

Valorized Indigenous Waste Materials: Potentially Cheap and Environmentally Friendly Adsorbents for the Removal of Toxic Ions from Wastewater



Department of Chemical and Forensic Science
Doctor of Philosophy in Chemistry
College of Science

Morlu G. F. Stevens
Student ID: 13100035

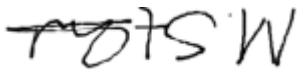
Based on research carried out under the supervision of Dr.
Bareki S. Batlokwa

A thesis submitted to Botswana International University of Science and Technology, Palapye in fulfillment of the requirement for the degree of Doctor of Philosophy in Chemistry

September 14, 2017

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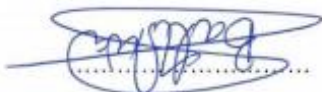
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The undersigned certifies that he/she has read and hereby recommends for acceptance by the Faculty of Science a dissertation/thesis titled: '**Valorized Indigenous Waste Materials: Potentially Cheap and Environmentally Friendly Adsorbents for the Removal of Toxic Ions from Wastewater**', in fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry of the BIUST.



Dr.
(Supervisor)

Date: 10/02/2018



Dr.
(Co-Supervisor)

Date:

DEDICATION

This thesis is dedicated to my loving wife **Mrs. Irene M. Stevens** and my beloved father **Mr. Paul F. Stevens**

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RESEARCH PUBLICATIONS

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2. Morlu Stevens, Bareki Shima Batlokwa, *Environmentally Friendly and Cheap Removal of Lead (II) and Zinc (II) from Wastewater with Fish Scales Waste Remains*; *International Journal of Chemistry*; (2017) Vol. 9, No. 4
3. Morlu Stevens, Bareki Shima Batlokwa, *Removal of Nickel (II) and Cobalt (II) from Wastewater Using Vinegar-Treated Eggshell Waste Biomass*; *Journal of Water Resource and Protection*, (2017), vol. 9, 931-944
4. Morlu Stevens, Bareki Shima Batlokwa, *Removal of Excess Toxic Chloride and Fluoride Anions from Wastewater Employing Eggshells Waste Remains*, *Journal of Open Chemistry* (2017), vol. 5 674-687
5. Morlu Stevens, Bareki Shima Batlokwa, *Removal of Toxic Sulphate and Bromate Anion from Wastewater by Vinegar-treated Fish Scales Waste Biomaterial*, *International Journal of Current Research* (2017), vol. 6 25278- 91
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7. Morlu Stevens, Bareki Shima Batlokwa, *Valorized eggshells for the Selective and Simultaneous Removal of Toxic Metallic Ions from Wastewater*, *International Journal of Environmental and Ecological Engineering* (2017), vol. 4, No. 5
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CONFERENCE PAPERS

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ABSTRACT

The aim of this thesis was to identify an abundant, easily available, cheap and environmentally friendly waste material(s) in our locality, Botswana, that could be valorized (rejuvenated) by subjecting it to a simple green procedure, then apply as an adsorbent to clean wastewater through the removal or reduction of ions Co, Ni, Zn, Cu, Hg, Cr, Ag, Fe, Pb, Al, As, Cd, Sn, Ti, Mg, F⁻, Cl⁻, SO₄²⁻, PO₄³⁻, NO₂⁻, BrO₃⁻, and NO₃⁻ that usually exist in wastewater. After an extensive search, eggshells and fish scales proved to be the most readily available and abundant. These waste remains were independently pulverized to attain uniform sized particles with increased surface area to volume ratio needed for efficient adsorption of the targeted ions. The particle sizes of the pulverized waste powders estimated from both the Laval standard sieves and the scanning electron microscope micrographs were found to be $\leq 10\ \mu\text{m}$ in each case, with spherical geometry and rough morphology, good features usually exhibited by good sorbents. The materials were further valorized by an optimal quantity (150 mL of vinegar for 80 mg of the valorized waste materials) of 12.7% vinegar for an optimal time (74 min). The procedure led to valorized waste materials (VWMs) with exposed functional groups on the surface of the waste powder particles that were attributed to the vinegar treatment and were thought to be the ones responsible for binding the targeted ions present in wastewater. Minitab 14 software was employed for the simultaneous modeling of the parameters of factors that affect sorption studies that included initial ion concentration, sorbent dose, contact time and solution pH which were found to be $\leq 28.44\ \text{mg/L}$, $\leq 84.29\ \text{mg/L}$, $\leq 88.63\ \text{min}$ and ≤ 8.75 respectively. Employing the optimized conditions, the VWMs exhibited high percentage removal efficiencies toward removing the selected ions from raw wastewater samples averaging 92.13 % with %RSD < 2 for n = 3(triplicate). Fourier transform infrared spectrometer, X-ray diffractometer and Raman spectrometer spectra of the VWMs displayed multiple functional groups such as amines, carboxylic, hydroxyl, and carbonyls which are well known to bond well with ions through hydrogen and oxygen bonding, as well as hydroxyapatite and calcite known to be a good ion-exchanger. Furthermore, the calculations and assessment of the kinetic and thermodynamic parameters of the adsorption of the selected ions by the VWMs showed that the adsorption process fitted the Langmuir isotherm model ($R^2 \sim 1$), fitted pseudo second order kinetics, was found to be spontaneous and endothermic respectively. All in all, the proposed VWMs with their high comparable percentage removal efficiencies, low cost (since they are collected from waste) and their environmental friendliness (since they are bio-materials thus biodegradable) presented themselves as potential replacements of the expensive, non-environmentally friendly, commercial adsorbents (represented by charcoal in this thesis) that are commonly employed for the removal of toxic ions from wastewater in wastewater treatment plants.

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CHAPTER ONE: BACKGROUND

1.0 Introduction

Fresh water for human, agricultural or industrial use is a scarce resource. Consequently, the use of treated wastewater effluent is currently, widely employed to compensate for the scarcity of safe and uncontaminated freshwater [1]. Wastewater treatment facilities have been set up to clean and recycle wastewater for use in irrigation, animal consumption, groundwater recharge, non-potable reuse and domestic activities [2]. However, the existence of toxic contaminants such as high concentrations of heavy metal ions (cations) and inorganic anions in the effluent pose a health hazard to animals and the environment [3]. Agricultural activities, discharge of untreated sanitary, toxic industrial wastes and household effluent, have constantly increased the addition of toxic inorganic ions in the aquatic ecosystems [4]. Such effluents containing toxic ions cause detrimental effects on all forms of life upon direct discharge to the environment and because of their toxicity and strong tendency to concentrate in the environment and food chains, have long lasting hazardous effects to the environment [5] [6]. Thus, it is essential that the concentration of contaminants in recycled wastewater be considerably reduced to acceptable levels as set out by international monitoring agencies such as the World Health Organization (WHO) [7], Food Agriculture Organization (FAO) [7] and Environment Protection Agency standard (EPA) [7].

In the past, several methods such as membrane assisted liquid extraction (MALE) [8] [9] liquid–liquid extraction [10] [11], membrane filtration [12] [8]; ion exchange [13] [14], adsorption [15] [16], chemical precipitation [17], electroplating [18], and evaporation [19] have been employed to remove pollutants, especially toxic ions within wastewater effluents [20]. However, these methods have been reported to have some challenges such as high cost [21] [22], requiring trained personnel [23], high energy consumption [8], using large quantities of chemicals [24] [25], poor removal rate that do not meet the pollution control limits [21] [26], low mechanical strength of adsorbents [11], weak hydrothermal stability [27], poor selectivity [28], time consuming [29] [30] and are often not easy to roll out to ordinary citizens especially in rural areas. Thus, our attempt in this thesis to consider naturally occurring, environmental friendly, readily available and cheaper indigenous knowledge based alternative materials that can decontaminate wastewater to a level where it can be useful to plants and animals. In this thesis,

we have identified such materials as eggshells and fish scales, normally thrown away. The waste materials were minimally pre-treated, physically and chemically characterized and applied to wastewater to evaluate their capability and performance to remove high levels of toxic ions that usually characterize wastewater.

1.1 Scope and Significance of the Thesis

The studies conducted in this thesis aimed at employing readily available and minimally pre-treated indigenous waste materials to provide relatively cheaper and effective solutions of removing contaminants, in particular high concentrations of ions that are usually present in wastewater. The realization of this project resulted in the tandem effect of valorizing, recycling and managing waste. Most inhabitants of the rural areas do not have access to the expensive conventional treatment technologies that are usually employed to purify wastewater such as gray-water for reuse for household or farming purposes. This implies that their health is at risk as a result of possibly consuming or their animals, water that is contaminated with high concentration of toxic ions. However, the availability of our minimally treated, eggshell and fish scale waste remains would alleviate the challenge of the removal or reduction of the high concentrations of ions and other associated contaminants that usually characterize wastewater, thus improving lives of communities through science. The findings of this research will be useful in developing and packaging minimally pre-treated eggshell and fish scale waste remains as an efficient, cheap, environmental friendly means of water purification for domestic and agricultural use.

1.2 Objectives

The thesis was set out to:

- Identify abundant, non-toxic, eco-friendly and easily available waste material(s) in our locality, Botswana.
- Valorize the waste materials employing simple green method(s).
- Optimize, characterize and evaluate the valorized waste materials (VWMs).

- Apply optimized parameters to evaluate the performance of the VWMs on a real, raw wastewater samples.

CHAPTER TWO: LITERATURE REVIEW

2.0 Wastewater

Wastewater refers to all seepage from household, hospitals, industries, commercial facilities, institutions and agricultural effluent [31] [32]. It also includes water from roof drainage, surface runoff, storm-water, urban runoff and sewage. Sewage refers to wastewater originating from toilets and bathroom fixtures, bathing, laundry, kitchen sinks, cleaners, and dirty water that is produced in households and public places [33]. Wastewater is categorized into three main categories, namely; black-water, gray-water and yellow-water [2].

Black-water refers to wastewater originating from toilet fixtures, dishwashers and food preparation sinks. It is usually highly contaminated with dissolved chemicals, particulate matter and is very pathogenic [1]. Gray-water, on the other hand, refers to wastewater that originates from bathroom sinks, laundry machines, sanitariums and bathtubs. It is considered a sewage that does not contain human waste (poop or urine). It is treated very differently from black-water and is usually suitable for re-use relative to black-water [34]. Meanwhile, yellow-water is essentially urine collected from specific conduits such as urinal and is usually not contaminated with either black-water or gray-water.

Due to shortage of freshwater and continuous water pollution the world over, many countries such as India and Tanzania, have now resorted to recycling wastewater to compensate for the shortage [2]. Therefore, a lot of research is now focused on cheaper strategies of recycling wastewater.

2.1 Recycled Wastewater Quality Parameters

Recycled wastewater quality refers to the value of wastewater to humans, animals and industrial usage as it relates to its physicochemical and microbiological characteristics [35][36]. In order to monitor wastewater quality for future use, there are parameters that national and international monitoring agencies such as Botswana Bureau of Standards (BOBS) [2], World Health Organization (WHO) and the United States Environmental Protection Agency (US-EPA) [32]

have set maximum acceptable levels for some wastewater quality parameters and in some cases have developed binding standards for wastewater quality.

Wastewater quality parameters are generally divided into physical, chemical and biological [37]. Physical water quality parameters include temperature, salinity and turbidity [22]. Biological include pathogens and indicator microorganisms [38] whilst chemical parameters include pH, dissolved solids, chemical oxygen demand, and conductivity [39]. In this thesis, a new, eco-friendly strategy for the improvement of the chemical wastewater quality parameters by removing or reducing the dissolved solids in the form of inorganic ions that are known to bio-accumulative and pose detrimental effects to animal, human and plant life due to their toxicity at relatively high concentrations is extensively studied.

2.1.1 pH

pH is a measure of a solution's acidity or alkalinity [20]. In water, small numbers of water molecules (H_2O) break apart or dissociate into hydrogen ions (H^+) and hydroxide ions (OH^-). Other compounds entering the water may react with these, leaving an imbalance in the numbers of hydrogen and hydroxide ions [40]. A large variety of aquatic organisms prefer a pH range between 6.5 and 8.0. The World Health Organization (WHO) and Environmental Protection Agency (EPA) have set their maximum acceptable limit for wastewater at pH 6.5 [41]. The EPA, has reported that a pH of 5.0 - 6.0 or lower is directly toxic to fish [42].

The pH of wastewater is also employed by biologist to determine the quantity of bacterial and organic matters present in wastewater effluent. For example, Travis Brand reported via Advanced Chemical Systems (ACS), that the pH of water can be employed to kill bacteria in wastewater. He pointed out that most organic matter and bacteria are best suited to a neutral pH, (pH 7.0) or slightly basic environment (pH 7.5 – 8.5). At an acidic pH, the excess hydrogen ions form bonds with the cell of the bacteria, which retard their growth or out rightly kill them. He concluded that after each wastewater treatment cycle, the pH must be adjusted to 6.5 or 7.0 to prevent damage to any living cell that consumes it [43].

The pH of water determines the solubility, toxicity and biological availability of chemical constituents [44]. For example, the degree to which heavy metals are soluble determines their

toxicity [45]. They tend to be more toxic at lower pH because they are more soluble [46]. Considerable changes in the wastewater pH usually occur as a result of industrial discharges. This in turn makes the water unsuitable for use [47].

2.1.2 Total dissolved solids

Total dissolved solids (TDS) is a measure of dissolved matter such as salts, organic matter and minerals in wastewater [34]. The total concentration of TDS is mostly made up of inorganic ions [48]. TDS can be naturally present in wastewater or as a result of human activities such as mining, oil, gas drilling, industrial and municipal treatment of water [49]. Under the United States of America (USA) federal safe water act, the U.S. Environmental Protection Agency (US EPA) classifies TDS as a secondary maximum contaminant level (sMCL). The US EPA recommends the maximum level of wastewater effluent sMCL of 900.00 mg/L [50]. TDS is not expected to harm human health at this sMCL, although may negatively affect the taste of recycled water. At elevated levels, TDS may damage water treatment equipment, reduce the effectiveness of treatment of other contaminants and as a result pose a serious health challenge to animals and humans. The toxicity of wastewater associated with high TDS results from increase in the wastewater salinity, changes in its composition, or the presence of other toxic substances. For example, TDS constituents such as arsenic, lead, and nitrate are known to cause serious health issues in animals, humans and plants at high concentration [45]. Due to the hazardous effect of high TDS levels on plants, the Food and Agricultural Organization (FAO) of the United Nation have set a maximum acceptable limit for TDS in wastewater effluent at 850 mg/L [1].

The total dissolved solids concentration is related to conductivity of water, but the relationship is not constant [49]. The relationship between total dissolved solids and conductivity is a function of the type and nature of the dissolved cations and anions in the wastewater and possibly the nature of any suspended materials [34]. Conductivity is measured through the use of a conductivity meter and is usually about 100 times the total cations or anions expressed as equivalents. TDS of wastewater is usually 0.5 to 1.0 times the electrical conductivity [39].

2.1.3 Conductivity

Conductivity is a measure of the ease with which water conducts electricity and as such it gives an indication of the total dissolved salt (TDS) content of the water [45]. The conducting ions come from dissolved salts and inorganic materials such as alkalis, chlorides, sulfides and carbonate compounds. The higher the concentration of the ions in wastewater, the higher the conductivity of the water. Conductivity of wastewater is mostly influenced by wastewater from sewage [39], urban runoff from roads (especially road salt) [11] and agricultural runoff with extremely high levels of dissolved salts from fertilizers [32][51]. The acceptable maximum levels of wastewater effluent conductivity as set out by the World Health Organization (WHO) is 2.50 dS/m [1]. It has been reported that the consumption of water with conductivity levels above 2.48 dS/m have detrimental effects on infants [49]. Adverse effects may include imbalance of salt and water in infants, heart patients and individuals with high blood pressure, and renal diseases [38].

2.1.4 Dissolved Oxygen

Dissolved oxygen (DO) refers to the relative measure of oxygen dissolved in wastewater available to sustain life, including living bacteria [38]. There are two main sources of dissolved oxygen in water, being atmospheric oxygen and oxygen from the aquatic plants as they photosynthesized [52]. The quantity of oxygen that can be dissolved in water is limited by physical conditions such as temperature and atmospheric pressure [53].

The most frequently employed unit of measure for dissolved oxygen in wastewater is parts per million (ppm), which is the number of oxygen (O_2) molecules per million total molecules in a sample. Percent saturation is another way of expressing dissolved oxygen levels. Percent saturation is the measured dissolved oxygen divided by the greatest quantity of oxygen that the water can hold at a particular temperature and atmospheric pressure, multiplied by 100% [36]. The concentration of dissolved oxygen in wastewater directly affects the existence of living organisms. For example, fish growth and activity usually require 5.0 – 6.0 mg/L of dissolved oxygen. Dissolved oxygen levels below 3 mg/L are deadly to most aquatic organisms. Levels below 2 mg/L will not support fish at all [54].

Low dissolved oxygen concentrations result from elevated temperature and excessive demand on the oxygen in the system, hence, the inability of the water to hold the available oxygen. Some pollutants such as acid mine drainage produce direct chemical demands on oxygen in the water for certain oxidation-reduction reactions [55] [56].

2.1.5 Turbidity

Turbidity refers to the transparency (clearness) of water. The greater the quantity of total suspended solids (TSS) in the water, the cloudier it appears and the higher the measured turbidity [34]. The major source of turbidity in open wastewater systems is phytoplankton. However, clays and silts from erosion, suspended bottom sediments and organic detritus from wastewater discharges are also sources of wastewater turbidity [45]. Dredging operations, channelization, increased flow rates, floods, or bottom-feeding fish such as carp may stir up bottom sediments and increase the cloudiness of water [42].

High concentrations of particulate matter can modify light penetration, cause smother benthic habitats thus, impacting both organisms and eggs. As particles of silt, clay, and other organic materials settle to the bottom, they can suffocate newly hatched larvae and fill in spaces between rocks which could have been used by aquatic organisms as habitat. Fine particulate material also can clog or damage sensitive gill structures, decrease their resistance to disease, prevent proper egg and larval development, and potentially interfere with particle feeding activities [57].

Turbidity often adds real costs to the treatment of surface water supplies used for drinking water since the turbidity must be virtually eliminated for effective disinfection of water usually by chlorine [58]. Pollution tends to reduce water clarity. Watershed development and poor land use practices cause increases in erosion, organic matter, and nutrients, all of which cause increases in suspended particulates and algae growth [51]. Particulates also provide attachment sites for heavy metals such as cadmium, mercury and lead, and many toxic organic contaminants [59].

2.1.6 Nutrients

Nutrients are substances that provide nourishment that is essential for the maintenance of life and growth. The most common examples of wastewater nutrients are nitrogen and phosphorous. Most nutrients in wastewater exist naturally in different forms or are converted to different forms. It should be noted that, a particular form may be toxic to an organism, but essential to another [5].

Nitrogen

Nitrogen is an essential nutrient that is required by all plants and animals for the formation of amino acids [60]. In its molecular form, nitrogen cannot be used by most aquatic plants, therefore it must be converted to another form; for instance, ammonia (NH_3). Ammonia on the other hand, may be taken up by plants or oxidized by bacteria into nitrates (NO_3^-) or nitrites (NO_2^-) [61]. Of these two forms, the nitrate is usually the most important, as it is more soluble and the one that is mostly used during photosynthesis. Excessive concentrations of nitrogen can lead to eutrophication and subsequent degradation of wastewater quality which result in high cost of recycling the wastewater. In addition, if water containing a nitrate concentration higher than 10.00 mg/L is used to prepare infant formula, it can result in methemoglobinemia [62].

Phosphorus

Phosphorus is essential for metabolic reactions of plants and animals. Once it enters wastewater systems, it quickly bonds to the fine suspended soil particles, making it temporarily unavailable to living organisms [55]. Since it occurs naturally in low levels, it is often the growth-limiting factor for plants. Phosphorus occurs in several forms, inorganic and organic. Inorganic orthophosphate (PO_4^{3-}) is the only form available to living organisms. However, the other forms of phosphate can be transformed into orthophosphates. For this reason, total phosphate is generally measured in addition to orthophosphate [63]. The measure of total phosphate provides an estimate of the amount of phosphorus potentially available to plants and animals. Since the phosphorus requirements of algae are minimal, rapid algal growth occurs when excess phosphorus is present in wastewater [64]. Common sources of excess phosphorus include

agricultural runoff from feed lots and fertilized fields, and sewage that contains organic phosphorus as well as inorganic phosphorus in products such as detergents. The resulting algal bloom can lead to eutrophication and the subsequent degradation of water quality which result in high cost of recycling the wastewater [56].

2.2 Composition of Raw Wastewater

Generally, the composition of wastewater is characterized by the presence of (i) macro-solid materials, mostly synthetic polymers such as plastics, sanitary napkins as well as debris; (ii) dissolved organic compounds such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) as well as dioxins; and (iii) dissolved inorganic ions such as methyl mercury, ferric and ferrous, mostly from leached fertilizers and manufacturing industries. These compounds are referred to as pollutants or contaminants of wastewater especially when present in concentrations that are higher than the critical or maximum levels set by international health monitoring agencies. A 1969 United Nations report define wastewater pollution as: “The introduction by man, directly or indirectly, of substances or energy into the marine environment resulting in such deleterious effects as harm to living resources, hazards to human health, hindrance to marine activities, including fishing, impairment of quality for use of wastewater and reduction of amenities” [65]. The main sources of these pollutants are from households, hospitals, commercial facilities, institutions, agricultural effluent and industrial waste [11]. Each year, the world generates 5–10 billion tons of industrial waste, most of which is pumped untreated into rivers, oceans, and other waterways [66]. Factories and industrial activities have been identified as major sources of water pollution due to the large quantities of chemical waste they produce and release into the environment [67].

2.2.1 Macro-solid Materials

Macro – solid materials in wastewater consist of insoluble solid debris, non-biodegradable synthetic polymers such as plastics, food containers, sanitary napkins, nappies/diapers, condoms, needles, children's toys, dead animals or plants, cigarettes, glass and metals. These solid materials are essential to our daily lives but become hazardous when they become waste within

the aquatic system [68]. For example, common plastic made from polythene, a compound which is part of almost every manufactured object, is non-biodegradable, light and floats easily, thus can travel enormous distances across the environment, threatening lives of many organisms as it gets in contact with them. Recent studies have shown the leaching of toxic, carcinogenic compounds such as bisphenol A (BPA) and dioxins from plastic food/beverage containers into surrounding water bodies including wastewater, thus rendering the water toxic for animal and human consumption [60]. Furthermore, some macro-solid materials pose physical challenges to birds, fish, and other aquatic creatures. For example, fishing lines and other debris found in wastewater strangle or choke fish as they move about the water or mistake it for food [69]. Because of their macro-solid nature, they are usually removed from wastewater via conventional filtration during recycling of water.

2.2.2 Organic Compounds

These are carbon based compounds that are biodegradable through oxidation by microorganisms excluding the inorganic carbon based compounds. Examples include; polychlorinated biphenyls (PCBs), polyaromatic aromatic hydrocarbons (PAHs) and dioxins which many international health monitoring agencies have categorized as organic pollutants [70]. Due to their numerous applications in human activities, organic compounds end up in wastewater. In high concentration, they cause an increase in turbidity and decrease the quantity of dissolved oxygen. Exposure of these compounds to humans and animals has major health consequences. For instance, PAHs have been reported to be highly toxic, mutagenic and carcinogenic to microorganisms and to higher forms of life including humans [9].

Due to their stability and unreactive nature, PCBs have been used as hydraulic fluids and coolant in transformers and plasticizers in paint. However, they have been found to cause chronic effects to the nervous system [71]. Dioxins on the other hand, accumulate in the food chain, mainly in the fatty tissues of animals. Studies have shown that they can cause reproductive and developmental problems, damage the immune system, interfere with hormones and also cause cancer.

There have been several researches (see Table 2.1) and numerous initiatives by international agencies geared toward removing or reducing organic pollutants from the environment including wastewater [72] [25]. For example, in 1990, the US-EPA set up a research lab; National Risk Management Research Laboratory (NRMRL), to exclusively focus on bioremediation strategies for the reduction of pentachlorophenol (PCP) and polycyclic aromatic hydrocarbons (PAHs) in soil and ground water in the United States of America. In 1995, the NRMRL launched the Bioremediation Field Initiative (BFI) which employed three effective methods; surface soil bioremediation, aboveground fixed-film bioreactor and in situ bioremediation for reduction/removal of PCP and PAHs from the soil and ground water [73]. To date, the methods are still being employed by the United Nations Environmental Programme (UNEP) in Asia, Africa and Eastern Europe (regions with high levels of PAHs and PCP) to remove/reduce the toxic organic pollutants [74].

Table 2.1: Effective removal methods for toxic organic pollutants from water.

Applications/Methods	Examples of Materials	Some of their Novel Properties
Adsorption	CNTs/nanoscale metal oxide and nanofibers [75]	High specific surface area and assessable adsorption sites, selective and more adsorption sites, short intraparticle diffusion distance, tunable surface chemistry, easy reuse.
Disinfection	Nanosilver/titanium dioxide (Ag/TiO ₂) and CNTs [76]	Strong antimicrobial activity, low toxicity and cost, high chemical stability ease of use.
Photocatalysis	Nano-TiO ₂ and Fullerene derivatives [77]	Photocatalytic activity in solar spectrum, low human toxicity, high stability and selectivity, low cost.
Membranes	Nano-Ag/TiO ₂ /Zeolites/Magnetite and CNTs [78]	Strong antimicrobial activity, hydrophilicity low toxicity to humans, high mechanical and chemical stability, high permeability and selectivity, photocatalytic activity.
Ozonation	Ozone-air or ozone-oxygen mixture [79]	Low toxicity, effective and easy to use.
Reverse Osmosis	Polyamide thin film composite [8]	Selective, chemically stability, strong antimicrobial activity.
Advanced oxidation processes	Natural bacterial strain [80]	High permeability, photocatalytic, readily available and low cost.

2.2.1.3 Dissolved Inorganic Ions

Human activities such as fertilizer and pharmaceutical manufacturing industries, mining, chemical storage sites and commercial enterprises as well as anthropogenic activities leach high concentrations of inorganic ions in the form of cations and anions into wastewater [55]. Inorganic ions are non-biodegradable, implying that they accumulate over time. Consequently, their concentration in wastewater increases gradually to high toxic levels thereby causing adverse health effects on exposure to humans and animals. These effects may include cancer, organ damage, nervous system damage, growth and development retardation, and in extreme cases, death [81] [82].

Dissolved inorganic ions in wastewater directly contribute to the total dissolved solids (TDS) and conductivity wastewater parameters. In high concentration they increase the wastewater TDS and conductivity to beyond acceptable levels. A study conducted by Uwidia *et al* established that the relationship between electrical conductivities and total dissolved salts concentration of raw domestic wastewater in Warri, Nigeria was linear [83]. Even though many countries and international health monitoring bodies such as WHO have established maximum contaminated level (MCL) standards for most toxic dissolved inorganic ions and the save use of wastewater as summarized in Table 2.2, there has been relatively limited research, geared towards removing/reducing the dissolved inorganic ions component of wastewater despite their toxicity. Thus, our endeavor through this thesis to initiate research geared towards developing innovative, cheap and environmental friendly materials based on valorizing any available and abundant waste materials in a locality to clean wastewater [4].

Table 2.2: WHO guidelines for the most toxic dissolved inorganic ions in wastewater and their potential health effects on human beings [6].

	Ions	MCL (mg/L)	Potential Effects of Excessive Discharge
1	Total Mercury	0.05	Kidney damage
2	Total Cadmium	0.1	Kidney damage
3	Total Chromium	1.5	Allergic dermatitis
4	Chromium (IV)	0.5	Under evaluation
5	Total Arsenic	0.5	Skin damage, inflammation of the circulatory system

	Ions	MCL (mg/L)	Potential Effects of Excessive Discharge
6	Total Lead	1.0	Delays in physical or mental development of infants/children, kidney problems and high blood pressure
7	Total Nickel	1.0	Lung inflammation and damage to the nasal cavity
8	Total Beryllium	0.005	Intestinal lesions
9	Total Silver	0.5	Skin discoloration
10	Chloride	250.0	hypertension
11	Fluoride	2.0	fluorosis
12	Sulfate	250.0	Dehydration
13	Nitrate	10.0	Methemoglobinemia or blue-baby syndrome

2.3 Methods for Wastewater Treatment

Treatment of wastewater involves decontamination, removal or reduction of excess wastewater constituents, most of which are toxic. In order to reduce the toxicity and contamination of wastewater and improve recycled effluents, researchers have over the last few decades prioritized pollution control and treatment of wastewater. As a result of tireless efforts, a number of methodologies with varying degrees of effectiveness have been developed and employed. Some of them includes membrane process [35], chemical coagulation [49], ion exchange [84], membrane assisted liquid extraction [85], chemical precipitation [7] and adsorption [68]

2.3.1 Membrane Process

Membrane process is an extraction method that involves the employment of a membrane as a selective barrier between two phases; the donor phase (sample) and the acceptor phase, which often consists of an aqueous or organic solvent [86]. Target analytes permeate from the sample through the membrane into the solvent. In this method, a liquid sample is in contact with a membrane made of semi-permeable material such as Teflon or silicone rubber [24]. There are two types of membranes that can be used; the porous and non-porous. Porous membrane has two phase solutions on either side of the membrane in physical contact through the pores of a

membrane while the non-porous membrane forms a separate phase (polymeric or liquid) between the donor and acceptor solutions [87].

For example, Ulbricht *et al* employed the metal oxides/Polyether sulfone (PES) [$\text{Al}_2\text{O}_3/\text{PES}$ and ZrO_2/PES] membranes for the extraction of the toxic ions; Cr^{3+} , Cd^{2+} and Pb^{2+} from wastewater. The membranes were employed as filters to trap ions and any undesired components thus preventing them from penetrating the pores of the membrane. The membrane demonstrated selectivity towards the desirable analytes of interest by allowing them through the pores and remove the toxic ions and the undesirable components [8]. However, high production and installation costs have hindered the full-scale application of this effective membrane process. Another example of membrane process is the membrane assisted liquid extraction (MALE) which is a three-phase extraction procedure that mimics the principles of liquid/liquid extraction (LLE), but with the addition of a membrane, partitioning the two liquid phases [88]. The membrane serves as a semi-permeable barrier separating two phases of different composition and is often used in separation and purification schemes. Among the popular membrane processes, liquid membrane (LM) is one of the important configurations which is further classified into bulk liquid membrane (BLM), and solid liquid membrane (SLM) [89].

Due to industrial suitability for continuous processing, the MALE configuration of SLM with hollow fiber membrane has been the most widely deployed in chemical, environmental and nuclear applications. SLMs are particularly important in instances where contaminant concentrations are extremely low and large volumes of solutions need to be processed [7]. The specific advantages of SLM based separation process are (a) high feed to strip volume ratio, (b) very low extractant (carrier) inventory, (c) no phase separation problem occurs as the organic and aqueous phases never mix, (d) negligible organic phase entrainment in the feed and strip aqueous solutions and (e) no moving parts. However, MALE has challenges of selectivity, automation, the use of non-environmentally friendly solvents (organic solvents) and high cost [90].

2.3.2 Ion Exchange

Ion exchange (IE) is an extraction technique that requires the interchange of ions between an adsorbent and the surrounding medium. Adsorbents employed are totally insoluble in most aqueous and organic solutions. They are usually constructed spherically, and are stress and strain free to resist physical degradation. They are stable at high temperatures and applicable over a broad pH range. IE adsorbents consist of cross linked polymer matrices to which charged functional groups are attached covalently. The ion exchangers which contain cations or anions as counter-ions are called cation exchangers or anion exchangers, respectively. In ion exchange extraction, a reversible interchange of ions between the solid and liquid phases occurs. An adsorbent removes ions of like charge in a chemically equivalent quantity without any morphological alterations of the adsorbents.

Ion exchange applications can be performed by column (flow continuous) and batch technique mode. In the flow continuous mode, the adsorbent is packed in the column and the aqueous medium is allowed to flow through it, whilst, in the batch mode, the adsorbent is sprinkled in the wastewater body and left for some time to equilibrate before it is reclaimed through filtration as a residue for regeneration and subsequent re-use. The batch mode is widely employed due to its simplicity and ease of application. For example, Dowex M 4195 and Diphonix resins were employed in the batch mode to evaluate their effectiveness in removing the toxic heavy metal ions; Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} in wastewater in the presence of complexing agents of a new generation; Baypure CX 100 (IDS) and Trilon M (MGDA) in comparison to reduction and precipitation removal techniques. The experiments were conducted in three parallel series with the reproducibility of the measurements within a % relative standard deviation (%RSD) of 95% for replicate measurements. Although ion exchange resins have proved to possess higher capacities for the removal of undesired components, their usage requires several pre-treatment procedures and specialized apparatus, thereby leading to high installation and operation costs [47][18].

2.3.3 Chemical Coagulation

Chemical coagulation is a unit process employed for the removal of colloidal solids from wastewater effluents. It involves: (i) the addition of chemicals as slurries, solutions or in a dry

form; a rapid mix to quickly disperse the chemicals throughout the effluent, (ii) flocculation (floc) or a slow agitation period to badge floc growth and agglomeration of particles, and (iii) separation of solids and liquid phases [49]. The main mechanisms of removal of pollutants by coagulation includes: the direct adsorption of pollutants (anion) in the hydrolysis products of the coagulant (cation), the formation of precipitates with the coagulant (metal salts), and the combination of the interaction and the adsorption of flocculated particles [7].

In the recent past, a successful coagulation/flocculation (Coag/Floc) and dissolved air flotation (DAF) using a pilot-scale wastewater reclamation plant in a high-tech industrial park in Gaborone, Botswana was employed to investigate the feasibility of improving the removal of the challenging high concentrations of anions from the secondary recycled effluent [91]. The pilot plant was equipped with units of Coag/Floc, DAF, activated carbon beds (AC), micro- filtration modules (MF) and a reverse-osmosis membrane (RO). It was operated in-situ continuously for around one year to evaluate the performance of anion removal in the two processes that were employed; the AC-RO process and the DAF-AC-RO process. Comparison of the performance of Coag/Floc-DAF-AC units in the DAF-AC-RO process with that of a single AC unit in the AC-RO process demonstrated that adding Coag/Floc-DAF units increased the removal efficiencies of the anions; phosphate, fluoride and silicate by approximately 70.0%, 42.7% and 70.1%, respectively. Most of the phosphate and fluoride were removed in the Coag/Floc-DAF units, while most of the silicate escaped from the Coag/Floc-DAF units, and was adsorbed and/or trapped in the AC unit [49].

The chemicals that are often employed in the process are: (i) the salts of a trivalent metal such as iron and aluminum, (ii) a control chemical for pH and alkalinity (mostly lime), and (iii) a coagulant aid such as activated silica or a polyelectrolyte [92].

Although, chemical coagulation has its degree of effectiveness, it also has a great deal of challenges. Too little chemical addition will not provide the desired quality whilst overfeeding of the chemicals will be a waste and may result in interference with filtration resulting in undesirable chemical residuals in the plant effluent [93].

2.3.4 Chemical Precipitation

Chemical precipitation is the most common method for removing dissolved ions from wastewater solution containing toxic ions. To convert the dissolved ions into solid particle form, a precipitation reagent is added to the mixture. A chemical reaction, triggered by the reagent, causes the dissolved ions to form solid particles. Filtration can then be used to remove the particles from the mixture [94]. The process is dependent upon the kind of ions present, the concentration of the ion, and the kind of reagent used. In hydroxide precipitation, for instance; a commonly used chemical precipitation process, calcium or sodium hydroxide is used as the reagent to create solid metal hydroxides. However, it can be difficult to create hydroxides from dissolved metal particles in wastewater because many wastewater solutions contain mixed metals [95].

Precipitation applications can be found in every sector where ions are found in the wastewater. For examples, (i) for surface water treatment on dissolved metals ions; milk of lime precipitation or for extreme cases, sulphate precipitation for end-of-pipe wastewater purification is employed. If milk of lime is employed, then the anions; fluoride, phosphate and sulphate can be removed simultaneously [96], (ii) in addition to end-of-pipe purification, precipitation can also be integrated into the process, for example, metal recuperation in rinse water from electrolysis processes or Fe removal from flux baths in thermal galvanization [97], (iii) precipitation is a suitable technique for the recuperation of silver from concentrated solutions (fixing baths) in the graphics sector [98], (iv) Precipitation is also applied when processing mineral products, including for the removal of metal ion and the anion; fluoride during purification of mica minerals [49]. Although chemical precipitation has proven to be effective, its application has some drawbacks including; relatively high effluent concentrations, the disruptive influence of surface-active substances and complex formers, high precipitant cost and toxic sludge formations [99].

2.3.5 Adsorption

Adsorption is the adhesion of molecules of dissolved solids to a surface which is usually referred to as an adsorbent. This process creates a film of the adsorbate (the adsorbed molecules) on the surface of the adsorbent. Adsorption can be a potential alternative to traditional treatment

processes of ions removal as it exhibits excellent characteristic for removal of ions. The process involves the use of synthetic materials [79] [100] or biomass [67] as adsorbents. However, the use of synthetic materials has some limitations including; the use of toxic chemicals as reagents, the production of toxic sludge and high cost, despite their excellent effectiveness. On the other hand, biomass which is environmentally friendly and cheaper has been employed to remove undesired materials from wastewater. For example, potato peel waste has been employed for the removal of Cr (VI) from aqueous solutions [95], untreated *Cocos nucifera* was employed for the removal of sulfate from industrial wastewater [55], orange peel has been found to be very effective for the removal of dissolved salts from water [13], crab shell has been employed for the removal of nickel and arsenic from wastewater[101], untreated coffee grounds, for the removal of mercury from environmental runoff [102], microbial cell, fungi and algae have been employed to remove heavy metals from wastewater [103][104][105], moss and yeast was employed for the removal of Cr(III) and Cr(VI) in water [106][60].

The use of biomass has proved to be an excellent way to treat industrial waste effluents, offering significant advantages such as the low-cost, availability, profitability, ease of operation and excellent efficiency [64] [95] [107]. Despite these advantages, the use of biomass to remove undesired materials from wastewater, especially dissolved ions has not been extensively applied. This is because biomass is often locality specific and as such, a certain biomass might not be available to be applied even though it would have demonstrated excellent performance in removing undesired species elsewhere [60] [108]. Thus, this thesis aimed at identifying biomass waste that is readily available in Botswana, after which it was valorized and applied as an adsorbent for the reduction or removal of toxic ions from household or even wastewater in general.

2.3.5.1 Factors Affecting Adsorption

Adsorption process of ions in wastewater is directly or indirectly influenced by operational parameters such as: contact time, ions concentration, surface area (particle size), temperature, and pH. Adjustment of any or all of these parameters increases or decreases the rate of adsorption of ions from wastewater.

pH

The pH value of the ions solution directly affects the whole adsorption process and particularly the adsorption capacity. The pH of the solution affects both the chemical interactions and the surface binding sites of the adsorbents. The effect of pH depends on the charge on the surface of the adsorbent. For example, if the adsorbent surface is negatively charged, at lower pH, the large number of H^+ ions present will neutralizes the negatively charged adsorbent surface. Hence diffusion interference is reduced and a better adsorption is obtained. If the surface charge of the adsorbent is positively charged, the H^+ ions may compete effectively with the cations of the solution causing a decrease in the quantity of metal ion adsorbed which might then lead to the high adsorption of anions [109] [110].

Contact Time

The quantity of ions adsorbed on to the adsorbent is always in the state of dynamic equilibrium with the quantity desorbed. The time required to attain this state of equilibrium is termed as the equilibrium time [111]. The quantity adsorbed at the equilibrium time reflects the maximum adsorption capacity.

Temperature

An increase in temperature, results in an increase in adsorption. The Le Chatlier's principle explains the fact that heat is adsorbed in the process of adsorption. As in the case of the heat of the solution the different heats of adsorption, hence, the differential and integral heat have to be evaluated to fully understand the infinitesimal changes of temperature versus the extent of adsorption [112].

Particle Size

Adsorbents with smaller particle size have a higher adsorptive ability due to their large external surface areas accessible to the ions to be removed [113].

Concentration

The extent of adsorption from a solution depends mainly on the available surface of the adsorbent, regardless of the mechanism. The process of adsorption is almost invariably reversible and a definite equilibrium is reached in a short time dependent on the concentration of the solution and quantity of the adsorbent; the higher the concentration, the lower the rate of adsorption and the vice versa [114].

2.3.5.2 Adsorbents

In the last few decades, alternative sorbents for the treatment of heavy metal ion contamination have been investigated [78][110][115]. Sorbents ranging from synthesized sorbents [116][117] to biosorbents [118][119] have been employed in many different ways to remove ions from wastewater effluent. Synthesized adsorbents are often developed and fashioned to remove particular target ion(s) [103]. For example, a multi-templated Pb-Zn-Hg ion imprinted sorbent was synthesized and employed to simultaneously remove lead, zinc and mercury ions from wastewater. The synthesized sorbents showed good selectivity towards the targeted metal ion by removing 90% - 98% of the templated ions as compared to 58% - 62% of the competitive ions [100]. However, the widespread use of the sorbent is challenged by; the high cost of reagents, and non-environmental friendly solvents and reagents. Thus the search for low cost, readily available and environmentally friendly adsorbents to remove toxic ions from water have over the last few years been a focus of the scientific world [104].

Biosorbents, with their low cost and environmentally friendly characteristics, have in the recent past proved to be materials of choice for the removal of variety of heavy metals ions. The agricultural residues seem to be preferred for the removal of ions and organics [103]. They are mainly comprised of cellulose materials that can adsorb ions in aqueous solution [120]. Numerous biomass waste materials whose adsorption properties have been reported; for instance, rice husk [108], saw dust [29], tea and coffee waste [121], orange peel [13], peanut shells [55], activated charcoal [122], and dry tree leaves [121] have been employed to remove undesired species from wastewater. For these, the adsorption process was found to be a function of adsorbent concentration, pH, metal ion concentration and temperature [55]. The kinetics of these materials together with their thermodynamic properties have not been widely studied.

2.3.5.2.1 Evaluation of the Performance of the Adsorbents

To investigate the performance of adsorbents at molecular level, the following parameters must be evaluated: adsorption equilibrium isotherms, kinetics and the adsorption thermodynamics.

2.3.5.2.1.1 Adsorption Equilibrium Isotherms

During adsorption a rapid equilibrium is established between the adsorbed ions and the adsorbent [103]. The equilibrium ion uptake q is calculated using the following equation:

$$q = \frac{(C_i - C_f)V}{M} \quad (2.1)$$

Where, V is the volume of the solution, C_i and C_f are the initial and the final equilibrium concentrations and M is the dry mass of the adsorbent [7]. The most widely employed isotherm equation for modeling the equilibrium is the Langmuir equation which is valid for monolayer sorption on to a surface with a finite number of identical sites and is given by equation:

$$q = \frac{q_{max}bC_f}{1+bC_f} \quad (2.2)$$

Where q_{max} is the maximum quantity of the ions per unit weight of the adsorbent to form a complete single layer on the surface (usually at the highest C_f) and b is a constant related to the affinity of the binding sites. q_{max} represents a practical limiting adsorption capacity when the surface is fully covered with ions and assists in the comparison of adsorption performance particularly in cases where the sorbent did not reach its full saturation in experiments [64].

The linearized form of equation 2.2 is given by:

$$\frac{C_f}{q} = \frac{C_f}{q_{max}} + \frac{1}{bq_{max}} \quad (2.3)$$

And from the linear equation, a plot of C_f/q versus $1/q_{max}$, can be obtained and b (affinity of binding sites constant) can then be determined from the plot as the inverse of the slope [47].

The empirical Freundlich model also considers simple molecular layer coverage of solute by the adsorbent. However, it assumes the adsorbent has a heterogeneous surface so that binding sites

are not identical [47]. This model takes the following equation forms for a single component adsorption.

$$q = KCf^{1/n} \quad (2.4)$$

Rearranged in the linearized form, equation 2.4 becomes;

$$\text{Log}q = \text{log}K + 1/n \text{log}C_f \quad (2.5)$$

Where K and n are the Freundlich constants characteristic of the system. K and n are indicators of adsorption capacity and adsorption intensity respectively can be obtained from the plot of $\text{Log}q$ versus $1/\text{log}C_f$ as the intercept and the inverse of the slope respectively [29]. The Freundlich isotherm provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model. Langmuir and Freundlich isotherms need additional models to explain the physical and chemical characteristics of adsorption. For instance, Langmuir isotherm constants cannot exclusively explain the chemical or physical properties of the adsorption process. However, the mean adsorption energy (E) calculated from the Dubinin – Radushkevich (D-R) isotherm provides important information about these properties. D-R isotherms are commonly used to describe the adsorption isotherms of single solute systems [123]. The D-R isotherms are expressed as:

$$q = q_{\max} \exp[-B[RT \ln[1 + \frac{1}{C_f}]]^2] \quad (2.6)$$

Rearranged in the linearized form, equation 2.6 becomes;

$$\ln q = \ln q_{\max} - Be^2 \quad (2.7)$$

$$\text{Where } e = RT \ln [1 + 1/C_f] \quad (2.8)$$

B is a constant related to the adsorption energy, R is the gas constant, T is the absolute temperature and e is the adsorption energy.

The mean adsorption energy (E) calculated from the Dubinin – Radushkevich (D-R) isotherm is given by;

$$E = \frac{1}{(2B)^{0.5}} \quad (2.9)$$

E gives information about the physical and chemical adsorption ability of the adsorbent. For the magnitude of $E \geq 8 \text{ kJ mol}^{-1}$ the adsorption process is said to follow chemical ion exchange, while for the values of $E < 8 \text{ kJmol}^{-1}$, the adsorption process is said to be of physical nature [47]. When Amarasinghe *et al* employed tea waste (TW) as an adsorbent to study its adsorption behavior of Cu and Pb from wastewater, they found out that the adsorption process is a function of pH, TW dose, contact time, initial Cu and Pb ions concentration and temperature. The Langmuir, Freundlich and Dubinin–Radushkevich models were applied to describe the equilibrium isotherms using nonlinear regression analysis [121].

2.3.5.2.1.2 Kinetic Models

The prediction of adsorption rate gives important information for designing batch adsorption systems in particular. The kinetics of adsorption is always studied based on the three kinetic models; first order, second order and intra particle diffusion models. These models take into account the adsorbed quantities that will enable the determination of the reactor volume [124]. The kinetics in most cases follows the first order rate equation,

$$\frac{dq}{dt} = k_1 (q_e - q) \quad (2.10)$$

Where q_e and q are the adsorption capacity at equilibrium and at time t respectively, and k_1 is the rate constant of the pseudo first order adsorption process [20]. The integrated linear form of equation 2.10 can be expressed as follows:

$$\log(q_e - q) = \log(q_e) - \frac{k_1}{2.303} t \quad (2.11)$$

A plot of $\log (q_e - q)$ vs. t gives a straight line for first order adsorption kinetics and the rate constant k_1 is obtained from the plot.

The sorption data may also be studied by second order kinetics [125],

$$\frac{dq}{dt} = k_2 (q_e - q)^2 \quad (2.12)$$

Where k_2 is the second order rate constant.

After integration,

$$\frac{1}{qe-q} = \frac{1}{qe} + k_2 t \quad (2.13)$$

This can further be written in the linear form;

$$\frac{t}{q} = \frac{1}{k_2 q e^2} + \frac{t}{q e} \quad (2.14)$$

The applicability of this equation can be studied by a plot of t/q verse t .

For the intra particle diffusion kinetic model;

$$q = k_d t^{1/2} \quad (2.15)$$

Where q is the adsorption capacity at time t , k_d is the distribution coefficient and $t^{1/2}$ is the adsorption half-life. The intra particle diffusion is obtained by investigating the relationship between the adsorption capacity (q) and the adsorption half-life ($t^{1/2}$).

Adsorption kinetics fully explains the entire adsorptive process of an adsorbent, which includes; the transfer of solute from the bulk solution to the boundary film that surrounds the adsorbent's surface, the transfer of solute from the boundary film to the adsorbent's surface, the transfer of solute from the adsorbent's surface to the active intra-particle sites and the interactions between the solute and the available adsorption sites on the internal surfaces of the adsorbent [55].

2.3.5.2.1.3 Adsorption Thermodynamics

The concept of thermodynamics assumes that in an isolated system, where energy cannot be gained or lost, the entropy change is the driving force. In environmental engineering practice, both energy and entropy factors must be considered in order to determine what processes will occur spontaneously. The Gibbs free energy change, ΔG is the fundamental criterion of spontaneity. A reaction occurs spontaneously at a given temperature if ΔG is a negative quantity [126]. The free energy of the sorption reaction considering the sorption equilibrium constant is given by the following equation:

$$\Delta G = -RT \ln b \quad (2.16)$$

Where ΔG is the change in Gibbs free energy, R is the gas constant, T (K) the absolute temperature and b (L/mol) the thermodynamic equilibrium constant. Considering the relationship between free energy and the equilibrium constant, change in equilibrium constant can be obtained in the differential form as follows [116]:

$$\frac{d \ln b}{dT} = \frac{\Delta H}{RT^2} \quad (2.17)$$

After integration,

$$\ln b = -\frac{\Delta H}{RT} + Y \quad (2.18)$$

The above equation can be rearranged to obtain

$$-RT \ln b = \Delta H - TRY \quad (2.19)$$

$$\text{Where } \Delta S = RY \text{ and } Y \text{ is a constant.} \quad (2.20)$$

Substituting equations (2.16) and (2.20) into (2.19), the Gibbs free energy change, ΔG , can then be represented as follows;

$$\Delta G = \Delta H - T\Delta S \quad (2.21)$$

A plot of Gibbs free energy (ΔG) versus temperature T will be linear. The values of enthalpy change ΔS and entropy change ΔH are then determined as the slope and the intercept of the plot respectively [127].

CHAPTER THREE: EXPERIMENTAL SECTION

3.0 Overview

This chapter gives a full account of the sampling and sample pre-treatment, reagents, instruments and procedures that were employed to valorize the bio-waste materials (eggshells and fish scales) that were identified as the abundant and readily available waste materials in our locality, Botswana. Furthermore, an account of the experimental procedures that were performed in evaluating the performance of the materials to remove the targeted ions of Co, Ni, Zn, Cu, Hg, Cr, Ag, Fe, Pb, Al, As, Cd, Sn, Ti and Mg as well as F^- , Cl^- , SO_4^{2-} , PO_4^{3-} , NO_2^- , BrO_3^- and NO_3^- is also discussed in this chapter.

3.1 Materials and Reagents

Ultra-pure water, of 18.0 M Ω /cm resistivity Type I, was prepared by an Elix 5 Millipore water purification system from Merck, (Darmstadt, Germany) and was employed to prepare all solutions. Reagents employed were of analytical grade; HCl (37%) and HNO₃ (60%) purchased from ACE (Johannesburg, South Africa), SPAR white spirit vinegar, which was employed to treat the waste materials was purchased from SPAR supermarket (Palapye, Botswana). 1000 mg/L elemental standard solutions for the targeted ions usually found in wastewater (Co, Ni, Zn, Cu, Hg, Cr, Ag, Fe, Pb, Al, As, Cd, Sn, Ti, Mg, F^- , Cl^- , SO_4^{2-} , PO_4^{3-} , NO_2^- , BrO_3^- , and NO_3^-) and NaOH (97%) pellets were purchased from Rochelle Chemicals (Johannesburg, South Africa). A 0.45 μ m pore sized Whatman filter papers (Hardened Ashless Circles 45 mm) that were employed for all filtering processes were purchased from Sigma-Adrich (Johannesburg, South Africa), pH meter was purchased from Crison (Liverpool, England), laboratory oven was purchased from Thermo Fisher Scientific Inc (Johannesburg, South Africa), hot plate was purchased from Benchmark Scientific, (Johannesburg, South Africa), micropipette from BOECO Ltd. (Berlin, Germany), analytical balance from Mettler Toledo, A W.S. Tyler™ (Johannesburg, South Africa), and Laval standard stainless steel sieves (63 – 300 μ m) purchased from Laval Lab (Minnesota, USA) were employed for sieving the waste materials. Minitab release 14 statistical software purchased from Minitab Inc. (Florida, USA) was employed for experimental

design and the simultaneous optimization of multiple parameters that affect adsorption efficiency of any adsorbent.

3.2 Instrumentation

An Elix 5 Millipore water purification system purchased from Chemetrix (Pty) Ltd (Johannesburg, South Africa) was employed for the production of ultrapure water. A Mars6 one touch microwave assisted extractor/digester purchased from CEM Microwave Technology Ltd (Johannesburg, South Africa) was employed for the digestion and extraction of ions from the VWMs and untreated waste materials. A Fritsch pulverisette-5 pulverizer purchased from Fritsch Ltd (Berlin, Germany) was employed to pulverize the waste materials. A JSM 1700 scanning electron microscope (SEM) coupled with an electron dispersive x-ray (EDX) purchased from JEOL Ltd (California, USA) was employed for the determination of size, morphology and elemental composition of the bio-waste materials. An E6700 Polaron range high vacuum evaporator sputter coater purchased from Quorum Technologies (London, United Kingdom), was employed to coat the VWMs and the untreated waste materials prior to SEM-EDX analysis. A Perkin Elmer fourier transform infrared (FTIR) spectrometer, Spectrum-Two, purchased from Perkin Elmer South Africa (Pty) Ltd (Johannesburg, South Africa). Additional investigation on the functional groups of the waste materials was carried out employing a Raman spectrometer, LabRAM HR evolution Raman S0 – TNO4 purchased from Jobin YVon Technology (Villeneuve d'Ascq, France). An iCAP 7000 series Thermo Scientific inductively coupled plasma optical emission spectrometer (ICP – OES) purchased from Perkin Elmer South Africa (Pty) Ltd. (Johannesburg, South Africa) was employed for the determination of all cations, while the concentration of all anions was determined with a Shimadzu S 150 ion chromatograph (IC) coupled with a conductivity detector (CDD – 10A), purchased from SHIMADZU, South Africa (Johannesburg, South Africa).

3.3 Sampling

The adsorbent employed for the experiments were brown eggshells collected from the Botswana International University of Science and Technology (BIUST) Moghul refectory (Palapye,

Botswana) and fish scales of *Tilapia ruweti* (Okavango tilapia) collected from Lake Ngami in Maun, Botswana. Since the thesis set out to identify bio-waste materials that were abundant and easily available in our locality, Botswana to be employed as adsorbents for removing common toxic ions usually found in wastewater. An extensive search covering most parts of Botswana was carried out after which several bio-waste materials were identified and assessed based on their abundance and ease of availability. Eggshell waste remains were found to be the most common in most locations in Botswana and fish scales waste remains were found to be common in the northern part of Botswana. 10 g of fish scales and 10 g eggshells were use throughout the research project. The identified waste remains were then subjected to sample pre-treatment procedures in order to rejuvenate (valorize) them for the adsorption and removal of toxic ions from wastewater.

To evaluate the intended applicability of the prepared VWMs to real samples, wastewater samples were obtained from Gaborone waste water treatment plant (wastewater), Gaborone, Botswana. At the treatment plant five sampling sites were identified (Inlet point, primary settling, secondary settling point, aeration point and effluent point). Random sampling technique was employed to obtain the samples from the plant. Grab sampling technique was employed to obtain the water samples from individual sampling sites. Each sample was transferred into a labeled brown glass bottle and acidified to $\text{pH} < 2$ in order to prevent further microbial activity which could have eventually affected the composition of the ions in the sample. Also, acidifying the samples ensured that undissolved ions that remained after sampling were dissolved. The wastewater samples were placed in the cold room at $-4\text{ }^{\circ}\text{C}$ to help immobilize any microbial activity or degradation of the sample. Samples were stored until analysis.

3.4 Pre-treatment of Waste Remains

The eggshell waste remains were thoroughly washed with deionized water to remove obvious dirt, dust and other impurities from their surfaces. They were then sun dried for 48 hrs and pulverized at 400 rpm for 45 min in both milling and reverse mode. The pulverized waste of eggshell remains was then sieved to obtain particles of < 63 micron only. There was further washing with deionized water to remove color and the very fine particles. The fish scale waste remains were similarly pre-treated.

For excellent adsorption of the ions, the pulverized waste materials (< 63 microns) had to be functionalized to expose the surface functional groups needed for the efficient adsorption of the targeted ions and their subsequent removal. Generally, functionalization of surfaces of potential adsorbent materials employ several methods that include strong mineral acid and base treatment, weak organic acids treatment, impregnation treatment, ozone treatment, surfactant treatment, plasma treatment, ashing, heat treatment and microwave treatment [128] [55]. All these methods but the weak organic acid treatment have several drawbacks such as high toxicity and cost of the solvents used, formation of toxic by-products, non-environmental friendliness and the denaturing or degradation of the biomass by the treatment method employed. Thus, our choice of the weak organic acid; vinegar coupled with its ease of availability and accessibility to everyone. Vinegar is primarily composed of 5%- 20% acetic acid (CH_3COOH), and water. The vinegar employed in this thesis was of concentration 12.7% acetic acid.

To effectively valorize the optimal quantity of the pulverized bio-waste materials (80 mg) to be employed for all batch optimization rebinding experiments, the optimal volume of the 12.67% acetic acid vinegar used for the valorization had to be optimized. To achieve that, increasing volumes of the vinegar ranging from 50 mL (set lower limit for Minitab experimental design) to 250 mL (set upper limit for Minitab experimental design) at 50 mL intervals, were each mixed with 80 mg of each of the two bio – waste materials separate conical flasks. The solution mixtures were equilibrated overnight, then filtered and left to dry in open air for 2 h. The dried, pre-treated bio-waste materials (80 mg) from each of the flasks were then introduced to 100 mL solutions of the selected ions at concentration 1000 mg/L and equilibrated overnight. Thereafter, the solution mixtures for each flask were filtered off to separate the residues (waste materials with bound ions) and the filtrate (solution containing unbound ions). The concentrations of the ions in the filtrates for the selected ions from each of the flasks were determined with ICP-OES and IC for each of the selected cations and anions respectively. To obtain the optimal volume of 12.7% acetic acid vinegar needed for optimal pre-treatment of the bio – waste materials, the percentage recoveries (% of ions bound/removed by the bio – waste materials) corresponding to increasing volumes of the acetic acid were calculated as per Equation 3.1 until the calculated percentage recoveries remained constant with increasing volume.

$$\%ions\ removed = \frac{conc.\ of\ ions\ before\ VWMs - conc.\ of\ ions\ after\ VWMs}{conc.\ of\ ions\ before\ VWMs} \times 100\% \quad 3.1$$

3.5 Physical Characterization of the Bio – Waste Materials

To fully evaluate the suitability of the valorized waste materials (VWMs) and the non-VWMs for adsorption and subsequent removal of the toxic ions, the favorable structural and chemical features of both the VWMs and non-VWMs were elucidated and compared, employing the following instruments; fourier transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD), scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX), Raman spectroscopy.

Fourier Transform Infrared Spectroscopy (FT-IR)

A Nicolet iS10 Thermo Scientific fourier transform infrared (FTIR) spectrometer was employed to identify the functional groups (responsible for the binding and uptake of selected ions) present on the surfaces of the non-VWMs and VWMs. Each of the materials (Eggshell and fish scale VWMs and their non-VWMs) were analyzed in point mode and their spectra collected in a single-beam at 2.0 cm^{-1} resolution after every 256 scans. The spectra were recorded in the wavelength range $400 - 4000\text{ cm}^{-1}$. This process was performed in triplicates ($n=3$) to ensure high precision of the analysis.

X-ray Powder Diffraction (XRD)

A powder D8 advanced powder x-ray diffractometer (XRD) analysis was employed to investigate the crystallinity of the non-VWMs and VWMs and also to investigate the treatment effect. The XRD with high efficiency linear detector of Lynx eye type, was operated with Cu $K\alpha$ emission ($\lambda = 1.54105\text{\AA}$, 40 kV, 40 mA per sec). The scanning mode employed was coupled with $2\theta/\theta$ in the scanning range of $10^\circ - 120^\circ$. The crystallite size of the sample was calculated by Deby-Scherrer method [109].

Scanning Electron Microscopy Coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDX)

Scanning electron microscope coupled with energy-dispersive x-ray spectrometer (SEM - EDX), was employed to determine the surface morphology, elemental composition and estimated particle sizes of the non-VWMs and VWMs. E6700 Polaron range, high vacuum pressure sputter coater was employed to coat the waste materials with carbon. The coated materials were mounted on 3.22 mm sample holders and were then taken for SEM-EDX analysis. The SEM was operated at a resolution of x430, imaging energy of 50 eV and amplification time of 5 microseconds under high vacuum with beam acceleration voltage of 10.0 kV (the recommended operating voltage for organic material samples) [5] utilizing a chamber gas (H_2O) for imaging, charge suppression and sample humidity. An EDX back scattering detector operated in point, shot and mapping mode (distribution of compounds) of the spectra mode (elemental composition) at a beam voltage of 1.0 kV LED was later employed for the investigation of the elemental composition of the materials.

Raman spectroscopy

To further elucidate the functional groups on the materials, Raman spectroscopic measurements were performed employing a LabRAM HR evolution raman spectrometer with 10X He-Cd laser at 525 nm excitation light source and 1400 gr/mm gratings. The spectra were acquired in the backscattering configuration employing thermo- electric cooled charge coupled device (CCD) detector.

3.6 Optimization and binding Studies

A multivariate optimization methodology, employing the Minitab statistical software for the simultaneous designing of optimization experiments for the parameters that usually affect efficient adsorption; contact time, pH, VWM dosage, as well as concentration. Empirical batch binding experiments were performed for each experimental simulation, for each of the selected ions to ascertain the optimal values of the parameters that usually affect efficient adsorption. Furthermore, the effect of Botswana weather temperature on the storage of the VWMs was also investigated.

3.6.1 Multivariate Optimization Methodology

Contact time, pH, VWM dosage and concentration were simultaneously optimized employing the *two-level ½ fractional factorial design* and the *central composite design (CCD)* of the Minitab statistical software. The two-level ½ fractional factorial screening design was employed for identification of the significance of each of the factors towards the experimental output. Following this, the face centered central composite design was performed to determine the optimum conditions for each factor that could result in maximum response of the experiments.

Two-level ½ fraction factorial screening design

The screening design was performed employing the experimental design that needed setting the lower and upper limit values for each parameter as displayed in Table 3.1 based on literature [7], thereafter Minitab simulated experiments within these limits for each of the ions.

Table 3.1: Set lower and upper limit values for each of the parameters that affect efficient adsorption for the two-level fractional factorial design

Variable	Factor	Low level	High level
A	Materials dosage (mg)	25	1000
B	pH	2	10
C	Contact time (minutes)	15	90
D	Concentration (mg/L)	0	50

A total of 62 experiments were designed by the software for each ion. The experiments were performed as batch binding experiments for each of the VWMs as per the design (see Appendix B, Table 6.3). At the end of each of the equilibrated times set by the design, the solution mixtures of the VWMs and the standard solutions of the selected ions were filtered off to separate the residues (waste materials with bound ions) and the filtrate (solution containing unbound ions). The concentrations of the ions in the filtrates for the selected ions were then determined with ICP-OES and IC for each of the selected cations and anions respectively. The experiments were performed in duplicates to enhance precision of the results. The concentrations of the ions by the

ICP-OES and the IC and were evaluated for the level of significance of each of the factors and that of the interaction of the factors employing the Minitab statistical software.

Central composite design (CCD)

The significant factors obtained from the screening phase (two-level $\frac{1}{2}$ fraction factorial design) were further evaluated to obtain the optimal parameters for the highest performance of the VWMs by employing the optimization phase (CCD). Once again, the conditions as described by Table 3.1 were employed and a further total of 62 experiments were designed by the software. The experiments were performed as per the design (see Appendix B, Table 6.4). At the end of each of the equilibrated time set out by the design, the concentrations of the ions were determined in a similar manner as described in the *Two-level $\frac{1}{2}$ fraction factorial screening design*. The concentrations of the ions by the ICP-OES and IC were evaluated for the level of significance of each of the factors and that of the interaction of the factors employing the Minitab statistical software.

3.6.2 Optimization of the Effect of Storage Temperature on the VWMs

In order to establish the effect of temperature on the VWMs based on their storage within the harsh extremes weather conditions in Botswana, stability tests were performed. Two sets of VWMs were prepared; one set stored in a cold room at -4°C , while the other set was stored at 45°C for 35 days. The optimal parameters were employed to 100 mL solution mixtures of the VWMs and selected ions (50 mg/L). Thereafter, the solution mixtures were filtered off employing a whatman No. 1 filter paper and the solution mixtures of the VWMs and the standard solutions of the selected ions were filtered off to separate the residues and the filtrate. The concentrations of the ions in the filtrates for the selected ions were then determined with ICP-OES and IC for each of the selected cations and anions respectively. The percentage recoveries (% of ions bound/removed) by the VWMs were calculated by subtraction as per equation 3.1. The experiments were performed in duplicates to determine precision of the results. Concentration determinations were performed for a period of 35 days (5 weeks) in the following manner: for the first week, concentrations were determined daily, for the second week, they were

determined for 3 days (first, third and last day) out of the 7 days, while for the third and fourth weeks, they were determined for 2 days (third and last day) of each week and for the last week, they were determined just once on the fourth. Scatter graphs of absorbance (concentration) Vs days on which the concentrations were determined were constructed.

3.6.3 Comparative Studies of the VWMs and non-VWMs

To evaluate and compare the performance of the VWMs and the non-VWMs in efficiently adsorbing and subsequently removing the selected ions from pure standard solutions of the ions and wastewater samples, batch binding experiments were performed. The experiments involved mixing an optimized dosage (80 mg) of the VWMs or the non-VWMs with a known volume of either a pure standard solution of each of the selected ions of an optimized concentration (28.44 mg/L) for an optimized equilibration time (74 min). The experiments were performed in triplicates (n=3) to enhance precision. The solution mixtures of the VWMs and standard solutions of the selected ions were filtered off to separate the residues (waste materials with bound ions) and the filtrate (solution containing unbound ions). The concentrations of the ions in the filtrates for the selected ions were then determined with ICP-OES and IC for each of the selected cations and anions respectively. Statistical methods were then employed to determine the mean values and the percentage standard deviations (%RSD). From the values, the percentage recoveries (% of ions bound/removed) by the VWMs were calculated by subtraction as per equation 3.1. A bar graph of percentage recovery against the VWMs and the nVWMs was constructed.

3.7 Determination of Anions and Cations of the Raw Wastewater Sample

To evaluate the concentration of dissolved ions present in the wastewater sample, 50 mL of the wastewater sample was digested employing a MARS6 microwave assisted digester in 50 mL aqua regia solution [129]. The solution mixture was transferred in 100 mL TFM sample vessel and digested at a pressure of 600 psi, temperature of 100 °C and 1200 W. The ramp time was set at 20.0 min with a hold time of 10.0 min [130]. The solution mixtures of the VWMs and standard solutions of the selected ions were filtered off to separate the residues (waste materials with

bound ions) and the filtrate (solution containing unbound ions). The concentrations of the ions in the filtrates for the selected ions were then determined with ICP-OES and IC for each of the selected cations and anions respectively. Statistical methods were then employed to determine the mean values and the percentage standard deviations (%RSD). From the values, the percentage recoveries (% of ions bound/removed) by the VWMs were calculated by subtraction as per equation 3.1. A bar graph of concentration of the selected ions in the wastewater against the selected ions was constructed.

3.8 Method validation

To validate the method the following parameters were evaluated; linearity, detection limits and recovery.

Linearity

The linearity of the method for each selected ion was evaluated by calculating correlation coefficients (R^2) from calibration plots of absorbance against the prepared pure standards ion concentrations of the selected ions within a chosen working range of 0 – 500 mg/L for each of the ions. The working range of 0 – 500 mg/L was selected based on the fact that the ion concentrations of the selected ions are usually below 500 mg/L in wastewater [131][132]. The concentrations of the ions were determined by ICP-OES and IC for each of the selected cations and anions respectively.

Detection Limits

Three detection limits were evaluated for the developed method; the limit of detection (LOD), limit of quantification (LOQ) and method detection limit (MDL). The LODs and LOQs were evaluated by identifying the Y-axis intercepts (Y_B) and calculating the slopes (m) of the calibration plots employing equation 3.3 and 3.4.

$$Y_{LOD} = Y_B + 3S_D \quad (3.3)$$

$$LOD = (Y_{LOD} - Y_B)/m \quad (3.4)$$

Where: Y_B is the Y-axis intercept and m is the slope of the plot.

The limit of quantification (LOQ) values was calculated employing equation 3.5 and 3.6.

$$Y_{LOQ} = Y_B + 10S_D \quad (3.5)$$

$$LOQ = (Y_{LOQ} - Y_B)/m \quad (3.6)$$

The *method detection limit (MDL)* on the other hand was calculated by employing 8 times the standard error of regression line and computing a *t-test* to obtain the *t-value* through equation 3.7.

$$MDL = T_{(n-1, 1-\alpha=0.99)} \times SD \quad (3.7)$$

Where: $T_{(n-1, 1-\alpha=0.99)}$ is the student's *t* value at 99% confidence level, n is the number of replicates measured and S_D is the standard deviation.

Recovery Studies

The extraction efficiency (removal efficiency) of the VWMs were evaluated by calculating the percentage (%) recoveries (% bound/removed) of the selected ions (Co, Ni, Zn, Cu, Hg, Cr, Ag, Fe, Pb, Al, As, Cd, Sn, Ti, Mg, F^- , Cl^- , SO_4^{2-} , PO_4^{3-} , NO_2^- , BrO_3^- , and NO_3^-) from pure standards of concentration 500 mg/L taken as the highest concentration that each of the ions can exist at in wastewater. Both the eggshell and fish scale VWMs under optimal conditions were evaluated separately by adding them to separate reaction vessels, each containing 100 mL of 500 mg/L pure standard of the selected ions. After equilibration, the solution mixtures of the VWMs and pure standard samples were filtered off to separate the residues and the filtrates. The concentrations of the ions in the filtrates for the selected ions were then determined with ICP-OES and IC for each of the selected cations and anions respectively. The experiments were performed in triplicates. Statistical methods were then employed to calculate the mean values for the % recoveries and the percentage standard deviations (%RSD) as per equation 3.8. From the values, bar graphs of percentage recoveries for the selected ions were constructed.

$$\% \text{Recovery (\%ions removed)} = \frac{\text{conc. of ions in pure standard before VWMs} - \text{conc. of ions in the filtrate after VWMs}}{\text{conc. of ions in pure standard before VWMs}} \times 100\% \quad (3.8)$$

3.9 Application of the Valorized Waste Materials (VWMs) to Raw Wastewater Samples from Gaborone Sewage Treatment Plant

To evaluate the efficiency of the VWMs in removing ions from real wastewater samples, the same procedure as the one described under the recovery studies section, section 3.8 was followed except that instead of the 500 mg/L standard that was employed, raw wastewater samples from Gaborone sewage treatment plant were employed. The experiments were performed in triplicates. Statistical methods were then employed to calculate the mean values for the percentage recoveries and the percentage standard deviations (%RSD) as per equation 3.1. From the values, bar graphs of percentage recoveries for the selected ions were constructed.

3.10 Adsorption Equilibrium Isotherms

Adsorption equilibrium studies were performed to determine the nature of the adsorption isotherms and the adsorption capacity of the VWMs for the removal of ions. For the isotherm studies, the initial ion concentrations were varied from 0 to 500 mg/L at intervals of 100 mg/L in separate reaction vessels. The optimal quantity of the VWMs (80 mg) was added to 100 mL of the prepared standard solutions and equilibrated for the optimal time at 200 rpm. The solution mixtures of the VWMs and standards were filtered off to separate the residues and the filtrates. The concentrations of the ions in the filtrates for the selected ions were then determined with ICP-OES and IC for each of the selected cations and anions respectively. The experiments were performed in triplicates. Various adsorption equilibrium parameters were calculated as explained in section 2.4 and a table of the calculated parameters was constructed.

3.11 Kinetic Models

Three models including the first order kinetic model, second order kinetic model and the intra particles kinetic model were evaluated to ascertain the adsorption kinetics of the adsorption

reaction of the VWMs and the selected ions in the wastewater samples. The optimal quantity of the VWMs (80 mg) was added to five (5) separate reaction vessels containing 100 mL of the wastewater samples and equilibrated for increasing time ranging from 15 min – 90 min at 200 rpm at interval of 15 min. The solution mixtures of the VWMs and the wastewater were filtered off to separate the residues and the filtrates. The concentration of the ions in each of the solution mixture for the selected ions were then determined with ICP-OES and IC for each of the selected cations and anions respectively. Various adsorption kinetics parameters were calculated as explained in section 2.5. A table of the calculated parameters was constructed.

3.12 Adsorption Thermodynamic

Thermodynamic studies were performed to investigate the spontaneity and thermal adsorption conditions of the adsorption of the selected ions by the VWMs. The optimal quantity of the VWMs (80 mg) was added to 100 mL of wastewater and equilibrated for the optimal time at different temperatures ranging from 0 °C – 50 °C, at intervals of 10 °C. The solution mixtures of the VWMs and the wastewater samples were filtered off to separate the residues and the filtrates. The concentration of the ions in each of the solution mixtures for the selected ions were then determined with ICP-OES and IC for each of the selected cations and anions respectively. Various thermodynamic parameters were calculated as explained in section 2.6. A table of the calculated parameters was constructed.

3.13 Desorption and Regeneration Studies

To evaluate the reusability of the VWMs, Mata *et al* regeneration studies method, employing five (5) adsorption-desorption cycles was followed [133]. Desorption experiments in which 50 mL of 1.0 M HCl, 1.0 M HNO₃, deionized water, EDTA, and 1.0 M NaOH solutions separately as the desorption mediums were mixed with 3 g of already used VWMs (after application for the removal of the selected ions) and equilibrated at 200 rpm for 120 min. The solution mixtures containing the used VWMs and the desorption medium were then filtered off to separate the residues and the filtrates. The concentrations of the ions in the filtrates were then determined with ICP-OES and IC for each of the selected cations and anions respectively. After each

desorption experiment, the VWMs (that was employed for the desorption experiment) were conditioned for the adsorption experiments [47]. For the adsorption experiments, the optimal quantity of the conditioned VWMs (80 mg) was added to 100 mL of the wastewater and equilibrated for the optimal time at 200 rpm. The solution mixture of the conditioned VWMs and the wastewater samples were filtered off to separate the residues and filtrates. The concentrations of the ions in each of the filtrates for the selected ions were then determined with ICP-OES and IC for each of the selected cations and anions respectively. The experiments were performed in triplicates. Statistical methods were then employed to determine the mean values and the percentage standard deviations (%RSD).

After each adsorption–desorption cycles, the percentage adsorption and the percentage desorption were calculated by employing equation 3.1. The values were then recorded in a tabular form.

3.14 Comparative Studies of the Proposed VWMs and the Commonly Applied Activated Charcoal

To compare the extraction efficiency of the proposed VWMs and the commonly applied, commercial grade activated charcoal in removing ions from waste water, 3 g of each of the adsorbents were separately applied to 500 mL of wastewater samples for the removal of the selected ions following the charcoal manufacturer`s application of the adsorbent procedure [47]. Each of the solution mixtures (the mixture of the VWMs and the wastewater as well as the mixture of the Activated charcoal and the wastewater in separate reaction vessels) were equilibrated at 200 rpm for 90 min [108]. Thereafter, they were filtered off to separate the residues and the filtrates. The concentrations of the ions in the filtrates for the selected ions were then determined with ICP-OES and IC for each of the selected cations and anions respectively. The experiments were performed in triplicates. Statistical methods were then employed to determine the mean values and the percentage standard deviations (%RSD). From the values, the percentage recoveries (% of ions bound/removed) by the VWMs and activated charcoal were calculated employing equation 3.1. A table (see Table 4.19) showing percentage removal of ions by each of the adsorbents (VWMs and the activated charcoal) employed was constructed.

CHAPTER FOUR: RESULTS AND DISCUSSIONS

4.0 Pre-treatment of the Collected Eggshell and Fish scale Waste Remains

Pulverization and Sieving

Following the procedures described in Section 3.4 to valorize (rejuvenate) the collected materials, pulverization and sieving of the collected waste materials of eggshells and fish scales were the first procedures that were conducted. The procedures resulted in off-white powdery materials (see Figure 4.1, a camera picture of the eggshell powder, the fish scale powder, not included was similar to eggshell picture) of smaller particle sizes of $< 63 \mu\text{m}$ for both the eggshell and fish scale remains as estimated from the sieve's mesh sizes.



Figure 4.1: A camera picture of pulverized eggshell powder

Further elucidation on the particle size, shape and morphology of the particles was achieved by employing the SEM-EDX which revealed morphologically rough particles of spherical geometry and particle sizes of about $10 \mu\text{m}$ for both waste materials as evidenced in the SEM micrographs in Figures 4.2 and 4.3 below which display similar features of the particles for both the fish scale and the eggshell pulverized waste remains.

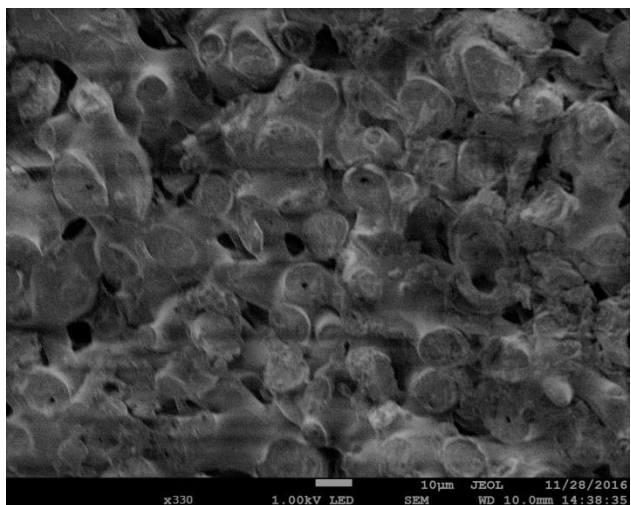


Figure 4.2: Typical SEM images of the pulverized fish scale waste remains

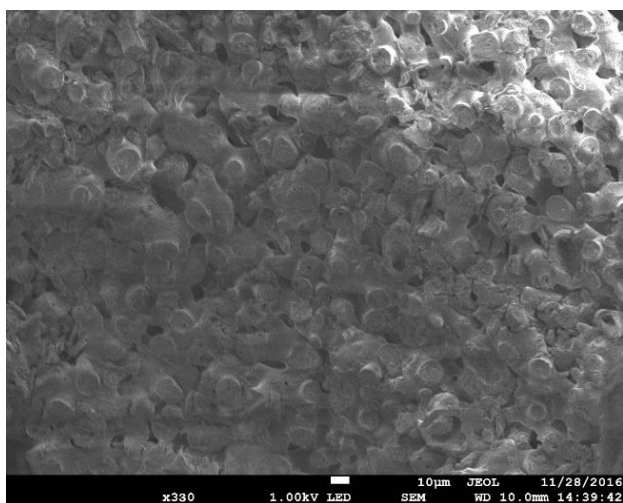


Figure 4.3: Typical SEM images of the pulverized eggshell waste remains

The spherical geometry and smaller particle sizes are known to be good characteristics for effective sorbents as they result in high surface area to volume ratio as well as a larger exposed surface area of the adsorbent to the targeted species [134]. The smaller the particles, the higher the rate of reactions [135], hence in this case the rate of adsorption was expected to be faster as the particles sizes of the waste materials were highly reduced during pulverization. Powders are generally good for sorption during binding studies [136], thus the existence of the waste materials in powder form was advantageous in other areas of this thesis (for example during

binding studies). The other advantage of the powder form was the improved handling of the waste materials after they were converted to powders during pulverization. In powder form the waste materials were presenting themselves as materials that could be included in miniaturized pieces of equipment for easy automation. Automation is advantageous in all scientific procedures, thus it is highly sought after in process development [131]. The large eggshell and fish scale remains that were originally collected (before pulverization and sieving) were cumbersome to handle, thus pulverization of the waste remains achieved preliminary valorization of the waste materials. To valorize a waste material is to put to use or to improve (rejuvenate) its usage after it had being deemed useless and regarded as waste. Since the eggshell and fish scale waste materials that were pulverized could be better handled in powder form, they were thereafter treated with vinegar to further valorize them.

Vinegar treatment of the pulverized waste materials

Vinegar treatment was performed to further valorize the waste materials in order to expose the surface functional groups needed for adsorption that could have been embedded in the structures of the waste remains. The volume of the 12.7% vinegar needed to effectively wash the waste remains such that maximum adsorption or removal efficiency of the selected ions was achieved were optimized as described in Section 3.4. The point at which plots of percentage adsorption or removal efficiency versus volume of acid plateaued, marked the optimized volume of vinegar that was needed to wash the pulverized waste remains for maximum valorization as represented by high adsorption percentage efficiencies in Figures 4.4A and 4.4B.

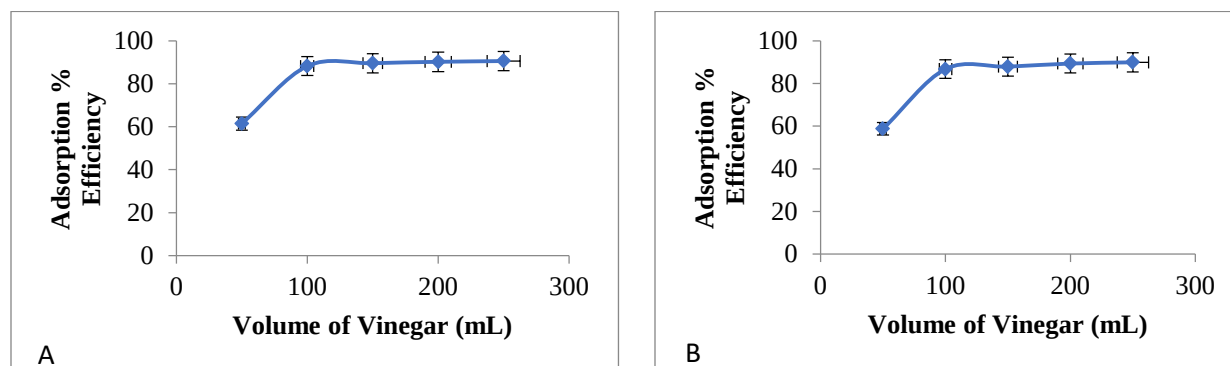


Figure 4.4A and B: Volume of vinegar needed to optimally valorize fish scale (A) and eggshell waste (B) remains to achieve maximal efficiency at $n = 3$

For both plots, 150 mL of the vinegar achieved highest efficiency, hence was the optimized volume of vinegar needed for optimal valorization of the waste materials. The pulverized vinegar waste materials which were optimally treated with vinegar as evidenced by the achieved maximal efficiency in Figures 4.4A and 4.4B were optimally valorized at this point and from here on were referred to as valorized waste materials (VWMs) whilst the pulverized waste materials that were untreated with vinegar were referred to as non-VWMs.

4.1 Physical Characterization of VWMs

Physical characterization of the VWMs included characterization of the morphology, shape and particle size employing SEM which were dealt with in Section 4.1 as well as identifying the functional groups with FTIR, Raman and XRD.

Fourier Transform Infrared Spectroscopy (FT-IR) of the VWMs

Fourier transform infrared spectrometer (FTIR) was employed to determine the functional groups on the VWMs responsible for the adsorption of the targeted ions. The FTIR spectra of the eggshell and fish scale VWMs showed stronger vibrational bands that were shifted when compared to the spectra of their non-VWMS counterparts (see Figures 4.5 and 4.6 below). The shifted, strong bands were attributed to the freed, non-bonded functional groups on the VWMs that were exposed by treating the pulverized waste materials with vinegar. Usually, the functional groups occur naturally coordinated (bonded) to various ions as supported by the Raman spectra (see Figures 4.7 and 4.8 below) and the XRD diffractogram (see Figures 4.9 and 4.10) as well as EDX spectra (see Figures 6.1 and 6.2 in Appendix A).

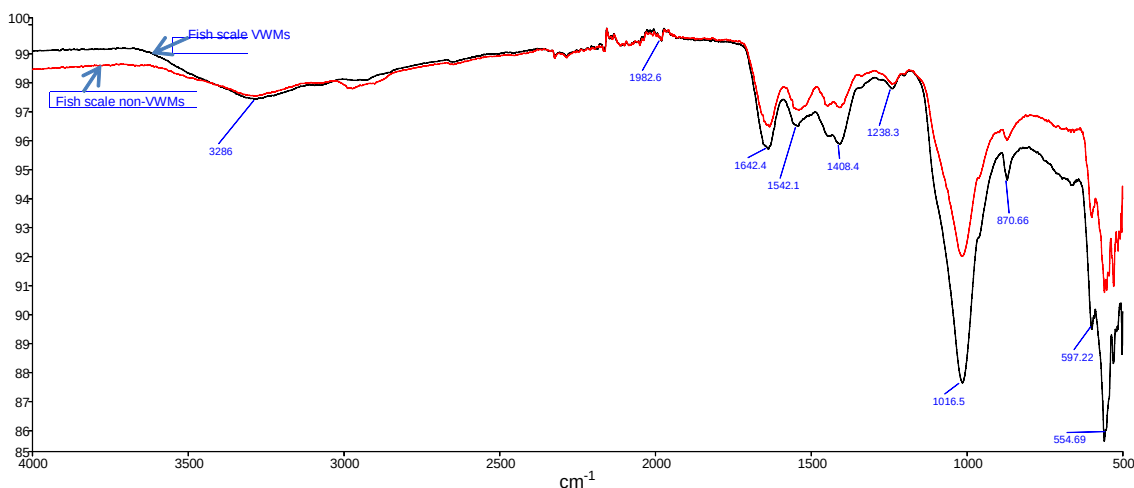


Figure 4.5: FTIR spectra of the fish scale VWM and non-VWM.

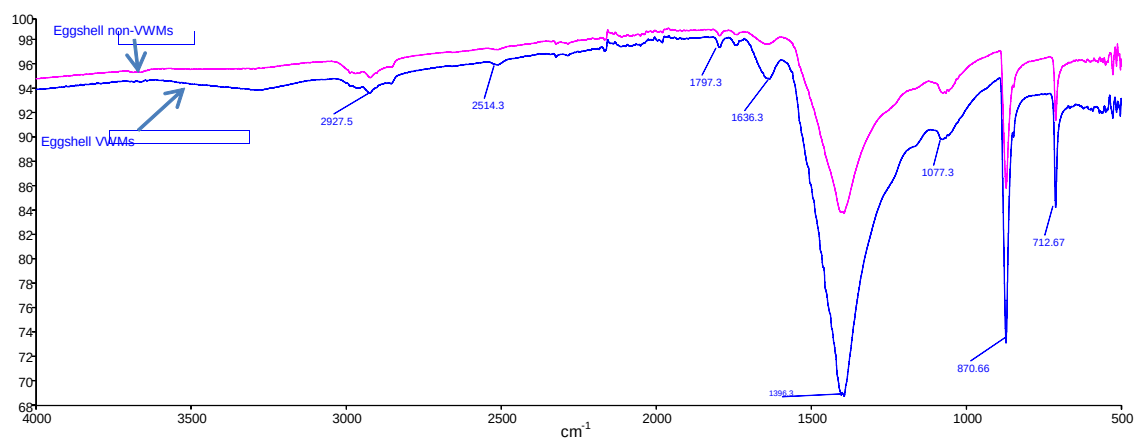


Figure 4.6: FTIR spectra of the eggshell VWM and non-VWM.

The FTIR spectra of the eggshell and fish scale VWMs were found to possess similar functional groups as evidenced by similar vibrational bands in their spectra. For instance, the most prominent bands found in both spectra (Figure 4.5 and 4.6) were the carboxyl groups located around 1016 cm^{-1} , primary amines around 554 cm^{-1} , amide groups around 3286 cm^{-1} , alkanes at 870 cm^{-1} , and hydroxyl groups around 1542 and 1642 cm^{-1} which are known to form coordinate bonds with ions through their lone pairs as well as hydrogen bonding for the ones with hydrogen atoms in their structures [137][109][138]. Alkene groups which are known to form coordinate

bonds with metal ions were also found at 1408.4 cm^{-1} in both VWMs [139]. However, the eggshell VWMs spectra had two other significant bands that were located at 1396 cm^{-1} and 712.67 cm^{-1} , associated with carbonate groups from calcium carbonate and valerite respectively [140][141]. It should be noted that, the 1396 cm^{-1} vibrational band found in the FTIR spectra of the eggshell VWMs has been reported elsewhere [142][143], where it was associated with carbonate minerals.

Raman Spectroscopy and Powder X-ray Diffraction (XRD) of the VWMs

To further characterize the VWMs, Raman spectrometer and x-ray diffractometer were employed for further investigation of VWMs for the presence of important species that could be essential for the uptake of ions [16][68]. The Raman spectra and the x-ray diffractograms supported each other by showing the presence of the same species of hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_5(\text{OH})_2$] for both the fish scale VWMs and non-VWMs (see Figures 4.7 and 4.8), except that the VWMs displayed reduced intensities of the two species relative to the non-VWMs increased intensities. There was an extra visible peak that was attributed to hydroxyproline ($\text{C}_5\text{H}_9\text{O}_3\text{N}$) found in the Raman spectra of both the fish scale VWMs and non-VWMs (see Figure 4.7). Hydroxyapatite and hydroxyproline are known for their excellent ion-exchange performance; they exchange calcium ion sites with cations and hydroxyl or phosphate sites for anions [144].

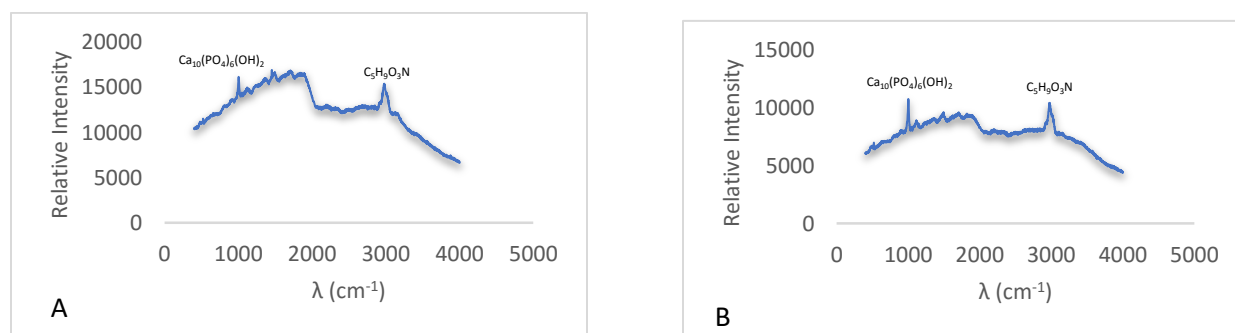


Figure 4.7: Raman spectrum for the fish scale non-VWMs (A) and fish scale VWMs (B)

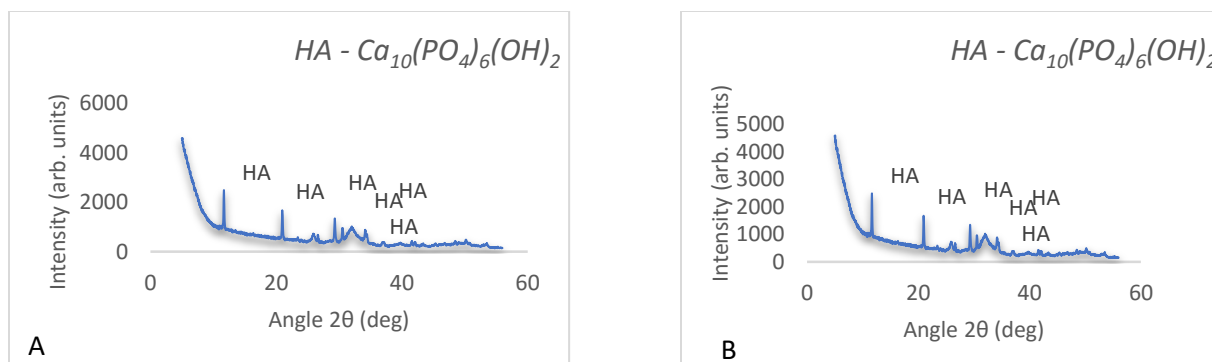


Figure 4.8: XRD diffractogram for the fish scale non-VWMs (A) and fish scale VWMs (B)

Similarly, the Raman spectra and the x-ray diffractograms for both the eggshell VWMs and non-VWMs (see Figures 4.9 and 4.10) complemented each other by showing the presence of the same species of calcite (CaCO_3), except that, just as in the fish scale, the VWMs displayed reduced intensities of the species relative to the non-VWMs. There was an extra visible peak that was attributed to ovocleidin 17 (OC-17) found in the Raman spectra of both the eggshell VWMs and non-VWMs (see Figure 4.9). Ovocleidin 17 and calcite are known for their ability to uptake ions by employing their amino functional groups and carbonate groups respectively to bond to ions via coordinate bonding [145][93].

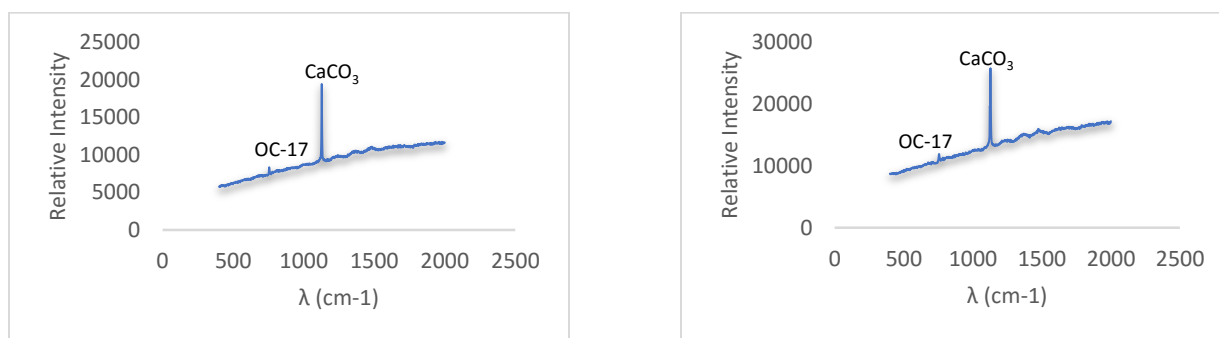


Figure 4.9: Raman spectrum for the eggshell VWMs (A) and eggshell non-VWMs (B)

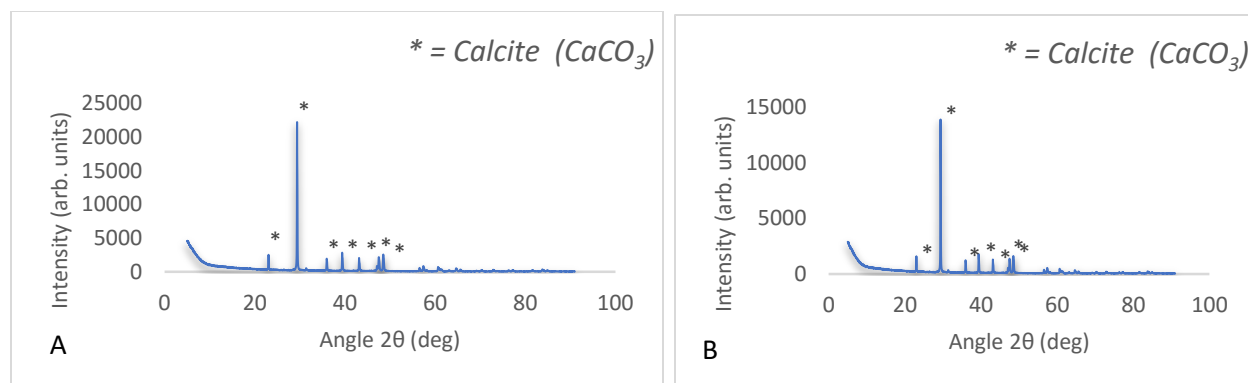


Figure 4.10: XRD diffractogram for the eggshell VWMs (A) and eggshell non-VWMs (B)

4.2 Binding Studies Experimental Design and Optimization Studies

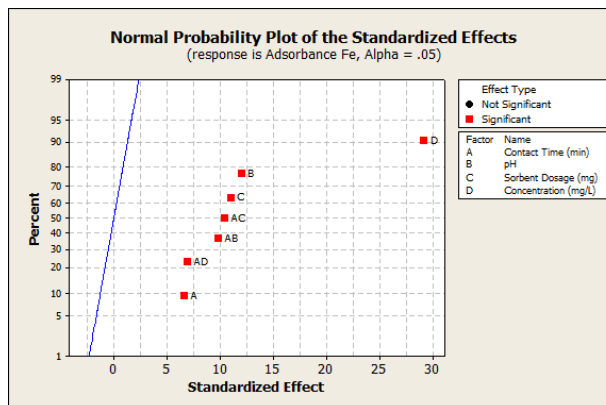
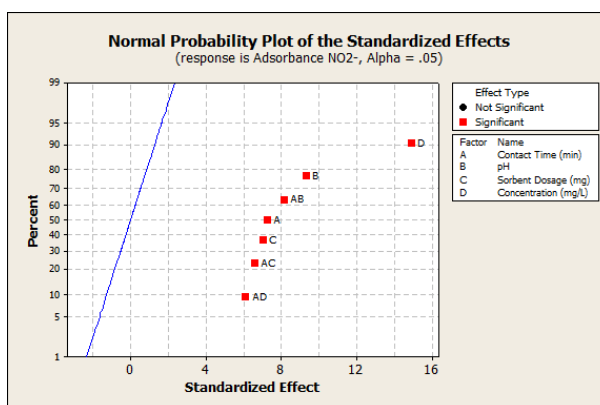
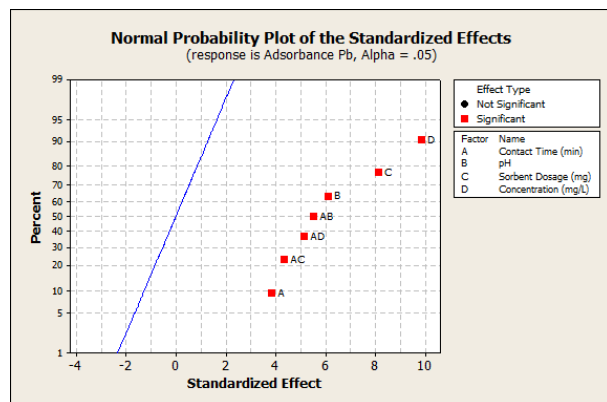
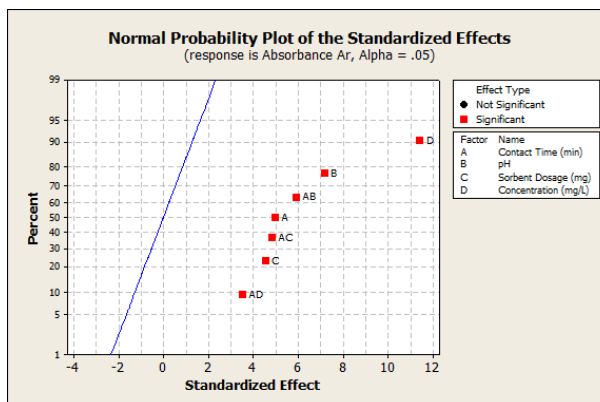
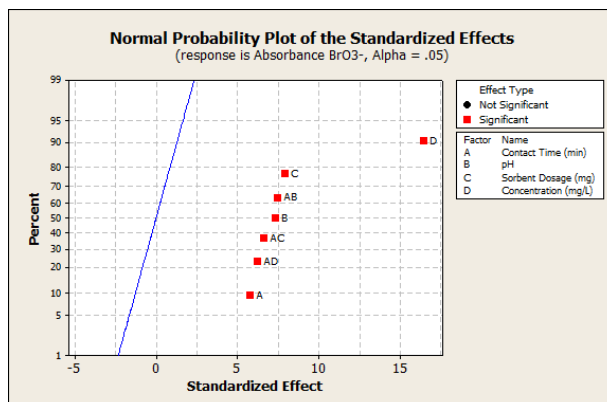
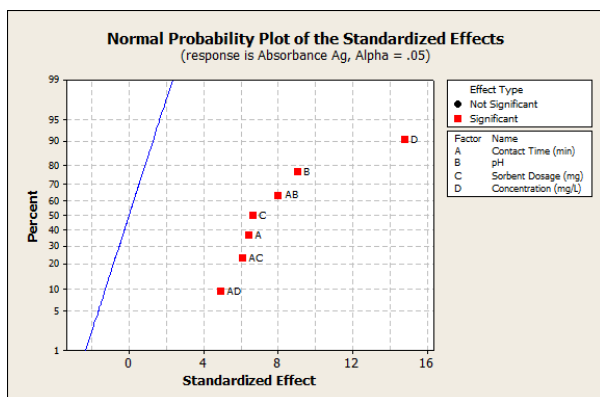
In order to optimize the practical experiments that were to be carried out with the VWMs, Minitab statistical software employing *Two-level ½ Fraction Factorial Design* and *Central Composite Design (CCD)*, was employed to theoretically design and optimize the experimental parameters (discussed in Section 3.6) that influence binding/adsorption.

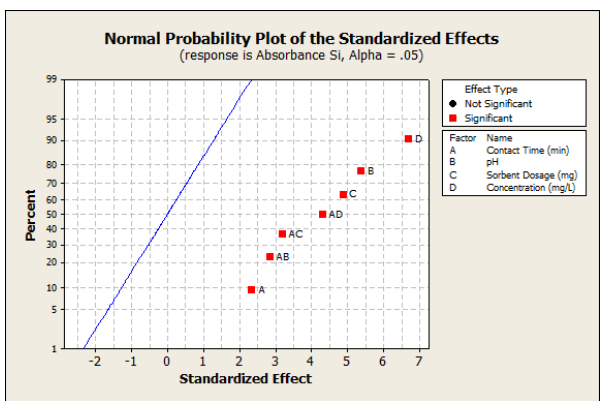
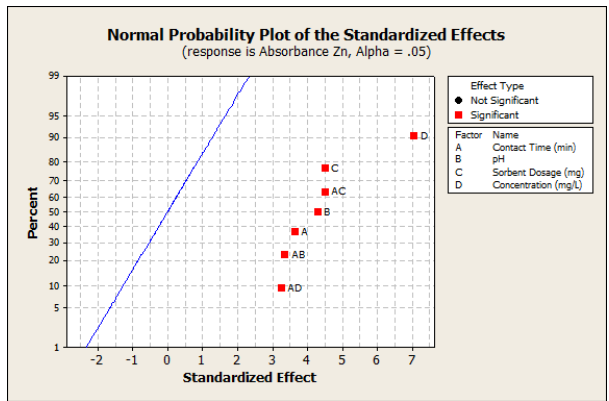
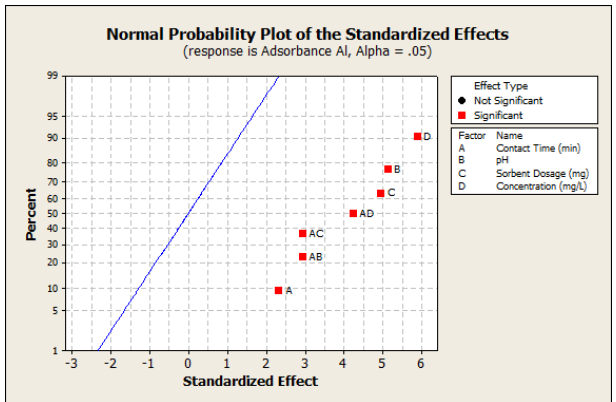
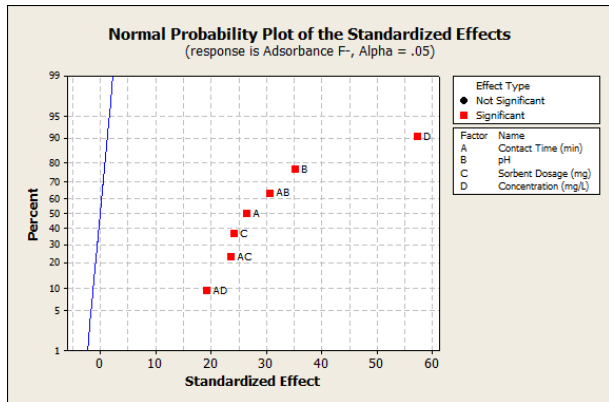
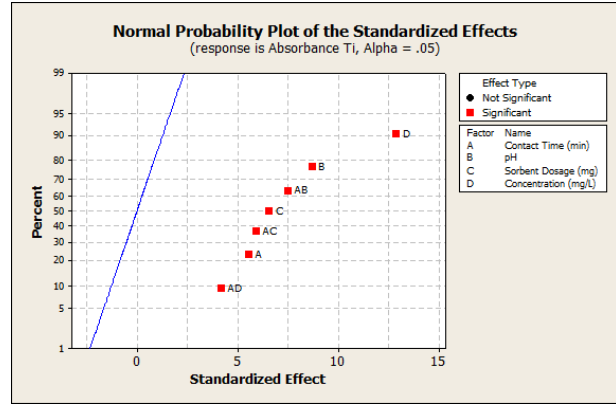
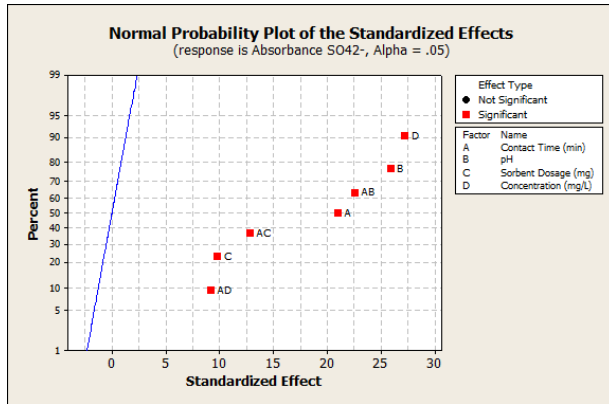
Two-level ½ Fraction Factorial Design

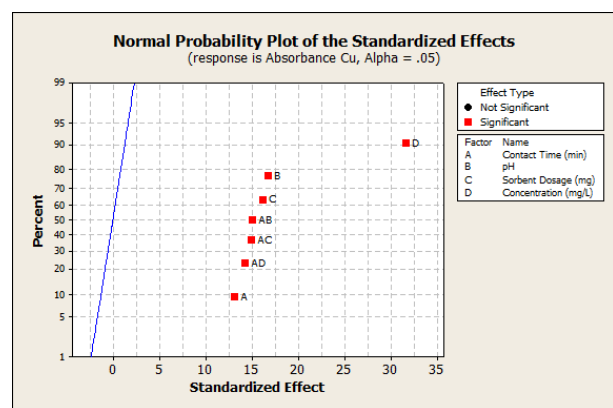
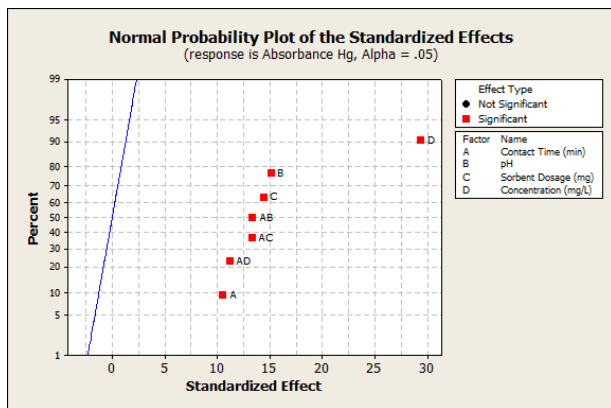
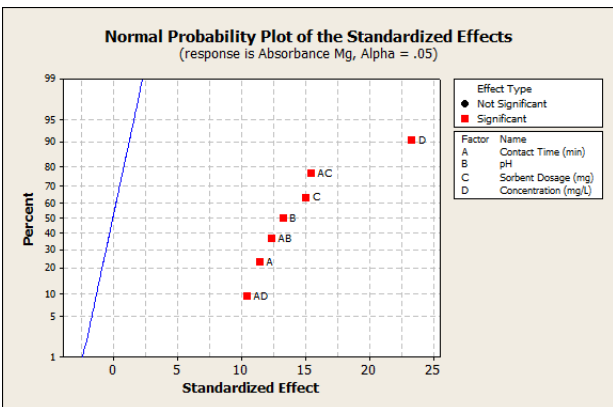
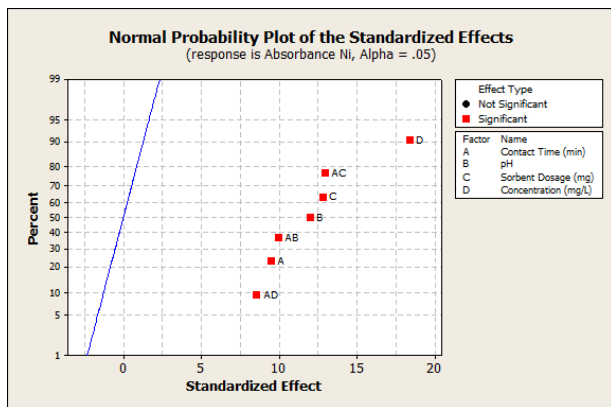
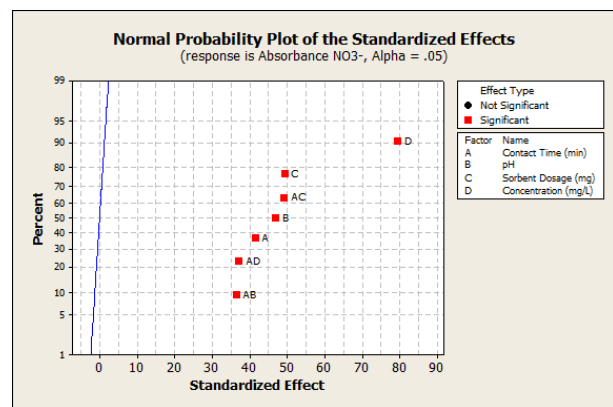
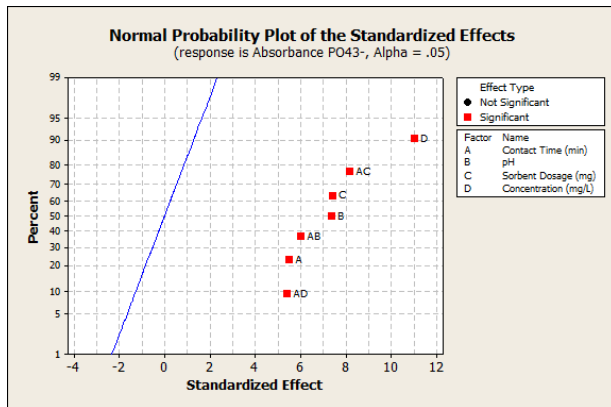
Prior to performing the practical optimization experiments, a *Two-level ½ Fraction Factorial Design* was performed to assess the level of significance of each investigated factor. The factorial design was employed as a screening phase which allowed a relatively large number of factors in a relatively small number of experiments that covered the whole experimental domain. The output identified the most influential factors towards the obtained yields. The design matrices, including the yields that followed performance of each experiment for each ion and each VWM were summarized in Appendix B (Tables 6.3 and 6.4). Analysis of the designed matrices was in the form of normal probability plots of standardized effects, Pareto charts of standardized effects and residual plots; as shown by Figures 4.11, 4.12 and 4.13, respectively. From the normal probability plots of standardized effects in Figures 4.11A (for fish scale VWMs) and 4.11B (for eggshell VWMs), the magnitude of the main effects of each factor as well as the effects brought about by the interaction of factors towards the obtained yields were investigated. The magnitude of each type of effect was represented by its distance from the solid

line, as well as the side on which the effect lay with respect to the solid line. Negative effects lay to the left while positive effects lay to the right of the solid line. The solid line indicated where the points would have fallen if the effects were zero, while the percentage on the y-axis signified the weightage of each of the factor's contribution towards the obtained yields. All the investigated effects showed a positive magnitude as they all lay to the right of the plots. The main effects, due to Factor A (contact time); B (pH), C (VWMs dosage) and D (concentration) were significant for the selected ions. Figure 4.11A and B showed that Factor D for the fish scale and the eggshell VWM powders lay furthest to the right of the solid line, signifying that factor D had a greater positive magnitude towards contribution of the yields obtained. However, the contribution of each of the factors (Factors; A, B, C, and D) showed higher weightage towards the output when compared to that of the effects brought about by the interaction of factors for both VWMs. The fish scale VWMs' normal probability plots of standardized effects of Ag, Cl⁻, NO₂⁻, F⁻, Ti, SO₄²⁻, Cr, BrO₃⁻ and As; showed that there was a significant contribution towards the obtained yields as a result of interactions between the factors; Factor A and Factor B, while, that of Cd, Zn, PO₄³⁻, NO₃⁻, Ni and Mg showed that there was a significant contribution towards the obtained yields as a result of the interactions between the factors; Factor A and Factor C.

The eggshell VWM powders' normal probability plots of standardized effects of Mg, Cl⁻, NO₂⁻, Fe, Si, SO₄²⁻, Cr, Cd, Co, PO₄³⁻ and As; showed that there was a significant contribution towards the obtained yields as a result of the interactions between the factors; Factor A and Factor B, while, that of Ag, Zn, Ti, NO₃⁻, BrO₃⁻, and Pb showed that there was a significant contribution towards the obtained yields as a result of the interactions between the factors; Factor A and Factor C.







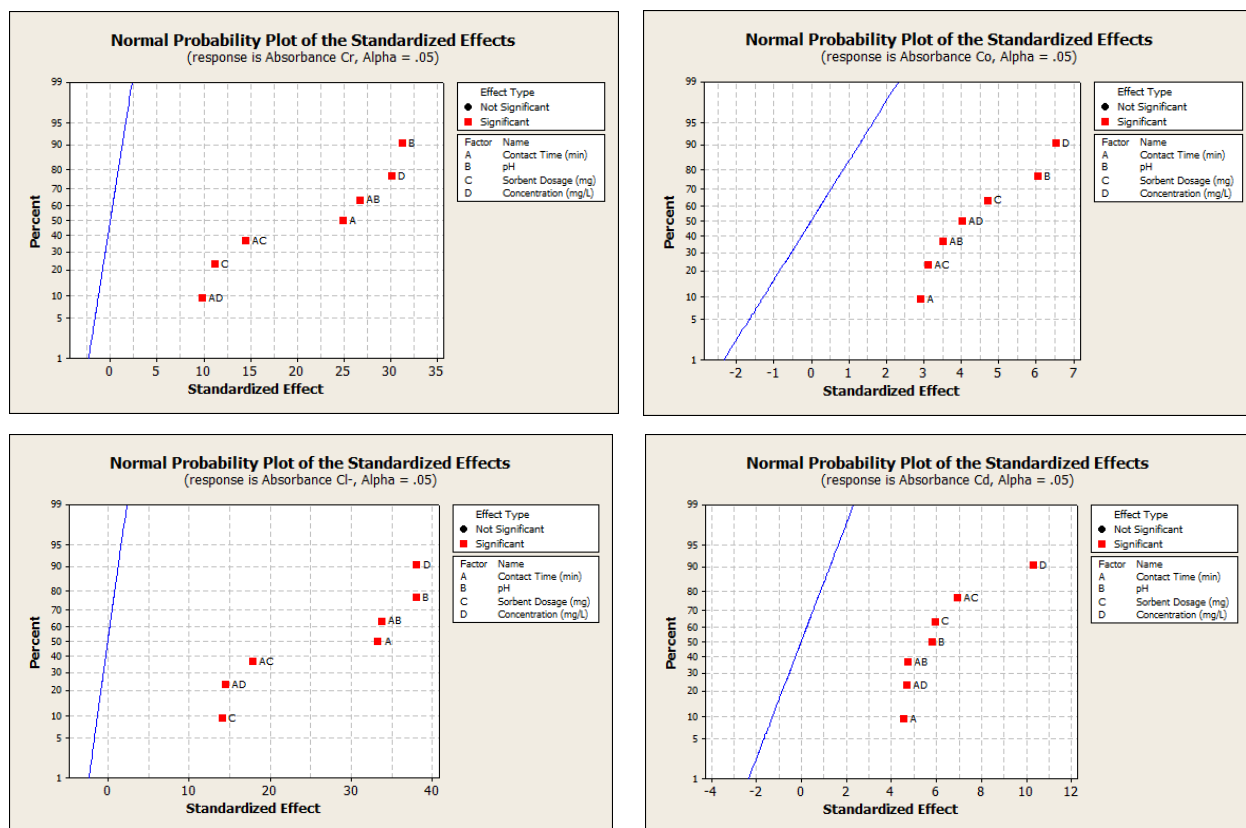
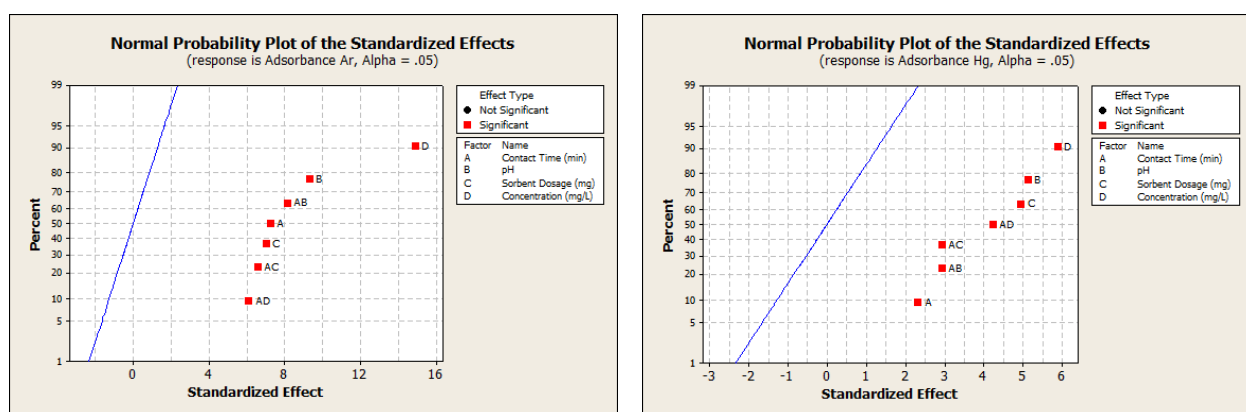
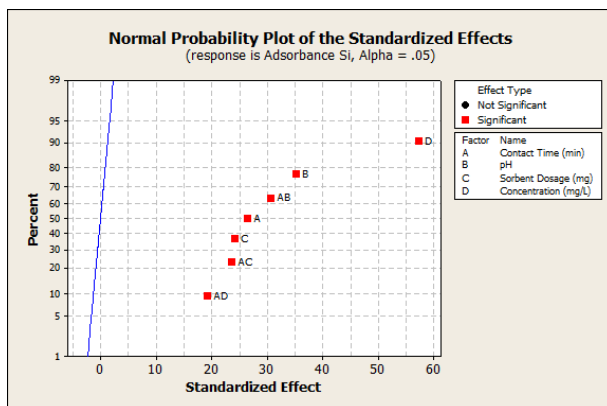
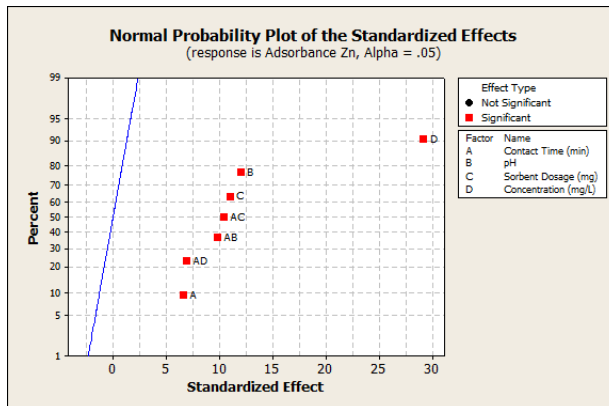
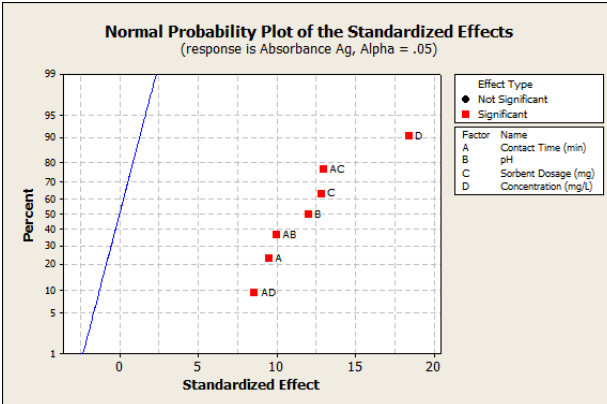
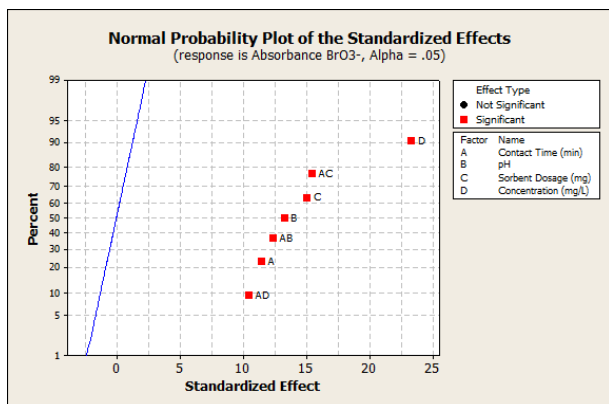
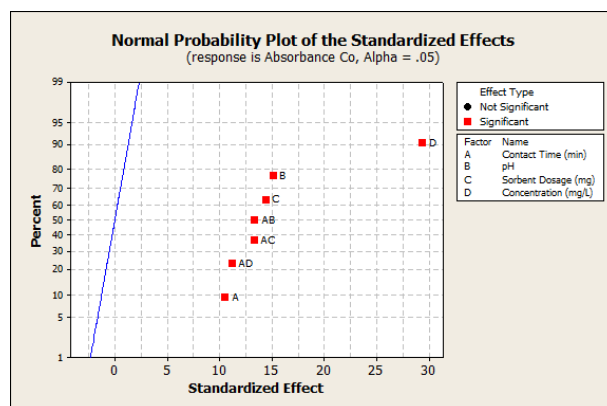
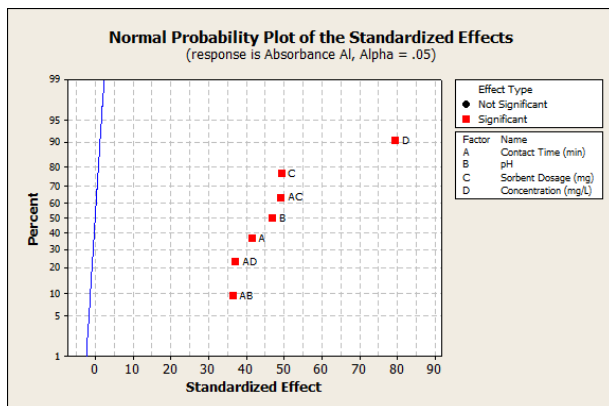
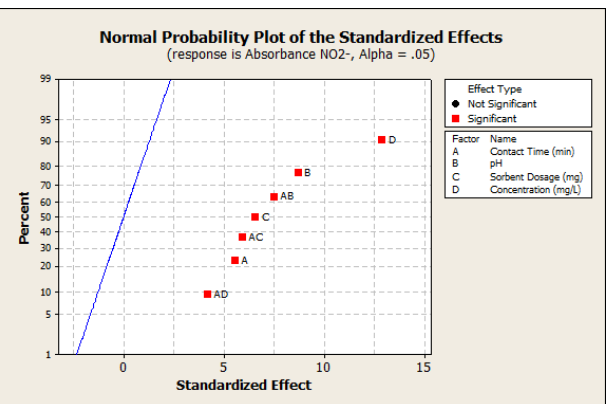
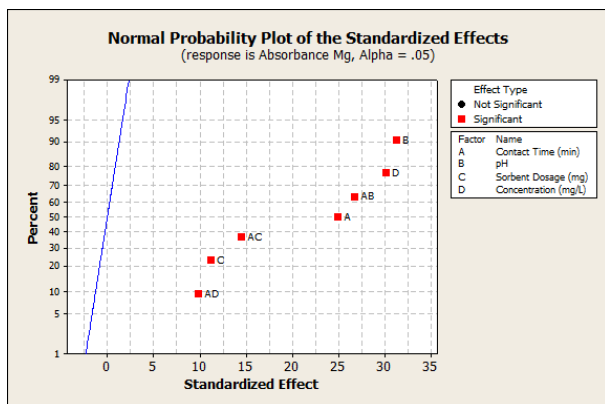
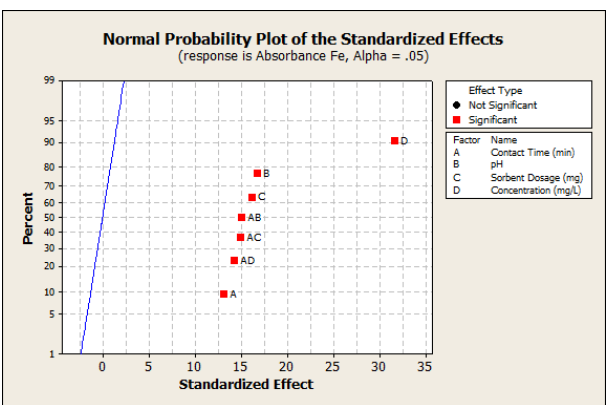
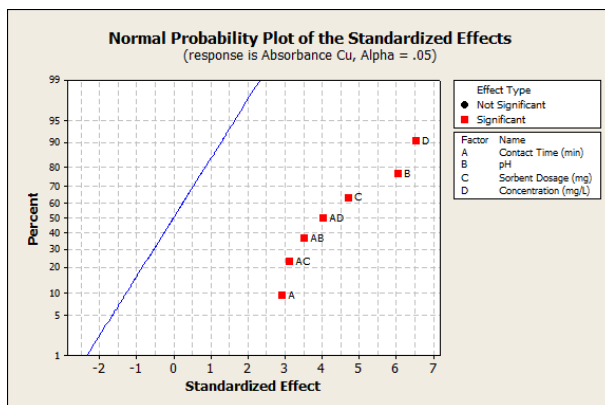
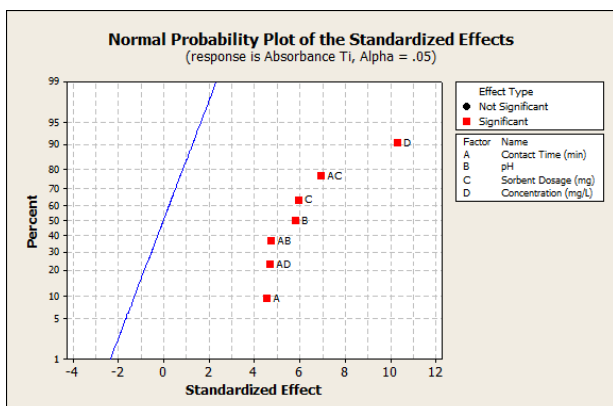
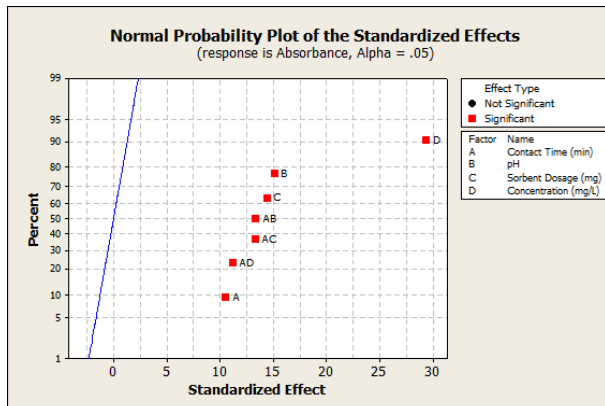
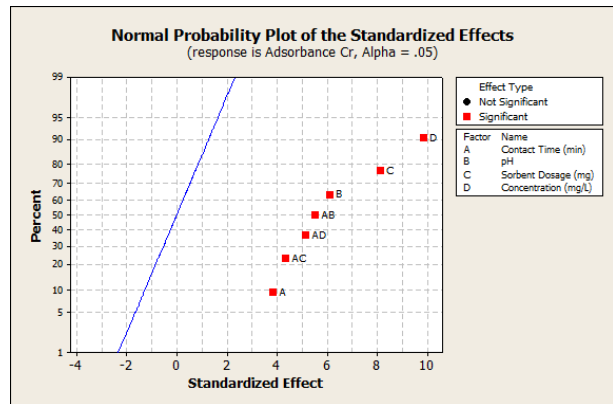
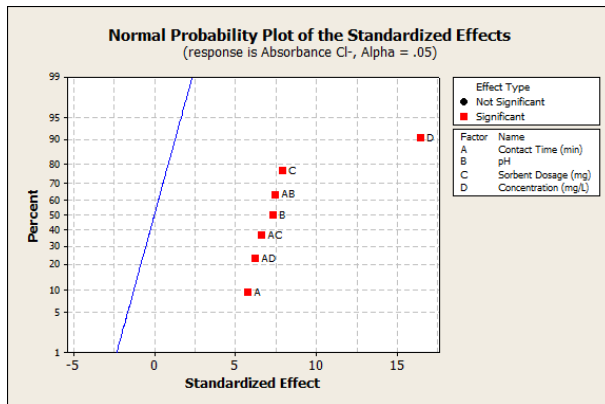


Figure 4.11A: The normal probability plots of standardized effects of the selected ions for the fish scale VWMs







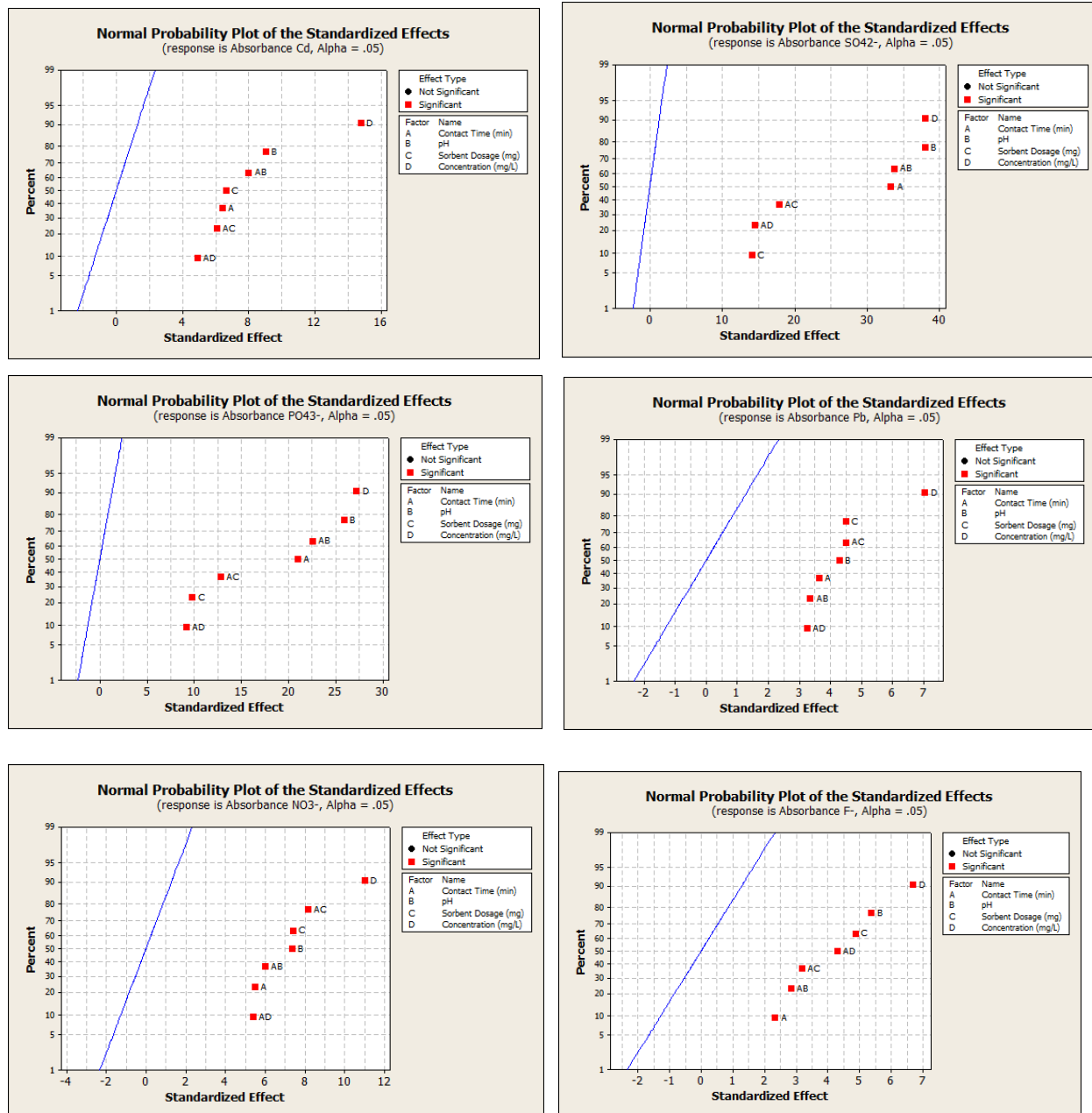
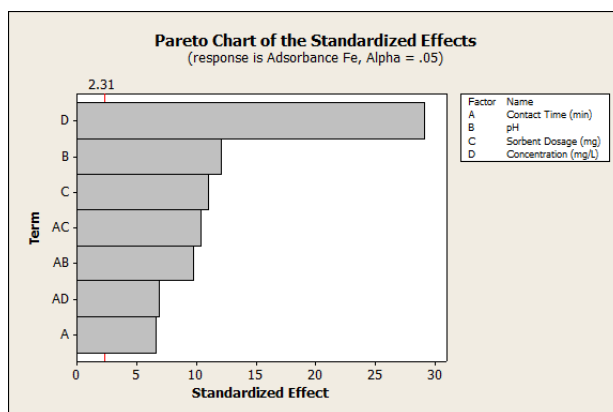
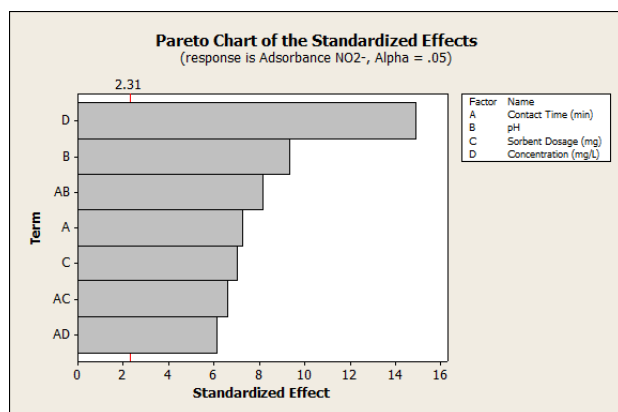
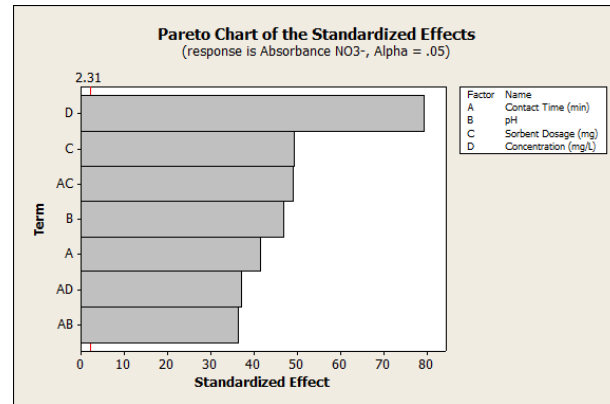
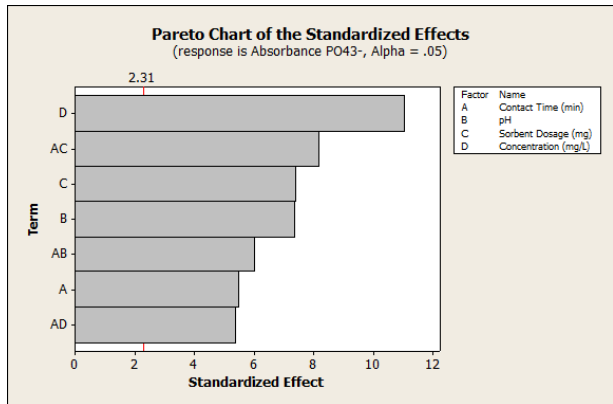
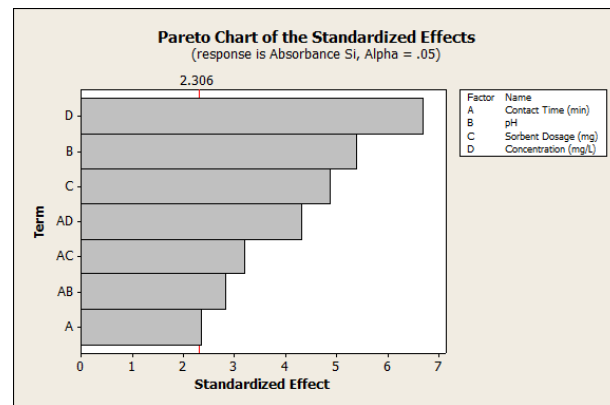
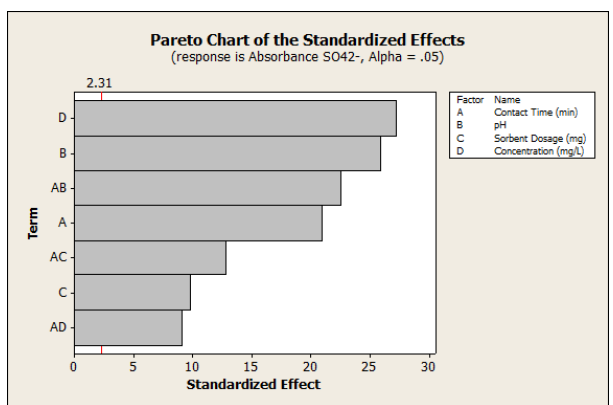
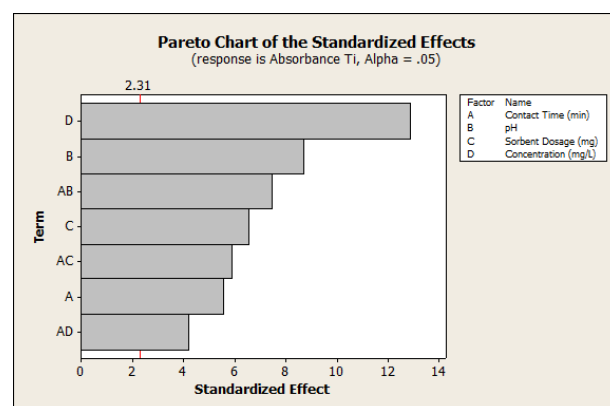
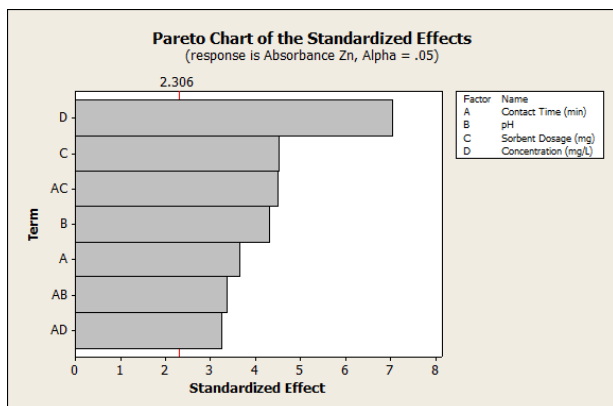
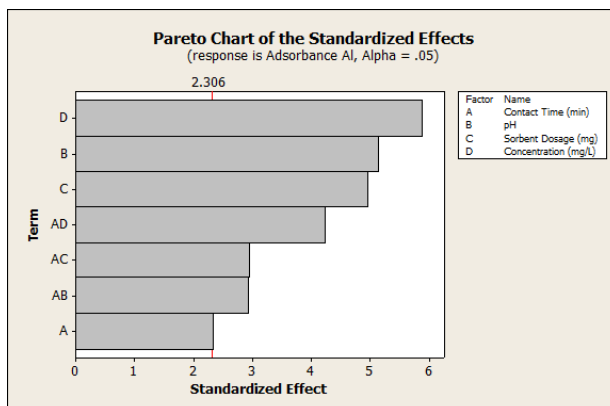
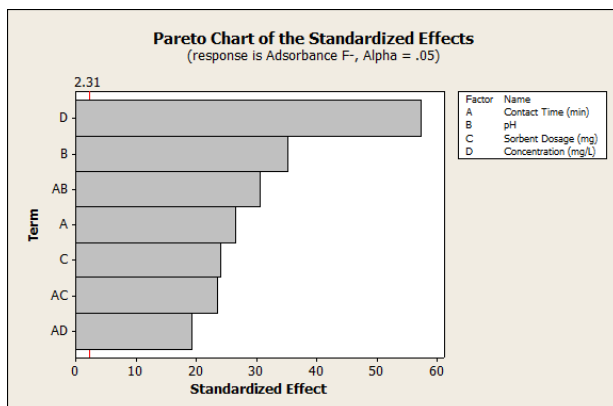


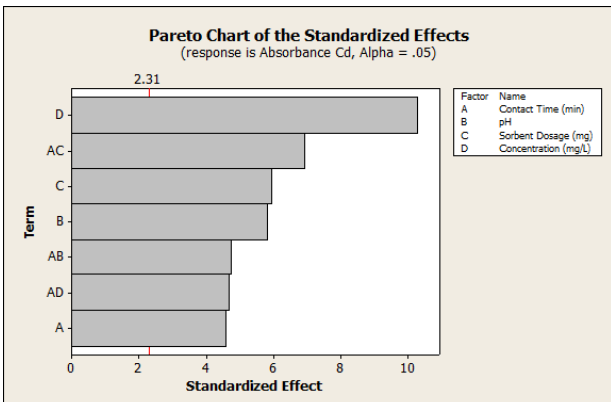
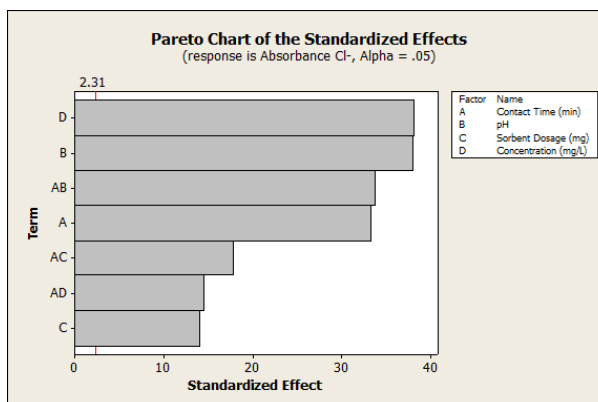
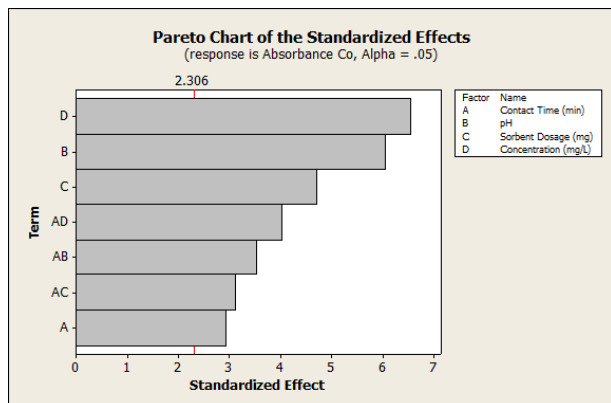
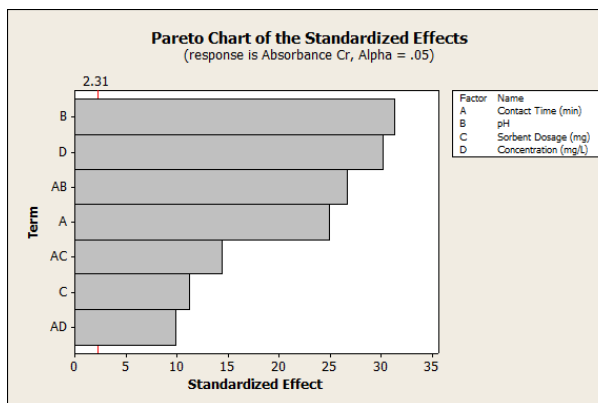
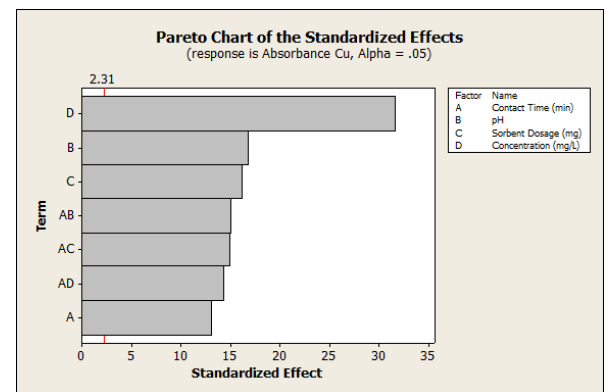
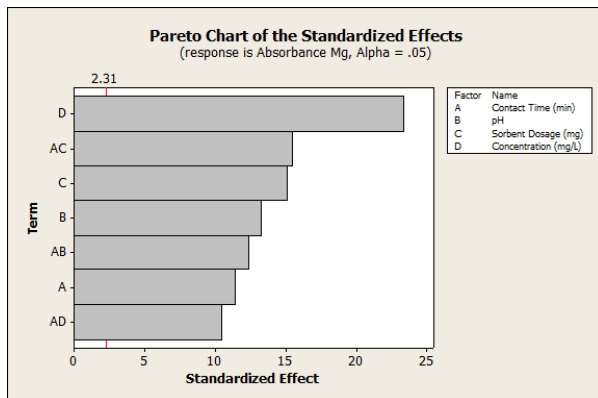
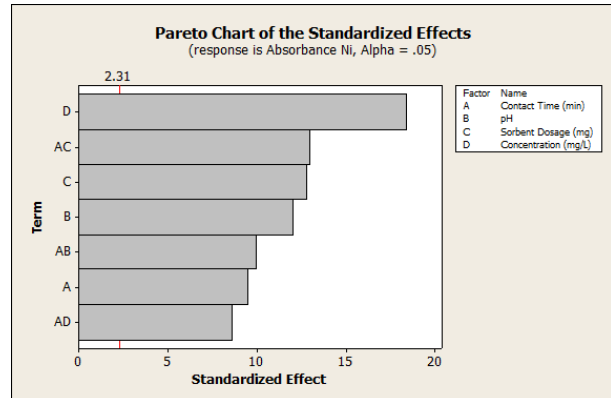
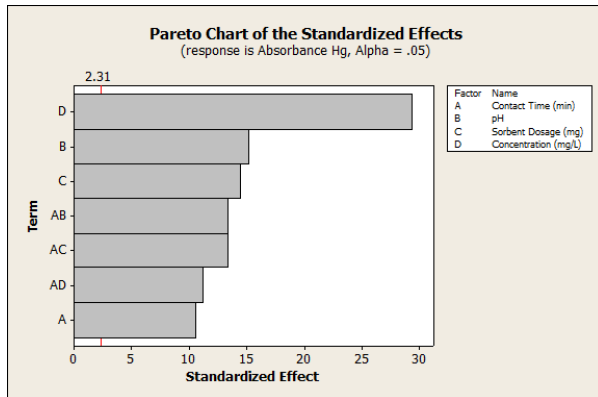
Figure 4.11B: The normal probability plots of standardized effects of the selected ions for the eggshell VWMs

Pareto charts of standardized effects in Figures 4.12A and 4.12B were employed for the identification of factors and the interactions of effects that were significant in the study. Only the absolute values of the effects were displayed. For each Pareto chart, a reference line was drawn on the chart, beyond which any effect that crossed it was significant. The reference line was

calculated by Minitab based on the standardized effects for cases where an error term existed or through the use of the Lenth's pseudo-standard error for cases where no error term was present [146]. The Pareto charts works hand-in-hand with the *p-value* test at a particular confidence level (commonly at 95 % confidence level). The chart display relevant effect of each factor on the response signal (yield), sorted from largest to smallest; with the reference line corresponding to a *p-value* of 0.05. Information deduced from the interpretation of the Pareto charts is always expected to corroborate the information deduced from the normal probability plots of standardized effects [147], which was the case with the Pareto charts in Figures 4.12A and 4.12B when compared to the normal probability plots of standardized effects in Figures 4.11A and 4.11B respectively. From the Pareto charts, the main effects due to Factors; A (contact time), B (pH), C (sorbent dosage) and D (concentration) were all found to be significant as each term crossed the solid reference line (see Figures 4.12A and 4.12B). The same significance for each of the factors was noted under the normal probability plots of standardized effects (see Figures 4.11A and 4.11B). The effect of Factor D showed the highest significance towards adsorption efficiency of both the eggshell and the fish scale VWMs. There were also effects due to interactions between combination of any two factors (for example, AB, AC, BC, CD etc.). The most significant of the combination interactions were the ones with Factor A.







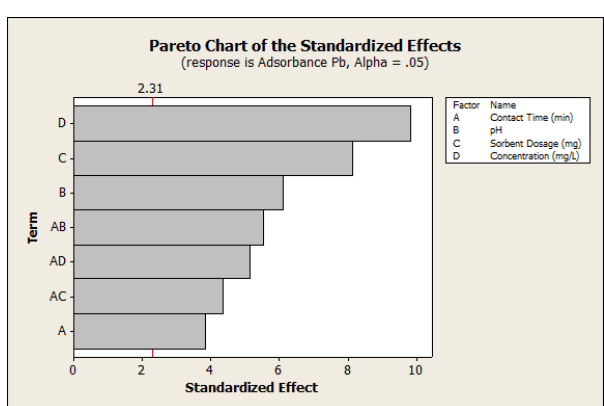
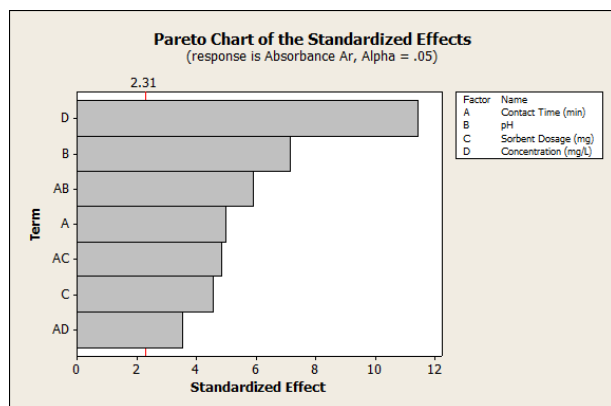
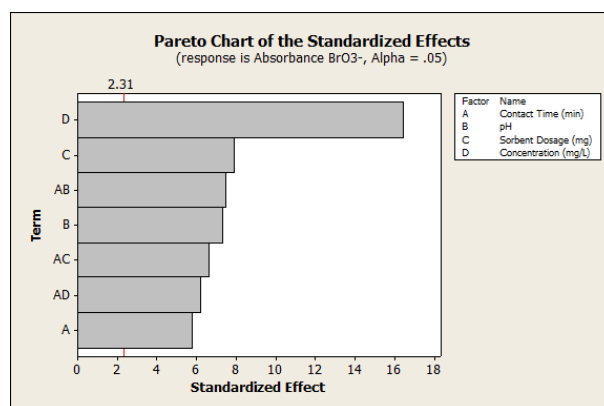
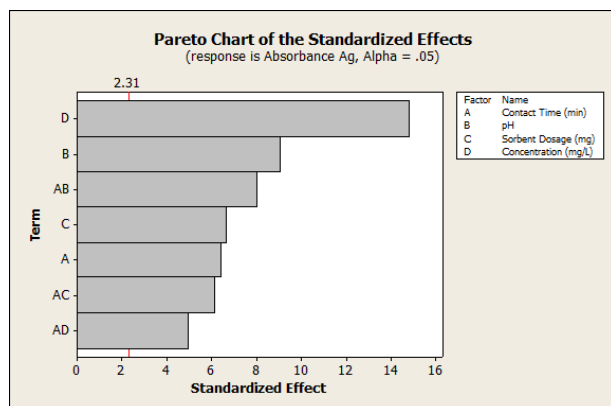
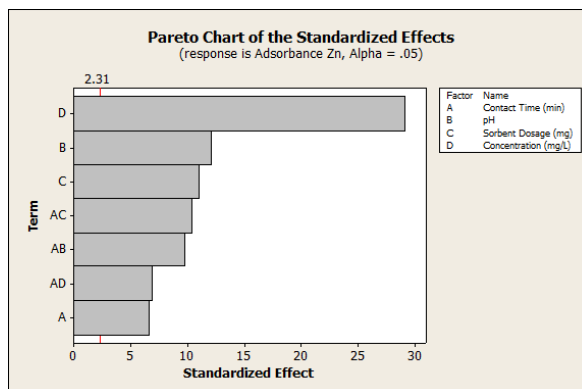
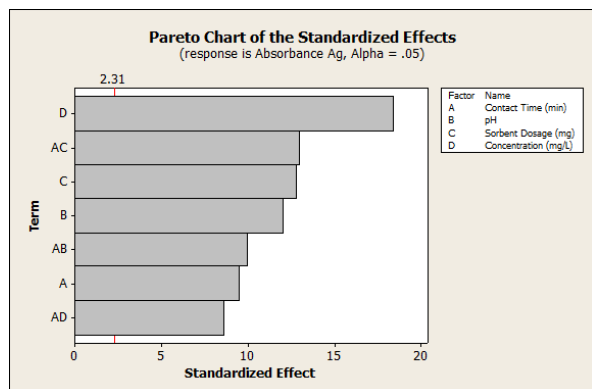
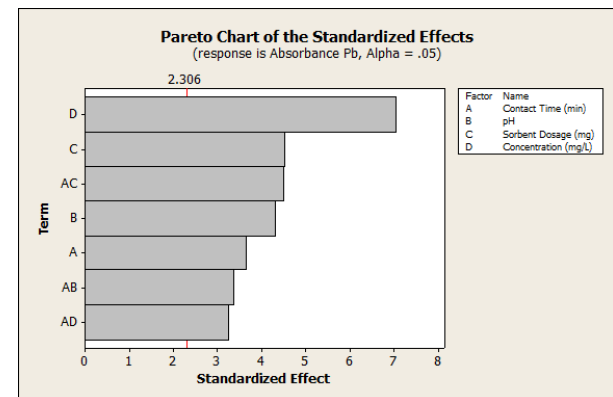
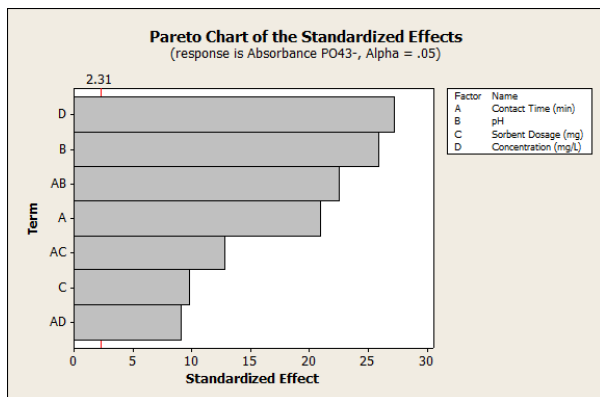
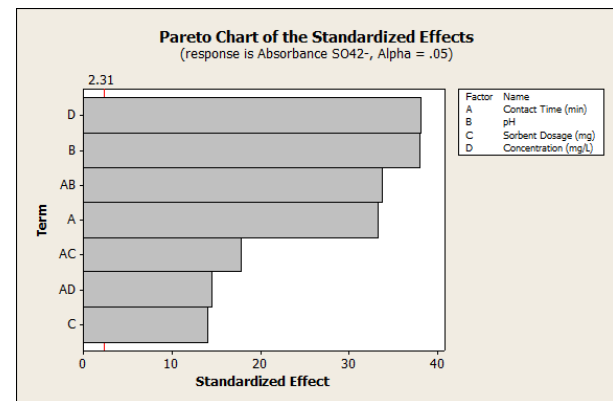
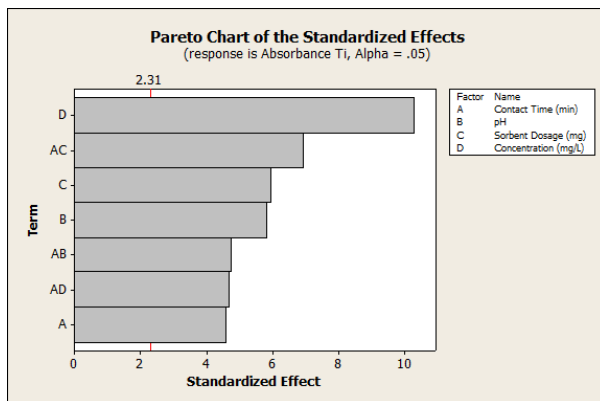
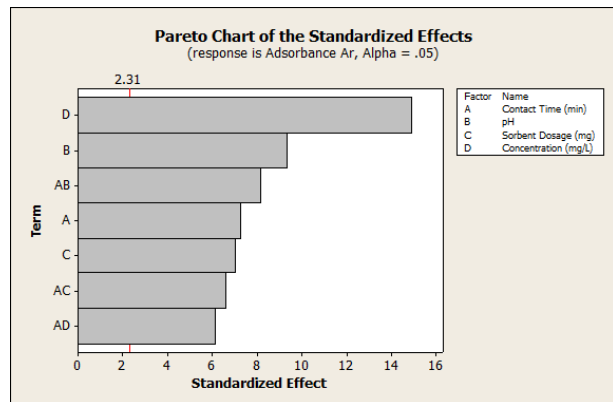
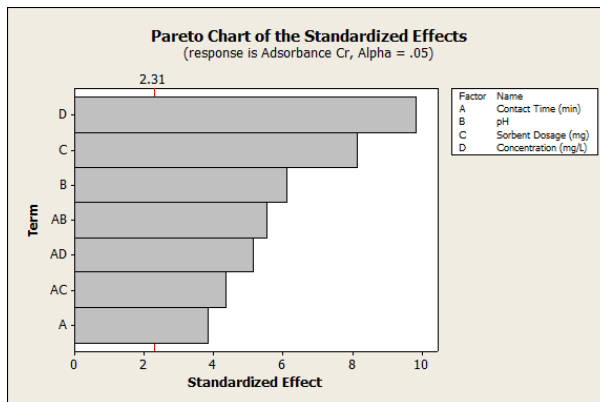
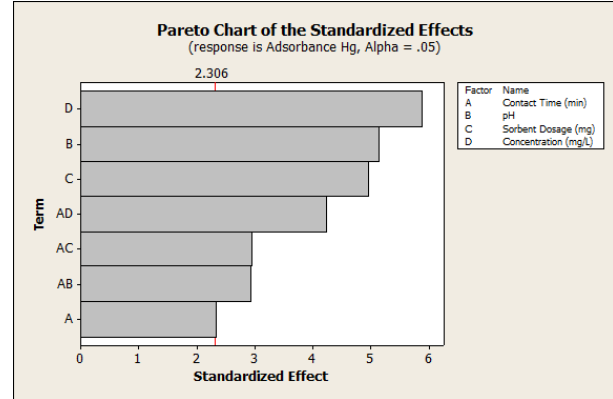
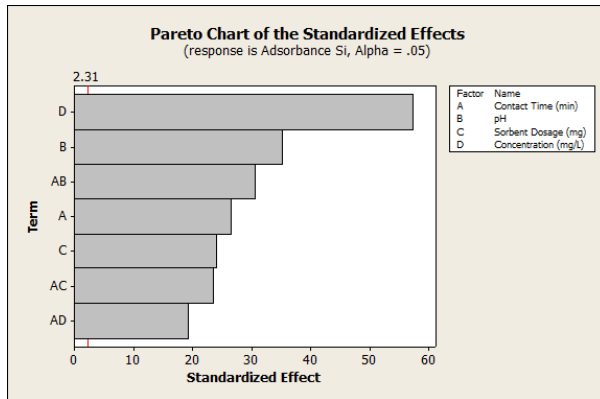
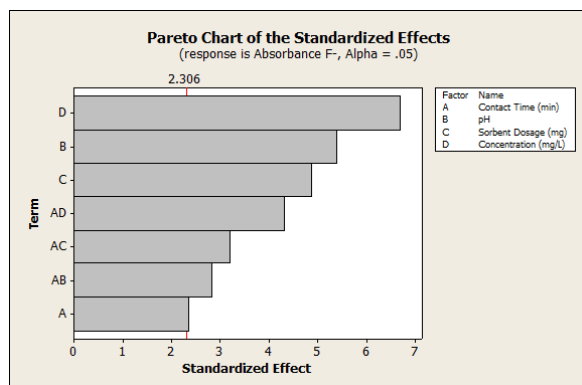
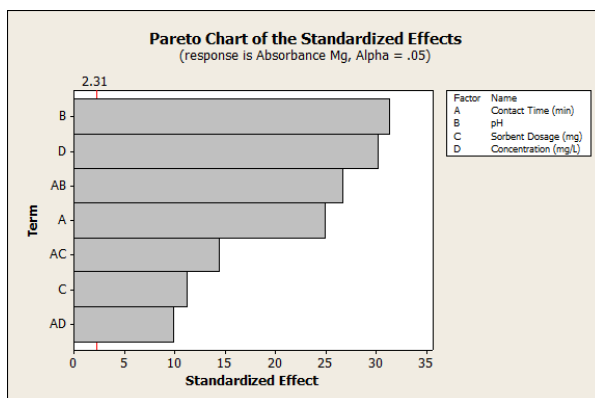
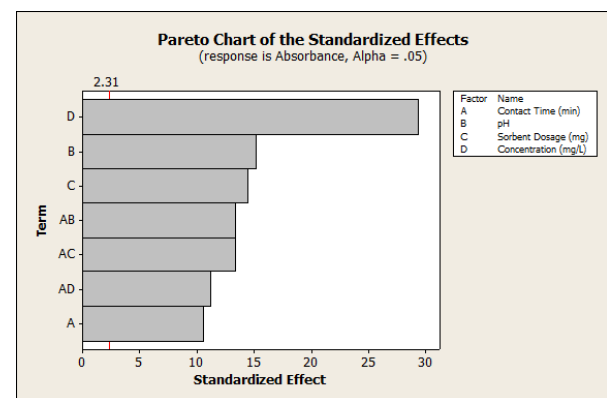
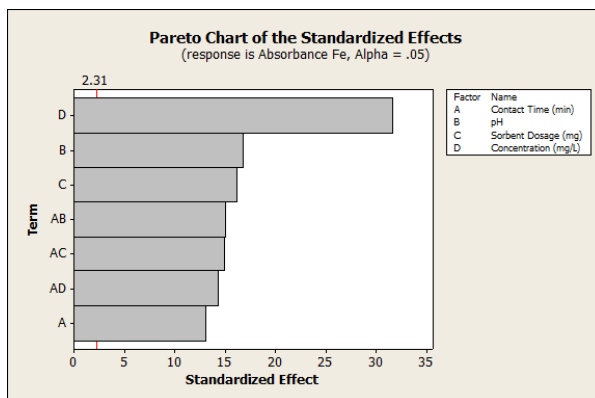
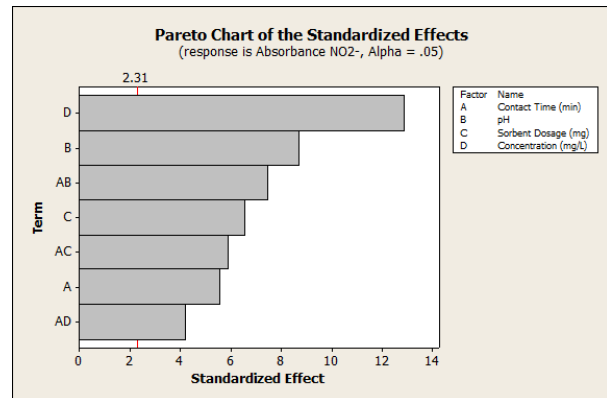
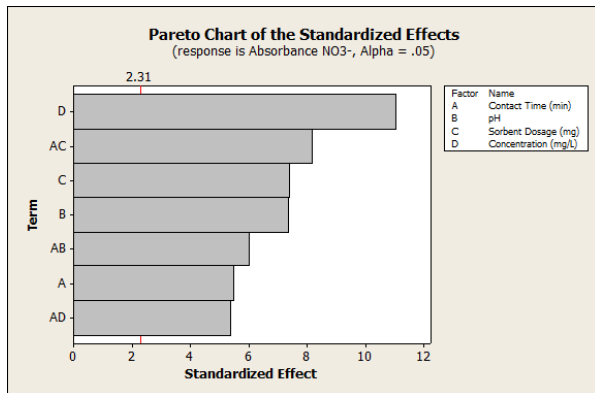


Figure 4.12A: Pareto charts of standardized effects of the selected ions for the fish scale VWMs







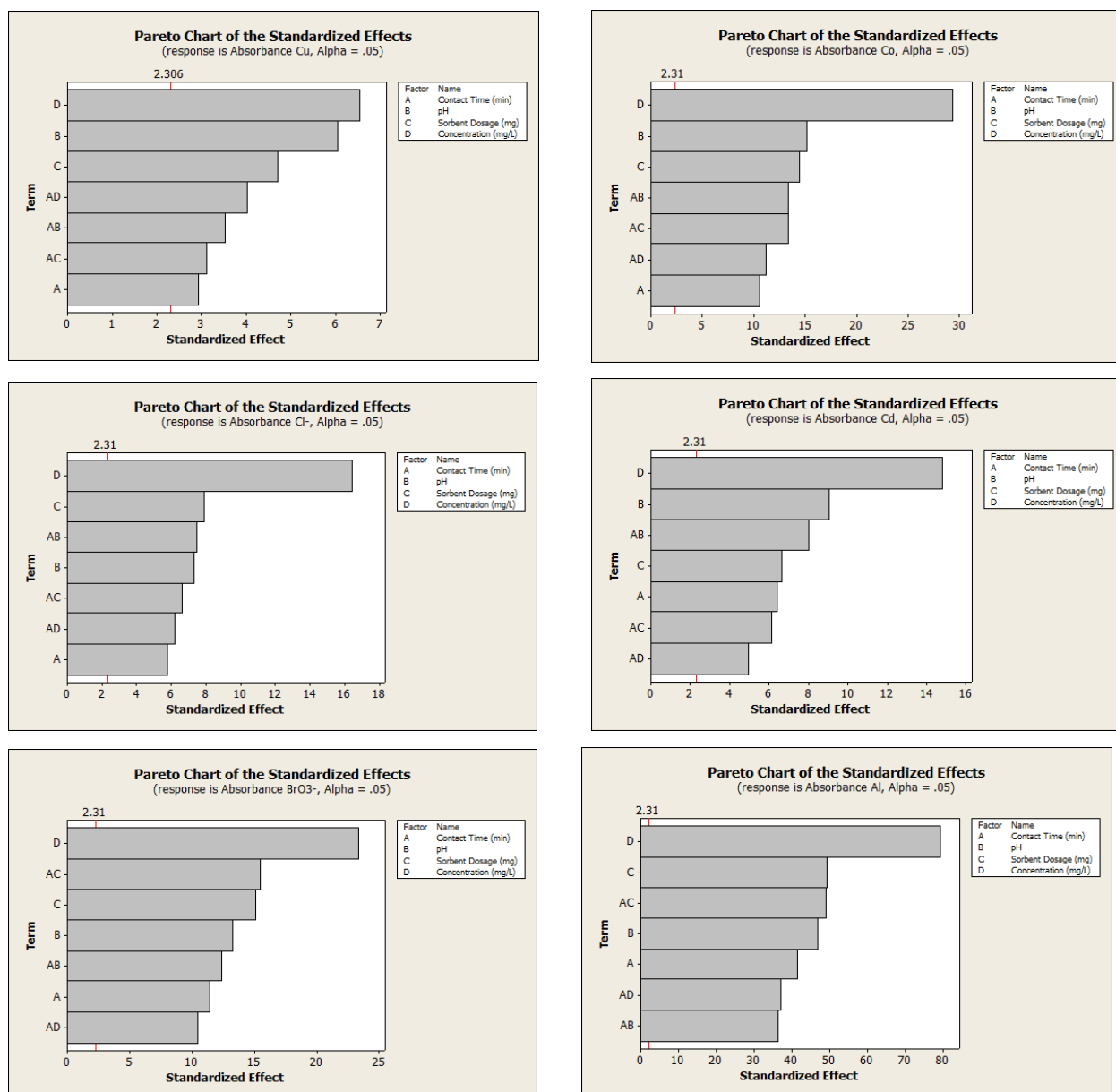
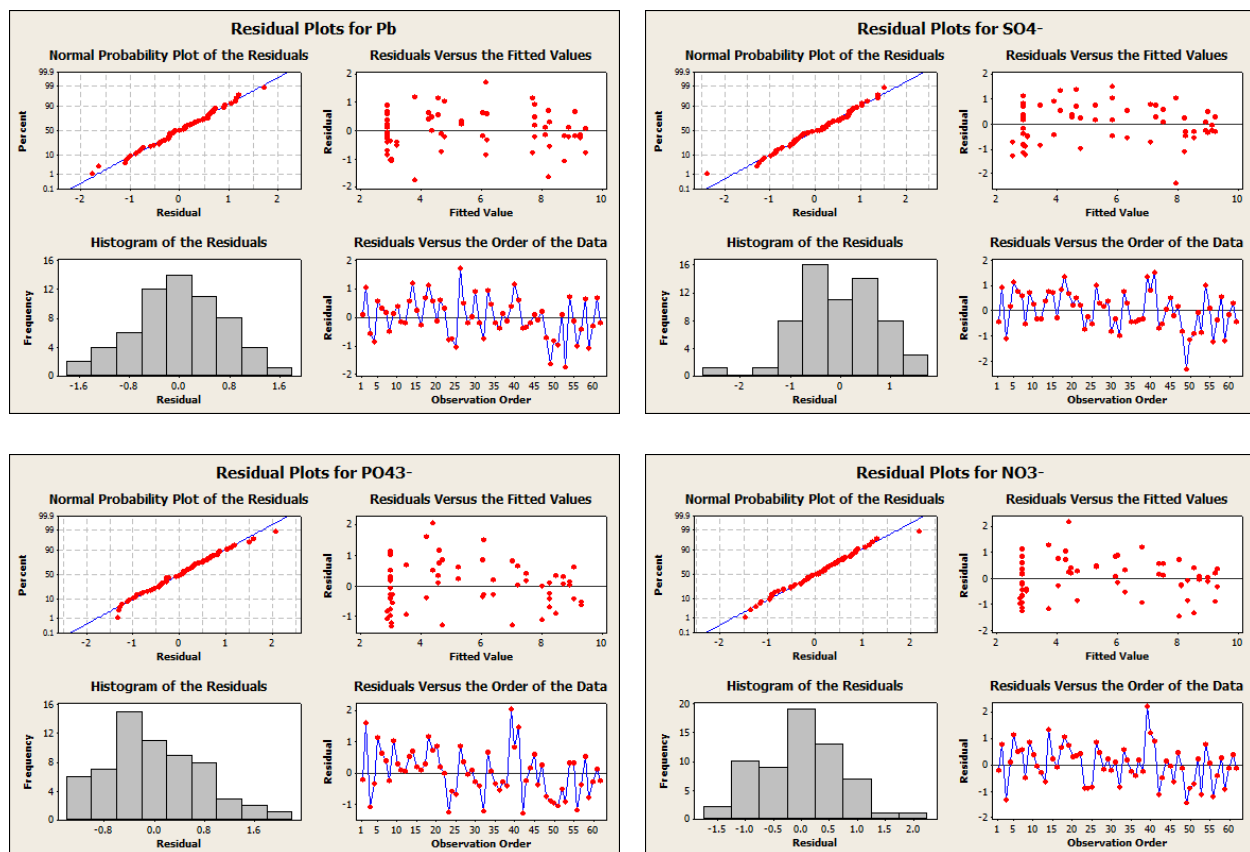
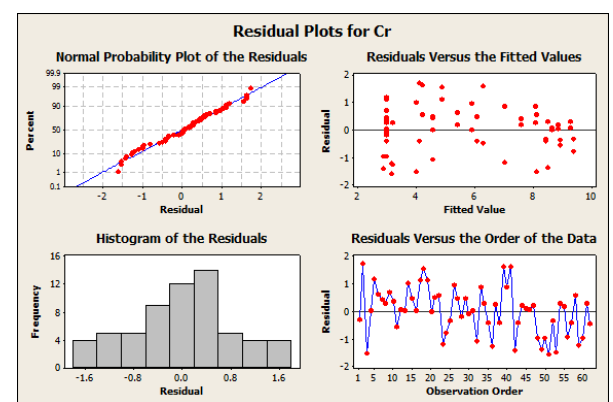
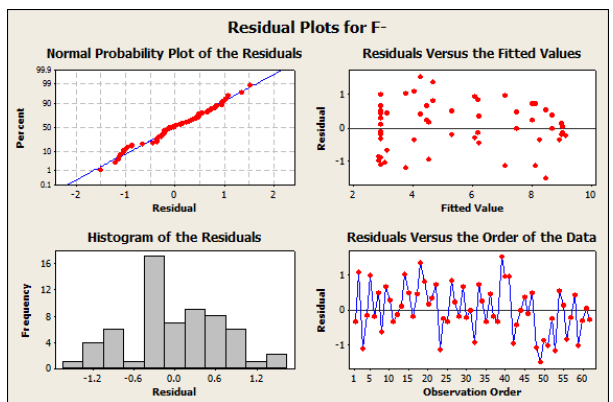
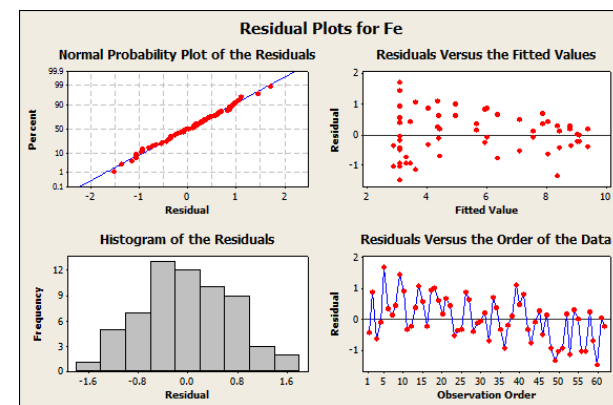
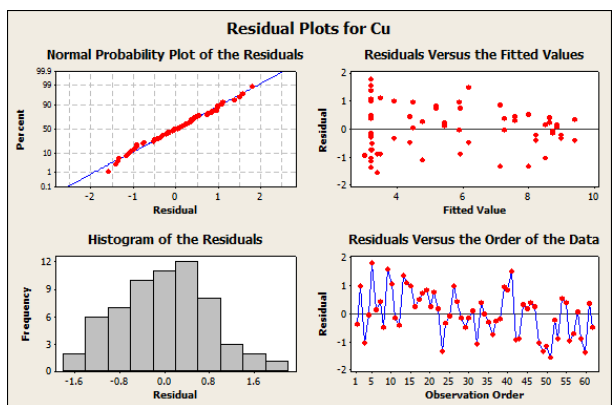
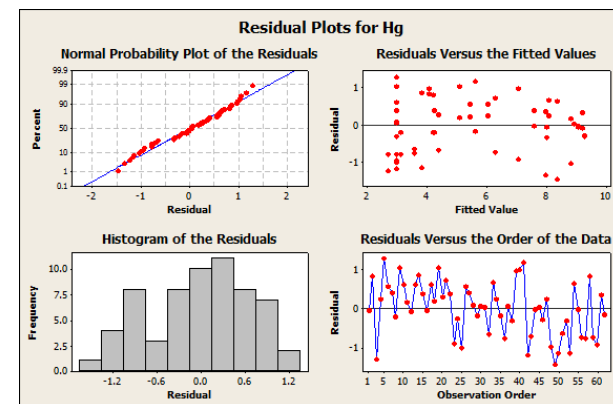
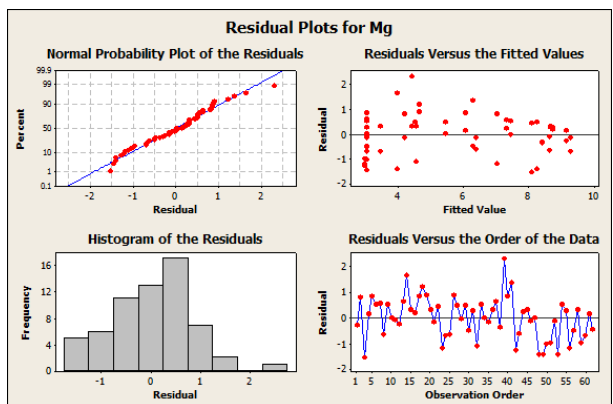
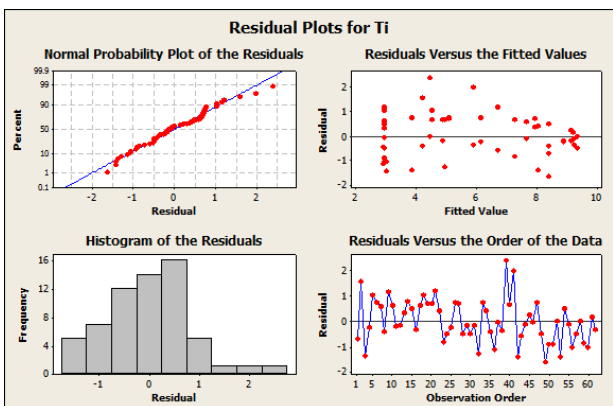
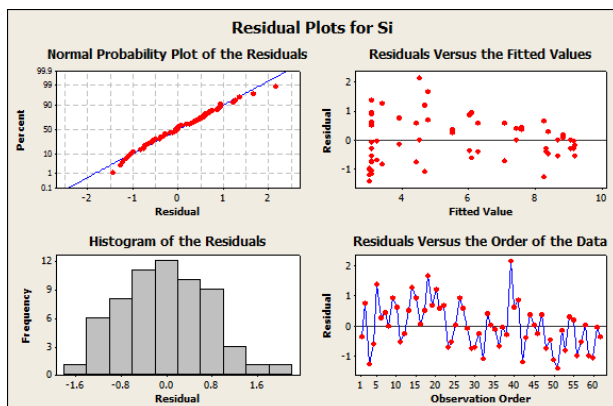


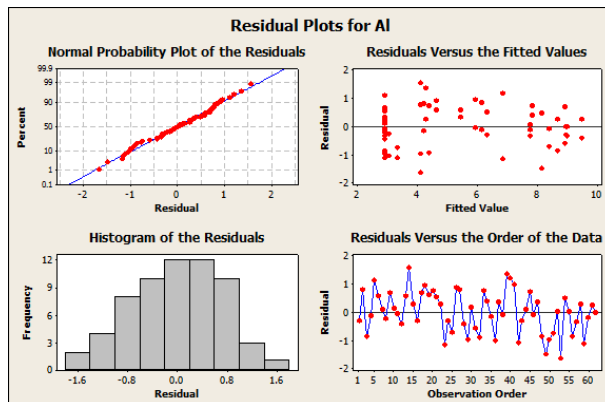
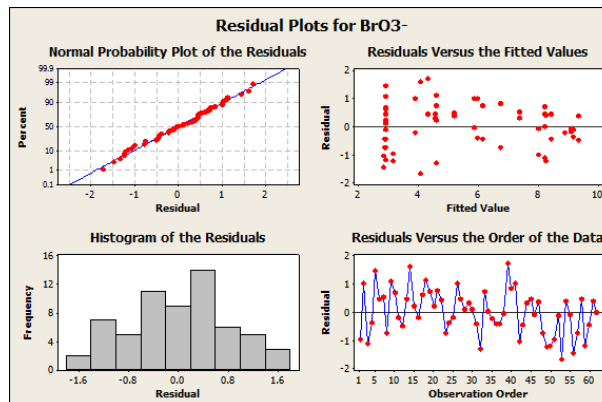
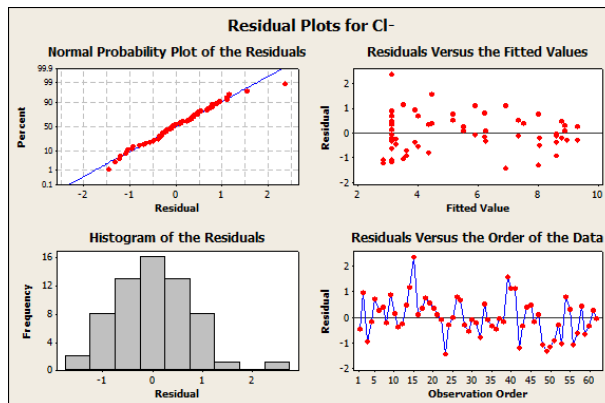
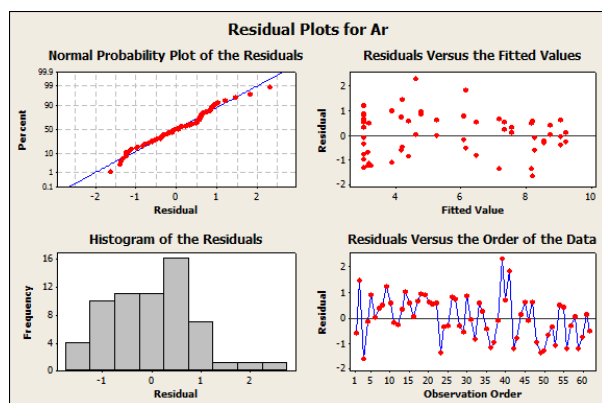
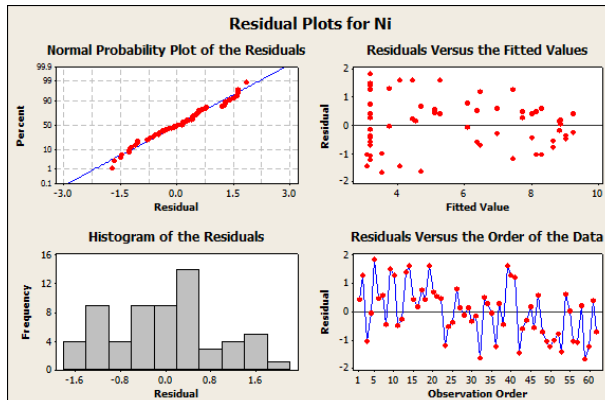
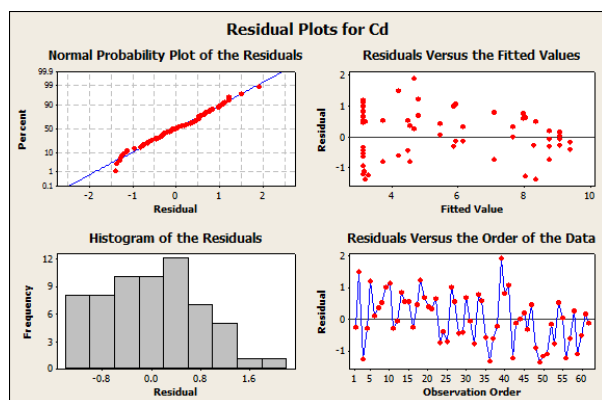
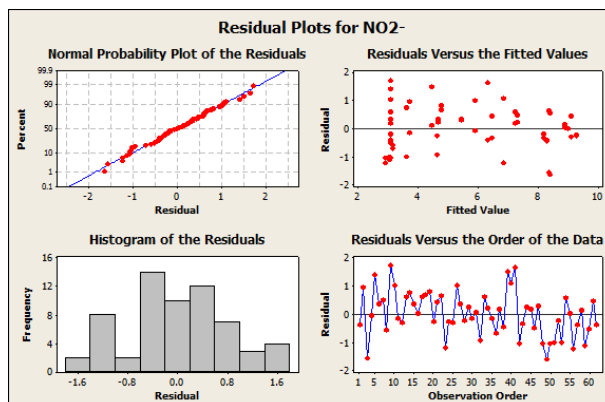
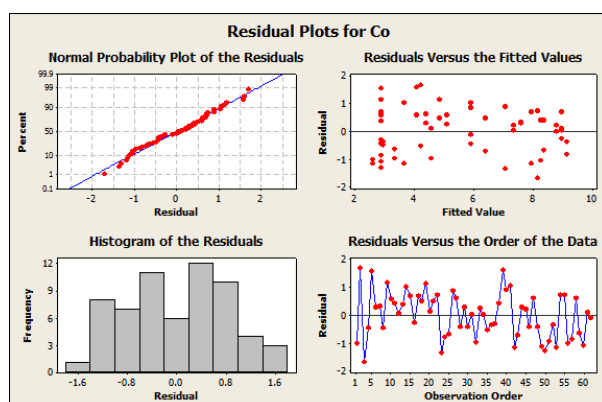
Figure 4.12B: Pareto charts of standardized effects of the selected ions for the eggshell VWMs

Residual plots (Figures 4.13A and 4.13B) for the VWMs yields (absorbance) obtained from Minitab were also studied. The plots showed the distribution patterns of data points based on the use of residuals which are the differences between the observed and the fitted values. The normal probability and histogram plots of the residuals were to confirm whether the data obtained exhibited standard Gaussian distribution or not. For the normal probability plots of the residuals, if the data points fell approximately along the straight line, then the residuals were said to be

normally distributed, and adhering to Gaussian distribution [148]. On the other hand, the plots of residuals versus fitted values were employed to detect unequal error variances and outliers, whilst the plots of residuals versus order of the data was to confirm whether there was correlation between the fitted and the observed residual data. The residuals versus fitted values plots revealed constant variances of the residuals about the center lines, signifying strong correlation between the fitted and the observed residual data. For the plots of residuals versus order of the data, randomized fluctuation of patterns about the center lines were observed, signifying that the data was uncorrelated. All the plots of the residuals versus order of the data for both the eggshell and fish scale VWMs showed randomly distributed residuals, thus signifying the absence of systematic errors and hence adequacy of the model [148].







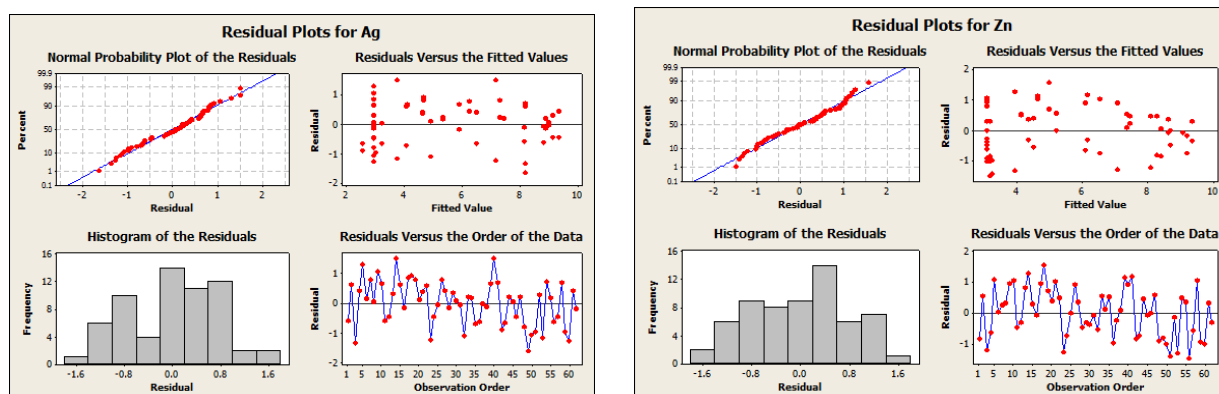
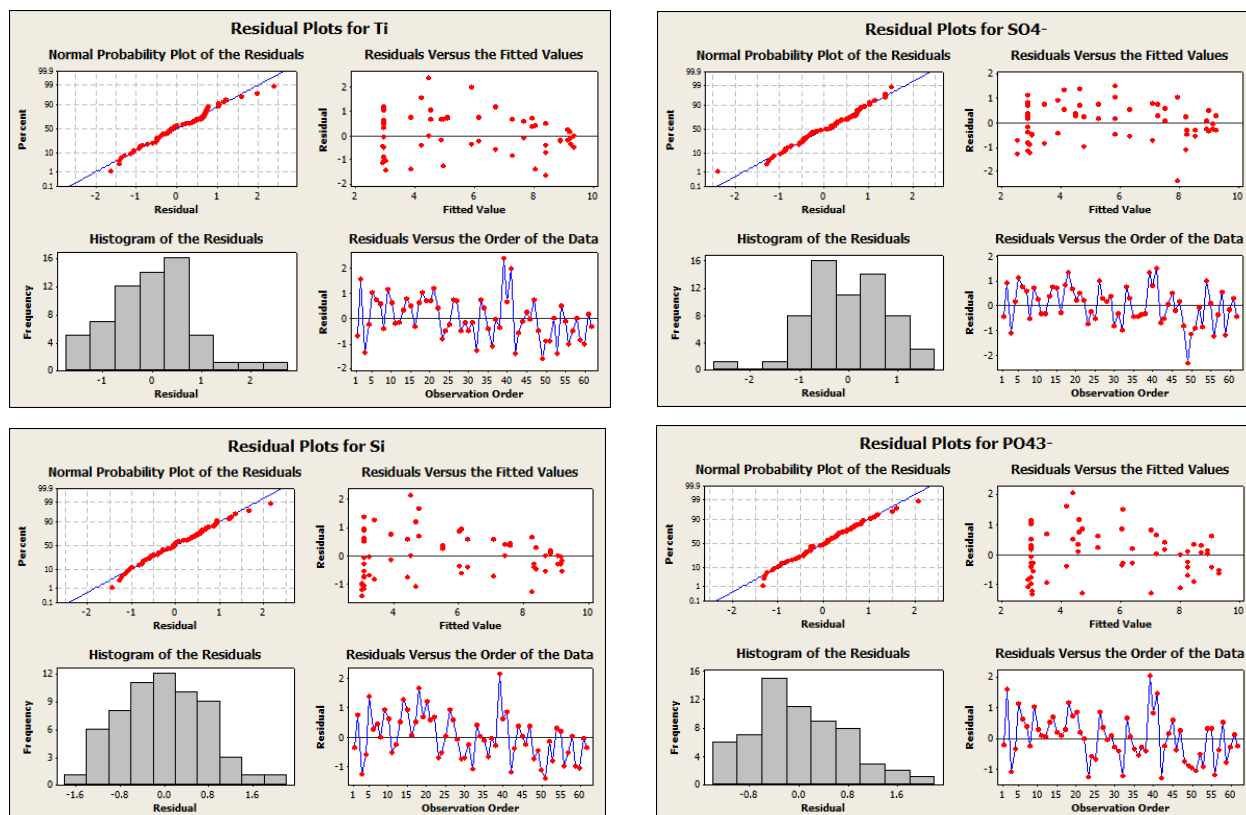
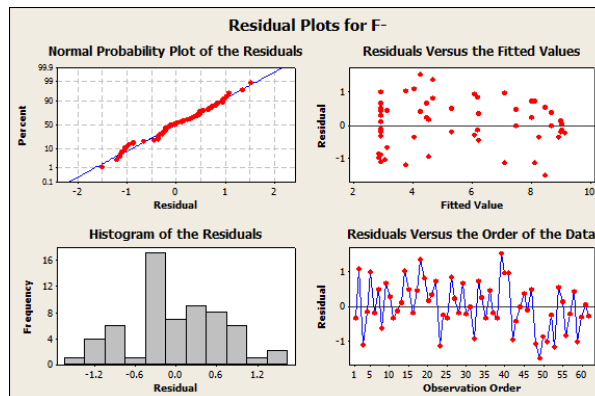
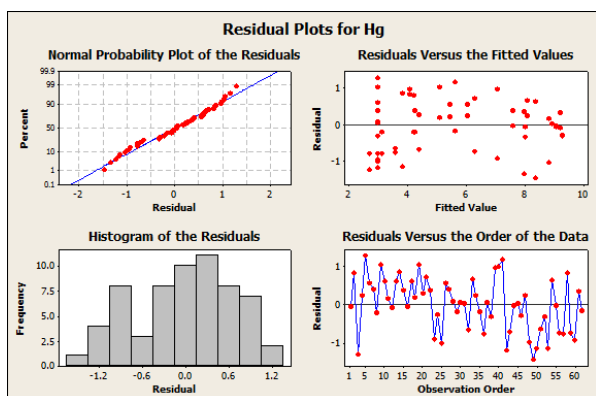
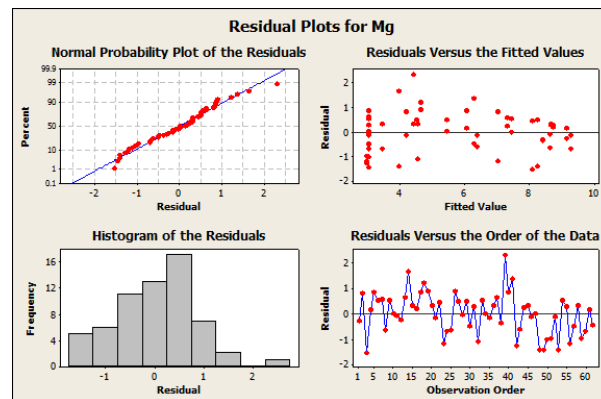
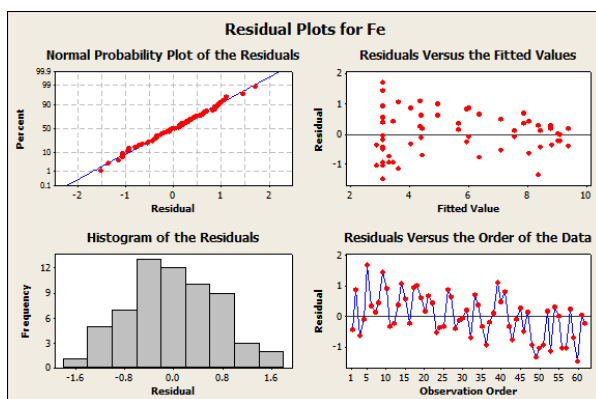
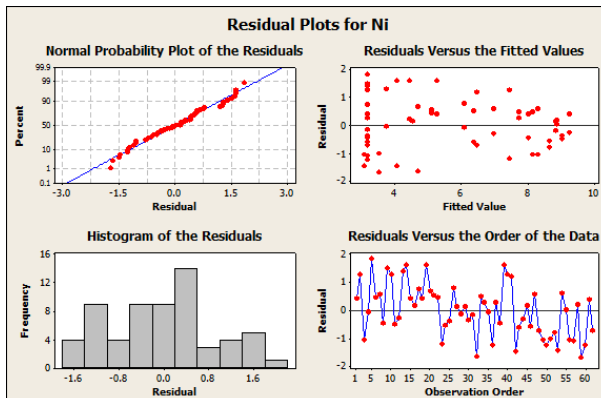
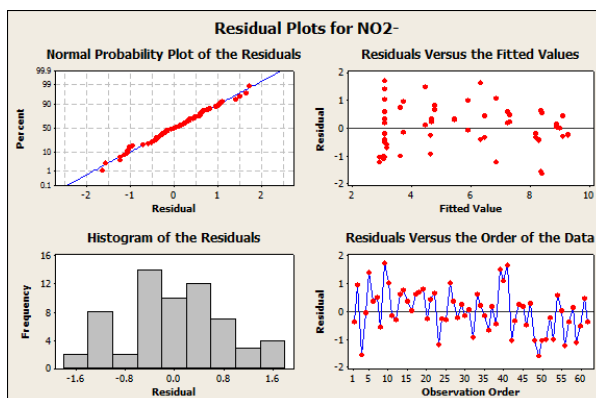
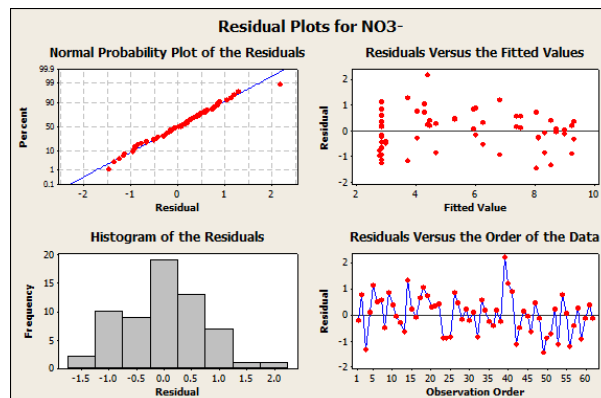
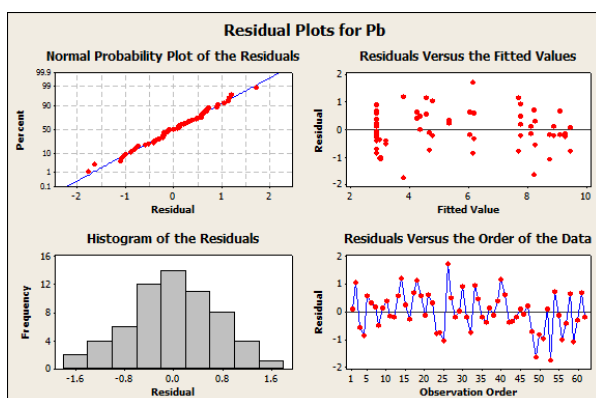
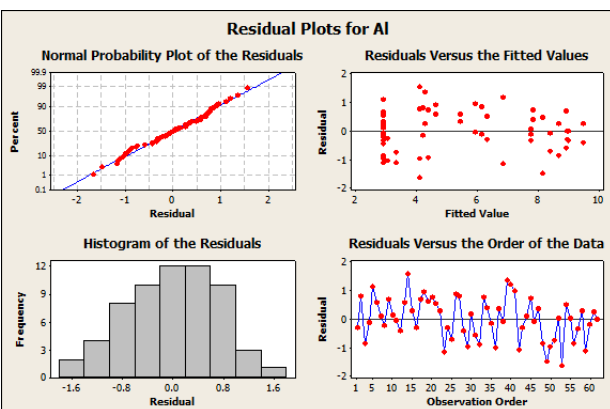
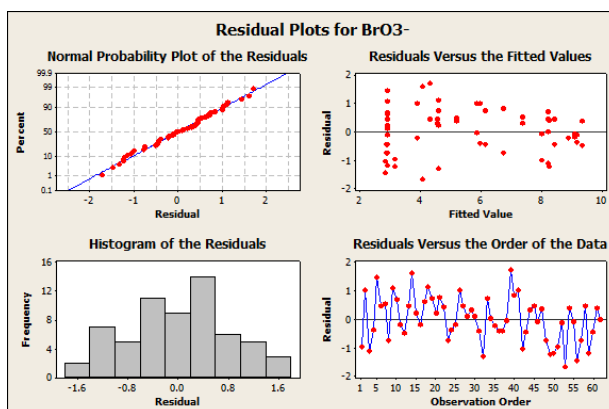
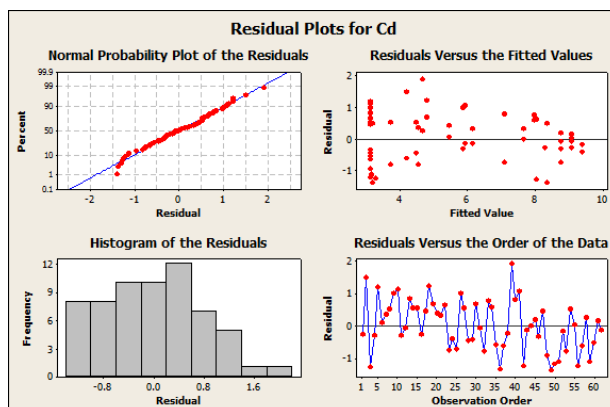
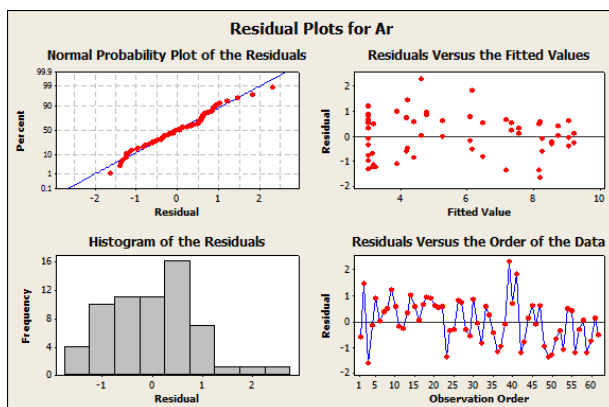
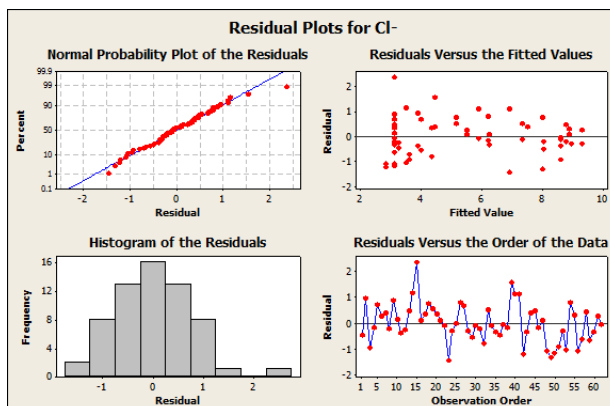
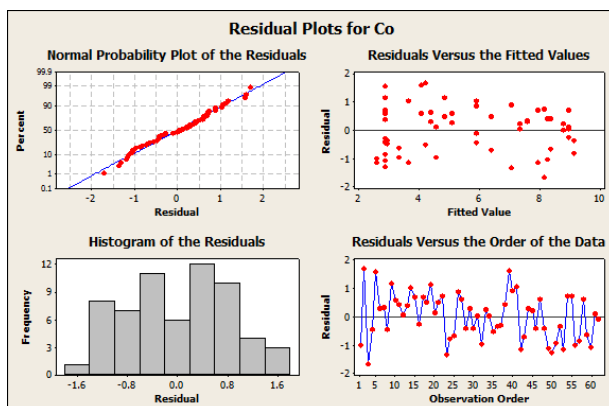
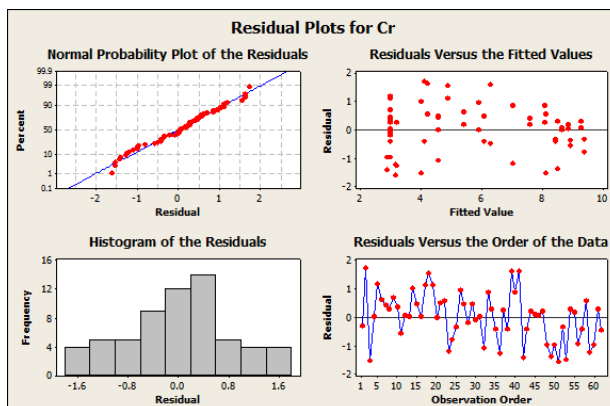
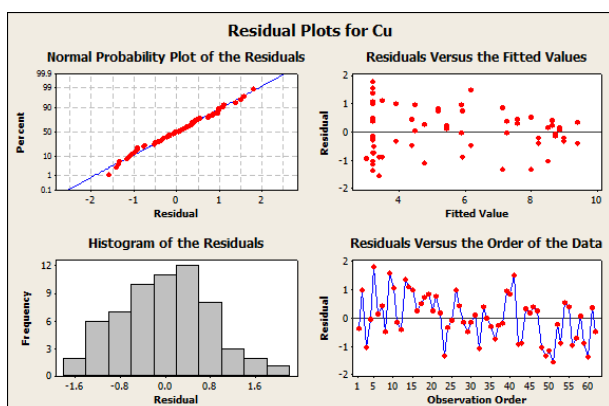


Figure 4.13A: Residual plots of standardized effects of the selected ions for the eggshell VWMs







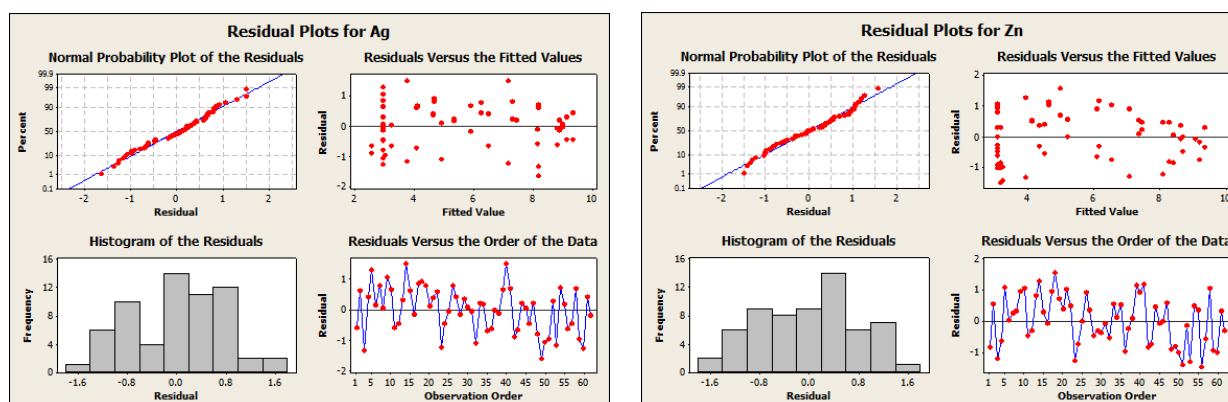


Figure 4.13B: Residual plots of standardized effects of the selected ions for the fish scale VWMs

Central composite design (CCD)

Following the screening of significant factors, a response surface design; CCD, was then created to determine the optimal values of each factor. The yields (optimal values), obtained following performances of the practical experiments were then captured in Tables 4.1.

Table 4.1: A summary optimal values for the parameters affecting adsorption efficiency of the fish scale (Fs) and eggshell (Es) VWMs

Ions	Parameters affecting adsorption efficiency of VWMs							
	Fs	Es	Fs	Es	Fs	Es	Fs	Es
	pH		Sorbent Dosage (mg)		Contact Time (min)		Concentration (mg/L)	
Ag	8.36	8.17	75.17	80.64	76.66	71.19	25.67	25.67
Al	6.71	7.00	74.26	75.17	65.72	77.57	23.85	23.85
Ar	7.78	7.52	78.82	81.56	63.89	70.28	23.85	23.85
BrO ₃ ⁻	7.78	8.17	83.38	78.82	71.19	69.37	22.02	23.23
Cd	8.27	7.68	80.64	77.91	63.89	68.46	25.06	23.24
Cl ⁻	7.19	8.27	79.73	85.20	74.84	69.37	24.45	26.26
Co	7.68	7.49	80.64	77.91	76.66	64.81	27.43	21.41
Cr	7.78	7.68	78.82	76.99	70.28	88.63	26.91	23.85
Cu	8.07	8.36	78.82	82.48	72.10	63.89	23.85	26.93
F ⁻	6.07	7.97	81.56	81.56	70.28	70.28	23.24	24.74
Fe	7.29	8.46	75.17	77.91	71.19	64.81	23.24	25.79
Hg	7.29	8.36	76.99	77.91	74.84	73.01	22.63	27.02

Ions	Parameters affecting adsorption efficiency of VWMs							
	Fs	Es	Fs	Es	Fs	Es	Fs	Es
	pH		Sorbent Dosage (mg)		Contact Time (min)		Concentration (mg/L)	
Mg	8.17	7.88	76.09	81.56	69.37	68.46	23.24	25.06
NO₂⁻	8.27	7.97	83.38	79.73	78.48	65.72	24.45	28.44
NO₃⁻	8.27	7.00	79.73	80.64	71.19	74.84	23.85	28.29
Pb	7.97	7.59	72.44	76.99	62.99	79.39	24.45	26.28
PO₄³⁻	8.75	7.88	84.29	83.39	70.28	78.48	24.45	25.67
Si	8.56	8.07	79.73	84.29	71.19	72.10	23.85	22.63
SO₄²⁻	7.97	8.46	79.73	81.56	71.19	77.57	23.23	24.45
Ti	8.36	7.49	83.38	77.91	71.19	67.54	23.85	25.31
Zn	7.52	7.97	76.99	79.73	69.37	75.75	27.49	23.24
Ni	7.19	8.07	76.18	80.64	52.96	73.01	26.06	25.06
All at once	7.19	7.51	76.17	74.36	72.96	75.12	26.06	25.67

Evaluation of the statistical significance of the Minitab models

The statistical significance of the models applied was evaluated through the use of Fisher distribution (*F-test*) for the analysis of variance (ANOVA) to validate the linear models at 95% confidence level. The obtained *F-test* values for the fish scale and eggshell VWMs were recorded in Appendix C1. Furthermore, the regression coefficients; R^2 and *Lack-of-fit (LOF)* were also employed to confirm the correlation of the model and the experimental data as well as to confirm if any error derived from contribution by regressor-response relationship was accounted for respectively and were recorded in Appendix C1 and C2. The R^2 values, which were all > 0.96 for all the selected ions for the VWMs, suggested that the models fitted adequately to the experimental data [147]. The *p-values* of the selected ions for the LOF were found to be 0.000 for the fish scale VWMs; with the exception of Ti which was 0.001, while, the *p-values* of the selected ions were 0.000 for all the ions. This signifies adequacy of the models in that there is relatively no LOF shown by the applied models [129].

Effect of extreme temperatures resembling Botswana temperatures on the efficiency of the VWMs

The VWMs were subjected to two different, extreme temperatures to determine the effect of extreme temperatures; one at low temperature of -4 °C and the other at a high temperature of 45 °C, both temperatures resembling extreme Botswana temperature on the adsorption percentage efficiency of the VWMs. The effect of extreme temperatures on the VWMs was evaluated over varying periods totaling 35 days as described in detail in Section 3.6.2. The results were summarized into graphs contained in Appendix D (Figures 6.3 – 6.10). From the graphs it was clear that the extreme temperatures had no significant effect on the VWMs, as the adsorption percentage efficiencies of the VWMs for the selected ions under the extreme temperatures (32% - 96%) were statistically comparable to the percentage efficiencies obtained under optimal conditions in Section 4.5 (33% - 95%).

4.3 Method validation

Linearity Studies

The regression equations and correlation coefficients (R^2) of the selected ions for both VWMs in Tables 4.2 and 4.3 were deduced from the calibration curves in Appendix F (Figures 6.11 and 6.12) for the working range of 0 to 500 mg/L. The calibration curves of the selected ions showed good linearity with correlation coefficients (R^2) of greater than 0.99 in all cases, demonstrating strong correlation between the instrumental absorbance (concentrations) obtained and the concentrations of the selected ions in the prepared standards. According to Miller and Miller, R^2 values between 0.8 and 1 indicate strong correlation, whilst R^2 values < 0.8 indicate weak correlation [149][150].

Table 4.2: A summary of the regression equations and correlation coefficients (R^2) for the selected ions for fish scale VWMs

Cations	R^2	Regression Equation	Anions	R^2	Regression Equation
Co	0.992	$y = 0.9152x - 7.3938$	F ⁻	0.9998	$y = 0.951x + 0.3586$
Ni	0.9953	$y = 0.9728x - 7.5557$	Cl ⁻	0.9995	$y = 0.9665x - 2.6976$
Zn	0.9993	$y = 0.9693x - 2.7429$	SO ₄ ²⁻	0.9993	$y = 0.9747x - 3.6795$

Cations	R ²	Regression Equation	Anions	R ²	Regression Equation
Cu	0.9983	y = 0.9782x - 7.3076	PO₄³⁻	0.9996	y = 0.9841x - 3.1933
Hg	0.9991	y = 0.9469x - 0.4119	NO₂⁻	0.9987	y = 0.9556x - 0.6533
Ag	0.9996	y = 0.9259x + 0.9481	BrO₃⁻	0.9994	y = 0.933x + 0.7767
Fe	0.9981	y = 0.9601x - 0.9481	NO₃⁻	0.9991	y = 0.9692x - 4.8605
Pb	0.9997	y = 0.9646x - 2.2138			
Cr	0.9996	y = 0.978x - 3.9305			
Mg	0.9995	y = 0.9564x - 3.4938			
Al	0.9996	y = 0.9669x - 3.13			
As	0.9992	y = 0.9612x - 2.7186			
Cd	0.9991	y = 0.977x - 5.6519			
Si	0.9996	y = 0.9668x - 3.3748			
Ti	0.9998	y = 0.9519x - 1.379			

Table 4.3: A summary of the regression equations and correlation coefficients (R²) for the selected ions for eggshell VWMs

Cations	R ²	Regression Equation	Anions	R ²	Regression Equation
Co	0.9978	y = 0.9422x - 4.27	F⁻	0.9994	y = 0.9746x - 1.9271
Ni	0.996	y = 0.9557x - 2.9367	Cl⁻	0.9974	y = 0.9731x - 4.5071
Zn	0.9975	y = 0.9776x - 3.9976	SO₄²⁻	0.9993	y = 0.9804x - 1.7748
Cu	0.9993	y = 0.9708x - 3.1171	PO₄³⁻	0.9999	y = 0.9655x - 1.0505
Hg	0.9996	y = 0.9583x - 0.6024	NO₂⁻	0.9998	y = 0.9727x - 1.6057
Ag	0.9999	y = 0.9621x - 1.6233	BrO₃⁻	0.9994	y = 0.9304x + 2.491
Fe	0.9995	y = 0.9684x - 2.1862	NO₃⁻	0.9997	y = 0.9755x - 1.4319
Pb	0.9997	y = 0.9786x - 3.5281			
Cr	0.9997	y = 0.9669x - 0.9781			
Mg	0.9986	y = 0.9799x - 5.0176			
Al	0.9999	y = 0.9755x - 2.6062			
As	0.9995	y = 0.9707x - 3.5757			
Cd	0.9975	y = 0.9724x - 5.8424			
Si	0.999	y = 0.9662x - 0.8986			
Ti	0.9995	y = 0.9648x - 2.4267			

Recovery Studies in Pure Standards

The ability of the fish scale and eggshell VWMs to adequately remove the selected ions from pure standards was investigated as described in Section 3.8. The percentage recoveries of the selected ions from the pure standards by the VWMs were calculated and summarized in Tables 4.4 and 4.5. High percentage recoveries of between 79.50% and 106.10% for $n = 3$ and %RSD of $\leq 2.67\%$ for all cases were recorded demonstrating effective wastewater treatment method as per the EPA method 40, which states that percentage recoveries of 70 – 130% for the validation of wastewater treatment methods, reflect an effective wastewater treatment method [151].

Table 4.4: A summary of the percentage recoveries of the selected anions from pure standards by the VWMs

Anions	FS Recoveries (%)	ES Recoveries (%)
F^-	104.65 ± 1.32	89.34 ± 2.85
Cl^-	95.32 ± 2.13	90.02 ± 3.56
SO_4^{2-}	94.95 ± 2.45	94.65 ± 2.34
PO_4^{3-}	79.64 ± 0.89	99.72 ± 1.54
NO_2^-	99.03 ± 1.56	98.73 ± 1.89
BrO_3^-	99.01 ± 2.09	95.70 ± 2.67
NO_3^-	98.01 ± 2.43	85.70 ± 2.67

Table 4.5: A summary of the percentage recoveries of the selected cations from pure standards by the VWMs

Cations	FS Recoveries (%)	ES Recoveries (%)
Co	99.940 ± 0.342	94.635 ± 2.176
Ni	94.900 ± 1.452	91.095 ± 3.562
Zn	97.690 ± 0.674	92.385 ± 2.511
Cu	97.330 ± 1.453	95.525 ± 1.563
Hg	98.750 ± 2.432	98.445 ± 1.023
Ag	95.380 ± 1.214	100.075 ± 2.784
Fe	105.450 ± 1.674	102.645 ± 0.735
Pb	101.335 ± 0.969	96.030 ± 2.331
Cr	106.050 ± 1.451	98.995 ± 1.454
Mg	101.170 ± 2.003	90.365 ± 1.673

Cations	FS Recoveries (%)	ES Recoveries (%)
Al	95.499 ± 3.217	100.194 ± 2.782
Ar	106.020 ± 1.042	99.195 ± 1.089
Cd	105.100 ± 0.997	104.795 ± 3.109
Si	104.890 ± 1.741	103.085 ± 2.651
Ti	100.005 ± 1.433	99.7 ± 1.450

Detection Limits

The limits of detection (LODs), limits of quantification (LOQs) and the method detection limits (MDLs) for all the selected ions were investigated as per Section 3.8 and summarized in Table 4.6 for each VWMs. All detection limits were found to be below the maximum acceptable concentrations set for toxic ions in wastewater, demonstrating that the method could be employed for the analysis of these ions. If the detection limits are above the maximal acceptable levels of ions in wastewater, then the method cannot be employed for removal of ions from wastewater as it will be out of working range concentration [151].

Table 4.6: A summary of the detection limits of the selected ions employing the VWMs

Cations	LODs (mg/L)	MDL (mg/L)		LOQ (mg/L)	RSD (%)	
		Fs	Es		Fs	Es
Co	0.0018 ± 0.002	0.0105 ± 0.012	0.0167 ± 0.001	0.01833 ± 0.021	1.62 ± 0.011	1.50 ± 0.016
Ni	6.67E-02 ± 0.001	0.0063 ± 0.003	0.0140 ± 0.003	0.00067 ± 0.001	2.00 ± 0.001	3.00 ± 0.019
Zn	3.33E-02 ± 0.02	0.0877 ± 0.013	0.0098 ± 0.002	0.00033 ± 0.007	2.71 ± 0.003	2.01 ± 0.002
Cu	0.00017 ± 0.004	0.0741 ± 0.006	0.0084 ± 0.001	0.00167 ± 0.002	5.01 ± 0.016	2.00 ± 0.011
Hg	0.0005 ± 0.003	0.0053 ± 0.006	0.0084 ± 0.003	0.005 ± 0.019	1.01 ± 0.001	4.00 ± 0.007
Ag	0.00017 ± 0.003	0.0028 ± 0.021	0.0083 ± 0.016	0.00167 ± 0.003	2.00 ± 0.002	4.52 ± 0.001
Fe	1.66E-02 ± 0.016	0.605 ± 0.001	0.0081 ± 0.002	0.00017 ± 0.021	4.21 ± 0.011	3.00 ± 0.003
Pb	0.0012 ± 0.015	0.0821 ± 0.011	0.0101 ± 0.001	0.017 ± 0.007	2.80 ± 0.001	1.00 ± 0.003
Cr	0.0048 ± 0.011	0.167 ± 0.002	0.0224 ± 0.021	0.04833 ± 0.003	1.09 ± 0.002	1.00 ± 0.002
Mg	6.67E-05 ± 0.021	0.105 ± 0.003	0.0084 ± 0.019	0.0007 ± 0.011	1.22 ± 0.003	1.90 ± 0.003
Al	0.015 ± 0.002	0.271 ± 0.016	0.0090 ± 0.001	0.147 ± 0.007	1.8 ± 0.016	3.40 ± 0.021
Ar	1.70E-05 ± 0.021	0.048 ± 0.002	0.0083 ± 0.004	0.0002 ± 0.003	1.65 ± 0.02	2.11 ± 0.007
Cd	0.0003 ± 0.23	0.105 ± 0.007	0.0080 ± 0.003	0.003 ± 0.02	2.48 ± 0.003	4.42 ± 0.001
Si	0.0002 ± 0.02	0.022 ± 0.004	0.0111 ± 0.011	0.0017 ± 0.007	1.19 ± 0.021	2.20 ± 0.007
Ti	0.0003 ± 0.034	0.65 ± 0.002	0.0136 ± 0.002	0.0033 ± 0.007	1.04 ± 0.004	1.20 ± 0.003
F ⁻	0.006 ± 0.003	0.823 ± 0.001	0.0215 ± 0.004	0.06 ± 0.002	1.31 ± 0.002	2.10 ± 0.008

Cations	LODs (mg/L)	MDL (mg/L)		LOQ (mg/L)	RSD (%)	
		Fs	Es		Fs	Es
Cl ⁻	0.001 ± 0.025	0.123 ± 0.007	0.0099 ± 0.001	0.01 ± 0.004	1.45 ± 0.022	1.90 ± 0.007
SO ₄ ²⁻	0.02 ± 0.002	0.038 ± 0.001	0.0083 ± 0.002	0.2 ± 0.02	2.01 ± 0.002	2.47 ± 0.001
PO ₄ ³⁻	0.004 ± 0.0031	2.016 ± 0.007	0.0234 ± 0.001	0.04 ± 0.007	7.00 ± 0.001	2.94 ± 0.011
NO ₂ ⁻	0.024 ± 0.001	0.031 ± 0.002	0.0125 ± 0.002	0.24 ± 0.004	6.00 ± 0.004	1.99 ± 0.02
BrO ₃ ⁻	0.01 ± 0.004	0.014 ± 0.001	0.0139 ± 0.004	0.01 ± 0.02	6.04 ± 0.007	2.10 ± 0.002
NO ₃ ⁻	0.025 ± 0.001	0.019 ± 0.003	0.012 ± 0.0074	0.25 ± 0.002	4.13 ± 0.004	2.53 ± 0.003

4.4 Comparative Studies of the VWMs and non-VWMs Adsorption of Selected Ions from Wastewater

A comparison of the eggshell and fish scale VWMs and their non-VWMs counterparts graphically represented in Figure 4.14 showed the superiority of the VWMs over the non-VWMs for both the eggshells and fish scale in removing the selected ions from wastewater. The VWMs recorded higher adsorption percentage efficiencies averaging 86.73% than their non-VWMs counterparts averaging 58.92% (see Figure 4.14) [152]. The superiority of the VWMs over the non-VWMs was attributed to the presence of functional groups that were exposed during the treatment of the VWMs with vinegar and making them more available for binding with the selected ion during their removal. Since the non-VWMs were not treated with vinegar, it meant that their functional groups were not exposed, thus, less or non-available for binding the ions.

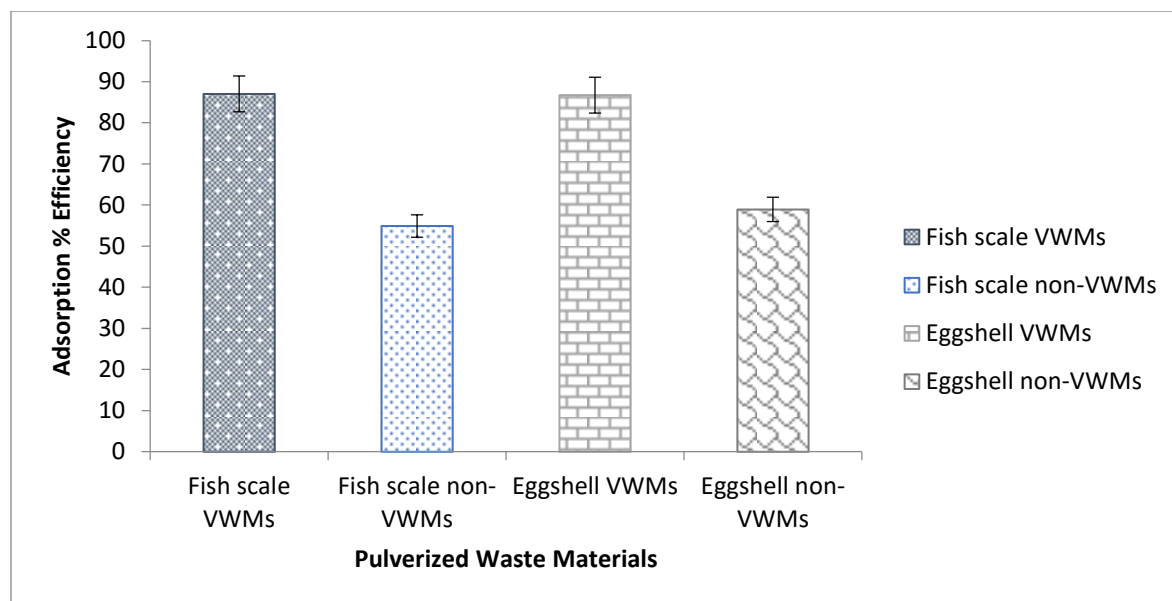


Figure 4.14: Adsorption percentage efficiencies of the VWMs and their non-VWMs counterparts

4.5 Application of the Valorized Waste Materials (VWMs) in Removing the Selected Ions from Raw Wastewater Samples from Gaborone Sewage Treatment Plant

Prior to applying the VWMs to the raw wastewater samples collected from the Gaborone sewage treatment plant, the concentrations of the selected ions in the raw wastewater samples were determined employing ICP-OES for the selected cations and IC for the selected anions as described in Section 3.9. Figures 4.15 and 4.16 are graphical representations of the concentrations of the selected ions in the raw wastewater (that is before removal with the VWMs). It should be noted that the concentrations of the selected ions in the wastewater samples were found to be within the allowed concentrations of ions in wastewater as set by Botswana Bureau of Standards and US EPA wastewater specifications [153].

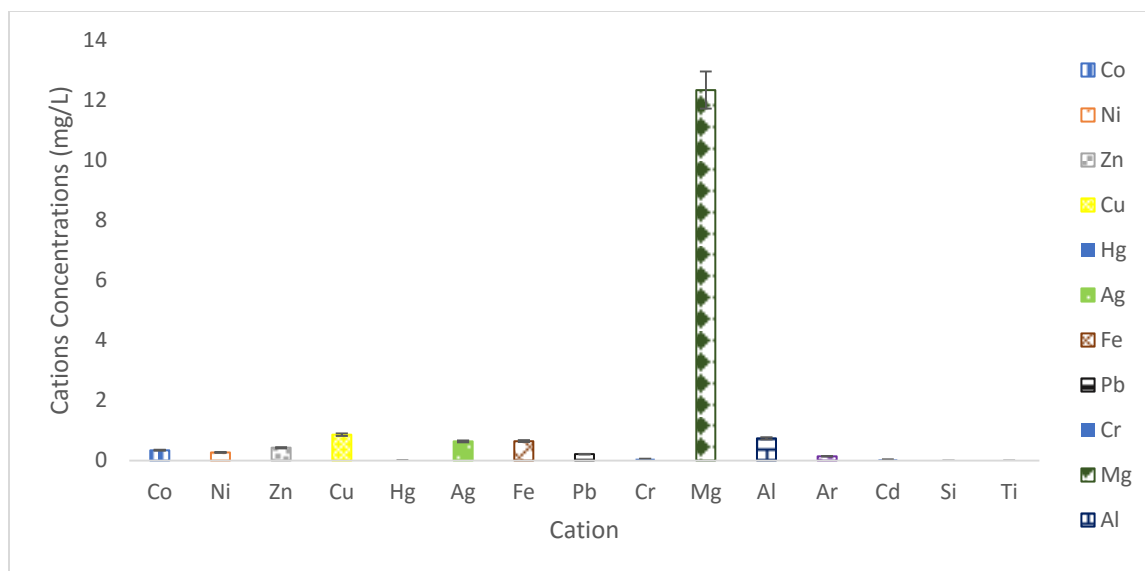


Figure 4.15: Concentrations of cations in raw wastewater samples

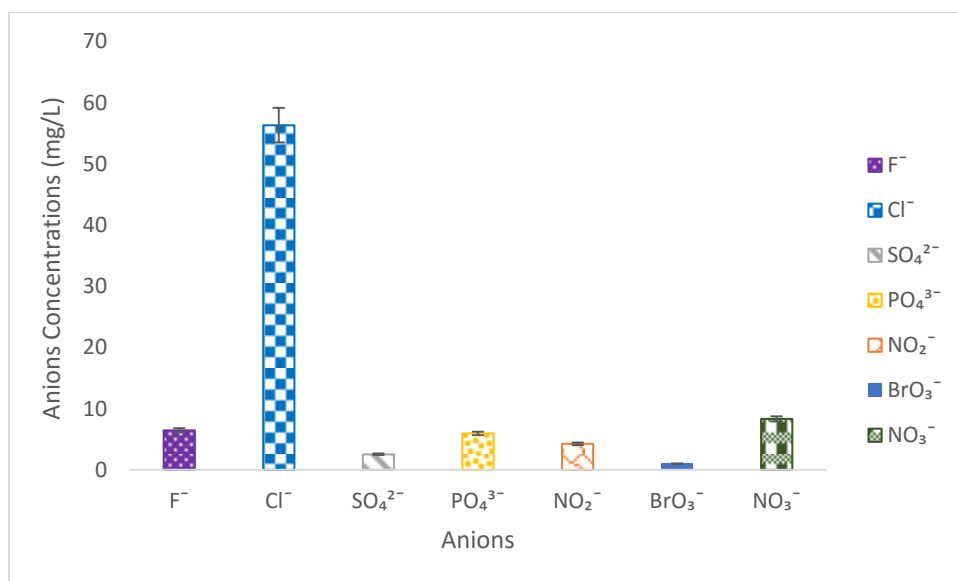


Figure 4.16: Concentrations of anions in raw wastewater samples

After the concentrations of the selected ions in the raw wastewater samples were determined, the VWMs for the eggshells and fish scales were applied and the percentage adsorption/removal efficiencies of each of the selected ions in the raw wastewater by each of the VWMs under

optimal conditions were calculated as per Equation 3.5. A summary of the percentage efficiencies of the VWMs for each of the selected ions were recorded in Table 4.7.

Table 4.7: A summary of the percentage adsorption/removal efficiencies (%) of each of the selected ions in the raw wastewater by each of the VWMs

Cations	Eggshell VWMs	Fish scale VWMs	Anions	Eggshell VWMs	Fish scale VWMs
Co	78.70	83.85	F ⁻	80.70	92.82
Ni	76.53	82.71	Cl ⁻	93.18	95.77
Zn	81.97	76.93	SO ₄ ²⁻	91.04	88.84
Cu	74.71	77.52	PO ₄ ³⁻	85.33	33.07
Hg	69.13	85.05	NO ₂ ⁻	85.34	91.42
Ag	84.07	76.72	BrO ₃ ⁻	88.55	82.97
Fe	76.98	69.90	NO ₃ ⁻	76.09	74.60
Pb	80.37	80.71			
Cr	86.96	93.02			
Mg	84.90	88.55			
Al	63.67	68.56			
Ar	74.48	60.92			
Cd	59.04	52.19			
Si	90.91	90.73			

The fish scale VWMs showed higher percentage ion removal towards Co, Ni, Cu, Hg, Cr, Mg, F, Cl⁻, NO₂⁻ removal in comparison with eggshell VWMs. Meanwhile, the eggshell VWMs proved to be more effective towards the removal of Zn, Ag, Fe, Ar, SO₄²⁻, PO₄³⁻, and BrO₃⁻ when compared to the fish scale VWMs. Both VWMs showed statistically the same removal percentages towards Pb, Al Cd, Si and NO₃⁻ (see Figures 4.17, 4.18 4.19 and 4.20).

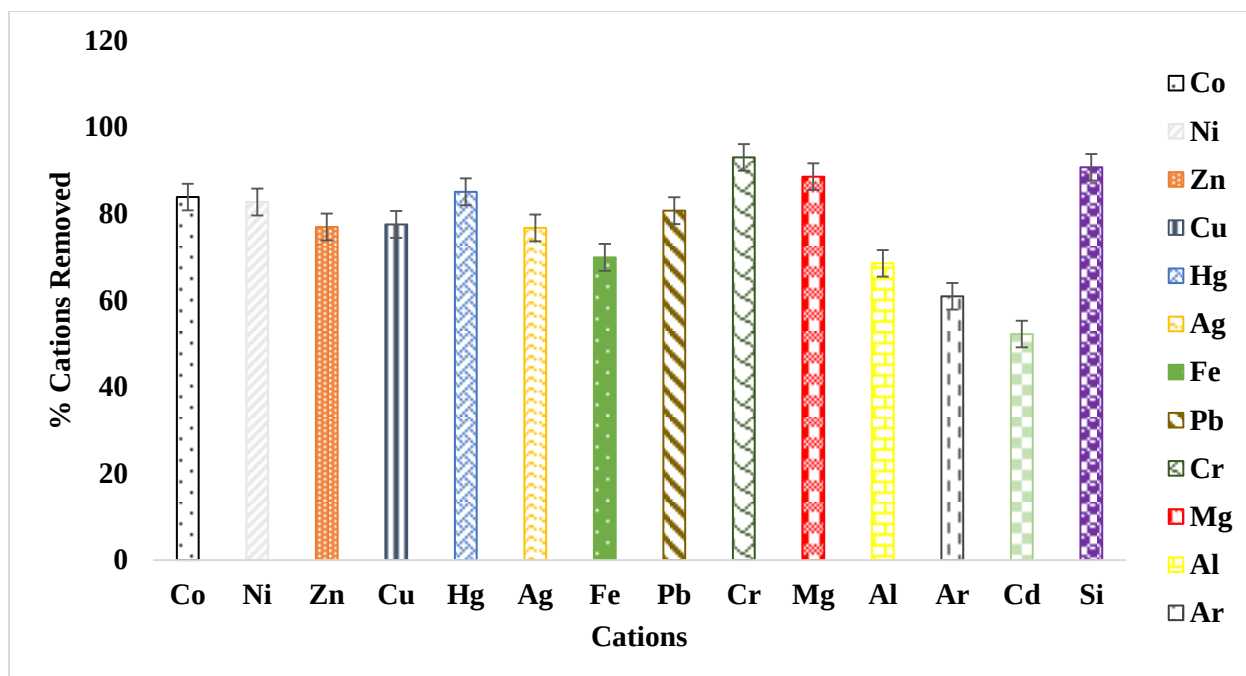


Figure 4.17: Percentage cations removal employing the fish scale VWMs

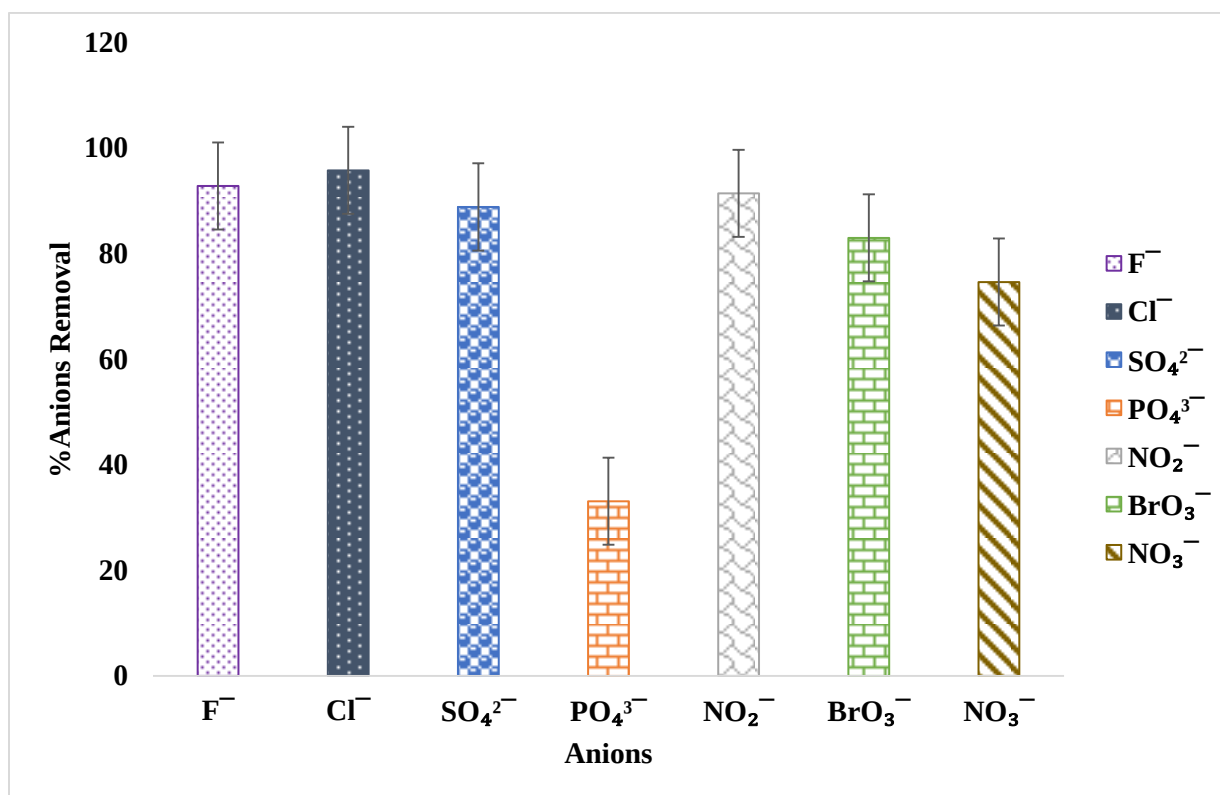


Figure 4.18: Percentage anions removal employing the fish scale VWMs

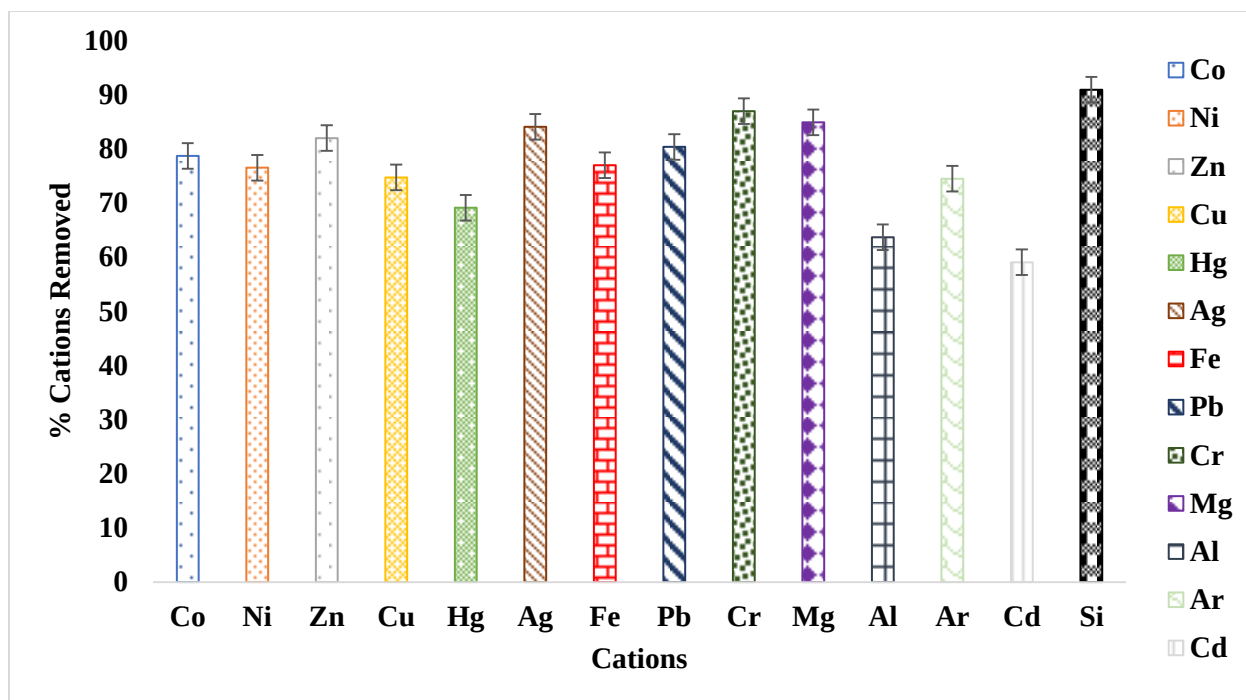


Figure 4.19: Percentage cations removal employing the valorized eggshells

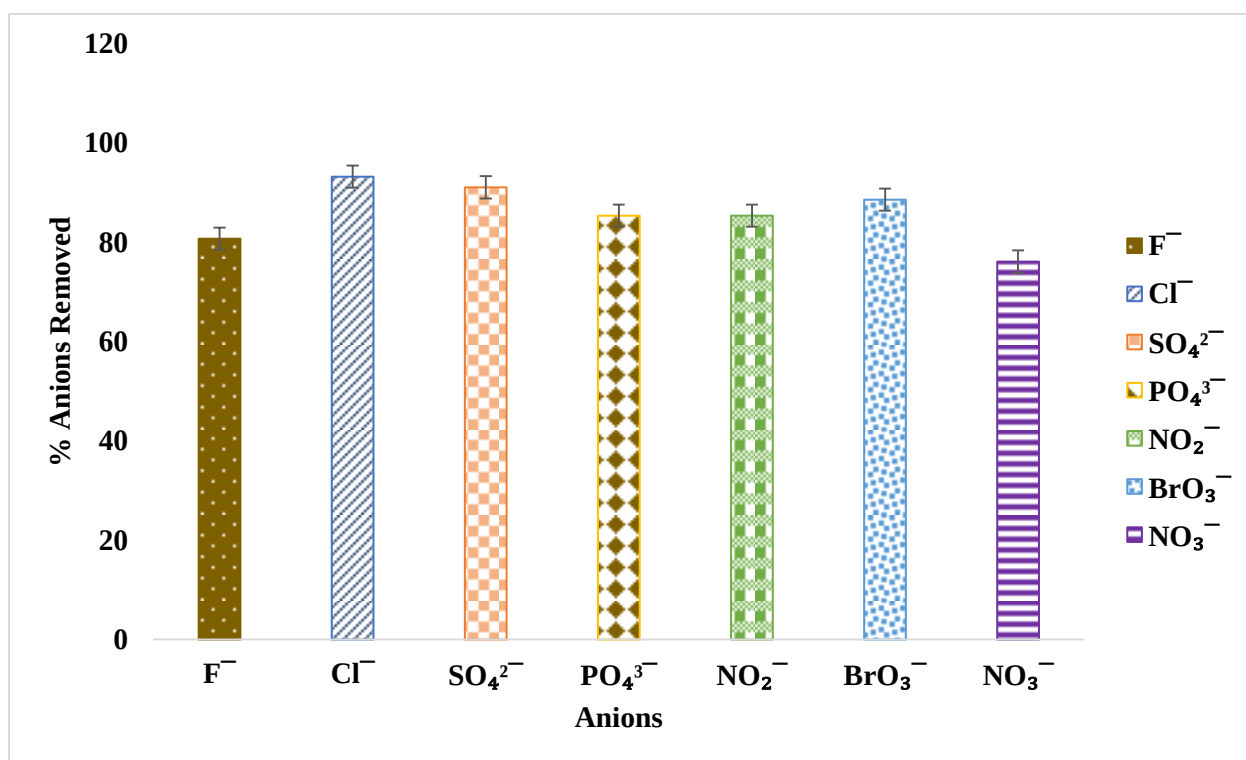


Figure 4.20: Percentage anions removal employing the valorized eggshells

Percentage ion removal for most of the selected ions was above 70% with exception of Al, PO_4^- and Cd which were observed to be lower than 70% for both VWMs.

4.6 Adsorption Equilibrium Isotherms

Adsorption isotherm models were applied to experimental data as described Section 2.5. A summary of linearized Langmuir and Freundlich adsorption isotherms parameters obtained for the eggshell and fish scale VWMs were recorded in Tables 4.11 and 4.12 respectively. In view of the values of the linear regression coefficients, Langmuir model fitted the sorption data far more than the other models as supported by the higher R^2 values > 0.9 of the Langmuir than the other models [55].

The affinity order of the eggshell VWMs based on the highest $q_{\max}$ (see Section 2.3.5.2.1.1 for calculations of $q_{\max}$) was found to be $\text{Si} > \text{Hg} > \text{Mg} > \text{Fe} > \text{Cd} > \text{Cu} > \text{NO}_3^- > \text{PO}_4^{3-} > \text{Co} > \text{Zn} > \text{SO}_4^{2-} > \text{Cr} > \text{Cl}^- > \text{Ti} > \text{Ag} > \text{Pb} > \text{Ar} > \text{BrO}_3^- > \text{NO}_2^- > \text{Ni} > \text{Al} > \text{F}^-$. and $\text{SO}_4^{2-} > \text{Cl}^- > \text{Si} > \text{Ar} > \text{Hg} > \text{Ag} > \text{Zn} > \text{Pb} > \text{Fe} > \text{Ti} > \text{NO}_2^- > \text{F}^- > \text{Al} > \text{Cu} > \text{Co} > \text{NO}_3^- > \text{Ni} > \text{Cd} > \text{Cr} > \text{Mg} > \text{BrO}_3^- > \text{PO}_4^{3-}$ for the fish scale VWMs.

The constant K which was determined by linear regression equations from the plot of $\log q_e$ against $\log C_e$ (Freundlich model) for each ion, measured the degree or strength of adsorption (small value of K indicates more adsorption) [154], and was found to be < 2 for both VWMs (fish scales and eggshells), indicating high degree of adsorption by the VWMs. The magnitudes of the experimental $q_{\max}$ for the VWMs were found to be comparable with the theoretically calculated $q_{\max}$, which also indicated a high degree of adsorption of the selected ions by the VWMs [129].

The applicability of Langmuir isotherms implies that monolayer adsorption existed under the experimental conditions [134][155]. The adsorption energies (E) (obtained from the Dubinin-Radushkevich model) which explain the physical or chemical characteristics of an adsorption process, were found to be $< 2 \text{ kJ mol}^{-1}$ for implying that the adsorption process was of a physical nature all ions.

Table 4.8: A summary of the calculated adsorption isotherm parameters for the adsorption of the selected ions unto the eggshell VWMs

Ions	Langmuir Model				Freundlich Model			Dubinin – Radushkevich Model		
	Temp. (K)	R ²	q _{max} (mg/g)	b (L/mg)	R ²	K	1/n	R ²	E (kJ/mol)	q _{max} (mg/g)
Co	298.15	0.9853	23.86	0.08	0.7256	0.51	1.11	0.9502	357.08	14.40
	308.15	0.9981	31.97	0.03	0.8552	0.68	1.14	0.9762	461.63	14.27
	318.15	0.9718	31.35	0.05	0.9134	0.96	1.06	0.9457	650.42	14.40
	333.15	0.9920	36.67	0.01	0.9681	1.53	1.02	0.9855	926.98	13.12
Ni	298.15	0.9236	24.15	0.19	0.636	0.46	0.97	0.947	345.90	14.88
	308.15	0.9997	28.57	0.01	0.9366	0.86	1.23	0.9041	533.88	15.18
	318.15	0.9969	34.84	0.03	0.9952	1.45	1.20	0.9972	745.73	14.84
	333.15	0.09916	15.27	0.04	0.9182	0.93	1.13	0.9576	1101.96	14.80
Zn	298.15	0.9541	26.74	0.16	0.6484	0.47	0.97	0.9737	348.84	14.80
	308.15	0.9759	26.32	0.11	0.7759	0.62	0.96	0.9944	456.70	13.38
	318.15	0.995	30.86	0.04	0.9891	1.26	1.24	0.9994	702.38	15.06
	333.15	0.9877	37.14	0.00	0.943	1.29	1.18	0.997	974.58	17.14
Cu	298.15	0.9616	31.65	0.13	0.6674	0.46	1.04	0.9995	339.91	12.54
	308.15	0.9946	24.95	0.04	0.8571	0.69	1.12	0.9583	471.61	15.14
	318.15	0.9811	29.85	0.07	0.8987	0.84	1.02	0.9816	602.78	15.18
	333.15	0.9982	41.84	0.02	0.9909	1.48	1.08	0.9999	914.66	15.26
Hg	298.15	0.9711	34.48	0.13	0.626	0.43	1.02	0.9012	320.35	15.75
	308.15	0.9940	48.31	0.05	0.8454	0.68	1.09	0.9705	469.35	15.15
	318.15	0.9831	30.21	0.07	0.8933	0.82	1.02	0.98	592.81	15.17
	333.15	0.9894	34.03	0.01	0.9465	1.30	1.09	0.9823	952.45	15.18
Ag	298.15	0.9584	27.93	0.16	0.6347	0.46	0.97	0.9671	340.53	15.33
	308.15	0.9905	32.37	0.06	0.8299	0.66	1.08	0.972	456.85	14.80

Ions		Langmuir Model			Freundlich Model			Dubinin – Radushkevich Model		
	318.15	0.9883	36.63	0.06	0.8903	0.79	1.05	0.9779	573.82	15.12
	333.15	0.9162	17.51	0.06	0.8401	1.73	1.00	0.979	928.07	15.14
Fe	298.15	0.9919	37.80	0.04	0.8339	0.64	1.16	0.9937	426.82	15.09
	308.15	0.9922	24.64	0.06	0.8289	0.65	1.08	0.9689	456.01	15.12
	318.15	0.9720	25.25	0.10	0.8325	0.70	0.99	0.9613	536.32	15.98
	333.15	0.9908	48.08	0.02	0.979	1.96	1.00	0.9851	845.97	15.15
Pb	298.15	0.9341	25.06	0.18	0.6451	0.47	0.98	0.9824	347.64	13.51
	308.15	0.9525	24.33	0.11	0.8147	0.69	1.02	0.9844	484.31	14.84
	318.15	0.9964	34.84	0.03	0.9893	1.26	1.24	0.9902	704.11	14.84
	333.15	0.9693	27.78	0.04	0.925	1.56	0.97	0.9936	944.94	15.12
Cr	298.15	0.9712	35.59	0.10	0.7378	0.53	1.09	0.9771	373.36	15.12
	308.15	0.9847	37.17	0.07	0.8312	0.67	1.08	0.985	462.89	14.84
	318.15	0.9325	15.55	0.14	0.8498	1.19	0.88	0.9948	623.44	14.50
	333.15	0.9883	28.57	0.00	0.9447	1.29	1.04	0.9759	971.51	15.38
Mg	298.15	0.9784	39.84	0.11	0.6685	0.45	1.08	0.9677	328.24	15.15
	308.15	0.9981	38.74	0.03	0.8693	0.71	1.12	0.9806	482.64	15.18
	318.15	0.9983	38.89	0.01	0.9541	0.98	1.12	0.9764	644.53	15.38
	333.15	0.9944	24.10	0.03	0.9672	1.22	1.15	0.9761	958.20	15.57
Al	298.15	0.9325	23.31	0.20	0.6031	0.45	0.91	0.9241	340.26	15.57
	308.15	0.9784	35.59	0.06	0.864	0.74	1.09	0.9656	501.98	15.36
	318.15	0.949	18.83	0.13	0.8361	0.75	0.92	0.9445	576.61	16.76
	333.15	0.9962	23.58	0.05	0.9894	1.36	1.13	0.9668	922.58	15.75
Ar	298.15	0.9528	28.82	0.15	0.6468	0.46	1.01	0.966	337.12	15.98
	308.15	0.9717	27.70	0.09	0.8447	0.72	1.03	0.9756	499.02	15.42
	318.15	0.9983	32.46	0.02	0.9848	1.28	1.18	0.9801	717.88	15.38
	333.15	0.9955	22.32	0.04	0.9948	1.46	1.14	0.9798	900.97	15.36
Cd	298.15	0.9647	35.59	0.13	0.6529	0.44	1.07	0.9356	322.43	15.75

Ions		Langmuir Model			Freundlich Model			Dubinin – Radushkevich Model		
Si	308.15	0.9950	40.25	0.04	0.854	0.71	1.06	0.9772	487.88	15.38
	318.15	0.9758	26.39	0.09	0.8515	0.73	1.00	0.982	552.17	15.18
	333.15	0.9964	29.24	0.03	0.9951	2.11	1.18	0.9818	833.00	15.15
	298.15	0.9539	36.76	0.11	0.6827	0.47	1.13	0.9657	334.64	15.15
	308.15	0.9926	45.05	0.05	0.8612	0.71	1.08	0.9827	486.01	14.84
	318.15	0.9817	26.81	0.08	0.8696	0.77	0.98	0.9873	574.27	15.18
	333.15	0.9919	42.63	0.01	0.9435	1.16	1.08	0.9678	1003.10	16.76
Ti	298.15	0.9452	25.45	0.17	0.6555	0.48	0.97	0.9983	353.98	13.50
	308.15	0.964	27.62	0.09	0.8298	0.68	1.04	0.9821	476.17	17.48
	318.15	0.9547	22.78	0.09	0.8609	0.80	1.00	0.9967	587.89	14.84
	333.15	0.9759	39.88	0.01	0.8991	1.27	1.19	0.9652	940.36	16.80
F ⁻	298.15	0.959	30.12	0.14	0.6557	0.46	1.02	0.9918	338.85	16.09
	308.15	0.9761	44.07	0.05	0.8516	0.72	1.11	0.9448	485.80	15.59
	318.15	0.8857	14.35	0.18	0.788	0.74	0.88	0.9445	584.91	17.68
	333.15	0.9907	1.30	0.45	0.91	0.89	1.15	0.9352	1125.10	17.50
Cl ⁻	298.15	0.9628	32.26	0.14	0.6395	0.44	1.03	0.9464	325.45	15.68
	308.15	0.9715	31.15	0.08	0.8464	0.72	1.07	0.9873	492.38	15.15
	318.15	0.9417	17.39	0.12	0.8718	0.86	0.92	0.9024	638.17	18.18
	333.15	0.9908	36.08	0.00	0.9548	1.31	1.01	0.9267	977.47	17.10
SO ₄ ²⁻	298.15	0.9246	25.00	0.20	0.6097	0.44	0.97	0.9537	329.56	14.33
	308.15	0.9769	31.85	0.08	0.8302	0.68	1.06	0.9576	472.10	15.38
	318.15	0.9967	29.44	0.02	0.9869	1.80	1.15	0.9556	792.74	16.80
	333.15	0.9786	31.97	0.01	0.9213	1.31	1.04	0.9842	970.73	16.10
PO ₄ ³⁻	298.15	0.9773	22.19	0.11	0.6526	0.43	1.10	0.912	313.98	16.70
	308.15	0.9971	28.03	0.03	0.8582	0.69	1.13	0.9057	467.80	15.87
	318.15	0.9960	34.03	0.02	0.9587	1.04	1.10	0.9325	670.99	16.76

Ions		Langmuir Model			Freundlich Model			Dubinin – Radushkevich Model		
NO₂⁻	333.15	0.9880	39.89	0.01	0.9255	1.12	1.05	0.9464	1027.41	17.14
	298.15	0.9403	24.27	0.18	0.6374	0.47	0.95	0.9207	350.81	12.35
	308.15	0.994	26.95	0.05	0.8415	0.69	1.06	0.9685	477.11	16.70
	318.15	0.9914	32.91	0.03	0.9533	1.05	1.07	0.9075	681.14	17.50
	333.15	0.9953	19.05	0.04	0.9729	1.14	1.12	0.9078	995.52	18.18
BrO₃⁻	298.15	0.9857	24.64	0.07	0.7763	0.57	1.12	0.9325	389.24	17.10
	308.15	0.9863	37.74	0.07	0.8262	0.66	1.07	0.9402	458.15	17.45
	318.15	0.9639	23.98	0.09	0.8692	0.80	1.00	0.9486	587.60	17.42
	333.15	0.9918	22.08	0.03	0.9534	1.18	1.18	0.9296	960.96	17.14
NO₃⁻	298.15	0.9215	26.60	0.20	0.5863	0.41	0.98	0.9216	311.30	16.63
	308.15	0.9926	43.10	0.06	0.8339	0.68	1.04	0.9201	475.32	15.73
	318.15	0.9729	23.98	0.09	0.8831	0.82	0.98	0.9882	601.24	15.99
	333.15	0.9981	30.58	0.02	0.969	1.12	1.02	0.9115	1035.34	17.45

Table 4.9: A summary of the calculated adsorption isotherm parameters for the adsorption of the selected ions unto the fish scale VWMs

Ions		Langmuir Model			Freundlich Model			Dubinin – Radushkevich Model		
	Temp. (K)	R ²	q _{max} (mg/g)	b (L/mg)	R ²	K	1/n	R ²	E (kJ/mol)	q _{max} (mg/g)
Co	298.15	0.993	27.80	0.05	0.8241	0.63	1.15	0.9821	418.94	13.25
	308.15	0.9996	28.73	0.01	0.9338	0.88	1.13	0.9818	555.54	13.34
	318.15	0.9978	32.86	0.01	0.9879	1.50	1.13	0.9815	769.42	13.53
	333.15	0.9932	21.14	0.03	0.9365	1.03	1.11	0.9814	1055.17	13.54
Ni	298.15	0.9755	36.23	0.07	0.8201	0.65	1.10	0.9019	438.19	14.95
	308.15	0.9938	25.77	0.04	0.8938	1.37	1.13	0.9577	666.40	14.51
	318.15	0.9975	33.09	0.01	0.9889	2.70	1.13	0.9571	791.45	14.91

Ions		Langmuir Model			Freundlich Model			Dubinin – Radushkevich Model		
	333.15	0.9915	15.06	0.04	0.9162	0.93	1.14	0.99589	1105.82	15.15
Zn	298.15	0.9975	32.46	0.03	0.8617	0.69	1.13	0.959	454.97	15.61
	308.15	0.9964	46.51	0.03	0.9796	1.16	1.18	0.9406	640.06	14.91
	318.15	0.9948	27.52	0.01	0.9796	1.86	1.16	0.9399	795.17	14.91
	333.15	0.9893	27.11	0.01	0.9355	1.17	1.05	0.9397	1007.40	15.12
Cu	298.15	0.9917	36.96	0.03	0.8443	0.65	1.22	0.92	422.95	15.78
	308.15	0.9929	24.45	0.05	0.9867	1.41	1.34	0.9804	657.68	14.91
	318.15	0.9981	27.27	0.01	0.987	1.39	1.12	0.9054	753.33	15.61
	333.15	0.9947	21.95	0.01	0.9692	1.37	1.05	0.9062	948.36	15.75
Hg	298.15	0.9925	36.50	0.10	0.8276	0.62	1.19	0.9805	413.51	15.76
	308.15	0.9967	34.67	0.03	0.9758	1.09	1.23	0.9483	612.62	16.81
	318.15	0.9985	35.56	0.02	0.9934	1.50	1.16	0.9326	760.50	15.20
	333.15	0.994	28.99	0.03	0.9527	1.13	1.11	0.9933	1001.85	14.38
Ag	298.15	0.9956	30.42	0.04	0.8342	0.64	1.17	0.9804	422.11	14.91
	308.15	0.9968	38.14	0.04	0.8798	0.75	1.08	0.9517	505.98	15.20
	318.15	0.9999	32.56	0.01	0.98	1.20	1.09	0.9859	720.39	14.79
	333.15	0.9785	33.33	0.00	0.8866	1.05	1.04	0.9761	1070.03	15.12
Fe	298.15	0.9907	34.92	0.06	0.8216	0.64	1.08	0.9931	434.44	15.20
	308.15	0.9983	40.42	0.02	0.9625	-2.01	1.20	0.9276	586.41	15.61
	318.15	0.9982	36.92	0.01	0.9921	1.67	1.13	0.9713	786.36	15.70
	333.15	0.9919	13.16	0.05	0.9357	0.95	1.15	0.9912	1081.80	15.18
Pb	298.15	0.9966	26.15	0.02	0.8586	0.64	1.33	0.9752	409.58	14.51
	308.15	0.9953	27.72	0.02	0.9284	0.88	1.14	0.98834	554.30	14.91
	318.15	0.9982	36.08	0.02	0.9958	1.61	1.16	0.9689	774.50	15.59
	333.15	0.9809	41.73	0.01	0.929	1.30	1.01	0.9927	982.53	15.12
Cr	298.15	0.9892	37.88	0.05	0.916	0.78	1.35	0.9757	473.29	14.91

Ions		Langmuir Model			Freundlich Model			Dubinin – Radushkevich Model		
	308.15	0.9979	24.34	0.02	0.9321	0.88	1.12	0.9503	557.87	15.61
	318.15	0.993	28.54	0.03	0.9697	1.18	1.03	0.9828	728.80	15.59
	333.15	0.9918	13.30	0.05	0.9304	0.94	1.15	0.9841	1090.50	15.38
Mg	298.15	0.9516	27.62	0.17	0.6185	0.44	0.97	0.9418	330.40	15.61
	308.15	0.9965	26.18	0.04	0.9004	0.80	1.08	0.9686	526.88	15.42
	318.15	0.99	22.89	0.02	0.9584	1.15	1.09	0.9395	707.49	15.89
	333.15	0.9938	24.39	0.03	0.9594	1.17	1.14	0.9765	976.69	15.61
Al	298.15	0.997	31.94	0.04	0.8273	0.63	1.15	0.9619	420.94	15.42
	308.15	0.9956	26.23	0.03	0.9257	0.87	1.11	0.953	556.14	15.76
	318.15	0.9985	29.29	0.01	0.9919	1.57	1.13	0.9431	777.49	17.18
	333.15	0.9937	33.33	0.02	0.9523	1.15	1.10	0.9755	996.32	15.74
Ar	298.15	0.9854	44.44	0.06	0.8098	0.62	1.13	0.9332	416.39	16.12
	308.15	0.9996	33.33	0.00	0.9494	0.94	1.14	0.9907	577.41	15.09
	318.15	0.9978	36.96	0.01	0.9894	1.61	1.14	0.9807	778.90	15.55
	333.15	0.9957	28.57	0.03	0.9654	1.17	1.10	0.9902	989.51	15.38
Cd	298.15	0.9997	29.09	0.00	0.8507	0.63	1.28	0.9499	409.43	15.42
	308.15	0.9992	33.33	0.00	0.9557	0.99	1.11	0.9649	602.46	16.81
	318.15	0.9981	33.33	0.00	0.984	1.32	1.11	0.9971	743.30	14.87
	333.15	0.9897	10.75	0.06	0.9449	0.95	1.19	0.9923	1071.57	15.15
Si	298.15	0.9972	30.91	0.03	0.7994	0.57	1.20	0.9727	384.15	14.91
	308.15	0.9984	38.48	0.02	0.9748	1.07	1.22	0.9936	609.40	14.91
	318.15	0.9984	34.34	0.01	0.9915	1.57	1.13	0.9933	777.43	14.80
	333.15	0.9925	40.51	0.02	0.9444	1.14	1.07	0.9556	1009.45	17.14
Ti	298.15	0.9947	28.97	0.04	0.8356	0.64	1.17	0.981	423.08	15.20
	308.15	0.9962	31.94	0.02	0.9301	0.88	1.11	0.9924	561.32	14.51
	318.15	0.9979	36.21	0.01	0.9899	1.60	1.14	0.9676	778.71	16.63
	333.15	0.9748	27.27	0.00	0.8986	1.24	1.12	0.9122	966.85	17.18

Ions		Langmuir Model			Freundlich Model			Dubinin – Radushkevich Model		
F⁻	298.15	0.9574	27.40	0.13	0.725	0.54	1.02	0.9479	386.58	16.81
	308.15	0.997	41.49	0.03	0.9801	1.13	1.26	0.9365	616.87	16.81
	318.15	0.9982	39.93	0.02	0.9924	1.67	1.14	0.9179	785.28	17.50
	333.15	0.9907	12.76	0.05	0.9091	1.89	1.15	0.9119	1128.11	17.66
Cl⁻	298.15	0.9992	28.33	0.01	0.833	0.62	1.21	0.9295	412.05	16.91
	308.15	0.9993	37.14	0.00	0.952	0.96	1.15	0.9752	582.26	16.81
	318.15	0.9982	39.37	0.01	0.9916	1.63	1.14	0.9947	781.86	16.12
	333.15	0.993	41.52	0.01	0.9524	1.21	1.03	0.98	999.98	17.42
SO₄²⁻	298.15	0.9815	41.84	0.07	0.8129	0.63	1.13	0.9657	421.99	16.40
	308.15	0.9885	38.46	0.05	0.9026	0.83	1.06	0.9527	544.77	16.81
	318.15	0.9974	35.24	0.01	0.9888	1.73	1.13	0.9315	793.21	17.22
	333.15	0.9819	41.94	0.01	0.9306	1.30	1.01	0.9255	980.90	17.45
PO₄³⁻	298.15	0.9925	10.61	0.04	0.838	0.65	1.16	0.931	429.22	16.81
	308.15	0.9973	14.84	0.03	0.901	1.12	1.23	0.9151	621.04	17.22
	318.15	0.9984	15.56	0.20	0.9946	1.63	1.15	0.9776	779.56	16.95
	333.15	0.978	15.36	0.01	0.9128	1.21	1.01	0.9339	1010.03	17.91
NO₂⁻	298.15	0.9996	39.93	0.03	0.889	0.74	1.16	0.9604	474.48	16.12
	308.15	0.9999	32.58	0.00	0.9598	0.99	1.16	0.9468	592.27	15.20
	318.15	0.9982	36.23	0.02	0.9926	1.66	1.14	0.9252	784.16	17.42
	333.15	0.9934	15.13	0.05	0.9688	1.08	1.14	0.9463	1013.08	16.00
BrO₃⁻	298.15	0.9624	29.07	0.11	0.7433	0.56	1.04	0.9275	393.30	16.81
	308.15	0.9892	19.34	0.06	0.9555	1.46	1.30	0.9029	673.26	17.22
	318.15	0.9983	25.36	0.02	0.993	1.66	1.14	0.999	783.87	14.80
	333.15	0.9905	11.27	0.08	0.9288	0.91	1.17	0.9137	1102.77	17.06
NO₃⁻	298.15	0.9974	22.50	0.02	0.9244	0.79	1.36	0.9461	471.00	16.81
	308.15	0.9973	32.46	0.02	0.9259	0.86	1.10	0.9265	554.14	17.22

Ions		Langmuir Model			Freundlich Model			Dubinin – Radushkevich Model		
	318.15	0.9984	41.67	0.03	0.9928	1.66	1.14	0.9469	784.74	17.87
	333.15	0.992	13.77	0.04	0.9315	0.95	1.15	0.9666	1085.74	17.19

4.7 Kinetics Models

The plot of $\log (q_e - q)$ vs. t gave a straight line for first order adsorption kinetics and the rate constant k_1 was then obtained from the plot. A summary of the comparison of experimental sorption capacities (q_{exp}) and the predicted values (q_{cal} , k_1 , k_2 , k_d , R^2) from pseudo first order, pseudo second order and intra particle diffusion constants were recorded in Tables 4.10 and 4.11 for the fish scale and eggshell VWMs respectively. The second order equation was found to be the best fitted kinetic model for the VWMs due to the fact that the calculated, q_{cal} values were very close to the experimental (q_{exp}) values as well as the high R^2 values when compared to the other employed models [20][156].

Table 4.10: A summary of the calculated kinetic models parameters for the adsorption of the selected ions onto the fish scale VWMs

Ions	q_{exp} (mg/g)	Second Order			First Order			Intra Particle Diffusion	
		R^2	K_2 (gmg ⁻¹ min ⁻¹)	q_{cal} (mg/g)	R^2	K_1 (min ⁻¹)	q_{cal} (mg/g)	R^2	K_d (mgL ⁻¹ min ^{-1/2})
Co	13.13	0.9974	0.033	13.51	0.9415	0.020	0.13	0.8767	0.660
Ni	12.04	0.9988	0.016	12.94	0.9218	0.022	0.16	0.7424	0.488
Zn	11.90	0.9997	0.024	12.03	0.8853	0.025	0.22	0.6063	0.470
Cu	13.16	0.995	0.015	13.31	0.9475	0.020	0.14	0.6121	0.325
Hg	11.43	0.9777	0.017	12.01	0.7446	0.030	0.32	0.5305	0.220
Ag	12.11	0.9974	0.043	13.45	0.9332	0.020	0.13	0.7509	0.533
Fe	9.86	0.9587	0.018	10.66	0.9118	0.028	0.63	0.5457	0.138
Pb	12.42	0.9909	0.041	13.31	0.9641	0.020	0.13	0.6645	0.348
Cr	11.51	0.9983	0.026	12.91	0.9251	0.022	0.16	0.5759	0.159
Mg	10.77	0.9952	0.015	13.02	0.9455	0.020	0.15	0.4908	0.154
Al	12.70	0.991	0.015	13.49	0.9634	0.019	0.13	0.5234	0.161
Ar	11.33	0.9983	0.027	12.73	0.9209	0.023	0.16	0.5758	0.234
Cd	12.13	0.9999	0.016	12.22	0.8793	0.024	0.20	0.6554	0.413
Si	11.56	0.999	0.028	12.39	0.9067	0.023	0.19	0.9452	0.518
Ti	11.60	0.9989	0.016	12.51	0.8628	0.024	0.19	0.8076	0.464
F⁻	13.89	0.9895	0.015	13.96	0.9747	0.018	0.12	0.7696	0.348
Cl⁻	12.09	0.9958	0.026	12.71	0.9252	0.023	0.18	0.8357	0.443
SO₄²⁻	13.87	0.9983	0.017	12.67	0.9204	0.022	0.17	0.5572	0.187
PO₄³⁻	10.41	0.9948	0.017	11.70	0.8007	0.028	0.29	0.4834	0.141
NO₂⁻	12.47	0.9976	0.036	12.92	0.9278	0.022	0.15	0.6343	0.288
BrO₃⁻	12.76	0.9957	0.016	12.91	0.9397	0.021	0.15	0.9355	0.420
NO₃⁻	12.10	0.9976	0.046	12.95	0.9297	0.022	0.15	0.5898	0.108

Table 4.11: A summary of the calculated kinetic models parameters for the adsorption of the selected ions onto the eggshell VWMs

Ions	q_{exp} (mg/g)	Second Order			First Order			Intra Particle Diffusion	
		R^2	K_2 (gmg ⁻¹ min ⁻¹)	q_{cal} (mg/g)	R^2	K_1 (min ⁻¹)	q_{cal} (mg/g)	R^2	K_d (mgL ⁻¹ min ^{-1/2})
Co	12.96	0.9915	0.022	13.14	0.9605	0.020	0.14	0.8484	0.452
Ni	11.71	0.999	0.010	12.70	0.9105	0.023	0.18	0.8537	0.391
Zn	10.27	0.9974	0.025	11.85	0.9072	0.025	0.22	0.7411	0.376
Cu	12.07	0.995	0.019	13.11	0.9483	0.020	0.14	0.6929	0.269
Hg	10.76	0.9805	0.024	11.83	0.7494	0.030	0.32	0.5896	0.194
Ag	12.61	0.9986	0.003	13.26	0.929	0.021	0.14	0.7629	0.376
Fe	9.94	0.9587	0.014	10.66	0.9118	0.028	0.63	0.6426	0.093
Pb	12.00	0.9951	0.002	13.08	0.9473	0.021	0.15	0.7102	0.264
Cr	12.22	0.9912	0.003	12.64	0.9518	0.021	0.16	0.6686	0.118
Mg	11.39	0.9907	0.012	12.82	0.9578	0.021	0.15	0.5377	0.129
Al	12.33	0.9928	0.002	13.31	0.9585	0.019	0.13	0.6188	0.130
Ar	11.83	0.994	0.002	12.53	0.942	0.022	0.17	0.612	0.165
Cd	11.87	0.9965	0.004	11.93	0.9157	0.024	0.21	0.8643	0.303
Si	11.81	0.9985	0.002	12.36	0.9113	0.023	0.19	0.6621	0.186
Ti	10.93	0.9959	0.003	12.61	0.8453	0.025	0.19	0.84	0.389
F ⁻	12.46	0.9763	0.012	13.66	0.9848	0.017	0.12	0.7539	0.289
Cl ⁻	12.02	0.9974	0.002	12.53	0.9202	0.023	0.18	0.7208	0.262
SO ₄ ²⁻	11.56	0.998	0.002	12.51	0.9189	0.023	0.18	0.5966	0.115
PO ₄ ³⁻	10.04	0.9885	0.003	11.79	0.7787	0.029	0.29	0.5812	0.076
NO ₂ ⁻	11.79	0.9978	0.005	12.77	0.9103	0.022	0.16	0.7205	0.203
BrO ₃ ⁻	12.11	0.9893	0.002	12.76	0.9609	0.020	0.15	0.8698	0.309
NO ₃ ⁻	12.07	0.9958	0.022	12.88	0.9408	0.021	0.15	0.6152	0.048

4.8 Adsorption Thermodynamics

The thermodynamic parameters (ΔG , ΔH and ΔS) for the adsorption of the selected ions onto the VWMs were calculated using Equation 2.21 as described in section 2.3.5.2.1.3 and were summarized in Tables 4.12 and 4.13 for the fish scale and eggshell VWMs respectively. From the calculated values of ΔG , ΔH and ΔS , the adsorption process was found to be spontaneous and endothermic based on the negative values of the Gibbs free energy and the positive values of ΔH observed and recorded in Tables 4.12 and 4.13 for all cases. ΔS values were found to be positive signifying the feasibility of the adsorption process occurring in an orderly fashion [127].

Table 4.12: A summary of the calculated thermodynamic parameters for the adsorption of the selected ions by the fish scale VWMs

Ions	Temp. (K)	b (L/mol)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/molK)	R^2
Co	298.15	5054.29	-21.14	58.26	0.4733	0.9884
	308.15	12923.90	-24.25			
	318.15	31181.50	-27.37			
	333.15	59709.20	-30.46			
Ni	298.15	4504.22	-20.85	45.47	0.3771	0.9971
	308.15	8865.56	-23.29			
	318.15	16393.90	-25.67			
	333.15	30938.30	-28.64			
Zn	298.15	5452.88	-21.33	72.12	0.6252	0.9704
	308.15	13076.00	-24.28			
	318.15	63475.70	-29.25			
	333.15	115922.00	-32.30			
Cu	298.15	4767.14	-20.99	52.25	0.4362	0.9999
	308.15	9196.24	-23.38			
	318.15	17950.80	-25.91			
	333.15	43644.20	-29.59			
Hg	298.15	18607.60	-24.37	43.96	0.3678	0.9832
	308.15	34668.20	-26.78			
	318.15	66907.90	-29.39			
	333.15	119898.00	-32.39			
Ag	298.15	8278.45	-22.36	44.24	0.3633	0.997

Ions	Temp. (K)	b (L/mol)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/molK)	R^2
	308.15	16723.80	-24.91			
	318.15	28612.30	-27.14			
	333.15	53988.10	-30.18			
Fe	298.15	4332.43	-20.76	48.16	0.3986	0.9897
	308.15	9562.50	-23.48			
	318.15	19323.50	-26.10			
	333.15	33360.20	-28.85			
Pb	298.15	16200.20	-24.03	49.58	0.4091	0.998
	308.15	34361.50	-26.76			
	318.15	63950.60	-29.27			
	333.15	132481.00	-32.67			
Cr	298.15	3972.19	-20.54	44.14	0.3649	0.999
	308.15	7557.56	-22.88			
	318.15	13064.30	-25.07			
	333.15	25791.70	-28.14			
Mg	298.15	1939.74	-18.77	50.83	0.4214	0.9927
	308.15	4309.40	-21.44			
	318.15	8902.93	-24.05			
	333.15	16727.50	-26.94			
Al	298.15	2269.30	-19.15	57.95	0.4842	0.9904
	308.15	5439.92	-22.04			
	318.15	13423.90	-25.14			
	333.15	26452.90	-28.21			
Ar	298.15	6126.08	-21.62	54.18	0.4481	0.9896
	308.15	14924.70	-24.62			
	318.15	32717.00	-27.50			
	333.15	60862.70	-30.51			
Cd	298.15	9080.05	-22.59	48.81	0.4122	0.968
	308.15	20327.50	-25.41			
	318.15	53275.40	-28.79			
	333.15	71874.00	-30.97			
Si	298.15	8703.08	-22.49	45.29	0.3753	0.9955
	308.15	17483.10	-25.03			
	318.15	32792.80	-27.50			
	333.15	59325.30	-30.44			

Ions	Temp. (K)	b (L/mol)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/molK)	R^2
Ti	298.15	3684.91	-20.36	49.96	0.4141	0.9925
	308.15	8126.83	-23.07			
	318.15	16620.50	-25.71			
	333.15	30625.10	-28.61			
F ⁻	298.15	1349.29	-17.87	37.31	0.3044	0.9901
	308.15	2624.03	-20.17			
	318.15	4193.82	-22.06			
	333.15	6557.82	-24.34			
Cl ⁻	298.15	2663.64	-19.55	56.58	0.4618	0.9917
	308.15	7076.45	-22.71			
	318.15	14013.00	-25.25			
	333.15	29300.00	-28.49			
SO ₄ ²⁻	298.15	7703.29	-22.18	57.31	0.4751	0.9991
	308.15	17370.70	-25.01			
	318.15	35977.50	-27.75			
	333.15	87406.70	-31.52			
PO ₄ ³⁻	298.15	8563.70	-22.45	62.45	0.5327	0.9708
	308.15	21341.90	-25.54			
	318.15	75977.10	-29.73			
	333.15	120829.00	-32.41			
NO ₂ ⁻	298.15	3637.15	-20.32	46.19	0.3837	0.9899
	308.15	7630.18	-22.90			
	318.15	15336.70	-25.49			
	333.15	25761.50	-28.13			
BrO ₃ ⁻	298.15	10207.70	-22.88	43.32	0.3583	0.9871
	308.15	21388.50	-25.54			
	318.15	41126.40	-28.10			
	333.15	64015.50	-30.65			
NO ₃ ⁻	298.15	4855.51	-21.04	51.25	0.4252	0.9975
	308.15	10317.00	-23.68			
	318.15	20531.40	-26.27			
	333.15	42615.10	-29.53			

Table 4.13: A summary of the calculated thermodynamic parameters for the adsorption of the selected ions by the eggshell VWMs

Ions	Temp. (K)	b (L/mol)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/molK)	R^2
Co	298.15	4554.10	-20.88	44.04	0.3603	0.991
	308.15	9676.52	-23.51			
	318.15	16741.48	-25.73			
	333.15	29450.27	-28.50			
Ni	298.15	4507.68	-20.86	54.01	0.4454	0.9898
	308.15	11094.52	-23.86			
	318.15	23665.32	-26.64			
	333.15	44462.12	-29.64			
Zn	298.15	6019.37	-21.57	63.02	0.5182	0.9955
	308.15	16437.50	-24.87			
	318.15	36179.89	-27.76			
	333.15	86997.46	-31.50			
Cu	298.15	4895.69	-21.06	41.52	0.3412	0.9837
	308.15	10383.33	-23.69			
	318.15	19025.75	-26.06			
	333.15	28444.94	-28.41			
Hg	298.15	17549.43	-24.22	66.76	0.5802	0.962
	308.15	41188.91	-27.22			
	318.15	194747.60	-32.22			
	333.15	297170.40	-34.91			
Ag	298.15	8049.87	-22.29	47.55	0.3946	0.994
	308.15	16828.11	-24.93			
	318.15	33292.65	-27.54			
	333.15	60396.53	-30.49			
Fe	298.15	5180.43	-21.20	41.37	0.3448	0.9918
	308.15	9842.26	-23.56			
	318.15	18602.60	-26.00			
	333.15	29911.62	-28.55			
Pb	298.15	15901.77	-23.98	48.36	0.3976	0.9961
	308.15	34533.33	-26.77			
	318.15	63363.91	-29.25			
	333.15	123480.30	-32.47			
Cr	298.15	4149.72	-20.65	54.69	0.4455	0.9969

Ions	Temp. (K)	b (L/mol)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/molK)	R^2
	308.15	10115.95	-23.63			
	318.15	17991.70	-25.92			
	333.15	42136.14	-29.49			
Mg	298.15	1974.41	-18.81	45.63	0.3739	0.9935
	308.15	4241.71	-21.40			
	318.15	7501.54	-23.60			
	333.15	13654.49	-26.37			
Al	298.15	2061.27	-18.92	45.59	0.3753	0.9973
	308.15	4176.78	-21.36			
	318.15	7332.07	-23.54			
	333.15	14231.01	-26.49			
Ar	298.15	6126.08	-21.62	58.96	0.4839	0.9992
	308.15	14576.26	-24.56			
	318.15	27443.96	-27.03			
	333.15	74549.25	-31.08			
Cd	298.15	9817.56	-22.79	53.03	0.4340	0.9805
	308.15	26387.56	-26.08			
	318.15	55925.87	-28.92			
	333.15	92901.65	-31.68			
Si	298.15	9706.46	-22.76	52.51	0.4329	0.986
	308.15	24128.05	-25.85			
	318.15	51838.43	-28.71			
	333.15	89863.74	-31.59			
Ti	298.15	3866.48	-20.48	50.55	0.4315	0.9723
	308.15	8072.01	-23.05			
	318.15	22685.78	-26.53			
	333.15	32943.57	-28.81			
F⁻	298.15	1398.97	-17.96	39.37	0.2744	0.9917
	308.15	2904.89	-20.43			
	318.15	4193.82	-22.06			
	333.15	7421.09	-24.68			
Cl⁻	298.15	2789.38	-19.67	53.26	0.4366	0.9871
	308.15	7119.08	-22.73			
	318.15	14589.71	-25.36			

Ions	Temp. (K)	b (L/mol)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/molK)	R^2
	333.15	26656.39	-28.23			
SO_4^{2-}	298.15	7734.30	-22.19	57.24	0.4722	0.9967
	308.15	18725.15	-25.20			
	318.15	38890.69	-27.95			
	333.15	87486.34	-31.52			
PO_4^{3-}	298.15	8563.72	-22.45	62.45	0.5393	0.9671
	308.15	19581.77	-25.32			
	318.15	77845.57	-29.79			
	333.15	120829.00	-32.41			
NO_2^-	298.15	3755.92	-20.40	57.28	0.4800	0.9997
	308.15	7630.18	-22.90			
	318.15	16550.36	-25.69			
	333.15	42562.44	-29.52			
BrO_3^-	298.15	10458.14	-22.94	50.26	0.4114	0.9982
	308.15	22921.68	-25.72			
	318.15	39845.17	-28.02			
	333.15	88026.84	-31.54			
NO_3^-	298.15	4855.90	-21.04	53.10	0.4372	0.9983
	308.15	10859.88	-23.81			
	318.15	20533.08	-26.27			
	333.15	46104.01	-29.74			

4.9 Desorption and Regeneration Studies

The desorption-regeneration studies were performed to evaluate the reusability of the VWMs. The VWMs were found to be reusable since after five (5) cycles and at each cycle the percentage efficiency of the removal of ions were statistically not significantly different for both VWMs and all the selected ions (see Tables 4.14 and 4.15 for the fish scale VWMs and eggshell VWMs respectively). Thus the VWMs could be several times (5 times) with regenerative washing off the adsorbed (desorption) after every cycle as described in Section 3.13.

Table 4.14: A summary of the percentage of ions adsorbed and desorbed by the fish scale VWMs for each cycle

Ions	Cycle I		Cycle II		III		IV		V	
	% Adsorp.	% Desorp.	% Adsorp.	% Desorp.	% Adsorp.	% Desorp.	% Adsorp.	% Desorp.	% Adsorp.	% Desorp.
Co	78.70	94.67	73.67	89.78	66.56	78.64	52.45	58.53	36.77	32.87
Ni	76.53	89.76	71.45	75.46	63.45	67.46	46.78	47.83	28.67	26.57
Zn	81.97	90.56	76.83	84.67	60.44	73.45	48.65	60.23	33.81	48.98
Cu	74.71	97.68	64.67	90.83	50.41	79.98	35.45	64.57	23.70	47.82
Hg	69.13	88.68	62.01	80.11	51.64	69.76	39.65	54.35	20.00	33.63
Ag	84.07	91.68	76.84	83.52	67.65	70.35	50.83	51.34	36.43	29.78
Fe	76.98	93.44	73.11	84.67	63.13	69.50	49.99	55.72	22.64	30.93
Pb	40.37	83.78	75.43	69.75	62.84	45.76	50.67	33.49	30.96	15.94
Cr	86.96	96.68	80.67	84.78	71.65	64.78	63.61	53.09	41.89	32.83
Mg	84.90	70.86	79.43	57.99	62.33	43.56	48.67	31.89	31.89	13.45
Al	63.67	69.54	59.21	51.78	43.86	41.98	31.09	32.56	19.67	17.84
Ar	74.48	85.78	68.93	67.83	54.89	50.37	42.36	40.13	20.56	29.76
Cd	59.04	82.16	52.56	77.01	43.87	62.43	29.78	50.01	14.35	21.83
Si	90.91	93.89	83.58	81.56	70.98	70.65	59.89	58.67	27.84	38.61
Ti	89.88	78.99	80.56	60.88	71.89	50.02	62.07	40.82	40.78	19.86
F⁻	87.82	89.88	80.23	80.35	72.45	68.68	63.89	40.72	49.99	24.12
Cl⁻	95.77	90.46	91.78	82.68	79.99	72.24	59.88	59.02	36.56	37.68
SO₄²⁻	88.83	82.56	78.46	73.56	65.89	61.45	50.42	48.16	28.67	25.45
PO₄³⁻	73.08	70.99	66.45	62.23	56.45	49.89	42.13	37.34	26.57	19.95
NO₂⁻	91.42	86.74	89.56	76.55	70.65	68.56	50.78	49.88	30.72	30.56
BrO₃⁻	82.97	92.65	74.34	78.56	53.45	71.56	41.87	60.67	23.67	38.02
NO₃⁻	74.60	85.55	61.34	72.34	50.65	60.56	34.89	51.45	19.00	20.56

Table 4.15: A summary of the percentage of ions adsorbed and desorbed by the eggshell VWMs for each cycle

Cations	I		II		III		IV		V	
	% Adsorp.	% Desorp.	% Adsorp.	% Desorp.	% Adsorp.	% Desorp.	% Adsorp.	% Desorp.	% Adsorp.	% Desorp.
Co	81.25	97.22	76.22	92.33	69.11	81.19	55.00	61.08	39.31	35.42
Ni	77.99	91.21	72.90	76.91	64.90	68.91	48.23	49.28	30.12	28.02
Zn	84.76	93.35	79.62	87.46	63.23	76.24	51.44	63.02	36.60	51.77
Cu	76.50	99.46	66.45	92.61	52.19	81.76	37.24	66.35	25.49	49.61
Hg	72.73	92.27	65.61	83.71	55.24	73.35	43.25	57.95	23.60	37.22
Ag	86.06	93.66	78.82	85.50	69.63	72.33	52.81	53.32	38.41	31.77
Fe	80.19	96.65	76.32	87.88	66.34	72.71	53.20	58.93	25.85	34.14
Pb	82.84	86.25	77.90	72.22	65.31	48.23	53.14	35.96	33.42	18.41
Cr	89.72	99.43	83.43	87.54	74.41	67.54	66.37	55.85	44.65	35.59
Mg	86.46	72.42	81.00	59.55	63.89	45.13	50.23	33.45	33.45	15.02
Al	68.35	74.21	63.88	56.45	48.53	46.65	35.76	37.23	24.35	22.51
Ar	79.04	90.34	73.49	72.39	59.45	54.93	46.92	44.70	25.13	34.33
Cd	64.91	88.02	58.43	82.88	49.74	68.30	35.65	55.88	20.22	27.70
Si	93.78	96.76	86.45	84.43	73.85	73.52	62.76	61.54	30.71	41.48
Ti	88.87	77.98	79.56	59.87	70.88	49.01	61.06	39.82	39.77	18.86
Anions										
F⁻	86.92	88.98	79.34	79.45	71.56	67.78	63.00	39.83	49.09	23.22
Cl⁻	93.09	87.78	89.11	80.00	77.32	69.56	57.21	56.34	33.89	35.00
SO₄²⁻	90.47	84.19	80.09	75.20	67.53	63.09	52.06	49.79	30.30	27.09
PO₄³⁻	74.08	71.99	67.45	63.23	57.45	50.89	43.13	38.34	27.57	20.95
NO₂⁻	88.86	84.18	87.00	73.99	68.09	66.00	48.22	47.32	28.16	28.00
BrO₃⁻	84.74	94.42	76.11	80.33	55.22	73.33	43.64	62.44	25.44	39.79
NO₃⁻	76.62	87.57	63.36	74.36	52.67	62.58	36.91	53.47	21.01	22.58

4.10 Comparative Studies of the Proposed VWMs and the Commonly Applied Activated Charcoal

For comparative studies, the percentage adsorption/removal efficiency of activated charcoal which is commonly employed for the removal of dissolved ions from wastewater in wastewater treatment plants [47] was compared with that of the proposed VWMs in this thesis. The VWMs showed relatively similar percentage removal efficiency of 69% – 92% ion removals to 70% - 95% of the activated charcoal in removing the selected ions from the raw wastewater samples (see Figures 4.21, 4.22 and Table 4.16) for comparison. Hence, going forward the proposed VWMs presented themselves as potential replacements of the activated charcoal as adsorbents for the removal of toxic ions in wastewater treatment plants since activated charcoal is expensive and production toxic byproducts during activation. The VWMs on the other hand, have proved to be cheap as they are waste materials which could be collected for free and are also environmentally friendly as they occur naturally.

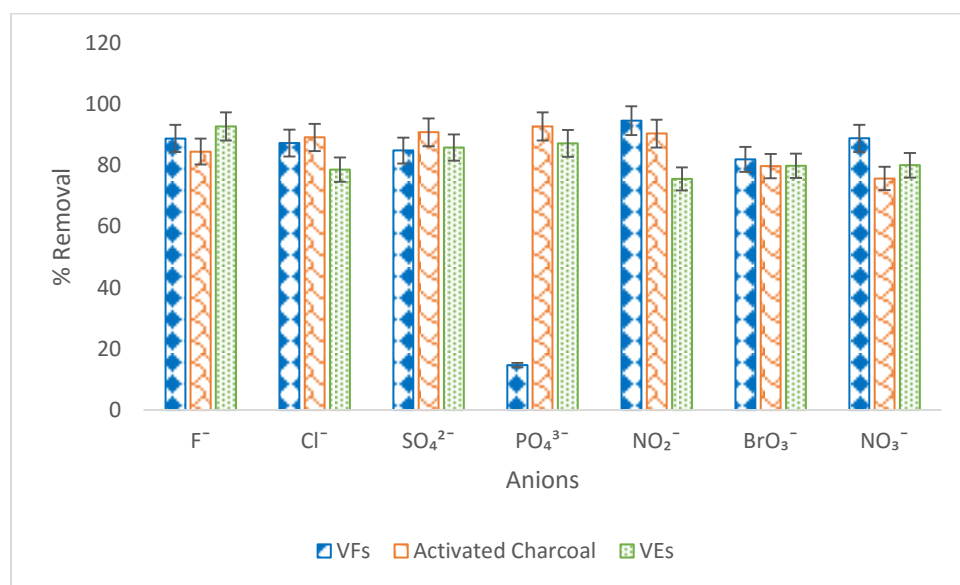


Figure 4.21: Percentage of anions removed by the VWMs and activated charcoal.

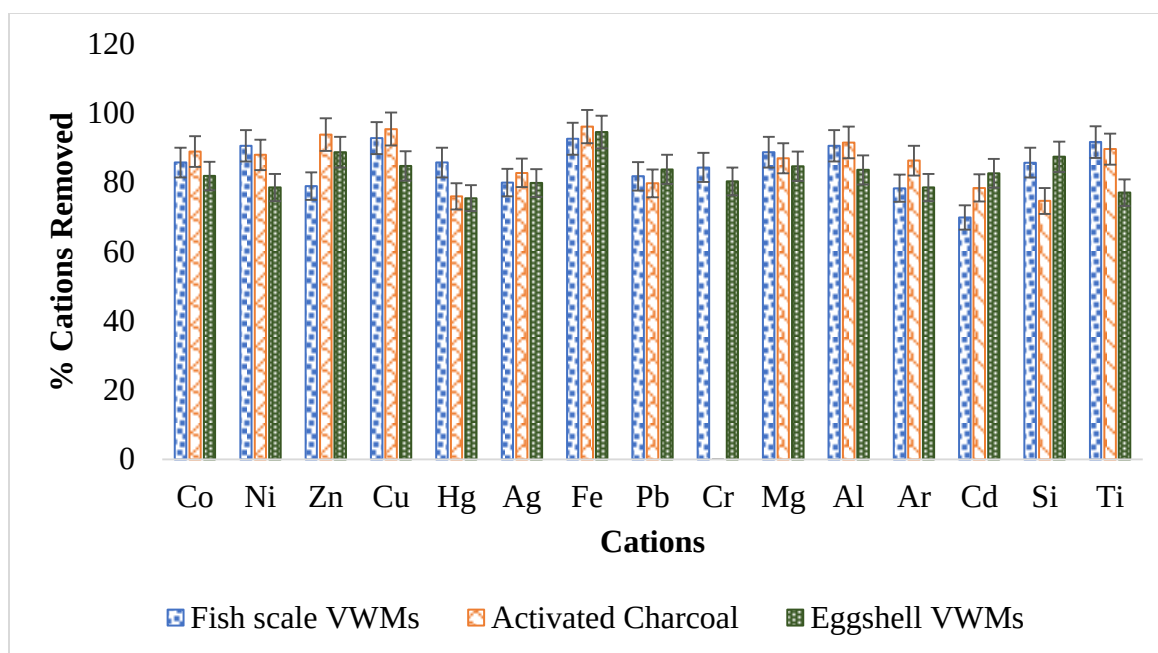


Figure 4.22: Percentage of cations removed by the VWMs and activated charcoal

Table 4.16: A summary of the percentage of the ions removed by the VWMs and activated charcoal

Cations	Fish scale VWMs	Activated charcoal	Eggshell VWMs	Anions	Fish scale VWMs	Activated charcoal	Eggshell VWMs
Co	85.78	88.95	81.89	F ⁻	88.74	84.45	92.67
Ni	90.64	87.99	78.56	Cl ⁻	87.24	89.09	78.56
Zn	78.95	93.86	88.79	SO ₄ ²⁻	84.79	90.78	85.78
Cu	92.85	95.46	84.79	PO ₄ ³⁻	14.69	92.67	87.15
Hg	85.78	75.99	75.49	NO ₂ ⁻	94.56	90.34	75.49
Ag	79.99	82.79	79.84	BrO ₃ ⁻	81.89	79.67	79.84
Fe	92.67	96.19	94.56	NO ₃ ⁻	88.79	75.67	79.99
Pb	81.78	79.76	83.79				
Cr	84.35	70.54	80.32				
Mg	88.75	86.98	84.67				
Al	90.56	91.56	83.65				
Ar	78.35	86.32	78.56				
Cd	69.89	78.43	82.67				
Si	85.73	74.67	87.42				
Ti	91.67	89.67	77.08				

CHAPTER FIVE: CONCLUSIONS

5.0 Conclusions of the Thesis

The main objectives of this thesis which was to (i) identify waste material(s) that were abundant and easily available in our locality, Botswana (ii) valorize the waste materials (iii) thereafter characterize and evaluate the valorized waste materials` (VWMs) efficiency in removing the selected toxic ions from wastewater, were successfully achieved as evident from the obtained high average percentage removal of 92.13% for the selected ions by the VWMs employing optimized conditions. The achieved high % removal by the identified eggshell and the fish scale VWMs were attributed to the functional groups existent on the structures of the waste materials which were exposed and made even more accessible to bonding the ions by a simple eco-friendly valorization strategy that involved pulverization and treatment of the waste materials with 12.67% vinegar. Several functional groups including carboxylic, hydroxyl and carbonyls that are known to bind with ions were revealed by fourier transform infrared (FTIR) and corroborated by Raman spectrometer and x-ray diffractometer (XRD). Scanning electron microscope (SEM) micrographs showed spherical geometry and rough morphology of the valorized waste materials which are excellent characteristics associated with superior sorbents. Furthermore, the calculations and assessment of the kinetic and thermodynamic parameters of the adsorption of the selected ions by the VWMs showed that the adsorption process fitted the Langmuir isotherm model because $R^2 \sim 1$, fitted pseudo second order kinetics, was found to be spontaneous and endothermic respectively.

All in all, the proposed VWMs with their high comparable %removal efficiencies, low cost (since they are collected from waste) and their environmental friendliness (since they are bio-materials thus bio-degradable) presented themselves as potential replacements of the expensive, non-environmentally friendly, commercial adsorbents (represented by charcoal in this thesis) that are commonly employed for the removal of toxic ions from wastewater in wastewater treatment plants. Consequently, it is our recommendation that from here on the VWMs can be rolled out and adapted right away by rural communities with scarce fresh water, to purify grey water for domestic purposes as the procedure proved to be simple, cheap and easy to use.

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CHAPTER SIX: APPENDICES

Appendix A

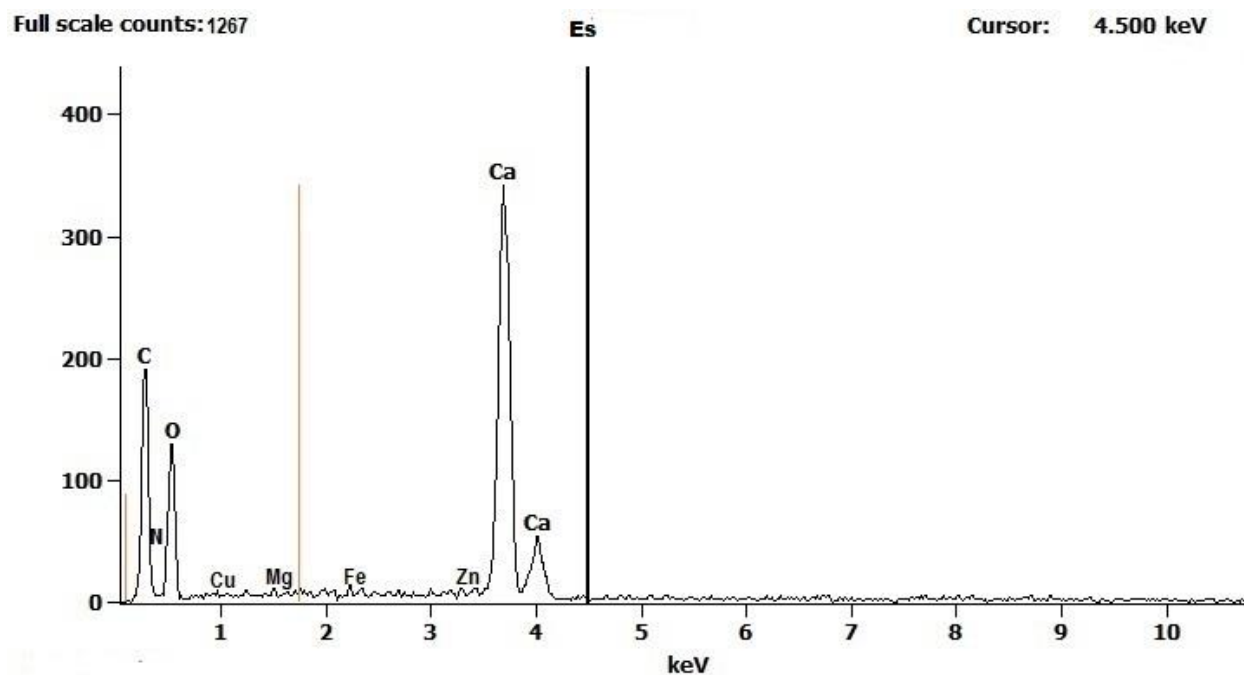


Figure 6.1: SEM - EDX for the eggshell VWMs

Table 6.1: SEM - EDX quantitative results for the eggshell VWMs

<i>Element Line</i>	<i>Weight %</i>	<i>Atom %</i>
<i>C</i>	19.84	21.82
<i>O</i>	13.78	19.18
<i>Ca</i>	52.40	22.45
<i>N</i>	5.21	13.76
<i>Cu</i>	1.34	4.12
<i>Mg</i>	2.56	5.49
<i>Fe</i>	3.01	8.35
<i>Zn</i>	1.86	4.81
<i>Total</i>	100.00	100.00

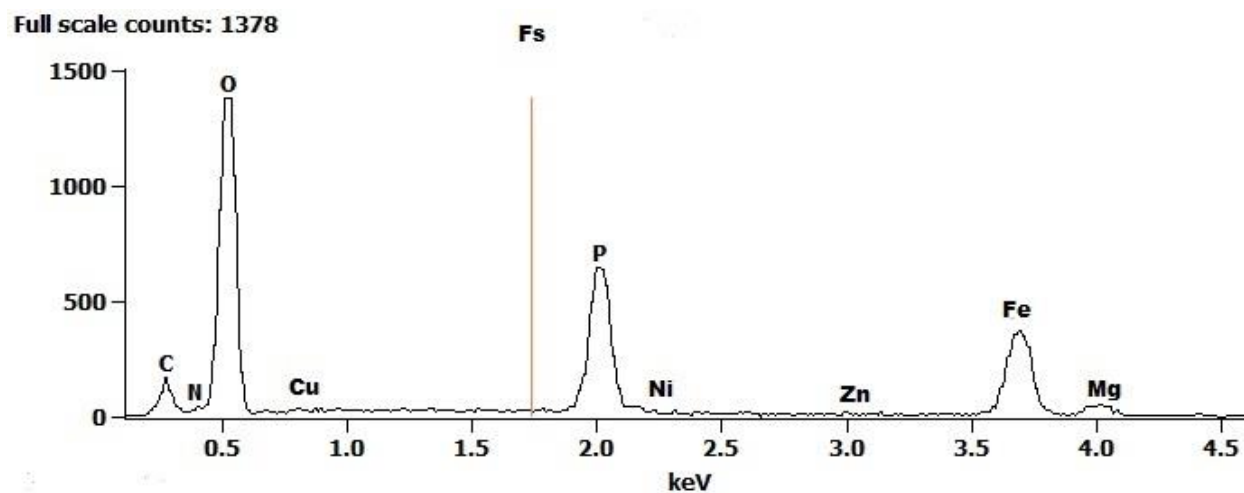


Figure 6.2: SEM - EDX for the fish scale VWMs

Table 6.2: SEM - EDX quantitative results for the fish scale VWMs

<i>Element Line</i>	<i>Weight %</i>	<i>Atom %</i>
<i>C</i>	9.56	16.39
<i>O</i>	40.32	27.12
<i>P</i>	21.17	18.65
<i>N</i>	1.51	4.14
<i>Cu</i>	0.92	3.27
<i>Mg</i>	6.88	9.09
<i>Fe</i>	15.76	17.22
<i>Zn</i>	1.46	4.12
<i>Ni</i>	2.42	7.13
<i>Total</i>	100.00	100.00

Appendix B

Table 6.3: Matrix design for the two-level $\frac{1}{2}$ fraction factorial design for the fish scale VWMs

StdOrder	RunOrder	PtType	Blocks	pH	Sorbent Dosage (mg)	Contact Time (min)	Concentration (mg/L)	Co	Ni	Zn	Cu	Hg	Cr	Ag	Fe
11	1	1	1	2	100	15	50	7.213	8.4512	7.5634	7.8153	7.9453	8.1109	7.5623	8.0014
39	2	1	1	10	100	90	0	5.893	5.0145	4.6734	4.8891	5.0114	5.8368	4.6732	4.8935
33	3	1	1	10	25	15	0	6.453	7.1123	6.868	7.4527	6.6498	6.5638	6.8345	7.3724
4	4	1	1	10	100	15	0	5.454	6.0145	5.4456	5.8345	6.2861	5.8945	6.6734	5.895
62	5	0	1	6	62.5	52.5	25	4.453	5.0014	4.1342	5.0001	4.2453	4.1673	4.2359	4.7824
50	6	-1	1	6	25	52.5	25	5.345	5.5634	5.1998	5.5648	6.0023	6.0244	5.4894	5.9983
6	7	1	1	10	25	90	0	7.893	7.5634	7.6745	8.0123	7.998	8.002	8.1342	7.6746
20	8	-1	1	6	100	52.5	25	2.454	2.6784	3.4523	2.6748	2.8896	3.4523	3.2453	3.841
57	9	0	1	6	62.5	52.5	25	4.044	4.673	3.9967	4.7832	3.9984	3.6784	4.0016	4.529
59	10	0	1	6	62.5	52.5	25	3.453	4.4231	4.1002	4.2673	3.5644	3.3326	3.5689	3.9967
3	11	1	1	2	100	15	0	8.785	8.5647	8.1999	8.5648	8.9845	8.3564	8.2341	8.4563
32	12	1	1	2	25	15	0	9.001	8.9967	9.0234	8.9846	9.1453	9.3452	8.8945	8.784
26	13	0	1	6	62.5	52.5	25	3.253	4.563	3.8734	4.563	3.5673	3.0134	3.2453	3.452
16	14	1	1	10	100	90	50	4.673	5.6473	5.1843	4.5738	4.6739	5.0142	5.2378	4.6734
56	15	0	1	6	62.5	52.5	25	3.563	3.5693	3.3425	4.1856	3.3321	3.425	3.5623	3.6345
10	16	1	1	10	25	15	50	8.685	9.0456	8.5647	8.8856	9.0345	8.8956	8.7561	8.8856

StdOrder	RunOrder	PtType	Blocks	pH	Sorbent Dosage (mg)	Contact Time (min)	Concentration (mg/L)	Co	Ni	Zn	Cu	Hg	Cr	Ag	Fe
27	17	0	1	6	62.5	52.5	25	3.563	3.8965	4.0235	3.6745	3.5638	4.1023	3.7845	4.0241
17	18	-1	1	2	62.5	52.5	25	5.356	5.6748	6.5452	5.8945	5.2673	6.4389	5.5799	5.9547
48	19	-1	1	2	62.5	52.5	25	5.998	6.8945	5.6783	5.9998	6.122	6.001	5.4532	5.5634
54	20	-1	1	6	62.5	52.5	0	4.674	5.3426	4.8956	5.0245	4.6734	4.534	5.0021	4.5634
43	21	1	1	10	100	15	50	6.896	6.8935	7.5641	6.6745	7.001	6.5648	6.8956	7.0023
2	22	1	1	10	25	15	0	8.896	8.634	8.5634	8.6794	8.3452	8.6758	8.7856	8.4532
38	23	1	1	2	100	90	0	5.673	6.2341	5.7834	5.7845	6.1235	5.8345	5.8962	6.537
9	24	1	1	2	25	15	50	8.342	8.112	8.4533	8.6734	9.0023	8.5935	8.6745	9.0001
34	25	1	1	2	100	15	0	7.674	8.6745	8.6745	8.645	7.7846	8.5648	8.7845	8.4634
35	26	1	1	10	100	15	0	6.785	6.856	7.0023	6.856	6.599	6.856	7.0345	6.856
24	27	-1	1	6	62.5	52.5	50	5.011	4.6739	4.6734	4.7845	4.6244	5.0245	5.0444	5.0001
31	28	0	1	6	62.5	52.5	25	2.452	3.0023	2.5638	3.0241	3.0241	2.7785	2.7845	2.6548
55	29	-1	1	6	62.5	52.5	50	4.673	4.6734	4.0132	3.866	4.0244	5.0324	4.986	4.2341
58	30	0	1	6	62.5	52.5	25	2.453	2.7845	2.6745	3.0023	3.0023	2.8894	2.9973	3.0024
36	31	1	1	2	25	90	0	8.785	8.6745	9.0034	8.946	8.956	8.6674	8.946	8.9674
23	32	-1	1	6	62.5	52.5	0	3.563	3.0024	3.9564	3.6473	3.724	3.4544	3.7893	3.675
14	33	1	1	10	25	90	50	7.565	8.2349	7.899	7.645	8.7457	8.9456	7.6745	8.5647
45	34	1	1	10	25	90	50	7.365	7.9982	7.453	7.2341	8.334	8.3421	7.645	8.218
8	35	1	1	10	100	90	0	3.652	3.6524	4.634	3.5634	4.0002	3.6743	3.3425	3.673
51	36	-1	1	6	100	52.5	25	2.563	1.899	2.134	2.435	2.314	1.8993	2.5634	2.4534

StdOrder	RunOrder	PtType	Blocks	pH	Sorbent Dosage (mg)	Contact Time (min)	Concentration (mg/L)	Co	Ni	Zn	Cu	Hg	Cr	Ag	Fe
29	37	0	1	6	62.5	52.5	25	2.563	3.4251	2.786	2.8945	3.0023	3.2314	2.8945	2.8745
42	38	1	1	2	100	15	50	8.675	7.5634	8.4836	7.9987	7.6749	8.0234	8.0445	8.546
21	39	-1	1	6	62.5	15	25	5.675	6.0345	5.7845	5.436	5.0345	5.846	4.7634	5.453
7	40	1	1	2	100	90	0	7.946	8.7456	8.0045	7.995	8.034	7.8959	8.6745	7.5648
46	41	1	1	2	100	90	50	6.957	7.6857	7.3457	7.674	6.785	7.896	6.563	6.753
22	42	-1	1	6	62.5	90	25	1.435	1.564	2.3241	2.034	1.435	1.4352	1.634	2.491
12	43	1	1	10	100	15	50	5.674	5.7452	5.7835	4.997	5.5647	5.6354	5.8356	5.5473
37	44	1	1	10	25	90	0	7.863	6.6745	7.895	7.8945	7.5692	7.7856	7.5483	7.4563
5	45	1	1	2	25	90	0	8.996	9.023	8.9978	9.0345	8.9456	8.7456	9.0546	9.0657
61	46	0	1	6	62.5	52.5	25	2.435	2.5645	3.0436	3.5634	2.645	3.0221	2.4623	2.5645
19	47	-1	1	6	25	52.5	25	5.675	5.673	5.7834	5.6783	5.6745	5.5835	5.5487	5.7845
30	48	0	1	6	62.5	52.5	25	2.423	2.433	2.1453	2.1342	1.9564	1.998	2.1324	2.1323
44	49	1	1	2	25	90	50	6.785	7.2341	7.4563	6.6745	6.8945	7.109	6.546	7.0023
25	50	0	1	6	62.5	52.5	25	1.563	1.895	2.0342	2.0156	1.785	1.998	1.867	2.0134
49	51	-1	1	10	62.5	52.5	25	2.351	2.453	1.785	1.7845	2.8964	1.5477	2.00245	2.336
40	52	1	1	2	25	15	50	8.785	7.883	9.0456	8.7856	8.9564	9.0564	9.436	9.5634
47	53	1	1	10	100	90	50	2.454	2.5895	2.5647	2.5487	2.645	2.463	2.5634	2.45
13	54	1	1	2	25	90	50	8.645	8.8945	8.7546	8.5634	9.0045	8.785	8.8945	8.6574
41	55	1	1	10	25	15	50	9.675	8.8977	9.0067	9.0564	9.0675	9.045	9.102	9.102
53	56	-1	1	6	62.5	90	25	1.563	1.9986	1.685	2.0013	1.895	1.8975	1.887	1.786

StdOrder	RunOrder	PtType	Blocks	pH	Sorbent Dosage (mg)	Contact Time (min)	Concentration (mg/L)	Co	Ni	Zn	Cu	Hg	Cr	Ag	Fe
60	57	0	1	6	62.5	52.5	25	2.001	2.0435	2.4523	2.453	2.1786	2.564	2.453	2.0167
52	58	-1	1	6	62.5	15	25	4.673	4.6371	5.6734	4.5234	4.8954	4.7835	4.7863	4.5894
18	59	-1	1	10	62.5	52.5	25	2.675	1.7854	2.2341	2.4537	2.7824	1.8896	2.009	2.544
28	60	0	1	6	62.5	52.5	25	1.785	1.8895	2.0436	1.7845	1.9984	2.0023	1.6533	1.5634
1	61	1	1	2	25	15	0	9.056	9.674	9.6735	9.745	9.564	9.574	9.784	9.0457
15	62	1	1	2	100	90	50	5.785	5.7456	5.846	5.673	5.4537	5.7845	5.699	5.6745
StdOrder	RunOrder	PtType	Blocks	pH	Sorbent Dosage (mg)	Contact Time (min)	Concentration (mg/L)	F ⁻	Cl ⁻	SO ₄ ²⁻	PO ₄ ³⁻	NO ₂ ⁻	BrO ₃ ⁻	NO ₃ ⁻	
11	1	1	1	2	100	15	50	7.895	7.5643	7.7845	8.0342	7.903	6.9991	7.8945	
39	2	1	1	10	100	90	0	5.116	4.8563	4.7893	5.7636	4.6732	4.8936	4.7844	
33	3	1	1	10	25	15	0	6.998	7.6745	7.0984	6.8884	6.7834	7.1023	7.2009	
4	4	1	1	10	100	15	0	6.01	6.0234	5.9917	5.6732	5.8244	5.5698	6.0004	
62	5	0	1	6	62.5	52.5	25	3.892	3.7893	4.0023	4.0899	4.4783	4.3455	3.9554	
50	6	-1	1	6	25	52.5	25	5.096	5.7835	6.0122	5.8354	5.7845	5.6735	5.7845	
6	7	1	1	10	25	90	0	7.965	7.8945	8.1263	7.8885	7.784	7.8989	8.1111	
20	8	-1	1	6	100	52.5	25	2.454	3.001	2.4536	2.7563	2.5611	2.1142	2.4531	
57	9	0	1	6	62.5	52.5	25	3.563	3.9854	3.5678	3.9984	4.7832	3.9984	3.6784	
59	10	0	1	6	62.5	52.5	25	3.178	3.2341	3.1024	3.2341	4.111	3.5634	3.1782	
3	11	1	1	2	100	15	0	8.564	8.2411	8.2341	8.3452	7.9998	8.6746	8.231	
32	12	1	1	2	25	15	0	8.887	9.0345	8.9345	8.9745	8.7856	8.856	9.0034	

StdOrder	RunOrder	PtType	Blocks	pH	Sorbent Dosage (mg)	Contact Time (min)	Concentration (mg/L)	Co	Ni	Zn	Cu	Hg	Cr	Ag	Fe
26	13	0	1	6	62.5	52.5	25	2.999	3.5623	3.2389	3.4831	3.6754	3.3452	2.1444	
16	14	1	1	10	100	90	50	4.784	4.6734	4.1722	4.1893	4.3562	5.6734	5.0134	
56	15	0	1	6	62.5	52.5	25	3.384	5.4634	3.5623	3.1342	3.4251	3.1123	3.0345	
10	16	1	1	10	25	15	50	8.786	9.0056	8.6745	8.7845	9.0023	8.8973	8.8957	
27	17	0	1	6	62.5	52.5	25	3.334	3.4537	3.6783	3.2451	3.6845	3.5243	3.4524	
17	18	-1	1	2	62.5	52.5	25	6.005	5.8943	5.9957	5.7845	5.4285	5.7234	5.3332	
48	19	-1	1	2	62.5	52.5	25	5.453	5.6735	5.321	5.3458	5.5634	5.3251	5.0023	
54	20	-1	1	6	62.5	52.5	0	4.676	4.6895	5.0035	5.5643	4.3564	4.7856	4.9078	
43	21	1	1	10	100	15	50	6.563	6.3452	6.8564	6.5634	6.8954	6.8956	6.5647	
2	22	1	1	10	25	15	0	8.845	8.5234	8.4537	7.9999	9.0034	8.6745	8.9781	
38	23	1	1	2	100	90	0	5.935	5.456	6.3422	5.7356	5.6345	5.9673	5.8999	
9	24	1	1	2	25	15	50	8.893	8.6745	8.9044	8.6845	9.0099	8.7845	8.3459	
34	25	1	1	2	100	15	0	8.563	8.598	8.0002	7.5647	7.8467	8.6745	7.457	
35	26	1	1	10	100	15	0	7.024	7.002	6.856	6.8945	6.8945	7.0023	6.7845	
24	27	-1	1	6	62.5	52.5	50	4.674	4.6734	4.7855	4.8995	5.0012	5.0342	4.8872	
31	28	0	1	6	62.5	52.5	25	2.683	2.7834	3.0023	2.8945	2.845	2.9981	2.645	
55	29	-1	1	6	62.5	52.5	50	5.111	3.4456	4.876	4.645	4.896	4.873	4.6735	
58	30	0	1	6	62.5	52.5	25	2.675	2.9999	1.9898	2.6745	2.8945	3.0024	2.5745	
36	31	1	1	2	25	90	0	8.645	8.5645	8.6745	8.645	8.9444	7.9989	8.7846	
23	32	-1	1	6	62.5	52.5	0	3.563	3.562	3.7821	3.4222	3.6734	3.2453	3.7834	
14	33	1	1	10	25	90	50	8.745	7.8456	8.035	7.856	7.846	8.945	7.945	

StdOrder	RunOrder	PtType	Blocks	pH	Sorbent Dosage (mg)	Contact Time (min)	Concentration (mg/L)	Co	Ni	Zn	Cu	Hg	Cr	Ag	Fe
										6			6		
45	34	1	1	10	25	90	50	8.245	7.2311	7.5634	7.2341	7.4523	8.2422	7.5342	
8	35	1	1	10	100	90	0	3.674	3.5281	3.425	3.782	3.5521	3.6453	3.7245	
51	36	-1	1	6	100	52.5	25	3.563	2.7734	2.523	2.451	2.4533	2.4311	2.534	
29	37	0	1	6	62.5	52.5	25	2.68	3.0244	2.4523	2.6745	3.2423	2.45	3.001	
42	38	1	1	2	100	15	50	7.896	7.845	7.9456	7.846	7.8456	7.9456	7.8456	
21	39	-1	1	6	62.5	15	25	5.785	6.0235	5.4537	6.4532	5.947	6.0356	6.563	
7	40	1	1	2	100	90	0	8.035	8.0121	7.8956	7.856	7.956	7.5647	8.0345	
46	41	1	1	2	100	90	50	7.023	6.998	7.342	7.564	7.946	6.865	6.897	
22	42	-1	1	6	62.5	90	25	1.846	1.5894	1.7845	1.6894	1.8456	1.7468	1.674	
12	43	1	1	10	100	15	50	5.785	5.9046	5.7845	6.0998	6.1002	5.6745	5.735	
37	44	1	1	10	25	90	0	7.456	7.8956	7.5846	7.6473	7.5386	7.6756	7.648	
5	45	1	1	2	25	90	0	9.045	9.267	9.537	9.675	9.0453	8.889	8.657	
61	46	0	1	6	62.5	52.5	25	2.786	2.8956	2.6574	2.546	2.563	2.7845	2.1563	
19	47	-1	1	6	25	52.5	25	5.783	5.6113	5.4389	5.453	5.7359	5.5648	5.745	
30	48	0	1	6	62.5	52.5	25	1.786	1.998	2.0234	2.1786	2.0234	2.1453	2.652	
44	49	1	1	2	25	90	50	6.946	6.6745	5.574	7.548	6.756	7.0234	6.5634	
25	50	0	1	6	62.5	52.5	25	2.012	1.896	1.674	1.967	2.0001	1.6845	1.896	
49	51	-1	1	10	62.5	52.5	25	2.002	2.674	1.9967	1.785	2.0132	2.132	1.978	
40	52	1	1	2	25	15	50	8.898	8.6856	9.0784	8.7835	9.0435	9.0453	9.453	
47	53	1	1	10	100	90	50	2.546	2.452	2.547	2.5623	2.564	2.341	2.549	

StdOrder	RunOrder	PtType	Blocks	pH	Sorbent Dosage (mg)	Contact Time (min)	Concentration (mg/L)	Co	Ni	Zn	Cu	Hg	Cr	Ag	Fe
13	54	1	1	2	25	90	50	9.006	8.786	8.99	8.786	8.956	8.658	8.7846	
41	55	1	1	10	25	15	50	9.111	9.2341	9.0341	9.0234	9.001	9.003	9.0443	
53	56	-1	1	6	62.5	90	25	1.966	1.745	1.2341	1.785	1.674	1.3367	1.564	
60	57	0	1	6	62.5	52.5	25	2.671	2.4453	2.4533	2.5643	2.674	2.1453	2.376	
52	58	-1	1	6	62.5	15	25	4.673	4.8725	4.6399	4.8935	4.563	4.7835	4.6274	
18	59	-1	1	10	62.5	52.5	25	1.99	2.904	1.6745	2.0344	1.8974	1.897	1.786	
28	60	0	1	6	62.5	52.5	25	2.563	2.7435	2.6745	2.675	2.5467	2.438	2.6745	
1	61	1	1	2	25	15	0	9.045	9.564	9.5392	9.0564	9.5647	9.7462	9.674	
15	62	1	1	2	100	90	50	5.785	5.8345	5.3427	5.784	5.8945	5.835	5.844	
StdOrder	RunOrder	PtType	Blocks	pH	Sorbent Dosage (mg)	Contact Time (min)	Concentration (mg/L)	Pb	Al	As	Cd	Si	Ti	Mg	
11	1	1	1	2	100	15	50	8.234	7.4521	7.6734	8.0034	7.9462	7.6734	8.1423	
39	2	1	1	10	100	90	0	5.835	4.9985	5.6735	5.6735	4.6739	5.7834	4.9974	
33	3	1	1	10	25	15	0	7.674	7.811	6.563	6.7356	6.9944	6.6738	6.5632	
4	4	1	1	10	100	15	0	5.245	6.0024	5.8931	5.5459	5.4532	5.8969	6.2341	
62	5	0	1	6	62.5	52.5	25	3.453	4.0012	3.8945	4.3174	4.4436	3.9832	3.897	
50	6	-1	1	6	25	52.5	25	5.673	6.0234	5.2324	5.528	5.7834	5.8156	5.9562	
6	7	1	1	10	25	90	0	7.94	7.845	7.8943	8.0012	8.0344	8.2341	7.8945	
20	8	-1	1	6	100	52.5	25	2.675	2.7845	3.6745	3.6734	3.2163	2.4536	2.7845	
57	9	0	1	6	62.5	52.5	25	3	3.5628	4.2109	4.1098	3.9854	4.1078	3.5678	

StdOrder	RunOrder	PtType	Blocks	pH	Sorbent Dosage (mg)	Contact Time (min)	Concentration (mg/L)	Co	Ni	Zn	Cu	Hg	Cr	Ag	Fe
59	10	0	1	6	62.5	52.5	25	3.256	3.0034	3.5624	4.2453	3.6734	3.5623	3.0562	
3	11	1	1	2	100	15	0	8.565	8.3459	8.3426	8.453	8.1234	8.6743	8.5648	
32	12	1	1	2	25	15	0	8.905	9.0564	8.9456	9.0023	8.8946	9.0456	8.9054	
26	13	0	1	6	62.5	52.5	25	3.458	3.4529	3.3343	3.9561	3.564	3.2461	3.672	
16	14	1	1	10	100	90	50	5.001	5.6734	4.8945	4.2389	4.6734	4.6354	5.6345	
56	15	0	1	6	62.5	52.5	25	3.11	3.152	3.5623	3.6344	4.0023	3.432	3.3421	
10	16	1	1	10	25	15	50	9.003	8.678	8.785	8.7845	8.9045	8.8856	8.9563	
27	17	0	1	6	62.5	52.5	25	3.563	3.5634	3.658	3.5634	3.5637	3.568	3.9023	
17	18	-1	1	2	62.5	52.5	25	5.694	5.5645	5.738	6.0023	6.4335	5.564	5.884	
48	19	-1	1	2	62.5	52.5	25	5.122	5.2311	5.6734	5.4536	5.4536	5.2011	5.5634	
54	20	-1	1	6	62.5	52.5	0	4.537	5.1342	4.9987	4.8967	5.8956	5.647	4.8967	
43	21	1	1	10	100	15	50	6.785	6.8563	7.0034	6.4563	6.8456	7.8945	6.2343	
2	22	1	1	10	25	15	0	8.567	8.9576	8.7856	8.6745	8.9521	8.4537	8.5344	
38	23	1	1	2	100	90	0	6.893	5.6745	5.8122	6.3457	6.3412	6.4322	5.8445	
9	24	1	1	2	25	15	50	8.675	8.675	8.6745	9.002	8.645	8.8443	8.5746	
34	25	1	1	2	100	15	0	7.675	7.6734	8.231	8.0013	8.6745	8.645	7.998	
35	26	1	1	10	100	15	0	7.856	6.9856	6.8864	6.856	7.0231	6.8895	6.9567	
24	27	-1	1	6	62.5	52.5	50	4.846	4.8745	4.8935	4.9956	5.0023	5.5478	4.9991	
31	28	0	1	6	62.5	52.5	25	2.675	2.4421	2.6734	2.645	2.991	2.453	3.0044	
55	29	-1	1	6	62.5	52.5	50	4.352	3.099	3.5634	4.0013	3.674	4.673	5.0034	

StdOrder	RunOrder	PtType	Blocks	pH	Sorbent Dosage (mg)	Contact Time (min)	Concentration (mg/L)	Co	Ni	Zn	Cu	Hg	Cr	Ag	Fe
58	30	0	1	6	62.5	52.5	25	3.784	3.0324	3.8451	3.7845	2.345	2.453	2.553	
36	31	1	1	2	25	90	0	8.673	8.3564	9.002	8.675	8.7784	8.9846	8.9467	
23	32	-1	1	6	62.5	52.5	0	3.893	3.4555	3.5634	3.724	3.5634	3.6723	3.4532	
14	33	1	1	10	25	90	50	8.687	8.5647	7.8945	8.7456	7.856	8.6745	7.9932	
45	34	1	1	10	25	90	50	8.234	8.2221	7.563	8.5634	7.4523	8.342	7.4532	
8	35	1	1	10	100	90	0	4.563	4.0234	3.7456	3.5634	3.7861	3.7884	4.0244	
51	36	-1	1	6	100	52.5	25	2.783	1.9995	2.0134	1.7834	2.5634	1.7456	3.7822	
29	37	0	1	6	62.5	52.5	25	3.002	3.231	2.0234	2.453	3.013	2.8934	3.674	
42	38	1	1	2	100	15	50	7.998	7.6745	8.162	8.0345	8.0342	8.0092	8.0674	
21	39	-1	1	6	62.5	15	25	4.635	5.645	6.957	6.5645	6.6743	6.856	6.7356	
7	40	1	1	2	100	90	0	8.857	8.0456	7.856	7.8989	7.6749	7.956	7.8878	
46	41	1	1	2	100	90	50	6.674	6.8956	7.9908	6.9945	6.8956	7.8956	7.675	
22	42	-1	1	6	62.5	90	25	2.564	1.784	2.0134	2.0113	1.784	1.584	1.684	
12	43	1	1	10	100	15	50	5.836	6.0245	5.6749	5.9908	5.8602	6.101	5.7846	
37	44	1	1	10	25	90	0	7.549	7.8456	7.6589	7.6584	7.9467	7.535	7.5648	
5	45	1	1	2	25	90	0	8.997	9.674	9.674	8.9468	9.056	9.3786	8.999	
61	46	0	1	6	62.5	52.5	25	2.789	2.785	2.8945	2.749	2.785	2.8944	2.896	
19	47	-1	1	6	25	52.5	25	5.548	5.7845	5.8567	5.8956	5.8954	5.8356	5.4637	
30	48	0	1	6	62.5	52.5	25	2.145	2.013	2.034	2.1564	2.3109	2.452	1.599	
44	49	1	1	2	25	90	50	6.575	6.6755	6.7845	6.956	7.8945	6.784	6.856	

StdOrder	RunOrder	PtType	Blocks	pH	Sorbent Dosage (mg)	Contact Time (min)	Concentration (mg/L)	Co	Ni	Zn	Cu	Hg	Cr	Ag	Fe
25	50	0	1	6	62.5	52.5	25	2.011	1.896	1.679 3	1.893 4	1.907 8	2.031 4	2.001	
49	51	-1	1	10	62.5	52.5	25	1.991	2.564	2.452 3	1.995 7	1.564 7	2.001 3	1.9944	
40	52	1	1	2	25	15	50	9.537	8.9965	8.684 5	9.216	9.034 5	9.345 2	9.1342	
47	53	1	1	10	100	90	50	2.01	2.45	2.754	2.895	2.564 5	2.448 7	2.564	
13	54	1	1	2	25	90	50	8.956	8.658	8.677	8.856	8.674 5	8.904 5	8.78	
41	55	1	1	10	25	15	50	9.135	9.0234	9.13	9.107	9.023 4	9.110 2	9.0342	
53	56	-1	1	6	62.5	90	25	1.905	2.0053	2.001 3	2.002 3	2.001 3	1.945 3	1.785	
60	57	0	1	6	62.5	52.5	25	2.454	2.537	2.674	2.452 3	2.513 4	2.453 1	2.543	
52	58	-1	1	6	62.5	15	25	4.895	4.5362	4.673	4.895 2	4.524	4.437	4.7245	
18	59	-1	1	10	62.5	52.5	25	1.889	2.19	1.895 5	2.002 3	2.002 4	2.023 4	1.9978	
28	60	0	1	6	62.5	52.5	25	2.563	2.674	2.214	2.564 4	2.001 3	1.889	2.342	
1	61	1	1	2	25	15	0	9.786	9.7456	9.352	9.234 1	9.134 2	9.345 2	9.3115	
15	62	1	1	2	100	90	50	5.845	5.8945	5.634	5.784 5	5.649 8	5.548 9	5.8345	

Table 6.4: Matrix design for the two-level ½ fraction factorial design for the eggshell VWMs

StdOrder	RunOrder	PtType	Blocks	pH	Sorbent Dosage (mg)	Contact Time (min)	Concentration (mg/L)	Co	Ni	Zn	Cu	Hg	Cr	Ag	Fe
11	1	1	1	2	100	15	50	8.003	7.7845	8.0014	8.0034	7.9462	8.1109	8.0342	7.8945
39	2	1	1	10	100	90	0	5.674	4.7893	4.8935	5.6735	4.6739	5.8368	5.7636	4.7844
33	3	1	1	10	25	15	0	6.736	7.0984	7.3724	6.7356	6.9944	6.5638	6.8884	7.2009
4	4	1	1	10	100	15	0	5.546	5.9917	5.895	5.5459	5.4532	5.8945	5.6732	6.0004
62	5	0	1	6	62.5	52.5	25	4.317	4.0023	4.7824	4.3174	4.4436	4.1673	4.0899	3.9554

StdOrder	RunOrder	PtType	Blocks	pH	Sorbent Dosage (mg)	Contact Time (min)	Concentration (mg/L)	Co	Ni	Zn	Cu	Hg	Cr	Ag	Fe
50	6	-1	1	6	25	52.5	25	5.528	6.0122	5.9983	5.528	5.7834	6.0244	5.8354	5.7845
6	7	1	1	10	25	90	0	8.001	8.1263	7.6746	8.0012	8.0344	8.002	7.8885	8.1111
20	8	-1	1	6	100	52.5	25	3.673	2.4536	3.841	3.6734	3.2163	3.4523	2.7563	2.4531
57	9	0	1	6	62.5	52.5	25	4.11	3.5678	4.529	4.1098	3.9854	3.6784	3.9984	3.6784
59	10	0	1	6	62.5	52.5	25	4.245	3.1024	3.9967	4.2453	3.6734	3.3326	3.2341	3.1782
3	11	1	1	2	100	15	0	8.453	8.2341	8.4563	8.453	8.1234	8.3564	8.3452	8.231
32	12	1	1	2	25	15	0	9.002	8.9345	8.784	9.0023	8.8946	9.3452	8.9745	9.0034
26	13	0	1	6	62.5	52.5	25	3.956	3.2389	3.452	3.9561	3.564	3.0134	3.4831	2.1444
16	14	1	1	10	100	90	50	4.239	4.1722	4.6734	4.2389	4.6734	5.0142	4.1893	5.0134
56	15	0	1	6	62.5	52.5	25	3.634	3.5623	3.6345	3.6344	4.0023	3.425	3.1342	3.0345
10	16	1	1	10	25	15	50	8.785	8.6745	8.8856	8.7845	8.9045	8.8956	8.7845	8.8957
27	17	0	1	6	62.5	52.5	25	3.563	3.6783	4.0241	3.5634	3.5637	4.1023	3.2451	3.4524
17	18	-1	1	2	62.5	52.5	25	6.002	5.9957	5.9547	6.0023	6.4335	6.4389	5.7845	5.3332
48	19	-1	1	2	62.5	52.5	25	5.454	5.321	5.5634	5.4536	5.4536	6.001	5.3458	5.0023
54	20	-1	1	6	62.5	52.5	0	4.897	5.0035	4.5634	4.8967	5.8956	4.534	5.5643	4.9078
43	21	1	1	10	100	15	50	6.456	6.8564	7.0023	6.4563	6.8456	6.5648	6.5634	6.5647
2	22	1	1	10	25	15	0	8.675	8.4537	8.4532	8.6745	8.9521	8.6758	7.9999	8.9781
38	23	1	1	2	100	90	0	6.346	6.3422	6.537	6.3457	6.3412	5.8345	5.7356	5.8999
9	24	1	1	2	25	15	50	9.002	8.9044	9.0001	9.002	8.645	8.5935	8.6845	8.3459
34	25	1	1	2	100	15	0	8.001	8.0002	8.4634	8.0013	8.6745	8.5648	7.564	7.457
35	26	1	1	10	100	15	0	6.856	6.856	6.856	6.856	7.0231	6.856	6.8945	6.7845
24	27	-1	1	6	62.5	52.5	50	4.996	4.7855	5.0001	4.9956	5.0023	5.0245	4.8995	4.8872
31	28	0	1	6	62.5	52.5	25	2.645	3.0023	2.6548	2.645	2.991	2.7785	2.8945	2.645
55	29	-1	1	6	62.5	52.5	50	4.001	4.876	4.2341	4.0013	3.674	5.0324	4.645	4.6735
58	30	0	1	6	62.5	52.5	25	3.785	1.9898	3.0024	3.7845	2.345	2.8894	2.6745	2.5745
36	31	1	1	2	25	90	0	8.675	8.6745	8.9674	8.675	8.7784	8.6674	8.645	8.7846
23	32	-1	1	6	62.5	52.5	0	3.724	3.7821	3.675	3.724	3.5634	3.4544	3.4222	3.7834
14	33	1	1	10	25	90	50	8.746	8.0356	8.5647	8.7456	7.856	8.9456	7.856	7.945

StdOrder	RunOrder	PtType	Blocks	pH	Sorbent Dosage (mg)	Contact Time (min)	Concentration (mg/L)	Co	Ni	Zn	Cu	Hg	Cr	Ag	Fe
45	34	1	1	10	25	90	50	8.563	7.5634	8.218	8.5634	7.4523	8.3421	7.2341	7.5342
8	35	1	1	10	100	90	0	3.563	3.425	3.673	3.5634	3.7861	3.6743	3.782	3.7245
51	36	-1	1	6	100	52.5	25	1.783	2.523	2.4534	1.7834	2.5634	1.8993	2.451	2.534
29	37	0	1	6	62.5	52.5	25	2.453	2.4523	2.8745	2.453	3.013	3.2314	2.6745	3.001
42	38	1	1	2	100	15	50	8.035	7.9456	8.546	8.0345	8.0342	8.0234	7.846	7.8456
21	39	-1	1	6	62.5	15	25	6.565	5.4537	5.453	6.5645	6.6743	5.846	6.4532	6.563
7	40	1	1	2	100	90	0	7.899	7.8956	7.5648	7.8989	7.6749	7.8959	7.856	8.0345
46	41	1	1	2	100	90	50	6.995	7.342	6.753	6.9945	6.8956	7.896	7.564	6.897
22	42	-1	1	6	62.5	90	25	2.011	1.7845	2.491	2.0113	1.784	1.4352	1.6894	1.674
12	43	1	1	10	100	15	50	5.991	5.7845	5.5473	5.9908	5.8602	5.6354	6.0998	5.735
37	44	1	1	10	25	90	0	7.658	7.5846	7.4563	7.6584	7.9467	7.7856	7.6473	7.648
5	45	1	1	2	25	90	0	8.947	9.537	9.0657	8.9468	9.056	8.7456	9.675	8.657
61	46	0	1	6	62.5	52.5	25	2.749	2.6574	2.5645	2.749	2.785	3.0221	2.546	2.1563
19	47	-1	1	6	25	52.5	25	5.896	5.4389	5.7845	5.8956	5.8954	5.5835	5.453	5.745
30	48	0	1	6	62.5	52.5	25	2.156	2.0234	2.1323	2.1564	2.3109	1.998	2.1786	2.652
44	49	1	1	2	25	90	50	6.956	5.574	7.0023	6.956	7.8945	7.109	7.548	6.5634
25	50	0	1	6	62.5	52.5	25	1.893	1.674	2.0134	1.8934	1.9078	1.998	1.967	1.896
49	51	-1	1	10	62.5	52.5	25	1.996	1.9967	2.336	1.9957	1.5647	1.5477	1.785	1.978
40	52	1	1	2	25	15	50	9.216	9.0784	9.5634	9.216	9.0345	9.0564	8.7835	9.453
47	53	1	1	10	100	90	50	2.895	2.547	2.45	2.895	2.5645	2.463	2.5623	2.549
13	54	1	1	2	25	90	50	8.856	8.99	8.6574	8.856	8.6745	8.785	8.786	8.7846
41	55	1	1	10	25	15	50	9.107	9.0341	9.102	9.107	9.0234	9.045	9.0234	9.0443
53	56	-1	1	6	62.5	90	25	2.002	1.2341	1.786	2.0023	2.0013	1.8975	1.785	1.564
60	57	0	1	6	62.5	52.5	25	2.452	2.4533	2.0167	2.4523	2.5134	2.564	2.5643	2.376
52	58	-1	1	6	62.5	15	25	4.895	4.6399	4.5894	4.8952	4.524	4.7835	4.8935	4.6274
18	59	-1	1	10	62.5	52.5	25	2.002	1.6745	2.544	2.0023	2.0024	1.8896	2.0344	1.786
28	60	0	1	6	62.5	52.5	25	2.564	2.6745	1.5634	2.5644	2.0013	2.0023	2.675	2.6745
1	61	1	1	2	25	15	0	9.234	9.5392	9.0457	9.2341	9.1342	9.574	9.0564	9.674

StdOrder	RunOrder	PtType	Blocks	pH	Sorbent Dosage (mg)	Contact Time (min)	Concentration (mg/L)	Co	Ni	Zn	Cu	Hg	Cr	Ag	Fe
15	62	1	1	2	100	90	50	5.785	5.3427	5.6745	5.7845	5.6498	5.7845	5.784	5.844
StdOrder	RunOrder	PtType	Blocks	pH	Sorbent Dosage (mg)	Contact Time (min)	Concentration (mg/L)	F ⁻	Cl ⁻	SO ₄ ²⁻	PO ₄ ³⁻	NO ₂ ⁻	BrO ₃ ⁻	NO ₃ ⁻	
11	1	1	1	2	100	15	50	6.999	7.6734	7.903	7.8153	8.2341	8.1423	7.5643	
39	2	1	1	10	100	90	0	4.894	5.7834	4.6732	4.8891	5.8354	4.9974	4.8563	
33	3	1	1	10	25	15	0	7.102	6.6738	6.7834	7.4527	7.6735	6.5632	7.6745	
4	4	1	1	10	100	15	0	5.57	5.8969	5.8244	5.8345	5.2453	6.2341	6.0234	
62	5	0	1	6	62.5	52.5	25	4.346	3.9832	4.4783	5.0001	3.4528	3.897	3.7893	
50	6	-1	1	6	25	52.5	25	5.674	5.8156	5.7845	5.5648	5.673	5.9562	5.7835	
6	7	1	1	10	25	90	0	7.899	8.2341	7.784	8.0123	7.9403	7.8945	7.8945	
20	8	-1	1	6	100	52.5	25	2.114	2.4536	2.5611	2.6748	2.6754	2.7845	3.001	
57	9	0	1	6	62.5	52.5	25	3.998	4.1078	4.7832	4.7832	2.9999	3.5678	3.9854	
59	10	0	1	6	62.5	52.5	25	3.563	3.5623	4.111	4.2673	3.2561	3.0562	3.2341	
3	11	1	1	2	100	15	0	8.675	8.6743	7.9998	8.5648	8.5647	8.5648	8.2411	
32	12	1	1	2	25	15	0	8.856	9.0456	8.7856	8.9846	8.9045	8.9054	9.0345	
26	13	0	1	6	62.5	52.5	25	3.345	3.2461	3.6754	4.563	3.4582	3.672	3.5623	
16	14	1	1	10	100	90	50	5.673	4.6354	4.3562	4.5738	5.0012	5.6345	4.6734	
56	15	0	1	6	62.5	52.5	25	3.112	3.4322	3.4251	4.1856	3.1099	3.3421	5.4634	
10	16	1	1	10	25	15	50	8.897	8.8856	9.0023	8.8856	9.003	8.9563	9.0056	
27	17	0	1	6	62.5	52.5	25	3.524	3.568	3.6845	3.6745	3.5634	3.9023	3.4537	
17	18	-1	1	2	62.5	52.5	25	5.723	5.564	5.428	5.8945	5.6935	5.884	5.8943	
48	19	-1	1	2	62.5	52.5	25	5.325	5.2011	5.5634	5.9998	5.1221	5.5634	5.6735	
54	20	-1	1	6	62.5	52.5	0	4.786	5.647	4.3564	5.0245	4.5366	4.8967	4.6895	
43	21	1	1	10	100	15	50	6.896	7.8945	6.895	6.6745	6.7845	6.2343	6.3452	
2	22	1	1	10	25	15	0	8.675	8.4537	9.0034	8.6794	8.5671	8.5344	8.5234	
38	23	1	1	2	100	90	0	5.967	6.4322	5.6345	5.7845	6.893	5.8445	5.456	
9	24	1	1	2	25	15	50	8.785	8.8443	9.0099	8.6734	8.6745	8.5746	8.6745	

StdOrder	RunOrder	PtType	Blocks	pH	Sorbent Dosage (mg)	Contact Time (min)	Concentration (mg/L)	Co	Ni	Zn	Cu	Hg	Cr	Ag	Fe
34	25	1	1	2	100	15	0	8.675	8.645	7.8467	8.645	7.6745	7.998	8.598	
35	26	1	1	10	100	15	0	7.002	6.8895	6.8945	6.856	7.8564	6.9567	7.002	
24	27	-1	1	6	62.5	52.5	50	5.034	5.5478	5.0012	4.7845	4.8456	4.9991	4.6734	
31	28	0	1	6	62.5	52.5	25	2.998	2.453	2.845	3.0241	2.6745	3.0044	2.7834	
55	29	-1	1	6	62.5	52.5	50	4.873	4.673	4.896	3.866	4.3523	5.0034	3.4456	
58	30	0	1	6	62.5	52.5	25	3.002	2.453	2.8945	3.0023	3.784	2.553	2.9999	
36	31	1	1	2	25	90	0	7.999	8.9846	8.9444	8.946	8.6734	8.9467	8.5645	
23	32	-1	1	6	62.5	52.5	0	3.245	3.6723	3.6734	3.6473	3.8934	3.4532	3.562	
14	33	1	1	10	25	90	50	8.946	8.6745	7.846	7.645	8.687	7.9932	7.8456	
45	34	1	1	10	25	90	50	8.242	8.342	7.4523	7.2341	8.2341	7.4532	7.2311	
8	35	1	1	10	100	90	0	3.645	3.7884	3.5521	3.5634	4.5634	4.0244	3.5281	
51	36	-1	1	6	100	52.5	25	2.431	1.7456	2.4533	2.435	2.783	3.7822	2.7734	
29	37	0	1	6	62.5	52.5	25	2.45	2.8934	3.2423	2.8945	3.0023	3.674	3.0244	
42	38	1	1	2	100	15	50	7.946	8.0092	7.8456	7.9987	7.998	8.0674	7.845	
21	39	-1	1	6	62.5	15	25	6.036	6.856	5.947	5.436	4.6345	6.7356	6.0235	
7	40	1	1	2	100	90	0	7.565	7.956	7.956	7.995	8.8567	7.8878	8.0121	
46	41	1	1	2	100	90	50	6.865	7.8956	7.946	7.674	6.674	7.675	6.998	
22	42	-1	1	6	62.5	90	25	1.747	1.584	1.8456	2.034	2.564	1.684	1.5894	
12	43	1	1	10	100	15	50	5.675	6.101	6.1002	4.997	5.8356	5.7846	5.9046	
37	44	1	1	10	25	90	0	7.676	7.535	7.5386	7.8945	7.5487	7.5648	7.8956	
5	45	1	1	2	25	90	0	8.889	9.3786	9.0453	9.0345	8.997	8.999	9.267	
61	46	0	1	6	62.5	52.5	25	2.785	2.8944	2.563	3.5634	2.7894	2.896	2.8956	
19	47	-1	1	6	25	52.5	25	5.565	5.8356	5.7359	5.6783	5.5476	5.4637	5.6113	
30	48	0	1	6	62.5	52.5	25	2.145	2.452	2.0234	2.1342	2.145	1.599	1.998	
44	49	1	1	2	25	90	50	7.023	6.784	6.756	6.6745	6.5748	6.856	6.6745	
25	50	0	1	6	62.5	52.5	25	1.685	2.0314	2.0001	2.0156	2.011	2.001	1.896	
49	51	-1	1	10	62.5	52.5	25	2.132	2.0013	2.0132	1.7845	1.9908	1.9944	2.674	
40	52	1	1	2	25	15	50	9.045	9.3452	9.0435	8.7856	9.537	9.1342	8.6856	

StdOrder	RunOrder	PtType	Blocks	pH	Sorbent Dosage (mg)	Contact Time (min)	Concentration (mg/L)	Co	Ni	Zn	Cu	Hg	Cr	Ag	Fe
47	53	1	1	10	100	90	50	2.341	2.4487	2.564	2.5487	2.01	2.564	2.452	
13	54	1	1	2	25	90	50	8.658	8.9045	8.956	8.5634	8.9564	8.78	8.786	
41	55	1	1	10	25	15	50	9.003	9.1102	9.001	9.0564	9.135	9.0342	9.2341	
53	56	-1	1	6	62.5	90	25	1.337	1.9453	1.674	2.0013	1.9054	1.785	1.745	
60	57	0	1	6	62.5	52.5	25	2.145	2.4531	2.674	2.453	2.4537	2.543	2.4453	
52	58	-1	1	6	62.5	15	25	4.784	4.437	4.563	4.5234	4.895	4.7245	4.8725	
18	59	-1	1	10	62.5	52.5	25	1.897	2.0234	1.8974	2.4537	1.8894	1.9978	2.904	
28	60	0	1	6	62.5	52.5	25	2.438	1.889	2.5467	1.7845	2.563	2.342	2.7435	
1	61	1	1	2	25	15	0	9.746	9.3452	9.5647	9.745	9.7856	9.3115	9.564	
15	62	1	1	2	100	90	50	5.835	5.5489	5.8945	5.673	5.845	5.8345	5.8345	
StdOrder	RunOrder	PtType	Blocks	pH	Sorbent Dosage (mg)	Contact Time (min)	Concentration (mg/L)	Pb	Al	As	Cd	Si	Ti	Mg	
11	1	1	1	2	100	15	50	7.213	7.9453	7.5634	7.4521	8.4512	7.5623	7.6734	
39	2	1	1	10	100	90	0	5.893	5.0114	4.6734	4.9985	5.0145	4.6732	5.6735	
33	3	1	1	10	25	15	0	6.453	6.6498	6.868	7.811	7.1123	6.8345	6.563	
4	4	1	1	10	100	15	0	5.454	6.2861	5.4456	6.0024	6.0145	6.6734	5.8931	
62	5	0	1	6	62.5	52.5	25	4.453	4.2453	4.1342	4.0012	5.0014	4.2359	3.8945	
50	6	-1	1	6	25	52.5	25	5.345	6.0023	5.1998	6.0234	5.5634	5.4894	5.2324	
6	7	1	1	10	25	90	0	7.893	7.998	7.6745	7.845	7.5634	8.1342	7.8943	
20	8	-1	1	6	100	52.5	25	2.454	2.8896	3.4523	2.7845	2.6784	3.2453	3.6745	
57	9	0	1	6	62.5	52.5	25	4.044	3.9984	3.9967	3.5628	4.673	4.0016	4.2109	
59	10	0	1	6	62.5	52.5	25	3.453	3.5644	4.1002	3.0034	4.4231	3.5689	3.5624	
3	11	1	1	2	100	15	0	8.785	8.9845	8.1999	8.3459	8.5647	8.2341	8.3426	
32	12	1	1	2	25	15	0	9.001	9.1453	9.0234	9.0564	8.9967	8.8945	8.9456	
26	13	0	1	6	62.5	52.5	25	3.253	3.5673	3.8734	3.4529	4.563	3.2453	3.3343	
16	14	1	1	10	100	90	50	4.673	4.6739	5.1843	5.6734	5.6473	5.2378	4.8945	
56	15	0	1	6	62.5	52.5	25	3.563	3.3321	3.3425	3.152	3.5693	3.5623	3.5623	

StdOrder	RunOrder	PtType	Blocks	pH	Sorbent Dosage (mg)	Contact Time (min)	Concentration (mg/L)	Co	Ni	Zn	Cu	Hg	Cr	Ag	Fe
10	16	1	1	10	25	15	50	8.685	9.0345	8.5647	8.678	9.0456	8.7561	8.785	
27	17	0	1	6	62.5	52.5	25	3.563	3.5638	4.0235	3.5634	3.8965	3.7845	3.658	
17	18	-1	1	2	62.5	52.5	25	5.356	5.2673	6.5452	5.5645	5.6748	5.5799	5.738	
48	19	-1	1	2	62.5	52.5	25	5.998	6.122	5.6783	5.2311	6.8945	5.4532	5.6734	
54	20	-1	1	6	62.5	52.5	0	4.674	4.6734	4.8956	5.1342	5.3426	5.0021	4.9987	
43	21	1	1	10	100	15	50	6.896	7.001	7.5641	6.8563	6.8935	6.8956	7.0034	
2	22	1	1	10	25	15	0	8.896	8.3452	8.5634	8.9576	8.634	8.7856	8.7856	
38	23	1	1	2	100	90	0	5.673	6.1235	5.7834	5.6745	6.2341	5.8962	5.8122	
9	24	1	1	2	25	15	50	8.342	9.0023	8.4533	8.675	8.112	8.6745	8.6745	
34	25	1	1	2	100	15	0	7.674	7.7846	8.6745	7.6734	8.6745	8.7845	8.231	
35	26	1	1	10	100	15	0	6.785	6.599	7.0023	6.9856	6.856	7.0345	6.8864	
24	27	-1	1	6	62.5	52.5	50	5.011	4.6244	4.6734	4.8745	4.6739	5.0444	4.8935	
31	28	0	1	6	62.5	52.5	25	2.452	3.0241	2.5638	2.4421	3.0023	2.7845	2.6734	
55	29	-1	1	6	62.5	52.5	50	4.673	4.0244	4.0132	3.099	4.6734	4.986	3.5634	
58	30	0	1	6	62.5	52.5	25	2.453	3.0023	2.6745	3.0324	2.7845	2.9973	3.8451	
36	31	1	1	2	25	90	0	8.785	8.956	9.0034	8.3564	8.6745	8.946	9.002	
23	32	-1	1	6	62.5	52.5	0	3.563	3.724	3.9564	3.4555	3.0024	3.7893	3.5634	
14	33	1	1	10	25	90	50	7.565	8.7457	7.899	8.5647	8.2349	7.6745	7.8945	
45	34	1	1	10	25	90	50	7.365	8.334	7.453	8.2221	7.9982	7.645	7.563	
8	35	1	1	10	100	90	0	3.652	4.0002	4.634	4.0234	3.6524	3.3425	3.7456	
51	36	-1	1	6	100	52.5	25	2.563	2.314	2.134	1.9995	1.899	2.5634	2.0134	
29	37	0	1	6	62.5	52.5	25	2.563	3.0023	2.786	3.231	3.4251	2.8945	2.0234	
42	38	1	1	2	100	15	50	8.675	7.6749	8.4836	7.6745	7.5634	8.0445	8.162	
21	39	-1	1	6	62.5	15	25	5.675	5.0345	5.7845	5.645	6.0345	4.7634	6.957	
7	40	1	1	2	100	90	0	7.946	8.034	8.0045	8.0456	8.7456	8.6745	7.856	
46	41	1	1	2	100	90	50	6.957	6.785	7.3457	6.8956	7.6857	6.563	7.9908	
22	42	-1	1	6	62.5	90	25	1.435	1.435	2.3241	1.784	1.564	1.634	2.0134	
12	43	1	1	10	100	15	50	5.674	5.5647	5.7835	6.0245	5.7452	5.8356	5.6749	

StdOrder	RunOrder	PtType	Blocks	pH	Sorbent Dosage (mg)	Contact Time (min)	Concentration (mg/L)	Co	Ni	Zn	Cu	Hg	Cr	Ag	Fe
37	44	1	1	10	25	90	0	7.863	7.5692	7.895	7.8456	6.6745	7.5483	7.6589	
5	45	1	1	2	25	90	0	8.996	8.9456	8.9978	9.674	9.023	9.0546	9.674	
61	46	0	1	6	62.5	52.5	25	2.435	2.645	3.0436	2.785	2.5645	2.4623	2.8945	
19	47	-1	1	6	25	52.5	25	5.675	5.6745	5.7834	5.7845	5.673	5.5487	5.8567	
30	48	0	1	6	62.5	52.5	25	2.423	1.9564	2.1453	2.013	2.433	2.1324	2.034	
44	49	1	1	2	25	90	50	6.785	6.8945	7.4563	6.6755	7.2341	6.546	6.7845	
25	50	0	1	6	62.5	52.5	25	1.563	1.785	2.0342	1.896	1.895	1.867	1.6793	
49	51	-1	1	10	62.5	52.5	25	2.351	2.8964	1.785	2.564	2.453	2.0025	2.4523	
40	52	1	1	2	25	15	50	8.785	8.9564	9.0456	8.9965	7.883	9.436	8.6845	
47	53	1	1	10	100	90	50	2.454	2.645	2.5647	2.45	2.5895	2.5634	2.754	
13	54	1	1	2	25	90	50	8.645	9.0045	8.7546	8.658	8.8945	8.8945	8.677	
41	55	1	1	10	25	15	50	9.675	9.0675	9.0067	9.0234	8.8977	9.102	9.13	
53	56	-1	1	6	62.5	90	25	1.563	1.895	1.685	2.0053	1.9986	1.887	2.0013	
60	57	0	1	6	62.5	52.5	25	2.001	2.1786	2.4523	2.537	2.0435	2.453	2.674	
52	58	-1	1	6	62.5	15	25	4.673	4.8954	5.6734	4.5362	4.6371	4.7863	4.673	
18	59	-1	1	10	62.5	52.5	25	2.675	2.7824	2.2341	2.19	1.7854	2.009	1.8955	
28	60	0	1	6	62.5	52.5	25	1.785	1.9984	2.0436	2.674	1.8895	1.6533	2.214	
1	61	1	1	2	25	15	0	9.056	9.564	9.6735	9.7456	9.674	9.784	9.352	
15	62	1	1	2	100	90	50	5.785	5.4537	5.846	5.8945	5.7456	5.699	5.634	

Appendix C

C.1 Analysis of Variance for the Fish Scales

R denotes an observation with a large standardized residual.

Table 6.5: Analysis of Variance for Co

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	325.34	325.34	23.2385	28.64	0.000
Linear	4	88.61	88.61	22.1513	27.30	0.000
Square	4	223.17	223.17	55.7925	68.76	0.000
Interaction	6	13.56	13.56	2.2607	2.79	0.021
Residual Error	47	38.13	38.13	0.8114		
Lack-of-Fit	10	14.29	14.29	1.4293	2.22	0.039
Pure Error	37	23.84	23.84	0.6444		
Total	61	363.47				
Unusual Observations for Co						
Obs	StdOrder	Co	Fit	SE Fit	Residual	St Resid
2	39	5.674	4.170	0.517	1.503	2.04 R
39	21	6.565	4.643	0.442	1.921	2.45 R
S = 0.9008		R-Sq = 89.5%		R-Sq(adj) = 86.4%		

Table 6.6: Analysis of Variance for Ni

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	350.55	350.55	25.0390	32.44	0.000
Linear	4	95.87	95.87	23.9664	31.05	0.000
Square	4	241.87	241.87	60.4675	78.35	0.000
Interaction	6	12.81	12.81	2.1350	2.77	0.022
Residual Error	47	36.27	36.27	0.7718		
Lack-of-Fit	10	14.04	14.04	1.4043	2.34	0.030
Pure Error	37	22.23	22.23	0.6008		
Total	61	386.82				
Unusual Observations for Ni						
Obs	StdOrder	Ni	Fit	SE Fit	Residual	St Resid
41	46	7.342	5.814	0.504	1.528	2.12 R
49	44	5.574	7.954	0.504	-2.380	-3.31 R
S = 0.8785		R-Sq = 90.6%		R-Sq(adj) = 87.8%		

Table 6.7: Analysis of Variance for Zn

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	332.917	332.917	23.7798	35.76	0.000
Linear	4	90.280	90.280	22.5699	33.94	0.000
Square	4	228.030	228.030	57.0074	85.72	0.000
Interaction	6	14.608	14.608	2.4346	3.66	0.005
Residual Error	47	31.256	31.256	0.6650		
Lack-of-Fit	10	7.473	7.473	0.7473	1.16	0.346
Pure Error	37	23.782	23.782	0.6428		
Total	61	364.173				
Unusual Observations for Zn						
Obs	StdOrder	Zn	Fit	SE Fit	Residual	St Resid
5	62	4.782	3.076	0.171	1.706	2.14 R
49	44	7.002	8.371	0.468	-1.369	-2.05 R
S = 0.8155		R-Sq = 91.4%		R-Sq(adj) = 88.9%		

Table 6.8: Analysis of Variance for Cu

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	325.34	325.34	23.2385	28.64	0.000
Linear	4	88.61	88.61	22.1513	27.30	0.000
Square	4	223.17	223.17	55.7925	68.76	0.000
Interaction	6	13.56	13.56	2.2607	2.79	0.021
Residual Error	47	38.13	38.13	0.8114		
Lack-of-Fit	10	14.29	14.29	1.4293	2.22	0.039
Pure Error	37	23.84	23.84	0.6444		
Total	61	363.47				
Unusual Observations for Cu						
Obs	StdOrder	Cu	Fit	SE Fit	Residual	St Resid
2	39	5.674	4.170	0.517	1.503	2.04 R
39	21	6.565	4.643	0.442	1.921	2.45 R
S = 0.9008		R-Sq = 89.5%		R-Sq(adj) = 86.4%		

Table 6.9: Analysis of Variance for Hg

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	332.29	332.29	23.7347	30.34	0.000
Linear	4	95.34	95.34	23.8350	30.47	0.000
Square	4	224.40	224.40	56.0989	71.71	0.000
Interaction	6	12.55	12.55	2.0917	2.67	0.026
Residual Error	47	36.77	36.77	0.7823		
Lack-of-Fit	10	12.98	12.98	1.2985	2.02	0.059
Pure Error	37	23.79	23.79	0.6428		

Total	61	369.06				
Unusual Observations for Hg						
Obs	StdOrder	Hg	Fit	SE Fit	Residual	St Resid
18	17	6.434	4.758	0.434	1.676	2.17 R
39	21	6.674	4.509	0.434	2.165	2.81 R
S = 0.8845		R-Sq = 90.0%		R-Sq(adj) = 87.1%		

Table 6.10: Analysis of Variance for Cr

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	343.81	343.81	24.5577	25.84	0.000
Linear	4	87.72	87.72	21.9308	23.08	0.000
Square	4	244.10	244.10	61.0254	64.22	0.000
Interaction	6	11.98	11.98	1.9971	2.10	0.071
Residual Error	47	44.66	44.66	0.9502		
Lack-of-Fit	10	20.46	20.46	2.0460	3.13	0.005
Pure Error	37	24.20	24.20	0.6541		
Total	61	388.47				
Unusual Observations for Cr						
Obs	StdOrder	Cr	Fit	SE Fit	Residual	St Resid
2	39	5.837	4.093	0.559	1.743	2.18 R
41	46	7.896	6.267	0.559	1.629	2.04 R
S = 0.9748		R-Sq = 98.5% R		R-Sq(adj) = 95.1%		

Table 6.11: Analysis of Variance for Ag

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	328.25	328.25	23.4461	31.85	0.000
Linear	4	87.13	87.13	21.7826	29.59	0.000
Square	4	230.76	230.76	57.6906	78.38	0.000
Interaction	6	10.35	10.35	1.7254	2.34	0.046
Residual Error	47	34.59	34.59	0.7361		
Lack-of-Fit	10	15.34	15.34	1.5343	2.95	0.008
Pure Error	37	19.25	19.25	0.5203		
Total	61	362.84				
Unusual Observations for Ag						
Obs	StdOrder	Ag	Fit	SE Fit	Residual	St Resid
2	39	5.764	4.155	0.492	1.608	2.29 R
39	21	6.453	4.383	0.421	2.070	2.77 R
41	46	7.564	6.064	0.492	1.500	2.13 R
S = 0.8579		R-Sq = 90.5%		R-Sq(adj) = 87.6%		

Table 6.42: Analysis of Variance for Fe

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	347.072	347.072	24.7909	35.42	0.000
Linear	4	92.186	92.186	23.0465	32.93	0.000
Square	4	246.233	246.233	61.5583	87.95	0.000
Interaction	6	8.653	8.653	1.4422	2.06	0.076
Residual Error	47	32.895	32.895	0.6999		
Lack-of-Fit	10	13.085	13.085	1.3085	2.44	0.024
Pure Error	37	19.810	19.810	0.5354		
Total	61	379.968				
Unusual Observations for Fe						
Obs	StdOrder	Fe	Fit	SE Fit	Residual	St Resid
39	21	6.563	4.383	0.410	2.180	2.99 R
49	44	6.563	8.036	0.480	-1.472	-2.15 R
S = 0.8366		R-Sq = 91.3%		R-Sq(adj) = 88.8%		

Table 6.13: Analysis of Variance for Pb

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	332.24	332.24	23.7315	27.53	0.000
Linear	4	82.23	82.23	20.5569	23.85	0.000
Square	4	238.55	238.55	59.6382	69.19	0.000
Interaction	6	11.46	11.46	1.9102	2.22	0.058
Residual Error	47	40.51	40.51	0.8619		
Lack-of-Fit	10	12.30	12.30	1.2302	1.61	0.141
Pure Error	37	28.21	28.21	0.7624		
Total	61	372.75				
Unusual Observations for Pb						
Obs	StdOrder	Pb	Fit	SE Fit	Residual	St Resid
2	39	5.893	4.184	0.533	1.709	2.25 R
3	33	6.453	8.154	0.533	-1.701	-2.24 R
S = 0.9284		R-Sq = 99.1%		R-Sq(adj) = 95.9%		

Table 6.14: Analysis of Variance for Al

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	342.799	342.799	24.4856	38.66	0.000
Linear	4	87.840	87.840	21.9600	34.67	0.000
Square	4	241.377	241.377	60.3443	95.27	0.000
Interaction	6	13.582	13.582	2.2636	3.57	0.005
Residual Error	47	29.771	29.771	0.6334		
Lack-of-Fit	10	9.402	9.402	0.9402	1.71	0.116
Pure Error	37	20.369	20.369	0.5505		

Total	61	372.570				
Unusual Observations for Al						
Obs	StdOrder	Al	Fit	SE Fit	Residual	St Resid
3	33	6.650	7.980	0.457	-1.330	-2.04 R
49	44	6.895	8.353	0.457	-1.459	-2.24 R
S = 0.7959		R-Sq = 92.0%		R-Sq(adj) = 89.6%		

Table 6.15: Analysis of Variance for As

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	323.469	323.469	23.1050	28.54	0.000
Linear	4	85.323	85.323	21.3307	26.35	0.000
Square	4	228.998	228.998	57.2495	70.72	0.000
Interaction	6	9.149	9.149	1.5248	1.88	0.103
Residual Error	47	38.046	38.046	0.8095		
Lack-of-Fit	10	13.882	13.882	1.3882	2.13	0.047
Pure Error	37	24.164	24.164	0.6531		
Total	61	361.515				
Unusual Observations for Ar						
Obs	StdOrder	Ar	Fit	SE Fit	Residual	St Resid
18	17	6.545	4.974	0.441	1.571	2.00 R
S = 0.8997		R-Sq = 99.5%		R-Sq(adj) = 96.3%		

Table 6.16: Analysis of Variance for Cd

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	343.170	343.170	24.5121	34.59	0.000
Linear	4	85.051	85.051	21.2626	30.01	0.000
Square	4	249.817	249.817	62.4541	88.14	0.000
Interaction	6	8.303	8.303	1.3838	1.95	0.092
Residual Error	47	33.305	33.305	0.7086		
Lack-of-Fit	10	10.497	10.497	1.0497	1.70	0.117
Pure Error	37	22.807	22.807	0.6164		
Total	61	376.474				
Unusual Observations for Cd						
Obs	StdOrder	Cd	Fit	SE Fit	Residual	St Resid
14	16	5.673	4.108	0.483	1.565	2.27 R
49	44	6.676	8.164	0.483	-1.488	-2.16 R
53	47	2.450	4.108	0.483	-1.658	-2.41 R
S = 0.8418		R-Sq = 91.2%		R-Sq(adj) = 88.5%		

Table 6.17: Analysis of Variance for Si

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	312.24	312.24	22.3030	20.02	0.000
Linear	4	79.78	79.78	19.9445	17.90	0.000
Square	4	217.73	217.73	54.4335	48.85	0.000
Interaction	6	14.73	14.73	2.4550	2.20	0.059
Residual Error	47	52.37	52.37	1.1142		
Lack-of-Fit	10	16.67	16.67	1.6674	1.73	0.111
Pure Error	37	35.69	35.69	0.9647		
Total	61	364.61				
S = 1.056		R-Sq = 95.6%		R-Sq(adj) = 91.4%		

Table 6.18: Analysis of Variance for Ti

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	343.891	343.891	24.5636	33.99	0.000
Linear	4	88.415	88.415	22.1038	30.58	0.000
Square	4	244.492	244.492	61.1231	84.57	0.000
Interaction	6	10.983	10.983	1.8305	2.53	0.033
Residual Error	47	33.968	33.968	0.7227		
Lack-of-Fit	10	9.450	9.450	0.9450	1.43	0.207
Pure Error	37	24.518	24.518	0.6627		
Total	61	377.858				
Unusual Observations for Ti						
Obs	StdOrder	Ti	Fit	SE Fit	Residual	St Resid
14	16	5.238	3.726	0.488	1.512	2.17 R
40	7	8.675	7.152	0.488	1.523	2.19 R
49	44	6.546	8.182	0.488	-1.636	-2.35 R
S = 0.8501		R-Sq = 95.0%		R-Sq(adj) = 92.3%		

Table 6.19: Analysis of Variance for Mg

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	323.217	323.217	23.0870	24.60	0.000
Linear	4	80.890	80.890	20.2226	21.55	0.000
Square	4	232.539	232.539	58.1347	61.95	0.000
Interaction	6	9.788	9.788	1.6314	1.74	0.133
Residual Error	47	44.106	44.106	0.9384		
Lack-of-Fit	10	13.997	13.997	1.3997	1.72	0.113
Pure Error	37	30.108	30.108	0.8137		
Total	61	367.323				
Unusual Observations for Mg						
Obs	StdOrder	Mg	Fit	SE Fit	Residual	St Resid

3	33	6.563	8.202	0.556	-1.639	-2.07 R
39	21	6.957	4.624	0.475	2.333	2.76 R
41	46	7.991	6.156	0.556	1.835	2.31 R
S = 0.9687		R-Sq = 98.0%		R-Sq(adj) = 94.4%		

Table 6.20: Analysis of Variance for F⁻

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	344.25	344.25	24.5894	29.95	0.000
Linear	4	88.67	88.67	22.1675	27.00	0.000
Square	4	243.00	243.00	60.7490	74.00	0.000
Interaction	6	12.59	12.59	2.0975	2.55	0.032
Residual Error	47	38.59	38.59	0.8210		
Lack-of-Fit	10	14.95	14.95	1.4949	2.34	0.030
Pure Error	37	23.64	23.64	0.6388		
Total	61	382.84				
Unusual Observations for F⁻						
Obs	StdOrder	F ⁻	Fit	SE Fit	Residual	St Resid
14	16	5.673	4.050	0.520	1.623	2.19 R
39	21	6.036	4.318	0.444	1.717	2.17 R
53	47	2.341	4.050	0.520	-1.709	-2.30 R
S = 0.9061		R-Sq = 99.9%		R-Sq(adj) = 96.9%		

Table 6.21: Analysis of Variance for Cl⁻

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	358.24	358.24	25.5888	27.33	0.000
Linear	4	85.71	85.71	21.4285	22.89	0.000
Square	4	257.91	257.91	64.4767	68.86	0.000
Interaction	6	14.62	14.62	2.4370	2.60	0.029
Residual Error	47	44.01	44.01	0.9363		
Lack-of-Fit	10	17.06	17.06	1.7060	2.34	0.029
Pure Error	37	26.95	26.95	0.7283		
Total	61	402.25				
Unusual Observations for Cl⁻						
Obs	StdOrder	Cl ⁻	Fit	SE Fit	Residual	St Resid
2	39	5.783	4.196	0.555	1.587	2.00 R
39	21	6.856	4.448	0.474	2.408	2.86 R
41	46	7.896	5.907	0.555	1.989	2.51 R
49	44	6.784	8.417	0.555	-1.633	-2.06 R
S = 0.9676		R-Sq = 99.1%		R-Sq(adj) = 95.8%		

Table 6.22: Analysis of Variance for SO_4^{2-}

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	324.18	324.18	23.1555	28.95	0.000
Linear	4	94.76	94.76	23.6905	29.62	0.000
Square	4	219.28	219.28	54.8211	68.55	0.000
Interaction	6	10.13	10.13	1.6883	2.11	0.070
Residual Error	47	37.59	37.59	0.7998		
Lack-of-Fit	10	13.48	13.48	1.3485	2.07	0.053
Pure Error	37	24.11	24.11	0.6515		
Total	61	361.77				
Unusual Observations for SO_4^{2-}						
Obs	StdOrder	SO_4^{2-}	Fit	SE Fit	Residual	St Resid
3	33	6.783	8.367	0.513	-1.583	-2.16 R
41	46	7.946	6.301	0.513	1.645	2.25 R
49	44	6.756	8.392	0.513	-1.636	-2.23 R
S = 0.8943		R-Sq = 99.6%		R-Sq(adj) = 96.5%		

Table 6.23: Analysis of Variance for PO_4^{3-}

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	312.74	312.74	22.3384	25.83	0.000
Linear	4	95.92	95.92	23.9791	27.73	0.000
Square	4	205.59	205.59	51.3986	59.43	0.000
Interaction	6	11.23	11.23	1.8712	2.16	0.063
Residual Error	47	40.65	40.65	0.8648		
Lack-of-Fit	10	11.46	11.46	1.1458	1.45	0.197
Pure Error	37	29.19	29.19	0.7889		
Total	61	353.39				
S = 0.9300		R-Sq = 98.5% R		R-Sq(adj) = 95.1%		

Table 6.24: Analysis of Variance for NO_2^-

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	355.18	355.18	25.3700	38.68	0.000
Linear	4	79.22	79.22	19.8059	30.20	0.000
Square	4	263.01	263.01	65.7518	100.26	0.000
Interaction	6	12.95	12.95	2.1582	3.29	0.009
Residual Error	47	30.82	30.82	0.6558		
Lack-of-Fit	10	10.25	10.25	1.0255	1.84	0.086
Pure Error	37	20.57	20.57	0.5559		
Total	61	386.00				
Unusual Observations for NO_2^-						
Obs	StdOrder	NO_2^-	Fit	SE Fit	Residual	St Resid

26	35	7.856	6.125	0.465	1.731	2.61 R
49	44	6.575	8.223	0.465	-1.649	-2.49 R
53	47	2.010	3.788	0.465	-1.778	-2.68 R
S = 0.8098		R-Sq = 92.0%		R-Sq(adj) = 89.6%		

Table 6.25: Analysis of Variance for BrO_3^-

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	319.083	319.083	22.7917	26.76	0.000
Linear	4	80.603	80.603	20.1508	23.66	0.000
Square	4	229.887	229.887	57.4717	67.47	0.000
Interaction	6	8.593	8.593	1.4322	1.68	0.147
Residual Error	47	40.035	40.035	0.8518		
Lack-of-Fit	10	15.784	15.784	1.5784	2.41	0.026
Pure Error	37	24.251	24.251	0.6554		
Total	61	359.118				
Unusual Observations for BrO_3^-						
Obs	StdOrder	BrO_3^-	Fit	SE Fit	Residual	St Resid
3	33	6.563	8.094	0.530	-1.531	-2.03 R
14	16	5.635	3.975	0.530	1.660	2.20 R
39	21	6.736	4.412	0.453	2.324	2.89 R
S = 0.9229		R-Sq = 98.9%		R-Sq(adj) = 95.5%		

Table 6.26: Analysis of Variance for NO_3^-

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	319.462	319.462	22.8187	31.69	0.000
Linear	4	93.020	93.020	23.2549	32.30	0.000
Square	4	215.698	215.698	53.9246	74.89	0.000
Interaction	6	10.744	10.744	1.7907	2.49	0.036
Residual Error	47	33.842	33.842	0.7200		
Lack-of-Fit	10	9.998	9.998	0.9998	1.55	0.160
Pure Error	37	23.843	23.843	0.6444		
Total	61	353.304				
Unusual Observations for NO_3^-						
Obs	StdOrder	NO_3^-	Fit	SE Fit	Residual	St Resid
15	56	5.463	3.090	0.178	2.374	2.86 R
23	38	5.456	6.902	0.487	-1.446	-2.08 R
39	21	6.024	4.462	0.416	1.561	2.11 R
S = 0.8485		R-Sq = 95.4%		R-Sq(adj) = 92.6%		

Appendix C

C.2 Analysis of Variance for the Eggshells

Table 6.27: Analysis of Variance for Co

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	332.24	332.24	23.7315	27.53	0.000
Linear	4	82.23	82.23	20.5569	23.85	0.000
Square	4	238.55	238.55	59.6382	69.19	0.000
Interaction	6	11.46	11.46	1.9102	2.22	0.058
Residual Error	47	40.51	40.51	0.8619		
Lack-of-Fit	10	12.30	12.30	1.2302	1.61	0.141
Pure Error	37	28.21	28.21	0.7624		
Total	61	372.75				
Unusual Observations for Co						
Obs	StdOrder	Co	Fit	SE Fit	Residual	St Resid
2	39	5.893	4.184	0.533	1.709	2.25 R
3	33	6.453	8.154	0.533	-1.701	-2.24 R
S = 0.9284		R-Sq = 94.1%		R-Sq(adj) = 90.9%		

Table 6.28: Analysis of Variance for Ni

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	312.24	312.24	22.3030	20.02	0.000
Linear	4	79.78	79.78	19.9445	17.90	0.000
Square	4	217.73	217.73	54.4335	48.85	0.000
Interaction	6	14.73	14.73	2.4550	2.20	0.059
Residual Error	47	52.37	52.37	1.1142		
Lack-of-Fit	10	16.67	16.67	1.6674	1.73	0.111
Pure Error	37	35.69	35.69	0.9647		
Total	61	364.61				
S = 0.8997		R-Sq = 99.5%		R-Sq(adj) = 96.3%		

Table 6.29: Analysis of Variance for Zn

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	323.469	323.469	23.1050	28.54	0.000
Linear	4	85.323	85.323	21.3307	26.35	0.000
Square	4	228.998	228.998	57.2495	70.72	0.000
Interaction	6	9.149	9.149	1.5248	1.88	0.103

Residual Error	47	38.046	38.046	0.8095		
Lack-of-Fit	10	13.882	13.882	1.3882	2.13	0.047
Pure Error	37	24.164	24.164	0.6531		
Total	61	361.515				
Unusual Observations for Zn						
Obs	StdOrder	Zn	Fit	SE Fit	Residual	St Resid
18	17	6.545	4.974	0.441	1.571	2.00 R
S = 0.9300 R-Sq = 88.5%			R-Sq(adj) = 85.1%			

Table 6.30: Analysis of Variance for Cu

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	312.74	312.74	22.3384	25.83	0.000
Linear	4	95.92	95.92	23.9791	27.73	0.000
Square	4	205.59	205.59	51.3986	59.43	0.000
Interaction	6	11.23	11.23	1.8712	2.16	0.063
Residual Error	47	40.65	40.65	0.8648		
Lack-of-Fit	10	11.46	11.46	1.1458	1.45	0.197
Pure Error	37	29.19	29.19	0.7889		
Total	61	353.39				
S = 0.7959		R-Sq = 92.0%		R-Sq(adj) = 89.6%		

Table 6.31: Analysis of Variance for Hg

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	342.799	342.799	24.4856	38.66	0.000
Linear	4	87.840	87.840	21.9600	34.67	0.000
Square	4	241.377	241.377	60.3443	95.27	0.000
Interaction	6	13.582	13.582	2.2636	3.57	0.005
Residual Error	47	29.771	29.771	0.6334		
Lack-of-Fit	10	9.402	9.402	0.9402	1.71	0.116
Pure Error	37	20.369	20.369	0.5505		
Total	61	372.570				
Unusual Observations for Hg						
Obs	StdOrder	Hg	Fit	SE Fit	Residual	St Resid
3	33	6.650	7.980	0.457	-1.330	-2.04 R
49	44	6.895	8.353	0.457	-1.459	-2.24 R
S = 0.9748		R-Sq = 88.5%		R-Sq(adj) = 85.1%		

Table 6.32: Analysis of Variance for Cr

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	343.81	343.81	24.5577	25.84	0.000

Linear	4	87.72	87.72	21.9308	23.08	0.000
Square	4	244.10	244.10	61.0254	64.22	0.000
Interaction	6	11.98	11.98	1.9971	2.10	0.071
Residual Error	47	44.66	44.66	0.9502		
Lack-of-Fit	10	20.46	20.46	2.0460	3.13	0.005
Pure Error	37	24.20	24.20	0.6541		
Total	61	388.47				
Unusual Observations for Cr						
Obs	StdOrder	Cr	Fit	SE Fit	Residual	St Resid
2	39	5.837	4.093	0.559	1.743	2.18 R
41	46	7.896	6.267	0.559	1.629	2.04 R
S = 0.8501		R-Sq = 91.0%		R-Sq(adj) = 88.3%		

Table 6.33: Analysis of Variance for Ag

Source	DF	Seq SS	Adj SS	Adj MS	P	F
Regression	14	343.891	343.891	24.5636	33.99	0.000
Linear	4	88.415	88.415	22.1038	30.58	0.000
Square	4	244.492	244.492	61.1231	84.57	0.000
Interaction	6	10.983	10.983	1.8305	2.53	0.033
Residual Error	47	33.968	33.968	0.7227		
Lack-of-Fit	10	9.450	9.450	0.9450	1.43	0.207
Pure Error	37	24.518	24.518	0.6627		
Total	61	377.858				
Unusual Observations for Ag						
Obs	StdOrder	Ag	Fit	SE Fit	Residual	St Resid
14	16	5.238	3.726	0.488	1.512	2.17 R
40	7	8.675	7.152	0.488	1.523	2.19 R
49	44	6.546	8.182	0.488	-1.636	-2.35 R
S = 0.8155		R-Sq = 91.4%		R-Sq(adj) = 88.9%		

Table 6.34: Analysis of Variance for Fe

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	332.917	332.917	23.7798	35.76	0.000
Linear	4	90.280	90.280	22.5699	33.94	0.000
Square	4	228.030	228.030	57.0074	85.72	0.000
Interaction	6	14.608	14.608	2.4346	3.66	0.005
Residual Error	47	31.256	31.256	0.6650		
Lack-of-Fit	10	7.473	7.473	0.7473	1.16	0.346
Pure Error	37	23.782	23.782	0.6428		
Total	61	364.173				
Unusual Observations for Fe						

Obs	StdOrder	Fe	Fit	SE Fit	Residual	St Resid
5	62	4.782	3.076	0.171	1.706	2.14 R
49	44	7.002	8.371	0.468	-1.369	-2.05 R
S = 0.8098		R-Sq = 92.0%		R-Sq(adj) = 89.6%		

Table 6.35: Analysis of Variance for Pb

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	355.18	355.18	25.3700	38.68	0.000
Linear	4	79.22	79.22	19.8059	30.20	0.000
Square	4	263.01	263.01	65.7518	100.26	0.000
Interaction	6	12.95	12.95	2.1582	3.29	0.009
Residual Error	47	30.82	30.82	0.6558		
Lack-of-Fit	10	10.25	10.25	1.0255	1.84	0.086
Pure Error	37	20.57	20.57	0.5559		
Total	61	386.00				
Unusual Observations for Pb						
Obs	StdOrder	Pb	Fit	SE Fit	Residual	St Resid
26	35	7.856	6.125	0.465	1.731	2.61 R
49	44	6.575	8.223	0.465	-1.649	-2.49 R
53	47	2.010	3.788	0.465	-1.778	-2.68 R
S = 0.8418		R-Sq = 91.2%		R-Sq(adj) = 88.5%		

Table 6.36: Analysis of Variance for Al

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	343.170	343.170	24.5121	34.59	0.000
Linear	4	85.051	85.051	21.2626	30.01	0.000
Square	4	249.817	249.817	62.4541	88.14	0.000
Interaction	6	8.303	8.303	1.3838	1.95	0.092
Residual Error	47	33.305	33.305	0.7086		
Lack-of-Fit	10	10.497	10.497	1.0497	1.70	0.117
Pure Error	37	22.807	22.807	0.6164		
Total	61	376.474				
Unusual Observations for Al						
Obs	StdOrder	Al	Fit	SE Fit	Residual	St Resid
14	16	5.673	4.108	0.483	1.565	2.27 R
49	44	6.676	8.164	0.483	-1.488	-2.16 R
53	47	2.450	4.108	0.483	-1.658	-2.41 R
S = 0.9687		R-Sq = 98.0%		R-Sq(adj) = 94.4%		

Table 6.37: Analysis of Variance for As

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	323.217	323.217	23.0870	24.60	0.000
Linear	4	80.890	80.890	20.2226	21.55	0.000
Square	4	232.539	232.539	58.1347	61.95	0.000
Interaction	6	9.788	9.788	1.6314	1.74	0.133
Residual Error	47	44.106	44.106	0.9384		
Lack-of-Fit	10	13.997	13.997	1.3997	1.72	0.113
Pure Error	37	30.108	30.108	0.8137		
Total	61	367.323				
Unusual Observations for Ar						
Obs	StdOrder	As	Fit	SE Fit	Residual	St Resid
3	33	6.563	8.202	0.556	-1.639	-2.07 R
39	21	6.957	4.624	0.475	2.333	2.76 R
41	46	7.991	6.156	0.556	1.835	2.31 R
S = 0.9008		R-Sq = 89.5%		R-Sq(adj) = 86.4%		

Table 6.38: Analysis of Variance for Cd

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	325.34	325.34	23.2385	28.64	0.000
Linear	4	88.61	88.61	22.1513	27.30	0.000
Square	4	223.17	223.17	55.7925	68.76	0.000
Interaction	6	13.56	13.56	2.2607	2.79	0.021
Residual Error	47	38.13	38.13	0.8114		
Lack-of-Fit	10	14.29	14.29	1.4293	2.22	0.039
Pure Error	37	23.84	23.84	0.6444		
Total	61	363.47				
Unusual Observations for Cd						
Obs	StdOrder	Cd	Fit	SE Fit	Residual	St Resid
2	39	5.674	4.170	0.517	1.503	2.04 R
39	21	6.565	4.643	0.442	1.921	2.45 R
S = 0.8845		R-Sq = 90.0%		R-Sq(adj) = 87.1%		

Table 6.39: Analysis of Variance for Si

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	332.29	332.29	23.7347	30.34	0.000
Linear	4	95.34	95.34	23.8350	30.47	0.000
Square	4	224.40	224.40	56.0989	71.71	0.000
Interaction	6	12.55	12.55	2.0917	2.67	0.026
Residual Error	47	36.77	36.77	0.7823		

Lack-of-Fit	10	12.98	12.98	1.2985	2.02	0.059
Pure Error	37	23.79	23.79	0.6428		
Total	61		369.06			
Unusual Observations for Si						
Obs	StdOrder	Si	Fit	SE Fit	Residual	St Resid
18	17	6.434	4.758	0.434	1.676	2.17 R
39	21	6.674	4.509	0.434	2.165	2.81 R
S = 1.056		R-Sq = 95.6%		R-Sq(adj) = 91.4%		

Table 6.40: Analysis of Variance for Ti

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	358.24	358.24	25.5888	27.33	0.000
Linear	4	85.71	85.71	21.4285	22.89	0.000
Square	4	257.91	257.91	64.4767	68.86	0.000
Interaction	6	14.62	14.62	2.4370	2.60	0.029
Residual Error	47	44.01	44.01	0.9363		
Lack-of-Fit	10	17.06	17.06	1.7060	2.34	0.029
Pure Error	37	26.95	26.95	0.7283		
Total	61	402.25				
Unusual Observations for Ti						
Obs	StdOrder	Ti	Fit	SE Fit	Residual	St Resid
2	39	5.783	4.196	0.555	1.587	2.00 R
39	21	6.856	4.448	0.474	2.408	2.86 R
41	46	7.896	5.907	0.555	1.989	2.51 R
49	44	6.784	8.417	0.555	-1.633	-2.06 R
S = 0.9676		R-Sq = 99.1%		R-Sq(adj) = 95.8%		

Table 6.41: Analysis of Variance for Mg

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	319.083	319.083	22.7917	26.76	0.000
Linear	4	80.603	80.603	20.1508	23.66	0.000
Square	4	229.887	229.887	57.4717	67.47	0.000
Interaction	6	8.593	8.593	1.4322	1.68	0.147
Residual Error	47	40.035	40.035	0.8518		
Lack-of-Fit	10	15.784	15.784	1.5784	2.41	0.026
Pure Error	37	24.251	24.251	0.6554		
Total	61	359.118				
Unusual Observations for Mg						
Obs	StdOrder	Mg	Fit	SE Fit	Residual	St Resid
3	33	6.563	8.094	0.530	-1.531	-2.03 R
14	16	5.635	3.975	0.530	1.660	2.20 R
39	21	6.736	4.412	0.453	2.324	2.89 R

S = 0.9229	R-Sq = 88.9%	R-Sq(adj) = 85.5%
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Table 6.42: Analysis of Variance for F⁻

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	346.11	346.11	24.7222	39.03	0.000
Linear	4	83.86	83.86	20.9646	33.10	0.000
Square	4	248.00	248.00	61.9998	97.89	0.000
Interaction	6	14.25	14.25	2.3756	3.75	0.004
Residual Error	47	29.77	29.77	0.6333		
Lack-of-Fit	10	11.59	11.59	1.1591	2.36	0.028
Pure Error	37	18.18	18.18	0.4913		
Total	61	375.88				
Unusual Observations for F⁻						
Obs	StdOrder	F⁻	Fit	SE Fit	Residual	St Resid
39	21	5.785	4.253	0.390	1.532	2.21 R
49	44	6.946	8.459	0.457	-1.513	-2.32 R
S = 0.7958		R-Sq = 92.1%		R-Sq(adj) = 89.7%		

Table 6.43: Analysis of Variance for Cl⁻

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	319.462	319.462	22.8187	31.69	0.000
Linear	4	93.020	93.020	23.2549	32.30	0.000
Square	4	215.698	215.698	53.9246	74.89	0.000
Interaction	6	10.744	10.744	1.7907	2.49	0.036
Residual Error	47	33.842	33.842	0.7200		
Lack-of-Fit	10	9.998	9.998	0.9998	1.55	0.160
Pure Error	37	23.843	23.843	0.6444		
Total	61	353.304				
Unusual Observations for Cl⁻						
Obs	StdOrder	Cl⁻	Fit	SE Fit	Residual	St Resid
15	56	5.463	3.090	0.178	2.374	2.86 R
23	38	5.456	6.902	0.487	-1.446	-2.08 R
39	21	6.024	4.462	0.416	1.561	2.11 R
S = 0.8485		R-Sq = 90.4%		R-Sq(adj) = 87.6%		

Table 6.44: Analysis of Variance for SO₄²⁻

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	350.55	350.55	25.0390	32.44	0.000
Linear	4	95.87	95.87	23.9664	31.05	0.000
Square	4	241.87	241.87	60.4675	78.35	0.000

Interaction	6	12.81	12.81	2.1350	2.77	0.022
Residual Error	47	36.27	36.27	0.7718		
Lack-of-Fit	10	14.04	14.04	1.4043	2.34	0.030
Pure Error	37	22.23	22.23	0.6008		
Total	61	386.82				
Unusual Observations for SO₄²⁻						
Obs	StdOrder	SO₄²⁻	Fit	SE Fit	Residual	St Resid
41	46	7.342	5.814	0.504	1.528	2.12 R
49	44	5.574	7.954	0.504	-2.380	-3.31 R
S = 0.8785		R-Sq = 90.6%		R-Sq(adj) = 87.8%		

Table 6.45: Analysis of Variance for PO₄³⁻

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	328.25	328.25	23.4461	31.85	0.000
Linear	4	87.13	87.13	21.7826	29.59	0.000
Square	4	230.76	230.76	57.6906	78.38	0.000
Interaction	6	10.35	10.35	1.7254	2.34	0.046
Residual Error	47	34.59	34.59	0.7361		
Lack-of-Fit	10	15.34	15.34	1.5343	2.95	0.008
Pure Error	37	19.25	19.25	0.5203		
Total	61	362.84				
Unusual Observations for PO₄³⁻						
Obs	StdOrder	PO₄³⁻	Fit	SE Fit	Residual	St Resid
2	39	5.764	4.155	0.492	1.608	2.29 R
39	21	6.453	4.383	0.421	2.070	2.77 R
41	46	7.564	6.064	0.492	1.500	2.13 R
S = 0.8579		R-Sq = 90.5%		R-Sq(adj) = 87.6%		

Table 6.46: Analysis of Variance for NO₂⁻

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	324.18	324.18	23.1555	28.95	0.000
Linear	4	94.76	94.76	23.6905	29.62	0.000
Square	4	219.28	219.28	54.8211	68.55	0.000
Interaction	6	10.13	10.13	1.6883	2.11	0.070
Residual Error	47	37.59	37.59	0.7998		
Lack-of-Fit	10	13.48	13.48	1.3485	2.07	0.053
Pure Error	37	24.11	24.11	0.6515		
Total	61	361.77				
Unusual Observations for NO₂⁻						
Obs	StdOrder	NO₂⁻	Fit	SE Fit	Residual	St Resid
3	33	6.783	8.367	0.513	-1.583	-2.16 R

41	46	7.946	6.301	0.513	1.645	2.25 R
49	44	6.756	8.392	0.513	-1.636	-2.23 R
S = 0.8943		R-Sq = 89.6%		R-Sq(adj) = 86.5%		

Table 6.47: Analysis of Variance for BrO_3^-

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	344.25	344.25	24.5894	29.95	0.000
Linear	4	88.67	88.67	22.1675	27.00	0.000
Square	4	243.00	243.00	60.7490	74.00	0.000
Interaction	6	12.59	12.59	2.0975	2.55	0.032
Residual Error	47	38.59	38.59	0.8210		
Lack-of-Fit	10	14.95	14.95	1.4949	2.34	0.030
Pure Error	37	23.64	23.64	0.6388		
Total	61	382.84				
Unusual Observations for BrO_3^-						
Obs	StdOrder	BrO_3^-	Fit	SE Fit	Residual	St Resid
14	16	5.673	4.050	0.520	1.623	2.19 R
39	21	6.036	4.318	0.444	1.717	2.17 R
53	47	2.341	4.050	0.520	-1.709	-2.30 R
S = 0.9061		R-Sq = 89.9%		R-Sq(adj) = 86.9%		

Table 6.48: Analysis of Variance for NO_3^-

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	347.072	347.072	24.7909	35.42	0.000
Linear	4	92.186	92.186	23.0465	32.93	0.000
Square	4	246.233	246.233	61.5583	87.95	0.000
Interaction	6	8.653	8.653	1.4422	2.06	0.076
Residual Error	47	32.895	32.895	0.6999		
Lack-of-Fit	10	13.085	13.085	1.3085	2.44	0.024
Pure Error	37	19.810	19.810	0.5354		
Total	61	379.968				
Unusual Observations for NO_3^-						
Obs	StdOrder	NO_3^-	Fit	SE Fit	Residual	St Resid
39	21	6.563	4.383	0.410	2.180	2.99 R
49	44	6.563	8.036	0.480	-1.472	-2.15 R
S = 0.8366		R-Sq = 91.3%		R-Sq(adj) = 88.8%		

Appendix D

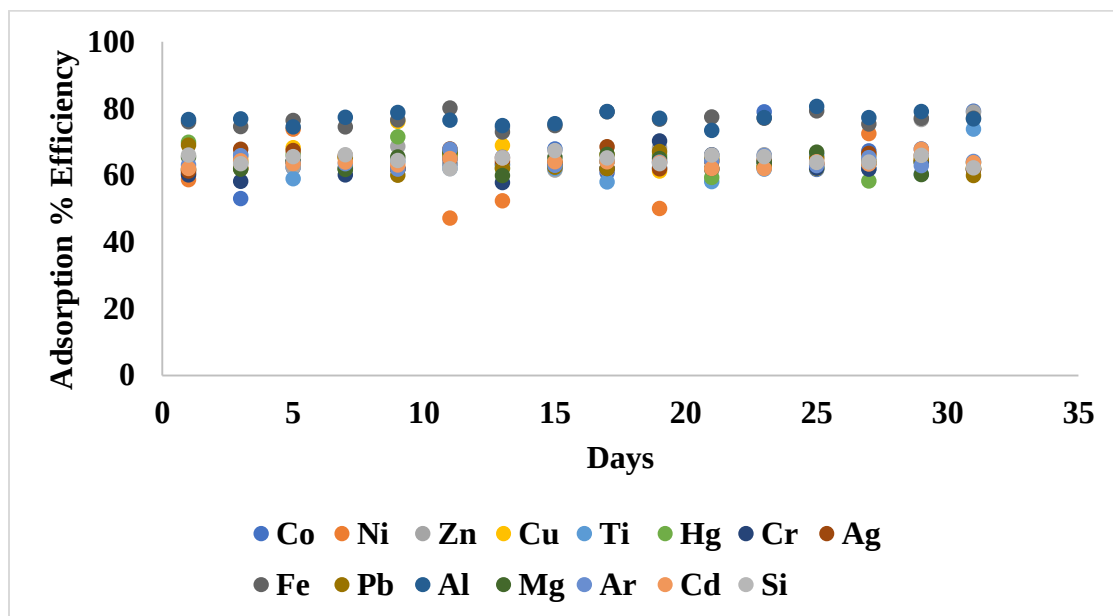


Figure 6.3: Adsorption percentage efficiency of cations by the fish scale VWMs stored in the cold room at -4°C

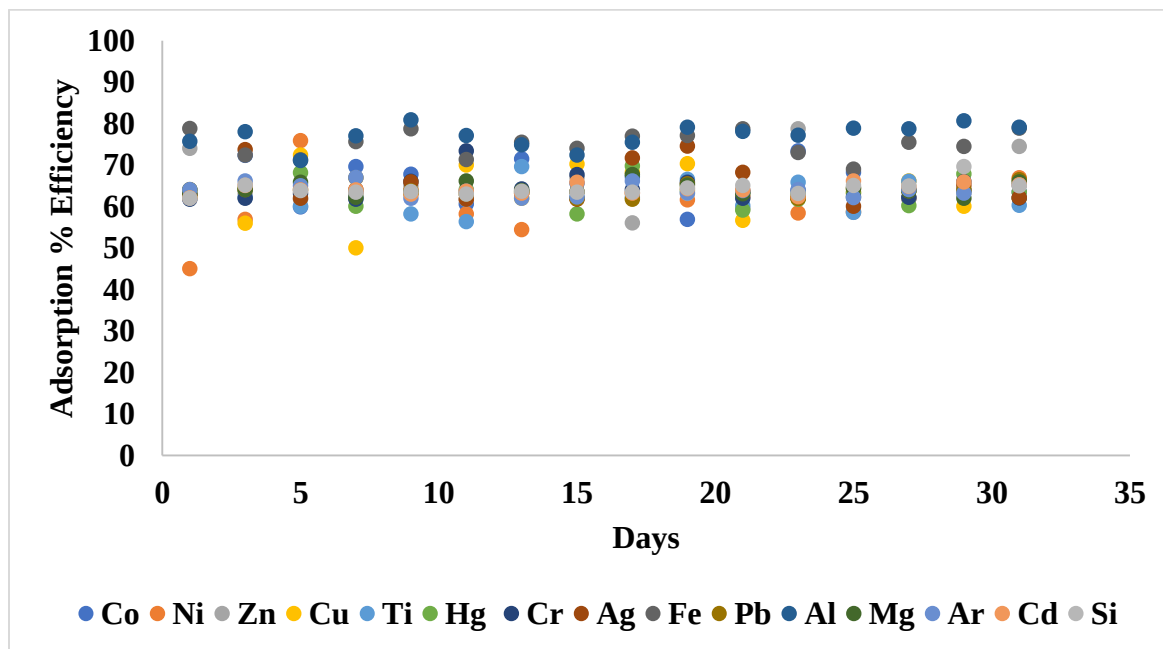


Figure 6.4: Adsorption percentage efficiency of cations by the fish scale VWMs stored at room temperature 45 °C

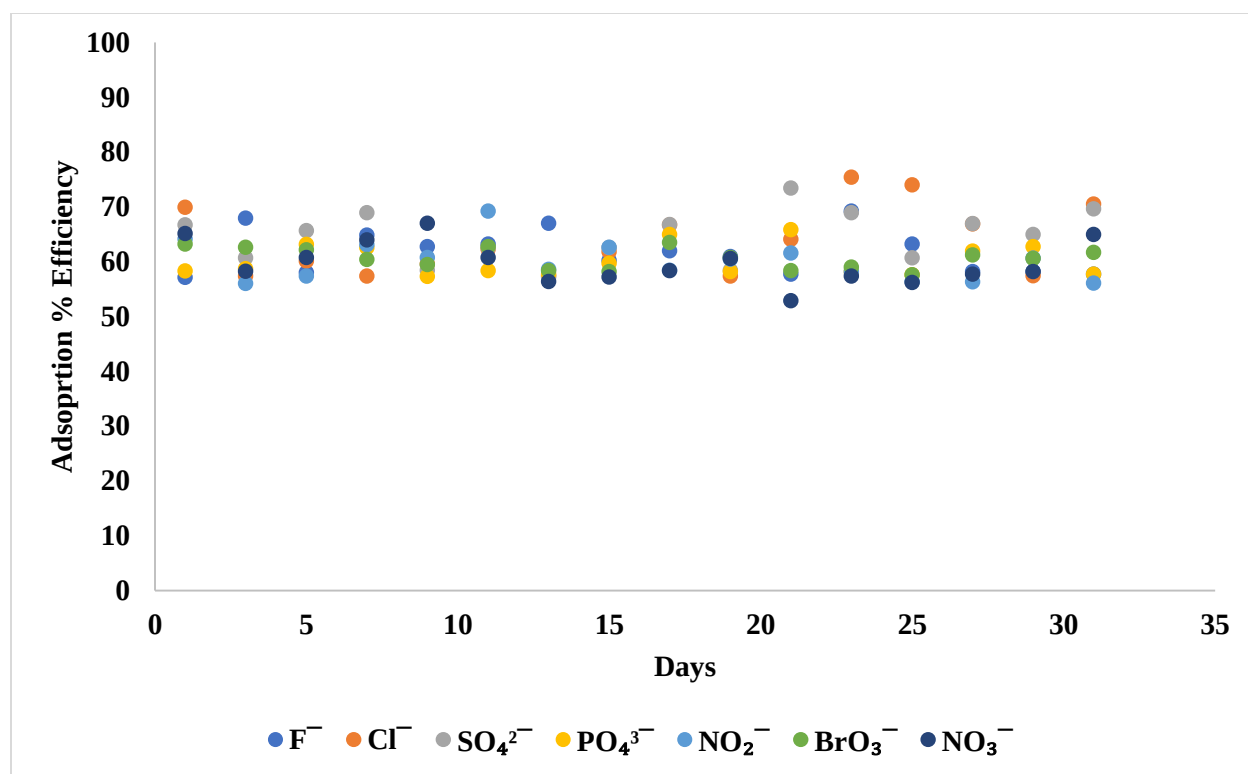


Figure 6.5: Adsorption percentage efficiency of anions by the fish scale VWMs stored in the cold room at -4°C

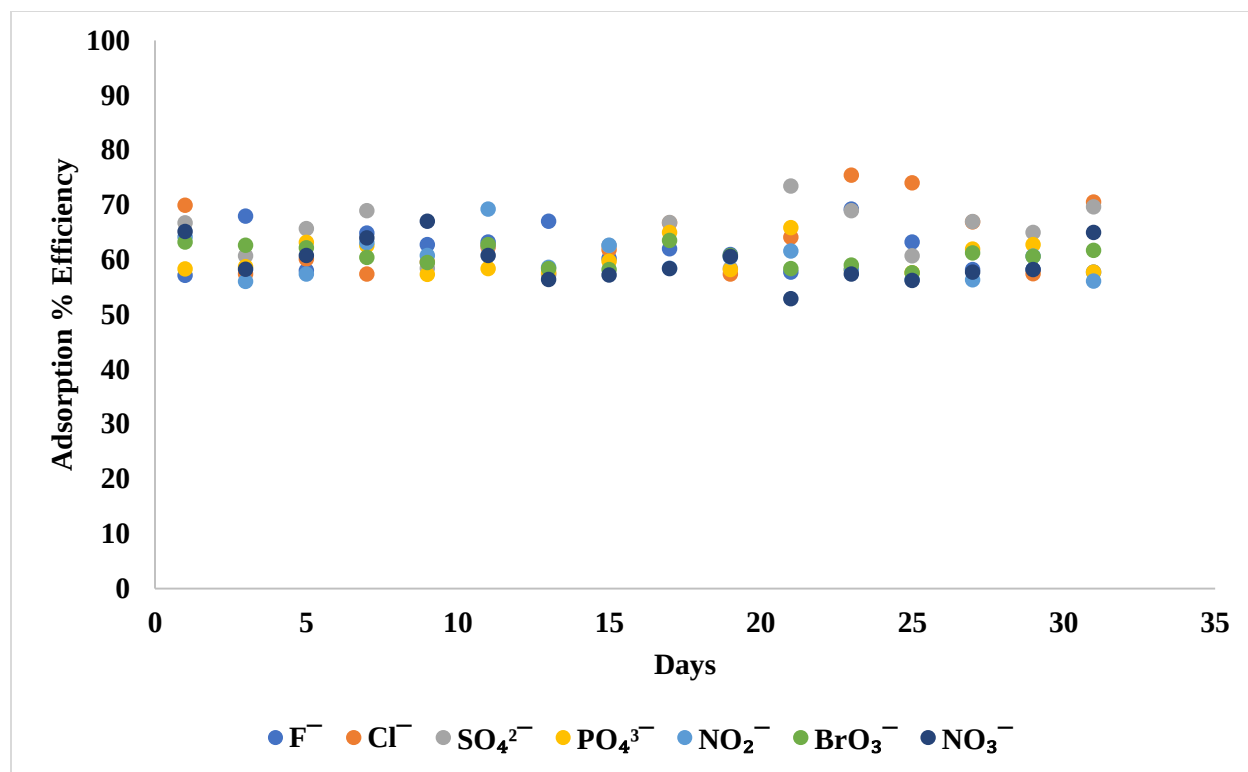


Figure 6.6: Adsorption percentage efficiency of anions by the fish scale VWMs stored at 45 °C

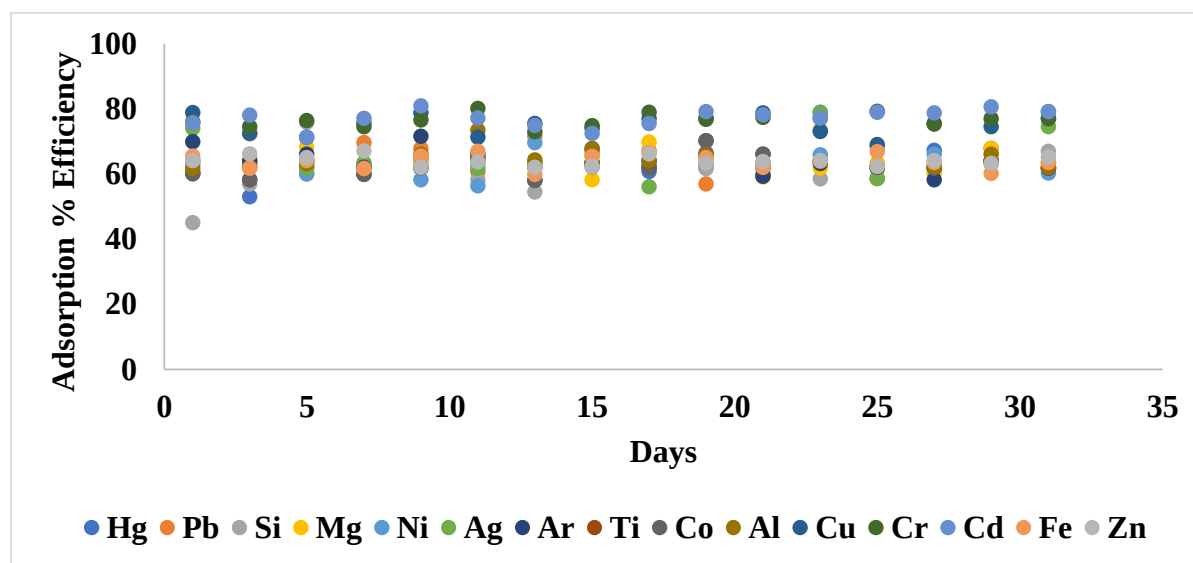


Figure 6.7: Adsorption percentage efficiency of cations by the eggshell VWMs stored in the cold room at -4 °C

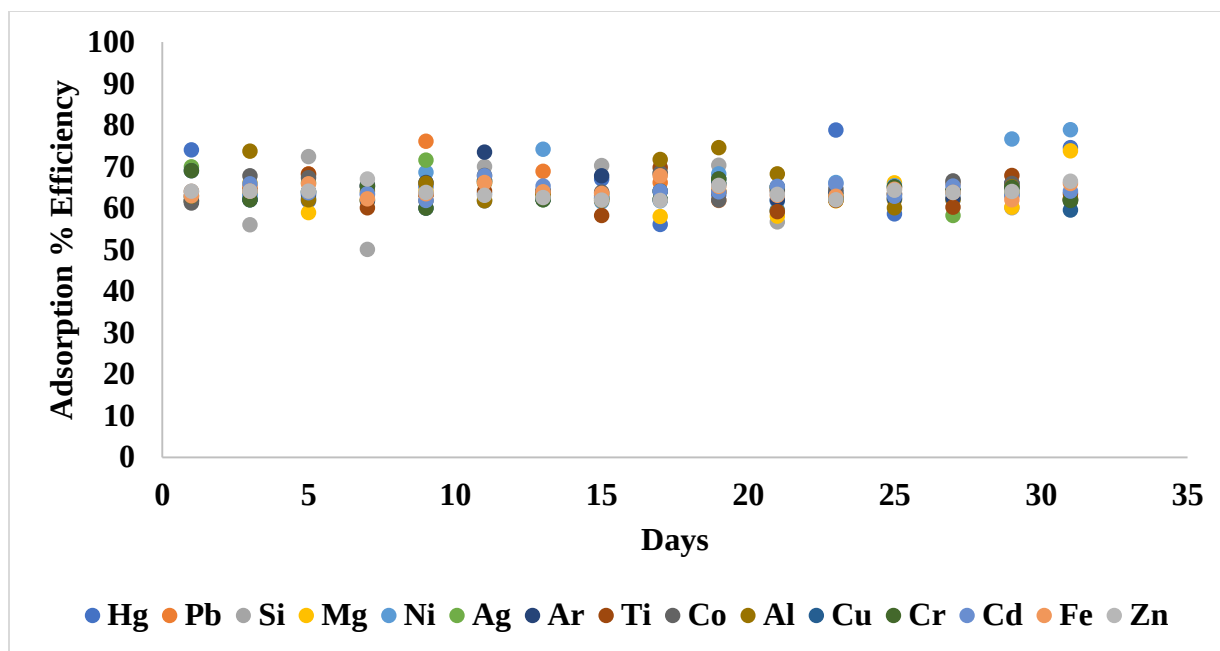


Figure 6.8: Adsorption percentage efficiency of cations by the eggshell VWMs stored at 45 °C

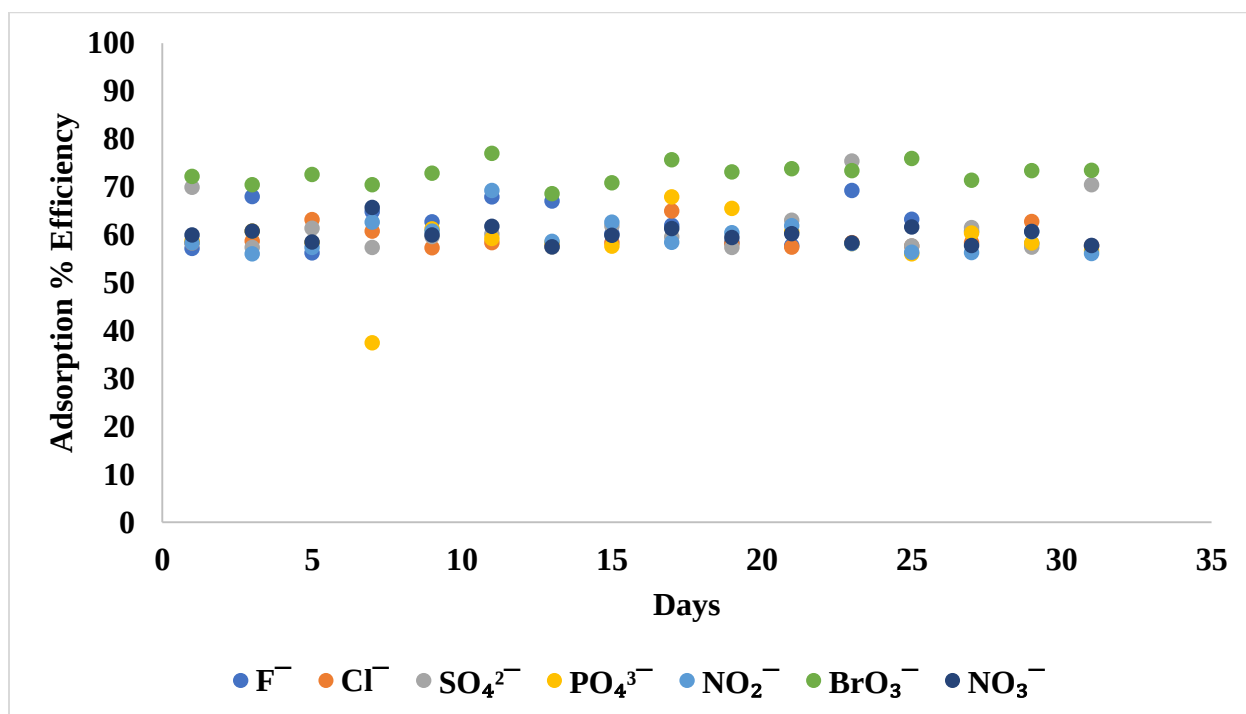


Figure 6.9: Adsorption percentage efficiency of anions by the eggshell VWMs stored at 45 °C

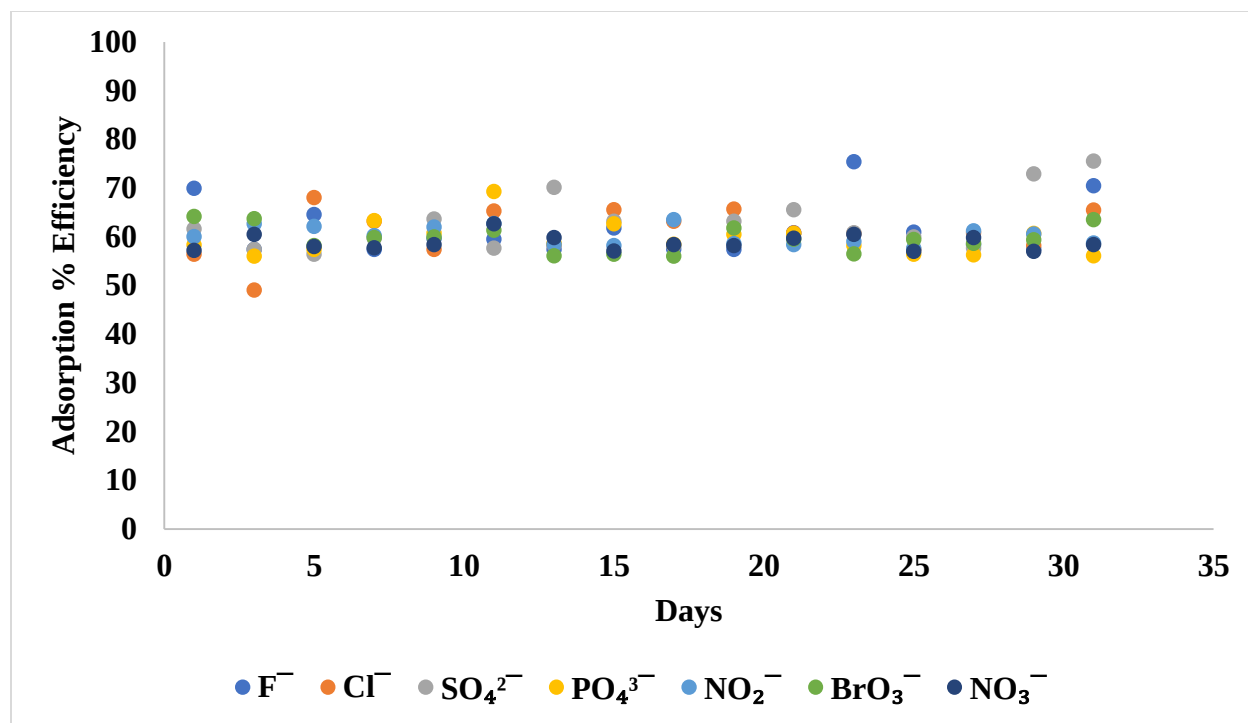


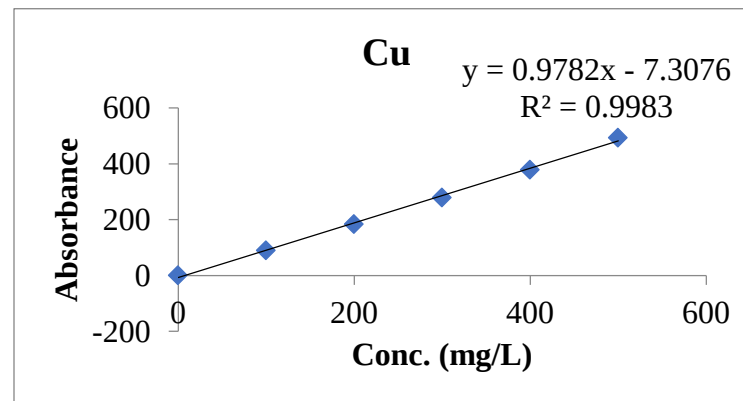
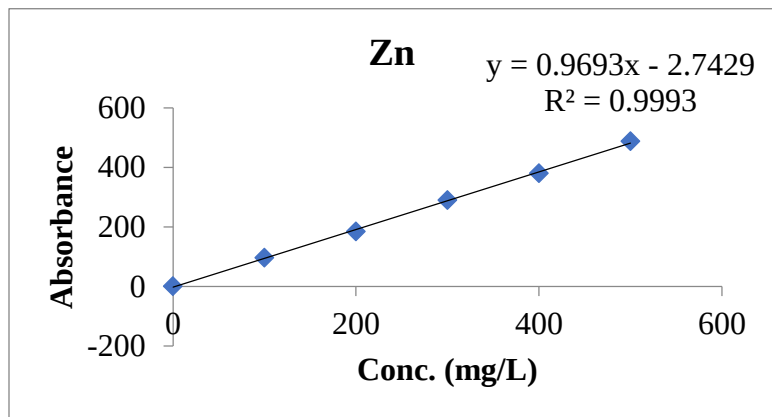
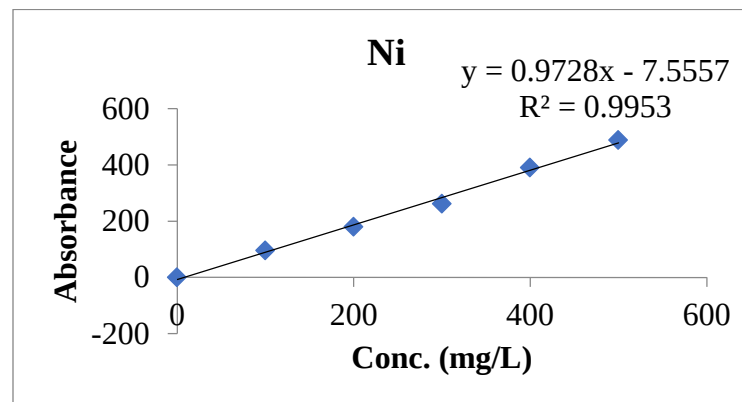
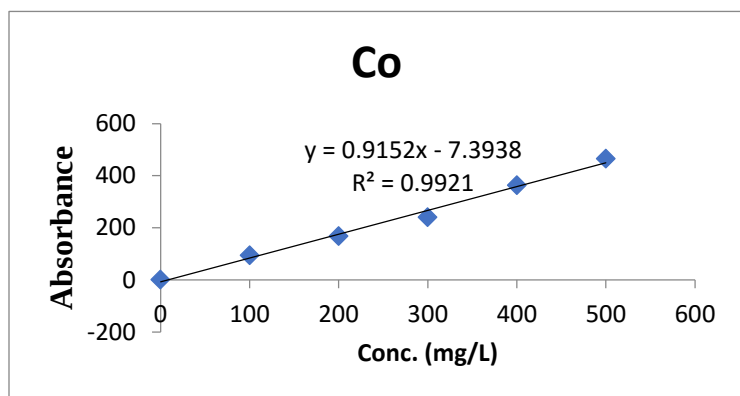
Figure 6.10: Adsorption percentage efficiency of anions by the eggshell VWMs stored in the cold room at $-4^{\circ}C$

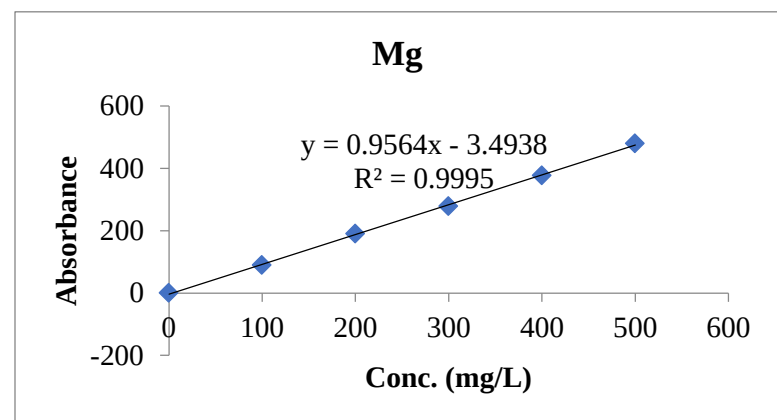
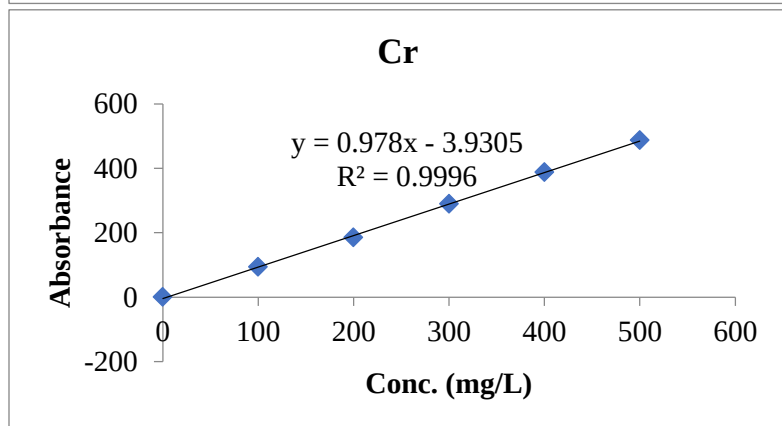
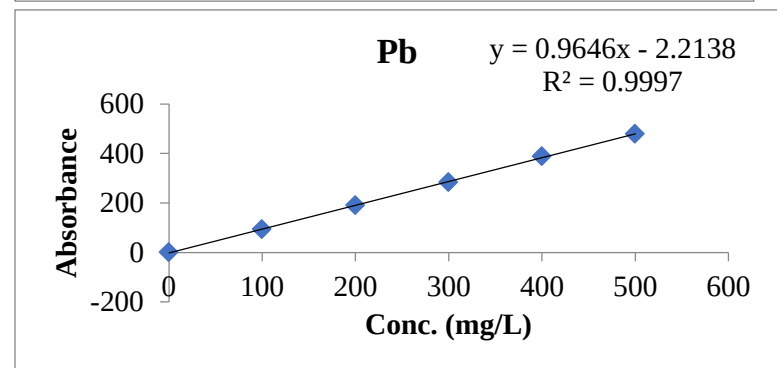
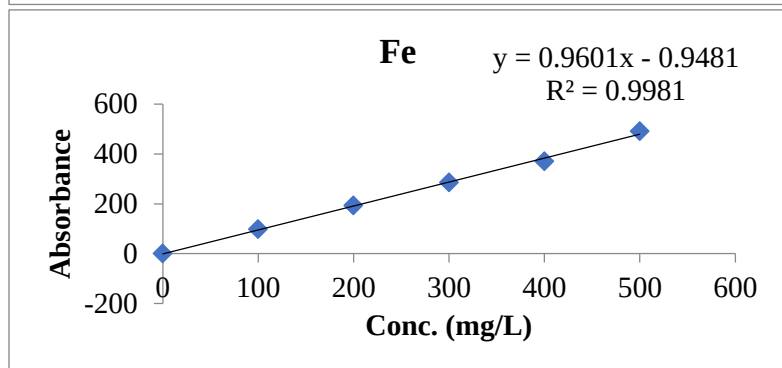
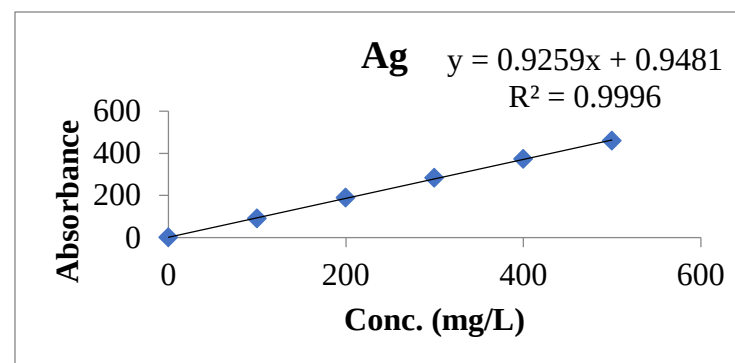
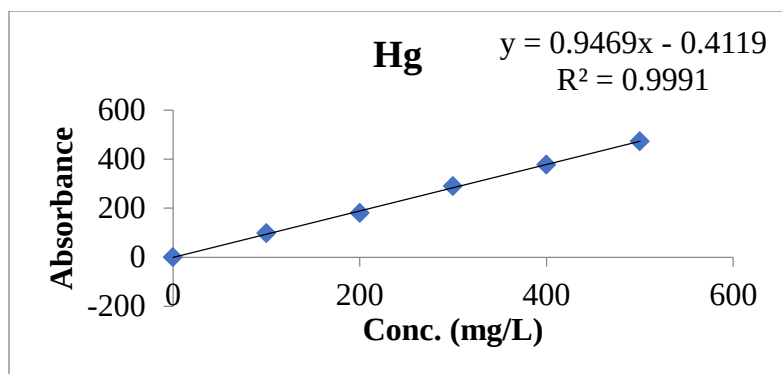
Appendix E

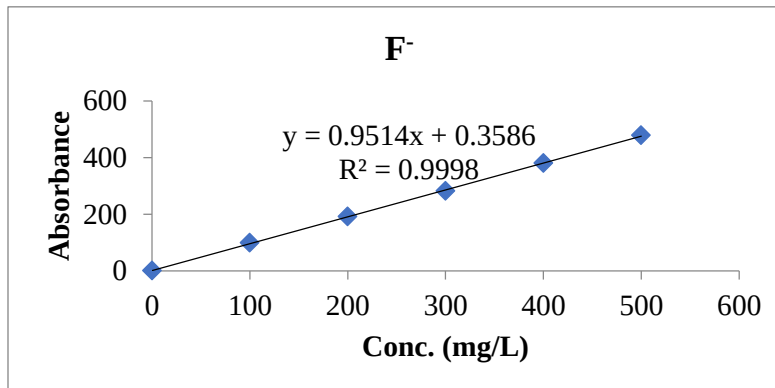
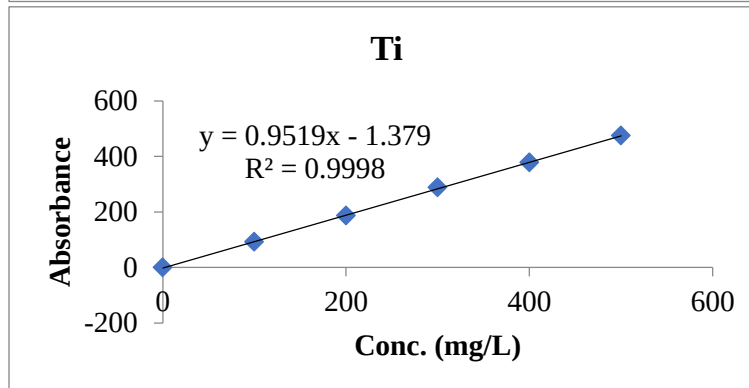
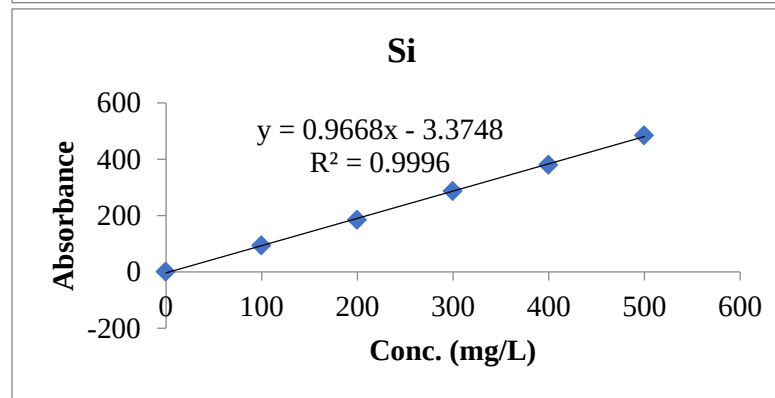
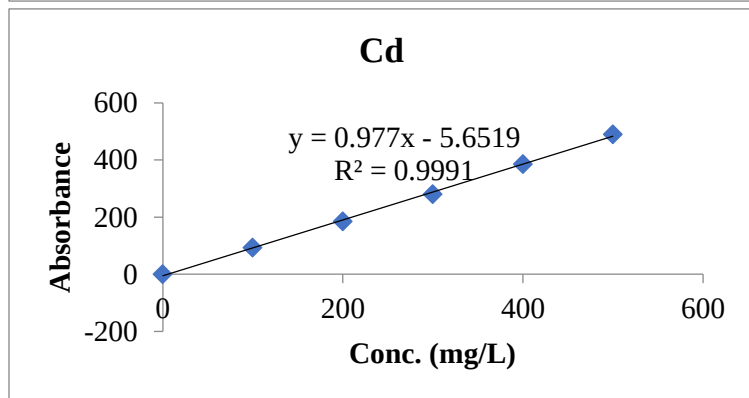
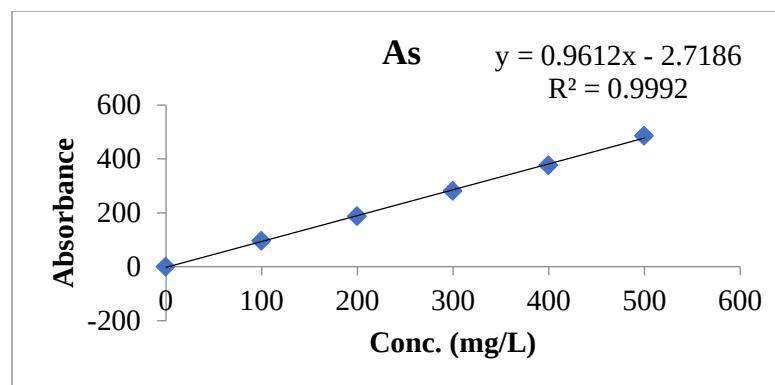
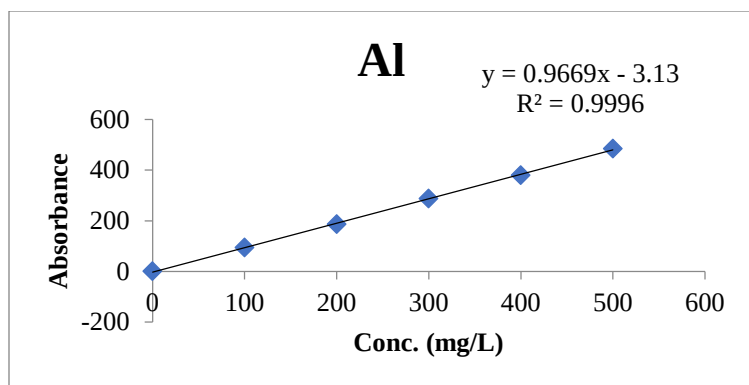
Table 6.49: Initial total ions concentration of the wastewater sample

Cations	Conc. (mg/L)	Anions	Conc. (mg/L)
Co	0.342 ± 0.0023	F ⁻	6.453 ± 0.056
Ni	0.271 ± 0.0081	Cl ⁻	56.318 ± 0.017
Zn	0.431 ± 0.0013	SO ₄ ²⁻	2.523 ± 0.0081
Cu	0.864 ± 0.0006	PO ₄ ³⁻	5.946 ± 0.0019
Hg	0.007 ± 0.0002	NO ₂ ⁻	4.256 ± 0.0112
Ag	0.641 ± 0.0008	BrO ₃ ⁻	0.978 ± 0.061
Fe	0.645 ± 0.009	NO ₃ ⁻	8.331 ± 0.002
Pb	0.216 ± 0.0030		
Cr	0.0645 ± 0.0033		
Mg	12.342 ± 0.0092		
Al	0.742 ± 0.0053		
As	0.142 ± 0.0034		
Cd	0.043 ± 0.0035		
Si	0.002 ± 0.0006		
Ti	ND		

Appendix F







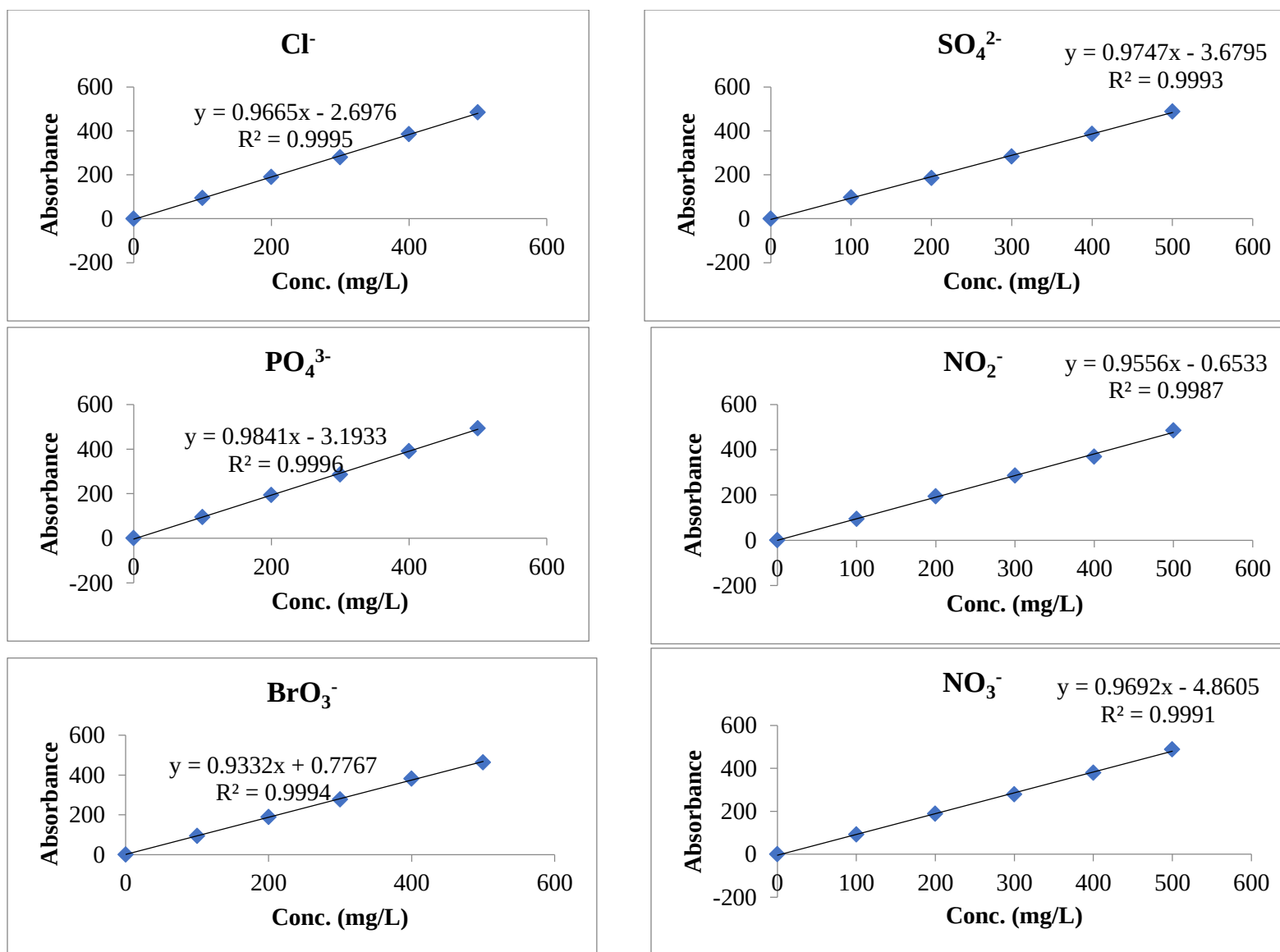
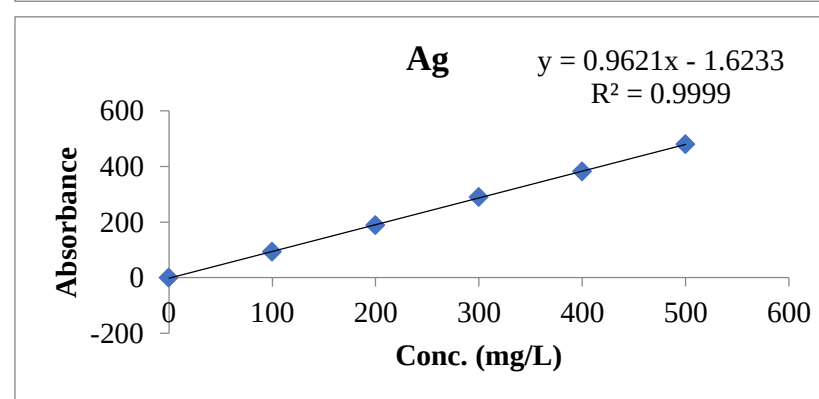
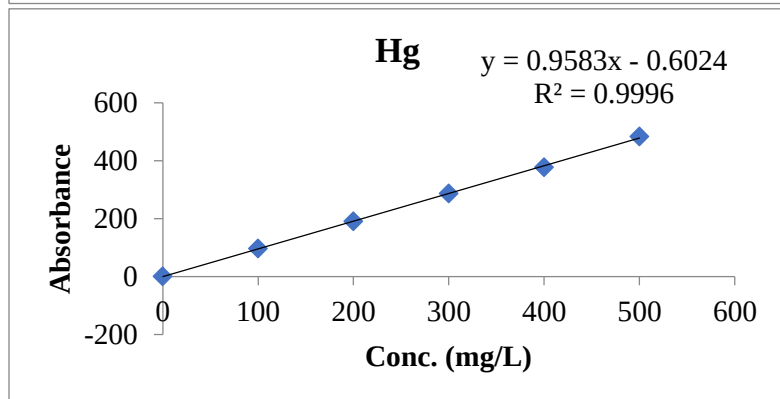
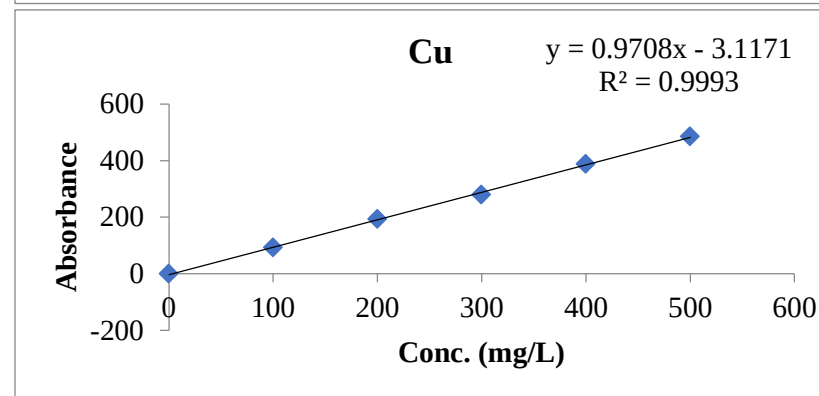
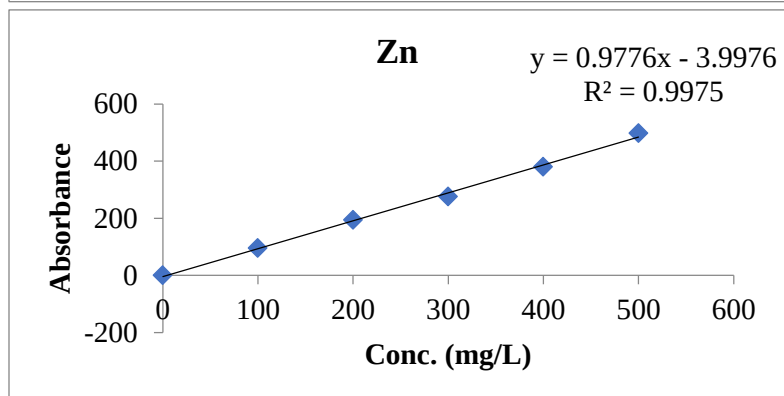
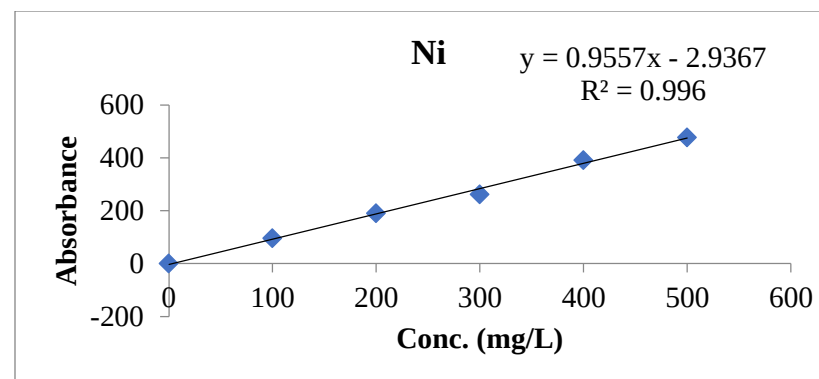
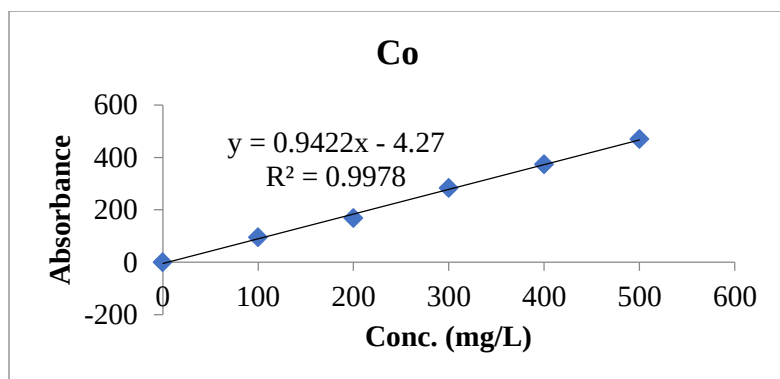
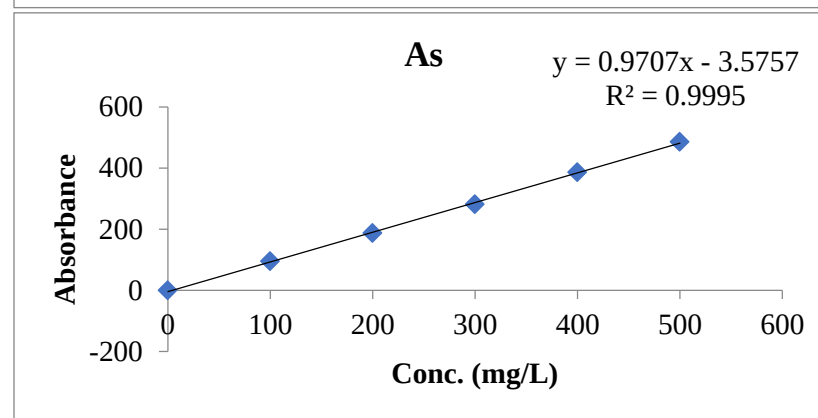
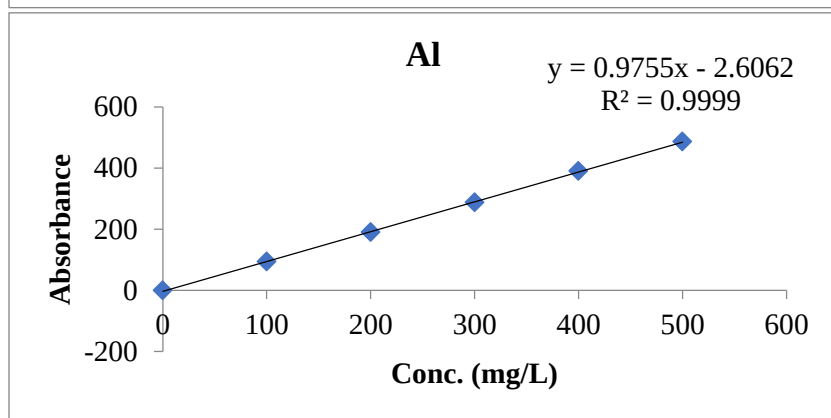
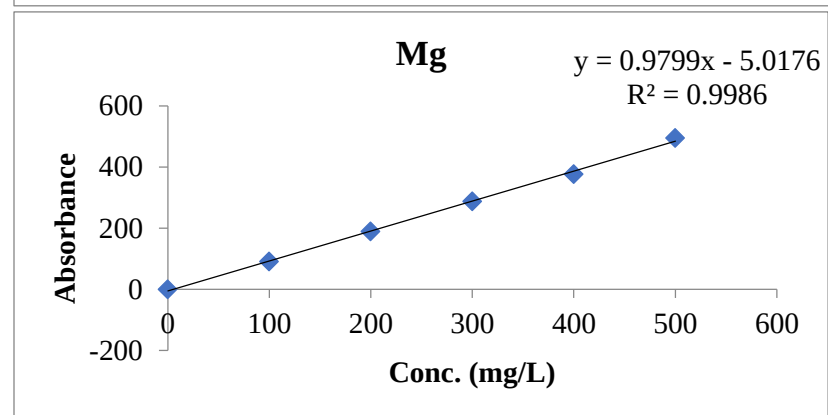
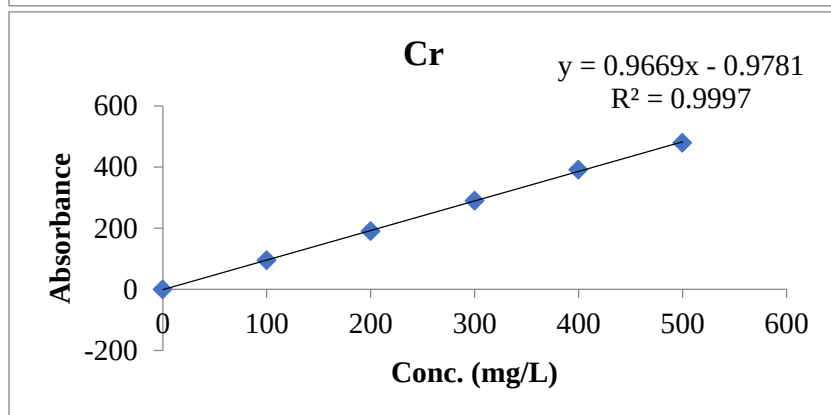
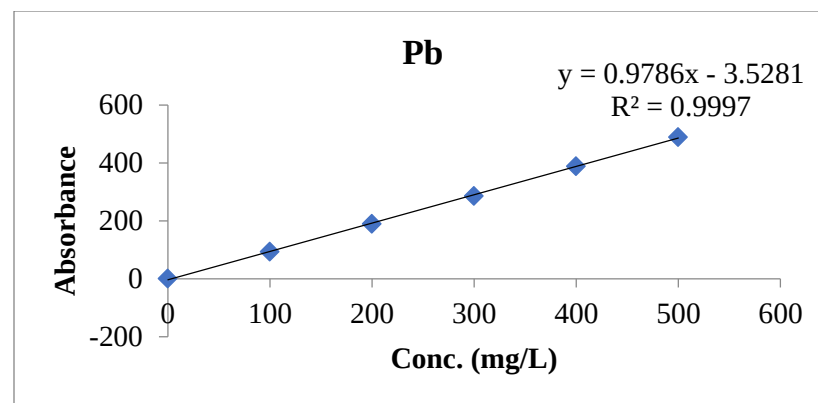
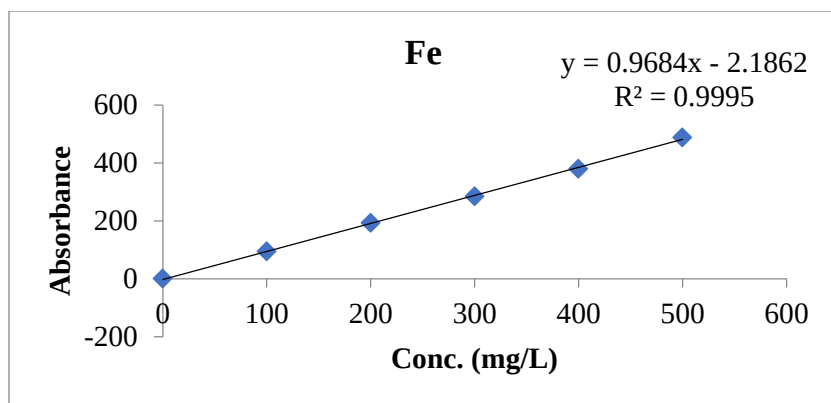
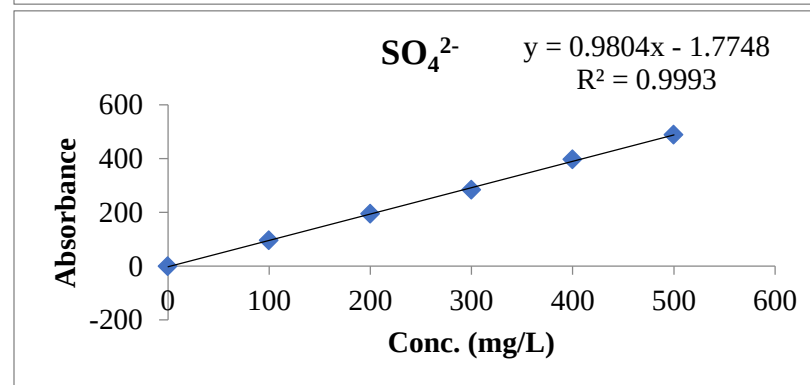
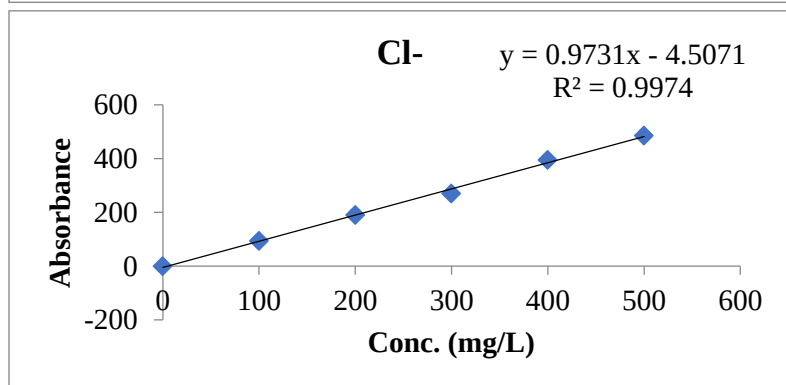
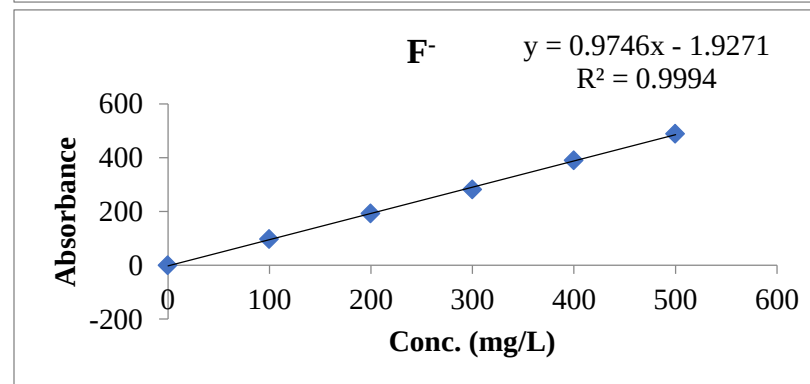
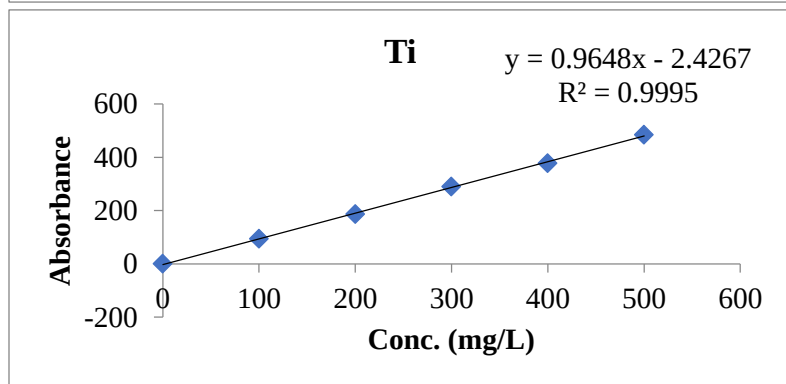
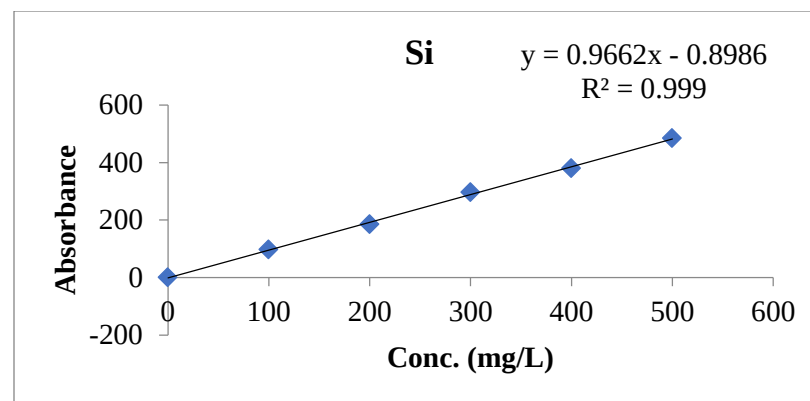
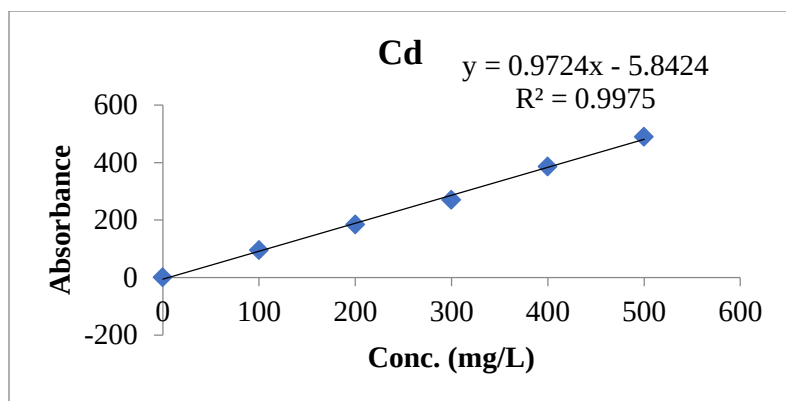


Figure 6.11: Calibration curves of the selected ions for the fish scale VWMs







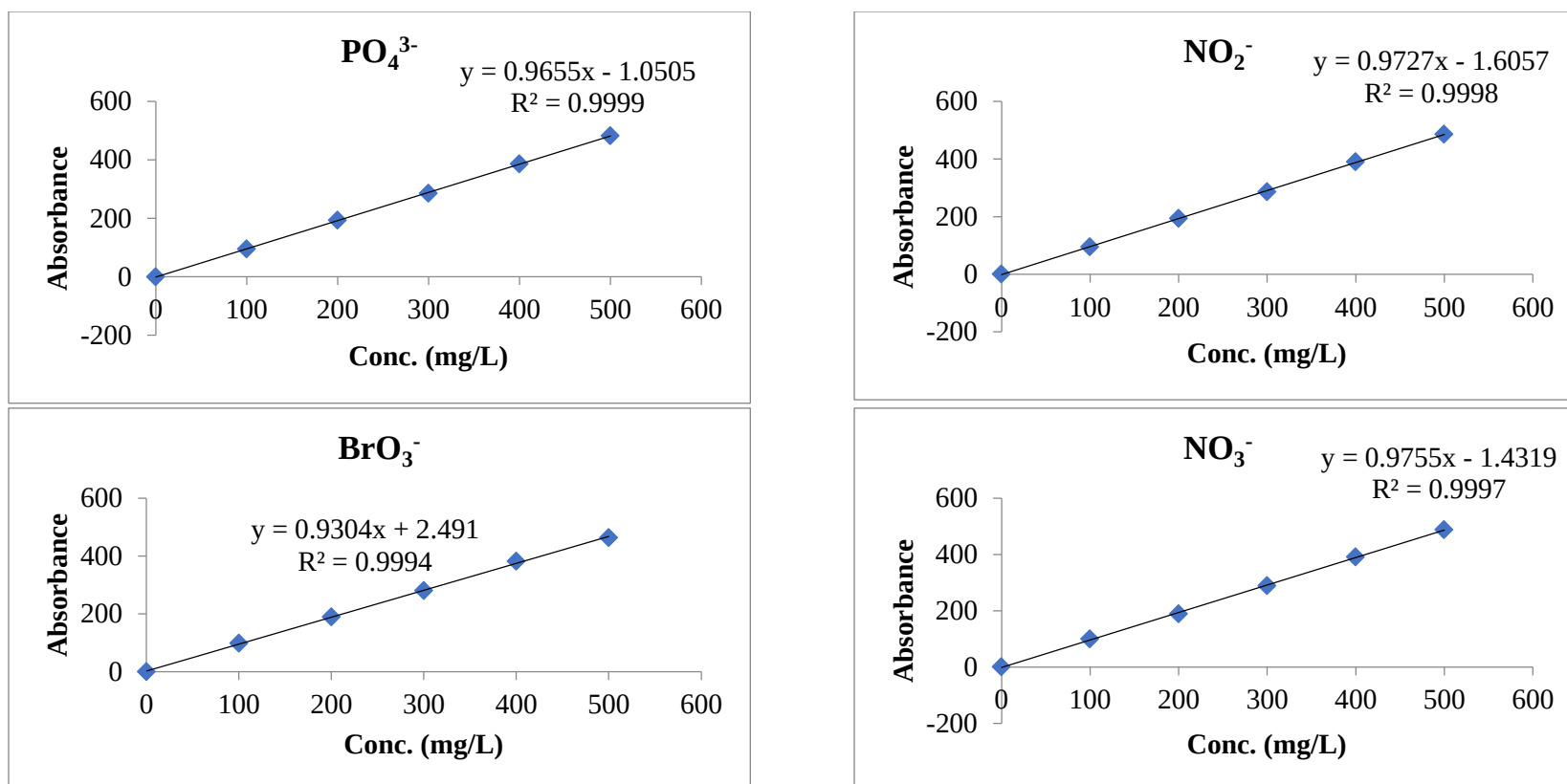


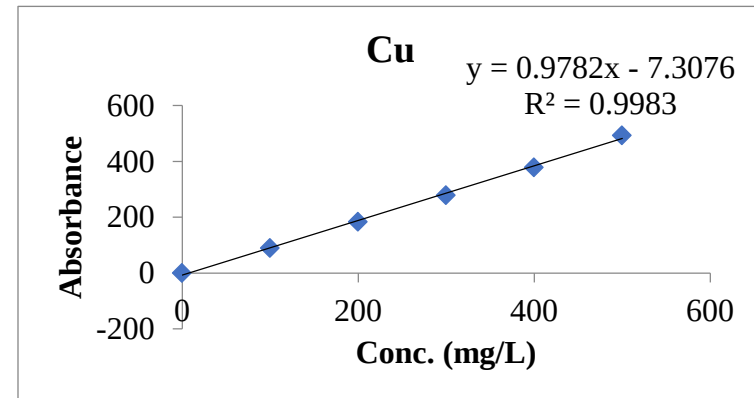
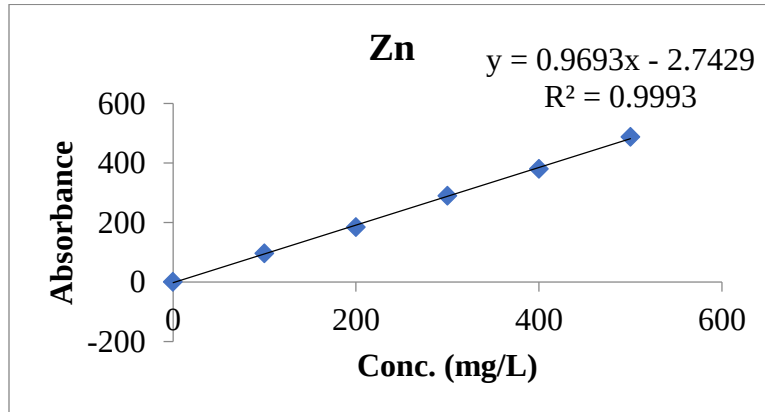
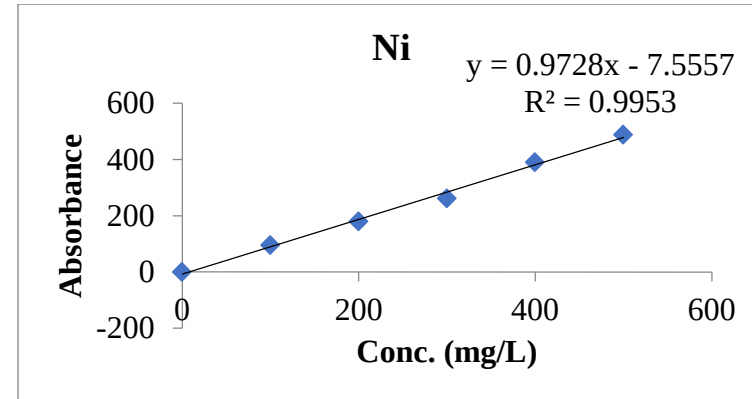
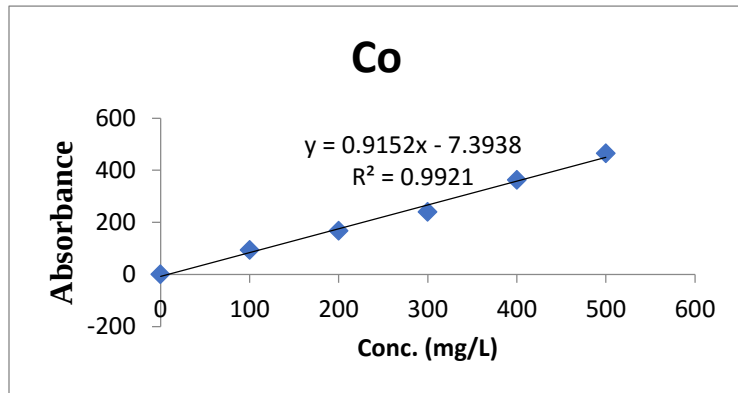
Figure 6.12: Calibration curves of the selected ions for the eggshell VWMs

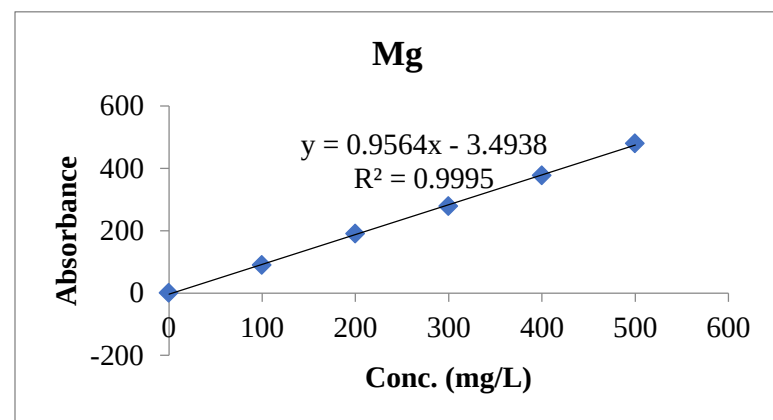
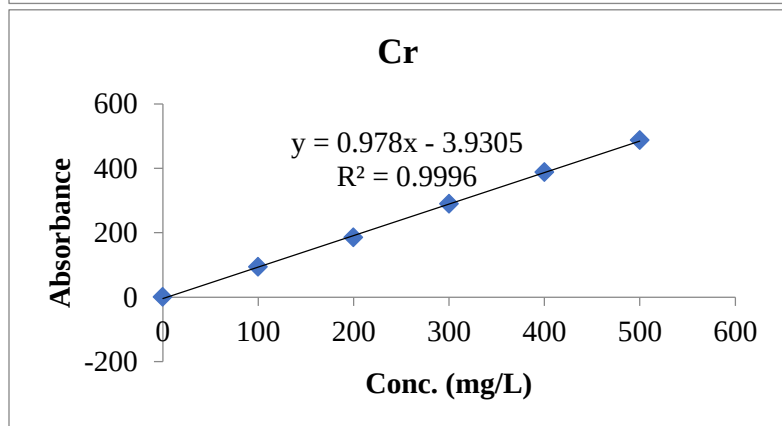
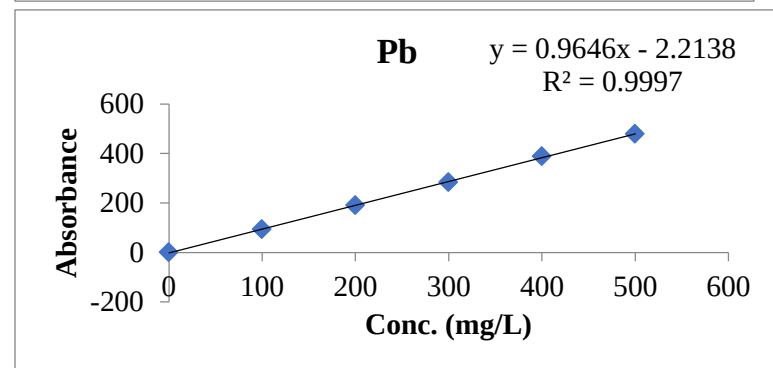
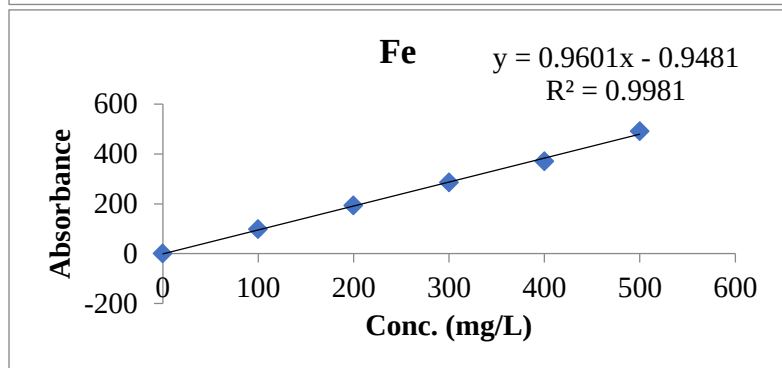
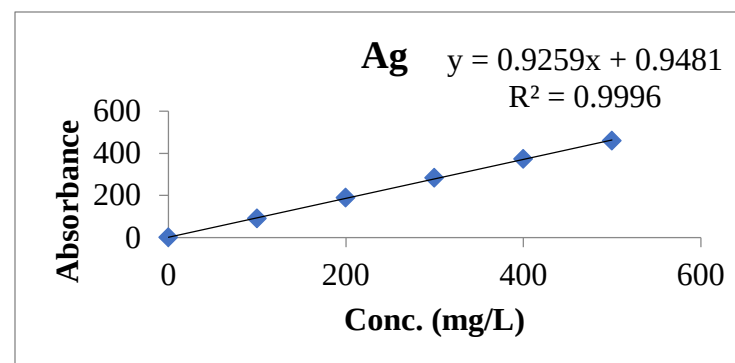
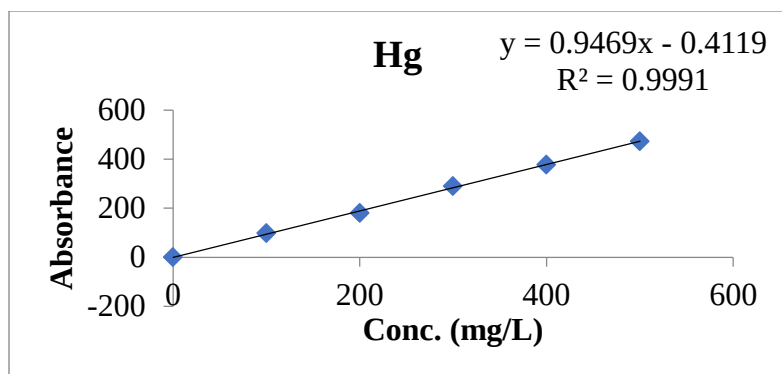
Appendix E

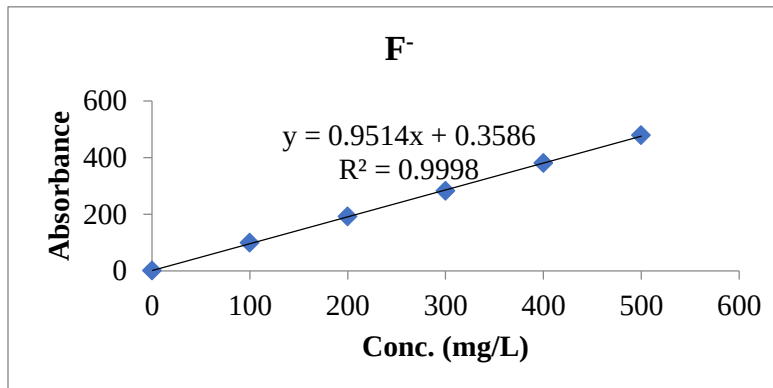
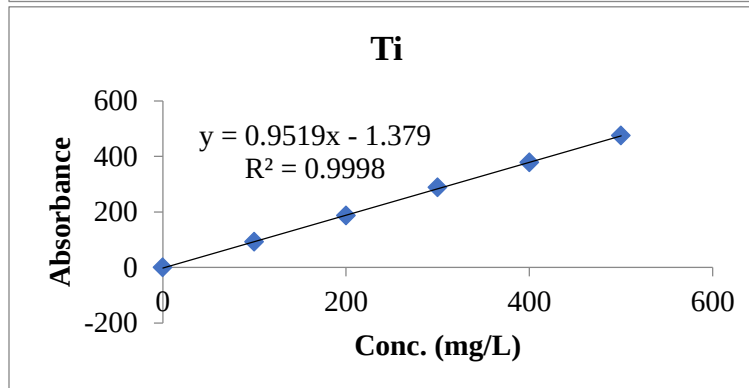
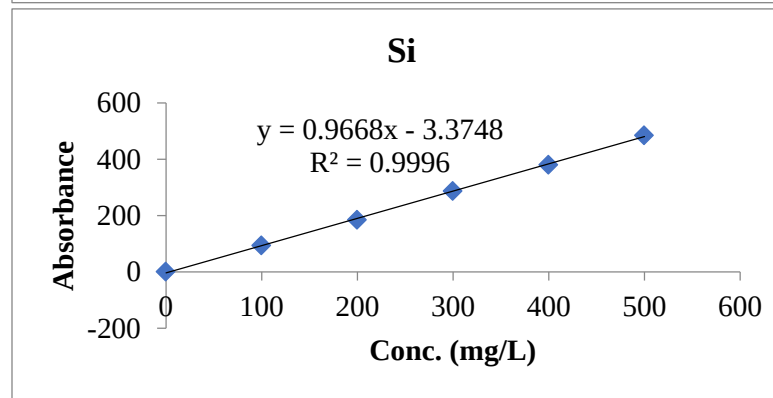
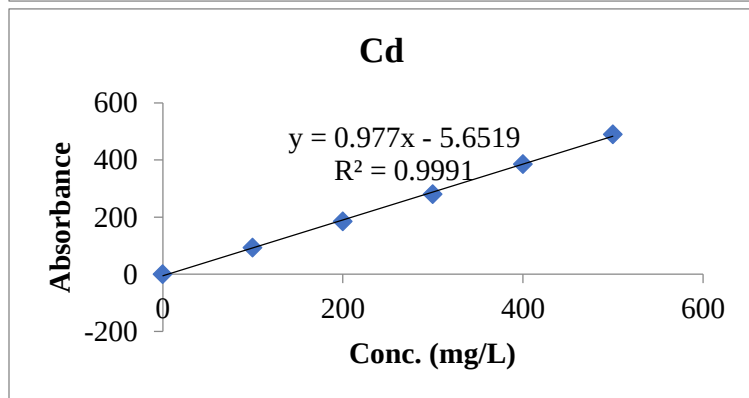
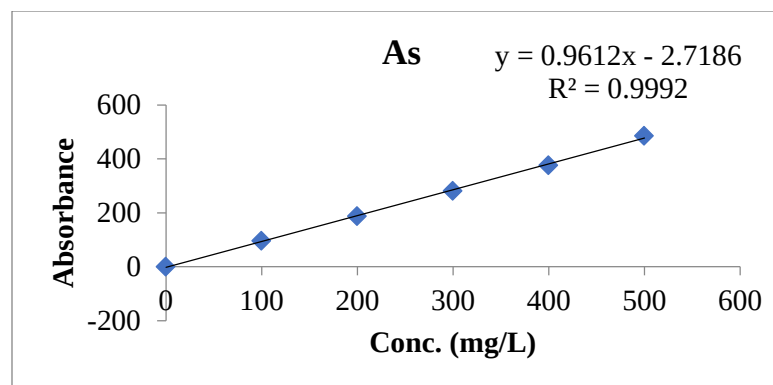
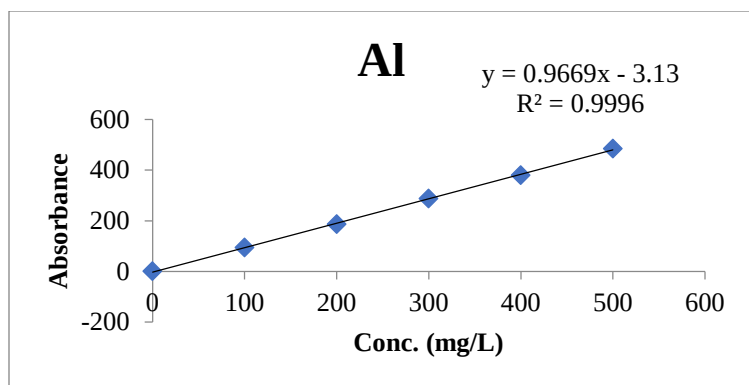
Table 6.50: Initial total ions concentration of the wastewater sample

Cations	Conc. (mg/L)	Anions	Conc. (mg/L)
Co	0.342 ± 0.0023	F ⁻	6.453 ± 0.056
Ni	0.271 ± 0.0081	Cl ⁻	56.318 ± 0.017
Zn	0.431 ± 0.0013	SO ₄ ²⁻	2.523 ± 0.0081
Cu	0.864 ± 0.0006	PO ₄ ³⁻	5.946 ± 0.0019
Hg	0.007 ± 0.0002	NO ₂ ⁻	4.256 ± 0.0112
Ag	0.641 ± 0.0008	BrO ₃ ⁻	0.978 ± 0.061
Fe	0.645 ± 0.009	NO ₃ ⁻	8.331 ± 0.002
Pb	0.216 ± 0.0030		
Cr	0.0645 ± 0.0033		
Mg	12.342 ± 0.0092		
Al	0.742 ± 0.0053		
Ar	0.142 ± 0.0034		
Cd	0.043 ± 0.0035		
Si	0.002 ± 0.0006		
Ti	ND		

Appendix F







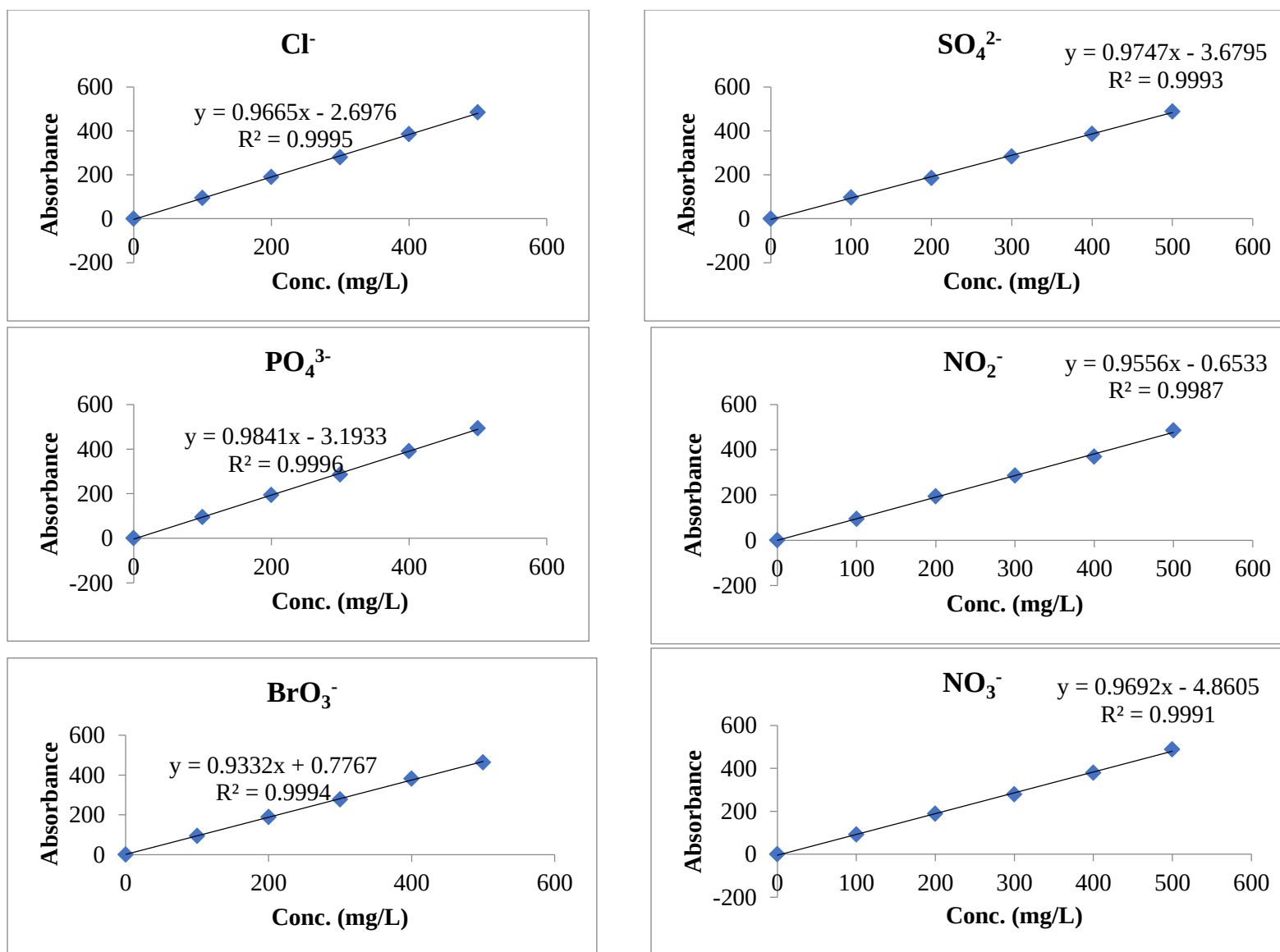
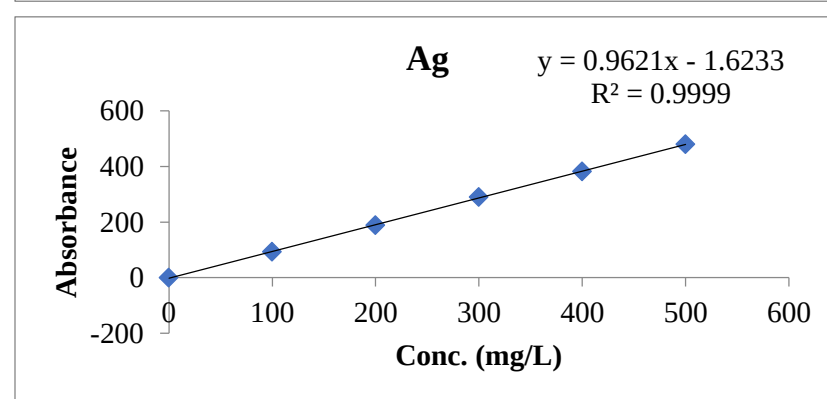
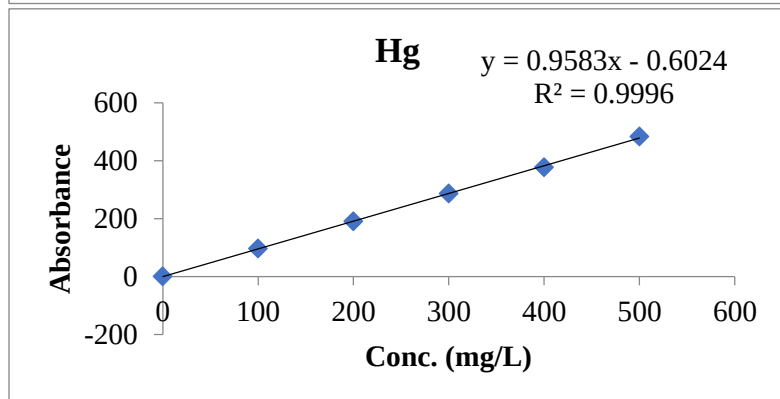
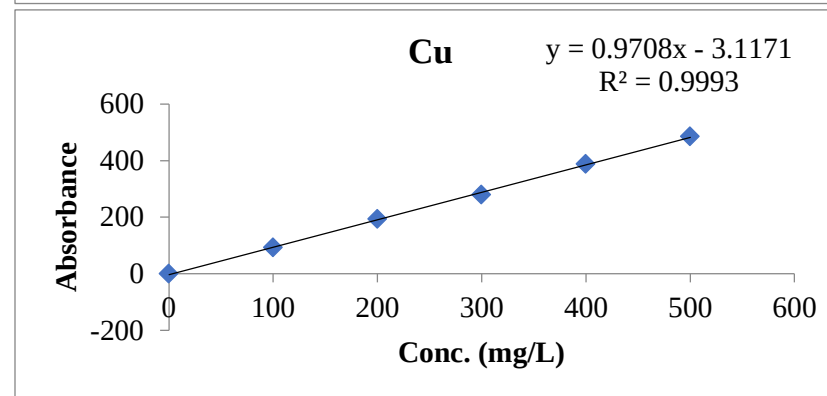
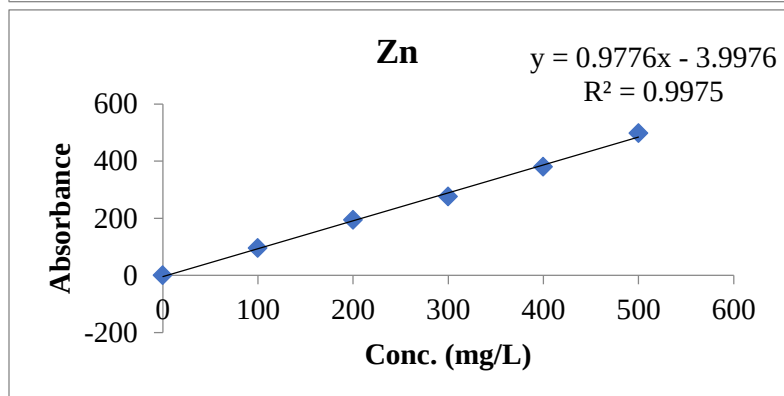
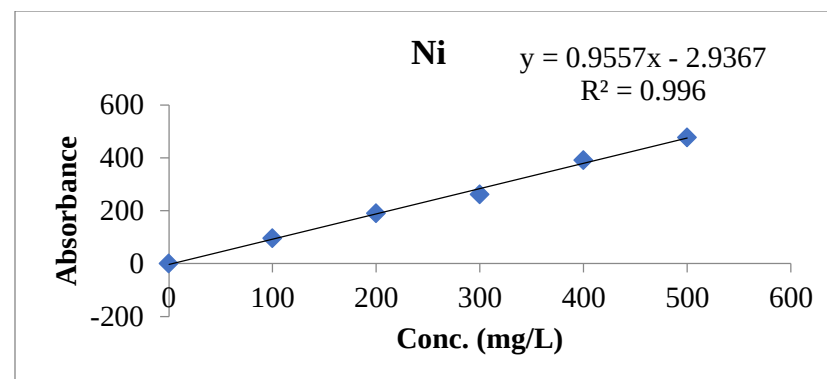
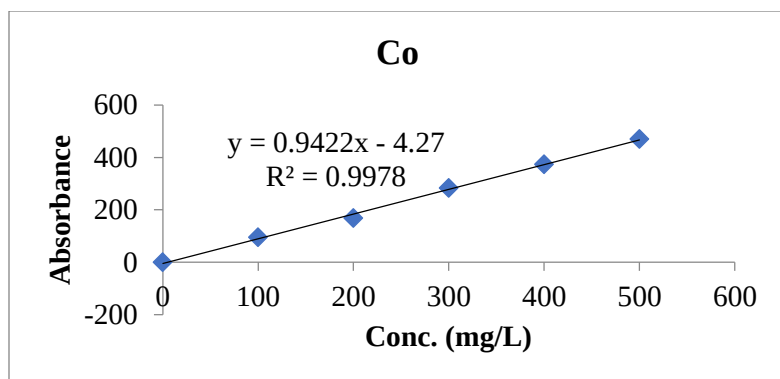
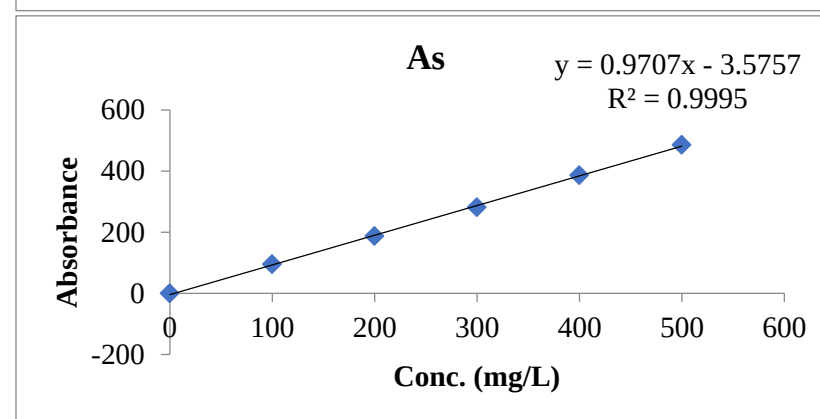
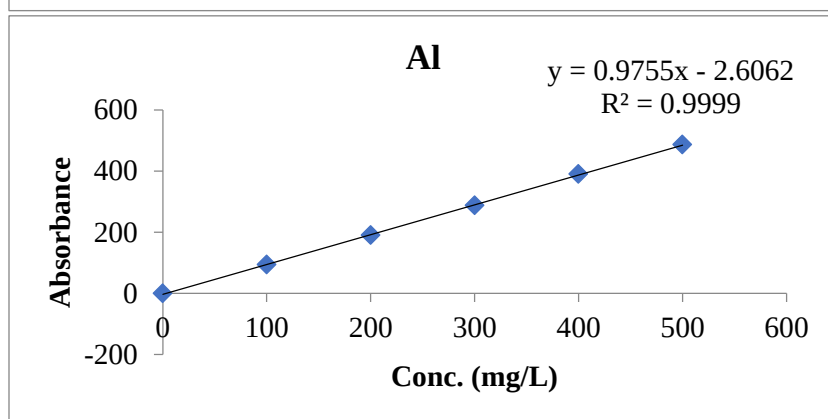
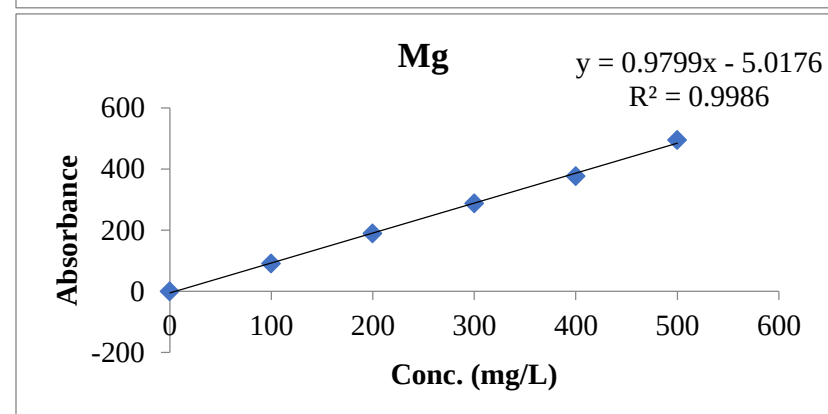
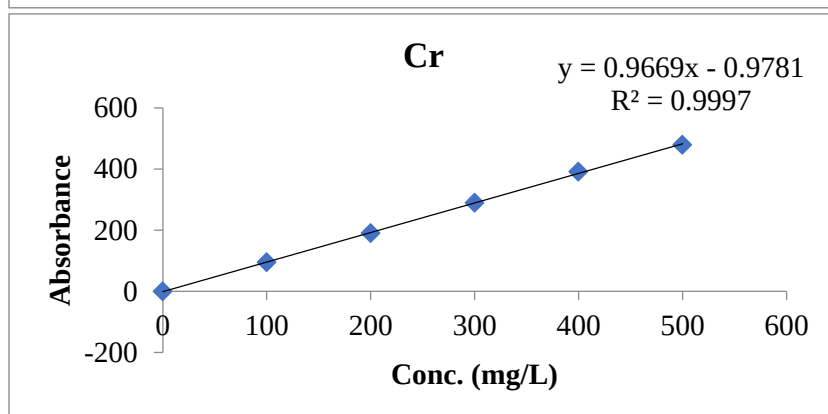
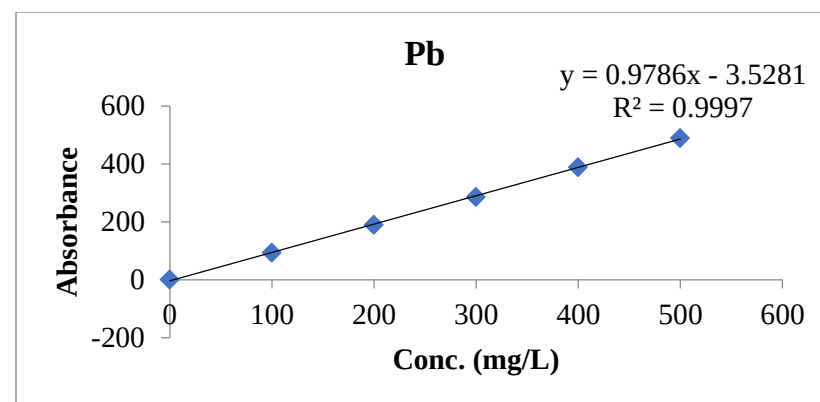
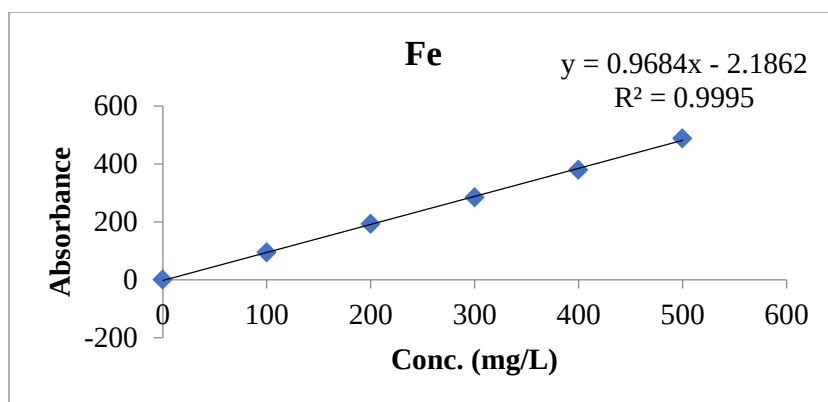
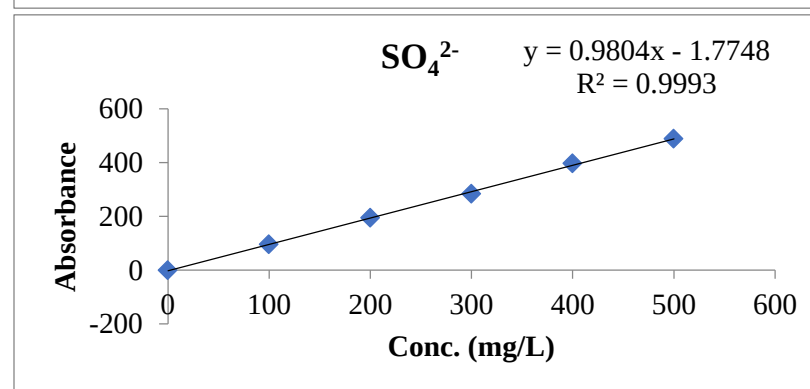
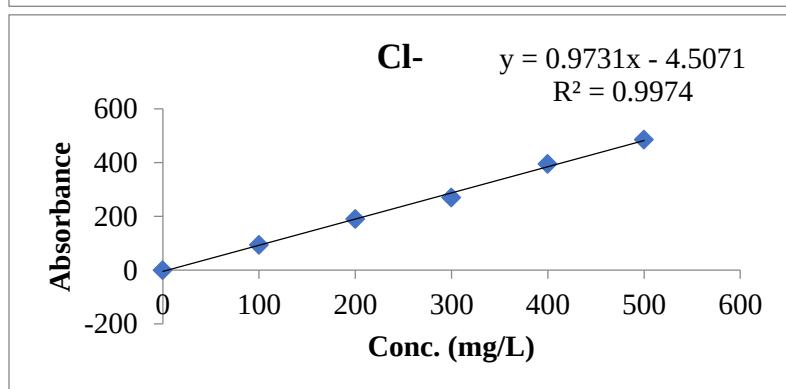
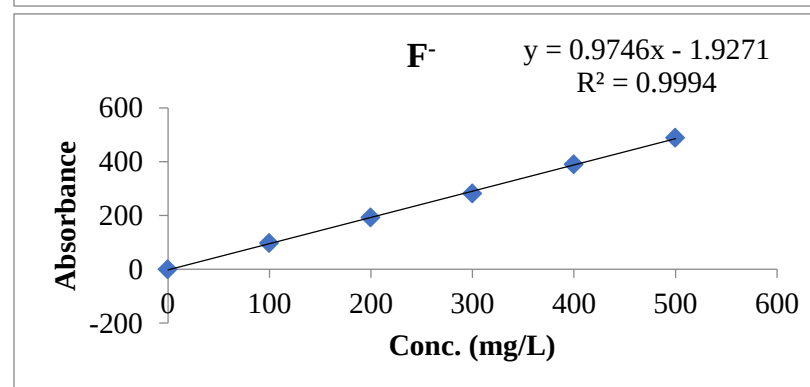
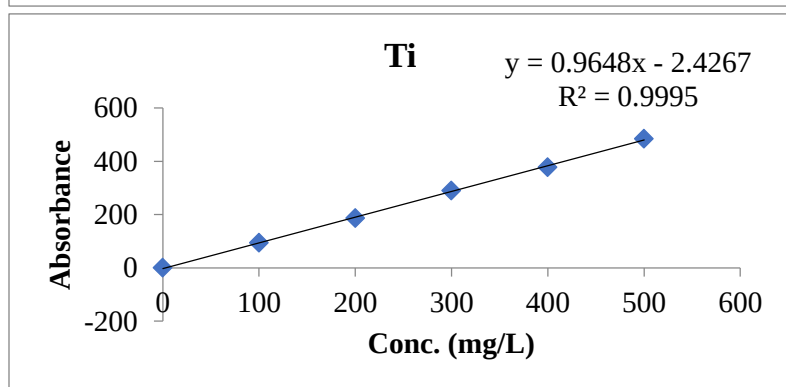
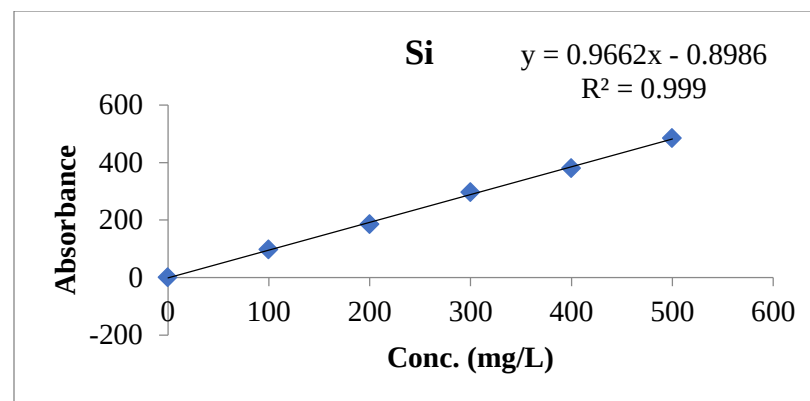
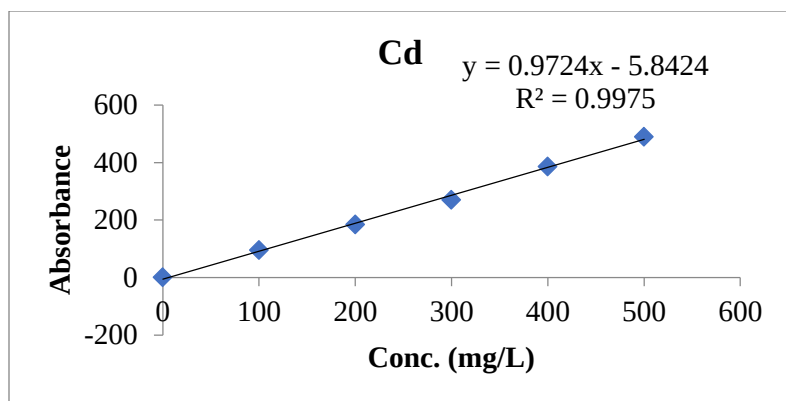


Figure 6.13: Calibration curves of the selected ions for the fish scale VWMs







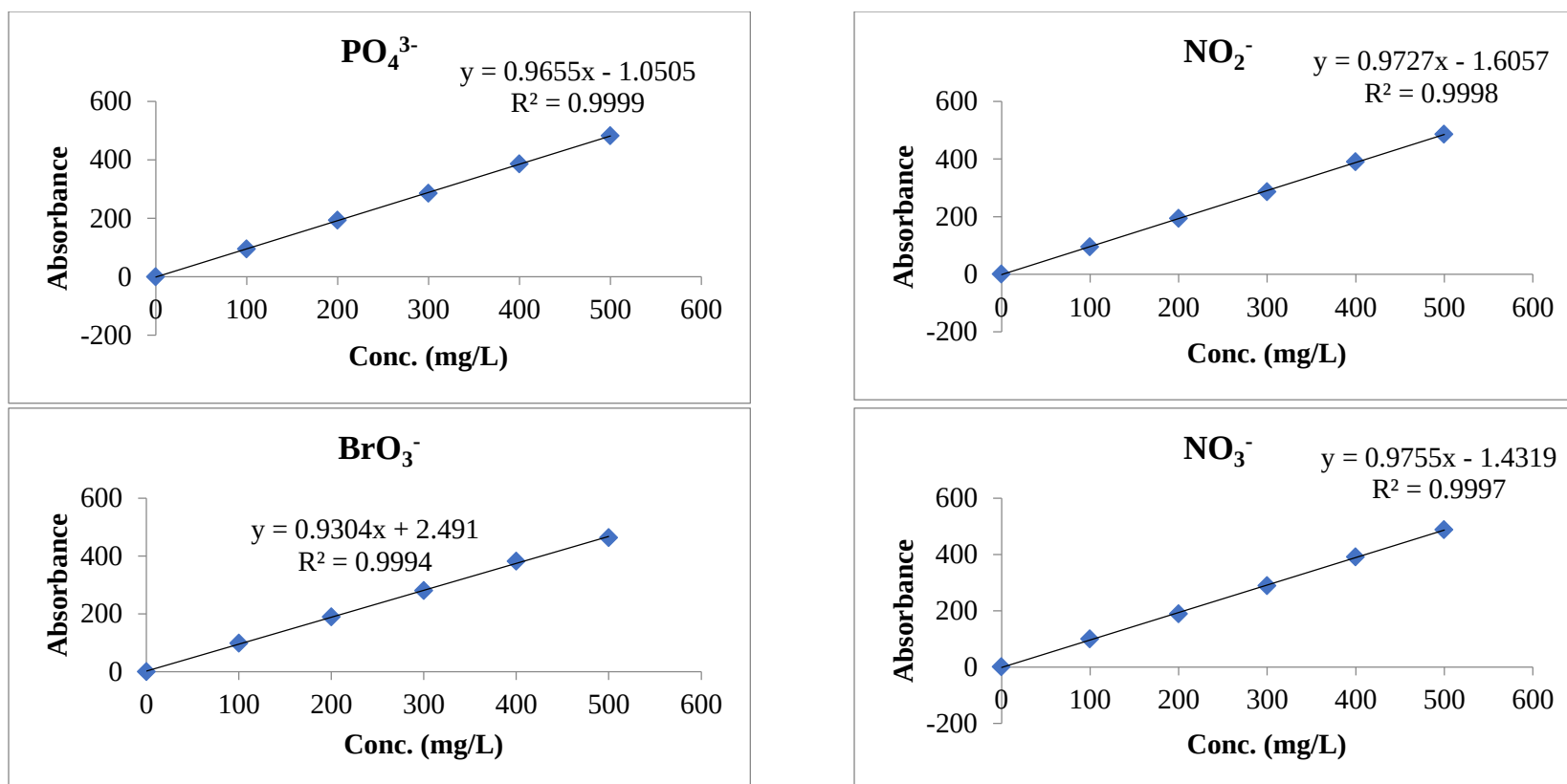


Figure 6.14: Calibration curves of the selected ions for the eggshell VWMs

