)-based removal of arsenate for decantation.

Factor	Coefficient Estimate		Standard Error	t for H0	
		DF		Coeff=0	Prob > t
Intercept	99.99	1	6.176E-04		
pH	4.688E-04	1	2.674E-04	1.75	0.1031
Ca : As	-3.437E-04	1	2.674E-04	-1.29	0.2211
Cr : As	-2.937E-04	1	2.674E-04	-1.10	0.2919
[As]	6.144E-03	1	2.674E-04	22.98	<0.0001
[As] ²	-1.585E-03	1	7.320E-04	-2.17	0.0458

Table 5.5 (b) The initial polynomial equation that describes the chromium (III) and calcium (II)-based removal of arsenate for filtration.

Factor	Coefficient Estimate		Standard Error	t for H0	
		DF		Coeff=0	Prob > t
Intercept	99.99	1	1.249E-03		
pH	7.875E-04	1	5.408E-04	1.46	0.1690
Ca : As	2.375E-04	1	5.408E-04	0.44	0.6677
Cr : As	-5.000E-04	1	5.408E-04	-0.92	0.3720
[As]	7.400E-03	1	5.408E-04	13.68	<0.0001
[As] ²	-7.983E-03	1	1.368E-03	-5.84	<0.0001

ANOVA was performed to observe whether the process parameters were statistically significant or not. The pH, Ca : As and Cr : As mole ratios were not statistically significant, which means that they do not have a significant effect on the arsenic removal within the experimental domain. These factors were therefore removed from the initial model.

5.4.2 Estimated coefficients for the final models that described the chromium (III) and calcium (II)-based removal of arsenate.

Tables 5.6 (a) and (b) show the estimated coefficients for this final models for decantation and filtration.

Table 5.6 (a) The final polynomial equation that describes the chromium (III) and calcium (II)-based removal of arsenate for decantation.

Factor	Coefficient Estimate		Standard Error	t for H0	
		DF		Coeff=0	Prob > t
Intercept	99.99	1	6.718E-04		
[As]	6.144E-03	1	2.909E-04	21.12	<0.0001
[As] ²	-1.585E-03	1	7.320E-04	-2.17	0.0458

Table 5.6 (a) The final polynomial equation that describes the chromium (III) and calcium (II)-based removal of arsenate for filtration.

Factor	Coefficient Estimate		Standard Error	t for H0	
		DF		Coeff=0	Prob > t
Intercept	99.99	1	1.255E-03		
[As]	7.400E-03	1	5.436E-04	13.61	<0.0001
[As] ²	-7.983E-03	1	1.368E-03	-5.84	<0.0001

Tables 5.6 (a) and (b) show a square factor which is {[As]²}. This indicates that a curvature is present in the model and this curvature is statistically significant (p<0.0001). Initial arsenic concentration is the principal variable which is significant, and {[As]²} indicates a very significant quadratic model term.

Thus the final model describing the data may be described by the following general equation:

$$\hat{Y} = b_0 + b_1D + b_2D^2 \dots\dots\dots Eqn \dots 5.2$$

5.5 VALIDATION OF THE MODEL

5.5.1 Graphic validation

To statistically validate these models, the following graphic tests have been performed: normal probability, residuals versus predicted response and half normal plot effect graphs.

(I) Full normal probability of studentized residuals

Figures 5.1 (a) and (b) show that errors are distributed normally i.e the residuals fall on a line, thus validating the adequacy of the least-square fit.⁴

Figure 5.1 (a) A plot of normal percentage probability versus studentized residuals for the decanted solutions of the coagulation of aqueous arsenate using a binary coagulant of chromium (III) and calcium (II)-based coagulation for decantation.

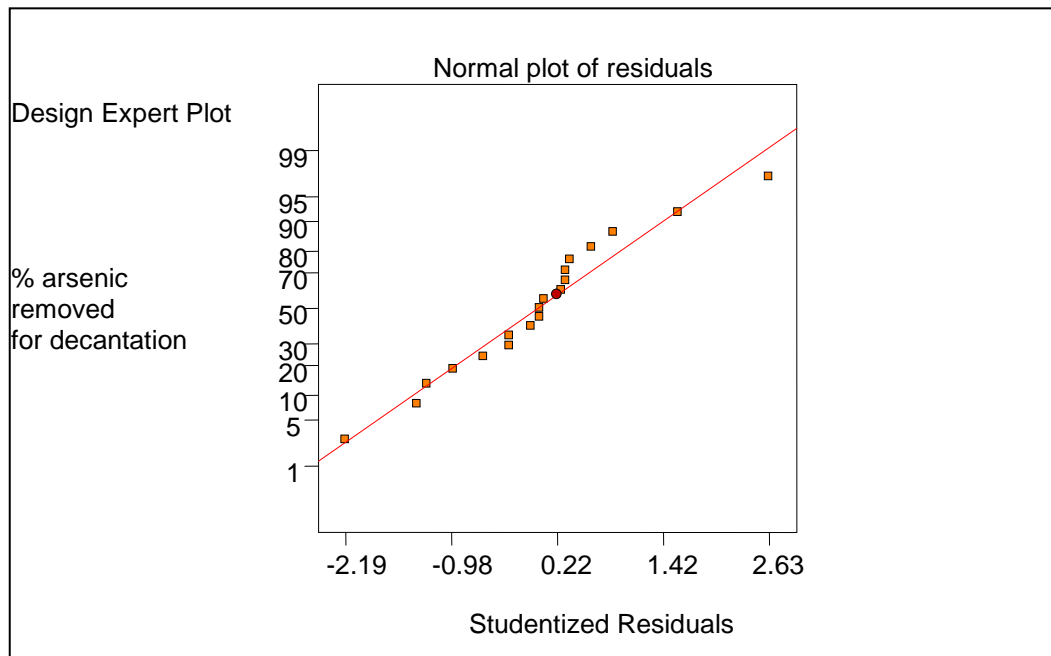
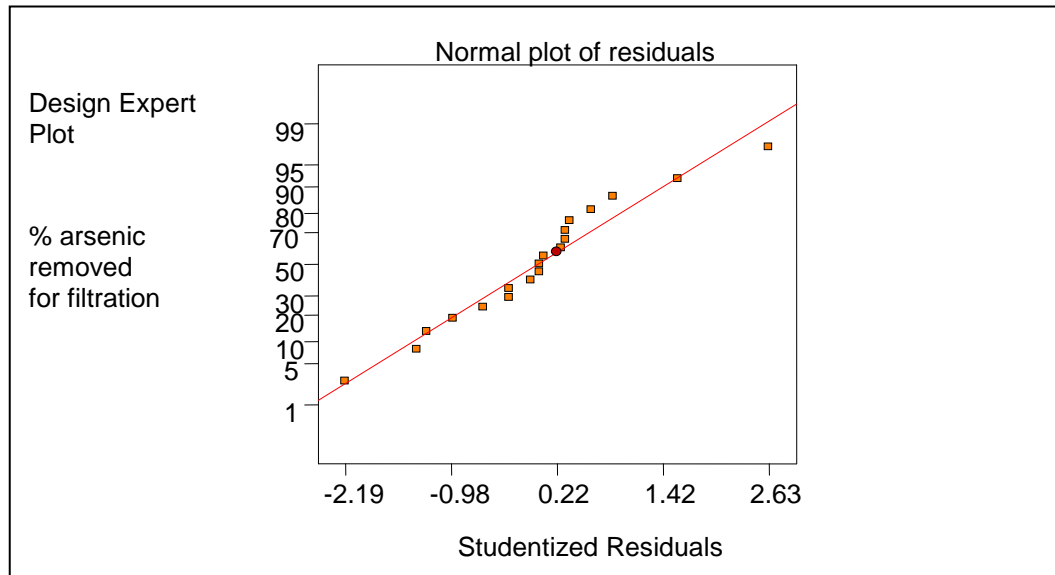


Figure 5.1 (b) A plot of normal percentage probability versus studentized residuals for the filtrated solutions of the coagulation of aqueous arsenate using binary coagulant chromium (III) and calcium (II)-based coagulation for filtration.



(II) Studentized residuals versus predicted response

Figures 5.2 (a) and (b) describes a plot of residuals *versus* predicted response showing points falling into an inverted funnel-shaped pattern (non-constant variance) for both decantation and filtration.⁵ There is a trend to higher absolute residuals as the value of the response increases. According to the literature survey the other action that may be taken is to transform the response, by modeling its logarithm or square root. Transforming a response in this method often simplifies its relationship with a predictor variable and leads to simpler models.⁶

Figure 5.2 (a) A plot of residuals *versus* predicted response for the model using a binary coagulant of chromium (III) and calcium (II)-based coagulation for decantation.

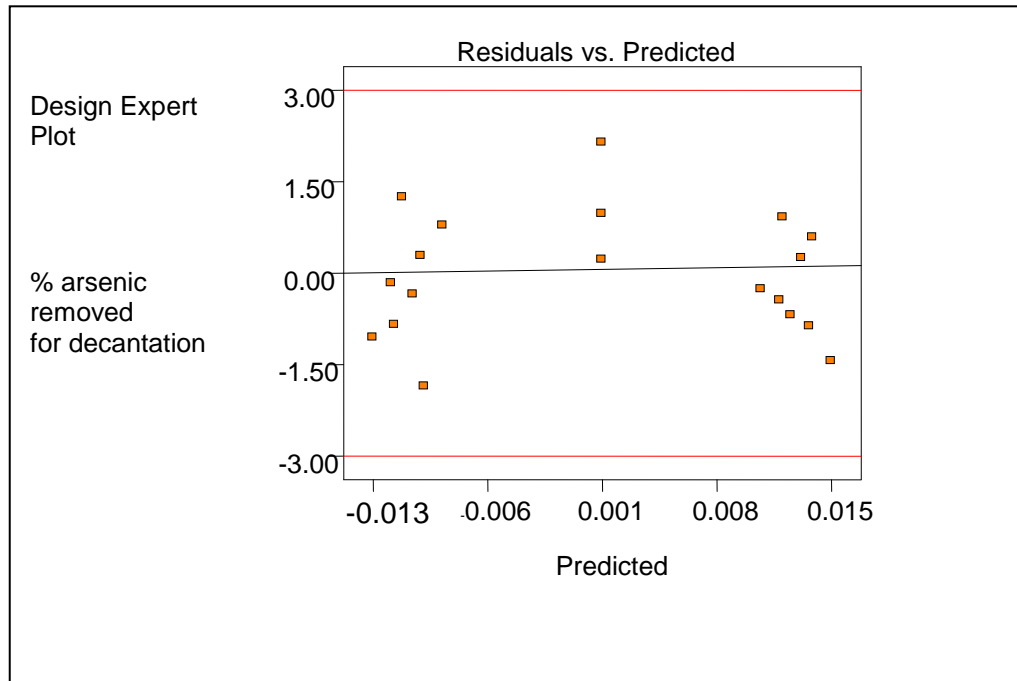
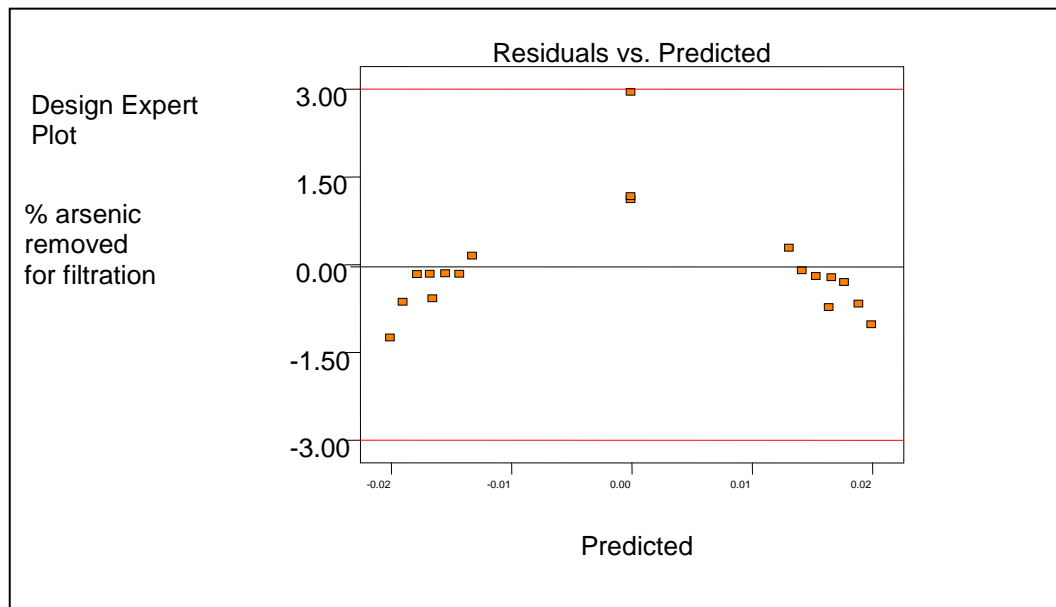


Figure 5.2 (b) A plot of residuals *versus* predicted response for the model using a binary coagulant of chromium (III) and calcium (II)-based coagulation for filtration.



(III) Half normal plot

A half-normal probability plot was used to identify the significant factors from the main factors. In a half-normal plot, the main factors are plotted against their expected normal values, while the significant effects are positioned as outliers, that is points far away from the best-fit straight line of the plot.⁶ Figures 5.3 (a) and (b) show half normal plots for chromium (III) and calcium (II)-based coagulation of arsenate for decantation and filtration respectively. In both half normal plots factor D (initial concentration of arsenic) is statistically significant. All the other factors which are insignificant fall on the line.

Figure 5.3 (a) A half normal plot for the model describing chromium (III) and calcium (II)-based coagulation of arsenate with decantation.

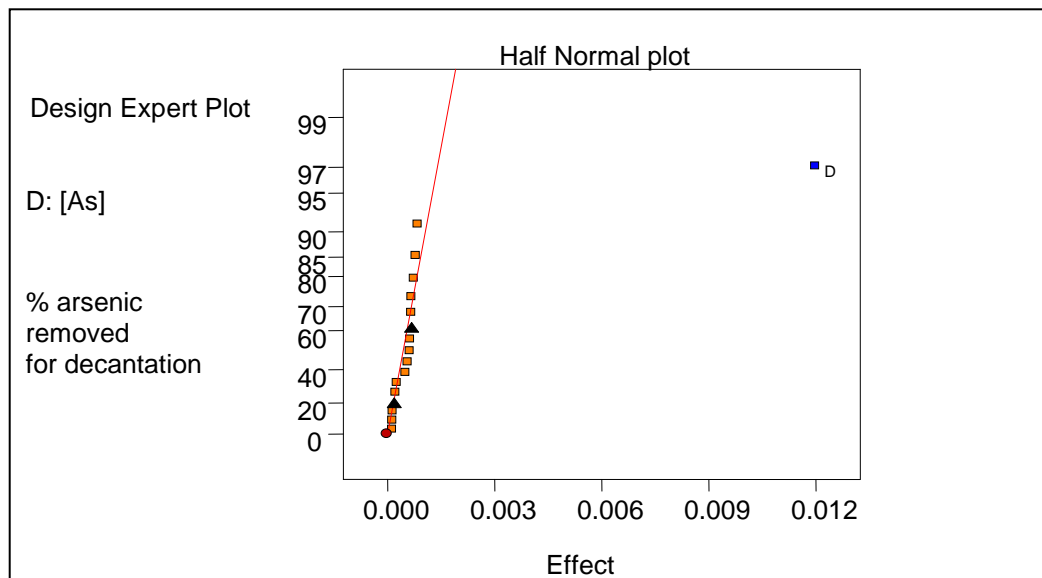
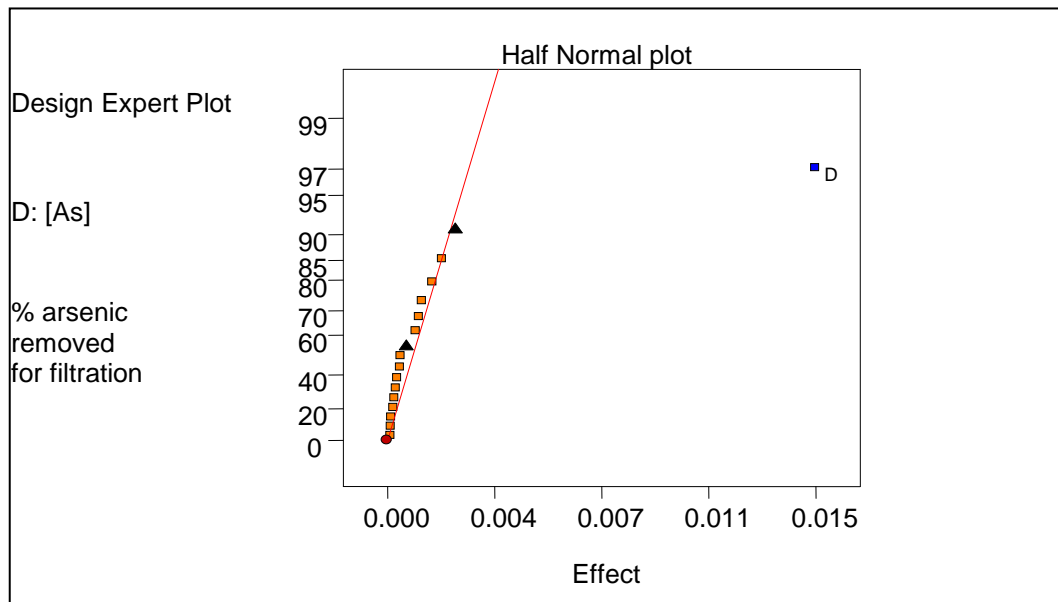


Figure 5.3 (b) A half normal plot for the model describing chromium (III) and calcium (II)-based coagulation of arsenate with filtration.



5.5.2 The final model describing chromium (III) and calcium (II)-based coagulation of arsenate

Once the important factor had been identified, the next step was to determine the settings for this factor that result in the optimum value of the response. The optimum value of the response was found at maximum value.

5.5.3 Optimization of chromium (III) and calcium (II)-based coagulation of arsenate

The optimization process was successfully determined to maximum of arsenate removal. The results from the second order polynomial models were developed using Equation 3.5 in chapter 3.⁷

5.6 EXPERIMENTAL VALIDATION

Confirmatory experiments were carried out in triplicate at selected variable settings. Table 5.7 shows results of the confirmatory experiments used to validate the model describing chromium (III) chloride and calcium (II) chloride - based coagulation of arsenate for decantation and filtration.

Table 5.7 Results of the confirmatory experiments used to validate the model describing chromium (III) chloride and calcium (II) chloride-based coagulation of arsenate for decantation and filtration.

Factors				Predicted 95% CL		Predicted		Responses	
A	B	C	D	CL Low	CL High	% As	% As	%As	% As
pH	Ca:As	Cr:As	[As] ppm	%As Removal (decant)	% As Removal (filtrated)	% As Removal Decant	% As Removal Filtrate	%As Removal (decant)	% As Removal (filtrated)
6.50	1.30	1.40	600.00	99.9996- 99.9998	99.9998- 99.9999	100.00	100.00	99.9894	99.9889
7.50	2.00	2.00	700.00	99.9996 99.9998	99.9996- 99.9998	100.00	100.00	99.9910	99.9897
11.50	1.80	1.70	800.00	99.9998 100.000	99.9996 99.9998	100.00	100.00	99.9906	99.9891

5.7 CONCLUSION

The removal of arsenate by combined chromium (III) and calcium (II)-based chloride coagulation was successfully investigated using four factors, half-factorial design. In order to test the predicted results, confirmation experiments were carried out. There was a good agreement in terms of concentration difference, despite the confidence limits between the predicted values and experimental values being slightly out. The results of confirmatory experiments were under the range of 95% confidence limits predicted by the model and the experimental procedure. Initial arsenic concentration was identified as a significant factor.

5.8 REFERENCES

1. Anodic and cathodic reactions in molten calcium chloride, D.J. Fray, The Canadian Metallurgical Quarterly, Volume 41, No.4, 2002, pp 433-439.
2. Application of response surface methodology in describing the performance of thin film composite membrane, Ani Idris, Farida Kormin and M.Y. Noordin, Separation and purification technology, Volume 49, Issue 3, 2006, pp 271-280.
3. Application of statistical experimental design for optimization of alkaline protease production from Bacillus sp. RGR-14, Bhavna Chauhan and Rani Gupta, Process Biochemistry, Volume 39, Issue 12, 2004, pp 2115-2122.
4. Influence of variable of combined coagulation-fenton-sedimentation process in the treatment of trifluraline effluent, Ayrton F. Martins, Tibirica G., Vasconcelos and Marcelo L. Wilde, Journal of hazardous materials, Volume 127, Issue 1-3, 2005, pp 111-119.
5. Factorial experimental design for recovering heavy metals from sludge with ion-exchange resin Hsien Lee, Yu-Chung Kuan and Jia-Ming Chern, Journal of hazardous materials, Volume 138, Issue 3, 2006, pp 549-559.
6. Engineering Statics Handbook Statistical Methods in the Work of Mary Natrella Carroll Croarkin and Will Guthrie,
7. Concrete mixture optimization using statistical methods, Marcia J. Simon, International symposium on high performance concrete, 1997, pp 230-244.

CHAPTER 6

THE MODELLING OF ARSENIC (VI) REMOVAL FROM AQUEOUS MEDIA USING MAGNESIUM (II) CHLORIDE

6.1. INTRODUCTION

In the field of waste water treatment magnesium chloride is a less commonly used coagulant.¹ In the literature survey, it was discovered that magnesium chloride removes arsenic more effectively than calcium chloride as using magnesium chloride raises the pH from pH 9 to 11 thereby producing improved removals. Magnesium has been used in this study as a coagulant to investigate its effectiveness in chemical precipitation of aqueous arsenate. Parameters studied using a three variable factorial design include initial arsenic concentration, pH, and Mg:As mole ratio.

6.2 EXPERIMENTAL

6.2.1 Coagulation procedure

The coagulation was carried out as in section chapter 2 in section 2.7.1 and 50% of MgCl₂ was used as coagulant. A white precipitate was formed and the pH was adjusted until it was stable for 30 seconds, 1 ml of anionic organic flocculent concentration (500 ppm) was added, stirred for two minutes and allowed to settle for an hour. Both decantates and filtrates were analyzed using inductively coupled plasma mass spectrometer.

6.2.2 Mechanism of arsenate removal by magnesium coagulation

As described in section 1.5, in solutions in pH ranges of 7 to 11,5 the predominant arsenate species is HAsO₄²⁻, which is negatively charged. Magnesium removes arsenic more effectively at pH 11-12. Arsenic precipitates out magnesium as the hydroxide, however it settles poorly.³

6.3 EXPERIMENTAL DOMAIN

6.3.1 Factorial design for magnesium (II)-based coagulation of arsenic

A three variable half factorial design (2^3) was performed in order to determine the influence of factors and the presence of interactions on the residual of arsenic. Three factors were studied: pH, initial concentration of arsenic and Mg:As mole ratio.

6.3.2 Coded values of the magnesium (II)-based coagulation

The experimental domain is shown in Table 6.1 Design Expert was used to estimate the response of dependent variables.

Table 6.1 The experimental domain used in the study of magnesium (II)-based coagulation of arsenate.

Factor	Name	Units	Low value	Middle Value	High Value
A	pH	-	9.30	10.45	11.60
B	Mg: As	-	1	2	3
C	Initial[As ^v]	ppm	250	550	850

Table 6.2 depicts the coded half factorial design used to investigate the magnesium (II)-based coagulation of arsenate.

Table 6.2 The coded values of the experimental design used to optimise magnesium (II)-based coagulation of arsenate.

Standard Order	Run Order	pH	B [As] ppm	C Mg:As Mole ratio	Type of point
1	1	-1	-1	1	F
2	6	1	-1	-1	F
3	2	-1	1	-1	F
4	3	1	1	1	F
5	7	0	0	0	Cp
6	4	0	0	0	Cp
7	5	0	0	0	Cp

F= factorial point

Cp= centre point

6.3.3 Results of the half factorial design using magnesium chloride (II)-based as coagulant

The experimental responses are shown in Table 6.3

Table 6.3 Results of the half factorial design used to model the removal of aqueous arsenate using magnesium (II) as coagulant.

Std Order	Run Order	pH	Mg:As	[As]	Conc As Left Decantate	% As Removed Decatante	Conc As Left Filtration	% As Removed Filtrate
		-	mol	ppm	ppm	%	ppm	%
1	1	9.30	3	250	0.0605	99.9758	0.0706	99.9716
2	6	11.60	1	250	0.0775	99.9749	0.0907	99.9704
3	2	9.30	1	850	0.0627	99.9928	0.0737	99.9914
4	3	11.60	3	850	0.0611	99.9950	0.0727	99.9999
5	7	10.45	2	550	0.0804	99.9927	0.1173	99.9874
6	4	10.45	2	550	0.0422	99.9859	0.0677	99.9835
7	5	10.45	2	550	0.0399	99.9854	0.0693	99.9787

6.4 RESULTS AND DISCUSSION

6.4.1 Factorial design and ANOVA

The main factors affecting arsenate removal during coagulation were determined by using a two-level half factorial 2^3 design. Significances of the effects were determined by ANOVA, which was important in determining the adequacy of the model. Tables 6.4 (a) and (b) show the ANOVA for the decanted and filtered solutions. The low p-values for the model indicate a highly significant linear association between the initial concentration of arsenic and the percentage of arsenic removed. The quality of the overall fit of the model is described in ANOVA Tables. The low p-value associated with the F-test statistic indicate that this model fits well.

Table 6.4 (a) ANOVA for the factorial model describing magnesium chloride (II)-based coagulation of arsenate for the decantation model.

Source	Sum of Squares	DF	Mean Squares	F Value	Prob > F
Model	3.441E-04	1	3.441E-04	316.36	<0.0001 (significant)
Residual	4.351E-06	4	1.088E-06		
<i>Lack of Fit</i>	<i>4.226E-06</i>	<i>3</i>	<i>1.409E-06</i>	<i>11.27</i>	<i>0.2148</i>
<i>Pure Error</i>	<i>1.250E-07</i>	<i>1</i>	<i>1.250E-07</i>		
Cor Total	3.485E-04	5			
Root MSE	1.043E-03		R-Squared	0.9875	
Dep Mean	99.98		Adj R-Squared	0.9844	
C.V.	1.043E-03		Pred R-Squared	0.9679	
PRESS	1.120E-05		Adeq Precision	30.807	Desire > 4

Table 6.4 (b) ANOVA for the factorial model describing magnesium chloride (II)-based coagulation of arsenate for the filtration model.

Source	Sum of Squares	DF	Mean Squares	F Value	Prob > F
Model	6.076E-04	1	6.076E-04	42.22	0.0027 (significant)
Residual	5.497E-05	4	1.374E-05		
<i>Lack of Fit</i>	<i>4.345E-05</i>	<i>3</i>	<i>1.448E-05</i>	<i>1.26</i>	<i>0.5618</i>
<i>Pure Error</i>	<i>1.152E-05</i>	<i>1</i>	<i>1.152E-05</i>		
Cor Total	6.626E-04	5			
Root MSE	3.707E-03		R-Squared	0.9170	
Dep Mean	99.98		Adj R-Squared	0.8963	
C.V.	3.708E-03		Pred R-Squared	0.7922	
PRESS	1.377E-04		Adeq Precision	11.515	Desire > 4

The large respective “F-values” of 316.36 for decantation and 42.22 for filtration implied that the models were significant. As in previous models in this research the “Adeq Precision” measures the signal to noise ratio, which should exceed 4. The ratios of 30.807 for decantation and 11.515 for filtration indicated an adequate signal to noise ratio. The mathematical models are reliable with an R² value of 0.9875 for decantation and 0.9170 for filtration in which 98.75 % and 91.70% of variation is explained by the models respectively. The adjusted R² value of 0.9844 for decantation and 0.8963 for filtration also suggested that the model was significant.

6.4.2 Defining the polynomial equation describing the magnesium (II)-based removal of arsenate.

Tables 6.5 (a) and (b) show the initial polynomial equations describing the magnesium (II)-based removal of arsenate for decantation and filtration respectively. Initial equation of the model is as follows:

$$\hat{Y} = b_0 + b_1A + b_2B + b_3C + b_4D + b_5A^2 \dots\dots\dots Eqn \dots 6.1$$

Table 6.5 (a) The initial polynomial equation that describes the magnesium (II)-based removal of arsenate for decantation.

Factor	Coefficient Estimate		Standard Error	t for H0	
		DF		Coeff=0	Prob > t
Intercept	99.99	1	2.354E-03		
pH	7.250E-03	1	2.039E-03	0.36	0.7562
[As]	9.275E-03	1	2.039E-03	4.55	0.0451
Mg:As	-1.725E-03	1	2.039E-03	-0.85	0.4866
pH ²	-6.275E-03	1	3.115E-03	-2.01	0.1815

Table 6.5 (b) The initial polynomial equation that describes the magnesium (II)-based removal of arsenate for filtration.

Factor	Coefficient Estimate		Standard Error	t for H0	
		DF		Coeff=0	Prob > t
Intercept	99.98	1	2.516E-03		
pH	1.825E-03	1	2.179E-03	0.84	0.4904
[As]	0.012	1	2.179E-03	5.66	0.0299
Mg:As	2.425E-03	1	2.179E-03	1.11	0.3816
pH ²	1.250E-04	1	3.328E-03	0.038	0.9735

As will be noted in Tables 6.5 (a) and (b), the terms representing pH, Mg:As mole ratio and pH² are statistically insignificant (p>0.05), which means that they do not have a significant effect on the response of arsenic removal in both models. These factors were therefore removed from the initial model.

6.4.3 Estimated coefficients for final models that described the magnesium (II)-based removal of arsenate.

Tables 6.6 (a) and (b) show the estimated coefficients for this final model for decantation and filtration.

Table 6.6 (a) The final polynomial equation that describes the magnesium (II)-based removal of arsenate for decantation.

Factor	Coefficient Estimate		Standard Error	t for H0	
		DF		Coeff=0	Prob > t
Intercept	99.99	1	1.047E-03		
B-[As]	4.637E-03	1	2.607E-06	17.79	<0.0001

Table 6.6 (b) The final polynomial equation that describes the magnesium (II)-based removal of arsenate for filtration.

Factor	Coefficient Estimate		Standard Error	t for H0	
		DF		Coeff=0	Prob > t
Intercept	99.99	1	1.775E-03		
B-[As]	6.162E-03	1	9.267E-03	6.65	0.0027

Thus both final models describing the data are given by the general equation of the model:

$$\hat{Y} = b_0 + b_1 B \dots \dots \dots Eqn \dots \dots 6.2$$

In both final models initial arsenic concentration is the only factor influencing the response. The linear model provides a good fit to the data ($R^2=0.9875$) for decantation and ($R^2=0.9170$) for filtration. One outlier (run #5) has been removed from the data.

6.5 VALIDATION OF THE MODEL

6.5.1 Graphic validation

Before a regression model can be accepted, it must be validated. For a simple regression model, this means that the residuals must be normally distributed and randomly distributed around zero, and also the independent variable must be shown by using a normal-half plot.

(f) Full normal probability plot of studentized residuals

Plot of studentized residual *versus* normal probability for model of magnesium (II) coagulation of arsenate show the distribution adequately describes the least-square fit. The studentized residuals should appear to follow a straight line on such a probability plot. The normal probability plots of residuals points are linearly distributed for both decantation and filtration.

Figure 6.1 (a) A plot of studentized residuals versus accumulative frequency for the model of magnesium (II)-based coagulation of arsenate with decantation.

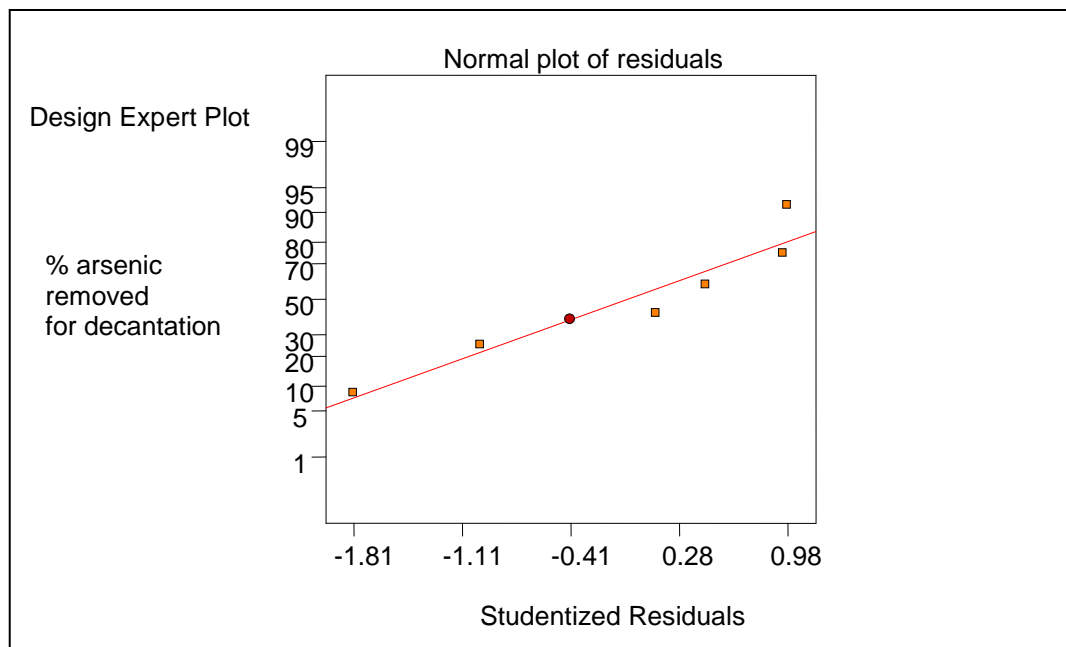
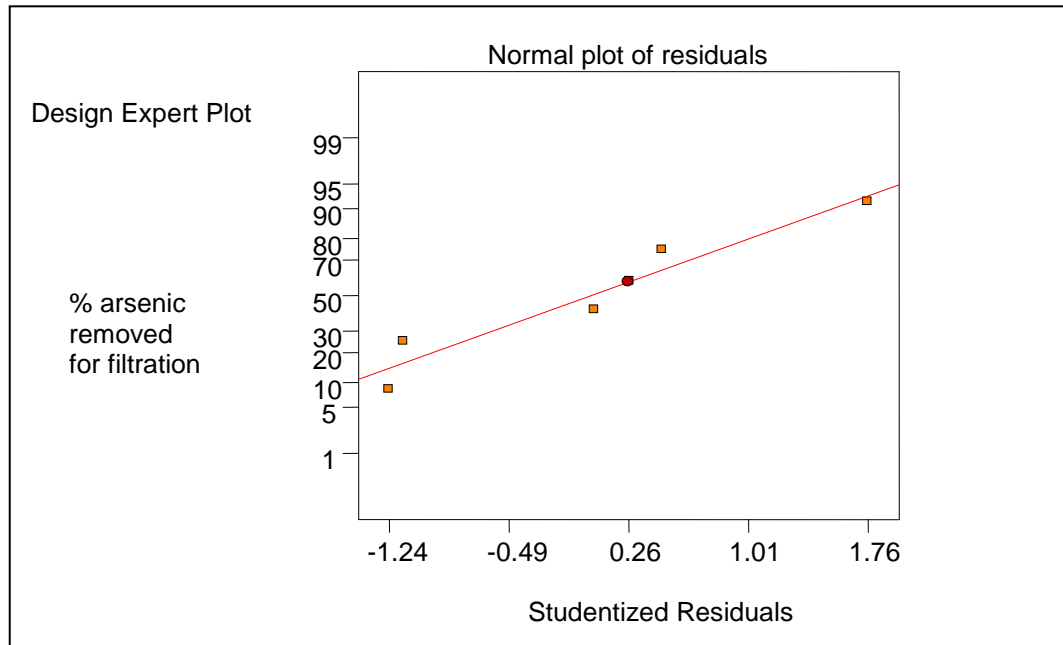


Figure 6.1 (b) A plot of studentized residuals versus accumulative frequency for the model of magnesium (II)-based coagulation of arsenate with filtration.



(II) Studentized residuals *versus* predicted responses

Figures 6.2 (a) and (b) show plots of residuals *versus* predicted responses for decantation and filtration respectively. Figure 6.2 (a) shows that the semi-circle shape of decantation indicates an inadequate model.⁴ The filtration plot makes a fan shape (<) opening to the right. A fan shape in the residuals indicates that the amount of error is not constant along the regression line.⁵ On the left, the errors are small; while on the right, the errors are large. Quadratic terms were insignificant.

Figure 6.2 (a) A plot of residual *versus* predicted response for the model of magnesium (II)-based coagulation of arsenate for decantation.

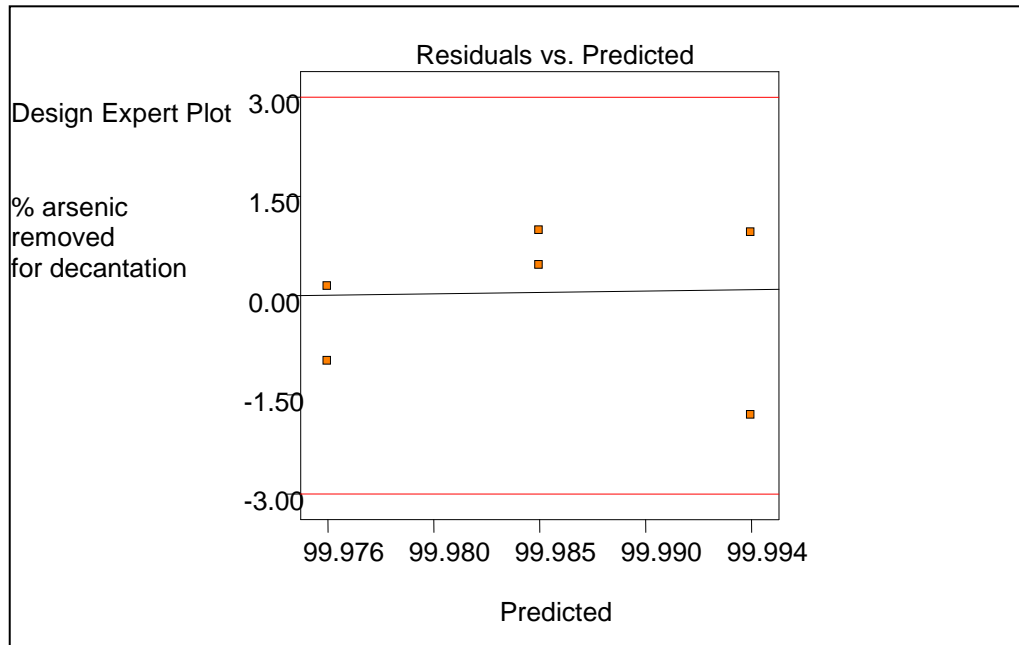
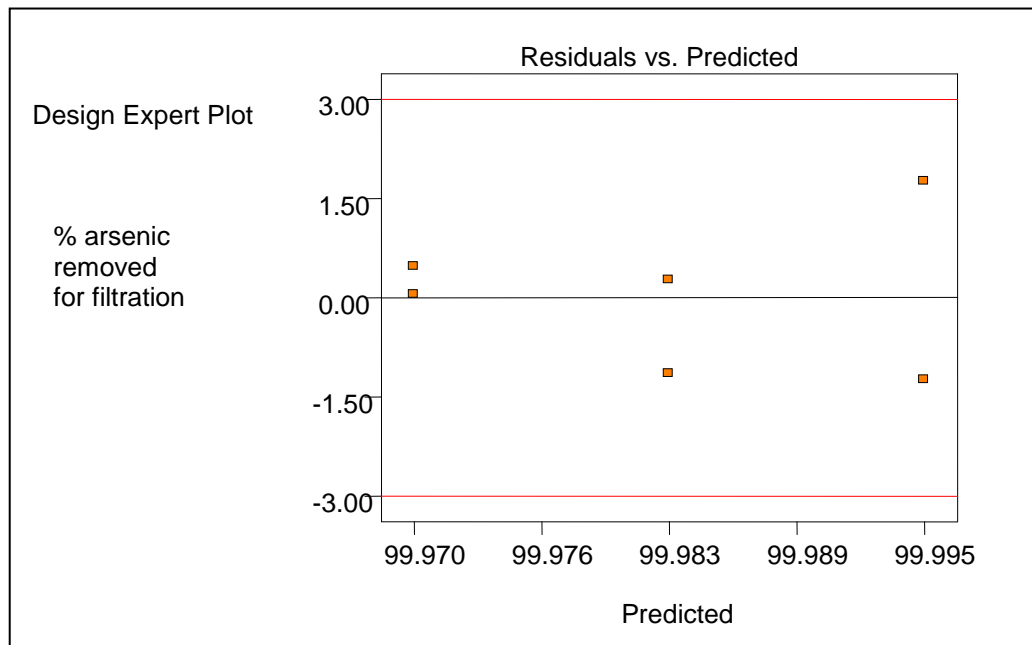


Figure 6.2 (b) A plot of residual *versus* predicted response for the model of magnesium (II)-based coagulation of arsenate for filtration.



(III) Half normal plot

Figures 6.3 (a) and (b) show half normal plots for magnesium (II)-based coagulation of arsenate for decantation and filtration respectively. Half normal plots reveal that only the important significant effect is the initial arsenate concentration term B.

Figure 6.3 (a) A half normal plot for the model of magnesium (II)-based coagulation of arsenate with decantation.

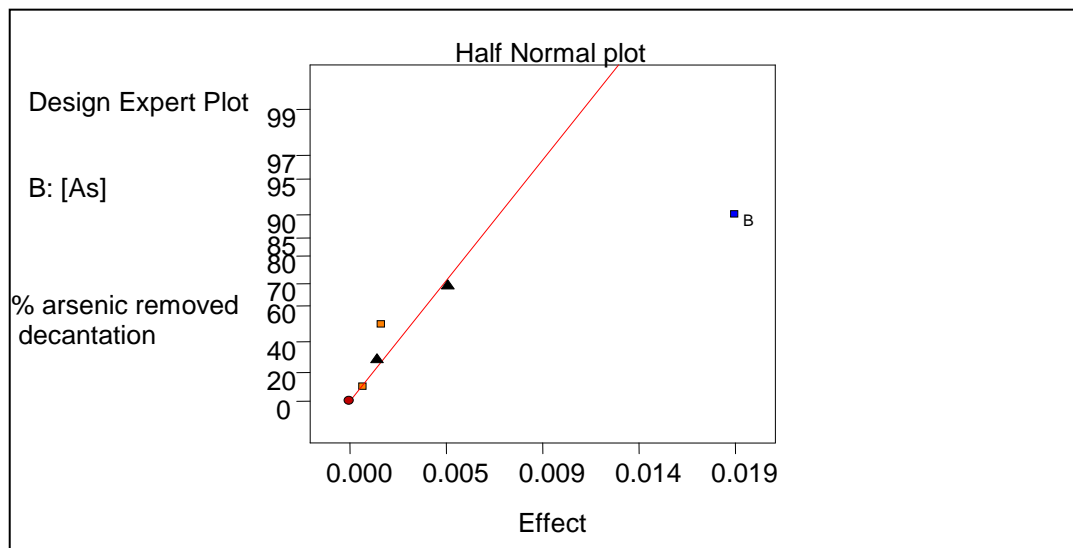
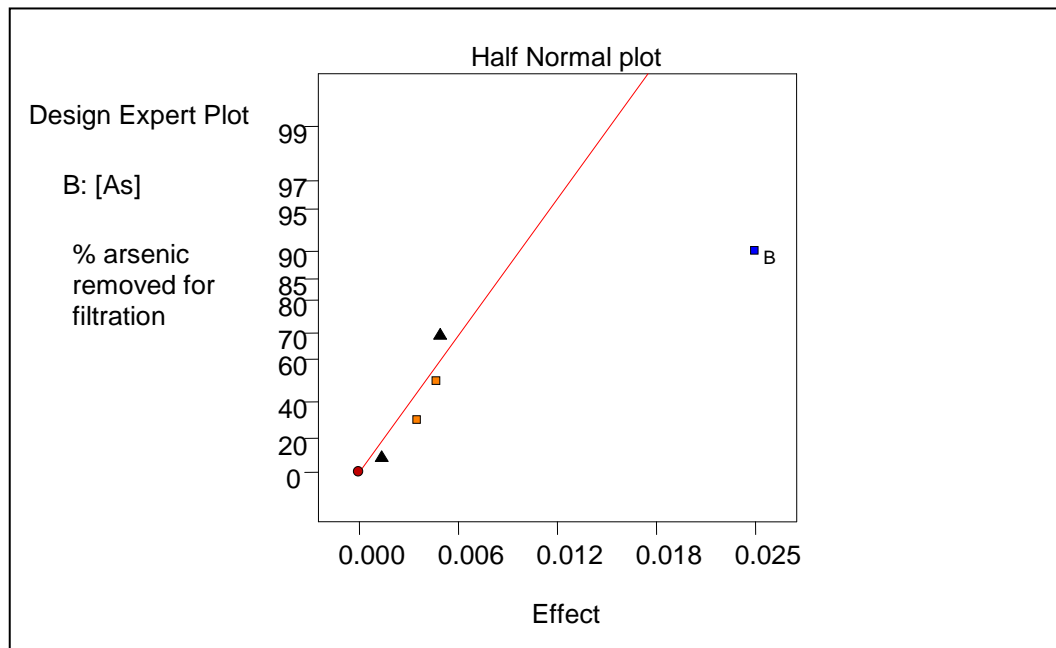


Figure 6.3 (b) A half normal plot for the model of magnesium (II)-based coagulation of arsenate with filtration.



6.5.2 Optimization of magnesium (II)-based coagulation of arsenate

The statistical analysis results in the development of first-order model that describes the mathematical relationship between the response and the factor. A general form of the model is given in Eqn 3.5. By using this equation, the maximum for both decantation and filtration was found respectively.

6.6 EXPERIMENTAL VALIDATION

Confirmatory experiments were run for validation and cross checked by using the Design Expert software for the prediction of arsenic removal and corresponding confidence intervals. Table 6.7 shows the results of the confirmatory experiments used to validate the model describing magnesium (II) chloride- based coagulation of arsenate.

Table 6.7 Results of the confirmatory experiments used to validate the model describing magnesium (II)-based coagulation of arsenate.

Factors			Predicted 95% CL		Predicted		Responses	
A	B	C	CL Low	CL High	% As	% As	%As	% As
pH	Mg:As Mole	[As] ppm	%As Removal (decant)	% As Removal (filtrated)	% As Removal Decant	% As Removal Filtrate	%As Removal (decant)	% As Removal (filtrated)
9.60	1.40	650.00	99.9996-99.9998	99.9996-99.9998	99.9996	99.9998	99.9871	99.9849
10.00	2.50	750.00	99.9996-99.9998	99.9998-100.0000	99.9998	99.9998	99.9880	99.9859
11.40	3.00	850.00	99.9998-100.0000	99.9998-100.0000	99.9998	100.0000	99.9906	99.9897

6.7 CONCLUSION

Magnesium-based models were derived to predict the removal of arsenate by magnesium chloride-based coagulation using a three factor, half-factorial design. The percentage of arsenic removed ranged from 99.9716 to 99.9999. The models were tested statistically and the response values were outside the CL limit but close enough to be accepted as it has a symmetric error. The results obtained from confirmatory experiments were lower than predictions estimation.

6.8 REFERENCES

1. Removal of dyes and industrial dye wastes by magnesium chloride, Water Research, Boon Hai Tan, Tjoon Tow Teng and A. K. Mohd Omar , Volume 34, Issue 2, 2000, pp 597-601.
2. Predicting arsenic removal during metal hydroxide precipitation, L.Mc Neil & M. Edwards, Journal of the American water works, Volume 89, No.1, 1997, pp 75-86.
3. High-pH–magnesium coagulation–flocculation in wastewater treatment L. Semerjian and G. M. Ayoub, Advances in Environmental Research, Volume 7, Issue 2, 2003, pp 389-403.
4. Projection Pursuit Regression, Jerome H. Friedman and Werner Stuetze, Journal of the american statistical association, Volume 76, Issue 376, 1981, pp 817-823.
5. The use of simulated annealing in chromosome reconstruction experiments based on binary scoring, A J Cuticchia, J Arnold and W E Timberlake, Genetic society of america, Volume 132, No.2, 1992, pp 591-601.

CHAPTER 7

CONCLUSION

7.1 LITERATURE REVIEW

Chapter 1 reveals the extent of the literature survey, particularly with respect to the latest developments in arsenic removal as well as a literature review of the relevant chemistry. A literature survey focusing on new developments within coagulation did not reveal any investigations of the use of a binary coagulant consisting calcium chloride and chromium (III) chloride. The modelling studies are thus a novel contribution to coagulation methods for arsenic removal.

7.2 MODELLING STUDIES

7.2.1 Introduction

The removal of arsenic from aqueous media containing monosodium methyl arsenate (MSMA) was not only investigated by performing modelling studies of Cr^{3+} , Ca^{2+} and Mg^{2+} as single coagulants, but also by studying efficacy of efficacy mixtures of two ions (Cr^{3+} and Ca^{2+}) as a binary coagulant. Experimental design methodology was used to investigate various operational parameters that affect the removal of arsenic such as pH, initial metal ion to arsenic mole ratio, coagulant type (Cr^{3+} , Mg^{2+} , Ca^{2+}) and dose.

7.2.2 Statistical analysis

The results of the experiments were assessed by appropriate statistical analysis. The goal of the investigative analyses was to identify models from the data while the goal of the confirmatory experiments was to validate to the design model. The effects of varying flocculant concentration, metal ion: arsenic mole ratio, initial concentration of arsenic and pH were investigated using experimental designs. ANOVA revealed the main effects which were significant. The models developed using design methods were reasonably accurate and were very helpful when visualizing the main effects of the factors that most affected arsenic removal.

7.2.3 Chromium (III)-based coagulation

The initial concentration of arsenic, the concentration of organic flocculent, pH and Cr:As mole ratio were systematically varied during the coagulation process using a central composite design. The formation of green precipitates upon raising the pH removed 99.85%-99.99% of arsenate initially present. The confirmatory experiments yielded a response of 99.00% arsenic removal from decantation and filtration experiments, which falls within the predicted range of the model. The mechanism by which arsenate is removed by Cr(III) involves initial formation of an insoluble ion pair between the Cr ion and arsenate.¹ The pH is one of the most important parameters affecting the coagulation. Since the surface charge of arsenate can be modified by changing the pH of the solution and this change affects the degree of ionization and speciation of the arsenate.² This behavior is due to the formation of different arsenate species in aqueous solution such as H_3AsO_4 , $H_2AsO_4^-$ etc. At $pH < 6$ arsenate has mostly negative one charge and $Cr(OH)_3$ has a very positive surface charge hence moderate to good removal of arsenate.³

A second order equation was used to find the maximum percentage of arsenic removed. The experimental design for the model and the final equations for the models are shown in Tables 7.1 and 7.2 respectively. Equation 3.4 the equation below shows the final polynomial equation which describing the response surface of chromium (III)-based coagulation of arsenate with decantation and filtration.

$$\hat{Y} = b_0 + b_1D + b_2D^2 \dots\dots\dots Eqn \dots 3.4$$

Table 7.1: The experimental validation for the modelling of chromium (III)-based coagulation of arsenate

	Factors				Predicted Responses		Actual Responses	
	A pH	B [Floc] ppm	C Cr:As Mole	D [As] ppm	% As Removal Decant	% As Removal Filtrate	%As Removal (decant)	%As Removal (filtrated)
Range	4.5- 8.5	1.5- 3.5	1.0- 5.0	50- 850				
Prediction	5.6	3.00	3.50	600.00	99.9700	100.0000	99.9788	99.9789
Experiments	6.0	2.55	3.20	314.00	99.9700	99.9600	99.9789	99.9699
	7.0	2.00	4.00	550.00	100.0000	100.0000	99.9899	99.9899

Table 7.2 The final equations for the predicted model with their P-values for chromium (III)-based coagulation of arsenate

Factors	Decanted Solution	P-value	Filtrated Solution	P-value
	% As Removed =	<0.0001 significant	% As Removed =	<0.0001 significant
Intercept	99.95		99.96	
[As]	1.14×10^{-04}		7.35×10^{-5}	
[As] ²	-7.60×10^{-8}		-3.8×10^{-8}	

One of the major findings in this study was that the final equations for chromium (III) and other coagulants for both the decantation and filtration models only show initial arsenate concentration as the factor that was significant in the model. It can be concluded that chromium is a good coagulant for arsenic and may find use in treating aqueous as effluent.

7.2.4 Calcium (II)-based coagulation

Removal of arsenic by calcium coagulation was investigated by factorial design using parameters including pH, Ca:As mole ratio and initial concentration of arsenic. ANOVA was used to validate the model. The “F-value” was very small <0.0005 (less than the 0.05). This low F value indicates that the equation is very significant and its factor describes the change in response. The arsenic removal

ranged from 95.17% to 98.58%. A confirmatory experiment was made in order to verify the results obtained from the statistical analysis and the results were within the 95% confidence limit. The results indicate that very low arsenic removal could be achieved at pH 12.5 when the initial arsenic concentration was 250 mg/l and was highly dependent on initial concentration. At an initial concentration of 850 mg/l, the percentage removal of arsenic was significantly higher at pH 10.0 for both decantate and filtrate. Calcium chloride added to MSMA waste water can form complexes with arsenic in form of $\text{CaH}_2\text{AsO}_4^+$, CaHAsO_4 , CaAsO_4^- , $\text{Ca}_3(\text{AsO}_4)_2$.⁴ Experiments were conducted with 250ppm arsenic and at pH 10.0 - 11.5 in solution with a small amount sludge present due to not a lot of $\text{Ca}(\text{OH})_2$ forming. At pH 12.50 a large amount of sludge was present and arsenic may be sorbing to lime $\text{Ca}(\text{OH})_2$ that did not dissolve and CaHAsO_4 could be forming. As the pH increases, the arsenate species is soluble ion with no surface as such and the charge concentration of the 2- minus charge remains 2- HAsO_4^{2-} . Calcium neutralizes this negative charge forming $\text{Ca}_3(\text{AsO}_4)_2$ and allows the arsenic to be removed from solution.⁴

To find the maximum arsenic removal for the decantation and filtration, a second order derivative equation 4.2 was used. The experimental domain for the predicted model and the final equations for the predicted models are shown in Table 7.3 and 7.4.

$$\hat{Y} = b_0 + b_1A + b_2B + b_3A^2 \dots\dots\dots \text{Eqn}\dots 4.2$$

Table 7.3: The experimental validation for the modelling of calcium (II)-based coagulation of arsenate

	Factors			Predicted Responses		Actual Responses	
	A pH	B Ca:As Mole	C [As] ppm	% As Removal Decant	% As Removal Filtrate	%As Removal (decant)	%As Removal (filtrated)
Range	10.00- 12.50	0.50- 3.00	250- 850				
Prediction	10.50	2.00	600.00	96.6200	97.6100	96.9652	96.873
Experiments	11.00	3.00	700.00	96.6200	97.6100	97.4905	97.5302
	12.00	2.50	750.00	97.6100	97.9000	97.4752	97.7852

Table 7.4 The final equation for the predicted model with their P-values for calcium (II)-based coagulation of arsenate

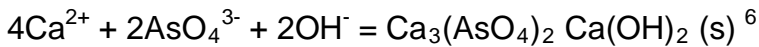
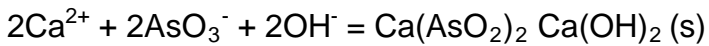
Factors	Decanted Solution	P-value	Filtrated Solution	P-value
	% As Removed =	<0.0099 significant	% As Removed =	<0.0001 significant
Intercept	97.60		97.75	
pH	-0.16		-0.14	
[As]	+1.98		+1.74	
pH ²	-1.30		-1.01	

7.2.5 Combined chromium (III) and calcium (II)-based coagulation

Two coagulants, chromium chloride and calcium chloride, were used in various combinations for this study. Removal of arsenic using a binary mixture of chromium (III) chloride and calcium (II) chloride was investigated by varying the pH, initial concentration of arsenate, Cr:As mole ratio and Ca:As mole ratio by factorial design. Decantation and filtration had P-values smaller than 0.05 and were significant and the percentage arsenate removed range from 99.70% – 99.99%. Experimental validation was performed to test the model. The results obtained were close to the predicted range of 99.99%. It was observed that, chromium chloride-based arsenic removal increased from the pH value of 4.5 to 8.5 in Table 3.4. It has been reported that below pH 2, almost all the metal

hydroxides are solubilized by protons and the metal binding could not be expected.⁵ As the pH value increased, Cr (III) began to bind to the hydroxide forming Cr(OH)₃. However, binding of arsenate to Cr(OH)₃ gradually increased with the pH. This finding suggested that, the adsorbent surface of Cr(OH)₃ might have different affinities for As(V) present in the solution and their affinities to chromium species are strongly affected by the pH value of the solution.

For calcium as a coagulant it was reported ⁶ that the precipitation of arsenic by calcium proceeds according to the following reactions:



The optimum arsenic removal was found by using a second order polynomial model. Equation 5.2. was used to find the maximum arsenic removal for the decantation and filtration. The experimental domain for the predicted model and the final equations for the models are shown in Tables 7.5 and 7.6 respectively.

$$\hat{Y} = b_0 + b_1D + b_2D \dots \dots \dots \text{Eqn} \dots 5.2$$

Table 7.5 The experimental validation for the modelling for calcium (II)- based and chromium (III)-based coagulation of arsenate

	Factors				Predicted Response		Actual Responses	
	A pH	B Ca:As moles	C Cr:As moles	D [As] ppm	% As Removal Decant	% As Removal Filtrate	%As Removal (decant)	% As Removal (filtrated)
Range	5.5- 7.5	0.5- 2.0	0.5- 2.0	250- 650				
Prediction	6.50	1.30	1.40	600.00	100.00	100.00	99.9894	99.9889
Experiments	7.50	2.00	2.00	700.00	100.00	100.00	99.9910	99.9897
	11.50	1.80	1.70	800.00	100.00	100.00	99.9906	99.9891

Table 7.6 The final equation for the predicted model with their P-values for calcium (II)-based and chromium (III)-based coagulation of arsenate

Factors	Decanted Solution	P-value	Filtrated Solution	P-value
	% As Removed =	<0.0001 significant	% As Removed =	<0.0001 significant
Intercept	99.99		99.96	
[As]	6.144×10^{-3}		7.40×10^{-3}	
[As] ²	-1.58×10^{-3}		-7.98×10^{-3}	

A disadvantage of the use of calcium in coagulation is that it may require use considerable base to reach the pH for precipitation and to meet effluent discharge criteria sufficient acid may be required to neutralize the base thus contributing to increased salt levels in the final effluents.

7.2.6 Magnesium (II)-based coagulation

Parameters studied included pH, initial concentration of arsenic and Mg:As mole ratio were investigated for the removal of arsenic using magnesium (II) chloride . The results show that magnesium chloride coagulation is capable of removing up to 99.99% of arsenate initially present. Magnesium chloride was shown to be more effective on its own than a combination of calcium chloride and chromium chloride and the percentage removed range from 99.70% – 99.99%. However, there is evidence that magnesium hydroxide settles poorly which could hamper plant processes.⁶ The removal of arsenic from 250.0 mg/l to 850 mg/l of initial concentration of arsenic by an aqueous MgCl₂ solution has been studied at various pH levels.

Table 6.3 from chapter 6 shows variation of percentage removal of arsenic with the pH of the solution. Little precipitate was observed at pH 9.30 - 10.45. As the pH value of the solution increases from 10 to 11, the amount of precipitate increases as the percentage arsenic removal increases. The arsenic removal decreases as the pH increases beyond 11. This is probably due to the formation of magnesium hydroxide precipitate that can be expected at pH values greater than 10.5, due to its solubility constant. When the alkalinity of the solution

containing $MgCl_2$ is increased by adding NaOH, $Mg(OH)_2$ precipitates are formed. The solubility of $Mg(OH)_2$ is given by $K_{sp} = [Mg^{2+}][OH^-]^2$ where K_{sp} is the dissociation constant of the hydroxide. An increase in Mg^{2+} ion or OH^- ion concentration beyond the K_{sp} value favours the formation of the hydroxide, $Mg(OH)_2$. When the pH value falls in the range 10.5–11.0, good flocculation occurs.⁷ At this pH value, almost all the magnesium ions are converted into precipitable hydroxide. It has been reported that the precipitate of $Mg(OH)_2$ acts to remove contaminants through an adsorptive coagulating mechanism.⁸ Its structure provides a large adsorptive surface area and its positive electrostatic surface charge⁸ enables it to act as a powerful and efficient coagulant. Beyond pH 11.0, the results show a lower arsenic removal rate. This phenomenon is probably due to the increase in the solubility of magnesium precipitate. The arsenate removal is shown to increase with the $MgCl_2$ dosage.⁸ It is evident that for the quantitative removal of more than 99.99% of 850.0 mg/l initial arsenic concentration solution, a higher dosage of $MgCl_2$ of solution is required.

The significance and adequacy of the linear models were confirmed by the ANOVA. Confirmation experiments were carried out in order to verify the model obtained from the statistical analysis. A first order model was used to calculate the maximum concentration of arsenic removed for both decantation and filtration as per equation 6.2. The experimental domain for the models and the final equations for the predicted model are shown in Tables 7.7 and 7.8 respectively.

$$\hat{Y} = b_0 + b_1B \dots \dots \dots Eqn \dots 6.2$$

Table 7.7 The experimental validation for the modelling for magnesium (II)-based coagulation of arsenate

	Factors			Predicted Responses		Actual Responses	
	A pH	B Mg:As Mole	C [As] ppm	% As Removal Decant	% As Removal Filtrate	%As Removal (decant)	%As Removal (filtrated)
Range	9.3- 11.6	1.0- 3.0	250- 850				
Prediction	6.60	1.40	600.00	99.9996	99.9998	99.9871	99.9849
Experiments	10.00	2.50	750.00	99.9998	99.9998	99.9880	99.9859
	11.40	3.00	850.00	99.9998	100.000	99.9906	99.9897

Table 7.8 The final equation for the predicted model with their P-values for magnesium (II)-based based coagulation of arsenate

Factors	Decanted Solution	P-value	Filtrated Solution	P-value
	% As Removed =	<0.0001 significant	% As Removed =	<0.0027 significant
Intercept	99.99		99.96	
[As]	1.775×10^{-3}		6.162×10^{-3}	

7.2.7 Comparisons of the coagulant systems

In this research different coagulants such as chromium chloride, calcium chloride and magnesium chloride were applied to select suitable ones with optimum arsenate removal efficiency. Therefore, in this study four models were derived and each was validated statistically and experimentally. Results showed that, high arsenic removals were obtained and the models are well suited to predict removal of arsenate in effluent containing high levels of arsenate. Each coagulant was efficient as individuals but chromium (III) and magnesium are the preferred coagulants due to their as high removal efficiency. Chromium chloride (III)-based and calcium chloride-(II) based as binary systems are shown to remove from 99.97% up to 99.99% of arsenate. Calcium proves less efficient removing up to 98.54% of the initial arsenic present. By combining calcium with chromium (III) this coagulant system was able to remove up to 99.99% of the

initial arsenic present. At pH 11-12 arsenic removal was more effective as it neutralizes the surface charge of arsenate but poor magnesium hydroxide settlement occurs. Below pH 11, less sludge produced but as pH increased magnesium arsenate formed.

The factor that most affected arsenic removal was found to be the initial concentration of arsenic and it plays important role in chromium (III)-based, calcium (II)-based and magnesium (II)-based coagulation. The effective range of the pH for chromium (III), calcium (II) and magnesium (II) are 5.5 - 7.5, 10.0 - 12.5 and 10.5 - 11.6 respectively. If the coagulant such as chromium (III), calcium (II) and magnesium (II) is added to water during coagulation, the pH of the water is depressed due to the presence of excess hydrogen ions. Therefore, alkali is always added to resist the pH depression that occurs during coagulation. In this case, the alkali used is NaOH. Calcium (II) and magnesium (II) are more effective in a higher pH ranges. However the amount of alkalinity required is less as compared to calcium (II).⁹ Chromium coagulation is more practical from the point of view of effluent treatment an outgoing effluent must be within a certain pH range typically 5-9. If calcium / magnesium were used then acid, (along with the disadvantage of increased cost and salt formation) will need to be added later to lower the pH to the correct range to meet effluent discharge criteria. As the part of the investigation of waste water removal, magnesium (II) chloride coagulant was able to achieve up to 99.99% arsenate removal when the pH is high enough to precipitate $Mg(OH)_2$ (i.e near pH 11). However, when only $Ca(OH)_2$ precipitated As (V) removal was between 95.00-98.00%.

7.3 Model comparison with other research work

According to Rubidge's finding As (v) can be removed effectively by coagulation with iron (III), Al (III) and binary mixtures of Al (III) and Fe (III).¹⁰ These coagulants were hydrolyzed to form hydroxides on which the As (v) was adsorbed and co-precipitated with other metallic ions. The coagulation process using aluminum sulphate and iron chloride were dependant on the initial concentration of arsenic, pH, settling time and dosage of the coagulant. Of the

two coagulants used Fe (III) was more effective than Al (III). The removal efficiencies of As (v) using ferric chloride as a function of coagulant dose, pH, initial concentration and flocculent are shown in Table 7.5 which indicates that the removal of As (v) was influenced by all factors. The percentage removal of As (v) with 450-650 mg/l iron (III) dosage at pH 6.5 produced a very good adsorption of arsenic. The Fe(OH)_3 and Al(OH)_3 precipitates were the end product of hydrolysis of coagulation using $\text{Al}_2(\text{SO}_4)_3$ and FeCl_3 . The Fe(OH)_3 floc at pH < 6.5 has positive surface charge and predominant ferric species are Fe^{+3} , FeOH^{2+} and Fe(OH)_2^+ which favor the adsorption of arsenate ions. Better arsenic removals were also obtained at pH 7.0 -7.5 where removal of arsenic took place through co-precipitates of both cations (Fe^{+3} and Al^{+3}) form and Fe(OH)_3 hydroxide and Al(OH)_3 precipitates with which arsenic co-precipitates rapidly.¹⁰ Removal of arsenic by coagulation with aluminum sulphate took place with greater efficiency at pH < 7.0 where the most effective cationic forms of aluminum are present and competition from the hydroxyl group was reduced.

The difference between the models of this research and those of Rubidge¹¹ was that the final models obtained in this research were simple with the initial arsenic concentration being the most significant factor. In contrast Rubidge's final equations are complex with more factors dictating the final arsenate level. Rubidge also concluded that pH, initial arsenate concentration, flocculent concentration has considerably had weaker influences on the response than iron (III) to arsenate mole ratio. The decantation models in Rubidge's work are more complex than the filtration system. The pH has a greater influence in decantation model and the concentration of flocculant is more significant in the filtration model. The initial arsenate concentration has considerable effect on the performance of removal of arsenic and it shows a similar effect in both models. However, percentage removal had no direct relation with initial arsenate concentration.¹¹ Table 7.9 shows the models obtained by Rubidge. It is clear that they are far more complex than the models obtained in this research.

Table 7.9: The final polynomial equation for iron (III) coagulant of arsenate with decants and filtrate as per Rubidge¹¹

Factors	Filtered Solution	Decanted Solution
	% As Removed =	% As Removed =
Intercept	94.88	95.12
pH	0.47	-1.91
[Floc]	0.86	0.29
Fe:As mole ratio	2.62	5.71
[As]	1.00	1.00
pH ²	1.24	-0.90
[floc] ²	0.75	0.54
Fe:As mole ratio ²		-1.49
[As] ²		-0.94
pH x [As]		-1.22
[floc] x Fe:As mole ratio		-1.20
[floc] x [As]	-1.65	-0.77
Fe:As mole ratio x [As]	-1.90	-1.15

7.4 COST CONSIDERATIONS

The determination of the economic feasibility of using these salts as coagulant for arsenic removal was evaluated by comparing the costs of industrial reagents grades: chromium (III) chloride cost approximately R6.50 per kg,¹² calcium (II) chloride of 25kg cost R5.85 per kg¹³ and magnesium (II) chloride of 25kg cost R8.00 per kg¹³ hence comparing chromium (III) chloride and magnesium (II) chloride as coagulants for As (v) removal chemical costs for magnesium (II) chloride were found to be approximately 1.5:1 greater than chromium (III) chloride. In this research, coagulation has offered a simple and cost effective way to remove As (V) from aqueous solution.

7.5 CONCLUSION

In this investigation, of the four coagulant systems investigated and modeled, chromium (III) chloride-based coagulation and magnesium chloride-based coagulation were shown to be the most efficient coagulants for removal of arsenate from aqueous media, although the combined chromium (III) chloride and calcium chloride system also gave very efficient arsenic removals. Calcium chloride on its own is less effective compared to the other coagulation systems.

An advantage of using chromium chloride is that it works over a wide range of pH. pH affected removal efficiency by changing the charge of the arsenate when K_{sp} being considered such as $CrAsO_4$, $Cr(H_2AsO_4)_3$, as it affects the coagulations process. According to the literature survey, calcium and magnesium actually enhanced removal of arsenate at high pH values.¹⁴ Formation of calcium arsenate solids has been observed. As (v) gets removed by $MgCl_2$ as $HAsO_4^{2-}$ at pH 11. Ca (II) and Mg (II) reduce the electrostatic repulsion for negatively charged arsenate and permit coagulation.

Comparing this work with Rubidge's work¹¹ shows that Cr (III) and Fe (III) can be regarded as the most efficient coagulants. A significant advantage of iron salts and chromium salts over aluminium, magnesium and calcium chloride is the broader pH range for good coagulation.

7.6 FUTURE RESEARCH

- To scale up and test the resultant sludges from each coagulation system for leachability with respect to arsenic and the metal ions.
- To investigate co-disposal of tannery effluent containing chrome (III) and arsenic effluent containing arsenate to study synergy in disposal.
- To develop a model suitable for lower initial arsenic concentration levels
- Repeat Rubidge's model studies at higher Fe (III) / As (v) ratios

7.7 REFERENCES

1. Spectroscopic Investigation of Cr(III)- and Cr(VI)-Treated Nanoscale Zerovalent Iron, Brucea Manning, Jonr Kiser, Hancheolkwon and Sushil Raj Kane, *Environ. Sci. Technol*, Volume 41, 2007, 586-592.
2. Effect of temperature on the removal of arsenate from aqueous solution by titanium dioxide nanoparticles, Valencia Trej, M. Villicana Mendez, R. Alfarocuevas Villanueva. M.G. Garnica Romo and R. Cortes Martinez, *Journal of Applied Sciences in Environmental Sanitation*, Volume 5, Issue 2, 2010, pp 171-184.
3. Removal of organic and inorganic pollutants from groundwater using permeable reactive barriers, Part 1. Treatment processes for pollutants, Franz-Georg Simon and Tamás Meggyes, *Land contamination and reclamation*, Volume 8, Issue 2, 2000, pp 103-116.
4. Calcium effect on arsenic (v) adsorption on coal fly ash, Tian Wang, Tingzhi Su, Jianmin Wang and Ken Ladwing, *World of coal ash*, 2007
5. Efficiency of different coagulants combination for the treatment of tannery effluents: A case study of Bangladesh, K. M. Nazmul Islam, Khaled Misbahuzzaman, Ahemd Kamruzzaman Majumder and Milan Chakrabarty, *African Journal of environmental science & technology*, Volume 5, Issue 6, 2011, pp 409- 419.
6. Solubility and stability of calcium arsenates at 25 degree, Y.N. Zhu, X.H.Zhang, Q.L.Xie, D.Q. Wang and G.W.Cheng, *Water, Air, and Soil Pollution*, Volume 169, 2006, pp 221–238.

7. High-pH–magnesium coagulation–flocculation in wastewater treatment
L. Semerjian and G. M. Ayoub, *Advances in Environmental Research*, Volume 7, Issue 2, 2003, pp 389-403.
8. Arsenic removal from drinking water by coagulation / filtration and lime softening plants, Keith A Field, Abraham Chen, Lili Wang, EPA/600/R-00/063, pp. 1- 96.
9. Arsenic disposal practices in the metallurgical industry, P.A. Riveros, J.E. Dutrizac and P. Spencer, *Research Scientist, Mining and Mineral Sciences* Volume 40, 2001, pp 395-420.
10. Arsenic removal from water using manganese greensand: Laboratory scale batch and column Studies, New Mexico State University, Water Treatment Technology Program Report, No. 41, 1999, pp 1-53.
11. Evaluation and optimization of selected methods of arsenic removal from industrial effluents by Dr Gletwyn Robert Rubidge. A dissertation submitted in fulfilment of the requirements for Doctors Degree in Technology, Chemistry. In the faculty of Applied Science at the Port Elizabeth, January 2004, Promoter Dr N Vorster, Co-promoter Prof B. Zeelie
12. Halley industrial limited
<http://madeinchina.tradekey.com/basic-chromium-chloride.htm>
13. Crest chemicals
<http://www.crestchem.co.za>
14. Arsenic Removal during Precipitative Softening, L. McNeill and M. Edwards, *Journal of Environmental Engineering*, Volume 123, Issue 5, 1997, pp 453-460.

APPENDIX 1- LIST OF FIGURES

CHAPTER 1

Figure 1.1	Acid-base chemistry of As^{5+}	7
Figure 1.2	Acid-base chemistry of As^{3+}	7
Figure 1.3	Transformation and mobilization of arsenic in the environment	11

CHAPTER 2

Figure 2.1	The calibration curve of initial concentration of MSMA.	43
------------	---	----

CHAPTER 3

Figure 3.1	Scatter diagram showing the outlier for decantation.	56
Figure 3.2	Scatter diagram show without an outlier for decantation.	57
Figure 3.3	A plot of studentized residual <i>versus</i> % normal probability for the model of chromium (III)-based coagulation of arsenate with decantation and filtration.	64-65
Figure 3.4	A plot of residual <i>versus</i> predicted for the model of chromium (III)-based coagulation of arsenate for decation and filtration.	66

CHAPTER 4

Figure 4.1	A plot of studentized residual <i>versus</i> accumulative frequency for the model of calcium (II)-based coagulation of arsenate with decantation and filtration.	79
Figure 4.2	A plot of residual <i>versus</i> predicted response for the model of calcium (II)-based coagulation of arsenate for decantation and filtration.	80-81

Figure 4.3	A half plot for the model of calcium (II)-based coagulation of arsenate with decantation and filtration.	82
Figure 4.4	Functional relationships between initial concentration of arsenic <i>versus</i> % As removed for decantation and filtration.	82
CHAPTER 5		
Figure 5.1	A plot of residual <i>versus</i> predicted response for the model of binary coagulant of chromium (III) calcium (II)-based coagulation of arsenate for decantation and filtration	93-94
Figure 5.2	A plot of residual <i>versus</i> predicted response for the model using binary coagulant of chromium (II) and calcium (II)-based coagulation of arsenate for decantation and filtration	95
Figure 5.3	A half plot for the model describing chromium (III) and calcium (II)-based coagulation of arsenate with decantation and filtration.	96-97
CHAPTER 6		
Figure 6.1	A plot of studentized residual <i>versus</i> accumulative frequency for the model of magnesium (II)-based coagulation of arsenate with decantation and filtration.	106-107
Figure 6.2	A plot of residual <i>versus</i> predicted response for the model of magnesium (II)-based coagulation of arsenate for decantation and filtration	108
Figure 6.3	A half plot for the model of magnesium (II)-based coagulation of arsenate with decantation and filtration	109-110

APPENDIX 2- LIST OF TABLES

CHAPTER 1

Table 1.1	pKa values	8
Table 1.2	MSMA material safety data sheet	9
Table 1.3	Technologies available for arsenic treatment	23-24

CHAPTER 2

Table 2.1	List of chemicals used for analysis.	34
Table 2.2	The Settings used on the Varian Spectra AA-10 atomic absorption spectrometer.	37
Table 2.3	Settings used on the ICP-AES Spectroscopy.	39
Table 2.4	Settings used on the ICP-MS.	41
Table 2.5	AAS results showing the determination of initial concentration of MSMA.	43
Table 2.6	Overview of the experimental design used in this research.	48

CHAPTER 3

Table 3.1	Natural values of experimental domain for chromium (III)-based coagulation.	51
Table 3.2	The coded design matrix for chromium (III)-based coagulation.	52
Table 3.3	The coded values of the experimental design used to optimise chromium (III)-based coagulation of arsenate solution.	53
Table 3.4	Results of the factorial design used to the model of the removal of aqueous arsenic (v) using chromium (III)-based as a coagulant.	55
Table 3.5	The initial polynomial equation that describe the chromium (III)-based removal of arsenate for decantation and filtration.	58
Table 3.6	The final polynomial equation that describe the	59

	chromium (III)-based removal of arsenate for decantation and filtration.	
Table 3.7	Definition of Anova terms.	60-61
Table 3.8	ANOVA for the factorial model describing the chromium (III)-based coagulation of arsenate for the decantation and filtration model.	62
Table 3.9	Results of the confirmatory experiments used to validate the 2^{4-1} model describing chromium (III)-based coagulation of arsenate.	69
CHAPTER 4		
Table 4.1	The experimental domain used in this study of calcium (II)-based coagulation.	73
Table 4.2	The coded values of the experimental design used to optimise calcium (II)-based coagulation of arsenate solution.	73
Table 4.3	Results of the factorial design used to model the removal of aqueous arsenic (v) using calcium (II)-based as a coagulant.	74
Table 4.4	ANOVA for the factorial model describing the calcium (II)-based coagulation of arsenate for decantation and filtration model.	74 -75
Table 4.5	The initial polynomial equation that describe the calcium (II)-based removal of arsenate for decantation and filtration.	76
Table 4.6	The final polynomial equation that describe the calcium (II)-based removal of arsenate for decantation and filtration.	77
Table 4.7	Results of the confirmatory experiments used to validate the model describing calcium (II)-based coagulation of arsenate.	84

CHAPTER 5

Table 5.1	Experimental domain used in this study of chromium (III) and calcium (II)-based coagulation of arsenate.	87
Table 5.2	The coded values of the factorial design used to optimize chromium chloride (III) and calcium chloride (II)-based coagulation of arsenate.	87-88
Table 5.3	Results of the factorial design used to model the removal of aqueous arsenate using binary mixture of chromium (III) and calcium (II)-based as a coagulants.	88
Table 5.4	ANOVA for the factorial model describing the combined chromium (III) and calcium (II)-based coagulation of arsenate for decantation and filtration.	89
Table 5.5	The initial polynomial equation that describe the chromium (III) and calcium (II)-based removal of arsenate for decantation and filtration.	90-91
Table 5.6	The final polynomial equation that describe the chromium (III) and calcium (II)-based removal of arsenate for decantation and filtration.	91-92
Table 5.7	Results of the confirmatory experiments used to validate the model describing chromium (III) and calcium (II)-based coagulation of arsenate.	98

CHAPTER 6

Table 6.1	The experimental domain used in the study of magnesium (II)-based coagulation	101
Table 6.2	The coded values of the experimental design used to optimise magnesium (II)-based coagulation of arsenate solution.	101

Table 6.3	Results of the half factorial design used to model the removal of aqueous arsenate using magnesium (II)-based as a coagulant.	102
Table 6.4	ANOVA for the factorial model describing magnesium chloride(II)-based coagulation of arsenate for decantation and filtration.	103
Table 6.5	The initial polynomial equation that describe the magnesium (II)-based removal of arsenate for decantation and filtration.	104
Table 6.7	The final polynomial equation that describe the magnesium (II)-based removal of arsenate for decantation and filtration.	105
Table 6.8	Results of the confirmatory experiments used to validate the model describing magnesium (II)-based coagulation of arsenate	111

CHAPTER 7

Table 7.1	The experimental validation for the modelling of chromium (III)-based coagulation of asrenate	115
Table 7.2	The final equations for the predicted model with their P-value for chromium (III)-based coagulation of asrenate	115
Table 7.3	The experimental validation for the modelling of calcuim (II)-based coagulation of asrenate	117
Table 7.4	The final equations for the predicted model with their P-value for chromium (III)-based coagulation of asrenate	117
Table 7.5	The experimental validation for the modelling of calcuim (II)-based and chromium (III)-based coagulation of asrenate	118
Table 7.6	The final equations for the predicted model with their P-value for calcuim (II)-based and chromium (III)-based coagulation of asrenate	119

Table 7.7	The experimental validation for the modelling of magnesium (II)-based coagulation of arsenate	121
Table 7.8	The final equations for the predicted model with their P-value for magnesium (II)-based coagulation of arsenate	121
Table 7.9	The final polynomial equation for iron (III) coagulant of arsenate with decants and filtrate as per Rubidge	124

APPENDIX 3- LIST OF EQUATION

Chapter 2	Equation 2.1	45
	Equation 2.2	46
Chapter 3	Equation 3.1	51
	Equation 3.2	51
	Equation 3.3	54
	Equation 3.4	59
	Equation 3.5	68
Chapter 4	Equation 4.1	75
	Equation 4.2	77
Chapter 5	Equation 5.1	90
	Equation 5.2	92
Chapter 6	Equation 6.1	104
	Equation 6.2	105