UTILIZATION OF *BRACHYSTEGIA SPICIFORMIS* (MSASA) LEAF POWDER IN THE REMOVAL OF NITRATES FROM WASTEWATERS: AN EQUILIBRIUM STUDY

by

Isheanesu Hungwe

(R092183V)

Submitted in partial fulfilment of the requirements for the degree of

Bachelor of Science Honours in Chemical Technology

Department of Chemical Technology

in the

Faculty of Science and Technology at the

Midlands State University

Supervisor: Mr M Shumba

Co-supervisor: Dr E Muleya

May 2014

DEDICATION

To my mother and in loving memory of my late father.

ACKNOWLEDGEMENTS

Firstly I would like to thank Almighty God for the gift of life and leading me through daily tragedy life experiences as well as the guidance during the course of my first degree. Really "To God be the Glory". I would like to extent my acknowledgement to my mother and my late father who made my school studies worth-doing through their prayers, financial support, daily encouragement and patience. I acknowledge Reginah, Nyaradzo, Fortune, Faith and Takunda. I would also like to thank my project supervisors, Mr. M. Shumba and Dr. E. Muleya their handful during the course of this project. Also not forgetting my immediate friends, Mr. T. Ndumo, Mr. M. Zivurawa and Mr. P. Tendayi, who were associates. My thanks extends to the Midlands State University in particular the Department of Chemical Technology for opportunity to carry out academic research.

ABSTRACT

The investigation of nitrate adsorption onto *Brachystegia spiciformis* leaf powder from waste waters was performed. Characterization for the functional groups of the biomass before and after nitrate sorption as well as after desorption was done using an FTIR spectrophotometer. The effect of pH, contact time, dosage and initial nitrate concentration was investigated. The *Brachystegia spiciformis* leaf powder had amine, carboxylic and hydroxyl groups that were involved in nitrate removal from aqueous environment. Optimum conditions for nitrate uptake were at pH 4, contact time of 30 minutes and biosorbent dose of 1.5 g and varying nitrate initial concentrations from 5 to 50 mg L^{-1}. The equilibrium data generated from the nitrate initial concentrations fitted the isotherms in the order Dubinnin-Radushkevich < Halsey = Freundlich < Langmuir < Temkin with correlation coefficient, R^2, values 0.9683, 0.9686, 0.9686, 0.9692 and 0.9792 respectively. The Freundlich`s adsorption intensity, n, ($0.1 < {}^{1}/_{n} < 1$) and the Langmuir`s separation factor, R_L, ($0 < R_L < 1$) revealed nitrate sorption favourability onto *Brachystegia spiciformis* leaf powder with the Langmuir`s sorption capacity of 1.6297 mgg^{-1}. Halsey and Freundlich isotherms evidenced surface heterogeneity and that the *Brachystegia spiciformis* had macro and micro pores. The Temkin and Dubinnin-Radushkevich isotherms indicated that the sorption process was based on physisorption and it was evidenced by heat of sorption constant, b_v. Nitrate desorption from the loaded *Brachystegia spiciformis* was achieved by increasing pH to alkaline conditions and the highest desorption ratio was achieved at 91.26 % at pH 11. After desorption the FTIR spectrum of *Brachystegia spiciformis* did not retain back its original spectrum.

DECLARATION

I, **Isheanesu Hungwe,** hereby declare that I am the sole author of this thesis. I authorize Midlands State University to lend this dissertation to other institutions or individuals for the purpose of scholarly research.

Signature ……..

Date ……..

APPROVAL

This dissertation entitles **"Utilization of *Brachystegia spiciformis* (Msasa) leaf powder in the removal of nitrates from wastewaters: An equilibrium study"** by **Isheanesu Hungwe** meets the regulations governing the award of the degree of **Bachelor of Science in Chemical Technology Honours** of the Midlands State University and is approved for its contribution to knowledge and literal presentation.

Supervisor ……..

Date ……..

TABLE OF CONTENTS

TITLE **PAGE**

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.0 Background

Farming activities and industrialization has resulted in the pollution of the environment. This is mainly due to the disposal of domestic and industrial wastes with high concentrations of organic and inorganic chemicals in to the environment and water bodies (Shao *et al*., 2009).

Waste water frequently contains nitrogen based compounds such as ammonia, nitrates and nitrites. Nitrates are a common toxic pollutant to humans and are introduced into natural waters from a variety of industrial activities such as fertilizer manufacturing, explosives, pharmaceuticals and nitro-organic compounds (Namasivayam and Sangeetha, 2005). Other sources of nitrate in drinking water are sewage, landfill leachate and animal manure. Most nitrogen containing compounds in natural waters tend to be converted to nitrate by the nitrification process (Gomez *et al*., 2000). Nitrates also occurs naturally in the environment, in mineral deposits, soil, seawater freshwater system and the atmosphere (Shao *et al*., 2009).

Water treatment costs are gradually increasing as the demand for water treatment chemicals is increasing and the supply is decreasing. Hence accessibility of quality drinking water is becoming a challenge particularly in developing countries like Zimbabwe (Utete *et al*., 2013). Consequently, diseases are spreading in humans due to contaminants in drinking water. The nitrate removal from water bodies is essential before being utilized. A large amount of nitrate in drinking water results in healthy disorders such as hypertension, thyroid disorder, stomach cancer, increased infant mortality (Shao *et al*., 2009), cytogenetic defects, birth defects and methemoglobinemia (Namasivayam and Sangeetha, 2005) .

Biological and physicochemical processes have been developed for nitrate removal from wastewaters (Namasivayam and Sangeetha, 2005). Generally separation processes of nitrates from waste waters includes reverse osmosis (Kesseru *et al*., 2002), ion exchange (Chatterjee *et al*., 2008), electrodialysis, electro-deionisation (Elmidaoni *et al*., 2004), distillation, Donnan dialysis (Ismail., 2007) and chemical denitrification. Known technologies employed are effective in nitrate removal from contaminated waters are very expensive (Kesseru *et al*., 2002). These drawbacks in nitrate removal from water and/or wastewater results in biological denitrification being the mostly used technology due to its cost effectiveness (Mateju *et al*., 2005).

The effects of carbon sources on the removal of nitrate from water and/or wastewater for biological processes have been studied before. Namasivayam and Sangeetha (2005) reported the potential use of $ZnCl_2$ activated carbon from coconut coir pith in the removal of nitrate from wastewaters. Use of high-area carbon cloth, protonated cross-linked chitosan and zeolite in nitrate removal was reported (Afkhami., 2003). Godini *et al*. (2010) stated the use of natural materials such as agar, agarose, collagen alginates and chitosan as well as synthetic polymeric materials for example polyacrylamide, polyurethane, polyethylene glycol and polyvinyl alcohol have been applied as media for nitrates removal. It is therefore of much interest of this research to determine the efficacy of *Brachystegia spiciformis* leaf powder in the removal of nitrates from aqueous solution.

1.1 Aim

To investigate the potential use of *Brachystegia spiciformis* leaf powder in the removal of nitrates from waste waters.

1.2 Objectives

- To characterize for functional groups of the *Brachystegia spiciformis* leaf powder before and after biosorption as well as after desorption using Fourier Transform Infrared Spectrometer (FTIR).
- To optimize pH, contact time, biosorbent dosage and initial concentration for the sorption of nitrates from solutions of known nitrate concentration.
- To investigate desorption of nitrates from the nitrate loaded *Brachystegia spiciformis* leaf powder.
- To assess the effective use of *Brachystegia spiciformis* leaf powder as an adsorbent on industrial effluent water (Sable Chemicals).

1.3 Problem Statement

The industries are unable to achieve the discharge limits of nitrates especially fertilizer manufacturing in their effluents using conventional treatment technologies (Godini *et al*., 2010). This is mainly due to the fact that industries will be focusing on their core business since it will be an extra expense to focus on water treatment. About 50% of water pollution are being caused by fertilizer run-off and from agricultural fields. Utete *et al*. (2013) and the Zimbabwe Ministry of Environment and Natural Resources Management (2011) reported high concentration levels of nitrates of well above 40 mg L^{-1} and 53 mg L^{-1} at Lake Kariba and Lake Chivero respectively. The World Health Organization (2011) have set the permissible limits to 45 mg L^{-1} and drinking water containing nitrate levels above the limit is unacceptable to consumers. High levels of nitrates in water causes severe problems such as eutrophication (Chatterjee *et al*., 2008). Bryan and van Grinsven (2013), Chatterjee *et al*. (2008) and Fewtrell (2004) stated the health effects of nitrates exposure through drinking water resulting in infectious diseases. These include cancer of the alimentary canal, cyanosis and methemoglobinemia or blue baby`s syndrome in pregnant women and children. Jensen and Darby (2012), Namasivayam and Sangeetha (2005) and Mateju *et al*. (2005) recommended conventional methods for the removal of nitrates from their studies. These include biological denitrification, chemical reduction, reverse osmosis, electrodialysis and anion exchange. They are all expensive (Pakniker *et al*., 2003) hence there is need for a cost effective method for nitrate remediation from aqueous environments.

1.4 Justification

Nitrates are discharged into the environment through agricultural and industrial activities. Conventional methods used to remediate the nitrates are expensive for example anion exchange, reverse osmosis as well electrodialysis. Previous researches by Moyo *et al*. (2012), Shao *et al*. (2011) and Namasivayam and Sangeetha (2005) proved the potential use of sunflower seed husks, rice husks and coconut coir pith respectively to be successful for the removal of nitrate from contaminated wastewaters. The potential use of *Brachystegia spiciformis* might be possible because it is suspected to contain hydroxyl, amine and carboxylic groups as the previously studied biosorbents. Thus the functional groups aid in the sorbate-sorbent interaction as stated by Chigondo *et al*. (2013). *Brachystegia spiciformis* is abundantly an indigenous plant covering more than 60% of the Southern Africa`s woodlands (Saidi and Ramatshimbila, 2006; Mabveni *et al*., 2004 and Garwe *et al*., 2009). The plant can survive in semiarid environments hence can be grown in all parts of Zimbabwe. It being in abundance and inexpensive, *Brachystegia spiciformis* as a biosorbent can be an alternative to nitrate removal from waste waters compared to expensive commercial methods for industrial water treatment. Also the nitrate rich plant powder can be used as fertilizer after the biosorption so as to increase plant growth and yields. The use of *Brachystegia spiciformis* as a biosorbent for the removal of nitrate ions has not been reported as yet and this gives motive to venture on this research.

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

This chapter gives the background information on nitrates pollution, conventional methods for treatment of nitrates from waste waters and the structural composition of the *Brachystegia spiciformis* leaves. It also covers the chemistry of the *Brachystegia spiciformis* leaves with respect to biosorption process and reports findings by other researchers and mechanism behind biosorption.

2.1 Nitrate and environmental pollution

Nitrate (NO_3^-) is an ion that contains nitrogen and oxygen arranged in a trigonal planner manner having a molecular weight of 62.0049 g mol^{-1}. The structure of a nitrate ion is as shown below.

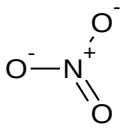

Figure 2.1: Chemical structure of a nitrate ion

Inorganic nitrates salts are water soluble at room temperature and pressure and they involve salts of nitric acid such as KNO_3, $NaNO_3$ and $Ca(NO_3)_2$. Nitrate ion is produced when nitrogen from ammonia or from different source reacts with oxygenated water. It is contained in water in plants in different levels. Usually livestock droppings, domestic wastes, industrial waters, potassium nitrate and ammonium nitrate contributes nitrates as fertilizers to plants. When nitrates are in excess, depending on plant, they stimulate plant growth and gives rise to eutrophication as well as death of aquatic organisms. This is as a result of depriving the aquatic life of oxygen.

World Health Organisation (2011) highlighted that higher concentration of nitrates exceeding 45 mg L^{-1} in drinking water results in blood disorder in humans. The disorder takes place via nitrate

eutrohepatic metabolism that gives rise to ammonia having nitrate being the intermediate. Nitrates are absorbed in bloodstream where they oxidize ferrous iron, Fe^{2+}, in haemoglobin to ferric iron, Fe^{3+}. This inhibits haemoglobin from oxygen access and consequently the organ tissues will be deprived of oxygen giving rise to a condition called methemoglobinemia. Methylene blue can however be used to treat the disorder and it reduces Fe^{3+} ion in blood cells to Fe^{2+}. Generally infants are at risk to higher nitrate levels than adults. This is mainly due to their stomachs that are less acidic resulting in nitrates being simply converted to nitrites by the *Eschericia coli* bacteria (Kim-shapiro *et al*., 2005; WHO, 2011).

Methemoglobinemia concentrations exceeding 25 % results in bluish skin and lips in infants and the condition can also be referred to as the blue baby`s syndrome. Nitrates affects animals as well and they cause intestinal disorder in rats, pigs, depression, body weight loss and reduced water consumption particularly in chicken (Tejero *et al*., 2012).

2.2.0 Current nitrates removal methods

The removal of nitrates from waste waters is achieved by physico-chemical processes before discharging the effluent into natural water body systems. There are quite a number of commonly used treatment technologies available for the reduction of nitrates in drinking water as well as the effluent industrial waters. These include ion exchange, biological denitrification, electrodialysis, reverse osmosis and chemical reduction (Chatterjee *et al*., 2008).

2.2.1 Ion Exchange

In ion exchange, water is passed through synthetic bed of resins which plays a role in removal of anions including nitrates from water, exchanging them for equivalent amounts of chlorides (Onyango *et al*., 2010). The resin bed is then taken out of service once the exchange capacity of the resin is reached. The resin is regenerated using sodium chloride solution, which returns back

to the chloride form. After being rinsed with clean water the bed is returned to service. The spent regenerant contains a high concentration of sodium chloride together with the anions removed from the resin bed (Jensen and Darby, 2012).

2.2.2 Denitrification

Denitrification is a biological process that exploits the ability of certain naturally occurring heterotrophic bacterial to use nitrate for respiration under anoxic conditions. Denitrification is achieved using both heterotrophic (*Paracoccus denitrificans*) and autotrophic (*Thiobacillus denitrificans and Thiomicrospira denitrificans*) bacteria. In heterotrophic denitrification, an organic carbon substrate such as methanol, ethanol or acetic acid is required as food source for the bacteria. Chemical equation 2.1 represents the process of heterotrophic denitrification.

$$6NO^{-}_{3(aq)} + 5CH_3OH_{(aq)} \rightarrow 3N_{2(g)} + 5CO_{2(g)} + 7H_2O_{(aq)} + 6OH^{-}_{(aq)} \text{.....(2.1)}$$

In autotrophic denitrification an inorganic source such as sulphur, reduced sulphur species for example thiosulphate or hydrogen is required (Deodyvet, 2009). The carbon needed for bacterial growth is obtained from bicarbonate in water. Once the bacteria breaks down the nitrates to gain the oxygen, the nitrate is reduced to nitrous oxide and in turn nitrogen gas. Nitrogen has a lower solubility in water, hence it escapes to the atmosphere as bubbles and it does not cause any environmental effect. The process occurs at pH values ranging from 7.0 to 8.5. Chemical equation 2.2 shows the process of autotrophic denitrification.

$$55S_{(s)} + 20CO_{2(g)} + 50NO^{-}_{3(aq)} + 38H_2O_{(aq)} + 4NH^{+}_{4(aq)} \rightarrow 4C_5H_7O_2N_{(s)} + 25N_{2(g)} + 55SO^{2-}_{4(aq)} + 64H^{+}_{(aq)} \text{.....(2.2)}$$

Autotrophic denitrification is advantageous over heterotrophic denitrification in that, an external carbon source such as methanol and ethanol which may result in lowering of costs. Also there less risk of sludge production hence handling of sludge is minimized.

Biological denitrification proved to be feasible, advanced, selective and most effective process for removing nitrates. The process has two major disadvantages as it is only efficient at high temperatures and the treatment process is slow (Jensen and Darby, 2012).

2.2.3 Electro-dialysis

It is an electrically driven process that utilizes high voltage to promote the movement of charged ions through a semi-permeable membrane, thereby reducing the contaminants in water. It makes use of alternating semipermeable cation and an anion transfer membranes in a direct voltage potential field. Uncharged particles are not removed (Pakniker *et al*., 2003). This technology is advantageous in that it involves the separation of ions without phase change which results in relatively low energy consumption and it is suitable for the separation of non-ionized and ionized components. Batista and Pinter (2007) stated a major disadvantage of this method of giving rise to membrane clogging due to formation of metal hydroxides. Hence there is need for a cheap clogging-free method for the removal of nitrates.

2.2.4 Reverse Osmosis

It is a process for the removal of dissolved ions from water in which pressure is used to force water through a semi-permeable membrane element which will pass the pure water but reject most of the dissolved materials. The separation of the ions is aided by charged particles thus the dissolved ions that carry a charge are likely to be rejected by the membrane than those that are not charged such as organics (Ryan, 2002). Reverse osmosis is advantageous in that there is high regeneration rate for a wide range of contaminants and very cost effective in the long term. However it has drawbacks of being expensive and the process is slow and it is not applicable for large sums of waste. The process also requires sediment and carbon pre-filtration to prevent membrane fouling.

2.3.0 Biosorption

It is a process by which ions are bound from aqueous environments by dead, inactive, microbial biomass. The process involves a biological solid phase material referred to as the biosorbant as well as a liquid phase containing a dissolved species to be sorbed. The sorbate species is attracted and bond through different types of mechanisms to the sorbent (Pollard *et al*., 2001). The process takes place up to equilibrium establishment between the amount of solid-bound sorbate species and its portion remaining in the solution (Pollard *et al*., 2001).

2.3.1 Biosorption mechanisms

The biosorption process involves several mechanisms that differ quantitatively and qualitatively according to the sorbent type, its origin and processing. The mechanism of biosorption can be classified as metabolism dependent or non-metabolism dependent. The mechanisms involves physisorption, chemisorption, ion exchange, chelation, coordination, micro-precipitation and entrapment in inter or intra-fibrillar capillaries and spaces of the structural polysaccharides networks of the biosorbent (Atkins and de Paula, 2010; Ong *et al*., 2010).

2.3.2 Physisorption

If the interaction between the solid surface and the adsorbed molecules has a physical nature the process is called physisorption .In this case the attraction interactions between the adsorbate and the substrate are van der Waals forces which are weak and the process is reversible. It is also referred to as a physical adsorption process (Atkins and de Paula, 2010). The change of enthalpy of physisorption ranges around the 20 $kJmol^{-1}$ region and the energy is not enough to promote bond breakage resulting in a molecule that have been sorbed to retain its identity.

2.3.3 Chemisorption

It is a process that involves the attraction forces between the adsorbed molecules and the solid surface are due to chemical bonding and the adsorption process can also be referred to as chemical adsorption (Atkins and de Paula, 2010). Chemisorption occurs as a monolayer, substances chemisorbed on solid surface are hardly removed because of stronger covalent bonds. The molecules chemisorbed finds sites that may results in their coordination number being maximized from the substrate. The energy change of chemisorption greater than that of physisorption and usually have values that are around the 200 kJ mol^{-1}, having shorter distance between the surface and the nearest adsorbate atom as compared to that of physisorption (Atkins and de Paula, 2010).

2.3.4 Ion exchange

In ion exchange, counter ions of the polysaccharides exchanges with the bivalent ions. For example anion exchange on biopolymers occurs onto variety of organic-nitrogen-based groupings. In proteins, amino, imidazole and guanidine groupings are common centers of positive charge. Centers of positive charge in nucleic acids will occur with protonation of amino groups on purine or pyrimidine rings or with protonation of heterocyclic nitrogen atoms. Polysaccharides as a group are acidic or neutral macromolecules with basic functional groups being rare and arising as un-acetylated amino-sugars. Chitin is the notable example where a proportion of glucosamine residues are reportedly un-acetylated and which provides on deacetylation chitosan with a high proportion of protonisable positive charge centers (Setshedi *et al*., 2010)

2.3.5 Factors affecting Biosorption

Knowledge of the factors that affect biosorption process is of importance to promote industrial application since it gives a picture of the equilibrium process such that the equipment design will

be easy. There a number of factors that affect biosorption process and they include initial concentration, pH, temperature, contact time, sorbent dosage and particle size.

The amount of anions adsorbed per unit mass increases with an increase in initial ion concentration. This increase could be due to the increase in electrostatic interaction involving sites of progressively lower affinity for ions. Ions adsorbed increases with an initial concentration increase since the ionic molecules migrates into macro and meso porous structure of the biosorbent at high initial anion concentrations in aqueous environment (Pehlivan *et al*., 2008).

pH is also an important parameter that affect the solution chemistry of the anions, activity of functional groups in the biomass and competition of the metallic ions .The sorption of anions mainly occurs at lower pH values. Setshedi *et al*. (2010) highlighted that at low pH, high electrostatic attractions are as a result of positively charged groups of the biomass` surface and the adsorbate which will be negatively charged. Hence pH affects the interactions of ions or species in solution and the adsorbent sites by either protonation or deprotonation.

The extant of adsorption is proportional to the specific surface area which is defined as that of the total surface that is available for adsorption. Thus the more finely divided and more porous is the solid biosorbent the faster the rate of sorption (Park *et al*., 2002).

Generally ion uptake increases with an increase in contact time upto when a constant uptake is attained. Initially ion removal is faster due to the availability of more vacant sites for sorption process (Park *et al*., 2002).

Also temperature affects biosorption process. An increase in temperature results in increase in the diffusion of the adsorbate across the external boundary layer and in the internal porous adsorbent particle, since there will a decrease in solution viscosity (Setshedi *et al*., 2010).

2.4 Mechanism of nitrate sorption by *Brachystegia Spiciformis*

Recently much have not been reported on the anionic removal from aqueous using *Brachystegia Spiciformis*. Previously Chigondo *et al*. (2013) investigated the potential use of *Brachystegia Spiciformis* in the removal of Zn^{2+} ions from an aqueous environment. In their study the biosorbent was found to be useful through electrostatic attractions between the sorbent and the Zn^{2+} ions. Moreover, quite a number of biosorbents were used utilized in the removal of nitrates from aqueous solution. These involve sunflower seed hulls (Moyo *et al*., 2012), rice hulls (Shao *et al*., 2011) and coconut pith (Namasivayam and Sangeetha, 2005). They found out that hydroxyl, amine, carboxyl, and carbonyl groups were responsible for binding with the nitrate ions with the help of protons in aqueous phase. Hence in this research such types of interactions are also expected to happen during the nitrate sorption on to *Brachystegia Spiciformis* in acidic conditions.

2.5.0 Biosorbent characterization and nitrate determination in aqueous solutions

Fourier transform infrared spectroscopy is a technique used for characterization of functional groups in a given compound. Different analytical methods are employed for nitrate determination in aqueous solution. Ultraviolet-visible spectroscopy and ion chromatography are widely used (Narayana and Sunil, 2009; Lastra, 2003 and Yang *et al*., 2004).

2.5.1 Functional group determination

Fourier transform infrared spectroscopy technique is used for the determination of the functional groups responsible for the sorption process. Adsorption in the infrared region occurs due to vibrational and rotational motions giving rise to stretching and bending of molecular groups (Pavia *et al*., 2007).

The pressed-disk is applied as a solid sample handling technique on fourier transform infrared spectroscopy. The technique makes use of dry powdered potassium bromide or other alkali metal

halides that is compacted under pressure to form a transparent disk. The sample is thoroughly mixed with powdered KBr in the ratio 1:10 (Silverstein *et al*., 2005). Mixing is effected by grinding in smooth agate mortar using a pestle after which the mixture is compacted under a pressure of 11000-14000 psi using a bolt while in a nut having one bolt in place until a transparent disk is achieved. The transparent disk is referred to as the cell and the quality of spectrum depends on the degree of mixing as well as particle size reduction to less than 2 µm. The cell is analyzed on calibrated spectrophotometer to promote appearance of bands at their appropriate frequencies. Calibration is done using polystyrene film standards. Generally care must be greatly taken in cell or disk handling, use of moisture free samples as well as prevention of contaminants such as silicones that are difficult to remove and they give rise to strong absorption patterns. (Silverstein *et al*., 2005).

2.5.2 Nitrate determination using ultraviolet visible spectrophotometer

Nitrate can be determined by coupling it to salicylic acid in concentrated sulphuric acid to produce a nitro derivative. Sodium hydroxide is added to the mixture and results in a yellow colour. The yellow colour is as a result of the rearrangement of the nitro derivative structure and it obeys the Beer Lambert`s law which is states that absorbance is directly proportional to the concentration of the analyte in a sample. Using an ultra-violet visible spectrophotometer the concentration of nitrates is determined at a wavelength of 410 nm (Lastra, 2003; Yang *et al*., 2004).

2.6.0 Biosorption equilibrium models

Biosorption isotherm models closely describes the adsorption behavior of a adsorbate to the adsorbent and the model has been applicable without exception The equilibrium biosorption process is often described by fitting the experimental points with models usually for representation of isotherm adsorption equilibrium. The widely used isotherms are:

2.6.1 Langmuir

It is an isotherm that is used to describe the relationship between the adsorbed material and its equilibrium concentration in solution (Dada *et al*., 2012; Oladoja *et al*., 2009). It works under the assumption that the biosorbent homogenous surface that have identical sites are energetically equivalent. It also assumes that adsorption occurs on open surface and molecules easily access the adsorption site. Each vacant site carries equivalent number of adsorbed molecules and there will never be any interaction between molecules of the adsorbate that occurs (Oladoja *et al*., 2009). Langmuir is represented by a general mathematical relationship as shown by equation 2.1.

$$Q_e = {}^{Q_M b C_e}/_{1 + bC_e} \quad \text{..... (2.1)}$$

Where: C_e is the concentration in ppm at equilibrium of the adsorbate,

Q_e is the amount of the adsorbent at equilibrium in mg g^{-1},

b is the Langmuir isotherm constant in L mg^{-1},

Q_M is the maximum sorption capacity of the adsorbate in mg g^{-1}

(Nidheesh *et al*., 2012; Das *et al*., 2008).

The characteristics of the Langmuir model can as well be expressed in terms of the equilibrium parameter or separation factor, R_L, given by equation 2.2:

$$R_L = {}^{1}/_{1 + bC_i} \quad \text{..... (2.2)}$$

Where C_i is the initial nitrate concentration in mgL^{-1}. If the $R_L > 1$, the isotherm will not be favourable, if $R_L = 1$, the isotherm will be linear, if $R_L = 0$, the isotherm will be irreversible and if $0 < R_L < 1$, the isotherm will be favourable (Samarghandi *et al*., 2009; Nharingo *et al*., 2013)

2.6.2 Freundlich

Freundlich isotherm model works under the assumption that the adsorption process that takes place on a heterogenous surface of adsorption capacity is related to the concentration of the adsorbent (Oladoja *et al*., 2009). The Freundlich is represented by the mathematical relationship as shown by equation 2.3.

$$Q_e = F_F C_e^{\frac{1}{n}} \quad \text{(2.3)}$$

Where: Q_e is the amount adsorbed in mg g^{-1} at equilibrium,

C_e is the equilibrium concentration of the adsorbate in mg g^{-1},

n is the adsorption intensity in g L^{-1} and,

K_F is the adsorbent capacity in (mg g^{-1})(L mg^{-1})^n

The value of n represents the parameter that characterize the quasi-Gaussian enegetic heterogeneity of the surface of adsorption. Moyo *et al*. (2012) and Samarghandi *et al*. (2009) highlighted that the adsorption intensity, n, should be within the range of 1 to 10 in order to the classify the favorability of the adsorption process. Also the value of $1/n$ should fall within the heterogeinity range of $0.1 < 1/n < 1$ for the sorption process to be favourable of the sorption process (Moyo *et al*., 2012).

2.6.3 Dubinin-Radushkevich

It is an isotherm that estimates the biomass` characteristic porosity as well as the energy of adsorption (Ho *et al*., 2009; Itodo and Itodo., 2010). It is given by a mathematical expression as shown by equation 2.4.

$$Q_e = Q_W e^{-K_{ad}\varepsilon^2} \quad \text{..... (2.4)}$$

Equation 2.4 can be linearized to the form shown by equation 2.5.

$$\ln Q_e = \ln Q_W - 2B_W RT \ln\left[1 + {}^{1}/_{C_e}\right] \quad \text{.....(2.5)}$$

Where: Q_e is the amount of the adsorbed nitrates at equilibrium in mg g^{-1},

Q_W is the adsorption capacity in mg g^{-1},

C_e is the nitrate equilibrium concentration in mg L^{-1},

B_W is the adsorption energy constant in $mol^2\ kJ^{-2}$ and

R and T are the ideal gas constant (8.314 kJ $mol^{-1}\ K^{-1}$) and the temperature (298 K) respectively (Oladoja *et al*., 2009).

The mean free energy is obtained from a mathematical relationship given by equation 2.6 (Nharingo *et al*., 2013).

$$E_W = {}^{1}\Big/_{[2B_W]^{1/2}} \quad \text{.....(2.6)}$$

2.6.4 Temkin

Temkin isotherm estimates the heat of sorption and the indirect adsorbate-adsorbate interaction on process of adsorption (Itodo and Itodo., 2010). It works under the assumption that heat of sorption is linear and binding energy is uniformly distributed up to when a maximum binding energy is attained (Vadi *et al*., 2011). It is given by a mathematical relationship as shown by equation 2.7.

$$Q_e = {RT}/{b_v} \ln[K_t C_e] \quad \ldots\ldots(2.7)$$

Where: T is the absolute temperature (298 K),

R is the ideal gas constant (8.314 kJ mol^{-1} K^{-1}),

K_t is the equilibrium binding constant (L mg^{-1}),

Q_e is the amount adsorbed at equilibrium (mg g^{-1}),

C_e is the equilibrium concentration (mg L^{-1}) and,

b_v is constant that is related to the heat of sorption (kJ mol^{-1}).

2.6.5 Halsey

It is an isotherm that predicts multilayer adsorption (Oladoja *et al*., 2009). Equilibrium data fitting to this model gives the heteroporocity of the surface of the adsorbent (Samarghandi *et al*., 2009). It is given by a general mathematical relationship as shown by equation 2.8.

$$Q_e = e^{\left[{[\ln K_h - \ln C_e]}/{n}\right]} \quad \ldots\ldots(2.8)$$

Where: n and K_h are the exponent and adsorption isotherm constant respectively,

Q_e is the amount adsorbed during sorption in mg g^{-1} and,

C_e is the equilibrium concentration in mg L^{-1}.

2.7 Advantages of biosorption

- It involves use of unused biomass leading to it being very inexpensive to use.
- It has proved to be highly efficient for quite a number of contaminants in industrial effluents for example removal of zinc ions from aqueous environment using *Brachystegia spiciformis* (Chigondo *et al*., 2013) and well as rremoval of dyes from an aqueous environments (Abdullah, 2005) .
- Minimization of chemical and biological sludge.
- Regeneration of biosorbent for reusability.
- Addition nutrient is usually not required since the biosorbent makes use of the functional groups on its entire structure hence there will always be higher probability of anionic recovery.

2.8 Desorption

Desorption is the detachment of adsorbed molecules or particles from a solid surface (Atkins and de Paula, 2010). It is the opposite of adsorption. Anion elution is of importance to ensure reusability of loaded adsorbent as well as recovery of adsorbed nitrates. Desorption studies also gives an evidence if the nitrate loaded biosorbent can desorb the nitrates after having been used as an organic fertilizer in agricultural fields Adsorbate by the ion exchange mechanism are desorbed and the desorption of molecules that were once as a result of chemisorption is difficult (Yu *et al*., 2007). Hence there is need for activation of particles from their foot of potential well that may result in vibration of the physisorbed molecules or particles from being shaken off the surface of

the substrate after a short period of time (Atkins and de Paula, 2010). This can be activated inform of alkaline condition if the sorption process was well favored in acidic condition. The rate of desorption of particles can be expressed as a percentage as shown by equation 2.9:

$$\%\text{age desorption} = {}^{Q_{des}}/_{Q_{ads}} \times 100\% \quad \text{.....(2.9)}$$

Where Q_{des} and Q_{ads} is the amount of particles desorbed and adsorbed respectively (Hale *et al*., 2013; Namasivayam and Sangeetha, 2005 and Woo *et al*., 2008).

CHAPTER 3

METHODOLOGY

3.0 Introduction

This chapter focuses on the procedure to be carried out in order to provide information by which this research will be judged its validity. This include sampling, preparation and preservation, characterization of the biosorbent as well as the sorption of the nitrates under different conditions. It also addresses how desorption is carried out as well as sorption of nitrates from industrial effluent under optimized conditions onto *Brachystegia spiciformis* leaf powder.

3.1 Sampling, preparation and preservation of biosorbent

Polythene bags were cleaned using tap water followed by cleaning three times with doubly distilled water. The bags were allowed to dry at room temperature. Dark green coloured *Brachystegia spiciformis* leaves were collected from Midlands State University field grounds. The leaves were collected while in cleaned polythene bags that were repeatedly washed with distilled water to remove dust as well as soluble impurities. The leaves were stored in a shade at room temperature and were sun dried until crisp and were ground using a pestle and mortar and passed through a 250 µm particle size sieve. The powdery leaf form was repeatedly washed with distilled water so as to remove colour and turbidity. The powder was oven dried at 92 ˚C until a constant mass was attained. The powder was put in air tight bottles and stored in a desiccator for further use (Chigondo *et al.*, 2013).

3.2 Biosorbent Characterization

Fourier Transform Infrared Spectrometer (Nicolet 6700) was used for functional group determination on *Brachystegia spiciformis* biosorbent. Three samples were prepared: (a) sample of *Brachystegia spiciformis* before sorption, (b) sample after sorption and (c) after nitrate

desorption. The pellet technique was used. Masses of 0.0500 g of the two powdered *Brachystegia spiciformis* were mixed with 0.5000 g powdered potassium bromide. Effective mixing was done by thoroughly mixing using a pistil and mortar and the mixture was transferred into the dry die and pressure was applied onto the die using the bolt and spanner. The compacted transparent discs were scanned from the range of 4000 cm^{-1} to 400 cm^{-1} on a Fourier Transform Infrared Spectrometer. The spectra were recorded (Quasier *et al*., 2009; Chigondo *et al*., 2013).

3.3 Preparation of nitrate stock solution and calibration solutions

Nitrate solution of 1000 mg L^{-1} was prepared by dissolving a mass of 1.6469 g potassium nitrate that was obtained by calculation using the formula in Appendix A4 in 1000 ml distilled water. The solution was diluted to 1000 ml volumetric flask mark using distilled water. From a 1000 mg L^{-1} stock solution, 100 mg L^{-1} was prepared by pipetting 100 ml of the 1000 mg L^{-1} stock solution into a 1000 ml volumetric flask and diluted to mark using distilled water. Working standards of concentrations of 5, 10, 20, 30, 40, 50 and 60 mg L^{-1} were prepared from 100 mg L^{-1} standard solution (Chatterjee *et al*., 2008).

3.4 Preparation of 2 M, 0.05 M and 0.1 M NaOH solution

Concentrations of 2 M, 0.05 M and 0.1 M NaOH solutions were prepared according to the procedure in Appendix A5.

3.5 Preparation of 0.05 M HCl solution

Concentration of 0.05 M HCl solution was prepared according to procedure in Appendix A5.

3.6 Preparation of 5% (w/v) salicylic acid in concentrated sulphuric acid

A concentration of 5% (w/v) salicylic acid in concentrated sulphuric acid was prepared according to procedure in Appendix A6. The solution was transferred into a dark brown bottle for storage (Lastra, 2003; Yang *et al*., 2004).

3.7 Procedure for nitrates determination using an ultraviolet visible spectrophotometer

Volumes of 2.5 ml of sample solutions were thoroughly mixed with 0.8 ml of 5 % (w/v) salicylic acid in concentrated sulphuric acid solution while in 50 ml Erlenmeyer flasks. After 20 minutes volumes of 19 ml 2 M NaOH were added slowly at room temperature to each of the solutions. Solutions were cooled to room temperature and the absorbances of the resultant yellow coloured solutions were noted on an ultraviolet visible spectrometer set at a wavelength of 410 nm (Lastra, 2003; Yang *et al*., 2004).

3.8 Calibration of the ultraviolet-visible spectrophotometer (Shangai Youko Instruments UV 752 PC)

The uv-vis was turned on and let to warm-up for 15 minutes. The wavelength was set at 410 nm. The above procedure described in section 3.7 was used to obtain the absorbances of 0, 5, 10, 20, 30, 40, 50 and 60 mg L^{-1} NO_3^-N solutions.

3.9 Preparation of pH meter calibration buffer solutions

The pH calibration solutions were prepared using the formula in Appendix A7 (Chang and Cruickshank, 2005; Silbereberg, 2009; Mohan, 2008 and De Lloyd, 2004).

3.9.1 pH 2 buffer solution

A volume of 30.6 ml of 0.1 M sodium citrate was pipetted into 100 ml volumetric flask and 0.1 M HCl solution was added to 100 ml mark (Chang and Cruickshank, 2005; Silbereberg, 2009; Mohan, 2008 and De Lloyd, 2004).

3.9.2 pH 4 buffer solution

A volume of 284.4 ml of 1 M acetic acid was measured and put into 500 ml volumetric flask. A volume of 50 ml of 1 M NaOH will be added and the solution was diluted up to 500 ml mark with

distilled water (Chang and Cruickshank, 2005; Silbereberg, 2009; Mohan, 2008 and De Lloyd, 2004).

3.9.3 pH 7 buffer solution

A volume of 62.5 ml of 0.1 M potassium dihydrogen phosphate was pippeted into 250ml volumetric flask. A volume of 36.4 ml of 0.1 M NaOH was pipetted into flask and then diluted to mark with distilled water (Chang and Cruickshank, 2005; Silbereberg, 2009; Mohan, 2008 and De Lloyd, 2004).

3.10 Effect of pH on nitrate sorption

Volumes of 50 ml of 50 mg L^{-1} nitrate solution was pipetted into twenty four labelled 250 ml conical flasks and the solutions were adjusted to different pH in the range of 1-8 with 0.05 M NaOH or 0.05 M HCl (Moyo *et al*., 2012; Chatterjee *et al*., 2008). Masses of 1.0000 g of *Brachystegia spiciformis* powder were added into twenty four different flasks and were ran on a rotary shaker set at 150 rpm for 24 hours. After agitation the mixtures were vacuum-filtered and the filtrates were collected in well labelled 50 ml Erlenmeyer flasks. The procedure described above in section 3.7 was used to determine the residual nitrate within the filtrates obtained.

3.11 Effect of contact time on nitrate sorption

Volume of 50 ml of 50 mg L^{-1} nitrate solution were placed into thirty nine labelled different Erlenmeyer flasks. Masses of 1.0000 g of biosorbent were added into thirty nine Erlenmeyer flasks containing the nitrates solutions. The mixtures were buffered at pH 4. The flasks were closed and shaken on a rotary shaker at 150 rpm. Shaking time was varied between 0 to 140 minutes (0, 1, 2, 3, 4, 5, 6, 10, 20, 50, 80 100, 120 and 140 minutes) and each flask was withdrawn after an appropriate time had lapsed. After agitation the mixture were vacuum-filtered and the filtrates were

collected in labelled 50 ml Erlenmeyer flasks. The procedure described above in section 3.7 was used to determine the residual nitrate within the filtrates obtained.

3.12 Effect of *Brachystegia spiciformis* dosage on nitrate sorption

Volumes of 50 ml of 50 mg L^{-1} nitrate solution were pipetted into twenty one 250 ml Erlenmeyer flasks. The solutions were buffered at pH 4. The flasks were closed and shaken on a rotary shaker at 150 rpm. Masses of 0.25, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 g of *Brachystegia spiciformis* leaf powder were weighed and placed into twenty one respective 250 ml Erlenmeyer flasks and each dose was being represented by three flasks. The solutions were left to agitate at 150 rpm under an optimized contact time of 30 minutes (Moyo *et al*., 2012; Chatterjee *et al*., 2008). After agitation the mixtures were vacuum-filtered and the filtrates were collect into labelled 50 ml Erlenmeyer flasks. The procedure described above in section 3.7 was used to determine the residual nitrate within the filtrates obtained.

3.13 Effect of initial concentration on nitrate sorption

Volumes of 50 ml varying nitrate concentration of 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 mg L^{-1} were placed into thirty 250 ml Erlenmeyer flasks. The solutions` pH were adjusted to 4 and an optimized mass of 1.5 g of the biosorbent obtained above was weighed and placed in thirty different 250 ml Erlenmeyer flasks. The flasks were stoppered and allowed to agitate for 30 minutes (Chatterjee *et al*., 2008) at 150 rpm. After agitation the mixtures were vacuum-filtered and the filtrates were collected in labelled 50 ml Erlenmeyer flasks. The procedure described in section 3.7 was used to determine the residual nitrate within the filtrates obtained.

3.14 Desorption

After the equilibrium study with an initial nitrate concentration 50 mg L^{-1}, nitrate-adsorbed *Brachystegia spiciformis* was collected by filtration by thoroughly washing with distilled water. Loaded biosorbent was transferred to different 250 ml Erlenmeyer flasks, each flask contained 50 ml distilled water and the pH was adjusted to 9.0, 10.0, 11.0 , 12.0 and 13.0, having a single pH represented by three 250 ml Erlenmeyer flask. The flasks were agitated at 100 rpm for 24 hours. The procedure described in section 3.7 was used to determine the eluted nitrate within the filtrates obtained. The desorbed nitrates from the *Brachystegia spiciformis* was calculated and expressed as a percentage.

3.15 Sampling of Effluent Water

A 2000 ml plastic container was thoroughly cleaned with tap water followed by soaking in 10 % H_2SO_4 for 24 hours and it was rinsed thrice with distilled water. Effluent water was collected from a local fertilizer manufacturing company (Sable Chemical Industries Ltd). Figure 3.1 shows the sampling point that was accessed during effluent water collection.

At the sampling point, the container was cleaned thrice with the effluent water. The container was filled up to the brim with the effluent water using a scoop. The sample was taken to the laboratory and stored in a refrigerator awaiting analysis.

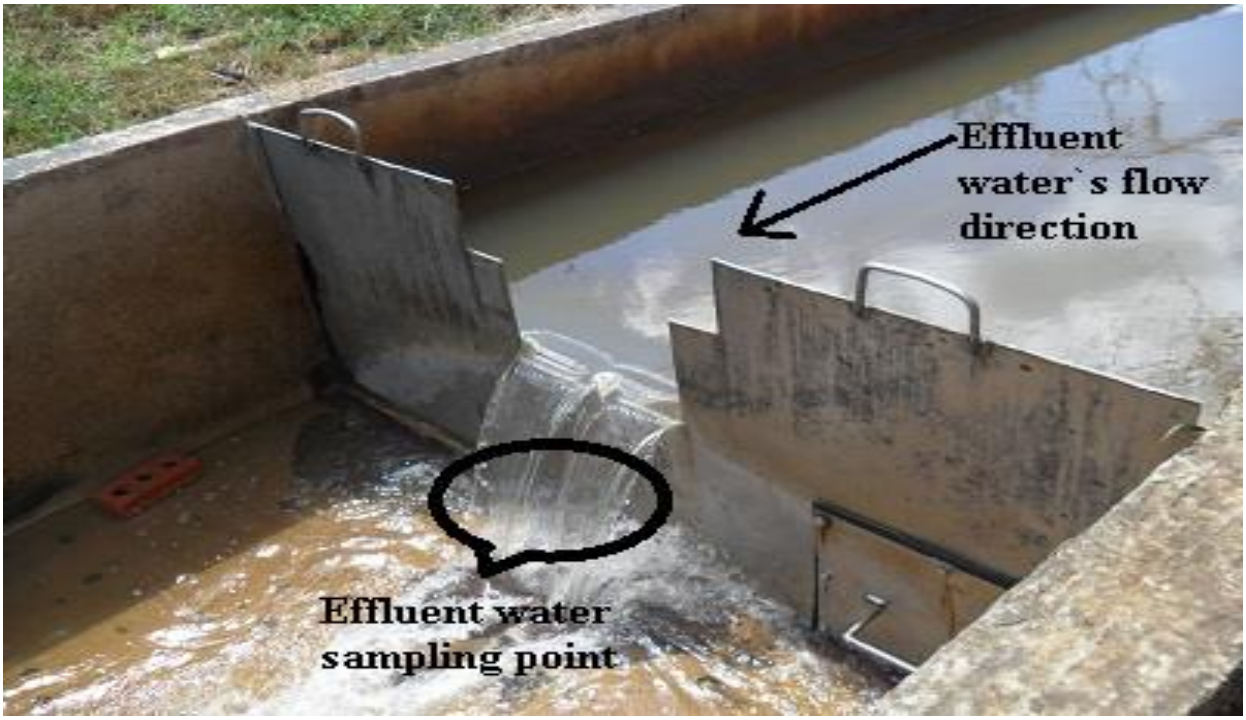

Figure 3.1: Sampling point of the water effluent

3.16 Treatment of the effluent water with *Brachystegia spiciformis* leaf powder

The optimum biomass determined in the batch experiment was weighed and placed into three 250 ml Erlenmeyer flasks. Volumes of 50 ml of effluent water were measured and placed into three 250 ml Erlenmeyer flasks and the solutions` pH were adjusted to 4 using 0.05 M NaOH and 0.05 M HCl. To each 250 ml Erlenmeyer flask containing effluent water, a mass of 1.5000 g of the *Brachystegia spiciformis* leaf powder was measured and added. The solutions were left to agitate at an optimized contact time of 30 minutes (Chatterjee *et al*., 2008). After agitation the mixtures were vacuum-filtered and the filtrates were collected in labelled 50 ml Erlenmeyer flasks. The procedure described in section 3.7 was used to determine the residual nitrates within the filtrates obtained.

3.17 Data treatment

Analysis of samples and filtrates was done in triplicate and the average values were calculated. The standard deviations of the results were calculated using the formula in Appendix A9 and were presented in form of error bars on the experimental data obtained. All this was done using Microsoft Excel.

CHAPTER 4

RESULTS AND DISCUSSION

4.0 Introduction

This chapter reports the results obtained from characterization of *Brachystegia spiciformis* before and after nitrate sorption and after nitrate desorption, optimization of pH, contact time, dosage and initial concentration from synthetic water, the effectiveness of the desorption of nitrates from the loaded *Brachystegia spiciformis* leaf powder as well as applicability of *Brachystegia spiciformis* on industrial effluent water. The results are presented in form of tables and graphs. The adsorption behavior between the nitrates and *Brachystegia spiciformis* leaf powder combination is described by five sorption isotherm equations of the Langmuir, Halsey, Dubinin-Radushkevich, Temkin and Freundlich models.

4.1 Characterization of *Brachystegia spiciformis* leaf powder

Fourier Transform Infrared Spectrometer (Nicolet 6700) was used in the characterization of leaf powder before and after biosorption of nitrates as well as after nitrate desorption. Table 4-1 shows the results obtained with their respective functional group assignments. There was a notable broad band at wavenumber of 3393.33 cm^{-1} that falls in the range 3300-3600 cm^{-1} for the spectra of *Brachystegia spiciformis* before sorption. The stretching motions of the N-H and O-H bonds absorbs best in the range 3300-3600 cm^{-1}. After nitrate sorption there was a change in band position from 3393.33 to 3418.33 cm^{-1} showing that there was involvement of the amino and hydroxyl groups during nitrate sorption since the band lost its initial intensity. Hence the likely reactions between the lateral chain of the *Brachystegia spiciformis* leaf powder and nitrates that resulted in change in band position are as shown by equations 4.1 and 4.2

Table 4-1: Characterization of *Brachystegia spiciformis* leaf powder

Wavenumber / cm^{-1}				Bond Assignment	Functional group	References
Before Sorption	**After sorption**	**After desorption**	**Band position (Silvestein *et al*., 2005)**			
3393.33	3418.33	3418.68	3200-3500	O-H and N-H stretching	Carboxylic acid, amino	Moyo *et al*., 2012, Chigondo *et al*., 2013
2920.67	2921.32	-	2500-3100	C-H asymmetric stretching vibration, O-H	methyl, methylene and methoxy groups, carboxylic acid	Yu *et al*., 2007, Chigondo *et al*., 2013,
1650.59	1651.08	1639.85	1650-1780	>C=O stretching -C-C=C- symmetric stretch	Carboxylic acid, carbonyl, Alkenes, aromatic alkenes	Yu *et al*., 2007

$$BSp - OH_{(aq)} + H^{+}_{(aq)} + NO^{-}_{3(aq)} \rightarrow BSp - OH^{+}_{2} \cdots NO^{-}_{3(s)} \text{.....(4.1)}$$

$$BSp - NH_{2(aq)} + H^{+}_{(aq)} + NO^{-}_{3(aq)} \rightarrow BSp - NH^{+}_{3} \cdots NO^{-}_{3(s)} \text{.....(4.2)}$$

Where: BSp represents the *Brachystegia spiciformis* lateral chain and

(⋯) is the electrostatic attraction between the nitrate and the functional group.

After desorption there was a slight change from the spectra after sorption of nitrates. The band position slightly changed from 3418.33 to 3418.68 cm^{-1}, which was not significant. However the biosorbent failed to retain to its original band position of 3393.33 cm^{-1} and it shows that the bonding was irreversible at this particular active groups (hydroxyl and amine) due to the nitrates that might have been chemisorbed.

Bruce (2007) stated that the range 2500-3100 cm^{-1} corresponds to the absorption due to O-H stretching of the carboxylic group and C-H stretching vibration of alkanes, methylene and methoxy groups. Hence the band at 2920.67 cm^{-1} before nitrate sorption could be due to O-H group of the carboxylic group. After nitrate sorption there was a change from 2920.67 to 2921.32 cm^{-1} and this might be due to O-H group that was involved in the nitrates being involved in electrostatic attraction. This is explained by chemical equation 4.3.

$$BSp - COOH_{(aq)} + H^{+}_{(aq)} + NO^{-}_{3(aq)} \rightarrow BSp - COOH^{+}_{2} \cdots NO^{-}_{3(s)} \text{.....(4.3)}$$

After desorption the band disappeared and failed to retain back its original band position. This was maybe due to the nitrates that were also chemisorbed.

The band at 1650.59 cm^{-1} falls in the range 1650-1780 cm^{-1} and it corresponds to >C=O stretching of either carboxylic or carbonyl groups, -C=C- and =C-H stretch of alkenes. After sorption of nitrates the band lost its intensity and changed to 1651.08 cm^{-1}. This might be due to >C=O stretching vibrations of the carboxylic acid as a result of electrostatic attractions that occurred between the hydrogen on carboxylic acid and oxygen of the nitrate. Hence the >C=O of the

carboxylic might have contributed much in band shifting. After desorption the band position changed from 1651.08 to 1639.85 cm^{-1}. The band at 1639.85 cm^{-1} is within in the range of 1560-1640 cm^{-1} which corresponds to the N-H stretching vibrations of the primary amines. This shows that the nitrates adsorbed were further converted to amines under alkaline conditions and were difficult to desorb.

The band before nitrate sorption at 1383.01 cm^{-1} is contained in the region 1300-1400 cm^{-1}. It corresponds to C-N stretching vibrations and N=O bending of the tertiary amino and nitro groups respectively. After nitrate sorption there was no significant change in band position hence none was involved in nitrate sorption. After desorption there was no significant change in band position (1384.10 cm^{-1}) but rather kept with the range limits (1300-1400 cm^{-1}) with which the tertiary and nitro groups are contained.

The band at 1284.70 cm^{-1} falls in the range 1050-1300 cm^{-1} corresponds to C-O stretching of primary and secondary alcohols as well as carboxylic acids. After nitrate sorption, the band lost its intensity and changed to 1162.40 cm^{-1}. This as well indicates that there was binding of the nitrates with the carboxylic and hydroxyl groups of the alcohols. After desorption the band further lost its intensity and disappeared. At this particular active groups the nitrates might have been chemisorbed and however failed to retain back to its original functional group characteristics before biosorption of nitrates. This could have been necessitated by the chemisorbed nitrates.

The band at 1070.79 cm^{-1} corresponds to the C=O stretching of the carboxylic acid that falls in range 1050-1300 cm^{-1}. Its intensity changed and shifted to 1062.07 cm^{-1} after nitrate sorption showing its participation in sorption process. After desorption the band lost its intensity and changed to 1032.79 cm^{-1} showing that it failed to retain to its original form.

The above information shows that the amine, carboxylic and hydroxyl might be the functional groups involved during the sorption of nitrates by the *Brachystegia spiciformis*. Similar functional groups were previously reported by Yu *et al*. (2007), Kaesarn *et al*. (2008) and Chigondo *et al*. (2013) and Moyo *et al*. (2012). Figure 4.1 shows the FTIR spectrum obtained for *Brachystegia spiciformis* before and after biosorption respectively.

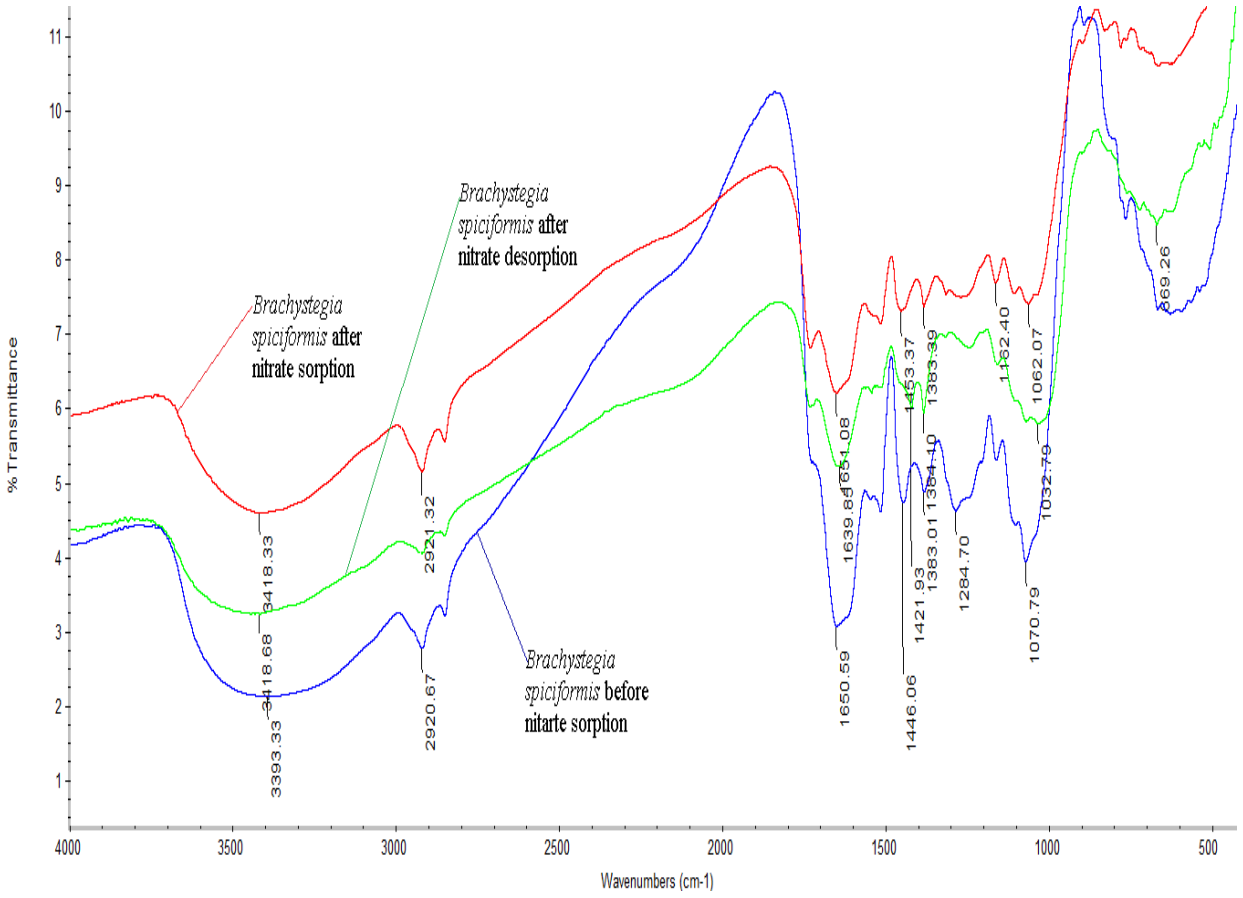

Figure 4.1: FTIR spectra of *Brachystegia spiciformis* leaf powder

4.2.0 Factors that affect nitrate sorption

Different factors that affect nitrate sorption were investigated. These included pH, contact time, biosorbent dosage and initial concentration. The values of C_i and C_e for a specific parameter are shown in Appendix B and the values of Q_e and R% are calculated as well using the formulae

shown in Appendix A8. The standard deviation was also calculated and the reliability of the results was determined. Formula for the standard deviation is shown in Appendix A9.

4.2.1 Effect of pH on nitrate sorption

Generally pH affects the activity of functional groups on the cell wall, chemistry of ions as well as the competition of ions for the binding sites. From figure 4.2 there was an increase in pH from 2-4 with an increase in nitrates uptake by the *Brachystegia spiciformis*. A further pH increase beyond pH 4 resulted in sudden decrease in nitrates removal. At low pH, more protons were ready for protonation of the *Brachystegia spiciformis*` surface and slightly below pH 4, approximately more than 93% of the active sites were protonated. Thus an increase in electrostatic attractions between negatively charged nitrates and the positively charged active groups of the sorbent resulted in increased nitrate uptake. The chemical equation 4.2 is the likely equation for the sorption of nitrates and lateral *Brachystegia spiciformis* adsorption sites under acid condition.

Beyond pH 4 all the active groups remained protonated (Guibal, 2004) and there was a decrease in electrostatic attractions between positively charged groups of the *Brachystegia spiciformis* with negatively charged nitrates. Hence there was less nitrate adsorption. As pH increased to 8, hydroxide ions increased in solution and led to deprotonation of the active groups (amine groups) of the sorbent. Deprotonated groups and negatively charged nitrates caused a repulsive effect thereby reducing the adsorption capacity (Chatterjee *et al*., 2009). The same trend was observed for the removal of nitrates (Moyo *et al*., 2012; Chatterjee *et al*., 2009) and orange 16 reactive dye (Suteu *et al*., 2011) from aqueous environment using sunflower seed husks.

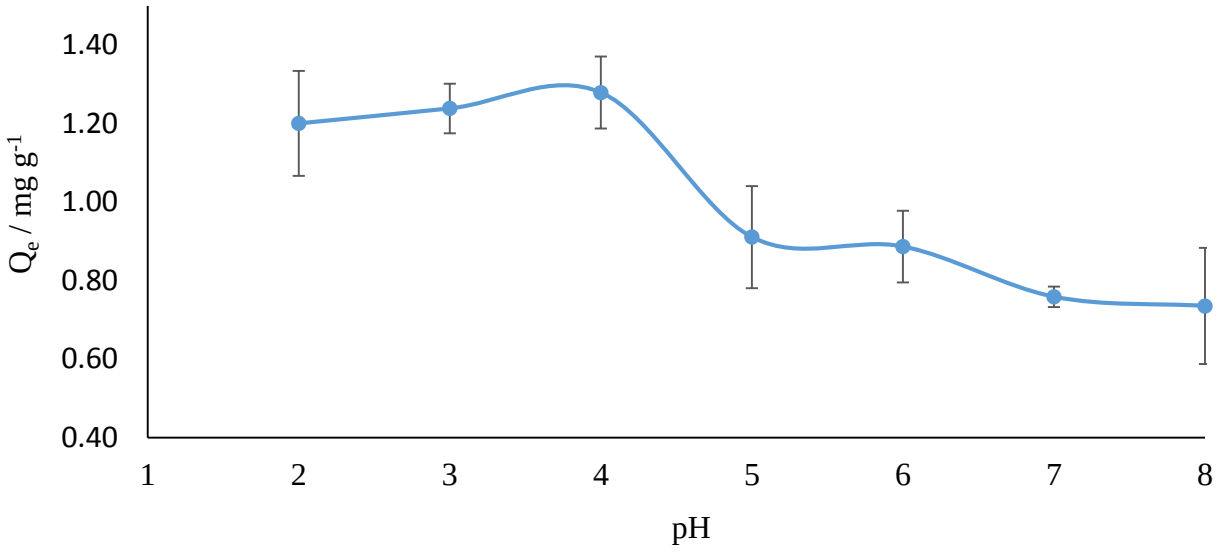

Figure 4.2: Effect of pH

4.2.2 Effect of contact time on nitrate sorption

Contact time is also one of the factors that affects the sorption process. It gives the minimum time required for adsorption process to occur as well as the control mechanism that takes place between nitrate ions as they move within the flow system. This parameter was investigated using the initial nitrate concentration of 50 mg L^{-1} with the sorbent dosage of 1.0000 g at pH 4 over a period of 140 minutes. From figure 4.3, there was a sudden increase in uptake of nitrates and decreased slowly with time until it became constant after 20 minutes. Initially the *Brachystegia spiciformis* sites were unoccupied and gave rise to an increase in sorption rate due to the higher diffusion of nitrates from the nitrate solution to the *Brachystegia spiciformis* sites. There were less number of vacancies or adsorption sites on the adsorbent and resulted in the diffusion gradient being decreased hence sorption rate decreased as time progressed until the equilibrium point was attained at 20 minutes. Beyond 20 minutes the sorption rate became zero (Nharingo *et al*., 2013) and approximately all the adsorption sites were occupied.

To ensure that equilibrium was well attained, agitation time of 30 minutes was used throughout this study. Similar trend was also observed from other findings that focused on cationic or anionic removal using different biosorbents (Chatterjee *et al*., 2008; Suteu *et al*., 2011 and Nharingo *et al*., 2013).

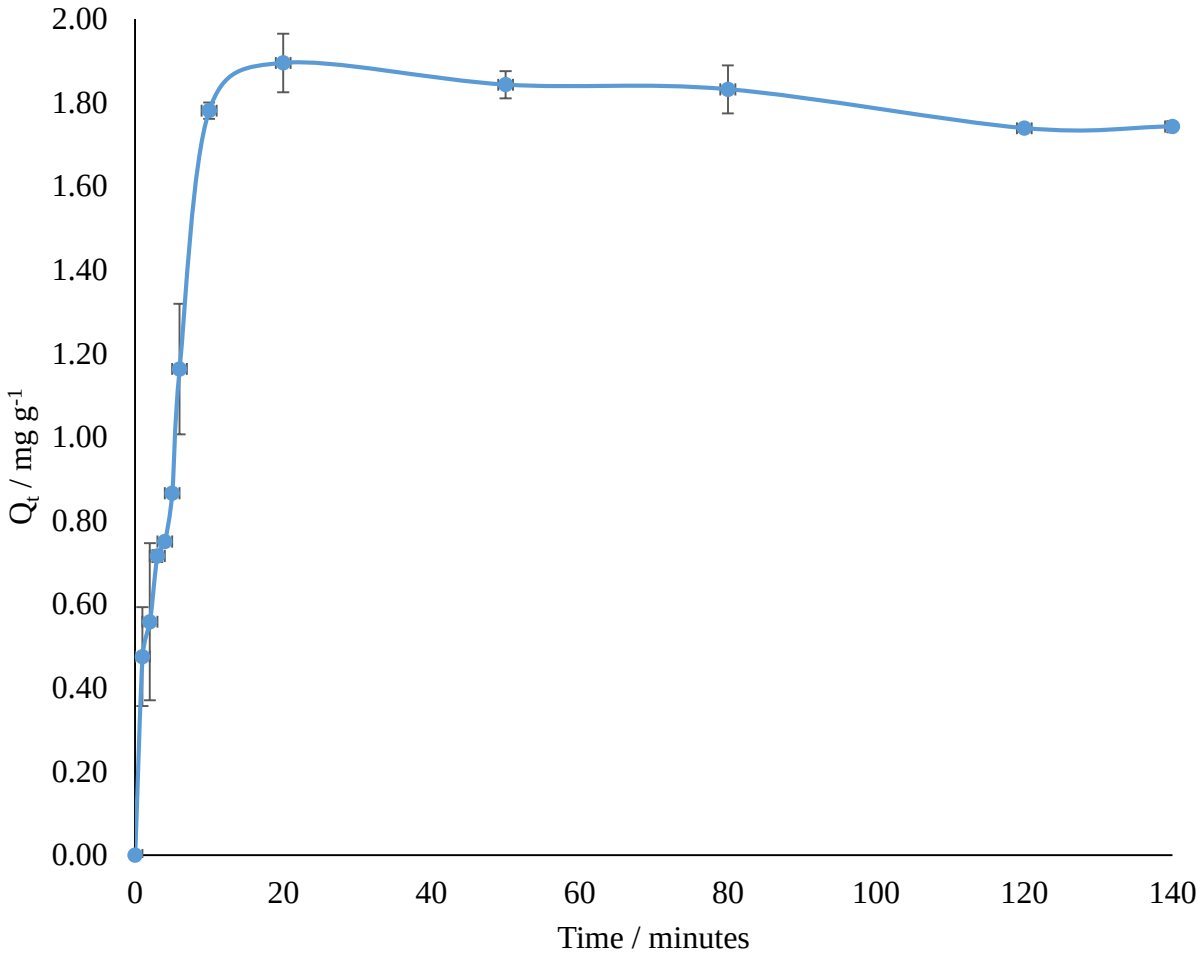

Figure 4.3: Effect of contact time

4.2.3 Effect of *Brachystegia spiciformis* dosage on nitrate sorption

Effect of *Brachystegia spiciformis* dosage on the removal of nitrates is as shown in figure 4.4. At initial sorbent dose the nitrate uptake remained almost constant and latter decreased as the dose increased. The constant uptake was as a result of the active sites which were sufficient for the nitrates that were present.

Beyond a 0.25 g dose, there was a decrease in amount of nitrates adsorbed with an increase in *Brachystegia spiciformis* dosage. This was mainly due to adsorbent overlapping sites that caused a decrease in total adsorbent surface ready for biosorption. According to Rajamohan (2009) a decrease was as a result of the solute transfer rate of the sorbent`s surface being splitted as the dosage increased. Also Nharingo *et al*. (2013) highlighted that according to the calculation formula of the amount of nitrates adsorbed, Q_e, the trend was as a result of rapid increase in dosage, m, so much that it overweighed the increase in nitrates adsorbed on sorbent`s surface $v[C_i - C_e]$.

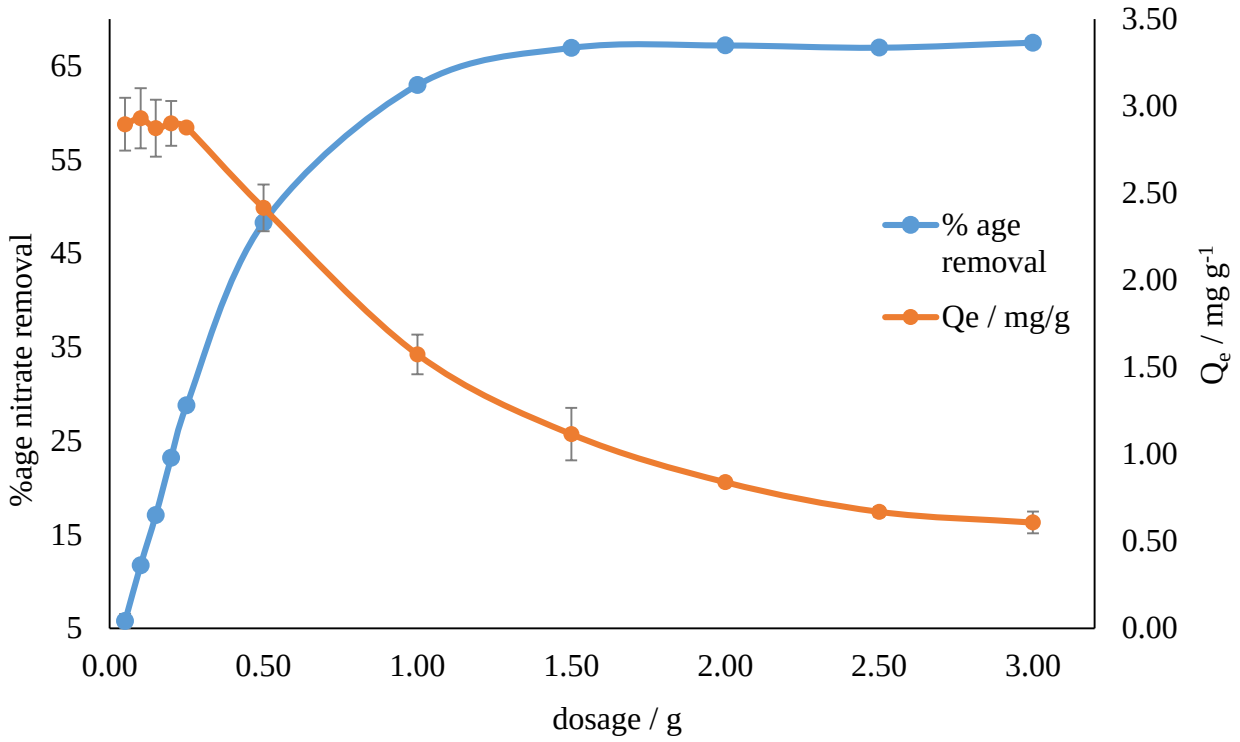

Figure 4.4: Effect of dosage on nitrate sorption

Figure 4.4 also shows an increase in the percentage removal of nitrates from 5.79 % to 66.92 % as the dosage increased from 0.05 g to 1.5 g and after which a constant trend was attained. The percentage increase was due to the presence of active groups that were ready for adsorption. Beyond a 1.5 g dose, no further increase in percentage removal was observed since the nitrates

were a limiting factor. Similar trend was observed from other research findings (Nharingo *et al*., 2013; Chatterjee *et al*., 2009 and Moyo *et al*., 2012).

4.2.4 Effect of initial concentration on nitrate sorption

The effect of nitrate initial concentration was investigated under optimized conditions of pH 4, 30 minutes contact time and a dosage of 1.5 g. Figure 4.5 shows the effect of initial nitrate concentration on nitrate sorption. Nitrates movement from the bulk solution to the *Brachystegia spiciformis* increased with an increase in diffusion gradient as the nitrate initial concentration increased from 5 mg L^{-1} to 40 mg L^{-1}. This was as a result of an increase of nitrates migration into the vacant biosorbent sites at high initial nitrate ions concentration. Beyond a 40 mg L^{-1} concentration the uptake became almost constant since enough sites were fully occupied by the nitrates. This was also the similar case for *Helianthus annuus* when used for the removal of nitrates (Moyo *et al*., 2012) and Orange 16 reactive dye (Suteu *et al*., 2011) from aqueous solutions.

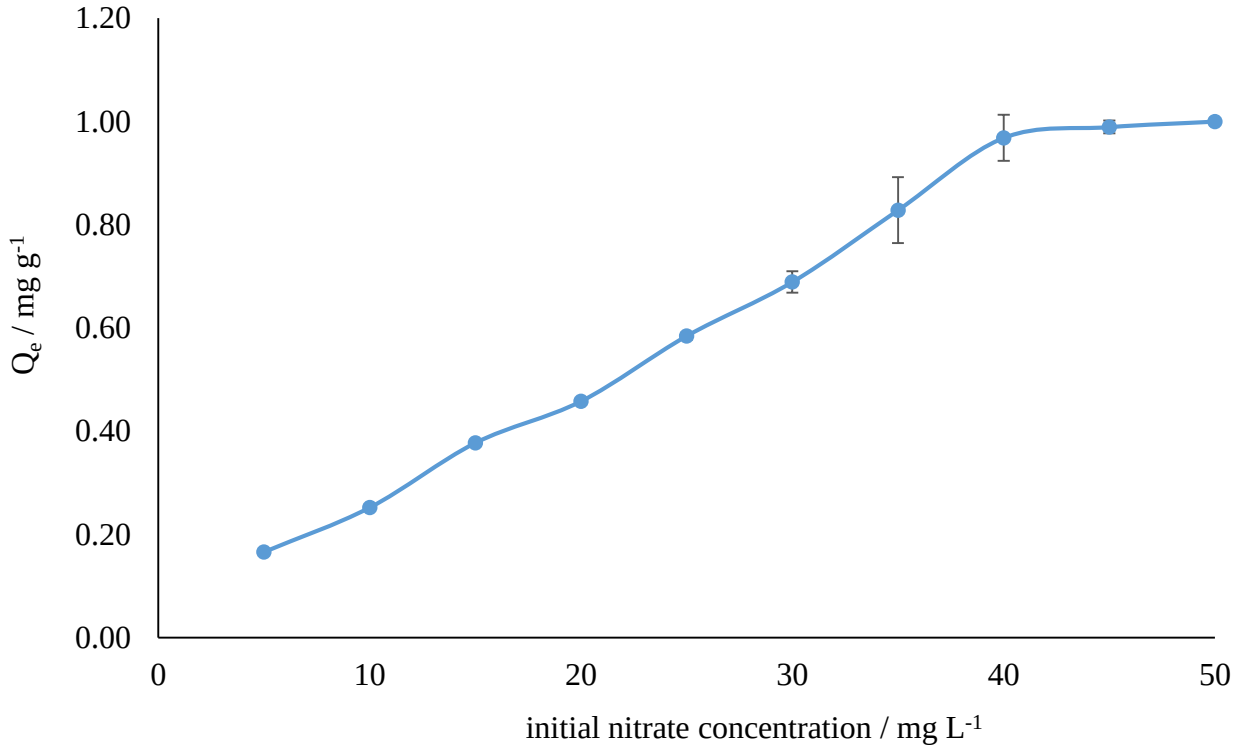

Figure 4.5: Effect of initial concentration

4.3.0 Adsorption isotherms of nitrate onto *Brachystegia spiciformis* leaf powder

Adsorption isotherms describes the adsorbate`s interaction with the adsorbent. The equilibrium studies determine the nature the mechanism of adsorbate and adsorbent`s interactions through sorption parameters evaluation. The relationship between the sorbed nitrates and the equilibrium was described by the Langmuir, Halsey, Dubinin-Radushkevich, Temkin and Freundlich models. The calculations on the constants and other parameters as well as the data used to come up with the isotherm models plots are shown in Appendix C.

4.3.1 Langmuir

It is represented by a general mathematical relationship as shown by equation 2.1.

The model can be linearized to the form shown by the equation 4.1.

$$C_e/Q_e = 1/Q_M \cdot C_e + 1/bQ_M \quad \text{.....(4.1)}$$

Where: C_e is the concentration in mg L^{-1} at equilibrium of the nitrates,

Q_e is the amount of nitrates adsorbed in mg g^{-1},

b is the Langmuir isotherm constant in L mg^{-1},

Q_M is the maximum sorption capacity of the adsorbate in mg g^{-1}.

Figure 4.6 shows a plot of C_e/Q_e against C_e. From the plot of the Langmuir isotherm, the correlation coefficient, R^2 is 0.9692 showing that the isotherm describes the sorption of nitrates by *Brachystegia spiciformis*. The slope of the graph is 0.6136. This implies that the maximum sorption capacity, Q_M, of the *Brachystegia spiciformis* for the nitrates was 1.6297 mg g^{-1}. The value obtained for the Langmuir isotherm constant, b, (0.09233 L mg^{-1}) was less than 0.1 L mg^{-1}. This implies that there was less surface energy within the sorption process (Sajidu *et al*., 2006). This indicated that there were high chances of having the nitrates ions bonding onto *Brachystegia spiciformis* sites (Chigondo *et al*., 2013). The possibility of adsorption of the nitrates onto the

Brachystegia spiciformis was also investigated using the separation factor, R_L, that was found to be 0.1781 L mg^{-1}. The separation factor falls within the favorability of sorption range of $0 < R_L < 1$ (Samarghandi *et al*., 2009; Nharingo *et al*., 2013).

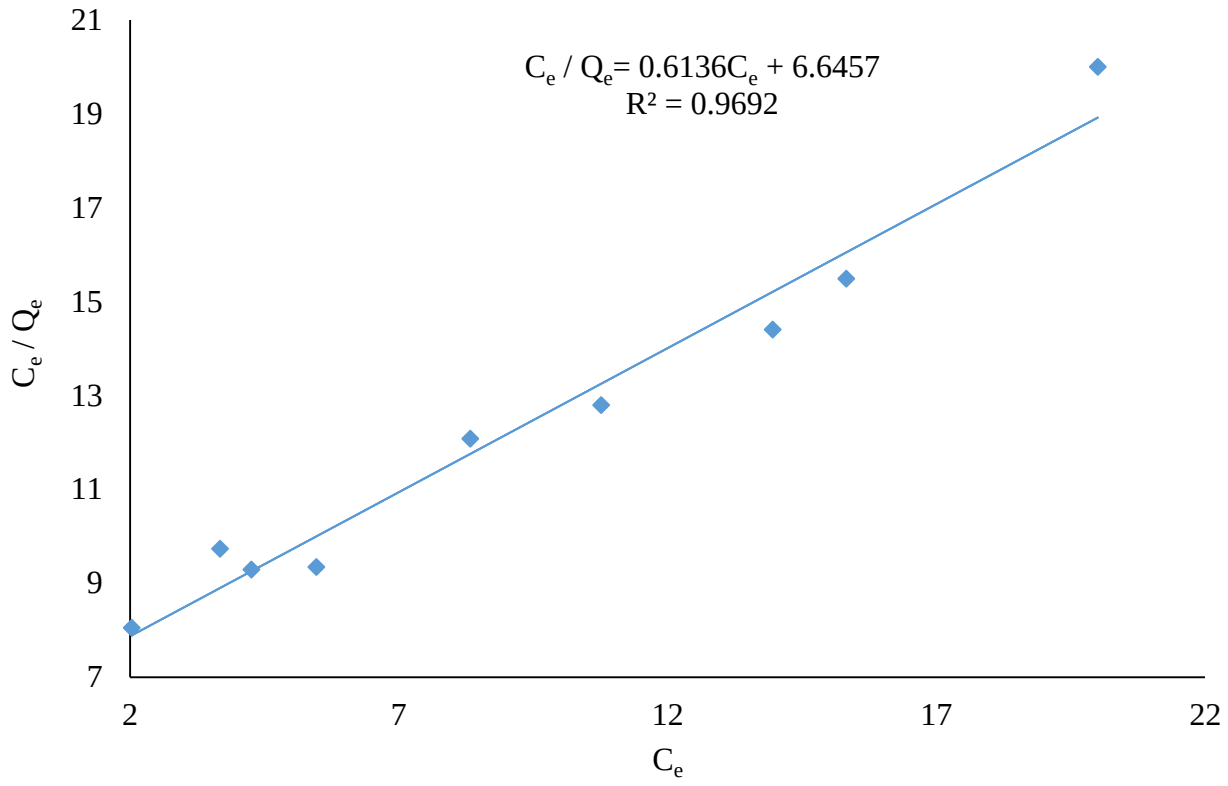

Figure 4.6: A linearized plot of the Langmuir model

4.3.2 Halsey

The generalized form of the Halsey is as shown by equation 2.8 (Samarghandi *et al*., 2009).

The model can also be given by a linearized mathematical relationship as shown by equation 4.2

$$\ln Q_e = {}^{1}/_{n} \ln K_h - {}^{1}/_{n} \ln C_e \quad \text{.....(4.2)}$$

Where: n and K_h are the exponent and adsorption isotherm constant respectively,

Q_e is the amount of nitrates adsorbed in mg g^{-1} and,

C_e is the equilibrium constant in mg L^{-1}.

Figure 4.7 shows a plot of $\ln Q_e$ against$\ln C_e$. The equilibrium data fitted the Halsey isotherm model with the correlation coefficient, R^2, being 0.9686. This however gives the evidence that there were higher chances of multilayer sorption and the heterogeneity of the *Brachystegia spiciformis*. The sorbent had macro pores and micro pores might have been used for nitrate sorption.

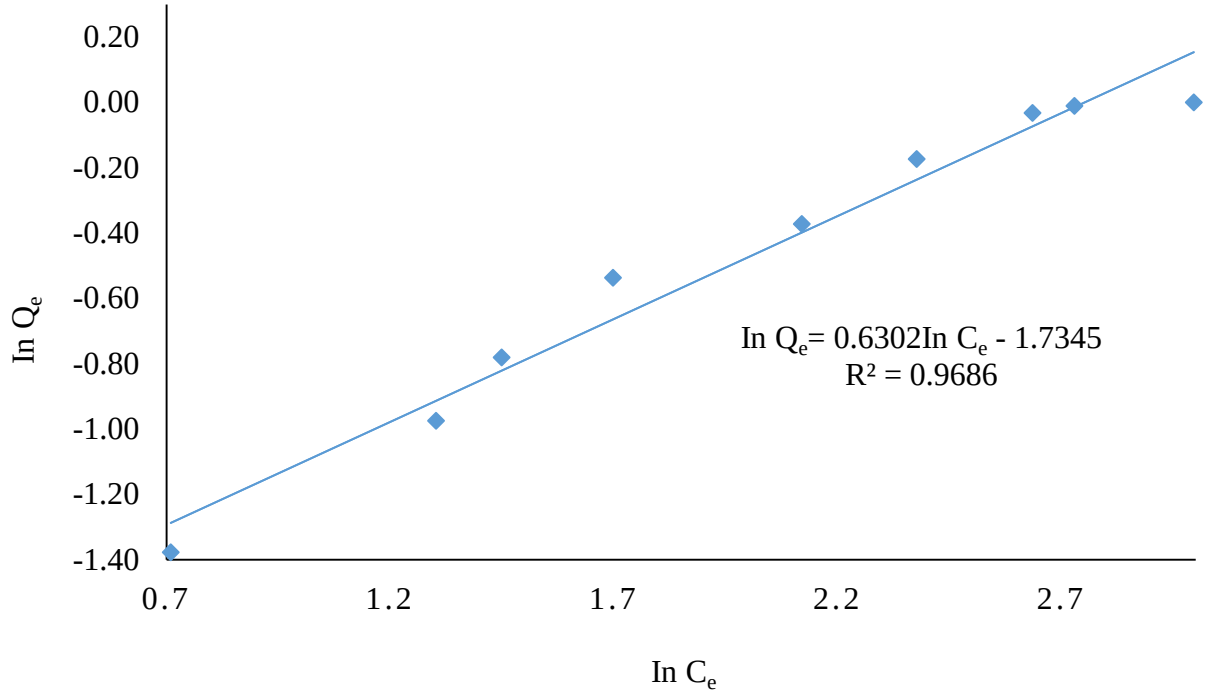

Figure 4.7: Plot of equilibrium data for Halsey isotherm model

4.3.3 Dubinin-Radushkevich

The isotherm is given by a general mathematical expression as shown by equation 2.4 and it can be linearized to the form shown by equation 4.3.

$$\ln Q_e = \ln Q_W - 2B_W RT \ln\left[1 + {}^{1}/_{C_e}\right] \quad \text{.....(4.3)}$$

Where: Q_e is the amount of the adsorbed nitrates at equilibrium in mg g^{-1},

Q_W is the adsorption capacity in mg g^{-1},

C_e is the nitrate equilibrium concentration in mg L^{-1},

B_W is the adsorption energy constant ($mol^2\ kJ^{-2}$) and

R and T are the ideal gas constant and the temperature (K) respectively.

(Oladoja *et al*., 2009).

Figure 4.8 shows a linear plot of In $Q_e$against $\ln\left[1 + {}^{1}/_{C_e}\right]$ having B_W as the slope and $\ln Q_W$ as the intercept. From the graph, the slope (also adsorption energy constant, B_W) obtained was 0.0008 $mol^2\ kJ^{-2}$ and the correlation coefficient, R^2, being 0.9683. The R^2 value indicates that the model fits the equilibrium data. The isotherm also shows that the adsorption capacity, Q_W was 1.2006 mg g^{-1}. The mean free energy was obtained from a mathematical relationship given by equation 4.4.

$$E_W = {}^{1}/_{[2B_W]^{1/2}} \quad \text{.....(4.4)}$$

Where B_W is the adsorption energy constant (Nharingo *et al*., 2013). The value of the mean free energy, E_W was 24.2667 kJ mol^{-1} and it falls in the region of 20 kJ mol^{-1} of the enthalpy change of physisorption (Atkins and de Paula., 2010). The enthalpy change was not enough to promote bond breakage and the adsorbate might have retained its originality although the surface might distort it (Atkins and de Paula., 2010). Chowdhury and Saha (2012) reported the mean free energy, E_W ranging from 13.52 to 15.67 kJ mol^{-1} after the sorption of methylene blue dye using hen feathers.

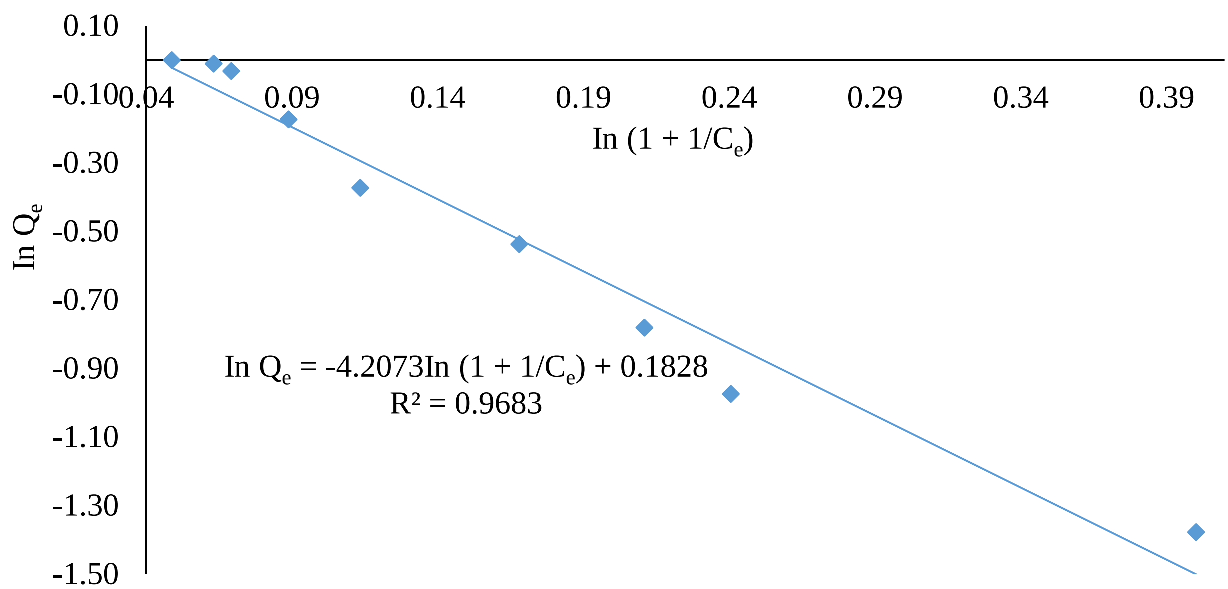

Figure 4.8: A linearized plot of the Dubinin-Radushkevich model

4.3.4 Temkin

The model is given by a general mathematical relationship as shown by the equation 2.7 and can be linearized to the form shown by the equation 4.5.

$$Q_e = {}^{RT}/_{b_v} \ln K_t + {}^{RT}/_{b_v} \ln C_e \ldots\ldots (4.5)$$

Where: T is the absolute temperature (298 K),

R is the ideal gas constant (8.314 J mol^{-1} K^{-1}),

K_t is the equilibrium binding constant in L g^{-1},

Q_e is the amount of nitrates adsorbed at equilibrium in mg g^{-1}

C_e is the equilibrium concentration in mg L^{-1} and,

b_t is constant that is related to the heat of sorption (kJ mol^{-1})

Figure 4.9 is a plot of ln C_e against $Q_e$having the correlation coefficient of 0.9792. This gives an indication that the adsorption sites were occupied by the nitrates before the less energetic ones (Nharingo *et al*., 2013). The heat of sorption constant, b_t and the intensity of sorption, K_t, were obtained as 6.7380 kJ mol^{-1} and 0.9999 L g^{-1} respectively. The value of b_t falls within range of bonding energy for ion-exchange, 6 – 15 kJ mol^{-1}, hence ion exchange mechanism was involved during nitrate sorption onto *Brachystegia spiciformis* leaf powder (Ho *et al*.,1995).

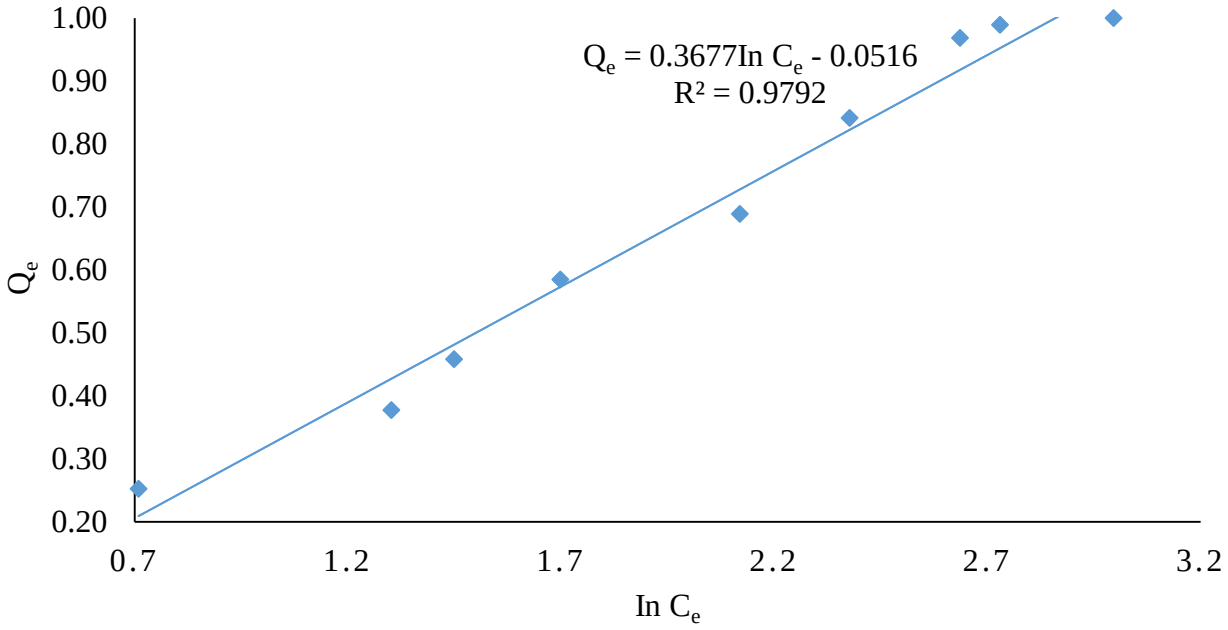

Figure 4.9: A linearized plot of the Temkin model

4.3.5 Freundlich

The model is represented by the mathematical relationship shown by equation 2.3.

The equation is linearized to the form shown by equation 4.6.

$$\log[Q_e] = \log[K_F] + {}^{1}/_{n} \log[C_e] \quad \text{.....(4.6)}$$

Where: Q_e is the amount adsorbed in mg g^{-1} at equilibrium

C_e is the equilibrium concentration of the adsorbate in mg L^{-1},

n is the adsorption intensity in g L^{-1} and,

K_F is the adsorbent capacity in (mg g^{-1})(L mg^{-1})^n.

Figure 4.10 is a plot of $\log[Q_e]$ against $\log[C_e]$ having $\log[K_F]$ and n as the intercept and reciprocal of the slope respectively. The equilibrium data fitted the isotherm model with the correlation coefficient, R^2, being 0.9686. The R^2 value shows that the sorption process was fairly heterogeneous resulting in the isotherm model fitting well or being more applicable for the sorption of nitrates using *Brachystegia spiciformis*. The value of K_F, adsorbent capacity measure was calculated from the intercept and obtained as 0.1765 mg g^{-1}. Also the value of ${}^{1}/_{n}$ being 0.6302 was obtained as the slope and it falls within the heterogeneity range of $0.1 < {}^{1}/_{n} < 1$ and thus it points to the favourability of the sorption process (Moyo *et al*., 2012). Also the value of n being equal to 1.5868 g L^{-1} was calculated as the reciprocal of the slope and indicates that the process is less heterogeneous although it is within the range ($1< n < 10$). This was the case for Moyo *et al*. (2012) on the nitrate sorption using *Helianthus annuus*.

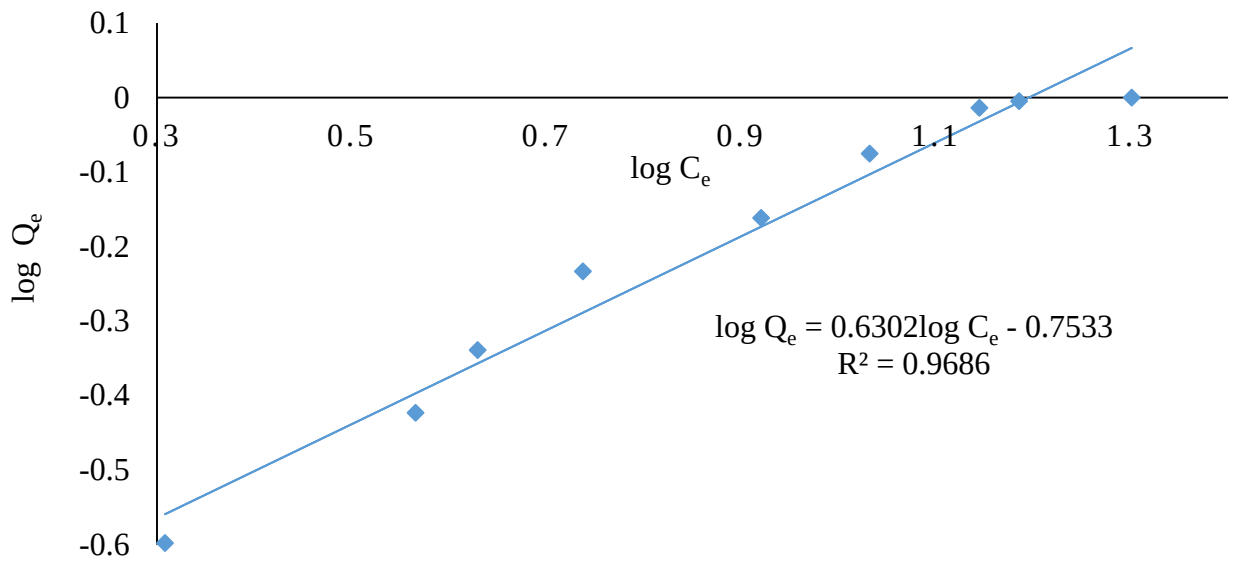

Figure 4.10: A linearized plot of the Freundlich model

Table 4.2 shows the parameters obtained after having plotted the sorption isotherm models.

Table 4-2: Sorption isotherm models with their respective parameters

Isotherm Model	Parameter	Value
Freundlich	K_F (mg g^{-1})(L mg^{-1})^n	0.1765
	n (g L^{-1})	1.5868
	R^2	0.9686
Langmuir	Q_M (mg g^{-1})	1.6297
	b (L mg^{-1})	0.0923
	R^2	0.9692
	R_L(L mg^{-1})	0.1781
Temkin	K_t (L g^{-1})	0.9999
	b_t (kJ mol^{-1})	6.7380
	R^2	0.9792

Dubinin-Radushkevich	B_w ($mol^2\,kJ^{-2}$)	0.0008
	E_w ($kJ\,mol^{-1}$)	24.2667
	Q_w($mg\,g^{-1}$)	1.2006
	R^2	0.9683
Halsey	K_H($L\,mg^{-1}$)	0.063781
	n	1.586798
	R^2	0.9686

4.4.0 Desorption Study

Desorption study was done and verified by studying at a wide range of alkaline conditions. After desorption, *Brachystegia spiciformis* was characterized using a Fourier Transform Infrared Spectrometer.

4.4.1 Variation of percentage desorption with pH

Desorption study was done at pH ranging from 9 to13. The percentage of desorbed nitrates from the *Brachystegia spiciformis* was calculated using the formula in Appendix A8 (Namasivayam and Sangeetha, 2005; Woo *et al*., 2008).

Figure 4.11 shows a variation of pH and the percentage of the nitrates desorbed. The amount of nitrate desorbed from the loaded *Brachystegia spiciformis* increased with an increase in pH to more alkaline pH condition. Maximum desorption percentage of 91.26 % was attained at pH 11. This indicated that electrostatic interaction predominantly played an important role between the nitrate and *Brachystegia spiciformis* (Namasivayam and Sangeetha, 2005; Chatterjee *et al*., 2009). Also from the effect of pH and desorption studies gives an evidence that chemisorption as well as

the ion exchange mechanism are the keys to the process of adsorption (Namasivayam and Sangeetha, 2005). This can however be supported by chemical equations 4.4 and 4.5.

$$BSp - COH^{+}_{2(aq)} + NO^{-}_{3(aq)} \rightarrow BSp - CNO_{3(s)} + H_2O_{(l)} \text{.....(4.4)}$$

(chemisorption)

$$BSp - COH_{(aq)} + NO^{-}_{3(aq)} \rightarrow BSp - CNO_{3(aq)} + OH^{-}_{(aq)} \text{.....(4.5)}$$

(ion exchange)

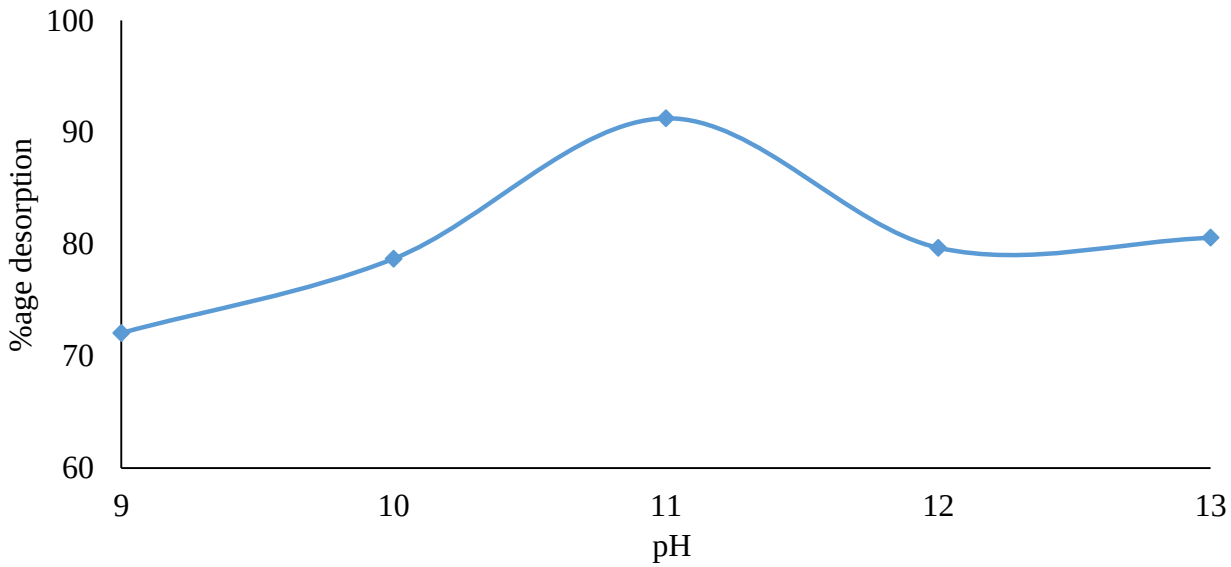

Figure 4.11: Nitrate desorption ratio from the loaded *Brachystegia spiciformis* at different pH condition.

4.5 Industrial effluent water analysis

The effluent water was filtered and analyzed for nitrates. The effluent water samples were optimized to pH 4 and were exposed to optimum *Brachystegia spiciformis* dosage of 1.5 g and were left to agitate on a rotary shaker for 30 minutes. The industrial water effluent was found to have an average concentration of 36.871 mg L^{-1} and it was below 45 mg L^{-1} of the WHO acceptable limits. *Brachystegia spiciformis* was exposed to the effluent and the concentration decreased to 19.913 ± 1.454 mg L^{-1} and the amount of nitrates adsorbed was 0.5653 mg g^{-1}. However the

calculated maximum sorption capacity,Q_M, (1.6297 mg g^{-1}) of the Langmuir model was not attained and it was necessarily due to the interfering ions within the industrial water effluent which were competing for sorption sites with the nitrates.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Brachystegia spiciformis leaf powder has been identified to be an effective biosorbent in nitrate removal from an aqueous environment. The fourier transform infrared spectrometry revealed that amine, hydroxyl and carboxylic groups took part in nitrate sorption on to the *Brachystegia spiciformis.* The biosorption of nitrates depended on optimum pH of 4, contact time of 30 minutes and an optimised dosage of 1.5 g. The equilibrium data best fitted the Temkin isotherm (R^2 = 0.9792). The data also fitted to Langmuir, Halsey, Debinnin- Radushkevich and Freundlich models with correlation coefficient (R^2) values of 0.9692, 0.9686, 0.9683 and 0.9686 respectively. The adsorption intensity, n, (1.5868 g L^{-1}) derived from Freundlich confirmed the sorption favorability. Debinnin- Radushkevich and Temkin models proved that the sorption of nitrates by the *Brachystegia spiciformis* was physisorption and endothermic in nature. Halsey model revealed that multilayer sorption process occurred on heterogeneous surface that had macro and micro pores. The *Brachystegia spiciformis* leaf powder was applicable to the industrial water effluent and the amount of nitrates adsorbed was 0.5653 mg g^{-1}. The desorption percentage was 91.26 % and was attained under alkaline condition of pH 11.

5.2 Recommendations

- The *Brachystegia spiciformis* leaves can be used for nitrates removal from waste waters without chemically modifying.
- Investigation on the effects of interferences and the kinetics during nitrate sorption onto *Brachystegia spiciformis* should also be explored.

- Further studies should be carried out to synthesize an organic fertilizer from the *Brachystegia spiciformis* droppings (leaves) after having loaded them with nitrates from industrial waste waters so that they can be used in agricultural fields.

REFERENCES

Adediran, G. O., Owalude, S. O., Tella, A. C. and Olaremu, A. G. (2011). Equilibrium sorption of lead and nitrate ions from aqueous solution using chemically modified rice husks. *Journal of Biotechnology*, 24 (3): 120-132.

Atkins, P. and de Paula, J. (2010). *Atkins` Physical Chemistry*, 9th ed. Oxford University Press, New York, pg 888-897.

Batista, J. and Pinter, A. (2006). Improvement of an integrated ion exchange or catalytic process for nitrate removal by introducing a two stage denitrification step. *Application in Catalysis Environment*, 63 (4): 150-159.

Bruce, D. Y. (2007). *Organic Chemistry*, 5th ed. Pearson Prentice Hall, Upper Saddle River, New York, pg 540-548.

Bryan, N. S. and van Grinsven, H. (2013). The Role of Nitrate in Human Health. *Advances in Agronomy*, 119 (4): 153-182.

Chang, R. and Cruickshank, B. (2005). *Chemistry*, 8th ed. Mc Graw-Hill Higher Education, New York, pg 680-682.

Chatterjee, S., Lee, D. S., Lee, M. W. and Woo, S. H. (2008). Nitrate removal from aqueous solution by cross-linked chitosan beads conditioned with sodium bisulphate. *Journal of Hazardous Material*, 166 (21): 508-513.

Chigondo, F., Nyambuya, T. and Chigondo, M. (2013). Removal of Zinc (ii) ions from aqueous solution using Msasa tree leaf powder: Equilibrium Studies. *Journal of Asian Scientific Research***,** 3 (2): 140-150.

Chowdhury, S. and Saha, P. D. (2012). Biosorption of methylene blue from aqueous solutions by a waste biomaterial: hen feathers. *Journal of Applied Water Science*, 2: 209-219.

Dada, A. O., Olalekan, A. P., Olutunya, A. M. and Dada, O. (2012). Lngmuir, Frendlich, Temkin and Dubinin-Radushkevich Isotherm Studies of Equilibrium Sorption of Zn^{2+} onto Phosphoric Acid Modified Rice Husk. *Journal of Applied Chemistry*, 3 (2): 38-45.

Delloyd, D. (2004). Lab Tech Resources Reagents and Solutions. *Preparation of pH buffer solutions,* [Online] Available at: http://delloyd.50megs.com/moreinfo/buffer2.html. [Accessed on 12/09/13].

Deodyvet, P. (2009). Nitrogen Removal from Wastewater: Nitrogen Chemistry. *The Water Planet Company*, 118-121.

Fewtrell, L. (2004). Drinking-water nitrate, methemoglobinemia and global burden of disease: a discussion. *Journal of Environmental and Health Perspectives*, 112 (14): 1371-1374.

Galun, N.T., Hefny, M. M. and Chaghaby, E. G. A. (2008). Removal of metal ions from synthetic wastewater by adsorption onto Eucalyptus tree leaves. *Journal of Chemical Society*, 53 (3):1585-1587.

Garwe, D., Chawira, M. A. and Kusena, K. (2009). Development, Ministry of Agriculture, Mechanisation and Irrigation Development. *The Zimbabwe Country Report on the State of Plant Genetic Resources for Food and Agriculture*, pg 13-23.

Gholizadeh, A., Kermani, M., Gholami, M. and Farzadkia, M. (2013). Kinetic and isotherm studies of adsorption and biosorption process in the removal of phenolic compounds from aqueous solutions: Comparative study. *Journal of Environmental Health Science and Engineering*, 11 (29): 1-10.

Godini, H., Rezaee, A., Jafari, A. and Mirhousaini, S. H. (2010). Denitrification of wastewater containing high nitrate using a bioreactor system packed by microbial cellulose. *Journal of World Academy of Science, Engineering and Technology*, 38 (7): 283-287.

Gomez, M., Gonzalez-Lopez, J. and Hontoria-Garcia, E. (2000). Influence of carbon source on nitrate removal of contaminated ground water in a denitrifying submerged filter. *Journal of Hazardous Material*, 80 (2): 69-80.

Guibal, E. (2004). Interactions of metal-ions with chitosan-based sorbents: a review. *Journal of Purification Technology*, 38 (3): 43–74.

Hale, S. E., Alling, V., Martisen, V. and Cornelissen, G. (2013). The sorption and desorption of phosphate-P, ammonium-N and nitrate in cacao shell and corn cob biochars. *Chemosphere*, 91 (11): 1612-1619.

Hammer, J. M. (2004). *Water and waste water technology*, 4th ed. Prentice Hall, India, pg 275.

Ho, Y. S., Porter, J. F. and Mckay, G. (2009). Equilibrium isotherm studies for the sorption of divalent metal onto peat: Copper, Nickel and Lead Single Component System. *Journal of Water, Air and Soil Pollution*, 141(9): 1-33.

Ismail, K. (2007). *Journal of Environmental Science Health*, 32 (3): 1347-1358.

Itodo, A. U. and Itodo, H. U. (2010). Sorption Energies Estimation Using Dubinin-Radushkivich and Temkin Adsorption Isotherms. *Life Science Journal*, 7 (4): 31-48.

Jagessar, R. C. and Sooknundun, L. (2011). Determination of nitrate anion in waste water from nine selected areas of coastal guyana via a spectrophotometric method. *International Journal of Applied Science*, 7 (2): 203-212.

Jensen, B. V. and Darby, J. L. (2012). Drinking Water Treatment for Nitrate Technical Report 6. In: Addressing Nitrate in California`s Drinking Water with a focus on Tulare Lake Basin and Salinas Valley Groundwater. Report for the State Water Resource Control Board Report to the Legislature Centre for Watershed Sciences, University of California,

Davis. [Online]. Available at: http://groundwaternitrate.ucdavis.edu. [Accessed on 30/06/13].

Kapoor, A. and Viraraghavan, T. (1997). Nitrate removal from drinking water-review. *Journal of Environmental Engineering*, 123 (5): 371-380.

Kaya, C., Ashraf, M., Sonmez, O., Aydemir, S., Tuna, A.L. and Cillu, M.A. (2009). The influence of Arbuschular mycorrhizal colonisation on key growth parameters and fruit yield of pepper plants grown at high salinity. *Journal of Scientific Horticulture,* 121:1-6.

Kesseru, P., Kiss, L., Bihari, Z. and Polyak, B. (2002). Investigation of the denitrification activity of immobilised Pseudomonas butanovora cells in the presence of different organic substrates. *Journal of Water Research*, 36 (4): 1565-1571.

Kim-shapiro, D. B., Gladwin, M. T., Patel, R. P. and Hogg, N. (2005). Between nitrate and haemoglobin: The role of nitrate in haemoglobin-mediated hypoxic vasodilation. *Journal of Inorganic Biochemistry*, 99: 237-246.

Lastra, O. C. (2003). Derivative spectrophotometric determination of nitrates in plant tissue, pg 1101-1105.

Mabveni, A. R. S. (2004). Mashroom Cultivation in Zimbabwe. *Mashroom Grower`s Handbook: Regional Research*, pg 213-219.

Malakootian, M., Yousef, N. and Fatehizadeh, A. (2011). Survey efficiency of electrocoagulation on nitrate removal from aqueous solution. *International Journal of Environmental Science Technology*, 8 (2): 107-114.

Mateju, V., Cizinska, S., Krejci, J. and Janoch, T. (2007). Biological water denitrification: A review. *Journal of Enzyme Microbiogical Technology,* 14 (2): 170-183.

Mohan, C. (2008). *Buffers: A guide for the preparation and use of buffer in biological systems*, Macmillan Press Ltd, London, pg 3-16.

Monteiro, M. N. M., Ferreira, F. N., Oliveira, N. M. M. and Avilla, A. K. (2003). Simplified version of the sodium salicylate method for nitrate analysis in drinking water. *Analytica Chimica Acta*, 477: 125-128.

Moyo, M., Maringe, A., Chigondo, F., Nyamunda, B. C., Sebata, E and Shumba, M. (2012). Adsorptive Removal of Nitrate Ions from Aqueous Solutions Using Acid Treatment Sunflower Seed Husk *(Helianthus Annuus*). *International Journal of Advances in Science and Technology*, 5 (6): 47-66.

Namasivayam, C. and Sangeetha, D. (2005). Removal and recovery of nitrate from water by $ZnCl_2$ activated carbon from coconut coir pith, an agricultural solid waste. *Indian Journal of Chemical Technology*, 12 (3): 513-521.

Narayana, B. and Sunil, K. (2009). A spectrophotometric Method for the Determination of Nitrite and Nitrate. *Eurasian Journal of Analytical Chemistry*, 4 (2): 204-214.

Nharingo, T., Shoniwa, V., Hunga, O. and Shumba, M. (2013). Exploring the biosorption of methylene blue dye onto acid treated sugarcane bagasse. *International Journal of Current Research*, 5 (8): 2169-2175.

Oladoja, N. A., Ashogbon, A.O., Oladimeji, J. B. and Aboluwoye, C. O. (2009). Studies on the sorption of basic dye by rubber (*Hevea brasiliensis*) seed shell. *Turkish Journal of Engineering and Environmental Science*, 32: 143-152.

Ong, S. T., Keng, P. S., Ming, H. and Yung, T. H. (2010). Equilibrium studies for the removal of basic dye by sunflower seed husk. *Journal of Hazardous Materials*, 163: 187-198.

Onyango, M. S., Masukume, M., Ochieng, A. and Otieno, F. (2010). Functionalised natural zeolite and its potential for treating drinking water containing excess amount of nitrate. *Journal of Agrochemical, Archaelogy, Green Chemistry and Water*, 36 (5): 655-662.

Pavia, D. L., Lampman, G. M., Kriz, G. S. and Engel, R. G (2007). *Introduction to Organic Laboratory Techniques. A Microscale Approach*, 4th ed. Thomson Brooks / Cole, Singapore, pg 833-867.

Pollard, S. J. T., Folwler, G. D., Sollars, C. J. and Perry, R. (2001). Low cost adsorbents for waste and wastewater treatment. *Science Total Environment*, 116: 31-52.

Rajamohan, N. (2009). Equilibrium studies on sorption of an anionic dye onto acid activated water hyacinth roots. *African Journal of Environmental Science and Technology*, 3 (11): 399-404.

Ryan, W. J. (2002). *Water treatment and purification technology*, 2nd ed. Agrobios, India, pg 103-109.

Saidi, T. A. and Ramatshimbila, T. V. (2006). Ecology and Management of a Remnant Brachstegia Spiciformis (Miombo) Woodland in North Eastern Soutpansberg, Limpopo Province. *South African Geographical Journal*, 88 (2): 205-212.

Sajidu, S. M. I., Henry, E. M. T., Persson, I., Masamba, W. R. L. and Kayambazinthu, D. (2006). pH dependence of sorption of Cd^{2+}, Zn^{2+}, Cu^{2+} and Cr^{3+} on crude water and sodium chloride extracts of *Moringa stenopetala* and *Moringa oleifera*. *African Journal of Biotechnology*, 5 (23): 2397-2401.

Samarghandi, M. R., Hadi, M., Moayedi, S. and Askari, F. B. (2009). Two-parameter isotherns of methyl orange sorption by pinecone derived activated carbon. *Iran Journal of Environmental Science Engineering*, 6 (4): 285-294.

Setshedi, M., Onyango, B., Gabriela, C. and Simona, N. (2010). Removal of heavy metals from aqueous solutions using hydrotalcite–like nano-structured materials. *Journal of Hazardous Materials*, 61 (3): 278-290.

Shanthi, K., Ayyasamy, P. M., Rajakumar, S., Lakshmanaaperumalsamy, P. and Ramasamy, K. (2005). Influence of various carbon sources on nitrate reduction with sludges. *Asian Journal of Microbiology and Biotechnology Environmental Science*, 7 (2): 431-438.

Shao, L., Xu, Z. X., Jin, W. and Yin, H. L. (2009). Rice Husk as Carbon Source and Biofilm Carrier for Water Denitrification. *Polish Journal of Environment Studies*, 18 (4): 693-699.

Silberberg, M. S. (2009). *Chemistry The Molecular Nature of Matter and Change*, 5th ed. Mc Graw-Hill Higher Education, New York, pg 832-840.

Silvestein, R. M., Webster, X. F. and Kiemle, D. J. (2005). *Spectrometric Identification of Organic Compounds*, 7th ed. John Wiley and Sons, Inc, New York, pg 72-108.

Suteu, D., Zaharia, C. and Malutan, T. (2011). Removal of Orange 16 reactive dye from aqueous solutions by waste sunflower seed shells. *Journal of the Serbian Chemical Society*, 76 (4): 607-624.

Tejero, J., Basu, S., Helms, C., Hogg, N., King, S. B., Kim-shampiro, D. B. and Gladwin, M. T. (2012). Enzymology: Low NO concentration-dependance of the reductive nitrosylation reaction of haemolobin. *The Journal of Biological Chemistry*, 6 (3): 1-29.

Utete, B., Mutasa, L., Ndlovhu, N. and Tendaupenyu, I. H. (2013). Impact of Aquaculture on Water Quality in Lake Kariba Zimbabwe. *International Journal of Aquaculture*, 3 (4): 11-16.

WHO, (2011). *Nitrate In: Guidelines for drinking water quality*, 3rd ed. Incorporating 1st and 2nd addenda, 1:317-319.

Woo, S. H. and Chatterjee, S. (2008). The removal of nitrate from aqueous solutions by chitosan hydrogel beads. *Journal of Hazardous Material*, 164 (9): 1012-1018.

Yang, X., Zhan, M. J., Kong, L. R. and Wang, L. S. (2004). Determination of hydroxyl radicals with salicylic acid in aqueous nitrate and nitrite solutions. *Journal of Environmental Science*, 16 (4): 687-689.

Yu, W., Bao-yu, G., Yue, W. and Yue, Q. (2007). Preparation and utilisation of wheat straw anionic sorbent for the removal of nitrate from aqueous solution. *Journal of Environmental Sciences*, 19 (2): 1305-1310.

APPENDIX

APPENDIX A

AI Apparatus

Polythene bags, 250 µm sieve, pestle and mortar, 2000 ml plastic container, Whatman filter papers, spatula, 50 ml, 100 ml and 1000 ml volumetric flasks, desiccator, 1ml, 10ml and 20 ml graduated pipettes, burette, wash bottle, vacuum filtration flasks, Buchner funnels, 50ml and 250 ml Erlenmeyer flasks, retort stand and beakers.

A2 Reagents

Table A-1: Reagents used

Chemical Name	Chemical Formula	Manufacturer	Concentration
Salicylic acid	$C_7H_8O_3$	Rochelle	138.13 g mol^{-1}
Potassium nitrate	KNO_3	Alpha Chemika	101.1 g mol^{-1}
Sodium hydroxide	NaOH	Associated Chemical Enterprises	40 g mol^{-1}
Hydrochloric acid	HCl	Scientific Masters	32%
Sulphuric acid	H_2SO_4	Glassworld	98%
Sodium citrate	CH_3COONa	Cosmo Chemicals	82.034 g mol^{-1}
Potassium dihydrogen phosphate	KH_2PO_4	Associated Chemical Enterprises	136.09 g mol^{-1}
Acetic acid	CH_3COOH	Skylabs	65.05 g mol^{-1}
Potassium bromide	KBr	Buck Scientific	119.01 g mol^{-1}

A3 Instrumentation

Table A-2: Instrumentation used

Instrument Name	Model	Manufacturer	Use in project
Digital analytical balance	GA110	OHAUS	Accurate mass measurements
Mechanical shaker	HY-4	Griffin	Shaking of samples
Oven	DHG-9070A	Labcon	Drying of samples
pH meter	BT-675	Boeco Germany	pH measurement
Hot plate	MSH 10	Labcon	Sample heating
Ultra-violet visible spectrometer	UV 752 PC	Shangai Youko Instruments	Nitrates quantification
Fourier Transform Infrared spectrometer	Nicolet 6700	Thermoscientific	Functional group determination on *Brachystegia spiciformis* leaf powder

A4 Stock and calibration solutions preparation

Preparation of 1000 mgL^{-1} nitrate stock solution was done using the following formula

$$\text{mass of } KNO_3 \text{ (g)} = 1g \times {M_{r(KNO_3)}}/{M_{r(NO_3^-)}} \times {100}/{t}$$

Where: t is the purity,

$M_{r(KNO_3)}$ is the relative molecular mass of potassium nitrate and,

$M_{r(NO_3^-)}$ is the relative molecular mass of the nitrate.

The mass of 1.6469 g calculated was transferred to 1000 ml a volumetric flask and was filled up to mark with distilled water to come up with 1000 mg L^{-1}.

Calibration solutions were prepared from 1000 mg L^{-1} stock solution using the following formula:

$$C_1V_1 = C_2V_2$$

Where C_1 and C_2 are the initial and final concentrations respectively and V_1 and V_2 are the initial and final volumes respectively. Concentrations of 5, 10, 20, 30, 40, 50 and 60 mg L^{-1} for nitrate calibration solutions were prepared.

A5 Preparation of 0.05 M HCl and 2 M, 0.1 M and 0.05 M NaOH solutions

A concentration of 0.05 M HCl was prepared basing on the following formula:

$$\text{volume to collect of 32 \% HCl} = x \times {100}/{y} \times {M_r}/{\rho}$$

Where: x is the molarity to be prepared,

y is the percentage of the stock solution,

M_r is the relative molecular mass of HCl and,

ρ is the density of HCl.

A solution of 2 M NaOH was prepared by dissolving 40 g of NaOH in 500 ml distilled water. Solutions of 0.1 M and 0.05 M NaOH were prepared in 100 ml volumetric flask from 2 M solution using the following formula:

$$C_1V_1 = C_2V_2$$

Where C_1 and C_2 are the initial and final concentrations respectively and V_1 and V_2 are the initial and final volumes respectively.

A6 Preparation of 5% (w/v) salicylic acid in concentrated sulphuric acid

A mass of 5.0000 g of salicylic acid was dissolved in concentrated sulphuric acid up to a 100 ml mark of a volumetric flask.

A7 Preparation of pH meter calibration solutions

pH buffer 2, 4 and 7 were prepared basing on the Henderson-Hasselbalch equation which is given by a general mathematical relationship as:

$$pH = pK_a + \log\left({[\text{conjugate base}]}/{[\text{acid}]}\right)$$

A8 Formulae used in calculation of the amount adsorbed (Q_e), percentage removal and the desorption percentage

$$Q_e = \left[{(C_i - C_e) \times v}/{m}\right] \text{ and } R\% = 100\,{[C_i - C_e]}/{C_i}$$

Where: C_i is the initial nitrate concentration (mg L^{-1}),

C_e is the equilibrium nitrate concentration (mg L^{-1}),

$R\%$ is the percentage removal of nitrates at equilibrium,

v is the volume (L) and,

m is the mass (g)

$$\%\text{age desorption} = {Q_{des}}/{Q_{ads}} \times 100\%$$

Where: Q_{des} is the amount of nitrates desorbed (mg L^{-1}) and,

Q_{ads} is the amount of nitrates adsorbed (mg L^{-1})

A9 Statistical Treatment of Data

The following formula was used for the determination of standard deviation (sd)

$$sd = \sqrt{\sum(x - \bar{x})^2 / n - 1}$$

$$= \sqrt{\left(\sum x^2 - \frac{[\sum x]^2}{n}\right) / n - 1}$$

Where $x, \bar{x}$, n and $n - 1$ is the sample result, sample mean, sample size and degrees of freedom respectively.

APPENDIX B: Batch Experiments

Calibration data

Table B-1: Calibration data

Concentration / mg L^{-1}	Absorbance
0	-0.001
5	0.038
10	0.080
20	0.163
30	0.249
40	0.329
50	0.381
60	0.500

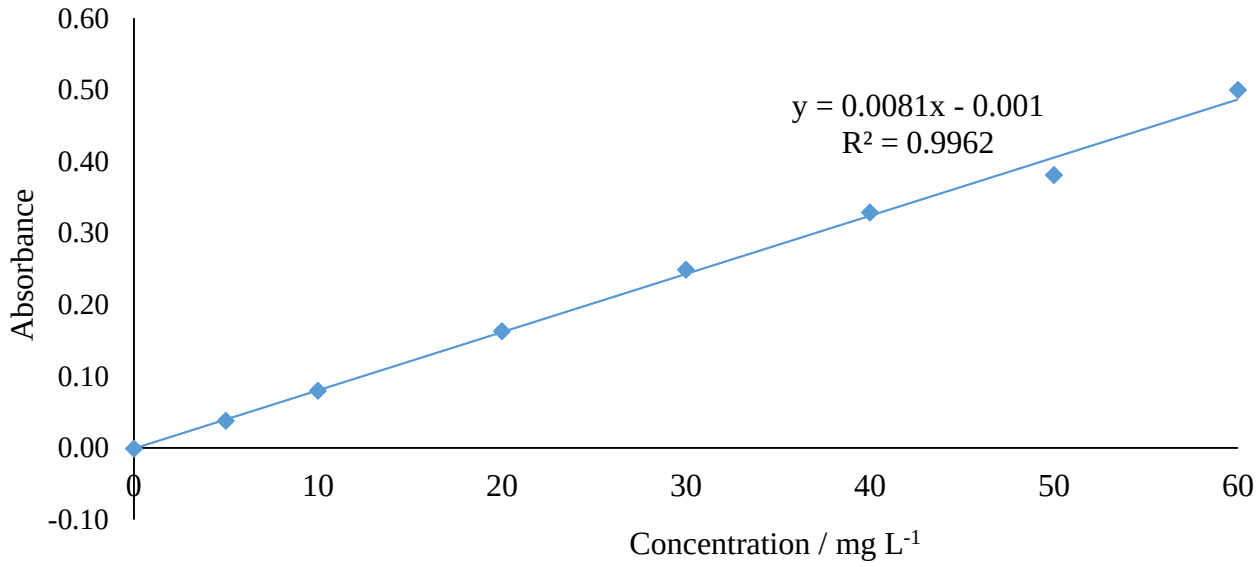

Figure B.1: Calibration curve

Table B-2: Effect of pH on nitrate sorption at a contact time of 24 hours

pH	C_i / mg L^{-1}	Dosage / g	C_{e_1}/ mg L^{-1}	C_{e_2}/ mg L^{-1}	C_{e_3}/ mg L^{-1}	$C_{e_{ave}}$/ mg L^{-1}	Standard Deviation	Q_e / mg g^{-1}
2	47.303	1.0011	23.385	23.196	25.643	23.921	±0.134	1.201
3	47.303	1.0005	26.554	22.713	22.341	22.527	±0.063	1.239
4	47.303	1.0006	21.653	21.783	25.258	21.718	±0.092	1.279
5	47.303	1.0013	28.343	28.910	29.260	29.085	±0.131	0.911
6	47.303	1.0010	29.701	30.192	29.431	29.566	±0.091	0.887
7	47.303	1.0011	32.143	32.106	32.353	32.125	±0.026	0.759
8	47.303	1.0011	32.697	34.831	32.488	32.593	±0.148	0.736

Table B-3: Effect of contact time on nitrate sorption at pH 4

Time / minates	C_i / mg L^{-1}	Dosage / g	C_{e_1}/ mg L^{-1}	C_{e_2}/ mg L^{-1}	C_{e_3}/ mg L^{-1}	$C_{e_{ave}}$/ mg L^{-1}	Standard deviation	Q_t / mg g^{-1}
0	50.802	0.0000	50.802	50.802	50.802	50.802	±0.000	0.000
1	50.802	1.0014	41.006	41.532	41.365	41.301	±0.118	0.475
2	50.802	1.0000	41.296	38.432	39.465	39.731	±0.188	0.554
3	50.802	1.0002	36.981	36.230	36.250	36.487	±0.014	0.716
4	50.802	1.0002	35.751	35.822	35.815	35.796	±0.005	0.750
5	50.802	1.0006	32.450	33.993	34.006	33.483	±0.009	0.866
6	50.802	1.0002	27.136	27.854	27.633	27.541	±0.156	1.163
10	50.802	1.0001	15.289	15.261	14.996	15.182	±0.020	1.781

20	50.802	1.0003	12.770	12.869	13.067	12.902	±0.070	1.895
50	50.802	1.0003	13.920	13.874	14.032	13.942	±0.032	1.843
80	50.802	1.0000	14.153	14.072	14.261	14.162	±0.057	1.832
120	50.802	1.0002	15.983	16.112	15.971	16.022	±0.008	1.739
140	50.802	1.0003	15.843	16.001	15.982	15.942	±0.013	1.743

Table B-4: Effect of *Brachystegia spiciformis* dose on nitrate sorption at pH 4 and contact time of 30 minutes

Dose / g	**C_i / mg L^{-1}**	**C_{e_1} / mg L^{-1}**	**C_{e_2} / mg L^{-1}**	**C_{e_3} / mg L^{-1}**	**$C_{e_{ave}}$ / mg L^{-1}**	**Standard deviation**	**Q_t / mg g^{-1}**	**%age removal**
0.0504	49.998	46.789	47.945	46.573	47.102	±0.152	2.896	5.79
0.1006	49.998	43.997	44.332	44.088	44.139	±0.173	2.930	11.72
0.1503	49.998	41.445	41.678	41.081	41.379	±0.164	2.873	17.06
0.2003	49.998	38.267	38.402	38.524	38.398	±0.128	2.900	23.20
0.2502	49.998	35.623	35.602	35.613	35.613	±0.010	2.877	28.77
0.5003	49.998	25.872	25.973	25.706	25.851	±0.134	2.415	48.30
1.0004	49.998	18.640	18.413	18.522	18.525	±0.113	1.573	62.95
1.5003	49.998	16.700	16.403	16.513	16.539	±0.150	1.115	66.92
2.0003	49.998	16.417	16.400	16.412	16.409	±0.008	0.840	67.18
2.5002	49.998	16.500	16.555	16.531	16.529	±0.028	0.669	66.94
3.0002	49.998	16.230	16.330	16.216	16.259	±0.062	0.607	67.48

Table B-5: Effect of initial concentration on nitrate sorption at pH 4, contact time of 30 minutes and dosage of 1.5 g

Theoretical C_i/ mg L^{-1}	**Measured C_i/ mg L^{-1}**	**Dosage / g**	**C_{e_1}/ mg L^{-1}**	**C_{e_2}/ mg L^{-1}**	**C_{e_3}/ mg L^{-1}**	**$C_{e_{ave}}$/ mg L^{-1}**	**Standard deviation**	**Q_e / mgg^{-1}**
5	5.033	1.5006	0.015	0.017	0.016	0.016	±0.001	0.166
10	10.009	1.5004	2.437	2.427	2.433	2.432	±0.005	0.252
15	15.003	1.5004	3.672	3.681	3.677	3.677	±0.005	0.377
20	20.067	1.5003	6.165	6.259	6.251	6.258	±0.005	0.458
25	25.033	1.5005	7.458	7.472	7.463	7.464	±0.007	0.584
30	30.003	1.5004	9.337	9.341	9.303	9.327	±0.020	0.689
35	34.974	1.5007	9.875	8.988	9.435	9.655	±0.098	0.845
40	39.945	1.5003	10.996	10.907	10.956	10.953	±0.044	0.968
45	45.033	1.5002	15.311	15.331	15.334	15.326	±0.012	0.989
50	50.039	1.5004	19.997	20.010	20.009	20.005	±0.007	1.000

APPENDIX C: Equilibrium sorption data and calculations

Langmuir isotherm

$$Q_e = {Q_M b C_e}/{1 + b C_e}$$

The linearized equation is as follows:

$${C_e}/{Q_e} = {1}/{Q_M} \cdot C_e + {1}/{b Q_M}$$

Where: ${1}/{Q_M}$ and ${1}/{b Q_M}$ is the slope and the ${C_e}/{Q_e}$ intercept respectively.

But the linearized equation on ${C_e}/{Q_e}$ against C_e plot is as follows:

$${C_e}/{Q_e} = 0.6136 C_e + 6.6457$$

Hence ${1}/{Q_M} = 0.6136$

$\therefore Q_M = {1}/{0.6136} = 1.629726 \text{ mg g}^{-1}$

Also ${1}/{b Q_M} = 6.6457$

Hence $b = {1}/{6.6457 \times 1.629726}$

$\therefore b = 0.0923330 \text{ L mg}^{-1}$

Also separation factor, $R_L = {1}/{1 + b C_i}$

Where b and C_i is the separation factor and initial concentration respectively.

$\therefore R_L = {1}/{1 + (0.0923330 \times 49.998)} = 0.1781 \text{ L mg}^{-1}$

Table C-1: Langmuir isotherm data

C_e / mg L^{-1}	Q_e / mg g^{-1}	${Q_e}/{C_e}$
2.432	0.2523	8.0561

3.677	0.3774	9.7410
4.258	0.4581	9.2962
5.464	0.5845	9.3481
8.327	0.6890	12.0841
9.655	0.8411	12.9998
13.953	0.9682	14.4110
15.326	0.9891	15.4937
20.005	0.9998	20.0091

Halsey isotherm

$Q_e = e^{[\ln K_h - \ln C_e]/n}$

The linearized equation is as follows:

$\ln Q_e = {}^{1}/_{n} \ln K_h - {}^{1}/_{n} \ln C_e$

Where: ${}^{1}/_{n}$ is the slope of $\ln Q_e$ against $\ln C_e$ plot

${}^{1}/_{n} \ln K_h$ is the $\ln Q_e$ intercept

But the equation of the graph is as follows:

$\ln Q_e = 0.6302 \ln C_e - 1.7345$

Hence ${}^{1}/_{n} = 0.6302$

$\therefore n = {}^{1}/_{0.6302} = 1.586798$

Also $^{1}/_{n} \ln K_h = -1.7345$, but $^{1}/_{n} = 0.6302$

Hence $K_h = e^{-2.752300857} = 0.063780941 L\ mg^{-1}$

Table C-2: Halsey isotherm data

C_e / mg L^{-1}	Q_e / mg g^{-1}	ln C_e	ln Q_e
2.432	0.2523	0.7091	-1.3773
3.677	0.3774	1.3020	-0.9743
4.258	0.4581	1.4489	-0.7808
5.464	0.5845	1.6982	-0.5370
8.327	0.6890	2.1195	-0.3724
9.655	0.8411	2.3764	-0.1730
13.953	0.9682	2.6357	-0.0323
15.326	0.9891	2.7295	-0.0109
20.005	0.9998	2.9960	-0.0002

Dubinnin-Radushkevich isotherm

$Q_e = Q_W e^{-K_{ad}\varepsilon^2}$

The linearized equation is as follows:

$$\ln Q_e = \ln Q_W - 2B_W RT \ln\left[1 + {}^{1}/_{C_e}\right]$$

Where: B_W and is the slope and $\ln Q_W$ is the $\ln Q_e$ intercept.

But the equation of the graph is as follows:

$$\ln Q_e = -4.2073 \ln\left[1 + {}^{1}/_{C_e}\right] + 0.1828$$

But $2B_W RT = 4.2073$

$$\therefore B_W = {}^{4.2073}/_{(2 \times 298 \times 8.314)} = 0.000849077 \text{mol}^2\ \text{kJ}^{-2}$$

Also $\ln Q_W = 0.1828$

$$\therefore Q_W = e^{0.1828} = 1.200574269\ \text{mg g}^{-1}$$

$$\text{Also } E_W = {}^{1}/_{[2B_W]^{1/2}} = {}^{1}/_{[2 \times 0.000849077]^{1/2}} = 24.2667415\ \text{kJ mol}^{-1}$$

Table C-3: Dubinnin-Radushkevich isotherm data

C_e / mg L^{-1}	Q_e / mg g^{-1}	$\ln\left[1 + {}^{1}/_{C_e}\right]$	$\ln Q_e$
2.432	0.2523	0.4002	-1.3773
3.677	0.3774	0.2406	-0.9743
4.258	0.4581	0.2109	-0.7808
5.464	0.5845	0.1681	-0.5370
8.327	0.6890	0.1134	-0.3724
9.655	0.8411	0.0888	-0.1730
13.953	0.9682	0.0692	-0.0323
15.326	0.9891	0.0632	-0.0109
20.005	0.9998	0.0488	-0.0002

Freundlinch isotherm

$Q_e = K_F C_e^{\frac{1}{n}}$

The linearized equation is as follows:

$\log[Q_e] = \log[K_F] + {}^{1}/_{n} \log[C_e]$

Where ${}^{1}/_{n}$ and $\log[K_F]$ is the slope and the $\log[Q_e]$ intercept

But the equation of the graph is as follows:

$\log Q_e = 0.6302 \log C_e - 0.7533$

But ${}^{1}/_{n} = 0.6302$

$\therefore n = 1.586797842$

Also $\log[K_F] = -0.7533$

Hence $K_F = 0.17648183$(mg g^{-1})(L mg^{-1})^n

Table C-4: Freundlinch isotherm data

C_e / mg L^{-1}	Q_e / mg g^{-1}	log C_e	log Q_e
2.432	0.2523	0.3080	-0.5982
3.677	0.3774	0.5654	-0.4232
4.258	0.4581	0.6292	-0.3391
5.464	0.5845	0.7375	-0.2332
8.327	0.6890	0.9205	-0.1617
9.655	0.8411	1.0321	-0.0818

13.953	0.9682	1.1447	-0.0140
15.326	0.9891	1.1854	-0.0047
20.005	0.9998	1.3011	-7.8614E-05

Temkin isotherm

$$Q_e = {RT}/{b_t} \ln[K_t C_e]$$

The linearized equation is as follows:

$$Q_e = {RT}/{b_v} \ln K_t + {RT}/{b_t} \ln C_e$$

Where ${RT}/{b_t}$ and ${RT}/{b_t} \ln K_t$ is the slope and the $\ln C_e$ intercept respectively of the Q_e against $\ln C_e$ plot.

But the equation of the graph is as follows:

$$Q_e = 0.3677 \ln C_e - 0.0516$$

But ${RT}/{b_t} = 0.3677$

$$\therefore b_t = {(298 \times 8.314)}/{0.3677} = 6\,738.025564 \text{Jmol}^{-1} = 6.738 \text{kJmol}^{-1}$$

Also ${RT}/{b_t} \ln K_t = -0.0516$

$$\ln K_t = {-0.0516}/{367.7} = -0.000140331$$

$$\therefore K_t = 0.999859678 \text{ L g}^{-1}$$

Table C-5: Temkin isotherm data

C_e / mg L^{-1}	ln C_e	Q_e / mgg^{-1}
2.432	0.7091	0.2523
3.677	1.3020	0.3774
4.258	1.4489	0.4581
5.464	1.6982	0.5845
8.327	2.1195	0.6890
9.655	2.3764	0.8411
13.953	2.6357	0.9682
15.326	2.7295	0.9891
20.005	2.9960	0.9998

APPENDIX D: Desorption studies and industrial effluent water analysis

Table D-1: Desorption

pH	C_i / mg L^{-1}	C_e / mg L^{-1}	Ave C_e / mg L^{-1}	Amount adsorbed / mg L^{-1}	Average amount adsorbed / mg L^{-1}	Amount desorbed / mg L^{-1}	Average amount desorbed / mg L^{-1}	%age desorption
9	48.659	35.817		12.842		9.872		
		35.800		12.859		8.346		
		35.818	35.811	12.847	12.850	9.563	9.260	72.07
10	49.081	38.650		10.431		8.588		
		37.560		11.521		8.634		
		38.850	38.353	10.728	10.893	8.501	8.754	78.71
11	49.732	43.330		6.402		5.608		
		43.353		6.379		5.912		
		43.449	43.378	6.283	6.354	5.877	5.799	91.26
12	49.811	42.546		7.265		5.824		
		42.442		7.369		5.930		
		42.446	42.478	7.365	7.333	5.778	5.844	79.69
13	49.006	42.317		7.599		6.119		
		42.256		7.660		6.202		
		42.426	42.333	7.490	7.583	6.010	6.110	80.58

Table D-2: Industrial effluent water analysis

Volume of industrial effluent water / ml	**Brachystegia spiciformis Dosage / g**	**$[NO_3^-]$ before sorption / mgL^{-1}**	**$[NO_3^-]$ after sorption / mgL^{-1}**	**Average $[NO_3^-]$ after sorption / mgL^{-1}**	**Standard deviation**	**Q_e / $mg\ g^{-1}$**
50	1.5002	36.871	18.349			
		36.871	18.351			
		36.871	18.349	18.349	±0.001	0.6174
50	1.5009	36.871	21.225			
		36.871	21.225			
		36.871	21.221	21.225	±0.002	0.5215
50	1.5003	36.871	20.165			
		36.871	20.165			
		36.871	20.165	20.165	±0.000	0.5569

APPENDIX E: Fourier Transform Infrared Spectra for *Brachystegia spiciformis* before and after nitrate sorption as well as after desorption

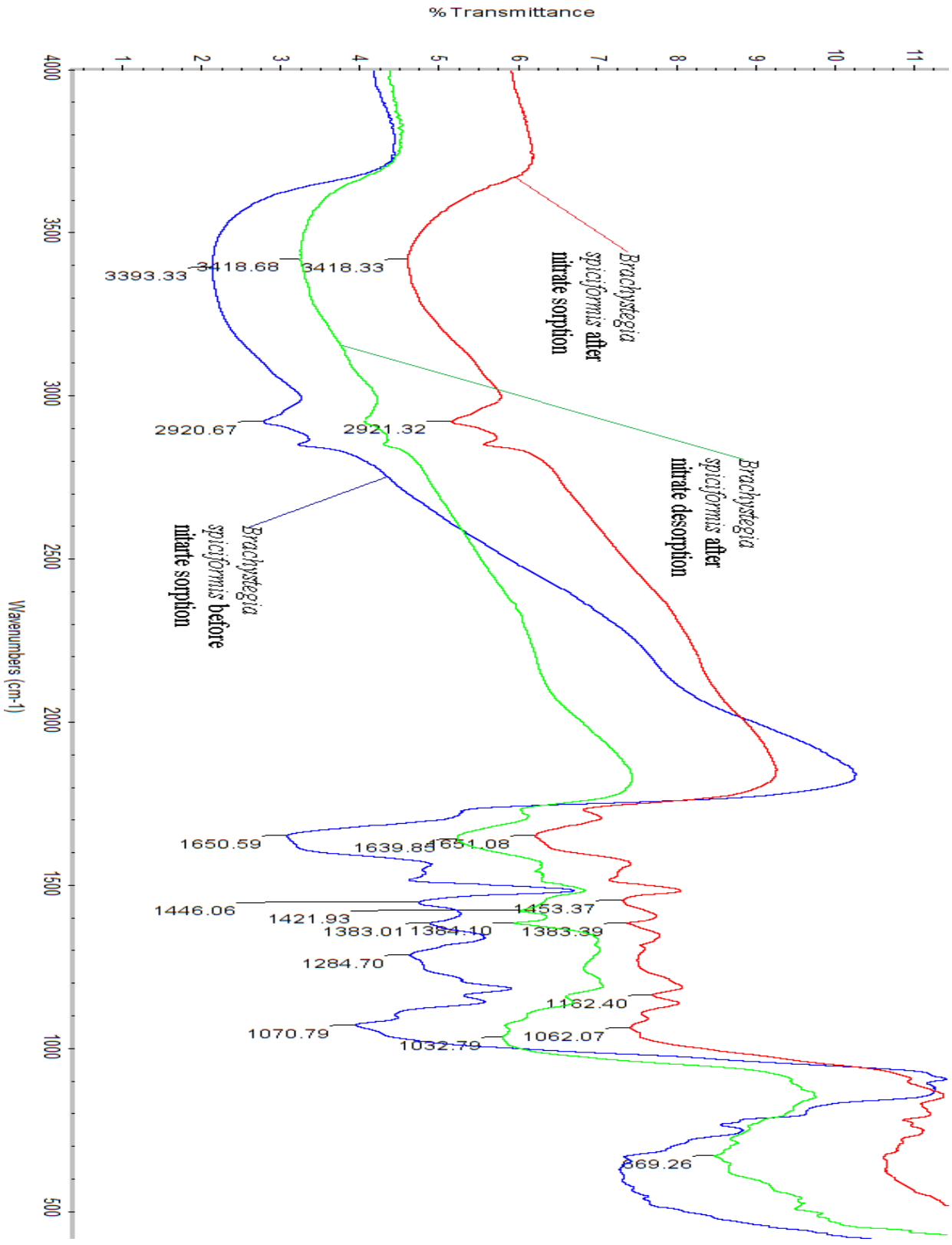

Figure E.1: *Brachystegia spiciformis* leaf powder spectrum