

Nickel pollution abatement from landfill leachate using biomaterials

By

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ABSTRACT

Batch experiments were conducted to assess the removal of Ni(II) from aqueous solutions and landfill leachates using low cost adsorbents eggplant peel (EGP), sweet potato peel (SWP) and banana peel (BNP). Preliminary studies were carried out to optimize biosorbent mass, pH, Ni(II) concentration, temperature and contact time for Ni(II) removal. The optimized conditions were then applied to landfill leachates using the selected low cost adsorbents.

Ni(II) removal efficiency for each biosorbent was investigated for each parameter. Results indicated that biosorbents masses, pH, initial concentration as well as solution temperature were important factors influencing Ni(II) removal from aqueous solutions. Percentage Ni(II) removal was 66 ± 0.30 , 38 ± 3.97 and 33 ± 1.20 using EGP, SWP and BNP, respectively. Ni(II) removal efficiency increased significantly ($P \leq 0.05$) with increasing biosorbent mass, pH and Ni(II) initial concentration while it decreased significantly ($P \leq 0.05$) with increasing temperature. Although Ni(II) removal efficiency varied significantly with time and the biosorbents no significant ($P > 0.05$) difference was observed between the time interval whether the experiment was conducted in batch or semi batch mode.

Results of FTIR studies indicated that several binding and chelating functional groups such as carboxyl, carbonyl and hydroxyl groups on the biomaterials surfaces could be responsible for Ni(II) biosorption.

The optimum biosorbent mass for EGP and SWP was 0.4 g and for BNP was 0.05 g. The values for initial concentration, pH, temperature and contact time were 100 mg/L, 5, 22°C and 2 hours, respectively. Ni(II) removal efficiencies using EGP, SWP and BNP were 66, 38 and 33%, respectively.

Taking into account the result and optimum condition obtained on Ni(II) removal efficiency from aqueous solution using EGP, SWP and BNP, the Ni(II) removal efficiency using these biosorbents from landfill leachate was investigated. It was found to be significantly ($P \leq 0.05$) lower than what was found from aqueous solution.

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DEDICATION

I wish to dedicate this work to my entire family who have given me support and encouragement throughout my study.

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GLOSSARY

Abbreviations	Definition
ρ_b :	Bulk density (g/mL)
ρ_s :	Particle density (g/mL)
ρ_w :	Water density (g/mL)
1/n:	Freundlich intensity parameter (dimensionless)
ANOVA:	Analysis of variance
BNP:	Banana peel
$C_{ad, ed}$:	Metal concentration on the biosorbent
C_{de} :	Metal concentration desorbed (mg/L)
C_e :	Metal equilibrium concentration (mg/L)
C_{ed} :	Residual metal concentration at equilibrium
C_o :	Initial metal concentration (mg/L)
DI:	Deionised water
DMRT	Duncan multiple range test
EGP:	Egg plant peel
FAAS:	Flame atomic absorption spectrometer
FIL:	Filtered
FTIR:	Fourier transform infrared
GLM	Generalised linear model
IARC:	International Agency for Research on Cancer
ICP-MS:	Inductively coupled plasma-mass spectrometry
K:	Kelvin
K_1 :	First order rate constant (min^{-1})
K_2 :	Second order rate constant (min^{-1})
K_c :	Equilibrium constant
K_f :	Freundlich constant (empirical constant)
K_L :	Langmuir constant (empirical constant)
m:	Mass of the biosorbent (g)
M_{f+w} :	Mass of flask filled to volume with distilled water (g)
M_s :	Oven-dried biosorbent mass (g)
M_{s+f+w} :	Mass of flask, oven dried biosorbent and distilled water (g)
M_t :	Oven-dried sample mass (g)
n:	Porosity (dimensionless)
NA	Not available
ND:	No detected

q:	Capacity of biosorbent (mg/g)
q _e :	Amount of metal adsorbed at equilibrium (mg/g)
q _m :	Maximum biosorbent capacity (mg/g)
q _t :	Amount of metal adsorbed at time t (mg/g)
R:	Universal gas constant (J mol ⁻¹ K ⁻¹)
RDS:	Relative standard deviation
SAS:	Statistical Analysis Software
SD:	Standard deviation
SWP:	Sweet potato peel
T:	Temperature (K)
t:	Time (min)
TDS:	Total dissolved solids
UNF:	Unfiltered
V:	Volume of metal ion (L)
VFA:	Volatile fatty acids
V _t :	Beaker volume (mL)
ΔG°:	Standard Gibbs free energy change (J)
ΔH°:	Standard enthalpy change
ΔS°:	Standard entropy change

CHAPTER ONE

INTRODUCTION

1.1 Background

Heavy metal pollution from wastewaters such as landfill leachate is of concern due to their presence and toxicity in the environment. Residual metals in the environment pose a threat not only to human health, but can also have serious detrimental effects on aquatic ecosystems (Papageorgiou *et al.*, 2006). Each landfill produces a liquid stream called leachate which is a highly complex and polluted wastewater. Substances that make up leachate can either be useful or harmful to the environment. An example of a useful component of leachate is water. Water is essential in plant and animal life. Without water there will be no life. Metals are used in a variety of applications and are thus present in municipal and industrial landfills. The main sources of heavy metals in landfill sites are garden pesticides, pharmaceuticals, photographic chemicals, certain detergents, personal care products, fluorescent tubes, waste oil, batteries, chemically treated wood, electronic waste, electrical equipments, paint and many other house hold goods (Slacka *et al.*, 2005). These metals commonly include manganese, arsenic, cadmium, nickel, lead, chromium, mercury, cobalt, copper and many others (Baun and Christensen, 2004). They have been reported to have toxic and/or carcinogenic effects on human health. Therefore, their removal from landfill leachate is of importance. Ni(II) ion is frequently encountered in raw wastewater streams from landfill leachate, mine drainage, metal finishing and forging. Concentrations up to 130 mg/L have been reported in these water streams. It is bio-accumulated by marine animals and may directly enter food chains thus presenting high health risk to consumers (Dean *et al.*, 1972). Even at low concentration it can be toxic to organisms. Acute poisoning by Ni(II) causes headache, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough, shortness of breath, cyanosis and extreme weakness (Malkoc and Nuhoglu, 2005). There is thus a need to find sustainable leachate treatment options to avoid or minimize pollution and its accompanying health effects.

Traditionally, conventional landfill leachate treatment processes have been similar to those that have been used for regular wastewater. The main approaches include biological, physical and chemical (physicochemical) treatment processes. The main disadvantages for leachate treatment processes are high running costs for chemical processing and a consistent high sludge volume which is produced after concentration of the metal (Farinella *et al.*, 2008). Adsorption onto activated carbon is one of the most extensively applied physicochemical processes for the removal of pollutants from leachates and wastewaters (Forster and Wase, 1997). Although activated carbon is widely applied for pollutant removal, biomaterials which are relatively cheaper and eco-friendly have also been successfully

employed as biosorbents for heavy metal removal from aqueous solutions and wastewaters due to their availability, low-cost, unique chemical composition and renewability (Juang and Shiau, 2000; Lacour *et al.*, 2001 and King *et al.*, 2007). The reduced running cost has been the focal point for research on application of biomaterials. Cost is a very important factor when considering material for use as biosorbents. The recent attention in this field is evident in the number of research currently being done on the use of low cost agricultural wastes for metal removal from aqueous solution (Gupta *et al.*, 2003; Iqbal *et al.*, 2009 and Jiang *et al.*, 2009).

Peels, also known as skin, are the outer protective layers of fruit or vegetables currently gaining wide attention as biosorbents in wastewater treatment. Peelings of different fruit such as, orange, banana, water melon, cassava, mango and many others, have been used as adsorbents for the removal of different pollutants from wastewaters (Juang and Shiau, 2000 and King *et al.*, 2007). These peels have no known commercial purposes and so, are discarded as waste thus becoming a source of pollution. They contain pectin, polyphenols, cellulose, hemicelluloses and lignin (Anwar *et al.*, 2009). These biopolymers are rich in functional groups such as hydroxyl, carboxylic and carbonyl, and are known to be responsible for metal ion binding from aqueous matrices (Deng *et al.*, 2007). Banana, eggplant and sweet potato are inexpensive crops which are available in many regions. They are among the most important food crops grown in both tropical and subtropical regions and are ranked among the top six in terms of production output (FAO stat, 2008). Banana is rich in sugar. It contains about 70% water, 27% carbohydrate, 1.2% protein and 0.3% of fat and 1 cal/g energy value. Several vitamins have been recorded and the fruit is considered a good source of vitamins A, B1, B2 and C. Eggplant, also known as aubergine, brinjal or Guinea squash ranks 5th in the world's vegetable crops production. Its nutritious value is comparable to other common vegetables (Collonnier, 2001). Its fresh weight is composed of 92.7% moisture, 1.4% protein, 1.3% fibre, 0.3% fat, 0.3% minerals, and the remaining 4% consists of various carbohydrates and vitamins (Khan, 1979). Sweet potato is an essential source of provitamin A that has been proven to improve the vitamin A status of children. Peels from these crops are composed of complex materials such as pectin, polyphenols, cellulose, hemicelluloses and lignin. They contain functional groups that are responsible for biosorption of metal ions. The main functional groups of these biopolymers include, carboxylic acids (R-COOH), phenolic hydroxides (Ar-OH), alcohols (R-CH₂-OH), aldehydes (R-C=O(-H)), ketones (R-C=O(-R)) and ethers (R-CH₂-O-CH₂-R') (Pehlivan *et al.*, 2008; Iqbal *et al.*, 2009). These functional groups are negatively charged, which allows for the strong attraction of metal ions to these peels. Therefore, eggplant, sweet potato and banana peels, due to their high pectin, polyphenol and cellulose content offer the potential for use as biosorbent for the removal of heavy metal from aqueous solution.

In this study, these three biomaterials (egg plant, sweet potato and banana peels) were tested for Ni(II) removal from aqueous solutions and landfill leachates. Effect of mass adsorbents, pH, initial concentration, contact time and temperature were studied. Ni(II) was selected for this study due to its prevalence in wastewaters and a heavy metal commonly found in landfill leachates. Also, available literature on Ni(II) removal from aqueous solutions showed that complete removal of this metal during treatment was seldom reported, indicating that this metal could pose a serious problem during water treatment processes.

1.2. Research questions

The key questions to be answered in this research are:

- I. How can biosorption conditions be modified in order to achieve the maximum biosorption of Ni(II) removal from aqueous matrices?
- II. Is nickel present in landfill leachate?
- III. Can these low cost adsorbents (EGP, SWP and BNP) remove Ni(II) from aqueous solutions and landfill leachate?
- IV. Is it a promising approach to treat landfill leachate with biosorbents in order to make the process of removal of Ni(II) more economical?

1.3. Objectives of the study

The main objective of this research was to investigate the use of three biosorbent materials in the removal of Ni(II) from landfill leachate using a series of batch studies under various experimental conditions. The specific objectives were:

- I. To study the biosorption mechanism, thermodynamic parameters, kinetics and other variables important for the removal of Ni(II) from aqueous matrices.
- II. To quantify levels of Ni(II) in leachates from selected landfill sites.
- III. To investigate the potential recovery of Ni(II) from biosorbent.
- IV. To identify the best biosorbent for Ni(II) removal from landfill leachate.

1.4. Delimitations

These investigations were focused on sweet potato, egg plant and banana peels' effectiveness for Ni(II) removal based on optimizing experimental conditions. Experiments were carried out using standard solutions to validate the method before application to landfill leachates. The role of microorganisms in the removal of heavy metals from wastewater has been reported (Ludvigsen *et al.*, 1999). This study was however focused on the removal of the remaining portion of metal waste using biosorption. Thus the influence of microorganisms was not considered in this study. The effect of other metals present in the leachates on the biosorption of Ni(II) by biomaterials was also not investigated.

CHAPTER TWO

LITERATURE REVIEW

2.1 Heavy metals

Heavy metals are metals that have specific gravity of 5, atomic number from 23 to 92 in period 4 to 7 of periodic table. They include arsenic, cadmium, antimony, bismuth, cerium, chromium, cobalt, copper, gold, gallium, iron, lead, manganese, mercury, platinum, nickel, tellurium, silver, thallium, uranium, tin, vanadium, and zinc (Erzsebet *et al.*, 2011). With the exception of mercury, all heavy metals are solid at room temperature. Some of these heavy metals such as copper, zinc, iron and manganese are required by humans for proper biological functions. However, excessive amounts of any of them may cause acute or chronic toxicity. Toxic heavy metals are capable of imitating the actions of essential elements in the body, interfering with the metabolic process and hence cause illness.

2.1.1 Nickel

Nickel is a metallic element with symbol Ni and relative atomic mass 58.69. Nickel is found in the first transition series of group VIIIb of the periodic table and is naturally present in the earth's crust. Five natural isotopes are known, of which ^{58}Ni (68.27%) and ^{61}Ni (26.10%) are the most abundant.

2.1.1.1 Occurrence properties and uses of nickel

Nickel is found in one of several oxidation states ranging from -1 to +4. However, the +2 oxidation state is the most prevalent form of nickel in biosystems. Solubilized Ni(II) in aqueous media at neutral pH are hydrated to the greenish hexahydrate $[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$. Pure nickel is ductile and malleable and can be polished, forged and welded. It is inert against corrosion by air, water, non-oxidizing acids, alkalis and many organic solvents (Denkhaus and Salnikow, 2002). It dissolves slowly in dilute nitric acid but not in concentrated nitric acid due to passivation of the metal surface. Nickel occurs combined with sulphur in millerite, with arsenic in the mineral niccolite, and with arsenic and sulphur in nickel glance. Nickel compounds are widely used in electroplating, electroforming, and for production of nickel-cadmium batteries and electronic equipment due to its unique physical and chemical properties. Nickel alloys, like stainless steel, are used in the production of tools, armaments, machinery, and appliances. They are also used to cast coins, and to produce jewellery and medical prostheses.

2.1.1.2 Effects of nickel

The high consumption of products containing nickel has inevitably led to the environmental pollution by nickel and its by-products at all stages of production, recycling and disposal. Human exposure to nickel occurs primarily via inhalation and ingestion. Since nickel has not been recognized as an essential element in humans it is not clear how nickel compounds are metabolized. It is known however, that exposure to nickel compounds can have adverse effects on human health. Nickel allergy in the form of contact dermatitis is the most common and well-known reaction. Although the accumulation of nickel in the body through chronic exposure can lead to lung fibrosis, cardiovascular and kidney diseases, the most serious concerns relate to nickel's carcinogenic effect (Denkhaus and Salnikow, 2002).

2.1.1.3 Nickel in the environment

The sources of environmental nickel contamination include production and processing of nickel and its by-products, the recycling of nickel-containing products and disposal of nickel containing wastes. Nickel compounds are also found in soils and are present in both soluble and insoluble forms such as sulfides and silicates (Garrett, 2000). Nickel is also present in the atmosphere and the species of nickel present is dependent on the source of contamination. Combustion of fossil fuels produces the greatest contribution of nickel compounds in ambient air (Merian, 1984). Significant concentrations of nickel in water where it is present in dissolved forms as well as suspended insoluble particles can be produced by direct leaching from rocks and sediment. Nickel concentration in deep-sea water usually range from 0.1 to 0.5 ppb Ni, whereas surface water contains 15–20 ppb Ni (Denkhaus and Salnikow, 2002). Ni(II) is the predominant form of nickel in aquatic sources (Förstner *et al.*, 1983). The existence of other nickel compounds depends on the pH and the organic or inorganic binding partners. Epidemiological studies have noted an increased risk of respiratory tract and nasal cancer in miners and workers in nickel refineries (Easton *et al.*, 1992 and Anderson, 1992).

2.1.1.4 Nickel in organisms

Nickel's occurrence in higher organisms is questionable. Nickel ranks as the 24th element in order of abundance in the earth's crust. Therefore, humans are constantly exposed to this ubiquitous element although in variable amounts. Moreover, a nickel-deficient diet is difficult to maintain because of nickel's abundance in all types of food (Denkhaus and Salnikow, 2002). Chronic nickel poisoning can affect several organs including the cardiovascular and respiratory systems, skin, and the kidneys (Antico *et al.*, 1999). Experiments with high nickel intake have shown that nickel is teratogenic and has carcinogenic potential. Nickel fumes are respiratory irritants and may cause pneumonitis. Exposure to nickel and its compounds may result in the development of a dermatitis known as "nickel itch" in sensitized individuals. The

first symptom is usually itching, which occurs up to 7 days before skin eruption occurs. The primary skin eruption is erythematous, or follicular, which may be followed by skin ulceration.

2.2 Landfill leachate

2.2.1 Landfills

More than 90% of municipal solid waste is directly disposed off at landfill sites. Open and burning dumps are common in many developing countries and these contribute to water and air pollution (Idriss *et al.*, 2009). The presence of these dumps often reduces the market value of nearby land and residences. A landfill is defined as an area of land disposal site that employ an engineering method of solid waste disposal to minimize environmental hazards and protect the quality of surface and subsurface waters (Pankratz, 2001). Landfills are typically used for the disposal of municipal or industrial solid waste materials.

2.2.2 Leachate

Leachate is defined as toxic liquid that is collected at the bottom of a landfill. Its generation is a result of rain water percolating through the waste layers in a landfill (Kjeldsen *et al.*, 2002). Leachate contains a variety of chemical constituents derived from the solubilization of the materials deposited in the landfill and from the products of the chemical and biochemical reactions occurring within the landfill under anaerobic conditions (Idris *et al.*, 2009).

2.2.3 Composition of leachate

The composition of leachate is of great interest because through it, leachate components that pollute surface and ground water bodies will be known and techniques for reducing or eliminating such components applied. Leachate is composed of organic and inorganic substances. The chemical compositions of leachates depend on factors such as age of landfill, the kind of waste deposited, location (country) etc (Irene, 1996 and Iaconi *et al.*, 2006).

The age of a landfill greatly influences the chemical composition of a leachate. Landfills that are less than five years old are said to be in the acidogenic phase (Renou *et al.*, 2008). In this phase landfills contain large amounts of biodegradable organic matter which normally undergo anaerobic fermentation facilitated by water content of the landfill resulting in the production of volatile fatty acids (VFA). As the landfill goes beyond five years, it moves to the methanogenic phase. Methanogenic microorganisms develop in the waste, converting the VFAs to methane and carbon dioxide and the organic fraction of the leachate becomes mostly non-biodegradable compounds known as refractory compounds.

The kind of waste deposited in a landfill is a factor that determines the chemical composition of leachate from the landfill. Organic materials in the waste are mostly kitchen waste while inorganic constituent comes from glass, plastics, metals, etc. Waste from different sources have different ratio of these organic and inorganic materials (Al-Yaquot and Hamoda, 2003).

It is expected that leachate characteristics will vary from country to country. This is because of the variation in soil composition under a landfill site, the composition of the disposed waste, the climate or seasonal weather variation, as well as sampling and landfill management for different countries (Idris *et al.*, 2004).

2.2.4 Conventional landfill leachate treatment

Many landfills pollute water bodies by discharging untreated leachate. When leachate percolates through the ground, it entrains landfill components such as decaying organic matter, microorganisms, heavy metals and inorganic compounds into the underlying groundwater, causing serious environmental problems (Idris *et al.*, 2009). As previously mentioned, several methods have been used for leachate treatment. The main applicable methods are biological and physicochemical treatment processes (Forgie, 1988).

2.2.4.1 Biological treatment

Biological methods involve the use of microorganisms or microbial processes to degrade environmental waste. These processes require a suitable environment for growth of microorganism that has the potential for pollutant removal (Vidali, 2001). The biological processes have shown to be efficient in removing pollutant from fresh leachate. The method becomes less effective in the removal of heavy metals and refractory compounds. Aerobic biological processes such as activated sludge reactors, aerobic or lagoons, bio rotors and some anaerobic treatment systems have been used to treat leachate (Wiszniowski *et al.*, 2006).

Activate sludge is extensively used for domestic wastewater treatment or co-treatment of leachate treatment. The principle of activated sludge system is that oxygen is injected through the aeration tank as the leachate is mixed with re-circulated sludge biomass. The microorganisms which are developed in the tank consume the organic matter in the leachate and transform it into a new microbial biomass, carbon dioxide and water (Wiszniowski *et al.*, 2006). This method has been shown in the more recent decades to be non effective for landfill leachate treatment (Lin *et al.*, 2000).

A lagoon is normally an artificial pond with microorganisms as in an activated sludge system for leachate treatment. It can be anaerobic or aerobic, natural or artificial. A lagoon is aerobic

when dissolved oxygen is present throughout much of its depth while in anaerobic lagoon oxygen is absent throughout much of its depth. The use of lagoon has generally been claimed as effective and of low cost for leachate treatment (Maynard *et al.*, 1999). Although it has been claimed effective, temperature dependence of lagoons causes significant limitation because it mainly affect microbial activity.

A bio rotor, also known as a rotating biological contractor is an attached growth technology. It has circular plastic discs mounted on a shaft which is partially submerged in a tank containing the leachate and this shaft is rotated slowly to stir the leachate. Microorganisms from leachate adhere to the plastic disc and then form bio-films, assimilating and treating organics from leachate as they pass over the surface of the disc. When the disc rotates out of leachate, it is oxygenated thereby maintaining aerobic conditions. After reaching a critical thickness, a portion of the bio film sloughes off the discs due to gravity and the shear forces generated by the rotating action (Wiszniewski *et al.*, 2006). Generally performance is lower than with an activated sludge technique.

Anaerobic treatment processes have also been found to be effective in removing organic compounds from landfill leachate (Alkalay *et al.*, 1998). These processes involve the use of microorganisms in the absence of oxygen to convert organic compounds in the leachate to biogas (methane and carbon dioxide).

Leachate biodegradation using biological treatment processes can primarily reduce high concentrations of organic compounds present in the leachate. However, many organic compounds and other pollutants such as heavy metals cannot be removed using biological processes. Physicochemical treatment are used along with the biological processes in order to make the treatment effective when biological oxidation processes are negatively affected by bio-refractory compounds such as heavy metals (Wiszniewski *et al.*, 2006). Hence, a combination of physicochemical and biological processes is often required for successful treatment of landfill leachate (Kargi and Pamukoglu, 2003).

2.2.4.2 Physical and chemical treatment

Physicochemical methods are conducted by oxidizing contaminants with chemicals after which physical separation processes are applied. They can be very costly, because large quantities of chemicals are required. Flotation, coagulation-flocculation, chemical oxidation, membrane processing, ion exchange and adsorption onto activated carbon have been used as the principal physico-chemical techniques for the reduction of heavy metals from landfill leachate (Dean *et al.*, 1972 and Renou *et al.*, 2008).

Flotation has been extensively used for many years and focused on the decrease of colloids, ions and macromolecules from landfill leachate (Rubio *et al.*, 2002). However, very few studies have been devoted to the application of flotation for the treatment of landfill leachate (Renou *et al.*, 2008).

Coagulation and flocculation may be used successfully in treating stabilized and old landfill leachates (Silva *et al.*, 2004). Aluminium sulphate, ferrous sulphate, ferric chloride and ferric chloro-sulphate were commonly used as coagulants (Amokrane *et al.*, 1997). Several studies have been reported on the examination of coagulation-flocculation for the treatment of landfill leachates, aiming at process optimization, i.e., selection of the most appropriate coagulant (Tatsi *et al.*, 2003). However, this treatment presents some disadvantages: consistent sludge volume is produced and an increase on the concentration of aluminium or iron in the liquid phase may be observed (Silva *et al.*, 2004).

Chemical oxidation in wastewater treatment typically involves the use of oxidizing agents (oxidants) to oxidize the organic contaminants. Ozone (O_3), hydrogen peroxide (H_2O_2), permanganate (MnO_4^-), chloride dioxide (ClO_2), chlorine (Cl_2), and oxygen (O_2) are typical oxidants. Chemical oxidation is effective for the treatment of wastewaters containing soluble organics which cannot be removed by physical separation, as well as for non-biodegradable and/or toxic substances (Wiszniewski *et al.*, 2006). In general, efficient treatment via chemical oxidation has been shown to be very cost effective for reducing toxic compounds in leachate (Chen xi, 2008).

Membrane processes usually consist of microfiltration, ultra-filtration, nanofiltration and reverse osmosis. The basis of these processes is that higher molecular weight organics cannot pass through when pressured wastewater is forced through the membrane. Reverse osmosis systems are the most widely used membrane processes for leachate treatment (Bohdziewicz *et al.*, 2008). The drawback of membrane processes is that the membranes are susceptible to fouling due to the formation of biological slimes (Renou *et al.*, 2008). Their construction and operation are very costly compared to traditional biological treatment processes.

Ion exchange resins are available for selective removal of metal ions whereby cations are exchanged for H^+ or Na^+ . Cation exchange resins are mostly synthetic polymers containing an active ion group such as SO_3H . The modified zeolites like zeocarb and chalcarb have greater affinity for metals like Ni(II) and Pb(II) (Groffman *et al.*, 1992). The limitations of the use of ion exchange for inorganic effluent treatment are primarily high cost and the requirements for appropriate pre-treatment systems. These methods have been found to be

limited, since they frequently involve high capital and operational costs. They may also result in the production of secondary wastes which present treatment problems.

Adsorption onto activated carbon is one of the most extensively applied physical-chemical processes for the removal of pollutants from leachate (Enzminger *et al.*, 1987). Although activated carbon is widely applied for pollutant removal, natural low-cost materials have also successfully been employed as biosorbents for heavy metal removal from aqueous solutions and wastewaters such as landfill leachate. As such, the use of low-cost natural adsorbents would be beneficial for the removal of heavy metals from landfill leachate.

2.2.5 Biosorption of heavy metals

Heavy metals are among the most common pollutants in landfill leachate. Heavy metals can cause severe public health problems. They are toxic to aquatic life and can pollute natural waters (Papageorgiou *et al.*, 2006). As previously discussed various treatment methods have been optimised and applied for heavy metal removal from aqueous solutions (Papageorgiou *et al.*, 2006). However, some of these methods are impracticable and uneconomical. Improved and innovative methods which are economically feasible for heavy metal removal have been developed in recent decades (Ulmanu *et al.*, 2003). The use of biological materials (biomaterials) in adsorption processes for the removal of heavy metals has been the subject of research interests. Lately, attention has been diverted towards the use of biomaterials which are by-products from large scale industrial operations and agricultural waste materials. The idea of using various agricultural products and by-products for the removal of heavy metals from solution has been investigated by a number of authors (Friedman and Waiss, 1972; Randall *et al.*, 1974). The process of heavy metal removal from aqueous solution using these biomaterials (often called biosorption) involves surface attachment (adsorption) of metals to biological adsorbent (biosorbent). Biosorption is becoming a potential alternative to the existing technologies for the removal and recovery of toxic metals from wastewater. Biosorption is an innovative technology that employs inactive dead biomass for the removal and recovery of heavy metals from wastewater (Yuan *et al.*, 2009). Major advantages of biosorption compared to conventional treatment methods include high efficiency, low cost, minimization of chemical or biological sludge, no additional nutrient requirement as well as regeneration of biosorbent and possibility of metal recovery.

Studies on the treatment of heavy metals have revealed biosorption to be a highly effective, cheap and easy method among the physicochemical treatment processes (Ajmal *et al.*, 2000). Orange peel was tested as low-cost adsorbent for Ni(II) removal from electroplating wastewater (Ajmal *et al.*, 2000). Ni(II) biosorption was found to be dependent on biosorbent dose, initial metal concentration, pH and temperature. The biosorption process of Ni(II)

showed a maximum biosorption of 96% at 50°C for initial concentration of 50 mg/L at pH 6. The potential of potato peel waste for the removal of Ni(II) from aqueous solution has been investigated (Prasad and Abdullah, 2009). It was found to be dependent on process parameters such as pH, initial concentration of Ni(II), biosorbent dosage and contact time. Metal uptake increased from 0.07 to 0.20 mmol/g as concentration of Ni(II) increased from 20 to 120 mg/L. Pavan *et al.* (2006) used waste ponkan mandarin (*Citrus reticulata*) peel as biosorbent to extract Ni(II), Co(II) and Cu(II) from aqueous solutions. Maximum biosorption capacities of the biosorbent were 1.92, 1.37 and 1.31 mmol/g for Ni(II), Co(II) and Cu(II), respectively. The mandarin peel demonstrated a great ability for extracting metallic ions from simulated industrial effluent contaminated individually with Ni(II), Co(II) or Cu(II) solutions or in mixtures. Hanif *et al.* (2007) studied the potential of *Cassia fistula* biomass to remove Ni(II) from aqueous solutions under different experimental conditions. The potential of *Cassia fistula* biomass to remove Ni(II) was found to be dependent on parameters such as pH, metal ion concentration, contact time and biomass size. *Cassia fistula* biomass was reported to be an excellent biomaterial for removing Ni(II) from aqueous solutions. Waste tea leaves were also tried for sequestering of Pb(II), Fe(II), Zn(II) and Ni(II) from aqueous solutions (Ahluwalia *et al.*, 2005). The order of metal adsorption was found to be: Pb > Fe > Zn > Ni from 5 to 100 mg/L. The use of tea waste for the biosorption of Ni(II) from aqueous solution has been examined by Malkoc *et al.* (2005). The capacity of biosorption of Ni(II) increased with increasing temperature and pH. The maximum biosorption capacity was obtained at pH 4.0.

Mavhi *et al.* (2005) studied the removal of Cd(II), Pb(II) and Ni(II) from industrial wastewater using tea waste as biosorbent. Experimental data indicated that tea waste like most other biosorbents can be used in the treatment of wastewater. Sõukand *et al.* (2009) investigated the removal of Cu(II), Cd(II), Ni(II) and Pb(II) from landfill leachate using the following natural materials: peat material (Peat A and Peat B), waste materials (carbon-containing ash, paper pellets, pine bark and semi-coke called blue) and synthetic materials (based on urea-formaldehyde resins called red adsorbents) or their mixtures. It was found that Peat A, a mixture of Peat B and carbon-containing ash and a mixture of Peat A and blue biosorbent were the biosorbents that gave the highest metal removal efficiencies. The results have shown that peat A alone (an inexpensive adsorbent) was a good biosorbent for heavy metal ions. Langmuir monolayer biosorption capacities, q_m , on Peat A was found to be 0.57, 0.37, and 0.36 mmol/g for Pb(II), Cd(II), and Ni(II), respectively. Sahnurova *et al.* (2007) used algae of *Enteromorpha Compressa* as biosorbent for Cd(II) and Zn(II) removal from landfill leachate. The optimum conditions for the removal for both metals ions Cd(II) and Zn(II) was found to be at pH 4; contact time 60 min and temperature 25°C.

Furthermore, a biomatrix prepared from rice husk, a lignocellulosic waste from agro-industry, has been evaluated for the biosorption of metal ions such as Pb(II), Hg(II), Cd(II), Cu(II), Zn(II), Co(II), Mn(II) and Ni(II) as a function of pH and metal concentrations. Values obtained from Langmuir isotherm increase in the following order (mmol/g): (0.094), (0.124), (0.149), (0.151), (0.162), (0.172), (0.180) and (0.280) for Ni(II), Zn(II), Cd(II), Mn(II), Co(II), Cu(II), Hg(II) and Pb(II), respectively. The biomatrix also reduced the Cr(VI) to Cr(III) in acidic medium (Krishnani *et al.*, 2008). However, due to very low cost of biomatrix, it was reported to be an interesting material in the treatment of metal contaminated water and represents an advantageous aspect when designing water treatment systems. Opeolu *et al.* (2009) investigated the potential of Maize (*Zea mays*) to remove Pb(II) removal from aqueous solutions and industrial effluents (Opeolu *et al.*, 2009). The study showed that the heavy metal biosorption capacity of maize (*Zea mays*) cob was influenced by parameters such as contact time, pH, Pb(II) concentration and shaking period. Equilibrium was attained after two hours contact time at pH 6. The percent adsorption tends to be constant with increasing Pb(II) concentration for maize cob while it increased steadily for Dowex and it was greatly enhanced by shaking. The same researchers also studied the removal of zinc (Opeolu *et al.*, 2011). They reported that the adsorption efficiency was increased by increasing contact time, pH, adsorbent dose, metal concentration and agitation speed, while it decreased by increasing particle size and temperature.

Agricultural waste such as peanut, pecan, walnut, hazelnut and groundnut shells in natural or modified form were also utilized for biosorption (Demirbas *et al.*, 2002; Shukla *et al.*, 2005 and Kurniawan *et al.*, 2006). Chamrathy *et al.* (2001) studied the efficiency of peanut shell prepared by thermal treatment in the presence of phosphoric acid or citric acid for the adsorption of Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II). The phosphoric acid-modified shells showed large amounts of adsorbed metal ions compared to citric acid-modified shells. A biosorbent prepared from powdered coconut shell was examined to remove cadmium from water over a wide concentration range (20 – 1000 mg/L). The prepared biosorbent exhibited a high biosorption capacity (285.7 mg/g) for Cd(II). The results showed that initial pH highly affected the uptake capacity of the biosorbent and the optimum pH for maximum uptake was 7 for Cd(II) ions (Pino *et al.*, 2006). Coir pith was evaluated for its biosorption potential for Co(II), Cr(III) and Ni(II) from a single and a mixture of ion solutions (Parab *et al.*, 2006). The maximum biosorption capacity of coir pith was found to be 12.82, 11.56 and 15.95 mg/g for Co(II), Cr(III) and Ni(II), respectively. Optimum pH values for maximum metal-ion biosorption were reported as 3.3, 4.3 and 5.3 for Cr(III), Co(II) and Ni(II), respectively.

2.2.5.1 Factors affecting biosorption

The investigation of the efficacy of the metal uptake by the biomaterial is essential for the industrial application of biosorption process, because it gives information about the equilibrium of the process which is necessary for the design of the equipment (Ahalya *et al.*, 2003). The metal uptake is usually measured by the parameter 'q' which indicates the amount of adsorbate in milligrams, per amount of biosorbent used in gram. The following factors affect the biosorption process: pH, biomaterial concentration, metal concentration, temperature, metal ion interaction with biosorbent and activation of adsorbent.

Several authors have indicated that biosorption is favoured by increasing pH, but only up to certain limit. pH is the main factor in the biosorption process because it affects the behaviour of metal ions in solution, the competition between metal ions for the biosorption sites, solution chemistry of the metals and the activity of the functional groups in the biomaterial (Das *et al.*, 2008).

Specific metal uptake seems to be affected by biomaterial concentration. A low biomaterial concentration increases specific metal uptake. Gadd *et al.* (1998) suggested that an increase in biomaterial concentration leads to interference between the binding sites. This suggestion is however in contradiction with another hypothesis by Fourest and Roux (1992), which attribute the specific uptake decrease to metal concentration shortage in solution.

The concentration, as well as the number of metals to be adsorbed by the adsorbent also affects the rate of biosorption. Since biosorption is mainly used to treat wastewater, it is expected that more than one type of metal ions would be present.

Temperature does not seem to influence the biosorption performance in the range of 20-35°C (Aksu *et al.*, 1992). Its effect on biosorption is profound, although most measurements are usually at room temperature.

Many studies have provided evidence in support of metal ions interaction with specific functional groups at the biosorbent surface. Several authors have used shifts in the maxima of infrared light adsorption as evidence for specific interactions (Iqbal *et al.*, 2009). NMR spectra also have been used to substantiate the involvement of specific chemical sites in the binding of metal ions (Araújo *et al.*, 2007). The interaction of the biosorbent with the metal determines the amount of metal that will be taken up by the biosorbent.

Activation of the biosorbent surface increases the number of vacant sites on the surface of the biosorbent. It can involve breaking the solid crystal into small pieces, heating solid material at high temperature, grinding lump of solid into powder, chemical modification of the

biomaterial or other methods suitable for a particular biosorbent. The rate of biosorption increases with increase in surface area of biosorbent. It also improves the performance of the biomaterial by introducing more functional groups.

2.2.5.2 Mechanism of biosorption

An important factor in metal uptake is the electrostatic attraction binding between metal cations and negatively charged sites at the cell surface (Schiewer *et al.*, 1999). Metal ion biosorption could take place due to an electrostatic attraction between metal cations and negatively charged sites on the biosorption surface such as phosphoryl, phosphate, carboxyl, sulphate, amino and hydroxyl groups (Tunali *et al.*, 2006). Possible biosorption mechanisms are ion-exchange, physical adsorption, chemisorptions, and complexation. Ion-exchange refers to a class of mechanism in which adsorbing metal ions replace other species already associated with the biosorbent surface. Physical adsorption is due to weak Van der Waal forces. The forces involves in chemical adsorption are much stronger and involve electron exchange and the formation of chemical bonds between the adsorbate and the adsorbent (Ruthven, 2006). As a result, chemisorption is highly specific and the adsorption energies are generally substantially greater than those for physical adsorption. Chemical adsorption is by its very nature limited to less than a monolayer coverage of the surface, while in physical adsorption, multilayer adsorption is common. Biosorption takes place in three steps: (1) bulk solution transport which moves the adsorbate through the bulk liquid by means of advection and dispersion, to the fixed film boundary layer surrounding the biosorbent media; (2) diffusive transport which moves the adsorbate across the fixed film boundary layer; and (3) bounding processes which act to attach the adsorbate to the media surface. Metal ion biosorption could take place due to an electrostatic attraction between metal cations and negatively charged sites on the biosorbent surface such as phosphoryl, phosphate, carboxyl, sulphate, amino and hydroxyl groups (Tunali *et al.*, 2006).

2.2.6 Biosorption equilibrium model

When any biosorption system reaches a state of equilibrium, there is a defined distribution of adsorbate molecules at the solid-liquid interface and also in the bulk at a particular temperature. The maximum possible accumulation of the adsorbate at the solid surface is a function of its concentration at a constant temperature, and it can be expressed by the following generalized Equation (2.1):

$$q_e = f(C_e) \tag{2.1}$$

Where q_e is the amount of adsorbate at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L). This type of relation is named as an adsorption isotherm, which represents equilibrium between the concentration of a solute in solution and

its concentration on the adsorbent, at a given temperature. Adsorption isotherms are used to describe equilibrium data and are important for developing equations that can be used to compare different biosorbents under different operational conditions. Several equilibrium models have been used to describe the metal transfer between the solution and solid phase during the biosorption process (Martin *et al.*, 2011). The simplest forms of these isotherms are Freundlich and Langmuir isotherms which in most cases are used to obtain maximum biosorption capacity of the biosorbent.

2.2.6.1 Langmuir isotherm model

The Langmuir model suggests that a monomolecular layer is formed when the biosorption occurs without any interaction between the adsorbed species (Aksu *et al.*, 2002). It assumes that every biosorption site is equivalent and the ability of sorbate to get bound is independent on whether or not the neighbouring sites are occupied (Langmuir, 1918).

The Langmuir model is given by the Equation (2.2):

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (2.2)$$

Equation (2.2) can be linearised as follows:

$$\frac{1}{q_e} = \frac{1}{q_m K_L} \left[\frac{1}{C_e} \right] + \frac{1}{q_m} \quad (2.3)$$

Where C_e is the concentration of the adsorbate solution (mg/L) at equilibrium, q is the biosorption capacity (mg/g) and K_L is related to the energy of biosorption (L/mg). Values of q_m can be calculated from the linear plot of $1/q_e$ against $1/C_e$ (Lawal *et al.*, 2010).

2.2.6.2 Freundlich isotherm model

The Freundlich isotherm model describes the biosorption of a solute from a liquid to a solid surface under the assumption that the stronger binding sites are occupied first and that the binding strength decreases with an increasing degree of site occupation. The Freundlich model proposes a monolayer adsorption with a heterogeneous energetic distribution of active sites, and/or interactions between adsorbed species, i.e. multilayer biosorption (Freundlich, 1907). This model is usually chosen to estimate the biosorption intensity of the biosorbent towards the adsorbate.

The Freundlich model can be expressed by the following empirical equation (2.4):

$$q_e = K_f C_e^{1/n} \quad (2.4)$$

Equation (2.4) can be expressed by the following form,

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (2.5)$$

Where $K_f(\text{mg}^{1-n}/\text{g L}^n)$ and n (dimensionless) represent the Freundlich constants characteristic of the system. K_f is indicative of the relative biosorption capacity, whereas n is the measure of the nature and strength of the biosorption process and the distribution of active sites.

2.2.7 Kinetic studies

In order to investigate the mechanism of biosorption and its potential rate-controlling steps that include mass transport and chemical reaction processes, kinetic models have been used to analyze the experimental data. These empirical mathematical models which describe adsorption data have been proven as useful tools for scale up process optimization (Sciban and Klasnja, 2003 and Senthilkumar *et al.*, 2006). The rate of biosorption is an important factor in wastewater remediation. In addition, selecting optimum conditions for full-scale batch metal removal processes requires information on the kinetics of metal uptake (Febrianto *et al.*, 2009). It is therefore necessary to establish the time dependence of contaminant capture under process conditions. The kinetic models such as pseudo-first and pseudo-second-order have been used to determine the biosorption mechanism. The equation of the two models is expressed as follows:

2.2.7.1 Pseudo first order kinetic model

The equation of the pseudo-first order (Lagergren, 1898) is express as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2.6)$$

Where q_e and q_t are amount of the adsorbate adsorbed at equilibrium and at time t , respectively, in mg/g, k_1 is the first order rate constant (min^{-1}) and t is time (min).

2.2.7.2 Pseudo-second-order model

The pseudo second order kinetic model as proposed by Ho and McKay (Ho and Mckay, 1999) is express as follow:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2.7)$$

Where k_2 is the pseudo second order rate constant.

2.2.8 Thermodynamic study

Thermodynamic study is reportedly done by carrying out equilibrium studies at various temperatures to obtain corresponding $C_{ad,eq}$ and C_{ed} . From these values, the equilibrium constant K_c can be calculated using the following relationship:

$$K_c = \frac{C_{ad,eq}}{C_{ed}} \quad (2.8)$$

where K_c is the equilibrium constant, $C_{ad,eq}$ and C_{ed} are the concentration of Ni(II) on the biosorbent and residual Ni(II) concentration at equilibrium, respectively.

$$\Delta G^\circ = -RT \ln K_c \quad (2.9)$$

where ΔG° is standard Gibbs free energy change (J); R the universal gas constant (8.314 J mol⁻¹ K⁻¹) and T the absolute temperature (K)

$$\ln K_c = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (2.10)$$

The plot of $\ln K_c$ as a function of $1/T$ yields a straight line from which standard enthalpy (ΔH°) and entropy (ΔS°) can be calculated from the slope and intercept, respectively.

2.2.9 Desorption studies

As the biosorption process is to be used as an alternative to wastewater such landfill leachate treatment, the regeneration of the biosorbent is important for keeping the process costs down and in opening the possibility of recovering the metals extracted from the liquid phase. For this purpose it is desirable to desorb the adsorbed metals and to regenerate the biosorbent material for another cycle of application. Desorption studies help in further elucidating the mechanism of adsorption and the feasibility of regenerating the biosorbent. Namasivayam and Yamuna (1992) reported if the adsorbed ions on the solid surface can be desorbed by water, the attachment of the ion on the adsorbent can be demonstrated by weak bonds such as Van der Waals forces. If acid or alkaline desorbs the ion, then the adsorption occurs through an ion exchange process. Dilute solutions of mineral acids like hydrochloric acid, sulphuric acid, acetic acid and nitric acid can be used for metal desorption from the biomaterial (Gadd *et al.*, 1998).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Cleaning of glassware

All glassware and containers were thoroughly washed with detergent and tap water, rinsed with distilled water and thereafter soaked in 10% HNO₃ for 72 hours after which they were thoroughly rinsed with distilled-deionised water and dried.

3.1.1 Reagent and residues preparation

- 1) All chemicals used were of analytical grade. Stock solution (1000 mg/L) of Ni(II) was prepared by dissolving 4.4786 g NiSO₄·6H₂O in distilled-deionised water in a beaker. The solution was then transferred to a one litre volumetric flask. Standard solutions of Ni(II) in the range of 5.00 – 217.50 mg/L were prepared from the stock solution by pipetting calculated volume of solutions into volumetric flasks and making up to the mark with distilled-deionised water.
- 2) Batch samples of banana, egg plant and sweet potato peels were collected from a local fruit and vegetable market. The three biosorbents were procured as batch samples. They were first thoroughly washed with tap water, followed by distilled deionised water. The samples were then dried to constant weight in convection oven at 60°C, cut into small pieces, ground and screened to 45-75 µm. They were then kept in plastic stoppered bottles and preserved in desiccators until the time of use to minimize the influence of humidity. Powder from the peels of egg plants, sweet potato and banana were labelled EGP, SWP and BNP, respectively.

3.1.2 Sample locations and sampling

Wastewater samples were collected from Bellville, Vissershok and Coastal Park landfill sites in Cape Town and they were collected in triplicates at specified time intervals. The leachates were collected in 1 L plastic bottles which were rinsed several times with the leachate before being filled with the leachate. The leachates were immediately preserved by adding concentrated HNO₃ to each bottle and the pH adjusted to 2.0 using a pH meter (model Crison). The samples were then stored in a refrigerator at about 4°C before the time of use. Some physicochemical parameters such as pH, temperature, salinity, turbidity, conductivity, total dissolved solid and resistivity of the landfill leachate were measured.

3.2 Analytical procedures

3.2.1 Determination of Ni(II) in biosorbents

Each of the biosorbent was washed with tap water and then, with distilled-deionised water and oven-dried at 120°C for 24 hours. 1 g of each biosorbent was weighed into 100 mL volumetric flask, and 10 mL of analytical grade nitric acid was added. The beakers were covered overnight. Digestion was carried out at a temperature of about 90°C. After cooling, the solution was filtered and made up to a final volume (100 mL) with distilled-deionised water. Ni(II) concentrations were determined by flame atomic absorption spectrometry (FAAS) (Model Perkin Elmer 3300).

3.2.2 Physicochemical analysis and chemical composition of landfill leachates

Physicochemical parameters such as pH, temperature, total dissolved solids (TDS), salinity, conductivity, turbidity and resistivity were determined. For heavy metal analysis landfill leachates were digested with a mixture of concentrated nitric and hydrochloric and the metal concentration was determined by inductively coupled plasma mass spectrometry (Agilent 7700 ICP-MS).

3.2.3 Precision studies

Spiked and unspiked leachate samples were analyzed for Ni(II). For the preparation of 50 mL of 10 mg/L Ni(II) solution, 0.5 mL of 1000 mg/L Ni(II) was accurately measured into a 50 mL volumetric flask containing landfill leachate. The flask was made to the mark with the respective landfill leachate. Triplicate samples of each landfill leachate were analyzed using a FAAS instrument.

3.2.4 Quality assurance/ quality control

The following quality control measures were taken.

- 1) Filtered and unfiltered samples were compared in order to determine whether the filter paper used in our experiment adsorbs or releases any metal. Filtered and unfiltered distilled-deionised water was analyzed to determine if Ni(II) was leached from the filter papers. Also, samples of filtered and unfiltered 100 mg/L of Ni(II) were analysed to determine whether metals were retained by filter paper.
- 2) A blank containing 25 mL of 100 mg/L of Ni(II) solutions without the biosorbents were placed on the shakers with other samples to determine any adsorption of Ni(II) onto the walls of the flasks used during our experiment. Control samples were prepared where three 50 mL Erlenmeyer flasks containing each 25 mL deionised water and the biosorbents were also placed on the shakers to determine any leaching of Ni(II) from the biosorbents.

- 3) Each sample was analyzed in triplicate using FAAS and the mean concentration was calculated.
- 4) Nickel Standard solutions containing each 2, 5, 7 and 10 mg/L of Ni(II) were prepared from 1000 mg/L stock solution. The results were used to plot the calibration curve to determine the linearity of concentration with absorbance.
- 5) The detection limit of the instrument used was also determined. Seven distilled-deionised water blanks were analyzed for Ni(II). Detection limit was calculated as three times the standard deviation of the seven blanks. Blank samples were analyzed after every 10 measurements.
- 6) An internal standard method for ICP-MS was used in order to correct for instrument drift due to matrix effects.

3.2.5 Preliminary equilibrium studies

Equilibrium conditions of biosorbent mass, pH, adsorbate concentrations, temperature and contact time were conducted using Ni(II) solutions. Batch experiments were conducted in 50 mL Erlenmeyer flasks using 25 mL of metal solutions. Agitation of the solution was achieved by shaking on an orbital shaker at 140 rpm.

3.2.5.1 Capacity studies

Different mass of each of the biosorbents (EGP, SWP and BNP) 0.025 g, 0.050 g, 0.100 g, 0.200 g, 0.400 g, 0.600 g corresponding to 1 g/L, 2 g/L, 4 g/L, 8 g/L, 16 g/L and 24 g/L, respectively, was added in each of 50 mL conical flask containing 25 mL of 100 mg/L Ni(II) solution. An optimal time of 2 hours was maintained for all the experiments. The mixture was then filtered through a Whatman filter paper and the filtrate analyzed for residual Ni(II) using a FAAS instrument.

Percentage Ni(II) removal was calculated according to Equation (3.1):

$$\text{Biosorption}\% = \frac{C_o - C_e}{C_o} \times 100 \quad (3.1)$$

Where C_o and C_e are initial and equilibrium metal concentrations, respectively

The amount of Ni(II) adsorbed by the biosorbent was then calculated using the Equation (3.2):

$$q_e (\text{mg/g}) = \frac{(C_o - C_e)V}{m} \quad (3.2)$$

Where q_e is the amount of metal ion adsorbed on the biosorbent in (mg/g)

C_o is the initial metal ion concentration in (mg/L)

C_e is the equilibrium concentration of Ni(II) in solution (mg/L)

V is the volume of Ni(II) solution used (L) and

m is the mass of the biosorbent used (g).

3.2.5.2 Effect of pH on Ni(II) biosorption

A 100 mg/L Ni(II) solution was prepared from 1000 mg/L stock solution by dilution. The pH of the solution was adjusted to the desired value and kept constant by adding either 0.1M HCl or 0.1M NaOH. The pH was monitored using a pH meter. The pH values investigated varied from 2 to 8. The biosorbent was weighed (0.4 g) and added to 25 mL solution of 100 mg/L Ni(II) at the desired pH and left for 2 hours. The mixture was then filtered and the filtrate analyzed for Ni(II) using a FAAS instrument.

3.2.5.3 Effect of Ni(II) concentration on biosorption

Six Ni(II) standard solutions with concentration ranging from 5 – 217.50 mg/L were prepared from the stock solution. Biosorbent mass of 0.4 g in 25 mL solution was used for adsorption isotherm studies with a contact period of 2 hours after which the mixture was filtered for analysis using a FAAS instrument.

Adsorption isotherms

It is generally possible to express the results of experimental adsorption measurements in the form of one or more equilibrium adsorption isotherm theories. It represents the equilibrium between the concentration of a solute (adsorbate) in solution and its concentration on the sorbent, at a specified temperature. Langmuir and Freundlich principles were applied for biosorption isotherm studies.

The Langmuir model suggests that a monomolecular layer is formed when adsorption takes place without any interaction between the adsorbed molecules (Aksu *et al.*, 2002). The Freundlich isotherm model, though empirical has been found more appropriate to several biosorption processes where non- uniformity of actual surface expected, and its application is limited to solutions of moderate concentrations. The Freundlich model assumes multiple layers at the biosorbent surface and that adsorption will increase as long concentration increases (Freundlich, 1907).

3.2.5.4 Effect of temperature on Ni (II) biosorption

The effect of temperature, a major factor influencing the adsorption process, was studied in the range of 30 to 60°C. The thermodynamic parameters, such as enthalpy (ΔH^0), entropy (ΔS^0) and Gibb's free energy (ΔG^0) were estimated using equations (2.9) and (2.10).

3.2.5.5 Effect of contact time

The effect of contact time on the adsorption process was studied in both batch and semi-batch mode. Batch experiments were conducted by varying contact time of optimized biosorbents doses with 50 mL of 100 mg/L Ni(II) ion solution at a pH 5 and 298 K. Contact times were 1, 3, 5, 10, 15, 20, 25, 30, 60, 90 and 120 min. Semi-batch experiments were conducted by contacting 0.8 g, 0.8 g and 0.1 g of EGP, SWP, BNP, respectively, with 50mL of 100 mg/L Ni(II) solution in a conical flask and samples were drawn from the flask at regular intervals. The mixture was filtered, then analyzed for residual Ni(II), and percentage removal of Ni(II) was estimated. Contact time was varied for the experiment to determine rates of biosorption of Ni(II) to a specific biosorbent. In order to investigate the mechanism of biosorption and its potential rate-controlling steps that include mass transport and chemical reaction processes, kinetic models have been used to analyze the experimental data.

3.2.6 Effect of modification of the biosorbents

Eggplant, sweet potato and banana peels were found to adsorb less Ni(II) than expected. They were therefore modified for further studies. This was to assess possible effects of chemical modification of biosorbents. The methods of Yeneneh *et al.* (2011) and Shafqat *et al.* (2008) were used and applied for chemical modification of the biosorbents.

The chemical modification of the biosorbents was carried out by shaking 4 g of each biosorbent with 80 mL of NaOH and HCl for 90 minutes at room temperature. This treatment was repeated twice. Excess NaOH and HCl were removed by washing the by-products with distilled deionised water until neutral pH was obtained. Modified biosorbents were then used to biosorption experiments using previously established optimal conditions.

3.3 Characterization of biosorbents

3.3.1 Functional group characterization

Fourier Transform Infrared (FTIR) absorption spectra of EGP, SWP and BNP were obtained using the potassium bromide (KBr) pellet method. Approximately 1 mg of finely powdered dry sample was mixed with 250 mg of dry potassium bromide and ground to fine powder in an agate mortar. The mixture was transferred into a die and compressed to form a pellet (13 mm diameter) using a hydraulic press. The pellet was carefully removed from the die, placed

in the holder and the spectra of the samples were recorded over the range 400 to 4000 cm^{-1} using an FTIR instrument (Perkin ElmerTM Spectrum 1000).

3.3.2 Physico-chemical properties of the biosorbents

Some physico-chemical properties of the biosorbents such as bulk density, particle density, porosity and pH were determined for each of the biosorbent.

3.3.2.1 Bulk density

To determine the bulk density (ρ_b), a glass beaker was emptied, dried and weighed. It was then filled to overflowing with oven-dried biosorbents (EGP, SWP and BNP). The sides of the beaker were tapped lightly ten times with a glass rod, then levelled by rolling the rod across the top edge of the beaker six times. The beaker was then reweighed, and the bulk density of biosorbent was calculated according to Equation (3.3) (Yoshiyuki and Yukata, 2003).

$$\rho_b = \frac{M_t}{V_t} \quad (3.3)$$

Where ρ_b is the bulk density (g/cm^3), M_t is the oven dried biosorbent mass (g), and V_t is the beaker volume (mL).

3.3.2.2 Particle density

To determine the particle density of the biosorbents three 100 mL stoppered volumetric flasks were weighed. 4 g of each of the oven-dried biosorbent was added to the each flask using 40 mL distilled water. The flasks were sealed with plastic stoppers, and the solution heated to boiling. The solution was boiled for 10 min, cooled to room temperature, and then filled to a 100 mL volume with pre-boiled and cooled distilled water. The flasks were reweighed and then emptied, cleaned, dried and filled to volume of 100 mL with pre-boiled distilled water and reweighed. Particle density was calculated according to Equation (3.4).

$$\rho_s = \frac{\rho_w M_s}{M_s - (M_{s+f+w} - M_{f+w})} \quad (3.4)$$

where ρ_s is the particle density (g/mL), ρ_w is the density of water (g/mL), M_s is the mass of oven-dried biosorbent, M_{s+f+w} is the mass of flask, oven-dried biosorbent and distilled water (g) and M_{f+w} the mass of the flask filled to volume with distilled water (g).

3.3.2.3 Porosity

Porosity (n) values were determined according to Equation (3.5)

$$n = [1 - (\frac{\rho_b}{\rho_s})] \times 100\% \quad (3.5)$$

Where n is the porosity (unitless)

3.3.2.4 Biosorbent pH

To measure the biosorbents pH, 5 g of each biosorbent was placed in a 100 mL glass Erlenmeyer flask with 25 mL of distilled water. The flasks were sealed and shaken at 100 rpm for 30 minutes. After filtration using a Whatman filter paper, the pH of biosorbent was measured.

3.4 Adsorption studies on the landfill leachate

For each landfill leachate, the optimized parameters for each of the biosorbents were put in contact with 25 mL of the digested leachate in 50 mL Erlenmeyer flasks. The mixtures were then placed on an orbital shaker for 2 hours, after which, they were filtered and the filtrates analyzed for residual Ni(II) using a FAAS instrument.

3.5 Desorption Studies

Desorption studies were carried out to assess recovery of Ni(II). The concentration of adsorbate at equilibrium C_{ad} (mg/L) was calculated as the difference between the initial and the equilibrium concentration ($C_o - C_e$). Ni(II)-loaded biosorbent were separated and gently washed with distilled deionised water to remove any unadsorbed Ni(II). Each biosorbent was then agitated in de-ionised water and 100 mL of 0.1M HCl for 1 hour and the amount of desorbed Ni(II) C_{de} (mg/L) estimated. The percentage of desorption was calculated using Equation (3.6) (Li *et al.*, 2010):

$$Desorption (\%) = \frac{C_{de}}{C_{ad}} \times 100 \quad (3.6)$$

3.6 Data and Statistical Analysis

Even though the traditional approach of “one-factor-at-a-time” experimentation, can be useful in finding predominant factors in a given situation, it is a time-and energy-consuming method (Diamond, 1989). Furthermore, since the results are valid only under fixed experimental conditions, prediction based on them for other conditions is uncertain

(Robinson, 2000). Design of experiments is a process of testing using a structured plan in which the input factors are varied in an organized manner to efficiently optimize output responses of interest with minimal variability (Frey et al., 2003). Design of experiments is therefore, an essential requirement used to optimize the performance, quality, and cost in situations where multiple variables are involve.

Factorial two way experimental design was used for all main effects and interactions up to order two for both independent variables factored. Percent removal of Ni(II) removed or Ni(II) removal efficiency was treated as the dependent variable in all the designs. Biosorbents (EGP, SWP and BNP) were the main treatment and mass, concentration, pH, temperature and contact time as sub-treatment.

Descriptive statistics breakdowns consisted of mean, standard deviation and standard errors. Statistical Analysis Software (SAS 9.0) was used to generate statistics. The Generalised Linear Model (GLM) procedure was used for ANOVA and Duncan Multiple Range Test (DMRT) was used for means comparison at 95 % significance level ($P \leq 0.05$).

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Biosorbents physicochemical properties

The biosorbents physicochemical properties were determined and are presented (Appendix A). The results are reported as the average values of the analysed samples obtained from the duplicate experiments.

4.2 Quality assurance or quality control

Results of quality assurance samples indicated that Ni(II) was not present in distilled-deionised water used, did not leach from filter paper and was not adsorbed or leached onto or from the filter paper. The R^2 of the calibration curve was higher than 0.99. The metal ion concentrations in the blank (25 mL of Ni(II) solution without any biosorbents) solutions and the control (25 mL deionised water no Ni(II) added and the biosorbents) were not found to change significantly after the shaking period as shown in Appendices B and C, which indicated that the effect of adsorption onto the beaker and the leaching of Ni(II) from the biosorbents were negligible and could be neglected throughout the experiment (Appendices B and C).

4.3 Effect of biosorbent mass

The number of available sites and exchanging ions for biosorption of metals depend upon the amount of biosorbent for the biosorption process. To examine the effect of biosorbents mass on Ni(II) biosorption, experiments were conducted at constant pH, initial concentration, time and temperature. The effect of biosorbent mass on the biosorption of Ni(II) by EGP, SWP and BPN biosorbents is shown in Figure 4.1. Biosorbent masses were varied from 0.025 g to 0.6 g for the three biomaterials. The percentage Ni(II) removal due to varied biosorbents masses and the biosorbent are presented (Table 4.1). The Ni(II) removal efficiency varied significantly ($P \leq 0.05$) with mass and the biosorbents. In two biosorbents (EGP and SWP), it was observed that Ni(II) removal efficiency increased with increase in biosorbent mass. The Ni(II) removal efficiency reached an optimum at 0.4 g for EGP and SWP, corresponding to $62 \pm 1.51\%$ and $41 \pm 1.46\%$ removal, respectively. The increase in removal efficiency may be attributed to the availability of biosorption sites for the ions as the mass increases (Karthikeyan *et al.*, 2007; Lata *et al.*, 2008). These results are similar to those reported by Mahvi *et al.* (2005), Nuhoglu and Malkoc, (2009) and Opeolu *et al.* (2011). The authors suggested that the increase in biosorption with the biosorbent mass may be due to increased number of unsaturated active sites as well as high accessibility of metals to the binding sites. The Ni(II) removal efficiency at biosorbent mass of 0.025 g presented lower

removal efficiency. However there was no significant difference between the biosorbent mass of 0.2, 0.4 and 0.6 g ($P > 0.05$).

Although there was significant ($P \leq 0.05$) Ni(II) removal by biosorbents (Figure 4.1), a careful examination of the data reveals that the mean Ni(II) removal efficiency using BNP was very low. The Ni(II) removal efficiency for BNP did not increase significantly with increasing biosorbent mass, and it reached a maximum at 0.05 g which corresponds to $29\% \pm 0.52$ Ni(II) removal. At biosorbent masses higher than 0.4 g for EGP and SWP, and 0.05 for BNP, there was no significant ($P > 0.05$) increase in the percentage Ni(II) removed by the biosorbents. These respective values for EGP, SWP and BNP were therefore selected as optimum biomaterial masses utilized in other aspects of this study. The difference in Ni(II) removal efficiency between EGP, SWP and BNP may be due to differences in their physicochemical properties (bulk density, porosity, etc) (Sõukand *et al.*, 2009) as well as to the chemistry of their original plant material (Ringqvist *et al.*, 2002).

Table 4.1: Percentage Ni(II) removal efficiency with varying biosorbents masses and the biosorbent

		Mass (g)						
		0.025	0.05	0.1	0.2	0.4	0.6	Mean Biosorbent
Ni(II) % Removal	EGP	31.31	35.66	48.26	57.38	62.60	62.18	49.47
	SWP	23.14	28.25	37.82	40.87	41.74	39.14	35.16
	BNP	27.83	29.56	28.69	19.13	16.52	14.79	22.75
	Mean Mass	27.43	31.16	38.26	39.13	40.28	38.70	
	CV%	5.41						
	$P \leq 0.05$	***						***
	Interaction	***						

***: significant

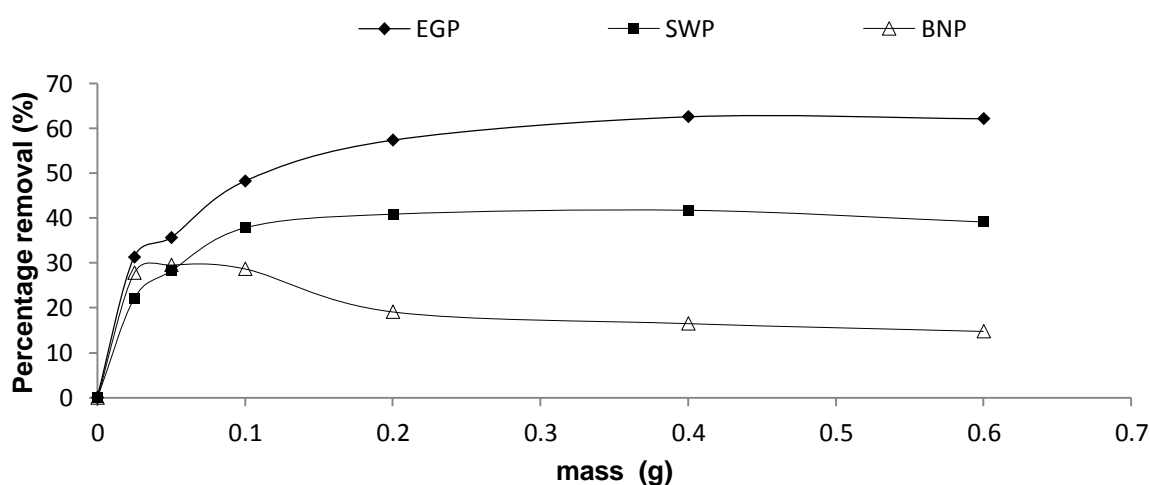


Figure 4.1: Effect of biosorbent mass on biosorption of Ni(II) ions from aqueous solution at pH 5

4.4 Effect of pH

To examine the effect of pH on the biosorption efficiency, several experiments were performed at varied pH ranging from 2 to 8 (Figure 4.2). pH has been reported to be the most important variable affecting the biosorption of metal ions by the biosorbent (Martinez *et al.*, 2006). It influences metal ions biosorption due to the competition between the metal and H⁺ ions for active biosorption sites. The result of Ni(II) removal efficiency at different pH values and the use of the biosorbents (EGP, SWP and BNP) are presented (Table 4.2). The Ni(II) removal efficiency varied significantly ($P \leq 0.05$) with pH values and the biosorbents. The mean Ni(II) removal efficiency at pH 2 was significantly lower than those at other pH values. At this low pH the overall surface of functional groups on the biosorbent are closely associated with H⁺ which in return reduces the approach of Ni(II) ions as a result of the repulsive force (Sheng *et al.*, 2004). The results indicate that relatively little biosorption took place at pH 2 and only $32.7 \pm 2.67\%$, $10.7 \pm 2.32\%$ and $1.9 \pm 0.49\%$ of Ni(II) were removed by EGP, SWP and BNP, respectively. Increasing the pH from 2 to 6 showed a rapid increase in the removal efficiency. Increasing solution pH resulted in de-protonation of functional groups on the biosorbent making biosorption sites more available for Ni(II) ions. Ni(II) removal efficiency at pH 5 was significantly ($P \leq 0.05$) higher than those at pH of 2, 3, 4, 6, 7 and 8. However, there was no significant ($P > 0.05$) difference between pH 4 and 8 with pH 5. Biosorption of Ni(II) on the biomaterials reached its maximum at the following pH values: pH 5, pH 4-5 and pH 5 for EGP ($61 \pm 2.58\%$ removal), SWP ($40 \pm 0.89\%$ removal) and BNP ($31 \pm 1.47\%$ removal), respectively. After pH 6 cloudy precipitates of Ni(II) were visible in solution and thus were inaccessible for Ni(II) biosorption by the biomaterials. Several researchers have investigated the effect of pH on the biosorption of metal ions using different types of peels (Li *et al.*, 2008; Prasad and Abdullah, 2009). The authors reported that maximum biosorption occurred in the pH range 4-6. pH 5 was therefore selected for further studies.

Table 4.2: Ni(II) removal efficiency at different pH values and the use of the biosorbents (EGP, SWP and BNP)

		pH							
		2	3	4	5	6	7	8	Mean Biosorbent
Ni(II) % Removal	EGP	32.75	58.61	61.20	61.20	58.61	61.20	61.20	56.40
	SWP	10.77	38.75	40.51	40.51	40.51	36.64	39.21	35.27
	BNP	1.96	15.88	21.47	31.37	26.47	28.92	29.80	22.28
	Mean pH	15.16	37.75.25	41.10	44.36	41.87	42.25	43.41	
	CV%	5.24							
	P ≤ 0.05	***							***
	Interaction	***							

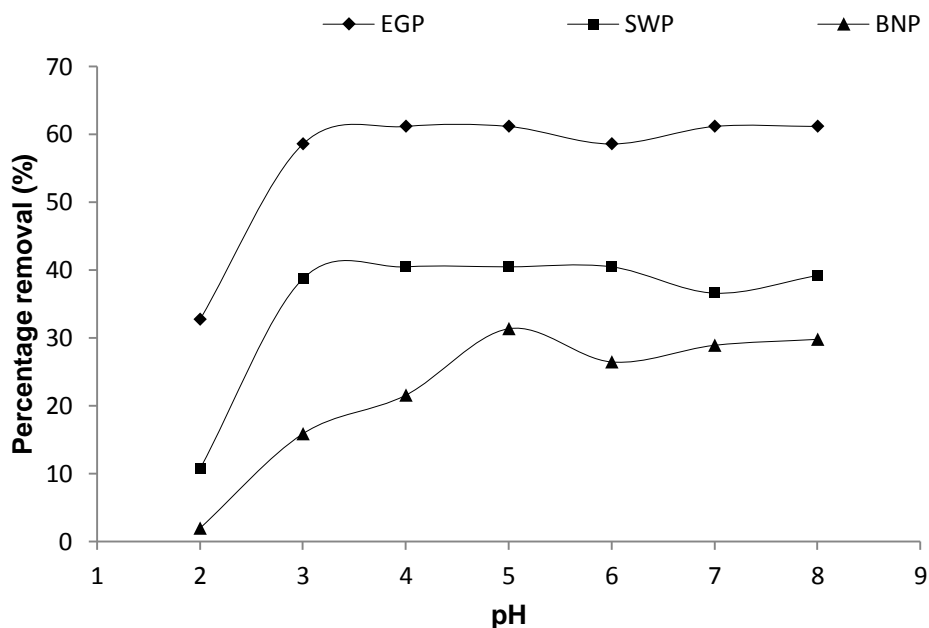


Figure 4.2: Effect of pH on biosorption of Ni(II) from solution using EGP, SWP and BNP

4.5 Effect of initial Ni(II) concentration

The effect of varying initial concentration (5 mg/L -217.50 mg/L) of Ni(II) on the biosorption onto EGP, SWP and BNP are presented (Figure 4.3). The result of Ni(II) removal efficiency at different concentrations using the biosorbents (EGP, SWP and BNP) is presented (Table 4.3). The removal efficiency varied significantly ($P \leq 0.05$) with metal concentration and the biosorbents. As a result, significant ($P \leq 0.05$) interaction effect was observed for Ni(II) removal indicating a non-uniform response pattern. For all biosorbents, Ni(II) removal efficiency increased with increasing concentration of Ni(II) reaching a maximum removal at 100 mg/L. The initial Ni(II) concentration provided an important driving force to overcome all mass transfer resistance of Ni(II) between the aqueous and solid phases as Ni(II) concentration increases. As mass transfer driving force increased, resistance to Ni(II) uptake decreased, resulting in higher Ni(II) removal (Nouri *et al.*, 2007). The mean Ni(II) removal efficiency at 100 mg/L was significantly ($P \leq 0.05$) higher than those at other concentration.

At higher concentration than 100 mg/L the Ni(II) removal efficiency declined. This behaviour indicates that saturation of the available sites on the surface of the biosorbents was preventing further biosorption of Ni(II) (Voleski, 2003). Therefore Ni(II) concentration of 100 mg/L was used in our subsequent experiments. The results are, however, in contrast with those reported by Nuhoglu and MalKoc, (2009) and Prasad and Abdullah, (2009). Both reported that Ni(II) removal efficiency decreased with increase in initial Ni(II) concentration. Nuhoglu and MalKoc, (2009) also reported that the percentage of metal ion removal is inversely related to the initial metal ion concentration. The data obtained from this experiment was then used to test the fitness of the biosorption process to Langmuir and Freundlich biosorption isotherms.

Table 4.3: Ni(II) removal efficiency at different metal concentration and the biosorbents

		Concentration (mg/L)							
		4.90	9.96	18.00	42.50	100.00	217.50	Mean Biosorbent	
Ni(II) % Removal	EGP	50.61	57.83	58.77	61.08	62.5	54.02	57.47	
	SWP	19.39	21.69	29.18	34.43	40.26	36.78	30.28	
	BNP	12.24	13.25	19.42	23.98	26.19	20.25	19.22	
	Mean Concentration	27.42	30.92	35.79	39.83	42.97	37.01		
	CV%							5.78	
	P ≤ 0.05							***	****
	Interaction							***	

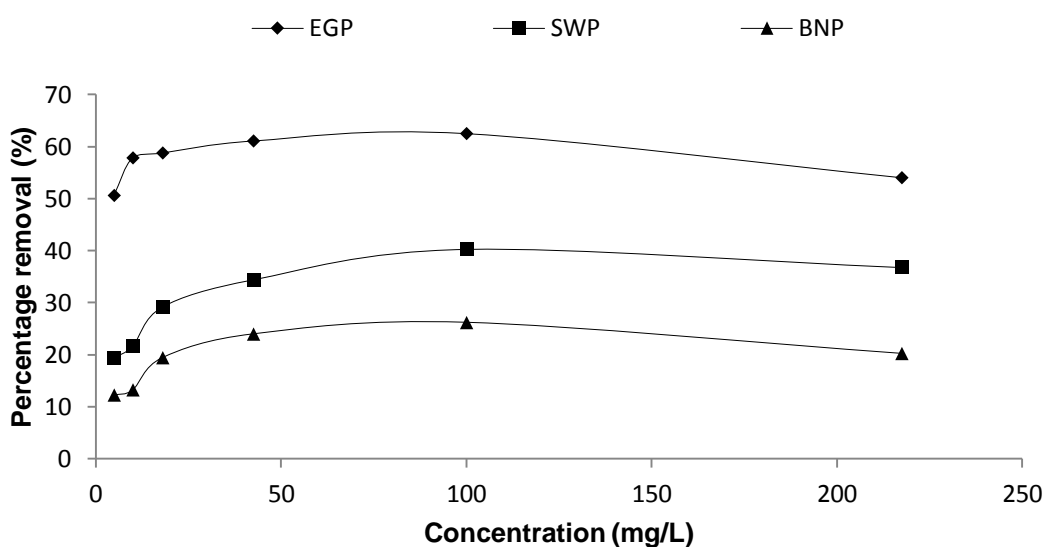


Figure 4.3: Effect of initial metal concentration on biosorption of Ni(II) from solution at pH = 5 and 298 K

4.5.1 Biosorption isotherms

Biosorption isotherms are used to describe equilibrium data and are important for developing equations that can be used to compare different biosorbents under different operational conditions. The Langmuir and Freundlich models were employed. Data from results of

varying initial concentration was fitted to adsorption isotherm in order to predict the theoretical biosorption capacities.

Figures 4.4 and 4.5 show the Langmuir and Freundlich plots for the biomaterials, respectively. A summary of the calculated parameters for each model is presented in Table 4.4. Comparing the fitness (R^2) of the experimental data of Ni(II) biosorption onto EGP and SWP, it can be seen that the Freundlich isotherm better describes the nature of the biosorption process between Ni(II) and EGP or SWP as is shown by the R^2 value which were greater than 0.98 ($R^2 > 0.98$) (table 4.4), while the Langmuir isotherm describes the nature of the biosorption process between Ni(II) and BNP ($R^2 = 0.99$). The Freundlich model assumes a multi-layer coverage of the biosorbent surface. Therefore, the biosorption process of Ni(II) onto EGP and SWP may be interpreted as multilayer adsorption.

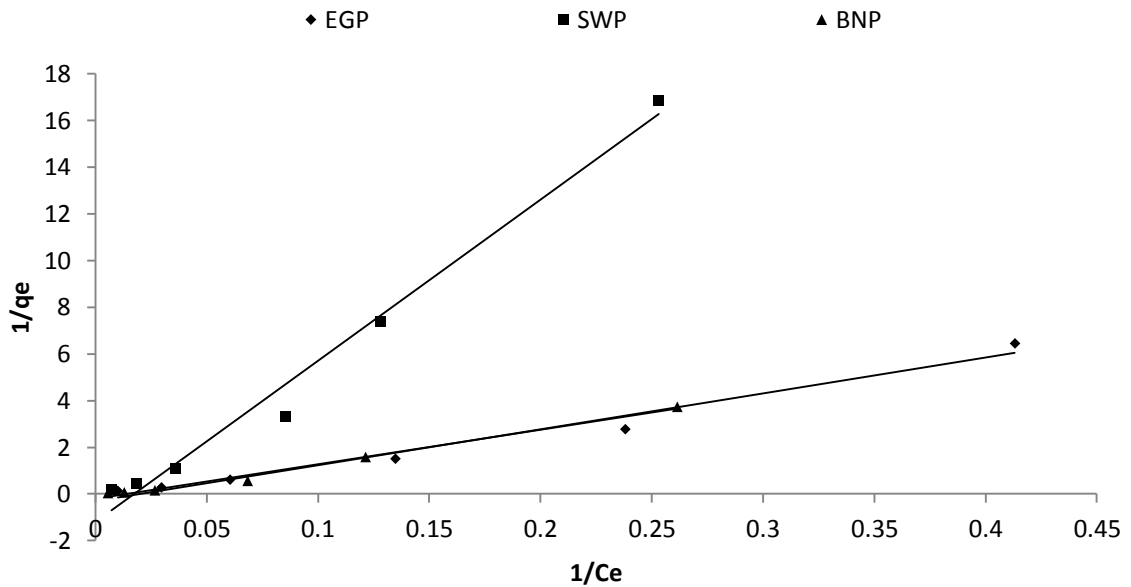


Figure 4.4: Langmuir isotherm for biosorption of Ni(II) ion onto EGP, SWP and BNP

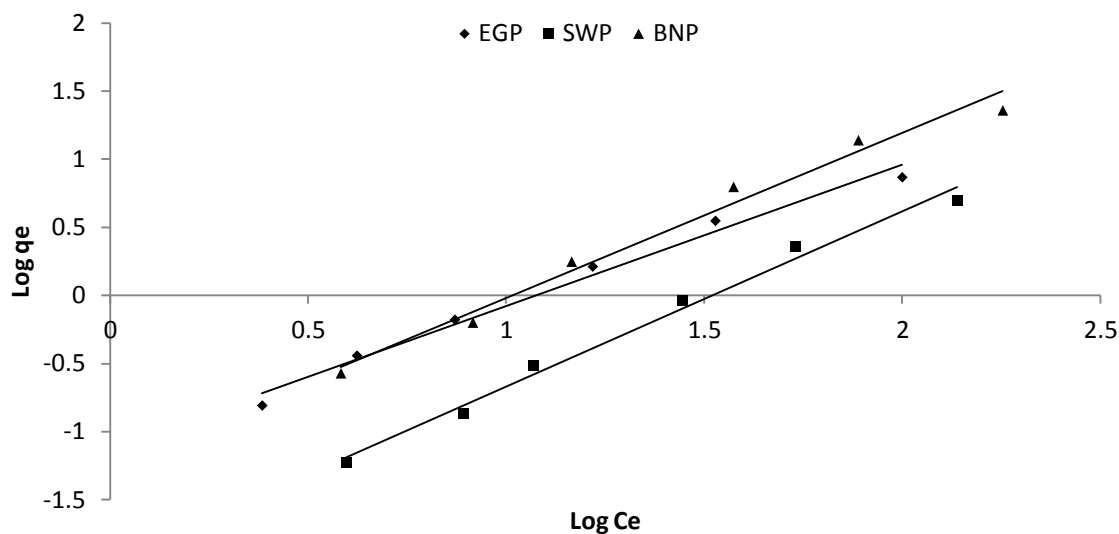


Figure 4.5: Freundlich isotherm for biosorption of Ni(II) ion onto EGP, SWP and BNP

Table 4.4: biosorption isotherm parameters for Ni(II) removal by EGP, SWP and BNP

Biosorbents	Langmuir				Freundlich		
	q_{exp}	q_m	K_L	R^2	K_F	$1/n$	R^2
EGP	7.344	-3.205	-0.020	0.977	0.077	0.962	0.986
SWP	4.989	-0.509	-0.009	0.984	0.011	0.776	0.989
BNP	22.016	-5.133	-0.013	0.991	0.059	0.825	0.982

4.6 Effect of temperature

The effect of temperature on biosorption of Ni(II) onto EGP, SWP and BNP was investigated in the range 295 to 333 K is presented (Table 4.5). Ni(II) removal efficiency varied significantly ($P \leq 0.05$) with temperature and biosorbents. It was observed for EGP and SWP (Figure 4.6) that Ni(II) removal efficiency decreased sharply as the temperature increased from 295-303 K, remaining fairly constant from 303 to 323 K, and decreased sharply again at 333 K. For BNP the percentage removal increased slightly as the temperature increased from 295 to 303 K, reaching a maximum at 313 K, and then decreased sharply as temperature was increased from 323 to 333 K.

The decrease in Ni(II) removal efficiency for the three biosorbents as temperature increases suggests that low temperature favours Ni(II) biosorption on the three biomaterials. Higher temperatures tend to decrease the boundary layer thickness. Metal ions, therefore, have an increased tendency to escape from the biosorbent surface to the solution phase (Opeolu *et al.*, 2011). This means that the biosorption process was an exothermic reaction.

Table 4.5: Ni(II) removal efficiency at different temperature and the biosorbent

		Temperature(K)					
		295.15	303.15	313.15	323.15	333.15	Mean Biosorbent
Ni(II) % Removal	EGP	64.92	54.40	53.07	48.34	40.14	52.17
	SWP	42.86	28.02	27.78	19.05	8.57	25.26
	BNP	26.38	27.14	26.67	14.76	10.95	21.18
	Mean Temperature	44.72	36.52	35.84	27.38	19.89	
	CV%			8.91			
	P ≤ 0.05			***			***
	Interaction			***			

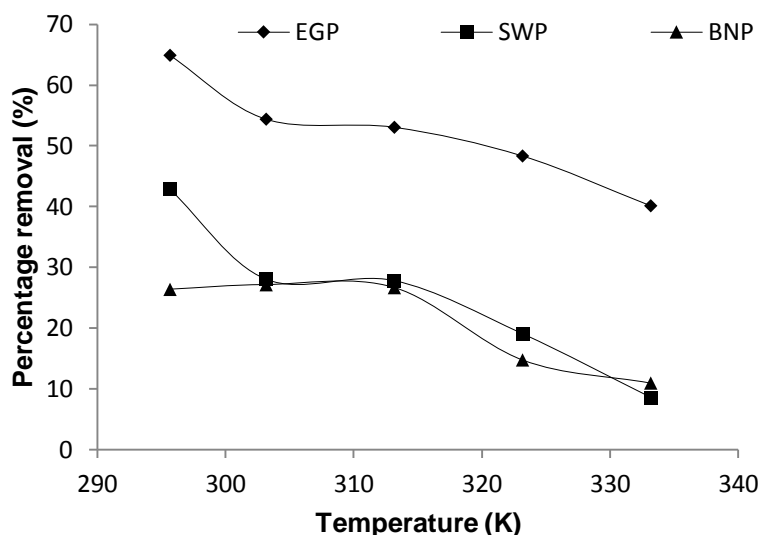


Figure 4.6: Effect of temperature (K) on the biosorption of Ni(II) ions by EGP, SWP and BNP

4.6.1 Thermodynamic studies

The results for Ni(II) biosorption as a function of temperature were modelled according to equations 2.9 and 2.10 to obtain the thermodynamic parameters, Gibbs free energy change ΔG° , enthalpy change ΔH° and entropy change ΔS° of the biosorption process.

The plots of $\ln K$ versus $1/T$ for the three biosorbents are presented (Figure 4.7). The thermodynamic parameters obtained from the plots are also presented (Table 4.6). The ΔG° for Ni (II) biosorption by the three biomaterials was temperature dependent. The change in enthalpy (ΔH°) and entropy (ΔS°) were negative. This implies that the reaction was exothermic and thus unfavourable at higher temperatures (Jiang *et al.*, 2009). The decreased biosorption with increases in temperature has been attributed to a weakening of adsorptive forces between the active sites of the biosorbents and adsorbate species and also between adjacent molecules on the adsorbed phase (Jiang *et al.*, 2009).

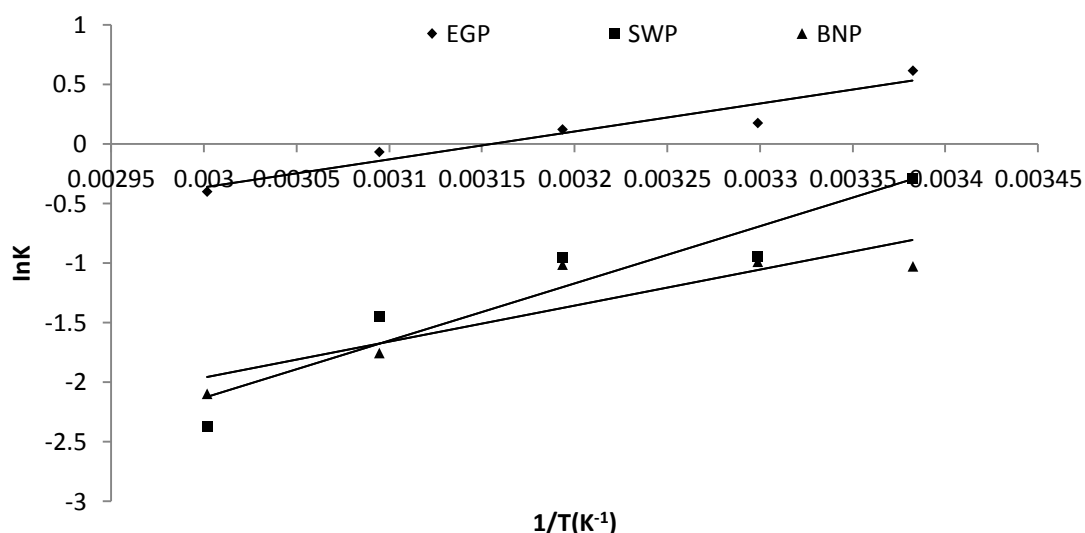


Figure 4.7: Thermodynamic profile of Ni(II) removal using EGP, SWP and BNP

Table 4.6: Thermodynamic parameters (ΔH° , ΔS° and ΔG°) for the biosorption of Ni(II) ion on EGP, SWP and BNP

	ΔH° (kJmol ⁻¹)	ΔS° (JK ⁻¹ mol ⁻¹)	ΔG° kJ/mol at various Temperatures (K)				
			295.65	303.15	313.15	323.15	333.15
EGP	-19.39	-61.21	-1.51	-0.44	-0.32	0.18	1.11
SWP	-39.87	-137.33	0.71	2.38	2.49	3.89	6.56
BNP	-25.14	-91.74	-2.52	-2.49	-2.63	-4.71	-5.80

4.7 Effect of time

Several authors have reported the effect of contact time on the biosorption of heavy metals separately either by batch or semi-batch mode. To the best of our knowledge, no work has been done so far, comparing both modes of experiment. Therefore, in this study, two modes of experiment (batch and semi-batch) were conducted simultaneously to find out if the result is different whether the experiment is conducted by batch or semi batch mode.

4.7.1 Batch experiments

The results of Ni(II) removal efficiency at different time intervals for the biosorbents are presented (Table 4.7). Removal efficiency varied significantly ($P \leq 0.05$) with time and the type of biosorbent. Mean Ni(II) removal efficiencies at 5, 10, 15, 20, 25, 30 and 120 min were slightly higher than those at 1, 3, 60 and 90 min. However, there were no significant ($P > 0.05$) differences between the contact times of 1, 3, 60 and 90 min with 5, 10, 15, 20, 25, 30 and 120 min. The three biosorbents showed fast Ni(II) reduction within 20 min of contact (Figure 4.8). At the beginning of the biosorption process, the concentration gradient between the liquid film on the solid and the solid surface was large and hence the transfer of solute onto the solid surface was fast (Babu and Gupta, 2008). Maximum percentage removal for SWP ($39 \pm 1.49\%$) and BNP ($28 \pm 1.58\%$) occurred within 5 minutes of contact while maximum

percentage removal for EGP ($65\pm 1.58\%$) occurred after 20 minutes. A dynamic system existed between the Ni(II) and the biomaterials; Ni(II) percentage removal by each biosorbent reduced after reaching the optimum. Similar results have been reported using other biosorbents for uptake of different heavy metals (Prasanna *et al.*, 2006; Bueno *et al.*, 2008; Prasad and Abdullah, 2009 and Lawal *et al.*, 2010). Metal uptake by biomaterial has been reported to occur in phases, usually beginning with an initial fast biosorption phase where the adsorbate reaches a maximum within 5 to 15 minutes after solid liquid contact (Volesky and Holan, 1995). A further increase in contact time had a negligible effect on the sorption. According to these results, the contact time was fixed at 120 minutes for the rest of the batch experiments. The fast biosorption rate reflects accessibility of the binding sites of EGP, SWP and BNP to metal ions. This has practical advantages in terms of reducing reactor volumes and time (Zhu *et al.*, 2008). Equilibrium time is an important parameter for an economical wastewater treatment system. It helps to study the biosorption mechanism and is required to obtain an insight of the rate of biosorption.

Table 4.7: Ni(II) removal efficiency at different time interval for the biosorbents

		Time Batch mode (min)											
		1	3	5	10	15	20	25	30	60	90	120	Mean Biosorbent
Ni(II) % Removal	EGP	60.53	61.86	63.16	64.21	64.91	65.79	65.79	65.79	65.79	64.47	64.47	64.25
	SWP	38.60	39.92	39.92	39.47	39.47	39.47	39.47	38.16	36.84	39.47	39.47	39.12
	BNP	25.00	25.52	28.95	28.95	28.95	28.95	28.10	26.84	23.68	24.74	26.32	26.98
	Mean Time	41.38	42.44	44.01	44.19	44.44	44.74	44.46	43.60	41.23	42.89	43.43	
	CV%	8.75											
	P ≤ 0.05	***											
	Interaction	ns											

Ns: not significant

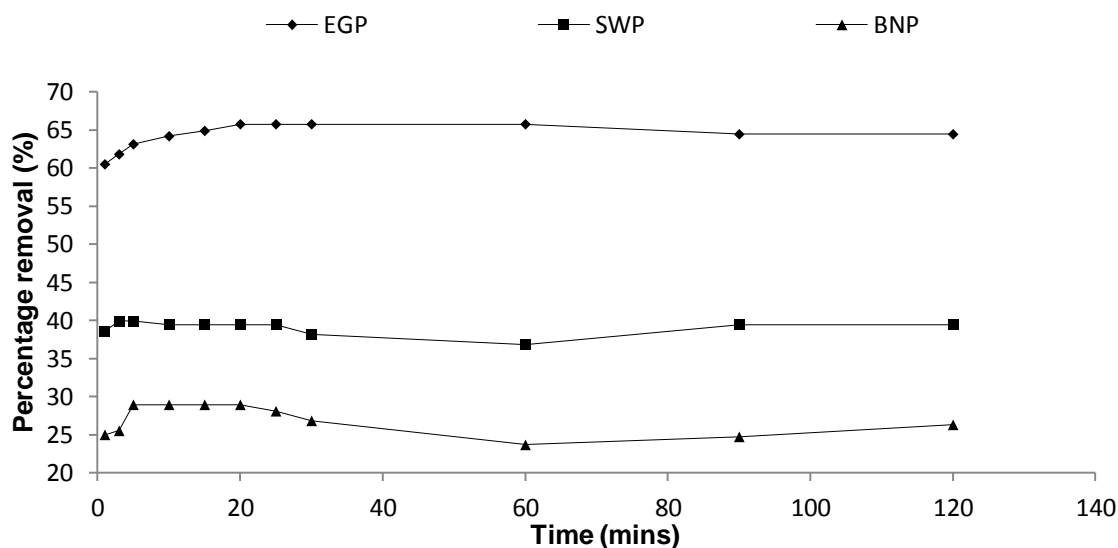


Figure 4.8: Effect of contact time (batch mode) on biosorption of Ni(II) ions by EGP, SWP and BNP

4.7.2 Semi-batch experiments

The results of Ni(II) removal efficiency at different times for the three biosorbents are presented in Table 4.8. Ni(II) removal efficiency varied significantly ($P \leq 0.05$) with the biosorbents. However, there was no significant ($P > 0.05$) difference over the time interval. The results show that the biomaterials reached their maximum percentage removal efficiencies very quickly, (< 25 minutes) (Figure 4.9). Reduction in percentage removal was observed after reaching the maxima and equilibrium was achieved after 60 minutes of contact time. Similar observation was noticed in the batch experiments. The reduction in percentage removal after reaching the maxima may be due to desorption of the metal from the surface of the biomaterial before attaining equilibrium with the Ni(II) solution.

Table 4.8: Ni(II) removal efficiency at different time and the biosorbents

		Time Semi-Batch mode (min)									
		5	10	15	20	25	30	60	90	120	Mean Biosorbent
Ni(II) % Removal	EGP	61.97	61.69	61.13	61.97	61.97	60.56	60.56	60.56	60.56	61.22
	SWP	37.99	37.99	38.55	37.99	37.99	37.99	35.17	35.17	35.17	37.11
	BNP	25.82	26.72	26.72	26.72	28.97	23.90	18.82	23.34	22.99	24.89
	Mean Time	41.93	42.13	42.13	42.22	42.98	40.82	38.19	39.69	39.58	
	CV%						9.21				
	$P \leq 0.05$						ns				***
	Interaction						ns				

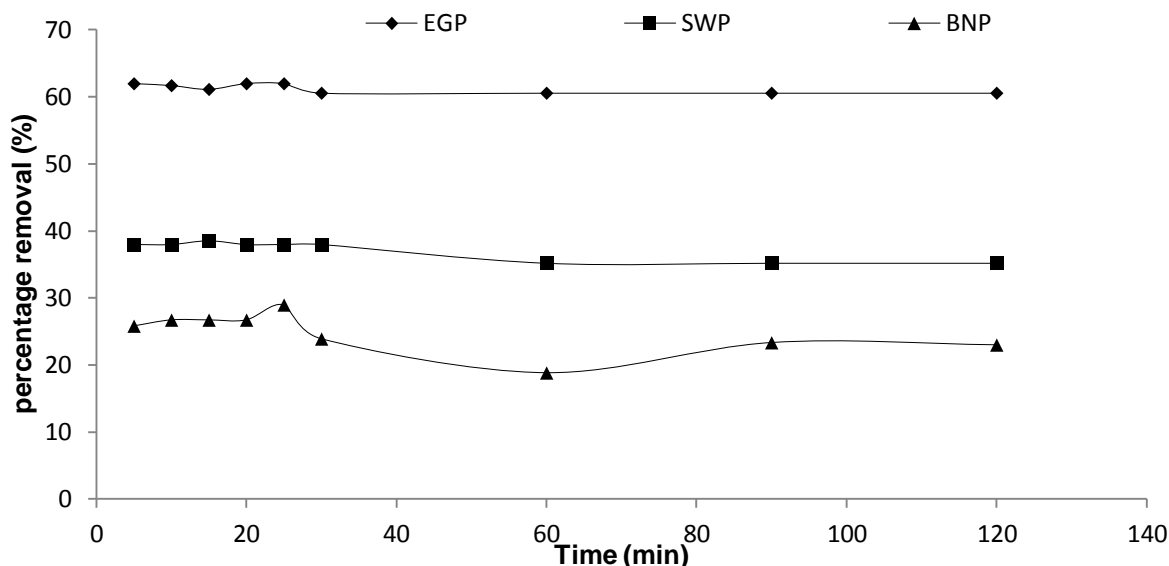


Figure 4.9: Effect of time on Ni(II) biosorption (Semi-batch mode) using EGP, SWP and BNP

Comparative results from the batch and semi batch process are presented in (Table 4.9). There was no significant difference from results obtained using both methods.

Table 4.9: Percentage removal and q_e for batch and semi-batch experiments

Biosorbents	Batch		Semi-batch	
	% Removal	q_e (mg/g)	% Removal	q_e (mg/g)
EGP	65	3.9	61	3.4
SWP	39	2.3	38	2.1
BNP	28	13.7	28	12.8

4.7.3 Kinetics of biosorption process

In order to investigate the mechanism of the biosorption of Ni(II) ions by EGP, SWP and BNP, pseudo first and pseudo second order kinetic models were used to evaluate the experimental biosorption data. These empirical mathematical models which describe biosorption data have been proven as useful tools to scale up process optimization (Sciban and Klasnja, 2003 and Senthilkumar *et al.*, 2006). Figures 4.10 and 4.11 show the pseudo-second plot for semi-batch and batch experiments, respectively.

The kinetic plots for the pseudo second order equations presented higher regression value ($R^2 > 0.995$) when compared to the pseudo first order plots ($R^2 \leq 0.802$). This suggests that the pseudo-second-order kinetic model, based on the assumption that the rate-limiting step may be chemical biosorption involving valance forces through sharing or exchange of electrons between heavy metal ions and the biosorbent provides the best correlation data for the heavy metal ions. A similar behaviour has been observed in the biosorption of heavy

metals from aqueous solutions by chemically modified orange peel (Feng *et al.*, 2011). The values of the pseudo second order parameters for the two semi-batch experiments and the batch experiment are presented (Table 4.10). The second order kinetic parameters were also dependent on the experimental method adopted as the batch and semi-batch experiments did not produce identical results. With the help of kinetic data, the rate determining step of the transport mechanism and thus the modelling and the design of the process can be described (Farooq *et al.*, 2011). One of the most important features of as biosorbent is the rate at which the solid phase adsorbs metal ions from the aqueous solution and attains equilibrium. A good correlation of the kinetic data explains the biosorption mechanism of the metal ion on the solid phase.

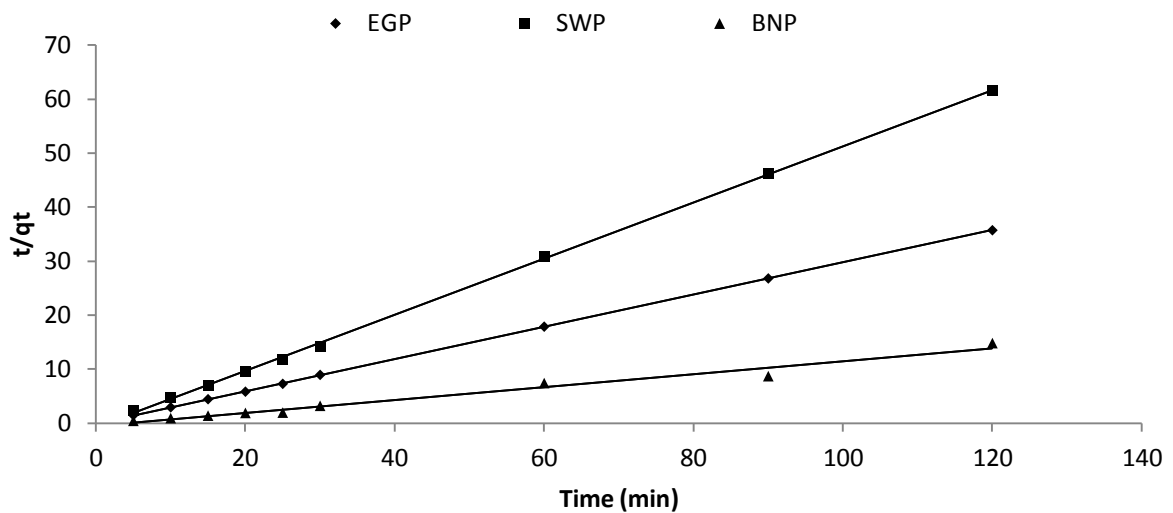


Figure 4.10:.Pseudo-second order plot for semi-batch experiments using EGP, SWP and BNP

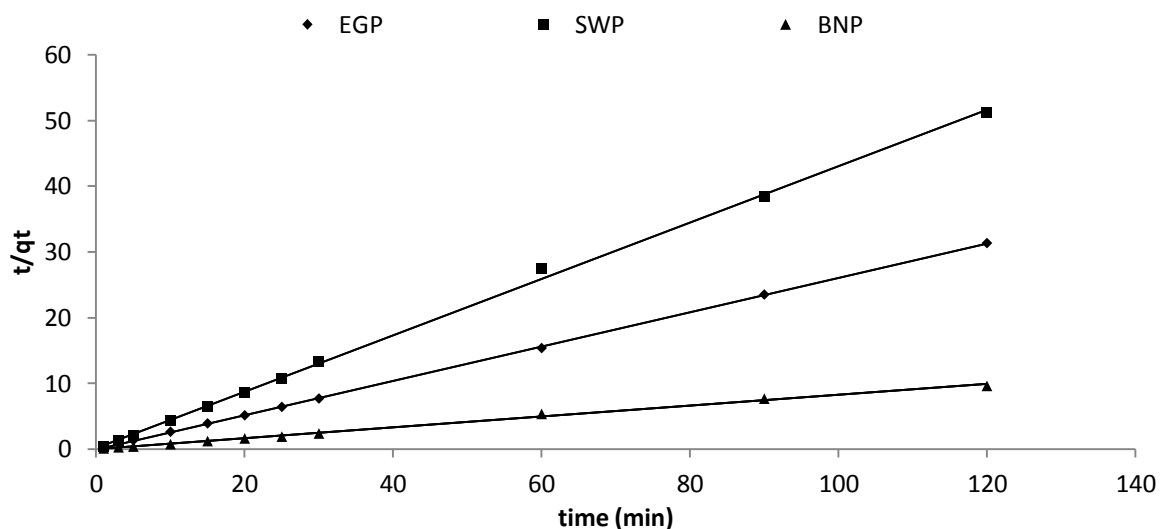


Figure 4.11:.Pseudo-second order plot for batch experiments using EGP, SWP and BNP

Table 4.10: Pseudo-second order parameters for semi-batch and batch biosorption of Ni(II) using EGP, SWP and BNP in 50 mL solution

	Semi-batch experiments			Batch experiments		
	0.8g	0.8g	0.1g	0.8g	0.8g	0.1g
	EGP	SWP	BNP	EGP	SWP	BNP
$K_2(\text{g mg}^{-1} \text{min}^{-1})$	1.109	0.372	0.031	1.567	1.820	0.219
$q_e(\text{mg g}^{-1})$	3.350	1.925	8.361	3.834	2.327	12.077
R^2	0.999	0.999	0.977	0.999	0.999	0.997

4.8 Effect of modification

The effect of chemical modifications on the Ni(II) removal efficiency using EGP, SWP and BNP are presented (Table 4.11). As can be seen from Table 4.11, the base modification resulted in improved Ni(II) removal using the three biosorbents. This improvement may be due to the formation of new functional groups and an increase in the number of binding sites which result in more available sites for biosorption (Yeneneh *et al.*, 2011). Acid modification of the biosorbents resulted in a decrease in Ni(II) removal efficiency using EGP. For SWP the removal efficiency did not change consistently. This difference of removal efficiency after a specific chemical modification may be due to the change in the nature of cell wall composition of the biosorbents (Shafqat *et al.*, 2008).

Table 4.11: Ni(II) percentage removal after modification by sodium hydroxide and hydrochloric acid

Biosorbents	Modifications	
	NaOH	HCl
EGP (%)	93.76	39.47
SWP (%)	57.02	36.84
BNP (%)	95.97	NA

4.9 FTIR data of biosorbents and Ni-loaded biosorbents

The FTIR spectra of EGP, SWP and BNP are presented (Figure 4.12). The band at 3416-3447 cm^{-1} was assigned to the OH group in free alcohols. The band at 2921-2929 cm^{-1} was assigned to the C-H stretching (Li *et al.*, 2007). The band at 1617-1637 cm^{-1} was assigned to the asymmetric stretching of $-\text{COO}-$ in ionic carboxylic group. The band at 1384 cm^{-1} was assigned to the symmetric $-\text{COO}-$ stretching in pectin (Farinella *et al.*, 2008). The band at 1021-1054 cm^{-1} was assigned to the C-OH stretching in alcohols. The deformation vibration of carbonyl stretching at 1245 cm^{-1} was observed in the FTIR spectrum of SWP Guilbaud *et al.* (2003). The FTIR spectra of the Ni(II) loaded biosorbents are presented in Figure 4.13. After metal loading, the C=O deformation band (1384 cm^{-1}) in pectin remained constant while shifts occurred in the ionic carboxylic bands indicating an interaction of this functional groups with the adsorbed Ni(II). Significant shifts were also observed in the O-H stretching band at

3416-3447 cm^{-1} . For example the 3447 cm^{-1} band in EGP shifted to 3421 cm^{-1} . After biosorption, the 1734 cm^{-1} band appeared in the spectra of all the biosorbents. This band has been attributed to the stretching vibration of C=O band due to non-ionic carboxylic groups such as in carboxylic acid or their esters (Li *et al.*, 2007 and Iqbal *et al.*, 2009a,b). The spectra in Figure 4.12 show that all the biomaterials possess ionic carboxylic functional groups. The appearance of the non-ionic C=O band in the metal loaded spectra may indicate the interaction of the ionic carboxylic acid group with Ni(II) ion, leading to a non-ionic C=O after metal loading. The functional groups in BNP were verified from earlier reports (Memon *et al.*, 2008). Those for EGP and SWP were unavailable in the literature. The FT-IR adsorption bands (wave numbers, cm^{-1}) of biomaterials and Ni(II) loaded biomaterials are presented (Table 4.12).

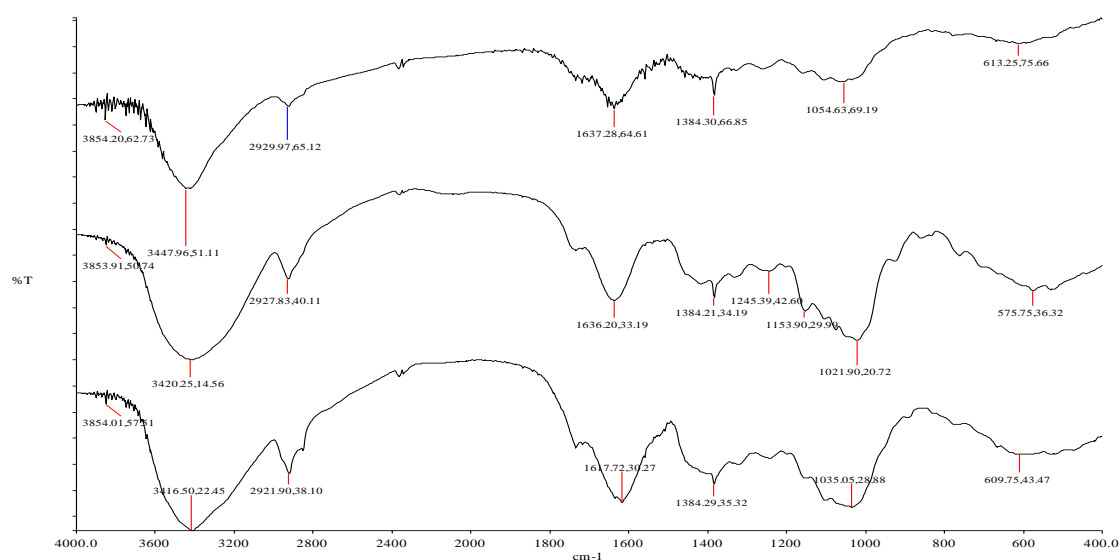


Figure 4.12: FTIR spectra of biomaterials; from above EGP, SWP and BNP

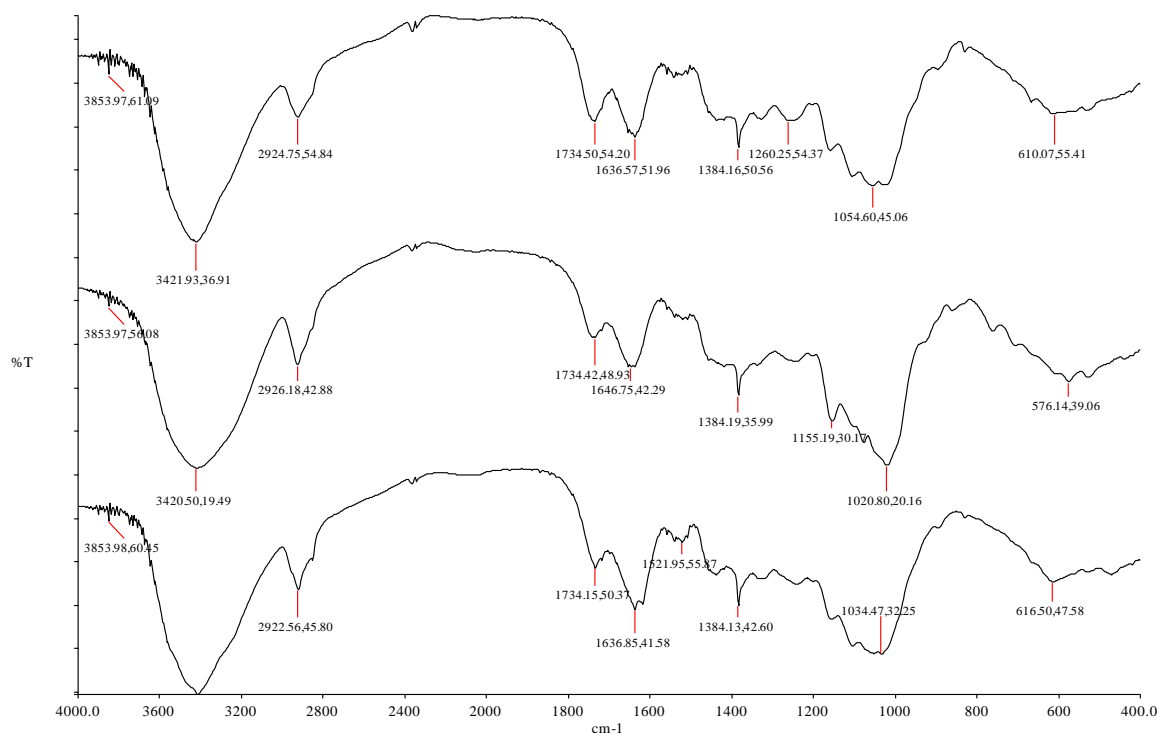


Figure 4.13: FTIR spectra of Ni(II) loaded biomaterials; from above EGP-Ni, SWP-Ni and BNP-Ni

Table 4.12: FT-IR biosorption bands (wave numbers cm^{-1}) of EGP, SWP and BNP and Ni(II) loaded EGP, SWP and BNP

Functional groups	EGP	EGP-Ni(II)	SWP	SWP-Ni(II)	BNP	BNP-Ni(II)
OH free alcohols	3447	3421	3420	3420	3416	3417
C-H stretching	2929	2924	2927	2926	2921	2922
C=O stretching vibration (non ionic)	-	1734	-	1734	-	1734
COO- asymmetric stretching (ionic)	1637	1636	1636	1646	1617	1636
COO- symmetric stretching	1384	1384	1384	1384	1384	1384
C=O deformation stretching	-	-	1245	-	-	-
C-OH stretching in alcohols	1054	1054	1021	1020	1035	1034

4.10 Desorption of Ni(II) from biosorbents

Table 4.13 shows the percentage desorbed Ni(II) from EGP, SWP and BNP using deionised water and HCl. From the result presented in table 4.13, it can be seen that Ni(II) desorption using HCl is significantly higher than when using deionised water. This result suggests that the adsorbed Ni(II) on the biosorbents were exchanged for H^+ in the desorbing solution. The biosorbent surfaces were protonated by H^+ under acidic conditions which could make desorption of positively charged Ni(II) possible. Therefore, ion exchange mechanism could play a significant role in the biosorption of Ni(II). This result is also in agreement with the chemisorptions pseudo-second order kinetic model which was very well fitted. One can

conclude from this observation that biosorption of Ni(II) to EGP, SWP and BNP is a chemical process that involves electrostatic interaction.

Table 4.13: Percentage of Ni(II) desorbed from EGP, SWP and BNP using H₂O and HCl

Biosorbents	C _o	C _e		%des	
		H ₂ O	HCl	H ₂ O	HCl
EGP	63.50	0.58	53.75	0.91	84.65
SWP	36.83	1.31	29.75	3.56	80.78
BNP	31.67	0.74	19.75	2.34	62.36

4.11 Ni(II) removal from landfill leachates using EGP, SWP and BNP

Mean responses of physicochemical parameters of landfill leachates (mean ± standard deviation values) are presented (Appendix D) and heavy metals in landfill leachates (mean ± standard deviation values) are also presented (Table 4.15 and 4.16). The result of Ni(II) removal efficiency from landfill leachate and aqueous solutions with the biosorbents are presented (Table 4.14). The Ni(II) removal efficiency varied significantly ($P \leq 0.05$) with landfill leachates and with biosorbents. The Ni(II) removal from the three leachate samples was highest using EGP. This is because EGP gave higher porosity than SWP and BNP (Table A-1). The porosity yields the surface areas on which adsorbate attaches (Yoshiyuki *et al.*, 2003). Percentage Ni(II) removal for the three landfill sites, Bellville, Vissershok and Coastal park (all in Cape Town) was 23.97 % 26.62 % and 21.33 %, respectively. The values were significantly lower than the control biosorption (65.97 % Ni(II)) in aqueous solution. The reason may be attributed to the fact that large amounts of lower molecular weight cations such as K⁺, Ca²⁺ and Mg²⁺ (Table 4.15) were found in the three landfill leachates. These cations may have competitive effect on Ni(II) removal from the selected landfill leachate. Furthermore, the landfill leachates also contain other metal ions (Table 4.16) in considerable concentration which may also compete with Ni(II) biosorption for the available biosorption sites on the biosorbent surface (Sōukand *et al.*, 2009). A Similar trend was also observed for SWP and BNP. Olu-owolabi *et al.* (2012) have previously reported that higher concentration of Na⁺ and K⁺ suppressed the biosorption of heavy metals by biomaterial and attributed this to the competition of these metal ions with those of heavy metals. The higher concentration of K⁺, Ca²⁺ and Mg²⁺ present in the leachates resulted in the reduction of the available biosorption sites for heavy metals. The data presented in Table 4.14 indicate that within landfill leachates there was a significant ($P \leq 0.05$) difference in Ni(II) removal. Similarly significant ($P \leq 0.05$) interaction effect was observed for Ni(II) removal efficiency indicating that the response patterns varied with different landfill leachate. Similar results have also been reported by Ringqvist *et al.* (2002) and Ishak and Hamzah, (2010).

Table 4.14: Ni(II) removal efficiency from landfill leachate and aqueous solution with the biosorbents

		Landfill leachates				
Ni (II) % Removal		Bellville	Vissershok	Coastal park	Control(aqueous solution)	Mean Biosorbent
		EGP	23.97	26.62	21.33	65.97
	SWP	12.60	18.83	14.73	38.37	21.41
	BNP	12.96	21.37	18.30	32.98	21.13
	Mean Landfill	16.51	22.27	18.12	45.78	
	CV%			15.21		
	P ≤ 0.05			***		***
	Interaction			***		

Table 4-15: Landfill leachate metal analysis in ppm (mean ± SD)

Metal	Vissershok	Coastal Park	Bellville
Ca	96.94±3.37	82.77±18.09	91.10±6.69
Fe	6.08±0.87	2.86±1.44	6.29±0.31
K	1656.50±24.75	2963.00±193.75	1396.67±84.76
Mg	145.90±0.99	337.60±22.35	220.77±13.65

Table 4-16: Landfill leachate heavy metal analysis in ppb (mean ± SD)

Metal	Vissershok	Coastal Park	Bellville
Al	1633.97±529.89	1260.54±922.05	390.39±20.80
V	135.54±9.29	58.56±4.27	53.00±4.43
Cr	314.14±40.36	52.76±5.03	175.86±4.25
Mn	187.81±5.79	35.05±24.23	77.26±5.20
Co	80.70±4.54	72.68±1.22	49.51±2.87
Ni	399.37±11.80	208.40±11.97	252.63±14.93
Cu	50.60±25.52	64.57±16.53	31.77±3.19
Zn	218.24±46.88	117.68±61.19	110.68±18.52
As	114.86±8.24	87.11±3.79	60.33±3.86
Sr	1591.00±16.74	1149.57±110.37	1472.92±90.69
Cd	10.23±3.95	4.28±1.43	19.74±17.98
Sn	50.60±16.49	5.29±0.13	37.61±3.00
Au	0.15±0.02	1.04±0.93	0.21±0.12
Hg	0.46±0.43	1.45±1.02	0.99±0.29
Pb	60.48±11.09	23.84±6.05	32.33±12.43

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Batch Ni(II) removal from aqueous solutions using natural low cost adsorbents was investigated. Based on statistical analysis Ni(II) removal efficiency was found to vary significantly ($P \leq 0.05$) with biosorbent mass, pH, Ni(II) initial concentration and temperature. At biosorbent mass of 0.4g, 0.4g and 0.05g for EGP, SWP and BNP, respectively, optimum pH was found to be 5 at a Ni(II) concentration of 100 mg/L.

Biosorption data of Ni(II) biosorption onto EGP and SWP fitted into the Freundlich isotherm model while those of BNP fitted into Langmuir the isotherm model.

The Gibbs free energy (ΔG°) was temperature dependent for the three biosorbents. The negative values of ΔH° recorded for Ni(II) suggested the exothermic nature of the biosorption process.

Kinetics model parameters were derived using pseudo-first order and pseudo-second order. Data fitted well into the pseudo-second order model for Ni(II) biosorption using EGP, SWP and BNP which suggests that the mechanism for Ni(II) removal from aqueous solutions using these biosorbents could be chemisorption.

Alkaline modification enhanced Ni(II) removal efficiency of the three biosorbents. Lesser mass of modified biosorbent were also required relative to unmodified biosorbents. Ni(II) recovery using 1 M HCl was found to be higher than when using deionised water.

Although Ni(II) removal efficiency was low for landfill leachates, EGP was found to be a better biosorbent for Ni(II) removal from aqueous solutions and leachates from the three selected landfill leachates.

5.2 Recommendations

Future studies should be conducted on the application of EGP, SWP and BNP for heavy metals removal in a multi-metal system.

To determine the competitive effect of some cations such as K^+ , Ca^{2+} , and Mg^{2+} on Ni(II) or other toxic metal biosorption from landfill leachate using EGP, SWP and BNP.

Future studies should be conducted to evaluate EGP, SWP and BNP efficiency to remove other metals or constituent from landfill leachate and other types of wastewater.

Further experiments need to be conducted to better understand the mechanism of Ni(II) removal from aqueous solution by EGP, SWP and BNP.

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APPENDICES

Appendix A: Biosorbents Characteristics

Table A-1: Adsorbent Properties

Biosorbent	Particle Density g/cm ³	Bulk Density g/cm ³	Porosity	Media pH
EGP	1.11	0.48	56.63	4.32
SWP	1.65	0.84	48.93	5.08
BNP	1.42	0.76	46.00	5.27

Appendix B: Determination of Ni(II) in biosorbents

Table B-1: Ni(II) in biosorbents (mean± SD)

EGP(mg/l)	SWP(mg/l)	BNP(mg/l)
0.095±0.01	0.105±0.02	0.085±0.01

Appendix C: Precision studies

Table C-1: Ni(II) concentration in spiked and unspiked leachates samples

Landfill leachates	Spike(mg/l)	Unspike(mg/l)	Spike distilled water(mg/l)
Bellville	10±0.14	0.27±0.03	9.7±0.13
Vissershok	11±0.11	0.34±0.04	9.7±0.13
Coastal park	9.90±0.15	0.21±0.03	9.7±0.13

Appendix D: Physicochemical Analysis of the Landfill leachate

Table D-1: Landfill leachates physicochemical parameters

	Temperature (°C)	pH	Conductivity (ms)	Salinity (psu)	TDS (ppt)	Turbidity	Resistivity (ohm)
Bellville	22.50	7.90	12.45	7.26	6.29	17.30	80.30
Vissershok	23.40	8.64	16.06	9.44	8.10	26.00	62.20
Coastal park	21.50	8.40	10.68	6.06	5.91	248.00	486.00

Appendix E: Quality assurance or quality control

Table E-1: Ni(II) in distilled-deionised water or leached from filter paper and adsorbed or leached onto or from filter paper

Ni(II) in DI	Ni(II) in FIL DI	UNF 100mg/l Ni(II)	FIL 100mg/l Ni(II)
ND	ND	99.98	99.94

Table E-2: Ni (II) leached from the biosorbents and adsorbed onto flask wall

N(II) leached from the biosorbents			N(II)adsorbed onto flask wall	
EGP	SWP	BNP	Initial conc	Final conc
ND	ND	ND	98.33±0.58	98.01±0.50

Appendix F: Statistical analysis of Ni(II) removal efficiency at different pH and the biosorbents

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BIOSORBENT X pH

The GLM Procedure

Class Level Information		
Class	Levels	Values
BIOSORBENTS	3	BNP EGP SWP
PH	7	2 3 4 5 6 7 8

Number of observations 63

The GLM Procedure

Dependent Variable: __REMOVAL_OF_Ni_ REMOVAL OF Ni

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	20	18539.47370	926.97369	193.36	<.0001
Error	42	201.34545	4.79394		
Corrected Total	62	18740.81916			

Source	R-Square	Coeff Var	Root MSE	__REMOVAL_OF_Ni_ Mean		
	0.989256	5.764048	2.189507	37.98557		
Source	DF	Type III SS	Mean Square	F Value	Pr > F	
BIOSORBENTS	2	12452.90186	6226.45093	1298.82	<.0001	
PH	6	5706.42549	951.07091	198.39	<.0001	
BIOSORBENTS*PH	12	380.14636	31.67886	6.61	<.0001	

The GLM Procedure

Duncan's Multiple Range Test for __REMOVAL_OF_Ni_

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.

Alpha	0.05	
Error Degrees of Freedom	42	
Error Mean Square	4.793939	
Number of Means	2	3
Critical Range	1.364	1.434

Means with the same letter are not significantly different.

Duncan Grouping	Mean	N	BIOSORBENTS
A	56.3995	21	EGP
B	35.2744	21	SWP
C	22.2829	21	BNP

The GLM Procedure

Duncan's Multiple Range Test for __REMOVAL_OF_Ni_

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.

Alpha	0.05					
Error Degrees of Freedom	42					
Error Mean Square	4.793939					
Number of Means	2	3	4	5	6	7
Critical Range	2.083	2.190	2.261	2.311	2.350	2.381

Means with the same letter are not significantly different.

Duncan Grouping	Mean	N	PH
A	44.363	9	5
B	43.409	9	8
B	42.254	9	7
B	41.867	9	6
	41.095	9	4
D	37.748	9	3
E	15.161	9	2

Breakdown of Means and Other Descriptive Statistics

1

----- Effect=BIOSORBENTS -----

BIOSORBENTS	PH	Mean of __REMOVAL_OF_NI_	Std. Dev. of __REMOVAL_OF_NI_	Std. Error of __REMOVAL_OF_NI_
BNP	.	22.2829	10.0604	2.19535
EGP	.	56.3995	10.2230	2.23083
SWP	.	35.2744	10.4248	2.27487

----- Effect=Overall -----

Mean of	Std. Dev. of	Std. Error of
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BIOSORBENTS	PH	__REMOVAL__ OF_NI_	__REMOVAL__ OF_NI_	__REMOVAL__ OF_NI_
.	.	37.9856	17.3860	2.19042
----- Effect=PH -----				
BIOSORBENTS	PH	Mean of __REMOVAL__ OF_NI_	Std. Dev. of __REMOVAL__ OF_NI_	Std. Error of __REMOVAL__ OF_NI_
2	2	15.1615	13.9189	4.63962
3	3	37.7481	18.6041	6.20136
4	4	41.0953	17.2663	5.75543
5	5	44.3633	13.3330	4.44433
6	6	41.8672	14.0870	4.69568
7	7	42.2543	14.7301	4.91003
8	8	43.4094	14.0762	4.69206
----- Effect=BIOSORBENTS*PH -----				
BIOSORBENTS	PH	Mean of __REMOVAL__ OF_NI_	Std. Dev. of __REMOVAL__ OF_NI_	Std. Error of __REMOVAL__ OF_NI_
BNP	2	1.9608	0.49020	0.28301
BNP	3	15.8824	1.89091	1.09172
BNP	4	21.5686	2.45098	1.41507
BNP	5	31.3725	1.47059	0.84904
BNP	6	26.4706	2.45098	1.41507
BNP	7	28.9216	2.45098	1.41507
BNP	8	29.8039	2.28455	1.31898
EGP	2	32.7540	3.39201	1.95838
EGP	3	58.6075	2.73136	1.57695
EGP	4	61.2042	2.58639	1.49325
EGP	5	61.2042	2.58639	1.49325
EGP	6	58.6178	2.73717	1.58031
Breakdown of Means and Other Descriptive Statistics				
----- Effect=BIOSORBENTS*PH -----				
BIOSORBENTS	PH	Mean of __REMOVAL__ OF_NI_	Std. Dev. of __REMOVAL__ OF_NI_	Std. Error of __REMOVAL__ OF_NI_
EGP	7	61.2042	2.58639	1.49325
EGP	8	61.2042	2.58639	1.49325
SWP	2	10.7697	2.93757	1.69601
SWP	3	38.7544	1.43352	0.82764
SWP	4	40.5131	0.89595	0.51728
SWP	5	40.5131	1.19311	0.68884
SWP	6	40.5131	1.03455	0.59730
SWP	7	36.6370	1.60757	0.92813
SWP	8	39.2199	1.29319	0.74663
The GLM Procedure				

Appendix G: Statistical analysis of Ni(II) removal efficiency at different biosorbents doses and the biosorbents

BIOSORBENT X MASS

Class		Class Level Information					
BIOSORBENTS	MASS	Levels	Values				
		3	BNP	EGP	SWP		
		6	0.1	0.2	0.4	0.6	0.05 0.025
Number of observations			54				
The GLM Procedure							

Dependent Variable: __REMOVAL_OF_Ni_ REMOVAL OF Ni

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	17	10777.41532	633.96561	191.51	<.0001
Error	36	119.17001	3.31028		
Corrected Total	53	10896.58533			

R-Square 0.989064 Coeff Var 5.078377 Root MSE 1.819417 __REMOVAL_OF_Ni_ Mean 35.82674

Source	DF	Type III SS	Mean Square	F Value	Pr > F
BIOSORBENTS	2	6481.485686	3240.742843	978.99	<.0001
MASS	5	1235.283254	247.056651	74.63	<.0001

BIOSORBENTS*MASS 10 3060.646380 306.064638 92.46 <.0001
The GLM Procedure

Duncan's Multiple Range Test for __REMOVAL_OF_Ni_

NOTE: This test controls the Type I comparison wise error rate, not the experiment wise error rate.

Alpha 0.05
Error Degrees of Freedom 36
Error Mean Square 3.310278

Number of Means 2 3
Critical Range 1.230 1.293

Means with the same letter are not significantly different.

Duncan Grouping	Mean	N	BIOSORBENTS
A	49.5651	18	EGP
B	35.1612	18	SWP
C	22.7539	18	BNP

The GLM Procedure

Duncan's Multiple Range Test for __REMOVAL OF Ni_

NOTE: This test controls the Type I comparison wise error rate, not the experiment wise error rate.

Alpha 0.05
Error Degrees of Freedom 36
Error Mean Square 3.310278

Number of Means 2 3 4 5 6
Critical Range 1.739 1.829 1.887 1.929 1.960

Means with the same letter are not significantly different.

Duncan Grouping	Mean	N	MASS
A	40.2853	9	0.4
B A	39.1255	9	0.2
B A	38.7010	9	0.6
B C	38.2603	9	0.1
	31.1598	9	0.05
D	27.4286	9	0.025

Breakdown of Means and Other Descriptive Statistics

1

----- Effect=BIOSORBENTS -----

BIOSORBENTS	MASS	Mean of __REMOVAL_ OF_NI_	Std. Dev. of __REMOVAL_ OF_NI_	Std. Error of __REMOVAL_ OF_NI_
BNP	.	22.753943401	6.345948681	1.4957544485
EGP	.	49.56506611	12.868705282	3.0331829234
SWP	.	35.161215495	7.3373771613	1.7294363823

----- Effect=MASS -----

BIOSORBENTS	MASS	Mean of __REMOVAL_ OF_NI_	Std. Dev. of __REMOVAL_ OF_NI_	Std. Error of __REMOVAL_ OF_NI_
	0.025	27.42855486	4.0423248382	1.3474416127
	0.05	31.159823707	3.8139527159	1.271317572
	0.1	38.26026444	8.6230140023	2.8743380008
	0.2	39.125492925	16.67935056	5.5597835199
	0.4	40.285316632	20.024775205	6.6749250685
	0.6	38.700997448	20.572491507	6.857497169

----- Effect=Overall -----

BIOSORBENTS	MASS	Mean of __REMOVAL_ OF_NI_	Std. Dev. of __REMOVAL_ OF_NI_	Std. Error of __REMOVAL_ OF_NI_
	.	35.826741669	14.338617425	1.9512386838

----- Effect=BIOSORBENTS*MASS -----

BIOSORBENTS	MASS	Mean of __REMOVAL_ OF_NI_	Std. Dev. of __REMOVAL_ OF_NI_	Std. Error of __REMOVAL_ OF_NI_
BNP	0.025	27.831941545	0.5777140794	0.3335433793
BNP	0.05	29.561586639	0.5231717781	0.3020533669
BNP	0.1	28.698677801	0.8429516996	0.4866783907

BNP	0.2	19.126652749	1.4088507037	0.813400333
BNP	0.4	16.517049408	1.5293730233	0.8829839267
BNP	0.6	14.787752262	1.4774442412	0.8530028304
EGP	0.025	31.315240084	3.117575057	1.7999327984
EGP	0.05	35.664578984	2.5998425669	1.5010198059
EGP	0.1	48.26026444	2.3255260698	1.3426431024
EGP	0.2	57.376478775	2.1093172674	1.2178148921
EGP	0.4	62.595685456	1.506655191	0.8698677801
EGP	0.6	62.178148921	1.4811271158	0.855129139
SWP	0.025	23.138482951	2.1904092882	1.2646333922

Breakdown of Means and Other Descriptive Statistics

2

----- Effect=BIOSORBENTS*MASS -----

(continued)

BIOSORBENTS	MASS	Mean of	Std. Dev.	Std. Error
		__REMOVAL__ OF_NI__	of __REMOVAL__ OF_NI__	of __REMOVAL__ OF_NI__
SWP	0.05	28.253305498	2.0517081403	1.1845542471
SWP	0.1	37.821851079	1.9704377362	1.1376327574
SWP	0.2	40.873347251	1.4860111965	0.8579489643
SWP	0.4	41.743215031	1.4644688456	0.8455114823
SWP	0.6	39.137091162	1.9281796173	1.1132350211

Appendix H: Statistical analysis of Ni(II) removal efficiency at different metal concentration and the biosorbents

The GLM Procedure
Class Level Information

BIO X CONCENTRATION

Class	Levels	Values
BIOSORBENTS	3	BNP EGP SWP
CONC	6	4.9 9.96 18 42.5 100 217.5

Number of observations 54

The GLM Procedure

Dependent Variable: __REMOVAL_OF_Ni__ REMOVAL OF Ni

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	17	15767.59396	927.50553	208.83	<.0001
Error	36	159.89074	4.44141		
Corrected Total	53	15927.48471			
R-Square	Coeff Var	Root MSE	__REMOVAL_OF_Ni__ Mean		
0.989961	5.909972	2.107465	35.65948		

Source	DF	Type III SS	Mean Square	F Value	Pr > F
BIOSORBENTS	2	13942.93772	6971.46886	1569.65	<.0001
CONC	5	1468.73713	293.74743	66.14	<.0001
BIOSORBENTS*CONC	10	355.91911	35.59191	8.01	<.0001

The GLM Procedure
Duncan's Multiple Range Test for __REMOVAL_OF_Ni__

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.

Alpha 0.05
Error Degrees of Freedom 36
Error Mean Square 4.44141

Number of Means 2 3
Critical Range 1.425 1.498

Means with the same letter are not significantly different.

Duncan Grouping	Mean	N	BIOSORBENTS
A	57.4674	18	EGP
B	30.2887	18	SWP
C	19.2224	18	BNP

The GLM Procedure

Duncan's Multiple Range Test for __REMOVAL_OF_Ni__

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.

Alpha 0.05
Error Degrees of Freedom 36
Error Mean Square 4.44141

Number of Means 2 3 4 5 6

Critical Range 2.015 2.118 2.186 2.234 2.271
 Means with the same letter are not significantly different.

Duncan Grouping	Mean	N	CONC
A	42.9765	9	100
B	39.8301	9	42.5
C	37.0166	9	217.5
C	35.7950	9	18
D	30.9237	9	9.96
E	27.4150	9	4.9

Breakdown of Means and Other Descriptive Statistics

1

----- Effect=BIOSORBENTS -----

BIOSORBENTS	CONC	Mean of __REMOVAL_ OF_NI__	Std. Dev. of __REMOVAL_ OF_NI__	Std. Error of __REMOVAL_ OF_NI__
BNP	.	19.2224	5.84389	1.37742
EGP	.	57.4674	4.37339	1.03082
SWP	.	30.2887	7.96621	1.87765

----- Effect=CONC -----

BIOSORBENTS	CONC	Mean of __REMOVAL_ OF_NI__	Std. Dev. of __REMOVAL_ OF_NI__	Std. Error of __REMOVAL_ OF_NI__
	4.9	27.4150	17.8221	5.94071
	9.96	30.9237	20.5568	6.85228
	18	35.7950	17.9256	5.97521
	42.5	39.8301	16.6834	5.56114
	100	42.9765	15.9012	5.30040
	217.5	37.0166	14.6498	4.88328

----- Effect=Overall -----

BIOSORBENTS	CONC	Mean of __REMOVAL_ OF_NI__	Std. Dev. of __REMOVAL_ OF_NI__	Std. Error of __REMOVAL_ OF_NI__
	.	35.6595	17.3355	2.35906

----- Effect=BIOSORBENTS*CONC -----

BIOSORBENTS	CONC	Mean of __REMOVAL_ OF_NI__	Std. Dev. of __REMOVAL_ OF_NI__	Std. Error of __REMOVAL_ OF_NI__
BNP	4.9	12.2449	4.08163	2.35653
BNP	9.96	13.2530	2.43461	1.40562
BNP	18	19.4259	4.77918	2.75926
BNP	42.5	23.9765	2.67067	1.54191
BNP	100	26.1889	1.56138	0.90146
BNP	217.5	20.2452	0.69017	0.39847
EGP	4.9	50.6122	2.15980	1.24696
EGP	9.96	57.8313	1.00402	0.57967
EGP	18	58.7739	1.02330	0.59080
EGP	42.5	61.0824	2.28381	1.31856
EGP	100	62.4815	1.19842	0.69191
EGP	217.5	54.0230	0.91954	0.53090
SWP	4.9	19.3878	0.40816	0.23565

Breakdown of Means and Other Descriptive Statistics

2

----- Effect=BIOSORBENTS*CONC -----

BIOSORBENTS	CONC	Mean of __REMOVAL_ OF_NI__	Std. Dev. of __REMOVAL_ OF_NI__	Std. Error of __REMOVAL_ OF_NI__
SWP	9.96	21.6867	1.00402	0.57967
SWP	18	29.1852	1.38926	0.80209
SWP	42.5	34.4314	1.66932	0.96378
SWP	100	40.2593	1.74389	1.00684
SWP	217.5	36.7816	1.14943	0.66362

The GLM Procedure

Appendix I: Statistical analysis of Ni(II) removal efficiency at different time and the biosorbents (batch mode)

BIO X TIME

Class	Class Level Information	
	Levels	Values
BIOSORBENTS	3	BNP EGP SWP
TIME	11	1 3 5 10 15 20 25 30 60 90 120
Number of observations		99

The GLM Procedure

Dependent Variable: REMOVAL_OF_Ni REMOVAL OF Ni

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	32	23746.43766	742.07618	234.52	<.0001
Error	66	208.84240	3.16428		
Corrected Total	98	23955.28006			

R-Square	Coeff Var	Root MSE	<u>REMOVAL_OF_Ni</u> Mean
0.991282	4.101578	1.778842	43.36970

Source	DF	Type III SS	Mean Square	F Value	Pr > F
BIOSORBENTS	2	23509.02421	11754.51211	3714.75	<.0001
TIME	10	141.22303	14.12230	4.46	<.0001
BIOSORBENTS*TIME	20	96.19041	4.80952	1.52	0.1043

The GLM Procedure

Duncan's Multiple Range Test for REMOVAL_OF_Ni

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.

Alpha	0.05
Error Degrees of Freedom	66
Error Mean Square	3.164279

Number of Means	2	3
Critical Range	.8744	.9199

Means with the same letter are not significantly different.

Duncan Grouping	Mean	N	BIOSORBENTS
A	64.0064	33	EGP
B	39.1171	33	SWP
C	26.9856	33	BNP

The GLM Procedure

Duncan's Multiple Range Test for REMOVAL_OF_Ni

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.

Alpha	0.05
Error Degrees of Freedom	66
Error Mean Square	3.164279

Number of Means	2	3	4	5	6	7	8	9	10	11
Critical Range	1.674	1.761	1.819	1.861	1.893	1.919	1.941	1.959	1.974	1.987

Means with the same letter are not significantly different.

Duncan Grouping	Mean	N	TIME
A	44.7368	9	25
A	44.7368	9	20
A	44.4444	9	15
B	44.1871	9	10
B	44.0094	9	5
B	43.5965	9	30
B	43.4269	9	120
B	42.8889	9	90
B	42.4363	9	3
	41.3754	9	1
	41.2281	9	60

Breakdown of Means and Other Descriptive Statistics

1

----- Effect=BIOSORBENTS -----

Mean of	Std. Dev. of	Std. Error of
---------	--------------	---------------

BIOSORBENTS	TIME	REMOVAL_ OF_NI_	REMOVAL_ OF_NI_	REMOVAL_ OF_NI_
BNP	.	26.9856	2.37033	0.41262
EGP	.	64.0064	2.38937	0.41594
SWP	.	39.1171	1.61800	0.28166

----- Effect=Overall -----

BIOSORBENTS	TIME	Mean of REMOVAL_ OF_NI_	Std. Dev. of REMOVAL_ OF_NI_	Std. Error of REMOVAL_ OF_NI_
.	.	43.3697	15.6346	1.57134

----- Effect=TIME -----

BIOSORBENTS	TIME	Mean of REMOVAL_ OF_NI_	Std. Dev. of REMOVAL_ OF_NI_	Std. Error of REMOVAL_ OF_NI_
	1	41.3754	15.6172	5.20575
	3	42.4363	15.8950	5.29834
	5	44.0094	15.2231	5.07436
	10	44.1871	15.7228	5.24094
	15	44.4444	16.0720	5.35734
	20	44.7368	16.5075	5.50251
	25	44.7368	16.4928	5.49761
	30	43.5965	17.4341	5.81136
	60	41.2281	17.4995	5.83317
	90	42.8889	17.4393	5.81309
	120	43.4269	16.8561	5.61870

----- Effect=BIOSORBENTS*TIME -----

BIOSORBENTS	TIME	Mean of REMOVAL_ OF_NI_	Std. Dev. of REMOVAL_ OF_NI_	Std. Error of REMOVAL_ OF_NI_
BNP	1	25.0000	1.46520	0.84593
BNP	3	25.5263	1.46520	0.84593
BNP	5	28.9474	1.57895	0.91161
BNP	10	28.9474	1.57895	0.91161
BNP	15	28.9474	1.57895	0.91161
BNP	20	28.9474	1.57895	0.91161
BNP	25	28.9474	1.57895	0.91161
BNP	30	26.8421	1.39250	0.80396

Breakdown of Means and Other Descriptive Statistics

2

----- Effect=BIOSORBENTS*TIME -----

(continued)

BIOSORBENTS	TIME	Mean of REMOVAL_ OF_NI_	Std. Dev. of REMOVAL_ OF_NI_	Std. Error of REMOVAL_ OF_NI_
BNP	60	23.6842	1.57895	0.91161
BNP	90	24.7368	1.57895	0.91161
BNP	120	26.3158	1.89766	1.09561
EGP	1	60.5263	2.63158	1.51934
EGP	3	61.8596	1.39780	0.80702
EGP	5	63.1579	2.63158	1.51934
EGP	10	64.1404	2.16835	1.25190
EGP	15	64.9123	1.51934	0.87719
EGP	20	65.7895	2.10526	1.21547
EGP	25	65.7895	1.57895	0.91161
EGP	30	65.7895	2.63158	1.51934
EGP	60	63.1579	2.63158	1.51934
EGP	90	64.4561	1.43688	0.82959
EGP	120	64.4912	1.49360	0.86233
SWP	1	38.6000	1.61252	0.93099
SWP	3	39.9228	1.48572	0.85778
SWP	5	39.9228	1.48572	0.85778
SWP	10	39.4737	1.65434	0.95513
SWP	15	39.4737	1.65434	0.95513
SWP	20	39.4737	1.65434	0.95513
SWP	25	39.4737	1.65434	0.95513
SWP	30	38.1579	1.64342	0.94883
SWP	60	36.8421	1.89766	1.09561

SWP	90	39.4737	1.57895	0.91161
SWP	120	39.4737	1.57895	0.91161

The GLM Procedure

Appendix J: Statistical analysis of Ni(II) removal efficiency at different time and the biosorbents (semi batch mode)

BIO X SEMIBATCH

Class	Class Level Information	
	Levels	Values
BIOSORBENTS	3	BNP EGP SWP
TIME_SEMI_BATCH_	9	5 10 15 20 25 30 60 90 120

Number of observations 81

The GLM Procedure

Dependent Variable: __REMOVAL_OF_Ni_ REMOVAL OF Ni

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	26	18729.93638	720.38217	119.28	<.0001
Error	54	326.12269	6.03931		
Corrected Total	80	19056.05907			

R-Square	Coeff Var	Root MSE	__REMOVAL_OF_Ni_ Mean
0.982886	5.982924	2.457501	41.07524

Source	DF	Type III SS	Mean Square	F Value	Pr > F
BIOSORBENTS	2	18453.48384	9226.74192	1527.78	<.0001
TIME_SEMI_BATCH_	8	184.22938	23.02867	3.81	0.0013
BIOSORBEN*TIME_SEMI_	16	92.22315	5.76395	0.95	0.5165

The GLM Procedure

Duncan's Multiple Range Test for __REMOVAL_OF_Ni_

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.

Alpha	0.05
Error Degrees of Freedom	54
Error Mean Square	6.039309
Number of Means	2 3
Critical Range	1.341 1.411

Means with the same letter are not significantly different.

Duncan Grouping	Mean	N	BIOSORBENTS
A	61.2207	27	EGP
B	37.1142	27	SWP
C	24.8908	27	BNP

The GLM Procedure

Duncan's Multiple Range Test for __REMOVAL_OF_Ni_

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.

Alpha	0.05
Error Degrees of Freedom	54
Error Mean Square	6.039309
Number of Means	2 3 4 5 6 7 8 9
Critical Range	2.323 2.443 2.522 2.580 2.624 2.660 2.689 2.713

Means with the same letter are not significantly different.

Duncan Grouping	Mean	N	TIME_SEMI_BATCH_
A	42.979	9	25
B	42.227	9	20
B	42.133	9	15
B	42.133	9	10

B	A	41.927	9	5
B	A	40.820	9	30
B	C	39.691	9	90
B	C	39.579	9	120
	C	38.188	9	60

Breakdown of Means and Other Descriptive Statistics

1

----- Effect=BIOSORBENTS -----

	TIME (SEMI BATCH)	Mean of __REMOVAL_ OF_NI_	Std. Dev. of __REMOVAL_ OF_NI_	Std. Error of __REMOVAL_ OF_NI_
BIOSORBENTS	.	24.8908	3.36730	0.64804
BNP	.	61.2207	1.92325	0.37013
EGP	.	37.1142	2.85279	0.54902

----- Effect=Overall -----

	TIME (SEMI BATCH)	Mean of __REMOVAL_ OF_NI_	Std. Dev. of __REMOVAL_ OF_NI_	Std. Error of __REMOVAL_ OF_NI_
BIOSORBENTS	.	41.0752	15.4338	1.71486

----- Effect=TIME_SEMI_BATCH -----

	TIME (SEMI BATCH)	Mean of __REMOVAL_ OF_NI_	Std. Dev. of __REMOVAL_ OF_NI_	Std. Error of __REMOVAL_ OF_NI_
BIOSORBENTS	5	41.9266	16.0158	5.33860
	10	42.1333	15.5423	5.18077
	15	42.1333	15.4216	5.14052
	20	42.2272	15.6734	5.22447
	25	42.9788	14.8667	4.95557
	30	40.8196	16.2006	5.40021
	60	38.1882	18.3563	6.11877
	90	39.6914	16.6300	5.54333
	120	39.5787	16.7463	5.58210

----- Effect=BIOSORBENTS*TIME_SEMI_BATCH -----

	TIME (SEMI BATCH)	Mean of __REMOVAL_ OF_NI_	Std. Dev. of __REMOVAL_ OF_NI_	Std. Error of __REMOVAL_ OF_NI_
BIOSORBENTS	5	25.8174	1.73560	1.00205
BNP	10	26.7193	1.69109	0.97635
BNP	15	26.7193	1.69109	0.97635
BNP	20	26.7193	1.69109	0.97635
BNP	25	28.9741	2.03244	1.17343
BNP	30	23.9048	3.26709	1.88626
BNP	60	18.8275	2.25479	1.30180
BNP	90	23.3371	2.25479	1.30180
BNP	120	22.9989	1.97536	1.14047
EGP	5	61.9718	1.56838	0.90551

Breakdown of Means and Other Descriptive Statistics

2

----- Effect=BIOSORBENTS*TIME_SEMI_BATCH -----

(continued)

	TIME (SEMI BATCH)	Mean of __REMOVAL_ OF_NI_	Std. Dev. of __REMOVAL_ OF_NI_	Std. Error of __REMOVAL_ OF_NI_
BIOSORBENTS	10	61.6901	1.49056	0.86058
EGP	15	61.1268	1.49056	0.86058
EGP	20	61.9718	1.40845	0.81317
EGP	25	61.9718	1.40845	0.81317
EGP	30	60.5634	2.81690	1.62634
EGP	60	60.5634	2.81690	1.62634
EGP	90	60.5634	2.81690	1.62634
EGP	120	60.5634	2.81690	1.62634
SWP	5	37.9906	2.31009	1.33373
SWP	10	37.9906	2.31009	1.33373
SWP	15	38.5540	5.42993	3.13497
SWP	20	37.9906	2.31009	1.33373

SWP	25	37.9906	2.31009	1.33373
SWP	30	37.9906	2.31009	1.33373
SWP	60	35.1737	2.81765	1.62677
SWP	90	35.1737	2.81765	1.62677
SWP	120	35.1737	2.81765	1.62677

Appendix K: Statistical analysis of Ni(II) removal efficiency at different temperature and the biosorbents

BIO TEMPERATURE

17:38 Sunday,

September 30, 2012 1

The GLM Procedure
 Class Level Information
 Class Levels Values
 BIOSORBENTS 3 BNP EGP SWP
 TEMPERATURE 5 295 303 313 323 333
 Number of observations 45
 The GLM Procedure

Dependent Variable: REMOVAL_OF_Ni REMOVAL OF Ni

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	14	12130.56914	866.46922	101.11	<.0001
Error	30	257.09787	8.56993		
Corrected Total	44	12387.66701			

Source	R-Square	Coeff Var	Root MSE	<u>REMOVAL_OF_Ni</u> Mean	Mean Square	F Value	Pr > F
BIOSORBENTS	0.979246	8.905998	2.927444	32.87048	4254.829878	496.48	<.0001
TEMPERATURE					812.651220	94.83	<.0001
BIOSORBEN*TEMPERATUR					46.288063	5.40	0.0003

The GLM Procedure
 Duncan's Multiple Range Test for REMOVAL_OF_Ni

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.

Alpha 0.05
 Error Degrees of Freedom 30
 Error Mean Square 8.569929

Number of Means	2	3	
Critical Range	2.183	2.294	
Means with the same letter are not significantly different.			
Duncan Grouping	Mean	N	BIOSORBENTS
A	52.175	15	EGP
B	25.255	15	SWP
C	21.181	15	BNP

The GLM Procedure
 Duncan's Multiple Range Test for REMOVAL_OF_Ni

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.

Alpha 0.05
 Error Degrees of Freedom 30
 Error Mean Square 8.569929

Number of Means	2	3	4	5
Critical Range	2.818	2.962	3.055	3.121
Means with the same letter are not significantly different.				
Duncan Grouping	Mean	N	TEMPERATURE	
A	44.721	9	295	
B	36.521	9	303	
B	35.838	9	313	
C	27.384	9	323	
D	19.889	9	333	

Breakdown of Means and Other Descriptive Statistics

1

----- Effect=BIOSORBENTS -----

BIOSORBENTS	TEMPERATURE	Mean of <u>REMOVAL_OF_Ni</u>	Std. Dev. of <u>REMOVAL_OF_Ni</u>	Std. Error of <u>REMOVAL_OF_Ni</u>
BNP	.	21.180952381	7.7260177858	1.9948492145
EGP	.	52.175238095	8.607866465	2.2225415644
SWP	.	25.255238095	11.967196931	3.0899169611

----- Effect=Overall -----

		Mean of __REMOVAL_ OF_NI_	Std. Dev. of __REMOVAL_ OF_NI_	Std. Error of __REMOVAL_ OF_NI_
BIOSORBENTS	TEMPERATURE	32.87047619	16.779090757	2.5012791688

----- Effect=TEMPERATURE -----

		Mean of __REMOVAL_ OF_NI_	Std. Dev. of __REMOVAL_ OF_NI_	Std. Error of __REMOVAL_ OF_NI_
BIOSORBENTS	TEMPERATURE			
	295	44.720634921	16.940415788	5.6468052627
	303	36.520634921	13.619413914	4.5398046382
	313	35.838095238	13.164928844	4.3883096147
	323	27.384126984	16.022530197	5.3408433991
	333	19.888888889	15.479981221	5.1599937402

----- Effect=BIOSORBENTS*TEMPERATURE -----

BIOSORBENTS	TEMPERATURE	Mean of __REMOVAL_ OF_NI_	Std. Dev. of __REMOVAL_ OF_NI_	Std. Error of __REMOVAL_ OF_NI_
BNP	295	26.380952381	3.365828009	1.943261707
BNP	303	27.142857143	3.1225897735	1.8028280463
BNP	313	26.666666667	2.8571428571	1.6495721977
BNP	323	14.761904762	3.5951592549	2.0756661636
BNP	333	10.952380952	4.2324735321	2.4436197331
EGP	295	64.923809524	1.9288242045	1.1136071737
EGP	303	54.4	2.0656789389	1.1926202914
EGP	313	53.066666667	2.8526790527	1.646995019
EGP	323	48.342857143	1.9152331226	1.1057603589
EGP	333	40.142857143	2.6964493324	1.5567957479
SWP	295	42.857142857	3.2991443954	1.9047619048
SWP	303	28.019047619	2.845882573	1.6430710696
SWP	313	27.780952381	2.8593483551	1.6508455425
SWP	323	19.047619048	2.8571428571	1.6495721977

----- Effect=BIOSORBENTS*TEMPERATURE -----

BIOSORBENTS	TEMPERATURE	Mean of __REMOVAL_ OF_NI_	Std. Dev. of __REMOVAL_ OF_NI_	Std. Error of __REMOVAL_ OF_NI_
SWP	333	8.5714285714	2.465894345	1.4236847639

Appendix L: Statistical analysis of Ni(II) removal efficiency at different landfill leachates and the biosorbents with synthetic solution (control).

BIO LEACHATE SYNTHETIC

The GLM Procedure

		Class Level Information			
Class	Levels	Values			
BIOSORBENTS	3	BNP EGP SWP			
LANDFILL_SITE	4	BELLVILLE COASTAL PARK SYNTHETIC VISSERSHOK			
		Number of observations 36			

The GLM Procedure

Dependent Variable: __REMOVAL_OF_Ni_ REMOVAL OF Ni

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	11	7299.654195	663.604927	43.51	<.0001
Error	24	366.061956	15.252581		
Corrected Total	35	7665.716150			

	R-Square	Coeff Var	Root MSE	__REMOVAL_OF_Ni_ Mean		
	0.952247	15.21377	3.905455	25.67053		
Source	DF	Type III SS	Mean Square	F Value	Pr > F	
BIOSORBENTS	2	1395.699797	697.849898	45.75	<.0001	
LANDFILL_SITE	3	5009.673658	1669.891219	109.48	<.0001	
BIOSORBEN*LANDFILL_S	6	894.280740	149.046790	9.77	<.0001	

The GLM Procedure

Duncan's Multiple Range Test for __REMOVAL_OF_Ni_

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.

Alpha	0.05
Error Degrees of Freedom	24
Error Mean Square	15.25258
Number of Means	2 3
Critical Range	3.291 3.456

Means with the same letter are not significantly different.

Duncan Grouping	Mean	N	BIOSORBENTS
A	34.475	12	EGP
B	21.406	12	BNP
B	21.131	12	SWP

The GLM Procedure

Duncan's Multiple Range Test for __REMOVAL_OF_Ni_

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.

Alpha	0.05
Error Degrees of Freedom	24
Error Mean Square	15.25258
Number of Means	2 3 4
Critical Range	3.800 3.991 4.114

Means with the same letter are not significantly different.

Duncan Grouping	Mean	N	LANDFILL_
A	45.775	9	SYNTHETIC
B	22.274	9	VISSERSHOK
C	18.121	9	COASTAL PARK
C	16.511	9	BELLVILLE

Breakdown of Means and Other Descriptive Statistics

1

----- Effect=BIOSORBENTS -----

BIOSORBENTS	LANDFILL SITE	Mean of __REMOVAL_ OF_NI_	Std. Dev. of __REMOVAL_ OF_NI_	Std. Error of __REMOVAL_ OF_NI_
BNP		21.4057	8.1514	2.35311
EGP		34.4747	19.4599	5.61758
SWP		21.1312	11.1745	3.22579

----- Effect=LANDFILL_SITE -----

BIOSORBENTS	LANDFILL SITE	Mean of __REMOVAL_ OF_NI_	Std. Dev. of __REMOVAL_ OF_NI_	Std. Error of __REMOVAL_ OF_NI_
	BELLVILLE	16.5111	7.3003	2.43345
	COASTAL PARK	18.1211	4.0132	1.33772
	SYNTHETIC	45.7755	15.4667	5.15558
	VISSERSHOK	22.2744	4.8358	1.61192

----- Effect=Overall -----

BIOSORBENTS	LANDFILL SITE	Mean of __REMOVAL_ OF_NI_	Std. Dev. of __REMOVAL_ OF_NI_	Std. Error of __REMOVAL_ OF_NI_
		25.6705	14.7993	2.46656

----- Effect=BIOSORBENTS*LANDFILL_SITE -----

BIOSORBENTS	LANDFILL SITE	Mean of __REMOVAL_ OF_NI_	Std. Dev. of __REMOVAL_ OF_NI_	Std. Error of __REMOVAL_ OF_NI_
BNP	BELLVILLE	12.9633	4.53169	2.61637
BNP	COASTAL PARK	18.3000	2.23242	1.28889
BNP	SYNTHETIC	32.9861	1.20281	0.69444
BNP	VISSERSHOK	21.3733	3.99312	2.30543

EGP	BELLVILLE	23.9700	6.39296	3.69098
EGP	COASTAL PARK	21.3333	4.48678	2.59045
EGP	SYNTHETIC	65.9722	0.30070	0.17361
EGP	VISSERSHOK	26.6233	4.06370	2.34618
SWP	BELLVILLE	12.6000	5.14746	2.97188
SWP	COASTAL PARK	14.7300	2.55572	1.47555
SWP	SYNTHETIC	38.3681	3.97793	2.29666
SWP	VISSERSHOK	18.8267	3.69622	2.13401