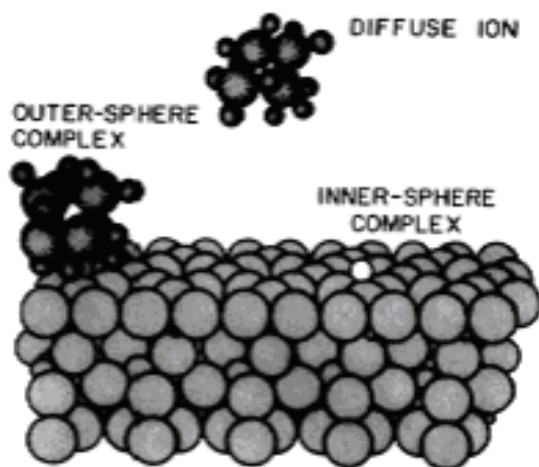


CHALMERS



Heavy Metals Adsorption by Fiber Ash

Master's Thesis in the International Master's Programme Applied Environmental Measurement Techniques

FRANCIS ETUTU NGOH

Department of Civil and Environmental Engineering
Division of Water Environment Technology
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden 2006
Master's Thesis 2006:74

MASTER'S THESIS 2006:74

HEAVY METALS ADSORPTION BY FIBER ASH

Master's Thesis in the '*Applied Environmental Measurement Techniques*'

FRANCIS ETUTU NGOH

Department of Civil and Environmental Engineering
Division of Water Environment Transport
CHALMERS UNIVERSITY OF TECHNOLOGY

Göteborg, Sweden 2006

Heavy Metals Adsorption by Fiber Ash

Masters Thesis in the '*Applied Environmental Measurement Techniques*'

FRANCIS ETUTU NGOH

© FRANCIS ETUTU NGOH, 2006

Master's Thesis 2006:74

Department of Civil and Environmental Engineering
Division of *Water Environment Transport*
Chalmers University of Technology
SE-412 96 Göteborg
Sweden
Telephone: +46 (0)31-772 1000

Department of Civil and Environmental Engineering
Göteborg, Sweden 2006

Heavy Metal Adsorption by Fiber Ash

Masters Thesis in the '*Applied Environmental Measurement Techniques*'

FRANCIS ETUTU NGOH

Department of Civil and Environmental Engineering

Division of *Water Environment Transport*

Chalmers University of Technology

Abstract

The problem of pollution by heavy metals is currently attracting global attention because of the deleterious effects it has on the environment and especially on human health. The prohibitive cost of the contemporary methods of their removal coupled with the fact that such methods are usually unsustainable has prompted the quest for environmentally friendly, sustainable, readily available and cost effective methods for the removal of heavy metals from contaminated wastewaters and soils.

Previous studies have been carried out on natural and rest-product materials but it was mostly comparative, trying to find out which of them adsorbs best. In this study, batch experiments are conducted with fiber ash to find out if it could be used to purify contaminated waters and the metals under consideration were Cd, Cu, Ni, Pb and Zn. During the batch runs, there was a manipulation of the different environmental parameters (pH, sorbate/sorbent mass ratio, metal concentration, mass of sorbent) to find how they influence the adsorption potentials of fiber ash.

Fiber ash was found to be efficient for all the considered metals at a neutral pH of 7.0 while poor adsorption at a slightly acidic pH of 5.6 was observed for Ni and Cd. The ash studied is recommended as an effective adsorbent for heavy metals at a neutral pH of the solution of the contaminated water.

Keywords: Fiber ash, adsorption, adsorption potentials, batch, pH

ACKNOWLEDGEMENTS

Very often people get favour or help but they fail to acknowledge it. Often too, people are over grateful. I do not know to which group I belong, but I know, for sure, I have one thing to say; I am overjoyed, Yuliya Kalmykova. Your immeasurable contribution, encouragement, expertise and ever-willing attitude to offer assistance culminated in the realization of this work. My thanks goes as well to my supervisor, Anne Margaret Strömvall.

My special gratitude extends to the Head of Department and my examiner, Prof. Greg Morrison for his fatherly considerations, constant assistance and encouragement. You gave me hope when I almost gave up hope. You made me belong.

I would also like to thank the staff of the Laboratory, Jesper Knutsson and Mona Zanders for their assistance during my lab work.

To my many friends who supported me morally and otherwise until the completion of this work, I am appreciative and will remember this for a long time to come. If I did not mention your name, well you know who you are.

Finally I would also like to thank my family, especially my late mum, who has always been there for me, to all whose love is undaunted, researchers of artificial intelligence.

To GOD, I extend my reverence, honour and praise.

Göteborg,
August 2006

Francis E. NGOH

TABLE OF CONTENTS

1	INTRODUCTION	1
2	REVIEW OF RELATED LITERATURE	4
3	THEORETICAL CONCEPTS.....	7
3.1	Adsorption Theory; Fundamentals.....	7
3.2	Potential of Ash as an Adsorbent Material	9
3.3	Factors affecting heavy metal adsorption on ash	11
4	METHODOLOGY.....	14
4.1	Outline of the study.....	14
4.2	Materials used	15
4.3	Experimental set up and Procedure.....	16
5	RESULTS AND DISCUSSION	18
5.1	Pilot experiment	18
5.2	Kinetic experiment.....	18
5.3	Reproducibility experiment.....	19
5.4	Adsorption of Cd, Ni, Pb, Zn and Cu.....	20
5.5	Adsorption of Cd at different initial concentrations	21
6	CONCLUSIONS AND RECOMMENDATIONS	22
7	REFERENCES.....	23
	Appendix I.....	27
	Appendix II.....	28

LIST OF TABLES

Table 1 Main Components in Fiber Ash and Fly Ashes.....	4
Table 2 Overview of selected studies in metal adsorption by different ashes including fiber ash.....	5
Table 3 Results of the Pilot Batch Experiment.....	18
Table 4 Reproducibility of the Results.....	19&20
Table 5 Adsorption of metals onto fiber ash at ph 5.6.....	20
Table 6 Adsorption of metals onto fiber ash at ph 7.0.....	20
Table 7 Adsorption of Cd at different Initial Concentrations.....	21

LIST OF FIGURES

Figure 1 Types of bonds involved in the adsorption of heavy metals to particulate surfaces.....	8
Figure 2 Flow chart of Experimental Procedure.....	17
Figure 3 Adsorption of metals onto fiber ash as a function of time.....	19

1 INTRODUCTION

Population expansion and increased industrialization have contributed to the release of increased heavy/trace metals content of many municipal wastewater treatment plant effluents and surrounding soils. Heavy metals discharged in wastewaters can be toxic to aquatic life and cause natural waters to be unfit as potable water sources. The ubiquitous nature of heavy metals, their toxicity even in trace quantities (for e.g. Cd damages the kidneys, Pb adversely affects red blood cells, the nervous system and the kidneys), their tendency for bioaccumulation in food chain, their non-biodegradability, their ability to undergo transformations, the economic impact and the stricter environmental regulations related to heavy metals discharges have prompted the development of processes for the removal of heavy metals from wastewaters and soils.

Contributions among many other sources come from facilities such as food processing industries, hospitals, printers, plastics and rubber, schools and universities, water treatment, metal fabrication and plating, battery manufacturing, photography shops, X-ray laboratories, leather tanning, paint etc., which are discharging heavy metals into the environment at an unprecedented and constantly increasing rate (P. Mavros et al., 1992).

Various methods for the removal of heavy metals from wastewaters include chemical precipitation, ion exchange, electro-dialysis, reverse osmosis, membrane filtration and absorption (R1). Adsorption, an all-encompassing term which we are going to employ in this study was one of the recognized efficient processes of heavy metals removal from aqueous solutions. In spite of the usefulness and effectiveness of alumina, silica, iron oxide and activated carbon as adsorbents of heavy metals, their prohibitive costs have restricted their widespread use. Therefore some studies have been carried out with the intention of developing new and especially cheap materials and sustainable adsorbents for the removal of heavy metals from wastewaters. These materials should have high affinity, selectivity and capacity towards metals. Fly ash was one of the materials that was extensively studied and approved as a good adsorbent. Its selection results in a two-fold benefit, i.e, the disposal of this ash which is a waste product and its usage as a low cost adsorbent for the treatment of wastewater and soils (Vinod K. G. et al., 2003).

Fiber ash, the main material of this study, is quite similar to fly ash in basic constituents but there are some slight differences in the percentages. The main constituents of ashes are SiO_2 , Al_2O_3 and CaO with fiber ash having a higher percentage of the latter. In one of the studies it was suggested that fly ash would be an even better adsorbent if its percentage of CaO increases. Fiber ash is a residual product of the production of toilet tissues, household towels, napkins etc of the SCA Hygiene Products in Sweden.

This project unlike most of the pioneer projects which were rather mostly aimed at rating the adsorbent potentials of some chosen natural materials for heavy metals, seeks to understand the contribution of the various parameters that influence adsorption by fiber ash (pH, sorbent mass, sorbate concentration while that of temperature was left out for technical reasons) using batch experiments for adsorption of the following heavy metals; *Ni*, *Cu*, *Zn*, *Pb* and *Cd*. This study sought to determine the optimal conditions for the selected parameters that would simultaneously give the highest removal of heavy metals with the lowest desorption. The experimental procedures were carried out at constant pH (either 5.6 or 7.0) in order to favour the adsorption of the metallic ions and to avoid precipitation within the milieu.

1.1.1 Background of the study

Fiber ash (used in this study) is a residual product of toilet tissues, household towels, facial tissues and napkins of the company SCA Hygiene Products AB. The main raw materials are wood and paper pulp. Basically, CaO, SiO₂, and Al₂O₃ are the three main constituents. This makes fiber ash similar to fly ash (from incineration plants) on which many adsorption studies have been carried out (Rio, 2002), the main difference being that the percentage CaO is much higher in fiber ash than in fly ash. Also, the presence of the mineral *Gehlenite* is what endows fiber ash with better adsorption qualities.

Previous investigations have been carried out in Chalmers to investigate the use of natural and rest-products materials as filters for metal-laden wastewaters and contaminated soils (Chauvet 2003, Kalmykova, 2004). This was prompted by the search for sustainable material (cost effective, environmentally sound and technically feasible) as against synthetic options which had prohibitive costs though efficient. This cost widely reduced the scale of application of these remediation methods. Precipitation, the commonest technology for metal expulsion falls below the stringent standards for the removal of toxic metals but the necessary polishing phases involves increased expenses to that of an already expensive sludge management (Pettersson, 1989; Brown et al., 2000a).

This project therefore sets to investigate the effect of the following; different environmental conditions, different metals, varying pH and varying adsorbent masses on the adsorbent properties of fiber ash as well as the contact time. It equally checks whether a mixture of fiber ash and peat will make a better adsorbent. The parameter, temperature, was not considered for technical reasons.

1.1.2 Objectives of the project

The objectives of this study are to carry out batch experiments with fiber ash in order to:

1. to check if ash could be used to purify contaminated soils and water
2. to find out how a manipulation of the different environmental conditions (pH, sorbate/sorbent mass ratio, metal concentration, mass of sorbent) influences the adsorption potentials of fiber ash

Pilot studies of fiber ash as an adsorbent showed its exceptionally high adsorption capacity compared to natural materials or even commercial adsorbents. Findings from this study will be a breakthrough in a greater project in the search for natural and rest products as possible alternatives for synthetic adsorbents based on sustainability and cost effectiveness.

1.1.3 Scope and Limitations of the Study

This study was purely laboratory based and results from previous study show that laboratory findings overestimated the adsorption efficiency of these natural rest-products as compared to when carried out in-situ. This pioneer study is aimed at finding out how a manipulation of the following parameters; pH, adsorbent mass, environmental conditions affect the adsorption potentials of fiber ash on the following five heavy metals, (*Cd, Ni, Cu, Zn and Pb*). Temperature was not included among these parameters for technical reasons. Langmuir and Freundlich adsorption isotherms were not empirically determined for the systems in the study but rather this information was extracted from previous literature.

In general, contaminated wastewaters contain more than one heavy metal. This study was done on single metal synthetic solutions which is a limitation because from the point of view of environmental protection, adsorption studies from multi-metal systems to which much work has been dedicated is imperative.

2 REVIEW OF RELATED LITERATURE

The study of fiber ash is relatively new and there is not much literature associated with it. However, many other types of ashes have been investigated for their sorption properties and adsorptive capacity on heavy metals (Bayat, 2002; Ricou-Hoeffler et al., 2001; Rio et al., 2002). Examples include fly ash, coal ash, bagasse, bottom ash etc. A large proportion of these literatures contained results of batch experiments for the following parameters; contact times, pH, metal concentrations, metal/adsorbent mass ratio, adsorbent/lime mixtures (Apak et al., 1998; Ricou-Hoeffler et al., 2000). In these studies, many authors reported the successful removal of copper, zinc, nickel, cadmium and lead. All these ashes are known to have basically these three main components; SiO₂, Al₂O₃ and CaO but their proportions vary (see Table 1 for their specific differences). These are also the three main components of fiber ash and therefore we can adopt the same results from fly ashes. Fly ashes in one of the studies were used for reducing trace metal concentrations in a wastewater treatment plant (Gupta and Torres, 1998) but generally there has been no in-depth investigation on the mechanism of adsorption of heavy metals onto fly ashes. The ability of fly ash to remove metal cations from wastewater has been demonstrated in many literatures (Bhattacharya and Venkobachar, 1984; Panday and Singh, 1985; Yadava et al., 1987) but for a limited number of metals. The mechanism or the removal was assumed to comprise of four steps (ref); (i) *surface precipitation* where most hydrolysable heavy metals are removed via co-precipitation of their insoluble hydroxides forming successive layers on the sorbent surface; (ii) *flocculation* by adsorption of hydrolytic products; formed on adsorbent surfaces as kinetic intermediates including [Fe₂(OH)₄]²⁺, [Fe₃(OH)₄]⁵⁺, [Al₄(OH)₈]⁴⁺ and [Al₈(OH)₂₀]⁴⁺ act as more effective flocculants than their parent ions due to their higher charge and strong specific absorptivities (iii) *chemical adsorption* based on surface complex formation, where metal ions are usually removed as uncharged hydroxides condensed onto the surfaces of -OH group bearing adsorbents ie, aluminium oxide, silica gel, ferric oxides and (iv) *ion exchange*, where the acid pre-treated sorbents may function as synthetic cation exchangers, (Apak et al., 1998).

Table 1. Main Components in Fiber and Fly ashes

	Fiber ashes	Fly ashes
	% TS	% TS
SiO ₂	28.9	44.9
Al ₂ O ₃	20.7	22.0
CaO	43.7	5.7

(Rio et al., 2002)

Several trends in the adsorptivity of the selected metals by ashes had been have been put forward by several authors and this depended on properties such as ionic size, redox potential etc. Depending on parameters such as ion exchange, chemical adsorption, surface precipitation or flocculation, a relative trend for the retention of the selected metals was proposed.

Generally, the experiments were carried out in single or multiple, natural or synthetic metal solutions. Many parameters were taken into consideration in the study for the adsorption capacities for the various types of ashes but it cannot be said with total certainty that this parameter is solely responsible for adsorption. Most of the parameters are linked and the process of adsorption is continuous. Majority of the literature quoted here are for other ashes as the adsorption study for fiber ash is relatively new and literature is limited. Many authors mentioned various parameters which include; calcium content, carbon content, pH, amount of adsorbent, initial concentration of metal, contact time, ash origin, the distribution ratios of the metals, inter-competition among metals, surface physical and chemical characteristics and processes such as ion exchange, chemical

reaction, etc. As earlier stated, most of these parameters and processes are interlinked, existing as a continuum, as will be noted later on.

Table 2 Overview of selected studies on metal adsorption by different ashes including fiber ash.

Author/year	Metals	C ₀ , mg/L	Time, hours	Experimental conditions/Relevant findings	pH	L/S, ml/g
(Mavros et al., 1993)	Ni	50	1/6	.time of final pH attainment depended on the amount of ash added .at lower mass of ash, addition of Ni ions into ash caused pH to drop	5.0 – 9.0 adjusted by adding H ₂ SO ₄	variable
Resat Apak et al., 1996	Cu, Pb, Cd	29	8	.hydrolytic metal precipitation reaction	7 – 12, not controlled	50
Julia Ayala et al., 1998	Cd, Cu	0.1-1.6	3	.metal cations hydrolyse with increase in pH .Cd and Cu removal capacity depended on pH	5.0 adjusted by H ₂ SO ₄ or NaOH	100
P. Ricou-Hoeffler et al., 2000	Ni, Cu, Zn, Cd, Pb	500	24	.adsorption increases with increase in sorbent .adsorption of Cu is endothermic	5.0 controlled by 1M HNO ₃	50
Chien-Jung et al., 2000	Cu	0.1M	3	.Cu removal could also be as a result of precipitation .Carbon fraction of ash influenced Cu removal at pH 5.	5.0 controlled by 0.1 HNO ₃	100
Belgin Bayat et al., 2002	Cr, Cd	55 Cr, 6 Cd	2	.Cd adsorption is greatest at pH 10	3.0 – 8.0 and adjusted by dilute 0.1 NaOH and HNO ₃	50
Belgin Bayat et al., 2002	Ni, Cu, Zn	25 Ni, Cu & 30 Zn	2	Removal of Ni & Zn increased with an increase of the metal initial concentration. .Removal of pollutants is pH dependent	3.0 – 8.0 and adjusted by dilute 0.1 NaOH and HNO ₃	50
Sebastien R et al., 2002	Pb, Cu, Cr, Ni, Zn, Cr	100	24	.Lime was added to increase stability of metallic ions	2.7 – 4.7 adjusted with 1M & 0.1M HCl	10
Young-Sook et al., 2002	Cu, Ni	100	6	.At reaction time 10mins, the bottom ash exhibits higher adsorption efficiency of Cu than that of Ni. .Adsorption rate of heavy metal increases with decreasing bottom ash particle size.	3.8 – 6.3	2 - 100
(Gupta and Sharma, 2003)	Zn	0.0003 - 0.003 M	24	.Adsorption increases with pH .50 to 60% of adsorption occurs within first one hour	1.0 – 6.0 and controlled by dilute NaOH and HNO ₃	10
P. Ricou-Hoeffler et	Ni	500	24	.Adsorption is influenced by pH, metal/adsorbent mass ratio and ash type	5.0 controlled	100

<i>al.</i> , 2000					by 10M NaOH and HCl 36%	
(Kalmykova et al., 2006)	<i>Pb, Cu, Zn, Cr, Cd</i>	1 – 10	2 – 4	.Grain size of adsorbent is an important factor in sorption. .Increase in pH increases the extent of precipitation .Adsorption is dependent on the <i>CaO</i> content	6 – 12 adjusted with 1M NaOH	20

3 THEORETICAL CONCEPTS

3.1 Adsorption Theory; Fundamentals

Adsorption has been defined by many authors but conventionally it is accepted as a phenomenon where molecules of the contaminants dissolved in water attach themselves to the surface of individual soil particles (McKay, 1996). In our case, the interaction of H^+ and metal ions between the solid fiber ash and the surrounding aqueous solution is the main focus. The surface attachment can be physical, chemical or exchange adsorption. Physical adsorption is caused by Van der Waals forces and is the easiest to separate because these forces are weak. It does not include the sharing or transfer of electrons and is essentially reversible. It has a low degree of specificity; thus adsorbed molecules are free to cover the entire surface of the adsorbent. A physically adsorbed molecule keeps its identity and upon desorption returns to the fluid phase in its original form. Chemical adsorption is formed by chemical bonding and requires significant efforts to separate. It is essentially irreversible. Chemically adsorbed species are fixed at specific sites and are linked to reactive parts of the adsorbent surface, confining the adsorption to a monolayer. The extent of chemical adsorption is dependent on the reactivity of the adsorbent and adsorptive (Jenny, 2006; Faust et al., 1987; Faust et al., 1988; Rouquerol et al., 1999). What is mostly obtained out in the field is actually an intermediate of physical and chemical adsorption, with both pore structure and reactive functional groups contributing to metal removal. Exchange adsorption is caused by the electrical attraction between adsorbate and the surface.

Metals exist in soil solutions as free metal ions, in soluble complexes with inorganic and organic ligands or associated with inorganic or organic colloidal material (Shuman, 1991). Examples of inorganic ligands in soils are anions (SO_4^{2-} , Cl^- , OH^- , PO_4^{3-} , CO_3^{2-}). Organic ligands include low molecular weight aliphatic, aromatic, amino acids and soluble constituents of fulvic acids. Colloidal particles include iron and manganese oxides, clay minerals and organic matter.

There are several processes that govern metal retention in soil. The removal of metal ions from aqueous solutions involves in principle the concentration of the solute on the solid surface governed by the following; precipitation, inclusion, adsorption, solid formation which are all distinguished by the type of association between metal and host mineral (Sposito, 1989). As adsorption proceeds, solutes are simultaneously adsorbed and desorbed. Eventually the rates of both processes will attain an equilibrium state called the adsorption equilibrium. At equilibrium, no change can be observed in the concentration of the solute on the solid surface or in the bulk solution. The position of equilibrium is characteristic of the entire system and is independent on the solute, adsorbent, temperature and pH among others (Faust and Aly, 1987). During this process therefore, metals can precipitate as pure solids; $CdCO_3$, $Pb(OH)_2$, ZnS_2 , or co-precipitate producing mixed solids, e.g. $(Fe_xCr_{1-x})(OH)_3$ or the occurrence of solid formation when metals are compatible with the host elements and can replace them throughout the mineral, example as in the substitution of Cd for Ca in $CaCO_3$. Metals have been shown to be able to adsorb onto organic matter, clay minerals, iron and manganese oxides and hydroxides, calcium carbonates and amorphous aluminosilicates, the organic matter in this case consisting of biochemicals and humic substances. They provide acid functional groups, carboxylic, phenolic, alcoholic and amino groups as adsorption sites.

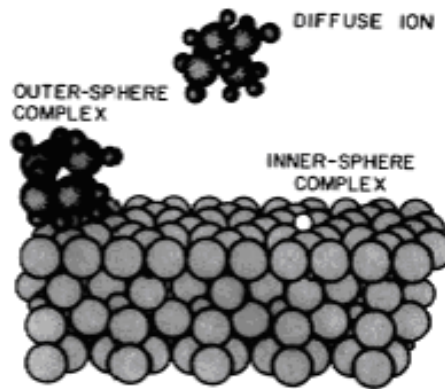


Figure 1. Types of bonds involved in the adsorption of heavy metals to particulate surfaces (Sposito, 1989).

Sorption is the general term used to describe the distribution of a substance in a media, between the solid and a dissolved phase, assuming that precipitation does not occur (Christensen, 2002). The substance sorbed is called *sorbate* and the media on which the phenomenon occurs is called *sorbent*. Sorption comprises two processes which are different from each other from a chemical/physical point of view; *Absorption*, which refers to bonding within the solid structure of the sorbent, and *Adsorption* which is the bonding to the surface of the particles. In this study, we are going to use the terminology “adsorption” though no insistence will be made on their difference.

Sorption to mineral surfaces and complexation by humic substances are two important processes influencing the cycling of potentially toxic trace metals in the environment (Adriano, 2001). In general, the bioavailability and mobility of trace metals depends strongly on chemical speciation. The toxicity of a metal is commonly directly proportional to the activity of the free metal ion. The mobility of trace metals in soils and aquatic environments is controlled mainly by their distribution between immobile solid phases, mobile colloidal particles and dissolved species (Kretzschmar et al., 1999). A quantitative assessment of the sorption behaviour of trace metals in aqueous systems containing clays and humic substances is therefore essential for understanding the biogeochemistry of trace metals.

Removal of heavy metals from water is possible by a number of processes such as chemical precipitation, ion exchange and others earlier mentioned. Adsorption is just another effective and selective process, capable of removing low metals from solutions. Sorption (adsorption) is related to three processes of the soils; Permanent negative charges, pH dependent charge of the surface and Adsorption of hydrophobic compounds. Permanent negative charge is usual for clay minerals and weakly soluble salts arising from “broken bonds” on the crystal surface and isomorphic substitutions. For example, Al^{3+} can substitute for Si^{4+} in a silica oxide, Mg^{2+} and Fe^{2+} ions can substitute for Al^{3+} in aluminosilicate clays resulting in permanent negative charge. pH dependent charged surfaces are associated with the edges of clay minerals, surfaces of oxides, hydroxides and carbonates and with organic matter. The charge arises from the association and dissociation of protons from surface functional groups. Negative charges are then produced due to dissociation at higher pH values. At low pH values, functional groups accept a proton, resulting in neutral or positive charged ions. For all pH dependent charged surfaces, as the pH decreases, the number of negatively charged sites also decreases. Under more alkaline conditions, the majority of sites will be negatively charged. On the other hand, adsorption of hydrophobic compounds is thought to be relevant for fulvic and humic acids. Their hydrophobic groups can bind to a particle surface while hydrophilic groups can serve as adsorption sites.

Metal adsorption behaviour is often described by a surface complexation model. (see figure 1). The three different complexes or bonding between metals and solid surface that can be formed are as illustrated in figure 1 above. Metals in diffuse ion association or in outer sphere complex are surrounded by coordination and are not directly bonded to the surface. These types of bonds represent “non specific” sorption when bonding is general and is related to the electrostatic strength; the attraction between dipoles. These reactions are rapid and reversible with only weak forces depending on the electronic configuration of the surface group and the adsorbed ion. They are therefore in exchangeable state or defined as “non-specific” sorption. Metals associated with exchangeable sites may, depending on the environment, be relatively mobile (Yuliya, 2004; Chauvert, 2003; McLean, 1992)

In inner sphere complexation, the metal is bound directly to the surface by an ionic and/or covalent binding, which implies a much higher bonding energy than in non-specific sorption. This adsorption mechanism is often called specific sorption because it depends on the electronic configuration of both metals and surface. At low concentrations, metals are adsorbed to the specific adsorption sites. With increasing concentration of the metal, the specific sites are saturated and the exchangeable sites are filled and become potentially mobile: affinity of metals for an adsorbent surface being concentration dependent.

3.2 Potential of Ash as an Adsorbent Material

The suitability of fly ash as an adsorbent for heavy metals ions from aqueous solutions has been examined by several authors (Ayala et al., 1998; Bayat, 2002). There is little literature on the adsorptive potentials of fiber ash but since it has the same composition as many of the studied fly ashes that have been proven to be able to adsorb heavy metals, it can be reasonably assumed that the same process of adsorption occurs with it. Basically, CaO (44%), SiO₂ (30%) and Al₂O₃ (21%) are the main constituents and this makes it very similar to fly ashes from incineration plants that have already been studied for their adsorptive properties (Rio, 2002). However as illustrated in Table 1 above, CaO is in a bigger proportion in fiber ashes than in typical fly ashes. Previous studies showed that fly ashes with higher CaO content would have a better adsorption capacity (see explanation in equations 2 & 3). It would be reasonable therefore, to imply that fiber ash can be even a better adsorbent than fly ash.

Most of the previous studies agreed that metal ions might adsorb on ash because of its high content of silica and alumina. These are present on the surface of ash as the functional group oxidized as SiO₂ and Al₂O₃. The silica surface is known to have a high affinity towards metal ions (Bayat, 2002; Gangoli et al) but the central ion of silicates (Si⁴⁺) has a strong affinity for electrons. Therefore the oxygen atoms that are bound to the silicon ions have a low basicity, causing the silica surface to act as a weak acid. The oxygen atoms react with water forming surface silanol (SiOH) groups. The acidity of these groups determines the dependence of the charge of silica surface on pH. This makes ashes a strong alkali material when added to water. At low pH, a positively charged silica prevails and at high pH a negative surface dominates. Fiber ash has higher percentage CaO (CaCO₃) content and this makes fiber ash a strong alkali material when added to water. Accordingly therefore, maximum adsorption of metals is observed at pH range 6-8 and therefore it can be expected that metal ions can be removed from aqueous solutions by *precipitation* and *electrostatic adsorption* since pH range (6-8) is known to contribute to the electrostatic interaction of the adsorbate with the surface, silicate, alumina and iron sites. Metal adsorption ions through SiO₂ bond may also involve the aminosilicates in ashes as shown below (Ricou-Heffer et al., 1999)



Ashes with high CaO contents are thought to have higher adsorption efficiency due to the formation of Ca and Si complexes such as Calcium silicates ($2\text{CaO}\cdot\text{SiO}_2$)

In neutral solutions;



In alkaline solutions;



Recent studies using Scanning Tunneling Microscope (STM) have pointed to the presence of Gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) in fiber ash. The elements present in gehlenite include Al(19.68%), Ca(29.23%), O(40.84%), and Si(10.24%) in the following proportions SiO_2 (21.91%), Al_2O_3 (37.19%), CaO (40.90%). Looking from the constituents of fiber ash as shown in table 1 and the aforementioned for gehlenite, there is a great similarity not only in the basic constituents but also of the percentage composition, making it the most prominent adsorption determining component in fly ash. X-ray diffraction of ash showed the presence of the following compounds in descending order of magnitude beginning with Gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$), Anorthite($\text{CaAl}_2\text{SiO}_8$), Calcite(CaCO_3), Calcium Silicate(Ca_2SiO_4), Potassium aluminium oxide(K_3AlO_3) and Wollastonite(CaSiO_3).

Gehlenite is a very interesting compound from a crystal-chemical point of view. Mineralogically, amorphous gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) is prepared by solid-state reaction of kaolinite with CaCO_3 and aluminium hydroxide. Kaolinite [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$] is a type of clay, an aluminosilicate hydrate. Recent studies index gehlenite (a layered-structure of the CaO- Al_2O_3 - SiO_2 system) as having showed high heavy metal ion uptake ability and a maximum sorption for Ni^{2+} (Jha et al., 2004). It showed high uptake selectivity for transition metals that makes it an effective candidate for the uptake of heavy metal ions from wastewaters. Also, layered-structures are thought to be more suitable than other structures as host materials for cation uptake because the release of the host cations may occur more readily and efficiently from the layered structures. Also, the fact that Ni^{2+} uptake capacity in one of the studies increases linearly with the basicity i.e. pH, is an indication that the presence of CaO in layered structures plays a major role in the uptake of Ni^{2+} from an aqueous solution.

Adsorption of metal ions from aqueous solution onto oxides and clay minerals has been a subject of interest in chemistry, geology and environmental sciences as well as other research areas. Clays are known for their ability to effectively remove heavy metals by specific adsorption and cation exchange in solution. They are fine particles with large surface reactivities and large surface areas. These particles have a diameter less than $1\mu\text{m}$ with a significant percentage of their atoms at the particle surfaces. The importance of surface properties in this case increases in proportion to the surface area of the clay particles and to its surface charge density or number of charged sites per unit area or weight. The three (3) causes for surface charge of clay being generally negative include; 1) isomorphous substitution in the crystal lattice – Al^{3+} replacing Si^{4+} in the tetrahedral layer or Mg^{2+} replacing Al^{3+} in the octahedral layer, 2) lattice imperfections or defects such as deficit in the octahedral Al^{3+} or interlayer K^+ which leads to net negative surface charge and 3) broken or unsatisfied bonds at crystal plate corners and edges which lead to the ionization of surface groups, usually resulting in a net negative surface charge due to exposed O^{2-} and OH^- . This is the chief source of surface charge for gehlenite.

Different uptake mechanisms have been reported of heavy metal ions by clay/aluminosilicate hydrates depending on the pH. Kaolinite (gehlenite) is a 1:1 clay mineral type with a chemically

simple structure; the tetrahedral sites are occupied by silicon and the octahedral sites by aluminium. The tetrahedral sheet carries a small permanent negative charge due to isomorphous substitution of Si^{4+} by Al^{3+} , leaving a single negative charge for each substitution. Both the octahedral and the crystal edges have a pH-dependent variable charge caused by protonation and deprotonation of surface hydroxyl groups. Thus tetrahedral sites of kaolinite become permanently negatively charged and allow electrostatic interaction with positively charged ions. Actually it is the layer edges where the OH groups exhibit acid-base behaviour which is primarily and predominantly responsible for interaction with heavy metals. Cation adsorption mainly occurs on proton-bearing surface functional groups such as silanols and aluminols via covalent bonding. Also the organic component of kaolinite may be responsible for some heavy metal retention but not of any significance. Confirmation of the occurrence of ion replacement reaction of Ca^{2+} by Ni^{2+} has been reported with emphasis on the fact that it is not an exchange reaction since the reverse reaction does not occur (Jha et al., 2004; Okada et al., 2003). Ni^{2+} is thought to condense on the fiber ash (gehlenite) surface by ion replacement with Ca^{2+} . This is what obtains at lower pH but at higher pH, precipitation is said to dominate. Metal adsorption decreases with decreasing pH reason being that the increasing H^+ ion concentrations compete more effectively with fixed metal cation concentrations for adsorption sites on gehlenite. With the isomorphous substitution of tetrahedral Al^{3+} for Si^{4+} , there is the creation of a negative charge within the lattice. Therefore, mono and divalent cations are weakly held and readily exchangeable, hence the occurrence of cation exchange which could be almost pH independent.

An increase in the pH of natural systems tends to favor the removal of most trace elements (especially cations) from solution. Their removal is usually by adsorption and or precipitation in solids that become insoluble with increasing pH. The adsorbing solid may already be present in the waste water or may be solids that have precipitated, such as metal carbonates and Al, Fe(III) and Mn(IV) oxyhydroxides. The trace elements may precipitate in their own pure solids, but most often are coprecipitated as trace species in their own pure solids.

It is maintained that heavy metal and ligand adsorption onto clays occur as a result of ion exchange, surface complexation, electrostatic interaction and hydrophobic interaction. Gehlenite's presence in one study with waste ash was known to decrease the amount of Pb leaching and its introduction into this through an inorganic matrix with silica content was encouraged. Therefore its existence in ash is a plus.

Because clays are able to exchange their alkali metal cations with protons, they are said to be efficient scavengers for heavy metals and this therefore makes fiber ash an efficient adsorbent (Stumm, 1992).

3.3 Factors affecting heavy metal adsorption on ash

The extent of heavy metal adsorption on fiber ash is a product of many factors combined. These factors include ; kinetics, pH, adsorbent nature, grain size distribution of the ash, temperature, clay, organic matter, redox potential, iron and manganese oxides and calcium carbonate content (Sposito, 1989; Chauvert, 2003; Yuliya, 2004).

Adsorption is a rapid process that can be described by an equilibrium equation. A kinetic investigation is recommended to avoid too short or unnecessarily long contact time between solid and liquid. It depends on temperature but unfortunately for logistical reasons, the thermodynamics aspect of this study was not delved into.

3.3.1 pH

The number of adsorption sites on fiber ash is pH dependent. Several studies have shown that cationic metal adsorption increases with pH (Harter, 1983). This as a matter of fact only occurs when the pH is greater than 7, the reason being partly due to preferential adsorption of the hydrolyzed metal in comparison to the free metal ion, nature of bonding and surface variable charges. Also, the proportion of the hydrolyzed metals increases with pH as seen in the hydrolysis of Cu occurring at pH6, Cd at pH8 and Zn at pH5.5. pH also impacts on adsorption sites which are known to be pH dependent. As pH reduces, the number of negative sites reduces. Also, as pH becomes more acidic, metal cations have to compete for available negatively charged sites with Al^{3+} and H^+ .

The effect of pH on metal cation adsorption is principally the result of changes in the net proton charge on particles. As pH increases, the amount of H^+ (and its associated positive charge) decrease and the electrostatic attraction of the adsorbent for a metal cation is enhanced (Sposito, 1989). pH is a very important parameter to control during batch experiments.

3.3.2 Initial concentration

Another significant factor influencing adsorption on ash would be the initial concentration of the metals in the aqueous solution. Literature from previous studies attests that the greater the initial concentration, the longer the contact time required for the removal of these metal contaminants. However, this does not mean that equal initial concentration for different metals implies that they will be equally removed from solution, quantity wise (Jenny, 2006).

3.3.3 Redox Potential

A chemical reaction in which electron transfer takes place is called a reduction-oxidation (redox) process. The redox potential of a system is the measure of the electrochemical potential or availability of electrons within the system (Sposito, 1989). A metal is said to be “reduced” when it gains electrons and loses in valency, while it is said to be oxidized when it loses electrons and gains in valency. Since most trace/heavy metals have more than one oxidation state they are said to be directly affected by changes in redox potential of the matrix. Anaerobic conditions often lead to reduction while aerobic leads to oxidization and so therefore, redox potential is closely related to microbial activity.

Redox reactions greatly affect contaminant transport in slightly acidic to alkaline conditions. For example, Fe(III) precipitates as a high adsorptive solid (Ferric hydroxide), while Fe(II) is very soluble and does not retain other metals. Generally therefore, oxidizing conditions favor retention of metals while reducing conditions accelerate migration.

3.3.4 Presence of cations

Alkaline and earth-alkaline metals such as Na, Ca and Mg together with NH_4^+ , Fe^{2+} and Mn^{2+} compete with heavy metals for adsorption sites, especially for non-specific sites. The contrary seems to be true for specific sites as trace cationic metals enjoy preferential adsorption over major cations and so also for trace anionic metals over major anions (SO_4^- , NO_3^-). However, when such specific sites are saturated, exchange reactions dominate and competition for these with major ions becomes important, e.g. Cu, Cd, Pb and Ni compete Ca (Harter, 1992; Yuliya, 2004). Also, there is competition among trace metal for adsorption sites such as Cu which is known to interfere with the adsorption of Zn and Cd (Kuo and Baker, 1980). The presence of competing metals is another

factor affecting adsorption. The preference by fiber ash for adsorption of one metal over another has been investigated by a few authors and properties such as electronegativity, ionic radius and redox potential are said to be of great influence.

The grain size distribution of the adsorbent (fiber ash) is an important factor as it represents the surface area of contact between the aqueous and solid phases. Generally, the smaller the grain, the higher the contact area as well as the number of adsorption sites. This would mean that the smaller the grain size, the higher the adsorption capacity.

3.3.5 Complex formation

Metal cations are known to form complexes with inorganic and organic ligands resulting in complexes with lower positive charge and free metal ions that may be uncharged or negatively charged. This decrease in positive charge of the complexed metal reduces adsorption to a negatively charged surface but there is an exception to this rule; this being the preferential adsorption of hydrolyzed metals (MeOH^+) vs the free bivalent metal (James and Healy, 1972). For example, the presence of Cl^- and SO_4^{2-} inhibit the adsorption of Cd, Ni, Cu and Zn to form complexes with Cl^- that decrease their adsorption (Hirsch et al., 1989). Also, high phosphate levels inhibit adsorption of Cu and Zn.

4 METHODOLOGY

4.1 Outline of the study

The study comprised:

1. Pilot batch experiment
2. Kinetic experiment
3. Reproducibility experiment
4. Adsorption studies for Cd, Ni, Zn and Cu at pH 5.6 and 7
5. Adsorption of Cd at different initial concentrations

4.1.1: Pilot batch experiment

Pilot experiment was conducted to decide amount of ash and metal to be used in the following experiments. A batch experiments with 0.1, 0.2, 0.3, 0.5, 0.75, 1 gram ash and 0.5L of 100 μ g/L Cd, in 0.02M acetate buffer of pH 5.7. pH was adjusted manually with HNO₃ and experiment was run for 12 hours. The aim of this pilot batch experiment carried out by Julia was to determine the mass of adsorbent and the initial concentrations of the synthetic metal solutions appropriate for use through out the experiment. The synopsis of reviewed literature as projected by table 2 was a guiding tool.

4.1.3: Kinetic experiment

Kinetic experiment was conducted to decide time needed to reach adsorption equilibrium. batch experiment with 0.1 g ash and single metal solution of Pb, Zn, Cu, Ni, Cd 100 μ g/L was run for 24 hours and samples taken after 0.5; 1; 2; 3; 4; 6; 7; 10; 24 hours. Acetate buffer solution of pH 5.6 was used.

4.1.4: Reproducibility

This is the repetition of a chosen experiment and it is generally done three times and the mean value is noted. The reasons for reproducibility experiments are, first of all to demonstrate that the material is homogeneous enough for only one tests to be done through out the laboratory experiments, that the materials will behave the same if subjected to the same conditions and that the laboratory procedure is accurate. This would imply that the results have proven to be the same even if done in another laboratory since the values are accurate enough, valid and representative.

4.1.5: Adsorption studies for Cd, Ni, Zn and Cu at pH 5.6 and 7

Limited literatures exist for adsorption studies on fiber ash as it is a relatively new material under study for its adsorptive potentials with respect to cost effectiveness and sustainability. Since fly ash has same basic constituents as fiber ash and much has been researched on it, an extrapolation of the parameters applied for fly ash was made to fiber ash. Based on our review of such literatures, we selected pH 5.6 and 7.0, both of which are fairly acidic and basic conditions, but most especially are the commonly existing ones. The Following experiments were conducted with 0.1, 0.2, 0.3, 0.4, 0.5 gram ash and 0.5L of 100 μ g/L metal, in 0.02M acetate buffer of pH=5.6 and 0.02M phosphate buffer of pH=7. The pH was adjusted manually with HNO₃ and NaOH. The experiment was run for 6 hours. The differences in their adsorptive capacities under these two pHs and the implications of these differences will be better x-rayed in the next chapter.

The removal of pollutants (heavy metals) from contaminated waters and soils by adsorption is highly dependent on the Ph of the solution, which affects the surface charge of the adsorbent, and

the degree of ionization and speciation of the adsorbate (Panday et al., 1985; Weng et al., 1990). Apparently therefore, the amount of metal removal by adsorption increases with an increase in pH level for up to about pH 8.0 for Ni(II), pH 7.0 for Zn(II) and pH 6.0 for Cu(II). These results correspond to the pH values at which the maximum removal is observed under equilibrium conditions. To avoid precipitation of the metal ions therefore, all the experiments were conducted at pH values less than 8.0. pH 5.6 and 7.0 to be precise were the selected pH.

4.1.6: Adsorption of Cd at different initial concentrations

There may not be any particular reason for the choice of Cd for adsorption experiments at various or different initial concentration. However it is worth noting that Cd is the most toxic among the 5 trace metals under study. The rationale for such a study is in consonance with the study objectives, one of which remains “finding out how a manipulation of metal concentrations influences the adsorption capacity of fiber ash”.

4.2 Materials Used

4.2.1 Characterization of Fiber ash adsorbent.

Fiber ash was characterized in a previous related study (Claire Chauvert, 2003). Ash is the rest product from recycled paper production, wood and paper being the main raw materials. Basically CaO, SiO₂ and Al₂O₃ are the three main constituents though it contains some amounts of various metals particularly Ba, Cr, Cu, Ni, Pb, S, Sr, Zn and Zr. It has a pH of 12.6 in nanopure water, making it a strong alkali when mixed with water. It has extremely low hydraulic conductivity of about $1 \cdot 10^{-11}$ m/s. See Appendix 1 for a complete table of its constituents as analyzed by the company SCA Hygiene Products AB.

4.2.2 Characterization of Peat adsorbent

This had also been conducted previously for a related study (Kalmykova et al.) and the material for this experiment was sphagnum peat of the same batch. It had a pH of 4.02 in nanopure water, humification degree H3, water content 77.5%, bulk density 0.0955 g cm⁻³, saturated hydraulic conductivity 0.034 cm min and cation exchange capacity of 30.85 meq/100g. The humic substance composition was 78% humic acid and 22% fulvic acid.

4.2.3: Stock Solutions used

The synthetic metal solutions or stock metal solutions for this study were prepared by dissolving nitrate salts for each of the prioritized metals (Cu, Cd, Ni, Pb and Zn). All the chemicals were of analytical reagent grade and were obtained from Merck, Germany.

4.2.4: Buffer Preparation

Chemicals:

-Acetate buffer (pH 5.6): Potassium acetate and acetic acid

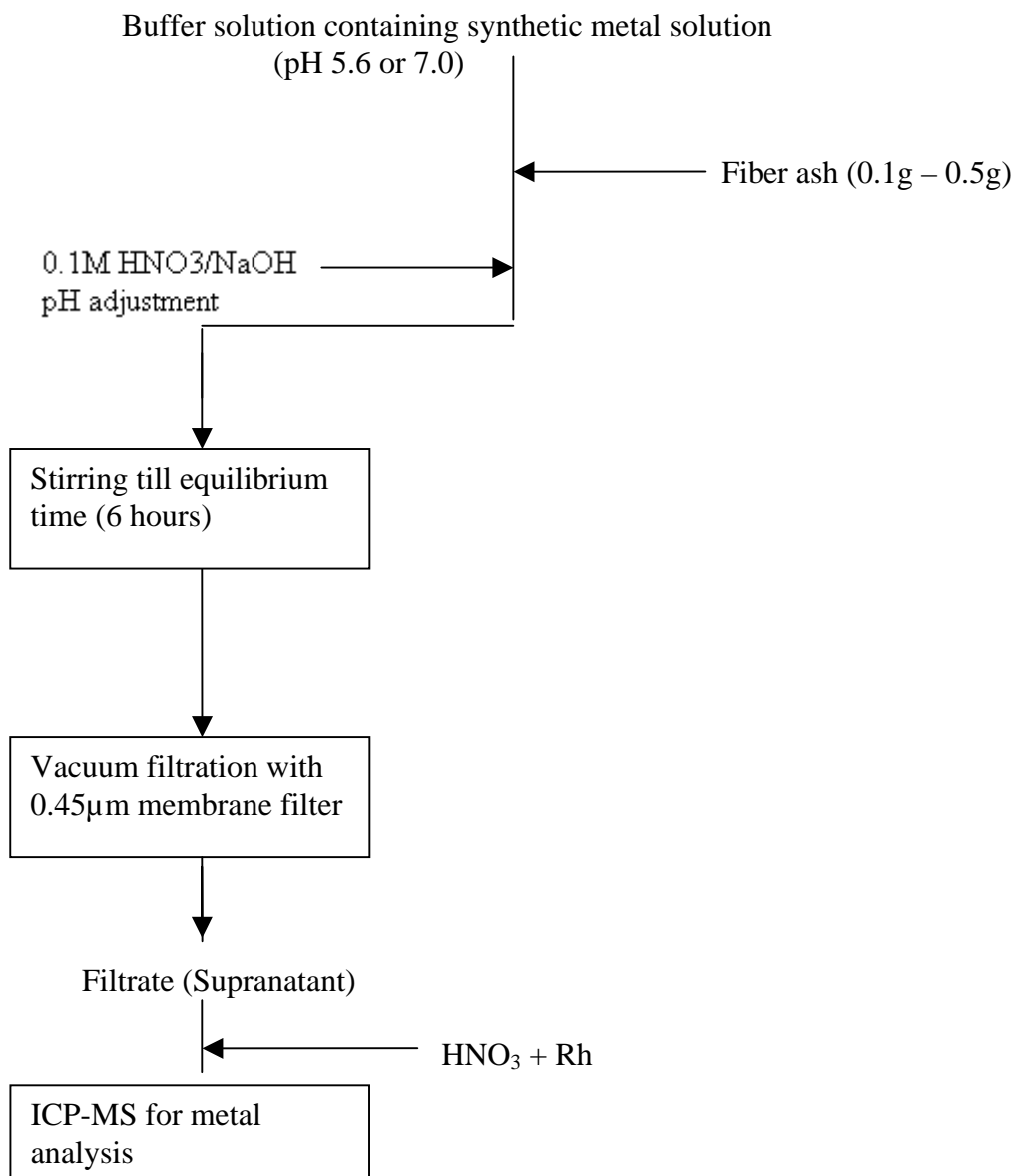
-Phosphate buffer (pH 7.0): Na₂HPO₄, HNO₃

4.3 Experimental set up and Procedure

Sorption studies were done in this case to evaluate the heavy metal retentive capability of fiber ash as well as a peat-ash mixture. These studies could also be used to generate adsorption coefficients for the fiber ash as well as the peat/fiber ash mixture. The set up in our case was basically a batch experiment, which consist of a number of flasks in which are put adsorbent, adsorbate and buffer solutions. Batch adsorption experiments were conducted to investigate the adsorptive characteristics and capacity of fiber ash. The principle of a batch experiment involves the placing in these beakers known mass of adsorbent with adsorbate (metal) solution of recorded initial pollutant concentration. It is capped and the contents are stirred at a determined speed by motor-run paddles. This runs for a predetermined time otherwise known as the equilibrium time, which was 6 hours based on preliminary kinetic studies. The equilibrium time is defined as the contact time required for the concentrations of the prioritized metals (Cd, Cu, Ni, Pb and Zn) in the synthetic solutions to reach an equilibrium value. During this time interval, there are periodic checks of the pH of the entire solution and any deviation from the accepted or defined normal is adjusted by applications of dilute HNO₃ solution or NaOH solution, depending on the direction of the deviation on the pH scale. The pH was monitored at the beginning, at determined intervals and at the end to ensure little fluctuations. It was read with the aid of a pH meter.

Samples for analysis of dissolved metals are collected in 12ml PE tubes following separation of adsorbent and the solution through filtration, by use of a 0.45µm cellulose acetate filter with the help of a vacuum pump. These samples were preserved with 1% concentrated suprapure HNO₃ and rhodium (Rh) was added before the analysis as internal standard. The metal concentrations were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The advantage of this technique's wide usage is that it is easy to operate and the data can be easily handled. This instrument can detect ultratrace compounds with a limit detection of about 0.1ngml⁻¹, for a large number of analytes in a very short time period. Its basic working principle simply put, is that the sample enters a plasma and gets ionized. The ions are directed under vacuum to a mass spectrometer and sorted into the mass- to- mass ratio. Finally the ions are detected by an electron multiplier (Fischer 1997). This ICP-MS however has some setbacks which include among others, results being sensitive to the adsorbent/solution ratio used- real adsorbent/solution ratios cannot be used in batch experiments, uncertainty in the scaling of results to real systems, sensitivity of results to the mixing rate, separation techniques can affect results and the coefficients generated are not often adequate to the metal behavior inflow through systems (Yuliya, 2004).

Figure 2 Flow Chart of the Experimental Procedure



5 RESULTS AND DISCUSSION

5.1 Pilot experiment

Pilot experiment was conducted to decide amount of ash and metal to be used in the following experiments. A batch experiments with 0.1, 0.2, 0.3, 0.5, 0.75, 1 gram ash and 0.5L of 100µg/L Cd were conducted and results are presented in Table 3. The percentage of metal adsorbed and the adsorption capacity were calculated according to:

$$\% = \frac{100 - C}{C_0} * 100,$$

Where C_0 is the initial metal concentration and C is the final metal concentration in the solution;

$$Q = \frac{(C_0 - C) \mu\text{g} / \text{L} * 0,5\text{L}}{m, \text{g}},$$

Where Q , µg/g is the adsorption capacity, C_0 is the initial metal concentration and C is the final metal concentration in the solution; 0.5 L is the volume of the solution, m is the mass of adsorbent in the beaker.

Table 3 Results of the pilot batch experiment

C_0	m, g	C	%	Q
94.20	0.1	82.68	12.2	57.59
	0.2	76.26	19.0	44.86
	0.3	61.89	34.3	53.85
	0.5	52.91	43.8	41.29
	0.75	10.38	89.0	55.88
	1.0	5.93	93.7	44.14

From the result of the pilot batch experiment an initial concentration of 100 µg/L of metal and adsorbent masses 0.1-0.5 were decided to be used in the following experiments.

5.2 Kinetic experiment

In order to decide the time necessary to reach the equilibrium state in the adsorption experiment a kinetic experiment was conducted. Adsorption was measured as a function of time and results are presented in Table 8 in Appendix and on a Figure 3.

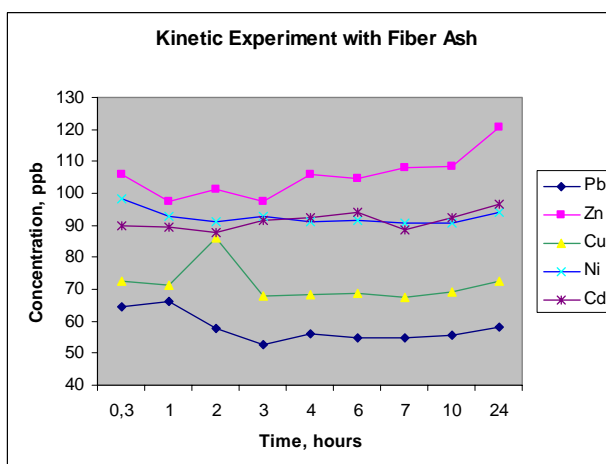


Figure 3 Adsorption of metals onto fiber ash as a function of time

Even though equilibrium seems to be reached in 3 first hours, 5 hours was chosen as experiment time to ensure that equilibrium is reached.

5.3 Reproducibility experiment

In order to check the reproducibility of the results three identical adsorption experiments were done on Cd adsorption onto ash. Standard deviation in percentage was used as indication of the variability of the results. The range of variability was 5-13 %, which is acceptable for experimental data. The range of variability for the parameters reported as result, i.e. uptake and adsorption capacity is very low and 0-0.4 %. These results demonstrate that results are reproducible; ash material is homogeneous enough for only single tests to be done through out the laboratory experiments, and that the material behave the same way if subjected to the same conditions and that the laboratory procedure is accurate.

Table 4 Reproducibility of the results

Reproducibility of final concentrations					
Mass of ash, g	Final concentration, C, $\mu\text{g/L}$			Average	STD, %
0.1	17.48	14.25	15.78	15.84	10
0.2	9.95	10.53	11.8	10.76	9
0.3	10.18	12.97	12.96	12.04	13
0.4	2.55	2.64	2.82	2.67	5

Reproducibility of uptake. %					
Mass of ash, g	Uptake. %			Average	STD. %
	%	%	%		
0.1	95.4	96.2	95.8	95.81	0.4
0.2	97.4	97.2	96.9	97.15	0.3
0.3	97.3	96.6	96.6	96.82	0.4
0.4	99.3	99.3	99.3	99.29	0

Reproducibility of adsorption capacity			
Mass	Adsorption capacity, $\mu\text{g/g}$	Average	STD. %

of ash. g	Q1	Q2	Q3		
0.1	1803	1820	1812	1812	0.4
0.2	920	919	916	919	0.3
0.3	613	609	609	610	0.4
0.4	470	470	469	469	0

5.4 Adsorption of Cd, Ni, Pb, Zn and Cu

Results of the adsorption tests for pH 5.6 are presented in Table 5 and at pH 7 in Table 6. All the metals were removed at high degree at pH 7 in the efficiency order Pb > Cd > Cu > Zn > Ni. However, adsorption was lower at lower pH = 5.6. Lead and Cu were adsorbed relatively well, while Ni and Cd were only slightly adsorbed. Zinc leached from the ash. These results suggest that some of the ash surface is positively charged at pH 5.6 and adsorption at pH lower than 7 is not effective. It should be noted, that fiber ash is a very alkaline material and only a very acidic water would bring solution with ash to as low pH as 5.6. Uptake, in %, of metal increased with the ash dose, as the same amount of metal, namely 50 µg/L was adsorbed by increasing amount of the adsorbent. In contrast, the adsorption capacities decreased with the ash dose, as adsorbent surface is more efficiently utilised at lower amount of adsorbent.

Table 5 Adsorption of metals onto fiber ash at pH 5.6

Adsorbent, g	Pb, % removed	Q, µg/g	Zn, % removed	Cu, % removed	Q, µg/g	Ni, % removed	Q, µg/g	Cd, % removed	Q, µg/g
0.1	45.99	206.56	-16.96	17.79	122	-2.28	-9.20	0.49	1.85
0.2	65.89	147.96	-1.64	31.76	109	-10.37	-20.90	4.67	8.84
0.3	77.23	115.62	-11.89	47.32	107.99	8.24	11.07	13.26	16.73
0.4	84.16	94.49	-10.63	57.36	98.18	0.56	0.56	14.29	13.53
0.5	87.30	78.41	-33.52	74.07	101.42	22.82	18.40	20.07	15.20

Table 6 Adsorption of metals onto fiber ash at pH 7

Adsorbent, g	Pb, % removed	Q, µg/g	Zn, % removed	Q, µg/g	Cu, % removed	Q, µg/g	Ni, % removed	Q, µg/g	Cd, % removed	Q, µg/g
0.1	99.6	425	62.3	222	75.7	282	35.0	123	82.7	294
0.2	99.3	212	71.5	128	86.0	160	45.0	79.0	91.2	162
0.3	99.9	142	83.5	99.3	88.5	110	57.2	67.1	94.8	112
0.4	99.9	106	77.9	69.5	89.6	83.6	65.0	57.1	96.6	85.8
0.5	99.9	85.2	80.3	57.3	90.3	67.4	71.0	49.9	98.1	69.8

5.5 Adsorption of Cd at different initial concentrations

Dependence of adsorption on initial metal concentration was investigated in the series of batch experiments with increasing Cd concentration. The results are presented in Table 7. More than 90% of Cd was removed in all the experiments. The uptake in % decreased only slightly with concentration. In contrast, the adsorption capacities increased proportionally to the amount of metal. This indicates that adsorption capacity obtained is a relative value, dependent on the experimental conditions, but the potential adsorption capacity would be higher. That nearly all the metal was removed from the water phase means that the adsorbent is not saturated and may adsorb much more of the metal.

Table 7 Adsorption of Cd at different initial concentrations

C ₀ , μM	Uptake, %	Q, mM/g
1	99.33	1.80
5	95.79	8.53
10	96.81	20.00
50	92.27	70.45
100	94.14	133.7

6 CONCLUSIONS AND RECOMMENDATIONS

Adsorption of heavy metals by fiber ash was investigated in batch experiments. Kinetic and equilibrium experiments were conducted. Study of the adsorption as a function of time showed that three hours was sufficient time to achieve equilibrium in the adsorption system with ash. This is in line with most of the reported equilibrium times for other types of ashes. Uptake of metals, in percentage, and adsorption capacities, as amount of metal adsorbed per unit mass of adsorbent was calculated. Metals were adsorbed in the efficiency order $Pb > Cd > Cu > Zn > Ni$. However, ash was found to be efficient for all the metals at neutral pH, while poor adsorption for Ni and Cd was observed at slightly acidic pH of 5.6. Zinc was leached from the ash at pH 5.6. Uptake was found to increase with the ash dose in the beaker, while adsorption capacity decreased.

The material proved to be an effective adsorbent in the range of metal concentrations studied of 1-100 μM . Almost all the metals were removed from the solution regardless of the increase in initial metal concentration. These results indicate that the adsorbent is not fully used and much higher adsorption capacities may be obtained.

The fiber ash studied is recommended as an effective adsorbent for heavy metals at neutral pH of the solution with the contaminated water. As fiber ash is an alkaline material and has pH of 12 in water, it may be effectively used to treat even very acidic contaminated waters, for example acid mine leachates.

7 REFERENCES

- Apak, R., Tutem, E., Hugul, M. and Hizal, J. (1998) Heavy metal cation retention by unconventional sorbents (red muds and fly ashes). *Water Research* **32**(2), 430-440.
- Adriano D. C. (2001) *Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability and Risks of Metals*. Spr
- Ayala, J., Blanco, F., Garcia, P., Rodriguez, P. and Sancho, J. (1998) Asturian fly ash as a heavy metals removal material. *Fuel* **77**(11), 1147-1154.
- Bayat, B. (2002) Comparative study of adsorption properties of Turkish fly ashes I. The case of nickel(II), copper(II) and zinc(II). *Journal of Hazardous Materials* **95**(3), 251-273.
- Benfield, L.D., Judkins, J.F., and Weand, B.L. (1982). *Process Chemistry for water and wastewater treatment*, Prentice-Hall, Inc. Eaglewood Cliffs, New Jersey, 07632
- Brower, J. B.; Pazirandeh, M., (1997) Comparison of Ion-Exchange Resins and Biosorbents for the removal of heavy metals from Plating Factory Wastewater. *Environ. Sci. Technol.* **31**, 910
- Brown P. L. and Markich S. J. (2000) Evaluation of the free ion activity model of metal-organism interaction: Extension of the conceptual model. *Aquat. Toxicol.* **51**, 177–194.
- Chauvert C., (2003), Treatment of contaminated leachate with natural and rest product adsorbent material, Masters thesis, Chalmers U. of Technology
- Connell D. W., (1997) *Basic concepts of Environmental Chemistry*, Lewis publishers: CRC Press
- Grover, M., and Narayanaswamy, M.S. (1982) Removal of hexavalent chromium by adsorption on fly ash, *J. Environ. Engrg. Div., Institution of Engineers (India)* **63**, 36=39
- Gupta, G. and Torres, N. (1998) Use of fly ash in reducing toxicity of and heavy metals in wastewater effluent. *Journal of Hazardous Materials* **57**(1-3), 243-248.
- Gupta, V.K. and Sharma, S. (2003) Removal of zinc from aqueous solutions using bagasse fly ash a low cost adsorbent. *Industrial & Engineering Chemistry Research* **42**(25), 6619-6624.
- Heechan Cho, Dalyoung Oh, Kwanho Kim (2005). “A study on removal characteristics of heavy metals from aqueous solution by fly ash”, *Journal of Hazardous Materials* **B127**, 187-195
- Heike B. Bradl (2004). “Adsorption of heavy metals on soils and soils constituents”, *Journal of Colloid and Interface Science* **277**, 1-18.
- Hirsch, D., Nir, S. and Banin, A. (1989) Prediction of Cadmium Complexation in Solution and Adsorption to Montmorillonite. *Soil Science Society of America Journal* **53**(3), 716-721.
- Ilona Heidmann, Iso Christl, and Ruben Kretzschmar , (2004) Sorption of Cu and Pb to kaolinite–fulvic acid colloids: Assessment of sorbent interactions *Geochimica et Cosmochimica Acta*, Vol. **69**, No. 7, pp. 1675–1686, 2005
- Jenny P. Holmberg, (2006), *Competitive Adsorption and Displacement Behaviour of Heavy Metals on Peat*, Masters thesis, Chalmers U. of Technology

James, R.O. and Healy, T.W. (1972) Adsorption of Hydrolyzable Metal-Ions at Oxide-Water Interface.1. Co(II) Adsorption on SiO₂ and TiO₂ as Model Systems. *Journal of Colloid and Interface Science* **40**(1), 42-&.

Jha, V.K., Kameshima, Y., Okada, K. and Mackenzie, K.J.D. (2004) Ni²⁺ uptake by amorphous and crystalline Ca₂Al₂SiO₇ synthesized by solid-state reaction of kaolinite. *Separation and Purification Technology* **40**(2), 209-215.

J. H. Potgieter, S. S. Potgieter-Vermaak, P.D. Kalibantonga (2005). "Heavy metals removal from solution by palygorskite clay", *Minerals Engineering* **19**, 463-470

Kalmykova Y., (2004), Leachate treatment of heavy metals by natural and residual product materials, Masters thesis, Chalmers U. of Technology

Kalmykova, Y., Strömvall, A.M. and Steenari, B.M. (2006) Alternative Materials for Adsorption of Heavy Metals and Petroleum Hydrocarbons from Contaminated Leachates. Sent for publication to *Environmental Technology*.

Karfa Traore, Tibo Simeon Kabre and Philippe Blanchart (2002). "Gehlenite and anorthite crystallization from kaolinite and calcite mix", *Ceramics International* **29**, 377-383

Kiyoshi Okada, Nagisa Watanabe, Kumar V. Jha, Yoshikazu Kameshima, Atsuo Yasumori, Kenneth J. D. Mackenzie (2003). "Effects of grinding and firing conditions on CaAl₂SiO₈ phase formation by solid-state reaction of kaolinite with CaCO₃", *Applied Clay Science* **23**, 329-336

Kretzschmar R., Borkovec M., Grolimund D., and Elimelech M. (1999) Mobile subsurface colloids and their role in contaminant transport. *Adv. Agron.* **66**, 121-193.

Kumar, S., Upadhyay, S. N. and Upadhyay, Y. D. (1987), Removal of phenols by adsorption on fly ash, *J. Chem. Tech. Biotechnol*, **37**, 281-290.

Kuo, S. and Baker, A.S. (1980) Sorption of Copper, Zinc, and Cadmium by Some Acid Soils. *Soil Science Society of America Journal* **44**(5), 969-974.

LaGrega M. D., Buckingham P. L. and Evans J.C. (1994a), *Hazardous Waste Management*, p. 408, McGraw-Hill, New York

Levenspiel, O., (1974) *Chemical Reaction Engineering*, Wiley Eastern Private Ltd., New Delhi, India.

Mavros, P., Zouboulis, A.I. and Lazaridis, N.K. (1993) Removal of Metal-Ions from Wastewaters - the Case of Nickel. *Environmental Technology* **14**(1), 83-91.

Mckay, (1996), *Use of Absorbents for the Removal of Pollutants from Wastewaters*, Boca Raton: CRC Press

N. Kantiranis, A. Filippidis, and A. Georgakopoulos (2005). "Investigation of the uptake of fly ashes produced after lignite combustion", *Journal of Environmental Management* **76**, 119-123.

- Okada, K., Watanabe, N., Jha, V.K., Kameshima, Y., Yasumori, A. and MacKenzie, K.J.D. (2003) Uptake of various cations by amorphous $\text{CaAl}_2\text{Si}_2\text{O}_8$ prepared by solid-state reaction of kaolinite with CaCO_3 . *Journal of Materials Chemistry* **13**(3), 550-556.
- Ricou-Hoeffler, P., Hequet, V., Lecuyer, I. and Le Cloirec, P. (2000) Adsorption and stabilization of nickel ions on fly ash/lime mixing. *Water Science and Technology* **42**(5-6), 79-84.
- Ricou-Hoeffler, P., Lecuyer, I. and Le Cloirec, P. (2001) Experimental design methodology applied to adsorption of metallic ions onto fly ash. *Water Research* **35**(4), 965-976.
- Rio, S., Delebarre, A., Hequet, V., Le Cloirec, P. and Blondin, J. (2002) Metallic ion removal from aqueous solutions by fly ashes: multicomponent studies. *Journal of Chemical Technology and Biotechnology* **77**(3), 382-388.
- S. Larous, A. –H. Meniai and M. Bencheikh Lehocine (2005). “Experimental study of the removal of copper from aqueous solutions by adsorption using sawdust”, *Desalination* **185**, 483-490
- Shaobin Wang, Hongwei Wu (2006). “Environmental-benign utilization of fly ash as low-cost adsorbents”, *Journal of Hazardous Materials* **xxx**, xxx-xxx
- Sposito, G. (1989). *The chemistry of soils*. New York, Oxford Univ. Press.
- Standard Methods for the Examination of Water and Wastewater, (1985) 16th Edition, American Public Health Association, Washington, D.C
- Stumm, W. (1992). *Chemistry of the solid-water interface: processes at the mineral-water and particle-water interface in natural systems*.
- Swedish Environmental Protection Agency, Guideline values or equivalents for levels in polluted groundwater. Related website: www.internat.environ.se/index.php3
- Tonni Agustiono Kurniawan, Gilbert Y. S. Chan, Wai-hung Lo and Snadhya Babel (2005). “Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals”, *Science of the Total Environment* **xx**, xxx-xxx
- Traina S. J. and Laperche V. (1999) Contaminant bioavailability in soil, sediments and aquatic environments. *Proc. Natl. Acad. Sci. USA* **96**, 3365–3371.
- V. Christian Taty-Costodes, Henri Fauduet, Catherine Porte, Alain Delacroix (2003), “Removal of Cd(II) and Pb(II) ions from aqueous solutions, by adsorption onto sawdust of *Pinus sylvestris*”, *Journal of Hazardous Materials* **B105**, 121-142
- Vinay Kumar Jha, Yoshikazu Kameshima, Akira Nakajima, Kiyoshi Okada and Kenneth J. D. Mackenzie (2005). “Effect of grinding and heating on Ni^{2+} uptake properties of waste paper sludge”, *Journal of Environmental Management* **xx**, xxx-xxx
- Vinay Kumar Jha, Yoshikazu Kameshima, Kiyoshi Okada and Kenneth J. D. Mackenzie (2004). “ Ni^{2+} uptake by amorphous and crystalline $\text{Ca}_2\text{Al}_2\text{SiO}_7$ synthesized by solid-state reaction of kaolinite”, *Separation and Purification Technology* **40**, 209-215.
- Vinay Kumar Jha, Yoshikazu Kameshima, Akira Nakajima, Kiyoshi Okada and Kenneth J. D. Mackenzie (2005). “Uptake properties of Ni^{2+} by $n\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ($n=1-4$) prepared from solid-state reaction of kaolinite and calcite”, *Journal of Hazardous Materials* **B123**, 281-287

Vinod K. Gupta et al, (2001), Removal of DDD and DDE from wastewater using bagasse fly ash, a sugar industry waste, Pergamon press, Wate Res. **35**(1), 33-40

World Health Organisation (WHO), Fact Sheet No 225 June 1999, Related Website:
www.who.int/inf-fs/en/fact225.html.

Yadava Ganoli, N., Markey, D.C and Thodos, G. (1975). Removal of heavy metal ions from aqueous solutions with fly ash, Proceedings of the 2nd National Conference on Complete on Complete Water Reuse: Water's Interface with Energy, Air and Solids, Chicago. Illinois.

Yadava, K.P., Tyagi, B.S., Panday, K.K., and Singh, V.N. (1987) Fly ash for the treatment of Cadmium II rich effluents, Environ. Tech. Lett., **8**, 225 – 234.

Yoshiaki Matsuzawa, Kazuhiro Mae, Shigeru Kitano, Satoshi Yoshihara, Shun-ichiro Ueno, Junya Nishino, Nobuhiko Kubota (2005). "Leaching behavior of heat-treated waste ash", Fuel **85**, 401-409

Appendix 1

Composition of the Ashes Results from SGAB Analytica

TS*	%	99.5
SiO₂	%TS	28.9 ± 0.1
Al₂O₃	%TS	20.1 ± 0.1
CaO	%TS	43.7 ± 0.1
Fe ₂ O ₃	%TS	1.14 ± 0.01
K ₂ O	%TS	0.868 ± 0.002
MgO	%TS	2.01 ± 0.01
MnO ₂	%TS	0.0711 ± 0.0001
Na ₂ O	%TS	0.257 ± 0.001
P ₂ O ₅	%TS	0.380 ± 0.003
TiO ₂	%TS	0.353 ± 0.001
Sum	%TS	98.4
LOI**	%TS	2.4
As	mg/kg TS	4.40
Ba	mg/kg TS	249
Be	mg/kg TS	2.18
Cd	mg/kg TS	0.994
Co	mg/kg TS	8.36
Cr	mg/kg TS	87.1
Cu	mg/kg TS	200
Hg	mg/kg TS	<0.1
La	mg/kg TS	14.1
Mo	mg/kg TS	<6
Nb	mg/kg TS	19.0
Ni	mg/kg TS	43.5
Pb	mg/kg TS	31.6
S	mg/kg TS	2240
Sc	mg/kg TS	1.53
Sn	mg/kg TS	<20
Sr	mg/kg TS	468
V	mg/kg TS	21.7
W	mg/kg TS	<60
Y	mg/kg TS	14.3
Zn	mg/kg TS	253
Zr	mg/kg TS	346

* Total Solid

** Lost of Ignition

Appendix 2

Table 8 Results of the kinetic experiment

Time, hours	Pb	%, removed	Zn	%, removed	Cu	%, removed	Ni	%, removed	Cd	%, removed
Co	64.48		105.86		72.50		98.13		89.98	
0.3	66.13	-2.55	97.32	8.07	71.37	1.56	92.84	5.39	89.58	0.45
1	57.94	10.15	101.17	4.43	85.87	-18.45	91.29	6.97	87.70	2.54
2	52.64	18.36	97.26	8.12	67.95	6.27	92.83	5.40	91.54	-1.74
3	56.15	12.91	105.79	0.07	68.34	5.74	90.99	7.28	92.22	-2.48
4	54.97	14.75	104.61	1.18	68.74	5.19	91.41	6.85	93.91	-4.37
6	54.68	15.20	107.92	-1.95	67.38	7.06	90.89	7.38	88.46	1.69
7	55.47	13.98	108.56	-2.55	69.05	4.76	90.84	7.43	92.47	-2.77
10	58.32	9.55	120.73	-14.04	72.73	-0.32	94.17	4.04	96.46	-7.20
24			121.68	-14.95			93.64	4.57	91.98	-2.22