Iron Oxide Based Materials for the Removal of Copper from Drinking Water
- A Study of Freundlich Adsorption Isotherms, Site Energy Distributions and Energy Frequency Distributions

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

NADER Z. A. YAGHI

Department of Civil and Environmental Engineering
Water Environment Technology
CHALMERS UNIVERSITY OF TECHNOLOGY
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Department of Civil and Environmental Engineering
Water Environment Technology
Chalmers University of Technology
SE – 41296, Göteborg
Sweden
Telephone: + 46(0)31-772 1000
Web: www.wet.chalmers.se

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ABSTRACT

This study describes experiments in which iron oxide coated sand and iron oxide coated LECA were used to study the removal of copper ion in drinking water. Two possible compounds were used to prepare Iron oxide coated with LECA and sand. The isotherm study results showed that the observed data fitted well with the Freundlich model. Isotherm studies were conducted by varying the mass of adsorbents and all experiments were conducted at room temperature, at pH =6.5, initial concentration 100µg/L and with a duration of 17 hours.

The results shows that LECA coated with ferric nitrate and LECA coated with ferric chloride seems to have higher removal than other adsorbents, whereas it gives efficiency of removal in the case of LECA nitrate rated from 82% to 98% and in the case of LECA Chloride rated from 80% to 96%. using adsorption isotherms and values of n and K_f (Freundlich constants), the third size of LECA coated with nitrate gave best value of n and K_f, estimated to 0.9997 and 3.4750 respectively and in second rank comes when LECA coated with ferric chloride size five which gave value for n and k_f of 0.9998 and 3.8645 respectively.

After studying the adsorption isotherm, site energy distribution and energy frequency distribution to all adsorbents using the theory of heterogeneity have been studied. The results shows that the loss occurs preferentially across sites having highest energy frequency distribution with the number of sites in the lowest energy range, as what is happened in uncoated LECA and uncoated sand. The final result and occurrence of the value of site energy distribution and energy frequency distribution showed that LECA coated nitrate is the best adsorbent among the other category and uncoated LECA is the worst.

Keywords: Copper, Drinking water, Iron oxide coated sand with, Iron oxide coated LECA, ferric nitrate, ferric chloride, Freundlich isotherm model, Freundlich constants, site energy distribution, and energy frequency distribution.

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1.0. Chapter one: Introduction

1.1. Background

Water is covered more than 70% of earth's surface, but the human use only less than 3.0 % for drinking, because most of these sources are salty, like the water of oceans and seas and can't be used for drinking or for domestic purposes. More than 78% of the water which can be used for drinking is locked up in polar ice caps and glaciers in sea ice.

Today, the industrial progress has released numerous harmful substances to the water body. Heavy metals represent one of the major example of these substances which although found in nature but heavy metals which are found in water with concentration above standard value comes from industrial sector . Metals cations in soluble form pose a great threat as these can easily transport and taken up by living ecosystem. Copper is considered one of the heavy metals and is widely used in daily life. Existence of copper in concentrations above the permissible level in natural water or drinking water may cause several health problems. Copper in drinking water comes from plumbing materials, from roof surface and also from copper pipes. Copper also enters ground water naturally; by leaching processes from ore's in the rock and soil in the earth crust.

Removal of heavy metals from water can be achieved by various processes like adsorption, chemical precipitation, ion exchange, membrane separation, and electrodialysis. Among these methods, adsorption is the most common technique being used in the treatment of drinking water. Adsorption is recognized as an efficient process of heavy metals removal from aqueous solution in spite of the usefulness and effectiveness of alumina, silica, iron oxide and active carbon as adsorbent of heavy metals. They are too expensive which restrict their widespread use.

Therefore a lot of studies have been carried out with the intention of developing new and especially the cheap adsorbent which must have high affinity, selectivity and capacity towards the removal of heavy metals.

Iron oxide coated sand and LECA (light expanded clay aggregate) were selected as the suitable materials to remove copper ion from water, because these materials are inexpensive, easily available, easy to handle and risk-free for the environment. In addition they give good results of efficiency in previous studies. Two possible compounds hydrate ferric nitrate $Fe\ (NO_3)_3.\ 9H_2O$ and hydrate ferric chloride $Fe\ (Cl)_3.\ 5H_2O$ were analyzed for coating LECA and sand materials in this study with a laboratory procedure. The compound with better adsorption was selected according to Freundlich adsorption isotherms and according to the site energy distribution and energy frequency distribution.

1.2. Aim and goals

1. Make comparison between different adsorbent materials; (sand, sand coated ferric nitrate, sand coated ferric chloride, LECA, LECA coated ferric nitrate and LECA coated ferric chloride).
2. Determine the suitable adsorbents material for removing copper.
3. Study the effect of size of adsorbent materials on removing copper from water.
4. Understand the mechanism of adsorption process.
5. Examine the adsorption isotherm equations (Freundlich) based on an adsorption process.
6. Study the site energy distribution and energy frequency distribution for each adsorbent.

2.0. Chapter Two: Water and Copper

2.1. Water and Drinking water

Water covers about approximately 70% of the Earth's surface. This amount of water exists in different forms (oceans, rivers, sea, lake, polar ice caps, sea ice, and ground water), Table 1 shows the distribution of water on earth and the amount of water different sources contain. But from all of these sources of water the human use less than 3.0 % for drinking, because most of these sources are salty, like the water of oceans and seas which cannot be used for drinking or in domestic purposes. More than 78% of the water which can be used for drinking is locked up in polar ice caps and glaciers in the sea ice. The available water for drinking for humans has is less than 0.08% of all the Earth's water ***(Bradley, 2004).***

Table 1: Distribution of water in earth and freshwater resource

Source of water	Percent	Source of fresh water	Percent
Oceans	97.59%	Ice and glaciers	78.19%
Ice and glaciers	1.90%	Groundwater	20.58%
Ground water	0.50%	River and lack	0.82%
River and lack	0.02%	Soil	0.41%
Soil	0.01%		

2.1.1. Physical and Chemical Properties of water

Water is colourless, odourless and tasteless which is an essential substance to life all organisms in the earth and is considered the universal solvent.

Water has unique properties. When it is in the form of solid it is less dense than liquid. That’s why lakes and the sea freeze from the top downwards. This property of water keeps the underwater in ocean and sea to be warm and keeps the living organisms and aquatic biota alive ***(Kenneth, 2000)***. The maximum density of water occurs at $4\,^{\circ}C$ which contain some of chemical and physical properties of water as shown in Table 2.

Water is considered a universal solvent because the hydrogen bond in water molecule interacts with all ionic and polar compounds, while it has not the ability to react and dissolve covalent and non polar compounds i.e. organic compounds ***(lee, a1996)***.

Table 2: The physical and chemical characteristics of water (David. R. Lide, a 1997).

Proprieties		Descriptions
Common name		Water
Chemical Name		Aqua, hydrogen hydroxide
Molecular formula		H_2O
Molar mass		$18.02\ g.mol^{-1}$
Density	**Liquid $4\,^{\circ}C$**	$1.00000\ g.cm^{-3}$
	Solid $0\,^{\circ}C$	$0.99987\ g.cm^{-3}$
Melting point		$0\ ^{\circ}C$
Boiling point		$100\ ^{\circ}C$
Specific heat capacity		$4184\ J.kg^{-1}K^{-1}$

2.1.2. Water in human body.

Water is a fundamental part of our lives. It is easy to forget how completely we depend on it as human survival is dependent on water. Water has been ranked by experts as second after oxygen as essential element for life. The average adult body contains 55% to 75% water so, 2/3 of body weight is water. A human embryo has more than 80% water. A newborn baby contains 74% water. The human brain tissue is comprised more than 80 % of water.

2.1.2.1. Importance of water to human

Water is important to human body because it

1. Regulates body temperature.
2. Regulates blood circulation.
3. Provides carrier’s nutrient and oxygen to cell.
4. Makes possible for various enzymatic and chemical reactions in the body.
5. Removes toxins and other wastes.
6. Provides cushion joints and protects tissues and organs.
7. Saves the organs from shocks and damages.

2.1.3. Water issue

The proportion of drinking water in earth is a very less and the sources of freshwater has been remained without increasing. Now or days human are facing many problems especially the pollution because of a rapid increase in the number of inhabitants on earth.

In pollution case, the most obvious types of water pollution affected oceans and seas are spill from oil tanker, which creates an oil spot that affect a vast area of the ocean, which caused the death of fish and other organisms in that area. The decomposing organisms cause increase in the amount of nutrient such as nitrates and phosphates. Most of small river and lake in urban area are polluting from runoff carrying the pollutant substances such as metal including copper, aluminium, etc or fertilizing nutrients (nitrate and phosphate), or chemical compounds from industrial sector. Acid rain and global warming are also considered sources of pollution for ground and surface water and the cause of shortage of drinking water.

2.2. Copper

2.2.1. Identify of copper

Copper is the 29th element and the first in group IB of the Periodic Table, changes four oxidation states described in table 3. Copper also forms organometallic compounds. The natural isotopic abundance is 69.17% of 63Cu and 30.83% of 65Cu, giving the element an average relative atomic mass of 63.546 ***(David, 1997).***

Copper is moderately abundant and is the twenty – fifth most abundant element in the earth's crust and it has been found in earth's crust in complexes and ores. The most common is chalcopyrite ($CuFeS_2$) ***(Lee, b.1996)***, since the natural abundance of copper in earth crust is approximately 60mg/kg and is 2.5×10^{-4} mg/litre in the sea ***(David, 1997)***.

Table 3: Oxidation states of copper and electronic configuration (cotton, 1988).

Oxidation state	Name	Electronic Configuration
$Cu^{(0)}$	Metallic copper	$1S^22S^22P^63S^2SP^6\ 4S^23d^9(3d^{10}4S^1)$
$Cu^{(+1)}$	Cuprous Ion	$1S^22S^22P^63S^2SP^63d^{10}$
$Cu^{(+2)}$	Cupric Ion	$1S^22S^22P^63S^2SP^63d^9$
$Cu^{(+3)}$	Trivalent Ion	$1S^22S^22P^63S^2SP^63d^8$

2.2.2. History of Copper

Copper is one of the first metals known to humans, it is the earliest metal worked by humans and remains in wide use throughout the human history. Copper was very important source for the Roman and Greeks, and was used in producing the mirror, cooking utensils and in the weapons. Copper was found in northern Iraq that dates to 8700 BC. Smelting became common in 3500 BC, producing relatively pure copper from oxidized copper ores with low arsenic content, ***(Donald, 1999)*** whereas in Europe it was found in copper tipped axe dated to 3200 BC, and the metal was 99.7% pure, and also copper was known in ancient china at least 2000 BC. Where excellent bronzes were being made in 1200 BC ***(Wikipedia, copper).***

2.2.3. Chemical and physical Properties of copper

Copper's unique chemical and physical properties have made it one of the most important metals. These properties have made copper malleable, ductile and a good conductor of heat and electricity. Copper is a reddish metal and it is a metallic chemical element with a face centred cubic crystalline structure. It is softer than iron and harder than zinc (***David, b 1997and Cotton, 1998)***.Table 4 described some of the important physical and chemical properties of copper and major copper compounds.

Tabell 4: Physical and chemical properties for copper and main compound *(David, 1997.*

	COPPER	COPPER(II) SULPHATE	COPPER(II) CHLORIDE
Molecular formula	Cu	$CuSO_4$	$CuCl_2$
Valancy	0	+2	+2
Molecular mass (g/mol)	63.55	159.6	134.45
Boiling point ^{o}C	2567	decomposes to CuO at 650 ^{o}C	decomposes at 993 ^{o}C
Melting Point ^{o}C	1083.4	Slightly decomposes at > 200 ^{o}C	620
Vapour pressure (kpa)	1.33 (1870 ^{o}C)	-----------------------	--------------------
Density (g/l)	8.94	3.603	
Water solubility	Insoluble	143g/l at 0 ^{o}C	706g/l

Copper is almost stable metal because it has single 4s electron outside a completed 3d shell. This property makes copper low chemical reactive with other compounds. Besides that copper is positioned below hydrogen in the electromotive force series; that's mean it can never displace hydrogen ions in dilute acid and will not dissolve in acid unless an oxidizing agent is present. But it is dissolved in concentrated nitric acid and hot concentrated sulphuric acid in absence of air and it is soluble in ammonium hydroxide, ammonium carbonate and potassium cyanide solutions in the presence of oxygen. In moist air it is oxidized slowly forming a greenish surface film and is mixed with carbonate, sulphate, hydroxides and oxides to form the patina compounds. This coating protects the metal from further attack. The most important chemical compound of copper is copper sulphate pentahydrate, copper chloride, copper cyanide, copper oxide and a basic carbonate ***(Cotton, 1998).***

2.3. Uses of copper

Copper are used widely in our ordinary life, where it is used in the manufacturing of water pipes, electrical wires, coins, valves, fittings, cooking utensils, in the roof of the houses and building material, in the plumbing of the household materials as bronze and also in household coatings materials. Copper compounds are also used as algaecides, fungicide, insecticide, wood preservatives and in electroplating, azo dye manufacturing, engraving, lithography, petroleum refining and pyrotechnics. Copper compounds can be added to fertilizers and animal feeds as a nutrient to support plant and animal growth ***(ASTDR, 2002).*** Copper compound also used as food additives (colour agent) ***(US FDA, 1994).*** Copper sulphate pentahydrate used as control algae in lakes and reservoirs ***(NSF, 2000)***.

2.4. Sources of copper in environmental and in human body

Copper is formed in environment naturally by leaching the copper from ore's in the rock and soil in the earth crust and from water and sediment in seas and rivers, this processing is done when the soil of earth crust are became highly acidic. Copper also enter to environment from anthropogenic sources.

2.4.1. Air

The main concentration of copper in atmosphere range from 5 – 200 ng/m$^{3.}$ This amount is releasing to atmosphere from two main sources; natural source (windblown dust 65%, volcanoes, forest fire and sea spray) and anthropogenic source (nonferrous metal production 3.3%, copper smelters and copper sulphate production 2.7%, coal and oil combustion 4.6%, iron and steel production 7.4%, municipal incinerators 1.9% others 2.3%). ***(Donald, 1999 and David, 1997)***

2.4.2. Water

Copper entered into drinking water primarily due to its usage in plumbing materials and also may be leached from copper pipes when they are in contact with non – aggressive water and make the colour of water blue. Corrosive toward copper depends primarily on the pH (acidity) of the water. High carbonate waters with an alkaline pH i.e. water with pH below 6.5 and hardness less than 60 mg of calcium carbonate per litter is very aggressive to copper. There are also many other factors that affect the amount of copper in drinking water such as the temperature of water in pipe and copper availability in the distribution system ***(World health Organization, 2004a).***

2.5. Environmental Fate of copper

2.5.1. Air

The fate of copper released to the atmosphere adsorbed to particulate matter depends on the particle size, the wind velocity, and the source characteristics. Generally, gravitational settling governs the dispersion of large particles (>5 µm). Combustion produces submicron particles containing copper oxides that may remain in the troposphere for up to 30 days and may travel far from the source of the particles ***(Donald, 1999)***.

2.5.2. Soil

Copper deposited in soil adsorbs strongly to clay minerals, iron and manganese oxides, and organic material. Several factors affect the balance of copper in the rock and mineral's and in derivative soil. These factors include: The degree of weathering, the nature and intensity of the soil formation, drainage, pH, oxidation-reduction potential, and the amount of organic matter in the soil. Copper in rocks is likely to be more mobile under acidic than alkaline conditions ***(David, 1997).***

2.5.3. Water

2.5.3.1. Copper speciation

Speciation of metal in water is meant the partitioning of metal in water phase and in colloidal phase. Speciation in water is important to understand the aquatic toxicity and bioaccumulation of metal in water. In copper case there is very small percentage of copper is present as the free aqua ion (Cu^{2+}), rather most of copper is adsorbed to organic and inorganic suspended particles with various ligands forming complex with strong bonding especially with fulvic and humic acid ***(Morrison, 1992).*** Iron oxides and humic acid substances most frequently bind copper in sediment and such tightly bound copper exerts little biological effects. The bioconcentration factor (10–100) of copper in fish is low but filter feeders such as molluscs possess high factors (up to 30,000). There is no evidence of biomagnification of copper in the food chain ***(Donald, 1999).***

2.6. Copper in Human Body

Copper in small amount is essential element of humans and living organism. Where it is an important catalyst for heme synthesis and iron absorption. Following zinc and iron, copper is the third most abundant trace element in the body ***(Donald, 1999)***. Copper enter human body either by drinking contaminated water or by food material which contain copper. Table 5 lists the average concentration of copper in human food, organisms and in the environment.

Table 5: Average concentration of copper in food, organism and environmental, (Donald, 1999).

	$\mu g / g$		$\mu g / g$
Food		**Food**	
Muscle meats	0.9 – 1.0	**Fruit**	0.4–1.5
Fish	2.0 – 3.0	**Vegetables**	0.3–3
Freshwater	0.3 – 3.0	**Potatoes**	2.1
Shellfish	12.0 – 37.0	**Environmental**	
Poultry	0.5 – 3.0	**Inorganic (Soil)**	≥4.0
Liver	4.6 – 6.2	**Organic (Soil)**	20 – 30
Nuts	6.0 – 37.0	**Sea water surface**	0.001
Grains and seeds	3.0–8.0	**Sea water 1000m**	0.1
Bran	15.0	**Algae**	0.05–0.29
Gem	6.0	**Yeast**	8.0
White flour	0.6	**Human**	1.7
Legumes	3.0 –7.0	Animal	1.5 – 2.5

In human body Copper never found in free ion, but always with bound with protein and organic compound. The compounds of copper are found in all human's organs and tissues, in varying concentration between few part per million to several hundred part per million. The high concentrations of copper are found in liver (3.2 – 9.9 mg/kg), blood (0.8 – 1.3 mg/kg, in red blood cell 0.76 mg/kg) and Hair (6.8 – 39 mg/kg) ***(Venkatesh Iyengar and Joost Wolttlez, 1988)***. Copper is found in several types of enzymes, at least ten enzymes are known to be dependent upon copper for their function, and table 6 describes some of those enzymes and their function in body.

Table 6: Enzymes in body contain copper and their function.

Enzyme name	Function
Cytochrome C oxidase	Using in produce energy from mitochondria in cell needed to drive biochemical resection ***(Piccoli, etc, 2006).***
Dopamine B hydroxylase	Conversion dopamine to noradrenalin (natural hormone plays a vital pare in transmission of nerve impulses), ***(Lamprecht, 1974).***
Lysyl oxidase	Proper the cross – linking in structural extra cellular matrix protein such as elastin and collagen during the building and repair of connective tissue ***(Sang Teak Jung, etc. 2006).***
Superoxide dismutase	Prevent the accumulation of superoxide radicals which cause cellular damage ***(Cai, 2006.)***

Copper also regulates the metabolism in the human body, and also is found in blood plasma. Since about 90% - 95% of the copper in the plasma is bound to ceruloplosmin, a plasma protein. There is a small amount of copper found in association with plasma albumin and amino acid but this small amount is not less important to function than other and all fluids of the body contain copper complexes.

2.7. Exposure pathways to copper and health effect

Human can be exposed to copper by breathing contaminated air with copper or drinking water containing high amount of copper. Human may also be exposed by skin contact with contaminated water, soil and other copper containing substances**.**

As well as copper is essential element in the human body so, it also has high toxicity to human and can cause adverse health effect. When the human are exposed to amount of copper above the limit value, the health problems ranging from stomach distress to much damage caused by vomiting, diarrhoea, stomach cramps and nausea. Copper is associated with liver damage and kidney disease. The human body has a natural mechanism for maintaining the proper level of copper. However, children under one year old have not yet developed this mechanism and are more vulnerable to the toxic effects of copper. People with Wilson's disease also have a problem with maintaining the proper balance and taking care to limit the exposure of copper. Concentration of Copper in drinking water with level of 5 to 8 mg/L make the water undrinkable ***(HDR Engineering Inc, 2001a).***

2.8. Guideline value

A guideline value represents the concentration of a chemical constituent that does not result in any significant risk to the health of the consumer over a lifetime of consumption. Guideline Values require adaptation because they relate to a "reference" human in a specified exposure environment ***(World health organization, 2004b).***

2.8.1. History of development guidelines value of copper

Guidelines for the recommended daily intake for copper have been proposed over the last 30 years by the joint Food and Agriculture Organization (FAO) and World Health Organization (HWO), ***(IPCS News, 1996a)***. Table 7 describes the development of such guidelines value of copper.

Table 7: Development guidelines value of copper. (World Health Organization, 2004c).

Year	Event
1958	WHO International Standards for Drinking-water suggested that concentrations of copper greater than 1.5 mg/litre would markedly impair the potability of the water.
1963	International Standards retained this value as a maximum allowable or permissible concentration.
1984	A guideline value of 1.0 mg/litre was established for copper, based on its laundry and other staining properties.
1993	Derived a provisional health-based guideline value of 2 mg/litre for copper from the PMTDI proposed by JECFA, based on a rather old study in dogs that did not take into account differences in copper metabolism between infants and adults.
2003	Conduct the risk assessment for copper.

The table 8 below describes the total normative requirement and maximum level for exposure to copper in diet of child, adult male and adult female.

Table 8: Total normative requirement and maximum level fro exposure to copper (IPCS, 1996b).

Exposure	Population	Normative requirement (mg/l)	Maximum Level (mg/l)
Total	Infant 10 kg	0.60	1.5
Diet	Child (6 – 10 year old)	0.75	3.0
	Adult male	1.35	12.0
	Adult female	1.15	10.0
Total Exposure		-	30.0
Drinking Water		-	2.0

2.8.2. Maximum contaminated level (MCL)

The maximum contaminated level (MCL) is calculated by equation 1, since the guidelines value for drinking water in many countries ranges from 1 – 2 mg Cu/l. MCL are used because of lack of both human and animal toxicity of copper and debate of guidelines value of copper. MCL value for copper is 1.3 mg Cu/l based on taste and to a lesser extent on limited toxicity data ***(Donald, 1999.)***

$$MCL = LOAEL \div Safty \text{ value (Guidelines value) * Daily water consumption}$$
$$= 5.3 \div 2.0 \text{ mg Cu/L * 2L/d}$$
$$= 1.3 \text{ mg Cu in L/d}$$

Equation 1: Calculated the maximum contaminated level

Where:

Lowest Observable Adverse Effect Level (LOAEL) = 5.3 mg

Safety Factor = 2 mg Cu/ l Guidelines value

Daily Water Consumption (adult) = 2L/d

3.0. Chapter Three: Adsorbent Material; Preparation and properties

3.1. Light Expanded Clay Aggregate (LECA)

The principle for LECA production was developed by the company Lemvigh – Muller & Munck A/S Copenhagen, Denmark, in 1939. LECA consists of small, lightweight, bloated particles of burnt clay. The thousands of small, air-filled cavities give LECA strength and thermal insulation properties. The base material is plastic clay which is extensively pre-treated and then heated and expanded in a rotary kiln. Finally, the product is burnt at 1100 °C to form the finished LECA product. LECA is an environment-friendly, entirely natural product incorporating the same benefits as tile in brick form.

3.1.1. Characteristics of LECA

LECA is a natural product containing no harmful substances. It is inert with a neutral pH value, resistant to frost and chemicals, will not break down in water, is non-biodegradable, non combustible and has excellent sound and thermal insulation properties.

3.1.2. Application of LECA in natural life

LECA is an incredibly versatile material and is utilised in ever-increasing number of applications:

3.1.2.1. Natural Product agriculture

LECA is used as a growing medium in Hydroponics systems and blended with other growing mediums such as soil and peat to improve drainage to retain water during periods of drought, to insulate roots during frost and to provide roots with increased oxygen levels promoting very vigorous growth.

3.1.2.2. Construction Industrial

LECA is also used extensively in the production of lightweight concrete blocks as well as for sound and thermal insulation material, and flue & chimney lining material. LECA is used in structural backfill against foundations, retaining walls, bridge abutments etc which can reduce earth pressure by 75% compared with conventional materials, and also increases stability while reducing settlement and land deformation.

3.1.2.3. Water Treatment

LECA is also used in water treatment facilities for the filtration and purification of municipal wastewater and drinking water as well as in other filtering processes, including those for dealing with industrial wastewater and fish farms.

It is also has superb water-draining properties because it has much lighter than alternatives such as gravel so it is easier to transport and handle. That’s why it is now the preferred aggregate for sports field drainage contractors.

3.2. Sand

Sand is a granular material made up of fine rock particles. Sand is a naturally occurring, finely divided rock, comprising particles or granules ranging in size from 0.0625 mm to 2 mm. Sand is commonly divided into five sub-categories based on size; very fine sand, fine sand, medium sand, coarse sand, and very coarse sand. These sizes are based on the Φ sediment size scale, where size in Φ = -log base 2 of size in mm. On this scale sand range from Φ = -1 to 4, with the divisions between sub-categories at whole numbers.

Table 9: Type and size of sand which are used in experiments

Φ – Scale	Size (mm)	Name	Name in Experiments
-1 to 0	1.0– 2.0	very coarse sand	SAND – 1
0 to 1	0.500– 1.0	coarse sand	SAND – 2
1 to 2	0.250– 0.50	medium sand	SAND – 3
2 to 3	0.125 – 0.250	fine sand	SAND – 4
3 to 4	0.0625 – 0.125	very fine sand	SAND – 5

3.2.1. Constituents of sand

Sand is a naturally occurring and a finely broken down rock by weathering. Sand is usually form from silicon dioxide (SiO_2) in quartz form and also contains several type of mineral like limestone, Feldspar, magnetite, chlorite, glauconitic, gypsum, and olivine. Therefore sand is considered chemical inertness, hardness and it is quite resistant to physical and chemical weathering. However the composition of sand varies according to local rock source and condition while the white sand contains high percent of limestone and the sands which are derived from lavas have content with high percent of olivine and it look greenish. While the sand which is derived from volcanic is rich in magnetite and has dark to black color.

3.2.3. Application of Sand in natural life:

3.2.3.1. Water Treatment:

Graded sand is used as an abrasive in sandblasting and is also used in media filters for filtering water.

3.2.3.2. Industrial Building material

Sand is often a principal component of the aggregate used in the preparation of concrete. Brick manufacturing plants also use sand as an additive with a mixture of clay and other materials for manufacturing bricks.

3.2.3.3. Agriculture

Sandy soils are ideal for certain crops such as watermelons, peaches, and peanuts and are often preferred for intensive dairy farming because of their excellent drainage characteristics.

3.2.3.4. Industrial

Sand is the principal component in glass manufacturing. Sometimes it also mixed with paint to create a textured finish for walls and ceilings or a non-slip surface.

3.2.3.5. Other Uses

Sand is using in railroads to improve the traction of the rails and in filling of the bags, calling Sandbags which are used for protection against floods and gun fire.

3.3. Preparation of Iron Oxide – Coated Sand and LECA

Iron – oxide coated sand was prepared by modifying the methods of ***Lai et al.,1994, Jea – kyu Yang et al.,2004 and Lai et al.,2000***. The process of coating sand and LECA were done in three main steps; sieving, washing and coating, with some of change in quantity of material in washing and coating process between sand and LECA.

3.3.1. Sieving and washing

3. 3.1.1. Sand

The sand was purchased from Baskarpsand AB, Baskarp. The raw sand was sieved to five geometric mean sizes , the diameter of sand ranged from 2mm - <0.125 mm, then sand was washed with 0.1 M HNO_3 for 24 h, and rinsed 5 times with DI water, after that it was dried in oven for 24 h at 105°C.

3.3.1.2. LECA

The LECA (2 – 6 mm) was bought from Hasselfors Garden AB, Göteborg, with diameter ranged between 2mm to 6mm, The LECA was ground in a mill machine and sieved into 5 different sizes with geometric size ranging between 2 mm and < 0.125mm. The LECA was soaked in acid solution (0.01 M HNO_3) for 48 h and then rinsed 8 times with DI water. After that it was dried in oven for 24 h at 105°C.

3.3.2. Coating Process

The total amount of sieved sand and LECA were divided into three equal parts. The first part was coated with hydrate ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) and the second part was coated with hydrate ferric chloride ($FeCl_3 \cdot 6H_2O$) and the last part remained without coating as a reference group.

3.3.2.1. Coating Sand

For coating the first part of sand with ferric nitrate, 0.5 M Fe(III) was prepared by dissolving $Fe(NO_3)_3.9H_2O$ in Milli – Q water *(* Solutions Preparation is in **appendix C**), and pH adjusted to 11.5-12.0 by adding concentrated NaOH drop wise during stirring. Then the solution was poured over the sand at weight ratio of sand: ferric nitrate 2:1. The mixture was then heated in an oven for 110°C for 24 h with stirring during the first four hours. After that the coated sand was washed with DI water several times to remove the excess amount of ferric nitrate and the runoff water became clear. The washed coated sand was dried at 105°C for 24 h, and the coated sand was saved in glass bottle ready for usage.

The second part of sand was coated with 0.5M $FeCl_3 .3H_2O$ and the pH of solution was adjusted to 11.5 – 12 by adding concentrated NaOH. The coating processing of second part of sand exactly was the same procedure of coating sand with ferric nitrate.

3.3.2.2. Coating LECA

The coated procedure of LECA exactly was done as the case of coated sand; first part of LECA was poured into 0.5M of ferric nitrate solution after adjusting the pH to 12, and second part was poured into 0.5M of ferric chloride solution after adjusting the pH to 12, both of two parts were poured to the solution at a weight ratio1:2. This was the opposite of sand which was poured at a weight ratio 2:1. This is done due to the some difference in physical properties between LECA and sand. For example the density as the density of sand is heavier than LECA, which means the same weight of LECA and sand will obtain volume of LECA much than sand. After that, the coating process of LECA was exactly the same as the process for coating sand.

3.6. Properties and characteristics of IOCS and IOCL

3.6.1. Iron Oxide Coated Sand (IOCS)

IOCS coating with ferric nitrate has a light red – brown color and appearance similar to uncoated sand, while IOCS coating with ferric chloride has a dark red –brown color. The IOCS coating with ferric nitrate hold iron more than IOCS coating with ferric chloride as shown in table 10.

Table 10: properties of iron coated sand

TYPE	SYMBOL	DIAMETER (MM)	IRON CONTAIN (MG/G)
UNCOATED SAND	US	-------------	0.1933
FERRIC NITRATE COATED SAND SIZE 1	NS1	1.0 – 2.0	1.1552
FERRIC NITRATE COATED SAND SIZE 2	NS2	0.5 – 1.0	1.2998
FERRIC NITRATE COATED SAND SIZE 3	NS3	0.25 – 0.5	1.7276
FERRIC NITRATE COATED SAND SIZE 4	NS4	0.125 – 0.25	1.6333
FERRIC NITRATE COATED SAND SIZE 5	NS5	<0.125	1.7655
FERRIC CHLORIDE COATED SAND SIZE 1	CS1	1.0 – 2.0	1.3299
FERRIC CHLORIDE COATED SAND SIZE 2	CS2	0.5 – 1.0	2.5569
FERRIC CHLORIDE COATED SAND SIZE 3	CS3	0.25 – 0.5	1.2161
FERRIC CHLORIDE COATED SAND SIZE 4	CS4	0.125 – 0.25	3.9485
FERRIC CHLORIDE COATED SAND SIZE 5	CS5	<0.125	0.8508

3.6.2. Iron Oxide Coating LECA (IOCL)

IOCL coating with ferric nitrate has a light red – brown color, while IOCL coating with ferric chloride has a dark red –brown to dark brown color. In addition to the IOCL coating with ferric nitrate hold iron more than IOCL coating with ferric chloride as shown in table 11.

Table 11: properties of iron coated LECA

TYPE	SYMBOL	DIAMETER (MM)	IRON CONTAIN (MG/G)
UNCOATED LECA	UL	---------------	1.1830
FERRIC NITRATE COATED LECA SIZE 1	NL1	1.0 – 2.0	6.7925
FERRIC NITRATE COATED LECA SIZE 2	NL2	0.5 – 1.0	7.6761
FERRIC NITRATE COATED LECA SIZE 3	NL3	0.25 – 0.50	11.038
FERRIC NITRATE COATED LECA SIZE 4	NL4	0.125 – 0.25	10.826
FERRIC NITRATE COATED LECA SIZE 5	NL5	<0.125	10.112
FERRIC CHLORIDE COATED LECA SIZE 1	CL1	1.0 – 2.0	7.4800
FERRIC CHLORIDE COATED LECA SIZE 2	CL2	0.5 – 1.0	7.2898
FERRIC CHLORIDE COATED LECA SIZE 3	CL3	0.25 – 0.50	8.8886
FERRIC CHLORIDE COATED LECA SIZE 4	CL4	0.125 – 0.25	9.6454
FERRIC CHLORIDE COATED LECA SIZE 5	CL5	<0.125	10.475

4.0. Chapter four: Literature review

4.1. Copper removal techniques

Several methods are used for removal of copper and heavy metals from water including thermal (evaporation), biological (biosorption), and physical/chemical methods (metal precipitation, ion exchange, adsorption, electrolysis, membrane separation process, chemical oxidation reduction, filtration, coagulation and flocculation). However most of these methods are expensive and has some limitation in practice ***(Tita, 2005).***

4.1.1. Metal precipitation

Copper like all heavy metals found in water may be in cationic or anionic forms, which may be precipitated as an insoluble salt at optimum conditions, usually an optimized pH level. The most common precipitating salts for copper are hydroxide and sulphide and bicarbonate ***(Chia, 2004)***. In hydroxide case the copper precipitate at pH less than 9 and larger than 8 forms copper hydroxide, but in sulphide case the maximum precipitation occurs at pH between 6 and 7 forming copper sulphide, which is insoluble in water shows the following equation ***(Roberts alley, 2000)***

$$\mathrm{Cu^{2+} + 2OH^{1-} \xrightarrow{9>pH>8} Cu(OH)_{2(PPt)}}$$

$$\mathrm{Cu^{2+} + S^{2-} \xrightarrow{7>pH>6} CuS_{(PPt)}}$$

In the metal precipitation if the concentrations of an insoluble salt is low and the solubility product of system is less than K_{sp} then the metal and precipitating metal remain in soluble forms, otherwise if the concentration of metal is higher than the solubility of salt in liquid exceeds and the precipitation occurs ***(Roberts alley, 2000).***

After precipitation process several methods are used to remove the precipitated salts from water. These methods include gravity settling, filtration and centrifugation etc etc ***(Roberts alley, 2000)***

4.1.3. Ion exchange

Ion exchange is defined as a process whereby an insoluble substance removes ions of positive or negative charge from an electrolytic solution and releases other ions of like charge into solution in a chemically equivalent amount. ***(HDR Engineering Inc, 2001b)***

The equilibrium reaction for the exchange ions A and B on a cation exchange resin is often represented as follows:

$$nR^{-}A^{n+} + B^{n+} \xleftrightarrow{k_{A^{+}}^{B^{n+}}} R_{n}^{-}B^{n+} + nA^{+} \qquad (2)$$

Equation 2: Equilibrium reaction for the exchange ion A and B on a cation

Where R^- is anionic group attached to the ion exchange resin, and A^+, B^{n+} are ions in solution.

In relatively dilute solution of ions the equilibrium constant expression for this reaction becomes:

$$k_{A^{+}}^{B^{n+}} = \frac{\left[R_{n}^{-}B^{n+}\right]_{R}\left[A^{+}\right]_{s}^{n}}{\left[R^{-}A^{n+}\right]_{R}^{n}\left[B^{n+}\right]_{s}} \qquad (3)$$

Where:

$\left[R_{n}^{-}B^{n+}\right]_{R}$: Concentration of B^{n+} in resin

$\left[A^{+}\right]_{s}^{n}$: Concentration of A^{+} in solution

$\left[R^{-}A^{n+}\right]_{R}^{n}$: Concentration of A^{n+} in resin

$\left[B^{n+}\right]_{s}$ Concentration of B^{n+} in solution

4.1.3.1. Types of ions exchange resins

Ion exchange may be considered the cheapest method among the methods which are used for removing copper from water. This occurs when we use cheaper exchanger, like natural zeolites ***(Osman, 2003)***. Today most ion exchange resins consist of synthesis material made up of polymeric matrix with soluble ionic function group attached to the polymer chain. The number and kind of functional group determine the exchange capacity and ion selectivity.

Resins are granular in nature and may have either a spherical or irregular shape to provide a larger surface and often a lower void volume, which increase the exchange capacity per unit of volume

Ion exchange resins are usually classified in the following manner ***(David Harvey, 2000)***:

1. Cation exchange resins:

    - Strong – Acid Exchange resins

- Weak – Acid Exchange resins

The strong acid contains functional group derived from a strong acid; normally sulphuric acid. Its degree of ionization is analogous to that of a strong acid, which permits the hydrogen to be dissociated and ready for exchange over a wide pH range, in weak acid the functional group derived from a weak acid and normally carboxylic or phenolic form.

2. Anion exchange resins

    - Strong – Base Exchange resins
    - Weak – Base Exchange resins

Functional group in strong Base Exchange resins is usually quaternary ammonium group, whereas weak Base Exchange resins contain primary, secondary and or tertiary amines as a functional group, strong Base Exchange resins are useful over a wide pH range, whereas weak Base Exchange resins are affective only within a fairly narrow pH range ***(HDR Engineering Inc, 2001b)***.

4.1.3. Adsorption

Adsorption is the binding of molecules or particles to a surface. The binding to the surface is usually weak and reversible. The most common industrial adsorbents are activated carbon, silica gel, sand and alumina, because they present enormous surface areas per unit weight. Activated carbon is produced by roasting organic material to decompose it to granules of carbon. The common sources of activated carbon are coconut shell, wood and bone. Silica gel is a matrix of hydrated silicon dioxide. Alumina is mined or precipitated aluminium oxide and hydroxide. **(More details for adsorption are in chapter five).**

4.2. Iron Oxide based material for removal of Copper from water

In removal of Copper from water using iron oxide coated material a very few studies are done. While a lot of these studies are doing on arsenic and other heavy metal and also all the studies were used iron oxide coated sand and never use iron oxide coated LECA in treatment processes.

One of the most important studies in removing of copper from water was done by ***Sutha Khaodhiar and other in 1999***. The coating procedure of sand was prepared by modifying the method of ***Edward and Benjamin 1989.*** IOCS was prepared by dissolving 20g of ferric nitrate in 50 ml deionised water. The solution was poured over 200g of pre – acid washed sand. The mixture was placed in an oven at $110\,^{o}C$ for 24h.

The equilibrium adsorption of copper on IOCS was reached in less than 24h. The equilibrium pH adsorption edge data shows that copper adsorption varies from less than 10% below pH 4 to more than 90% adsorbed above pH 6 reaching to more than 98% on pH 8.5.

Other study on removing copper from water was done by ***Lai, C.H, etc (1994)***. The iron oxide sand was prepared by pouring the solution of 0.5M ferric nitrate and 200g in 1L Pyrex glass beaker. The mixture was placed on drying oven at 50 ^oC for 96h and was stirred by Teflon mixer during the first 48h. The coated sand was washed with de – ionized water until run – off was clear and finally it was dried at 50^oC for 96h.

The maximum concentration of iron on the surface is about 5.8 ± 0.2 mg Fe/ g sand. Adsorption efficiency is strongly dependent on pH. The greater adsorption occurs at the higher pH, since the adsorption efficiency was reached above 95% at pH higher than 6.5

Jea – kue Yang and other (2004) was tested the iron oxide sand on four metal, arsenic, lead, cadmium and copper. The iron oxide coated sand was prepared by using ferric chloride. 500ml of 0.5M ferric chloride solution adjusted to pH 10 was poured to 1Kg sand in rotary evaporator, by rotating the rotary evaporator at 30 rpm and 70^oC, until approximately 10% of water remained in the suspension. After that the sand was dried at different baking temperature (110^oC; 24h – 550^oC; 1 – 4h).

The maximum concentration of iron on the surface varies with varying the baking time and temperature as shown in table 12.

Table 12: properties of iron coated sand with varying the baking time and temperature.

Sample	Temperature ^{o}C	Time (Hrs)	Content iron mg/kg
Sand – J (Blank)	25	-------------	2.440
IOCS – J1	110	24	8.550
IOCS – J2	550	1	6.610
IOCS – J3	550	2	6.220
IOCS – J4	550	3	6.430
IOCS – J5	550	4	6.990

The adsorption arsenic was completed within 20 min while copper and other heavy metal adsorption on IOCS were relatively slower than arsenic and strongly depended on initial pH. The adsorption of copper in IOCS was appeared when pH is above 6.

5.0. Chapter Five: Theory

5.1. Inductively coupled plasma – mass spectrometer.

Inductively coupled plasma – mass spectrometer (ICP – MS) is an inorganic analytical technique used primarily for the quantitation of trace elements (metals) in a variety of sample media. ***(West, B.M, 2004).***

5.1.1. Application

1. Quantitative analysis of main and ultra-trace elements in both organic and inorganic samples.
2. Survey analysis of main and ultra-trace elements in both organic and inorganic samples.
3. Depth profiles of elements in solids by using laser ablation as a sampling technique.
4. Isotope ratio analysis.

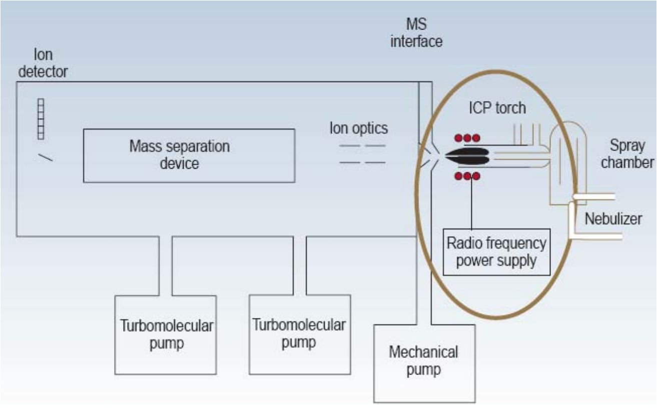


Figure 1: Schematic of an ICP-MS system showing the location of the plasma torch and radio frequency (RF) power supply. (Ropert, 2001).

5.1.2. Principle of work

5.1.2.1. The plasma Torch

The basic components that are used to generate the source: a plasma torch, a radio frequency (RF) coil and RF power supply. Figure 1 shows their proximity to the rest of the instrument.

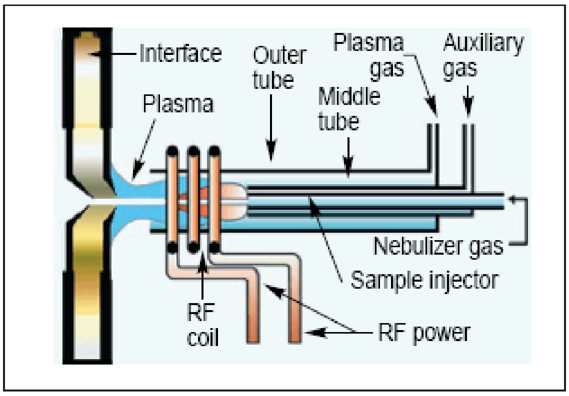


Figure 2: Detailed view of a plasma torch and RF coil relative to ICP – MS interface. (Ropert, 2001).

Figure 2 is a more detailed view of the plasma torch and RF coil relative to the MS interface. The plasma torch consists of three concentric quartz tubes (outer tube, middle tube, and sample injector). The torch can either be one – piece with all three tubes connected or it can be a demountable design in which the tubes and the sample injector are separated. The gas which is usually argon is passed between the outer and middle tubes at a flow rate of 12–17 L/min to form the plasma (plasma gas with temperature $8000^{o}C$). Between middle tube and the sample injection at; 1l/min a second gas was flowed (the auxiliary gas), and is used to change the position of the base of the plasma relative to the tube and the injector. A third gas flow, the nebulizer gas also flows at 1 L/min carries the sample, in the form of a fine-droplet aerosol, from the sample introduction system, and physically punches a channel through the centre of the plasma. The sample injector is often made from materials other than quartz, such as alumina, platinum, and sapphire, if highly corrosive materials need to be analyzed. It is worth mentioning that although argon is the most suitable gas to use for all three flows. There are analytical benefits in using other gas mixtures, especially in the nebulizer flow. The plasma torch is mounted horizontally and positioned centrally in the RF coil, approximately 10–20 mm from the interface ***(Ropert ,2001).***

5.1.2.2. Formation of an ICP discharge

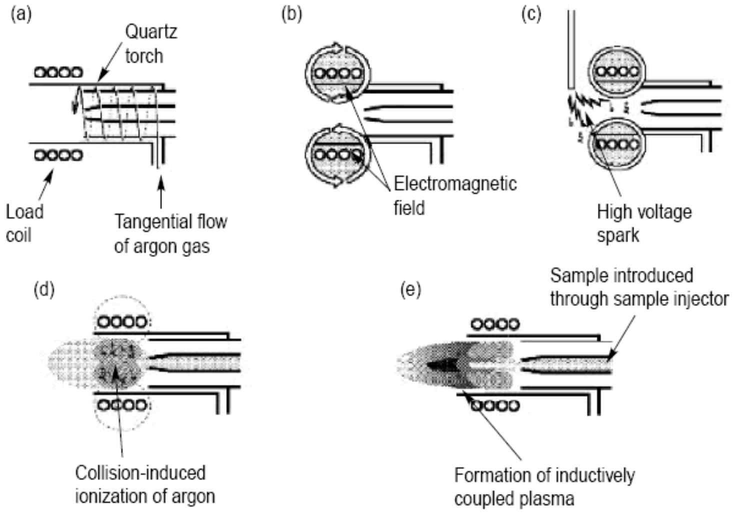


Figure 3: Schematic of an ICP torch and load coil showing how the inductively coupled plasma is formed (Ropert, 2001).

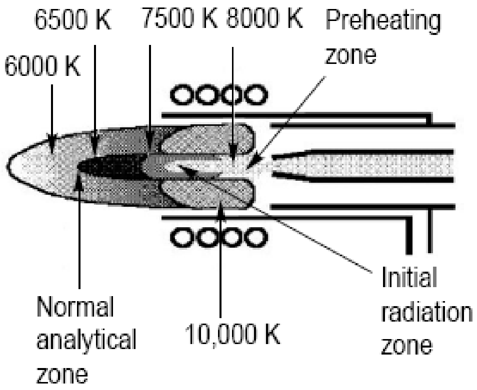
The whole process of formation of an ICP discharge is shown in fig.3, (a) A tangential flow of argon gas is passed between the outer and middle tube of the quartz torch. (b) RF power (typically 750–1500 W, depending on the sample) is applied to the load coil; an alternating current oscillates within the coil at a rate corresponding to the frequency of the generator. In most ICP generators this frequency is either 27 or 40 MHz. This RF oscillation of the current in the coil causes an intense electromagnetic field to be created in the area at the top of the torch. (c) A high – voltage spark with argon produced free electron by the RF field, causing collision and ionization of the argon gas. The free electrons are caught up and accelerate in the magnetic field and colloid with other argon atoms, stripping off stills more electrons. (e) This collision induced ionization of the argon continues in a chain reaction, breaking down the gas into argon atoms, argon ions, and electrons, forming what are known as an inductively coupled plasma discharge and this ICP is formed at the open end of quartz torch. The ICP discharge is then sustained within the torch and load coil as RF energy is continually transferred to it through the inductive coupling process. The sample aerosols are introduced into the plasma through a third tube called the sample injection ***(Ropert, 2001).***

5.1.2.3. Function of the RF generator

Although the principles of an RF power supply have not changed since the work of Greenfield, the components have become significantly smaller. Some of the early generators that used nitrogen or air required 5–10 kW of power to sustain the plasma discharge — and literally took up half the room. Modern generators use a solid-state electronic component, which means that vacuum power amplifier tubes are no longer required.

As mentioned previously, two frequencies have typically been used for ICP RF generators: 27 and 40 MHz. These frequencies have been set aside specifically for RF applications of this kind, so they will not interfere with other communication-based frequencies. The early RF generators used 27 MHz, while the more recent designs favour 40 MHz. This appears to be no significant analytical advantage of one type over the other. However, it is worth mentioning that the 40-MHz design typically runs at lower power levels, which produces lower signal intensity and reduced background levels. Because it uses slightly lower power, this might be considered advantageous when it comes to long-term use of the generator. The more important consideration is the coupling efficiency of the RF generator to the coil. The majority of modern solid-state RF generators are on the order of 70–75% efficient, meaning that 70–75% of the delivered power actually makes it into the plasma. This wasn't always the case, and some of the older vacuum tube–designed generators were notoriously inefficient. Some of them experienced more than a 50% power loss. Another important criterion to consider is the way the matching network compensates for changes in impedance (a material's resistance to the flow of an electric current) produced by the sample's matrix components or differences in solvent volatility. In older crystal-controlled generators, this was usually done with servo – driven capacitors. They worked very well with most sample types, but because they were mechanical devices, they struggled to compensate for very rapid impedance changes produced by some samples. As a result, the plasma was easily extinguished, particularly during aspiration of volatile organic solvents. These problems were partially overcome by the use of free-running RF generators, in which the matching network was based on electronic tuning of small changes in frequency brought about by the sample solvent or matrix components. The major benefit of this approach was that compensation for impedance changes was virtually instantaneous because there were no moving parts. This allowed for the successful analysis of many sample types that would probably have extinguished the plasma of a crystal-controlled generator ***(Ropert, 2001).***

5.1.2.4. Ionization of the sample



Figur 4: Different temperature zone in Plasma (Ropert, 2001).

As mentioned previously the samples aerosol enter the injection via the spray chamber, when the sample enter the injection it is move to the center of plasma discharge, then goes through a number of physical change in temperatures, starting at the preheating zone and continuing through the radiation zone before it eventually becomes a positive charge ion in the analytical zone as is shows in fig.4. ***(Ropert, 2001)***

The process in equation 4 is simplified the mechanism of conversion sample in liquid phase to positive ion in ICP – MS.

$$(\text{Droplet})\,M(H_2O)^+\,X^- \xrightarrow{\text{Disolvation}} (\text{Solid})(MX)_n \xrightarrow{\text{Vaporization}} (\text{Gas})\,MX$$

$$\xrightarrow{\text{Atomization}} (\text{Atom})\,M \xrightarrow{\text{Ionization}} M^+$$

$$\text{From Sample Injection} \xrightarrow{\hspace{5cm}} \text{To Mass spectrometer}$$

Equation 4: Mechanism of conversion of a droplet to a positive ion in the ICP – MS *(Ropert, 2001).*

5.1.2.5. Detector and ICP-MS spectrum

Finally, the ions are measured using an electron multiplier, and are collected by a counter for each mass number. An ICP-MS spectrum is a plot of ion intensity (y-axis) versus mass-to-charge ratio (x-axis). In argon plasma, predominantly singly charged ions are produced. This means in practice that the mass-to-charge ratio can be replaced by mass in the spectrum. Most elements have more than one isotope and each isotope has a specific mass. Copper (Cu), for example, has two isotopes: 63Cu with 34 neutrons and 65Cu with 36 neutrons in the nucleus. Thus, the mass spectrum of copper consists of two peaks, mass 63 and mass 65.

5.1.3. Limitations of ICP-MS Spectroscopy

1. The total dissolved salt content of the analyte solution must be kept low or else instrument performance is adversely affected; this dilution can result in less attractive detection limits for some elements.

2. Common matrix elements and other molecular species can interfere with the determination of some base metals; for example, chloride will interfere with a number of elements and ArCl (Argon chloride) has the same mass of As (Arsenic).

3. Some doubly charged ionic species create difficulties.

4. Ultra pure acids are required for leaches and digestions and this will increase the cost of measurements.

5.2. Adsorption

5.2.1. Fundamental adsorption

Adsorption is considered one of traditional techniques for controlling the release of organic compound, adsorption is a mass transfer process may be defined as; attraction and accumulation of one substance on the surface of another substance. Adsorption is a thermodynamic system in which various component are striving for equilibrium. The process of adsorption occurs in both steady – state and unsteady – state condition. The first primary force driving the interaction between the Adsorbate and the adsorbent is the electrostatic attraction and repulsion between molecular of the Adsorbate and the adsorbent. These driving forces can be either physical and called physical adsorption or chemical calling chemisorptions. ***(Roberts, 2000)***.

5.2.1.1. Physical adsorption:

Physical adsorption is a result of interaction between Adsorbate substances and adsorbent, these physical electrostatic forces the van der waals force, consisting weak attraction and long range and repulsion through dipole – dipole interaction and dispersing interaction, and hydrogen bonding ***(physical chemistry, 2002)***. Dipole – dipole interaction as a result of polar compound orienting themselves so that their charges result in lower combined free energy. Dispersing interactions are result of attractive forces between electron and nuclei of molecule in system. If the molecules come too close to each other, repulsion force can push the molecules apart. Hydrogen bonding is a special case of dipole – dipole interaction in which the hydrogen atom in a molecule has a partial positive charge, attractive another atom or molecule with a partial negative charge. In liquid phase system the van der waals force it is the primary physical force driving adsorption. Because physical adsorption dose not involve sharing of electron is include mono and multilayer and consider reversible reaction with low adsorption energy 20kJ /mol ***(Physical chemistry, 2002)*** and all these processes are done only when the intermolecular forces between a chemical molecule (Adsorbate) in a liquid stream and a solid (adsorbent) are greater than the forces between the molecules of the liquid stream ***(Water quality control hand book, 2000).***

5.2.1.2. Chemical adsorption:

In chemical adsorption the force between Adsorbate and adsorbent is often stronger than the force in physical adsorption; chemical adsorption is produced by transfer of electrons and the formation of chemical bond between Adsorbate and adsorbent. It may be irreversible reaction and have high adsorption energies grater than the adsorption energy in physical adsorption. The adsorption energy in chemical adsorption is estimated with 200KJ /mol. Chemical adsorptions have only a monolayer and is a site specific reaction occurring to the function group location ***(Water quality control hand book, 2000).***

Tabell 13: Summarizes distinguish between the chemical and physical adsorption.

	Physical adsorption	Chemical adsorption
Electrostatic force	Van der waals bond	Covalent bond
Interaction	Weak	Strong
Type of reaction	Reversible	Irreversible
Site reaction	Long rang (no location)	Specific (function group location)
Saturation Uptake	multilayer	Monolayer
Electron sharing	Dose not sharing electron	Have electrons sharing
Adsorption enthalpy	low	High
Kinetics of Adsorption	Fast - since it is a non-activated process	Very variable - often an activated process

5.2.2. Factors affecting adsorption capacity

Capacity of adsorption is the most important characteristic of an adsorbent; adsorption capacity can be simply defined as the amount of adsorbate taken up by the adsorbent, per unit of mass or volume of adsorbent ***(Bal, 1984)***. Adsorption capacity depends on fluid – phase concentration, polarity, pH, charge and molecular weight, but the most important factors in adsorption capacity are temperature, pore size distribution and surface area.

5.2.2.1.Temperature:

Temperature is especially necessary when the adsorption system contain volatile organic compounds. Adsorption capacity is inversely proportional to temperature, this principle is based upon Gibbs free energy; Gibbs free energy measures the spontaneous change in a system. The change in Gibbs free energy of system ΔG; at constant temperature, so when $\Delta G < 0$ a system react spontaneously and adsorption occurs, but if $\Delta G > 0$ a compound that does not react and no adsorption at given temperature, but may be happened some of adsorption at lower temperature.

5.2.2.2.Surface area

One of major considerations during selection of the adsorbent is the Surface area of material; this characteristic is related to adsorbent particle diameter. The particle diameter influences the rate of adsorption. Smaller diameter particle such as powder sand (sand V) have a shorter diffusion path resulting in more rapid adsorption. The mass transfer rate increases in inverse proportion to the particle diameter.

5.2.2.3.Pore size distribution

Pore size distribution is a measurement of the percent of the space of a particle occupied by microspores (pore diameter < 2 A^o), mesopores (pore diameter > $20A^o$ and < $500A^o$ and macrospores (pore diameter > $500A^o$). Figure 5 illustrates a portion of a typical particle cross section, a molecule cannot penetrate into a pore smaller than given minimum diameter, this process screens out large molecule and allows small molecule to penetrate further into the adsorbent particle or to adsorb in the smaller diameter pores.

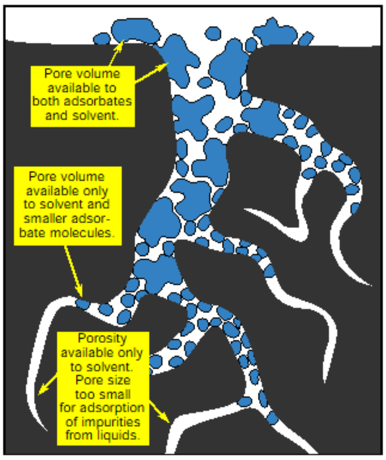


Figure 5: concept of molecular screening.

5.3. Adsorption isotherms

The adsorption of compound onto adsorbent can be described mathematically by an adsorption isotherm; adsorption isotherm simply defined as the quantity of adsorption that can be bound up on a particular of adsorbent is a function of the concentration of an adsorbate and the temperature.

Experimental data derived from adsorption isotherms experiments will typically fit one of five different curve, the five different curves are shown in figure 6, where q_m is define as the maximum loading and q is the concentration of adsorbed species on the adsorbent, C is the adsorbate concentration and C_{sat} is the saturation concentration of the adsorbent. Type I adsorption is convex upward throughout the curve and is considered the favourable for adsorption. Type II is convex upward throughout the curve and is considered the unfavourable for adsorption. Type III, IV, V, and VI adsorption curves have multiple inflection points and therefore both concave and convex portion. Type IV, and V curves can exhibit hysteresis, a condition where desorption occurs along different isotherm than adsorption.

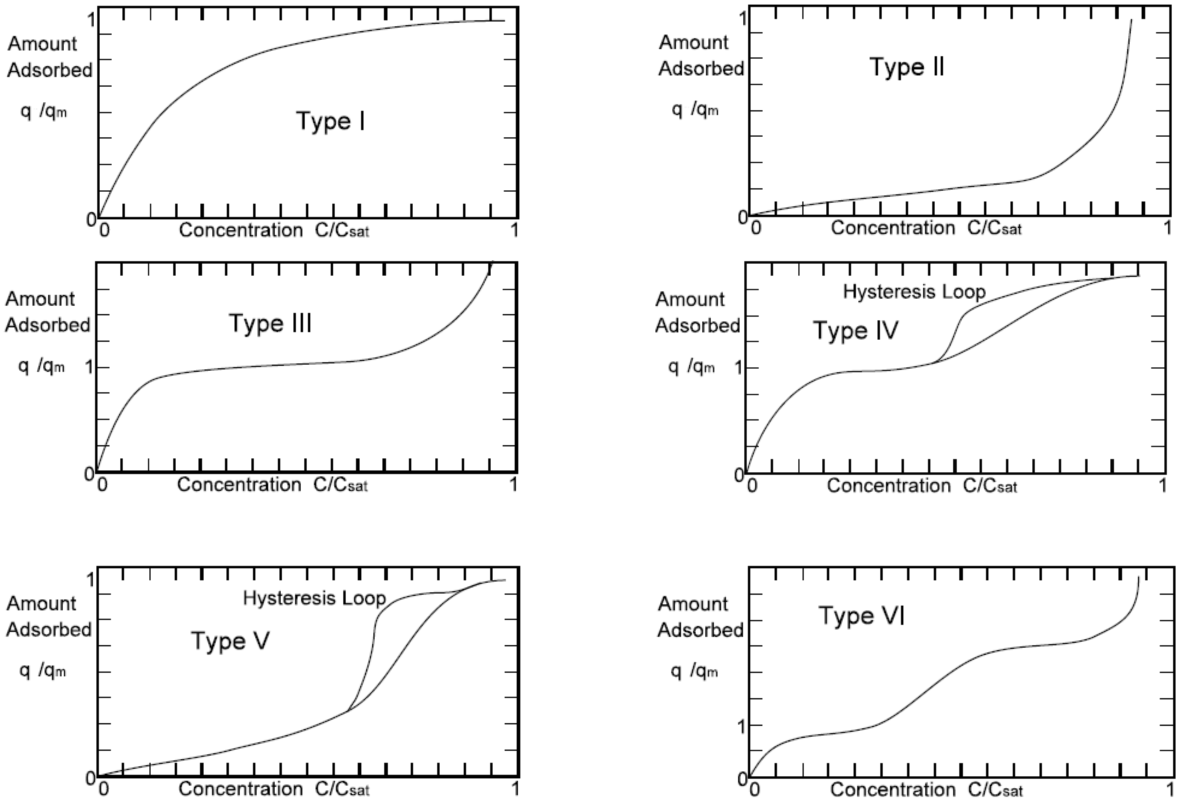


Figure 6: type of adsorption isotherm (kent S. knaebel).

Although several isotherms have been developed for use in modelling the adsorption isotherms, but three isotherms are consider the most common equation used to described the equilibrium between an adsorbent (surface) and an Adsorbate (chemical in solution). These isotherms are the Langmuir, Freundlich and Redlich – Peterson adsorption equations.

5.3.1. Freundlich isotherms equation

In 1906, Freundlich presented the earliest known adsorption isotherm equation. Freundlich is an empirically derived logarithmic model that attempts to factor in the effects of various adsorption energy levels. The model assumes that the number of sites associated with a particular free energy of adsorption decreases approximately as the free energy level increases, this empirical model can be applied to non – ideal sorption on heterogeneous surfaces as well as multilayer adsorption. And can be expressed this model by the following equation ***(Water quality control handbook, 2002 and Ho, etc., 2002)***:

$$q_e = K_f C_e^{1/n} \tag{5}$$

Where:

q_e = Equilibrium loading on the adsorbent (mg/g)

K_f = *Asorption* capacity at unit concentration (mg/g) (L/g)$^{1/n}$

C_e = Equilibrium concentration of adsorbate (mg/L)

n = Adsorption intesity

The equation fit straight line when plotted on ln – ln basis, the equation 3 can be written in following form:

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e \tag{6}$$

The slope of this line is 1/n, and the best value of 1/n in adsorption chemical is between 0 and 1. When the value of 1/n greater than 1, this mean the adsorbed chemical is unfavourably, and chemical that is not adsorbed, 1/n approaches infinity ***(Water quality control handbook, 2000).***

5.3.2. Langmuir Isotherms equations

In 1915 Langmuir developed equation to described the interaction between the adsorbent and adsorbate as a linear, reversible and mono layer chemical reaction, this equation is a relatively straightforward model that assume that the adsorbent surface is completely homogeneous, that each adsorbent site can bind a maximum of one adsorbate molecule, and that their no interaction between molecules of the adsorbate ***(water quality control handbook, 2000).***

This model can describe theoretically by following equation ***(Yuh-Shan Ho, 2005):***

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \tag{7}$$

Where:

q_e = Equilibrium loading on the adsorbent (mg/g)

C_e = Equilibrium concentration of adsorbate (mg/L)

q_m and K_a = characteristics of langmuir equation

Constant q_e and K_a can be determined from linearized form of equation 1, represented by

$$\frac{C_e}{q_e} = \frac{1}{q_m K_a} + \frac{C_e}{q_m} \tag{8}$$

A plot of C_e/q_e versus C_e should indicate a straight line of slope $1/q_m$ and an intercept of $1/(K_a q_m)$.

Advantage of the Langmuir equation includes simplicity and the applicability to a wide range of data. Limitations to the model include the monolayer assumption the reversibility of bonding and the constant uptake rate.

5.3.3. Redlich – Peterson isotherms equation

The Redlich–Peterson isotherm contains three parameters and involves the features of both the Langmuir and the Freundlich isotherms.

It can be described as follows:

$$q_e = \frac{A C_e}{1 + B C_e^g} \tag{9}$$

Then take the natural logarithm of both sides

$$\ln\left(A \frac{C_e}{q_e} - 1 \right) = g \ln(C_e) + \ln(B) \tag{10}$$

Although a linear analysis is not possible for a three parameter isotherm, three isotherm constants, A, B and g, can be evaluated from the pseudo-linear plot represented by Eq. 6 using a trial-and-error optimization method. A general trial-and-error procedure which is applicable to computer operations was developed to determine the coefficient of determination, r^2 for a series of values of A for the linear regression of $\ln(C_e)$ on $\ln\left(A\frac{C_e}{q_e}-1\right)$ and to obtain the best value of A which yields a maximum optimized value of r^2 ***(Yuh-Shan Ho, 2005).***

Table 14 is summarised the Isotherm constants for two-parameter models by linear regression for Langmuir model, Freundlich model and Redlich–Peterson.

Table 14: Isotherms constant for two - parameter by linear regression.

Isotherm	Transformed		Slope	Intercept
	X – values	Y – values		
Langmuir	C_e	C_e/q_e	$1/q_m$	$1/K_a q_m$
Freundlich	$\ln C_e$	$\ln q_e$	$1/n$	$\ln K_f$
Redlich – Peterson	$\ln\left[A\frac{C_e}{q_e}-1\right]$	$\ln C_e$	g	$\ln B$

5.4. Energy distribution (E*) and adsorption energy frequency F(E*)

Adsorption isotherms parameters n and K_f can thus be related to particular energy distribution, and their empirical determined values can be interpreted with respect to the energetic character of an adsorbent.

The basic integration equation underlying the theory of heterogeneous surface is ***(Weber, 1995)***

$$q_e(C_e)=\int_0^\infty q_h(E,C_e)F(E)dE \qquad (11)$$

This equation is defined the total adsorption q_e of an adsorbent by a heterogeneous surface as the integral of an energetically homogenous isotherm q_h multiplied by a site energy frequency distribution F(E) over range of energies, where E is the difference between adsorbate and adsorbent adsorption energies for a given site.

If local adsorption isotherm and site energy distribution function F(E) are known or assumed the integral given in previous equation may be solved to yield a corresponding overall adsorption isotherm. To derive the Freundlich adsorption isotherm model based on a local Langmuir adsorption isotherm model will be used the Halsey and Taylor approached ***(Halsey and Taylor, 1947)***. In this approach the exponential site energy distribution was used. Conversely if a set of data is found to confirm to a particular isotherm model the integral equation may be solved to drive the corresponding site energy distribution.

This approach and other were put to represent simplification of a more general isotherm relationship termed the generalized Langmuir model, which can be written. *(Weber, 1995)*

$$q_e = Q_g^o \left[\frac{(b_g C_e)^m}{1+(b_g C_e)^m} \right]^{n/m} \qquad (12)$$

Where Q_g^o is the generalized isotherm maximum adsorption capacity, m and n are heterogeneity parameter (n is Freundlich constant), b_g is a generalized form of the Langmuir energy constant that incorporates a characteristic site energy (E_o), the universal gas constant (R) and absolute temperature (T): ***(Weber, 1995)***

$$b_g = f\left(e^{-E_o/RT}\right) \qquad (13)$$

The constant E_o is the energy corresponding to the maximum site frequency and it determines the position of the energy distribution function on the energy axis, the heterogeneity parameter m characterized the shape of the site energy distribution in the direction of lower values of E_o , while the parameter characterized the shape of the site energy distribution in the direction of higher values of E_o. ***(Weber, 1995)***

From m and n values, the common Freundlich model was confirmed when the values of n range between 0 to 1, and the value of m = 1. ***(brouers, 2004)***

$$q_e = Q_g^o (b_g C_e) \qquad (14)$$

And for Langmuir – Freundlich isotherm the value of m are equal n (m = n),

$$q_e = Q_g^o \left[\frac{(b_g C_e)^m}{1+(b_g C_e)^m} \right] \qquad (15)$$

And for Generalized Freundlich isotherm for m = 1 and 0 < n < 1.

$$q_e = Q_g^o \left[\frac{(b_g C_e)}{1+(b_g C_e)} \right]^n \qquad (16)$$

5.4.1. Approximate site energy distribution

Cerofolini proposed an alternative technique for determining site energy distributions based on a method referred to as the condensation method. The method involves generating approximate distribution function from isotherm equations. The approximate distributions, unlike the exact distribution, are not normalized but rather are written directly in terms of the isotherm parameters (Q_g^o, b_g, m, and n). Each parameter from those are controlled one properties on distribution curve, since the area under the distributions is controlled by Q_g^o, the position of the distribution in the energy axis relative to the reference energy is controlled by b_g , and the spread of the distribution is controlled by m and n. under the assumption of the cerofolini approximation, the equilibrium liquid phase concentration is related to the energy of adsorption by ***(Weber, 1995)***

$$C_e = C_s \exp - \left[\frac{E - E_s}{RT} \right] = C_s \exp \left[\frac{-E^*}{RT} \right] \qquad (17)$$

Where C_s is the initial concentration of adsorbate, E_s is the value of the sorption energy corresponding to $C_s = C_e$. By incorporating equation 17 into equation 11 it can be shown that an approximate site energy distribution $F(E^*)$, is obtained by differentiating this isotherm, $q_e(E^*)$, with respect to E^*

$$F(E^*) = \frac{-dq_e(E^*)}{dE^*} \qquad (18)$$

Because the resulting site energy distributions are not normalized, the area under the distribution is equal to the maximum adsorption capacity Q_g^o (equilibrium loading on adsorbent).

$$\int_0^\infty F(E^*) dE^* = Q_g^o \qquad (19)$$

The Langmuir – Freundlich model incorporation of equation 17 into equation 15 followed the differentiation with respect to E^* yields

$$F(E^*) = \frac{Q_g^o n (b_g C_s)^n}{RT} * \exp\left(\frac{-nE^*}{RT}\right) \left[1 + (b_g C_s)^n \exp\left(\frac{-nE^*}{RT}\right)\right]^{-2} \qquad (20)$$

In the case of generalized Freundlich isotherm incorporation of equation 17 into equation 16 followed the differentiation with respect to E^* yields the approximation site energy distribution

$$F\left(E^*\right)=\frac{Q_g^o n\left(b_g C_s\right)^n}{RT} * \exp\left(\frac{-nE^*}{RT}\right)\left[1+\left(b_g C_s\right)\exp\left(\frac{-E^*}{RT}\right)\right]^{-(n+1)} \tag{21}$$

In the common Freundlich isotherm a simplification of Langmuir – Freundlich model, involves only two independent parameters, applying the same assumption and incorporation the equation 17 into equation 14 followed the differentiation with respect to E^* then yields the approximation site energy distribution in terms of the corresponding adsorption parameters:

$$F\left(E^*\right)=\frac{Q_g^o n\left(b_g C_s\right)^n}{RT} * \exp\left(\frac{-nE^*}{RT}\right) \tag{22}$$

All three isotherm model effectively determine Q_g^o and b_g from one set of adsorption data and the parameter b_g is depend on the value of Freundlich constant k_f

$$Kf = Q_g^o\left(b_g\right)^n \tag{23}$$

6.0. Chapter six: Methodology

In the present study, coating LECA with ferric nitrate (NL), coating LECA with ferric chloride(CL), coating sand with ferric nitrate(NS), coating sand with ferric chloride(CS), un-coating sand (UN), and un-coating LECA (UL), were evaluated through batch scale adsorption equilibrium and kinetic studies, in removing copper from drinking water. there were two objectives of this study, the first section in the procedure of experiment will be use in experiments to study the efficiency of materials in removing copper from the water and in the second section of the experiment will been use the data to calculate the site energy and energy frequency distribution for all adsorbent.

6.1. Stock and Batch of copper Solution preparation

Initial concentration of copper solution (100µg/l) was prepared from 1g/L stock solution of copper sulphate (CuSO4). Adjustment for pH was carried out with trace point of concentrate and dilutes nitric acid and sodium hydroxide (1 – N HNO3, 0.1 N HNO3, 1 – N NaOH and 0.1 – N NaOH). The pH of the solution was adjusted to the initial experimental value; the containers sealed and allowed to stand overnight. The following day the pH was readjusted to the initial experimental value before initiating batch experiments. **Appendix C.**

6.2. Experiments section

The experiments were carried out in 250ml Erlenmeyer flasks, The study of this experiment done with varying the adsorbent dose and fixes other parameters like pH

6.5, Initial concentration of copper solution = 100µg /L, Temperature =25C, and the conduct time at 17 hours. The modeling of Adsorption isotherms have been applied on the results of these experiment to choose the best material for removing copper according to the value of n and K_f.

The adsorbent dose was varied from 0, 0.125, 0.25, 0.5, 2.5, and 5.0 g for LECA coated with ferric nitrate, LECA coated with ferric chloride and uncoated LECA, and for uncoated sand as well as coated sand with ferric nitrate and ferric chloride the adsorbent dose were varied from 0, 0.25, 1.0, 5.0, 10, and 25 g. In the experiments, 250 ml of copper solution was transferred to 250 ml an Erlenmeyer flask which contains the adsorbent. After these samples were placed on the shake and shaken at 180 rpm.

6.3. Prepare sample for ICP – MS

After completion the of the conduct time, 9.8 ml from each flasks were pour out in clean plastic tube and 100 µL from super nitric acid was added to the sample and 100 µL from radium solution as a standard at concentration 1µg/l was added to sample also. Then Metal analysis was carried out by inductively coupled plasma-mass spectroscopy (ICP - MS) at m/z value of 63

7.0. Chapter seven: Results and Discussion

The results in this chapter are divided into two parts; the first part will contain the result of the first objective of the thesis which is stated in the previous chapter (Methodology) and the second part shows the site energy distribution which is depend on the result of first section, for that the result of second section in this thesis will be separate from first part and is discussed alone.

7.1. Affect the type of adsorbent on removal copper

The percentage of removing copper was arrived to more than 95% in some types of adsorbents. Fig 7 and fig. 8 shows the percent of removal copper vs. the adsorption dose using uncoated LECA size 1 and size 5, respectively as adsorbent. In general the percentage of removing copper was increased with decreasing the size of adsorbent, because the total surface area in small size is bigger than that in large size, and all of transport mechanism becomes diffused, the rate of which increases with decrease size of particles ***(Jozsef toth, 2002)***. Increasing the adsorption dose in sample helps to increase the surface area, for that the removing copper increases when increase the adsorption dose. The full results and graphs are in **appendix E**

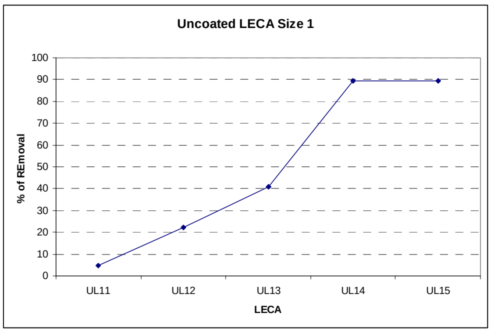


Figure 7: Percent of copper removal vs. Adsorption dose using Uncoated LECA size 1.

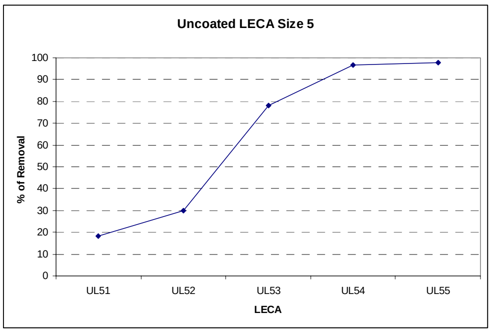


Figure 8: Percent of copper removal vs. Adsorption dose using Uncoated LECA size 5.

In contrary of uncoated LECA, uncoated sand shows high percentage of removing copper when we use adsorption dose less than 20g/L, but when we used adsorption dose larger than 20g/L the percentage of removing copper had been decreased, as shows in fig. 9 and fig.10. The reason for decreasing removal copper when we use large amount of adsorption dose is may be due to the precipitation of adsorbent, and since this type of adsorption is physical; the links are very weak and there is probability to happened reversible reaction.

In the same amount of adsorption dose, the percentage of removal copper in large size is more than percentage of removal copper in small size; this could been explained and because uncoated sand did not contains any anion for bonding it with copper, for that’s the adsorption of copper is being done only at these pores and this is due to the pore size, whereas in large size of uncoated sand. The pore size is enough to penetrate big amount of copper, in contrary in small size which has small pore size, and it not allows penetrating the ions of copper into this pores.

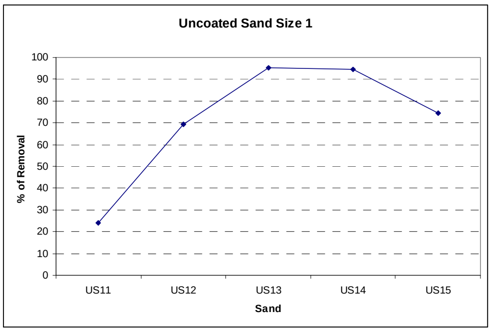


Figure 9: Percent of copper removal vs. Adsorption dose using Uncoated sand size 1.

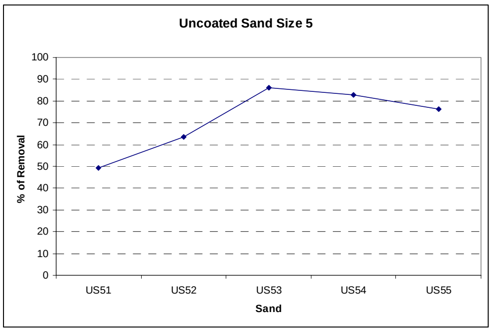


Figure 10: Percent of copper removal vs. Adsorption dose using Uncoated sand size 5.

In the case of using ferric nitrate coated LECA and ferric chloride coated LECA as adsorbent, the percentage of removal copper when we used ferric nitrate coated

LECA are greater than ferric chloride coated LECA. The percentages of removal in both types of coated LECA are increased with increasing the adsorption dose and the small size gave best adsorption. The reason of LECA coated ferric nitrate results better than LECA coated ferric chloride are due to the amount of iron oxide contain in LECA from coating. Table 15 shows the amount of iron in both types.

Table 15: Percent of removal copper with respect to the amount of iron contains in LECA nitrate and LECA chloride

Adsorbent type and size	Iron contains (mg/g)	Percent of removal in adsorption dose 0.5g
Ferric nitrate coated LECA size 1	6.7925	86.85
Ferric nitrate coated LECA size 2	7.6761	95.53
Ferric nitrate coated LECA size 3	11.038	97.17
Ferric nitrate coated LECA size 4	10.826	93.30
Ferric nitrate coated LECA size 5	10.112	93.24
Ferric chloride coated LECA size 1	7.4800	90.63
Ferric chloride coated LECA size 2	7.2898	91.83
Ferric chloride coated LECA size 3	8.8886	83.82
Ferric chloride coated LECA size 4	9.6454	84.25
Ferric chloride coated LECA size 5	10.475	94.06

In ferric nitrate and ferric chloride coating sand the copper removing is depending on the amount of iron contains in the sand from the coating. Whereas the amount of iron in sand size 5 from ferric nitrate is 1.7656mg iron /g sand, and the amount of iron in sand from ferric chloride are 0.8508 mg iron /g sand. For that sand coating ferric nitrate is removing more copper than sand coating ferric chloride as shown in fig. 11 and 12.

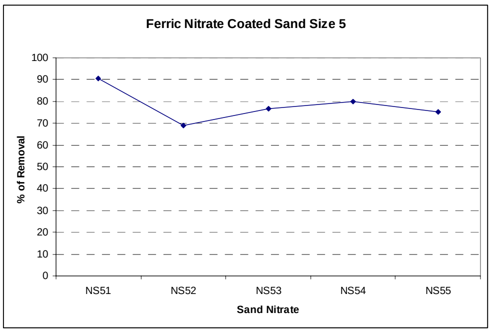


Figure 11: Percent of copper removal vs. Adsorption dose using ferric nitrate sand size 5.

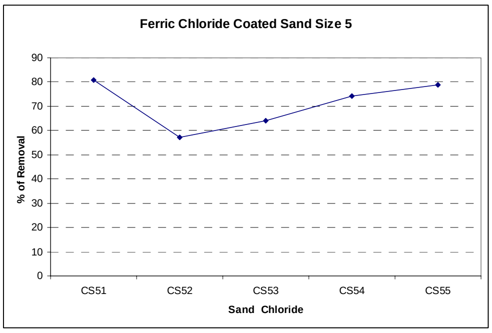


Figure 12: Percent of copper removal vs. Adsorption dose using chloride nitrate sand size 5.

7.2. Adsorption Isotherms Modelling and site energy Distribution

The linear Freundlich isotherm plots for the adsorption of the copper metal onto different adsorbent are presented in **appendix F**. In table 16 and figure 13 and 14 examination of the plot suggests that the linear Freundlich isotherm is a good model for the adsorption of copper into LECA coating ferric nitrate and some of adsorbent in LECA coating ferric chloride, but not for others adsorbent.

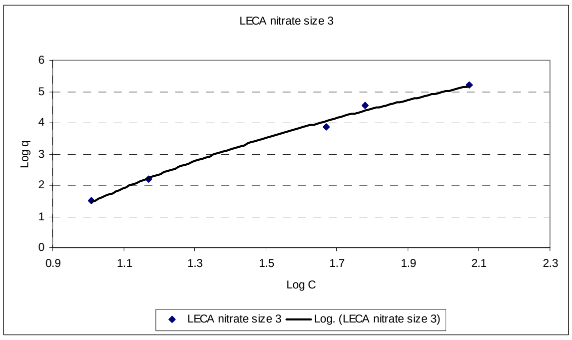


Figure 13: Adsorption isotherms modelling for LECA nitrate size 3.

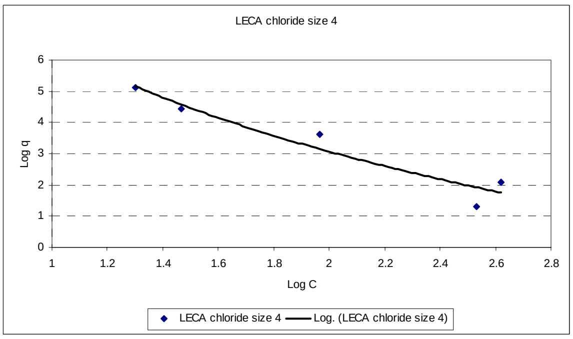


Figure 14: Adsorption isotherms modelling for LECA chloride size 4.

Table 1: Linear Freundlich sorption isotherm constants, coefficients of determination R^2

code	Adsorbent	n	K_f	code	Adsorbent	n	K_f
UL1	Uncoated LECA size 1	5.5928	74.989	**US1**	Uncoated sand size 5	1.0949	32.591
UL2	Uncoated LECA size 2	3.7594	76.983	**US2**	Uncoated sand size 5	0.9248	24.160
UL3	Uncoated LECA size 3	2.2624	33.227	**US3**	Uncoated sand size 5	1.1008	31.074
UL4	Uncoated LECA size 4	2.8994	38.690	**US4**	Uncoated sand size 5	0.9002	17.037
UL5	Uncoated LECA size 5	2.0534	23.393	**US5**	Uncoated sand size 5	0.9022	19.458
NL1	Nitrate coated LECA size 1	1.0267	4.0142	**NS1**	Nitrate coated sand size 1	0.8228	11.423
NL2	Nitrate coated LECA size 2	1.0222	3.6517	**NS2**	Nitrate coated sand size 2	0.9172	15.073
NL3	Nitrate coated LECA size 3	0.9998	3.4570	**NS3**	Nitrate coated sand size 3	0.8052	10.643
NL4	Nitrate coated LECA size 4	1.0223	3.6957	**NS4**	Nitrate coated sand size 4	0.7985	10.261
NL5	Nitrate coated LECA size 5	1.0282	3.7445	**NS5**	Nitrate coated sand size 5	0.7815	9.8355
CL1	Chloride coated LECA size 1	1.0250	4.3601	**CS1**	Chloride coated sand size 1	0.8263	13.261
CL2	Chloride coated LECA size 2	0.9933	3.8547	**CS2**	Chloride coated sand size 2	0.9430	18.582
CL3	Chloride coated LECA size 3	0.9817	3.8071	**CS3**	Chloride coated sand size 3	0.8056	12.209
CL4	Chloride coated LECA size 4	0.9765	3.8238	**CS4**	Chloride coated sand size 4	0.7982	11.713
CL5	Chloride coated LECA size 5	0.9998	3.8645	**CS5**	Chloride coated sand size 5	0.7789	11.171

Based on the n and K_f values, and since the value of n and k_f relate to energy of adsorption. So it is impossible to judge which adsorbent is better than other before calculating the site energy distribution and energy frequency distribution for every adsorbent. The site energy distribution and energy frequency distribution were calculated depending upon the common Freundlich isotherm model (equation 21).

Figure 15 and 16 shows the site energy distribution and energy frequency distribution for uncoated material.

In uncoated LECA and uncoated sand the adsorbent surface contains low energy sites, and high energy frequency distribution, this can be explain as

1- Almost all of these sites on the adsorbent surface are not available to the Adsorbate and large numbers of pores site are not occupied with Adsorbate.

2- The bond between sites on adsorbent surface and the molecules of Adsorbate are very weak for that's this system contains a lot of repulsion and attraction, that's mean reversible and irreversible reactions are done at same time.

With respect to the size of adsorbent, the larger size contains huge number of sites with comparable to smaller, then the larger size must have energy distribution frequency more than smaller size (the complete graph in appendix 3).

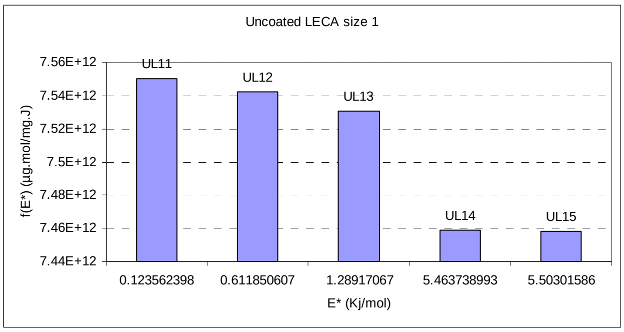


Figure 15: Site energy distributions for uncoated LECA size 1

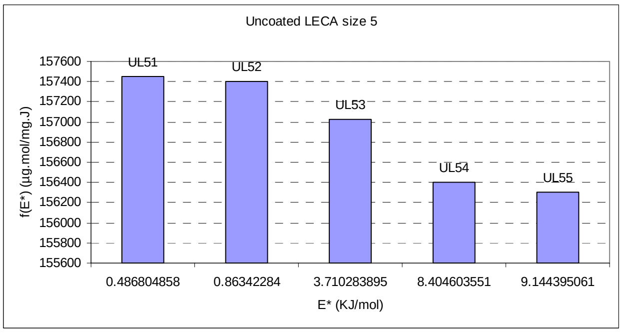


Figure 16: Site energy distributions for uncoated LECA size 5

In coating material with ferric nitrate the energy frequency distribution ranges between 120 – 190 µg.mol/mg.J, whereas the site energy in LECA nitrate is higher than site energy in sand nitrate, which mean the sites in the surface of LECA nitrate are occupied with adsorbate more than the sites in sand nitrate.

In the same type, for example LECA nitrate, the smaller size of adsorbent gives site energy higher than the results that we obtained from larger size although small size gives energy frequency distribution less than that's results from large size as shown in figure15. This is because the smaller size are completely coated but in large size due to the largest size the coating is reached only the upper surface, and inside part is remained without coating that means the large size of adsorbent is combined between coated and uncoated in the same pieces, for that's the smaller size is better for adsorption than larger size. The sites energy and energy frequency distribution in the materials coated with ferric chloride gives result similar to materials coated with ferric nitrate as shown in figure17 and 18.

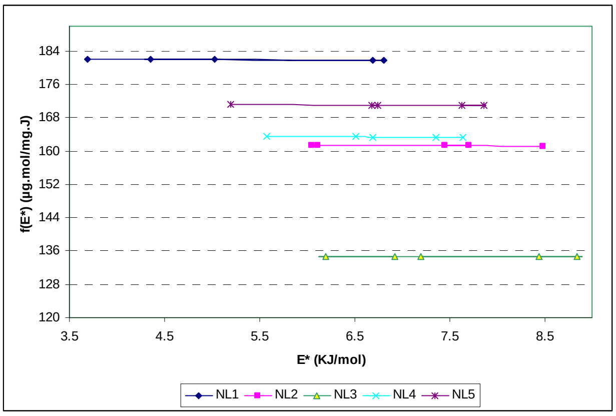


Figure 17: The order of Site energy distributions for LECA nitrate.

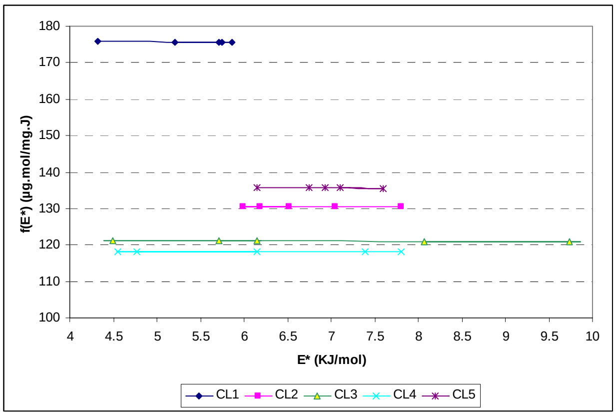


Figure 18: The order of Site energy distributions for LECA chloride.

8.0. Chapter eight: Conclusion

Copper comes to the drinking water from different source, one of these sources are the copper pipes which are used in drinking water system. The presence of copper in drinking water with high concentration exposes to the human causes several public health problems. Adsorption is the one of methods which is used to remove the heavy metal as well as the copper from drinking water.

Iron oxide coated LECA and coated sand was used as adsorbent for removal copper from drinking water, LECA and sand were sieved to five sizes and two possible compound were used in the coating process, one of the two is ferric nitrate and the other is ferric chloride, in the adsorption process iron oxide coated LECA with ferric nitrate is consider the best adsorbent among the other category in removing copper specifically the size three from that's type , since this type did not gave high percent of copper removal from water, and best value in Freundlich isotherm model only, but it also gave high site energy and low energy frequency.

With respect to the other adsorbent, uncoated sand is better than uncoated LECA, and the coated LECA is better than coated sand, and at the same time the material that coated with ferric nitrate is better than material which is coated with ferric chloride. Finally it is possible to make a daftly order to the adsorbent occurring to the efficiency of removing, Freundlich isotherms model, site energy distribution model and energy frequency distribution model to get this order:
Efficiency of removing: **NL** > **CL** > **NS** > **CS** > **US** > **UL**.
Freundlich isotherms model: **NL** > **CL** > **NS** > **CS** > **US** > **UL**.
Site energy distribution model: **NL** > **CL** > **NS** > **CS** > **US** > **UL.**

Energy frequency distribution model: **NL** > **CL** > **NS** > **CS** > **US** > **UL.**

And if we take more specific, depend on the size, we will get this order:

Efficiency of removing: **NL3** > **CL5** > **NL2** > **……….**

Freundlich isotherms model:

n Value: NL3 > **CL5** > **NL2** > **……….**

K_f Value: NL3 > **CL5** > **NL2** > **……….**

Site energy distribution model: **NL3** > **CL5** > **NL2** > **……….**

Energy frequency distribution model: **NL3** > **CL5** > **NL2** > **……….**

From that LECA coated with ferric nitrate size three and LECA coated with ferric chloride size five are the best adsorbent to complete the progress studies on removing copper from water.

9.0. Chapter nine: References

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10.0. Chapter ten: Appendices:

Appendix A: Glossary of terms

Appendix B: Type of adsorbent and definition of code

Appendix C: Solutions Preparation

Appendix D: Coating procedure

Appendix E: ICP – MS result

Appendix F: Freundlich adsorption isotherms modelling

Appendix G: Site energy distribution and frequency distribution modelling

Appendix A: Glossary of terms

Acceptable daily Intake	**Estimate of the largest amount of chemical to which a person can be exposed on a daily basis that is not anticipated to result in adverse effects (usually expressed in mg/kg/day).**
Adsorbate	The material that accumulate at an interface; it is the substances in the adsorbed state.
Adsorbent	Solid material on which adsorption occurs, like iron oxide and active carbon.
Adsorption	A surface phenomenon defined as the increase in concentration of a particular component at the surface on interface between two phases.
Adsorptive	Adsorbable substance in the fluid phase. A molecule or an ion in the soil solution that potentially can be adsorbed.
Aggregate:	A mass or cluster of soil particles, often having a characteristic shape.
Bioaccumulants	Substances that increase in concentration in living organisms as they take in contaminated air, water, or food because the substances are very slowly metabolized or excreted.
Chelation	A chemical complexing (forming or joining together) of metallic cations (such as copper) with certain organic compounds, such as EDTA (ethylene diamine tetracetic acid). Chelation is used to prevent the precipitation of metals (copper).
Chemisorptions	Adsorption involving chemical bonding
Copper	A chemical element in the periodic table that has the symbol **Cu** (Latin: *cuprum*) and atomic number 29. It is a ductile metal with excellent electrical conductivity, and finds extensive use as an electrical conductor, thermal conductor, as a building material, and as a component of various alloys.
Diffusion	The movement of suspended or dissolved particles from a more concentrated to a less concentrated area. The process tends to distribute the particles more uniformly.
Ecosystem	The interacting synergism of all living organisms in a particular environment; every plant, insect, aquatic animal, bird, or land species that forms a complex web of interdependency. An action taken at any level in the food chain, use of a pesticide for example, has a potential domino effect on every other occupant of that system.
Electrodialysis	A process that uses electrical current applied to permeable membranes to remove minerals from water. Often used to desalinize salty or brackish water
Enzyme	(a) Any of numerous proteins or conjugated proteins produced by living organisms and functioning as biochemical catalysts. (b) A protein that a living organism uses in the process of degrading a specific compound. The protein serves as a catalyst in the compound's biochemical transformation.
Exposure	Radiation or pollutants that come into contact with the body and present a potential health threat. The most common routes of exposure are through the skin, mouth, or by inhalation.
Falvic acid	The coloured material which reminds in solution after the remove of humic acid by acidification.
Humic acid	A type of humic substance, it is the dark coloured organic material which can be extract from soil by various reagents and which is insoluble in dilute acid.

Ion exchange treatment	A process whereby an insoluble substance removes ions of positive or negative charge from an electrolytic solution and releases other ions of like charge into solution in a chemically equivalent amount.
Leachate	A liquid that results from water collecting contaminants as it trickles through wastes, agricultural pesticides or fertilizers. Leaching may occur in farming areas, feedlots, and landfills, and may result in hazardous substances entering surface water, ground water, or soil
Leaching	The process by which soluble constituents are dissolved and filtered through the soil by a percolating fluid.
Ligands	A molecule or ion with at least one pair of unshared electron available for coordinate bonding with Cation
Maximum contaminant level (MCL)	The maximum permissible level of a contaminant in water which is delivered to the free flowing outlet of the ultimate user of a public water system, except in the case of turbidity where the maximum permissible level is measured at the point of entry to the distribution system. Contaminants added to the water under circumstances controlled by the user are excluded from this definition, except those contaminants resulting from the corrosion of piping and plumbing caused by water quality.
pH	A measure of the acidity of a solution. pH is equal to the negative logarithm of the concentration of hydrogen ions in a solution. A pH of 7 is neutral. Values less than 7 are acidic, and values greater than 7 are basic
pollutant	Generally, any substance introduced into the environment that adversely affects the usefulness of a resource.
Physisorption	Adsorption without chemical bonding
Surface coverage	Ration of the amount of adsorbed substance to monolayer capacity

Appendix B: Type of adsorbent and definition of code

Uncoated sand

US11	Uncoated sand size 1 weight 0.25g
US12	Uncoated sand size 1 weight 1g
US13	Uncoated sand size 1 weight 5g
US14	Uncoated sand size 1 weight 10g
US15	Uncoated sand size 1 weight 25g
US21	Uncoated sand size 2 weight 0.25g
US22	Uncoated sand size 2 weight 1g
US23	Uncoated sand size 2 weight 5g
US24	Uncoated sand size 2 weight 10g
US25	Uncoated sand size 2 weight 25g
US31	Uncoated sand size 3 weight 0.25g
US32	Uncoated sand size 3 weight 1g
US33	Uncoated sand size 3 weight 5g
US34	Uncoated sand size 3 weight 10g
US35	Uncoated sand size 3 weight 25g
US41	Uncoated sand size 4 weight 0.25g
US42	Uncoated sand size 4 weight 1g
US43	Uncoated sand size 4 weight 5g
US44	Uncoated sand size 4 weight 10g
US45	Uncoated sand size 4 weight 25g
US51	Uncoated sand size 5 weight 0.25g
US52	Uncoated sand size 5 weight 1g
US53	Uncoated sand size 5 weight 5g
US54	Uncoated sand size 5 weight 10g
US55	Uncoated sand size 5 weight 25g

Ferric nitrate coated sand

NS11	Nitrate coated sand size 1 weight 0.25g
NS12	Nitrate coated sand size 1 weight 1g
NS13	Nitrate coated sand size 1 weight 5g
NS14	Nitrate coated sand size 1 weight 10
NS15	Nitrate coated sand size 1 weight 25
NS21	Nitrate coated sand size2 weight 0.25g
NS22	Nitrate coated sand size2 weight 1g
NS23	Nitrate coated sand size2 weight 5g
NS24	Nitrate coated sand size2 weight 10g
NS25	Nitrate coated sand size2 weight 25g
NS31	Nitrate coated sand size3 weight 0.25g
NS32	Nitrate coated sand size3 weight 1g
NS33	Nitrate coated sand size3 weight 5g
NS34	Nitrate coated sand size3 weight 10g
NS35	Nitrate coated sand size3 weight 25g
NS41	Nitrate coated sand size4 weight 0.25g
NS42	Nitrate coated sand size4 weight 1g
NS43	Nitrate coated sand size4 weight 5g
NS44	Nitrate coated sand size4 weight 10g
NS45	Nitrate coated sand size4 weight 25g
NS51	Nitrate coated sand size5 weight 0.25g
NS52	Nitrate coated sand size5 weight 1g
NS53	Nitrate coated sand size5 weight 5g
NS54	Nitrate coated sand size5 weight 10g
NS55	Nitrate coated sand size5 weight 25g

Ferric chloride coated sand

CS11	Chloride coated sand size 1 weight 0.25g
CS12	Chloride coated sand size 1 weight 1g
CS13	Chloride coated sand size 1 weight 5g
CS14	Chloride coated sand size 1 weight 10
CS15	Chloride coated sand size 1 weight 25
CS21	Chloride coated sand size2 weight 0.25g
CS22	Chloride coated sand size2 weight 1g
CS23	Chloride coated sand size2 weight 5g
CS24	Chloride coated sand size2 weight 10g
CS25	Chloride coated sand size2 weight 25g
CS31	Chloride coated sand size3 weight 0.25g
CS32	Chloride coated sand size3 weight 1g
CS33	Chloride coated sand size3 weight 5g
CS34	Chloride coated sand size3 weight 10g
CS35	Chloride coated sand size3 weight 25g
CS41	Chloride coated sand size4 weight 0.25g
CS42	Chloride coated sand size4 weight 1g
CS43	Chloride coated sand size4 weight 5g
CS44	Chloride coated sand size4 weight 10g
CS45	Chloride coated sand size4 weight 25g
CS51	Chloride coated sand size5 weight 0.25g
CS52	Chloride coated sand size5 weight 1g
CS53	Chloride coated sand size5 weight 5g
CS54	Chloride coated sand size5 weight 10g
CS55	Chloride coated sand size5 weight 25g

Uncoated LECA

UL11	Uncoated LECA size1 weight 0.125g
UL12	Uncoated LECA size 1 weight 0.25
UL13	Uncoated LECA size 1 weight 0.5g
UL14	Uncoated LECA size 1weight 2.5g
UL15	Uncoated LECA size 1 weight 5g
UL21	Uncoated LECA size 2 weight 0.125g
UL22	Uncoated LECA size 2 weight 0.25
UL23	Uncoated LECA size 2 weight 0.5g
UL24	Uncoated LECA size 2 weight 2.5g
UL25	Uncoated LECA size 2 weight 5g
UL31	Uncoated LECA size 3 weight 0.125g
UL32	Uncoated LECA size 3 weight 0.26
UL33	Uncoated LECA size 3 weight 0.5g
UL34	Uncoated LECA size 3 weight 2.5g
UL35	Uncoated LECA size 3 weight 5g
UL41	Uncoated LECA size 4 weight 0.125g
UL42	Uncoated LECA size 4 weight 0.27
UL43	Uncoated LECA size 4 weight 0.5g
UL44	Uncoated LECA size 4 weight 2.5g
UL45	Uncoated LECA size 4 weight 5g
UL51	Uncoated LECA size 5 weight 0.125g
UL52	Uncoated LECA size 5 weight 0.28
UL53	Uncoated LECA size 5 weight 0.5g
UL54	Uncoated LECA size 5 weight 2.5g
UL55	Uncoated LECA size 5 weight 5g

Ferric nitrate coated LECA

NL11	Nitrate coated LECA size 1 weight 0.125g
NL12	Nitrate coated LECA size 1 weight 0.25g
NL13	Nitrate coated LECA size 1 weight 0.5g
NL14	Nitrate coated LECA size 1 weight 2.5g
NL15	Nitrate coated LECA size 1 weight 5.0g
NL21	Nitrate coated LECA size2 weight 0.125g
NL22	Nitrate coated LECA size2 weight 0.25g
NL23	Nitrate coated LECA size2 weight 0.5gg
NL24	Nitrate coated LECA size2 weight 2.5g
NL25	Nitrate coated LECA size2 weight 5.0g
NL31	Nitrate coated LECA size3 weight 0.125g
NL32	Nitrate coated LECA size3 weight 0.25g
NL33	Nitrate coated LECA size3 weight 0.5g
NL34	Nitrate coated LECA size3 weight 2.5g
NL35	Nitrate coated LECA size3 weight 5.0g
NL41	Nitrate coated LECA size4 weight 0.125g
NL42	Nitrate coated LECA size4 weight 0.25g
NL43	Nitrate coated LECA size4 weight 0.5g
NL44	Nitrate coated LECA size4 weight 2.5g
NL45	Nitrate coated LECA size4 weight 5.0g
NL51	Nitrate coated LECA size5 weight 0.125g
NL52	Nitrate coated LECA size5 weight 0.25g
NL53	Nitrate coated LECA size5 weight 0.5g
NL54	Nitrate coated LECA size5 weight 2.5g
NL55	Nitrate coated LECA size5 weight 5.0g

Ferric chloride coated sand

CL11	Chloride coated LECA size 1 weight 0.125g
CL12	Chloride coated LECA size 1 weight 0.25g
CL13	Chloride coated LECA size 1 weight 0.5g
CL14	Chloride coated LECA size 1 weight 2.5g
CL15	Chloride coated LECA size 1 weight 5.0g
CL21	Chloride coated LECA size2 weight 0.125g
CL22	Chloride coated LECA size2 weight 0.25g
CL23	Chloride coated LECA size2 weight 0.5g
CL24	Chloride coated LECA size2 weight 2.5g
CL25	Chloride coated LECA size2 weight 5.0g
CL31	Chloride coated LECA size3 weight 0.125g
CL32	Chloride coated LECA size3 weight 0.25g
CL33	Chloride coated LECA size3 weight 0.5g
CL34	Chloride coated LECA size3 weight 2.5g
CL35	Chloride coated LECA size3 weight 5.0g
CL41	Chloride coated LECA size4 weight 0.125g
CL42	Chloride coated LECA size4 weight 0.25g
CL43	Chloride coated LECA size4 weight 0.5g
CL44	Chloride coated LECA size4 weight 2.5g
CL45	Chloride coated LECA size4 weight 5.0g
CL51	Chloride coated LECA size5 weight 0.125g
CL52	Chloride coated LECA size5 weight 0.25g
CL53	Chloride coated LECA size5 weight 0.5g
CL54	Chloride coated LECA size5 weight 2.5g
CL55	Chloride coated LECA size5 weight 5.0g

Appendix C: Solutions Preparation

1- 0.5M Ferric nitrate solution:
For preparation ferric nitrate solution, ferric nitrate hydrated Fe (NO) $_3$. $9H_2O$ was used.
Preparation of 2 L 0.5M $\mathrm{Fe(NO_3)_3.9H_2O}$

$$2L\ \mathrm{Solution} \times 0.5\frac{mol\ \mathrm{Fe(NO_3)_3.9H_2O}}{1L\ Solution} \times 404\frac{g\ \mathrm{Fe(NO_3)_3.9H_2O}}{1\,\mathrm{mol}\ \mathrm{Fe(NO_3)_3.9H_2O}} = 404g\ \mathrm{Fe(NO_3)_3.9H_2O}$$

Then $404\,g\ \mathrm{Fe(NO_3)_3.9H_2O}$ were added in 2L of Milli – Q water

2- 0.5M Ferric chloride solution:
For preparation ferric nitrate solution, ferric chloride hydrated Fe (NO) $_3$. $9H_2O$ was used.

Preparation of 2 L 0.5M

$$2L\ \mathrm{Solution} \times 0.5\frac{mol\ \mathrm{Fe(Cl)_3.5H_2O}}{1L\ Solution} \times 258.5\frac{g\ \mathrm{Fe(Cl)_3.5H_2O}}{1\,\mathrm{mol}\ \mathrm{Fe(Cl)_3.5H_2O}} = 258.5g\ \mathrm{Fe(Cl)_3.5H_2O}$$

Then $258.5\mathrm{g\,Fe(Cl)_3.5H_2O}$ were added in 2L of Milli – Q water

3- Copper solution (100μg/L)
For the preparation of copper solution, copper sulphate $CuSO_4.5H_2O$ was used, but due to difficulties with weighting very small amount of $CuSO_4.5H_2O$ (about $3.95\times10^{-4}g$). For that we will prepare firstly stock solution with concentration 1g/L and later diluted to concentration 100μg/L

$$1L\ \mathrm{Solution} \times \frac{\mathrm{1g\ copper}}{1L\ Solution} \times \frac{\mathrm{249g\ CuSO_4.5H_2O}}{\mathrm{63g\ copper}} = 3.95g\ \mathrm{CuSO_4.5H_2O}$$

So $3.95g\ \mathrm{CuSO_4.5H_2O}$ will add to 1L Milli – Q water to get solution of copper with concentration 1g Cu/L

And for preparation 100μg Cu/L

$$(C_i \times \mathrm{V_i})_{concentrated\ \mathrm{solution}} = (C_d \times \mathrm{V_d})_{\mathrm{diluted\ solution}}$$

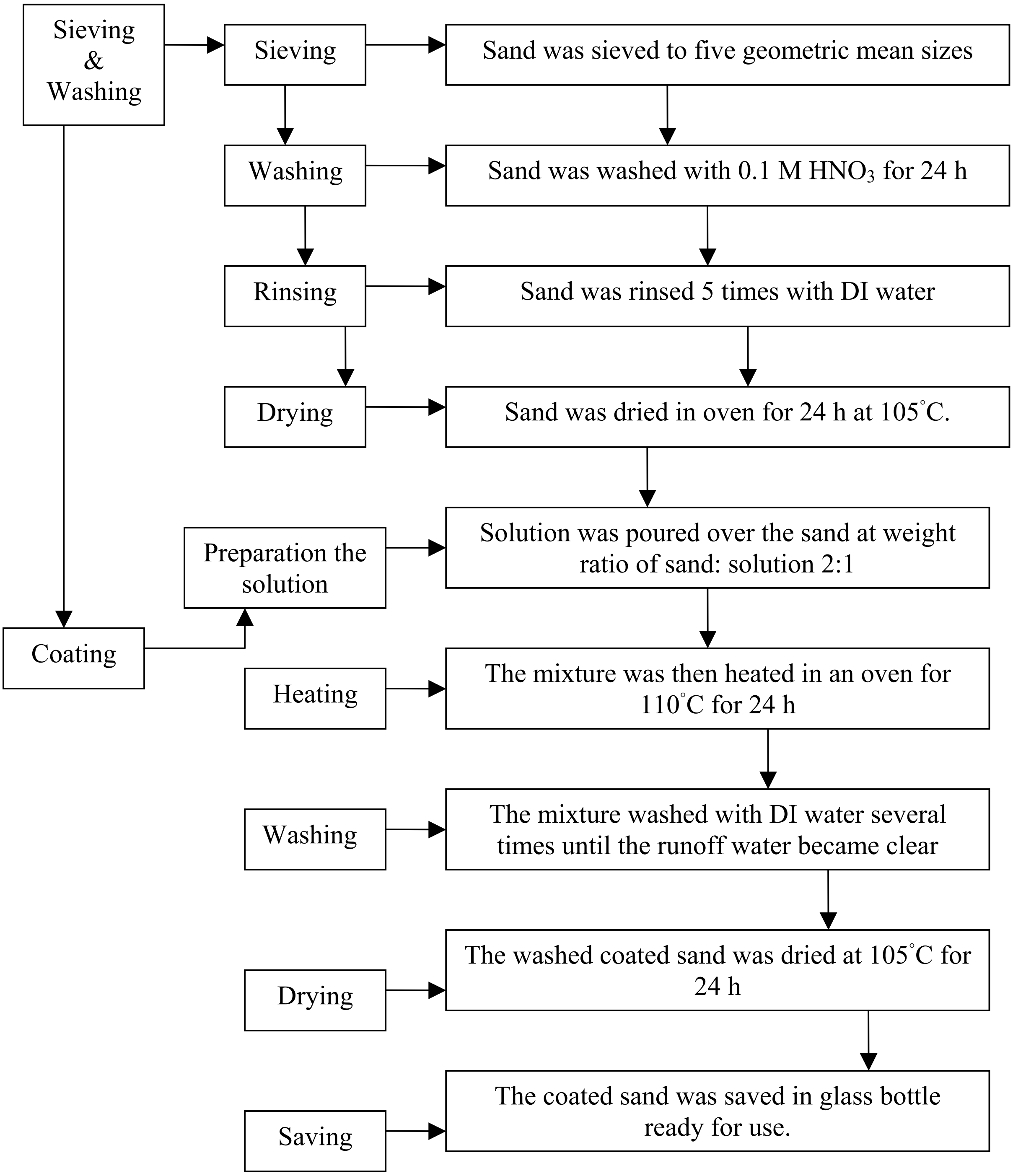
$$\left(1g\frac{\mathrm{Cu}}{\mathrm{L}} \times \mathrm{V_i}\right) = \left(100\mu g\frac{Cu}{L} \times 10L\right)$$

$$\mathrm{V_i} = 1\times10^{-3}L = 1ml$$

So we will tack 1ml from stock solution and add it to 10L Milli – Q water to get copper solution with concentration 100μg Cu/L

Appendix D: Coating procedure

Coating of sand



Sand was sieved to five geometric mean sizes

Sand was washed with 0.1 M HNO_3 for 24 h

Sand was rinsed 5 times with DI water

Sand was dried in oven for 24 h at 105°C.

Solution was poured over the sand at weight ratio of sand: solution 2:1

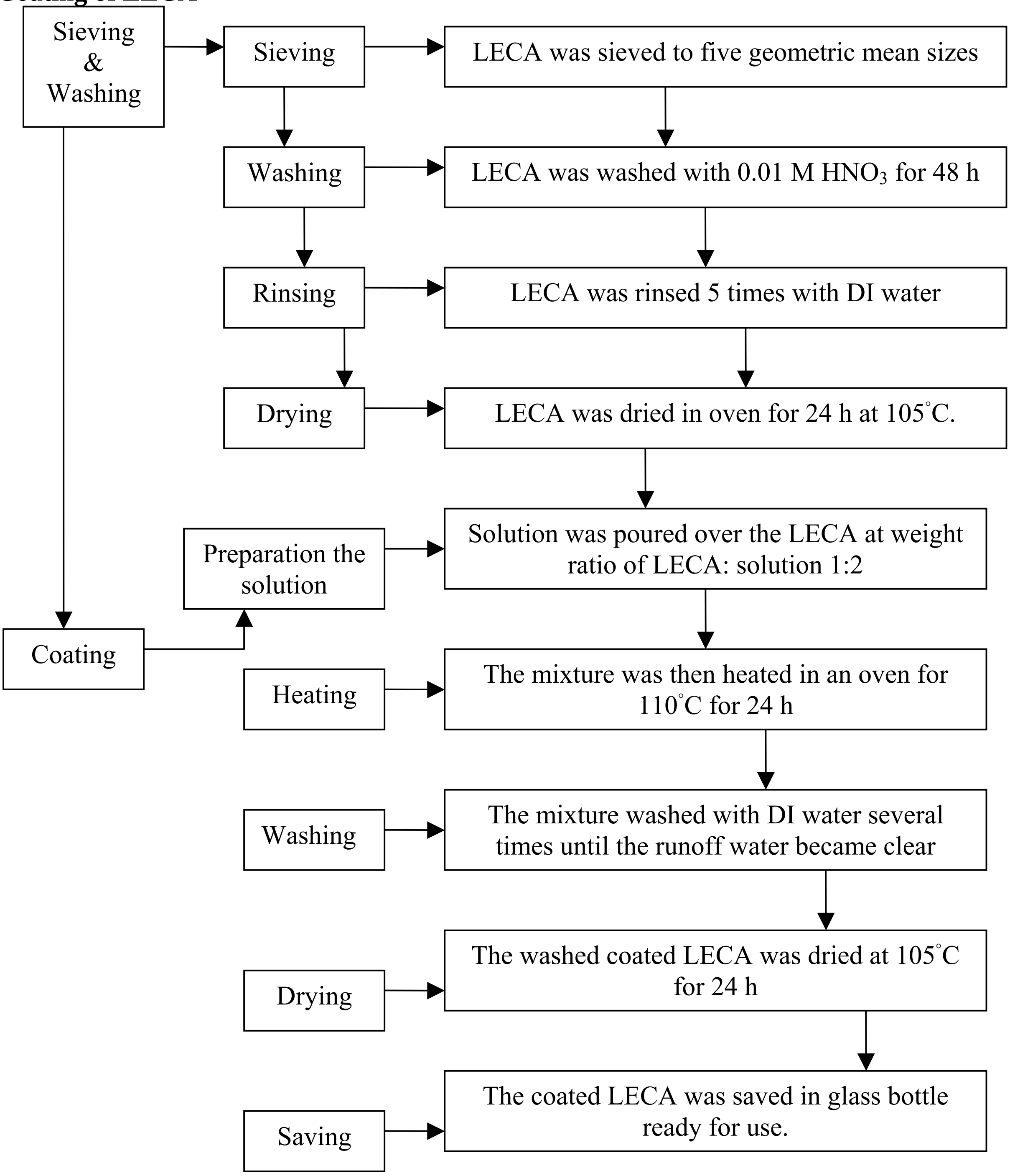
The mixture was then heated in an oven for 110°C for 24 h

The mixture washed with DI water several times until the runoff water became clear

The washed coated sand was dried at 105°C for 24 h

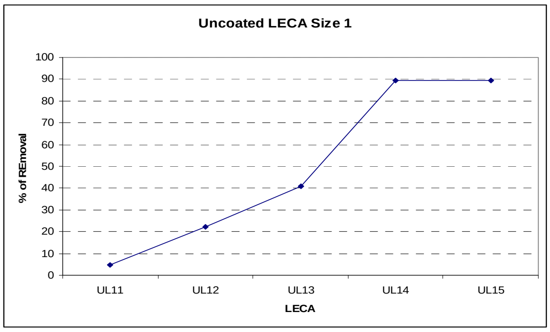
The coated sand was saved in glass bottle ready for use.

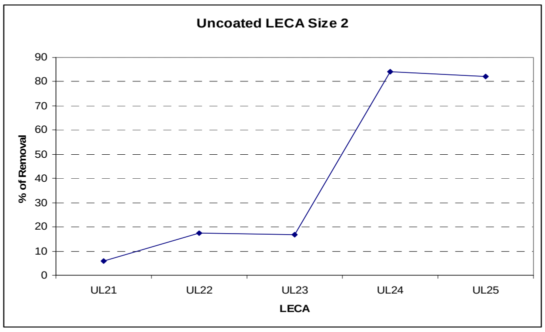
Coating of LECA

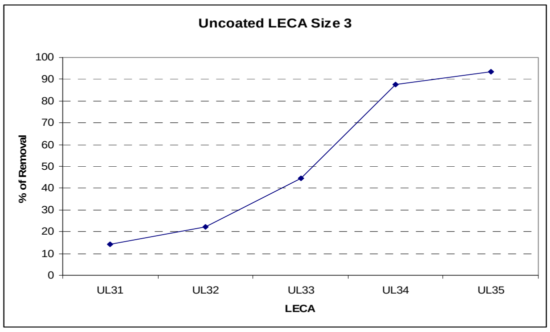


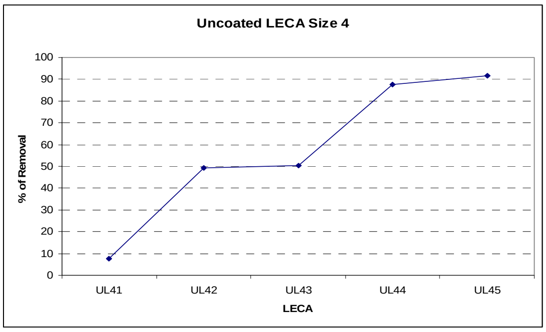
Appendix E: ICP – MS result

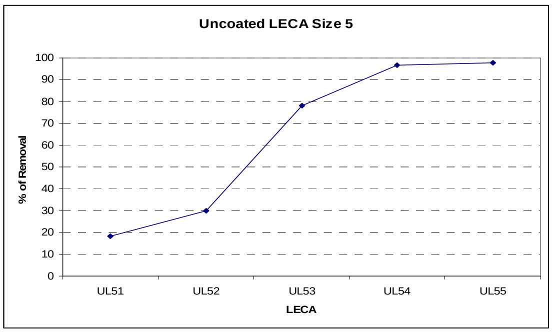
Uncoated LECA



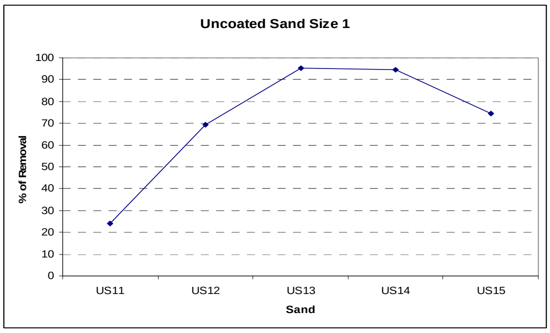


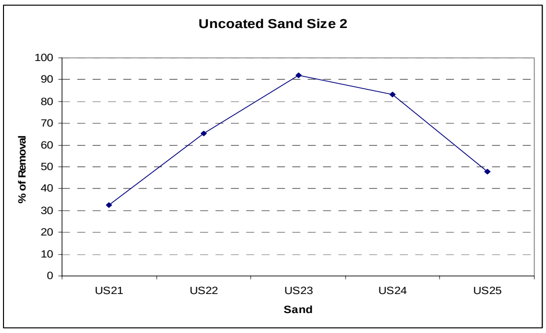


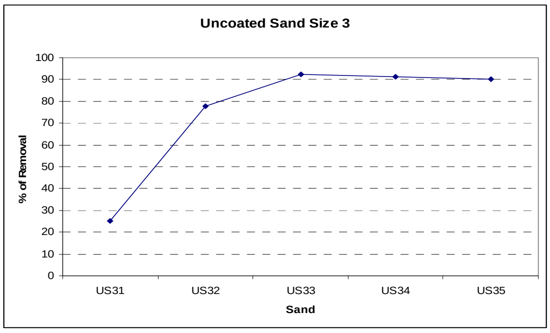


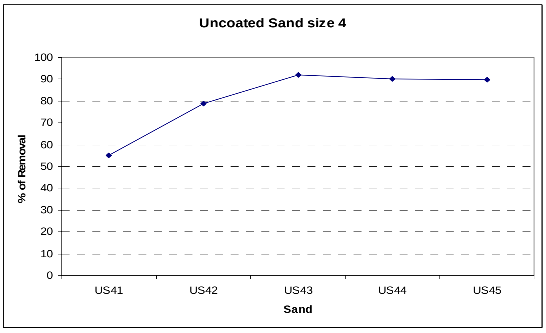


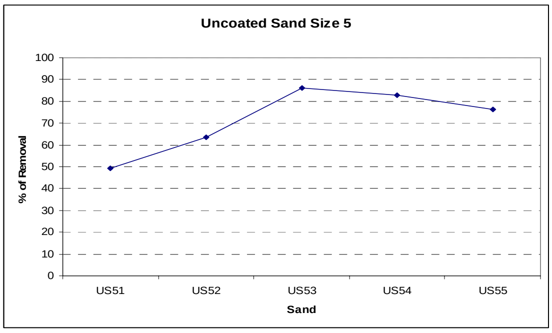
Uncoated sand



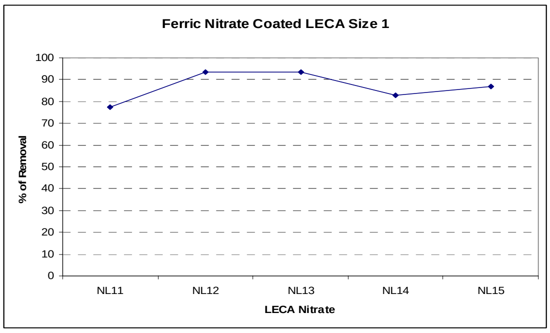


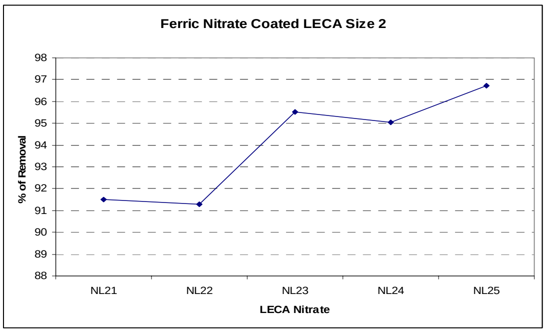


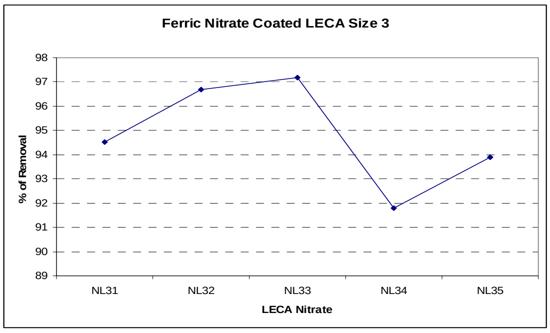


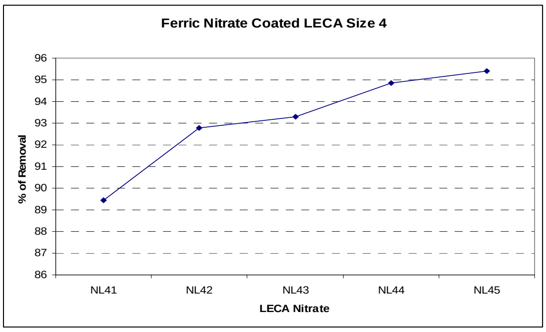


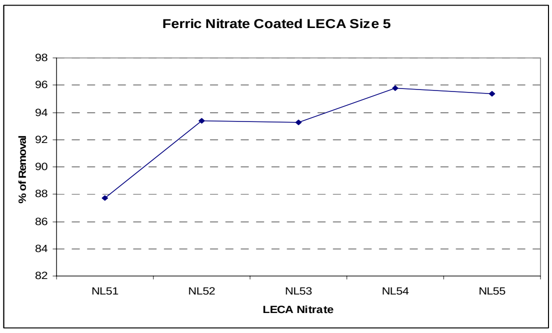
Ferric nitrate coated LECA



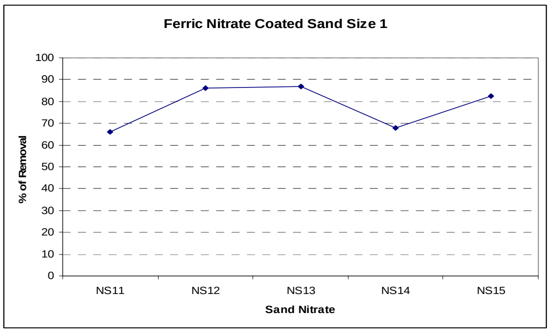


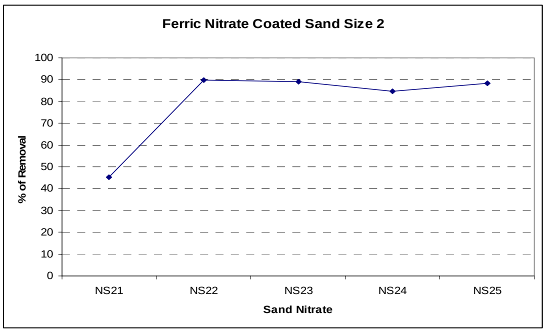


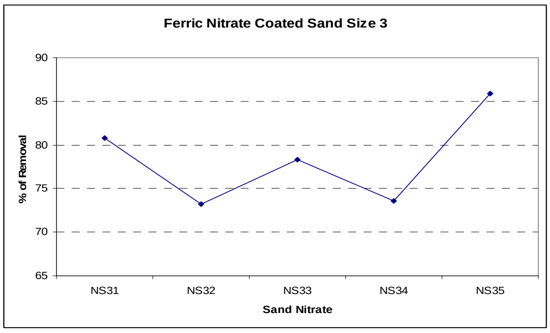


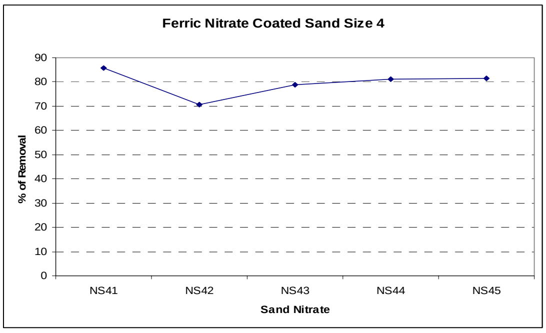


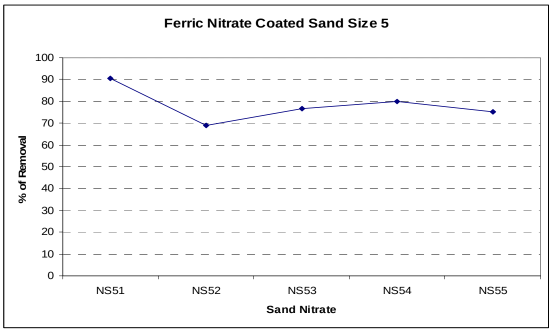
Ferric nitrate coated sand



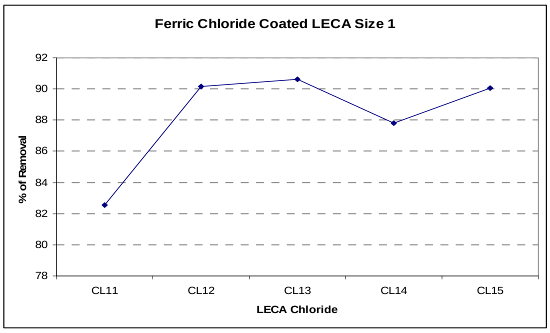


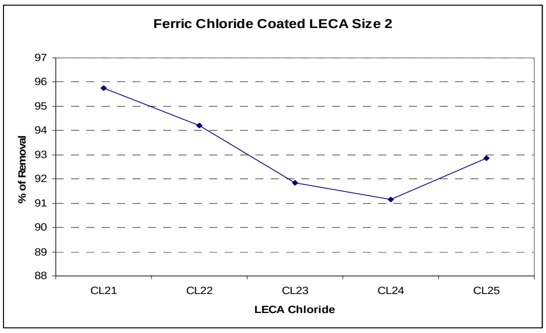


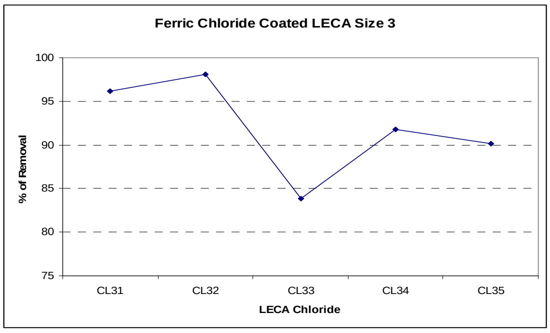


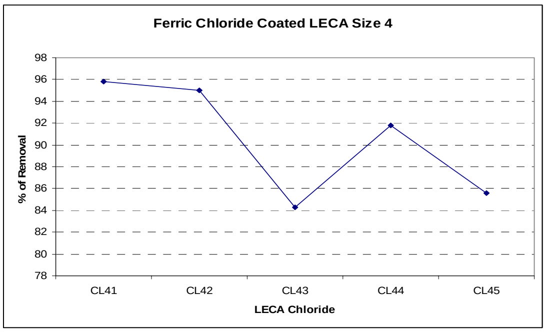


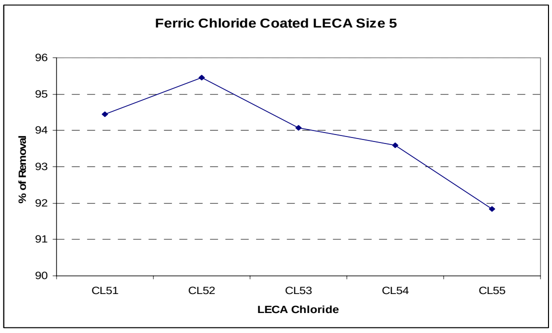
Ferric Chloride coated LECA



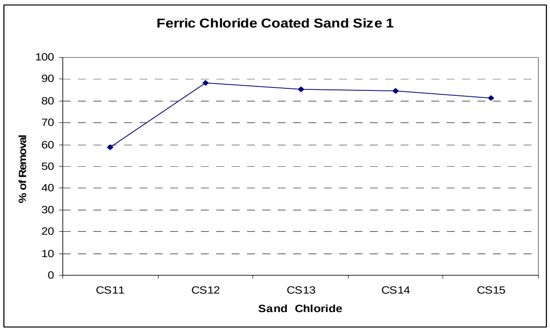


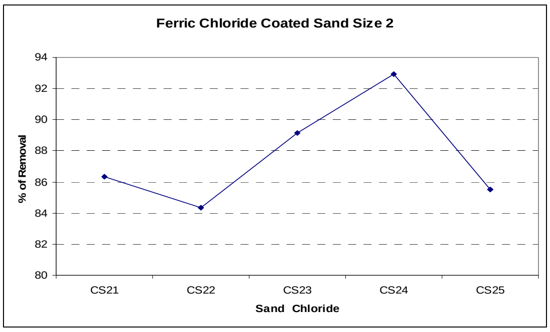


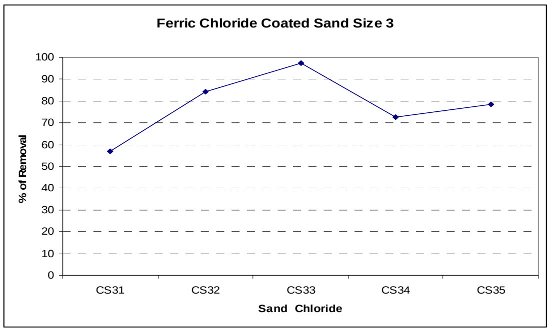


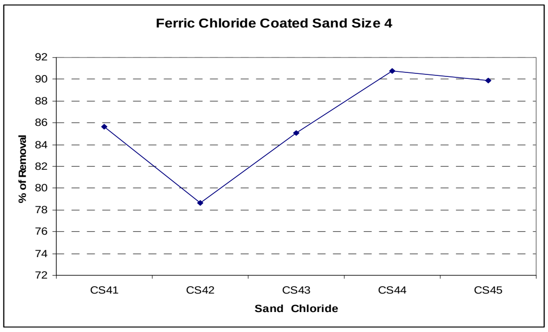


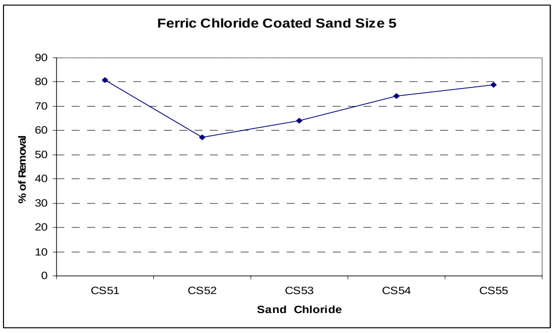
Ferric chloride coated sand





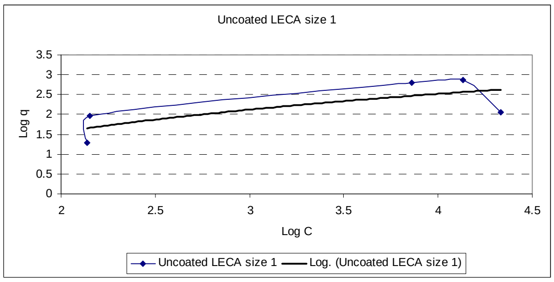


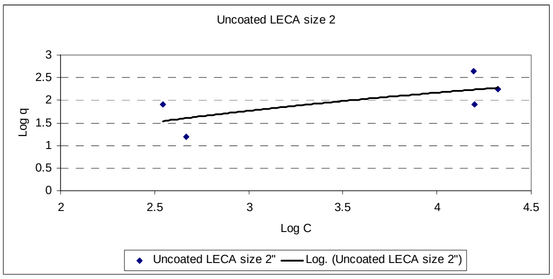


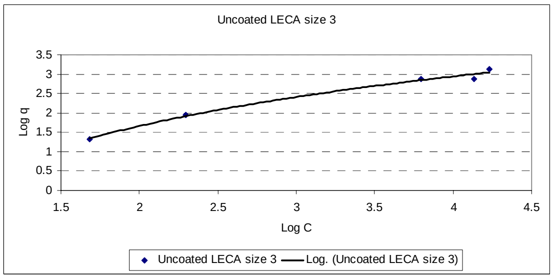


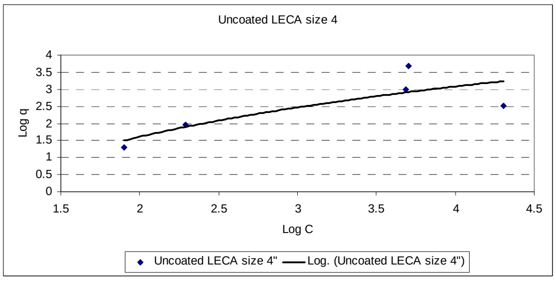
Appendix F: Freundlich adsorption isotherms modelling

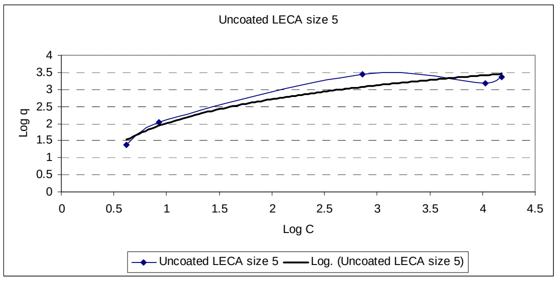
Uncoated LECA

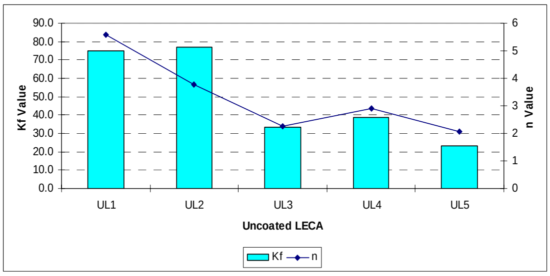






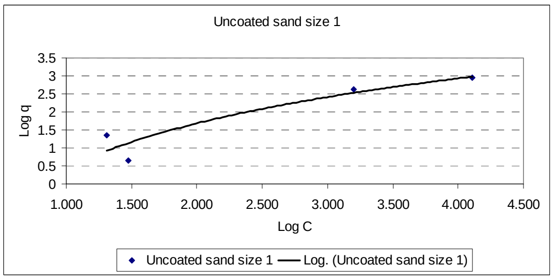


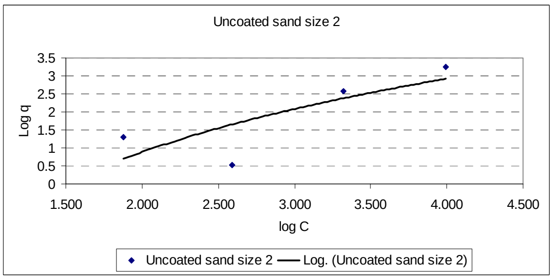


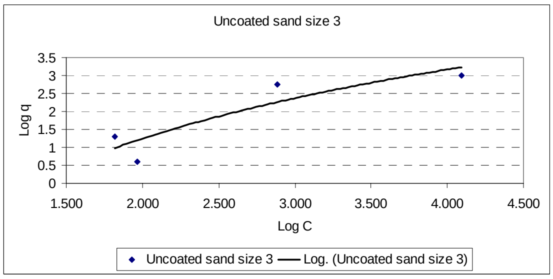


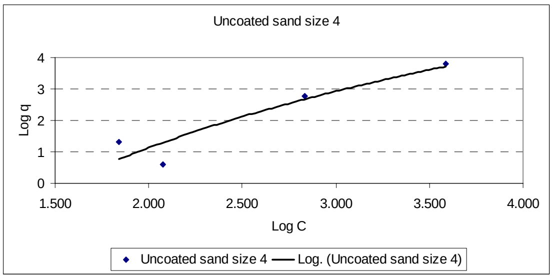
	n	K_f
UL1	5.5928	74.9894
UL2	3.7594	76.9839
UL3	2.2624	33.2277
UL4	2.8994	38.6901
UL5	2.0534	23.3938

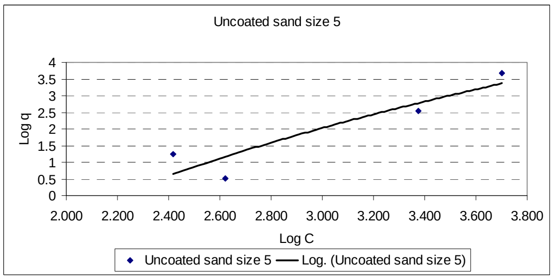
Uncoated sand

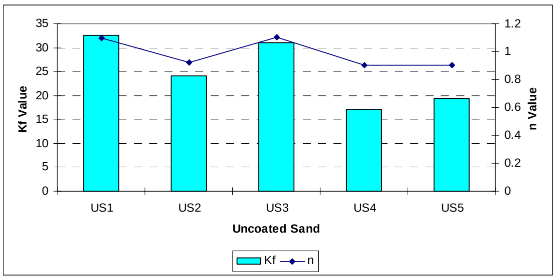






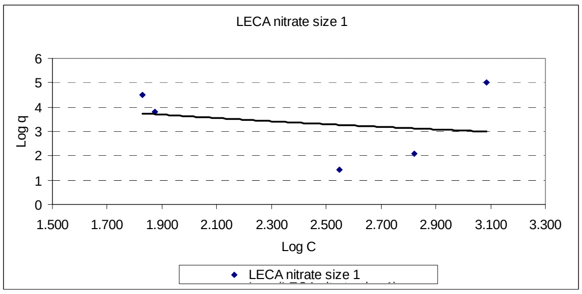


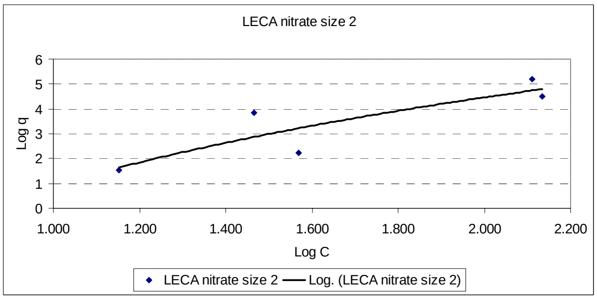


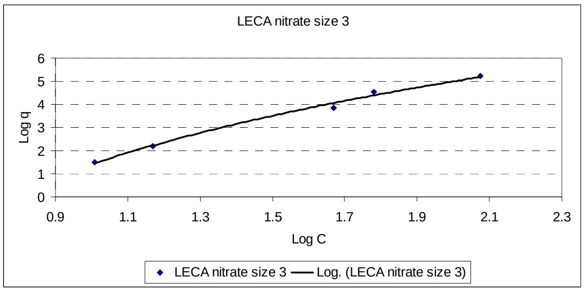


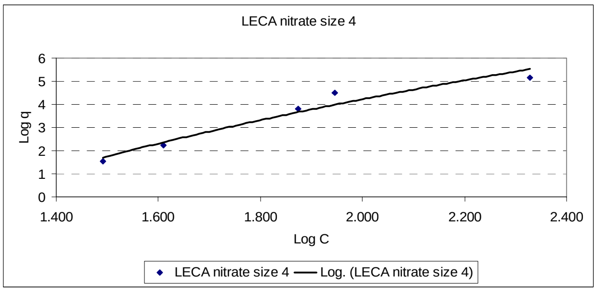
	n	K_f
US1	1.094930	32.59117
US2	0.924813	24.16017
US3	1.100837	31.07420
US4	0.900252	17.03727
US5	0.902201	19.45808

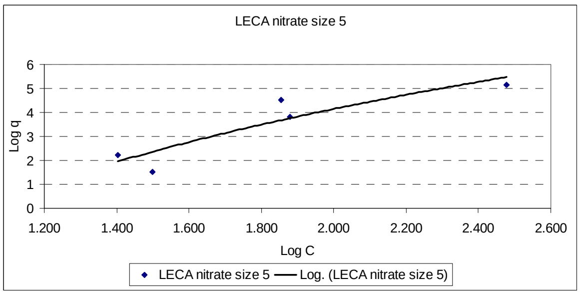
Ferric nitrate coated LECA

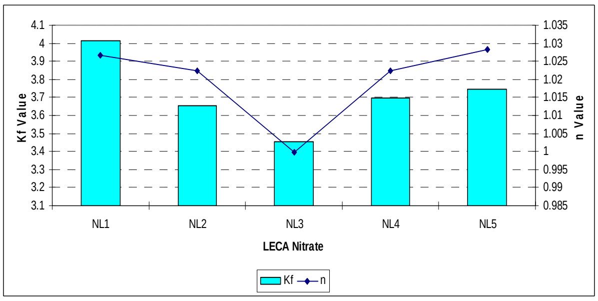






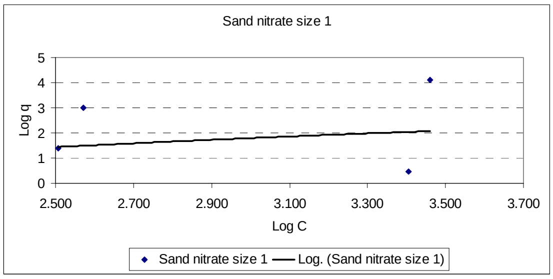


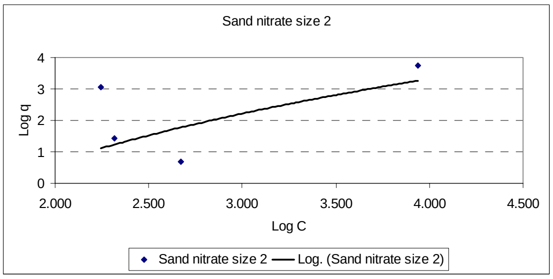


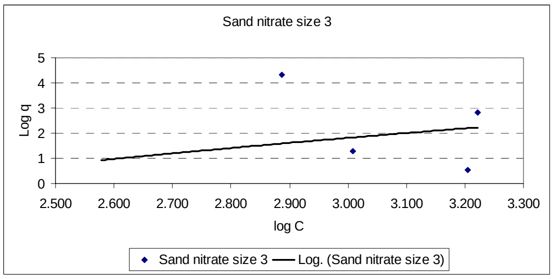


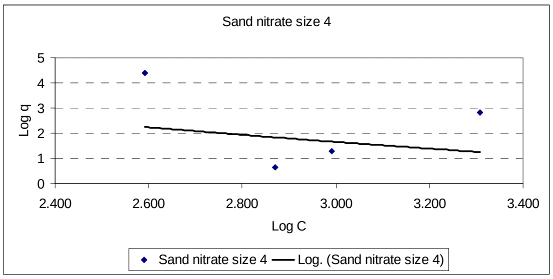
	n	K_f
NL1	1.026799	4.014209
NL2	1.022286	3.651741
NL3	0.999700	3.457005
NL4	1.022390	3.695728
NL5	1.028278	3.744553

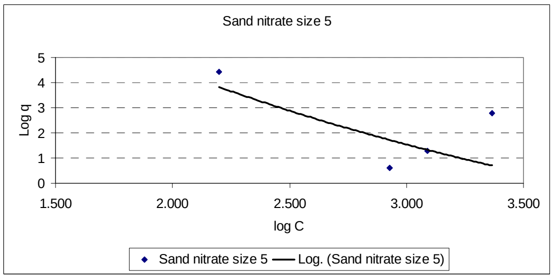
Ferric nitrate coated sand

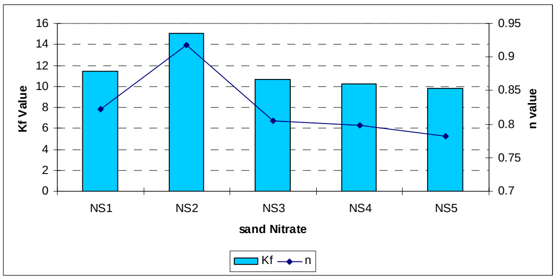






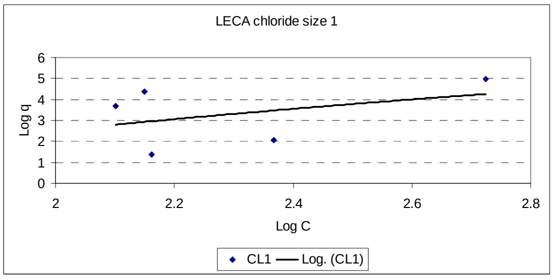


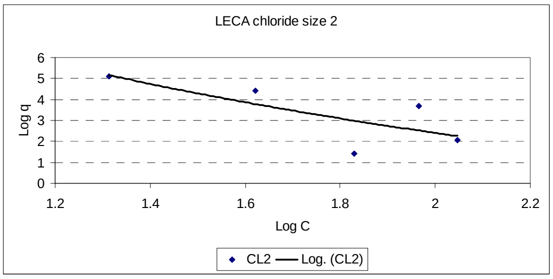


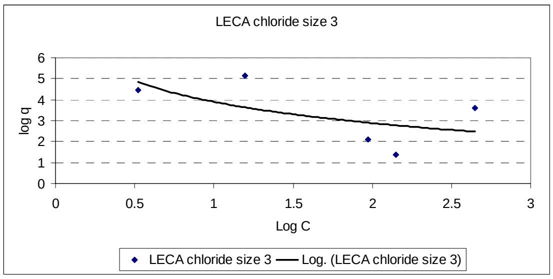


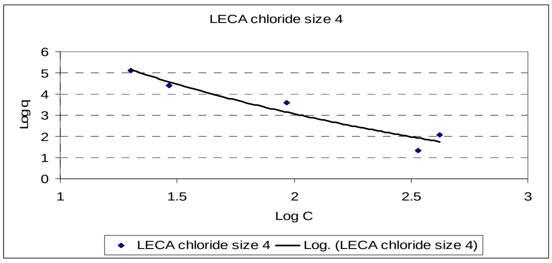
	n	K_f
NS1	0.822842	11.42352
NS2	0.917263	15.07301
NS3	0.805218	10.64388
NS4	0.798594	10.26124
NS5	0.781555	9.835581

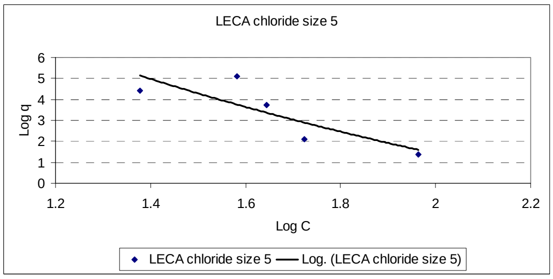
Ferric chloride coated LECA

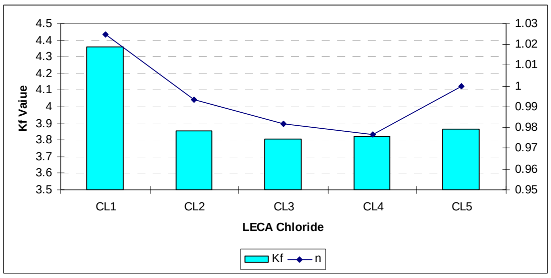






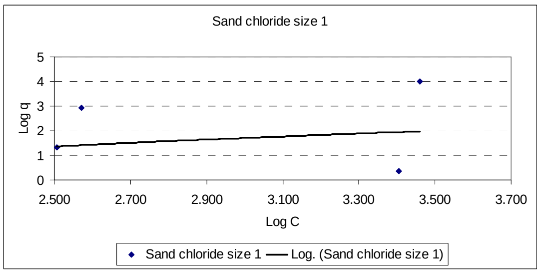


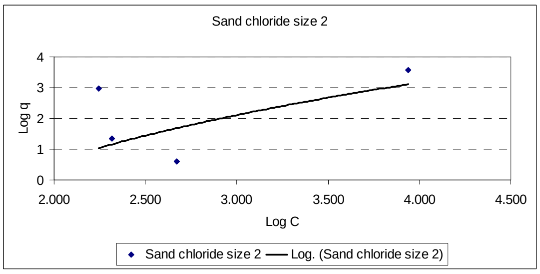


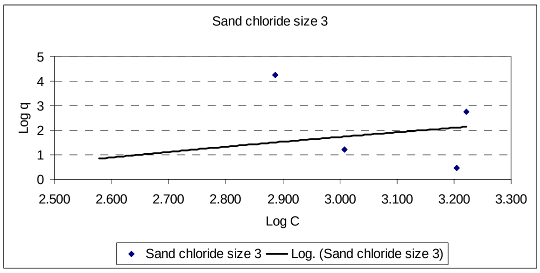


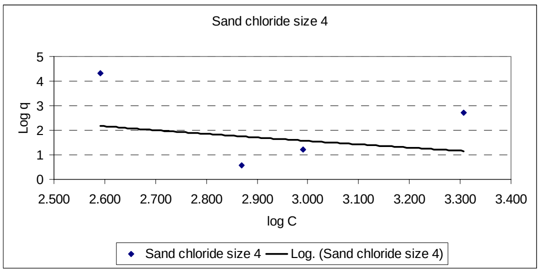
	n	K_f
CL1	1.025010	4.360136
CL2	0.993345	3.854784
CL3	0.981740	3.807150
CL4	0.976563	3.823843
CL5	0.999810	3.864560

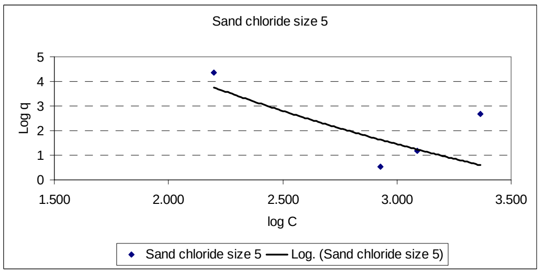
Ferric chloride coated sand

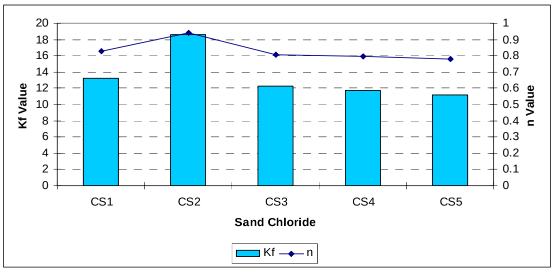








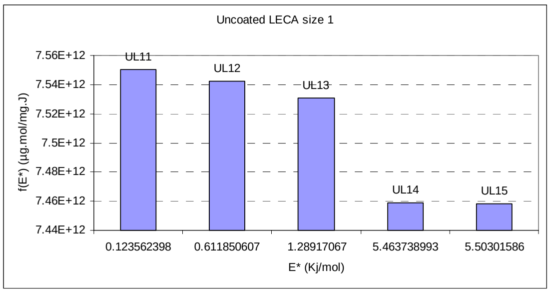


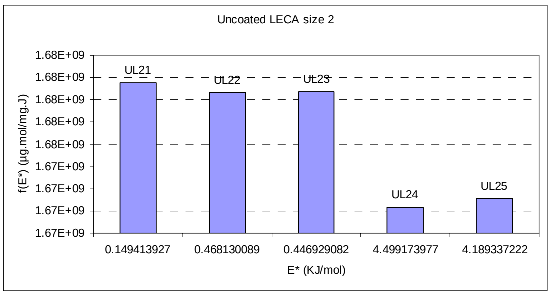


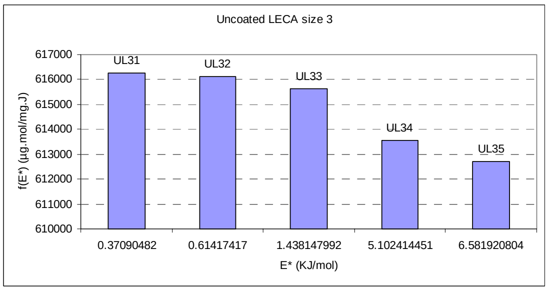
	n	K_f
CS1	0.826310	13.26172
CS2	0.943040	18.58232
CS3	0.805672	12.20956
CS4	0.798276	11.71386
CS5	0.778998	11.17120

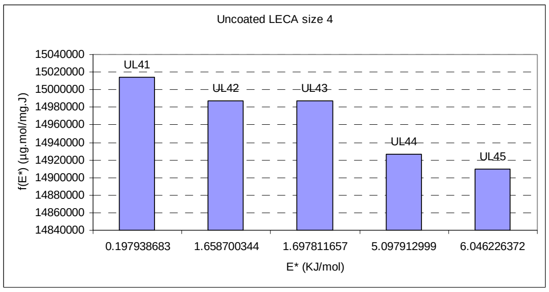
Appendix G: Site energy distribution and frequency distribution modelling

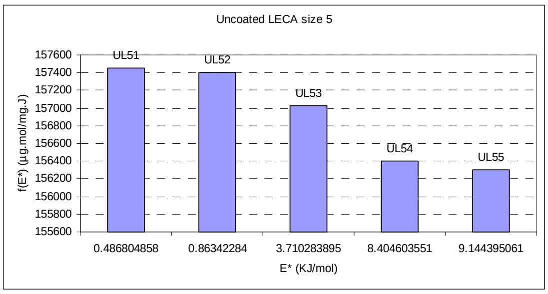
Uncoated LECA



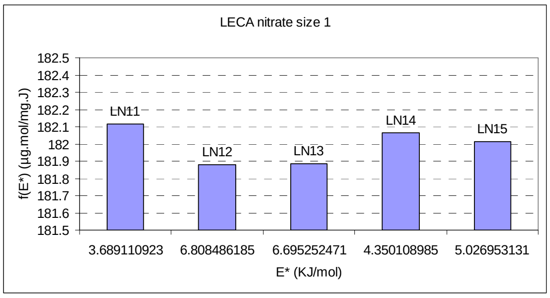


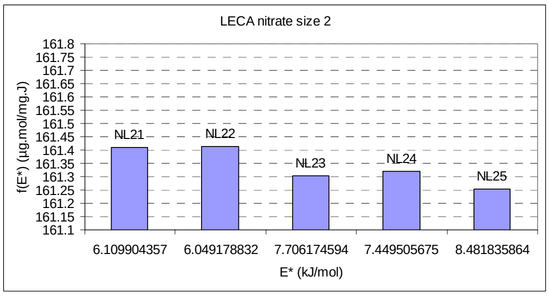


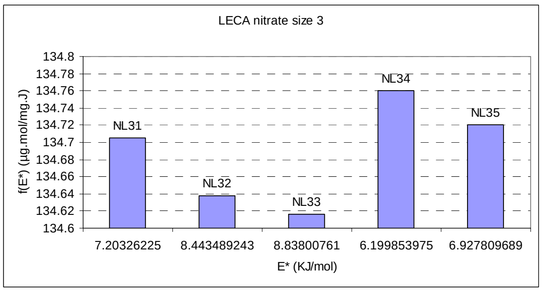


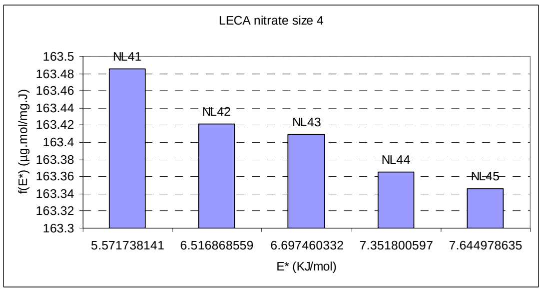


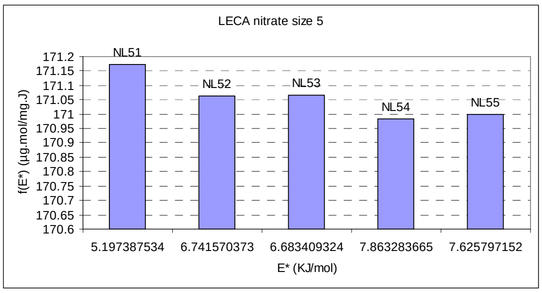
Ferric nitrate coated LECA



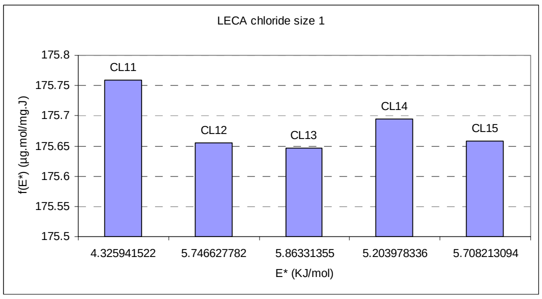


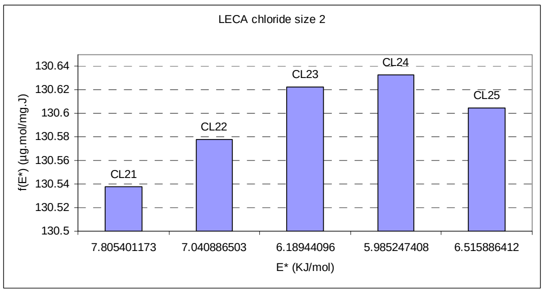


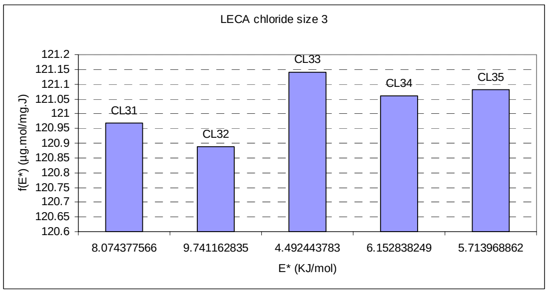


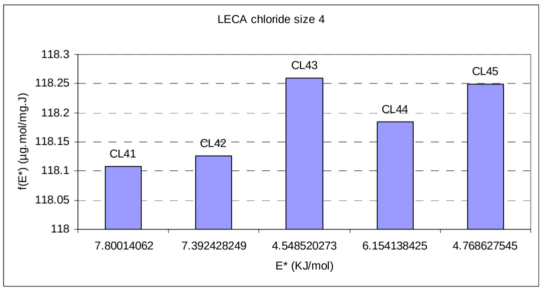


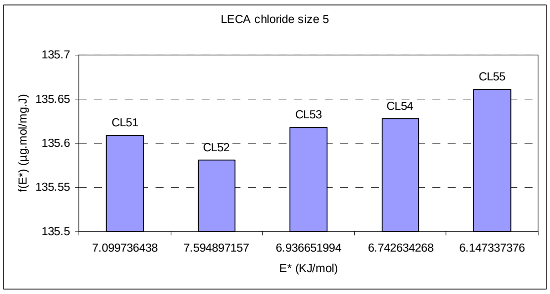
Ferric chloride coated LECA



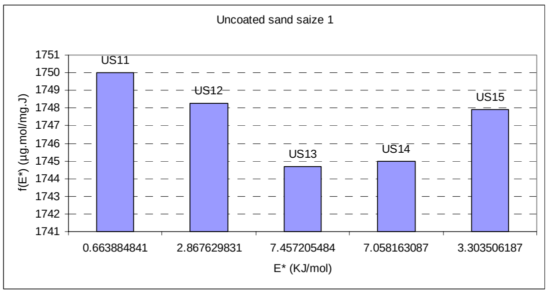


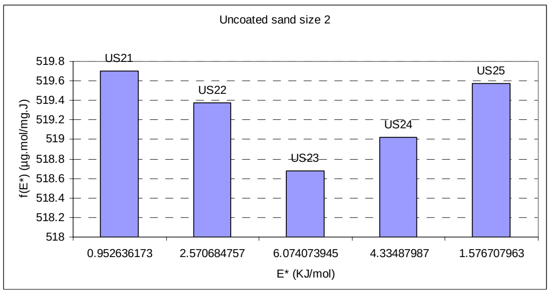


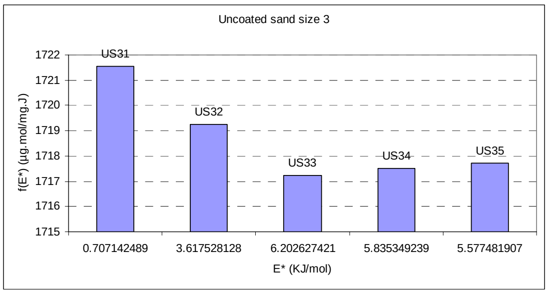


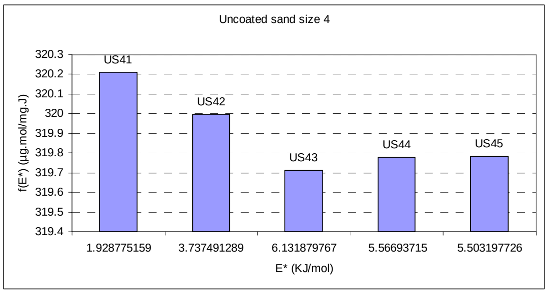


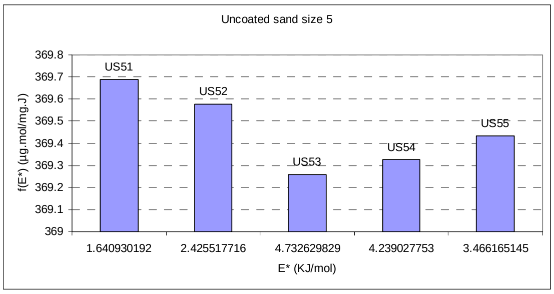
Uncoated sand



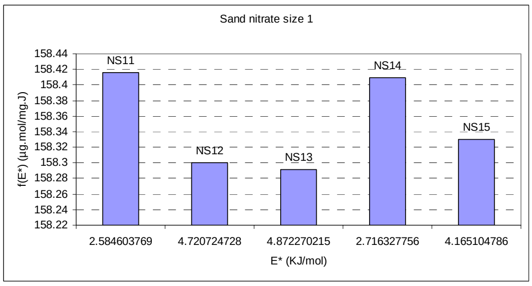


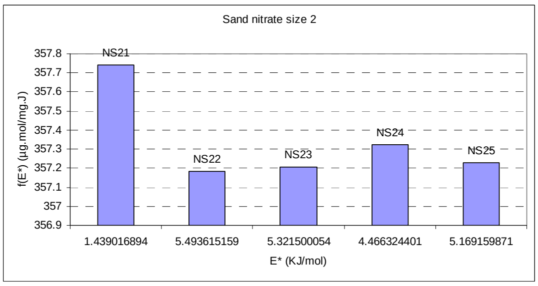


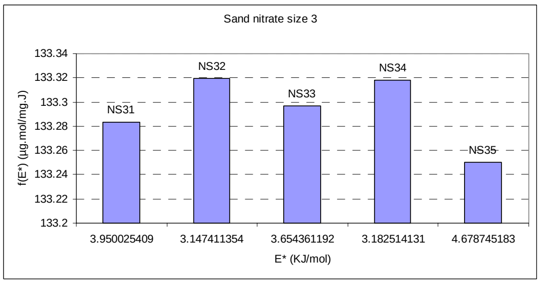


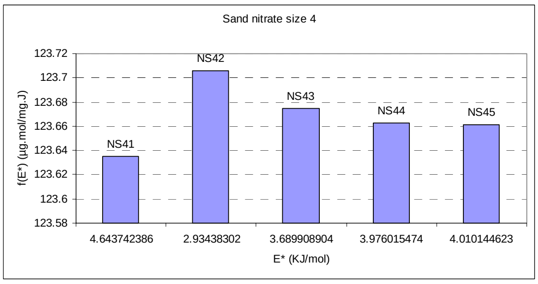


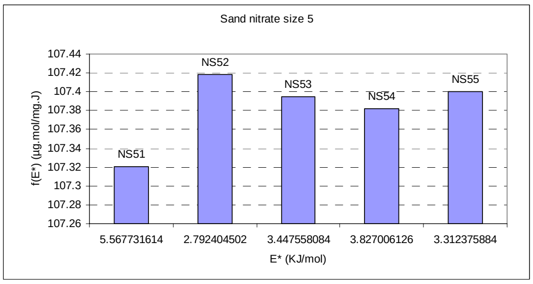
Ferric nitrate coated sand











Ferric chloride coated sand