



**VUT**

**DEVELOPMENT OF A SIMPLE TECHNIQUE FOR SELECTIVE  
REMOVAL OF CESIUM IN WASTEWATER IN THE  
PRESENCE OF MIXED ALKALI METALS.**

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## DECLARATION

I declare that this dissertation is my own, unaided work. It is being submitted for the Degree Magister Technologiae to the Department of Chemistry, Vaal University of Technology, Vanderbijlpark. It has not been submitted before for any degree or examination to any other University.

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## **DEDICATION**

I dedicate this work to my parents Mr and Mrs Diretse, my sisters Puleng and Dimpho and my niece Amogelang.

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- \* Finally to the Almighty God, who gave me strength to complete my research.

## PRESENTATIONS AND PUBLICATIONS

The work presented in this dissertation has been published in peer-viewed journal and presented at conferences and symposium. Poster presentation, 3<sup>rd</sup> water municipality conference held at Cape Town International Conference center, June 2011. Oral presentation, South African Chemical Institute (SACI) young chemists symposium held at Vaal University of technology, October 2011. Oral presentation, Water Institute of South Africa conference held at Cape Town International Conference center, May 2012. Poster presentation, IV SEANAC international conference “Analytical Chemistry for the Environment, Health and Water”, held at Maputo, 07 – 11 July 2012.

### **Publication**

Pholosi, A., Ofomaja, A.E., Naidoo, E.B., (2011) Effect of chemical extractants on the biosorptive properties of pine cone powder: Influence on lead(II) removal mechanism. Journal of Saudi Chemical Society, doi:10.1016/j.jscs.2011.10.017

## ABSTRACT

Amongst treatment technologies, adsorption is rapidly gaining prominence because it can remove metal pollutants at low concentrations, economical, ease of operation, and the adsorbent can be regenerated for reuse. This study therefore, aimed at developing a simple material for selective removal of cesium from wastewater. An agricultural waste material (pine cone) was used as a cheap solid support for transition metal hexacyanoferrate and applied as biosorbents for cesium removal. The preparation and characterization of biosorbent for cesium removal in the presence of alkali metals is reported.

The experimental procedure was carried out in three phases; the first phase described the sample preparation. Toluene-ethanol mixtures of different ratios were investigated as surface treatment method for pine cone and the optimum treatment ratio determined by measuring the improvement in surface properties of the pine cone such as bulk density, iodine number, and surface negative charge. The modification of pine cone with iron hexacyanoferrate was examined in the second phase. The preparation of potassium iron(III) hexacyanoferrate (KFeHCF) supported toluene-ethanol modified pine cone powder was studied in order to consider its application for cesium removal from aqueous solution. The biosorbent was designed to incorporate the hexacyanoferrate ligand which is known to have a high affinity for cesium ions in aqueous solution. Fe(III) was loaded onto the toluene-ethanol treated pine cone powder followed by hexacyanoferrate ligand incorporation on the biosorbent producing the potassium iron hexacyanoferrate supported toluene-ethanol treated pine cone.

The modified pine cone was characterized by FTIR, XRD and TGA analysis. The influence of solution pH and adsorbent dose were studied. The application of potassium iron hexacyanoferrate for the selective removal of cesium in the presence of sodium and calcium was investigated in the third phase. Batch adsorption kinetic studies were performed to determine the effect of modification on cesium removal. Coefficient of correlation,  $r^2$ , and Chi-square,  $\chi^2$ , methods were applied in the determination of the best fit kinetic method.

Increasing the ratio of toluene in the extractant mixture increased formation of esters and iodine capacity of the material, but reduced carboxylate ions and surface charge. Maximum cesium

adsorption was observed for the 2:1 toluene-ethanol treated sample. Structural characterization using FTIR, XRD and TGA confirmed the successful modification of KFeHCF pine cone powder. Cesium adsorption experiments indicate that KFeHCF supported toluene-ethanol modified pine was more efficient for cesium removal than the raw pine cone powder. Kinetic modeling of  $\text{Cs}^+$  adsorption was done using the pseudo-first, pseudo-second order and diffusion chemisorption kinetic models. The pseudo first order kinetics could not accurately predict the experimental data. The kinetics data fitted the pseudo-second order and diffusion-chemisorption models. The chemisorption diffusion model only accurately describes the experimental data after 5 min of contact whereas the pseudo second order describes the experimental data over the range of contact time. The application of the FeHCF modified pine cone for cesium removal from aqueous solution revealed that the FeHCF modified pine was less affected by the presence of competitive cations than the toluene-ethanol treated sample and the raw pine cone sample.

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## LIST OF ABBREVIATIONS AND SYMBOLS

PCP	Pine cone powder.
HCF	Hexacyanoferrate
KHCF	Potassium hexacyanoferrate
KFeHCF	Potassium iron hexacyanoferrate.
NiHCF	Nickel hexacyanoferrate.
KTiHCF	Potassium titanium hexacyanoferrate
KZnHCF	Potassium zinc hexacyanoferrate
KCuHCF	Potassium copper hexacyanoferrate
KCoHCF	Potassium cobalt hexacyanoferrate
NH <sub>4</sub> FeHCF	ammonium Iron hexacyanoferrate
K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	Potassium iron hexacyanoferrate
$q_e$	Equilibrium capacity.
$q_t$	Equilibrium capacity at time t.
$k_1$	Pseudo-first order rate constant.
$k_2$	Pseudo-second order rate constant.
$K_{DC}$	Diffusion-chemisorption constant
$t^{0.5}$	The time in min raised to the power of 0.5
$(P)_t$	Number of active sites occupied on the adsorbent at time t.
$(P)_0$	Number of equilibrium sites available on the adsorbent.
$r^2$	Correlation coefficient.
$\chi^2$	Chi- square

$C_o$	Initial Concentration.
$C_e$	Equilibrium concentration.
$m$	Mass of the adsorbent
$V$	solution volume
% R	Percentage removal
$h$	the initial sorption rate.
$S_{xx}$	sum of square of x
$S_{yy}$	sum of square of y
$S_{xy}$	sum of square of x and y
$C_s$	Saturation concentration of solute
$q_{e,m}$	Equilibrium capacity obtained by calculating from model
FTIR	Fourier Transformed Infrared.
BET	Brunauer, Emmett and Teller Isotherm
TGA	Thermogravimetric analysis
DTA	Derivative thermal analysis
XRD	X-Ray Diffraction
AAS	Atomic absorption spectrophotometer.

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# CHAPTER 1

## 1.0 INTRODUCTION

### 1.1 Introduction

The contamination of waters by industrial effluents rich in radionuclide has received much attention in the last decades. Even trace amounts of radionuclides can be enough to cause concern. Several sources of radionuclide in soils and water that have been identified include natural processes, global fall-out from nuclear weapon testing, discharges from nuclear installations, disposal of nuclear waste or leakage from storage tanks (Salvatores and Palmiotti, 2011; Vodyanitskii, 2011) and occasional nuclear accidents (Saleh, 2011). One radionuclide of concern is cesium.  $^{137}\text{Cs}$  is water-soluble and can rapidly enter the biological cycles and accumulate in terrestrial ecosystems, behaving in a very similar way to potassium and sodium (Bourcier *et al.*, 2010). The toxicity of  $\text{Cs}^{137}$  is mainly due to its radiological properties. A high dose of  $\text{Cs}^{137}$  is responsible for medullar dystrophy, disorders of the reproductive function, and effects on liver and renal functions. Disorders of bone mineralization and brain damages have also been described in human beings (Lestaevel *et al.*, 2010).

Considerable efforts have been directed towards the development of various physico-chemical methods for the removal and recovery of radioactive Cs isotopes from nuclear waste streams such methods include co-precipitation, coagulation, ion exchange, solvent extraction, electrochemical and membrane processes. However, in many cases, the products from these methods do not meet the legal limits imposed on the quality of radioactive wastewaters. Large amount of sludge, which is often difficult to handle are generated from the processes. More effective purification systems, such as ion-exchange columns, are often more expensive and, hence, unsuitable for these industries (Vejsada and Hradil, 2005). Adsorption has been found to be superior to other techniques in terms of initial cost, flexibility and simplicity of design, ease of operation, insensitivity to toxic pollutants (Rafatullah *et al.*, 2010) and does not result in the formation of harmful substances.

Several adsorbents have been employed in cesium removal from aqueous solution. The uses of natural minerals such as clays minerals and zeolites have been prominent. The drawback of these adsorbents is the mobility to cope with the competitive interaction of other monovalent and divalent cations, in particular  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$  which considerably interfere with  $\text{Cs}^+$  removal. Consequently, many researchers have studied the behavior of natural organic or inorganic materials that have high adsorption capacity and which are particularly abundant and inexpensive to use. Transition metal complex hexacyanoferrate has been immobilized on solid support material (Parab and Sudersanan, 2010, Vrtoch *et al.*, 2011). The advantage of this method is the high selectivity of hexacyanoferrate for cesium. The cost of most solid supports used for this purpose has limited their large scale application.

In recent times, agricultural waste materials are becoming feasible alternatives to expensive solid support materials. The advantage of supports from biological origin will be the cheap, readily available source of the support material and also the opportunity of regeneration offered by biosorbents as compared with other supports. Since agricultural adsorbents usually have low surface areas and sorption capacities, this could hinder its application as effective support for hexacyanoferrates; therefore raw agricultural adsorbents are treated by various methods to increase their sorption capacities to enhance their application. Different bases, acids and surfactants as chemical modifiers and thermal activation to enhance the adsorption capacity of agricultural biosorbents have been employed.

## **1.2 Problem statement**

The radioisotopes of Cesium bear high similarities to K, Na and Ca in simple chemistry and geochemistry. They are mobile in various environments and can be easily assimilated by plants and other terrestrial and aquatic organisms. Because of the close similarity in properties, the separation of these metal ions from the system containing mixed alkali metal ions, such as brine system is difficult. Therefore, the development of a simple, inexpensive, and practical method for the separation of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^+$  and cesium from water is very important. Studies (Parab and Sudersanan, 2010) have been done on removal of cesium using cyanoferrates but no research has looked into the competitive removal in the presence of alkali metals which is present in real life wastewater.

### **1.3 Aim**

The main aim of this research is to use the solvent extraction procedure for the removal of extractants from pine cone and design a simple material for selective removal of cesium in wastewater in the presence of competitive cations.

The objectivity aim of study was achieved by considering the following research objectives:

- To optimize the solvent extraction method for the modification of pine cone.
- To modify and optimize modification procedures of pine cone powder using potassium iron hexacyanoferrate.
- To determine the kinetic parameters of the sorption processes.
- To determine the competitive effect of Na and Ca ions in bi-soluble solutions.
- To determine the mechanism of uptake and recovery of cesium ions from solution.

### **I.4. Outline of the research**

Chapter 1:

This chapter covers the introduction and problem statement. It gives an insight into the research project. The aim and objective of the study are also presented in this chapter.

Chapter 2:

This chapter covers literature review of radioactive metal pollutants in aqueous system, methods of removal, and adsorption as an alternative method for removal of radioactive pollutant. A review of various adsorbents that have been used, the limitations, and the use of modified adsorbents are also discussed.

Chapter 3:

The experimental procedure which is divided into three sections is described. The first section describes the sample preparation and solvent extraction treatment. Section two involved the modification of pine cone with iron hexacyanoferrate. Section three involved the application of modified pine cone for the selective removal of cesium in the presence of sodium and calcium.

#### Chapter 4:

Results and discussion which is divided into three sections are discussed. The first section covers the results of the surface properties of different pine cone samples extracted with toluene-ethanol mixture of different ratios. The second section covers, the results of surface properties of the toluene-ethanol treated pine cone with potassium iron hexacyanoferrate and the surface characterization. The third section covers results of the application of pine cone for the selective removal of cesium in the presence of sodium and calcium.

#### Chapter 5:

This chapter covers the conclusion and recommendations from the results obtained.

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## CHAPTER 2

### 2.0 LITERATURE REVIEW

#### 2.1 Wastewater

Water is a source of life and energy. It is a unique substance, because it can naturally renew and cleanse itself by allowing pollutants to settle out through the process of sedimentation, or by diluting the pollutants to a point where they are not present in harmful concentration. However, this natural process is difficult when excessive quantities of harmful contaminants are added. The water industry has been faced with a series of great challenges. Heavy metals released into the environment have increased continuously as a result of the rapid development of various industrial activities and technologies, posing a significant threat to the environment and public health because of their toxicity, bioaccumulation in human bodies and persistence in nature (Bahadir *et al.*, 2007).

Wastewater is defined as water used in domestic and/or industrial processes. Wastewater includes water containing substances such as human waste, food scraps, oils, soaps and chemicals. The world supply of freshwater is limited and threatened by pollution as a result of indiscriminate discharge of untreated wastewater effluents. In South Africa, water is scarce and there is need to protect the available water resources from discharges of untreated wastewater. Businesses and industries contribute their share of used water that must be cleaned. Pollution has been very damaging to aquatic ecosystems, and may consist of agricultural, urban, and industrial wastes containing contaminants such as sewage, fertilizer, and heavy metals that have proven to be very damaging to aquatic habitats and species.

Water pollution due to the disposal of heavy metals continues to be a great concern worldwide. Consequently, the treatment of polluted industrial wastewater remains a topic of global concern since wastewater collected from municipalities, communities and industries must ultimately be returned to receiving waters or to the land. The laws that regulate maximum acceptable concentrations of toxic metals in wastewaters, discharged into rivers, streams or drinking waters

have therefore become more restrictive recently and at present acceptable maximum permissible levels are a fraction of  $\text{mg/dm}^3$  or  $\mu\text{g/dm}^3$  (Chojnacka, 2010).

## 2.2 Sources of pollutants in wastewater

The main sources of freshwater pollution can be attributed to discharge of untreated sanitary and toxic industrial wastes, dumping of industrial effluent, and runoff from agricultural fields. Many industrial activities such as mining and smelting, combustion of fossil fuel and gasoline, waste incinerators, surface finishing industry, energy and fuel production, fertilizer and pesticide industry, electroplating, electrolysis, electro-osmosis, coating and metal surface finishing, automotive, aeronautical and steel industry, atomic energy installation, leather working, photography, and electric appliance manufacturing discharge large quantities of wastewater containing various concentrations of heavy metals into the environment. (Hang *et al.*, 2006; Wang and Chen, 2006).

Humans also affect the natural geological and biological redistribution of heavy metals by altering the chemical form of heavy metals released into the environment. Such alterations often lead to increase in metal's toxicity which accumulates in plants and animals. It also bioconcentrate in the food chain and attack specific organs in the body. Apart from human and industrial effluents, weathering of soil and rocks and volcanic eruptions from which the released metals finds their way into the water bodies are also other main sources of heavy metals discharging into the marine environment. A large quantity of heavy metals also suspends in the atmosphere from where they can reach the waters through dry deposition and with the precipitation. The distribution of heavy metals in manufacturing industries is given in Table 1.

**Table: 2.1** General Distribution of Heavy metals in Particular Industrial Effluents

Industries	Ag	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Ti	Zn
<b>General Industry and Mining</b>				X	X	X		X		X			X
<b>Plating</b>			X	X	X				X	X			X
<b>Paint Products</b>				X						X		X	

<b>Fertilizers</b>			X	X	X	X	X	X		X			X
<b>Insecticides/ Pesticides</b>		X			X		X		X				
<b>Tanning</b>		X		X									
<b>Paper Products</b>				X	X		X		X	X		X	X
<b>Photographic</b>	X			X									
<b>Fibers</b>					X								X
<b>Printing / Dyeing</b>				X						X			
<b>Electronics</b>	X										X		
<b>Cooling Water</b>				X									
<b>Pipe Corrosion</b>					X					X			

### 2.2.1 Domestic wastewaters and urban run-off

Significant quantities of heavy metals are present in domestic wastewaters and sewage. A large number of heavy metals may also be contributed by corrosion of metal pipes. Sewage sludge if discharged into the waters may be a significant source of Cu, Ag, Cd, Zn and Pb. The urban runoff in general, carries organic load along with several hazardous chemicals which not only spoils the aesthetic sense of the river but at the same time also degrades the aquatic ecosystem. Due to high establishment and running cost of a sewage treatment plant, the majority of urban centres in developing world dispose urban runoff and sewerage water directly into urban rivers without any treatment or with partial treatments. Run-off from the urban areas during rainy season is rich in certain heavy metals; however their relative quantities depend upon the factors like road and traffic conditions. Harmful substances that wash off roads, parking lots, and rooftops can harm our rivers and lakes. Lead from automobile is released into the atmosphere, which later gets deposited at the surface and finds its way in the run-off.

### 2.2.2 Industrial wastewater

Industry is an important source of heavy metals. A number of heavy metals are used by various industries and a proportion of them find their way into the effluents. Few metals may also be disposed off as by-products, while some are released during industrial combustion of coal or other materials. For example, the mercury cells used in caustic soda production are the source of

mercury in the effluent released by the industry. Pit dumping and sanitary landfills allow the leaching of significant quantities of heavy metals, especially Cu, Zn, Pb and Hg into the surface and ground waters. Industrial air pollution releases a number of heavy metals into atmosphere and become potential source of water pollution after dry or wet deposition.

### *2.2.3 Mining*

By mining and extraction, a part of the heavy metals do end up in tailings and other waste products. The waste rocks left at the sites of mining and surface after the mining is over, are liable to greater weathering and oxidation that release most of the metals in the free state. In some cases, even long after mining activities have ceased, the emitted metals continue to persist.

### *2.2.4 Disposal of discarded product*

The main part of the heavy metals will still be present when the discarded products are disposed off. Heavy metals will either be collected for recycling or disposed of to municipal solid waste incinerators or landfills. A minor part will be disposed of as chemical waste and recycled or landfilled via chemical waste treatment.

### *2.2.5 Agricultural activities*

Agricultural soils are usually rich in heavy metals as a result of the use of various fungicides, herbicides, phosphatic fertilizers, organic manures and the presence of decaying plant and animal residue. The use of wastewater for irrigation and sewage sludge has further increased the quantities of heavy metals in agricultural soils. The agricultural run-off together with soil erosion is the potential source of water pollution.

## **2.3 Heavy metal pollution**

Studies on heavy metal pollution of water have recently attracted a lot of attention due to the need for acceptable drinking water quality and better understanding of environmental pollution of freshwater resources (Demirak *et al.*, 2006; Deheyn and Latz 2006; Grosbois *et al.*, 2006; Nicolau *et al.*, 2006; Adamo *et al.*, 2005; Nyangababo *et al.*, 2005; Okonkwo *et al.*, 2005; Jain 2004; Huang and Lin 2003; Powell and Alexander 2003; Reimann *et al.*, 2003; Neal *et al.*, 2000; Lee *et al.*, 1998).

Heavy metals are found in elemental form and in a variety of other chemical compounds. Heavy metals normally occurring in nature are not harmful to our environment, because they are only present in very small amounts. They only become pollutants when they show up in huge amounts due to industrialization. Contamination of water by toxic heavy metals through the discharge of industrial wastewater is a worldwide environment problem. Heavy metals have peculiar characteristics including that (1) they do not decay with time (2) they can be necessary to plants at certain levels but can become toxic when exceeding specific threshold, (3) they are always present at a background level of non-anthropogenic origin, and (4) they often occur as cations which strongly interact with the soil matrix, therefore, heavy metals in soil can become mobile as a results of changing environmental conditions (Facchinelli *et al.*, 2001).

Heavy metals such as lead, mercury, copper, cadmium, zinc, nickel, and chromium are among the most common pollutants found in the industrial effluents which cause serious threat to the environment, and affect, animals and human because of their extreme toxicity (Bahadir *et al.*, 2007; Liu *et al.*, 2006). Heavy metal toxicity can result in damage or reduced mental and central nervous function, lower energy levels and damage to blood composition, lungs, kidneys, liver and other vital organs. Presence of metals in water streams and marine water causes a significant health threat to the aquatic community. Various regulatory bodies have set the maximum prescribed limits for the discharge of toxic heavy metals in the aquatic systems. However, the metal ions are being added to the water stream at a much higher concentration than the prescribed limits by industrial activities, thus leading to the health hazards and environmental degradation. For example the permissible limit of Cu is  $2.5 \text{ mg/dm}^3$  in water (Prasad and Freitas, 2000) and that of lead being  $0.10\text{--}0.05 \text{ mg/dm}^3$  (Ucun *et al.*, 2003).

Lead occurs naturally in the environment. However, most lead concentrations that are found in the environment are a result of human activities. The major source of lead in the environment is from plastics, finishing tools, cathode ray tubes, ceramics, solders, pieces of lead flashing and other minor product, steel and cable reclamation. Lead salts enter the environment through the exhausts of cars. The larger particles will drop to the ground immediately and pollute soils or surface waters, the smaller particles will travel long distances through air and remain in the atmosphere. Lead can result in the wide range of biological effects depending upon the level and

duration of exposure (Friberg and Elinder, 1985). Lead poisoning in human causes severe damage to the kidney, nervous system, reproductive system, liver, and brain

Mercury is generally considered to be one of the most toxic metals found in the environment. Mercury enters the environment through the leaching of soil due to acid rain, coal burning, or industrial, household, and mining wastes. The major natural source of mercury is the degassing of the Earth's crust, emissions from volcanoes and evaporation from natural bodies of water. Mercury causes impairment of pulmonary function, and kidney, chest pain and dyspnoea (WHO, 1990). Several past disasters due to the contamination of heavy metals in aquatic streams are Minamata tragedy in Japan due to methyl mercury contamination (Friberg and Elinder, 1985; Kjellstrom *et al.*, 1977).

Copper is a widely used industrial metal for electrical wiring, plumbing, air conditioning tubing and roofing. Since copper is a widely used material, there are many actual or potential sources of copper pollution. Copper is introduced into water through pulp and paper board, wood and leather preserving, petroleum refining, copper smelter industries, etc (Panday *et al.*, 1985: 1986). Any processing or container involving copper material may contaminate the products such as food, water or drink. Copper is essential to human life and health but like all heavy metals, is potentially toxic as well. For example, continued inhalation of copper-containing spray is linked with an increase in lung cancer among exposed workers (Yu *et al.*, 2000). The World Health Organization (WHO) recommended a maximum acceptable concentration of Cu(II) in drinking water less than  $1.5 \text{ mg/dm}^3$  (Rao *et al.*, 2006).

Cadmium enters the water through waste disposal, hazardous waste sites, landfills, and waste streams. Cadmium derives its toxicological properties from its chemical similarity to zinc, which is an essential micronutrient for plants, animals and humans. Cadmium is biopersistent and, once absorbed by an organism, remains resident for many years (over decades for humans) although it is eventually excreted. Cadmium is found to cause cancer, hypertension, weight loss, bone lesions and *Itai-itai* disease. The average daily intake for humans is estimated as  $0.15 \mu\text{g}$  from air and  $1 \mu\text{g}$  from water. Smoking a packet of 20 cigarettes can lead to the inhalation of around 2-4  $\mu\text{g}$  of cadmium.

Zinc enters the air, water, and soil as a result of both natural processes and human activities. Most zinc enters the environment as the result of human activities, such as mining, purification of zinc, lead, and cadmium ores, coal burning, steel production and burning of wastes. Zinc is most toxic to microscopic organisms in the aquatic environments. It is also an essential element for aquatic and terrestrial biota and its removal from the environment below certain levels can also be harmful due to its deficiency. Zinc may bind to particulate matter. Soluble species of zinc are readily available for biological reactions and, therefore, considered as most toxic. It has been shown that zinc in water is a better predictor of fish tissue contamination than zinc in either sediment or invertebrates.

Small amounts of Nickel are needed by the human body to produce red blood cells, however, in excessive amounts, can become mildly toxic. Higher concentrations of nickel cause cancer of lungs, nose and bone. Acute poisoning of Ni (II) causes headache, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness (Al-Asheh and Duvnjak 1997; Beliles, 1979).

Chromium is a toxic heavy metal being released in the environment by applications like tanning, wood preservation and pigments, dyes for plastic, paints, and textiles. Chromium occurs in a number of oxidation states, but chromium (VI) and chromium (III) are of main environmental concern (Yu *et al.*, 2000). Low-level exposure can irritate the skin and cause ulceration. Long-term exposure can cause kidney and liver damage, and damage too circulatory and nerve tissue. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of chromium.

#### **2.4 Water pollution by radioactive elements**

With the development of nuclear science and technology, especially the wide application of nuclear power, the radioactivity contaminants threatens the human environment seriously. Even trace amounts of radionuclides can be enough to cause concern. A well-known example is a radiological accident in 1987 in Goiânia, Brazil where a number of people died, many more were injured and the environment became contaminated as a result of exposure to  $^{137}\text{Cs}$  found in an old medical radiation therapy source (Anjos *et al.*, 2004). A recent accident occurred in March

2011 in Japan where as many as 20,000 people died. Explosions and leaks of radioactive gas took place in three reactors at the Fukushima Daiichi Nuclear Power Station that suffered partial meltdowns, while spent fuel rods at another reactor overheated and caught fire, releasing radioactive material directly into the atmosphere.

The environmental radiation can be from different sources and can be natural or man-made. In the natural radiation, cosmic rays are involved and reach the surface of earth from space. Examples of radioactive elements include radioactive isotopes of iodine, radon, uranium, cesium, and thorium. These chemicals enter aquatic ecosystems through discharge from nuclear power plants, processing of uranium and other ores, nuclear weapons production, and natural sources. The harmful effects of radioactive waste when ingested through drinking water include genetic mutations, miscarriages, birth defects, and certain cancers.

Radioactive elements are produced in the environment and affect other materials. Gases and particles are produced by the radioactive materials and are carried by the wind and the rain brings down the radioactive particles to the ground which is referred as nuclear fallout. The soil transfers these radioactive substances to the plants and ultimately they reach the human body and cause many side effects. Iodine may affect the white blood cells, bone marrow, lymph, skin cancer and lead to tissue degeneration. The radioactive materials are passed through the land to water and cause an adverse effect on the aquatic animals.

The major sources of radioactive waste released into the environment includes the increasing use of radioactive isotopes in research, agricultural and medical applications, mining and processing of ores, for example uranium tailings and the nuclear power plants.

#### *2.4.1 Nuclear power plants*

The waste resulting from radioactivity produces hazards when unsafely maintained. In case of nuclear power plant accidents, if the radioactive core is exposed and meltdown occurs with the release of high amount of radioactivity, then danger is caused to life and surrounding environment. A recent example is the nuclear accident that took place in Japan in March 2011.

#### *2.4.2 Transportation*

Transportation of nuclear wastes from one place to another, by any forms of transportation (air, land, water and sea) will possibly bring serious hazards to the environment if they are not maintained carefully.

#### *2.4.3 Nuclear tests*

The radioactive products released in such an explosion thus comprise: unused explosive, fission products formed from these explosives, and activation products formed by neutron bombardment of elements present in soil or water. The force of the explosion and the very considerable rise in temperature that accompanies it convert these radioactive substances into gases or else eject them high onto the atmosphere in the form of more or less fine particles.

#### *2.4.4 Uranium mining*

Uranium, substance that is used in nuclear power plants, is harvested from uranium mining. Uranium mining results in radioactive waste that pollutes the surrounding environment.

### **2.5 Disposal of nuclear waste**

The decaying process of radioactive wastes takes a very long time in progress. Some radioactive substances have a half-life of more than 10,000 years, which means they are dangerous in that great amount of time. There are common ways to dispose nuclear waste (i) burying underground very deeply, (ii) burying under the sea, and (iii) sending them to outer space. However, these procedures are still dangerous and expensive.

### **2.6 Alkali and alkali earth metals**

Alkali metals (sodium, potassium, and cesium) are chemical elements that belong to the group 1 of the periodic table. They are silvery colored, soft metals of low density and low melting point. They are good conductors of heat and electricity. They have the lowest ionization energy, which makes them to be highly reactive and electropositive. Alkali earth metals are chemical elements that belong to the group 2 of the periodic table. The metals are silvery colored when pure and are harder than the alkali metals having high melting point. They are good conductor of heat and

electricity. Alkali earth metals are very reactive but not as reactive as the alkali metals (Liptrot, 1992)

Sodium (Na) is an abundant metallic element which is an important mineral for all living organisms. The soft metal also appears in abundance of compounds such as sodium chloride, known as salt. Its relative rarity on land is due to its solubility in water, thus causing it to be leached into bodies of long-standing water by rainfall. It exists in high concentration in seawater, and it is among the ten most abundant minerals in the earth's crust.

Potassium (K) is a very important mineral for the proper function of all cells, tissues, and organs in the human body. It is crucial to heart function and plays a key role in skeletal and smooth muscle contraction. It is a major nutrient which has to be accumulated in great quantity by roots and distributed throughout the plant and within plant cells (Gierth and Maser, 2007).

Calcium (Ca) plays an important role in building and maintaining strong bones and teeth, and also large part of human blood and extra cellular fluids. It is also necessary for normal functioning of cardiac muscles, blood coagulation, milk clotting and regulation of cell permeability.  $\text{Ca}^{2+}$  plays a key role in numerous cellular processes, such as maintaining membrane potentials and controlling hormonal secretion cellular (Brown and MacLeod, 2001).

## **2.7 Cesium in water**

Cesium is released into water bodies during the mining, milling, and production process of pollucite ore. The natural erosion and weathering of rocks also lead to cesium's introduction into ground and surface water. Radioactive cesium is released to the environment during the normal operation of nuclear power plants, explosion of nuclear weapons, and accidents involving nuclear power plants or nuclear powered satellites or submarines. In the past, the majority of radioactive cesium released to water surfaces in North America arose from deposition following atmospheric nuclear weapons testing conducted by the United States, primarily during the 1960s (Robbins et al. 1990).

Once released, these radioactive cesium isotopes persist in the environment, with the potential for adverse health effects. Following release to the atmosphere, radioactive cesium can travel thousands of miles before settling to earth, and is removed by wet and dry deposition. Radioactive cesium can also be released to soil or water in liquid effluents from spent fuel and fuel reprocessing plants. Cesium binds strongly to most soils and does not travel far below the surface of the soil. Consequently, cesium is not readily available for uptake by vegetation through roots. However, radiocesium can enter plants upon falling onto the surface of leaves.

### *2.7.1 Occurrence of Cesium*

Cesium is a naturally occurring element found in rocks, soil and dust at low concentrations. Natural cesium is present in the environment in only one stable form, as the isotope  $^{133}\text{Cs}$ . Cesium metal is a soft, silvery white-grey, ductile metal which was discovered spectroscopically in 1860 by German Chemists Robert Bunsen (1811-1899) and Gustav Kirchhoff (1824-1887) in mineral water from Durkheim. It is a liquid in a warm room, melting at  $28.4^{\circ}\text{C}$ . Cesium (Cs) is a very reactive metal, highly alkaline, and very electropositive. Cs reacts explosively with cold water producing cesium hydroxide ( $\text{CsOH}$ ) which is an extremely strong base that can attack glass. Cesium compounds do not react violently with air or water and are generally very soluble in water. Cesium compounds exist only in the +1 oxidation state.

Since cesium is highly reactive, it is not usually found in a pure form in nature; most of the world's cesium comes from minerals and nuclear fission. It is also released into the air, water and soil through mining and milling of ores. In minerals it is found in the pollucite and in an ore of lithium called lepidolite. Pollucite ( $\text{Cs}_4\text{Al}_4\text{Si}_9\text{O}_{26}$ ) contains the largest fraction of Cesium. Cesium is also found in small amounts in a mineral of boron called rhodizite.

In nature, cesium exist only as a non-radioactive or stable isotope known as cesium-133, however there are several cesium isotopes that are radioactive. Radioactive forms of cesium are produced by the fission of uranium in fuel elements (fuel rods) during the normal operation of nuclear power plants, or when nuclear weapons are exploded. Radioactive forms of cesium are unstable and eventually change into other more stable elements through the process of radioactive decay. The two most important radioactive isotopes of cesium are  $^{134}\text{Cs}$  and

<sup>137</sup>

Cs. The half-life is the time it takes for half of that cesium isotope to give off its radiation and change into a different element. The half-life of <sup>134</sup>Cs is about 2 years and the half-life of <sup>137</sup>Cs is about 30 years.

Cesium is used as a getter in bulb and evacuated tubes, in photoelectric cells, in atomic clocks (the most precise instrument of time-keeping), as a catalyst in the hydrogenation of certain organic compounds and in nuclear medicine. Cesium compounds are used in the production of glass and ceramics. Crystalline cesium iodide and cesium fluoride are used in scintillation counters, which convert energy from ionizing radiation into pulses of visible light for radiation detection and spectroscopy. <sup>137</sup>Cs is also well known as an excellent gamma source for some clinical and biotechnological applications like surgical instrument disinfection, radiotherapy and food sterilization (Ebner *et al.*, 2001).

### 2.7.2 Toxicity of cesium

Exposure to radioisotopes of cesium is of much greater human health concern. Energy released by radioactive isotopes can result in significant damage to living cells. Both Cs-134 and Cs-137 emit beta radiation and gamma radiation. Beta radiation travels short distance and can penetrate the skin and superficial body tissues while gamma radiation can travel long distance and can penetrate the entire body. The radiation dose can be classified as external or internal. External and internal exposures of humans to radiocesium have resulted in a spectrum of adverse health effects such as nausea, vomiting and diarrhea. The strong external gamma radiation associated with <sup>137</sup>Cs short-lived decay products barium-137 makes external exposure a concern, and shielding is often needed to handle materials containing large concentration of cesium. The main concern of cesium in the body is associated with the increased likelihood for inducing cancer. The three most possible modes of internal contamination of radiocesium are inhalation, oral ingestion and percutaneous absorption (Faustino *et al.*, 2008).

A number of people in Brazil, who handled radioactive cesium that was scavenged from a medical machine used for radiation therapy, became sick from exposure to the radiation; a few of them died. High levels of radioactive cesium have been released to the environment from the nuclear weapons testing and incidents such as the Chernobyl nuclear plant accident in 1986.

These isotopes can easily mix with soil, drinking water and rivers, increasing the risk of health problems such as contractions or death depending on the level of exposure (Casarett *et al.*, 2008). The transfer of radiocesium into the food chain and into sheep and reindeer may contribute to human cesium exposure.

## **2.8 Methods of cesium removal from wastewater**

Several methods used for Cesium removal includes nanofiltration (Bai *et al.*, 2006), semi-permeable dynamic membranes (Rudenko *et al.*, 2007), ultra filtration (Rao *et al.*, 2000), and membrane distillation (Zakrzewska-Trznadel *et al.*, 1999). Other conventional methods for removal of cesium ions from aqueous solutions are chemical precipitation, ion exchangers, chemical oxidation/reduction, reverse osmosis and electro dialysis (Gardea-Torresdey *et al.*, 1998; Zhang *et al.*, 1998). However these conventional techniques have their own inherent limitations such as less efficiency, sensitive operating conditions and production of secondary sludge and the membrane processes require high pressure with high-energy consumption and are expensive. It was found that alternative methods for removal of heavy metals and radionuclides, such as metal precipitation and chelating agents, have been ineffective for Cs removal (Avery *et al.*, 1995).

### *2.8.1 Chemical precipitation*

In chemical precipitation, the precipitation of metals is achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers. Chemical precipitation of heavy metals as their hydroxide using lime is widely used. Lime is generally favoured for precipitation purpose due to the low cost of precipitant, ease of pH control in the range of 8.0-10.0 and the excess of lime also serve as an adsorbent for the removal of metal ions. The large amount of sludge containing toxic compounds produced during the process is the main disadvantage.

### *2.8.2 Membrane process*

Important examples of membrane process applicable to inorganic wastewater treatment include reverse osmosis, electro dialysis and ultrafiltration. These processes involve ionic concentration by the use of selective membrane with a specific driving force. For reverse osmosis, pressure difference is employed to initiate the transport of solvent across a semi-permeable membrane.

The membrane pore size is very small allowing only small amounts of very low molecular weight solutes to pass through. It is an effective heavy metal removal technology proven through several bench-scale and pilot-scale studies, and is very effective in removing dissolved constituents (Ning, 2002). The disadvantage of this method is that it is expensive. Electro dialysis relies on ion migration through selective permeable membrane in response to a current applied to electrodes. The application of the membrane process described is limited due to pretreatment requirement. The methods are expensive and require a higher level of technical expertise to operate. Ultrafiltration designates a membrane separation process, driven by a pressure gradient in which the membrane fractionates components of a liquid as a function of their solvated size and structure. The process uses membrane with larger pore sizes which allow some components to pass through with the water. Ultrafiltration membrane removes high molecular weight substances, colloidal materials, organic and inorganic polymer molecules. The main disadvantage of this process is the generation of

### *2.8.3 Ion exchange*

Ion exchange resins are available and are selective for certain metal ions. In this process, metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the exchange resin. The cation exchange resins are mostly synthetic polymers containing an active ion group such as  $\text{SO}_3\text{H}$ . The limitations on the use of ion exchange for inorganic effluent treatment are primarily high cost and the requirements for appropriate pretreatment system. Ion exchange is capable of providing metal ion concentrations to parts per million levels. However, in the presence of large quantities of competing mono-and divalent ions such as Na and Ca, ion exchange is almost totally ineffective.

### *2.8.4 Solvent extraction*

Solvent extraction involves an organic and an aqueous phase. The aqueous solution containing the metal of interest is mixed with the appropriate organic solvent and the metal passes into the organic phase. In order to recover the extracted metal, organic solvent is contacted with an aqueous solution whose composition is such that the metal is stripped from the organic phase and is reextracted into the stripping solution. Solvent extraction techniques are not suitable for effluents containing less than  $1 \text{ g/dm}^3$  of targeted heavy metals (Mameri *et al.*, 1999).

Table 2.2: Disadvantages of conventional methods for wastewater treatment containing cesium (Mohan and Pittman, 2007).

<b>Removal methods</b>	<b>Disadvantages</b>
Distillation	Requires careful maintenance to ensure purity. Consumes large amount of energy. Some contaminants can be carried into the condensate.
Ultrafiltration	Will not remove dissolved inorganics.
Reverse osmosis	High tech operation and maintenance.
Nanofiltration	Very high-capital and running cost, pre-conditioning: high water rejection.
Electrodialysis	Toxic wastewater is produced.
Ion-exchange resin	High cost medium; high-tech operation and maintenance; regeneration creates a sludge disposal problem.

## 2.9 Adsorption technique

Adsorption is the process through which a substance originally present in one phase (liquid) is removed from that phase by accumulation at the interface between that phase and a separate (solid) phase. The substance that accumulates at the interface is called ‘adsorbate’ and the solid on which adsorption occurs is ‘adsorbent’. Unbalanced forces of attraction between the liquid and solid phases result in an increase of concentration of the particular component(s) on the solid phase. Because of the high affinity of the adsorbent for the adsorbate species, the adsorbate is attracted and bound to the adsorbent by different mechanisms. Adsorption due to weak van der Waals forces is called physical adsorption and adsorption due to chemical bonding between adsorbent and adsorbate molecule is referred as chemisorption (Bhatnagar and Sillanpaa 2010).

Adsorption, as a separation process, is operative in most natural physical, biological and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resin and water purification. It is a well known equilibrium separation process and an effective method for water decontamination applications (Ahmad *et al.*, 2007, 2009; Rafatullah *et al.*, 2009; Dabrowski, 2001).

Adsorption technique has played a very significant role on removing the heavy metals and radioactive pollutants and has been an effective alternate process for the treatment of contaminated wastewater. Selective adsorption processes utilizing biological materials, mineral oxides, activated carbons, or polymer resins, has generated increasing excitement (Dambies *et al.*, 2002).

### *2.9.1 Advantages of adsorption process*

The major advantages of adsorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive sorbents. Compared with conventional or some biological methods for removing metal ions from industrial effluent, the adsorption process offers significant advantages of cost effective (the cost of the sorbent is low since they are often made from naturally abundant or waste materials), profitability, high efficiency (Hashem *et al.*, 2007; Ravikumar *et al.*, 2005; Allen *et al.*, 2005; Mittal *et al.*, 2005), minimization of chemical or biological sludge, regeneration of adsorbents, possibility of metal recovery, ease of operation, no metal toxicity issues and simplicity of design (Faust *et al.*, 1987; Ahalya *et al.*, 2003). Adsorption can remove or minimize different type of pollutants and thus it has a wider applicability in water pollution control.

### *2.9.2 Adsorption mechanism*

The process of adsorption involves a solid phase (sorbent) and a liquid phase (solvent) containing a dissolved species to be adsorbed. Due to high affinity of the sorbent for the metal ion species, the latter is attracted and bound for the adsorbent surface. Metal adsorption is a rather complex process affected by several factors. Mechanisms involved in the adsorption process include chemisorption, complexation, adsorption–complexation on surface and pores, ion exchange, microprecipitation, heavy metal hydroxide condensation onto the biosurface, and surface adsorption (Gardea-Torresdey *et al.*, 2004; Volesky, 2000).

At the surface of the solids, there are unbalanced forces of attraction which are responsible for adsorption. Due to the higher affinity of the adsorbent for the adsorbate species, the latter is attracted and bound there by different mechanisms. The process continues till equilibrium is

established between the amount of solid-bound adsorbate species and its portion remaining in the solution.

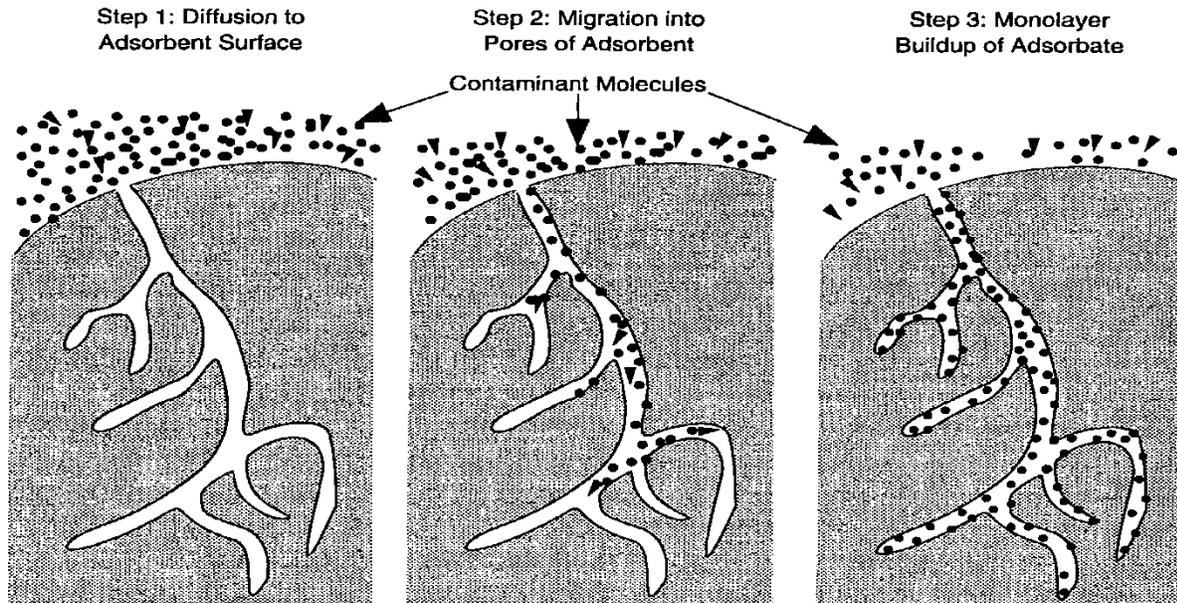


Figure 2.1: Adsorption mechanism

### 2.9.3 Factors affecting adsorption

The major factors that affect the adsorption process are: initial metal ion concentration, pH (the degree of ionization of a species is affected by the pH), surface area of adsorbent (Large size implies a greater adsorption capacity), particle size of adsorbent (smaller particle size reduces internal diffusional and mass transfer limitation to the penetration of the adsorbate inside the adsorbent), contact time or residence time (the longer the time the more complete the adsorption will be), solubility of adsorbate in wastewater, affinity of the solute for the adsorbent, and the number of carbon atoms. For substances in the same homologous series a larger number of carbon atoms is generally associated with a lower polarity and hence a greater potential for being adsorbed, size of the molecule with respect to size of the pores. Large molecules may be too large to enter small pores. This may reduce adsorption independently of other causes and degree of ionization of the adsorbate molecule. More highly ionized molecules are adsorbed to a smaller degree than neutral molecules. Aksu *et al.* (1992) reported that temperature does not influence the adsorption process in the range of 20-35 °C.

## 2.10. Types of adsorbents

An adsorbent is a substance, usually porous in nature with a high surface area, which can adsorb substances onto its surface by intermolecular forces. A number of materials have been extensively investigated as adsorbents in water pollution control. Some of the important ones are the commercial adsorbents which include silica gel, zeolites, activated alumina and activated carbon and the industrial by-products.

### 2.10.1 Commercial adsorbents

#### *Silica gel*

Silica gel is an amorphous form of silicon dioxide, which is synthetically produced in the form of hard irregular granules. Silica gel as a solid drying agent has been widely utilized in dehumidification process for their great pore surface area and good adsorption capacity (Chang *et al.*, 2008). Modified forms of silica have also been widely explored for the removal of different pollutants.

#### *Activated carbon*

Activated carbon has been the most widely used and popular adsorbent in effluent treatment throughout the world. Activated carbon is produced by a process consisting of raw material dehydration and carbonization followed by activation. The product obtained is known as activated carbon and generally has a very porous structure with a large surface area ranging from 600 to 2000 m<sup>2</sup>/g (Bhatnagar and Sillanpää, 2010). Activated carbon remains an expensive material since the higher the quality of activated carbon, the greater its cost. Activated carbon also requires complexing agents to improve its removal performance for inorganic matters. Therefore, this situation makes it no longer attractive to be widely used in small-scale industries because of cost inefficiency (Babel and Kurniawan, 2003).

#### *Zeolites*

Zeolites are naturally occurring crystalline aluminosilicates consisting of a framework of tetrahedral molecule, linked with each other by shared oxygen atoms. High ion-exchange capacity and relatively high specific surface areas, and more importantly their relatively cheap prices, make Zeolites more attractive adsorbents (Rafatullah *et al.*, 2009). Zeolites-based

materials are extremely versatile and their main use include detergent manufacture, ion-exchange resins, catalytic applications in the petroleum industry, separation process and as an adsorbent for water, carbon dioxide and hydrogen sulphide (Bhatnagar and Sillanpää, 2010). Various zeolites have been employed for the removal of pollutants. However, one disadvantage of the application of Zeolites relates to the competitive interactions of other monovalent cations, in particular  $\text{Na}^+$  and  $\text{K}^+$  in water effluent, which can considerably block  $\text{Cs}^+$  adsorption (Tomioka *et al.*, 1992; Avery, 1995).

#### *Activated alumina*

Activated alumina comprises a series of nonequilibrium forms of partially hydroxylated alumina oxide,  $\text{Al}_2\text{O}_3$ . It is also used to remove water from organic liquids including gasoline, kerosene, oils, aromatic hydrocarbons and many chlorinated hydrocarbons, having the surface area ranging from 200 to 300  $\text{m}^2/\text{g}$ . Activated alumina is receiving renewed attention as an adsorbent and a wealth of information has been published (Naiya *et al.*, 2009; Singh and Pant, 2004; and Ku and Chiou, 2002) on its adsorption characteristics.

Adsorption of heavy metals on conventional adsorbents such as activated carbon, silica gel, zeolites and activated alumina has been used widely in many applications as effective adsorbents. However, the high capital and regeneration costs of the materials limits their large-scale use for the removal of metals, this has encouraged researchers to look for low-cost adsorbing materials (Wang *et al.*, 2003; Babel and Kurniawan, 2003; Reddad *et al.*, 2002; Bailey *et al.*, 1999).

#### *2.10.2 Industrial by-products and wastes*

Industrial activities generate huge amount of solid waste materials as by-products. Some of this material is being put to use while others find no proper utilization and are dumped elsewhere. If the solid wastes could be used as low-cost adsorbents, it will provide a two-fold advantage to environmental pollution. Firstly, the volume of waste materials could be partly reduced and secondly the low-cost adsorbent if developed can reduce the pollution of wastewaters at a reasonable cost. Industrial waste requires little processing to increase its sorptive capacity. A number of industrial wastes have been investigated with or without treatment as adsorbents for

the removal of pollutants from wastewaters (Bhatnagar and Sillanpää, 2010). In India, various types of industrial wastes such as waste slurry, lignin, iron(III) hydroxide, and red mud, have been explored for their technical feasibility to remove heavy metals from contaminated water (Babel and Kurniawan, 2003). Table 3 summarises some of the industrial wastes that have been used for adsorption of heavy metals, and the sorption capacities exhibited by such materials.

Table. 2.3: Adsorption capacities of industrial waste (mg/g)

Material	Ni <sup>2+</sup>	Pb <sup>2+</sup>	Cr <sup>6+</sup>	Cd <sup>2+</sup>	Cu <sup>2+</sup>	Sources
Waste slurry				15.73	20.97	Lee and Davis, 2001
Iron (III) hydroxide			0.47			Namasivayam and Rangnathan, 1993
Blast furnace slag		40	7.5			Srivastava <i>et al.</i> , 1997
Sawdust					13.80	Ajmal <i>et al.</i> , 1998
Activated red mud	160					Zouboulis and Kydros, 1993
			1.6			Pradhan <i>et al.</i> , 1999
Bagasse fly ash			260			Gupta <i>et al.</i> , 1990

## 2.11 Biosorption and Biosorbents

Biosorption can be defined as the ability of biological materials to accumulate pollutants from wastewater through metabolically mediated or physico-chemical pathways of uptake (Fourest and Roux, 1995). Biosorption is an alternative low cost and eco-friendly technology to existing costly water treatment technologies and based on the biomaterial–pollutant interaction. Current researches in this field demonstrated that different kinds of biomaterials interact with dye molecules, heavy metals and other organic substances and they successfully remove these contaminants from aqueous media (Akar *et al.*, 2008; Herrero *et al.*, 2008; Ju *et al.*, 2008; Melgar *et al.*, 2007; Park *et al.*, 2007; Tunalı *et al.*, 2007; Quintelas *et al.*, 2006; Volesky *et al.*, 1999).

The performance of a biosorption process depends on various factors including the character of raw wastewater (for example, pH, temperature, metal species and ionic strength), type of

biomass (for example, size, structure and capacity) and the operation factors of the process (for example, the stirring speed). The most popular biosorbents encountered are microbial, bacterial fungal or algal biomass and lignocellulosic materials (Ho and Ofomaja 2006; 2005; Feng and Aldrich 2004; Ariff *et al.*, 1999).

Biosorbents are originally from the living organisms, which live in sea and fresh water. They are rich in carbon, hydrogen, oxygen, nitrogen and phosphorus. Dead biomass can also be used as alternative adsorbents. Dead cells accumulate heavy metals to an equal or greater extent than living cells. The bacterial cell surfaces are anionic due to the presence of ionized groups in the cell wall polymers, causing the cell to attract metal cations. The use of dead rather than live biomass eliminates the problems of waste toxicity and nutrient requirements.

### *2.11.1 Types of Biosorbent*

Abundant natural materials, particularly of cellulosic nature, have been suggested as potential biosorbent for heavy metals. Algae, fungi and bacteria are examples of biomass-derived sorbents for several metals. Such sorbents have produced encouraging results. Gadd, 1988 and Brierley, 1990 reviewed how bacteria, fungi and algae take up toxic metal ions. Recent investigation has reported that algae, fungi, and bacteria as biosorbents are eco-friendly, low-cost and effective (Das, *et al.*, 2008).

#### *2.11.1.1 Algae*

Algae include a large and diverse assemblage of organisms that contain chlorophyll and carry out oxygenic photosynthesis. Algae are classified on the nature of the chlorophyll(s), the cell wall chemistry, and flagellation. All types of algae contain chlorophyll *a*. Gupta *et al.*, (2001) studied Cr(VI) biosorption by biomass of filamentous algae *Spirogyra* species. Equilibrium isotherms were obtained and maximum removal of Cr(VI) was 1.47 g metal/kg of dry weight biomass at pH of 2.0.

#### *2.11.1.2 Fungi*

Fungi and yeast accumulate on the non-nutrient metals cadmium, mercury, lead, chromium, etc., in substantial amounts. Both living and dead fungal cells possess a remarkable ability for toxic

and precious metals uptake from wastewater. The fungi and yeast can be grown in substantial amounts using unsophisticated fermentation techniques and inexpensive growth media. Fungi are used in a variety of industrial fermentation processes. These processes could serve as economical biomass supply sources for the removal of metal ions. Therefore, fungal biomass could serve as an economical means for metal ion removal and recovery from aqueous solutions.

#### *2.11.1.3 Bacteria*

The use of bacteria for bioadsorption is a fast growing field in metal remediation because of their ability to grow under controlled conditions and smaller size, which leads to high surface area and fast rates. According to Volesky and Holan, (1995) who presented an extensive review of biosorption results, the strong biosorbent behavior of certain types of microbial biomass toward metallic ions is a function of the chemical makeup of microbial cells. *Thuringiensis* (S, ahin and O' ztu' rk, 2005), *Zoogloea ramigera* (Nourbakhsh *et al.*, 1994), *Bacillus* sp. (Nourbakhsh *et al.*, 2002), *Aeromonas caviae* (Loukidou *et al.*, 2004a; Loukidou *et al.*, 2004b), *Pantoea* sp. (Ozdemir *et al.*, 2004), *Aeromonas caviae* have been used for chromium remediation.

### **2.12 Agricultural wastes as biosorbents.**

Agricultural waste materials are now becoming promising alternatives to other sources of biosorbents since they are easily obtained, low in cost, prevent further chemical pollution to the environment (Atlas, 1995) and they have functional groups such as carboxylic acids, esters, carboxylates, phenolic and amino group that can act as adsorption sites for heavy metal ions. Agricultural waste materials have been of interest for their unique ability to bind many toxic metal ions and radionuclides at very low concentrations from contaminated sources (Balarama Krishna *et al.*, 2004). Conversion of agricultural wastes into low-cost adsorbents is a promising alternative to solve environmental problems and also to reduce the preparation costs.

The raw agricultural solid wastes such as leaves, fibers, fruits peels, seeds etc. and waste materials from forest industries such as sawdust, bark etc. have been used as adsorbents. These materials are available in large quantities and may be potential adsorbents due to their chemical characteristics and low cost. Adsorbents from agricultural waste materials may have a potential marketing advantage in the wastewater treatment over other adsorbents including synthetic

adsorbents, because they are of low cost, more biosafe, environmentally friendly, available in abundance and more efficient (Huang *et al.*, 2010).

Raw agricultural waste materials used as biosorbent have the following disadvantages as compared to other activated carbon and other adsorbents: (1) the sorption capacity of agricultural waste products are rather low and (2) after filtration with agricultural wastes biosorbents, the water is seen to have high chemical oxygen demand (COD) and biological oxygen demand (BOD) as well as total carbon (TOC) due to release of soluble organic compounds contained in the plant material. Hence chemical modification will be the significant method to overcome the limitations by improving surface properties and removing soluble organic components of plant wastes applied for biosorption (Ofomaja *et al.*, 2009).

### **2.13 Chemical composition of agricultural adsorbents**

Agricultural by-products usually are composed of lignin and cellulose as major constituents and may also include other polar functional groups of lignin, which includes hemicelluloses, extractives, alcohols, aldehydes, ketones, carboxylic, phenolic, and ether groups. These groups have the ability to bind metal ion by donation of an electron pair from these groups to form complexes with the metal ion in solution (Pagnanelli *et al.*, 2003). Some adsorbents are non-selective and bind to a wide range of heavy metals with no specific priority, whereas others are specific for certain types of metals depending upon their chemical compositions (Sud *et al.*, 2008).

Cellulose is a crystalline homo-polymer of glucose with 1 → 4 glycosidic linkage and intramolecular and intermolecular hydrogen bonds (Demirbas, 2000). These linkages thus form cellulose as the repeating unit of cellulose chain (Figure 3). By forming intermolecular hydrogen bonds, cellulose is insoluble in most solvents and has a low accessibility to acid and enzymatic hydrolysis. Hemicelluloses consist of different monosaccharide units. The polymer chains of hemicelluloses have short branches and are amorphous. Because of the amorphous morphology, hemicelluloses are partially soluble or swellable in water.

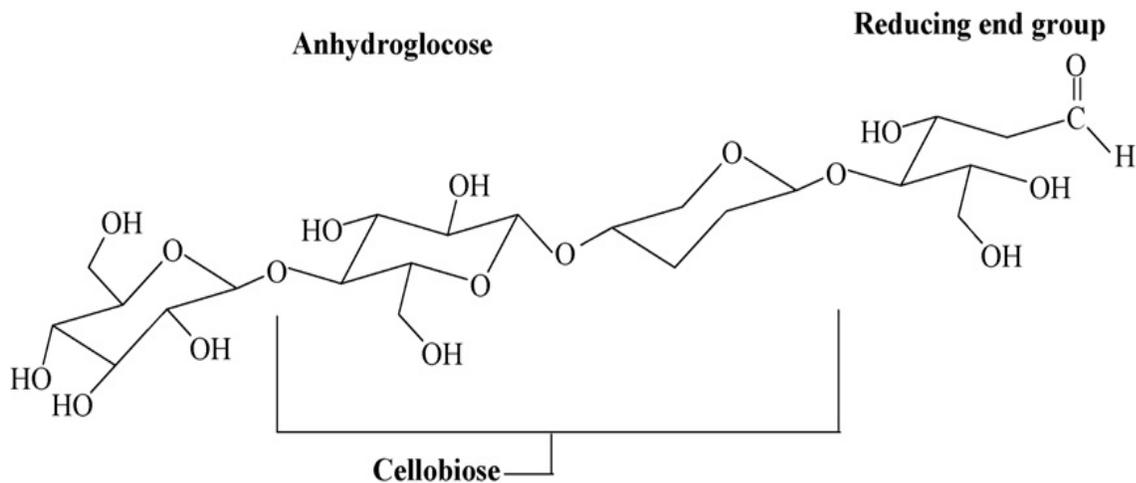


Figure 2.2: The structure of cellulose. Anhydroglucose is the monomer of cellulose, cellobiose is the dimer (Hashem *et al.*, 2007).

Lignin is a three dimensional polymer of aromatic compounds covalently linked with xylans in hardwoods and galactoglucomannans in softwoods (Garg *et al.*, 2007). Even though mechanically cleavable to a relatively low molecular weight, lignin is not soluble in water. It has a high surface area ( $180 \text{ m}^2/\text{g}$ ) and a strong resistance to chemical reactions. Its functions are to provide structural strength, provide sealing of water conducting system that links roots with leaves, and protect plants against degradation. These properties of lignin reveal that it has a potential to be used as a possible adsorption material to remove heavy metals from waste waters.

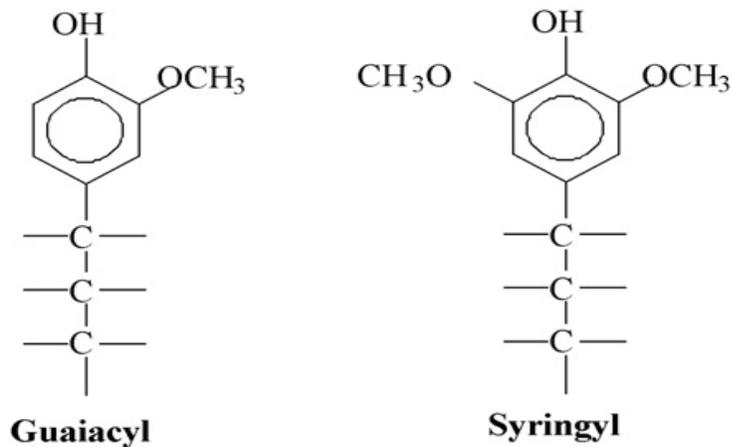


Figure 2.3. Schematic illustration of building units of lignin.

## 2.14 Application of agricultural waste as adsorbents

A low cost adsorbent is defined as one which is abundant in nature or is a by-product or waste material from another industry (Višekruna *et al.*, 2011). Removal of heavy metal ions from the aqueous streams by agricultural waste materials is an innovative and promising technology. At present, there is growing interest in using low-cost, commercially available materials for the adsorption of heavy metals. Research has been conducted on the variety of biosorbents for the removal of heavy metal ions as Cr, Cu, Ni, Pb, Cd, As, Hg and other metals.

Continuous attempts have been made to develop low cost non-conventional adsorbents for removal of toxic metal ions. Recently, Bhatnagara and Sillanpaa, (2010) and Sud *et al.*, (2008) reviewed a wide variety of low-cost adsorbents for the removal of heavy metals. A wide variety of materials such as pine cone powder (Ofomaja *et al.*, 2009), brown algae (Dabbagh *et al.*, 2008), wheat brean (Bulut and Baysal, 2006), tea-industry waste (Cay *et al.*, 2004, ) rice husk (Ajmal *et al.*, 2003), modified sawdust of walnut (Bulut and Tez, 2003) holly oak (Prasad and Freitas, 2000), animal bones (Al-Asheh *et al.*, 1999), sawdust (Ajmal *et al.*, 1998), pine bark (Al-Asheh and Duvnjak, 1998), modified bark (Gloaguen and Morvan, 1997), modified cellulosic materials (Okieimen *et al.*, 1985), and fly ash (Panday *et al.*, 1985), are being used as low-cost alternatives to expensive adsorbents. Table 2.4 shows the summary of adsorption capacities of different agricultural wastes as adsorbents for the removal of heavy metals from water.

Table 2.4: Adsorption capacities of different agricultural wastes as adsorbents for the removal of various pollutants from water.

Adsorbate	Adsorbent	Adsorption capacity (mg/g)	Reference
NaOH treated rice husk	Cd(II)	20.24	Kumar and Bandyopadhyay, 2006
Peanut hull	Cu(II)	21.25	Zhu <i>et al.</i> , 2009
Pomelo peel	Cd(II)	21.83	Saikaew <i>et al.</i> , 2009
Mango peel	Cd(II)	68.92	Iqbal <i>et al.</i> , 2009
	Pb(II)	99.05	

<b>Bael fruit shell</b>	Cr(VI)	17.27	Anandkumar and Mandal, 2009
<b>Chestnut shell</b>	Cu(II)	12.56	Yao <i>et al.</i> , 2009
<b>ZnCl<sub>2</sub>-modified walnut shells</b>	Hg(II)	151.5	Zabihi <i>et al.</i> , 2008
<b>Sugarcane bagasse</b>	Zn(II)	31.11	Mohan and Singh, 2002
<b>H<sub>3</sub>PO<sub>4</sub>-treated rice bran</b>	Ni(II)	102	Zafar <i>et al.</i> , 2007

Table 2.5: Summary of modified plant waste as biosorbents for the removal of cesium ion from aqueous solution.

<b>Biosorbents</b>	<b>Modifying agent</b>	<b>Biosorption capacity (mg/g)</b>	<b>Reference</b>
<b>Sargassum Glaucescens</b>	Formaldehyde (FA)	0.08	Dabbagh <i>et al.</i> , 2008
	Glutaraldehyde (GA)	31.7	
	Potassium hexacyanoferrate (HCF)	49.4	
	FA and HCF	62	
	GA and HCF	56.5	
<b>Cystoseira indica</b>	Formaldehyde (FA)	63.5	
	Glutaraldehyde (GA)	60.4	
	Potassium hexacyanoferrate (HCF)	37.3	
	FA and HCF	37.2	
	GA and HCF	39.7	

### **2.15 Disadvantages of the use of adsorbent for Cesium removal**

The main disadvantage of cesium removal using various adsorbents is the competitive interaction of other monovalent and divalent cations, in particular  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$ , which can considerably block  $\text{Cs}^+$  adsorption. These cations compete with cesium ions for the adsorption/exchange sites (Vrtoch *et al.*, 2011; Jalali-Rad *et al.*, 2004). The competition is attributed to the close similarity in the physical and chemical properties of sodium, potassium, calcium, and cesium, therefore the separation of cesium from systems containing mixed alkali metal ions, such as brine systems is difficult (Yea *et al.*, 2009). The problem of interference in cesium adsorption can be avoided by the use of complexes which can specifically or preferentially bind cesium ions in the presence of these alkali and alkali earth metals.

### **2.16 Multicomponent sorption of Cs in the presence of alkali and alkali earth metals**

Industrial effluents rarely contain a single component; hence, design of adsorption systems must be based on multi-component systems. Therefore, competitive adsorption is very important in water and wastewater treatment because most metal ions to be adsorbed exist in solution with other adsorbable metal ions. The removal of one metal ion may be influenced by the presence of other metal ions. For example: Uranium uptake by biomass of bacteria, fungi and yeast was not affected by the presence of manganese, cobalt, cadmium, mercury, copper and lead in solution (Sakaguchi and Nakajima, 1991). In contrast, the presence of  $\text{Fe}^{2+}$  and  $\text{Zn}^{2+}$  was found to influence uranium uptake by *Rhizopusarrhizus* (Tsezos and Volesky, 1982) and cobalt uptake by different microorganisms seemed to be completely inhibited by the presence of uranium, lead, mercury and copper (Sakaguchi and Nakajima, 1991).

Cesium has been shown to compete with potassium (K), sodium (Na), calcium (Ca) as well as the chemically similar element rubidium (Rb) for both active and passive membrane transport, although Cs is generally transported less readily than the other metals by these processes (Cecchi *et al.*, 1987; Latorre and Miller, 1983; Edwards, 1982; Sjodin and Beauge, 1967; Hodgkin, 1947). Calcium is adsorbed from the soil by plant and passed on to animals where it is used in the formation of bones and teeth. Man gets calcium from both plant and animal sources like milk, vegetables, and cereal grains. Cesium is produced from these sources and due to chemical similarities to calcium it is also deposited in bones and teeth. Cesium-137 which is chemically

similar to potassium is a common constituent of all living cells. Cs from fallout passes to man through contaminated meat and dairy products or contaminated grains and leafy vegetables. The soft parts of the body, especially the muscles, are badly affected by the presence of cesium.

Therefore separation and recovery of radioactive cesium from wastewater is a significant issue and has drawn particular attention of researchers. Cs uptake behaviour for several divalent cations was investigated by Shrivastava *et al.*, (1995). Terada *et al.*, (1998) studied the influence of alkali elements on the accumulation of radiocesium by mushroom and found that the Cs uptake was affected by a high concentration of potassium and Rubidium.

### **2.17 Application of hexacyanoferrate as adsorbents**

In the past few decades, attention has been shifted to the use of chemical precipitating agents for cesium removal from aqueous solution (Sun *et al.*, 1997). The most popular precipitating agent being the transition metal hexacyanoferrates (HCF) which are effective for cesium removal from aqueous solutions (Sharygin *et al.*, 2007; Milyutin *et al.*, 2007). The advantage of transition metal precipitants includes their high selectivity for cesium, high affinity over a wide range of pH, chemical and thermal resistance (Zhang *et al.*, 2009; Nilchi *et al.*, 2003).

Adsorbents of high selectivity maintain the ability to preconcentrate target species even in the presence of excess interfering cations or competing ligands (Lin *et al.*, 2005). It is assumed that the property which is responsible for the affinity of various hexacyanoferrates towards alkali metal ions is the intensity of the electrostatic field on the surface of the cation in the hexacyanoferrates. Transition metal hexacyanoferrates are required for Cs removal from solutions containing large amount of Na<sup>+</sup> and K<sup>+</sup> but the use of this ion exchangers is restricted to a narrow range of pH and in their usual form they have posed practical difficulties as sorbents (Jalali *et al.*, 2004).

Nickel hexacyanoferrate has been widely studied for separation and electrochemical sensing of Cs<sup>+</sup> owing to its strong selectivity for Cs<sup>+</sup> over other radionuclides and alkali cations. They also have high Cs<sup>+</sup> sorption capacity over many metal hexacyanoferrates (Ismail *et al.*, 1999). Recently, studies (Parab and Sudersanan, 2010; Faustino *et al.*, 2008; Chang *et al.*, 2008; Loos-

Neskovic *et al.*, 2004) have been carried out on the application of hexacyanoferrate for the removal of radioactive cesium from solution. Ferric hexacyanoferrate binds to cesium chemically, which resulted in its removal. Ferric hexacyanoferrates permeates small hydrated ions such as  $\text{Cs}^+$ , whereas larger hydrated ions like  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^+$  gets blocked (Jin *et al.*, 2003).

Although quite effective for cesium removal, hexacyanoferrate (HCF) precipitant has the disadvantage of high yields of colloidal sludge, which makes them difficult to remove from solution. The alternative to solving this problem was then to prepare the ferrocyanides in a granular or finely dispersed form. Again, these methods have the disadvantage of high power consumption when producing granulated hexacyanoferrates (HCF) suitable for cesium removal under dynamic conditions (Mardanenko *et al.*, 2004), while the poor mechanical strength, disintegration of grains along with the problem of clogging of the bed due to high hydrodynamic resistance of the finely dispersed form of the hexacyanoferrates remains a serious limitation.

### **2.18 Ferric hexacyanoferrate for cesium binding.**

Ferric hexacyanoferrate ( $\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3$ ), was first prepared in 1704 as a prospective dye and is considered to be the first synthetic coordination compound (Buser *et al.*, 1977). Ferric hexacyanoferrate is also known as Prussian blue (PB). Prussian blue is a very dark blue, colour fast, non-toxic pigment. Prussian blue is also known as iron blue, mineral blue, Paris blue and Brunswick blue. The PB crystal structure is a cubic lattice (Robin 1962) with the  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  atoms occupying the corners of the cube and the cyanide group placed at the sides (Fig. 2). The  $\text{Fe}^{\text{II}}$  atoms are bonded to the carbon atom in the cyano group and the  $\text{Fe}^{\text{III}}$  atoms are bonded to the nitrogen atom in the cyano group. The cubic structure is retained in aqueous media and due to the stability of the crystal lattice,  $\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3$  is insoluble.

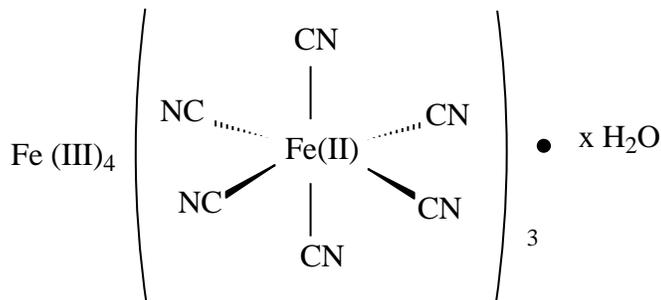


Figure: 2.4. The chemical structure of Prussian blue.

Literature review also showed that the potassium nickel hexacyanoferrate is the most widely applied supported hexacyanoferrate for cesium sorption. Studies carried out by Dresow *et al.* (1990) on the binding of  $^{134}\text{Cs}$  in rats, using different transition metals, showed that  $^{134}\text{Cs}$  inhibition increased in the order of  $\text{KZnHCF} < \text{KCuHCF} < \text{FeHCF} < \text{KCoHCF} < \text{KNiHCF} < \text{NH}_4\text{FeHCF} < \text{KFeHCF}$ , indicating that  $\text{KFeHCF}$  may also be very effective in its application for cesium adsorption from wastewater.

### 2.19 Binding of hexacyanoferrate into solid support materials

Various attempts have been made by researchers on the grafting of different metal hexacyanoferrates (HCF) onto various solid supports. Grafting of hexacyanoferrate (HCF) has been carried out on various materials such as silica gels (Milonjic *et al.*, 2002; Rajec *et al.*, 2000), zeolites and natural aluminosilicates (Kazemian *et al.*, 2006; Loos-Neskovic *et al.*, 1984) to improve mechanical strength, reduce cost and reduce hydrodynamic resistance of the product. Several types of metal ion combination with the hexacyanoferrate have also been tested for example, potassium zinc hexacyanoferrate ( $\text{KZnHCF}$ ) (Zhang *et al.*, 2009), potassium titanium hexacyanoferrate ( $\text{KTiHCF}$ ) (Sun *et al.*, 1997), potassium iron(III) hexacyanoferrate ( $\text{KFeHCF}$ ) (Mardanenko *et al.*, 2004) and potassium nickel hexacyanoferrate ( $\text{KNiHCF}$ ) (Vrtoch *et al.*, 2011) have been applied on various supports.

### 2.20 Binding of hexacyanoferrate into the agricultural waste biosorbents

The advantage of supports from biological origin is the cheap and readily available source as compared with other supports. Since biosorbents usually have low surface areas and sorption capacities, this could hinder its application as effective support for hexacyanoferrates; therefore

there is a need to improve their surface properties to enhance their application. Recent studies into the utilization of supports from biological origin have been reported. Parab and Sudersanan (2010) prepared potassium nickel hexacyanoferrate onto coir pith while Vrtoch *et al.*, (2011) prepared potassium nickel hexacyanoferrate onto *Agaricus bisporus* mushroom biomass and both authors successfully applied the exchangers for cesium removal from aqueous solution.

### **2.21 Pine cone as biosorbent of interest**

Pine is a genus of trees with about 115 species. Pine cone is an organ of the pine tree containing reproductive structures. It is an agricultural waste produced when pine tree seeds are removed from matured cones (Ofomaja *et al.*, 2010). Pine tree cones are produced in large quantities at forest industries as a litter. Pine trees are only one of the conifer, or cone bearing plants. Pine cones, like the reproductive organs of other conifers, come in male and female varieties. Male and female cones grow on the same tree. Male pine cones are smaller, not more than 5 cm long, more herbaceous and are short lived (lives for only few months). Male pine cones are covered with pollen sacs and after they release them they then fall off the trees. Female pine cones are woody with scaled structure. They are much harder than the male pine cones and are typically 3-60 cm long.

Pine cone is composed of mainly  $\alpha$  cellulose (18.8%), hemicellulose (46.5%), and lignin (37.4%) (Nagata *et al.*, 1990). The pine cones contain large quantities of glucose, derived from cellulose, and smaller quantities of mannose, galactose, and xylose probably derived from hemicelluloses (Pettersen, 1984). They also contain significant amount of ethanol/toluene extractive (Gonultas, 2008) and resin which is a sticky residue that is deposited on hands and fingers when pine cones are handled. Pine cone contains lignin which strengthens the cell walls and protects the microfibrils of the cell wall from chemical, physical and biological attack (Ofomaja *et al.*, 2009). Large quantities of cones are released in pine plantation annually with little or no use. Pine cone powder as adsorbent has the advantage of achieving maximum metal removal at short contact time (Ofomaja *et al.*, 2010).

Large quantities of cones are produced annually throughout the world, especially in pine plantations grown for the pulp and paper industry. Pine cones are collected, dried to facilitate

seed released, and generally discarded or burned in the stove in winter. New use for pine cone can provide extra income for forest landowners.

The chemical properties of pine cone has been determined on a percentage dry basis by Brebu *et al.*, (2010) and Nagata *et al.*, (1990) and is shown in Tables 3 below:

Table 2.6: Properties of pine cone

<b>Properties of pine cone.</b>	<b>Proximate analysis wt%</b>
<b>Moisture</b>	9.6
<b>Ash</b>	0.9
<b>Volatile</b>	77.8
<b>Elemental analysis wt%</b>	
<b>C</b>	42.62
<b>H</b>	5.56
<b>N</b>	0.76
<b>S</b>	0.05
<b>O</b>	51.01
<b>Main constituents wt %</b>	
<b>Lignin</b>	37.4
<b>Hemicellulose</b>	46.5
<b>Cellulose</b>	18.8
<b>Ethanol/toluene extractives</b>	15.4

### 2.21.1 Application of pine cone biomass as biosorbent

Pine cones contain some components such as lignin, cellulose and organic groups which leaches into the treated water and greatly increased chemical oxygen demand. Several modifying agents have been studied to reduce organic components of pine cone thereby increasing its adsorption capacity. Modified pine cone powder as biosorbent has been shown to have high affinity for many metal ions. For example Ofomaja *et al.*, (2010) treated pine cone powder surface with potassium hydroxide and applied it for copper(II) and lead(II) removal from solution, Argun *et*

*al.*, (2008) modified the pine cone with fentons reagent before applying it for cadmium and lead removal.

Pine cone powder a biosorbent has the advantage of achieving maximum metal removal at short contact time. For example Malkoc, (2006) achieved equilibrium for nickel (II) in 3 minutes while Uzun *et al.*, (2002) removed chromium(IV) from aqueous solution in 20 minutes. Literature research revealed that initial solution pH strongly affects metal sorption on to pine cone powder. Oguz, (2005) showed that pine cone powder capacity for chromium(VI) increased from 10.00 to 16.60 mg/g when solution pH decreased from 5.4 to 1.5 while Uzun *et al.*, (2003) observed an increase from 6.73 to 53.6 % of lead ion sorption as solution pH was increased from 2.0 to 4.0.

## **2.22 Surface modification of biosorbent**

Biosorbent modification is a process of chemically or physically manipulating the surface properties of plant materials to alter properties such as type and amount of functional groups, surface area and porosity by extraction of plant chemical components so as to improve its adsorptive ability. Agricultural waste adsorbents are modified by various methods to increase their adsorption capacities because metal binding is believed to take place through chemical functional groups present in the materials. Most studies show that agricultural wastes have been highly efficient for the metal ion removal in their modified form.

Several authors have investigated the use of numerous chemicals agents/extractants for modifying plant materials in their application as biosorbents and some of these include base solutions (sodium hydroxide, calcium hydroxide, sodium carbonate), mineral and organic acid solutions (hydrochloric acid, tartaric acid, nitric acid, sulphuric acid, citric acid), organic compound (ethylenediamine, formaldehyde, epichlorohydrin, methanol), dye and oxidizing agents for removing soluble organic compounds and increasing efficiency of metal adsorption (Wan Ngah and Hanafiah, 2008).

Various modification strategies have been employed, for example Laszlo and Dintzis (1994) treated hulls with sodium hydroxide and epichlorohydrin and observed an improvement in calcium(II) binding, Marshall and Johns (1996) exposed hulls to sodium hydroxide and noted an

increase in zinc(II) adsorption capacity. Recently, Ofomaja *et al.*, (2010) modified pine cone powder with potassium hydroxide and noted an increase in copper(II) and lead(II) removal.

Several investigations have been performed on the citric modification of agricultural wastes products. Wartelle and Marshall (2000) modified several common agricultural wastes (soybeans, rice hulls, sugarcane bagasse, cottonseed, rice straw and rice bran) with citric acid and determined their ability to adsorb copper ions.

### **2.23 Biosorbent surface treatment by solvent extraction**

A number of physical and chemical methods have been employed for modification of a variety of biosorbent materials. The physical treatments include heating/boiling, freezing/melting, and drying while the chemical treatment include washing with detergents, cross-linking with organic solvents, alkali or acid treatment, chemical reactions with a variety of organic and inorganic compounds (Deng and Ting, 2005; Lin and Rayson, 1998; Wang, 2002; Wang and Chen, 2006). Chemical treatment of adsorbents sourced from agricultural wastes is usually targeted at (i) extracting plant water soluble or organic soluble constituents which may leach into treated water thereby increasing the chemical oxygen demand (COD), biological chemical demand (BOD) and total organic carbon (TOC) (Gaballah *et al.*, 1997, Nakajima and Sakaguchi, 1990), (ii) improve the adsorption capacity of the biosorbent in question by swelling the material so as to increase the internal and external surfaces (Sciban *et al.*, 2006) (iii) improving the cation exchange capacity of agricultural by-product (Sessa and Wing, 1997, 1998; Wing 1996, 1997; Ahmedna *et al.*, 1997; Marshal and Johns, 1996; Laszlo and Dintzis, 1994) and (iv) modifying the biosorbent surface to allow for penetration of polyfunctional organic compounds into the matrix of the biosorbent to increase binding sites (Marshall and Wartelle, 2000; Marshal *et al.*, 1999).

Wood products especially products of pine wood have been treated using different kinds of chemical extractants to improve surface properties such as mechanical strength, chemical resistance and ability to incorporate organic acid anhydrides through esterification which act as wood preservation agents against decay etc (Papadopoulos *et al.*, 2010; Jebrane *et al.*, 2010). This chemical extraction has been shown to remove wood extractives such as plant pigments, coloured organic compounds, lignin, resin acids and water soluble tannins (Sciban *et al.*, 2006).

Recent studies have shown that these extraction methods have been applied for wood materials used as adsorbents for heavy metal removal from solution. For example, Sciban *et al.*, (2006) used formaldehyde-sodium hydroxide treatment of oak and black locust sawdust before applying it as an adsorbent for removing copper and zinc from aqueous solution. Marchetti *et al.*, (2000) extracted wood meal (*Picea abies*) with a mixture of toluene-ethanol and applied the modified material as an adsorbent for cadmium ions from aqueous solution. These authors reported an enhancement in the metal adsorption capacities and the ability of the extracted materials to be modified with polyfunctional organic acids and other modifying agents.

## **2.24 Kinetic models applied to predict the rate of cesium adsorption from aqueous solution.**

### *2.24.1 Introduction*

Adsorption is one of the most widely applied techniques for pollutants removal from contaminated aqueous solution, since it eliminates the need for huge sludge-handling processes. When adsorption is concerned, kinetic aspects should be involved to know more details about its performance and mechanisms. Predicting the rate at which adsorption takes place for a given system is probably the most important factor in adsorption system design, with adsorbate residence time and the reactor dimensions controlled by the system's kinetics. The kinetic parameter, which is helpful for the prediction of adsorption rate, gives important information for designing and modeling the processes.

Although equilibrium studies are important in determining the effectiveness of adsorption, it is also important to determine the type of adsorption mechanism within a given system (Khraisheh *et al.*, 2002). The study of adsorption kinetics in wastewater treatment is crucial as it provides understanding of the reaction pathways and the mechanisms of adsorption reactions (Sag and Aktay, 2002). The kinetics of adsorption processes is concerned with intermolecular forces between adsorption sites and adsorbate molecules and forms an important area of surface chemistry.

Numerous kinetic models have described the reaction order of adsorption systems based on solution concentration. These include first order (Saiers *et al.*, 1994) and second-order (Mccoy and Liapis, 1991) reversible ones, and first-order (Mohan *et al.*, 2002) and second-order (Chu

and Hashim, 2003) irreversible ones, pseudo-first-order (O'Shannessy and Winzor, 1996) and pseudo-second-order ones (Zaror, 1997) based on the solution concentration. On the other hand, reaction orders based on the capacity of the adsorbent have also been presented, such as Lagergren's first-order equation (Lagergren, 1898), Ho's second-order expression (Ho and McKay, 2000) and diffusion chemisorption model (Sutherland, 2004).

#### 2.24.1.1 Pseudo First Order rate equation

The pseudo-first order model considers the rate of occupation of biosorption sites to be proportional to the number of unoccupied sites. In order to determine the controlling mechanism of adsorption process such as mass transfer and chemical reaction, the first order kinetic model is used to test the experimental data. A simple kinetics of adsorption is given by Lagergren rate equation. Lagergren's first order rate equation has been called pseudo first order (Ho and McKay, 1998), and has been widely used to describe the adsorption of pollutants from wastewater in different fields. It is the earliest known pseudo order to describe the adsorption rate based on the adsorption capacity. The pseudo-first order equation is generally expressed as:

$$\int \frac{dq_t}{dt} = k_1 \int (q_e - q_t) \quad (2.1)$$

Where  $q_t$  and  $q_e$  ( $\text{mg g}^{-1}$ ) are the amount adsorbed at time  $t$  and at equilibrium and  $k$  ( $\text{min}^{-1}$ ) is the rate constant of the pseudo-first order sorption process. Equation (2.1) can be integrated with boundary conditions  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_e = q_e$ : the integrated form of equation (2.1) becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{kt}{2.303} \quad (2.2)$$

When the values of  $\log(q_e - q_t)$  were linearly correlated with  $t$ , the plot of  $\log(q_e - q_t)$  versus  $t$  will give a linear relationship from which  $k_1$  and  $q_e$  can be determined from the slope and intercept of the graph respectively.

### 2.24.1.2 Pseudo second order rate equation

The pseudo second-order model assumes that the adsorption process is a pseudo-chemical reaction process with the driving force being the difference between the average solid concentration and the equilibrium concentration with the overall adsorption rate proportional to the square of the driving force (Yang and Al-Duri, 2005). Ho and McKay, (2000) assumed that the adsorption capacity is proportional to the number of active sites occupied in the adsorbent and expressed the kinetic rate equation accordingly. The rate expression for the sorption described by Equations (2.3) and (2.4) is:

$$\frac{d(P)_t}{dt} = k[(P)_0 - (P)_t]^2 \quad (2.3)$$

Where  $(P)_t$  is the number of active sites occupied on the peat at time  $t$ ,  $(P)_0$  and is the number of equilibrium sites available on the peat.

The kinetic rate equations can be rewritten as follows:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2, \quad (2.4)$$

Where  $k$  is the rate constant of sorption, ( $\text{g mg}^{-1} \text{ min}^{-1}$ ),  $q_e$  is the amount of divalent metal ion adsorbed at equilibrium, ( $\text{mg g}^{-1}$ ),  $q_t$  is amount of divalent metal ion on the surface of the sorbent at any time,  $t$ , ( $\text{mg g}^{-1}$ ).

Separating the variables in Eq. (2.4) gives:

$$\frac{dq_t}{(q_e - q_t)^2} = k dt, \quad (2.5)$$

Integrating this for the boundary conditions  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$ , gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt, \quad (2.6)$$

which is the integrated rate law for a pseudo-second order reaction. Eq. (2.6) can be rearranged to obtain:

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

which has a linear form of

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t. \quad (2.8)$$

$h$  is defined to be the initial sorption rate ( $\text{mg g}^{-1} \text{min}$ ) as  $q_t/t$  approach to 0.

$$h = kq_e^2, \quad (2.9)$$

Then

Eqs. (2.8) and (2.9) become:

$$q_t = \frac{t}{\frac{1}{h} + \frac{t}{q_e}}, \quad (2.10)$$

and

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t. \quad (2.11)$$

Where  $h$  ( $\text{mg}/(\text{g}\cdot\text{min})$ ) is the initial adsorption rate. The constants can be determined experimentally by plotting  $t/q_t$  against  $t$ . Therefore, if the plot of the experimental forms a straight line, it is believed that the biosorption follow the pseudo-second order mechanism. If chemical adsorption is the rate controlling step, the pseudo-second-order model is more likely to predict the behavior over the entire concentration range of the adsorption process.

#### 2.24.1.3 Diffusion-chemisorption model

Sutherland (2004) developed an empirical diffusion chemisorption kinetic model to simulate adsorption of heavy metals unto heterogamous surfaces. Sutherland's expression is as follows:

$$\frac{t^{0.5}}{q_t} = \frac{t^{0.5}}{q_e} + \frac{1}{K_{DC}} \quad (2.12)$$

where  $q_t$  (mg/g), the rate of change of concentration of the solid phase is equated as a function of the rate of mass transfer of  $\text{Cs}^+$  ions from the liquid phase to the adsorption site ( $K_{DC}$  (mg/g  $t^{0.5}$ )) and  $q_e$  (mg/g) is the equilibrium capacity, while  $t^{0.5}$ , is the time in min raised to the power of 0.5. Therefore, the plot of  $t^{0.5}/q_t$  versus  $t^{0.5}$  will yield a straight line with slope equal to  $1/q_e$  and intercept equal to the diffusion-chemisorption constant,  $K_{DC}$ . The predicted equilibrium capacity value was then calculated by rearranging the above equation to form:

$$q_t = k_{DC} x \frac{t^{0.5}}{q_e} \quad (2.13)$$

## 2.25 Error methods

In the optimization kinetic models to experimental data, it is necessary to define an error function so as to evaluate the fit of the isotherm equation to the experimental data. The use of two error functions which are, (1) the linear coefficient of determination,  $r^2$  and (2) the nonlinear chi-square,  $\chi^2$ , were employed in this investigation. The coefficient of determination,  $r^2$ , represents the percentage of variability in the dependent variable that has been explained by the regression line. The value of the error model may vary from zero to unity. Therefore a coefficient of determination of one indicates that 100% of the variation of  $q_e$  has been explained by the regression equation. The linear coefficient of determination,  $r^2$ , can be obtained from evaluation of data by linear model, and calculated with aid of the equation:

$$r^2 = \frac{S_{xy}^2}{S_{xx}S_{yy}} \quad (2.14)$$

Where  $S_{xx}$  is the sum of squares x

$$S_{xx} = \sum_{i=1}^n x_i^2 - \frac{\sum_{i=1}^n X_i}{n} \quad (2.15)$$

Where  $S_{yy}$  is the sum of squares of y

$$S_{yy} = \sum_{i=1}^n y_i^2 - \frac{\sum_{i=1}^n y_i}{n} \quad (2.16)$$

Where  $S_{xy}$  is the sum of square of X and Y

$$S_{xy} = \sum_{i=1}^n x^2 y^2 - \frac{\left(\sum_{i=1}^n X_i\right)\left(\sum_{i=1}^n Y_i\right)}{n} \quad (2.17)$$

The chi-square,  $\chi^2$ , test statistic is based on the sum of the squares of the difference between the experimental data and data obtained by calculation using models, with each squared difference divided by the corresponding data obtained by calculating from models. The equivalent mathematical statement is:

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \quad (2.18)$$

where  $q_{e,m}$  is the equilibrium adsorption capacity obtained by calculation from models (mg/g),  $q_e$  is the equilibrium adsorption capacity of experimental data (mg/g). If the data from the model is close to the experimental data,  $\chi^2$  will give a small number and if they far apart in value,  $\chi^2$  will be a larger number. Therefore, it is necessary to also analyze the data set on the non-linear chi-square test to confirm the best kinetic model for the adsorption systems.

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## CHAPTER 3

### 3.0 EXPERIMENTAL PROCEDURE

#### 3.1 Introduction

This chapter is divided into three sections, the first section describes the sample preparation, in which the raw pine cones were obtained from pine plantation and treated by solvent extraction. Solvent extraction was applied as a surface treatment method and the extraction ratio of two solvents were optimized. The effect of extraction on surface properties such as bulk density, surface negative charge and iodine capacity were examined.

Section two involved the modification of solvent extracted pine cone with iron hexacyanoferrate. This section involved two steps. The first step involved the loading of  $\text{FeCl}_3$  onto the treated pine cone surface, and the second step involved the treatment of the iron(III) loaded pine cone powder with  $\text{K}_3[\text{Fe}(\text{CN})_6]$ . Iron(III) loaded pine cone and  $\text{K}_3[\text{Fe}(\text{CN})_6]$  modified pine cone concentrations were optimized and the best concentration were chosen. The modified pine cone was then characterized by FTIR, XRD and TGA analysis to confirm that modifications were successfully achieved.

Section three involved the application of potassium iron hexacyanoferrate for the selective removal of cesium in the presence of sodium and calcium. Kinetics experiments were performed.

#### 3.2 Sample Collection and preparation

##### 3.2.1 Collection

Pine tree cones were collected from a plantation in Sasolburg, Free State. The cones were washed to remove impurities such as sand and leaves. The washed cones were then dried at  $90^\circ\text{C}$  for 48 hours in the oven. The scales on the cones were removed and crushed by a pulveriser. The pine cone powder was then sieved and particles between 90 and  $45\ \mu\text{m}$  were collected and used for analysis.

### 3.2.2 Sample preparation

Pine cone powder (50g) was extracted with 250 cm<sup>3</sup> of a mixture of toluene: ethanol at different ratios (1:1, 2:1, 1:2 and 1:3 v/v) in a reflux apparatus at various contact time (2, 4, 8 h). The solid product from the extraction was then soaked in water for an additional 8 h, to remove all extractives. The pine cone was then oven-dried at 105 °C to constant weight and cooled to ambient temperature in a desiccator over phosphorus pentoxide. The pine cone powder was transferred to a flask containing pyridine set at 100 °C for 1 h. Pyridine swells the pine cone and acts as a catalyst for the modification reaction. The mixture was filtered and the pine cone was refluxed in acetone for 1 h to remove the pyridine. Pine cone powder was then filtered and oven-dried at 105 °C.

### 3.2.3 Bulk density determination

Bulk density of a powder material is a measure of the amount of void (pore) spaces present in the material. The larger the amount of void spaces, the lower the bulk density (Ofomaja *et al.*, 2010a). Plant materials are known to contain voids spaces that may be filled with plant components such as sugars, pigments, lignin, resin acids, water soluble tannins and so on (Wartelle and Marshall, 2000).

Bulk density measurement was carried out in a 25 cm<sup>3</sup> density bottle. The dry pine cone powder was added to the density bottle with gentle tapping to ensure that the particles settle to the bottom and all air spaces were filled. The mass of the density bottle containing the pine cone powder was then determined. The mass of pine cone powder that occupied 25 cm<sup>3</sup> was then obtained from the mass of the bottle and pine cone powder minus the mass of empty bottle.

Mass of PCP which occupies 25 cm<sup>3</sup> volume = (mass of bottle + pine cone powder) – mass of empty bottle.

$$\text{Bulk density} = \text{Mass of PCP occupying } 25 \text{ cm}^3 \text{ volume} / 25 \text{ cm}^3 \quad (3.1)$$

### 3.2.4 Iodine number determination

Significant information on the internal surface of powder materials can be obtained from the iodine capacity ( $I \text{ mg g}^{-1}$ ) of the material. In principle, 25 cm<sup>3</sup> of iodine solution of 0.015 mol/dm<sup>3</sup> was added to flasks, which contained different amount of pine cone powder ranging

from 0.031 to 0.500 g. The flasks were then shaken for 24 h to assure equilibrium adsorption of iodine onto pine cone powder. The iodine number ( $\text{mg g}^{-1}$ ) (or adsorption capacity) was determined from the titration of the residual solution of  $10 \text{ cm}^3$  with  $0.10 \text{ mol/dm}^3$  sodium thiosulfate in the presence of  $1 \text{ cm}^3$  of 1.00 wt % starch solution as an indicator. The iodine adsorption capacity was determined from the adsorbed iodine/unit mass of the adsorbent at the residual iodine concentration.

### 3.2.5 Surface negative charge

The surface negative charges on biological materials are attributed to ionization of acidic functional groups on the material surface (Ofomaja *et al.*, 2010b). These sites are usually responsible for interaction with positively charged species in solution (Ho and Ofomaja, 2007). A modification of the method of Boehm (1966) was used to determine total negative charge. That 'total' negative charge could be obtained only on samples at  $\text{pH} < 3.0$ . At this pH even the most easily ionizable negative groups (i.e. carboxyl groups) were fully protonated as indicated by no change in titratable negative charge when the pH was at or below 3.0. With fully protonated pine cone powder, the presence of a strong base (NaOH) deprotonated both strongly and weakly ionizable groups which contribute to the total negative charge.

One-half gram of pine cone powder, which had pH values  $< 3.0$ , was suspended in  $25 \text{ cm}^3$  of  $0.10 \text{ mol/dm}^3$  NaOH and stirred at 300 rpm for 16-20 h in glass stoppered  $100 \text{ cm}^3$  Erlenmeyer flasks. The flasks were kept stoppered during stirring to minimize the dissolution of carbon dioxide gas in the NaOH and the subsequent formation of  $\text{Na}_2\text{CO}_3$ . The flask contents were filtered by vacuum filtration through Whatman #4 filter paper and  $10 \text{ cm}^3$  of the filtrate added to  $15.0 \text{ cm}^3$  of  $0.10 \text{ mol/dm}^3$  HCl. The addition of excess HCl prevented any possible adsorption of carbon dioxide by the base and was particularly important if the solutions were required to stand for extended time periods before analysis. The solution was titrated with  $0.10 \text{ mol/dm}^3$  NaOH until an endpoint. The results were expressed in mmoles  $\text{H}^+$  neutralized by excess  $\text{OH}^-$  per gram of pine cone powder.

### 3.2.6 Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectra of pine cone before and after treatment were recorded on a Fourier Transform Infrared Spectrometer (Perkin-Elmer infrared spectrophotometer) to elucidate the functional group present on the pine cone powder.

### 3.2.7 Brunauer–Emmett–Teller (BET) Surface area

The Brunauer–Emmett–Teller (BET) surface area and pore size distribution were determined using computer-controlled nitrogen gas adsorption analyzer. Degassing was carried out for 1 hour at 90° and increased to 120° for 2 h. A mass of 0.2 g of pine cone was applied for analysis.

### 3.2.8 Cesium adsorption

A volume of 100 cm<sup>3</sup> of cesium solution of concentration 100 mg/dm<sup>3</sup> was added to six 250 cm<sup>3</sup> beakers. An amount (1.0 g) of the raw and toluene-ethanol extracted pine cone powder sample were then added to the prepared cesium solution. The mixtures were then shaken at room temperature for 2 h at 200 rpm. At the end of agitation, the mixture was separated by centrifugation at 100 rpm and the clear liquid was analysed by atomic absorption spectrophotometer for cesium left in the solution.

### 3.2.9 Cesium desorption

Desorption studies are vital in determining the mechanism of an adsorption process and its applicability in industrial practice. Desorption characteristics of an adsorbent can be evaluated by extracting adsorbed metal ions by different solvents. Biosorbent residue used in the system of 0.5 g of pine cone in contact with 100 cm<sup>3</sup> of 100 mg/dm<sup>3</sup> of cesium solution was separated by centrifugation and washed with distilled water. The washed residue solid was then stirred in 100 cm<sup>3</sup> of 0.1 mol/dm<sup>3</sup> of each of the desorbing solvents (NaOH, H<sub>2</sub>O, CH<sub>3</sub>COOH, Ca(OH)<sub>2</sub> and KOH). After shaking the flask for 2 h at 200 rpm, the pine cone solids were separated by filtration and the leached amount of cesium ions in the filtrate analyzed by atomic absorption spectrophotometer.

### 3.3 Modification of treated pine cone powder by iron hexacyanoferrate

The incorporation of potassium iron(III) hexacyanoferrate (KFeHCF) into the matrix of the modified pine cone was carried out in two steps. The first step involved the loading of  $\text{FeCl}_3$  onto the modified pine cone surface, while the second step of the synthesis involved the treatment of the iron(III) loaded pine cone powder with  $\text{K}_3[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ .

#### 3.3.1 Iron(III) chloride loading onto modified pine cone

In this experiment, 5.0 g of pine cone powder was added to 250  $\text{cm}^3$  beakers in which 100  $\text{cm}^3$  of  $\text{FeCl}_3$  solutions of varying concentrations (0.10, 0.15, 0.20, 0.25 and 0.50  $\text{mol}/\text{dm}^3$ ) have been placed and the initial solution pH set at 6, 7 or 8. The mixtures were then shaken at 120 rpm in a water bath for 6 h at 27 °C. After 6 h of contact, the mixture was filtered and washed with deionized water to remove excess  $\text{FeCl}_3$  and the residual solid dried at 105 °C for 24 h. The amount of  $\text{FeCl}_3$  left in solution was determined using Atomic absorption spectrophotometer (AAS) while the amount of  $\text{FeCl}_3$  loaded on the modified pine cone was taken as the difference.

#### 3.3.2 Treatment with KHCF

The modified pine cone sample with the highest amount of Fe(III) loading was chosen for this step. In this experiment, 5.0 g of the Fe(III) loaded pine cone was contacted with 100  $\text{cm}^3$  of  $\text{K}_3[\text{Fe}(\text{CN})_6] \cdot \text{H}_2\text{O}$  solution of different concentrations (0.10, 0.15, 0.20, 0.25 and 0.50  $\text{mol}/\text{dm}^3$ ) and agitated for 18 h at 120 rpm under room temperature. This resulted in the incorporation of KFeHCF in the matrix of the modified pine cone powder. Finally, the KFeHCF loaded pine cone was separated by filtration; washed with deionized water and dried at 80 °C.

#### 3.3.3 Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectra of pine cone before and after modification and potassium iron hexacyanoferrate incorporation were recorded on a Fourier Transform Infrared Spectrometer (Perkin-Elmer infrared spectrophotometer) to elucidate the functional group present on the pine cone powder.

### 3.3.4 X-Ray Diffraction (XRD)

The structural and crystallographic make up of substances can be determined by X-ray diffraction technique. Solvent extraction, iron(III) deposition and HCF modification of pine cone may lead to changes in its chemical structure, therefore understanding these changes in structural properties due to HCF modification will provide valuable information regarding the adsorption reaction (Ofomaja and Naidoo, 2011).

XRD was conducted to identify the chemical composition and crystallographic structure of the raw and modified pine powder. XRD patterns were obtained with an X'Pert PRO X-ray diffractometer (PANalytical, PW3040/60 XRD; CuK $\alpha$  anode;  $\lambda = 0.154$  nm). The samples were gently consolidated in an aluminium holder and scanned at 45 kV and 40 mA from 10° to 120° 2 $\theta$  the exposure time for each sample was 20 min and a step size of 0.02°. The diffraction patterns were analyzed using X'Pert High Score software (version 2.2.0) and plotted using OriginPro 7.0.

### 3.3.5 Thermal gravimetric analysis (TGA)

Thermogravimetric analysis is usually performed in the determination of mass change in the composite polymer as a function of time and temperature. This analytical technique gives an indication of the reactions which occurs at the molecular level of the materials. An STA 6000 Instrument was employed to measure the thermal analysis of pine cone powder, modified and KFeHCF incorporation modified pine cone. This instrument is capable of obtaining DSC and TGA measurements simultaneously. The raw pine, 2:1 toluene-ethanol treated pine and KFeHCF incorporation modified pine cone were weighed into quartz crucibles. Thermal scans were performed from 30 to 700 °C at a heating rate of 10 °C/min. An empty crucible was used as a reference.

### 3.3.6 Cesium adsorption experiment

A volume of 100 cm<sup>3</sup> of cesium solution of initial concentration 100 mg/dm<sup>3</sup> was added to six 250 cm<sup>3</sup> beakers and the initial solution pH's of the solutions adjusted to pH 8. An amount (1.0 g) of the raw, toluene-ethanol treated and KFeHCF incorporation modified pine cone samples were then added to the prepared cesium solutions. The mixtures were then shaken at room

temperature for 2 h at 200 rpm. At the end of the agitation, the mixture was separated by centrifugation at 1000 rpm and the clear liquid analyzed by Atomic absorption spectrophotometer for the cesium left in solution.

### **3.4 Optimization of cesium adsorption using raw, toluene-ethanol treated, Fe(III) loaded and potassium iron hexacyanoferrate modified pine cone powder.**

#### *3.4.1 Effect of biosorbent dose*

The effect of sorbent dose on the equilibrium uptake of cesium was investigated with sorbent masses of 0.10, 0.50, 0.10, 0.20, and 0.30 g. The experiments were performed by adding the known mass of pine cone powder to five 250 cm<sup>3</sup> beakers containing 50 cm<sup>3</sup> of 100 mg/dm<sup>3</sup> solution at pH 8.0. The flasks were shaken at 145 rpm and 291 K for 1 h and the equilibrium concentration of cesium remaining was determined by atomic absorption spectrometer.

#### *3.4.2 Effect of solution pH*

One of the most important parameters in the adsorption process is initial pH of solution. For each metal ion, there is a specific pH value at which the maximum adsorption of that ion takes place. The effect of solution pH on the equilibrium uptake of cesium was investigated between pH 1 and pH 10. Experiments were performed by adding a known mass of pine cone powder in to 500 cm<sup>3</sup> beakers containing 100 cm<sup>3</sup> of 100 mg/dm<sup>3</sup> cesium solution. The pH of the solution was adjusted using 0.1 mol/dm<sup>3</sup> HCl or NaOH. The flasks were shaken at 145 rpm and 291 K for 2h and the amount of cesium remaining in solution was measured by atomic adsorption spectrometer (AAS).

#### *3.4.3 Cation competition*

A volume of 100 cm<sup>3</sup> of cesium solution with concentration ranging from 50 to 250 mg/dm<sup>3</sup> was mixed with different concentration (0.1, 0.5, and 1.0 mg/dm<sup>3</sup>) of sodium and calcium. The mixture was placed in a conical flask and set at pH 8.0. An accurately weighed amount (1.0 g) of the raw pine cone, toluene-ethanol treated and FeHCF incorporated pine cone was added to the solutions. The conical flasks were then agitated at a constant speed of 145 rpm in a water bath set at 291 K. After shaking the flask for 2 h, the raw pine cone, toluene-ethanol treated and FeHCF

incorporated pine cone powder was separated by filtration. The filtrate was analysed for remaining cesium concentration by Atomic absorption spectrometer (AAS).

#### *3.4.4 Kinetic studies*

Kinetic experiments were carried out by agitating 100 cm<sup>3</sup> of cesium solution of concentration ranging from 50 to 250 mg/dm<sup>3</sup> with 1.0 g of pine cone powder in a 250 cm<sup>3</sup> beaker at 291 K at an optimum pH of 8.0 and at a constant agitation speed of 145 rpm for 30 min. Samples (2.0 cm<sup>3</sup>) were withdrawn out at different time intervals, centrifuged and the concentration of cesium was analyzed using atomic absorption spectrophotometer.

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## CHAPTER 4

### 4.0 RESULTS AND DISCUSSION

#### 4.1 Introduction

This chapter is divided into three sections. The first section covers the surface properties such as bulk density, iodine capacity and surface negative charge of different extracted samples. Fourier Transform infrared (FTIR) spectrophotometer was conducted to elucidate functional groups present on the pine cone powder before and after treatment. Thermal Gravimetric Analysis (TGA) was conducted to get the decomposition profile of the material heated. Atomic Absorption spectrophotometer (AAS) was conducted to determine the cesium adsorption and desorption studies.

The second section covers the modification of toluene-ethanol treated pine cone with potassium iron hexacyanoferrate. Pine cone modification involved two steps. Fe(III) was first loaded onto the toluene-ethanol treated pine cone powder followed by hexacyanoferrate ligand incorporation on the biosorbent producing the potassium iron hexacyanoferrate supported toluene-ethanol treated pine cone. The pine cone surface was characterized by Fourier Transform infrared (FTIR) spectrophotometer, Thermal Gravimetric Analysis (TGA) and X-Ray diffraction (XRD) before and after potassium iron hexacyanoferrate modification.

The third section covers the application of potassium iron hexacyanoferrate for the selective removal of cesium in the presence of sodium and calcium. Kinetic studies for the removal of cesium by raw pine, 2:1 toluene-ethanol treated pine, and HCF modified pine cone powder was conducted. Different kinetic models such as the Lagergen's pseudo-first order equation, second-order equation and empirical diffusion chemisorption model were tested to find out which model is in agreement with the experimental results of the kinetic study.

## 4.2 Surface properties

### 4.2.1 Bulk density

The effects of extracting pine cone powder with different ratios of toluene-ethanol mixtures at different time interval on the bulk density are shown in Fig. 4.1. The results revealed that the bulk density of pine cone powder is  $0.6457 \text{ g/cm}^3$ . On refluxing 50 g of pine cone powder with toluene-ethanol mixture of ratios 1:1, 2:1, 1:2 and 1:3 (v/v) for 2 h the bulk densities was found to have been altered. The bulk density for pine cone powder washed with toluene-ethanol mixture of ratios 1:1, 2:1, 1:2 and 1:3 reduced by 28.9 %, 32.9 %, 30.2 % and 31.6 % respectively. These results showed that pine cone treated with 2:1 mixture of toluene-ethanol produced the largest reduction in bulk density. Previous studies have shown that pine cone consists of about 15.4 % alcohol-benzene extractive (Micales *et al.*, 1994). The reduction of bulk density can be attributed to extraction of plant pigments, resin acids, tannins and sugars in the pine cone material. Wartelle and Marshall, (2000) observed a percentage decrease in bulk density of 31.0, 36.4 and 60.1% when corn cob, soybean hull and almond hull were treated with  $0.1 \text{ mol/dm}^3$  of NaOH for 1 h.

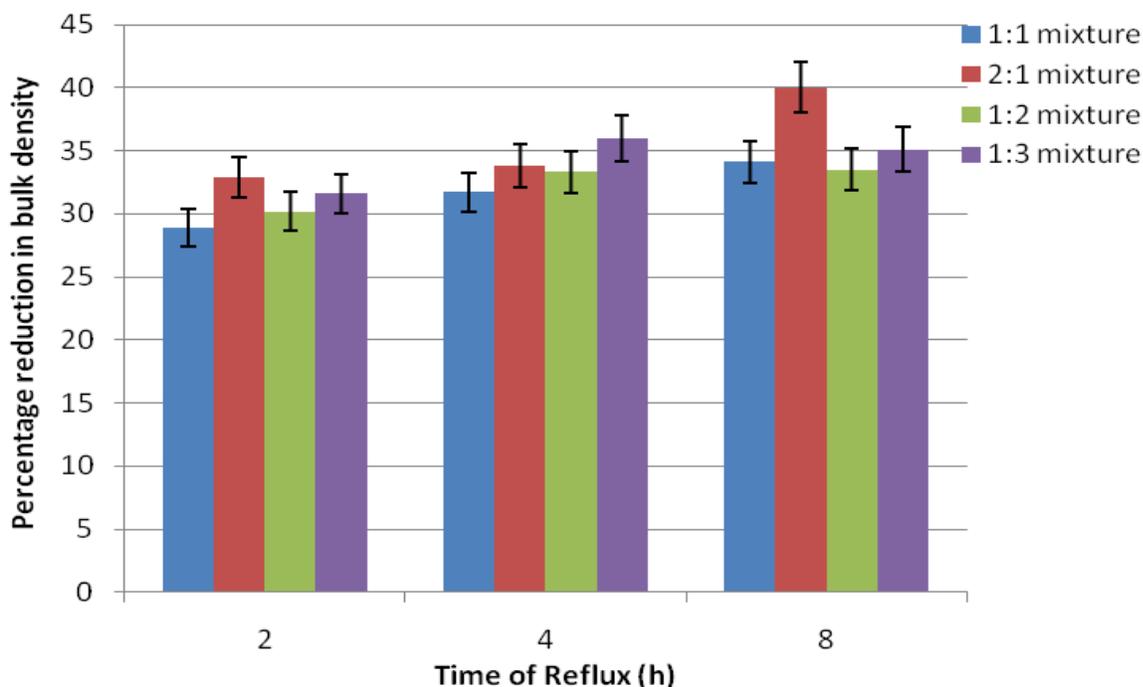


Fig. 4.1: Relationship between ratio of toluene-ethanol mixture, contact time and bulk densities of extracted pine cone powder

When refluxing time was increased from 2 to 4 h, the percentage reduction in the bulk density was found to increase for all samples except for the sample extracted with 2:1 mixture which had a slightly higher value as compared to the value after 2 h of extraction. The reduction in bulk densities of pine cone became 31.7 %, 32.3 %, 33.3 % and 36.0 % as the pine cone samples were extracted with 1:1, 2:1, 1:2 and 1:3 mixture of toluene-ethanol. The trend in these percentages was different from those observed for 2 h of reflux. The result for 4 h extraction reveals that greater extraction was observed for samples extracted with 1:2 and 1:3 mixtures than for the 1:1 and 2:1 mixtures.

On increasing the reflux time from 4 to 8 h, the bulk densities reduced further for the 1:1 (34.1 %) and 2:1 (33.5%) treatments. The reduction was almost constant for 1:2 (33.5 %), and the 1:3 treatment had a value of reduction of 35.4 % which was slightly less than that for 4 h treatment. The extraction of pine cone using 1:2 and 1:3 toluene-ethanol mixtures above 4 h did not alter the bulk densities much while 8 h of contact with 1:1 and 2:1 toluene-ethanol mixtures produced further reduction in bulk density.

From these results, it can therefore be concluded that for the 1:1, 2:1 and 1:2 mixtures, the reduction in bulk densities continues with increasing contact time, while for the 1:3 mixture, bulk density reduces to its optimum values at 4 h of contact and reduces only slightly at 8 h of contact.

#### 4.2.2 Iodine capacity (*I*)

The value of iodine capacity obtained for pine cone was  $23.7 \pm 0.09 \text{ mg g}^{-1}$ . When pine cone powder was treated with toluene-ethanol mixture of ratios 1:1, 2:1, 1:2 and 1:3 (v/v) for 2 h, the iodine capacities increased to  $24.39 \pm 0.10$  and  $24.96 \pm 0.07 \text{ mg g}^{-1}$  for toluene-ethanol mixtures of 1:1 and 2:1 but decreased to  $22.73 \pm 0.20$  and  $22.39 \pm 0.40 \text{ mg g}^{-1}$  for the 1:2 and 1:3 mixture (Fig. 4.2). It may be interpreted that the 1:2 and 1:3 toluene-ethanol mixtures caused contraction of the pine cone surface due to the higher ethanol ratio.

On increasing the contact time from 2 to 4 h, the iodine capacities increased to  $26.98 \pm 0.30$ ,  $26.1 \pm 0.30$ ,  $23.55 \pm 0.40$  and  $24.70 \pm 0.50 \text{ mg g}^{-1}$  for the 1:1, 2:1, 1:2 and 1:3, respectively. These results suggest that 4 h of heating may have increased the amounts of pore spaces in the pine

cone material by extracting more of the organic plant components as was observed from the high percentage reduction in bulk densities for all samples. The magnitude of increase was higher for samples treated with toluene-ethanol mixture of ratios 1:1, 2:1 than for the 1:2 and 1:3 treatments (Fig. 4.2).

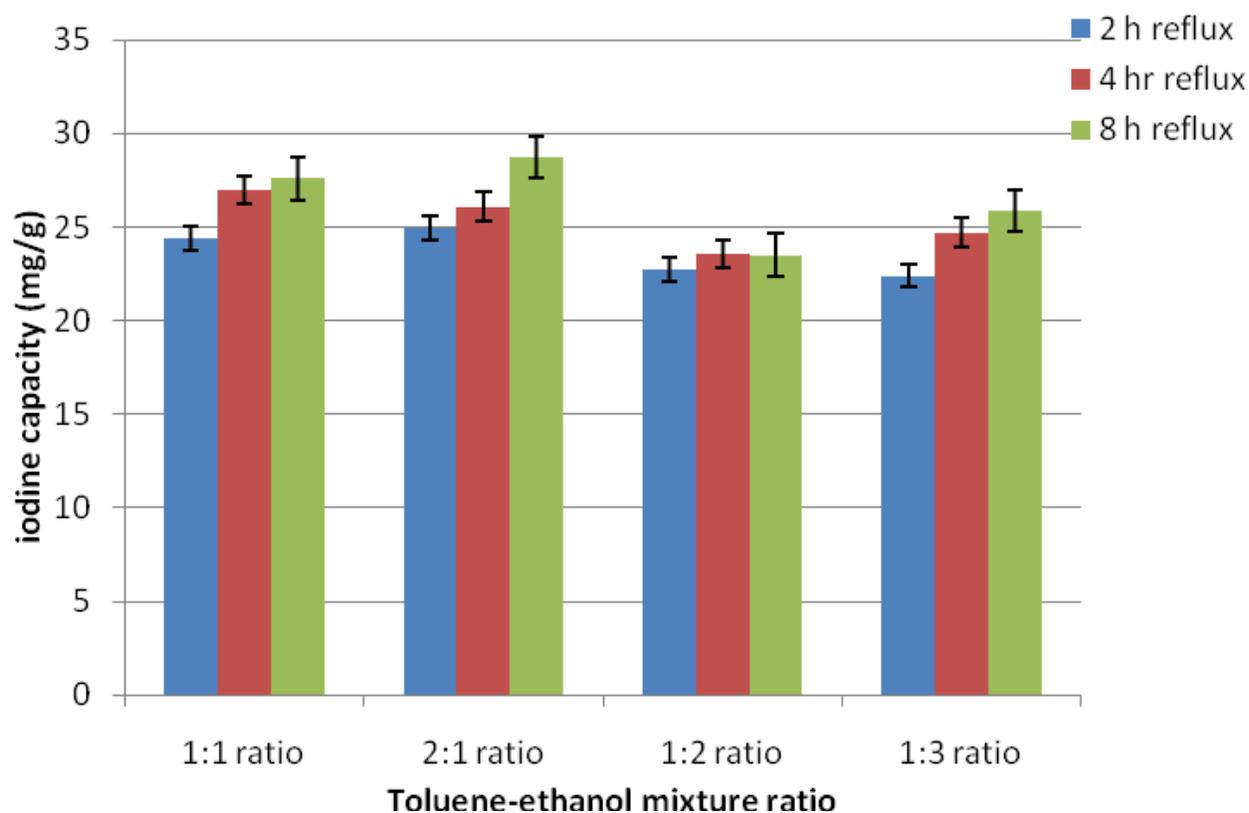


Fig. 4.2: Relationship between iodine capacity and toluene-ethanol mixture ratio at different reflux time.

Increasing the reflux time to 8 h, further increase in the iodine capacities for 1:1, 2:1 and 1:3 treated samples to  $27.60 \pm 0.40$ ,  $28.72 \pm 0.50$  and  $25.88 \pm 0.50$   $\text{mg g}^{-1}$  was observed while for the 1:2 mixture, the iodine capacity reduced slightly to  $23.49 \pm 0.50$   $\text{mg g}^{-1}$ . It was observed here that the increases in iodine numbers were not as rapid between 0 to 4 h and 4 to 8 h of reflux time as compared to the 2 to 4 h of reflux except with the 2:1 mixture treatment. The results showed that the iodine capacity increased continuously with increasing time of reflux and this trend is quite similar to the percentage decrease in bulk densities of the samples. The 2:1 mixture treatment producing the highest percentage decrease in bulk density at each reflux time also had the highest increase in iodine capacity. This can be attributed to the extraction of organic

components of pine cone present within the material matrix. This showed that the extraction procedure caused an opening of the pore spaces and increased the internal surface area of the pine cone. Similar extraction has been reported by Koncsag *et al.*, 2011.

#### 4.2.3 Surface negative charge

The surface negative charge value of the raw pine cone powder was  $3.82 \pm 0.02$  mmol/g. On treatment of pine cone powder with toluene-ethanol mixture of ratios 1:1, 2:1, 1:2 and 1:3 (v/v) for 2 h, the values of surface negative charge obtained were  $0.73 \pm 0.04$ ,  $0.68 \pm 0.03$ ,  $0.78 \pm 0.03$ ,  $0.77 \pm 0.04$  mmol/g. The results revealed that the values of surface negative charge reduced but did not change significantly from that of the raw pine cone with 2 h of extraction. The implication of these results is that the initial extraction may have removed only surface components of the pine cone samples that are negatively charged. For example, pine cone is known to contain diterpinoid resin acids which make up a percentage of the extractives and carry negative charges. These acids act as defense mechanism against fungi attack (Zinkel and Russell, 1989). Marshall *et al* (1999) observed a reduction in surface negative charge from  $1.33 \pm 0.00$  mmol/g to  $1.01 \pm 0.00$  for soybeans extracted with  $0.1 \text{ mol/dm}^3$  NaOH for 1 h at  $23^\circ\text{C}$ . Similar observation has been reported by Ofomaja *et al* (2009) in the extraction of pine cone powder using dilute NaOH solution.

When the contact time of reflux was increased, from 2 to 4 h, the values of surface negative charge increased slightly for all samples. The values of the new surface negative charge obtained were  $0.74 \pm 0.05$  mmol/g for ratio 1:1,  $3.78 \pm 0.03$  mmol/g for ratio 2:1,  $3.80 \pm 0.04$  mmol/g for ratio 1:2 and  $3.80 \pm 0.05$  mmol/g for ratio 1:3. It was explained earlier that the initial reduction in surface charge was attributed to removal of charged components such as resin acids. Therefore, further increase in surface negative charge with increased time of contact can be attributed to two possible reasons (i) extraction of plant components blocking the pore spaces in the pine cone particles which causes the exposure of hidden negative sites within the pores and (ii) release of functional groups on the material surface which leads to increased charges. From the calculated values of iodine number in the previous section, the increase in iodine capacities were highest between 2 to 4 h of reflux time than between 0 to 2 reflux times signifying that opening of block pores may have caused that increase in the magnitude of surface negative charge.

Finally, increasing contact time of refluxing to 8 h increased the values of surface negative charge of the samples extracted with toluene-ethanol mixtures of ratio 1:2 ( $4.02 \pm 0.02$  mmol/g) and 1:3 ( $3.92 \pm 0.04$  mmol/g) higher than the values for the raw pine cone. The surface negative charges for toluene-ethanol mixtures of ratio 1:1 ( $3.80 \pm 0.05$  mmol/g) and 2:1 ( $3.76 \pm 0.03$  mmol/g) had values lower than the original raw pine cone. The lower values of surface negative charge for samples treated with 1:1 and 2:1 mixtures may be attributed to the high formation of esters from carboxylic acid group which contributes largely of the total negative charge. On other hand, samples treated with 1:2 and 1:3 mixtures with lower proportions of esterification had higher surface charge values.

#### 4.2.4 FTIR analysis

Analysis of the raw pine cone powder using FTIR (Fig. 4.3); showed that the sample's spectra bands is divided into four main sections; (i) the section covering  $3100 - 3600 \text{ cm}^{-1}$  which is a broad band indicative of unbounded  $-\text{OH}$  group (Perez-Mariin *et al.*, 2007), (ii) the section covering between  $2700 - 2900 \text{ cm}^{-1}$  which is a peak to aliphatic C-H stretching (Brown *et al.*, 2001; Romero-Gonzalez *et al.*, 2001), (iii) the section between  $1500 - 1750 \text{ cm}^{-1}$  which represents the carbonyl group stretching (Shin *et al.*, 2007) and (iv) the finger print region which covers wave numbers below  $1500 \text{ cm}^{-1}$  (Min *et al.*, 2004).

Prominent peaks on the spectra includes the peak at  $3334.19 \text{ cm}^{-1}$  representing unbounded hydroxyl group ( $-\text{OH}$ ), peaks at  $2700 - 2900 \text{ cm}^{-1}$  which comprise the majority of aliphatic fraction of waxes (Inglesby *et al.*, 2005), peaks at  $1627.20$  and  $1547.68 \text{ cm}^{-1}$  which are indicative of asymmetric and symmetric stretching vibrations of ionic carboxylic acid groups ( $-\text{COO}^-$ ) (Iqbal *et al.*, 2009). The peak at  $1026.93 \text{ cm}^{-1}$  is associated with C-O-C functionalities (Moosavi-Nasab and Yousefi, 2011). The peak at  $1511.41 \text{ cm}^{-1}$  is due to aromatic ring vibrations likely from the lignin fraction of the plant material (Shin *et al.*, 2007), while peaks between  $812.30$  and  $659.47 \text{ cm}^{-1}$  represent bending modes of these aromatic compounds (Bansal *et al.*, 2009).

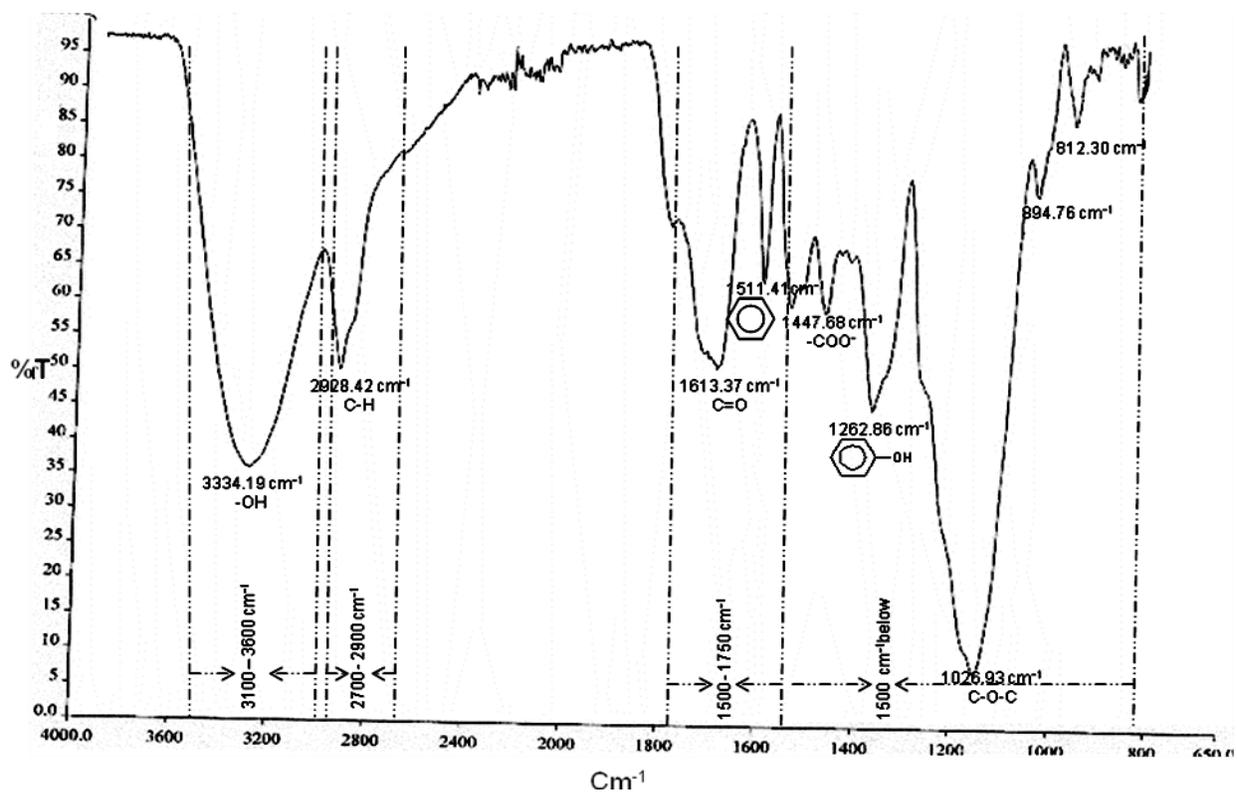


Fig. 4.3: FTIR spectra of raw pine cone powder.

The peak at  $1262.69\text{ cm}^{-1}$  is indicative of aliphatic acid group vibration due to deformation vibration of C=O and stretching formation of -OH of carboxylic acid and phenol (Iqbal *et al.*, 2009). The peak at  $1372.43\text{ cm}^{-1}$  is assigned to C-N stretching vibration, which corresponds to the amine groups (Xu *et al.*, 2011).

A comparison of the FTIR spectra for the extracted pine cone samples (8h treatment only) with the raw pine cone is presented in Fig. 4.4. The results showed that changes in peak intensities as well as a significant increase in intensity of the peak around  $1720\text{ to }1738\text{ cm}^{-1}$  were observed for the extracted samples.

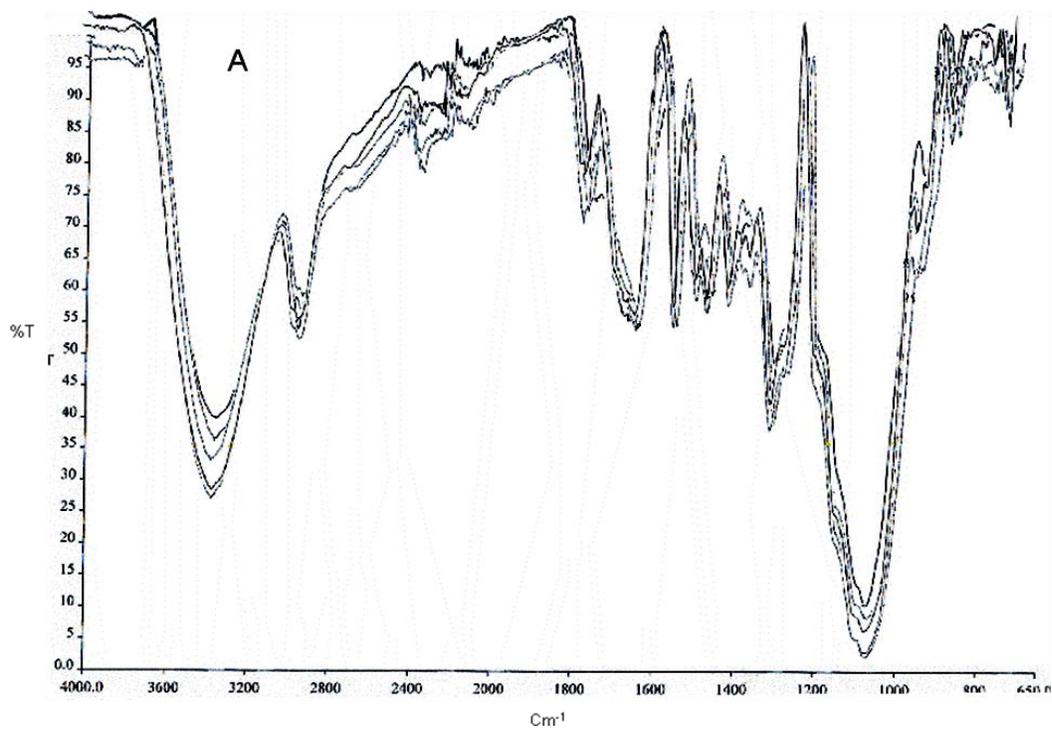


Fig. 4.4: Comparison of FTIR spectrum for raw and treated pine cone powder with various ratios of toluene-ethanol mixtures for 8h.

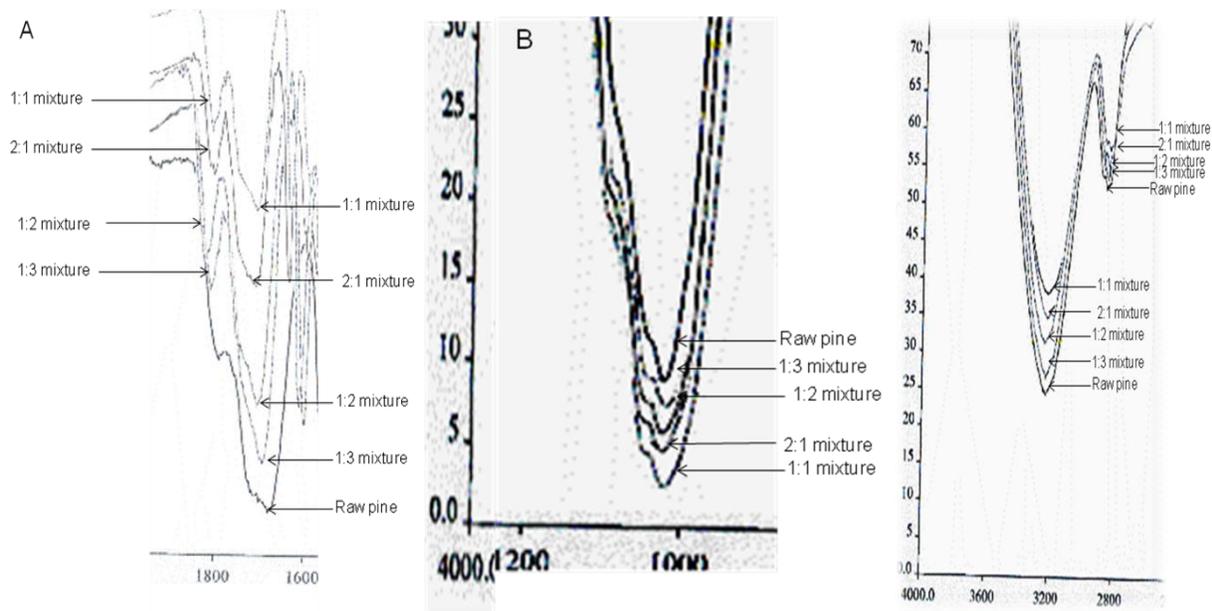


Fig.4.5: Comparison of characteristic peak for raw and extracted pine cone: (a) the peaks between 1800 and 1600 cm<sup>-1</sup>, (b) peaks between 1200 and 1000 cm<sup>-1</sup> and (c) peaks at 3334 cm<sup>-1</sup>.

The peak observed between 1720 to 1738  $\text{cm}^{-1}$  is attributed to C=O of esters and non-ionic carboxylic acid groups (-COOH, -COOCH<sub>3</sub>) stretching vibration (Iqbal *et al.*, 2009) (Fig. 4.5a). This means that toluene-ethanol extraction interacted with the pine cone to produce non-ionic carboxylic acid groups or esters (Fig. 4.5a). The increase in the intensity of the peak at 1020 to 1029  $\text{cm}^{-1}$  representing the C-O-C functionality (Fig. 4.5b) in all the extracted samples therefore confirmed that the peaks at 1720 to 1738  $\text{cm}^{-1}$  were due to ester formation on the pine cone surface. The raw pine cone contains more of the carbonyl ions than the extracted sample and little ester groups as can be seen from Fig. 4.3 and Fig. 4.5a. The intensity of the ester group increased in the order of raw < 1:3 < 1:2 < 2:1 < 1:1 (i.e., as the ethanol proportion decreased).

It was observed that the unbounded -OH peaks increased in intensity as compared with the raw sample, indicating the possibility of increase of hydroxyl groups during the extraction (Fig. 4.5c) (Inglesby *et al.*, 2005). Fig. 4.5c also showed peaks reduction at 2700 – 2900  $\text{cm}^{-1}$  for the extracted samples, as compared with the raw pine cone. It has been shown that the CH<sub>2</sub>-group stretching comprises the majority of aliphatic fraction of waxes. Inglesby *et al.*, (2005) in the solvent extraction of rice straw with toluene-ethanol mixture, observed a reduction of these peaks and associated the reduction to the extraction of waxes on the straw surface. The peaks, representing the carboxylate ions, at 1627.20 and 1547.68  $\text{cm}^{-1}$  also reduced in intensity for samples treated with toluene-ethanol mixture of ratios 1:1 and 2:1 while for samples treated with toluene-ethanol mixture of ratios 1:2 and 1:3 the intensities changed, slightly. This supports the above results above that ester formation occurred more with samples treated with 1:1 and 2:1 mixtures.

The intensities of the peaks lying between 1311 and 1375  $\text{cm}^{-1}$ , representing C-N stretching of amine also increased slightly, indicating that basic functional group of amine (C-N) was not extracted during the treatment process but was more exposed with increasing internal surface. Finally, the peaks between 1500 and 1513  $\text{cm}^{-1}$ , due to benzene ring and that between 1200 and 1260  $\text{cm}^{-1}$ , representing carboxylic/aromatic hydroxyl (-OH) stretching formation of phenol, decreased after extraction. This may likely be due to extraction of lignin containing pine cone material.

Table 4.1: Surface characteristics parameters for pine cone and toluene-ethanol treated pine cone powder

Sample	Property				
	<u>Bulk Density (g/cm<sup>3</sup>)</u>				
Raw	0.6457				
Toluene: ethanol treated	0.4296				
Surface area	<u>Pore Volume</u>				
	<u>BET (m<sup>2</sup>/g)</u>	<u>Langmuir (m<sup>2</sup>/g)</u>	<u>V<sub>total</sub>(cm<sup>3</sup>/g)</u>	<u>V<sub>micro</sub>(cm<sup>3</sup>/g)</u>	<u>V<sub>micro</sub>/V<sub>total</sub></u>
Raw Pine	4.39	4.60	0.004	0.011	2.707
Toluene: ethanol treated	26.30	28.90	0.173	0.245	1.416
	<u>Surface negative charge (mmol/g)</u>				
Raw	3.82 ±0.02				
Toluene: ethanol modified	3.76 ±0.03				

V<sub>total</sub> = Total pore volume; V<sub>micro</sub> = Micropore volume

#### 4.2.5 Brunauer–Emmett–Teller (BET) Surface area

From table 4.1 it is observed that both the BET and Langmuir surface area for the raw pine cone are 4.38 and 4.50 m<sup>2</sup>/g respectively and on treatment with toluene: ethanol mixture, the values increased to 26.30 and 28.90 m<sup>2</sup>/g, respectively. These results indicate that extraction of plant components improved both internal and external surface area to a large extent. Argun and Dursun, (2008) observed an increase in BET surface area for Fenton's activated pine cone as compared with the raw pine cone, while Ofomaja *et al.*, (2009) using NaOH treatment of pine cone powder also observed an increase in both external and internal surfaces.

#### 4.2.6 Adsorption experiments

Batch adsorption experiments of cesium ion removal from aqueous solution were performed using the raw and toluene-ethanol (1:1, 2:1, 1:2, 1:3 at 8 h) extracted samples. An amount (1 g) of each of the samples were contacted with 100 cm<sup>3</sup> of 100 mg/dm<sup>3</sup> cesium solution adjusted to pH 5 and agitated at 200 rpm for 2 h at room temperature. The results of the adsorption experiment revealed that the adsorption capacities were different for the various samples. The cesium adsorption capacities ( $q_e$ , mg g<sup>-1</sup>) obtained were 1.46, 1.55, 1.83, 1.09, and 1.18 mg g<sup>-1</sup> for the raw and toluene-ethanol extracted 1:1, 2:1, 1:2 and 1:3 samples respectively. From these results it can be seen that the sample with high toluene proportion (2:1) had the highest value for the equilibrium sorption capacity than the raw pine cone. Therefore it can be said that toluene-ethanol extraction improved the cesium adsorption capacity of pine cone powder. The order of increasing cesium adsorption capacity within the samples is 1:3 < 1:2 < raw < 1:1 < 2:1.

The trend in the percentage cesium removal from solution was compared with the surface properties of the samples. The comparison showed that the trend in the values of bulk density was not in line with the cesium equilibrium capacities, i.e. no correlation was observed between cesium adsorption capacity and bulk density. The relationship between cesium adsorption capacity and surface negative charge is shown in Fig. 4.6.

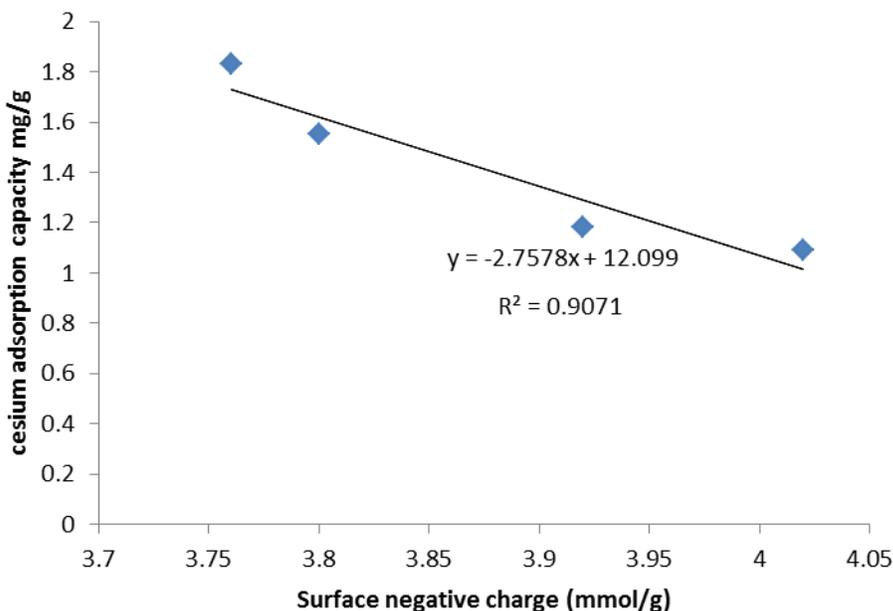


Fig. 4.6: Relationship between cesium adsorption capacity and surface charge.

When the trend in the values of surface negative charge of the extracted samples were compared with equilibrium cesium capacity, it was observed that the sample with the highest cesium adsorption capacity of  $1.83 \text{ mg g}^{-1}$  (2:1 toluene-ethanol extracted sample) corresponded to the least surface negative charge of  $3.76 \text{ mmol/g}$ . On the other hand, the sample with the least equilibrium cesium adsorption capacity of  $1.09 \text{ mg g}^{-1}$  (1:2 toluene-ethanol extracted sample) had the highest surface negative charge of  $4.02 \text{ mmol/g}$ . It was found that the trend in surface negative charge with cesium adsorption capacity gave an inverse relationship with a low correlation coefficient  $r^2 = 0.907$ . This suggests that the surface negative charge of the pine samples does not control the adsorption performance of the pine cone sample.

Comparing the trend of equilibrium cesium capacities with the iodine capacity of the extracted pine cone samples showed that a trend can be observed between equilibrium cesium capacity and iodine adsorption capacity. The highest value for iodine capacity, which is  $28.72 \text{ mg g}^{-1}$  (2:1 toluene-ethanol extracted sample), corresponded to the highest values for equilibrium cesium adsorption capacity of  $1.83 \text{ mg g}^{-1}$ , while the least value of iodine capacity of  $23.49 \text{ mg g}^{-1}$  (1:2 toluene-ethanol extracted sample) corresponded to the least equilibrium cesium adsorption

capacity of  $1.09 \text{ mg g}^{-1}$ . A relationship between cesium adsorption capacity and iodine capacity is shown in fig. 4.7.

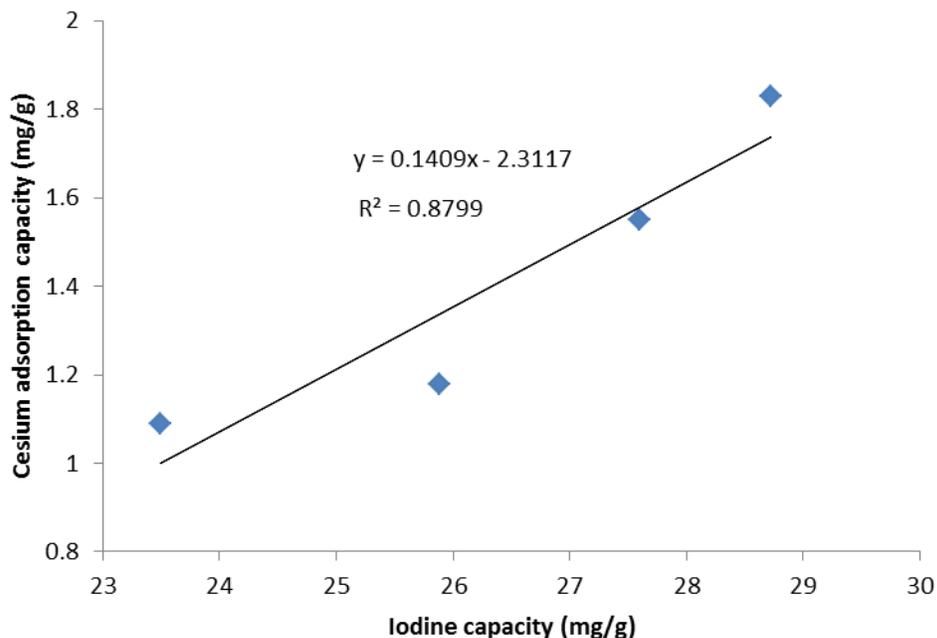


Fig. 4.7: Relationship between cesium adsorption capacity and iodine capacity.

When the relationship between iodine capacity and cesium equilibrium capacity were plotted, a linear relationship was found with correlation coefficient,  $r^2 = 0.879$ . The good correlation between the iodine capacity (I) and equilibrium cesium adsorption capacity suggests that the internal surface of the adsorbent controls the cesium adsorption onto the pine cone surface. One explanation to these results is that, although the 1:2 and 1:3 toluene-ethanol extracted samples has higher surface negative charges, their internal surface is smaller than those of the 1:1 and 2:1 extracted samples. This will therefore affect their ability to remove cesium from aqueous solution, while for the 1:1 and 2:1 toluene-ethanol the inner surface is larger and accounts for the higher cesium adsorption capacity.

#### 4.2.7 Desorption studies

The desorption experiment was carried out using 1.0 g of the raw and extracted pine cone used for the adsorption experiments after filtrating and washing with excess water to remove unbounded cesium ions. Results of the desorption analysis are shown in Fig. 4.8. The percentages of cesium ions desorbed from pine cone powder are compared for all five desorbing

agents used (sodium hydroxide, potassium hydroxide, calcium hydroxide, acetic acid and water). If a solution of strong acids such as KOH or NaOH can desorb the metal ion, it is believed that the attachment of metal is by ion-exchange. If a solution of  $\text{CH}_3\text{COOH}$  can desorb the metal, it is believed that the biosorption of metal is by chemisorption. If the metal ion adsorbed can be desorbed by water, it is believed that the attachment of the metal ion onto the adsorbent is by weak bonds (physical bonds) (Ansari and Mosayebzadeh, 2010).

From Fig. 4.8 it will be observed that the solution of KOH and NaOH desorbed the highest percentage of cesium from all samples, this mechanism accounted for the largest fraction of cesium desorbed with all pine samples. Desorption of cesium with KOH and NaOH had the highest percentage in 1:2, 1:3 and raw pine.

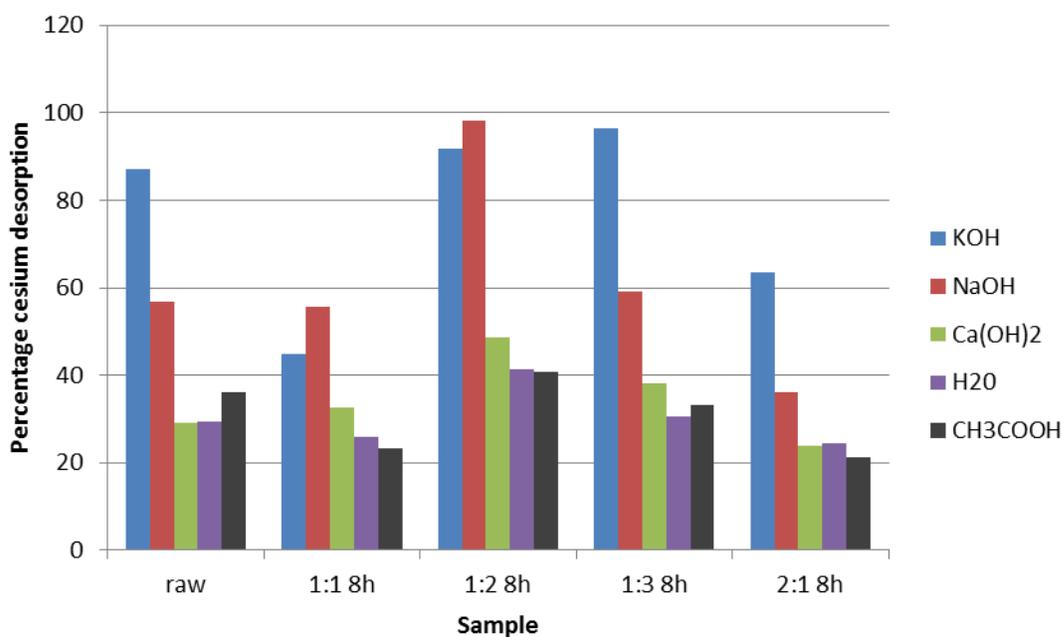


Fig. 4.8: Desorption efficiencies of cesium from pine cone and toluene-ethanol extracted pine cone powder by various solvents.

The prominence of ion-exchange mechanism amongst the samples is in the order 1:2 > 1:3 > raw pine > 2:1 > 1:1 toluene-ethanol treated sample. The desorption results revealed that the highest percentage of cesium desorbed was obtained for the 1:2 toluene-ethanol extracted pine cone powder (98.05 %), followed by 1:3 toluene-ethanol extracted pine cone powder (96.4 %), then the raw pine cone (87.2 %). This trend in the percentage of cesium bounded by cation exchange to the pine samples was observed to follow the trend in the surface negative charge of the

samples. Toluene-ethanol ratio 1:1 (44.8); (55.7 %) and 2:1 (63.6 %); (36.1) toluene–ethanol extracted pine cones had the least values of percentage cesium desorbed by KOH and NaOH respectively, these may be due to the extraction of negatively charge organic compounds that could contribute to the ion-exchange mechanism.

The sample extracted with 0.1 mol/dm<sup>3</sup> Ca(OH)<sub>2</sub> had the third highest fraction of cesium desorbed. The 1:2 (48.6 %) followed by 1:3 (38.2 %), then the 1:1 (32.5 %) had the highest values of percentage cesium desorbed by Ca(OH)<sub>2</sub>. Although bonded cesium ions desorbed by Ca(OH)<sub>2</sub> may also indicate ion-exchange mechanism, its lower percentage desorption may be due to its poor ionization in water. The percentage of cesium desorbed by acetic acid, which accounts for irreversibly bounded cesium, is the mechanism responsible for the least fraction of cesium desorbed from the pine samples. The irreversible mechanism was dominant in the 1:2 (40.7 %), raw (36.1 %), and 1:3 (33.14 %) toluene–ethanol extracted pine cone powder. Desorption, using acetic acid solution, removed small amount of cesium ions in the 1:1 (23.29 %) and 2:1 (21.17 %) ratio toluene– ethanol extracted pine cone powder. These may be due to certain components in lignin and tannin fraction such as (phenolic compounds) of the raw pine that may account for the greater chemisorption percentage in the raw pine. These components are leached out during the toluene-ethanol extraction process thereby reducing their quantities in the treated samples.

Finally, the trend was similar for the percentage cesium desorbed by water which accounted for the weakly bounded cesium. The results showed that there was a higher fraction of cesium held by weak adsorption on the 1:2 (41.4 %) and 1:3 (30.7 %) ratio toluene-ethanol extracted pine cone powder. While lower percentage desorption of cesium were recorded for the raw sample (29.3 %), 1:1 (25.9 %) and 2:1 (24.3 %) ratio toluene-ethanol extracted pine cone powder.

Table 4.2: FTIR peaks for unbounded water and acidic functional groups before and after cesium adsorption.

	Raw	1:1 8h	2:1 8h	1:2 8h	1:3 8h
FTIR peak					
<b>Hydroxyl (-OH)</b>					
Before	3334.19	3332.78	3332.15	3334.99	3333.49

After	3338.85	3334.05	3334.50	3338.97	3336.15
<b>Carboxylate (-COO-)</b>					
Before	1613.37	1607.20	1606.84	1606.73	1611.10
After	1609.91	1608.02	1604.56	1605.84	1604.44
<b>Carboxylic –OH</b>					
Before	1447.68	1422.59	1421.58	1423.29	1422.94
After	1451.86	1422.98	1422.22	1422.76	1422.72
<b>Phenol –OH</b>					
Before	1262.89	1264.01	1264.21	1263.29	1263.27
After	1263.02	1263.58	1264.01	1263.13	1263.65

The spectra peaks for the pine cone samples before and after cesium adsorption are recorded in Table 4.2. The peak values suggest that certain peaks have been shifted slightly after cesium adsorption from solution and the extent of the shift of the affected peaks were not the same in all samples. Peaks that were involved include the unbounded –OH peak, the carbonyl and carboxylate peaks, the amine peak and the carboxylic/phenolic –OH peaks. These suggest that both –OH groups and acidic functional groups on the pine cone samples are responsible for cesium binding.

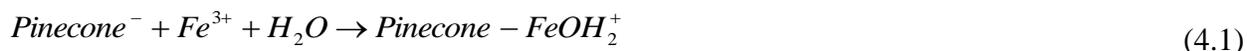
The peaks at 3334.19, 3332.78, 3332.15, 3334.99 and 3333.49  $\text{cm}^{-1}$ , representing the unbounded –OH in the raw, 1:1, 2:1, 1:2 and 1:3 ratio toluene-ethanol extracted pine cone samples shifted to 3338.85, 3334.05, 3334.50, 3338.7 and 3336.16  $\text{cm}^{-1}$  respectively. It was observed that change in the position of the peaks were higher for samples with higher percentage desorption of cesium when KOH,  $\text{CH}_3\text{COOH}$ , NaOH,  $\text{Ca}(\text{OH})_2$  and water was applied as desorption agent. This will suggest that the unbounded –OH groups actually played a role in the cation exchange and physical bonding to cesium.

The peaks for carbonyl/carboxylate groups at 1613.37/1447.68  $\text{cm}^{-1}$ , 1607.20/1422.59  $\text{cm}^{-1}$ , 1606.84/1421.58  $\text{cm}^{-1}$ , 1606.73/1425.29  $\text{cm}^{-1}$  and 1611.10/1422.94  $\text{cm}^{-1}$  also shifted slightly to 1609.91/1451.86  $\text{cm}^{-1}$ , 1608.02/1422.98  $\text{cm}^{-1}$ , 1604.56/1422.22  $\text{cm}^{-1}$ , 1605.84/1422.76  $\text{cm}^{-1}$  and 1604.44/1422.72  $\text{cm}^{-1}$ . It was found that raw, 1:2, 2:1 and 1:3 samples had higher shifts in the carbonyl/carboxylate peaks. Raw, 1:2, and 1:3 samples have been shown to have higher surface negative charges. The peaks representing the carboxylic/phenolic -OH bond shifted more for 1:1, 2:1 and 1:3 samples than for raw and 1:2 samples. Samples 1:2, and 1:3 had the lowest values for iodine capacity and higher intensities of the carboxylic/phenolic -OH peak, indicating that the carboxylic/phenolic -OH participated strongly in the sorption process.

### 4.3 Modification of toluene-ethanol treated pine cone with potassium iron hexacyanoferrate

#### 4.3.1 Theory of modification

Literature survey showed that the most employed hexacyanoferrates in preparation of exchangers have been the potassium nickel, potassium copper, potassium zinc and potassium titanium hexacyanoferrates (Dresow *et al* 1990, Joseph *et al.*, 1997, Loos-Neskovic *et al.*, 2004). But studies have shown that potassium iron(III) hexacyanoferrate also have high affinity and selectivity for cesium ions in solution (Dresow *et al.*, 1990). Therefore a new method was attempted to prepare the hexacyanoferrate supported pine cone powder in a two-step method below:



Where Pinecone<sup>-</sup> represent the negatively charged sites on the pine cone powder surface.

#### 4.3.2 Iron(III) chloride loading onto treated pine cone

In the present study, iron(III) loading was performed at solution pH between 6 and 8 and iron(III) solution concentrations of 0.5, 1.0, 1.5, 2.0 and 2.5  $\text{mol/dm}^3$ . Fig. 4.9 shows the plots of amount of iron(III) adsorbed per unit mass of modified pine cone versus the initial amounts of iron(III) added in the solution at various solution pH's. The plots revealed that as the amount of

iron(III) added into the solution increased, the amount of iron(III) adsorbed on the pine cone powder increased up to an almost saturated state when the iron(III) addition was higher than 2.0 mol/dm<sup>3</sup>. The solution pH affects the iron(III) removal from aqueous solution, for example, iron(III) uptake increased from pH 6 to pH 7 at all concentrations of iron(III) applied in this experiment. As the solution pH moved towards alkalinity the amount of iron(III) adsorbed reduced even below that observed at pH 6. The reduction in the amount of iron(III) adsorbed at pH 8 is likely due to the formation of FeO<sup>-</sup> which caused repulsion of the negatively charged pine cone ions.

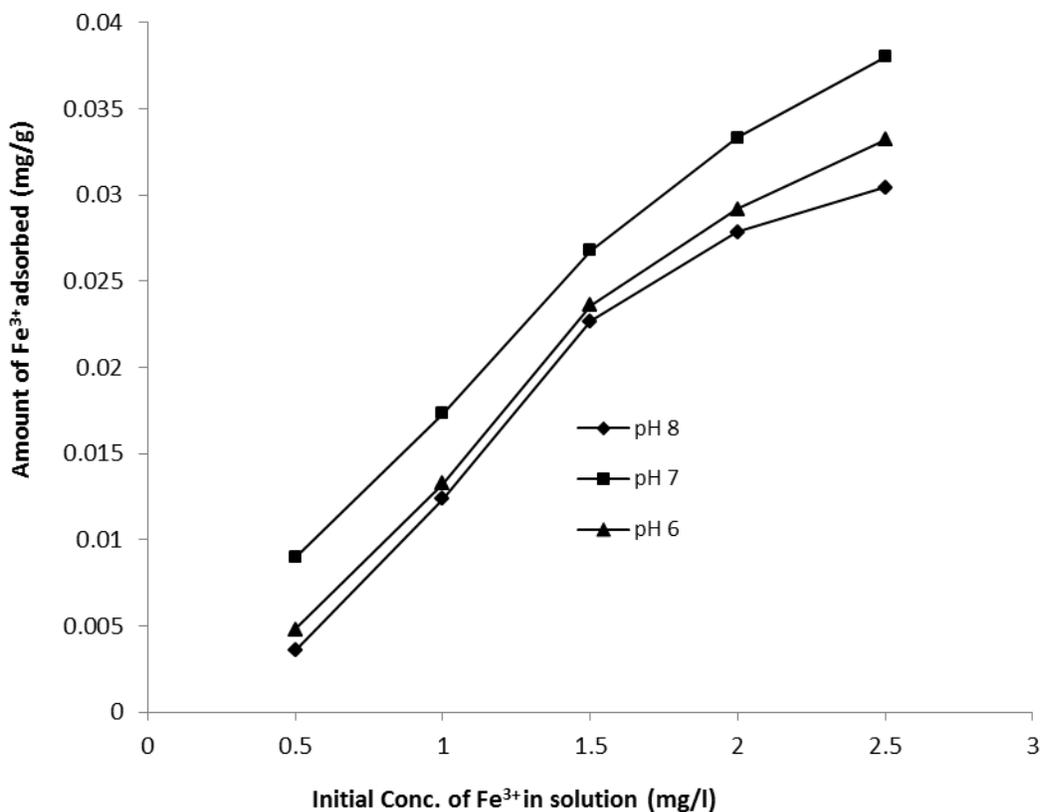


Fig. 4.9: Amount of Fe(III) deposited onto toluene: ethanol treated pine cone powder at various solution pH.

#### 4.3.3 Treatment of Fe(III) loaded pine cone with potassium hexacyanoferrate

The application of Hexacyanoferrate onto the Fe(III) modified pine cone surface was optimized by varying the initial concentration of hexacyanoferrate (0.6 to 1.0 mg/dm<sup>3</sup>) contacted with a

known mass of Fe(III) modified pine cone powder. The results of the uptake of different concentrations of hexacyanoferrate onto iron(III) modified pine cone are shown in Fig. 4.10.

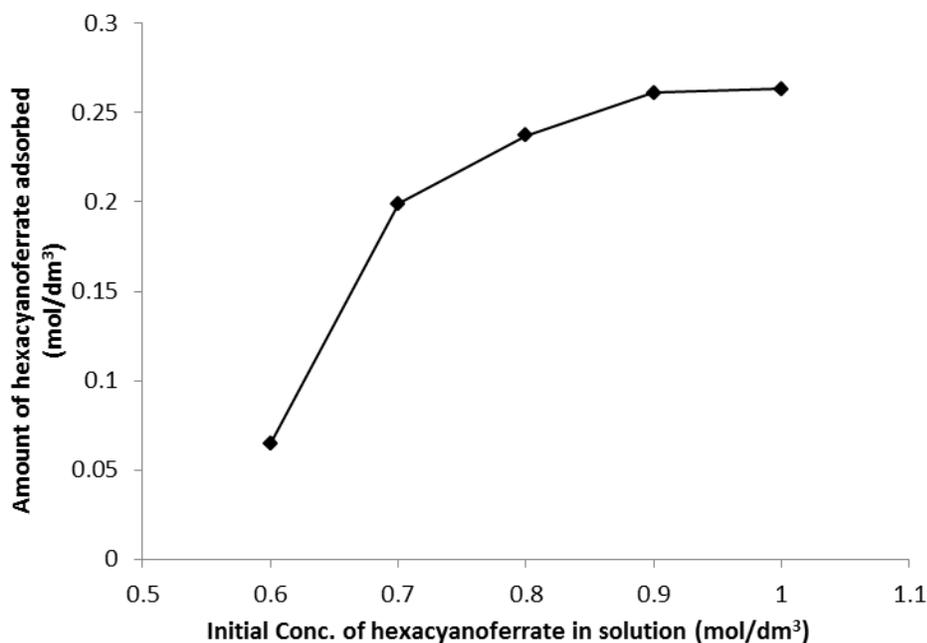


Fig. 4.10: Amount of hexacyanoferrate adsorbed onto Fe(III) loaded toluene: ethanol treated pine cone powder.

It was observed that there was a rapid uptake of hexacyanoferrate, when 0.6 and 0.8 mg/dm<sup>3</sup> of hexacyanoferrate was applied, as the concentration of hexacyanoferrate increased above 0.8 mg/dm<sup>3</sup>, the rate of uptake decreased. When 0.9 to 1.0 mg/dm<sup>3</sup> of hexacyanoferrate was applied there was no significant difference in the amounts of hexacyanoferrate removed from solution, therefore 0.90 mg/dm<sup>3</sup> was taken as the optimum hexacyanoferrate loading concentration when contacted with 5.0 g of Fe(III) loaded pine cone powder.

#### 4.3.4 Fourier Transform Infrared (FTIR) Spectroscopy

Fig. 4.11 shows the FTIR spectra of the raw pine and toluene: ethanol extracted pine cone. It is observed that the raw pine cone consist of different types of organic functional groups. Notable among these groups are the hydroxyl (-OH) at 3344 cm<sup>-1</sup>, carboxylic functional group detected by carbonyl (-C=O) at 1613.37 cm<sup>-1</sup> and carboxylate anion (-COO<sup>-</sup>) at 1447.68 and carbonyl -OH of esters at 1729 cm<sup>-1</sup>. Other functional groups are the -CN at 1372.43 cm<sup>-1</sup>, aromatic groups of

benzene ( $1511.40\text{ cm}^{-1}$ ) and phenol ( $1262.86\text{ cm}^{-1}$ ), aromatic bending at  $812.30$  and  $667.21\text{ cm}^{-1}$  while the  $-\text{CH}$  stretching of  $\text{C sp}^3$  appeared at  $2924\text{ cm}^{-1}$ .

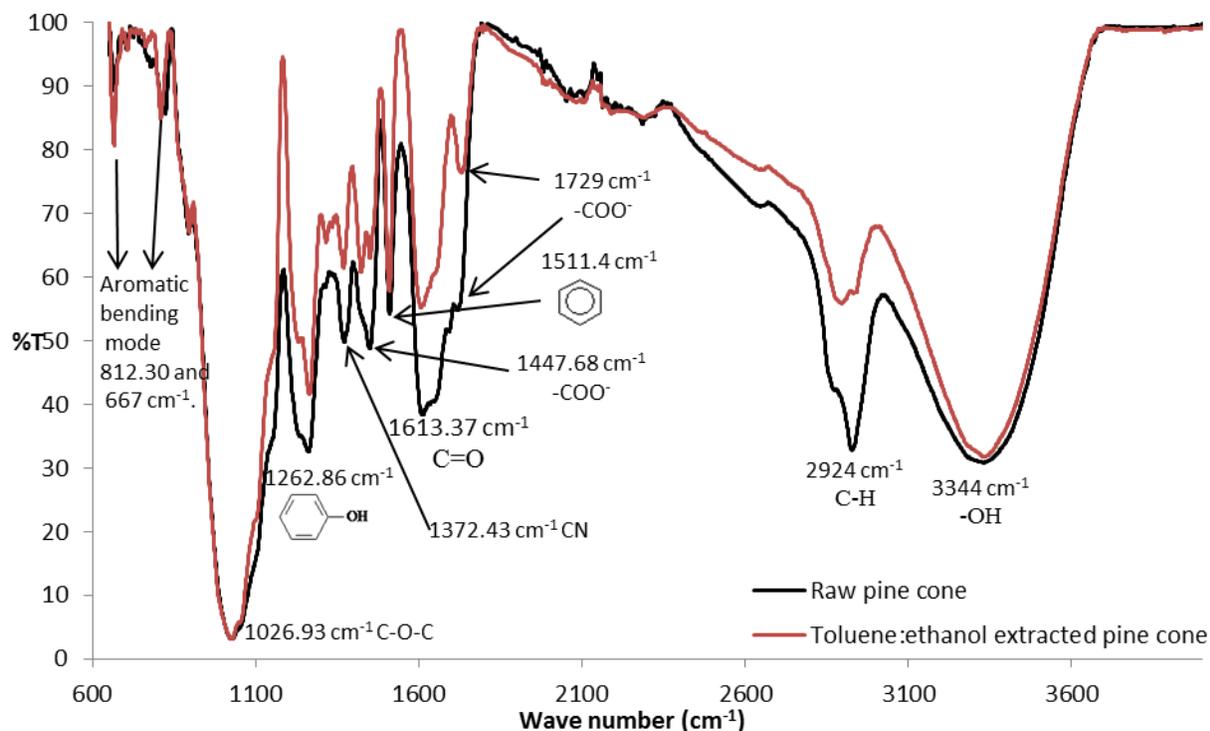


Fig. 4.11: Comparison of the FTIR spectra of raw and toluene-ethanol treated pine cone.

When toluene-ethanol extraction was performed on the raw pine cone, no new peaks were observed in the spectra of the extracted material, but increases in the intensities of some peaks/bands were noted. The functional groups with decreased intensities include  $-\text{CH}$  stretching ( $\text{C sp}^3$ ) at  $2924\text{ cm}^{-1}$  which comprises the majority of aliphatic fraction of waxes (Inglesby *et al.*, 2005). Inglesby *et al.* (2005), in the solvent extraction of rice straw with toluene-ethanol mixture observed a reduction of these peaks and associated the reduction to the extraction of waxes on the straw surface.

The carbonyl  $\text{C}=\text{O}$  of ester groups at  $1729\text{ cm}^{-1}$  increased in the toluene-ethanol extracted pine cone indicating some form of esterification process. The carbonyl ( $-\text{C}=\text{O}$ ) at  $1613.37\text{ cm}^{-1}$  and carboxylate anion ( $-\text{COO}^-$ ) at  $1447.68\text{ cm}^{-1}$  also decreased slightly in intensities, indicating that

carboxylic groups may have either been converted to esters or extracted out of the pine cone matrix. Finally the hydroxyl band at  $3344\text{ cm}^{-1}$  reduced slightly in intensity.

Fig. 4.12 shows a comparison of the FTIR spectra of the toluene-ethanol treated pine cone and the iron(III) loaded toluene-ethanol treated pine cone. The difference between these two samples is the interaction of iron(III) with the various functional groups on the pine cone surface. For example, Aryl *et al.* (2010) observed that iron(III) loaded onto staphylococcus xylosus biomass interacted majorly with the certain oxygen containing functional groups causing either a complete disappearance of these groups or leading to a shift in their peaks or bands.

From Fig. 4.12, it was observed that peaks at  $1729\text{ cm}^{-1}$  representing the carbonyl C=O of esters were found to disappear in the iron(III) loaded pine cone, which suggest that the carbonyl oxygen on esters are preferred sites for iron(III) binding on pine cone. This was confirmed by the strong reduction in the intensity of the peak at  $1026.39\text{ cm}^{-1}$  which represents the C-O-C linkage of esters in the iron(III) loaded pine cone.

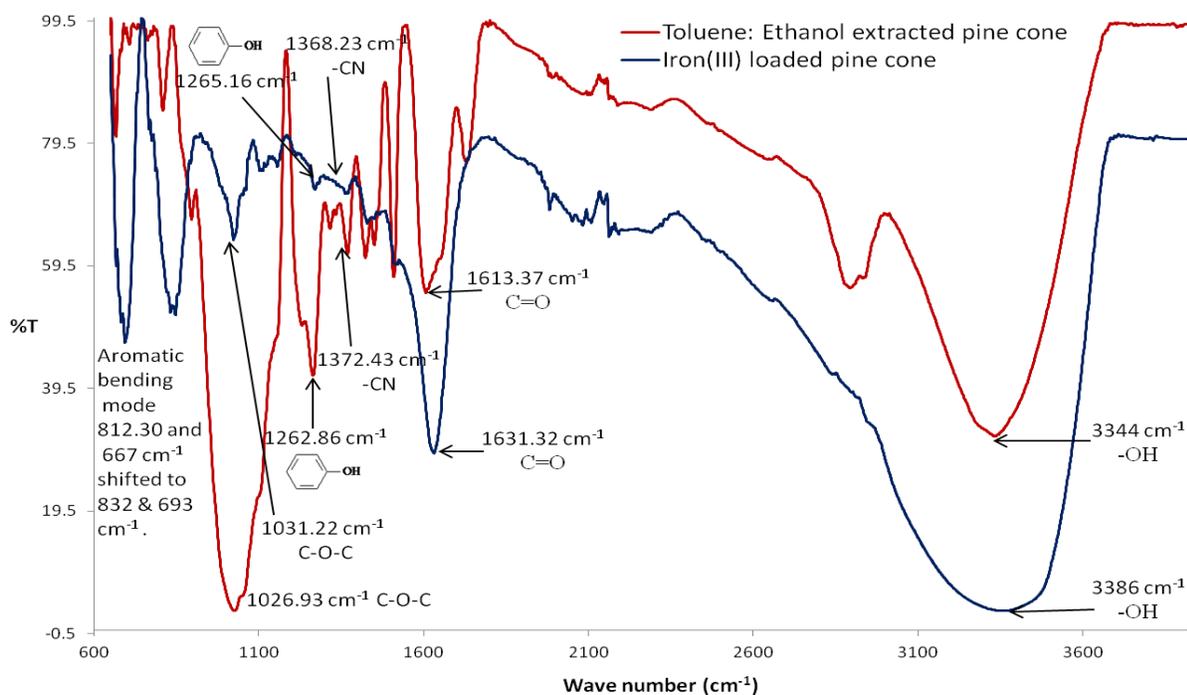


Fig. 4.12: Comparison of the FTIR spectra of toluene-ethanol treated and Fe(III) loaded toluene-ethanol treated pine cone.

Other functional groups with peaks experiencing slight shifts includes the hydroxyl group at  $3344\text{ cm}^{-1}$ , shifting to  $3386\text{ cm}^{-1}$ , the C=O of carboxylic acid, shifting from  $1613$  to  $1631\text{ cm}^{-1}$ , the -CN peak, shifting from  $1372.32$  to  $1368.23\text{ cm}^{-1}$ , the phenol peak, shifting from  $1265$  to  $1262\text{ cm}^{-1}$  and confirmed by the shift in aromatic bending peaks from  $812.30$  and  $669\text{ cm}^{-1}$  to  $832$  and  $693\text{ cm}^{-1}$  respectively. The shift in these peaks indicates that the iron(III) loaded on this material had interacted with these functional groups.

Fig. 4.13 shows a comparison of the FTIR spectra of the iron(III) loaded pine cone and the hexacyanoferrate modified pine cone. The major difference observed between these two samples is the very sharp peak at  $2045\text{ cm}^{-1}$  representing the cyanide stretching in the hexacyanoferrate modified pine cone which is absent in the iron(III) loaded sample. A similar peak was obtained by Parab and Sudersanan (2010) at  $2110\text{ cm}^{-1}$  for hexacyanoferrate modified coir pith.

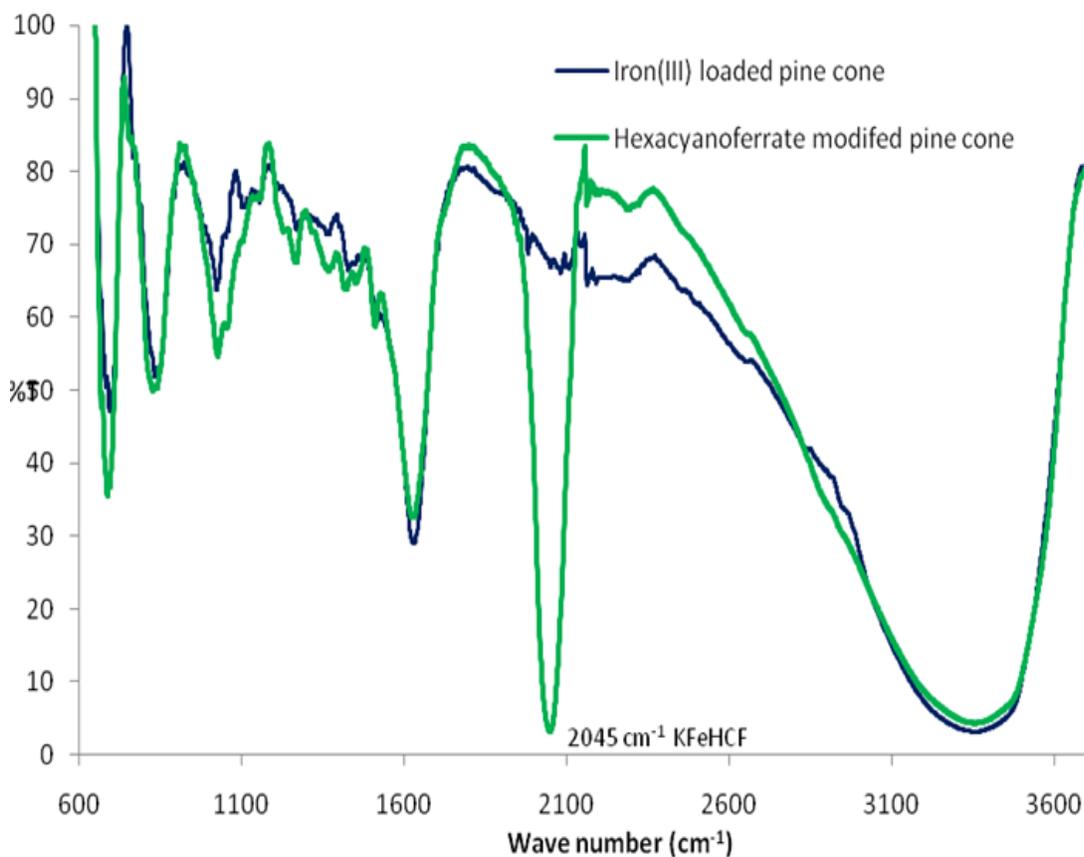


Fig. 4.13: FTIR spectra's for Iron(III) loaded and hexacyanoferrate modified pine cone powder.

#### 4.3.5 X-Ray Diffraction (XRD)

The results in Fig. 4.14 show the XRD pattern of raw pine and the 2:1 toluene- ethanol extracted pine cone. For the raw pine the characteristic main peaks of cellulose (I) at the  $2\theta$  of  $15.3^\circ$ ,  $21.3^\circ$  and  $34.0^\circ$  were observed. These peaks are indicative of highly organized crystalline cellulose (Zhu *et al.*, 2008). Secondary peaks corresponding to cellulose (II) which are indicative of less organized and amorphous polysaccharide materials were also observed at the  $2\theta$  of  $26.1^\circ$ ,  $36.2^\circ$  and  $40.1^\circ$  on the XRD spectra. The spectra indicate that the pine cone is composed basically of crystalline cellulose. When pine cone was treated with 2:1 toluene-ethanol solvent mixture, the characteristic main peaks of cellulose (I) reduced drastically. The primary peaks can still be seen slightly at  $2\theta$  at  $15.5^\circ$ ,  $22.2^\circ$  and  $34.1^\circ$ . The secondary peaks on the other hand were almost non-existent in the extracted pine cone except at  $2\theta$  at  $22.2^\circ$ ,  $44.7^\circ$ , indicating the solvent extraction may have removed the amorphous fraction of the pine cone.

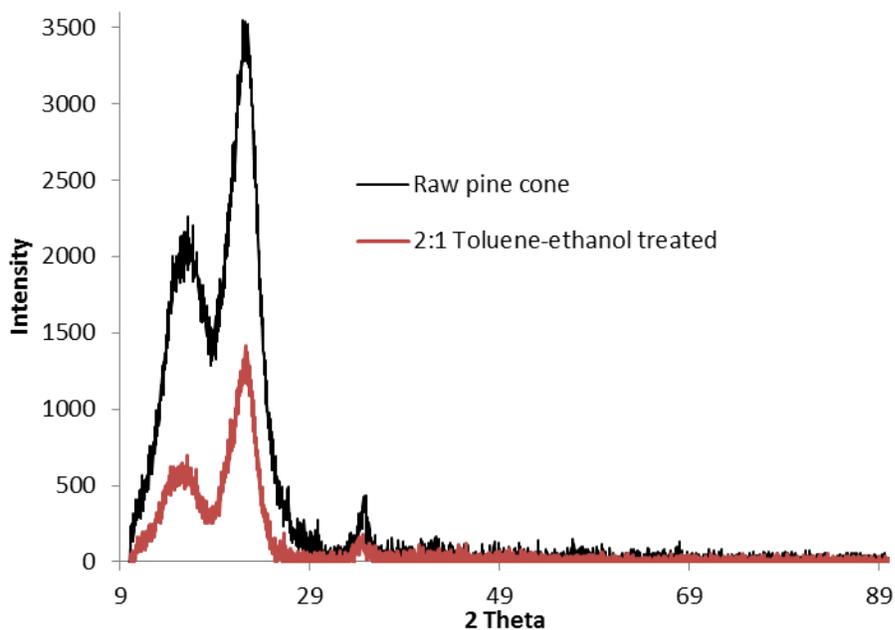


Fig. 4.14: X-ray diffraction spectra's of raw pine and 2:1 toluene-ethanol treated pine cone.

The XRD spectra for the 2:1 toluene-ethanol treated pine and the iron(III) loaded pine cone were compared in Fig. 4.15. It was observed that a very large difference between the two samples, for example, the primary peaks on the 2:1 toluene-ethanol treated pine were reduced to  $2\theta$  at  $11.83^\circ$ ,  $22.3^\circ$  and new sharp peaks at  $2\theta$  at  $31.6^\circ$ ,  $35.4^\circ$ ,  $45.4^\circ$ ,  $56.4^\circ$ ,  $75.2^\circ$  and  $83.9^\circ$ . These new peaks are

characteristic of iron(III) phase deposited on the pine cone. Bashmakov *et al.* (2008) also observed iron(III) phase XRD peaks at  $2\theta$  of 35.1, 41.4, 50.4, 67.2 and 74.1°, when iron(III) oxide was immobilized on cellulose.

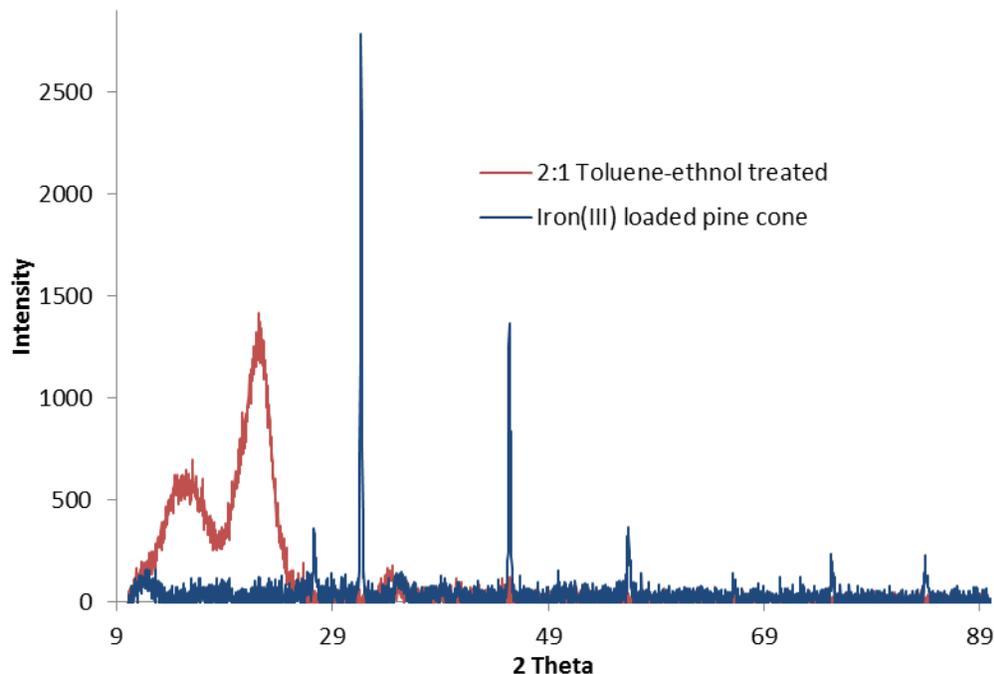


Fig. 4.15: X-ray diffraction spectra's of 2:1 toluene-ethanol treated pine cone and Fe(III) loaded pine cone

Finally, the XRD spectra's of the iron(III) loaded pine cone powder and the HCF modified pine cone are shown in Fig. 4.16. From Fig 4.16, it will be observed that the very prominent peaks in the iron(III) loaded sample at  $2\theta$  of 26.3, 31.6, 45.4, 56.4, 75.2 and 83.9 ° have all been drastically reduced. The only visible peaks remaining are those for  $2\theta$  at 11.9, 26.6 and 35.2 °. The result suggests that there has been some interaction between the loaded iron(III) phase and the hexacyanoferrate anions. The final product is less crystalline as seen from the very low XRD peaks, as compared with the initial pine material.

Similar results were obtained by Parab and Sudersanan (2010) in the incorporation NiHCF onto coir pith. The authors observed very low crystallinity in the modified sample and compared with the NiHCF spectra. The observable XRD peaks were found approximately at  $2\theta$  of 18, 26 and 36

° respectively. The peak signified NiHCF incorporation onto the structure of coir pith matrix. The peak positions and intensities were also similar to those observed in our present studies.

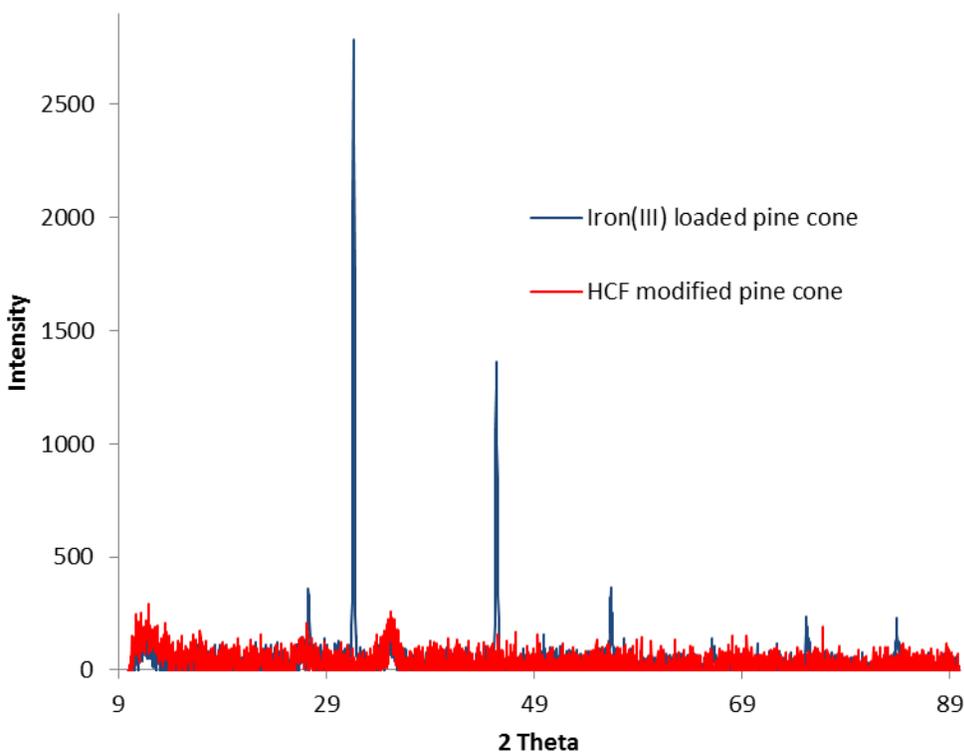


Fig. 4.16: X-ray diffraction spectra's of Fe(III) loaded pine and HCF modified pine cone.

#### 4.3.6 Thermal gravimetric analysis (TGA)

Fig. 4.17 shows the thermogravimetric curve for the raw pine cone, 2:1 toluene- ethanol treated, iron(III) loaded and hexacyanoferrate modified pine cone. The TGA curves (Fig. 4.17) showed an initial weight loss of 14 % (raw pine), 10 % (HCF modified pine), 5 % (2:1 ethanol: toluene treated) and 4 % iron(III) modified pine cone below 200 °C. This has been attributed to the elimination of water molecules retained in these materials. For the raw pine cone, the initial decomposition of the cellulose/ hemicellulose materials can be seen at 220 °C, while for 2:1 toluene: ethanol treated, iron(III) loaded and HCF modified the onset of decomposition were 228, 269 and 236 °C respectively. The final decomposition temperatures were also in the order of raw pine (395 °C), 2:1 toluene- ethanol treated (406 °C), iron(III) loaded (482 °C) and HCF modified (473 °C). The percentage decomposition of the plant materials were in the order of Raw (60 %), 2:1 toluene- ethanol (65 %), Iron(III) loaded (10.8 %) and HCF modified (20.8 %).

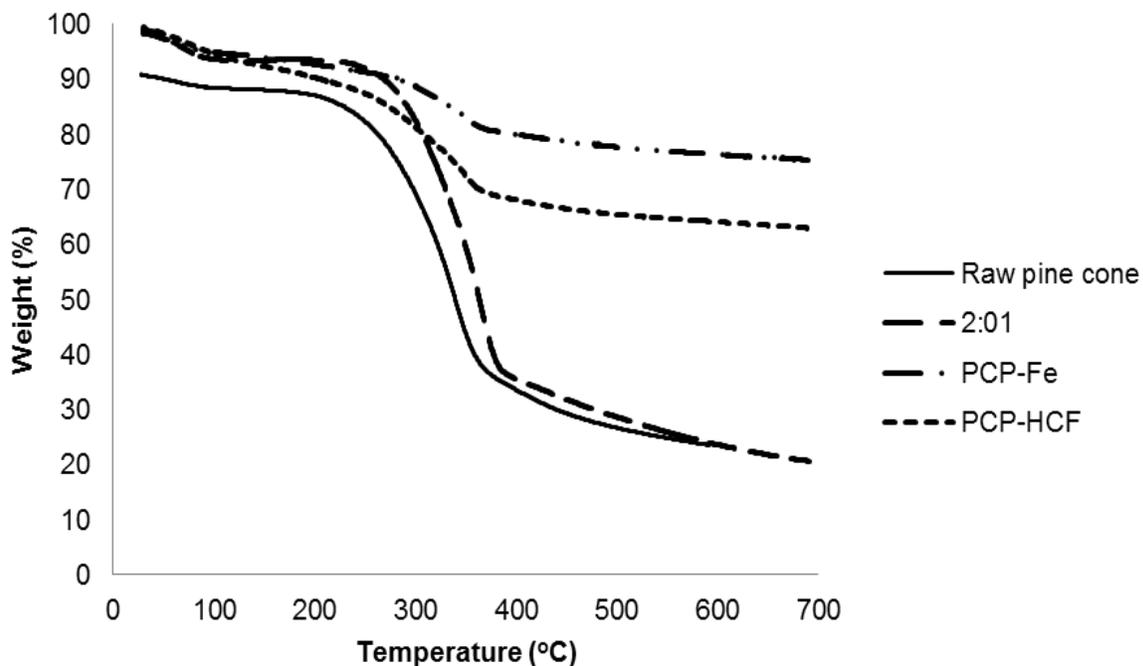


Fig. 4.17: TGA curve of raw, toluene- ethanol treated, Fe(III) loaded and hexacyanoferrate modified pine cone powder

The results indicate that toluene- ethanol treatment reduced the stability of the pine cone slightly, this may be due to extraction of the plant material. The addition of iron(III) to the pine cone introduced extra stability as seen from the reduction of percentage decomposition to 10.8%. Finally, the addition of HCF to the iron(III) loaded pine cone reduced the stability slightly.

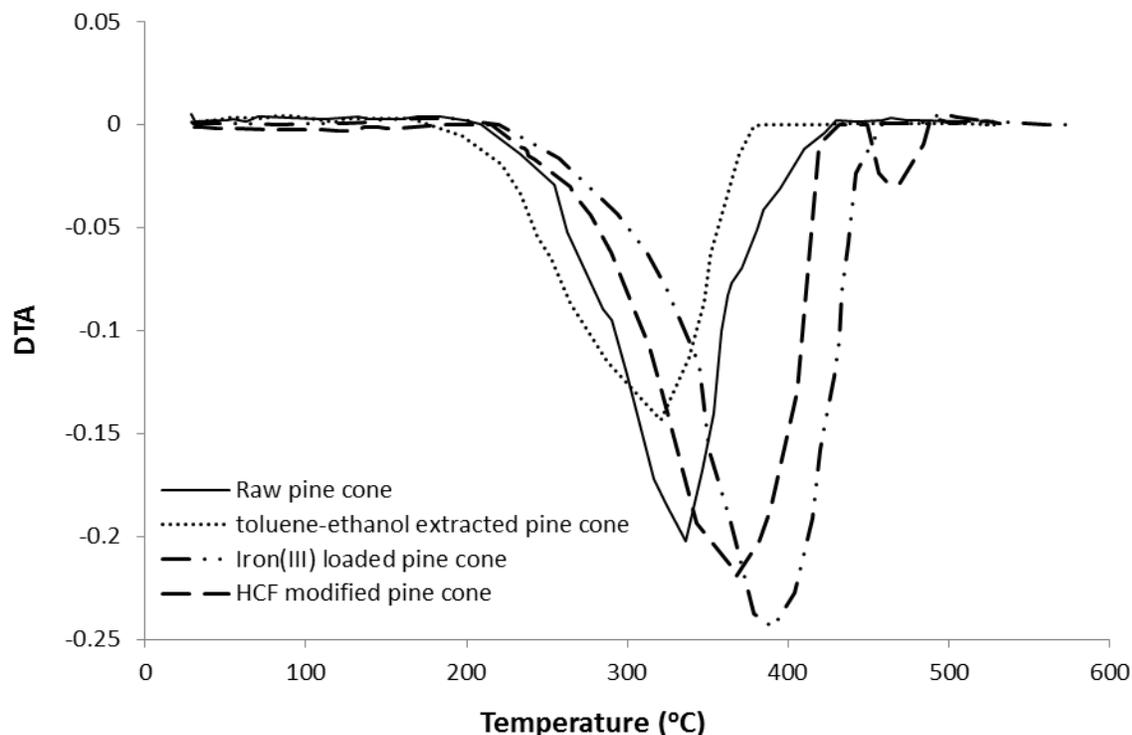


Fig. 4.18: DTA curve of raw, toluene- ethanol treated, Fe(III) loaded and hexacyanoferrate modified pine cone powder

The DTA curves of the raw pine, 2:1 toluene-ethanol treated pine, iron(III) loaded and HCF modified pine cone are shown in Fig. 4.18. The Figure shows endothermic peaks associated with the decomposition of the various materials. It will be observed that the raw pine, 2:1 toluene-ethanol and the Iron(III) loaded pine cone displayed one endothermic peak each, whereas the HCF modified sample showed one intense peak and a smaller peak at higher temperature. The temperature at which these peaks were observed are in the order of raw pine (336 °C), 2:1 toluene-ethanol treated pine (321 °C), iron(III) loaded pine cone (390 °C) and HCF modified pine cone (367 °C). This confirms that stabilization effect of the presence of iron(III) on the biomaterial.

#### 4.4 Optimization of cesium adsorption using raw, Fe(III) loaded and potassium iron hexacyanoferrate modified pine cone powder.

##### 4.4.1 Effect of biosorbent dose

The experiment on cesium adsorption from aqueous solution using the three different samples was carried out to test the efficiency of the products for cesium removal from aqueous solution. The Fe(III) loaded sample was not employed for cesium removal since repulsion between positively charged Iron(III) and  $\text{Cs}^+$  will render adsorption ineffective. From the results in Fig. 4.19, it will be observed that the percentage of cesium removed from aqueous solution increased with increasing amount of the adsorbent material introduced into the solution. From the solution of cesium in which 3.0 g of the adsorbent was added, the percentage removal of cesium were in the order of Raw pine (3 %), 2:1 toluene- ethanol treated (13 %) and HCF modified sample (60 %).

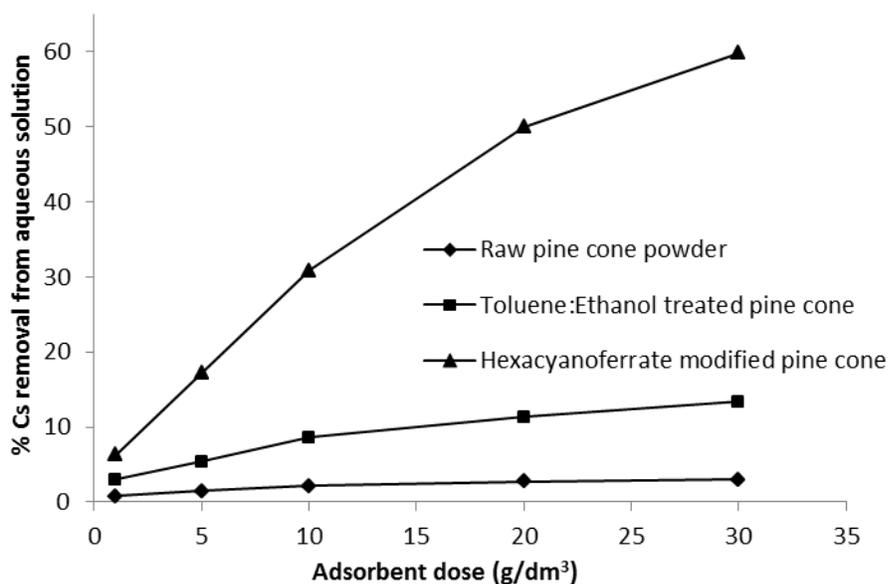


Fig. 4.19: Percentage removal of cesium for raw pine cone, toluene-ethanol treated pine cone, and hexacyanoferrate modified pine cone.

These results indicated that the incorporation of HCF into the treated pine cone increased the affinity of the adsorbent material for cesium ions in solution. The higher cesium percentage observed for the HCF modified pine cone and the 2:1 toluene- ethanol treated sample over the

raw sample can be attributed to the higher surface area of the treated and modified sample due to the availability of more active surface sites for adsorption.

#### 4.4.2 Effect of solution pH

The effect of pH on cesium adsorption onto raw pine, 2:1 toluene-ethanol treated pine and hexacyanoferrate modified pine cone was studied in the range pH 1-10 and are shown in Fig. 4.20.

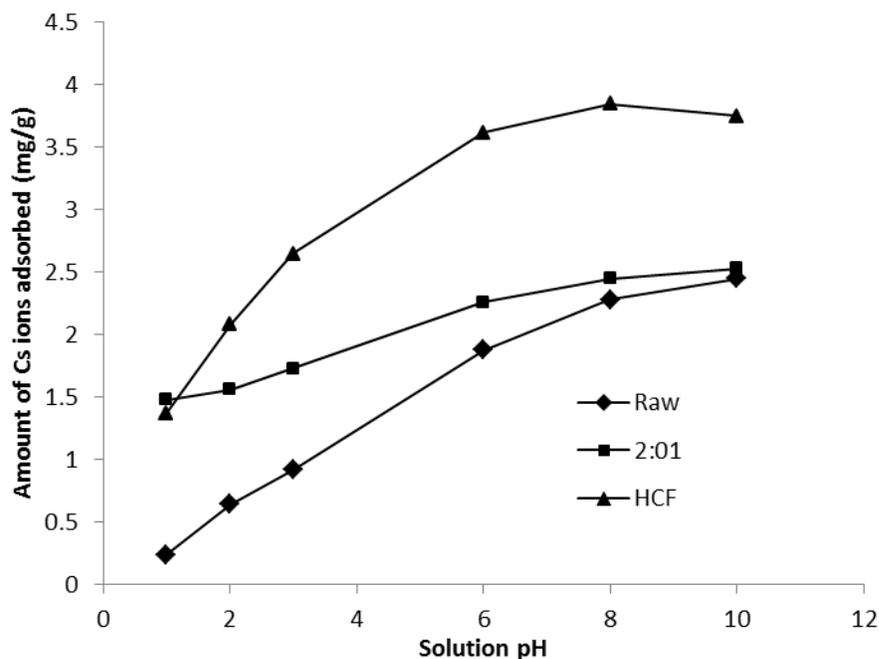


Fig. 4.20: Effect of initial solution pH on cesium uptake by raw pine, 2:1 toluene-ethanol treated and HCF modified pine cone powder.

As the solution pH increases, the amount of cesium removed from the solution increased in all the sorbent samples studied up to solution pH 8. This can be attributed to the increase in negative charges on the biosorbents' surface with increasing solution pH and the reduction in  $H^+$  competition for biosorption sites. By reducing the concentration of  $H^+$  ions, the surface deprotonation of biosorbent occurs, which results into increase in the number of effective sorption sites on the surface of biosorbent. The amount of cesium removed, increased up to pH 8 but got reduced at solution pH 10 for HCF modified pine cone, but increased steadily for raw

pine cone and 2:1 toluene-ethanol treated pine cone. Therefore pH of 8 was assumed to be the optimum solution pH for Cs removal from solution. Dahiya *et al.*, (2008) also observed that at low solution pH, Cs<sup>+</sup> adsorption onto pre-treated arca shell biomass was less than 1.0 mg/g and on increasing solution pH above 5.5 the removal of Cs<sup>+</sup> from solution increased rapidly.

#### **4.5 Kinetics and equilibrium studies of the competitive cesium biosorption onto iron(III) hexacyanoferrate immobilized pine cone powder**

##### *4.5.1 Adsorption Kinetic*

In the present study, batch contact was studied using 1.0 g of the raw, toluene-ethanol treated and HCF modified pine cone with 100 cm<sup>3</sup> of Cs<sup>+</sup> ions of concentrations varying between 50 and 250 mg/dm<sup>3</sup> and agitated at 120 rpm at 26 °C. The amount of cesium adsorbed at equilibrium can be obtained from the equation below:

$$q = \frac{(C_o - C_e)}{m}V \quad (4.3)$$

Where q is the equilibrium sorption capacity (mg/g), C<sub>o</sub>, the initial Cs concentration (mg/dm<sup>3</sup>) C<sub>e</sub>, the equilibrium Cs concentration (mg/dm<sup>3</sup>), V the solution volume (dm<sup>3</sup>) and m is the mass of the adsorbent (g). The percentage removal was calculated using the following equation:

$$\%R = \frac{(C_o - C_e)}{C_o} \times 100 \quad (4.4)$$

The results of the kinetic study were expressed as the percentage of Cs<sup>+</sup> ions removal from solution at different time intervals. Figs. 4.21a-c shows the plots of percentage Cs<sup>+</sup> ions removed against time. The results in Fig. 4.21a-c revealed that the percentage removal increased rapidly at the onset of the adsorption process and reduced gradually as time increased, and coming to an almost constant state at the end of the adsorption period. This behavior is attributed to the fact that at the initial stage of adsorption the surface of the adsorbent was empty and the adsorption sites were free. Therefore, the increase in percentage removal at this stage was due to concentration gradient between the bulk solution and the surface of the adsorbents. As the process continued with time, the percentage removal reduced due to saturation of the surfaces of the adsorbent with adsorbate molecules. Comparing the three adsorbents from Figs. 4.21a-c, it will be observed that the percentage removal of Cs<sup>+</sup> ions at all initial Cs concentrations were

higher for HCF modified sample than for the toluene-ethanol treated and raw samples. It was also observed that the  $\text{Cs}^+$  ions percentage removal reduced as the concentration of  $\text{Cs}^+$  ions in solution increased. Reduction in percentage removal with increasing concentration at a fixed mass of adsorbent can be attributed to complete saturation of adsorption sites on the adsorbent surface with increase in initial concentration. As initial concentration increases and sites become totally saturated, percentage removed as initial concentration increases will therefore reduce.

The order of increase in percentage  $\text{Cs}^+$  ion removal amongst the adsorbents at a particular  $\text{Cs}^+$  ion concentration is raw pine < toluene-ethanol treated < HCF modified. The result therefore, is an indication that the treatment and modification carried out on the raw pine cone surface enhanced the ability of the adsorbent to remove  $\text{Cs}^+$  ions from aqueous solution. The HCF modified pine cone removed about 38, 36, 31, 29 and 27 % of the  $\text{Cs}^+$  ions from solution as initial Cs concentration was increased from 50, 100, 150, 200 to 250  $\text{mg}/\text{dm}^3$ . For the toluene-ethanol modified sample percentage removal decreased from 22, 21, 20, 19, 18 % with increased in Cs ions in solution whereas for the raw sample, the percentage decrease were 17, 16, 15, 14 and 13 % as initial Cs concentration increased from 50 to 250  $\text{mg}/\text{dm}^3$ . At initial concentration of 250  $\text{mg}/\text{dm}^3$ , the increase in percentage removal of the HCF modified pine cone over the raw pine was 55.3 %, while at 50  $\text{mg}/\text{dm}^3$  it was 52 %.

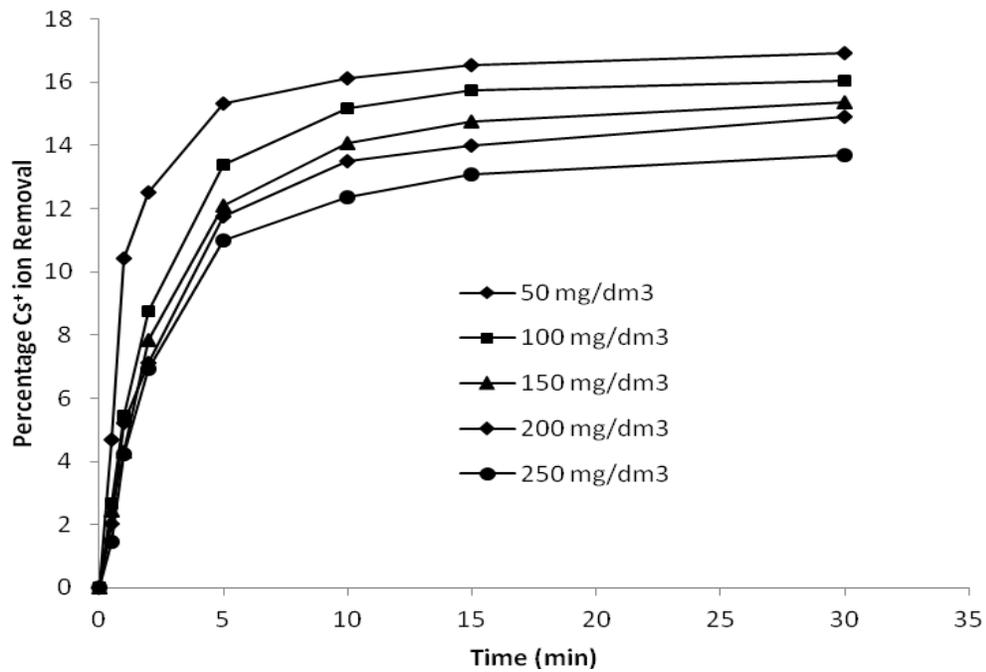


Fig. 4.21a: Percentage removal of Cs<sup>+</sup> ions from aqueous solution using raw pine cone. Adsorbent dose: 10 g/dm<sup>3</sup>; Solution pH: 8; Agitation Speed: 120 rpm; Temp: 26 °C.

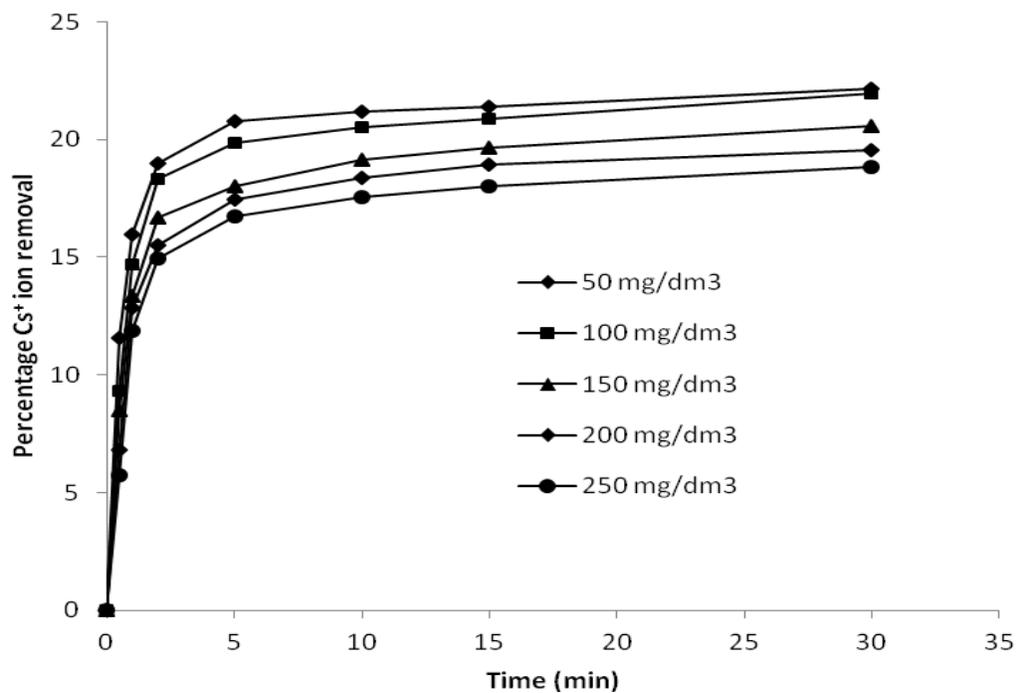


Fig. 4.21b: Percentage removal of Cs<sup>+</sup> ions from aqueous solution using toluene-ethanol treated pine cone. Adsorbent dose: 10 g/dm<sup>3</sup>; Solution pH: 8; Agitation Speed: 120 rpm; Temp: 26 °C.

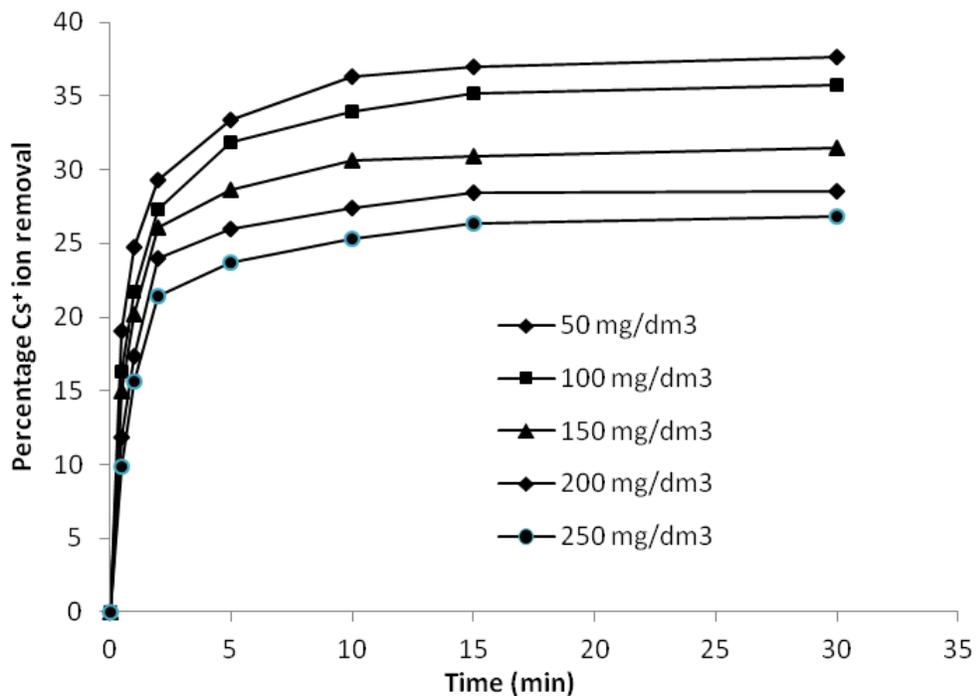


Fig. 4.21c: Percentage removal of Cs<sup>+</sup> ions from aqueous solution using HCF modified pine cone. Adsorbent dose: 10 g/dm<sup>3</sup>; Solution pH: 8; Agitation Speed: 120 rpm; Temp: 26 °C.

#### 4.5.2 Kinetic modeling

The kinetic data on the adsorption of  $\text{Cs}^+$  ions by raw, toluene-ethanol and HCF modified pine cone were plotted according to the pseudo-first-order, pseudo-second-order and diffusion-chemisorption kinetic models along with the experimental data. The kinetic parameters of the pseudo-first, pseudo-second-order and diffusion-chemisorption models were also calculated and given in Table 4.3a - c.

##### 4.5.2.1 Pseudo-first order kinetic model

The pseudo-first order constants and correlation coefficient,  $r^2$ , for the sorption of cesium onto pine cone from 50 to 250  $\text{mg}/\text{dm}^3$  of cesium were calculated from the plots of  $\log(q_e - q_t)$  versus  $t$  and are given in table 4.3a. The plot of  $\log(q_e - q_t)$  versus  $t$  for the raw pine cone, toluene-ethanol treated pine and HCF modified pine cone are shown in Fig. 4.22a-c. The pseudo-first order kinetic data on  $\text{Cs}^+$  ions adsorption by all samples showed that there was a deviation from the straight line of the experimental data using the pseudo-first order kinetic model after the first 2 min of contact. The observed deviation from the experimental data seen in the pseudo-first order plots are attributed to the sharp fall in concentration gradient at the initial rapid uptake stage of  $\text{Cs}^+$  ions removal due to large amount of vacant site for biosorption (Ofomaja, 2010) which is followed with a slow uptake stage after 2 min of contact. Within this time period, it is believed that there is a switch between mass transfer diffusion control and pore diffusion control (Ofomaja, 2007; 2008).

Values of the pseudo-first order kinetic parameters for  $\text{Cs}^+$  ions adsorption for all adsorbents are given in Table 4.3a. From Table 4.3a it can be observed that the pseudo-first order equilibrium capacity,  $q_e$ , increased from 0.69 to 1.94  $\text{mg}/\text{g}$  for the raw pine, from 0.70 to 2.00  $\text{mg}/\text{g}$  for toluene-ethanol treated pine and from 0.94 to 2.42  $\text{mg}/\text{g}$  for HCF modified sample as initial Cs concentration increased from 50 to 250  $\text{mg}/\text{dm}^3$ . The values for the equilibrium capacity,  $q_e$ , were least for the raw pine cone and highest for the HCF modified pine cone. The predicted values for equilibrium capacity using the Pseudo-first order model was seen to be very different from the experimental values for all samples.

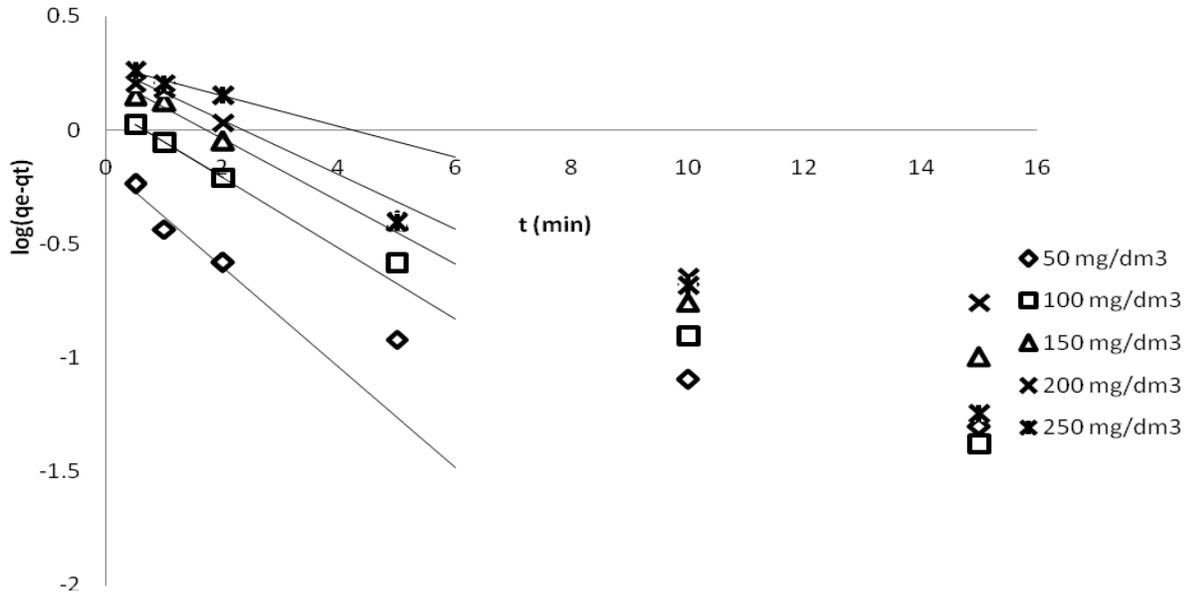


Fig.4.22a: Pseudo first order kinetics data for cesium adsorption by raw pine cone powder.

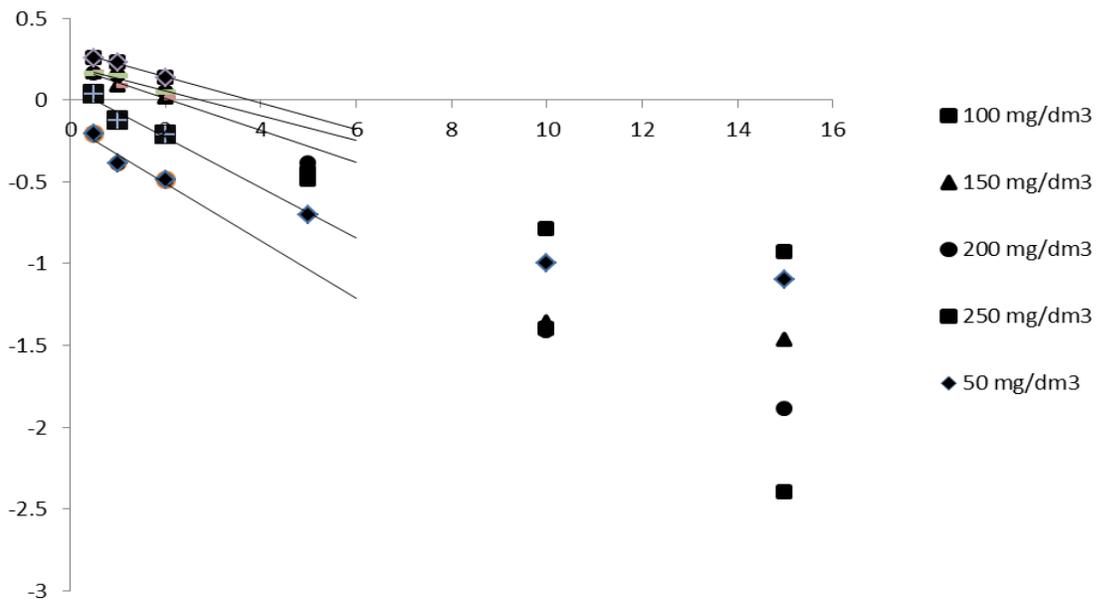


Fig.4.22b: Pseudo first order kinetics data for cesium adsorption by toluene-ethanol treated pine cone.

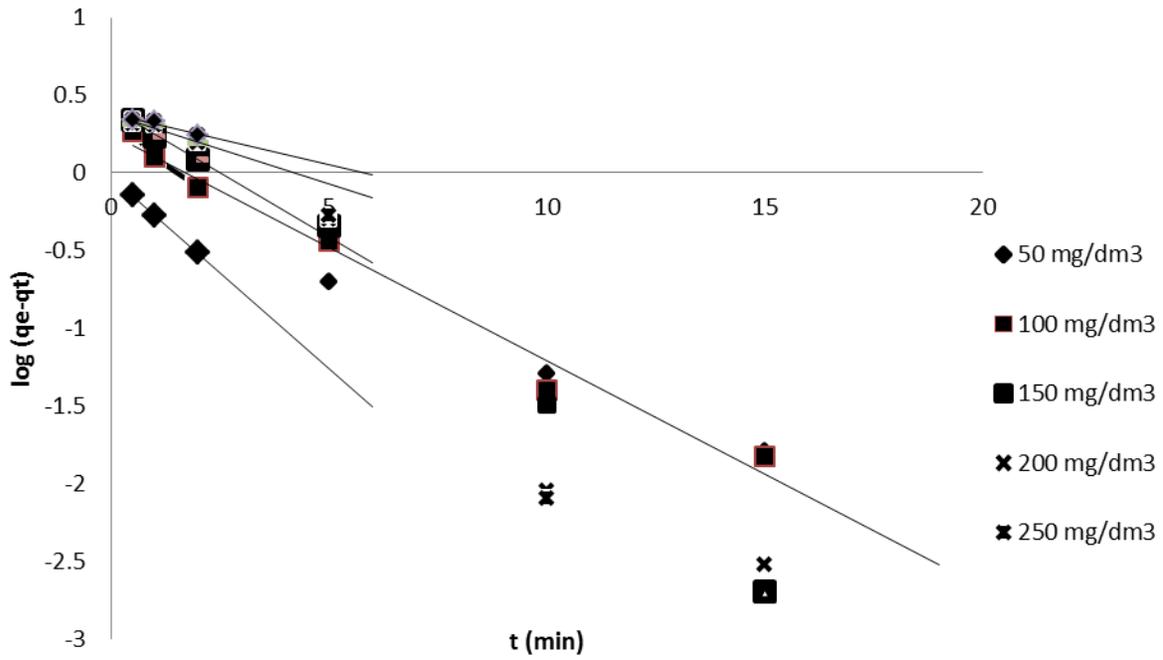


Fig.4.22c: Pseudo first order kinetics data for cesium adsorption by HCF modified pine cone.

The pseudo-first order rate constant,  $k_1$ , was found to decrease for all samples as initial concentration of  $\text{Cs}^+$  ions increase in solution. For the raw pine cone, the rate constant,  $k_1$ , decreased from 0.5067 to 0.1568  $\text{min}^{-1}$ , for toluene-ethanol treated pine its values reduced from 0.4049 to 0.1659  $\text{min}^{-1}$  while for the HCF modified sample the values reduced from 0.5685 to 0.1529  $\text{min}^{-1}$ . The relationship between the pseudo-first order equilibrium capacities,  $q_e$ , and rate constant,  $k_1$ , with the initial Cs concentration between the ranges of concentration applied can be represented by the equations below:

$$\text{Raw pine:} \quad q_e = 0.1372C_0^{0.4644} \quad (r^2 = 0.9963) \quad (4.5)$$

$$\text{Toluene-ethanol treated pine:} \quad q_e = 0.2984C_0^{0.3370} \quad (r^2 = 0.9821) \quad (4.6)$$

$$\text{HCF modified pine:} \quad q_e = 0.1906C_0^{0.4524} \quad (r^2 = 0.9618) \quad (4.7)$$

$$\text{Raw pine:} \quad k_1 = 8.2243C_0^{-0.6721} \quad (r^2 = 0.8969) \quad (4.8)$$

$$\text{Toluene-ethanol treated pine:} \quad k_1 = 6.8960C_0^{-0.5422} \quad (r^2 = 0.8931) \quad (4.9)$$

$$\text{HCF modified pine:} \quad k_1 = 2.4871C_0^{-0.4049} \quad (r^2 = 0.9771) \quad (4.10)$$

#### 4.5.2.2 Pseudo second order kinetic model

The pseudo-second order constants and correlation coefficient for the sorption of cesium onto pine cone from 50 to 250 mg/dm<sup>3</sup> of cesium were calculated from the plots of  $t/q_t$  against  $t$  and are given in table 4.3b. The plot of  $t/q_t$  against  $t$  for the raw pine cone, toluene-ethanol treated pine and HCF modified pine cone are shown in Fig. 4.23a-c. On application of the pseudo-second order model to the kinetic data, it was observed that the plots of  $t/q_t$  versus  $t$  were straight lines for all three samples, indicating that the pseudo-second order model was capable of describing the kinetic data for the whole range of contact time used in this experiment. From the tables it can be observed that an increase in cesium concentration caused an increase in equilibrium adsorption capacity,  $q_e$ , and initial adsorption rate,  $h$ , but reduced the adsorption rate  $k_2$ . For the raw sample, the equilibrium capacity increased from 0.91 to 2.68 mg/g, for toluene-ethanol treated the increase was from 1.32 to 4.11 mg/g, while for HCF modified the equilibrium capacity increased from 1.89 to 5.91 mg/g. The predicted values for equilibrium capacity using the Pseudo-second order model was seen to be very close to the experimental values for all the initial concentrations of Cs applied. This suggests that the pseudo-second order model accurately describes the adsorption process to a reasonable extent. The pseudo-second order equilibrium capacity,  $q_e$ , had higher values for HCF modified pine followed by the toluene-ethanol treated pine and the values increased with increasing initial Cs concentration.

The initial adsorption rate,  $h$ , had higher values for the HCF modified pine due to the higher affinity of HCF for Cs<sup>+</sup> ions on the pine surface and was least for the raw pine since it has the least value for surface area. The values of  $h$  increased from 0.92 to 1.42 mg/g min for raw pine cone, from 1.78 to 6.27 mg/g min for the toluene-ethanol treated pine while for the HCF modified pine cone the values increased from 4.30 to 10.68 mg/g min. The values of  $k_2$  reduced from 1.117 to 0.198 g /mg min for the raw pine, from 1.012 to 0.370 g /mg min for the toluene-ethanol treated pine while for the HCF modified pine cone the values reduced from 1.199 to 0.306 g /mg min.

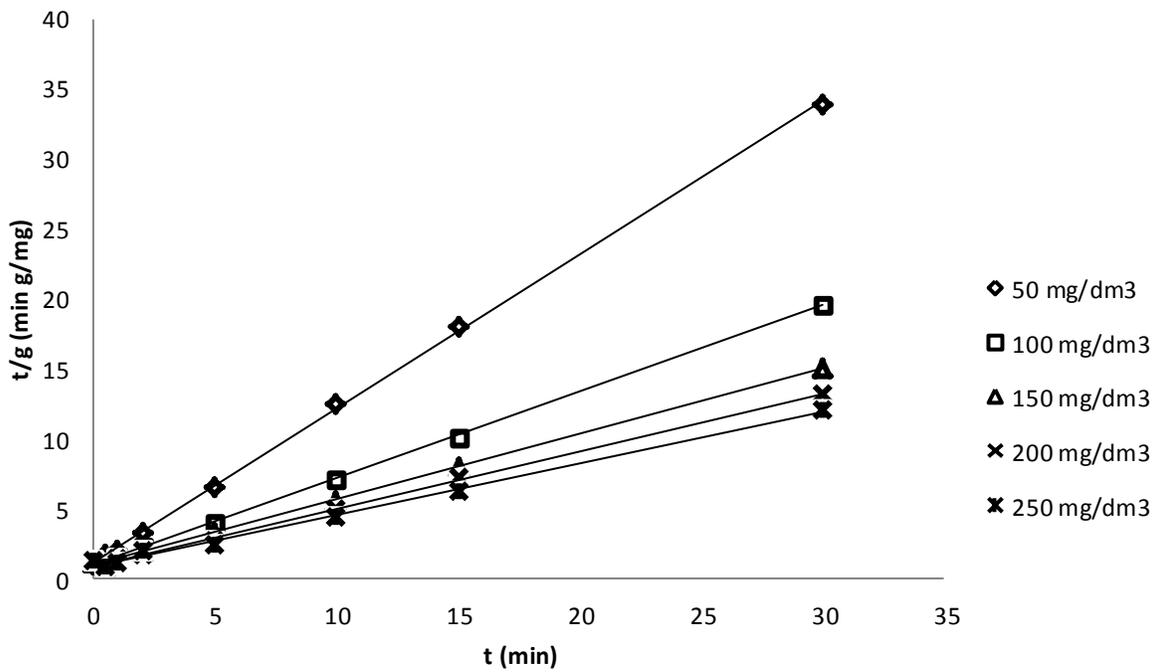


Fig.4.23a: Pseudo second order kinetics data for cesium adsorption onto raw pine cone powder.

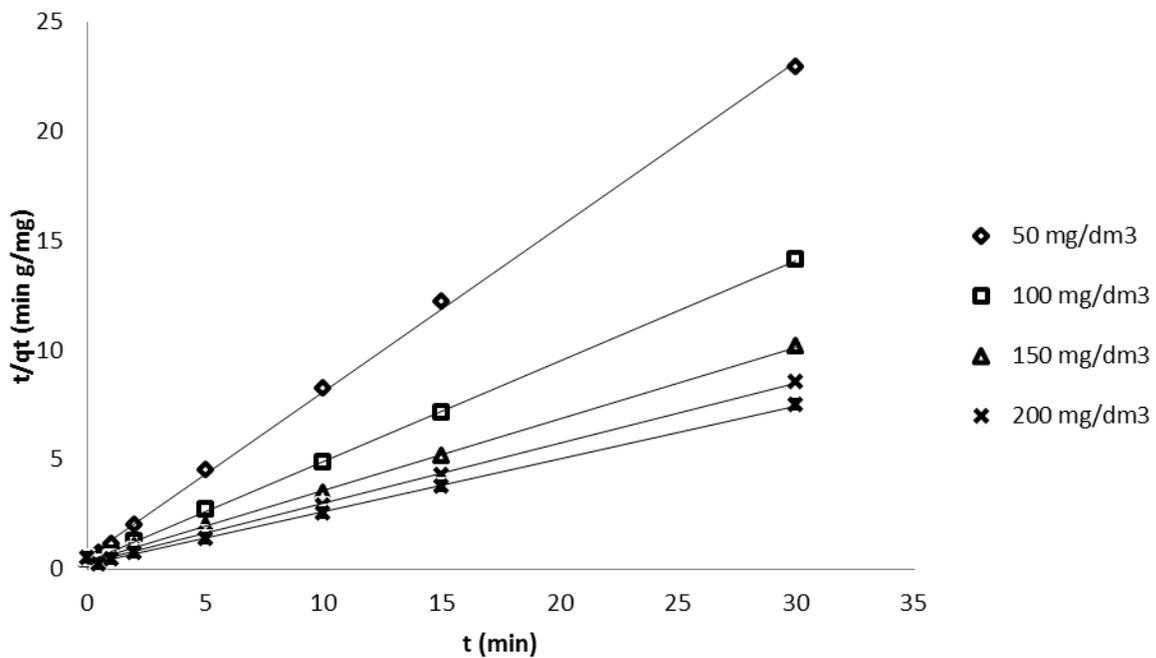


Fig.4.23b: Pseudo second order kinetics data for cesium adsorption onto toluene-ethanol treated pine cone powder.

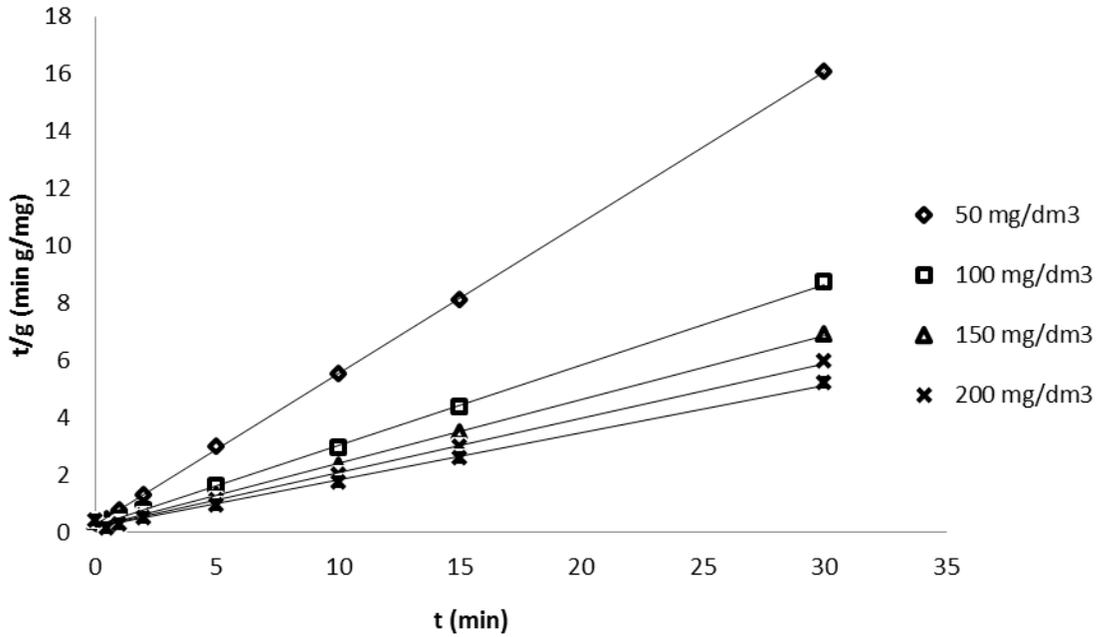


Fig.4.23c: Pseudo second order kinetics data for cesium adsorption onto HCF modified pine cone powder.

The relationship between the pseudo-second order predicted equilibrium capacities,  $q_e$ , and rate constant,  $k_2$ , with the initial Cs concentration between the ranges of concentration applied can be represented by the equations below:

$$\text{Raw pine:} \quad q_e = 0.0199C_0^{0.9689} \quad (r^2 = 0.9994) \quad (4.11)$$

$$\text{Toluene-ethanol treated pine:} \quad q_e = 0.0282C_0^{0.9455} \quad (r^2 = 0.9990) \quad (4.12)$$

$$\text{HCF modified pine:} \quad q_e = 0.0793C_0^{0.8244} \quad (r^2 = 0.9941) \quad (4.13)$$

$$\text{Raw pine:} \quad k_2 = 5.645C_0^{-0.21193} \quad (r^2 = 0.9971) \quad (4.14)$$

$$\text{Toluene-ethanol treated pine:} \quad k_2 = 6.511C_0^{-2.0677} \quad (r^2 = 0.9963) \quad (4.15)$$

$$\text{HCF modified pine:} \quad k_2 = 0.9078C_0^{-1.8013} \quad (r^2 = 0.9891) \quad (4.16)$$

#### 4.5.2.3 Diffusion-chemisorption model

Sutherland (2004) expression for the diffusion-chemisorption model was also applied in modeling the kinetic data and the model parameters displayed in Table 4.3c. The plot of  $t^{0.5}/q_t$  versus  $t^{0.5}$  for the raw pine cone, toluene-ethanol treated pine and HCF modified pine cone are

shown in Fig. 4.24a-c. The plot of  $t^{0.5}/q_t$  versus  $t^{0.5}$  did not yield straight lines; instead the lines became only linear after the first 2 min of contact.

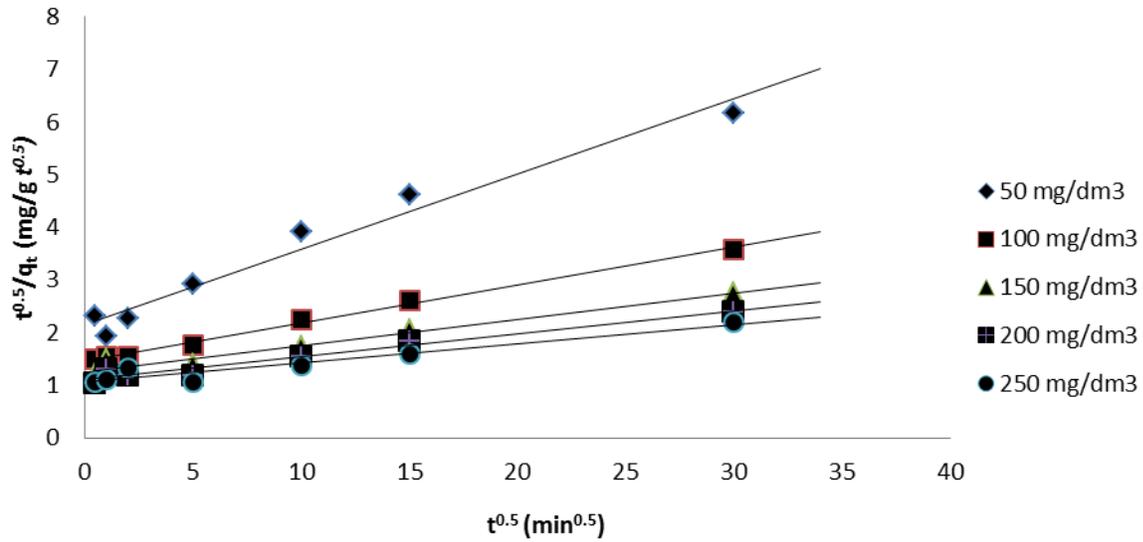


Fig. 4.24 a: Diffusion chemisorption data for cesium adsorption onto raw pine cone powder.

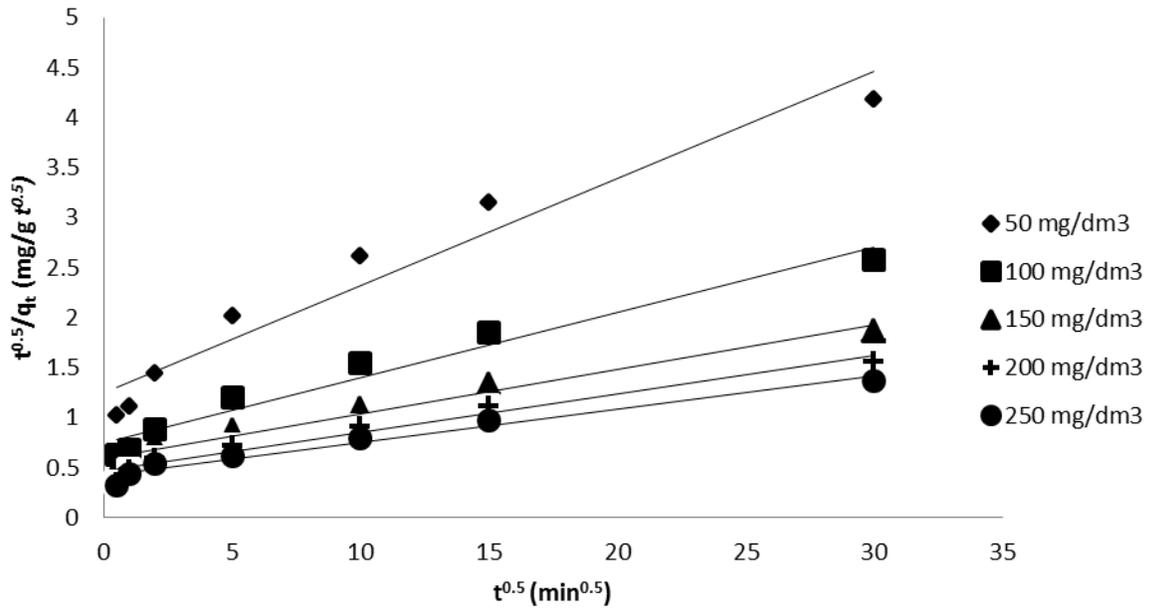


Fig. 4.24 b: Diffusion chemisorption data for cesium adsorption onto toluene-ethanol treated pine cone powder.

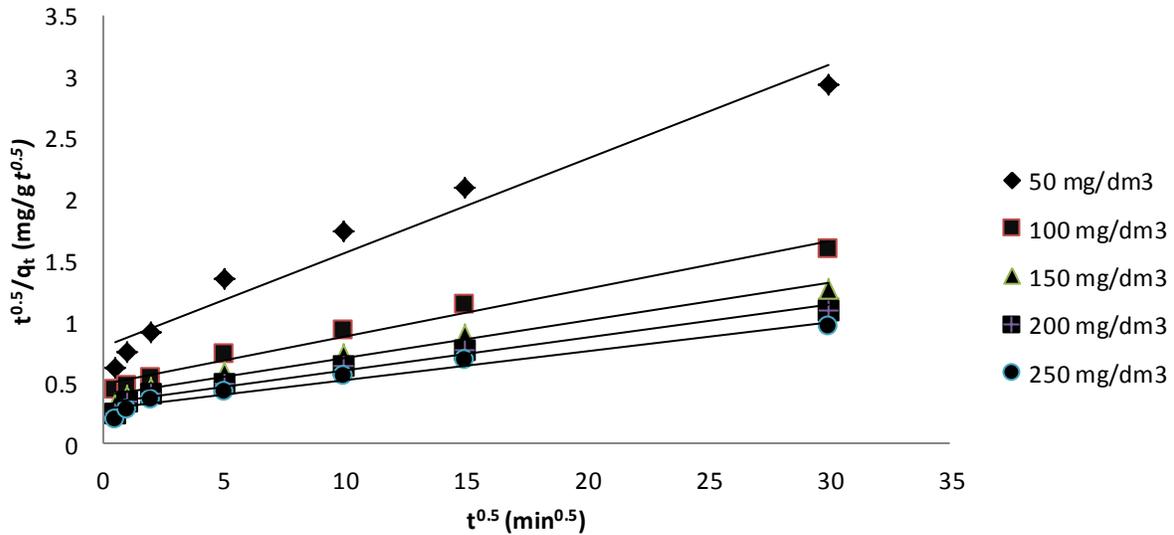


Fig. 4.24c: Diffusion chemisorption data for cesium adsorption onto HCF modified pine cone powder.

Values of diffusion-chemisorption equilibrium capacities and diffusion-chemisorption rate constant,  $K_{DC}$ , were found to increase with increasing initial concentration of cesium on solution for all samples. The values of chemisorption equilibrium capacities  $q_e$ , increased from 1.00 to 2.88 mg/g for raw pine cone, from 1.49 to 4.23 mg/g, for toluene-ethanol treated pine cone, while for HCF modified pine cone the  $q_e$  increased from 2.02 to 6.13 mg/g. The values of  $K_{DC}$ , are in the range of 1.394 to 3.655 (mg/g  $t^{0.5}$ ) for raw pine cone, for toluene-ethanol treated pine cone  $K_{DC}$  values increased for 1.947 to 15.482 (mg/g  $t^{0.5}$ ), while for HCF modified pine cone  $K_{DC}$  values increased for 4.943 to 20.7800 (mg/g  $t^{0.5}$ ). The values of the diffusion-chemisorption equilibrium capacities are closer to the experimental data than those predicted by the pseudo-first order model but not as close as compared with those predicted by the pseudo-second order model. HCF modified samples had higher equilibrium capacities and diffusion-chemisorption rate constant as compared with the toluene-ethanol and raw pine cone samples.

The relationship between the diffusion-chemisorption model predicted equilibrium capacities,  $q_e$ , and rate constant,  $K_{DC}$ , with the initial Cs concentration between the ranges of concentration applied can be represented by the equations below:

$$\text{Raw pine:} \quad q_e = 0.1068C_0^{1.1732} \quad (r^2 = 0.9967) \quad (4.17)$$

Toluene-ethanol treated pine:  $q_e = 0.0169C_0^{1.0756} \quad (r^2 = 0.9970)$  (4.18)

HCF modified pine:  $q_e = 0.0550C_0^{0.9276} \quad (r^2 = 0.9806)$  (4.19)

Raw pine:  $K_{DC} = 2.205C_0^{-0.0701} \quad (r^2 = 0.9919)$  (4.20)

Toluene-ethanol treated pine:  $K_{DC} = 30.9101C_0^{-0.4028} \quad (r^2 = 0.9623)$  (4.21)

HCF modified pine:  $K_{DC} = 5.2541C_0^{-0.0382} \quad (r^2 = 0.9984)$  (4.22)

Table 4.3a: Pseudo-first order parameters for the effect of Cs<sup>+</sup> concentration on the uptake of Cs<sup>+</sup> by Raw and modified pine cone.

	50 mg/dm <sup>3</sup>	100 mg dm <sup>-3</sup>	150 mg/dm <sup>3</sup>	200m g/dm <sup>3</sup>	250 mg/dm <sup>3</sup>
<b>Raw Pine Cone</b>					
$q_e$ (mg/g) ( <i>exp</i> )	0.85	1.60	2.33	2.98	3.57
$q_e$ (mg/g)	0.69	1.27	1.71	2.11	1.94
$k_l$ (min <sup>-1</sup> )	0.5067	0.3584	0.3148	0.2755	0.1568
<b>2:1 Toluene-ethanol Treated Pine cone</b>					
$q_e$ (mg/g) ( <i>exp</i> )	1.08	2.13	3.17	4.00	4.71
$q_e$ (mg/g)	0.70	1.20	1.60	1.61	2.00
$k_l$ (min <sup>-1</sup> )	0.4049	0.3539	0.2253	0.1739	0.1659
<b>HCF Modified Pine Cone</b>					
$q_e$ (mg/g) ( <i>exp</i> )	1.88	3.57	4.73	5.71	6.71
$q_e$ (mg/g)	0.94	2.31	2.60	2.39	2.42
$k_l$ (min <sup>-1</sup> )	0.5685	0.5334	0.3822	0.2082	0.1529

Table 4.3b. Pseudo-second order parameters for the effect of Cs<sup>+</sup> concentration on the uptake of Cs<sup>+</sup> by Raw and modified pine cone.

	50 mg/dm <sup>3</sup>	100 mg dm <sup>-3</sup>	150 mg/dm <sup>3</sup>	200m g/dm <sup>3</sup>	250 mg/dm <sup>3</sup>
<b>Raw Pine Cone</b>					
$q_e$ (mg/g) ( <i>exp</i> )	0.85	1.60	2.33	2.98	3.57
$q_e$ (mg/g)	0.91	1.61	2.11	2.41	2.68
$k_2$ (g /mg min)	1.1172	0.4582	0.2768	0.2372	0.1976
$h$ (mg/g min)	0.9238	1.1825	1.2133	1.3749	1.4197
<b>2:1 Toluene-ethanol Treated Pine cone</b>					
$q_e$ (mg/g) ( <i>exp</i> )	1.08	2.13	3.17	4.00	4.71
$q_e$ (mg/g)	1.32	2.17	3.03	3.61	4.11
$k_2$ (g /mg min)	1.0117	0.7783	0.4373	0.4295	0.3703
$h$ (mg/g min)	1.7821	3.6579	4.0264	5.5907	6.2686
<b>HCF Modified Pine Cone</b>					
$q_e$ (mg/g) ( <i>exp</i> )	1.88	3.57	4.73	5.71	6.71
$q_e$ (mg/g)	1.89	3.53	4.46	5.17	5.91
$k_2$ (g /mg min)	1.1988	0.4801	0.3604	0.3237	0.3061
$h$ (mg/g min)	4.3045	5.9681	7.1547	8.6695	10.6769

Table 4.3c. Diffusion Chemisorption kinetics parameters for the effect of Cs<sup>+</sup> concentration on the uptake of Cs<sup>+</sup> by Raw and modified pine cone.

	50 mg/dm <sup>3</sup>	100 mg dm <sup>-3</sup>	150 mg/dm <sup>3</sup>	200m g/dm <sup>3</sup>	250 mg/dm <sup>3</sup>
<b>Raw Pine Cone</b>					
$q_e$ (mg/g) ( <i>exp</i> )	0.85	1.60	2.33	2.98	3.57
$q_e$ (mg/g)	1.00	1.79	2.39	2.67	2.88
$K_{DC}$ (mg/g $t^{0.5}$ )	1.3936	2.0861	2.2643	2.7915	3.6547
<b>2:1 Toluene-ethanol Treated Pine cone</b>					
$q_e$ (mg/g) ( <i>exp</i> )	1.08	2.13	3.17	4.00	4.71
$q_e$ (mg/g)	1.49	2.34	3.22	3.81	4.23
$K_{DC}$ (mg/g $t^{0.5}$ )	1.9466	4.6011	7.1606	9.2846	15.4820
<b>HCF Modified Pine Cone</b>					
$q_e$ (mg/g) ( <i>exp</i> )	1.88	3.57	4.73	5.71	6.71
$q_e$ (mg/g)	2.02	3.71	4.66	5.3916	6.13
$K_{DC}$ (mg/g $t^{0.5}$ )	4.9426	10.1247	13.2926	16.824 0	20.7800

Table 4.4: A comparison of Chi-square and coefficient of determination,  $r^2$  for three kinetics model for  $\text{Cs}^+$  adsorption.

Sample	Pseudo-first order		Pseudo-Second order		Diffusion-chemisorption	
	$\chi^2$	$r^2$	$\chi^2$	$r^2$	$\chi^2$	$r^2$
Raw Pine						
50 (mg/dm <sup>3</sup> )	0.0591	0.9234	0.0011	0.9996	0.0083	0.9992
100 (mg/dm <sup>3</sup> )	0.0563	0.9990	0.0005	0.9998	0.0270	0.9977
150 (mg/dm <sup>3</sup> )	0.0574	0.9548	0.0028	0.9996	0.0427	0.9982
200 (mg/dm <sup>3</sup> )	0.1665	0.9404	0.0114	0.9989	0.0581	0.9987
250 (mg/dm <sup>3</sup> )	0.4752	0.9504	0.0117	0.9971	0.0758	0.9978
Toluene-ethanol Pine cone						
50 (mg/dm <sup>3</sup> )	0.6644	0.8868	0.0066	0.9992	0.0006	0.9999
100 (mg/dm <sup>3</sup> )	1.1022	0.8707	0.0035	0.9998	0.0062	0.9975
150 (mg/dm <sup>3</sup> )	2.0163	0.9680	0.0102	0.9995	0.0484	0.9893
200 (mg/dm <sup>3</sup> )	4.4880	0.9406	0.0193	0.9994	0.0374	0.9906
250 (mg/dm <sup>3</sup> )	4.4238	0.9867	0.0194	0.9993	0.0018	0.9855
HCF modified pine						
50 (mg/dm <sup>3</sup> )	1.1326	0.9994	0.0024	0.9999	0.0025	0.9988
100 (mg/dm <sup>3</sup> )	0.7011	0.9827	0.0009	0.9998	0.0525	0.9906
150 (mg/dm <sup>3</sup> )	1.5991	0.9903	0.0058	0.9997	0.0751	0.9922
200 (mg/dm <sup>3</sup> )	5.4589	0.9295	0.0237	0.9994	0.0807	0.9898
250 (mg/dm <sup>3</sup> )	9.9060	0.9182	0.0006	0.9994	0.0824	0.9906

#### 4.5.2.4 Comparison of kinetic models

The ability of the different kinetic models applied in this study to describe the experimental data was determined by plotting the predicted values of equilibrium capacities of  $\text{Cs}^+$  per unit mass (mg/g) using the different adsorbents at different time intervals,  $t$ , along with the experimentally determined values of equilibrium capacities of  $\text{Cs}^+$  (mg/g) per unit mass for the different adsorbents at the same time intervals,  $t$ . In the plots only the predicted values of the pseudo-second and diffusion-chemisorption models were compared with the experimental data since the chi-square error method suggested poor correlation between the pseudo-first order model with the experimental data. The figures showed that the predicted values of the two kinetic models were quite close to the experimental data especially with the pseudo-second kinetic model. The Pseudo-second order model gave close values to the experimental data over the total contact period, whereas a close look at the figures showed that at the initial contact period (between 0 and 5 min), the predicted values of the diffusion-chemisorption model were further away from the experimental data than for the period after 5 min. This result indicated that the diffusion-chemisorption mechanism only accurately describes the  $\text{Cs}^+$  ion adsorption after 5 min of contact.

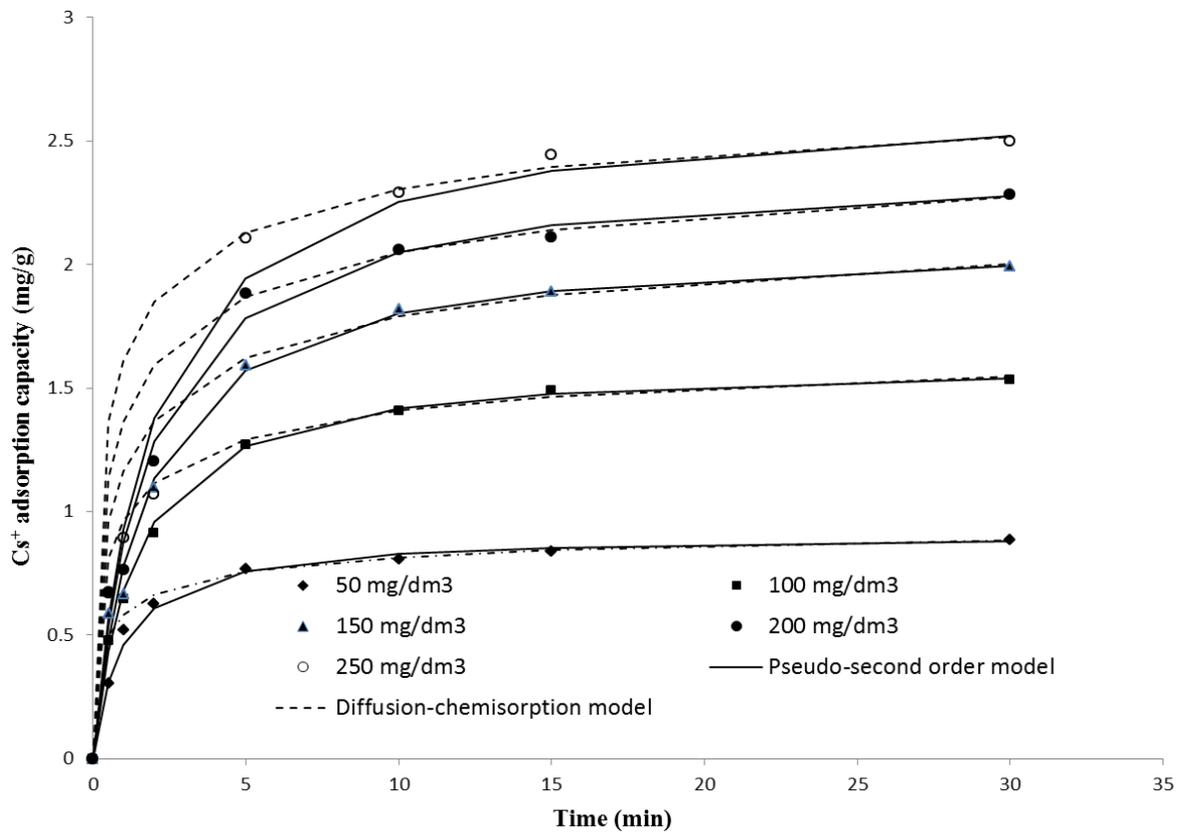


Fig. 4.25a: Cs adsorption capacity for Cs<sup>+</sup> ions removal from aqueous solution using raw pine cone. Adsorbent dose: 10 g/dm<sup>3</sup>; Solution pH: 8; Agitation Speed: 120 rpm; Temp: 26 °C.

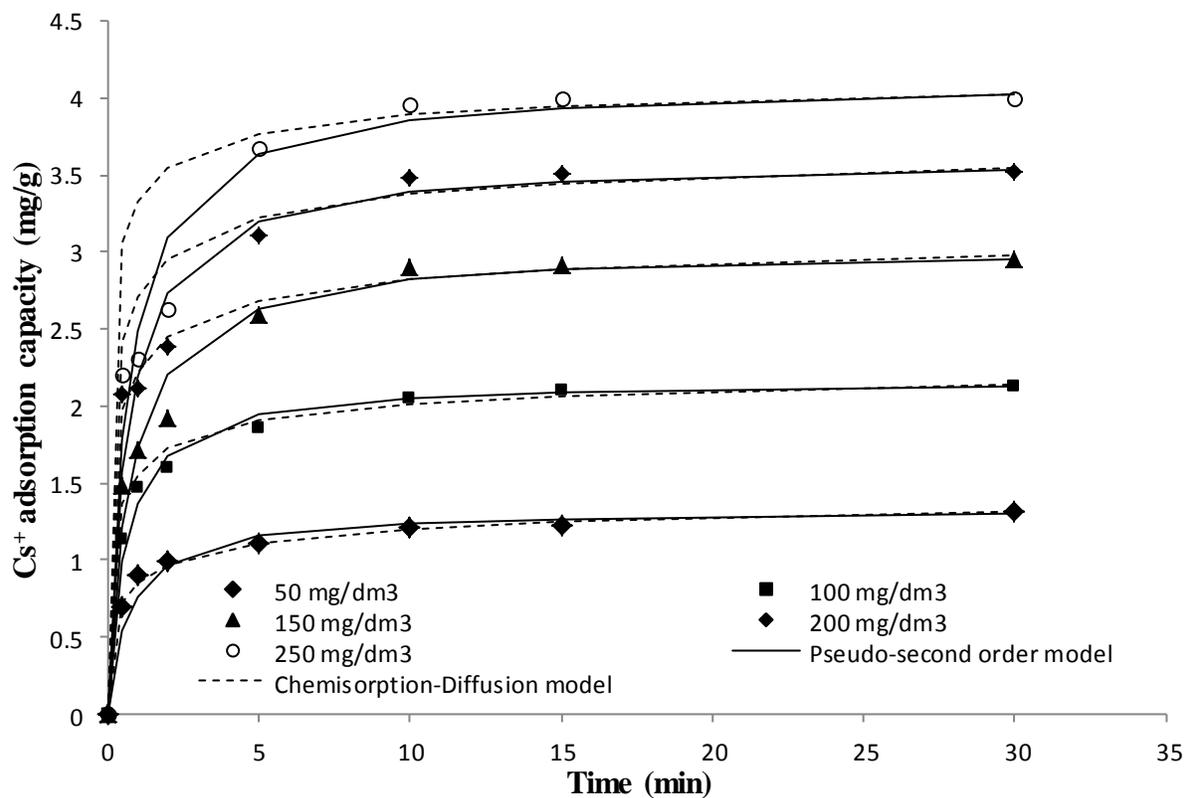


Fig. 4.25.b: Cs adsorption capacity for Cs<sup>+</sup> ions removal from aqueous solution using toluene-ethanol treated pine cone. Adsorbent dose: 10 g/dm<sup>3</sup>; Solution pH: 8; Agitation Speed: 120 rpm; Temp: 26 °C.

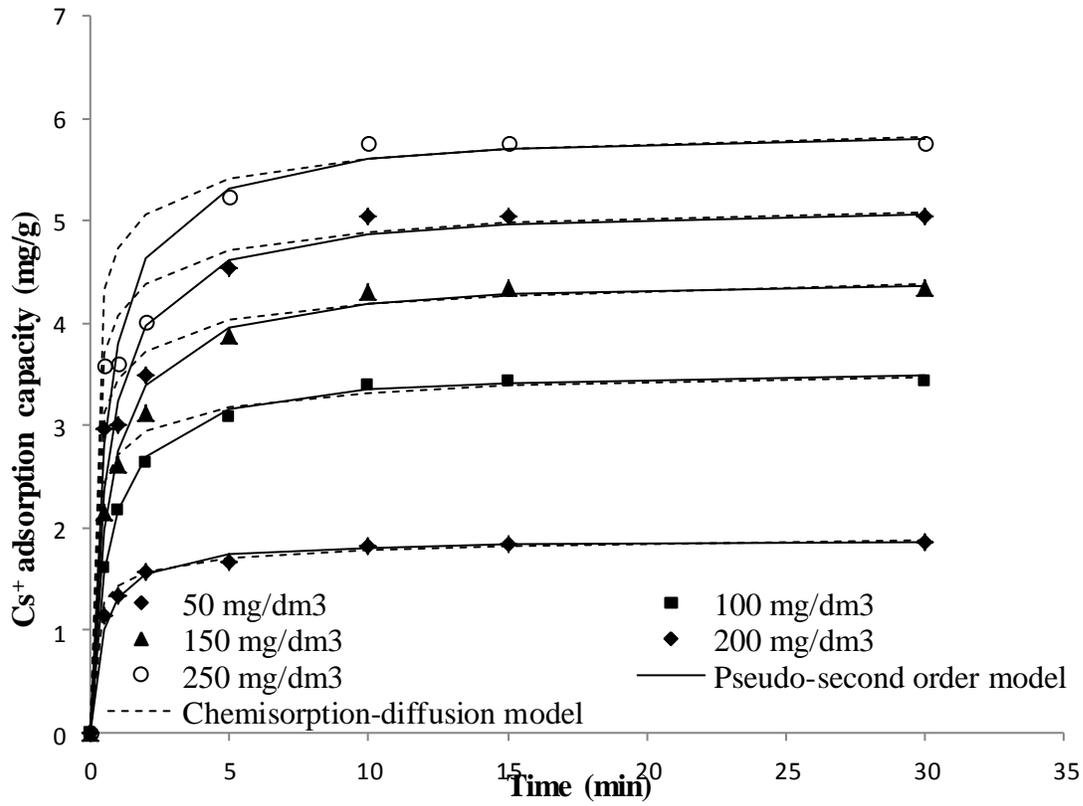


Fig. 4.25c: Cs adsorption capacity for Cs<sup>+</sup> ions removal from aqueous solution using HCF modified pine cone. Adsorbent dose: 10 g/dm<sup>3</sup>; Solution pH: 8; Agitation Speed: 120 rpm; Temp: 26 °C.

#### *4.5.3 Competitive biosorption of cesium using iron(III) hexacyanoferrate immobilized pine cone powder.*

The influence of interfering cations ( $\text{Na}^+$  and  $\text{Ca}^{2+}$ ) on the adsorption of  $\text{Cs}^+$  ion by iron(III) hexacyanoferrate modified pine cone were investigated by conducting the kinetic study, since the motive of this research was to develop a simple technique for selective removal of cesium in presence of competitive metals. The kinetic study was conducted using 1.0 g of raw, toluene-ethanol treated and hexacyanoferrate modified pine cone sample with  $100 \text{ cm}^3$  of cesium ion solution of concentrations 50, 150 and  $250 \text{ mg/dm}^3$  set at initial pH 8 to which either sodium ( $\text{Na}^+$ ) or calcium ( $\text{Ca}^{2+}$ ) ions of concentrations  $0.5 \text{ mg/dm}^3$  was added. The results of the kinetic study were then recorded as the percentage of  $\text{Cs}^+$  ions removal from solution at different time intervals. Figs. 4.26a-c, Figs. 4.27a-c, and Figs. 4.28a-c, showed the plots of percentage  $\text{Cs}^+$  ions removed at a given time interval for raw pine, toluene-ethanol treated pine and HCF modified pine cone at 50, 150 and  $250 \text{ mg/dm}^3$  respectively.

The figures revealed that for all samples, the percentage removal increased rapidly at the onset of the adsorption process and reduced gradually as time increased, and coming to an almost constant state at the end of the adsorption period. The figures showed that the competitive alkali metals reduced the percentage cesium removal from solution and the reduction was more for Ca interference than that caused by Na, this may be due to the charge and bigger atomic size of Ca compared to Na. The competitive effect of Ca and Na was more on the raw pine cone as compared to the toluene-ethanol treated pine cone and HCF modified pine cone.

Comparing the three pine cone samples at different concentrations, it was observed that the reduction in percentage removal of  $\text{Cs}^+$  ions was more for raw pine than for the toluene-ethanol treated and HCF modified pine cone. Comparing the three pine cone samples at different concentrations, 50, 150 and  $250 \text{ mg/dm}^3$ , it was observed that the  $\text{Cs}^+$  ions percentage removal reduced as the concentration of  $\text{Cs}^+$  ions in solution increased. An increase in  $\text{Cs}^+$  ion concentration reduced the cation competition. HCF modified pine cone was less affected by the cation competition for all concentration and the reduction in competitive effect reduced with an increase in concentration of the  $\text{Cs}^+$  ion present in solution. The results show that the HCF

modified pine cone is more selective and has high affinity for cesium removal than the raw pine cone and toluene-ethanol treated pine cone powder.

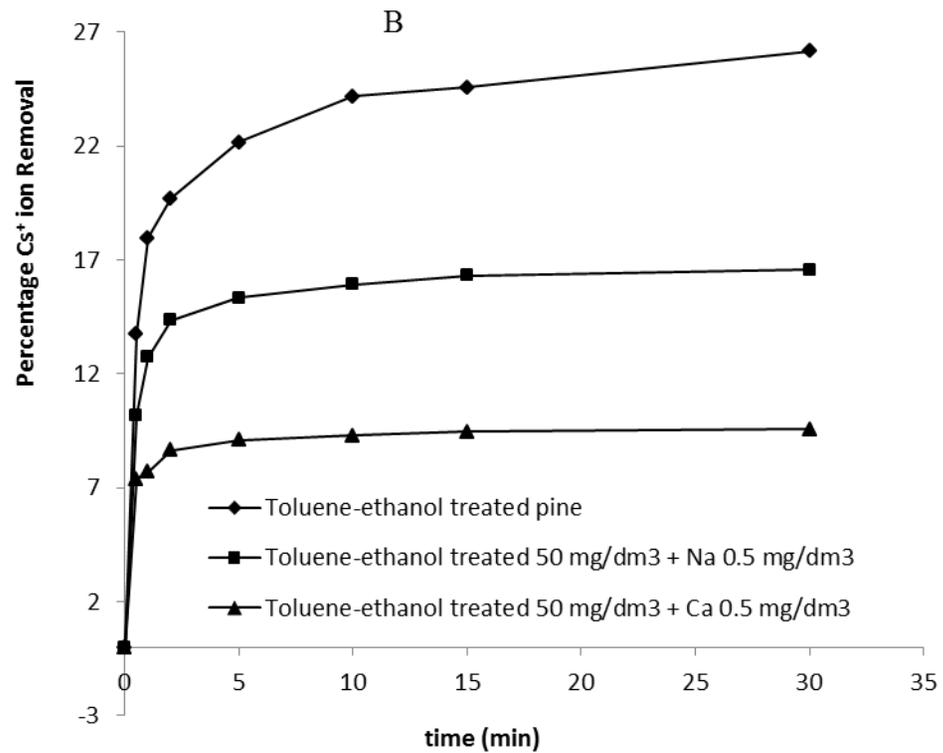
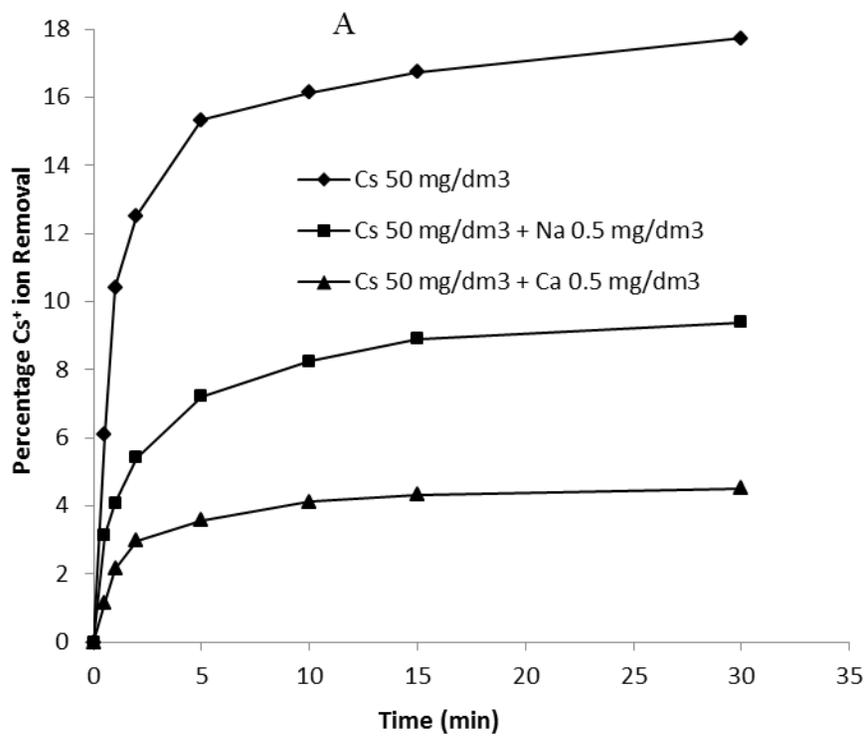


Fig. 4.26: (a) Percentage removal of Cs<sup>+</sup> ions from aqueous solution using 50 mg/dm<sup>3</sup> raw pine cone.

(b) Percentage removal of Cs<sup>+</sup> ions from aqueous solution using 50 mg/dm<sup>3</sup> toluene-ethanol treated pine cone.

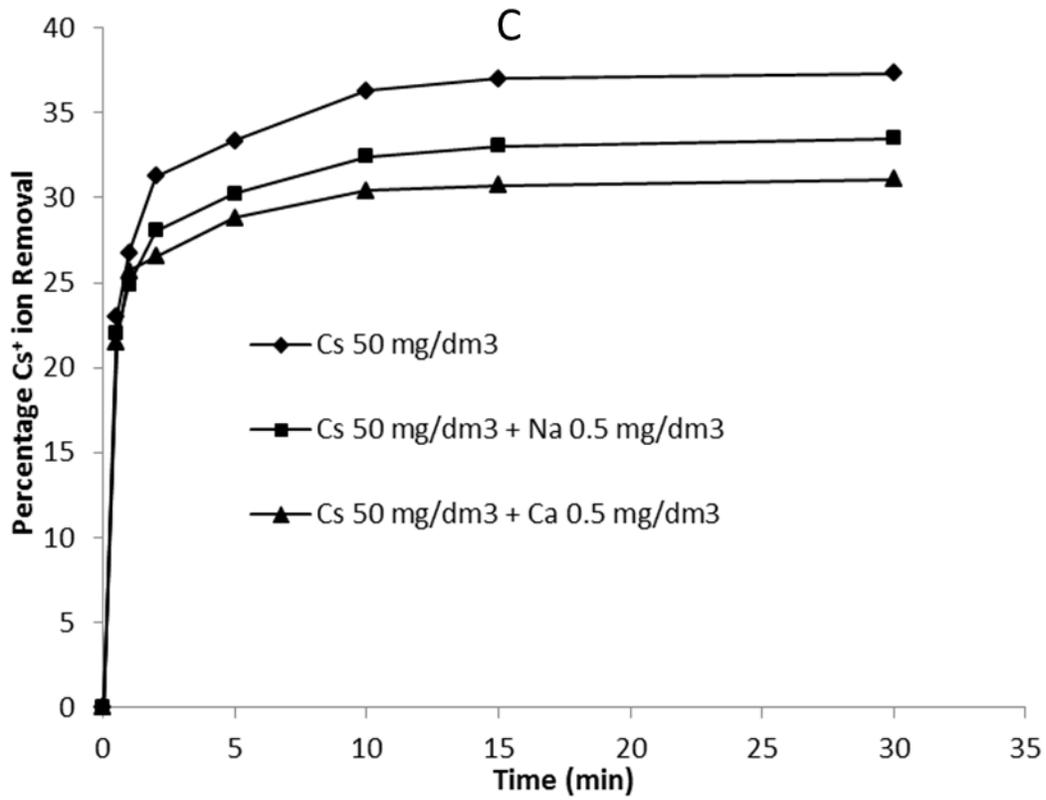


Fig: 4.26c: Percentage removal of Cs<sup>+</sup> ions from aqueous solution using 50 mg/dm<sup>3</sup> HCF modified pine cone.

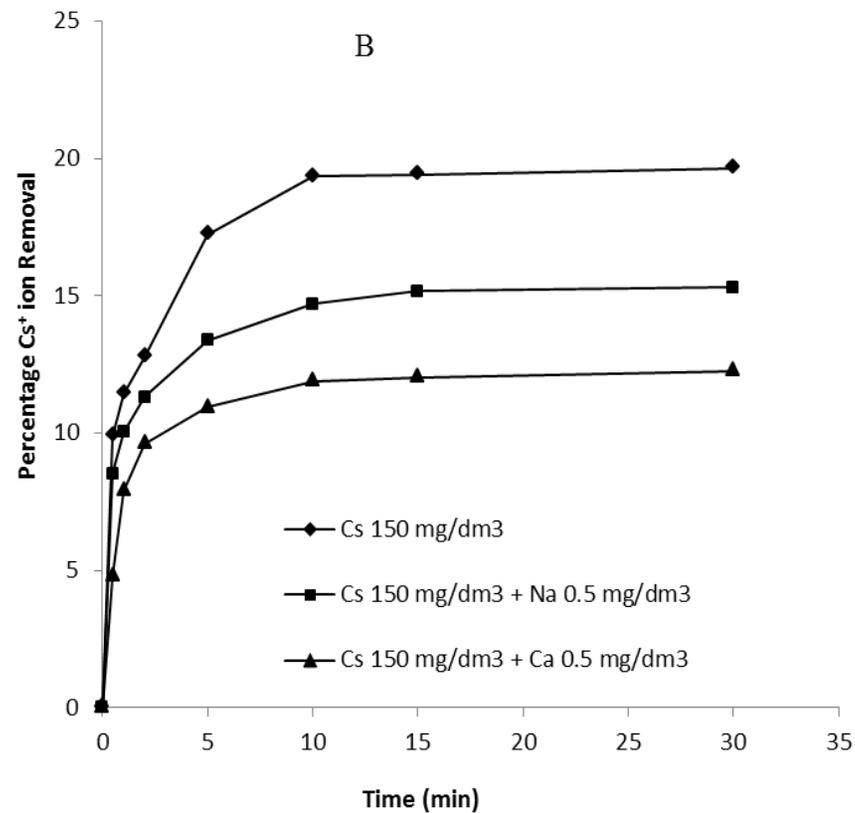
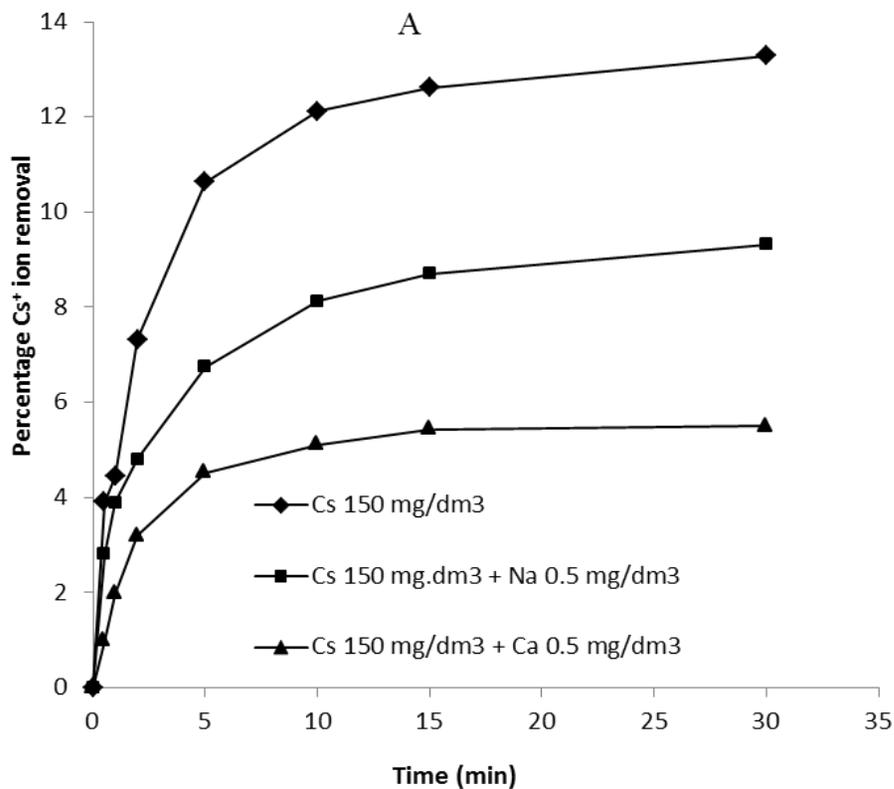


Fig: 4.27: (a) Percentage removal of Cs<sup>+</sup> ions from aqueous solution using 150 mg/dm<sup>3</sup> raw pine cone.  
 (b) Percentage removal of Cs<sup>+</sup> ions from aqueous solution using 150 mg/dm<sup>3</sup> toluene-ethanol treated pine cone.

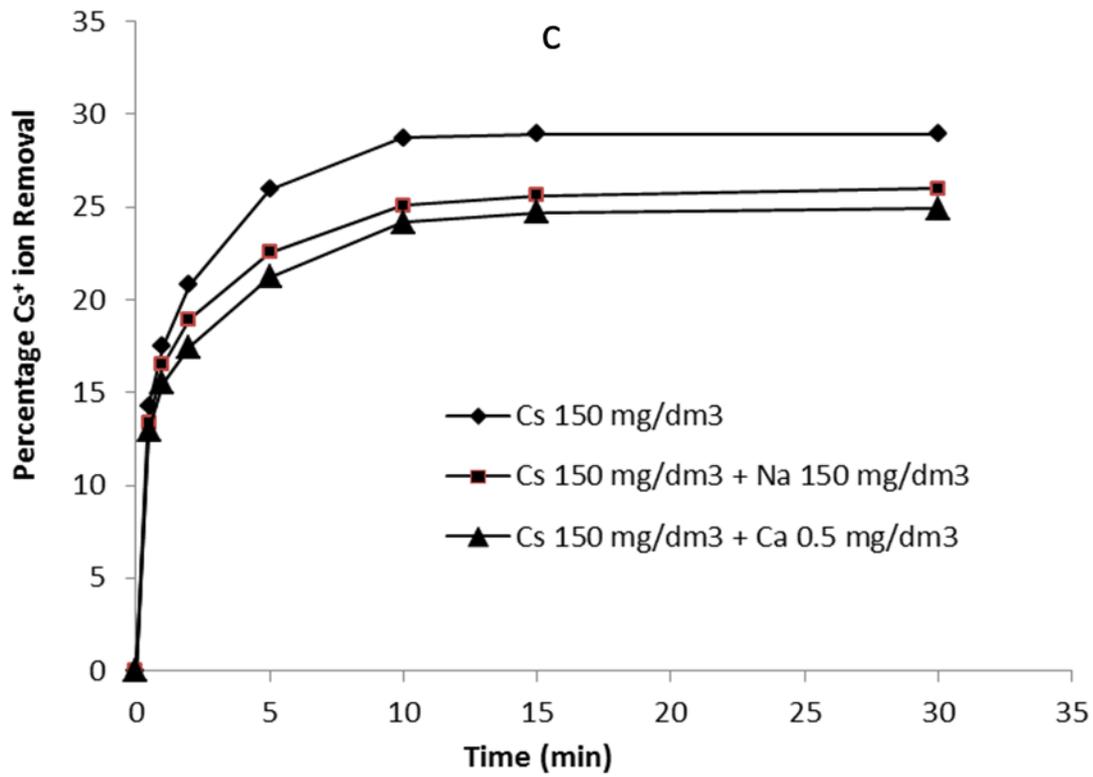


Fig: 4.27c:Percentage removal of Cs<sup>+</sup> ions from aqueous solution using 150 mg/dm<sup>3</sup> HCF modified pine cone.

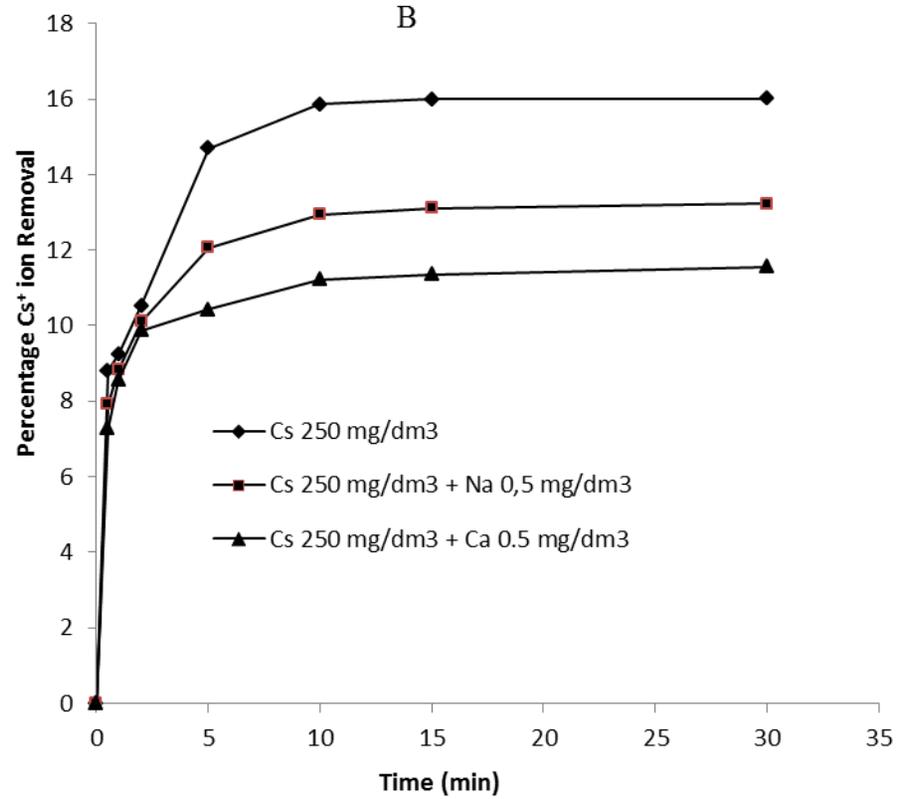
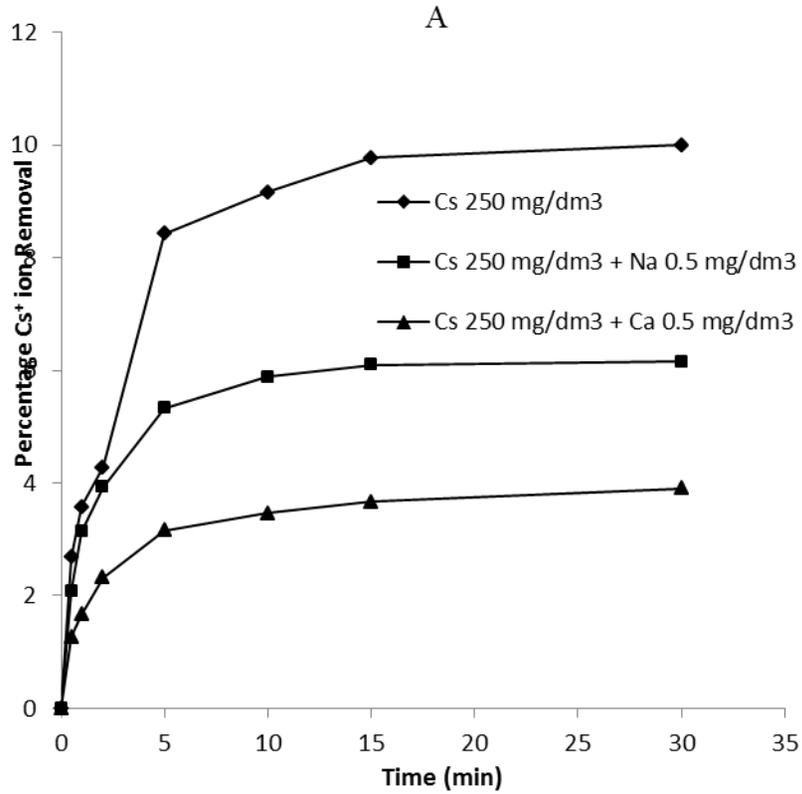


Fig: 4.28: (a) Percentage removal of Cs<sup>+</sup> ions from aqueous solution using 250 mg/dm<sup>3</sup> raw pine cone.

(b) Percentage removal of Cs<sup>+</sup> ions from aqueous solution using 250 mg/dm<sup>3</sup> toluene-ethanol treated pine cone.

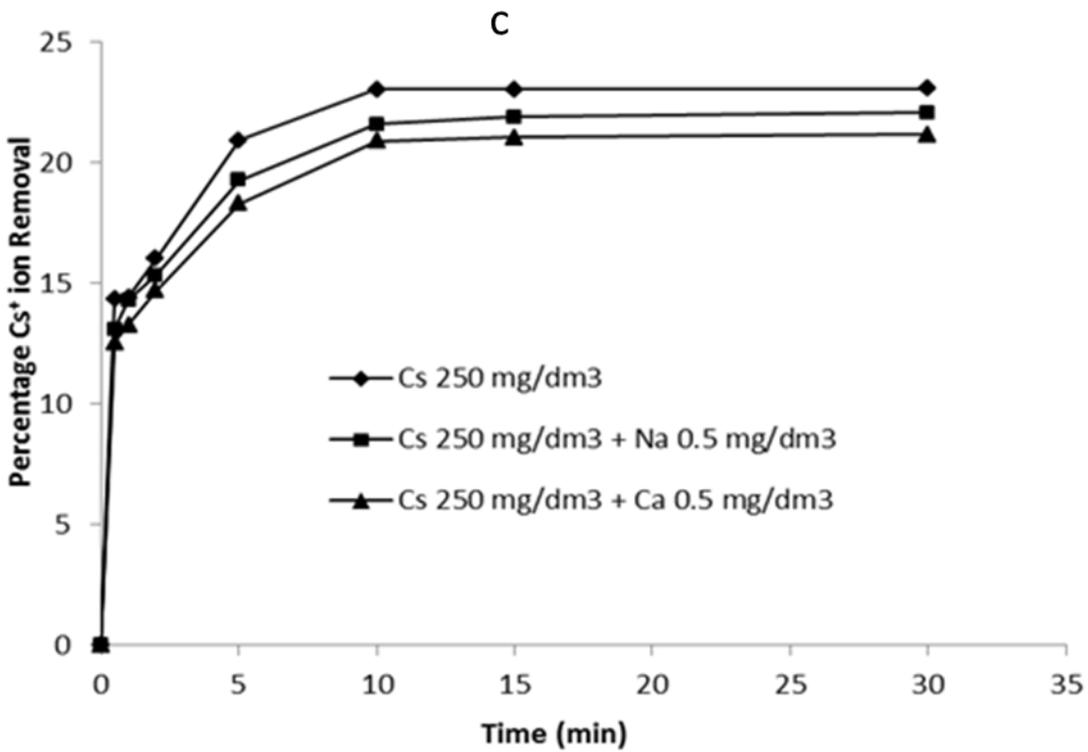


Fig: 4.28 c: Percentage removal of Cs<sup>+</sup> ions from aqueous solution using 250 mg/ dm<sup>3</sup> HCF modified pine cone.

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## CHAPTER 5

### 5.0 CONCLUSION AND RECOMMENDATION

#### 5.1 Conclusion

In this study toluene-ethanol treatment of the biosorbent surface was necessary to extract unwanted plant component and increase total surface area for interaction with the modifying agents. Decreasing the proportion of ethanol in the mixture improved the surface negative charge but reduced iodine capacity. Cesium adsorption was found to increase with increasing iodine capacity and reducing surface negative charge. Desorption studies revealed that cation-exchange accounts for a large percentage of the cesium binding mechanism. The 2:1, 8 h toluene-ethanol mixture was the best modifying procedure that gave the optimum biosorption properties. FTIR studies showed that there were changes in intensities of various peaks. FTIR studies before and after cesium adsorption revealed that unbounded -OH and acidic functional groups are responsible for the cesium binding.

The optimum solution pH for Fe(III) loading was found to be pH 8, and optimum concentration of Fe(III) solution was  $2.5 \text{ mg/dm}^3$ . HCF modification of the Fe(III) loaded pine cone surface was optimal at  $0.9 \text{ mol/dm}^3$  of HCF solution. The incorporation of FeHCF was confirmed by FTIR, TGA and XRD analysis. The preparation of FeHCF modified pine cone was successfully performed. The application of KFeHCF modified pine cone biosorbent showed higher effectiveness for cesium removal than the toluene-ethanol treated sample and the native pine sample.

FeHCF modification carried out on raw pine cone surface enhanced the ability of the adsorbent to remove  $\text{Cs}^+$  ions in the presence of alkali metals from aqueous solution. The pseudo first order kinetics could not accurately predict the experimental data; therefore, the adsorption of cesium onto pine cone is not likely controlled by film diffusion. It was found that the kinetic data fitted the pseudo-second and diffusion-chemisorption models. Therefore, removal of cesium onto pine cone is likely controlled by surface adsorption and internal diffusion mechanism. The

chemisorption diffusion model only accurately describes the experimental data after 5 min of contact whereas the pseudo second order describes the experimental data over the range of contact time. The application of the FeHCF modified pine cone for cesium removal from aqueous solution revealed that the FeHCF modified pine showed higher selectivity for cesium than the toluene-ethanol treated sample and the raw sample and it was not considerably affected by the presence of competitive cations. Finally a simple material for selective removal of cesium from aqueous solution in the presence of mixed alkali metals has been developed.

## **5.2 Recommendation**

FeHCF modified pine cone was found to be less affected by the presence of competitive cations. For this reason:

- Further studies should be done to explore the competitive effect of Ca and Na ion on tri and tetra-soluble solution since only bi-components solution was investigated.