SYNTHESIS OF ALUMINO-PHOSPHATES FROM BONES FOR USE IN WATER REMEDIATION

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156/22603/2012

A Thesis Submitted in Partial Fulfillment of the Requirements for the Award of the Degree of Master of Science in Chemistry in the School of Pure and Applied Sciences of Kenyatta University

MAY, 2015
DECLARATION

This thesis is my original work and has not been presented for an award of a degree in any other University / Institution.

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To my late mother Victoria Syombua, sister Cecilia Githinji, my husband Nelson Mwalimu, daughter Wendy Barbara, son Adrian Linus Mwalimu, brother Kelvin Githinji and all those who encouraged me to pursue this study to the end.
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# ABBREVIATIONS AND ACRONYMS

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<tr>
<td>AAS</td>
<td>Atomic absorption spectroscopy</td>
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<tr>
<td>AlPO₄</td>
<td>Alumino-phosphate</td>
</tr>
<tr>
<td>CDC</td>
<td>Centers for Disease Control and Prevention</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>KEMRI</td>
<td>Kenya Medical Research Institute</td>
</tr>
<tr>
<td>KNBS</td>
<td>Kenya National Bureau of Statistics</td>
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<tr>
<td>KSFR</td>
<td>Kenya Society for Fluoride Research</td>
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<tr>
<td>Kwh</td>
<td>kilowatts per hour</td>
</tr>
<tr>
<td>L</td>
<td>Litres</td>
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<tr>
<td>NIDR</td>
<td>National Institute of Dental Research</td>
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<tr>
<td>ppm</td>
<td>parts per million</td>
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<tr>
<td>PVC</td>
<td>polyvinyl chloride</td>
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<td>WHO</td>
<td>World Health Organization</td>
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ABSTRACT

More than two thirds of the earth is covered by water however, only 2.5% of all the water on earth is fresh. In Kenya, only 1.9% of land coverage is occupied by water, with more than 41% of the population lacking access to clean drinking water. A major risk arises from consumption of water containing high levels of fluorides or that contaminated with heavy metals. Conventional technologies such as reverse osmosis, ultrafiltration and electro dialysis used in water remediation are efficient but expensive. Greater attention has been given to alternative technologies such as biosorption for water remediation. The present work aimed at hydrothermal synthesis of alumino-phosphates molecular sieves adsorbent. Characterization was done using Fourier transform infrared spectroscopy. Batch experiments were carried out to determine the effect of initial ion concentration, pH, contact time, temperature, shaking speed, co-ions and adsorbent dose on adsorption process. Adsorption kinetics was done using pseudo-first order and pseudo-second order equations. Isotherm adsorption models were used to analyze the experimental data. The adsorption data for AlPO₄ fit very well to the Langmuir model for lead (II) and cadmium (II) ions, which indicated presence of a monolayer adsorbent. The maximum sorption capacity was 6.329 mg/g for lead (II) ions and 5.208 mg/g for cadmium (II) ions at 45±1 °C. A pseudo-second order model described the kinetic data. The initial ion concentrations have significant effect on the adsorption efficiency of the molecular sieves. The highest percentage adsorption occurred at initial ion concentration of 6 mg/L for fluoride ions. Adsorption increased with increase in initial ion concentration for both lead (II) and cadmium (II) ions. The adsorption for fluoride ions, lead (II) ions and cadmium (II) ions also increased with an increase in the AlPO₄ dosage and equilibrium reached at 1.00 g/100 ml for all adsorption experiments. The optimum pH was found to be between 5 and 7. Temperature variation played an important role in ion adsorption by the AlPO₄ molecular sieves. The amount of lead and cadmium (II) ions adsorbed increased from 84.50% to 89.25% and 79.50% to 83.17% respectively, when the temperature was increased from 25 to 45±1 °C. Defluoridation experiments showed increased adsorption from 77.67% to 78.50% as temperatures were raised from 20 to 30±1 °C. Further increase in temperature resulted to reduced percentage of ion adsorption in all experiments. The optimum shaking speed for both lead (II) ions and cadmium (II) ions was 6 revolutions per second. Optimum contact time was found to be 90 minutes. Other anions were found to affect adsorption of fluorides. The results of this work indicate that the alumino-phosphate (AlPO₄) molecular sieves constitute a promising material for the development of an adsorption technology for the removal of lead (II), cadmium (II) metal ions and fluoride ions from aqueous systems.
CHAPTER ONE
INTRODUCTION

1.1 Background information

Kenya has a population of 44,037,656 persons (KNBS, 2013). The population is expected to grow even higher with the estimated birth rate of 30.08 births/1,000 population versus a death rate of 7.12 deaths/1,000 population (KNBS, 2013). With the expected increase in population, by 2030, food demand is predicted to increase by 50% and 70% by 2050, while energy demand from hydropower and other renewable energy resources will rise by 60%. These issues are interconnected; increasing agricultural output will substantially increase both water and energy consumption, leading to increased competition for water between water-using sectors (APHA, 1992). Increased economic activity and industrialization has led to high population growth. This has created an increase in demand for fresh water as well as resulted in severe pollution of the available water resources (Fotso et al., 2007).

Water is typically referred to as polluted when it contains anthropogenic contaminants and either does not support human use, such as drinking water, or undergoes a marked shift in its ability to support its constituent biotic communities, such as fish. Water pollution occurs through contamination of aquatic environment by inorganic chemicals which are considered a major threat to the aquatic organisms as well as man and animals that drink the contaminated water (Volesky, 1994; Romieu et al., 1997). Water pollution affects plants and organisms living in water bodies. In almost all cases, the effect is damaging not only to individual species and populations, but also to the natural
biological communities. Among other pollutants, heavy metals pose a great threat to life.

Water scarcity is both a natural and a man-made phenomenon. There is enough freshwater on the planet for seven billion people but it is unevenly distributed making it inaccessible and too much of it is wasted, polluted with numerous contaminants and unsustainably managed (Keith and Telliard, 1979). Although all the contaminants that afflict the world are dangerous and potentially life threatening, heavy metal contamination is a pollutant that is commonly studied and assessed even in countries where water purification methods are effective.

Lead, mercury, arsenic and cadmium are examples of heavy metals which are found in water as pollutants. Drinking water with lead contaminants has adverse effect on human development which includes birth defects in unborn babies as well as brain damage and breakdown of the nervous system (Igwe and Abia, 2006). Cadmium affects the proper functioning of vital body organs such as the kidneys and lungs. Over the years, research shows that indiscriminate dumping of untreated waste water and chemical wastes directly into surface water bodies has lead to a rise in potential health and environmental problems. Contaminated water does not only disrupt aquatic life but also reduces its reproductive capability (Igwe and Abia, 2006; Keith and Telliard, 1979).

In addition to pollutants, most water supplies contain some naturally occurring fluoride ions. Fluoride ions also enter drinking water as discharge from fertilizer or aluminum
factories (Juncos and Donadio, 1972). Endemic fluorosis in Kenya has been a public health problem for many years. Exposure of the tooth enamel to too much fluoride ions leads to dental fluorosis, which is characterized by discoloring of tooth enamel (Juncos and Donadio, 1972). Children aged 8 years and younger exposed to excessive amounts of fluoride have an increased chance of developing pits in the tooth enamel (Hedlund and Gallagher, 1989). Excessive consumption of fluoride ions over a lifetime leads to bone fractures in adults, and may result in effects on bone leading to pain and tenderness (Hedlund and Gallagher, 1989). Rapid population growth and changes in rainfall patterns in many parts of Kenya have exacerbated the problem of water scarcity, forcing communities to turn to poor quality water sources for their needs. Communities in rural areas of Kenya use water from natural sources without treatment, and water monitoring is not possible because many rural areas are relatively inaccessible (KSFR, 2006). The world is rapidly running out of clean water; water that is free from any pollutants such as heavy metals among other pollutants. According to the United Nations, by the year 2030, the world will need at least 30 percent more of clean water. Water scarcity already affects every continent. Around 700 million people in 43 countries suffer today from water scarcity. While approximately a fifth of the world's population, live in areas of physical scarcity and 500 million people are approaching this situation. In addition, almost one quarter of the world's population, face economic water shortage. This is where countries lack the necessary infrastructure to take water from rivers and aquifers.
According to the United Nations, water use has grown at more than twice the rate of population increase in the last century. By 2025, an estimated 1.8 billion people will live in areas plagued by water scarcity, with two-thirds of the world's population living in water-stressed regions as a result of use, growth, and climate change. According to findings presented at the 2012 Conference on "Water Scarcity in Africa: Issues and Challenges", with the existing climate change scenario, it is estimated that by 2030, 75 million to 250 million people in Africa will be living in areas of high water stress, which will likely displace anywhere between 24 million and 700 million people as conditions become increasingly unlivable.

Over 41% of Kenya's population lack access to clean drinking water and this poses high risks to their health. According to the Joint Monitoring Programme’s 2012 report, access to safe water supplies throughout Kenya is 59%. There is still an unmet need in rural and urban areas for both water and sanitation. Kenya faces challenges in water provision with erratic weather patterns in the past few years causing droughts and water shortages. Kenya also has a limited renewable water supply and is classified as a water scarce country.

Precipitation, membrane filtration and ion exchange methods are used in water remediation processes (Keith and Telliard, 1979). Though the methods are effective in removal of undesirable ions from water, they are characterized with high operational cost. This has resulted to the need of more studies on synthesis of cheap natural-based sorbents. Examples of cheaper adsorbents that have been studied include activated
alumina, activated bauxite, bagasse fly ash and activated carbon. Earlier research (Xie et al., 1996) on alumino-phosphate molecular sieves has shown its ability in adsorbing metal ions from water.

1.2 Problem Statement and Justification

The limited clean water resources that are available are threatened by over-exploitation, poor management as well as ecological degradation. Bulk untreated chemical waste from industries and farms are often directed towards surface water bodies such as rivers and lakes. Scarcity of clean drinking water is a big problem all over the world. Kenya has an area of about 582,642 km², water occupies 1.9% leaving more than two thirds as either arid or semi arid. The impact of water shortage has manifested itself in increased water use conflicts, food shortages and power rationing in Kenya. Surface and ground waters resources in Kenya are becoming polluted by the activities of agriculture, urbanization, leachate from municipal dumping site, eutrofication of fertilizers and pesticide residue and heavy metals.

Large amounts of fluoride ions in drinking water, which occur naturally, have become of major concern globally. A WHO report in 2006 identifies the belt that stretches from Syria, through Jordan, Egypt, Libya, Algeria, Sudan, and Kenya as one of the main fluoride belts (NRC, 1993) Previous studies (Wambu and Muthakia, 2011) showed the presence of high fluoride water in the Gilgil area of Nakuru County, Kenya. Lake water had fluoride ion levels up to 200 mg/L. Of the other sources, the highest mean fluoride ion levels were in piped water (7.69 mg/L) and borehole water (6.57 mg/L). A study by
the KSFR (2006) indicated that 19 million Kenyans suffer from fluorosis. It reported the worst hit community is the smallest tribe in the world (the El-Molo) living near Lake Turkana, where 80 per cent of the 186 members suffer from the condition. The lowest levels were reported in Western Kenya, at 11.7 per cent of the population. The accessibility of a defluoridation technique of drinking water is of great necessity in the affected areas.

Studies have been conducted previously to determine levels of various pollutants in soils and water bodies. The major pollutants studied are heavy metals which pose a big risk to human health as well as aquatic life. Modern methods of removing these heavy metals are expensive; as a result, there is need for research on adsorbents which are readily available as well as affordable. Some natural-based sorptive media for heavy removal include: activated alumina, activated carbon, iron coated sand, kaolinite clay, hydrated ferric oxide and activated bauxite. This study seeks to investigate a cheaper and efficient method of water remediation by synthesizing alumino-phosphate sieves from bone ash as a source of phosphates and study their adsorption capacities of heavy metal ions and fluoride ions.

1.3 Hypothesis

Alumino-phosphate synthesized from bones as a source of phosphates fused with alumina can be used to remove excess fluoride ions and selected metal ions from contaminated water.
1.4 Objectives

1.4.1 General objective

To synthesize alumino-phosphate molecular sieves from bones as a source of phosphates fused with alumina and investigate their effectiveness in the removal of excess fluoride ions and selected metal ions from contaminated water.

1.4.2 Specific objectives

(i) To describe the kinetic data using pseudo – first order and pseudo – second order equations.

(ii) To determine the efficiency of alumino-phosphate molecules on fluoride ions, cadmium (II) ions and lead (II) ions adsorption by optimization of various parameters (time, temperature, agitation, pH, dosage and initial ion concentration).

1.5 Significance of the study

The purpose of this study was to:

(i) Purify contaminated water by removing excess fluoride ions, lead and cadmium metal ions using alumino-phosphate derived from locally available waste materials. This will ensure a clean environment as well as improve accessibility to clean and safe drinking water to a majority of citizens in many developing countries such as Kenya, whose total daily income is less than a dollar.

(ii) Provide a scientific pathway for research into inexpensive, efficient alternative method of defluoridation as well as removal of heavy metals from waste water.
1.6 Limitation and scope of work

Contaminated water has many undesirable properties, this research only considered the adsorption of fluoride ions, lead (II) ions and cadmium (II) ions from contaminated water. There are numerous sources of phosphorus in the environment, examples include rocks and soil mineral. This study was limited to waste bones as a source of phosphorus. The bone type and source were not considered.
CHAPTER TWO
LITERATURE REVIEW

2.1 Adsorbents

Most adsorbents (such as activated carbons) are manufactured, but a few, such as some zeolites, occur naturally. Each material has its own characteristics such as porosity, pore structure and nature of its adsorbing surfaces. Pore sizes in adsorbents may be distributed throughout the solid. They are classified generally into three pore categories: macro-pores which have diameters greater than 50.0 nm, meso-pores (also known as transitional pores) have diameters ranging between 2.0 – 50 nm and micro-pores have diameters of less than 2.0 nm. Many adsorbent materials, such as carbons, silica gels and alumina, are amorphous and contain complex networks of inter-connected micro-pores, meso-pores and macro-pores. In contrast, pores in molecular sieve adsorbents have precise dimensions. Adsorbents can be categorized by specific material types. Major types of adsorbents in use are: activated alumina, activated carbon, clay, polymeric adsorbents, silica gel, molecular sieves and zeolites

2.1.1 Activated alumina

Activated alumina is an adsorbent made of aluminum oxide (Al₂O₃). It is used as a desiccant for drying gases and as a fluoride filter for drinking water. It has specific use as a silica gel replacement in certain environments due to its thermal shock resistance and physical constancy when immersed in water.
2.1.2 Activated carbon

Activated carbon is roasted organic material (coconut shell, peels, wood) that forms porous granules. It is a versatile and inexpensive adsorbent that comes in many sizes and has a range of applications from gas, water, and metal purification to air filtration.

2.1.3 Clay

Clay or clay silicates are natural mineral adsorbents. They are inexpensive, inert, and have a quick capture rate. However, they begin to desorb at temperatures above 120°F.

2.1.4 Organic polymers

Organic polymers are chains of repeating carbon based molecules used as adsorbents in size-exclusion chromatography and gas separation processes with high retention power and selectivity. Most do not require disposal and the regeneration process is environmentally friendly.

2.1.5 Silica gel

Silica gel is a common desiccant used in food preservation, humidity control, and various medical devices. It has a higher water absorption capacity than clay silicates, it is very inert, and it can be regenerated through heating.

2.1.6 Molecular sieves and zeolites

Molecular sieves are adsorbents with uniform pore size that can be tuned to be highly selective. Naturally occurring molecular sieves are referred to as zeolites. They are used
as dehumidifiers and air purifiers due their high retention and adsorption capacities even at high temperatures (Wilson et al., 1982).

2.1.7 Bones

The chemical composition of bones; has both organic and inorganic components. It consists mainly of collagen fibers, an inorganic bone mineral in the form of small crystals and a small amount of other substances such as proteins and inorganic salts. *In vivo* bone (living bone in the body) contains between 10% and 20% water (John et al., 2002). Of its dry mass, approximately 60-70% is bone mineral; most of the rest is collagen. The major minerals of the intercellular composite are calcium and phosphate (John et al., 2002).

![Bone structure image](image)

**Figure 2.1:** Bone structure (John et al., 2002)

The composition of the mineral component is approximated as hydroxyapatite, with the chemical formula \( \text{Ca}_{10} (\text{PO}_4)_6 (\text{OH})_2 \) (John et al., 2002). However, whereas hydroxyapatite has a Ca:P ratio of 5:3 equivalent to 1.67, bone mineral itself has Ca:P
ratios ranging from 1.37 - 1.87. This is because the composition of bone mineral is much more complex and contains additional ions such as silicon, carbonate and zinc (Steele et al., 1988). The primary tissue of bone, osseous tissue, is made mostly of calcium phosphate in the chemical arrangement termed calcium hydroxyapatite.

2.2 Alumino-phosphates (AlPO₄)

![Structure of AlPO₄](image.png)

**Figure 2.2:** Structure of AlPO₄ (Wilson et al., 1982)

AlPO₄ are three-dimensional chemical compounds with a molecular weight of 121.953 g/mol. They are formed from corner-connected tetrahedral units each consisting of aluminium and phosphorus (Wilson et al., 1982). The various structures exhibit intra-crystalline adsorption pore volumes from 0.04 to 0.35 cm³/g, and pore sizes from 0.3 to 0.8 nm. The anhydrous form is found in nature as the mineral berlinite (Wilson et al., 1982). AlPO₄ is synthesized by means of hydrothermal process starting from reactive alumino-phosphate gels, or the individual aluminium, phosphorus components. Many synthetic forms of anhydrous alumino-phosphates are used as catalysts or molecular sieves (Wilson et al., 1982).
Alumino-phosphates are popularly used in dehydration reactions due to their good hygroscopic properties and their high adsorption power (Wilson et al., 1982). The adsorption power is particularly good due to the macro-porous framework structure of AlPO₄. A large number of molecules can be adsorbed on the large surface area. Adsorption and desorption are present in a concurrent equilibrium which can be controlled by adjusting parameters such as temperature and pressure. Earlier research on alumino-phosphate molecular sieves has shown its ability in adsorbing metal ions from contaminated water (Wilson et al., 1982).

2.3 Selection Criteria of adsorbents
Adsorbents are selected by considering their selectivity, surface area, and regeneration ability. Selective sorbent only removes specific substances. Surface area refers to the amount of material a sorbent has available for contact and determines the capacity of material a sorbent can adsorb, the adsorption rate of the sorbent, and the retention rate of the substance within the sorbent. Regeneration is the ability of a sorbent to be reused after capturing to its capacity (Herrero et al., 2008).

2.4 Adsorption isotherm models
Adsorption isotherm models are widely employed to examine the relationship between the adsorbed and the aqueous concentrations at equilibrium. Adsorption equilibrium is established when the concentration of the sorbent in a bulk solutions is in dynamic balance with that of the adsorbent interface (Ahalya et al., 2004). An adsorption isotherm is characterized by certain constants, the values of which describe the surface
properties and affinity of the adsorbent and can be used to compare adsorptive capacities of various adsorbents (Herrero et al., 2008). The degree of the adsorbent affinity to the sorbent determines its distribution between the solid and liquid phases. The analysis of equilibrium data is important to develop mathematical models, which could be used for predicting metal ion adsorption, reflecting the mechanism of metal adsorption and the influence of the variables such as pH, temperature, among others (Ahalya et al., 2004).

2.5 Fluorides

Fluoride compounds are salts that form when the element, fluorine, combines with minerals in soil or rocks. Some fluoride compounds, such as sodium fluoride and fluorosilicates, dissolve easily into ground water as it moves through pore and spaces between rocks. Besides drinking fluoridated water, there are various ways through which people are exposed to fluoride ions. Other sources of fluoride ions include food and beverages processed with fluoridated water (Heilman, 1999), fluoridated dental products (Barot, 1998), mechanically deboned meat (Fein and Cerklewski, 2001) and pesticide residues (e.g., from cryolite) on food (Barbier, 2010). Cryolite is primarily responsible for the fluoride contamination of our vegetables, fruits, fruit drinks, and wine. It is sprayed on grapes, potatoes and citrus fruit.

Fluoride is voluntarily added to some drinking water systems as a public health measure for reducing the incidence of cavities among the population (CDC, 2001). Fluoride is added to public water supplies either in the form of hydrofluosilicic acid or any other
form complying with the specification that may be approved by the Ministry of Health. The CDC, EAP as well as the WHO provide recommendations about the optimal levels of fluoride in drinking water in order to prevent tooth decay. Maximum contaminant level (MCL) for fluoride as set by the WHO's drinking water regulations for fluoride is 1.5 ppm equivalent to 1.5 mg/L. Different bodies in different countries have set varying MCL.

2.6 Fluoride toxicity

Fluoridation’s role in the decline of tooth decay is in serious doubt (Diesendorf, 1986). The largest survey ever conducted in the US (over 39,000 children from 84 communities) by the National Institute of Dental Research (NIDR) showed little difference in tooth decay among children in fluoridated and non-fluoridated communities (Hileman, 1999). According to NIDR researchers, the study found an average difference of only 0.6 in decayed, missing, and filled surfaces in the permanent teeth of children aged 5-17 residing their entire lives in either fluoridated or un-fluoridated areas. This difference is less than one tooth surface, and less than 1% of the tooth surfaces available in a child’s mouth (Brunelle and Carlos, 1990).

Fluoride is not an essential nutrient since there is no disease, not even tooth decay, associated with fluoride ions deficiency (NRC, 1993; Institute of Medicine, 1997). On the contrary there is extensive evidence that exposure to excessive fluoride ions can interfere with many important biological processes. Exposure to excessive consumption of fluoride ions over a lifetime may lead to increased likelihood of bone fractures in
adults, and may result in effects on bone leading to pain and tenderness (Hedlund and Gallagher, 1989). It also results to dental fluorosis which is characterized by discoloring of tooth enamel caused by too much fluoride ions (Juncos and Donadio, 1972). Children aged 8 years and younger exposed to excessive amounts of fluoride have an increased chance of developing pits in the tooth enamel (Brunelle and Carlos, 1990). Manji and Kapila (1984) undertook a research on dental fluorosis in an area of Kenya with 2 mg/L fluoride in the drinking water. 102 children born and reared in an area of rural Kenya in this area were examined for dental fluorosis. The prevalence of dental fluorosis was found to be 100%, 50% of the children had pitting or more severe enamel damage in at least half the teeth present.

Fluoride interferes with numerous enzymes (Carlsson, 1978). In combination with aluminum, fluoride interferes with guanosine nucleotide-binding proteins (a family of proteins involved in transmitting signals from a variety of different stimuli outside a cell into the inside of the cell). Such interactions give aluminum-fluoride complexes the potential to interfere with signals from growth factors, hormones and neurotransmitters (Kishi and Ishida, 1993). Studies by Jennifer Luke (1997) show that fluoride accumulates in the human pineal gland to very high levels. In her Ph.D. thesis, Luke has also shown in animal studies that fluoride ions reduce melatonin production and lead to an earlier onset of puberty (Luke, 1997).

2.6.1 Defluoridation methods
Fluoride ions can be removed from water by using various available methods which include reverse osmosis, electrochemical methods, distillation and the use of activated alumina de-fluoridation filter.

2.6.2 Reverse osmosis

This is a type of water filtration process that involves the use of osmotic pressure to remove certain elements from water. It occurs when water is moved across a membrane against the concentration gradient. Reverse osmosis is considered a highly effective water purifying process. Although there are reverse osmosis water filtration systems designed for homes’ water purification, it's most common use is to desalinate seawater to make it drinkable. Reverse osmosis is commonly used to purify several types of bottled water, though not all, and is characterized by high operation cost thus making it unaffordable for local home use (Sudhir and Bashir, 2006).

2.6.3 Electrochemical methods

The basic principle of the process is the adsorption of fluoride ions with freshly precipitated aluminum hydroxide, which is generated by the anodic dissolution of aluminum or its alloys, in an electrochemical cell. Though efficient in defluoridation, it is associated with high operational cost. Electrochemical methods use electricity hence; wherever electricity is not available the method becomes inaccessible. The process utilizes 0.3 to 0.6 kwh of electricity per 1000 liters of water containing 5 - 10 mg/L of fluoride ions (Sudhir and Bashir, 2006). Furthermore the anode is continuously
consumed and needs to be replenished. In addition the process generates sludge at the rate of 80 - 100 g per 1000 liters (Sudhir and Bashir, 2006).

### 2.6.4 Activated alumina

Activated alumina is a granular, highly porous material consisting essentially of aluminum trihydrate (Sudhir and Bashir, 2006). It can be regenerated with hydrochloric acid, sulphuric acid, alum or sodium hydroxide. The use of sodium hydroxide needs to be followed by a neutralization to remove residual sodium hydroxide from the bed. The ability of activated alumina to remove fluoride ions depends on other aspects of the chemistry of water as well. Such factors as hardness, silica and boron, if present in water will interfere with fluoride ion removal and reduce the efficiency of the system (Sudhir and Bashir, 2006).

### 2.7 Heavy metals

Heavy metals refer to metallic chemical elements that have a specific gravity greater than 5.0 g/cm³ and are toxic at low concentrations (Oehme, 1978). They include some metalloids, transition metals, basic metals, lanthanides and actinides. They can exist in soluble, colloidal or particulate phase and consequently reach every part of an aquatic ecosystem. Some of these metals play basic roles in organisms and are regarded as essential elements. Trace amounts of metals such as Zn, Cu and Fe are essential in the environment; they play a biochemical role in life processes. These elements, or some form of them, are commonly found naturally in foodstuffs, in fruits and vegetables, and
in commercially available multivitamin products (IOSHIC, 1999). Higher concentrations of these metals may cause pollution to life (Ambasht, 1990).

Heavy metals are effective pollutants which have drastic environmental impact on all organisms (Mason, 2002). Among the toxic heavy metals: mercury, lead and cadmium, called the big three, are in the limelight due to their major impact on the environment (Volesky, 1994). Others include arsenic, chromium and zinc.

2.7.1 Lead and cadmium applications and toxicology

Previous research has confirmed the presence of these heavy metals in water bodies. Lead and cadmium are some of the most poisonous metals, if their discharge in water systems is not controlled. The United States Environmental Protection Agency (USEPA) has classified them as priority pollutants (Keith and Tellierd, 1979). Drinking water with lead contaminants has adverse effect on human development which includes birth defects in unborn babies as well as brain damage and breakdown of the nervous system. It is also associated with seizures, encephalopathy, calcium loss and kidney dysfunction (Keith and Tellierd, 1979).

Cadmium affects the proper functioning of vital body organs such as the kidneys and lungs leading to hepatic damage and hypertension (Ambasht, 1990). Through bioaccumulation, small amounts of these heavy metals become concentrated in organisms to a level that affects their physiological state. Through agriculture, water containing pesticides and fertilizers is drained into rivers, lakes and streams. In the
Egyptian irrigation system, the main source of Cadmium (Cd) and lead (Pb) are industrial wastes as well as algaecides, for Pb, while that of Cd is the phosphatic fertilizers used in crop farms (Mason, 2002). Effluents of industrial activities and runoffs in addition to sewage effluents supply the water bodies and sediment with huge quantities of inorganic anions and heavy metals (Abdel-Baky et al., 1998; Hussein et al., 2005). The most anthropogenic sources of metals are industrial, petroleum contamination and sewage disposal (Santos et al., 2005).

Cadmium and lead find their way into water bodies as a result of their diverse applications and improper deposition of the materials containing these heavy metals. The most significant use of cadmium is in nickel/cadmium batteries, as rechargeable or secondary power sources. Cadmium coatings provide good corrosion resistance, particularly in high stress environments such as marine and aerospace applications where high safety or reliability is required; the coating is preferentially corroded if damaged (Guruswamy, 2000). Other uses of cadmium are as pigments, stabilizers for PVC, in alloys and electronic compounds. Cadmium is also present as an impurity in several products, including phosphate fertilizers, detergents and refined petroleum products (Zweifel, 2009).

Lead is added to brass to reduce machine tool wear. It is also used for the customization of tennis rackets. Sheet-lead is used as a sound deadening layer in some areas in wall, floor and ceiling design in sound studios where levels of airborne and mechanically produced sound are targeted for reduction or virtual elimination (Guruswamy, 2000).
Lead is frequently used in polyvinyl chloride (PVC) plastic, which coats electrical cords. This lead is composed of 12 – 28% lead (II) oxide (PbO). Lead, in either pure form or alloyed with tin, or antimony is used in the manufacture of bullets (Zweifel, 2009).

2.7.2 Methods of lead and cadmium recovery

2.7.2.1 Precipitation
This is the most frequently used method for heavy metal remediation in water. This method has reduced levels below the current USEPA guideline of 0.01 mg/L (Amorim et al., 2003). Also, it has the potential to reduce other contaminants that hinder the quality of drinking water, including turbidity, iron, phosphate manganese, fluoride, colour, and odour. Precipitation technologies include the use of a chemical treatment leading to the precipitation or co-precipitation of a solid and the subsequent separation of the solid from the water source. Chemicals used to precipitate a solid make the process to be costly.

2.7.2.2 Membrane Filtration
Membrane filtration is used mostly to treat ground water and is characterized by either filter membranes which are divided into four classes according to pore size: microfiltration, ultrafiltration, nanofiltration, or reverse osmosis. Membrane filtration is associated with high operating costs (Ruiz et al., 2008).
2.7.2.3 Ion exchange methods
It involves the exchange of ions between an electrolyte solution and a complex. Ion exchangers are either cation exchangers or anion exchangers (Hodi et al., 1995). There are also amphoteric exchangers that are able to exchange both cations and anions simultaneously. The simultaneous exchange of cations and anions is more efficiently performed in mixed beds that contain a mixture of anion and cation exchange resins, or passing the treated solution through several different ion exchange materials (Hodi et al., 1995). Ion exchangers can be unselective or have binding preferences for certain ions or classes of ions, depending on their chemical structure. This can be dependent on the size of the ions, their charge, or their structure (Hodi et al., 1995). The ion exchange process efficiency depends on an oxidation pre-treatment step. The disadvantage is regeneration with other chemicals and it is expensive (Hodi et al., 1995).

2.8 Adsorption
Sorptive filtration requires the use of a sorptive media for adsorption to take place. The adsorption process involves a solid phase, sorbent, and a liquid phase, a solvent which is normally water, containing a dissolved species to be sorbed (Ahalya et al., 2004). Due to higher affinity of the sorbent for sorbate species, the sorbate is attracted and bound there until equilibrium is established between the amount of solid bound sorbate species and its portion remaining in solution (Ahalya et al., 2004). The degree of sorbent affinity for the sorbate determines its distribution between the solid and liquid phases (Ahalya et al., 2004). Adsorption is relatively rapid and can be reversible (Kuyucak et al., 1998). Adsorption is of importance because the removal of potentially toxic metals, which can as well be valuable rare metals and nuclides from aqueous
effluents, can result in detoxification and therefore safe environmental discharge (Amorim et al., 2003).

### 2.9 Factors affecting ion adsorption

The factors that may affect binding of ions by molecular sieves and other sorbents include pH, temperature, co-ions in solution, sorbent dosage, initial ion concentration, shaking speed and contact time. Investigation on the effect of each of these parameters on adsorption processes is essential for industrial application. This gives information about the equilibrium of the process, which is necessary for the design of the equipment (Ahalya et al., 2004).

#### 2.9.1 Effects of pH on adsorption

Metal sorption depends on the pH because of the resulting changes that occur in the metal species and on the surface of the adsorbing media (Singh et al., 2006). When the pH is altered, mineral surfaces become more negatively charged with the increasing pH and the surface groups that have lost protons may be able to adsorb cations more readily, and anions less readily, from solutions (Singh et al., 2006). Control of pH therefore, is a major factor affecting defluoridation as well as the separation of metal ions from solution containing different metal ions. The pH dependence occurs when the fluoride ions and hydroxyl ions compete for adsorption site or when the metal ions and protons compete for the same active metal binding sites on the sorbents surface (Donmez and Aksu, 2002).
2.9.2 Effect of competing co-ions on adsorption

Adsorption is mainly used in aqueous systems where more than one type of cations or anions would be present and these include divalent metal ions such as magnesium or anions such as chloride, nitrite, sulphate and bicarbonate ions. However, removal of fluoride ions may be influenced by the presence of other anions; though the effects of these ions vary. Although the elimination of the anions is not the purpose of the adsorption studies, they can compete and interfere with the binding sites of the ion to be eliminated at a particular pH (Lodeiro et al., 2006). The presence of other cations may also have an effect on the adsorption of particular metal ions in solution. It has been reported that the influence of metal ions with a single charge is lower than the effect of ions with a double charge; this is because they have a weaker electrostatic attraction for the functional groups than the double charged ones (Xie et al., 1996).

2.9.3 Effect of initial ion concentration on adsorption

Initial ion concentration in solution has an influence on the specific adsorption. The adsorption capacity of ions is decreased with the increase in the ion concentration due to saturation of the binding sites, although the amount of ions adsorbed increases with the increase in the initial ion concentration (Fourest and Roux, 1992). At very high concentrations many adsorbent materials have been found to be quite ineffective compared to convectional sorbents probably due to saturation of the adsorption sites. At very low metal ion concentration however, they have very high efficiency (Gadd, 1990).
2.9.4 Effect of temperature on adsorption

Temperature has two main effects on the adsorption processes. Increasing the temperature is known to increase the diffusion rate of the sorbent within the pores as a result of decreasing the solution viscosity as well as mobility (Aksu, 2001). The other effect is that equilibrium between the adsorbent and the sorbent is attained within a shorter time due to the increase in the diffusion rate (Lodeiro et al., 2006). The effect of temperature on adsorption also depends on the heat of sorption. Usually for physical sorption, enthalpy of sorption is exothermic and preferred at lower temperature (Aksu, 2001).

For chemisorptions the overall heat of sorption is a combination of heat of various reactions taking place at sorption sites. It also depends on the type of ion and adsorbent because they contain more than one type of binding sites and some sites might be selective to particular ions (Ghodbane et al., 2008). The effect of temperature on the adsorption process found in literature presents differing behaviors. Aksu (2001) reported higher adsorption capacity as temperature increases while on the other hand; Aksu and Kutsal (1992) and Bosco et al. (2005) reported practically temperatures independent effect on adsorption capacity.

2.9.5 Effect of agitation speed on adsorption

Increase in the stirring rate increases the rate of the adsorption. Higher stirring rates are needed to eliminate the film resistance that prevents more ions to be adsorbed. When the stirring rate is increased the diffusion rate of the ions from the bulk liquid to the
liquid boundary layer surrounding sorbent particles become higher because of the enhancement of the turbulence and the decrease of the thickness of the liquid boundary layer (Ghodbane et al., 2008).

2.9.6 Effect of contact time on adsorption
According to Yang et al. (1999), a large number of vacant surface sites are available for adsorption during the initial stage and the solute concentration gradient is high. With the passage of time, there is a decrease in the number of adsorption sites and the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid phase and in the bulk liquid phase (Yang et al., 1999).

2.10 Adsorption equilibrium models
Adsorption studies are expressed in models known as adsorption isotherms. These isotherms are a plot of the amounts of sorbent adsorbed on the surface of adsorbent and concentration or pressure at constant temperature. Different adsorption isotherms are based on the adsorption surface. From the graphs, it can be predicted that after a certain concentration, saturation concentration, adsorption does not occur anymore. This can be explained by the fact that there are limited numbers of adsorption pores on the surface of the adsorbent (Pehlivan et al., 2008). In order to develop an operational procedure it is important to describe the adsorption equilibrium data employing adequate mathematical models. Ideally these models should be capable of predicting metal adsorption, reflecting the mechanism of the metal adsorption and the influence of various variables such as pH, ionic strength and temperature among others (Herrero et al., 2008).
Several Models have been used to interpret the adsorption equilibrium data. However, Langmuir (Katircioglu et al., 2008), Freundlich (Pehlivan et al., 2008) and Langmuir–Freundlich (Lodeiro et al., 2006) derived from combining Langmuir and Freundlich being the most commonly employed adsorption isotherms. Langmuir and Freundlich isotherms are the earliest known, and are therefore widely used to fit the equilibrium data because they have easily interpretable constants. Although these models shed no light on the mechanistic aspect, they remain a useful and convenient tool for comparing results from different sources on a quantitative basis. They also provide information on sorption potential (Singh et al., 2006). The Freundlich and Langmuir adsorption isotherms may exhibit an irregular pattern due to the complex nature of both sorbent material and its varied multiple active sites, as well as the complex solution chemistry of some metallic compounds (Oliveira et al., 2008).

### 2.10.1 Langmuir adsorption isotherm

Langmuir adsorption isotherm assumes that the adsorption surface has a finite number of adsorption sites with equal sizes and shapes. It is valid for monolayer sorption and it is expressed as equation 2.1.

\[
q_e = \frac{b Q_{\text{max}} C_e}{1 + b C_e}
\]  

(2.1)

Where \( q_e \) corresponds to the amount of the metal ion adsorbed per gram of the adsorbent at equilibrium (mg/L), \( C_e \) is the solute concentration (mg/L) in aqueous solution after equilibrium is reached, \( Q_{\text{max}} \) represents practical limitation adsorption capacity when the surface is fully covered with metal ions and assists in the comparison
of performance particularly in cases where the adsorbent did not reach its full saturation in the experiments; $b$ is an affinity constant for binding sites. A high value of $b$ indicates a high affinity of the adsorbent for the sorbent. The linearized Langmuir equation is expressed as in equation 2.2.

$$\frac{C_e}{q_e} = \frac{1}{bQ_{\text{max}}} + \frac{Q_{\text{max}}}{Q_{\text{max}}}$$  \hspace{1cm} (2.2)

A plot of $\frac{C_e}{q_e}$ against $C_e$ gives a straight line from which $Q_{\text{max}}$ and $b$ can be obtained (Yu et al., 1999; Oliveira et al., 2008).

### 2.10.2 Freundlich adsorption isotherm

Freundlich adsorption isotherm describes heterogeneous surface energies by multilayer adsorption. The empirical equation used to estimate the adsorption intensity of the sorbent towards the adsorbent and is given by equation 2.3

$$q_e = K_f C_e^n$$  \hspace{1cm} (2.3)

The linearized Freundlich equation is expressed as in equation 2.4

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$  \hspace{1cm} (2.4)

Where $K_f$ and $n$ are Freundlich constants representing adsorption capacity and intensity respectively; $n$ varies with the heterogeneity of the adsorbent. For values of $\frac{1}{n}$ in the range $0.1 < \frac{1}{n} < 1$ adsorption is favorable. $q_e$ is adsorption density and $C_e$ is the concentration of the metal in equilibrium. A plot of $\log q_e$ against $\log C_e$ gives a
straight line which can be used to determine $K_f$ and $n$. The data obtained is used to determine the recovery efficiency and predict the nature of the adsorbing surface for each model (Singh et al., 2007; Ghodbane et al., 2008).

2.11 Adsorption kinetics

Kinetic experiments are initially necessary in order to determine the time required to achieve the adsorption equilibrium. Several independent processes may control the kinetics of adsorption process such as, transport phenomenon (bulk, film or pore diffusion) and chemical reactions. To properly understand the adsorption kinetics, an accurate rate equation must be obtained for each step that takes place during the procedure (Herrero et al., 2008). The kinetics of heavy metals adsorption is modeled by first-order Lagergren equation, pseudo-second-order equation and the second-order rate equation.

2.11.1 First-order Lagergren equation

The linear form of first-order Lagergren equation is expressed by equation 2.5

$$\log(q_e - q_t) = \log q_e - \frac{K_L t}{2.303}$$  (2.5)

Where $K_L$ is the Lagergren constant expressed per minute, $q_e$ is the metal adsorbed at equilibrium expressed in mg/g, $q_t$ is the metal adsorbed at a given time in mg/g and $t$ is the time taken for the adsorption to take place (Li et al., 2008). Straight-line plots of $\log (q_e - q_t)$ against $t$ implies that the reaction follows first order kinetics, the gradient
giving the Lagergren constant and the y intercept giving the metal adsorbed at equilibrium.

### 2.11.2 Pseudo – second order equation

A linear form of the pseudo – second order equation is given by equation 2.6

\[
\frac{t}{q_t} = \frac{1}{K'q_e^2} + \frac{t}{q_e}
\]

(2.6)

Where \(K'\) is the pseudo – second order rate constant of adsorption, \(q_e\) is the metal adsorbed at equilibrium expressed in mg/g, \(t\) is the time taken for the adsorption to take place and \(q_t\) is the metal adsorbed at a given time expressed in mg/g (Li et al., 2008). A straight-line plot of \(\frac{t}{q_t}\) against \(t\) from this equation will confirm that the adsorption process follows pseudo – second order kinetics. The rate constants are determined from the y intercept.

The metal adsorption \(q_{e,i}\) can be expressed in different units depending on the purpose of the exercise. For practical and engineering process evaluation purposes, eventually concerned with process mass balances, it is customary to use weight per (dry) weight, which is the amount (mg) of metal adsorbed per gram of the (dry) adsorbent material. Ultimately, mainly because of reactor volume considerations, the adsorption may also be expressed on per volume basis as mg/l. It is relatively easy to convert among these units; the only problem may arise with the sorbent weight volume conversions. For scientific interpretations, the sorbent material dry-weight basis is thus preferred. The
metal ion adsorption capacity is calculated by material balance using equation 2.8 (Kuyucak et al., 1990).

\[ q_{e,t} = \frac{V(C_{e,t} - C_{e,d})}{M} \]  

(2.8)

Where \( q_{e,t} \) is the metal adsorption in mg /g, \( V \) is volume of metal solution in litres, \( C_{e,t} \) is the initial metal concentration in mg/l, \( C_{e,d} \) is the concentration of metal solution at a given time in mg/l.

2.12 Methods of analysis

2.12.1 Fourier transform infrared (FTIR) spectroscopy

Source energy is passed through an interferometer and onto the sample. IR light energy passes through a beamsplitter, which sends the light in two directions at right angles. One beam goes to a stationary mirror then back to the beamsplitter. The other goes to a moving mirror. The motion of the mirror makes the total path length variable versus that taken by the stationary-mirror beam. When the two meet up again at the beamsplitter, they recombine, but the difference in path lengths creates constructive and destructive interference. The recombined beam passes through the sample.

The sample absorbs all the different wavelengths characteristic of its spectrum, and this subtracts specific wavelengths from the interferogram. The detector reports variation in energy versus time for all wavelengths simultaneously. A laser beam is superimposed to provide a reference for the instrument operation. A mathematical function called a
Fourier transform allows us to convert an intensity-vs.-time spectrum into an intensity-vs.-frequency spectrum (Naja et al, 2005).

**Figure 2.3:** FTIR instrumentation (Naja et al, 2005).

### 2.12.2 Atomic absorption spectrometry (AAS) technique

The methods used in determination of lead (II) and cadmium (II) ions presences are divided into two classes, classical and instrumental methods. Atomic absorption spectrometry is highly sensitive and determines the concentration of metals down to parts per billion per gram in a sample (Skoog, 2004). The atomic absorption spectrometry technique measures the amount of the radiation absorbed by the ground state atoms resident in the flame. The amount of radiant energy absorbed by the photomultiplier detector is directly proportional to the concentration of the absorbing atoms in the flame hence, the number of elements in the sample (Skoog, 2004).

The technique makes use of absorption spectrometry to assess the concentration of an analyte in a sample. It relies heavily on the Beer–Lambert law. The electrons of the
atoms in the atomizer can be promoted to higher orbitals for a short amount of time by absorbing a set quantity of energy. This amount of energy is specific to a particular electron transition in a particular element and this ensures elemental selectivity.

In order to analyze a sample for its constituents, it has to be atomized. The sample is then illuminated by light. The light transmitted is finally measured by a detector. A spectrometer is placed between the atomizer and the detector to reduce the effect of emission from the atomizer.

![Diagram of AAS instrumentation](image)

**Figure 2.4:** AAS instrumentation

The intense resonance line (frequency), which corresponds to the transition ground state atoms of the analyte to an excited state, originates from the hollow cathode lamp. This resonance line ($\lambda$) is absorbed by atoms in the flame and is characteristic of the elements under investigation making AAS highly selective with a high degree of specificity. The amount of radiant energy absorbed by the Photo Multiplier Tube (PMT) detector is directly proportional to the concentration of the absorbing atoms in the flame. AAS technique has some advantages that include less spectral interference, versatile and has high sensitivity (can detect up to 0.1 mg/l). In the analysis of lead (II) ions and cadmium (II) ions, the signal is subject to interference from the other transition
metals, phosphates and formation of variable refractory oxides in air acetylene flame. Better sensitivity is achieved by use of reducing condition of nitrous oxide- acetylene flame.

2.12.3 Ion selective electrode (ISE)

Ion-selective electrode (ISE) is also known as a specific ion electrode (SIE). It is a transducer that converts the activity of a specific ion dissolved in a solution into an electrical potential, which can be measured by a voltmeter or by a pH meter. The voltage is theoretically dependent on the logarithm of the ionic activity, according to the Nernst equation. The ISE can also be calibrated to give readings of a particular ion present in a solution in mg/l. The sensing part of the electrode that is dipped into the sample solution is usually made of an ion-selective membrane.

2.12.4 Types of ion-selective membrane

2.12.4.1 Glass membranes

Glass membranes are made from an ion-exchange type of silicate or chalcogenide glass. The silicate glass membrane type of ISE has good selectivity, but only for several single-charged cations; mainly H\(^+\), Na\(^+\), and Ag\(^+\). Chalcogenide glass membrane also has selectivity for double-charged metal ions, such as Pb\(^{2+}\), and Cd\(^{2+}\). An example of this type of electrode is the pH glass electrode (Skoog, 2004).
2.12.4.2 **Ion-exchange resin membranes**

Ion exchange resins are based on special organic polymer membranes which contain a specific ion-exchange substance (resin). Usage of specific resins allows preparation of selective electrodes for tens of different ions, either single-atom or multi-atom. An example is the potassium selective electrode, based on valinomycin as an ion-exchange agent. The valinomycin has a hexagonal ring structure with an internal cavity which is almost exactly the same size as the diameter of the $\text{K}^+$ ion. Thus it can form complexes with this ion and preferentially conducts it across the membrane (Vogel, 1978).

2.12.4.3 **Crystalline membranes**

Crystalline membranes are made from mono or poly-crystallites of a single substance. They have good selectivity, because only ions which can introduce themselves into the crystal structure can interfere with the electrode response. Selectivity of crystalline membranes can be for both cation and anion of the membrane-forming substance. An example is the fluoride selective electrode based on lanthanum fluoride ($\text{LaF}_3$) crystals. In the fluoride ISE, the membrane consists of a single lanthanum fluoride crystal which has been doped with europium fluoride ($\text{EuF}_2$) to reduce the bulk resistivity of the crystal.

The inner surface of the crystal is in contact with the inner reference solution, and the outer surface of the crystal is in contact with the solution containing the analyte. A potential develops across the membrane that depends on the difference in the concentration of fluoride ion on each side of the membrane. Since the concentration of
the internal solution is fixed, the potential developed across the membrane is related to
the concentration of the analyte. It is 100% selective for fluoride ions and is only
interfered with by hydroxyl ions (OH\(^-\)) which react with the lanthanum to form
lanthanum hydroxide, with the consequent release of extra fluoride ions. This
interference is eliminated by adding a pH buffer to the samples to keep the pH in the
range 4 to 8 and hence ensure a low OH\(^-\) concentration in the solutions (Skoog, 2004).
CHAPTER THREE
MATERIALS AND METHODS

3.1 Sampling collection and pre-treatment

Fresh bone samples were randomly collected from butcheries in Githurai market, Nairobi county. The samples were washed with distilled water several times in order to remove dirt. The samples were then dried in an oven at 80°C for 24 hours to prevent growth of bacteria. The dry bone samples were later placed in a furnace and ignited at a temperature of 800 °C for 8 hours. They were then crashed and ground to fine ash which was stored in a plastic bag ready for use.

3.2 Hydrothermal synthesis

The bone ash rich in phosphates was fused with commercially obtained alumina by hydrothermal synthesis. The ash, alumina and 100 ml of brine water were put in a reaction bomb and placed in an oven set at 80°C for 24 hours. The contents in the reaction bomb were cooled then washed and filtered to obtain the solid molecular sieves.

3.3 Experimental procedures

All the chemicals used in preparation of the reagents were of analytical grade. The chemicals were purchased from Sigma Aldrich (Germany). Lead (II) standard stock solution of 1000 mg/L was obtained by dissolving 1.599 g of lead nitrate (Merck) in distilled water in a 1000 ml volumetric flask and the solution made up to the mark. A working solution of 200 mg/L was prepared from the stock by placing 20 ml of the
stock solution in a 100 ml volumetric flask and making it to the mark using distilled water. Working lead (II) standards of 10 mg/L, 20 mg/L, 50 mg/L, 100 mg/L and 200 mg/L were prepared by adding 5, 10, 25, 50 and 100 ml of the working solution into a 100 ml volumetric flask and diluting it to the mark using distilled water.

Cadmium (II) stock standard solution of 1000 mg/L was obtained by dissolving 2.744 g of cadmium nitrate (Merck) and diluted to 1 litre in 1000 ml volumetric flask using distilled water. A working solution and standards were prepared using the same procedure as in lead (II).

Fluoride ion stock standard solution of 1000 mg/L was obtained by dissolving 2.210 g of anhydrous sodium fluoride (Merck) and diluted to 1 litre in 1000 ml volumetric flask using distilled water. A working solution of 100 mg/L was prepared from the stock by placing 10 ml of the stock solution in a 100 ml volumetric flask and making it to the mark using distilled water. Working fluoride ion standard solutions of 0.1, 2, 4, 6, 8 and 10 mg/L were prepared by adding 0.1, 2, 4, 6, 8 and 10 ml of the working solution into a 100 ml volumetric flask and diluting it to the mark using distilled water.

Ionic strength adjustment buffer (ISAB) solution was prepared by adding 57 ml glacial acetic acid, 45 g sodium chloride and 4g CDTA (1, 2-diamino cyclohexan N,N,N,N-tetra acetic acid) in 500 ml distilled water in a 1000 ml beaker and the mixture stirred to dissolve. The pH was adjusted to 5.5 by adding drops of 5M NaOH. The contents in the beaker were transferred into a 1 litre volumetric flask and topped up to the mark with distilled water.
3.3.1 Experimental procedures on the determination of optimum temperature

1.00 g of alumino-phosphate was accurately weighed and added to 100 ml of fluoride solution at initial concentrations of 6 mg/L and pH of 6. The experiments were carried out in triplicates at temperatures of 20, 30, 40, 50 and 60 ± 1°C. The samples were collected and filtered after 90 minutes, and then analyzed for the remaining fluoride ions in solution using the fluoride ISE.

For metal ion adsorption, 1.00 g of alumino-phosphate was accurately weighed and added to 100 ml of either lead (II) or cadmium (II) solutions at initial concentrations of 100 mg/L and at an optimum pH of 6 for both lead (II) and cadmium (II) ions. The shaking speed was maintained at 6 rps and the experiments were carried out in triplicates at temperatures of 25, 35, 45, 55 and 65 ± 1°C. The samples were collected and filtered after 90 minutes, and then analyzed for the remaining metal ions in solution using the AAS.

3.3.2 Experimental procedures on the determination of optimum pH

Maintaining the temperature at 30 ± 1°C and initial fluoride concentration at 6 mg/L, the pH was varied between pH 2 and 13 by addition of 0.1 M nitric acid or 0.1 M sodium hydroxide drop wise until the desired pH of 2, 5, 7, 9 and 13 were obtained in which 1.00 g of alumino-phosphate weighed accurately was added to 100 ml sample solutions. After 90 minutes, each sample was filtered separately and analyzed with an ISE for the remaining fluoride ions. The experiments were done in triplicate and the average values used to calculate the optimum pH value.
For the metal ion adsorption, batch experiments were done maintaining the temperature at 45 ± 1°C and shaking speed of 6 rps the pH was varied in the range of 2 to 13 by addition of 0.1 M nitric acid or 0.1 M sodium hydroxide drop wise until the desired pH was obtained. 1.00g alumino-phosphate weighed accurately was added to 100 ml solution portions of either lead (II) or cadmium (II) ions at pH 2, 5, 7, 9 and 13. The mixtures were agitated for approximately 90 minutes then filtered and analyzed using AAS for the remaining metal ions in solution. The experiments were done in triplicate for three initial metal ion concentrations of 25 mg/L, 50 mg/L and 100 mg/L and the average values used to determine the optimum pH value. The highest yield value for each of the initial concentration was noted and used as the optimum pH value for each of the two metal ions.

3.3.3 Determination of optimum shaking speed on adsorption

An adsorbent dose of 1.00 g was placed in two 250 ml conical flask containing 100 ml of 100 mg/L of either lead (II) or cadmium (II) ions at a temperature of 45 ± 1 °C and pH 6. Three samples of the mixtures were shaken simultaneously for each metal ion. The shaking speed interval was varied from 2, 4, 6, 8 and 10 for 90 minutes. Thereafter which samples of the solution were filtered and analyzed for the remaining lead (II) and cadmium (II) ions using an AAS.

3.3.4 Experimental procedures on the determination of equilibrate time

Batch experiments were carried out to find the equilibrium time for adsorption of fluoride ions on alumino-phosphate molecular sieves. Alumino-phosphate of 1.00 g was
mixed with 100 ml of 6 mg/L fluoride solution at a temperature of 30 ± 1 °C and pH 6. Samples were then collected at predetermined time intervals of 30 minutes for 150 minutes. After completion of each batch of experiments, samples were filtered and the remaining fluoride concentrations were determined using a fluoride ISE. The experiments were carried out in triplicate and the average values used in all the calculations.

When carrying out fluoride ISE measurements, all standards and samples were mixed with equal volumes of ISAB solution and mixed thoroughly to compensate for any differences in activity coefficients between sample and standards. A constant agitation was maintained so as to allow a fresh supply of ions to be exposed to the sensing portion of the ISE. Magnetic stirrers can generate sufficient heat to change the solution temperature. To counteract this effect, a piece of styrofoam sheet was placed between the stirrer and the beaker to act as an insulating material. The electrode tip was rinsed and gently dabbed dry with a low-lint laboratory tissue between measurements using distilled water to ensure accurate readings.

Batch experiments were also carried out to find the equilibrium time for adsorption of lead (II) and cadmium (II) ions on alumino-phosphate molecular sieves. One g of alumino-phosphate was mixed with 100 ml solutions of lead (II) or cadmium (II) ions at initial concentrations of 25 mg/L, 50 mg/L and 100 mg/L at a temperature of 45 ± 1 °C and pH 6. The mixture was shaken constantly at a speed of 6 and samples were collected at predetermined time intervals of 15 minutes for 60 minutes and thereafter at
30 minutes interval for up to 150 minutes. After completion of each batch of experiments, samples were filtered and the absorbances were determined using an AAS, on the remaining solution for each of the metal ions. In this work air acetylene flame was used. The experiments were carried out in triplicate and the average values used in all the calculations.

3.3.5 Determination of the effect of interfering anions on fluoride ion adsorption

The effects of coexisting anions such as sulphate, nitrate, chloride, and bicarbonate on fluoride adsorption by the alumino-phosphate molecular sieves were examined in batch experiments.

The effect of chloride ions on the adsorption of fluoride ions by AlPO₄ adsorbent was studied by adding 1.00 g of the molecular sieves to a mixture of solution of 50 mg/L, 100 mg/L, 200 mg/L, 300 mg/L and 400 mg/L of chloride ions while maintaining fluoride ions at 6 mg/L, pH of 6 and a temperature of 30 ± 1°C for 90 minutes. The amount of fluoride ions adsorbed was determined and then compared with that of the blank (without interfering ions) for which the percentage reduction was calculated. The same procedure was repeated separately using nitrate, sulphate and bicarbonate ions.

3.3.6 Experimental procedures on the determination of optimum sorbent dose

The adsorbent dose was varied from 0.50 g, 1.00 g, 1.50 g, 2.00 g and 2.50 g per 100 cm³ in initial ion concentration of 6 mg/L fluoride solution to determine the dose for optimal removal of fluoride ions. The experiment was carried out in triplicates at a temperature of 30 ± 1 °C, pH of 6.0, and contact time of 90 minutes after which the
samples were removed from the water bath and filtered. The remaining solution was analyzed using a fluoride ISE for the remaining fluoride ion concentration.

The adsorbent dose was varied from 1.00, 2.00, 3.00, 4.00 and 5.00g in100 cm³ to determine the dose for optimal removal of lead (II) and cadmium (II) metal ions. The experiment was carried out in triplicates at a temperature of 45 ± 1 °C, pH of 6.0, 100 mg/L initial metal ion concentration; the shaking speed was maintained at 6 for 90 minutes after which the samples were removed from the water bath and filtered. The remaining solution was analyzed using an AAS for the remaining metal ions.

3.3.7 Experimental procedures on the determination of optimum initial ion concentration

For fluoride ion adsorption, the initial fluoride ion concentration was varied from 2 mg/L to 10 mg/L at optimum temperature of 30 ± 1°C and pH of 6. The experiments were done in triplicate using 1.00 g of adsorbent in 100 cm³. The samples were then filtered after about 90 minutes and the filtrate analyzed for the remaining fluoride ion concentration using a fluoride ISE. After the analyses the average values were used to calculate the amount and the percentage of fluoride ions adsorbed from each initial ion concentrations. The optimum value was obtained by taking the highest percentage amount of fluoride ion adsorbed per unit mass of the adsorbent.

For metal ion adsorption, samples of lead (II) and cadmium (II) ion with initial ion concentrations varying from 10 mg/L to 200 mg/L were prepared in triplicate volumes of 100 cm³. 1.00 g of AlPO₄ adsorbent was added to each sample and shaken at a speed
of 6 rps for about 90 minutes while maintaining the optimum temperature of 45 ± 1°C and the pH at 6 for each metal ion. The samples were then filtered and the filtrate analyzed for the remaining metal ion concentration using AAS. After the analyses the average values were used to calculate the amount and the percentage of metal ions adsorbed from each initial metal ion concentrations. The optimum value was obtained by taking the highest percentage amount of metal ion adsorbed per unit mass of the adsorbent.

3.3.8 Adsorption kinetics

The kinetics of adsorption of lead (II) ions adsorbed by alumino-phosphate was studied as follows; 1.00g of the adsorbent was mixed with 100 cm³ of 100 mg/L solution and contained in a 200 cm³ plastic bottles. The resultant mixture was at a pH of 6.0 and maintained at a temperature 45 ± 1°C and speed of 6 rps in the shaker. Volumes of 5.00 ml were removed from the water bath at 15 minutes intervals using a syringe fitted with a membrane filter for 60 minutes and intervals of 30 minutes for up to 150 minutes and then analyzed using an AAS for the remaining metal ions. The data obtained was modelled by first order Lagergren and pseudo- second order equations to determine the rate constant and the efficiency of the adsorbent. The procedure was repeated using cadmium (II) ions. This method was adopted from Loukidou et al, (2004).

3.4 Instrumentation

Atomic absorption spectrophotometer (AAS) (Buck, model 210 VGP) was used for analysis of lead (II) and cadmium (II) ions. The AAS was set at the recommended
instrumental settings; at wavelength 283.3 nm for lead and 228.90 nm for cadmium, the slit length for the two metal ions was maintained at 0.7 nm. Fluoride ions were analyzed using a calibrated Fluoride ISE Combined (Sentek, 48030/0001). General operating instructions of optimum pH range: pH 4 to pH 8, temperature range: 0 to 80 °C and preconditioning time: 5 minutes were maintained (Skoog, 2004). The recommended ISAB was prepared and mixed with sample solution in the volume ratio of 1:1 to ensure that all measured solutions have the same ionic strength and avoid errors due to differences between the measured activity and the actual concentration.

All pH measurements were performed using a calibrated (Jenway 3505) pH-meter equipped with a standard calomel electrode (SCE). Special buffer tablets for pH 4, 7 and 9 were each dissolved separately, in 100 cm\(^3\) of distilled water in a beaker and used to calibrate the pH meter. Before use, the pH electrode was conditioned with saturated potassium chloride solution over night to wet the membrane and improve its sensitivity. The pH meter was calibrated daily before any pH measurements were carried out in the laboratory (Vogel, 1978).

Constant shaker (model C.F.C 3018) was used in shaking the samples at the required speeds while the centrifuge model Centurion 6,000 series was used for separating the residue from the solution. A water bath model SB3D was used for temperature regulation.
Fourier Transform Infrared Spectrophotometer (FTIR 8400) was used for IR spectroscopy analysis of the chemical groups on the walls of the molecular sieves responsible for the adsorption process. Potassium bromide (KBr) was used as the background material in all the analysis. KBr was mixed with the molecular sieves in the ratio 1:50. This was done by mixing 1 mg of the dried sample of alumino-phosphate with 50 mg KBr, ground to fine powder and pressed under vacuum to a pellet. The pellet was analyzed using an FTIR spectrophotometer (FTIR-8400) in the range 400 cm$^{-1}$ - 4000 cm$^{-1}$ (Naja et al, 2005).
CHAPTER FOUR
RESULTS AND DISCUSSION

4.1 Characterization of synthesized alumino-phosphate (AlPO₄) molecular sieves

Figure 4.1: FTIR Spectrum of synthesized AlPO₄ molecular sieves

The FTIR spectra of the synthesized AlPO₄ molecular sieves gave peaks at 3861.2, 3813.0, 3747.4, 3568.1, 3444.6, 3300.0, 3093.6, 2937.4, 2518.9, 2378.1, 2275.8, 2202.6, 2077.2, 1733.9, 1651.0, 1512.1, 1461.9, 1413.7, 1045.3, 731.0, 605.6, 567.0 and 486.0 cm⁻¹ as shown in figure 4.1.

The absorption band at 1461.9 cm⁻¹ is attributed to C=O bending vibrations associated with ketones present in the organic bone structure(Ibrahim et al., 2010). The stretching band of C=O (which is the characteristic band of carboxyl group) appears at 1733.9 cm⁻¹. The peak at 2202.6 cm⁻¹ is attributed to the bridging oxygen atoms (Al–O–Al). Strong
and medium-strength base sites are characterized by peaks ranging between 2193 and 2217 cm$^{-1}$. The OH band, which is observed at 1413.7 cm$^{-1}$ might arise from phenol compounds (Ibrahim et al., 2009). The band at 1045 cm$^{-1}$ is assigned to the fundamental frequencies of the PO$_4^{3-}$ group due to P–O stretching. While that at 2378.1 cm$^{-1}$ to medium P-H stretching vibrations. The FTIR analysis results confirmed the synthesis of AlPO$_4$ molecules.

4.2 Adsorption of fluoride ions by AlPO$_4$ molecular sieves

4.2.1 Effect of Temperature on the adsorption of fluoride ions

The data obtained by variation of temperature of fluoride ion solution is given in figure 4.2. It is observed that by increasing the temperature from 20 °C to 60 °C ± 1°C there was an increase in the amount of fluoride ions adsorbed by the molecular sieves followed by a decline in the amount of percentage defluoridation. Adsorption of fluoride ions increased from 77.67% to 78.50% when the temperature was increased from 20 °C to 30 °C ± 1 °C. However this is followed by a decrease in percentage defluoridation from 78.50% to 38.67% when the temperature was increased from 30 °C to 60 °C ± 1 °C.

The graph (Figure 4.2) indicates that high temperatures work against defluoridation by AlPO$_4$ molecular sieves. This results are in agreement with Zhao et al. (2010) investigation on fluoride removal from aqueous solution using synthesized Fe$_3$O$_4$-Al(OH)$_3$ magnetic nanoparticles. The adsorption capacity decreased with temperature.
The decrease in the amount of fluoride ions adsorbed with temperature indicates an exothermic nature of the process. It is clear that the temperature of the adsorption medium could be important for energy dependent mechanisms in fluoride ion binding process.

![Figure 4.2: Effect of temperature on the adsorption of fluoride ions by AlPO₄ molecules](image)

### 4.2.2 Effect of pH on the adsorption of fluoride ions

The data generated from the effect of pH of the solution at a constant temperature of 30 °C± 1 °C (determined from experimental procedure described in section 4.2.1) is given in figure 4.3. There is an increase in the percentage amount of fluoride ions adsorbed increased from 50.33% to 78.33% when the pH was varied from 2 to 7 as shown in graph (Figure 4.3). This can be attributed to the formation of weakly ionized hydrofluoric acid in acidic conditions (Tor, 2006). Equilibrium was reached between pH 5 and 7 where a slight change in adsorption accompanied change in pH. As the pH was increased from 7 to 13, the amount of fluoride ions adsorbed by the AlPO₄
molecular sieves decreased from 78.33% to 30.00 %. The minimum amount of adsorbed fluoride ions occurred at pH of 13.0.

At higher pH values, the reduction in adsorption may be possible due to abundance of OH⁻ ions causing increased hindrance to diffusion of fluoride ions, due to the increasing electrostatic repulsion between the negatively charged surface sites of the adsorbent and fluoride ions (Raichur and Basu, 2001). The results is in agreement with fluoride removal studies on montmorillonite at optimum pH 6 where 82.00% of fluoride ions were removed at pH 7, 60.00% at pH 10 and 56.00% at pH 12, (Tor, 2006), carbon slurry at optimum pH 7 (Gupta and Sthacharyya, 2006) and mixed rare earth oxides at an optimum of about pH 6.5 (Raichur and Basu, 2001). This confirms that fluoride ion adsorption onto adsorbents from aqueous solutions is dependent on the pH of solution as it is with other ions. The pH of the solutions used was 6; this was recorded as the optimum value and maintained in all other defluoridation experiments.
4.2.3 Effect of contact time on the adsorption of fluoride ions

The data on the amounts of fluoride ions adsorbed as contact time was varied is given in figure 4.4. This experiment was done at constant temperature of 30 °C ± 1 °C and pH 6 (determined from experimental procedures described in sections 4.2.1 and 4.2.2). It was observed that the amount of fluoride ions adsorbed by AlPO₄ molecular sieves increased with increase in contact time. From the graph (Figure 4.4), a plateau was reached at about 90 minutes. Also the fluoride ions adsorption by AlPO₄ molecular sieves showed a fast initial adsorption to near saturation and then a little or no increase as equilibrium was approached. Time contact of 90 minutes was recorded as the optimum time and used in all fluoride adsorption experiments.

This data is in agreement with studies of Ibrahim et al. (2010) on agricultural waste adsorbent for the removal of lead (II) ions from aqueous solutions. In their study, a fast initial adsorption was followed by little or no increase as equilibrium time was
approached. This is attributed by the fact that a large number of vacant surface sites are available for the adsorption during the initial stage and the solute concentration gradient was high. With the passage of time, there is a decrease in the number of adsorption sites and the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid phase and in the bulk liquid phase (Tor, 2006).

![Figure 4.4: Effect of contact time on the adsorption of fluoride ions by AlPO₄ molecules](image)

**Figure 4.4:** Effect of contact time on the adsorption of fluoride ions by AlPO₄ molecules

### 4.2.4 Effect of sorbent dose on the adsorption of fluoride ions

The effect of varying the adsorbent mass on the percentage removal of fluoride ions using AlPO₄ molecular sieves at conditions temperature of 30 °C ± 1 °C, pH 6 and contact time of 90 minutes (determined from experimental procedures described in sections 4.2.1, 4.2.2 and 4.2.3) is given in figure 4.5. As shown, percent removal increased to an optimum value at with increase in sorbent dosage. There was a sharp increase in the percentage adsorption of fluoride ions from 71.33% to 78.83% when the
adsorbent dose was increased from 0.50 g to 2.50 g /100 ml. As the sorbent dose was increased from 1.00 g to 2.50 g, the graph assumed an almost straight line due to the minimal change in percentage of fluoride ions adsorbed.

Adsorbent dose of 1.00 g was taken as the optimal adsorbent dose and used for all the fluoride ion adsorption experiments where other parameters were varied. Alagumuthu et al. (2010) examined adsorbent obtained by burning, carbonization and thermal activation of Cynodon dactylon, and reported appreciable defluoridation efficiency with increase in adsorbent dose. This is attributed to availability of more adsorption sites due to increased surface area at higher dose of adsorbent.

Figure 4.5: Effect of adsorbent dose on the adsorption of fluoride ions by AlPO₄ molecules
4.2.5 Effect of initial ion concentration on the adsorption of fluoride ions

The mean amount of fluoride ions adsorbed by AlPO$_4$ sieves was determined at the following conditions: temperature 30 °C ± 1 °C, pH 6, contact time of 90 minutes and 1.00 g/100 ml adsorbent (determined from experimental procedure described in sections 4.2.1, 4.2.2, 4.2.3 and 4.2.4). Change in initial ion concentrations indicated an effect on the adsorption efficiency of the molecular sieve. As the initial concentration increased from 2 mg/L to 6 mg/L, there was an increase in the percentage quantity of fluoride ions adsorbed by the molecular sieves from 39.90% to 77.83% (Figure 4.6). An increase in initial ion concentration above 6 mg/L was accompanied by a decrease in percentage defluoridation.

The highest percentage adsorption of fluoride ions occurred at an initial ion concentration of 6 mg/L. At this initial fluoride ion concentration, 77.83% of the initial concentration of fluoride ions was adsorbed. Initial ion concentration of 6 mg/L was recorded as the optimum concentration and used in all fluoride adsorption experiments where other parameters were varied. There was an increase in adsorption due to an increase in the amount of the fluoride ions bound on the surface of the adsorbent. Lv et al. (2006) obtained a similar trend in their study on fluoride ion removal with MgAl-CO$_3$. According to Malakootian et al. (2011), removal of fluoride ions from aqueous solution by pumice showed an increase in adsorbed percentage as initial fluoride concentration was increased due to a raise in the driving force of the concentration gradient.
4.2.6 Effect of interfering co-ions on the adsorption of fluoride ions

The effects of coexisting anions (such as sulphate, nitrate, chloride, and bicarbonate) on fluoride adsorption by AlPO₄ molecular sieves were examined and the data presented in graphs. The effect of selected anions on the adsorption of fluoride ions by AlPO₄ adsorbent was studied by adding 1.00 g/100 cm³ of the molecular sieves to a mixture of solution of known concentrations of the interfering anions with fluoride ions. Other parameters maintained constant were pH 6, initial fluoride ions concentration of 6 mg/L, 90 minutes contact time and temperature of 30 °C ± 1 °C. The amount of fluoride ions adsorbed was noted and then compared with that of the blank (without interfering ions) for which the percentage reduction was calculated. From the graph (Figure 4.7), it is observed that, chloride ions and nitrate ions did not perceptibly interfere with the removal of fluoride ions even at a concentration of 400 mg/L. As chloride ions concentration increased from 0 mg/ L to 400 mg/L, the percentage of fluoride ions adsorbed remained almost constant varying from 78.00% to 77.50%.
A similar trend was observed when nitrate ions were introduced as interfering ions. An increase in nitrate ions from 0 mg/L to 400 mg/L was accompanied by a slight change in the percentage of fluoride ions adsorbed ranging from 78.00% to 75.00%. Sulphate ions showed some adverse effects on defluoridation when the concentration of these interfering ions was increased. An increase of sulphate ions from 0 mg/L to 400 mg/L caused variation in the percentage of fluoride ions adsorbed decreasing from 78.00% to 66.00%. However, the presence of bicarbonate ions showed great competitive adsorption with fluoride ions. The fluoride ions adsorbed by AlPO₄ molecular sieves decreased from 78.00% to 30.50% with the increase of bicarbonate ions concentration from 0 mg/L to 200 mg/L, and then decreased slightly to 20.50% with further increment of bicarbonate ions concentration to 400 mg/L.

The data obtained is in agreement with studies on fluoride ions removal on montmorillonite where defluoridation efficiency was found to decrease from 82.00% to 58.00% with increase in bicarbonate ions (Tor, 2006). According to Tor (2006), this may be attributed to the competition of bicarbonate ions with the fluoride ions at the active site, on the surface of the sorbents. The selective nature of the fluoride ions by the adsorbent depends on size, charge, polarizability and electronegativity difference. From the data obtained, the order of interference of fluoride ions removal by the AlPO₄ molecular sieve adsorbent was in the order, $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$. A similar trend was reported by Alagumuthu et al. (2010) while studying adsorption of fluoride ions by cynodon dactylon.
The data obtained indicated that in the presence of chloride ions, nitrate ions, sulphate ions and bicarbonate ions the sorptive capacity of AlPO₄ molecular sieves was decreased. The reduced binding capacity may be as a result of competition for binding sites according to Lodeiro et al. (2006). Industrial effluents as well as surface water may contain a mixture of anions, such as chloride, nitrate, sulphate and bicarbonate ions. Although the elimination of these anions is not the purpose of this adsorption studies, they can compete and interfere for binding sites with the fluoride ions.

![Figure 4.7: Effect of interfering co-ions on the adsorption of fluoride ions by AlPO₄ molecules](image)

**Figure 4.7:** Effect of interfering co-ions on the adsorption of fluoride ions by AlPO₄ molecules

### 4.3 Adsorption of lead (II) and cadmium (II) metal ions by AlPO₄ molecular sieves

#### 4.3.1 Effect of temperature on the adsorption of lead (II) and cadmium (II) metal ions

The data obtained by varying the temperature of solution in the adsorption of lead (II) and cadmium (II) metal ions by AlPO₄ molecular sieves is given in a graph. From the graph (figure 4.8) it is observed that by increasing the temperature from 25 °C to 45 °C ±
1°C there was a general increase in the amount of adsorbed metal ions. The increase was followed by a decline in the amount of metal ions adsorbed as temperature was further increased to 65 °C ± 1°C. The amounts of lead (II) ions adsorbed were higher than cadmium (II) ions.

Adsorption of lead (II) ions increased from 84.50% to 89.25% when the temperature was increased from 25 °C to 45 °C ± 1 °C. However, the adsorption decreased for temperature above 45 °C. These data was in agreement with the findings of Lodeiro et al. (2006), who observed that increasing the temperature favored the adsorption of lead (II) ions and cadmium (II) ions on marine macro-algae. Benhima et al. (2008) obtained similar results when they studied the adsorption of lead (II) ions and cadmium (II) ions onto micro-particles of dry plants as the adsorbent.

The percentage of cadmium (II) ions adsorbed increased from 79.50% to 83.17% when the temperature was increased from 25 °C to 45 °C ± 1 °C, but decreased at temperatures above 45 °C. Benguella and Benaissa (2002) and Herrero et al. (2008) made similar observations when they performed the adsorption of cadmium (II) ions by chitin and red alga respectively. They suggested that the adsorbents whose adsorption capacities had a small change accompanying temperature change could be desirable.

The enhancement of metal ion adsorption capacity with temperature is attributed to the possible increase in the number of active sites available for adsorption on the surface with increase in temperature up to a certain point. The kinetic energy of metal ions
increased with increasing temperature of solution. At 25 °C to 45 °C ± 1 °C, the collision frequency between the adsorbent and adsorbent increased: hence greater adsorption on the surface of the adsorbent particles (Ola, 2007). Further increase of temperature, above 45 °C worked against the removal of both ions.

Pandey et al. (1986) observed that decrease in adsorption with rise in temperature might be due to weakening of the adsorptive forces between the active sites of the adsorbent and adsorbate species and also between the adjacent molecules of the adsorbed phase. Very high temperature could cause deterioration of the matrix structure of the adsorbent, and then, it may probably result to loss of sorption sites, hence reducing the percentage of lead (II) and cadmium (II) ions removal according to Davis et al. (2003). The temperature of the adsorption medium could be important for energy dependent mechanisms in metal binding process.

![Figure 4.8](image)

**Figure 4.8:** Effect of temperature on the adsorption of lead (II) and cadmium (II) metal ions by AlPO₄ molecules
4.3.2 Effect of pH on the adsorption of lead (II) and cadmium (II) metal ions

The data generated on the effect of pH at constant temperature of 45 °C ± 1 °C (determined from experimental procedure described in section 4.3.1) on adsorption of lead (II) and cadmium (II) metal ions by AlPO₄ molecular sieves at different initial ion concentrations is given in graphs. From the graph (Figure 4.9) it is observed that the maximum percentage amount of lead (II) ions adsorbed at the initial concentrations of 100 mg/L, 50 mg/L and 25 mg/L ranged from about 87.00% to 91.00%, 64.50% to 66.06% and 25.00% to 28.00% respectively at approximately pH 5.0 to pH 7.0. The minimum amount of adsorbed lead (II) ions occurred at pH of 2.0.

Similar findings have been reported for other types of adsorbents. Singh et al. (2006) reported that the highest percentage of lead (II) ions adsorbed by phosphatic clay occurred at a pH of 5.0. Gupta and Sttacharyya (2006) suggested that at low pH the adsorbent surface would be completely covered with hydrogen ions (H⁺) and lead (II) ions cannot complete with them for adsorption sites. This could be partly due to the fact that protons are strong competing sorbate because of their higher concentration. This could probably explain the low lead (II) ions adsorption at low pH. Ghodbane et al. (2008) reported that the minimal adsorption obtained at low pH may be due to high mobility of protons and partly due to the fact that the solution pH influences the sorbent surface charge.

According to Li et al. (2008) the surface charge of the adsorbent is positive at pH < PZC (point of zero charge), neutral at pH = PZC and negative at pH > PZC. At pH >
PZC, the metal ions in solution are attracted to the surface of the sorbent, thus favoring sorption. At higher pH values, the lower number of protons and the greater number of negative charges could result in greater metal ion adsorption. At pH of 7, however, there was decrease in lead (II) ion adsorption, probably, due to hydrolysis accompanying the precipitation of metal hydroxides according to Pehlivan et al. (2008).

From the data, the maximum amount of cadmium (II) ions adsorbed occurred at pH of 5.0 for initial metal ion concentrations of 100 mg/L, pH 7.0 for both initial ion concentrations of 50 mg/L and 25 mg/L. The maximum percentage amounts of cadmium (II) ions adsorbed at these concentrations were 83.50%, 60.50% and 25.33% respectively. The least amount of cadmium (II) ions adsorbed occurred at the pH of 2.0 for all the initial ion concentrations studied. From the graph (Figure 4.10) it is observed that adsorption capacity of AlPO₄ molecular sieves increased remarkably with increasing pH. Optimum adsorption was reached at values ranging between pH 5.0 and pH 7.0.

Carrilho and Gilbert (2000) who investigated a filamentous free-living form of brown algae, found that sorptive capacity to be greatest at around pH 5.5 for Cr (III), Fe (III) and Cu (II) metal ions. Li et al. (2008) noted at higher pH, the formation of anionic hydroxide complexes decreases the concentration of free metal ions, thereby; the adsorption capacity of metal ions is decreased, figure 4.10 shows a similar trend. Herrero et al. (2008) observed that at pH above 6.0 low soluble hydroxyl species are
formed such as Cd(OH)$_2$ and Cd(OH)$_3^-$’. This probably contributed to the decline in cadmium (II) ion adsorption at values above pH 7.0.

From the data obtained, it is evident that the pH of the solution influence both metal binding sites on the adsorbent surface and the chemistry of the metal in solution. Metal ion adsorption onto adsorbents from aqueous solutions is dependent on the pH of solution as it affects adsorbent surface charge and degree of ionization.

**Figure 4.9:** Effect of pH on the adsorption of lead (II) ions from solutions of 100 mg/L, 50 mg/L and 25 mg/L by AlPO$_4$ molecules
Figure 4.10: Effect of pH on the adsorption of cadmium (II) ions from solutions of 100 mg/L, 50 mg/L and 25 mg/L by AlPO$_4$ molecules

4.3.3 Effect of shaking speed on the adsorption of lead (II) and cadmium (II) metal ions

The data obtained by varying the agitation speed during the adsorption of lead (II) ions and cadmium (II) ions by AlPO$_4$ molecular sieves is presented in a graph. The experiment was carried out at constant temperature of 45 °C ± 1 °C and pH 6 (determined from experimental procedures described in sections 4.3.1 and 4.3.2). The resulting graph given in figure 4.11 shows that the amount of metal ions adsorbed increased with the increase in the agitation speed. When the shaking speed was varied from 2 rps to 6 rps, the percentage cadmium (II) ions adsorbed increased from 64.67% to 80.67%. Further increase of the agitation speed from 6 rps to 10 rps resulted to minimal change of the percentage cadmium (II) ions adsorbed ranging between 80.67% and 80.33%. A similar trend was observed for the percentage adsorption of lead (II) ions when shaking speed was varied. When the shaking speed was varied from 2 rps to 6 rps, the percentage lead (II) ions adsorbed increased from 71.75% to 86.75%.
Further increase of the agitation speed from 6 rps 10 rps resulted to minimal change of the percentage lead (II) ions adsorbed ranging between 86.75% and 86.50%. The maximum amount adsorbed occurred at shaking speed 6 rps, for both lead (II) ions and cadmium (II) ions, which was taken as the optimum shaking speed and used in all experiments where shaking speed was maintained constant. Ghodbane et al. (2008) suggested that when increasing the agitation speed, the diffusion rate of metal ions from the bulk liquid to the liquid boundary layer surrounding sorbent particles become higher because of an enhancement of turbulence and a decrease of the thickness of the liquid boundary layer. Good diffusion of ions towards the sorbent particles is also ensured. Low and Lee (1997) suggested that increasing the agitation rate increases the external film mass transfer coefficient hence the rate of adsorption. This is due to reduction of the film boundary layer surrounding the sorbent particles. According to Mckay (1982), in a system where the agitation of solid in a solution is vigorous, intraparticle diffusion is likely to be the limiting step.

**Figure 4.11:** Effect of shaking speed on the adsorption of lead (II) and cadmium (II) metal ions by AlPO₄ molecules
4.3.4 Effect of contact time on the adsorption of lead (II) and cadmium (II) metal ions

The data generated from the variation of contact time in the adsorption of lead (II) and cadmium (II) metal ions is given graphs. A temperature of 45 °C ± 1 °C, pH 6 and agitation speed of 6 rps (determined from experimental procedures described in sections 4.3.1, 4.3.2 and 4.3.3) were maintained constant. In the graph (Figure 4.13) it is observed that the amount of cadmium (II) ions adsorbed by the AlPO4 molecular sieves increased with increase in contact time and reached a plateau value at about 100 minutes when the initial metal ion concentration was 100 mg/L but was reached much earlier; at about 90 minutes when the initial metal ion concentration was 50 mg/L and at about 60 minutes when the initial metal ion concentration was 25 mg/L. The same trend was observed, in the graph given by figure 4.12, for lead (II) ions although the plateau was reached at a shorter time. Initial metal ion concentration of 100 mg/L and 50 mg/L lead (II) ions took about 90 minutes while initial metal ion concentration of 25 mg/L lead (II) ions took about 45 minutes.

From the data obtained, lead (II) and cadmium (II) ions adsorption by AlPO4 molecular sieves, show a fast initial adsorption to near saturation and then little or no increase as equilibrium is approached. Oliveira et al. (2008) who studied the adsorption of Cd (II), Cu (II), Zn (II) and Cr (VI) by untreated coffee husks reported similar results. According to Gulipalli et al. (2011) in their study on the adsorption of selenium (IV) ions on iron (III) chloride coated rice husks, this is attributed by the fact that a large number of vacant surface sites are available for the adsorption during the initial stage
and with the passage of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid phase and in the bulk liquid phase.

**Figure 4.12:** Effect of contact time on the adsorption of lead (II) metal ions by AlPO$_4$ molecules

**Figure 4.13:** Effect of contact time on the adsorption of cadmium (II) metal ions by AlPO$_4$ molecules
4.3.5 Effect of sorbent dose on the adsorption of lead (II) and cadmium (II) metal ions

The data generated by variation of sorbent mass on the adsorption of lead (II) ions and cadmium (II) ions by AlPO₄ molecular sieves is presented in a graph. The sorbent dose was varied from 0.50 g/ml to 2.50 g/cm³ while maintaining constant parameters determined from experimental procedures described in sections 4.3.1, 4.3.2, 4.3.3 and 4.3.4.

There was an increase in the percentage adsorption of lead (II) from 86.50% to 92.00% when the adsorbent dose was increased from 0.50 g to 1.50 g/100 cm³. The adsorption of cadmium (II) ions increased from 79.67% to 84.33% when the adsorbent dose was increased from 0.50 g to 1.00 g/100 cm³. From the graph given in figure 4.14, it is observed that the adsorption of both lead (II) and cadmium (II) ions increased with increase in sorbent dosage. Slight changes in percentage adsorption were accompanied by increase in adsorbent dosage from 1.50 g to 2.50 g/100 cm³ for lead (II) ions and 1.00 g to 2.50 g/100 cm³ for cadmium (II) ions.

Increase in adsorption with the adsorbent dosage can be attributed to the availability of greater surface area and larger number of adsorption sites, (Puranik et al., 1997). At adsorbent dose less than the optimum amount, the adsorbent surface becomes saturated with metal ions and the residual metal ion concentration in the solution is large. With an increase in sorbent dosage, the metal ion adsorption increases due to increased metal ion adsorption by the increased amount of adsorbent. According to Davila- Jimenez et al.
(2003), the increment in metal ions removal becomes very small as the surface metal ions concentration and the solution metal ions concentration come to near equilibrium with each other. Higher metal ions adsorption at lower adsorbent mass has also been attributed to an increased metal to adsorbent ratio, which decreases upon an increase in adsorbent mass according to Puranik and Paknikar (1997).

At higher molecular sieves to solute concentration ratios, there is a very fast superficial adsorption onto the sorbent surface that produces a lower solute concentration in the solution than when the molecular sieve to solute concentration ratio is lower. This is because a fixed mass of adsorbent can only adsorb a certain amount of the metal ion (Davila- Jimenez et al., 2003). The decrease in amount of lead (II) and cadmium (II) ions adsorbed with increasing sorbent mass is due to the split in the concentration gradient between solute concentration in the solution and the solute concentration in the surface of the sorbent. Fourest and Roux (1992) observed that increased adsorbent concentration led to insufficiency of metal ions in solution with respect to binding metal ions. Thus with the increasing sorbent mass, the amount of lead (II) and cadmium (II) ions adsorbed onto unit weight of sorbent gets reduced causing a decrease in adsorption efficiency with increasing sorbent mass concentration. Adsorbent dose of 1.00 g was taken as the optimal adsorbent dose and used for all experiments.
4.3.6 Effects of initial ion concentrations on adsorption of lead (II) and cadmium (II) ions

The data generated by varying the initial metal ion concentrations on the adsorption of lead (II) and cadmium (II) by AlPO₄ molecular sieves is given in a graph. The experiment was carried out maintaining constant parameters determined from experimental procedures described in sections 4.3.1, 4.3.2, 4.3.3, 4.3.4 and 4.3.5). The remaining metal ion concentration in each case was measured separately. From the graph (Figure 4.15), it is observed that the highest percentage adsorption of lead (II) ions and cadmium (II) ions occurred at a concentration of 200 mg /L. At this initial metal ion concentration, 88.00% and 84.00% of the initial concentration of lead (II) cadmium (II) ions were adsorbed respectively. As the initial concentration increased from 10 mg/L to 200 mg/L for the two metal ions, there was an increase in the percentage quantity of metal ions adsorbed by the AlPO₄ molecular sieves. The increase in adsorption of lead (II) ions and cadmium (II) ions can be explained as a result of
increase in the amount of the metal ions bound. For the initial concentration of 10 mg/L, the percentages were 32.50% and 16.67% for lead (II) ions and cadmium (II) ions respectively. AlPO₄ molecular sieves have the highest adsorption capacity occurring at high concentrations of lead (II) and cadmium (II) ions. This may be explained by a progressive increase in electrostatic mutual interaction between sites that have lower affinity for metal ions as the population of occupied sites decreases (Al-Asheh et al., 1997).

![Figure 4.15](image)

**Figure 4.15**: Effect of initial ion concentration on the adsorption of lead (II) and cadmium (II) metal ions by AlPO₄ molecules

### 4.4 Kinetics of lead (ii) and cadmium (ii) ions adsorption

#### 4.4.1 Modeling of the data

Kinetics of lead (II) and cadmium (II) ions adsorption was modeled by the first-order Lagergren equation and the Pseudo-second-order equation and the graphs given in figures, 4.16, 4.17, 4.18 and 4.19 respectively. The first-order Lagergren was modeled by plotting log \((q_e - q_t)\) against \(t\) while Pseudo-second-order was modeled by plotting \(t/q_t\)
against t for both both lead (II) and cadmium (II) ions. Where $q_e$ and $q_t$ were calculated using equation 2.8.

**Figure 4.16:** Fit of Pseudo-1\textsuperscript{st} order-equation for the adsorption of lead (II) metal ions by AlPO\textsubscript{4} molecules

**Figure 4.17:** Fit of Pseudo-1\textsuperscript{st} order-equation for the adsorption of cadmium (II) metal ions by AlPO\textsubscript{4} molecules
From figure 4.16 it is observed that the first order Lagergren equation failed to fit the experimental data on the adsorption of lead (II) metal ions. However, figure 4.18 indicates that the pseudo- second – order equation provided a near perfect match between the theoretical and the experimental values. The lower R² value (0.890) for the first order Lagergren equation in comparison to the R² value (0.994) obtained from the
pseudo-second–order equation suggests that lead (II) metal ions adsorption onto AlPO$_4$ followed the pseudo-second–order equation. Comparable results were obtained when the data of cadmium (II) metal ions adsorption was fitted on the first order Lagergren equation and the pseudo-second–order equation.

From the graphs given in figures 4.17 and 4.19, it is observed that the $R^2$ value obtained from the first order Lagergren equation (0.973) was lower than the value obtained from the pseudo-second–order equation (0.995) suggesting poor pseudo-first–order fit to the data for cadmium (II) adsorption. The pseudo-second-order rate constant $K'$ for cadmium (II) ions adsorption was found to be 0.007 g/mg/min while that of lead (II) ions was 0.009 g/mg/min.

The adsorption described by the pseudo second-order model was developed based on the assumption that the rate limiting step may be chemisorption. This suggests that the adsorption involves two species, in this case, the metal ion and the adsorbent according to Babalola et al. (2009). The model considering metal–adsorbent reaction as a rate limiting step constitutes a significant alternative to the commonly used diffusion equations. In this case, metal diffusion both in the bulk solution and in the adsorbent is considered faster than the reaction that takes place in the active binding sites (Herrero et al., 2008).
4.4.2 Kinetics of the metal ions adsorption

Information of the kinetics of metal ions is required for selecting the optimum operating conditions for further experiments. The lead (II) ions and cadmium (II) ions adsorption process proceeded in one distinct phase. From the graph (Figure 4.20), it is observed that, for both metal ions the adsorption rates were very fast initially, and then become almost stable as contact time increased while maintaining other parameters constant (temperature of 45 °C ± 1 °C, pH 6, shaking speed of 6 rps, initial metal ion concentration of 100 mg/L and 1.00 g/100 ml adsorbent). According to Zhou et al. (1998), this trend shows an attainment of equilibrium.

![Figure 4.20: Adsorption of lead (II) and cadmium (II) metal ions against time by AlPO₄ molecules at optimum conditions](image)

It was found that the rate of the metal adsorption was rather fast, about 45.00% of lead (II) was adsorbed in the first 15 minutes and 88.25% of the total adsorption occurred in 90 minutes. After 90 minutes there was a slower adsorption rate. About 42.33% of cadmium (II) ions were adsorbed in the first 15 minutes while about 81.33% of
cadmium (II) ions were adsorbed in 90 minutes. After 90 minutes there was a slower adsorption rate and thereafter there was no significant adsorption noted.

The adsorption of lead (II) and cadmium (II) metal ions by AlPO$_4$ molecular sieves, as noted earlier increases sharply at the beginning of the process followed by a slower adsorption as the equilibrium is approached. Li et al. (2008) proposed that the fast initial rate might be due physical adsorption or ion exchange at the adsorbent surface. Because active sites in a system is a fixed number and each site can adsorb only one ion in a monolayer, the metal adsorption by the sorbent surface will be rapid initially, then slows down as the competition for decreasing availability of active sites intensifies by the metal ions remaining in solution.

It is observed that the amount of for lead (II) ions adsorbed was greater than cadmium (II) ions. Brasquet et al. (2002) and Rivera-utrilla et al. (2003) found the same order of preference when aqueous solutions of lead (II) and cadmium (II) ions were adsorbed on activated carbon. Benhima et al. (2008) who performed lead (II) and cadmium (II) ions adsorption onto inert organic matter (IOM) suggested that high hydrated ionic radius of cadmium (II) ions (2.75 Å) induces quick saturation of adsorption surface available for hydrated ionic radius due to steric hindrances. This may result to reduction of the adsorption surface available for cadmium (II) ions. They further noted that since the hydrated ionic radius for lead (II) ions (2.61 Å) is low, therefore it may fit several adsorption sites before saturation and could explain the greater amount of lead (II) ions
adsorbed. Lodeiro et al. (2006) gave similar explanation when they studied the adsorption of lead (II) and cadmium (II) ions by marine macro-alga.

Pseudo-second order equation proposed by Ho (2003) was able to fit the kinetic data in the whole data range. In this model, the rate limiting step is chemisorption, where metal from solution is due to purely physicochemical interactions between the adsorbent and the metal solution (Aksu, 2001). This model predicts the sorption behavior of lead (II) and cadmium (II) ions over all the concentration studies and enables the initial sorption rate to be evaluated. It depends on the initial metal ion concentration and the adsorption sites.

4.4.3 Adsorption isotherms for AlPO₄ molecular sieves

The adsorption data for both lead (II) and cadmium (II) metal ions were fit into Langmuir and Freundlich isotherm models. Equation 2.2 was used for the linear Langmuir fit while linear equation 2.4 was used for Freundlich model. Equation 2.8 was applied in calculation of the ions adsorbed at equilibrium (qₑ). The graphs that were obtained are given in figures 4.21, 4.22, 4.23 and 4.24.
Figure 4.21: Langmuir fit for lead (II) metal ions adsorption by AlPO$_4$ molecules

Figure 4.22: Freundlich fit for lead (II) metal ions adsorption by AlPO$_4$ molecules
Figure 4.23: Langmuir fit for cadmium (II) metal ions adsorption by AlPO₄ molecules

Figure 4.24: Freundlich fit for cadmium (II) metal ions adsorption by AlPO₄ molecules

Table 4.1: Freundlich and Langmuir parameters for lead (II) metal ions adsorption by AlPO₄

<table>
<thead>
<tr>
<th>Freundlich constants (lead (II) ions)</th>
<th>Langmuir constants (lead (II) ions)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_f$ (mg/g)</td>
<td>$Q_{\text{max}}$ (mg/g)</td>
</tr>
<tr>
<td>18.072</td>
<td>6.329</td>
</tr>
<tr>
<td>$\frac{1}{n}$</td>
<td>$\frac{1}{b}$</td>
</tr>
<tr>
<td>-0.274</td>
<td>-3.759</td>
</tr>
<tr>
<td>$N$</td>
<td>$b$</td>
</tr>
<tr>
<td>-3.650</td>
<td>-0.266</td>
</tr>
<tr>
<td>$R^2$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>0.921</td>
<td>0.997</td>
</tr>
</tbody>
</table>
Table 4.2: Freundlich and Langmuir parameters for cadmium (II) ions adsorption by AlPO$_4$

<table>
<thead>
<tr>
<th>Freundlich constants (cadmium (II) ions)</th>
<th>Langmuir constants (cadmium (II) ions)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_f$ (mg/g)</td>
<td>$Q_{\text{max}}$ (mg/g)</td>
</tr>
<tr>
<td>23.988</td>
<td>5.208</td>
</tr>
<tr>
<td>$\frac{1}{n}$</td>
<td>$\frac{1}{b}$</td>
</tr>
<tr>
<td>-0.366</td>
<td>-6.993</td>
</tr>
<tr>
<td>$N$</td>
<td>$b$</td>
</tr>
<tr>
<td>-2.732</td>
<td>-0.143</td>
</tr>
<tr>
<td>$R^2$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>0.994</td>
<td>0.998</td>
</tr>
</tbody>
</table>

Adsorption isotherm models describe the adsorption phenomena at the solid-liquid interface. They provide essential data for practical design of adsorption systems and understanding of the relation between adsorbent and sorbent. The Langmuir and Freundlich models were used to determine adsorption isotherm data. This analytical method is important in comparing of different adsorbents.

The $R^2$ values for Freundlich and Langmuir isotherms fit on the adsorption for lead (II) ions were 0.921 and 0.997 respectively, while those for the adsorption of cadmium ions were 0.994 and 0.998 respectively as indicated in tables 1 and 2. By comparison of the $R^2$ values, the Langmuir adsorption isotherm has higher values of $R^2$ hence it fits well to the experimental data obtained than the Freundlich adsorption isotherm, for both cadmium (II) and lead (II) ions. This indicates that the adsorption of both metal ions on the AlPO$_4$ molecular sieve is monolayer. Panda et al. (2008) and Oliveira et al. (2008) obtained similar results on the biosorption of cadmium and nickel by functionalized husk of *lathyrus sativas* and untreated coffee husks as biosorbents for the removal of heavy metals from aqueous solutions respectively.
The maximum adsorption, $Q_{\text{max}}$, of lead (II) ions was found to be 6.329 mg/g while that for cadmium (II) ions was 5.208 mg/g. The adsorption capacities of AlPO₄ molecular sieves for the removal of lead (II) and cadmium (II) have been compared with those of other adsorbents reported in the literature as presented in table 3. The experimental data of the present study compares favorably well with that of other adsorbents reported in literature. In some cases these values suggest that the adsorbent, AlPO₄ molecular sieves, have a higher adsorption capacity for the two metal ions than some conventional adsorbents. This is because most adsorbents contain micro pores and the adsorption process is affected by surface properties such as surface area and polarity. A large specific surface area is preferable for providing large adsorption capacity.

The size of the micro pores determines the accessibility of the sorbate molecules to the adsorption surface (Igwe and Abia, 2006). However $Q_{\text{max}}$ for lead (II) ions is greater than that of cadmium (II) ions Benhima et al. (2008) obtained similar result when they studied the removal of lead (II) and cadmium (II) ions from aqueous solution by adsorption onto micro-particles of dry plants. They proposed that the lower hydrated ionic radius of lead (II) ions bear a charge density that favors attractive electrostatic interactions between the adsorbent and the lead (II) ions. The higher charge density due to lower ionic radius could explain the greater maximum adsorption capacity of lead (II) ions. Rivera-utrilla et al. (2003) found the same order of preference when they studied the adsorption of lead (II) and cadmium (II) ions by activated carbon and gave the same explanation.


Table 4.3: $Q_{max}$ Values of some adsorbents reported in literature

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Maximum adsorption capacity $Q_{max}$ (mg/g)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated alumina</td>
<td>5.02</td>
<td>Gupta and Chen, 1978</td>
</tr>
<tr>
<td>Baggasse fly ash</td>
<td>2.5</td>
<td>Gupta and Sttacharyya, 2006</td>
</tr>
<tr>
<td>Activated carbon Darco</td>
<td>1.05</td>
<td>Houng and Fu, 1984.</td>
</tr>
<tr>
<td>Al$_2$O$_3$/Fe (OH)$_3$</td>
<td>0.09</td>
<td>Hodi et al., 1995.</td>
</tr>
</tbody>
</table>

Regarding Freundlich isotherm, the slope $\frac{1}{n}$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for $\frac{1}{n}$ below one indicates a normal Langmuir isotherm while $\frac{1}{n}$ above one is indicative of cooperative adsorption and it also implies that the adsorption is favorable. $\frac{1}{n}$ Values of -0.366 and -0.274 were observed for cadmium (II) and lead (II) ions respectively, indicating a normal Langmuir fit.
CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The results of this work indicate that the alumino phosphate (AlPO_4) molecular sieves constitute a promising material for the development of an adsorption technology for the removal of lead (II), cadmium (II) and fluoride ions from aqueous systems. The fast kinetics of the adsorption process together with the high adsorption capacities of these molecular sieves towards defluoridation, lead (II) and cadmium (II) ions removal can be compared favorably with other sorbents. Metal sorption kinetics was found to be dependent upon contact time, initial ion concentration, sorbent dose, solution pH, temperature, agitation speed and presence of co-ions.

Optimum pH was found to be 5-7, time contact of 90 minutes and agitation speed of 6 rps in a solution containing 1.00 g/ 100 ml of adsorbent dosage. The optimum initial ion concentration for metal ions, lead (II) and cadmium (II), was 100 mg/ L at an optimum temperature of 45± 1 °C. The optimum initial ion concentration for fluoride was found to be 6 mg/ L at an optimum temperature of at 30 ± 1 °C.

AlPO_4, an economical molecular sieve, may be particularly appropriate for the treatment of small quantities of drinking waters containing fluoride ions, lead (II) ions and cadmium (II) ions and the data reported here could be useful for the design of batch or stirred-tank flow reactors.
5.2 Recommendations

The study indicates that AlPO\textsubscript{4} molecular sieves have the ability to bind fluoride ions, lead (II) ions and cadmium (II) ions from aqueous systems. However the study did not use the industrial wastewater or show how the ions can be recovered and the adsorbent regenerated. Consequently it is recommended that,

i. further studies on the synthesized AlPO\textsubscript{4} to be carried out to determine its efficiency in purification of waste waters in local sewerage plants

ii. studies be conducted on regeneration, modification and reuse of the AlPO\textsubscript{4} adsorbent

iii. studies be conducted on the effect of the particle size of AlPO\textsubscript{4} molecular sieves on defluoridation as well as the metal ion adsorption.
REFERENCES


APPENDICES

Appendix 1A: Effect of temperature on the adsorption of fluoride ions by AlPO$_4$ molecules

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Amount of fluoride ions adsorbed (mg/L) Mean ± sd</th>
<th>% fluoride ions adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4.66 ± 0.02</td>
<td>77.67</td>
</tr>
<tr>
<td>30</td>
<td>4.71 ± 0.01</td>
<td>78.50</td>
</tr>
<tr>
<td>40</td>
<td>3.58 ± 0.00</td>
<td>59.67</td>
</tr>
<tr>
<td>50</td>
<td>3.14 ± 0.03</td>
<td>52.33</td>
</tr>
<tr>
<td>60</td>
<td>2.32 ± 0.02</td>
<td>38.67</td>
</tr>
</tbody>
</table>

Appendix 1B: Effect of pH on the adsorption of fluoride ions by AlPO$_4$ molecules

<table>
<thead>
<tr>
<th>pH</th>
<th>Amount of fluoride ions adsorbed (mg/L) Mean ± sd</th>
<th>% fluoride ions adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3.02 ± 0.02</td>
<td>50.33</td>
</tr>
<tr>
<td>5</td>
<td>4.61 ± 0.01</td>
<td>76.83</td>
</tr>
<tr>
<td>7</td>
<td>4.70 ± 0.17</td>
<td>78.33</td>
</tr>
<tr>
<td>9</td>
<td>3.97 ± 0.02</td>
<td>66.17</td>
</tr>
<tr>
<td>13</td>
<td>1.80 ± 0.00</td>
<td>30.00</td>
</tr>
</tbody>
</table>

Appendix 1C: Effect of contact time on the adsorption of fluoride ions by AlPO$_4$ molecules

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Amount of fluoride ions adsorbed (mg/L) Mean ± sd</th>
<th>% fluoride ions adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>4.02 ± 0.01</td>
<td>67.00</td>
</tr>
<tr>
<td>60</td>
<td>4.67 ± 0.02</td>
<td>77.83</td>
</tr>
<tr>
<td>90</td>
<td>4.79 ± 0.04</td>
<td>79.83</td>
</tr>
<tr>
<td>120</td>
<td>4.83 ± 0.00</td>
<td>80.50</td>
</tr>
<tr>
<td>150</td>
<td>4.83 ± 0.02</td>
<td>80.50</td>
</tr>
</tbody>
</table>
**Appendix 1D:** Effect of varying adsorbent dose on adsorption of fluoride ions by AlPO$_4$ molecules

<table>
<thead>
<tr>
<th>Mass of adsorbent (g/100 ml)</th>
<th>Amount of fluoride ions adsorbed (mg/L) Mean ± sd</th>
<th>% fluoride ions adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>4.28 ± 0.01</td>
<td>71.33</td>
</tr>
<tr>
<td>1.00</td>
<td>4.68 ± 0.00</td>
<td>78.00</td>
</tr>
<tr>
<td>1.50</td>
<td>4.7 ± 0.17</td>
<td>78.33</td>
</tr>
<tr>
<td>2.00</td>
<td>4.72 ± 0.01</td>
<td>78.67</td>
</tr>
<tr>
<td>2.50</td>
<td>4.73 ± 0.00</td>
<td>78.83</td>
</tr>
</tbody>
</table>

**Appendix 1E:** Effect of initial ion concentration on the adsorption of fluoride ions by AlPO$_4$ molecules

<table>
<thead>
<tr>
<th>Initial fluoride ions (mg/L)</th>
<th>Amount of fluoride ions adsorbed (mg/L) Mean ± sd</th>
<th>% fluoride ions adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3.99 ± 0.01</td>
<td>39.90</td>
</tr>
<tr>
<td>4</td>
<td>4.34 ± 0.03</td>
<td>54.25</td>
</tr>
<tr>
<td>6</td>
<td>4.67 ± 0.03</td>
<td>77.83</td>
</tr>
<tr>
<td>8</td>
<td>2.92 ± 0.01</td>
<td>73.00</td>
</tr>
<tr>
<td>10</td>
<td>1.53 ± 0.02</td>
<td>76.50</td>
</tr>
</tbody>
</table>

**Appendix 1F:** Effect of chloride co-ions on the adsorption of fluoride ions by AlPO$_4$ molecules

<table>
<thead>
<tr>
<th>Initial Cl$^-$ ion concentration (mg/L)</th>
<th>Amount of fluoride ions adsorbed (mg/L) Mean ± sd</th>
<th>% fluoride ions adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.68 ± 0.02</td>
<td>78.00</td>
</tr>
<tr>
<td>50</td>
<td>4.68 ± 0.00</td>
<td>78.00</td>
</tr>
<tr>
<td>100</td>
<td>4.68 ± 0.02</td>
<td>78.00</td>
</tr>
<tr>
<td>200</td>
<td>4.67 ± 0.01</td>
<td>77.85</td>
</tr>
<tr>
<td>300</td>
<td>4.67 ± 0.01</td>
<td>77.76</td>
</tr>
<tr>
<td>500</td>
<td>4.65 ± 0.01</td>
<td>77.50</td>
</tr>
</tbody>
</table>
**Appendix 1G:** Effect of nitrite co-ions on the adsorption of fluoride ions by AlPO₄ molecules

<table>
<thead>
<tr>
<th>Initial NO₃⁻ ion concentration (mg/L)</th>
<th>Amount of fluoride ions adsorbed (mg/L)</th>
<th>% fluoride ions adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.68 ± 0.02</td>
<td>78.00</td>
</tr>
<tr>
<td>50</td>
<td>4.63 ± 0.02</td>
<td>77.70</td>
</tr>
<tr>
<td>100</td>
<td>4.65 ± 0.02</td>
<td>77.50</td>
</tr>
<tr>
<td>200</td>
<td>4.62 ± 0.00</td>
<td>77.00</td>
</tr>
<tr>
<td>300</td>
<td>4.61 ± 0.01</td>
<td>76.88</td>
</tr>
<tr>
<td>500</td>
<td>4.50 ± 0.03</td>
<td>75.00</td>
</tr>
</tbody>
</table>

**Appendix 1H:** Effect of sulphate co-ions on the adsorption of fluoride ions by AlPO₄ molecules

<table>
<thead>
<tr>
<th>Initial SO₄²⁻ ion concentration (mg/L)</th>
<th>Amount of fluoride ions adsorbed (mg/L)</th>
<th>% fluoride ions adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.68 ± 0.00</td>
<td>78.00</td>
</tr>
<tr>
<td>50</td>
<td>4.53 ± 0.02</td>
<td>75.50</td>
</tr>
<tr>
<td>100</td>
<td>4.32 ± 0.01</td>
<td>72.00</td>
</tr>
<tr>
<td>200</td>
<td>4.21 ± 0.01</td>
<td>70.11</td>
</tr>
<tr>
<td>300</td>
<td>4.09 ± 0.01</td>
<td>68.24</td>
</tr>
<tr>
<td>500</td>
<td>3.96 ± 0.03</td>
<td>66.00</td>
</tr>
</tbody>
</table>

**Appendix 1I:** Effect of bicarbonate co-ions on adsorption of fluoride ions by AlPO₄ molecules

<table>
<thead>
<tr>
<th>Initial HCO₃⁻ ion concentration (mg/L)</th>
<th>Amount of fluoride ions adsorbed (mg/L)</th>
<th>% fluoride ions adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.68 ± 0.01</td>
<td>78.00</td>
</tr>
<tr>
<td>50</td>
<td>3.60 ± 0.02</td>
<td>60.00</td>
</tr>
<tr>
<td>100</td>
<td>2.92 ± 0.02</td>
<td>48.67</td>
</tr>
<tr>
<td>200</td>
<td>1.83 ± 0.03</td>
<td>30.50</td>
</tr>
<tr>
<td>300</td>
<td>1.44 ± 0.01</td>
<td>24.00</td>
</tr>
<tr>
<td>500</td>
<td>1.23 ± 0.03</td>
<td>20.50</td>
</tr>
</tbody>
</table>
Appendix 1J: Effect of temperature on the adsorption of lead (II) and cadmium (II) metal ions by AlPO₄ molecules

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Amount of Cd²⁺ adsorbed (mg/L) Mean ± sd</th>
<th>Amount of Pb²⁺ adsorbed (mg/L) Mean ± sd</th>
<th>% Cd²⁺ adsorbed</th>
<th>% Pb²⁺ adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>79.50 ± 0.03</td>
<td>84.50 ± 0.09</td>
<td>79.50</td>
<td>84.50</td>
</tr>
<tr>
<td>35</td>
<td>82.83 ± 0.06</td>
<td>88.25 ± 0.05</td>
<td>82.83</td>
<td>88.25</td>
</tr>
<tr>
<td>45</td>
<td>83.17 ± 0.10</td>
<td>89.25 ± 0.04</td>
<td>83.17</td>
<td>89.25</td>
</tr>
<tr>
<td>55</td>
<td>82.17 ± 0.02</td>
<td>88.50 ± 0.03</td>
<td>82.17</td>
<td>88.50</td>
</tr>
<tr>
<td>65</td>
<td>81.50 ± 0.27</td>
<td>87.75 ± 0.01</td>
<td>81.50</td>
<td>87.75</td>
</tr>
</tbody>
</table>

Appendix 1K: Effect of pH on the adsorption of lead (II) ions from solutions of 100 mg/L, 50 mg/L and 25 mg/L by AlPO₄ molecules

<table>
<thead>
<tr>
<th>pH</th>
<th>Amount of Pb²⁺ adsorbed (mg/L) Mean ± sd</th>
<th>% Pb²⁺ adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 mg/L solution</td>
<td>50 mg/L solution</td>
</tr>
<tr>
<td>2</td>
<td>82.75 ± 0.50</td>
<td>82.75</td>
</tr>
<tr>
<td>5</td>
<td>87.00 ± 0.00</td>
<td>87.00</td>
</tr>
<tr>
<td>7</td>
<td>91.00 ± 0.50</td>
<td>91.00</td>
</tr>
<tr>
<td>9</td>
<td>86.50 ± 0.87</td>
<td>86.50</td>
</tr>
<tr>
<td>13</td>
<td>84.50 ± 0.50</td>
<td>84.50</td>
</tr>
</tbody>
</table>

Appendix 1L: Effect of pH on the adsorption of cadmium (II) ions from solutions of 100 mg/L, 50 mg/L and 25 mg/L by AlPO₄ molecules

<table>
<thead>
<tr>
<th>pH</th>
<th>Cd²⁺ adsorbed (mg/L) Mean ± sd</th>
<th>% Cd²⁺ adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 mg/L solution</td>
<td>50 mg/L solution</td>
</tr>
<tr>
<td>2</td>
<td>69.50 ± 0.27</td>
<td>69.50</td>
</tr>
<tr>
<td>5</td>
<td>83.50 ± 0.10</td>
<td>83.50</td>
</tr>
<tr>
<td>7</td>
<td>84.00 ± 0.20</td>
<td>84.00</td>
</tr>
<tr>
<td>9</td>
<td>71.00 ± 0.00</td>
<td>71.00</td>
</tr>
<tr>
<td>13</td>
<td>68.33 ± 0.06</td>
<td>68.33</td>
</tr>
</tbody>
</table>
**Appendix 1M**: Effect of shaking speed on the adsorption of lead (II) and cadmium (II) metal ions by AlPO₄ molecules

<table>
<thead>
<tr>
<th>Speed (rps)</th>
<th>Amount of Cd²⁺ adsorbed (mg/L) Mean ± sd</th>
<th>Amount of Pb²⁺ adsorbed (mg/L) Mean ± sd</th>
<th>% Cd²⁺ adsorbed</th>
<th>% Pb²⁺ adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>64.67 ± 0.04</td>
<td>71.75 ± 0.39</td>
<td>64.67</td>
<td>71.75</td>
</tr>
<tr>
<td>4</td>
<td>77.17 ± 0.04</td>
<td>77.75 ± 0.32</td>
<td>77.17</td>
<td>77.75</td>
</tr>
<tr>
<td>6</td>
<td>80.67 ± 0.02</td>
<td>86.75 ± 0.44</td>
<td>80.67</td>
<td>86.75</td>
</tr>
<tr>
<td>8</td>
<td>80.33 ± 0.06</td>
<td>86.50 ± 0.01</td>
<td>80.33</td>
<td>86.50</td>
</tr>
<tr>
<td>10</td>
<td>80.66 ± 0.40</td>
<td>86.50 ± 0.04</td>
<td>80.66</td>
<td>86.50</td>
</tr>
</tbody>
</table>

**Appendix 1N**: Effect of contact time on the adsorption of lead (II) ions from solutions of 100 mg/L, 50 mg/L and 25 mg/L by AlPO₄ molecules

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Amount of Pb²⁺ adsorbed (mg/L) mean ± sd</th>
<th>% Pb²⁺ adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 mg/L solution</td>
<td>50 mg/L solution</td>
</tr>
<tr>
<td>15</td>
<td>45.00 ± 0.10</td>
<td>11.13 ± 0.01</td>
</tr>
<tr>
<td>30</td>
<td>69.50 ± 0.27</td>
<td>17.50 ± 0.27</td>
</tr>
<tr>
<td>45</td>
<td>80.00 ± 0.27</td>
<td>30.25 ± 0.00</td>
</tr>
<tr>
<td>60</td>
<td>85.75 ± 0.04</td>
<td>33.25 ± 0.04</td>
</tr>
<tr>
<td>90</td>
<td>88.25 ± 0.04</td>
<td>35.00 ± 0.36</td>
</tr>
<tr>
<td>120</td>
<td>88.75 ± 0.49</td>
<td>35.01 ± 0.01</td>
</tr>
<tr>
<td>150</td>
<td>89.00 ± 0.40</td>
<td>35.00 ± 0.00</td>
</tr>
</tbody>
</table>
Appendix 1O: Effect of contact time on the adsorption of cadmium (II) metal ions from solutions of 100 mg/L, 50 mg/L and 25 mg/L by AlPO₄ molecules

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>100 mg/L solution</th>
<th>50 mg/L solution</th>
<th>25 mg/L solution</th>
<th>100 mg/L solution</th>
<th>50 mg/L solution</th>
<th>25 mg/L solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>42.33 ± 0.06</td>
<td>10.00 ± 0.10</td>
<td>3.31 ± 0.01</td>
<td>42.33</td>
<td>20.00</td>
<td>13.22</td>
</tr>
<tr>
<td>30</td>
<td>58.50 ± 0.17</td>
<td>16.62 ± 0.02</td>
<td>6.25 ± 0.02</td>
<td>58.50</td>
<td>33.24</td>
<td>25.00</td>
</tr>
<tr>
<td>45</td>
<td>73.00 ± 0.36</td>
<td>24.05 ± 0.01</td>
<td>8.25 ± 0.03</td>
<td>73.00</td>
<td>48.10</td>
<td>33.00</td>
</tr>
<tr>
<td>60</td>
<td>80.00 ± 0.10</td>
<td>28.25 ± 0.05</td>
<td>8.72 ± 0.02</td>
<td>80.00</td>
<td>56.50</td>
<td>34.87</td>
</tr>
<tr>
<td>90</td>
<td>81.33 ± 0.06</td>
<td>28.55 ± 0.02</td>
<td>8.72 ± 0.01</td>
<td>81.33</td>
<td>57.10</td>
<td>34.87</td>
</tr>
<tr>
<td>120</td>
<td>82.33 ± 0.21</td>
<td>28.55 ± 0.00</td>
<td>8.72 ± 0.01</td>
<td>82.33</td>
<td>57.10</td>
<td>34.89</td>
</tr>
<tr>
<td>150</td>
<td>82.33 ± 0.15</td>
<td>28.55 ± 0.04</td>
<td>8.73 ± 0.02</td>
<td>82.33</td>
<td>57.10</td>
<td>34.90</td>
</tr>
</tbody>
</table>

Appendix 1P: Effect of adsorbent dosage on the adsorption of lead (II) and cadmium (II) metal ions by AlPO₄ molecules

<table>
<thead>
<tr>
<th>Adsorbent (g/100 ml)</th>
<th>Amount of Cd²⁺ adsorbed (mg/L) Mean ± sd</th>
<th>Amount of Pb²⁺ adsorbed (mg/L) Mean ± sd</th>
<th>% Cd²⁺ adsorbed</th>
<th>% Pb²⁺ adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>79.67 ± 0.02</td>
<td>86.50 ± 0.39</td>
<td>79.67</td>
<td>86.50</td>
</tr>
<tr>
<td>1.00</td>
<td>84.33 ± 0.06</td>
<td>90.75 ± 0.00</td>
<td>84.33</td>
<td>90.75</td>
</tr>
<tr>
<td>1.50</td>
<td>84.00 ± 0.27</td>
<td>92.00 ± 0.50</td>
<td>84.00</td>
<td>92.00</td>
</tr>
<tr>
<td>2.00</td>
<td>84.21 ± 0.02</td>
<td>92.00 ± 0.50</td>
<td>84.21</td>
<td>92.00</td>
</tr>
<tr>
<td>2.50</td>
<td>84.01 ± 0.01</td>
<td>91.50 ± 0.36</td>
<td>84.01</td>
<td>91.50</td>
</tr>
</tbody>
</table>

Appendix 1Q: Effect of initial ion concentration on the adsorption of lead (II) and cadmium (II) metal ions by AlPO₄ molecules

<table>
<thead>
<tr>
<th>Initial ion concentration (mg/L)</th>
<th>Amount of Pb²⁺ adsorbed (mg/L) Mean ± sd</th>
<th>Amount of Cd²⁺ adsorbed (mg/L) Mean ± sd</th>
<th>% Pb²⁺ adsorbed</th>
<th>% Cd²⁺ adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3.25 ± 0.00</td>
<td>3.33 ± 0.02</td>
<td>32.50</td>
<td>16.67</td>
</tr>
<tr>
<td>20</td>
<td>10.75 ± 0.01</td>
<td>29.83 ± 0.46</td>
<td>53.75</td>
<td>59.66</td>
</tr>
<tr>
<td>50</td>
<td>35.50 ± 0.30</td>
<td>68.33 ± 0.06</td>
<td>71.00</td>
<td>68.33</td>
</tr>
<tr>
<td>100</td>
<td>77.00 ± 0.20</td>
<td>168.00 ± 0.87</td>
<td>77.00</td>
<td>84.00</td>
</tr>
<tr>
<td>200</td>
<td>176.00 ± 0.87</td>
<td>168.00 ± 0.87</td>
<td>88.00</td>
<td>84.00</td>
</tr>
</tbody>
</table>