

ADSORPTION OF HEAVY METALS FROM AQUEOUS SOLUTION ONTO ACTIVATED CARBON DERIVED FROM *Balanites aegyptiaca* SEEDS

A series of batch experiments were conducted in order to investigate the feasibility of *Balanites aegyptiaca* seeds based activated carbon as compared with industrial activated carbon for the removal of chromium, lead, copper, cobalt, nickel, cadmium and manganese from aqueous solution by the adsorption process within 30 to 150 min contact time. The Activated samples were prepared using Zinc chloride and tetraoxophosphate V acid. Investigation was carried out by studying the influence of initial solution pH, adsorbent dosage and initial concentration of the various metal ions. The results obtained showed that the activated carbon of *Balanites aegyptiaca* seeds studied had relatively high adsorption capacities for these heavy metal ions. The percentage removal was Cr (VI), (64%, 70% and 71%), Cu (II), (75%, 78% and 80%), Pb (II), (86%, 69% and 69.61%), Cd (II), (69%, 72% and 69%), Ni (II), (72%, 78% and 77%), Co (II), (66%, 68% and 69%) and Mn (III), (80%, 79% and 77.8%) respectively. Adsorption equilibrium was established in 90 minutes for the heavy metal ions. The equilibrium data fitted pseudo- second order out of pseudo first order, pseudo second order, Natarajan and Khalaf and Elovich model tested. The investigation also showed that the adsorbents can effectively remove metal ions from similar wastewater and aqueous media

CHAPTER ONE

1.0

INTRODUCTION

1.1 Background of the Study

With rapid increase in global industrial activities, the pollution derived from uncontrolled substances containing heavy metals such as chromium, lead, copper and zinc has become a serious problem (Srivestava, Tyagi and Paul, 2010). Numerous metal ions such as that of chromium, copper, lead, manganese, mercury, cadmium, are known to be significantly toxic (Luqman, Najua, Zawani and Suraya, 2008). These heavy metals have harmful effect on human physiology and other biological systems when they exceed tolerance levels. It has been estimated that the toxicity due to metallic discharge annually into the environment far exceeds the combined total toxicity of all radioactive, and organic waste released into source of drinking water (Badmus, Audu and Anyata, 2007; Abdul-salam and Adekola, 2005). The most widely used methods for removing heavy metals from wastewaters includes chemical precipitation, complexation, solvent extraction, membrane processes, ion exchange, and ultra filtration (Gupta,

Jain, Ali and Saini, 2003). However, most of these methods are either economically prohibitive, generation of secondary wastes (sludge) or too complicated for the treatment of metals (Jang, Seo and Bishop, 2005).

Consequently, there is the need to urgently find new technologies or materials for removing heavy metal ions from wastewater. However, adsorption processes have shown many advantages over the physicochemical methods. They are quite selective, effective, efficient, regenerative, no sludge formation, economical and above all they can remove various levels of soluble heavy metals in solution (Jihyun - Lim, Hee-Man Kang, Lee-Hyung and Seok-Ohko, 2008).

1.2 Scope of the Study

This research uses *Balanites aegyptiaca* seeds to prepare activated carbon. The adsorbent prepared was used for its adsorptive feasibility on chromium, lead, copper, cadmium, cobalt, nickel and manganese. The kinetics of these metal adsorptions on the seeds used was studied.

1.3 Justification of the Study

Heavy metal pollution has become one of the most serious environmental problems today. Billions of gallons of wastewater containing heavy metals are produced each year by textile industries, metallurgical plants, gas operations, industries, washing operations and other processes. Most of the chemical methods used in cleaning up these heavy metals are not effective. Micro-organisms have been used extensively in cleaning of heavy metals in the environment (adsorption) but plants have not been used extensively in removing heavy metals from the environment. This justifies the use of *Balanites aegyptiaca* seeds with surface modification to improve their metal removal performance and to add to their economic values, reduce the cost of waste disposal and most importantly to provide a potentially inexpensive alternative to the existing commercial activated carbon.

1.4 Aim and Objectives of the Study

The research is aimed at preparing Activated charcoal from *Balanites aegyptiaca* seeds using zinc chloride ($ZnCl_2$) and tetraoxophosphoric acid (H_3PO_4) as activating agents, and at the same time using the prepared activated carbon to adsorb chromium, lead, copper, cadmium, cobalt, nickel and manganese from aqueous solution.

The objectives of this research were to:

- (1) Prepare the activated carbon using *Balanites aegyptiaca* seeds
- (2) Determine the Ash content of the *Balanites aegyptiaca* seeds
- (3) Characterized the Activated carbon using bulk density, % burn off, % carbon yield, pH and conductivity
- (4) Evaluate the Adsorption capacity of activated carbon from *Balanites aegyptiaca* seeds to ascertain it's carbon content effect on the heavy metal removal
- (5) Study the Adsorption kinetics using pseudo first order, pseudo second order, Elovich model and Nataranja and Khalaf first order equation.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Morphological Description of *Balanites aegyptiaca*

Balanites aegyptiaca is known by different names such as soap berry tree or desert date in English, *aduwa* in Nupe and *aduwa* in Hausa. The tree is about 10 m high with fluted trunk and spherical crown. The bark is grayish with ragged fissures. The slash is hard and pale yellow in colour. Younger branches are armed with green straight spines. Leaves are distinctive having two leaflets. Inflorescence consists of flowers that are greenish yellow in clusters between the leaf stalk and spine. The flowers are penta – sepalous with ten stamens and ovary of five – fused dark green carpel. The flowering occurs between March and June. Fruits contained one seed and resemble a date, usually green but yellow at maturity.

These plants are commonly found in the Sudan and sahelian parts of savanna. The plants are generally used medicinally in treating some diseases such as syphilis, malaria fever and other venereal diseases (Mann, Gbate and Umar, 2003).

2.2 Heavy Metals

Heavy metals are chemical elements with a specific gravity of at least five times that of water (Lenntech, 2012; Life extension, 2013; Wikipedia, 2013). Heavy metals are also refers to any metallic chemical element that has a relatively high density and can be toxic / poisonous at a very low concentration (Asio, 2009). Examples of heavy metals include: antimony, arsenic, bismuth, cadmium, chromium, cobalt, copper, lead, manganese, mercury, nickel, platinum, and silver, tin.

Heavy metals are toxic even at low concentrations. They are non-biodegradable and their threat is in multiple of their accumulation in the environment as well as through the food chain. Heavy metals may enter an organism's body through food, drinking water, and even air and once above

the tolerance level cause toxic reactions (Volesky and Naja, 2003). Heavy metals can enter a water supply by industrial and consumer waste disposal or even from acidic rain breaking down soils and releasing heavy metals in to streams, lakes, rivers, and ground water (Lenntech, 2012). These metals unlike organic pollutants do not decay and poses different kind of challenges for remediation.

2.3 Sources of Heavy Metal Pollution

Heavy metal pollution is a problem associated with areas of intensive industry. However, road ways and automobiles now are considered to be one of the largest sources of heavy metals. Zinc, copper, and lead are three of the most common heavy metals released from road travel, accounting for at least 90 % of the total metals in road run-off (Jacob,Ajai and Amadi, 2013). Sources of heavy metal pollutions are from geological and anthropological activities which includes industrial effluents, fuel production, mining, smelting processes, military operations, agricultural chemicals and metallurgical works (Dembitsky, 2003) Heavy metal pollution most commonly arises from the purification of metals, e.g., the smelting of copper and the preparation of nuclear fuels (Wikipedia, 2013) Electroplating is the primary source of chromium and cadmium. Lead and zinc are released in tiny particulates as dust from rubber tires on road surfaces; the small size allows these toxic metals on the wind to be inhaled, or transported on to top soil or edible plants.

For instance, sources of copper include motor vehicles, plumbing tube fitting, release from manufacturing processes such as in electrical companies during the production of electrical cables, metal plating, mining and manufacturing of computer heat sinks (Tumin *et al.*, 2008; Hadel and Chang, 2004)

Again, lead is emitted during mining and its smelting activities, lead paints, improper disposal of lead batteries (Hadel *et al.*, 2004). Other sources of lead include garbage burning, paint wood, wearing away of lead containing paints (Esakku, Palanivelu, and Joseph, 2003).

2.4 Toxicological Aspects of Heavy Metals

Due to their mobility in aquatic ecosystems and their toxicity to higher life forms, heavy metals in surface and groundwater supplies have been prioritized as major inorganic contaminants in the environment. Even if they are present in dilute, undetectable quantities, their recalcitrance and consequent persistence in water bodies imply that through natural processes such as biomagnifications, concentrations may become elevated to such an extent to begin exhibiting toxic characteristics. These metals can either be detected in their elemental state, which implies that they are not subject to further biodegradative processes or bound in various salt complexes. In either instance, metal ions can not be mineralized. Apart from environmental issues, technological aspects of metal recovery from industrial waters must be considered (Ramachandra, Ahalya and Kanamadi, 2005)

2.4.1 Effect of Heavy Metals on the Environment/Human Health

The detoxification of metal-bearing wastewater is of pressing environmental concern. All metal processing activities lose and/or discharge sometimes even large quantities of heavy metals hence the demand for metal sequestration and the need to immobilize the metals released into the environment (Volesky and Niu, 2003). Heavy metals are toxic even at low concentration, as they are non-biodegradable, their threat is multiplied by their accumulation in the environment through the food chain and other sources, therefore pose a serious threat to human health (Volesky and Kuyucak, 1990). Kuyucak also observed that heavy metal toxicity is frequently brought about by its long-term potential for bioaccumulation and biomagnifications causing heavier exposure for some organisms than is present in the environment alone. Individual heavy

metals have specific signs of their toxicity whose nature of effects can be toxic, carcinogenic, and mutagenic (Lenntech, 2013; McCluggage, 1991).

The heavy metals that are hazardous to humans include lead, mercury, cadmium, arsenic, copper, zinc, and cadmium. Such metals are found naturally in the soil in trace amounts, which can pose few problems. When concentrated in particular areas, however, they present a serious danger.

Arsenic and cadmium, for instance, can cause cancer. Mercury can cause mutations and genetic damage, while copper, lead, and mercury can cause brain and bone damage (Abia and Asuquo, 2006). The effects and health risks of some heavy metals are:

(A) Copper: This element is an essential substance to human life, but in high doses can cause anemia, liver and kidney damage, stomach and intestinal irritation. The suggested safe level of copper in drinking water for humans varies depending on the sources, but tends to be pegged at 1.5 to 2.0 mg/l (Najua, Luqman, Zawani and Suraya, 2008). People with wilson's disease are at greater risk for health effects from over exposure to copper (Lenntech, 2013).

(B) Lead: Human exposure to lead can result into a wide range of biological effects depending on the levels and duration of exposure. Various effects occur over a broad range of doses, with the developing foetus and infant being more sensitive than the adult. High levels of exposure may result in toxic biochemical effects in humans, which in turn cause problems in the synthesis of haemoglobin, effects on the kidneys, gastrointestinal tract, joint and reproductive system, and acute or chronic damage to the nervous system which may lead to loss of up to 2 IQ points in children (lenntech, 2012 and Udedi 2003).

(C) Nickel: Electroplating is one important process involved in surface finishing and metal deposition for better life of articles and for decoration. Although several metals can be used for electroplating, nickel, copper, zinc and chromium are the most commonly used metals; the choice depends upon the specific requirement of the articles. During washing of the electroplating tanks,

considerable amounts of the metal ions find their way into the effluent. Ni (II) is present in the effluents of silver refineries, electroplating, zinc base casting and storage battery industries.

Higher concentration of nickel causes cancer of lungs, nose and bone. Dermatitis (Ni itch) is the most frequent effect of exposure to nickel, such as coins and jewellery. Acute poisoning of Ni (II) causes headache, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness (Ramachandra, *et al.*, 2005).

(D) Chromium: Humans are exposing to chromium through breathing, eating or drinking and through skin contact with chromium compounds. The level of chromium in air and water is generally low. In drinking water the level of chromium is usually low as well, but contaminated well water may contain the dangerous chromium (IV) ie hexavalent chromium. For most people eating food that contains chromium (III), it is the main route of chromium uptake, as chromium (III) occurs naturally in many vegetables, fruits, meats, yeasts and grains. Various ways of food preparation and storage may alter the chromium contents of food, as in the case of food stored in steel tanks or cans leading to enhanced chromium concentrations. Chromium (VI) is a danger to human health, mainly for people who work in the steel and textile industry. Chromium (VI) is known to cause various health effects. When it is a compound in leather products, it can cause allergic reactions, such as skin rash. Inhaling chromium (VI) can cause nose irritations and nosebleeds. Other health problems that are caused by chromium (VI) are skin rashes, respiratory problems, weakened immune systems, kidney and liver damage, alteration of genetic material, lung cancer and death. The health hazards associated with exposure to chromium are dependent on its oxidation state. The metal form (chromium as it exists in this product) is of low toxicity. The hexavalent form is toxic. Adverse effects of the hexavalent form on the skin may include ulcerations, dermatitis, and allergic skin reactions. Inhalation of hexavalent chromium compounds can result in ulceration and perforation of the mucous membranes of the nasal

septum, irritation of the pharynx and larynx, asthmatic bronchitis, bronchospasms and edema. Respiratory symptoms may include coughing and wheezing, shortness of breath, and nasal itch.

Carcinogenicity- Chromium and most trivalent chromium compounds have been listed by the National Toxicology Program (NTP) as having inadequate evidence for carcinogenicity in experimental animals. According to NTP, there is sufficient evidence for carcinogenicity in experimental animals for the following hexavalent chromium compounds; calcium chromate, chromium trioxide, lead chromate, strontium chromate, and zinc chromate (Kumar *et al.*, 2009)

(E) Mercury: Mercury is generally considered to be the most toxic metals found in the environment (Ramachandra *et al.*, 2005). Once mercury enters the food chain, progressively larger accumulation of mercury compounds takes place in humans and animals. The major sources of mercury pollution in environment are industries like chloro-alkali, paints, pulp and paper, oil refining, rubber processing and fertilizer (Namasivayam and Periasamy, 1993), batteries, thermometers, fluorescent light tubes and high intensity street lamps, pesticides, cosmetics and pharmaceuticals ((Krishnan and Anirudhan, 2002). Methyl mercury causes deformities in offspring, mainly affecting the nervous system (teratogenic effects). Children suffer from mental retardation, cerebral palsy and convulsions. Mercury also brings about genetic defects causing chromosome breaking and interference in cell division, resulting in abnormal distribution of chromosome. Mercury causes impairment of pulmonary function and kidney, chest pain and dyspnoea (WHO, 1990). The harmful effect of methyl mercury on aquatic life and humans was amply brought out by the Minamata episode in Japan (WHO, 1991).

2.4.2 Effects of Heavy Metals on Aquatic Organisms

Aquatic organisms are adversely affected by heavy metals in the environment. The toxicity is largely a function of the water chemistry and sediment composition in the surface water system (Ramachandra *et al.*, 2005). Volesky (2003) shows how heavy metal ions can become bioaccumulated in an aquatic ecosystem. The metals are mineralized by microorganisms, which in turn are taken up by plankton and further by the aquatic organisms. Finally, the metals by now, several times biomagnified is taken up by man when he consumes fish from the contaminated water.

i) slightly elevated levels in natural waters may cause the following sub-lethal effects in aquatic organisms: histological or morphological change in tissues;

ii) Changes in physiology, such as suppression of growth and development, poor swimming performance, changes in circulation;

iii) Changes in biochemistry, such as enzyme activity and blood chemistry;

iv) Changes in behaviour, and

v) Changes in reproduction (Ramachandra, 2005).

Many organisms are able to regulate the metal concentrations in their tissues. Fish and crustacean can excrete essential metals, such as copper, zinc, and iron that are present in excess. Some can also excrete non-essential metals, such as mercury and cadmium, although this is usually met with less success (Ramachandra, 2005)

Research has shown that aquatic plants and bivalves are not able to successfully metal uptake. Thus, bivalves tend to suffer from metal accumulation in polluted environments. In estuarine systems, bivalves often serve as biomonitor organism in areas of suspected pollution (Kennish, 1990). Shell fishing waters are closed if metal levels make shellfish unfit for human consumption.

In comparison to freshwater fish and invertebrates, aquatic plants are equally or less sensitive to cadmium, copper, lead, mercury, nickel, and zinc. Thus, the water resource should be managed for the protection of fish and invertebrates, in aquatic order to ensure aquatic plant survivability (USEPA, 2002). Metal uptake rates will vary according to the organism and the metal in question. Phytoplankton and zooplankton often assimilate available metals quickly because of their high surface area to volume ratio. The ability of fish and invertebrates to adsorb metals is largely dependent on the physical and chemical characteristics of the metal (Kennish, 1990). With the exception of mercury, little metal bioaccumulation has been observed in aquatic organisms (Kennish, 1990). Metals may enter the system of aquatic organisms via three main pathways:

- i) Free metal ions that are absorbed through respiratory surface (e.g., gills) are readily diffused in to the blood stream.
- ii) Free metal ions that are adsorbed onto body surfaces are passively diffused into the blood stream.
- iii) Metals that are sorbed onto food and particulates may be ingested, as well as free ions ingested with water (Rahman, Saad, Shaidan and Rizai, 2005). For example, Chromium is not known to accumulate in the bodies of fish, but high concentrations of chromium, due to the disposal of metal products in surface waters, can damage the gills of fish that swim near the point of disposal.

2.4.3 Irrigation Effects of Heavy Metals

Irrigation water contaminated with sewage or industrial effluents may transport dissolved heavy metals to agricultural fields. Although most heavy metals do not pose a threat to humans through crop consumption, cadmium may be incorporated into plant tissue. Accumulation usually occurs in plant roots, but may also occur throughout the plant (Ramachandra, 2005). Most irrigation

systems are designed to allow for up to 30 percent of the water applied to it not be absorbed, and this can leave the field as return flow or either joins the groundwater or runs off the field surface (tail water). Sometimes tail water are rerouted into streams because of downstream water rights or a necessity to maintain stream flow. However, usually the tail water is collected and stored until it can be reused or delivered to another field (USEPA 1993a).

Tail water is often stored in small lakes or reservoirs, where heavy metals can accumulate as return flow is pumped in and out. These metals can adversely impact on aquatic communities. An extreme example of this is the Kesterson Reservoir in the San Joaquin Valley, California, which received subsurface agricultural drain water containing high levels of selenium and salts that, had been leached from the soil during irrigation. Studies in the Kesterson Reservoir revealed elevated levels of selenium in water, sediments, terrestrial and aquatic vegetation, and aquatic insects. The elevated levels of selenium were cited as relating to the low reproductive success, high mortality, and developmental abnormalities in embryos and chicks of nesting aquatic birds (Shukla and Sakherdaude, 1990).

2.5 Need for the Removal of Heavy Metals.

The continuous discharge of industrial, domestic and agricultural wastes in rivers and lakes causes deposit of pollutants in sediments. These pollutants may include heavy metals, which endanger public health when incorporated into food chain. Heavy metals are not destroyable through biological degradation, as is the case with most organic pollutants. Incidence of heavy metal accumulation in fish, oysters, mussels, sediments and other components of aquatic ecosystems have been reported from all over the World (Ramachandra *et al.*, 2005). Literature shows that excessive heavy metals can be toxic through either direct action of the metal or through their inorganic salts or via organic compounds from which the metal can become easily

detached or introduced into the cell. In either case, the exposure to different metals may occur in common circumstances, particularly in industrial setting. Accidents in some environments can result in acute, high level exposure. Some of the heavy metals are toxic to aquatic organisms even at low concentration. The problem of heavy metal pollution in water and aquatic organisms including fish, needs continuous monitoring and surveillance as these elements do not degrade and tend to biomagnify in man through food chain. Hence, there is a need to remove the heavy metals from the aquatic ecosystems (Meyer, 2007)

2.6 Conventional Methods for the Treatment of Heavy Metals

Over the last few decades, several methods have been devised for the treatment and removal of heavy metals. Numerous industries (e.g., electroplating, metal finishing operations, electronic-circuit production, steel and non-ferrous processes and fine-chemical and pharmaceutical production) discharge a variety of toxic metals into the environment.

For several years now, it is mandatory that industry is required to remove metal pollutants from liquid discharges. The commonly used procedures for removing metal ions from aqueous streams include chemical precipitation, ion exchange, reverse osmosis, electrodialysis, ultrafiltration, solvent extraction, lime coagulation (Gupta *et al.*, 2003; Sultan and Amer 1998). The process description of some of these methods is presented below.

2.6.1 Chemical Precipitation

Precipitation of metals is greatly achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers. The large amount of sludge containing toxic compounds produced during the process is the main disadvantage (Sultan, 1998).

i) Hydroxide Precipitation: Chemical precipitation of heavy metals as their hydroxides using lime or sodium hydroxide is widely used. Lime is usually favored for precipitation purposes due to the low cost of precipitant, ease of pH control in the range of 8.0 to 10.0 and the excess of lime also

serves as an adsorbent for the removal of metal ions. The efficiency of the process depends on a number of factors, which may include the ease of hydrolysis of the metal ion, nature of the oxidation states, pH, presence of complex forming ions, standing time, degree of agitation and settling and filtering and characteristics of the precipitate. The limitations of this method include difference between metals in the optimum pH for hydroxide formation may lead to the problems in the treatment of effluents containing combined metal ions. Variability in metal hydroxide solubility at a fixed pH is another drawback (Sultan, 1998).

ii) Carbonate Precipitation: Carbonate precipitation of metals using calcium or sodium carbonate is very limited because of deposit effect which causes blockages on the material used. Patterson (1997) reported improved results using carbonate precipitate for Cd (II) and Pb (II) from electroplating effluents. When the pH was brought to 7.5, residual concentration of Pb (II) and Cd (II) were 0.60 and 0.25 mg/l, respectively.

iii) Sulphate Precipitation: Since most heavy metals form stable sulphides, they can be excellently removed by sulphide precipitation. Treatment with sulphide is very advantageous when used as a polishing step after conventional hydroxide precipitation or when very high metal removals are required (Mano, 2008).

2.6.2 Chemical Reduction

Reduction of hexavalent chromium can be accomplished using electro-chemical units. This technique uses consumable iron electrodes and an electric current to generate ferrous ions that react with hexavalent chromium to give trivalent chromium as follows (USEPA, 1993a).



Another application of chemical reduction process is the use of sodium borohydride, which is considered effective for mercury, lead, silver and gold removal (Ramachandra *et al.*, 2005).

2.6.3 Solvent Extraction

The liquid – liquid extraction (also known as solvent extraction) of metals from solutions on a large scale has gain popularity in recent years due to the introduction of selective complexing agents (Ramachandra *et al.*, 2005). In addition to it use in hydrometallurgical applications, solvent extraction has gained widespread usage for waste reprocessing and effluent treatment.

Solvent extraction involves an organic and an aqueous phase. The aqueous solution containing the metal or metals of interest is mixed with the appropriate organic solvent and the metal passes into the organic phase. To recover the extracted metal, the organic solvent is contacted with an aqueous solution whose composition of such the metal is stripped from the organic phase and is re-extracted into the stripping solution. The concentration of the metal in the strip liquor may be increased, often 10 to 100 times over that of the original feed solution. When the metal of interest has been removed, the organic solvent is recycled or a fraction of it may be treated to remove the impurities (Dhiraj, Garinia and Kaur, 2008).

2.6.4 Membrane Process

Membrane process which is applicable to inorganic waste treatment includes reverse osmosis and electrodialysis (EPA, 1990). These processes involve ionic concentration by the use of selective membrane with a specific driving force. For the case of reverse osmosis, pressure difference is employed to initiate the transport of solvent across a semi permeable membrane and electro-dialysis relies on ion migration through selective permeable membranes in response to a current applied to electrodes. The application of these membrane processes is limited due to pretreatment requirements, primarily, for the removal of suspected solids. The methods are often expensive and sophisticated, and required a higher level of technical expertise to operate.

A liquid membrane is a thin film that selectively permits only the passage of a specific constituent from a mixture (Ramachandra *et al.*, 2005). Unlike solid membrane, however liquid

membranes separate by chemistry rather than size, and it is in many ways similar in technology to solvent extraction.

Though, liquid membrane technology is a recent development, a number of problems still remain unsolved. One major issue is the long-term stability of the membranes, whereas the efficient breakup of microspheres for product recovery is one of the difficulties encountered frequently with emulsion membranes (Gupta *et al.*, 2008)

2.6.5 Ion Exchange

Ion exchange resins are available selectively for certain metal ions. The cations are exchange for H^+ or Na^+ . The cation exchange resins are mostly synthetic polymers containing an active ion group such as SO_3H . Zeolite (natural material) can be used as ion exchange media (Van der Heen, 1997). The modified zeolites like zeocarb and chalcarb have greater affinity for metals like Ni and Pb (Groffman, Petterson and Brookins, 1992). The limitations on the use of ion exchange for inorganic effluent treatment are primarily high cost and the requirements for appropriate pretreatment systems. This method (ion exchange) is capable of providing metal ion concentrations to part per million levels. However, in the presence of mono- and divalent ions such as Na and Ca (large quantities), ion exchange is almost totally ineffective (Mano, 2008).

2.6.6 Electrodeposition

Some metals found in waste solution can be recovered by electrodeposition using insoluble anodes. For example, spent solutions resulting from sulphuric acid cleaning of copper may be saturated with copper sulphate in the presence of residual acid. These are mostly ideal for the case of electro-winning where high quality cathode copper can be electrolytically deposited while free sulphuric acid is regenerated (Gupta *et al.*, 2003).

2.6.7 Adsorption

Activated carbon possesses an affinity for heavy metals, therefore considerable attention are focused on the use of carbon for the adsorption of hexavalent chromium, complexed cyanides and metals present in various forms in wastewaters. The use of activated carbon for adsorption of heavy metals was first presented in 1929 by Watonable and Ogawa (Huang, Chung and Lio, 1996).

The mechanism of removal of hexavalent and trivalent chromium from synthetic solutions and electroplating effluents has been extensively studied by a number of researchers. Some researchers observed that the removal of Cr (VI) occurs through several steps of interfacial reactions (Huang *et al.*, 1996).

I) The direct adsorption of Cr^{6+} onto carbon surface.

II) The reduction of Cr^{6+} species to Cr^{3+} by carbon on the surface.

iii) The adsorption of the Cr^{3+} species produced, which occurs to a much lesser extent than the adsorption of the Cr^{6+} species.

Adsorption of Cr (III) and Cr (VI) on activated carbon from aqueous solutions has been studied (Toledo, Utrilla, Gracia and Cistilla, 1994). Grannular activated carbon was used for the removal of Pb (II) from aqueous solutions (Cheng, Subramania, Chakrabarti, Guo, Ma, Lu, and Pickering, 1993). The adsorption process is mostly inhibited by the presence of humic acid, iron (III), aluminum (III) and calcium (II).

2.7 Disadvantages of Conventional Methods for Treatment of Wastewater Containing Heavy Metals.

Heavy metals are a class of pollutants, often toxic and dangerous, and are widely present in industrial and household wastewaters. Large quantities of heavy metals are produce/ present in wastewaters from industrial processes such as electroplating and metal finishing operations, electronic circuit production, steel and aluminum processes to name but a few industries.

Although metal precipitation which uses cheap alkali such as lime (calcium hydroxide) is considered to be the most favoured option for metal sequestration, other separation technologies are now beginning to find favour. Precipitation, by adjusting the pH value is not selective and any iron (ferric ion) present in the liquid effluent will be precipitated initially followed by other metals. Precipitation consequently can or produces large quantities of solid sludge for disposal, for example precipitation as hydroxides of 100 mg/l of copper (II), cadmium (II) or mercury (II) produces as much as -10, -9 and 5 fold mg/l of sludge respectively (Mano, 2008). The metal hydroxide sludge resulting from treatment of electroplating wastewater has been classified as a hazardous waste (Sultan, 1998; Mano, 2008).

At present many of these technologies such as ion exchange represent significant capital investments by industry and as such conventional methods are ineffective in the removal of low concentrations of heavy metals and they are non-selective. Moreover, it is not possible to recover the heavy metals by the above mentioned methods (Gupta *et al.*, 2003).

2.8 Biosorptions

Biosorptions is a property of certain types of inactive, dead, microbial biomass to bind and concentrate heavy metals from even very dilute aqueous solutions (Volesky *et al.*, 2003 and Metcalf, 2005). The biomass acts as chemical substance, as well an ion exchanger of biological origin. The major binding techniques in operation here are simple adsorption as well as bioaccumulation. The most of the complexation phenomena of heavy metal ions onto a sorbent material involve a combination of several techniques. It was indeed investigated by Babel, Del Mundo and Acera (2006) ,that the sorption power of any given sorbent is determined by its ability to trap the heavy metal ion and this is related to its geometry and specific chemical compounds reacting with the heavy metal ions.

2.8.1 Sources of Biomass for Biosorptions

The biomass used in biosorption technique include: bacteria, fungi, yeast, molds, microorganisms, seaweeds activated sludge, fermented wastes and agricultural propagated biomasses. The basic components of the agricultural waste materials biomass include hemicellulose, lignin, extractives, lipids, proteins, simple sugars, water hydrocarbons, starch containing variety of functional groups that facilitates metal complexation which helps for the sequestering of heavy metals (Bailey, Olin, Bricka and Adrian, 1999; Huang *et al.*, 1996; Sudha and Abraham, (2003); Zhon and Kiff, 1991). The biosorbent employed must be hard enough and can withstand the application of pressures, and above all, must be porous, transparent to metal ion sorbate species, have high and fast sorption uptake even after repeated regeneration (Regine and Viera, 2005; Volesky *et al.*, 2003).

Studies reveal that various agricultural waste materials such as rice bran, rice husk, wheat bran, wheat husk, sawdust of various plants, bark of the trees, groundnut shells, coconut shells, black gram husk, hazelnut shells, walnut shells, cotton seed hulls, waste tea leaves, cassia fistula leaves, maize corn cob, jatropha deoiled cakes, sugar cane bigasse, apple, banana, orange peels, soybean hulls, grapes cotton stacks... has been tried(Mahan and singh,2002; Nigam and Rama,2002; Ahluwalia and Goyal, 2005; Egila and Okorie, 2002; Igwe and Abia,2007). These promising agricultural waste materials are used in the removal of metal ions either in their natural form or after some physical or chemical modification.

2.8.2 Biomass Types

The biomass types which serve as a basis for metal biosorption processes can accumulate in excess of 25 % of their dry weight in deposited heavy metals: Pb, Cd, U, Cu, Zn, even Cr and others. However, the assessment of the metal-binding capacity of some types of biomass has gained momentum since 1985 (Volesky and Holan (1995); Regine *et al.*, 2005). Indeed, some biomass types are very effective in accumulating heavy metals. Availability is a major factor to be taken into account to select biomass for clean-up purposes. The economy of environmental

remediation dictates that the biomass must come from nature or even has to be a waste material. Sea weeds, mold, yeasts, bacteria, crab shells, among other kinds of biomass, have been tested for metal biosorptions with very encouraging results. Some biosorbents can bind and collect a wide range of heavy metals with no specific priority, whereas others are specific for certain types of metals (Volesky *et al.*, 2003).

When choosing the biomass for metal biosorptions experiments, certain factors are to be considered. This ranges from origin, and the biomass type. This account for whether the biomass comes from:

- (i) industrial wastes which are obtained free of charge
- (ii) Organisms are easily available in large amounts in nature and
- (iii) Organisms are of quick growth, especially cultivated or propagated for biosorptions purposes (Regine *et al.*, 2006).

2.9 Biosorptions Mechanism

The removal of metal ions from aqueous streams using agricultural materials is based upon metal biosorptions (Volesky and Holan, 1995). Biosorptions of heavy metal ions occur as a result of physicochemical interaction, mainly by ion exchange or complexation (complex formation between metal ions and the functional groups present on the cell surface. Various functional groups involved are hydroxyl, carbonyl, phosphate, carboxyl, sulfhydryl, thioether, sulfonate, imidazole, phosphodiester, amine, and amides. Only ion exchange mechanism is considered the well known model of metal binding and proton releasing reaction (Tunali, Cabuk and Akar, 2006).

The degree of adsorption, rate of adsorption is influenced by many factors such as: solution concentration, pH of the solution, ionic strength, nature of adsorbates and the procedure for adsorbent modification. Others are physical properties of the adsorbent (surface area and

porosity), chemical nature of the adsorbent. From the aforementioned, therefore, the specific effect of adsorbent properties and their operating conditions depends on the adsorbent-metal ion system (Amarasinghe and Williams, 2007). Volesky *et al.*, (2003) postulated various metal binding mechanisms known as adsorption of gases on solids.

2.9.1 Adsorption on Solids

In this case, two types of adsorption behaviours occur. These are:

(i) Physical adsorption or physisorption: Physisorption is due to the operation of forces between the solid surface and the adsorbent forces which are caused by secondary attractive forces (vander Waals). They are undirected and non-specific. These weak forces ultimately lead to the condensation of the vapours of these gases to liquids when the exerted pressure p is equal to p_v , the vapour pressure of the adsorbent molecules (at a temperature of isotherm). The energies of adsorption involved are of the order of $300-350 \text{ jmol}^{-1}$ which means that the enthalpy change is less. Physical adsorptions are generally reversible and are established rapidly but the reduction of pressure leads to the dissolution of gases along the same isotherm curve with the exception which occurs when there are very few pores of the capillary of the adsorbate. It is independent of the chemical nature of the substance being adsorbed (Oura, Lifshits, Saranin, Zotov and Katayama,2003;SharmaandSharma,2006)

(ii) Chemisorptions: Chemisorptions results from much stronger binding forces which are comparable to those leading to the formation of chemical bonds. The chemisorptions could be by ion exchange, complexation, co-ordination and chelation. This involves stronger interaction between adsorbate and adsorbent usually accompanied by rearrangement of atoms within or between adsorbate. It is similar to chemical reaction and involves transfer of electronic charge between adsorbent and adsorbate. The most extreme form of chemisorptions occurs when integral numbers of electrons are transferred, forming a pure ionic bond. Chemisorptions is highly selective since only certain types of molecules will be adsorbed by a particular solid

(Sharma *et al.*, 2006). The energy of adsorption ranges from 40-400 J mol⁻¹. At low temperatures, chemisorptions are seldom reversible. To reverse the adsorption, the solid must be heated at high temperature and also pumped at high vacuum to suction out the dissolved gas. Sometimes, the gas that is actually dissolved is not the same as that adsorbed. For instance after the adsorption of oxygen on charcoal at 150 K, heating the charcoal and pumping it may lead to the dissolution of CO and not O₂. Chemisorptions is complete when the surface is covered by an adsorbed monolayer but sometimes, physical adsorption can take place on top of an adsorbed monolayer of a gas. It is possible for a system to display physical adsorption at one temperature and chemisorptions at some higher temperature. For instance, N₂ is physically adsorbed on iron at 78 K and adsorbed chemically with the formation of iron nitride at 800 K. Hence, physisorption and chemisorptions could be interchanged but they can be distinguished by direct IR spectroscopy of the adsorbed molecules (Retter and Auerbach, 1996).

2.10 Factors Influencing Heavy Metal Removal by Sorption

2.10.1 Effect of pH on the Removal of Heavy Metal Ions

The adsorptions of heavy metal ions were found to be strongly dependent on the pH of the solution because it affects biosorbent surface charge, the degree of ionization, and the species of biosorbate (Karnitz, Gurgel, Melo, Botaro, Melo, Rossimiriam, Freitas and Laurent, 2007). The acidity of solution pH is one of the most important parameters controlling the uptake of heavy metals from wastewater and aqueous solutions. The uptake of metals increases with increase in pH until at a pH 6 but decreases slightly in pH range of 6 to 9, because at pH above this, the precipitation of metal ions would occur. As the pH increases, more negatively charged surface becomes available thus facilitating greater metal removal (Luqman *et al.*, 2008).

It is commonly agreed that the sorption of metal cations increases with increasing pH as the metal ionic species become less stable in the solution (Jihyun Lim *et al.*, 2008). However, the pH effect on the metal sorption causes a change on the active sites when the binding ions are acidic, thus this depends on the availability of free sites. At lower pH the active sites are protonated, therefore, competition between protons and metal ions for sorption sites occurs (Kazemeipour, Anseni, Shabnam, Majdzadeh and Kemani, 2008). At a low enough pH, virtually all sites become protonated and complete desorption of the bound metal ion is possible, which is why acid treatment is a method for metal elution and regeneration of sorbent material. The decrease in the pH value by 2 units can in some cases result in 90 % reduction of metal binding (Kazemeipour *et al.*, 2008).

It was believed that at extreme pH values the regeneration of the sorbent may completely damage the structure of the biosorbent material. Microscopic observation has shown distorted cells, significant weight loss and decrease in the sorption capacity (Kuyucak and Volesky, 1990).

2.10.2 Effect of Temperature on the Removal of Heavy Metal Ions

Physisorption is an exothermic process i.e. the equilibrium constant decreases with increase in temperature. The amount of metal ion removed from the solution decreases as the temperature of the solution increases. The reason is that the adsorption process is inversely related to temperature (Okuo and Ozioko, 2007). Also, an increase in temperature brings about an increase in kinetic energy of the system and this perhaps causes desorption rather than adsorption. It was observed that the adsorption of Cu (II) onto HCl using treated palm kernel fibre increases with increase in temperature which is an indication that the ability of Cu (II) ions to get adsorbed increases with a rise in temperature (Ho and Afajama, 2006).

2.10.3 Effect of Biosorption Dosage on the Removal of Heavy Metal

Babalola, Babarinde, Oninia and Popoola (2008), observed that the biomass added into the solution determine the number of binding sites available for biosorption. The metal uptake therefore increases with increase in biomass dosage due to the complex interactions of several factors.

An increase in biosorptions quantities strongly affects the quantities of metal ion removed from aqueous solutions. This could be attributed to the fact that at high biosorbent dosages the available metal ions are insufficient to cover all the exchangeable sites on the biosorbent, usually resulting in to low metal uptake (Luqman *et al.*, 2008; Fourest and Roux, 1992; Vijaraghavan, Palanivelu and Velan, 2006).

2.10.4 Effect of Initial Metal Concentration on the Removal of Heavy Metal

At low concentrations, the sorption sites took up the available metal more quickly. However, at higher concentrations, the metal ions needed to diffuse to the biomass surface by intraparticle diffusion and greatly hydrolyzed ions will diffuse at a slower rate (Luqman *et al.*, 2008).

2.11 Applications of Metal Biosorptions

Since biosorptions of heavy metals from aqueous solutions is a new technology, it has wide areas of application such as in the treatment of wastewater (Schiewer and Volesky, 2000). Adsorption is operative in most natural, physical, biological, and chemical systems and it is most used in industrial applications such as activated carbon, synthetic resins and water purifications. Other industries which are dependent on adsorption include agriculture, mining, paper making, painting and photography (Sharma *et al.*, 2006)

2.12 Advantages of Biosorptions Mechanism

Biosorptions is recommended as cheaper and more effective technique (Artola, Balaguer and Rigola, 1997) though it is highly competitive with the presently available technologies like ion-exchange, electrodialysis, reverse osmosis, ultrafiltration. The knowledge of the metal sequestering

mechanism would assist in the manipulation of the biosorbent in order to optimize its performance, cost effectiveness, heavy metal selectivity, regenerative and no additional nutrient requirement when compared with other conventional processes.

This mechanism could lead to exploring the possibility of using simple analogous materials, either synthetic or natural, for metal sequestering (Volesky and Niu, 2003).

2.13 Equilibrium Modeling

Generally, isotherm adsorption models are frequently used in the wastewater treatment to predict and determine the ability of adsorbent in the removal of pollutant down to a specific discharge value. When certain mass of adsorbent and that of wastewater are in contact for a long time, the equilibrium between the amounts of pollution adsorbed and the amount remaining in the solution will be developed (Ho and Mckay, 1998; Demirbas, 2008). It is certain that for any system in equilibrium, the amount of material adsorbed onto the adsorbent can be calculated using the balance equation (Pastircakova, 2004).

$$Q_e = (C_o - C_e) V/M \text{ _____ (1)}$$

Where Q_e = Mass of the pollutant per mass of adsorbent (mg per unit adsorbent).

C_o = Initial concentration of the adsorbates in solution (mg/dm³)

C_e = Concentration of the adsorbate in solution after equilibrium has been reached (mg/dm³);

V = Volume of the solution to which the adsorbent is exposed.

M = Mass of the adsorbent (g).

Using the above equation, the relationship between equilibrium binding and the concentration of ions at constant temperature can be calculated by isotherm plot of Q_e versus C_e . When metal concentration increases in the solution, the binding capacity also increases from zero to the maximum. It is therefore required that the sorbent should have high sorption capacity and greater

affinity for sorbate species, which is a reflection of the isotherm curve at low equilibrium concentration.

Some simple isotherm models frequently used are Langmuir model, Freundlich, Radke and Prausnitz, Radlich Peterson, and the combination of Langmuir and Freundlich. The same model may not be applied to all situations but some times more than one model may be applied to explain the biosorptions mechanism. Though there is no critical reason to use a more complex model if a two parameter model can fit the data considerably and reasonably well.

2.14 Activated Carbon

Activated Carbon is one of the commonest materials which have been used to purify different products since Roman times (Calgon, 2007). The first known use of activated carbon dates back to the Ancient Egyptians who utilized its adsorbent properties for purifying oils and medicinal purposes as adsorbent for toxic substances in human body (Cameron Carbon, 2006). It is very effective adsorbent for many pollutant species (organic, inorganic and biological) which are of concern in water and wastewater treatment (Calgon, 2007; Bansode, Losso, Marshal, Rao and Mat, 2003). Activated carbons are efficient and versatile adsorbent for the purification of water, air (air purified with activated carbon is actually purer than much of the outside air we normally consider fresh and sweet) and chemical as well as natural products (Malik, Ramtells and Wate, .2007; Green bank, 2007). It is use in gas masks and for deodorization. Disposed activated carbon filters are being widely used in forced air furnaces and air conditioners.

Commercially activated carbon (CAC) is widely used for adsorbing various substances including heavy metals from industrial effluent (Frank, 2000). However, activated carbon is known as the broad spectrum agent (in technology applications such as nuclear power plant containment systems) and can effectively remove toxic and bio-refractive substances such as herbicides, insecticides, chlorinated hydrocarbons present in many water supplies (Frank, 2000; Cameron Carbon, 2006).

Granular activated carbon (GAC) is commonly the typical form of activated carbon used for removing organic constituents and residual disinfectants in water supplies. According to Frank (2000), GAC does not only improves taste but also minimizes health hazards and protects other water treatment units such as reverse osmosis, membranes and ion exchange resins from possible damage due to oxidation or organic fouling. Activated carbon is a favored water treatment technique because of its multifunctional nature and for the fact that it adds nothing detrimental to the treated water. Granular activated carbon was used during the First World War to develop suitable respiratory devices for personnel protection and for the entrapment of both war and nerve gases.

Granular activated carbon has tremendous surface area and this characteristic helps in adsorption since the process is a surface phenomenon and these increases its effectiveness and make it slow to settle but difficult to remove once added (Khalkhali and Omidavi, 2005).

2.14.1 Sources and Production of Activated Carbon

The most commonly used raw materials are coal (anthracite, bituminous and lignite), coconut shells, wood (both soft and hard), peat and petroleum based residues or other carbonaceous materials (Cameron carbon, 2006). Almost all materials containing high fixed carbon content can potentially be activated. Many other raw materials have been evaluated such as walnut shells, peach pills, babassu nutshell and palm kernels but invariably their commercial limitation lies in raw material supply. This is illustrated by considering that 1,000 tons of untreated shell type raw materials will only yield about 100 tons of good quality activated carbon (Cameron carbon, 2006).

Activated carbon can be produced from many raw materials i.e. soft wood, Coconut shell and Peat lignite (both mineral and coal). The raw material must be relatively low cost and source of raw material should be closed to the factory location to minimize the transport cost.

The majority of Activated Carbon used through out the World is produced by two stage process. First the material is carbonized and coke is produced. The pores of produced coke are too small; hence, the next is a process of enlarging the pore structure so that an accessible internal surface is created. This is achieved by semi product with steam at temperature between 900⁰C to 1200⁰C. At this temperature rate determination factor is the chemical reaction between steam and carbon. This reaction takes place at the internal surface of the carbon removing carbon from the pore walls and there by enlarging them. The more highly activated the carbon, the greater the surface and pore volume (Calgon, 2007)

2.14.2 Selection of Activated Carbon for Use

The selection of the right grade of activated carbon depends solely on some factors such as the general class of application, type and concentration of contaminants, efficiency required, resistance to liquid or gas flow, heat transfer, thickness of bed used, method of support for carbon bed, and operating conditions. The laboratory test helps to determine the final selection for the best type and mesh size. It is most necessary to compare several grades (Calgon, 2007).

Typical surface area for activated carbon is approximately 1,000 square meters per gram (m² / gm). However, different raw materials produce different types of activated carbon varying in hardness, density, pore and particle sizes, surface areas, extractables, ash and pH. These differences in properties make certain carbons preferable over others in different applications (Frank, 2000).

2.14.3 Factors Affecting the Performance of Activated Carbon

Frank (2000) showed that there are two principal mechanisms through which activated carbon removes contaminants from water. These are adsorption and catalytic reduction. Organics are removed by adsorption and residual disinfectants are removed by catalytic reduction.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Sample Collection

The *Balanites aegyptiaca* seeds based precursor was randomly selected at different places within Edati Local Government Area of Niger State, Nigeria.

3.2 Equipments / Apparatus

The laboratory equipments and apparatus used are listed below:

Muffle furnace (lenton)

Atomic Absorption Spectrophotometer (HULK 211)

Gallen kamp (ov 880 England)

Wweighing balance (Scout Pro SPU601)

pH Meter (3015 Jenway)

Conductivity Meter (Windaus 3302)

Hot plate (Consair)

Sieve (2.00 mm)

Distiller, all glass (Purehit Still OD/ 131)

Plastic rubber Bowls (Dana plast)

Crucible (Ceramic)

Beakers (Pyrex)

Volumetric flask (Pyrex)

Polyethylene bottles (Dana plast)

Plastic tray (Dana plast)

Deionizer (Permutit 250)

Measuring cylinder (Pyrex)

Sample bottles (Dana plast)

Funnels (Dana plast)

Mutter and pestle (Wood)

3.3 Sample Pretreatment

The sample used as adsorbent was pre-treated using the method of Hameed, Mahmoud and Ahmed (2008). The *Balanites aegyptiaca* seeds were washed with ordinary water and with de-ionised water to remove soil and other adhering impurities, sun dried and oven dried at 100°C overnight. The sample was then ground and sieved in to fine powder. This was to allow shorter diffusion path, thus allowing the adsorbent (*Balanites aegyptiaca* seeds) to penetrate deeper into the aqueous solution more quickly, resulting in a higher rate of adsorbent (Oboh, Emmanuel and Thomas, 2009), the ground sample was stored in air tight container.

3.4 Determination of Ash Content

5.00 g of the blended raw sample was weighed into an empty crucible. This was then introduced into a Muffle furnace at 500⁰C for three hours until grayish white ash was obtained. It was removed and allowed to cool at room temperature, then in dessicator before weighing (AOAC, 1990).

3.5 Preparation of the Adsorbent

The ground sample was carbonized by measuring 5 g in to a clean and weighed crucible, and then introduced into Muffle furnace set at 600⁰C for 5 min, after which it was transferred into a container, and washed with a bath of ice water and the excess was drained off. The carbonized sample was further washed using 0.1M HCl to remove the surface ash, followed by hot water and then distilled water respectively in order to remove the acidic residue (Rahman *et al.*, 2005). The carbonized samples were then sun dried, Oven dried at 100⁰C for 1 h (Odebunmi and Okeola, 2001). This process was repeated until a substantial amount of the carbonized sample was obtained (Gimba, Ocholi and Nok, 2004; Turoti, Gimba, Ocholi and Nok, 2007).

The carbonized sample was then divided into two parts. 5 g from the first part of the carbonized sample was mixed with 5 cm³ of 1M tetraoxophosphate V acid as activating agent (H₃PO₄) in a crucible and allowed to stand for 2 h. It was introduced into Muffle furnace set at 800⁰C for 10 min. The sample was cooled with ice-water, washed with 0.1M HCl followed by hot water washed and the distilled water, and the excess water was drained off, sun dried and finally oven dried at 100⁰ C. This continued until sufficient activated carbon was obtained and stored in airtight container for sorption studies (Vaughan, Seo and Marshall, 2001). The activated carbon obtained is labeled AC₁. 5 g from the second part of the carbonized sample was also mixed with 5 cm³ of 1M zinc chloride as activating agent (ZnCl₂) in a crucible and allowed to stand for 2 h. It was then introduced into Muffle furnace set at 800⁰C for 10 min. The sample was cooled with

ice water and undergoes other processes as that above and the activated carbon obtained was labeled AC₂. The commercial activated carbon used was obtained from Chemistry Laboratory Kontagora.

3.6 Adsorbent Characterization

3.6.1 Bulk Density

The bulk density was determined using the method of Ahmedna, Marsihall and Rao., (2003). A 25 cm³ cylinder was filled to its mark with activated carbon. The cylinder was tapped for at least 1 to 2 min to compress the carbon to a steady volume. The compressed sample was weighed and the mass (m) was divided by the volume occupied in the cylinder

$$\text{Bulk density (gcm}^{-3}\text{)} = \frac{\text{weight of activated carbon (g)}}{\text{Volume of packed dry material (cm}^3\text{)}} \text{-----(2)}$$

(Apipreeya, Phussadee and Prasert, 2006)

3.6.2 pH and Conductivity Measurement

The approach for pH determination was based on the approach of Okiemen, Ojokoh, Okiemen and Wuana (2004). 1.0 g of activated carbon was weighed into a beaker and 20.0 cm³ of distilled water was added to each. These were macerated with glass rod to uniformly wet the samples. The water quantity was increased to 100 cm³. The sample was stirred for 30 s and allowed to stand for 1 h. The beakers were covered with clean watched glasses during the period and 10.00 cm³ of the extract was decanted into a clean dry beaker. The pH was determined using pH meter and the conductivity was taken using conductivity meter at room temperature.

3.6.3 Activated Burn off

Burn off refers to the weight difference between the original char and the activated carbon divided by the weight of the original sample with both weights on dry basis (Ioannidou and Zabaniotou, 2006).

This is expressed as:

$$\% \text{ Burn off} = \frac{W_0 - W_1}{W_0} \times 100 \quad \text{_____} (3)$$

W_0 = weight of charcoal after pyrolysis, washing and drying and W_1 = weight of carbon after activation, washing and drying (Ioamidou and Zabaniotou, 2006).

3.6.4 Yield of Activated Carbon

The yield of activated carbon is the ratio of the resultant activated carbon to the original precursor with weight on a dry basis (Yulu, Waluwender and Fan, 2001).

$$\% \text{ Yield} = \frac{W_1}{W_0} \times 100 \quad \text{_____} (4)$$

W_0 = Original mass of precursor on a dry basis, W_1 = Weight of carbon after activation, washing and drying (Apipreeya *et al.*, 2006).

3.7 Preparation of Standard Solutions

3.7.1 Lead Nitrate [Pb (NO₃)₂] Stock Solution

1.60 g of Pb (NO₃)₂ salt was weighed and poured into a 1000 cm³ volumetric flask and dissolved with de-ionized water to the mark to give a stock solution (1000 ppm). A solution of 100 ppm was prepared from the stock solution by measuring 10 cm³ of the solution into a 100 cm³ volumetric flask and diluted with de-ionized water to the mark. Various concentrations of working solutions of 5, 10, 20, 30, 40 and 50 ppm were also prepared by sequential dilution of the 100 ppm solution (Peter, Whiteside and Bruce, 1984).

3.7.2 Hydrated Nickel Chloride [NiCl₂. 6H₂O] Stock Solution

4.02 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ salt was weighed and poured into a 1000 cm^3 volumetric flask and dissolved with de-ionized water to the mark to give a stock solution (1000 ppm). A solution of 100 ppm was prepared from the stock solution by measuring 10 cm^3 of solution into a 100 ml volumetric flask and diluted with de-ionized water to the mark. Various concentrations of working solutions of 5, 10, 20, 30, 40, and 50 ppm were also prepared by sequential dilution of the 100 ppm solution respectively (Peter, Whiteside and Bruce, 1984).

3.7.3 Copper II Sulphate [CuSO_4] Stock Solution

3.90 g of CuSO_4 was weighed using electronic weighing balance and poured into a 1000 ml volumetric flask, dissolved with de-ionized water and was make up to mark to give a stock solution (1000 ppm). A solution of 100 ppm was prepared from the 1000 ppm by measuring 10 cm^3 of solution into a 100 cm^3 volumetric flask and diluted with de-ionized water to the mark. Various concentrations of working solutions of 5, 10, 20, 30, 40, and 50 ppm were also prepared by sequential dilution of the 100 ppm respectively (Peter *et al.*, 1984).

3.7.4 Hydrated Chromium Nitrate [$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] Stock Solution

7.70 g of $[\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ salt was weighed and dissolved with de-ionized water in 1000 cm^3 volumetric flask and was made up to mark with de-ionized water. The solution was shaken thoroughly to ensure homogenous mixing. Other concentrations (5, 10, 20, 30, 40 and 50 ppm) were obtained from this solution by serial dilution (Peter *et al.*, 1984).

3.7.5 Hydrated Cobalt Chloride [$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$] Stock Solution

4.03 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ salt was dissolved in 1000 ml volumetric flask and was made up to mark with de-ionized water and other concentrations as above were prepared by serial dilution (Peter *et al.*, 1984).

3.7.6 Cadmium Nitrate [$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$] Stock Solution

2.76 g $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ salt was weighed and prepared into a 1000 cm^3 volumetric flask and diluted with de-ionized water to the mark to give a stock solution (1000 ppm). A solution of 100 ppm was prepared from stock solution by measuring 10 cm^3 of the solution into a 100 cm^3 volumetric flask and diluted with de-ionized water to the mark. Various concentrations of working solutions, 5, 10, 20, 30, 40 and 50 ppm were also prepared by sequential dilution of the 100 ppm solution (Peter *et al.*, 1984).

3.7.7 Manganese Chloride ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) Stock Solution

3.92 g $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ salt was weighed and prepared into a 1000 cm^3 volumetric flask and diluted with de-ionized water to the mark to give a stock solution (1000 ppm). Other procedure as above was followed to prepared various concentrations of working solutions of 5, 10, 20, 30, 40 and 50 ppm were also prepared by sequential dilution of the 100 ppm solution (Peter *et al.*, 1984).

3.8 Sorption Experiment

3.8.1 Variation of Contact Time

0.5 g of the activated carbon was taken and mixed with metal ion solution in a volumetric flask; these were allowed to stand at various time intervals of 30, 60, 90, 120 and 150 min at a room temperature. This mixture was filtered using Whatman Filter Paper No 42 and the filtrate was analyzed for metals using Atomic Absorption Spectrophotometer. The experiments were performed in triplicates (Vaughan *et al.*, 2001).

3.8.2 Variation of Metal Ion Concentration

A multiple batch sorption was carried out for the measurement of adsorption capacities at different concentrations of 10 ppm, 20 ppm, 30 ppm, 40 ppm and 50 ppm for the various heavy metals studied. 100 cm^3 of the various metal solutions was measured into a volumetric flask and 0.5 g of the adsorbent added. The volumetric flask was kept undisturbed for 90 min at 33°C . The mixture was filtered using Whatmann Filter Paper No 42 and the filtrate stored in a refrigerator

prior to analysis using an Atomic Absorption Spectrophotometer. The experiment was performed in triplicates and the average taken for the purpose of quality control.

3.9 Adsorptive Capacity (Q) of Metal Ions per Unit Adsorbent

The adsorptive capacity for metal ions per unit adsorbent (mg/g) was calculated by the following formular:

$$Q = V (C_i - C_t)/W \text{ _____ (5)}$$

Where Q is the adsorptive capacity at time t (mg/g)

V = Volume of the metal solution (l)

C_i = Concentration of metallic ions before interaction with activated carbon (mg/l)

C_t = Concentration of metal ion after interaction with the activated carbon (mg/l)

W = weight of the activated carbon (g) (Hameed *et al.*, 2008).

3.10 Percentage Removal of Heavy Metal Ions

This is calculated using the formular :

$$\% \text{ Removal} = \frac{C_i - C_t}{C_i} \times 100 \text{ _____ (6)}$$

Where C_i is the initial metal ions concentration in mg/dm³ and C_t is the metal ion concentration at time t in mg/dm³

3.11 Adsorption Isotherm

In order to describe the adsorption kinetics for the various metal ions under study on the prepared activated carbons (AC₁ and AC₂) and commercial activated carbon (CAC), pseudo first-

order (Lagergren, 1898), pseudo second-order (Ho and Mckay, 2000), Natarajan and Khalaf first order (Raji, Manju, and Amirudhan, 1986) and Elovic Model (Chien and Clayton, 1980) were applied to the experimental data.

Pseudo first- order equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (7)$$

Pseudo second-order equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

Natarajan and Khalaf first order equation:

$$\log \frac{C_t}{C_i} = \frac{k_1}{2.303 t} \quad (9)$$

Elovic model equation:

$$q_t = \frac{1}{\beta \ln(\alpha \beta)} + \frac{1}{\beta \ln(t)} \quad (10)$$

Where q_e = amount of adsorbate adsorbed at equilibrium (mg/g), q_t = amount of adsorbate after time t , k_1 = Adsorption rate constant for first-order (min^{-1}), k_2 = Adsorption rate constant for second-order ($\text{g.mg}^{-1} \text{min}^{-1}$), α = Initial adsorption rate ($\text{mg.g}^{-1} \text{min}^{-1}$), C_i = initial concentration of the adsorbent, C_t = Concentration of the adsorbent after time t , β = desorption constant (g.mg^{-1}) during any experiment.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Results

4.1.1 Characteristics of Activated Carbon

The characteristics of activated carbon are presented in Table 4.1. The values obtained for ash content, bulk density, percentage burn off, pH, percentage yield and conductivity were all shown in Table 4.1 for the activated carbons labeled AC₁, AC₂ and CAC, respectively.

Table 4.1 Characteristics of the Activated Carbon Produced Using Different Activating Agent

Parameters	AC ₁	AC ₂	CAC
Ash Content (%)	6.78	6.91	6.68
Bulk density (g/cm ³)	0.52	0.53	0.51
% burn off	43.89	54.10	40.39
pH	6.52	6.60	6.42
% yield	56.11	45.90	42.50
Conductivity (μs/cm)	2.40	2.50	2.39

AC₁: Activated Carbon Prepared using H₃PO₄ as Activating Agent

AC₂: Activated Carbon Prepared using ZnCl₂ as Activating Agent

CAC: Commercial Activated carbon

4.1.2 Heavy Metal Composition of the *Balanites aegyptiaca* seeds

The results of the sorbents in heavy metal composition are given in Table 4.2. The Table shows that the activated carbons prepared from *Balanites aegyptiaca* seeds contain the heavy metal in varying amounts. The AC₁ contained 0.44, 0.31, 0.14, 0.10, 0.12, 0.33 and 0.42 mg/kg respectively of Cr (IV), Pb (II), Cu (II), Cd (II), Ni (II), Co (II) and Mn (III). AC₂ contained 0.48, 0.24, 0.16, 0.42, 0.15, 0.32 and 0.36 mg/kg of the metal ions above while CAC contained 0.43, 0.35, 0.16, 0.31, 0.24, 0.22 and 0.45 mg/kg of the respective metal ions. In all the activated carbons, Cr (VI) ion concentration using the highest while Cd (II) was the smallest in AC₁, Ni (II) was the smallest in AC₂ and Cu (II) was the smallest in CAC.

Table 4.2 Heavy Metal Composition of the *Balanites aegyptiaca* seeds

	Amount of metal ions AC ₁	adsorbed (mg/kg) AC ₂	CAC
Cr (VI)	0.44	0.48	0.43
Pb (II)	0.31	0.24	0.35
Cu (II)	0.14	0.16	0.16
Cd (II)	0.10	0.42	0.31
Ni (II)	0.12	0.15	0.24
Co (II)	0.33	0.32	0.22
Mn (II)	0.42	0.36	0.45

AC₁: Activated Carbon Prepared using H₃PO₄ as Activating Agent

AC₂: Activated Carbon Prepared using ZnCl₂ as Activating Agent

CAC: Commercial Activated Carbon

4.1.3 Effect of Contact Time of AC₁, AC₂ and CAC on the Removal Percent of Cr, Pb, Cu, Cd, Ni, Co and Mn Ions

The results obtained shows that at a constant concentration of metal ions and fixed amount of adsorbent, the adsorption efficiency increased with increasing contact time up to a certain level until it reached equilibrium and then decreased until removal started to manifest. The Tables 4.3.1, 4.3.2 and 4.3.3 show various percentage removals with their respective contact times.

In Table 4.3.1, the rapid removal of Cr for AC₁ was noticed from 43% to 64% with the contact time variation from 30 to 150 min. The optimum contact time was 90 min with 64% adsorption. In Table 4.3.2, the removal of chromium ion for AC₂ was observed from 48% to 70% and the optimum time was 90 min with 70% adsorption. In table 4.3.3, the removal of chromium ion for CAC was observed from 48% to 62% and the optimum time was 90 min with 62% adsorption respectively.

Table 4.3.1 shows the uptake of lead ion as it increased with contact time until at equilibrium. For AC₁, the percentage removal of lead II ion ranged from 38% to 60% with contact time variation from 30 to 150 min. The optimum contact time was 90 min with 60% adsorption. For AC₂ in table 4.3.2, the removal of lead ions was observed from 51% to 66% and the optimum time was 90 min with 66% adsorption. For CAC in table 4.3.3, the removal of lead II ion was observed from 38% to 60% and the optimum time was 90 min with 60% adsorption.

The uptake of copper ion for AC₁ increased from 30% to 58% with contact time 30 to 90 min and started decreasing from 36% to 22% at contact time between 120 to 150 min. Also for AC₂, it increased from 49% to 66% at contact time between 30 to 90 min and decreased from 56% to 28% at contact time of 120 to 150 min. For CAC, the increased in percentage was from 30% to 58% at between contact time of 30 to 90 min then decreased from 32% to 30% at contact time of 120 and 150 min, respectively

For Cadmium ion, percentage removal for AC₁ at contact times 30 to 90 min increased from 40% to 56% until it decreased from 36% to 22% at contact time 120 to 150 min. For AC₂, the percentage removals of cadmium ion ranged between 52% to 62% at contact time 30 to 90 min and get reduced from 52% to 38% at contact time 120 to 150 min while that of CAC ranged from 30% to 58% at contact time 30 to 90 min until the removal percentage reduced from 32% to 30% at contact time 120 to 150 min.

For AC₁, the percentage removal of nickel ion ranged between 28% to 50% at contact time 30 to 90 min and decreased from 30% to 20% at contact time 120 to 150 min. For AC₂, Nickel ion percentage removal at contact time 30 to 90 min is 47% to 62% and hence decreased from 52% to 38% at contact time 120 to 150 min. For CAC, percentage removal of nickel ion is 40% to 55% at contact time 30 to 90 min and decreased from 33% to 28% at contact time 120 to 150 min.

AC₁ also showed percentage removal of cobalt ion at contact time 30 to 90 min ranged from 12% to 47% before the observed decreased in the percentage removal of 32% to 21% at contact time of 120 to 150 min. For AC₂, the percentage removal of cobalt ion was between 39% to 55% at contact time 30 to 90 min and decreased from 49% to 22% at contact time 120 to 150 min. CAC also removes cobalt ion ranged from 25% to 48% at 30 to 90 min and the percentage removal of cobalt ion decreased between 30% to 20% at 120 to 150 min contact time.

AC₁ removed manganese ion at 18% to 48% at contact time between 30 and 90 min while the percentage removal reduced from 48% to 40% at contact time 120 to 150 min. AC₂ also showed percentage removal of 51% to 55% at contact time 30 to 90 min then there was decrease in the percentage removal from 28% to 22% at 120 to 150 min contact time. CAC removed manganese ion from 28% to 38% at contact time 30 to 90 min then the percentage removal decreased from 22% to 20% at 120 to 150 min contact time.

Table 4.3.1 Effect of Contact Time of AC₁ on the Removal Percent of Named Metal Ions

Time (s)	AC ₁ (%)						
	Cr	Pb	Cu	Cd	Ni	Co	Mn
30	43	38	30	40	28	12	18
60	45	37	36	45	32	34	25
90	64	60	58	56	50	47	67.8
120	63	30	36	36	30	32	48

150	58	20	22	22	20	21	40
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Table 4.3.2 Effect of Contact Time of AC₂ on the Removal of Named Metal Ions

Time (s)	AC ₂ (%)						
	Cr	Pb	Cu	Cd	Ni	Co	Mn
30	48	51	49	52	47	39	51
60	58	56	35	45	38	40	40
90	70	66	67	67	62	60	67.5
120	58	56	46	46	52	36	49
150	40	28	32	32	38	20	22

Table 4.3.3 Effect of Contact Time of CAC on the Removal of Named Metal Ions

Time (s)	CAC (%)						
	Cr	Pb	Cu	Cd	Ni	Co	Mn
30	48	38	30	30	40	25	28
60	49	49	47	47	49	32	22
90	71	60	60	58	55	50	68
120	60	48	31	32	33	20	22
150	58	58	31	30	28	22	20

4.1.4 Adsorptive Capacity of Metal Ions on the AC₁, AC₂ and CAC

The result of the effect of contact time on adsorptive capacity of metal ions on AC₁, AC₂ and CAC are presented on Tables 4.4.1, 4.4.2 and 4.4.3. Adsorptive capacity of AC₁, AC₂ and CAC at 30 min contact time for all the metal ions (Cr, Pb, Cu, Cd, Ni, Co and Mn) ranged from 0.12 to 0.48 mg/kg. Adsorptive capacity at 60 min contact time for all the metal ions listed above ranged from 0.20 to 0.58 mg/kg. The adsorptive capacity at 90 min contact time for all metal ions (Cr, Pb, Cu, Cd, Ni, Co and Mn) ranged from 0.26 to 0.73. The adsorptive capacity at 120 min contact time for all the metal ions ranged from 0.20 to 0.63 mg/kg. The adsorptive capacity at 150 min contact time for all the metal ions listed above ranged from 0.20 to 0.58 mg/kg. Chromium ion had the highest adsorptive capacity of 0.73 mg/kg at 90 min contact time while lead II ion had the lowest adsorptive capacity at 30 min contact time and then adsorptive decreased there after.

Table 4.4.1 Adsorptive Capacity of AC₁ on the Various Metal Ions

Contact		AC ₁					
time		(mg/kg)					
(s)	Cr	Pb	Cu	Cd	Ni	Co	Mn
30	0.48	0.12	0.40	0.14	0.34	0.23	0.38
60	0.43	0.18	0.39	0.23	0.36	0.20	0.40
90	0.45	0.26	0.47	0.32	0.49	0.26	0.44
120	0.60	0.20	0.30	0.32	0.31	0.43	0.43
150	0.57	0.20	0.22	0.30	0.31	0.31	0.31

Table 4.4.2 Adsorptive Capacity of AC₂ on the Various Metal Ions

Contact		AC ₂					
time		(mg/kg)					
(s)	Cr	Pb	Cu	Cd	Ni	Co	Mn
30	0.38	0.38	0.30	0.31	0.20	0.30	0.20

60	0.58	0.55	0.38	0.50	0.41	0.28	0.26
90	0.70	0.68	0.66	0.65	0.60	0.50	0.51
120	0.58	0.55	0.43	0.58	0.50	0.20	0.22
150	0.40	0.25	0.32	0.28	0.28	0.32	0.33

Table 4.4.3 Adsorptive Capacity of CAC on the Various Metal Ions

Contact time (s)	CAC (mg/kg)						
	Cr	Pb	Cu	Cd	Ni	Co	Mn
30	0.43	0.18	0.48	0.24	0.31	0.20	0.23
60	0.45	0.36	0.56	0.36	0.58	0.35	0.55
90	0.73	0.71	0.68	0.66	0.60	0.58	0.55
120	0.63	0.56	0.58	0.36	0.36	0.30	0.29
150	0.58	0.40	0.38	0.23	0.24	0.20	0.21

4.1.5 Effect of Initial Metal Ions Concentration on Adsorption by AC₁, AC₂ and CAC for 90 min

The uptake mechanism of metal ions solely depended on the initial metal ion concentration. From the result of this study, metal ions were adsorbed by specific sites at low concentrations but the adsorption amount did not increase proportionally for higher metal ion concentrations since the active sites were filled and saturated. This was a proof that percentage removal of metal ions decreases with increase in metal ion concentration (El-Ashtouky, Amin and Abdelwahab, 2008).

The Tables 4.5.1 to 4.5.3 reveals that for AC₁, the chromium ion percentage removal decreased from 74% to 48%, the percentage removal of lead II ion decreased from 75% to 42%, copper II ion percentage removal was from 70% to 43%, cadmium was from 56% to 22%, nickel ion was

from 50% to 20%, cobalt ion from 47% to 12% and manganese ions decreased in percentage removal from 48% to 18%, respectively.

For AC₂, the chromium ion percentage removal decreased from 76% to 49%, lead II ion decreased from 73% to 43%, Copper II ion decreases from 70% to 44%, cadmium ion was from 68% to 41%, nickel ion from 63% to 41%, cobalt ion from 60% to 42%, and manganese ion from 58% to 32%, respectively.

For CAC, the chromium ion percentage removal decreased from 78% to 50%, lead II ion from 73% to 49%, copper II ion from 71% to 45%, cadmium ion from 72% to 46%, nickel II ion from 68% to 39%, cobalt ion from 60% to 42% and finally manganese decreased from 52% to 33%, respectively.

The decreased in percentage adsorption can be attributed to lack of sufficient surface area to accommodate more metal ions available in the solution as the concentration increases. At lower concentrations, all metal ions present in the solution could interact with the functional groups present and the available binding sites on the surface of the adsorbent (Babalola *et al*, 2008). The percentage adsorption was higher than those at higher metal ion concentrations and thus at higher concentrations lower adsorption yield is as a result of the saturation of adsorption sites.

Table 4.5.1 Effect of Initial Metal Ions Concentration on Adsorption by AC₁ for 90 min (100 g/cm³)

Conc.	AC ₁ (%)						
	Cr	Pb	Cu	Cd	Ni	Co	Mn
10	74	75	70	63	62	58	56
20	70	71	64	58	56	52	49
30	68	66	62	50	51	50	48
40	58	60	55	40	42	45	44
50	48	42	43	30	41	43	41

Table 4.5.2 Effect of Initial Metal Ions Concentration on Adsorption of AC₂ for 90 min (100 g/cm³)

Conc.	AC ₂ (%)						
	Cr	Pb	Cu	Cd	Ni	Co	Mn
10	76	73	70	68	63	60	58
20	72	71	68	59	55	52	50
30	69	69	58	43	45	46	44
40	59	59	56	41	43	44	42
50	49	49	44	38	41	42	32

Table 4.5.3 Effect of Initial Metal Ion Concentration on Adsorption of CAC for 90 min (100 g/cm)

Conc.	CAC(%)						
	Cr	Pb	Cu	Cd	Ni	Co	Mn
10	78	73	71	72	68	60	52
20	71	70	68	59	52	51	48
30	68	65	55	54	46	48	42

40	53	52	48	49	41	44	38
50	50	49	45	46	39	42	33

4.1.6 Effect of Variation of Mass of Adsorbent on the Adsorption of Metal Ions Using AC₁, AC₂ and CAC for 90 min

Biosorption capacity is strongly affected by the amount of biosorbent. The effect of the adsorbent dosage was studied at room temperature by varying the sorbent amounts from 0.5 g to 2.5 g. For all the runs, initial concentration of the metal ions was kept constant. Tables 4.5.1 to 4.5.3 showed that the adsorption of different metal ions increased rapidly with increase in the amount of adsorbent. This increase is as a result of greater availability of the surface area at higher concentration of the adsorbent (El- Ashtoukhy *et al.*, 2008). There is significant increase in uptake when the dosage was increased from 0.5 g to 2.5 g and after this, any further addition of the adsorbent beyond this did not cause any significant change in the adsorption. This is due to the overlapping of adsorption sites resulted from overcrowding of the adsorbent particles. These

resultant results are an indication that removal efficiency is directly related or proportional to the number of available adsorption sites. Thus once equilibrium is attained, there is no further effect on adsorption efficiency (Zafar, Nadeem and Hanif, 2006).

For chromium, minimum percentage removal was 30% for AC₁, 48% for AC₂ and 52% for CAC for the dosage of 0.5 g while the maximum percentage removal was 78% for AC₁, 78% for AC₂ and 77% for CAC at 2.5 g dosage.

For lead, the minimum percentage removal was 28% for AC₁, 30% for AC₂ and 38% for CAC for the dosage of 0.5 g while the maximum percentage removal is 76% for AC₁, 72% for AC₂ and 73% for CAC at 2.5 g dosage.

For copper, minimum percentage removal was 35% for AC₁, 38% for AC₂ and 36% for CAC for the doses of 0.5 g while the maximum percentage removal was 75% for AC₁, 78% for AC₂ and 80% for CAC at 2.5 g dosage.

For cadmium, the minimum percentage removal was 38% for AC₁, 40% for AC₂ and 41% for CAC for the dose of 0.5 g while the maximum percentage removal was 66% for AC₁, 67% for AC₂ and 68% for CAC at 2.5 g dosage.

For nickel, the minimum percentage removal was 36% for AC₁, 36% for AC₂ and 42% for CAC at 0.5 g dosage. The maximum percentage removal was 60% for AC₁, 67% for AC₂ and 63% for CAC at 2.5 g dosage, respectively.

For cobalt, the minimum percentage removal was 22% for AC₁, 20% for AC₂ and 38% for CAC at 0.5 g dosage while the maximum percentage removal was 57% for AC₁, 58% for AC₂ and 52% for CAC at 2.5 g dosages.

For manganese, the minimum percentage removal was 24% for AC₁, 22% for AC₂ and 37% for CAC at 0.5 g dosage while the maximum percentage removal was 52% for AC₁, 59% for AC₂ and 61% for CAC at 2.5 g dosage, respectively.

Results obtained from above showed that the adsorption capacity of the AC₁ and AC₂ prepared and CAC can be compared to give efficient maximum removal of the metal ions at all levels of adsorbent dosages. Among metal ions chromium get adsorbed at higher rate followed by manganese, copper, nickel, cadmium, lead and cobalt, respectively.

Table 4.6.1 Effect of Variation of Mass of Adsorbent on the Adsorption of Metal Ions Using AC₁

Dosage(g)	AC ₁ (%)						
	Cr	Pb	Cu	Cd	Ni	Co	Mn
0.5	30	28	35	38	36	22	24
1.0	44	40	48	47	45	38	38
1.5	58	60	55	54	50	38	39
2.0	68	66	64	60	58	51	49
2.5	78	76	70	66	60	50	52

Table 4.6.2 Effect of Variation of Mass of Adsorbent on the Adsorption of Metal Ions Using AC₂

Dosage(g)	AC ₂ (%)						
	Cr	Pb	Cu	Cd	Ni	Co	Mn
0.5	48	30	38	40	36	20	22
1.0	53	41	46	45	46	28	30
1.5	62	58	56	55	54	55	40
2.0	66	62	63	64	60	52	48
2.5	78	72	68	67	67	58	59

Table 4.6.3 Effect of Variation of Mass of Adsorbent on the Adsorption of Metal Ions Using CAC

Dosage(g)	CAC(%)
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	Cr	Pb	Cu	Cd	Ni	Co	Mn
0.5	52	38	36	41	42	38	37
1.0	55	43	38	43	44	39	38
1.5	64	51	53	49	48	40	41
2.0	67	63	62	60	52	48	52
2.5	77	73	71	68	63	52	61

4.1.7 Effect of pH of Solution on Adsorption of Metal Ions on AC₁, AC₂ and CAC

Tables 4.7.1, 4.7.2 to 4.7.3 showed the effect of pH of the solution on adsorption of the metal ions from aqueous solution. For AC₁, the highest sorption percentage removal observed for chromium ion, lead II ion and copper II ion occurred at pH 3.0, while that of cadmium ion, cobalt ion, nickel II ion and manganese ion occurred at pH 4.0, pH 5.0, pH 4.0 and pH 5.0, respectively.

For AC₁, the percentage removal for chromium ion increased from 51.2% to 54.3% as pH increased from 2.0 to 3.0 and decreased from 50.6% at pH 6.0. Percentage removal of lead II ion increased from 50.2% to 54.6% as pH increased from 2.0 to 3.0 and decreased from 50.6% at pH 6.0. Similarly for copper II ion, there was increased from 18.1% to 19.9% as pH increased from 2.0 to 4.0 and decreased from 15.1% at a pH 7.0. Also cadmium ion percentage removal increased from 90.1% to 95.6% as pH increased from 2.0 to 5.0 and decreased from 90.8% at pH 6.0. The percentage removal of cobalt ion increased from 36.48% to 63.80% as the pH increased from 2.0 to 5.0 and then decreased from 60.92 at pH of 6.0. The percentage removal of nickel ion increases from 64.80% to 76.78% between the pH 2.0 to 4.0 and then start to decreased from 60.88% at the pH 5.0. Finally for manganese ion, the increased was from 53% to 61% at pH 5.0 and started decreasing from 49% when the pH was 6.0.

For AC₂, the highest sorption percentage removal was observed for chromium ion at pH 3.0, lead II ion at pH 4.0, copper II ion at pH 5.0, cadmium ion at pH 4.0, cobalt at pH 5.0, Nickel at pH 5.0 and manganese at the pH 5.0.

The percentage removal of chromium ion for AC₂ increased from 50.2% to 51.3% as the pH increased from 2.0 to 4.0 before it started decreasing from 51.1% downward at pH 5.0. Lead II ion has it's percentage removal from 80.0% up to 83.8% as the pH increased from 2.0 to 4.0 and then started decreasing from 80.8% at pH 5.0. Similarly, copper II ion percentage removal increases from 69.3% to 73.3% at pH 5.0 then it decreased downward from 68.0% at pH 6.0. Cadmium ion equally followed the same trend by increasing from 33.10% to 71.51% and hence decreased from 62.22% at pH 5.0. Cobalt percentage removal increased also from 35.40% to 62.30% as the pH increased from 2.0 to 5.0 and started decreasing from 60.77% at the pH 6.0. Nickel percentage removal increased from 69.20% to 74.18% as the pH increased from 2.0 to 5.0 then reduction in percentage removal started from 62.38% downward at pH 6.0. Finally the

manganese ion percentage removal commenced from 55% to 65% as the pH get increased from 2.0 to 5.0 and hence decreased from 53% downward at pH 6.0.

For CAC, the highest sorption percentage removal observed for chromium, lead II, copper II, cobalt, nickel and manganese ions occurred at pH 5.0 while that of cadmium occurred at pH 4.0. The percentage removal of chromium ion by CAC was from 51.4% to 61.0% as pH increased from 2.0 to 5.0 until it eventually started decreasing from 55.3% at pH 6.0. For lead II ion the percentage removal took the trend from 90.5% to 94.6% as pH increased from 2.0 to 5.0 and thus decreased again from 90.1% downward at the pH 6.0. Copper in the other hand has it's percentage removal from 50.5% to 55.2% as the pH increased from 2.0 to 4.0 and started decreasing with percentage removal from 54.8% at pH 5.0. Cadmium ion has percentage removal from 33.0% to 70.32% as the pH increased from 2.0 to 4.0 before it decreased from 62.0% at pH 5.0. Cobalt percentage removal also increased from 34.0% to 71.38% as pH increased from 2.0 to 5.0 then the percentage removal reduced from 66.30% at pH 6.0. Nickel ion had a trend of percentage removal from 51.28% to 58.38% as the pH increased from 2.0 to 5.0 until there was decreased in the percentage removal from 45.39% at pH 6.0. Finally the manganese ion had it percentage removal from 54% to 66% at the pH trend of 4.0 to 5.0 and the percentage removal decreased from 57% at pH 6.0

The increase in chromium, lead II, copper II, cadmium II, cobalt II, nickel II and manganese III ions removal as pH increased can be explained on the basis of a decrease in competition between proton and the metal cat ion for the surface sites and as well as by the decrease in positive surface charge which results in a lower coulombic repulsion of the sorbing metal cations (Ali Shafaghat, Farshid, Mahdi, Jabar and Masoud, 2012). In 1997, Wase and Forster reported similar result for the adsorption of lead and chromium onto activated carbon. At pH below 6.0, the stated metal ions would predominate and pH values just below 8.0, the metal ions would start precipitating out as their hydroxides (Parvathi, Nagendran and Nareshkumar, 2006).

Literature showed that pH value greater than pH point of zero charge (pH_{zero}), the functional groups on biosorbents have net negative charge and at pH values lower than pH_{pzc} , the functional groups on the surface of biosorbents have net positive charge (Horsfall and Spiff, 2004). These therefore accounted for high percentage removal of the various named metal ions at pH 3.0 to pH 5.0. The decreased in percentage removal of metal ions at lower pH value may be attributed to repulsion between positively charged adsorbents surfaces and positive metal ions. Many literatures showed that at low pH values in aqueous medium, surfaces of adsorbents are closely associated with hydroxonium ions (H_3^+O) which may hinder the accessibility of metal cations by repulsive forces to the surface functional groups and this may cause the decreased in the percentage metal removal (Yu, Zhang, Shukla, and Dorris, 2001). Furthermore, the decrease in percentage removal at pH value greater than 6.0 is as a result of precipitation been dominant or both ion exchange and aqueous metal hydroxide formation (Ali, Farshid, Mahdi, Jaber and Masoud, 2012). This condition is often not desirable as the metal precipitation could result in copper and chromium having confusion for the adsorption capacity. Chromium (VI) exhibited different types of pH dependence in aqueous solution. At pH range of 1 to 4, the dominant species of Cr (VI) ions in solution are $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^{-1} and $\text{Cr}_2\text{O}_7^{-1}$. Some functional groups in biomass are amines among others and they are positively charged when protonated and may electro-statically bind with negatively charged metal complexes (Popuri, Srinivasa, Jammala, Ajithapriya, Reddy, Kachireddy, Abburi, 2007). At lower pH, the biosorbents is positively charged due to protonation and as dichromate ion exists as anion, this may lead to an electro-static attraction between them (Boddu, Abburi, Talbott, Smith and Haasch, 2008). Also at very low pH value, the surface of sorbent would be surrounded with hydroxonium ion which would enhance the chromium VI ion interaction with the binding sites of the biosorbents by greater attractive forces (Babalola *et al.*, 2008).

These reasons accounted for the high Cr (VI) sorption percentage observed at a lower pH up to pH 4.0 where highest sorption capacity occurs. Also a sharp decrease in adsorption above pH 4.0 is attributed to occupation of the adsorption sites by anionic species like HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} etc which causes the retardation of such ions further toward the sorbent surface (Donmez and Aksu, 1999). The decrease in adsorption at high pH values may also be due to the competitiveness of the oxyanion of chromium and OH^- ions in the bulk (Popuri *et al.*, 2007). Similar report was made in 2006 by Aganwal, Bhuptawat and Chaudhari that optimum pH of 4.0 was observed in the biosorption of chromium VI by tamarind shell. Levent, Denizii, Omer and Bektas (2002) also reported similar optimum pH of 6.0 for the sorption of cadmium onto *Pleutorus sapidus*. Ali, Farshid, Mahdi, Jaber and Masoud (2012) also reported optimum pH for the adsorption of Pb, Cu and Cr using five plants to be about 4.0 which were rather acidic. Several other investigations have been reported that provided similar pH range for the sorption of the metal ions studied onto different biomass systems (Taty- Costodes, Fauduet, Porte and Delacrois 2003). At this junction, it can therefore be concluded that activated carbons (AC_1 and AC_2) prepared in this work could be used to remove Cr, Pb, Cu, Cd, Co, Ni and Mn effectively from aqueous solution compared with commercially activated carbon. It was also observed from the results of this study that the removal of the metal ions is pH dependent with each metal having a characteristic pH range within which it is mostly removed

Table 4.7.1 Effect of pH on the Removal Percentage of AC₁, AC₂ and CAC on Cr, Pb and Cu

pH	Cr			Pb			Cu		
	AC ₁	AC ₂	CAC	AC ₁	AC ₂	CAC	AC ₁	AC ₂	CAC
1	51.2	50.2	51.4	90.1	80.0	90.5	70.8	69.3	50.5
2	52.3	52.3	56.2	91.2	81.6	91.8	71.7	70.0	51.5
3	54.3	54.6	58.8	92.0	81.8	92.6	73.8	71.2	52.5
4	51.2	51.3	66.9	92.6	83.8	93.9	74.5	71.8	55.2
5	51.0	51.1	61.0	95.6	80.8	94.6	75.8	73.3	54.8
6	50.6	50.6	55.3	90.8	72.2	90.1	72.0	68.0	52.3
7	49.3	49.4	49.1	89.2	70.1	89.2	70.7	67.3	51.8
8	48.5	47.8	44.8	86.8	67.6	88.3	68.2	66.1	50.6

Table 4.7.2 Effect of pH on the Removal Percentage of AC₁, AC₂ and CAC on Cd, Co, Ni and Mn

Cd	Co	Ni	Mn
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pH	AC ₁	AC ₂	CAC	AC ₁	AC ₂	CAC	AC ₁	AC ₂	CAC	AC ₁	AC ₂	CAC
1	32.25	33.10	33.00	36.48	35.40	34.00	64.80	69.20	51.28	53.0	55.0	54.0
2	42.85	40.23	41.20	43.98	42.88	43.20	74.55	70.38	52.88	55.0	57.0	56.0
3	62.32	60.12	61.80	45.60	45.29	48.20	78.28	71.28	54.90	57.0	59.0	58.0
4	73.26	71.51	70.32	58.76	57.25	56.20	76.78	73.28	55.36	60.0	62.0	61.0
5	60.58	62.22	62.00	63.80	62.30	71.38	60.88	74.18	58.38	61.0	65.0	66.0
6	52.36	50.34	51.04	60.92	60.77	66.30	58.28	62.38	45.39	49.0	53.0	57.0
7	43.32	42.12	40.30	57.81	56.72	55.80	43.28	53.90	43.28	45.0	51.0	54.0
8	30.70	31.23	31.00	55.38	54.29	50.60	32.18	48.88	41.88	42.0	48.0	50.0

4.8 Parameters of Estimated kinetics Models for Different Adsorbent Types for the Various Metals under Study

Heavy metals	Types of adsorbent	1 st order		2 nd order		Elovich equation			Natarajan/kahalaf equation	
		R ²	k ₁	R ²	K ₂	R ²	a	b	R ²	K ₁
Cr	AC ₁	0.773	-0.054	0.907	-6.357	0.008	0.056	0.006	0.812	-8.634
	AC ₂	0.024	-0.010	0.645	4.395	0.000	0.175	0.001	0.041	-2.371
	CAC	0.750	-0.070	0.982	6.757	0.837	0.522	-0.075	0.808	-5.902
Pb	AC ₁	0.275	0.025	0.575	3.388	0.111	0.064	0.029	0.164	-9.407
	AC ₂	0.723	0.043	0.908	8.178	0.581	0.054	0.071	0.007	1.056
	CAC	0.007	-0.005	0.768	8.759	-0.06	0.218	0.000	0.0031	-1.649
Cu	AC ₁	0.278	0.029	0.704	3.272	0.05	0.251	0.000	0.049	-2.345
	AC ₂	0.102	-0.014	0.601	8.778	0.029	0.151	0.015	0.005	-0.902
	CAC	0.058	-0.012	0.474	2.368	0.112	0.074	0.043	0.019	-1.469
Cd	AC ₁	0.418	-0.028	0.738	8.025	0.156	0.106	0.030	0.026	1.520
	AC ₂	0.532	0.043	0.819	4.058	0.125	0.112	0.019	0.016	0.979
	CAC	0.005	-0.004	0.785	8.446	0.211	0.523	0.058	0.009	-0.927
Ni	AC ₁	0.456	-0.005	0.489	2.726	0.044	0.17	0.025	0.021	1.567
	AC ₂	0.100	-0.015	0.621	2.937	0.232	0.044	0.044	0.064	2.886
	CAC	0.231	-0.009	0.848	3.129	0.170	0.138	0.027	0.071	1.881
Co	AC ₁	0.004	0.001	0.577	2.596	0.008	0.311	0.012	0.228	-4.097
	AC ₂	0.000	-0.001	0.737	3.512	0.022	0.181	0.011	0.025	-1.211
	CAC	0.008	-0.002	0.812	2.853	0.006	0.21	0.005	0.025	-1.211
Mn	AC ₁	0.332	0.016	0.960	4.813	0.725	0.576	0.073	0.817	-8.170
	AC ₂	0.3-09	0.041	0.855	3.070	0.508	0.015	0.051	0.324	4.948
	CAC	0.101	-0.001	0.840	3.111	0.142	0.225	0.022	0.149	0.850

4.2

Discussion

4.2.1 Characteristics of the Activated Carbons

The ash contents of the activated carbons prepared from the sampled *Balanites aegyptiaca* seeds labeled AC₁ and AC₂ were 6.78% and 6.91 % (Table 4.1). This result proves that the ash contents of the sample were low which indicate high carbon yield. The % burn off was not too high and this was an indication that there was high % yield and as a result less chars were released due to less high burn off. It was observed that the bulk density of AC₁ and AC₂ was low and this could be linked to corrosive effect of the chemical on the biomass during pore formation. The pH for the various activated carbon was shown to have been 6.52% (AC₁) and 6.60% (AC₂) and this trend is not far from what Kobya, Demirbas and Senturk (2005) reported. The Conductivity values for the activated carbons was low which indicated that the ash content of the carbon was low i.e. the conductivity values of activated carbons is always dependent on the values of their ash content.

4.2.2 Heavy Metal Composition of Sorbent

Heavy metal concentration of the sample studied was determined in order to give the idea of the amount of those metals present. Table 4.2 shows the percentage heavy metal composition of *Balanites aegyptiaca* seeds to have ranged from 0.10 to 0.44 mg/kg (AC₁) while that of AC₂ ranged from 0.15 to 0.48 mg/kg. Chromium ion is more prevalent in the two prepared activated carbons i.e. 0.44 mg/kg (AC₁), 0.48 mg/kg (AC₂) and cadmium ion was the least in AC₁ with 0.10 while nickel is the least in AC₂ with 0.15 mg/kg. The range of Heavy metal composition in AC₁ is shown in decreasing order as: Cr > Mn > Co > pb > Cu > Ni > Cd while the range in AC₂ is: Cr > Cd > Mn > Co > pb > Cu > Ni.

4.2.3 Effect of Contact Time on Adsorption of Metal Ions

Contact time was varied from 30 min to 150 min and a sharp increase in the percentage removal was observed though optimum value was at 90 min. However, further increase of contact time beyond 90 min generally results to a decrease in the adsorption of metal ions (Shukl and Pai, 2005). As a result of this, contact time of 90 min was set for all other experiments. From the result obtained for AC₁, chromium ion

had the highest percentage removal at the end of 90 min, followed by lead, then copper, then cadmium, nickel, manganese and cobalt ions, respectively. For AC₂, chromium had the highest percentage removal followed by copper, then cadmium, lead, nickel, cobalt and finally manganese ions respectively. For CAC, the order is that lead had the highest percentage removal, followed by copper, then cadmium, then nickel, chromium, cobalt, and manganese.

The observed fast rate of biosorption kinetics is in line/ consistent with biosorption of metals which involve non- energy mediated reaction where metal removal from solution is purely a physicochemical interaction between biomass and metal solution (Igwe and Abia,2003; Oboh and Aluyor, 2008). At 90 min, little or no increase in percentage adsorption was observed with increase in contact time. Furthermore, chromium had the highest percentage removal in all the adsorbents (AC₁, AC₂ and CAC). This trend can be explained by considering that chromium ion has a smaller ionic radius than other metal ions. As a result that chromium has a smaller ionic radius, it tends to diffuse more onto the potential adsorption sites easily than other adsorbents. Additionally, Abia and Osuguo (2006) had reported that when there are interaction between various metal ions and the adsorbent, ions with smaller ionic radii tend to be more strongly attracted to the adsorbent sites and since chromium ion has smaller ionic radii hence a larger percentage of it was removed. Cobalt has the least adsorptive capacity compared with other metal ions in AC₁, AC₂ and CAC.

The order of metal uptake in the adsorbents (AC₁) was Cr> Mn>Pb> Cu>Cd>Ni>Co and that of AC₂ was Cr>Mn>Cu>Cd>Pb>Ni>Co and finally that of CAC was Cr>Mn>Pb>Cu>Cd>Ni>Co. The difference in adsorptive capacity of the adsorbents was as a result of differences in their ionic size of the metal ions, their nature and the distribution of active groups on the biosorbent and finally the mode of interaction between the metal ions and the biosorbent (Abia and Osuguo, 2006).

4.2.4 Effect of Initial Metal Ions Concentration on Adsorption

The result of percentage removal of the various metal ions under study at different initial metal ion concentrations for the various adsorbents (AC₁, AC₂ and CAC) are shown in Tables 4.5.1, 4.5.2 and 4.5.3,

respectively. The result obtained showed that as the metal ion concentrations increased from 10 mg/kg to 50 mg/kg the sorption capacity increased with increased in initial metal ion concentrations. This was an indication that surface saturation depends upon the initial metal ion concentrations. At low concentrations, adsorption sites took up the available metal more quickly and when the concentrations become high the rate of diffusion becomes slow. This is attributed to the fact that ions diffused to biomass surface by intraparticle diffusion and the greatly hydrolyzed ions would tend to diffuse at a slower rate (Oyebamiji, Adesola, Olalekan, Pappala, Vincent and Oninlo 2008). The level of metal ions uptake and percentage removal followed this order. For AC₁, Pb>Cr>Cu>Cd>Ni>Mn>Co and that of AC₂ is shown as Cr>Pb>Cu>Cd>Ni>Co>Mn while that of CAC is Cr>Pb>Cu>Cd>Ni>Co>Mn, respectively. This trend is as a result of electrostatic interaction between the metal ions and the adsorbent active sites. For the three adsorbents, the differences in the uptake levels of the metal ions can be explained in terms of their differences in the ionic sizes and atomic weight of the metal ions, their mode of interaction between the metal ions and the substrate (Gong, Jin, Chen, Chen and Liv, 2005). The result obtained showed that as the initial metal ion concentrations increased there was corresponding increase in the amount of metal ions adsorbed and this could be due to availability of the uncovered surface area of the adsorbent since adsorption kinetics depends on the surface area of the adsorbent (Qadeer and Akhtar, 2005).

Furthermore, the increase in percentage removal could be explained in terms of the progressive increase in the electrostatic interaction between the metal ions and the adsorbent active sites and hence more adsorption sites were being covered as the metal ion concentration get increased (Gong *et al.*, 2005). In addition, higher initial concentrations may lead to an increase in the affinity of the metal ions toward the active sites (Al-Aashel, Banat, Al-omari and Duvnjak, 2003). A comparison of the three substrates (AC₁, AC₂ and CAC) clearly showed that at any given metal ion concentrations, AC₁ could bind more of the metal ions than the AC₂ and CAC. This confirmed further that the nature of activating agents on various activated carbons prepared may play an important role in the rate of adsorption mechanism.

4.2.5 Effect of Variation of Adsorbent Dosage on Adsorption

The effects of sorbent dose on the percentage removal of metal ions are shown in Tables 4.6.1, 4.6.2 and 4.6.3. As the sorbent dose was increased from 0.5 to 2.5 g/100 cm³, the percentage removal of the metal ions increased. This increase in the sorption percentage of metal ions compared with adsorbent dose could be attributed to increase in sorbent surface area and availability of more sorption sites (Gong *et al.*, 2005). This could explain why there is high percentage removal of heavy metal. AC₁, AC₂ and CAC were able to achieve the percentage removal of metal ions in the order AC₁>AC₂>CAC. This trend could be as a result of availability of more adsorption sites in the various activated carbons (Gong *et al.*, 2005). In addition it might be attributed to the fact that the larger the surface area of adsorbent, the more the adsorption (Gong *et al.*, 2005). Furthermore, the dose of biomass added into the solution determined the number of binding sites available for biosorptions (Zafar *et al.*, 2006). A similar trend in metal uptake with variation in biosorbent dosage has been reported for Pb (II) biosorptions from its synthetic aqueous solutions by *Spirullina maxima* as dose increased from 0.5 to 2.5 g/100 cm³ (Gong *et al.*, 2005). This result was in agreement with studies by El- Ashtoukhy *et al.*, 2008.

4.2.6 Adsorptive Capacity (Q) of Metal Ions per Unit Adsorbent

The values obtained for adsorptive capacity of all the metal ions by AC₁, AC₂ and CAC increased as the metal ion concentrations increased for all the metal ions. The trend observed could be as a result of the interaction between the metal ions and the adsorbent active sites and also due to saturation of the adsorption sites after 90 min after which there was no increase in adsorption observed as the contact time increased.

The result showed that chromium ion has smaller ionic size was adsorbed at a faster rate and had highest adsorptive capacity in AC₁, AC₂ and CAC respectively. The order of adsorptive capacity (Q) is Cr>Mn>Cu>Cd>Ni>Co>Pb in all the adsorbents. This could be explained considering the ionic radius of Cr (VI) and Mn (III) with high Q than Cu (II), Cd (II), Ni (II), Co (II), and Pb (II) as reported by Abia *et al.*, 2003. This therefore showed that the smaller the ionic radii the greater the affinity to the reactive sites and since Cr (VI), Mn (III) ions have smaller ionic radii, it could be possible that they would diffuse

faster through the adsorbent surface than the bulkier ions like Cu (II), Cd (II), Ni (II), Co (II) and Pb (II) and hence the ions of smaller radii would tend to move faster to potential adsorption sites (Abia and Osuguo, 2006).

4.2.7 Adsorption Kinetics

The adsorption isotherms described how the adsorbed molecules are been distributed between the liquid phase and the solid phase when adsorption process reaches an equilibrium state (Hameed *et al.*, 2008). Equilibrium studies are described by sorption isotherm characterized by certain constants whose values express the surface properties and affinity for the sorbent as well as a step to find the suitable model that can be used for design purpose. The results obtained in this study were tested with four isotherm equations namely: Pseudo first-order equation (Lagergren, 1898), Pseudo second- order equation (Ho and Mckay, 1999), Natarajan and Khalaf first order equation (Raji, Manju and Amirudhan, 1986), and Elovich model equation (Chien and Clayton, 1980; Sparks, 1986). The result showed that the equilibrium data fitted pseudo second order compared to pseudo first order, Natarajan and Khalaf and Elovich model tested (Table 4.8).

4.2.8 Effect of pH on the Percentage Removal

The pH of the solution has a significant impact on the uptake of heavy metals. This is because it is the determinant factor for the surface charge of the adsorbent, degree of ionization and speciation of the adsorbate (Karnitz *et al.*, 2006). From the result of the effect of pH on the biosorptions of Cr (III), Pb (II), Cu (II), Cd (II), Co (II), Ni (II) and Mn (III) ions by AC₁, AC₂ and CAC shown in the Tables 4.7.1 and 4.7.2, it was observed that the removal for percentage the respective ions increased with increase in pH value. The minimum removal of the metal ions observed at low pH of 1.0 to 2.0 could be attributed to the protons competing with metal ions for active sites i.e. there is a high H⁺ concentration and the adsorbent surface becomes more positively charged thus reducing the attraction between adsorbent and metal ions. But as the pH increases there is availability of more negatively charged surface and this

reduces the competition between proton and metal ions and thus facilitate greater metal uptake. pH effect on biosorptions equilibrium has been reported to be necessary for an accurate evaluation of biosorptions process (Wase and Forster, 1997). The highest adsorption of Pb (II) at pH 5.0 and Ni (II) at pH 4 and as the pH increased further, adsorption reduced is in line with what was reported by Rozaini, Jain, Tan, Azraa and Tong, 2010 who studied the possibility of using modified mangrove barks to optimize the removal of Ni (II) and Cu (II) ions. The highest adsorption for Cd (II) and Pb (II) ions occurred at pH 4.0 and pH 5.0 respectively and with further increase in pH there was decreased in adsorption. Similar result was obtained when effect of pH on sorption of Cd (II), Pb (II), Ni (II) and Cr (III) ions by unmodified African white star apple were studied by Onwu and Ogah, 2010. Above all it was well documented that the high pH favours both adsorption and precipitation of heavy metal cations (Malamis, Katsou, Stylianou, Haralambous and Loizidou 2010).

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this study, the ability of *Balanites aegyptiaca* seeds to bind Cr (VI), Pb (II), Cu (II), Cd (II), Ni (II), Co (II) and Mn (II) ions from aqueous solution was investigated and found to be an effective biosorbent for the removal of heavy metals in aqueous system. The adsorption on *Balanites aegyptiaca* seeds increased with increase in sorbate concentration and pH. The optimum pH range for Cr (VI), Pb (II), Cu (II), Cd (II), Co (II), Ni (II) and Mn (III) ions biosorption was pH 4.0 and pH 5.0 using activated carbon prepared from tetraoxophosphate V acid as activating agent (AC₁), activated carbon prepared from activating agent zinc

chloride (AC₂) and commercial activated carbon (CAC), respectively. The kinetic study showed that the biosorptions study could be better explained using pseudo second order kinetics compared with pseudo first order, Elovic model, Natarajan and Khalaf models. Due to the high correlation coefficient obtained by using the pseudo-second order kinetic model, the results can be represented well by the pseudo-second order model. The adsorption capacity of metals varied from one metal system to another, and depended upon the presence of other metals in the solution. Also, intraparticle diffusion plots indicate that both surface adsorption and pore diffusion are involved in metal adsorption on AC₁, AC₂ and CAC. The results of this study suggest that an adsorption system utilizing *Balanites aegyptiaca* seeds can be an economically feasible technique for the treatment of heavy metals in aqueous solution and above all, this result can be considered as a fundamental step for the representation of the experimental behavior and for development of process design since the main adsorption mechanism is probably a chemisorptions reaction.

5.2 Recommendations

As a result that the *Balanites aegyptiaca* plant has not been efficiently utilized in the field of adsorption process but rather in medical and biodiesel production, it is therefore recommendations that apart from plant seed used in this study, other parts of the plant should be investigated to ascertain its feasibility for biosorptions process. The particle size of the prepared activated carbon and the functional groups present in the activated carbon which is responsible for its adsorptive capacity should be investigated. Furthermore, more biosorptions models and isotherms should be employed to test further the feasibility of this plant for adsorption. Finally, the raw powdered sample and activated charcoal prepared from the sampled seed should be used on both industrial effluent and aqueous solution to compare their adsorption efficiencies.

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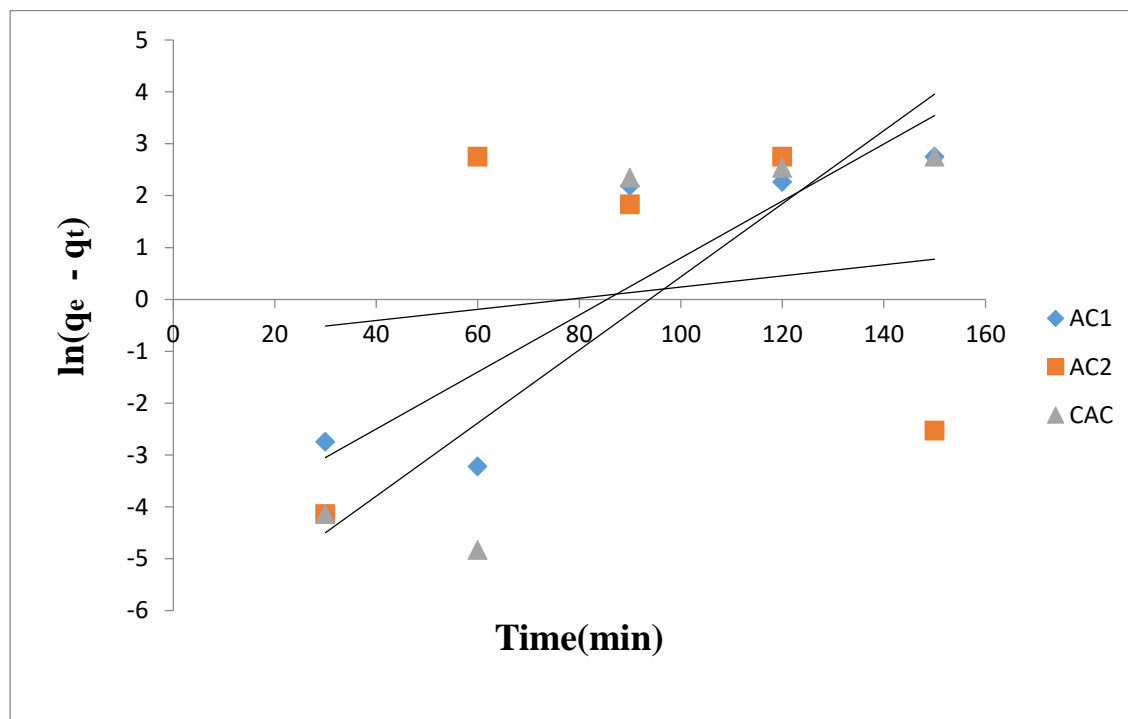
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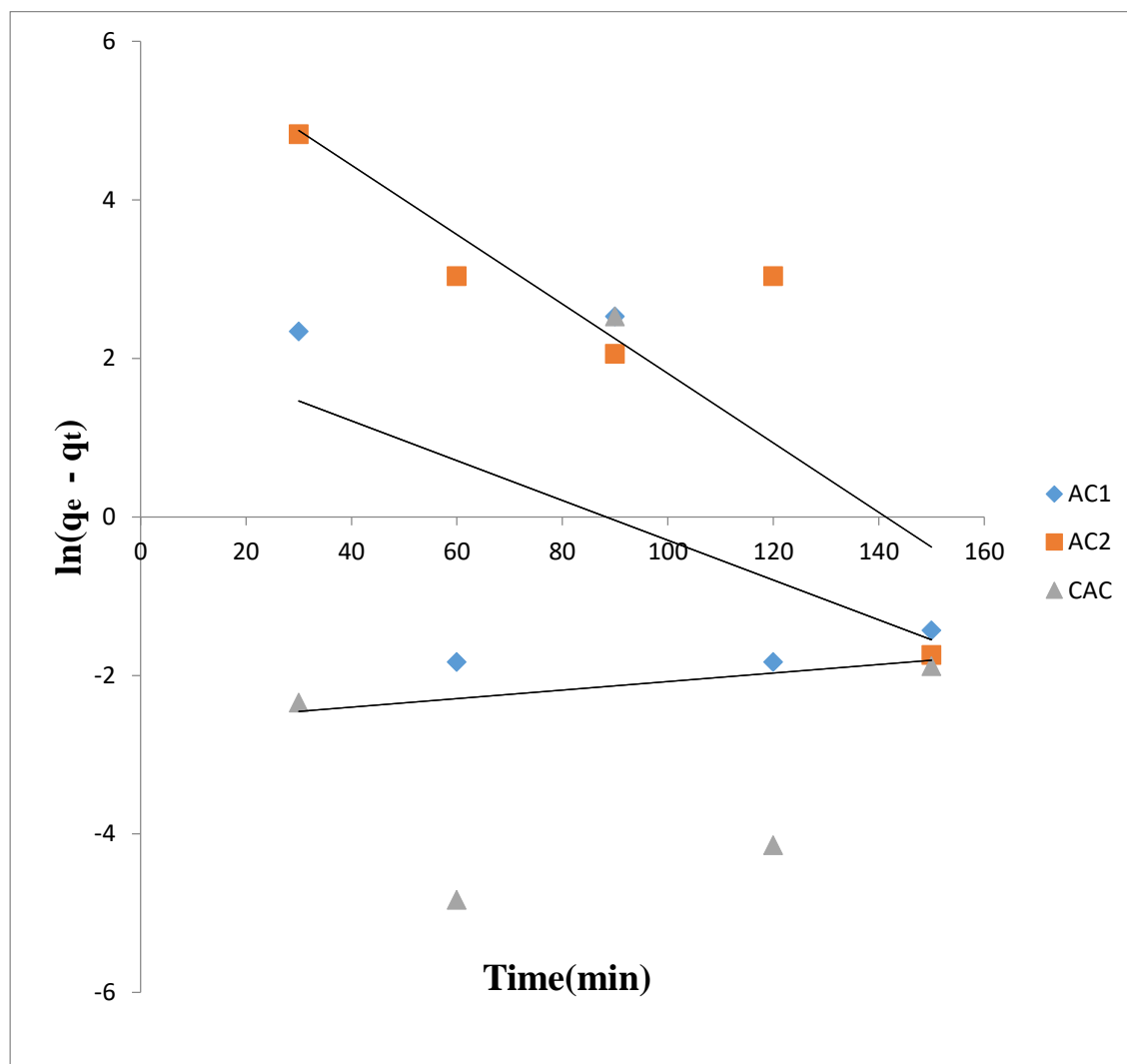
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Appendix A1



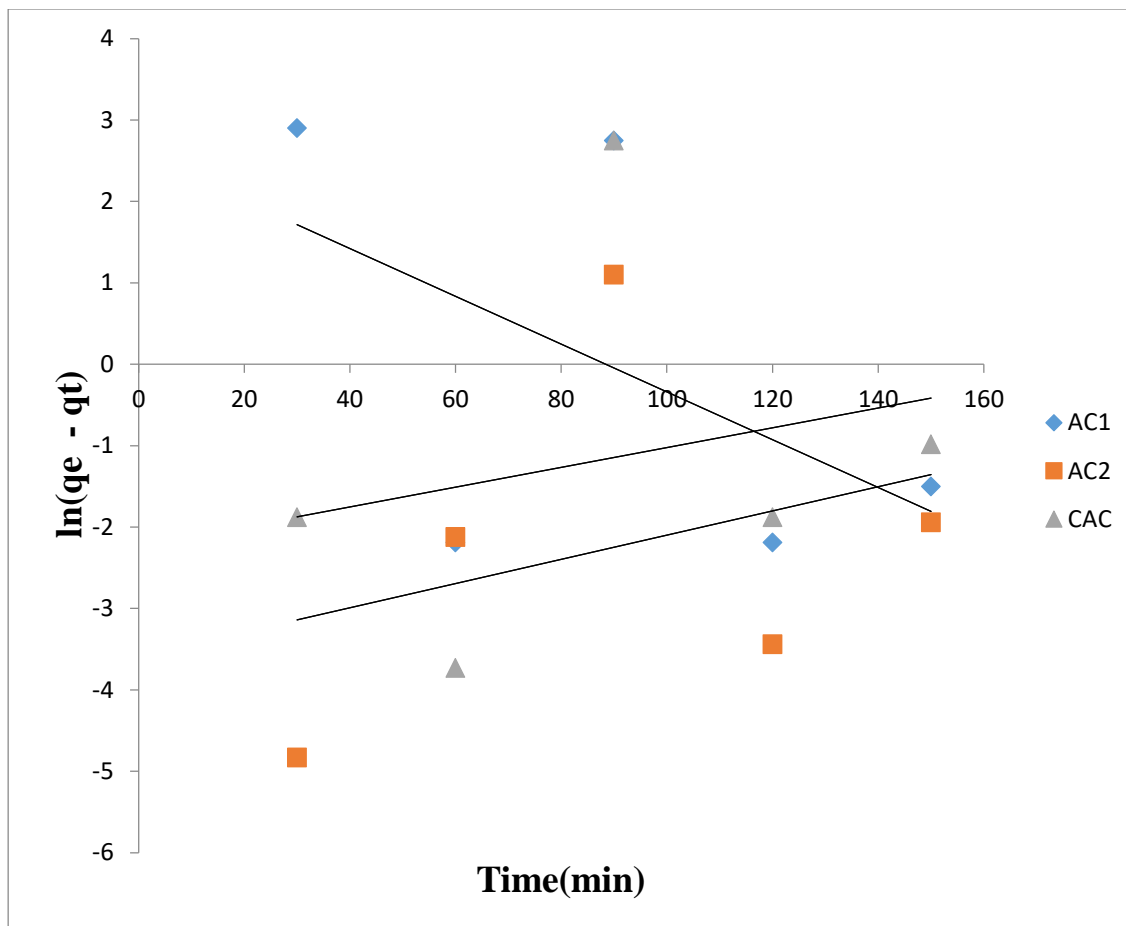
First order plots for adsorption of Chromium onto different types of adsorbents.

Appendix A2



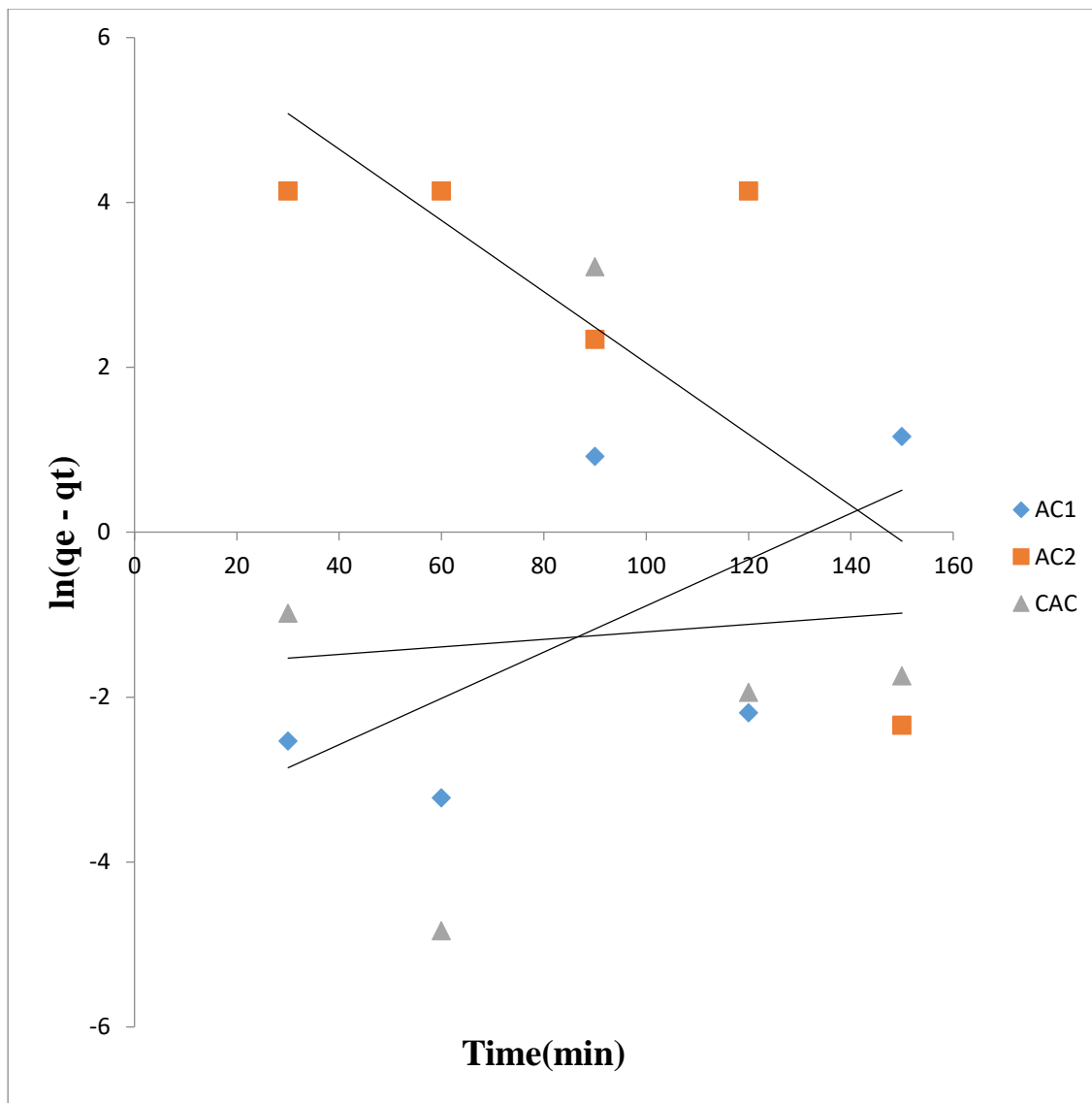
First order plots for adsorption of Lead onto different types of adsorbents.

Appendix A3



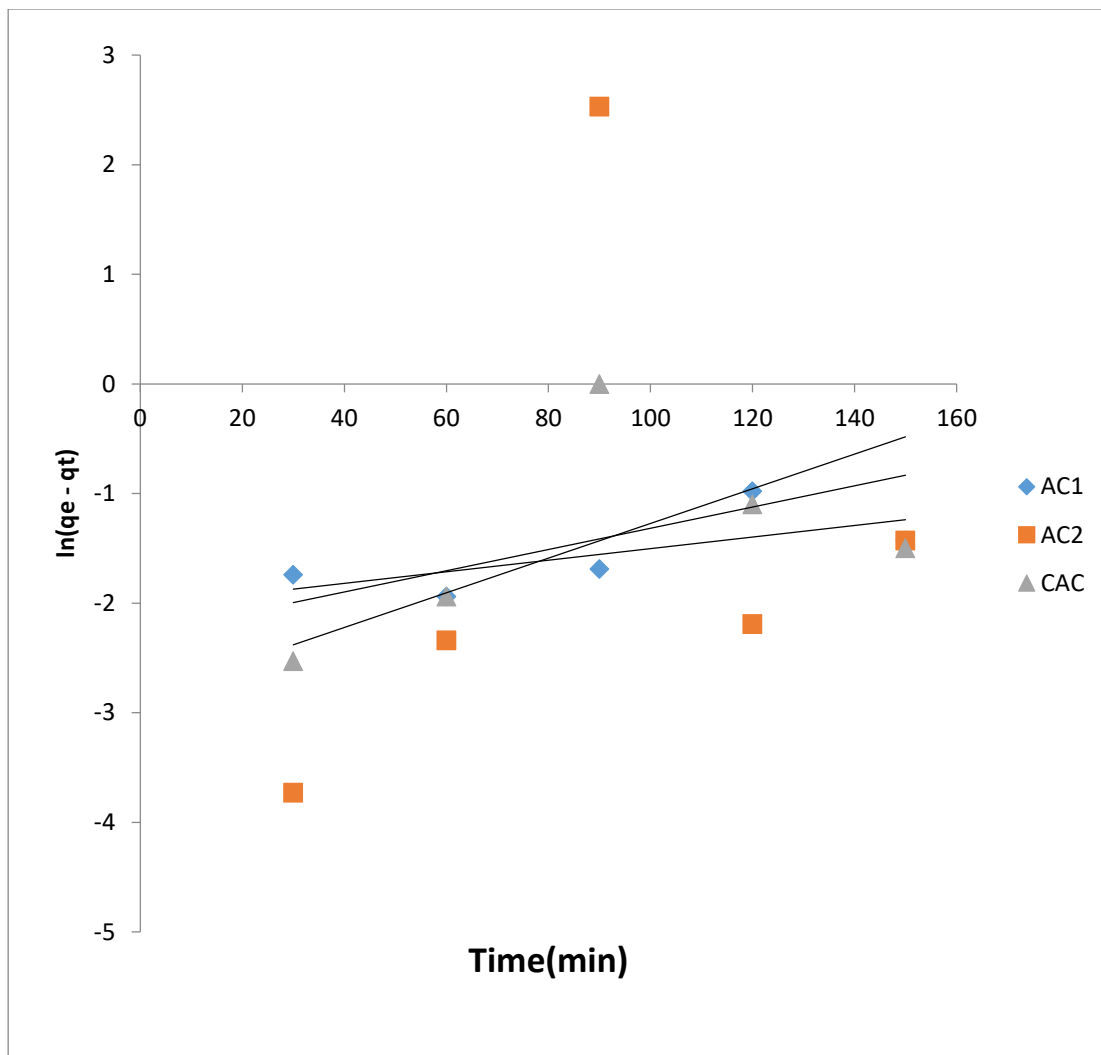
First order plots for adsorption of Copper onto different types of adsorbents.

Appendix A4



First order plots for adsorption of Cadmium onto different types of adsorbents.

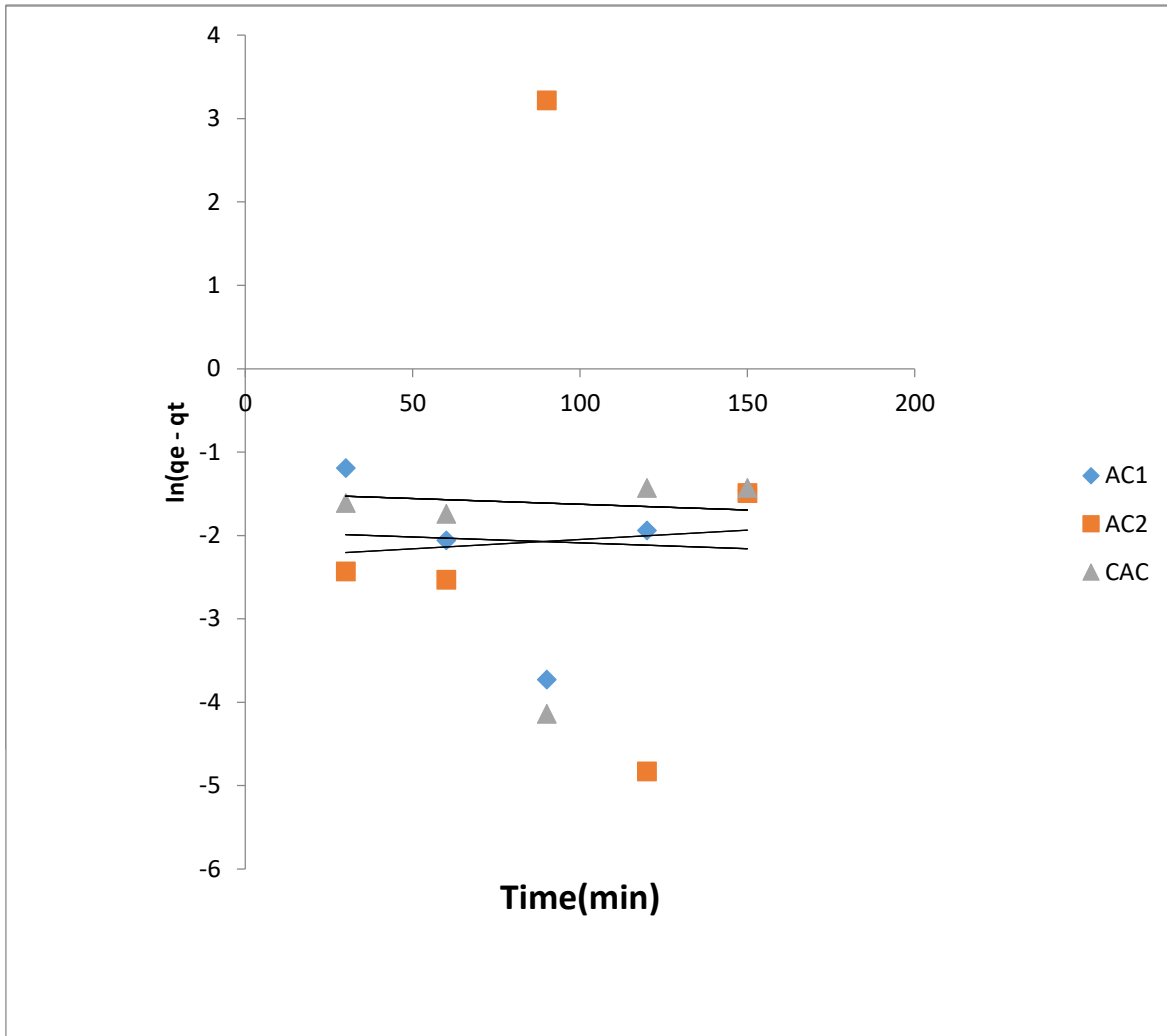
Appendix A5



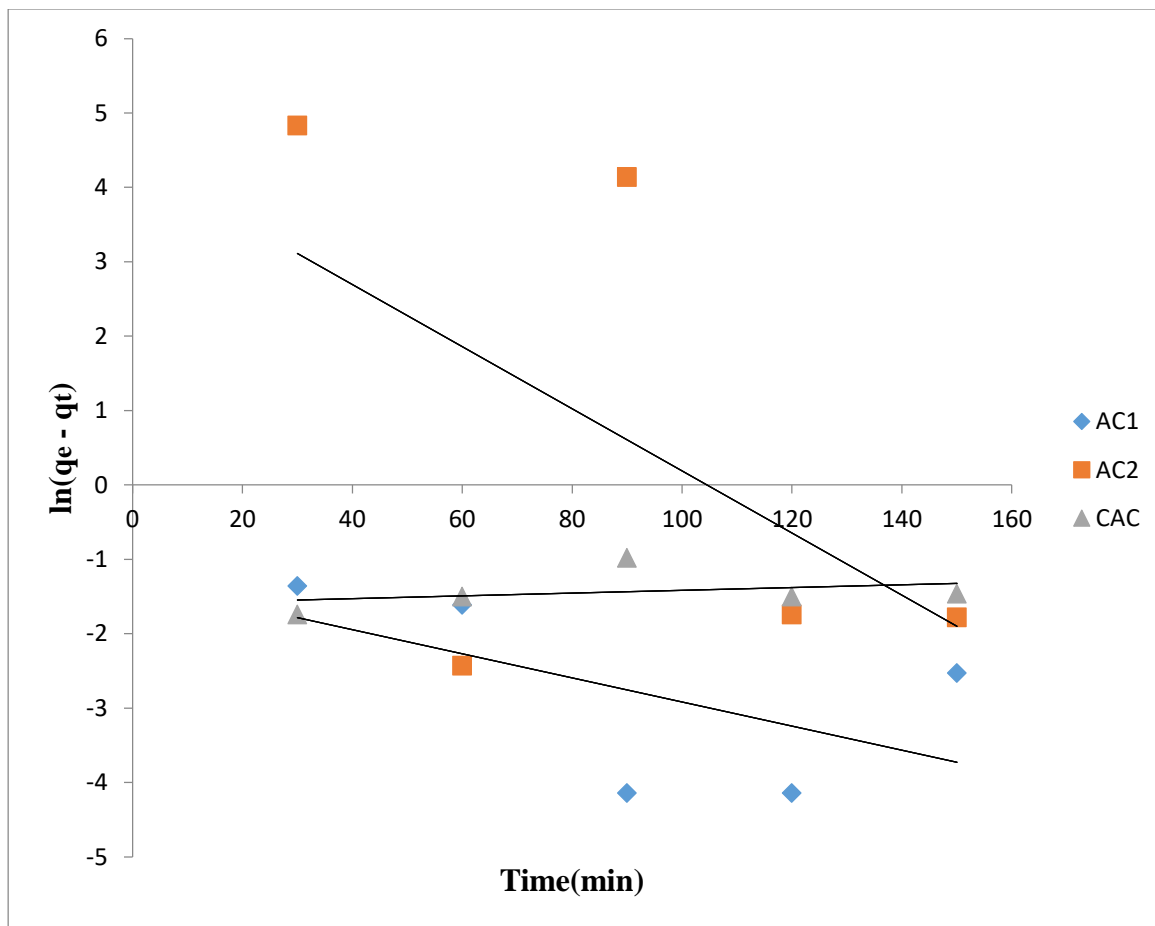
First order plots for adsorption of Nickel onto different types of adsorbents.

Appendix A6

First order plots for adsorption of cobalt onto different types of adsorbents

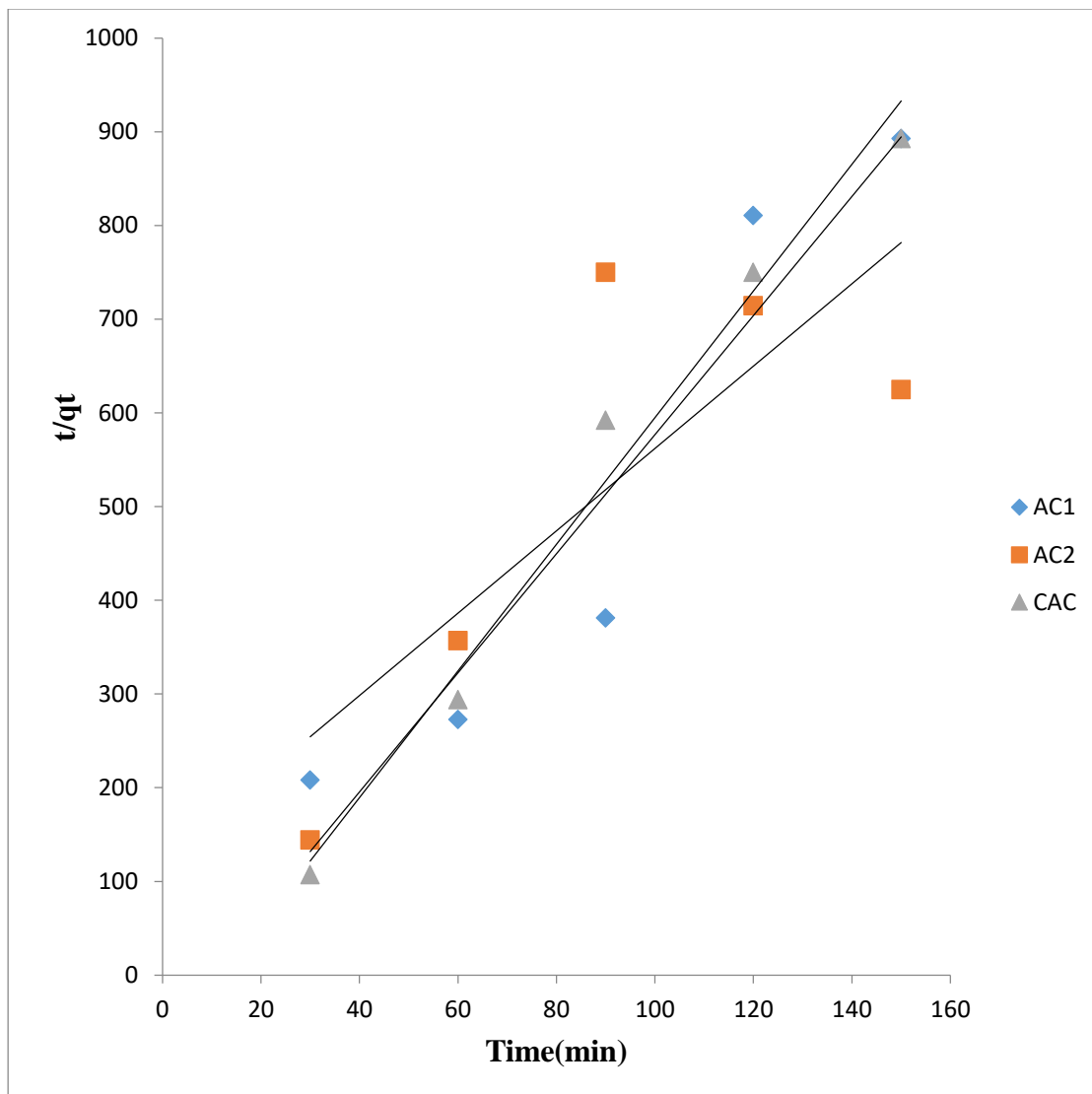


Appendix A7



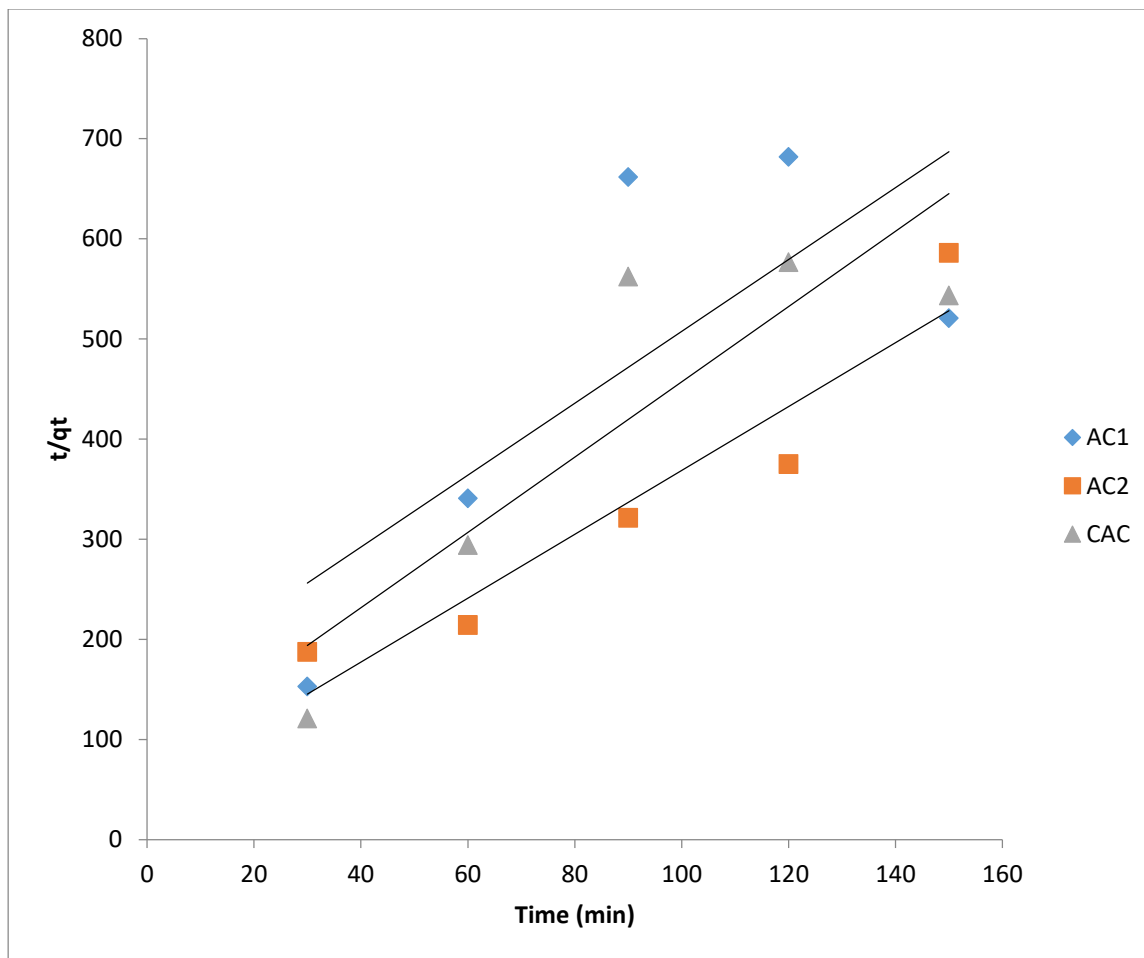
First order plots for adsorption of Manganese onto different types of adsorbents

Appendix A8



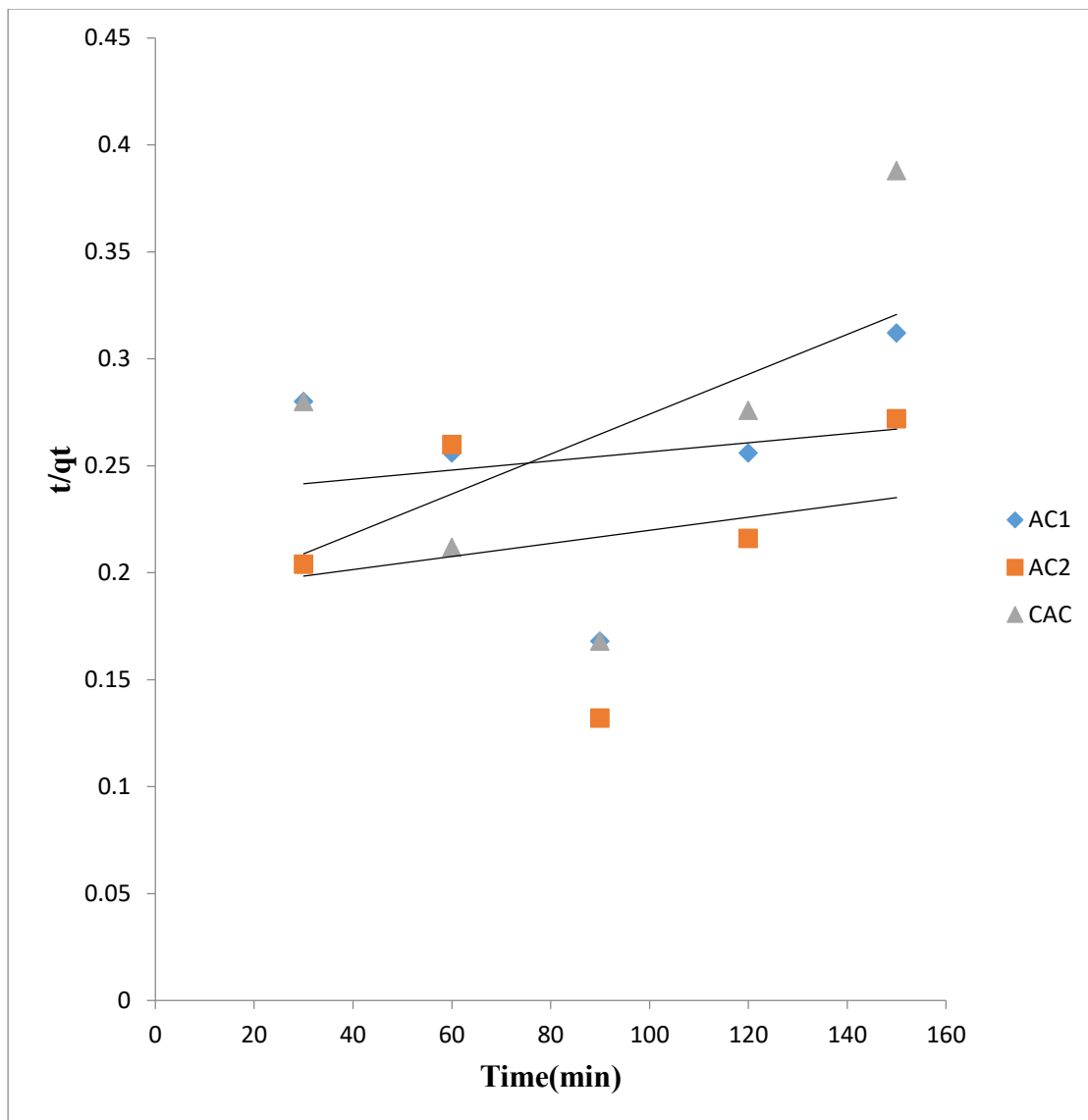
Second order plot of Chromium onto different types of adsorbents

Appendix A9



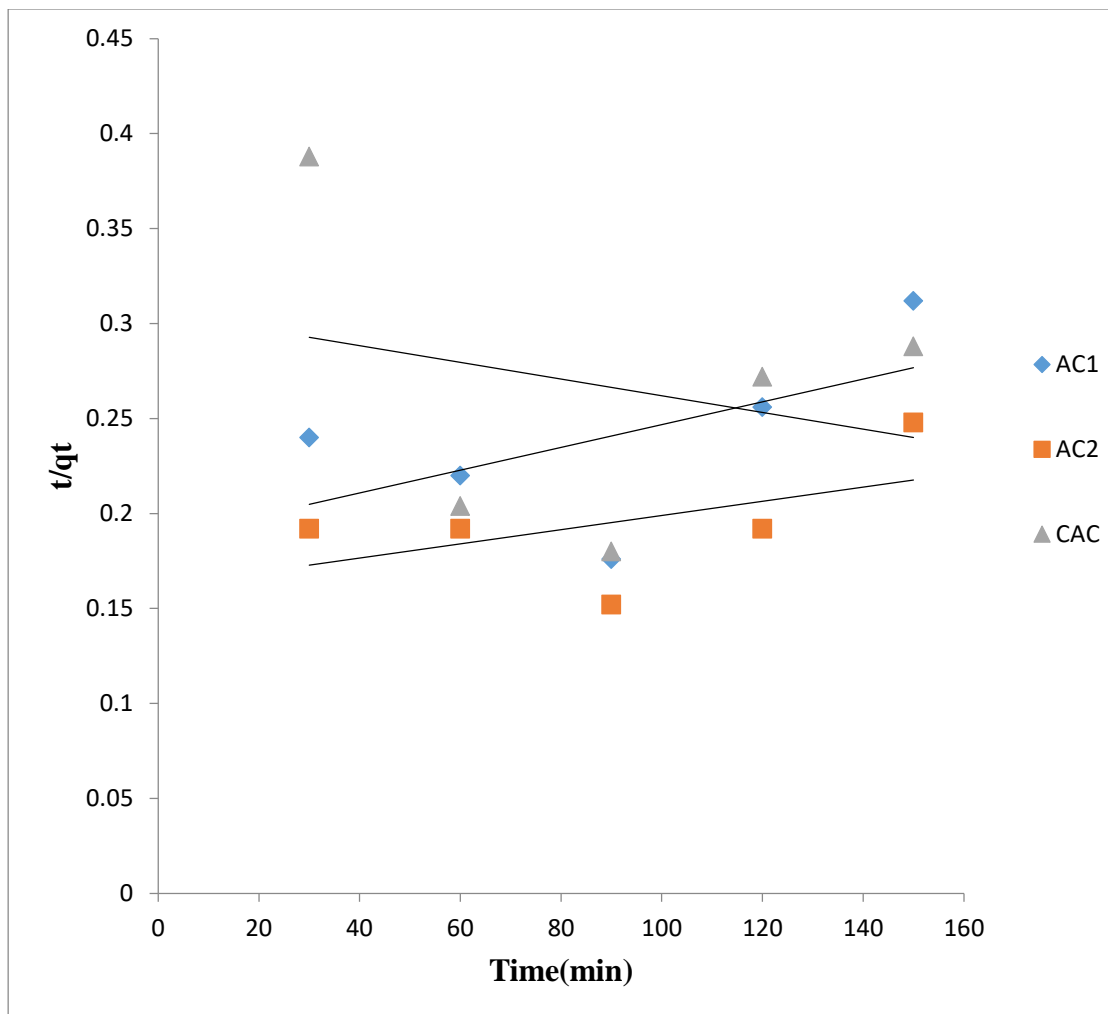
Second order plot of Lead onto different types of adsorbents.

Appendix A10



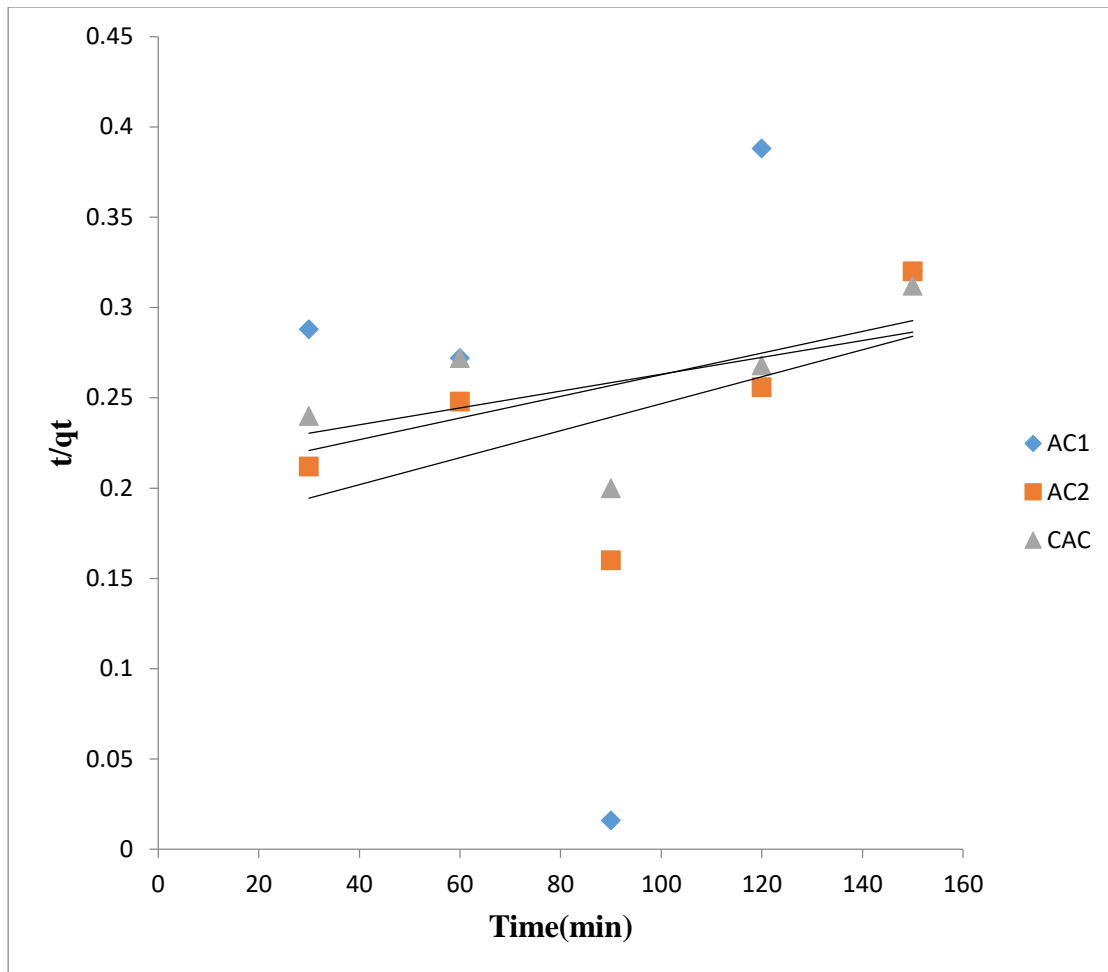
Second order plot of Copper onto different types of adsorbents.

Appendix A11



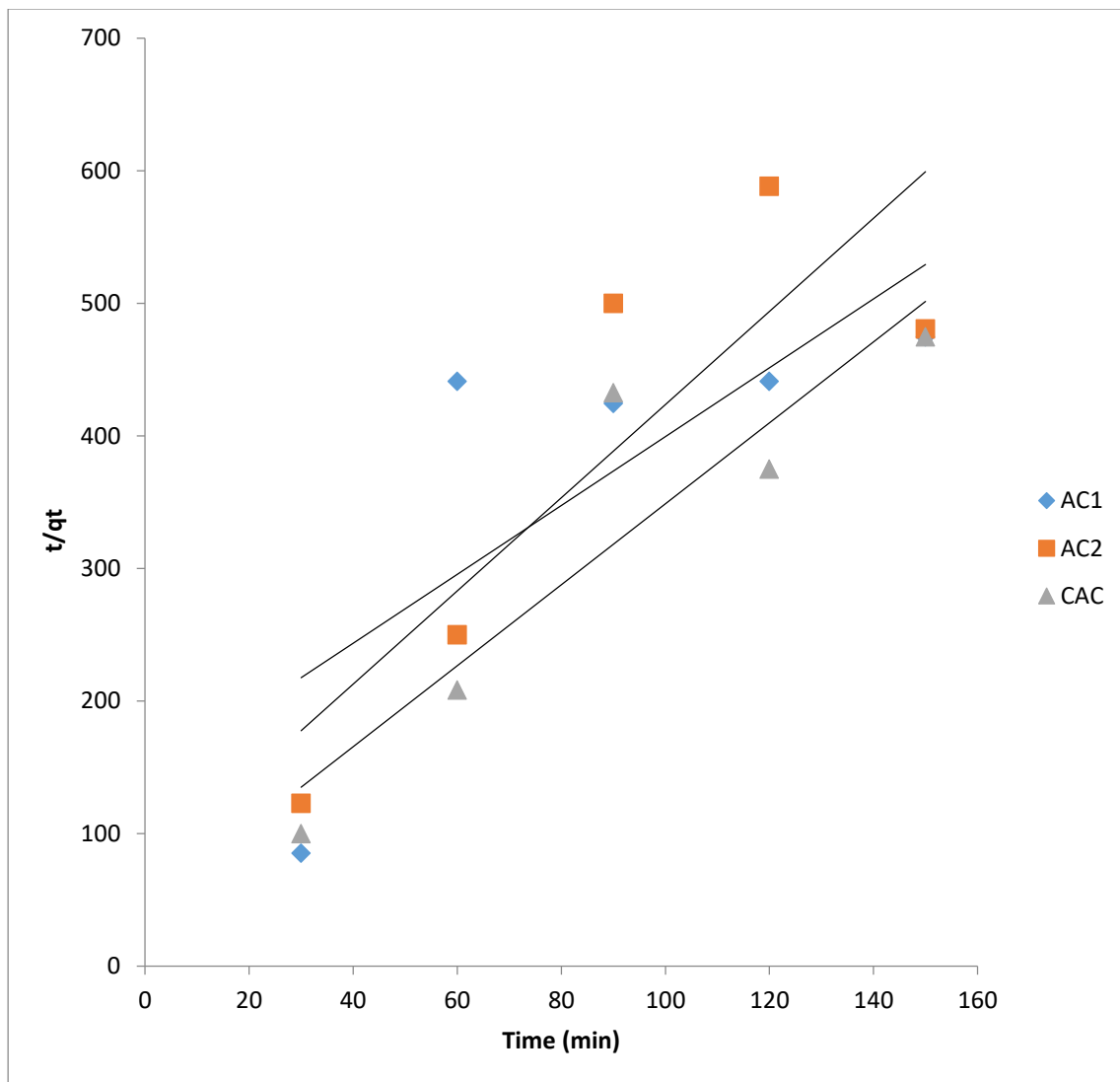
Second order plot of Cadmium onto different types of adsorbents.

Appendix A12



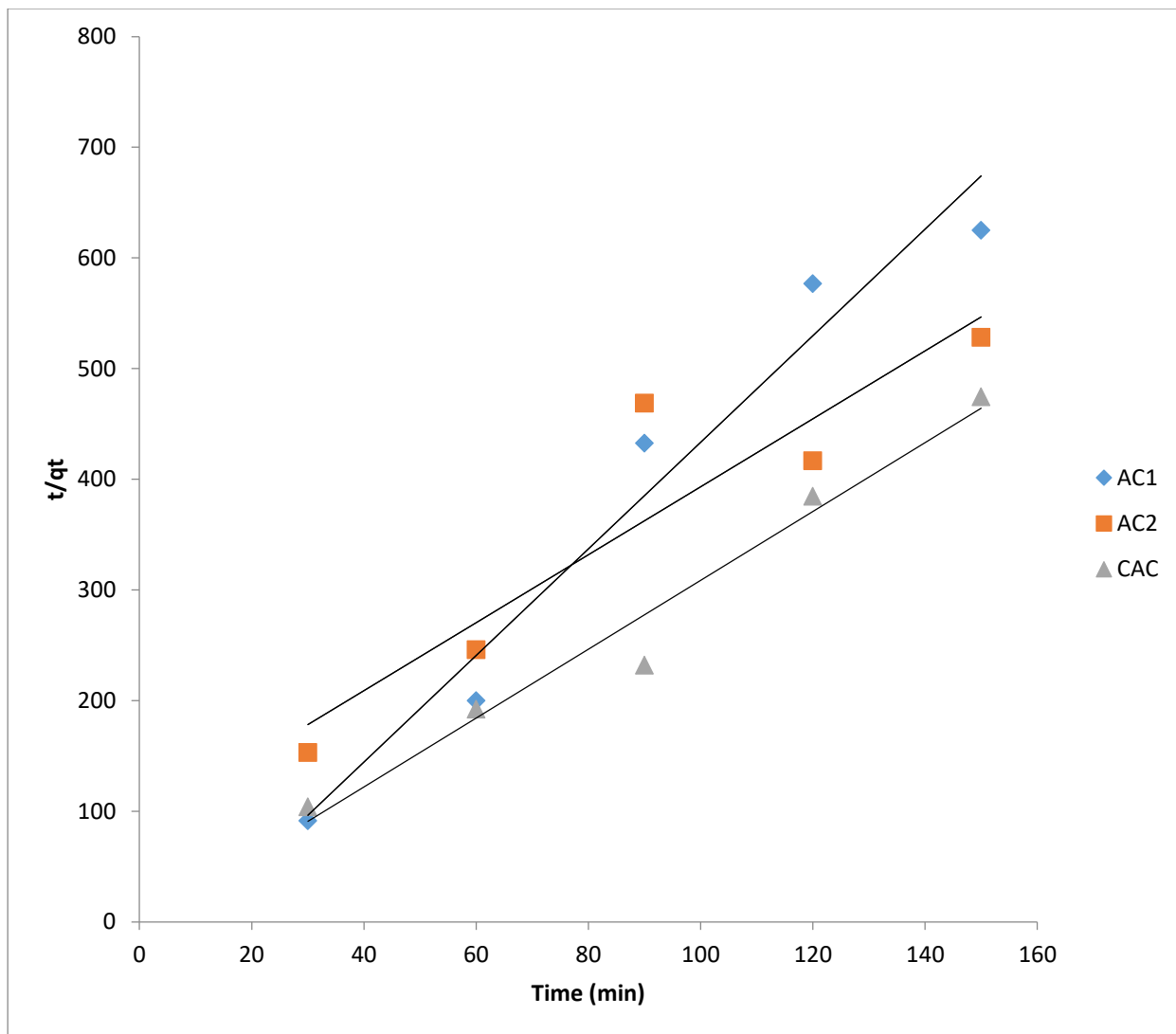
Second order plot of Nickel onto different types of adsorbents.

Appendix A13



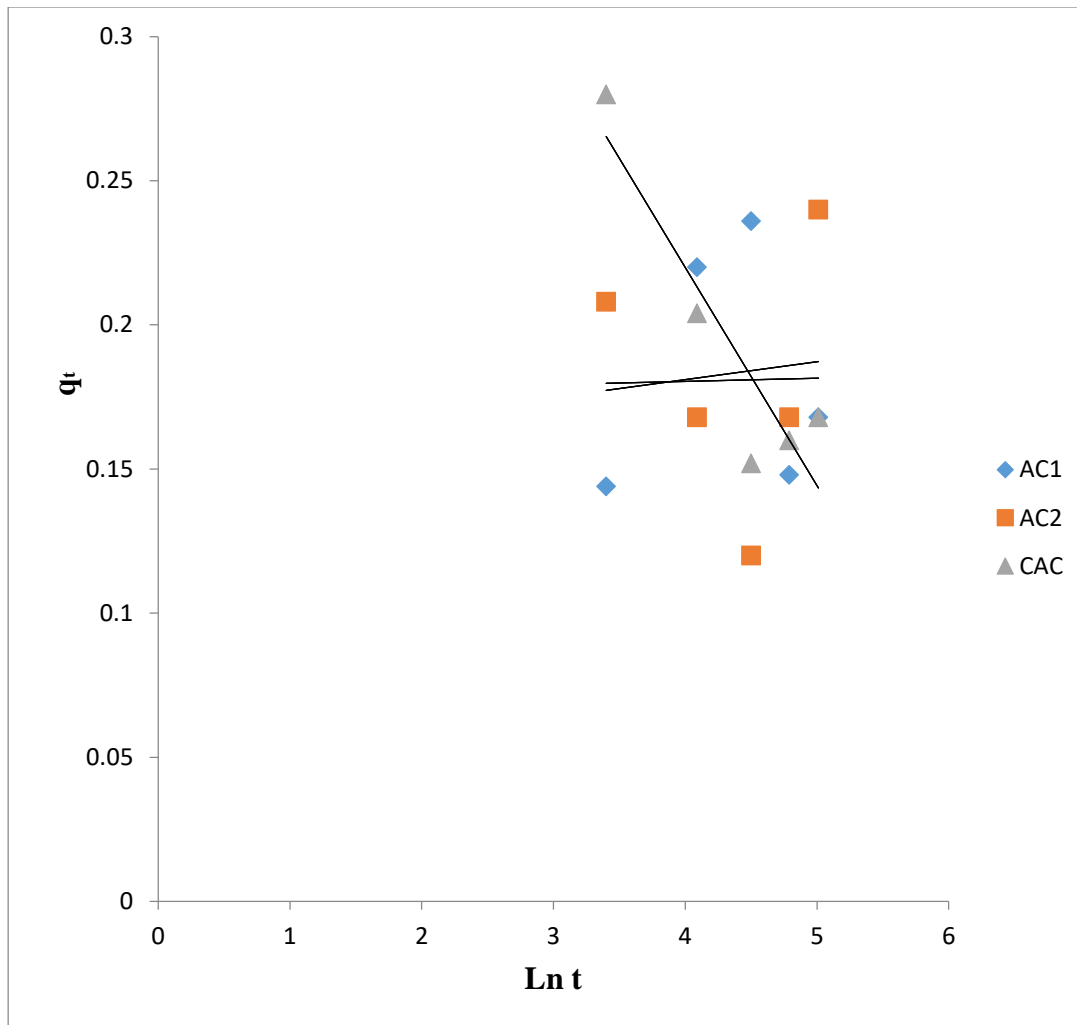
Second order plot of Cobalt onto different types of adsorbents.

Appendix A14



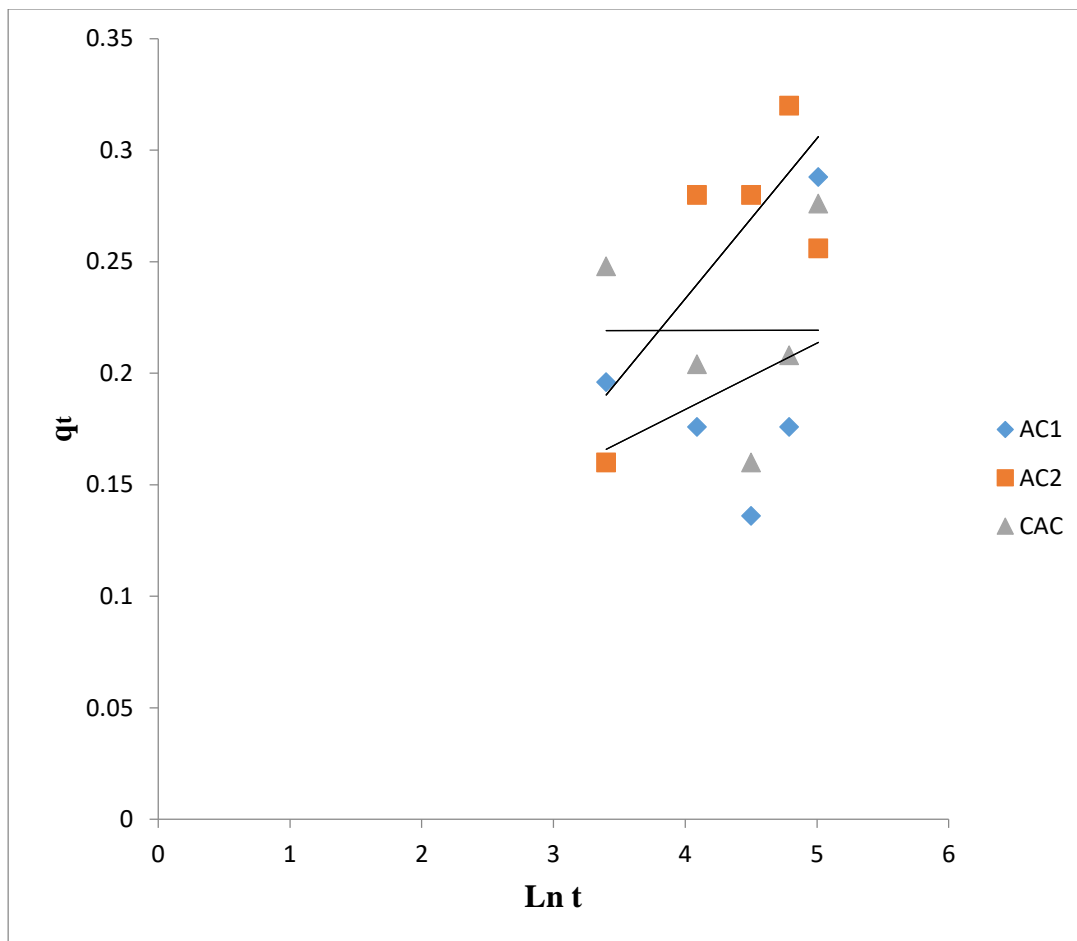
Second order plot of Manganese onto different types of adsorbents.

Appendix A15



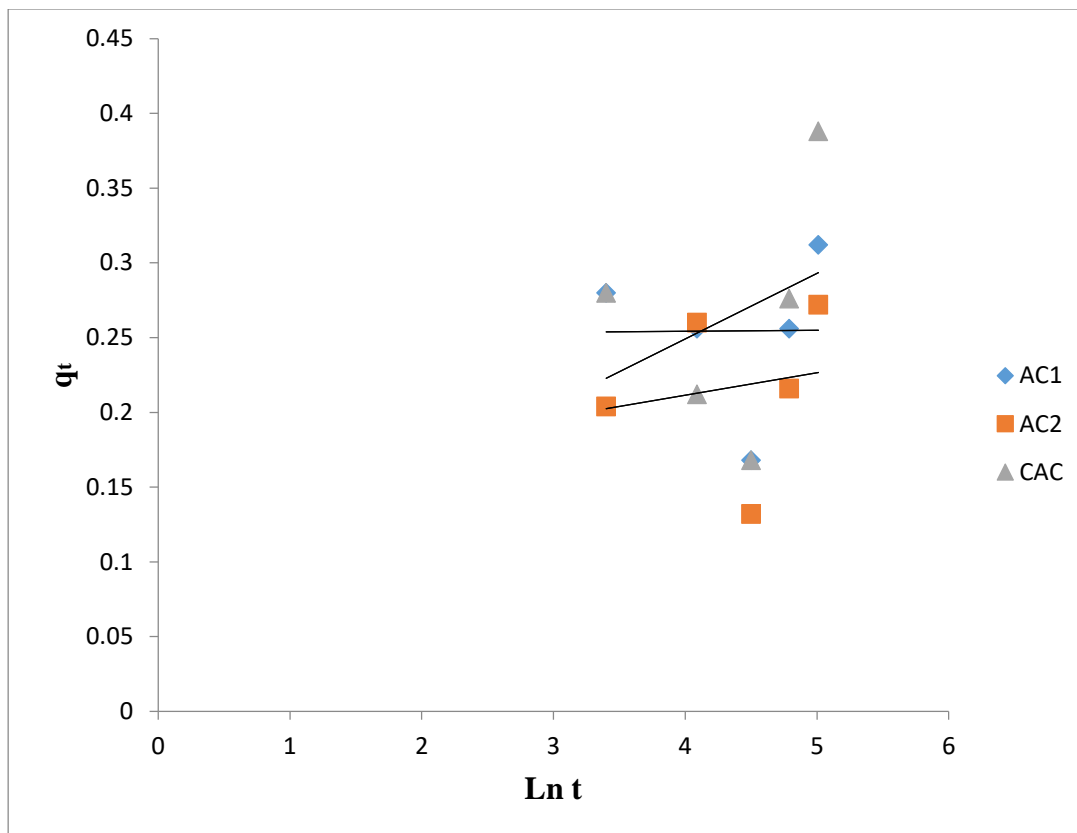
Elovich plot for adsorption of chromium onto different types of adsorbents.

Appendix A16



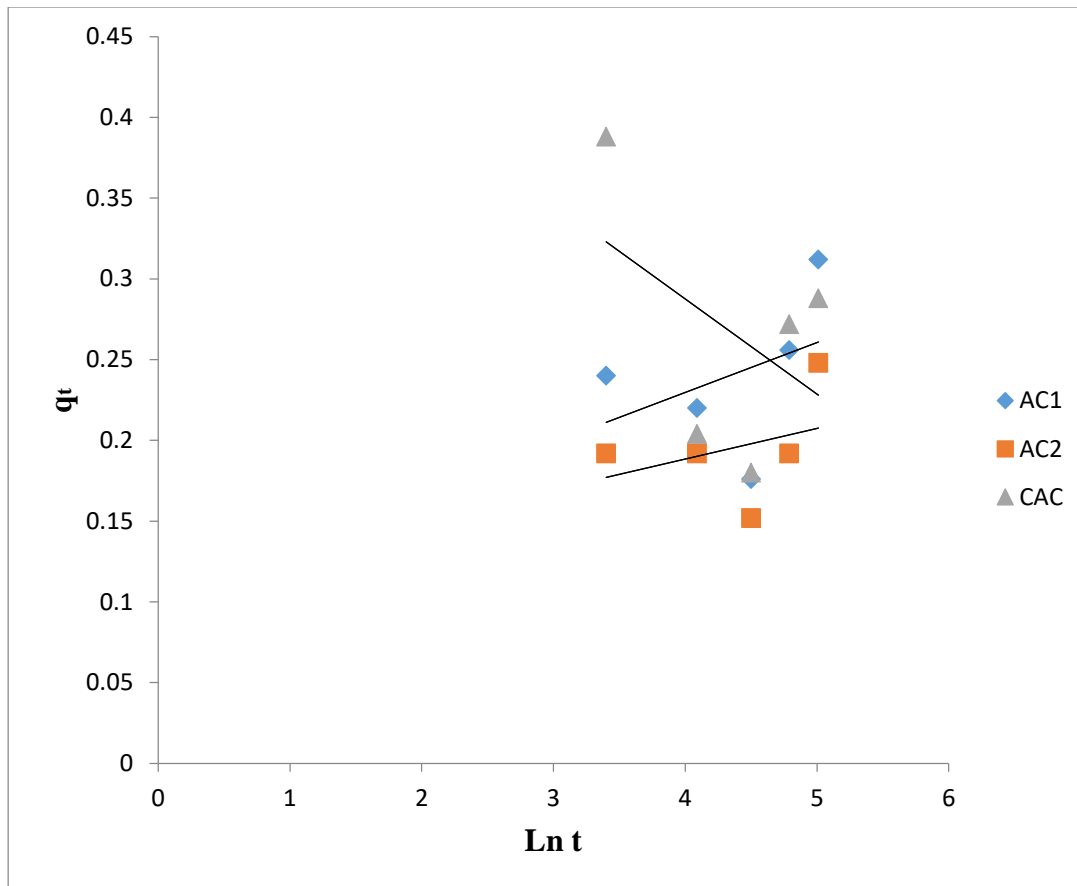
Elovich plot for adsorption of lead onto different types of adsorbents.

Appendix A17



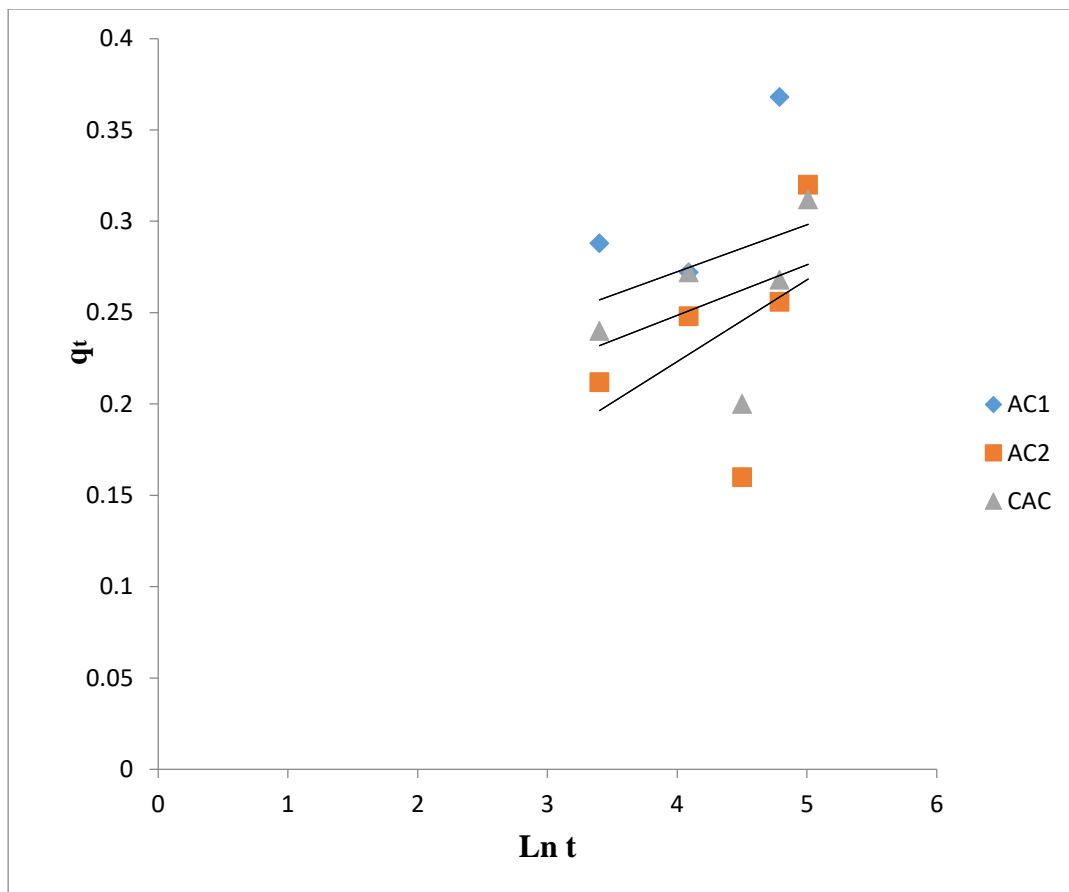
Elovich plot for adsorption of copper onto different types of adsorbents.

Appendix A18



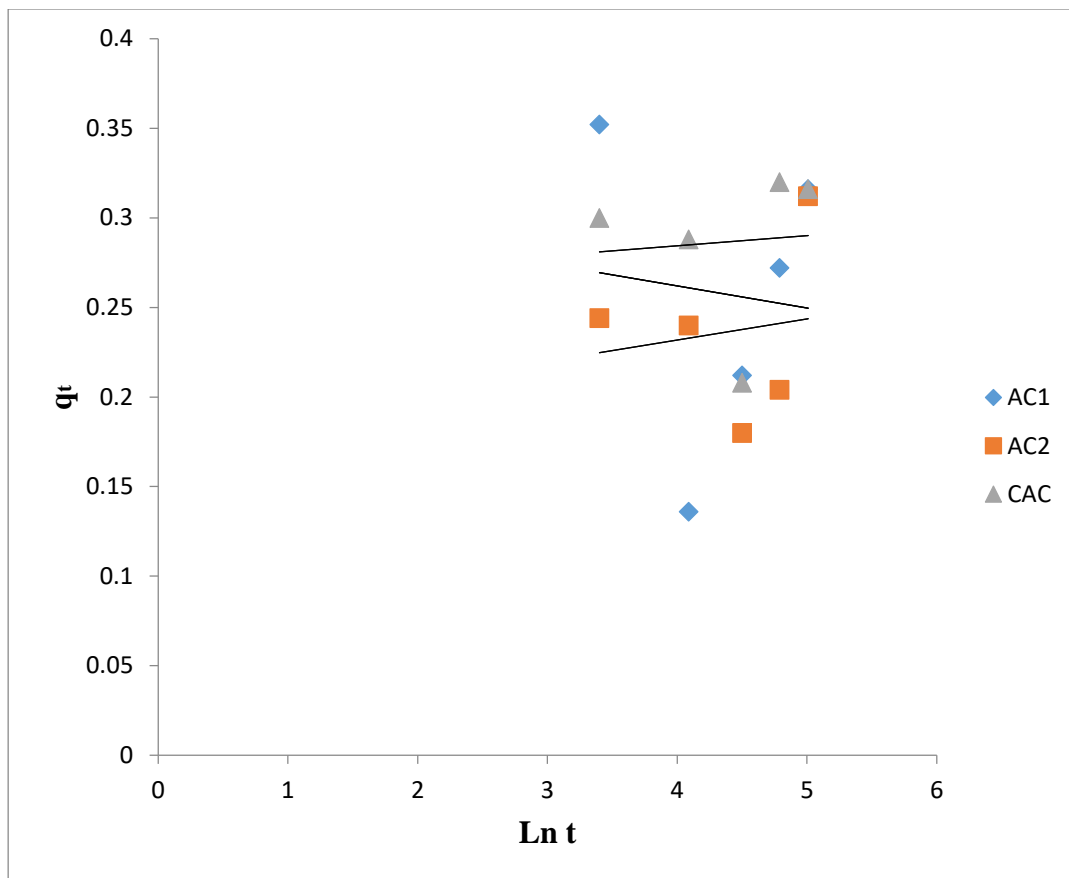
Elovich plot for adsorption of cadmium onto different types of adsorbents.

Appendix A19



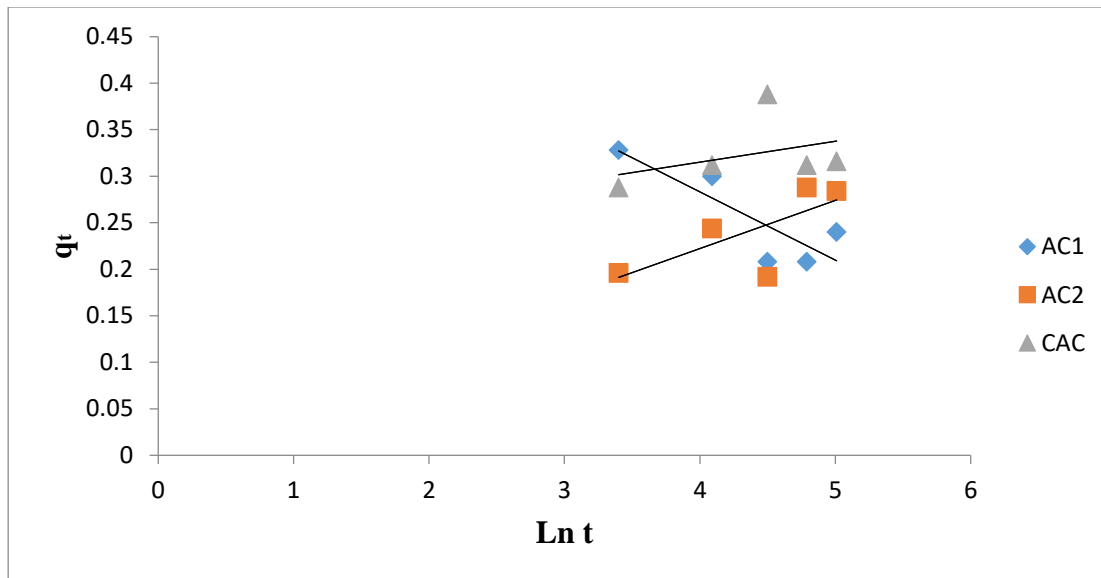
Elovich plot for adsorption of Nickel onto different types of adsorbents.

Appendix A20



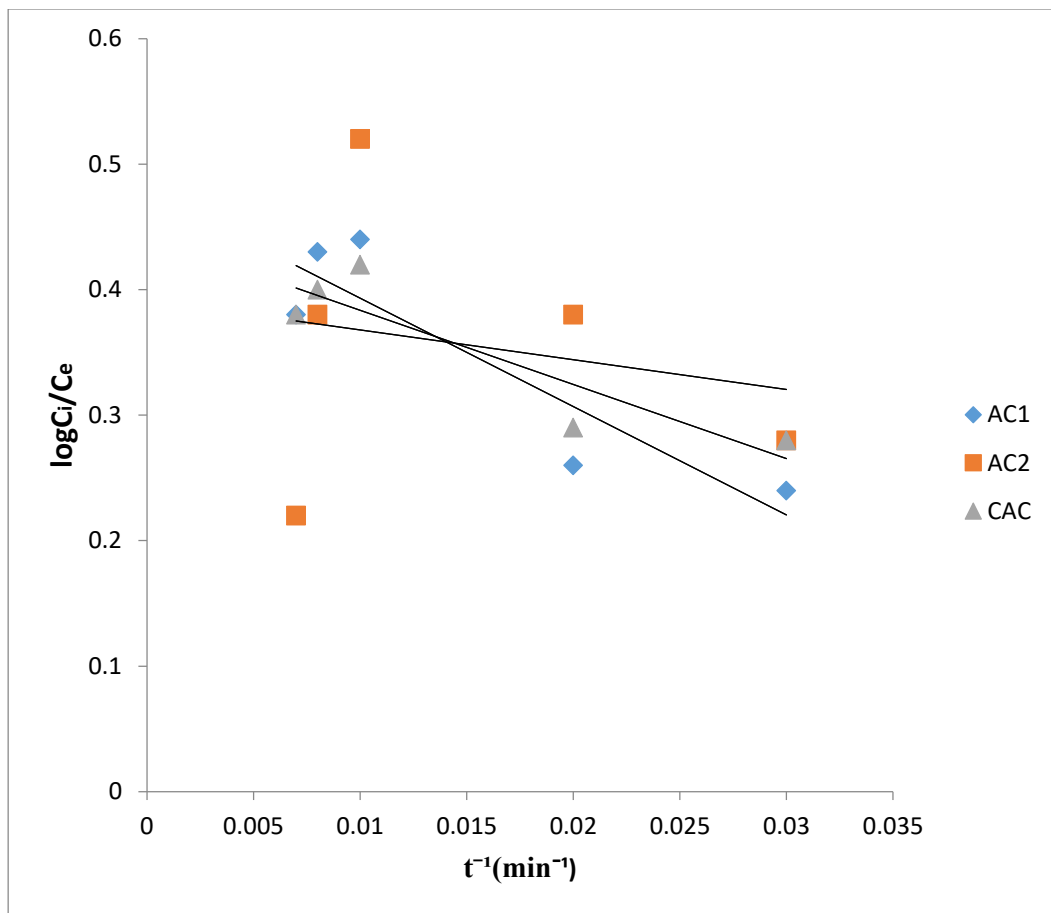
Elovich plot for adsorption of cobalt onto different types of adsorbents.

Appendix A21



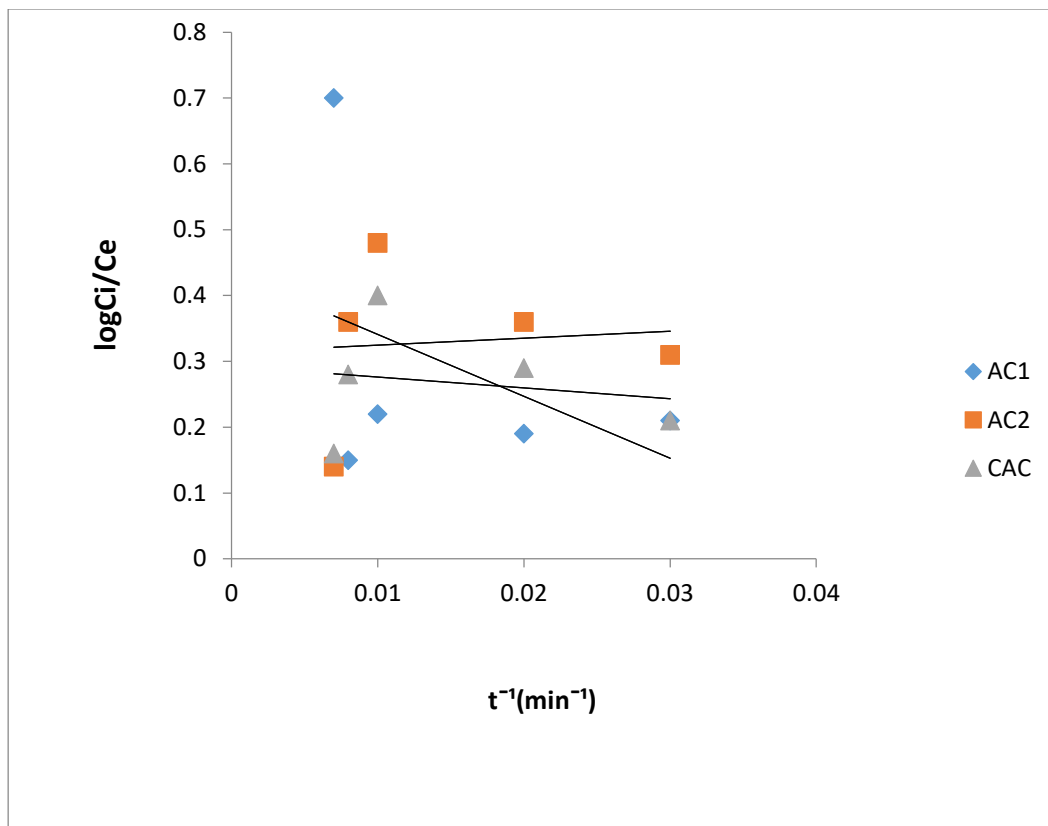
Elovich plot for adsorption of manganese onto different types of adsorbents.

Appendix A22



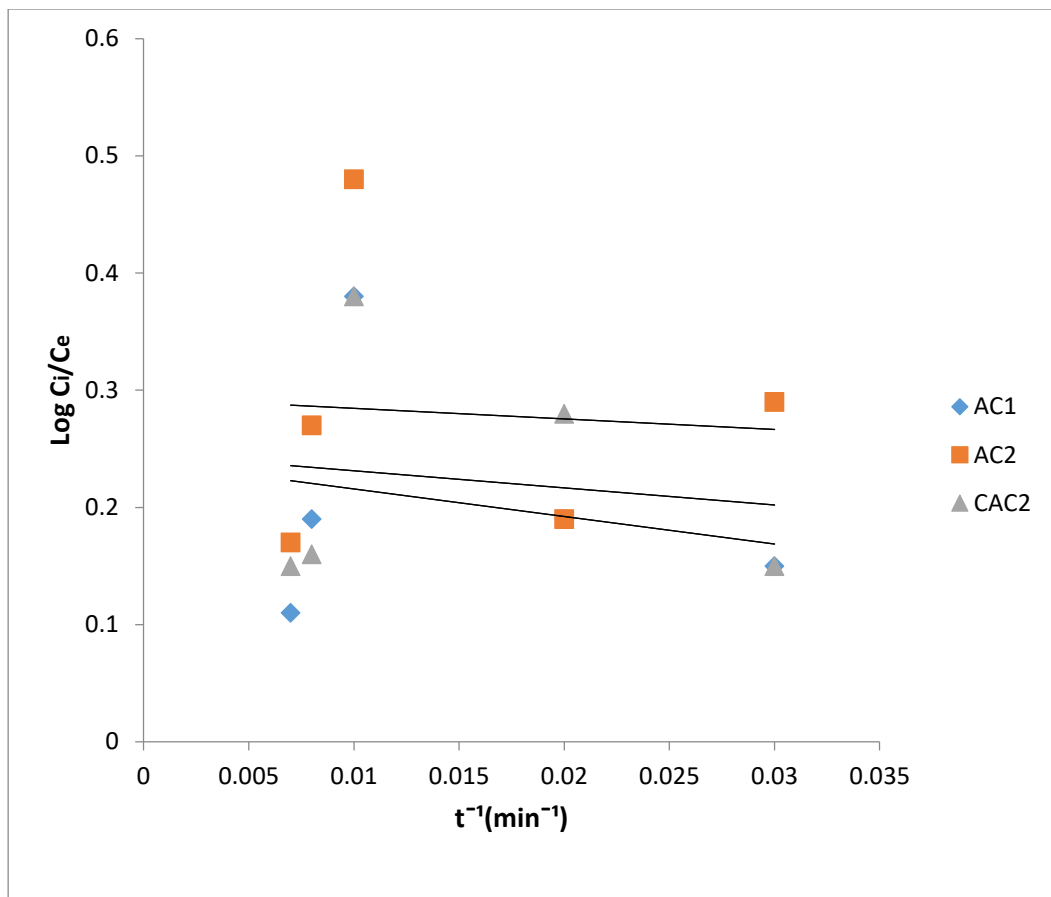
Natarajan plot for adsorption of chromium onto different types of adsorbents.

Appendix A23



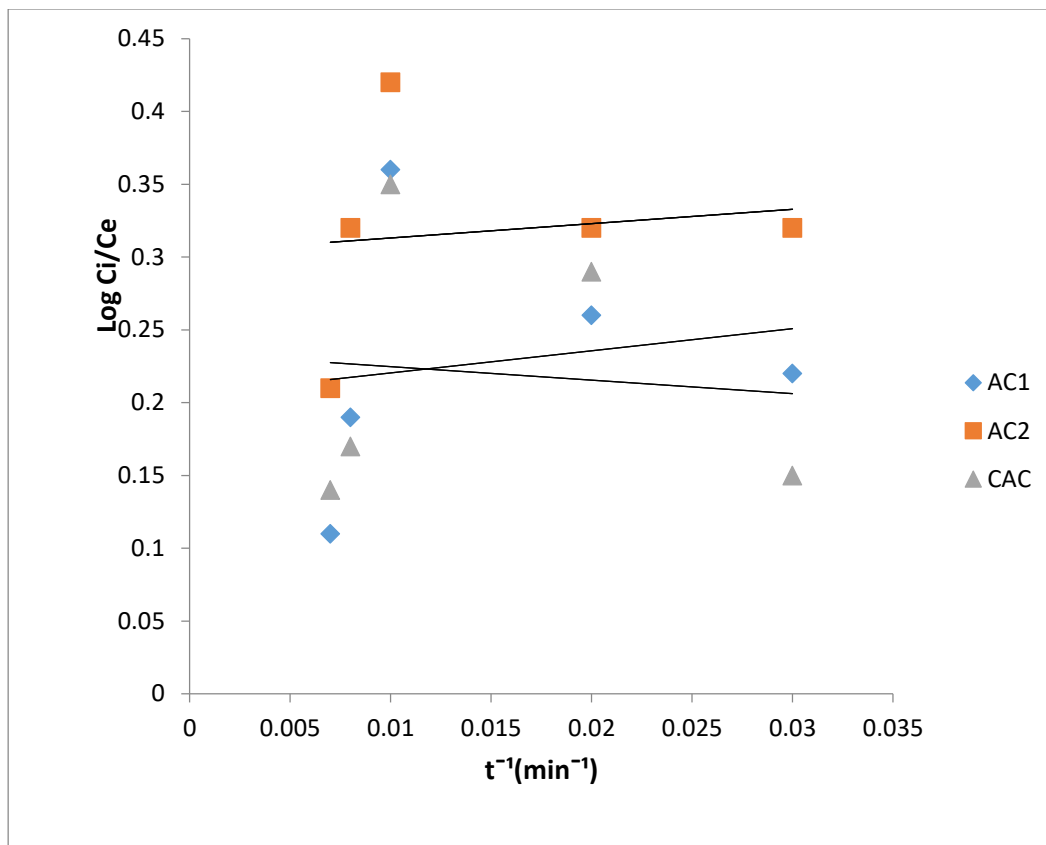
Natarajan plot for adsorption of lead onto different types of adsorbents.

Appendix A24



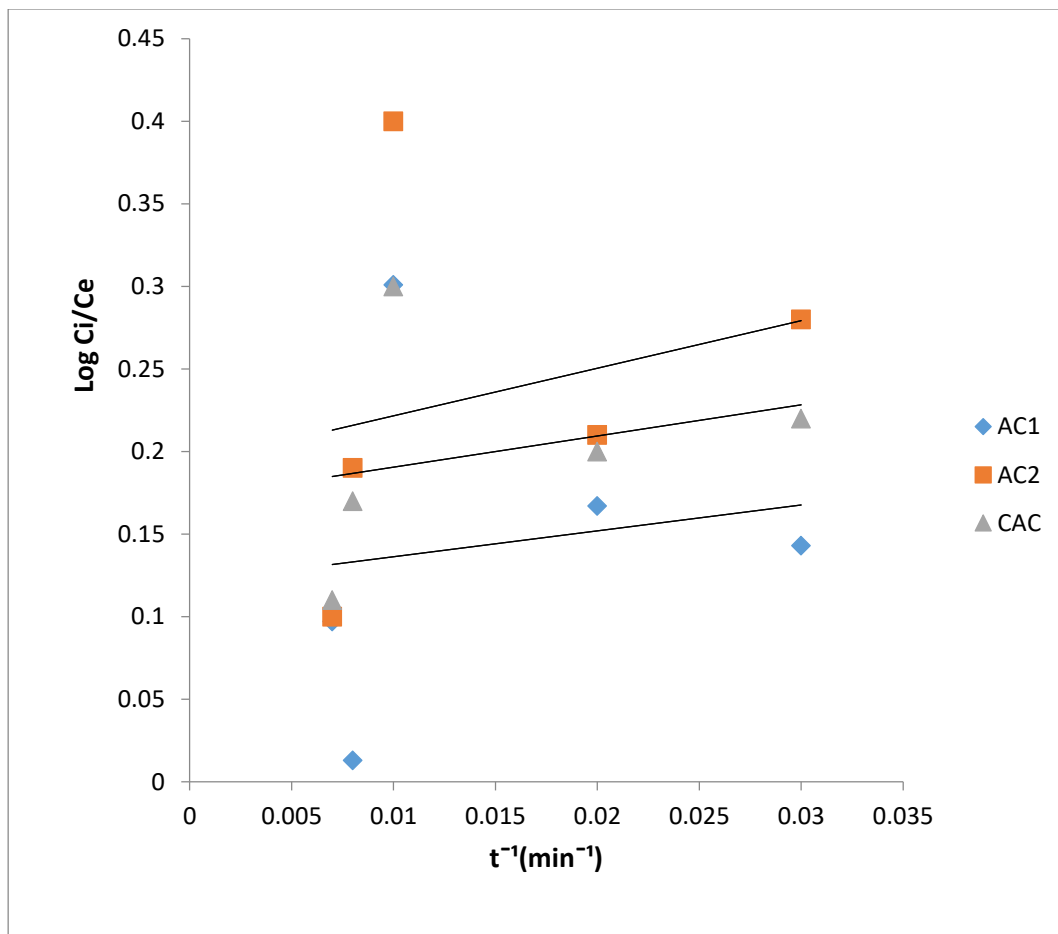
Natarajan plot for adsorption of copper onto different types of adsorbents.

Appendix A25



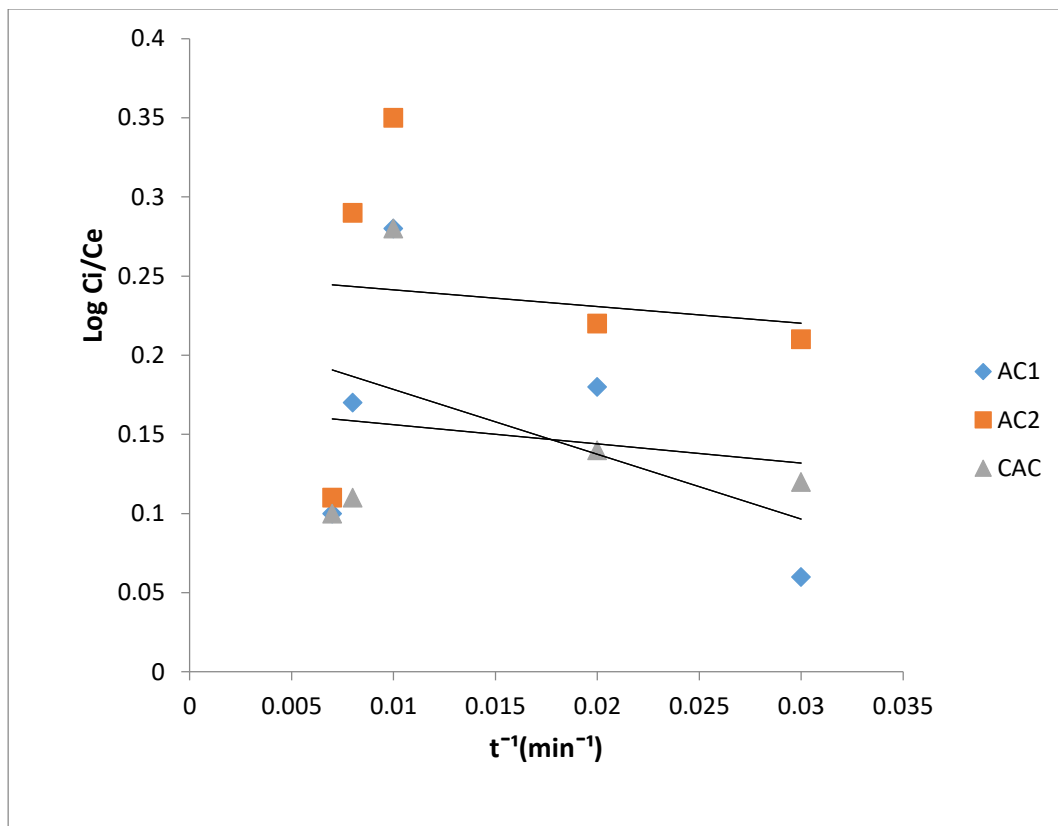
Natarajan plot for adsorption of cadmium onto different types of adsorbents.

Appendix A26



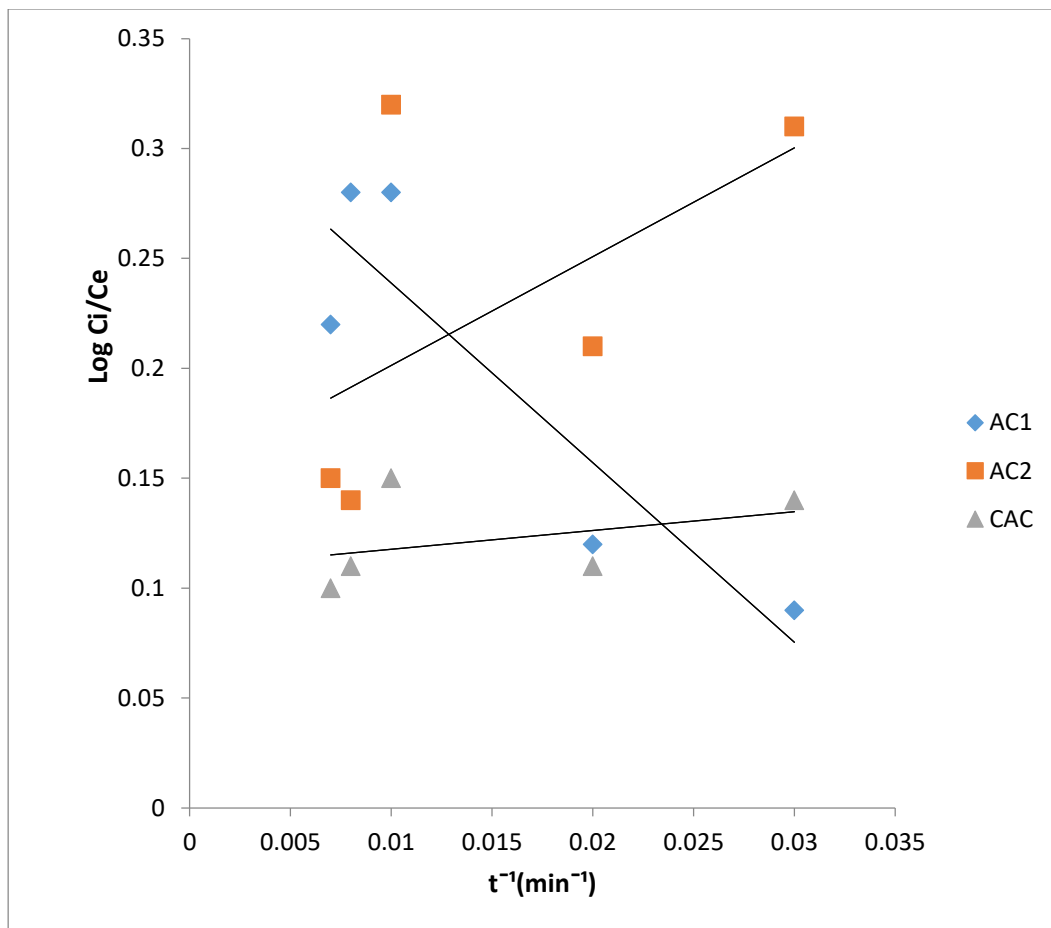
Natarajan plot for adsorption of Nickel onto different types of adsorbents.

Appendix A27



Natarajan plot for adsorption of cobalt onto different types of adsorbents.

Appendix A28



Natarajan plot for adsorption of Manganese onto different types of adsorbents.

