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Certificate

This is to certify that the work presented in the thesis entitled, “***STUDIES ON SOME NON-CONVENTIONAL ADSORBENTS AND THEIR POSSIBLE USE IN THE REMOVAL OF HEAVY METALS AND ORGANIC POLLUTANTS FROM WASTEWATER***” is the original work of Mr. Moonis Ali Khan, carried out under my supervision and guidance. The work is suitable for the submission to the award of Ph.D degree.

(**RIFAQAT ALI KHAN RAO**)
Supervisor

Acknowledgment

Praise be to Allah for his blessings which has been bestowed on me in completing my work with success.

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List of Publications

Nomenclature

AAS	Atomic absorption spectrophotometer
AR Grade	Analytical Reagent Grade
BSS	British Standard System
b	Langmuir constant for energy of adsorption (l/mg)
C_e	Equilibrium concentration of adsorbate in the solution (mg/l)
C_o	Initial concentration of adsorbate in the solution (mg/l)
C_{Ac}	Equilibrium concentration of adsorbate on the adsorbent surface (mg/l)
C	Amount of adsorbate in the solution (mg/l)
DDW	Double Distilled Water
ΔG°	Standard Free energy change (KJ/mole)
ΔH°	Standard Enthalpy change (KJ/mole)
HPLC	High performance liquid chromatography
K_f	Freundlich adsorption constant
K_c	Equilibrium constant
K₁	Lagergren / Pseudo- first-order rate constant (1/min)
K₂	Pseudo-second-order rate constant (g/mg-min)
m	Amount of adsorbent (g)
N	Number of observations
n	Freundlich exponent

P	Percentage relative deviation
q_e	Amount of adsorbate adsorbed per unit weight of adsorbent at equilibrium or Adsorption capacity (mg/g)
$q_{e(\text{exp})}$	Experimental value
$q_{e(\text{theo})}$	Theoretical value
q or q_t	Amount of adsorbate adsorbed per unit weight of adsorbent at time (t) (mg/g)
q_m	Langmuir constant
R	Universal gas constant (8.314 J/ mol-K)
R_L	Separation constant
RSD	Relative standard deviation
ΔS°	Standard Entropy change (KJ/ mole-K)
T	Absolute temperature (K)
t	Time (min)
V	Volume of solution (litre)
W	Mass of adsorbent (g)
x	Mass of adsorbate adsorbed on the adsorbent (mg)
θ°	Langmuir constant for fractional monolayer coverage (mg/g)

Units

°C	Degree Celsius
cm	Centimeter
g	Gram
g/mg-min	Gram per milligram-minute
hrs	Hours
J /mole-K	Joules per mole-Kelvin
K	Kelvin
KJ/mol-K	Kilo joule per mole- Kelvin
KJ/mol	Kilo joule per mole
mg/l	Milligram per litre
ml	Millilitre
mA	Microampere
mol² / J²	Mole square per joule square
moles /g	Moles per gram
1/min	Per minute
l /mg	Litre Per milligram
l /g	Litre per gram
min	Minute

mins	Minutes
mole/ l	Moles per litre
mmols /g	Millimoles per gram
mg /g	Milligram per gram
mM	Millimoles
M	Moles
nm	Nanometer
rpm	Revolutions per minute
µg	Microgram
µl	Microlitre
%	Percentage

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Chapter –1

Introduction

*When the earth is sick and polluted,
human health is impossible....
To heal ourselves we must heal our planet,
and to heal our planet we must heal ourselves*

The term pollution is derived from the Latin word "Pollutioneum" which means "Defile" or "to make dirty". **Environmental pollution** may be defined as an introduction of contaminants into an environment that causes harm to human health, other living organisms, and the environment. Few authors defined pollution as, "An unwelcome concentration of substances that are beyond the environmental capacity to handle. These substances are detrimental to people and other living organisms" or "Undesirable state of natural environment being contaminated with harmful substances as a consequence of human activities" or "Pollution is the runner of predition"

Pollution can be in the form of chemical substances or energy as noise, heat or light. Pollutants can be naturally occurring substances or energies, but are considered contaminants when in excess of natural levels.

Pollution has always been a factor of concern since Paleolithic era (or Prehistoric era). Making of tools by human beings led to the practice of metal grinding and results in minor accumulation of discarded material probably dispersed without too much impact on the nature.

Pollution is one of the most serious problem that human beings are facing today. Many countries from all over the world are studying ways to save the constantly deteriorating environment. Even though a lot of methods have been implemented but all the current ways of cleaning up the environment are simply moving pollutants from one environment to the other and are not able to eliminate the factors that led to the pollution in the first place. In order to completely resolve the problem fundamental reason has to be discovered (E.P.R, 2001)

Environmental scientists have come a long way in this direction. A challenging task of characterisation and estimation of toxic material often at trace levels in very complex matrix may be accomplished only by the analytical chemist. Today organic and inorganic pollutants have perhaps, become more important as they are not only toxic but often carcinogenic and effect physiological processes, in such a way that there are long run consequences, which are usually fatal.

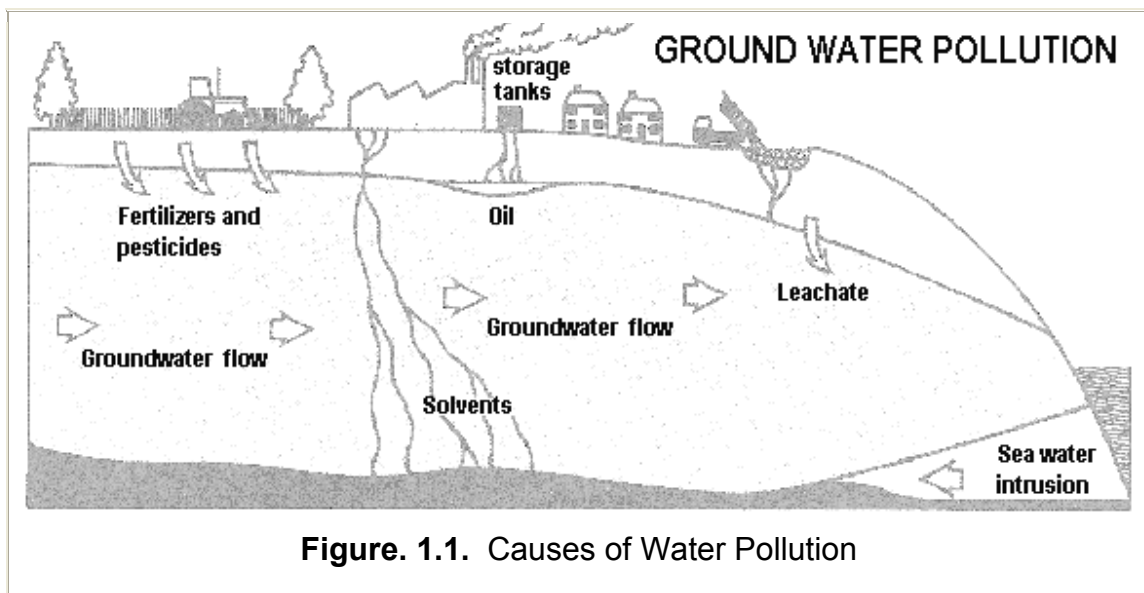
It is very difficult to separate and identify the complex mixtures. However, recent developments in instrumental techniques have made it much easier. Ultra performance liquid chromatography (ULPC), high performance liquid chromatography (HPLC), high performance thin layer chromatography (HPTLC), gas chromatography – mass spectroscopy (GC-MS) are the few instrumental techniques used for quantitative and qualitative determination of organic compounds. While atomic absorption spectrophotometer (AAS), atomic emission spectrophotometer (AES), Inductively coupled plasma – mass spectroscopy (ICP- MS) are effectively used for the analysis of inorganic matter.

Pollution can be classified as **air pollution, water pollution, soil contamination, radioactive pollution, noise pollution, thermal pollution**. One of the leading cause of air and noise pollution is motor vehicles, producing 90% of the all unwanted noise worldwide (E.P.R., 2001; Buchanan and Horwitz). Chlorinated hydrocarbons, heavy metals, benzene, phenols, petrochemical spills causes water and soil pollution. The primary source of radioactive pollution is nuclear power plant. The use of water as coolant in thermal power plants causes thermal pollution.

Water is an elixir of life. It covers about three quarters of the earth's surface area. About 95% of earth's water is in the oceans, which is unfit for human consumption and other uses because of its high salt content. Of the remaining 5%, about 4% is locked in the polar ice caps. The remaining 1% constitutes all the fresh water in the hydrological cycle including ground water reserves. Only 0.1% is available as fresh water in rivers, lakes and streams, which is suitable for human consumption (Tyagi et al., 1998).

Water is said to be polluted, if its physical and chemical properties are altered due to the addition of unwanted matter, which makes it unfit for its intended use. The sources of water pollution may be broadly categorised as **Point sources** and **Non-point sources**. Point sources occur when harmful substances are emitted directly into a water body like industrial effluents discharged directly into a river. Non-point sources deliver pollutants indirectly through transport or environmental changes like fertiliser from farm field is carried into a stream by rain. Point source is easy to monitor and regulate. Non-point sources are much more difficult to monitor and control and today they account for the majority of contaminants in streams and lakes.

There are innumerable commercial and domestic activities responsible for polluting water bodies (**Figure. 1.1**). Sewage and wastewater, marine dumping, industrial waste, radioactive waste, oil spills, underground storage leakages. Atmospheric deposition, global warming and eutrophication are the few of them.



Sewage is the term used for wastewater that often contains faeces, urine and laundry waste. There are billions of people on earth, disposal of sewage is a major problem in developing countries, as many people do not have an access to sanitary conditions and clean water. Untreated sewage wastewater in such areas is the major cause of diarrhoea.

Dumping of litter in the sea can cause huge problem as they can be caught in by marine animals and may result in death. Different items take different length of time to degrade like plastic takes about 400 years.

Industrial waste is the huge source of water pollution, it produces pollutants that are extremely harmful to people and the environment. Many industrial facilities use fresh water to carry away waste from the plant and into rivers, lakes and oceans. Pollutants from industrial sources include asbestos, lead, mercury, nitrates, phosphates, sulphur, oil, petrochemicals etc.

Eutrophication occurs when the environment becomes enriched with nutrients. This can be a problem in aquatic habitats such as lakes as it can cause algal bloom, which in turn consumes dissolved oxygen making water unfit for aquatic life.

Global warming causes the rise in the earth's water temperature. Global warming is the process where the average global temperature increases due to the green house effect. An increase in water temperature can result in the death of many aquatic organisms and disrupt many aquatic habitats.

Pollution some times may affect the environment hundreds of miles away from the source such as nuclear waste, this is called **trans boundary pollution**. Some of the important sources of water pollution are summarised in **Table.1.1**

Table. 1.1. Various sources and methods of water pollution

Sources	Methods	
Petroleum products	<ul style="list-style-type: none">• Manufacture of plastics• Manufacture of lubricants• Fractional distillation of crude oil• Vehicle fuel• Manufacture of solvents• Refinery gases for domestic cooking• Paraffin wax• Bitumen for road surfacing and roofing• Manufacture of synthetic fabrics	<ul style="list-style-type: none">• Accidental spills from ships, tankers, trucks, pipelines and leaky underground storage tanks.• Old and faulty machineries in industrial factories that are inefficient.• Improper refining processes with the production of toxic byproducts.
Synthetic agricultural chemicals	<ul style="list-style-type: none">• Pesticides• Herbicides• Insecticides• Fungicides	<ul style="list-style-type: none">• Accumulation of chemicals in plants and animals when die, will not decompose which will spread to water sources during rainfall, increasing toxicity of water source.

Contd.

Heavy metals	<ul style="list-style-type: none"> • Mining • Automobile exhaust • Metallurgy • Manufacture of batteries 	<ul style="list-style-type: none"> • Leak pipes • Unfiltered industrial discharge which flow into water sources • Emission of oxides of lead from tractors and machineries used during mining or in industries which dissolves in water • Improper storage of heavy metals in storage containers.
Hazardous wastes	<ul style="list-style-type: none"> • Radioactive materials • Corrosive materials • Reactive materials • Ignitable materials 	<ul style="list-style-type: none"> • Improper treatment of waste, which are still toxic upon release.
Excess organic matter	<ul style="list-style-type: none"> • Chemical fertilisers • Sewage sludge • Animal waste 	<ul style="list-style-type: none"> • Stimulate algae growth and during decomposition of algae it consumes oxygen that dissolves in the water, decreasing the level of oxygen in aquatic ecosystem and increase the mortality rate (death rate) of flora and fauna. At the same time, decaying material will turn the water murky. This is called eutrophication.

Contd.

<ul style="list-style-type: none">• Sediment	<ul style="list-style-type: none">• Soil erosion and soil• Particulates washed by storms and floodwaters from croplands, unprotected soils, strip mines, roads and bulldozed urban areas	<ul style="list-style-type: none">• Accumulation of sediments will turn the water murky.• Mass flow of mud into water source system will alter the clarity of water.
<ul style="list-style-type: none">• Infectious organisms	<ul style="list-style-type: none">• Microbes (virus, bacteria, protozoan)	<ul style="list-style-type: none">• Host for growth of these microorganisms, consuming nutrients in lakes, rivers, oceans• Infect plants and animals in the aquatic ecosystem, which die and upon decomposition, which accumulates sediments and organic matters which turns the water source murky thereby, polluting it.
<ul style="list-style-type: none">• Air pollution	<ul style="list-style-type: none">• Acid rain• Emission of greenhouse gases.	<ul style="list-style-type: none">• Dissolves into rainwater which alters the pH of water.• Dissolves into water sources which affects the aquatic ecosystem.

Contd.

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- | | | |
|---|---|---|
| <ul style="list-style-type: none">• Thermal pollution | <ul style="list-style-type: none">• Drawn from rivers and lakes to be used as coolants in factories and power plants. | <ul style="list-style-type: none">• Warmer water returned to rivers and lakes will alter the species makeup of the aquatic ecosystem, introducing infectious organisms and others which are adaptable to warmer temperature, which will alter the water composition in the lake or river.• Level of oxygen in water sources will be reduced, threatening the aquatic ecosystem, which will lead to the death of many species and in turn make the water murky. |
|---|---|---|

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- | | | |
|--|---|---|
| <ul style="list-style-type: none">• Soil pollution | <ul style="list-style-type: none">• Accumulation of sediments-• Non-biodegradable chemical fertilisers | <ul style="list-style-type: none">• Seeping of rainwater containing chemical pollutants from soil surface through underground soil which flows into water systems |
|--|---|---|
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Water pollution due to heavy metals and organic pollutants has been a major concern since long. Heavy metals are non-biodegradable and are the cause of many dreadful disorders on long run, on the other hand many organic pollutants are carcinogenic in nature.

The scientific world has widely accepted definition for '**heavy metals**'. However, it is generally accepted that the term 'heavy' refers to metals with an specific gravity that is at least five times the specific gravity of water. The specific gravity of water is one at 4°C (39°F). Simply stated, specific gravity is a measure of the density of a given amount of a solid substance when it is compared to an equal amount of water. In general terms, a 'heavy metal' has a specific weight higher than 8 gm/cm³.

In small quantities, certain heavy metals are nutritionally essential for a healthy life. Some of these are referred to as the trace elements (e.g., Fe, Cu, Mn and Zn). These elements, or some forms of them, are commonly found naturally in foodstuffs, fruits and vegetables, and in commercially available multivitamin products (I.O.S.H.I.C, 1999). Heavy metals are also common in industrial applications such as in the manufacture of pesticides, batteries, alloys, electroplated metal parts, textile dyes, steel, and so forth. (I.O.S.H.I.C, 1999). Many of these products are in our homes and actually add to our quality of life when properly used.

Heavy metals become toxic when they are not metabolised by the body and accumulate in the soft tissues. They may enter the human body through food, water, air or absorption through skin when they come in contact with humans in agriculture and in manufacturing, pharmaceutical, industrial or residual settings. Some of the important heavy metals with their sources and hazardous effects are tabulated in **Table.1. 2.**

Table.1.2. Sources and hazardous effects of some important heavy metals

Heavy metals	Sources	Effects
Aluminium	Alum, aluminium-cooking foils, animal feed, antacids, aspirin, auto exhaust, bleached flour, cans and tins, ceramics, dental amalgams, etc.	Alzheimer's disease, anaemia, appetite loss, memory loss, spleen pain, stomach pain, etc.
Arsenic	Burning of arsenate treated building materials, coal combustion, insect sprays	Abdominal pain, anorexia, brittle nails, chronic anemia, etc
Beryllium	Coal burning, manufacturing house holds products, industrial dust, etc.	Disturbance of calcium and vitamins.
Cadmium	Airborne industrial contaminants, batteries, ceramics, cigarette smoke, electroplating, fertilisers, welding metals, etc.	Alopecia, anaemia, cardiovascular diseases, enlarged heart, renal diseases, migraines, Itai-Itai disease.

Contd.

Copper	Electroplating industries, pulp and paper mills, fertiliser plants, steel work foundries, petroleum refineries.	Gastrointestinal catarrh, Cramps in calves, Hemochromatosis.
Chromium	Metal plating, cooling towers, leather tanning industries, paint industry etc.	Severe mucosal irritation, cancer, etc.
Lead	Battery manufacture, canned fruit and juice, cigarette smoke, electroplating, lead pipes, etc.	Abdominal pain, arthritis, blindness, Parkinson's disease, schizophrenia, unintentional weight loss.
Manganese	Coal mining, ceramics, dry battery cells, etc.	"Manganese psychosis" a brain disease.
Mercury	Adhesives, air conditioner filters, algicides, broken thermometers, burning newspapers and building materials, soft contact lens solution, tattooing, wood preservatives, etc.	Adrenal dysfunction, allergy, alopecia, brain damage, hearing loss, vision loss, etc. Minamata disease.

Contd.

Nickel	Industrial waste, kelp, Haemorrhages, margarine, nuclear device intestinal cancer, oral testing, tea, tobacco cancer, nausea, etc. smoke, etc.
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To understand the toxicity of metals, the electronic configuration must be in mind. Electrons bind molecules together. They are the rivets, bolts, nails and screws of the body. Electrons are usually intended in pair as they whiz around the outside of the atoms and give stability to form of the atom or molecule. When, for any reason, these paired electrons become separated, the molecule is damaged. These damaged molecules are called “**free radicals**” and are highly reactive, attacking other cellular structures to grab electron in order to become paired again. Usually there are enough free electrons in the vicinity to satisfy the demands of the free radicals, but when the level of free radicals increases beyond a certain point, the cellular protective electron donating mechanism which usually keeps these molecules in check is exceeded. When that happens, great numbers of these radicals are set free, all greedily looking for electrons whenever they can be found. So, when toxic metals are in body tissues, there is free radical destructive activity going on constantly resulting in rapid aging and degeneration. The ability of metals to disrupt the function of essential biological molecules such as protein, enzyme and DNA is the major cause of their toxicity. Displacement of certain metals essential for cell by similar metal is another cause of toxicity. For example: cadmium can substitute for the essential metal zinc in certain protein that requires zinc for their structure or function. The alteration in protein can lead to toxic consequences. In the same way, lead can substitute for calcium in the bones, and in other sites where calcium is required. (Zubair Ahmad; CPP).

Organic pollutants especially **persistent organic pollutants** (POPs) are organic compounds that are resistant to environmental degradation through chemical, biological

and photolytic processes, due to which they have been observed to persist in the environment and are capable of long range transport. Most of the organic pollutants are fat soluble and can accumulate in the fatty tissues of animals and human beings making significant impacts on health and environment. Some of the organic pollutants with their sources and hazardous impacts are listed in **Table. 1.3**.

Table. 1.3. Some organic pollutants with their sources and hazardous effects

Organic pollutants	Sources	Effects
α -naphthyl amine	Dye manufacture, colour film manufacture.	May cause bladder cancer.
β -naphthyl amine	Dye manufacture.	Bladder cancer.
Benzidine	Manufacture of dyes, rubber, plastic, printing ink.	Bladder cancer.
Ethylene imine	Paper and textile industry.	Causes cancer.
Chlorinated ethylene (such as Vinyl chloride)	Plastic manufacture, polymer industry.	Liver cancer

Contd.

Ethylene dichloride	Industrial solvents, gasoline additive for lead scavenging, grain fumigant.	Suspected carcinogen.
Phenols and chlorophenols	Coke distillation plant, petrochemical industry, municipal wastewater.	Pentachlorophenol, a derivative of chlorophenol is responsible to cause Hodgkin's disease and leukemia.
Benzene and lower alkyl benzenes (such as toluene and ethyl benzene)	Chemical industry, lower alkyl benzene are components of gasoline and are used as solvent for paints and coatings.	Chronic exposure to benzene results in anaemia and leucopenia. Acute exposure to toluene by the inhalation results in CNS depression.
Chlorinated alkanes (such as carbon tetrachloride; 1,2-Dichloroethane	Chemical industry (intermediate in the production of organochlorine compounds)	Acute toxicity effects skin, circulation, respiration blood and the function of kidneys, liver, eyes and pancreas.

There are various quality parameters, which are very essential to be checked before discharging water to commercial and domestic water supplies. These parameters include colour, odour, pH of water, temperature, transparency, turbidity, conductivity, taste, TDS (total dissolved solids), DO (dissolved oxygen), BOD (biological oxygen demand) and COD (chemical oxygen demand).

In natural water, **colours** are due to the presence of humic substances, fulvic ions, metal ions (like chromium is responsible for pale yellow colour) suspended matter, phytoplankton weeds and industrial effluents. Contamination of natural water by industrial effluents containing organic matter like chlorophenols and metal ions like iron, manganese causes offensive **odour and taste**. The drinking water must be odourless and tasteless.

The intensity of alkalinity or acidity is measured on a pH scale. **pH** is regarded as a measure of concentration of hydrogen ions in water or solution. pH of natural water is nearly 7 (i.e., neutral). However, the water is acidic if pH is below 7, above 7 the water is alkaline. The alkalinity of water is due to the presence of carbonates, bicarbonates, and silicates. Presence of weak organic acids is also responsible for the alkalinity of natural water.

Temperature is one of the most important parameter for aquatic environment as almost all the physical, chemical and biological properties are governed by it. These properties include density, surface tension, viscosity, solubility of solutes, dissolution of gases, etc. The rate of chemical reactions and biological activity such as corrosion, BOD, photosynthesis, growth and death of microorganisms are all dependent upon environmental temperature. Increase in water temperature increases oxygen demand, leading to serious oxygen depletion problem in water resources.

Transparency of water has been inversely proportional to the turbidity. Turbidity arises due to the presence of suspended solid matter such as clay, silt, organic matter, phytoplankton and other microorganisms. Turbidity refers to the expression of optical

property (Tyndall effect) in which the scattering of light occurs due to the suspended matter or particles in water.

Conductivity is reciprocal of electrical resistance. It is the measure of ability of water to convey electricity. It also becomes the measure of dissolved ionic solids as specific conductance of water increases with increase in concentration of dissolved ionic compounds.

Total dissolved solid (TDS) content is defined as residue left after evaporation of water at 103 to 105°C. It is an aggregated amount of the entire floating, suspended, separable and dissolved solids present in water. The solids may be organic or inorganic in nature.

The **dissolved oxygen (DO)** content shows the health and ability of a stream to purify itself through biochemical process. DO saturation value varies from 8 -15 mg/l. When DO level drops below 2 mg/l, environment shifts towards anaerobic species.

Biological oxygen demand (BOD) / Biochemical Oxygen demand has been used as an index of organic pollution. BOD may be defined as the amount of oxygen (in mgs) dissolved in water needed to break down the organic matter present in one litre of pure water for five days at 20°C. The BOD of pure water is 0 - 3 mg/l. In case BOD is 5 mg/l or more, then the water is some what contaminated. Water in vicinity of factories is found to have BOD as high as 1000 mg/l. i.e., highly contaminated.

Chemical oxygen demand (COD) is a measure of the capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of inorganic chemicals such as ammonia and nitrite. COD measurements are commonly made on samples of waste waters or of natural waters contaminated by domestic or industrial wastes.

To ensure desirable characteristics of products and services such as quality, environmental friendliness, safety, reliability, efficiency and interchangeability and at an economical cost **International Organisation for Standardisation** (ISO) was founded on February 23, 1947. The organisation promulgates worldwide industrial and commercial standards. Its short name “ISO”, is derived from a Greek word “ISOS”, meaning, “equal” The main aim of ISO is to develop international standards to make the development, manufacturing and supply of products and services more efficient, safer and cleaner, facilitate trade between countries and make it fairer, provide governments with a technical base for health, safety and environmental legislation, and conformity assessment, share technological advances and good management practice, disseminate innovation, safeguard consumers, and users in general, of products and services and make life simpler by providing solutions to common problems. The organisation is responsible for many thousands of the standards, which benefit the world. In India, Bureau of Indian standards (BIS) formerly known as ISI is doing the same job. **Table. 1.4.** Outlines Indian standards for packaged drinking water and packaged natural mineral water

Table.1.4. Indian standards for packaged drinking water and packaged natural mineral water

Standards	Specific Tests	Test Methods	Range/ Detection Limit	Accuracy
Packaged	Colour	IS: 3025(P-4)-1983	1-50 Units	+/- 1
Drinking	Odour	IS: 3025(P-5)-1983	N A	N A
Water	Taste	IS: 3025(P-8)-1984	N A	N A
IS: 14543- 1998 and	Turbidity	IS: 3025(P-10)-1984	0.1-1 NTU	+/- 0.1
			1- 10 NTU	+/- 1.0
	TDS	IS: 3025(P-16)-1984	10-50 mg/l	+/-30 %
			>50-100 mg/l	+/- 20 %
Packaged			<100-500mg/l	+/- 10 %
Natural			Above 500 mg/l	+/- 5%
Mineral				
Water				
IS:13428- 1998	pH	IS: 3025(P-11)-1983	1-14	+/- 0.1
	Barium	IS: 13428-1983 F	0.5 - 50 mg /l	+/- 20 %
	Copper	IS: 3025(P-42)-1992	0.02 – 20 mg/l	+/- 20 %
	Iron	AAS-APHA 19 th ED	0.05 – 20 mg/l	+/- 20 %
	Manganese	AAS-APHA 19 th ED	0.05 – 20 mg/l	+/- 20 %
	Nitrate	IS: 3025(P-34)-1988	0.1-1 mg /l	+/- 10 %
			> 1- 10 mg/l	+/- 8 %
			> 10 mg/l	+/- 5%

Contd.

Standards	Specific Tests	Test Methods	Range/ Detection Limit	Accuracy
Packaged Drinking Water IS: 14543-1998	Nitrite	IS: 3025(P-34)-1988	0.01-1mg /l	+/- 10 %
			> 1- 10 mg/l	+/- 8 %
			> 10 mg/l	+/- 5 %
and Packaged Natural Mineral Water IS:13428-1998	Fluoride	23 OF IS: 3025 (P-49)-1994	0.1-5 mg/l	+/- 20 %
	Zinc	IS: 3025(P-49)-1994	0.1-20 mg/l	+/- 20 %
	Silver	IS: 13428-1998 - J	0.005-20 mg/l	+/- 20 %
	Aluminium	31 OF IS: 3025 - 1964	0.01-20 mg/l	+/- 20 %
	Chloride	IS: 3025 (P-32)-1988	1-100 mg/l	+/- 10 %
			>100-500 mg/l	+/- 8 %
			> 500 mg/l	+/- 5 %
	Selenium	AAS-APHA 19 th ED	0.005 – 5 mg/l	+/- 20 %
	Sulphate	IS:3025 (P-24) -1986	10 – 500 mg/l	+/- 20 %
	Alkalinity	IS: 3025(P-23)-1986	1-100 mg/l	+/- 10 %
			>100-500 mg/l	+/- 8 %
			> 500 mg/l	+/- 5 %
	Calcium	IS: 3025(P-40)-1991	1-100 mg/l	+/- 10 %
			>100-500 mg/l	+/- 8 %
			> 500 mg/l	+/- 5 %

Contd.

Standards	Specific Tests	Test Methods	Range/ Detection Limit	Accuracy
Packaged Drinking Water IS: 14543- 1998	Manganese	IS: 3025(P-46)-1994	1-100 mg/l	+/- 10 %
			>100-500 mg/l	+/- 8 %
			> 500 mg/l	+/- 5 %
and	Sodium	IS:3025(P-45)- 1993	1-100 mg/l	+/- 10 %
			>100-500 mg/l	+/- 8 %
			> 500 mg/l	+/- 5 %
Packaged Natural Mineral Water IS:13428- 1998	Residual Free Chlorine	IS:3025(P-26)- 1986	0.05 -20 mg /l	+/- 20 %
	Phenolic compounds	54OF IS: 3025-1964	0.001 - 5 mg/l	+/- 20 %
	Mineral Oil	IS:3025(P-39)- 1991	0.01 - 10 mg/l	+/- 20 %
	Anionic Surface active agents	IS: 13428-1998-K	0.1 – 100 mg /l	+/- 30 %
	Mercury	IS:3025(P-48)- 1994	0.0005 -20 mg/l	+/- 20 %
	Cadmium	IS:3025(P-41)- 1992	0.002-20 mg/l	+/- 20 %
	Arsenic	IS:3025(P-37)- 1988	0.005-5 mg/l	+/- 20 %
	Cyanide	IS:3025(P-27)- 1986	0.02-20 mg/l	+/- 20 %
	Lead	IS:3025(P-47)- 1994	0.01-20 mg/l	+/- 20 %
	Chromium	IS:13428-1998-J	0.01-20 mg/l	+/- 20 %
	Nickel	IS:13428-1998-L	0.01-20 mg/l	+/- 20 %

Contd.

Standards	Specific Tests	Test Methods	Range/ Detection Limit	Accuracy
Packaged Drinking Water	Poly Chlorinated Biphenyls	AOAC–17 th Edition	0.001- 10 mg/l	+/- 30 %
IS: 14543-1998	Sulphide	IS:3025(P-29)-1986	0.02- 20 mg/l	+/- 20 %
and Packaged Natural Mineral Water	Antimony	AAS-APHA19 th ED	0.002- 20 mg/l	+/- 20 %
	Borate	IS:13428-1998-H	0.5-50 mg/l	+/- 20 %
	Pesticides	IS: 12616-1989	0.1 µg/l	+/- 30 %
	Residue	IS: 13832-1993		
IS:13428-1998		AOAC–17 th Edition		
Microbiological analysis	E. Coli	IS:5887(P-1)1976	NA	NA
	Coliform	IS: 5401-1969	NA	NA
	Faecal streptococci, Staphylococcus aureus	IS: 5887 (P-2) 1976	NA	NA
	Sulphite Reducing Anaerobes	IS:13428-1998 C	NA	NA
	Pseudomonas aeruginosa	IS:13428-1998 D	NA	NA
	Aerobic Microbial Count	IS: 5402-1969	NA	NA
	Yeast ,Mould	IS: 5403-1999	NA	NA
	Salmonella, Shigella	IS:5887(P-3)1999 IS: 5887(P-7)1999	NA	NA

In addition to the above stated standard tests, the content of different ions varies in different samples and is of importance due to specific reasons. **Table.1.5** outlines certain parameters with permissible limits for domestic water supplies.

Table. 1.5. Various water quality parameters.

Parameters	USPHS (1969)	ISI Standard (IS-2296-1963)
Colour	Colourless	-
Odour	Odourless	-
Taste	Tasteless	-
pH	6.0-8.5	6.0-9.0
Specific Conductance	300 μ mho/cm	-
DO	4-6 mg/l	3.0 mg/l
TDS	500	-
Suspended solids	5.0	-
Chlorides	250	600
Sulphates	250	1000
Cyanide	0.05	0.01

Contd.

Fluoride	1.5	3.0
Arsenic	0.05	0.2
Chromium (VI)	0.05	0.05
Lead	< 0.05	0.1
Iron	< 0.3	-
Selenium	0.01	0.05
COD	4.0	-
Carbon extract	0.15	-
Phenols	0.061	0.05
Caliform cell/ 100ml	100	< 500
Total bacteria count / 100ml	1×10^6	-

Concentrations are in mg/l or otherwise mentioned.

There are various methods used in sewage and industrial wastewater treatment. They are termed as preliminary treatment, primary treatment, secondary treatment and tertiary treatment. The principle objectives of **preliminary treatment** are the removal of gross solids such as large floating and suspended solid matter, grit, oil and grease if present in considerable quantities. Large quantities of floating rubbish such as cans, cloth, wood and other objects present in wastewater are usually removed under preliminary treatment.

Primary treatment involves the removal of gross solids, gritty materials and excessive quantities of oil and grease, the next step is to remove the remaining suspended solids as much as possible. This is aimed at reducing the strength of the wastewater and also to facilitate secondary treatment.

The suspended matter can be removed effectively and economically by sedimentation. This process is particularly useful for treatment of wastes containing high percentage of settleable solids or when the waste is subjected to combined treatment with sewage.

Finely divided suspended solids and colloidal particles cannot be removed by simple sedimentation by gravity. In such cases, mechanical flocculation or chemical coagulation is employed. Coagulation is the most effective and economical means to remove impurities. But recently, it is observed that coagulants containing polydiallyl dimethyl ammonium chloride breaks down to form allyl chloride, which affects the cell and is also a potent carcinogen (Das, B, 2008). Sometimes, in addition to the coagulants, other chemicals called “coagulant aids” are also used in very small quantities to promote the formation of large and quick settling floc and thereby enhancing coagulation. Activated silica and polyelectrolytes such as polymers of cyanamide, acrylic acids and their derivatives, and hydrolysed high molecular weight polymers having molecular mass 10^4 to 10^6 of acrylamide or acrylonitrile are the most commonly used coagulant aids.

Some industries produce different type of wastes, having different characteristics at different intervals of time. Hence, uniform treatment is not possible. In order to obviate this problem, different streams of effluents are held in big holding tanks for specified periods of time. Each unit volume of the waste is mixed thoroughly with other unit volumes of other wastes to produce a homogenous and equalised effluent.

Highly acidic and highly alkaline wastes should be properly neutralised before being discharged. Acidic wastes are usually neutralized by treatment with limestone or lime slurry or caustic soda, depending upon the treatment and quality of the waste. Alkaline

wastes may be neutralised by treatment with sulphuric acid or CO₂ or waste boiler flue gas. If both acidic and alkaline wastes are produced in the same plant or at nearby plants, storing them in separate holding tanks and mutual neutralisation by mixing them in appropriate proportion is the cheapest method.

In **secondary treatment**, biological processes involving bacteria and other microorganisms remove the dissolved and colloidal organic matter present in wastewaters. These processes may be aerobic or anaerobic. In aerobic process, bacteria and other microorganisms consume organic matter as food, causing coagulation and flocculation of colloidal matter, oxidation of dissolved organic matter to CO₂ and degradation of nitrogenous organic matter to ammonia, converted to nitrite and eventually to nitrate. Thus, aerobic treatment reduces BOD. It also removes appreciable amounts of oil and phenol. However, commissioning and maintenance of aerobic treatment systems are expensive. Anaerobic treatment is mainly employed for the digestion of sludge. Generally organic liquid wastes from dairy, slaughter houses etc., are treated economically and effectively by anaerobic treatment. The efficiency of anaerobic treatment process depends upon pH, temperature, waste loading, absence of oxygen and toxic materials.

Tertiary treatment is the final treatment, meant for “polishing” the effluent from the secondary treatment processes, to improve the quality further. The main objectives of tertiary treatment are the removal of fine suspended solids, bacteria, dissolved inorganic solids and final traces of organics. The final effluent before discharging is chlorinated. Though chlorination is essential to kill the disease causing bugs present in surface water, indiscriminate chlorination increases the risks for human health. It is found that on one hand chlorine kills microbes, it also reacts with organic matter present in the water to form toxic organochlorines, which are carcinogenic. The chlorinated disinfectants in drinking water could act as a co-carcinogen on epithelial cells in small intestine and modify the tumour suppressor gene, leading to cancer (Das, B, 2008). The effect of treated water on a particular species of yeast is observed. The yeasts are similar to mammalian cells with respect to growth. It is found that the chemicals used to

treat water damage the cells of yeast species *Schizosaccharomyces pombe* (Banerjee et al., 2008). The DNA of treated yeasts cells resembled a comet with distinct head, the nucleus and a tail containing fragments of DNA. The comet formation is a sure sign of cell damage.

Depending upon the required quality of the final effluent and the cost of treatment that can be afforded in a given situation, any of the following treatment methods can be employed:

Evaporation, an expensive process used only to recover solids or the concentrated solutions for their reuse, e.g., some electroplating wastes. This method is also employed for concentrating radioactive liquid wastes.

Ion-exchange process is used for the removal and recovery of toxic materials from wastewater. Ion exchange process is economical only when the recovered salts are reused in the process, as in electroplating industry. The method may not be economical if the objective of the treatment is only the removal of dissolved solids from wastewater.

Reverse osmosis. When a wastewater containing dissolved solids is allowed to pass through a semipermeable membrane, at a pressure over and above the osmotic pressure of the wastewater, only the water from the waste permeates through the membrane, leaving behind concentrated liquor, containing the dissolved solids. This process is particularly suitable and effective for the removal of dissolved solids from wastewater. The cost of the membranes and the fouling of the membranes are the major limitations of this process.

Chemical precipitation. Dissolved solids present in wastewater, particularly the heavy metal ions, can be removed by chemical precipitation. Cheap precipitating agent like lime is used to precipitate heavy metals as their hydroxide. Chromates in the electroplating waste are highly toxic and can be removed by treatment with FeSO_4 first to reduce the chromates to Cr (III), followed by precipitation with lime.

Adsorption is a power tool for the environmental engineer for the removal of trace amounts of organic and inorganic contaminants present in municipal and industrial wastewater. Adsorption is the partitioning process in which a contaminant is transferred from dissolved state in the aquatic phase to the surface of solid phase, where it accumulates for subsequent extraction or destruction. In adsorption a solid surface in contact with the solution has the tendency to accumulate a layer of solute molecules at the interface due to imbalance of surface forces. This accumulation of molecules is vectorial sum of the forces of attraction and repulsion between the solution and the adsorbent. Majority of the solute ions or molecules, accumulated at the interface, are adsorbed onto the large surface area within the pores of adsorbent and relatively a few are adsorbed on the outside surface of the particles.

Adsorption from an aqueous solution is influenced largely by the competition between the solute and the solvent molecules for adsorption sites. The tendency of a particular solute to get adsorbed is determined by the difference in the adsorption potential between the solute and the solvent. In general, the lower the affinity of the adsorbate for the solvents, the higher will be the adsorption capacity for solutes. Activated carbon and polymeric adsorbents have high adsorption capacities in water primarily because of a low adsorption potential. (Rai et al., 1998). Three distinct steps must take place for adsorption to occur:

- The adsorbed molecule must be transferred from the bulk phase of the solution to the surface of the adsorbent particle. In so doing, it must pass through a film of solvent that surrounds the adsorbent particle. This process is referred to as **film diffusion**.
- The adsorbate molecule must be transferred to an adsorption site on the inside of the pore. This process is referred to as **pore diffusion**.
- The particle must become attached to the surface of the solute, i.e., be **adsorbed**.

There are many factors that influence the rate of adsorption and the extent to which a particular solute can be adsorbed. Adsorbent characteristics, size and shape of adsorbent particles, solubility of solute, pH, temperature, concentration, and agitation time are few of the factors that influence the adsorption. Adsorption rate usually decreases as the size of adsorbent particle becomes large. Highly soluble compounds having strong affinity to solvent are less easily adsorbed. Adsorption capacity is inversely proportional to solubility. Rate of adsorption increases with increase in concentration. pH of the solution has strong influence on adsorption primarily due to change in the ionic concentrations of water and solutes. Temperature is also a factor that affects the rate and extent of adsorption.

Conventional and Non-conventional adsorbents are used in this approach. Activated carbon, a conventional adsorbent constitute one of the most important type of industrial carbon and is prepared by carbonisation and activation of large number of raw materials. (Rodriguez-Reinoso and Linares-Solano, 1988). Activated carbon is extensively used for the removal of organic molecules and heavy metals because of its high adsorption capacity. (Bansal et al.1988). Activated carbon is marketed in both powdered and granular form. The shortcoming of using activated carbon, as an adsorbent is its regeneration cost which makes it uneconomical. To make adsorption an economically feasible process non-conventional adsorbents have come into application. Non-conventional adsorbents include inorganic adsorbents, organic adsorbents and biosorbents. These adsorbents are capable of removing/retrieving of heavy metal ions and organic pollutants from wastewater. Materials like chitin, chitosan, modified cotton, keratin, fly ash, oil cakes, fruit peels, barks, etc. are few of the non-conventional adsorbents used for the removal of heavy metals and organic organic pollutants. These adsorbents are tabulated in **Table.1.6 and 1.7.**

Table. 1.6. Summary of various adsorbents used for the removal of heavy metals from wastewater (1998 – 2007)

Adsorbent	Metal removed	Adsorption / Desorption	Conditions	Reference
Fly ash	Cu, Pb, Zn, Cd, Cr (III) and Ni	40-100%	pH 1-10	Ricou et al., 1998
Red mud	Cu, Zn, Ni and Cd			Lopez et al., 1998
Cladophora sp.	Cu		Column process flow rate 1.12 ml/min	Asku and Yener, 1998
Biomass of <i>Medicago satavia</i> (alfalfa)	Cd, Cr, Pb and Zn	7.4 mg/g to 43 mg/g	pH. 5 Recovery by 0.1M HCl by column process	Gardea-Torresday et al., 1998
Fly ash	Cu, Pb, Zn			Gupta and Torres, 1998
Acid sandy Soil	Cd		pH 3.6-4.3	Wilkins et al., 1998
Hematite	Cd	98%	pH 9.2	Singh et al., 1998
Blast furnace slag	Pb, Zn, Cd, Cu and Cr (III)			Lopez et al., 1998
Biosorption by sea weeds	Cr (III) and Cr (VI)			Kratochvil et al., 1998
Carbon	Cr (III), Cr (VI) Pb, Zn			Lalvani et al., 1998

Formaldehyde cross linked <i>Saccharomyces cerevisiae</i>	Cr (VI)	Sorption capacity 6.3 mg/g pH 2.5	Zhao and Duncan, 1998
Biosorption on filamentous fungi	Ni		Mogollon et al., 1998
Peat	Co, Cd, Ni Cu and Zn		McKay et al., 1998
Apple residues	Cu, Pb, Cd		Lee et al., 1998
Modified titanium oxide	Pb, Cd, Hg		Subha et al., 1998
Crab shell particles	Pb	99% Removal	Lee et al., 1998
Rice husk	Pb		Khalid et al., 1998
<i>Rhizopus arrhizus</i>	Cu, Zn		Sag et al., 1998
Adsorption by different plant species	Cr (III), Cr (VI)		Kleiman and Cogliatti, 1998
Blast furnace slag	Pb (II)	95-97% adsorption at pH 5.9-6	Dimitrova and Mehandgiev, 1998

Biosorption by magnetite immobilized cell of <i>Pseudomonas putida</i>	Cu	96% adsorption. Recovery 95% with 6N HCl	Chua et al., 1998
Iron rich material	Cr (VI)		Sengupta, S. 1998
Chitosan	Cu (II)	4.7 mg/g of Cu (II) was adsorbed at pH 6.2	Wan Ngah and Isa, 1998
Living Mycelium of White-rot fungus <i>Phanerochaete crysosporium</i>	Cu (II)	3.9 mM Cu / g of dry mycelium was adsorbed	Sing and Yu, 1998
Sargassum algal biomass	Cu (II)		Kratochvil and Volesky, 1998
Activated carbon	Cr (VI)		Bandyopadhyay and Biswan, 1998
Fire clay	Ni		Bajpai, S.K., 1999
<i>Aspergillus niger</i>	As, Pb, Cd, Cu and Ni		Kapoor et al., 1999
Natural zeolite	Pb, Cu, Cd, Zn		Yuan et al., 1999

Bone charcoal	Cr (VI)	90% adsorption pH-1		Dahbi et al., 1999
Lime treated montmorillonite	Zn			Tsai and Vesiland, 1999
Dried <i>Chlorella vulgaris</i>	Cu, Cr (VI)	pH 2 for Cr (VI) pH 4 for Cu		Asku et al., 1999
Industrial biomass	Zn, Cu, Ni			Zonboulis et al., 1999
Japanese red pipes	Cr (VI)	95% adsorption pH 2-3		Aoyama et al., 1999
Quaternized rice hulls	Cr (VI)		Column process recovery with 0.5M NaOH solution	Low et al., 1999
Hydrocalcite	Cr (VI)	95.7% recovery by 0.1M NaOH		Manju et al., 1999
Fly ash and fly ash /line	Cu, Zn and Pb			Ricou et al., 1999
Rice husk	Hg			Khalid et al., 1999
Oak ridge Y-12 plant	Hg			Hollerman et al., 1999

Natural bentonite	Cd, (II), Zn (II)	pH is important factor	Xia and He., 2000
Sheep hair	Cr (VI)	Maximum adsorption at pH 0.75-1.25 and 3.25-3.75	Sarvanam et al., 2000
Black locus leaves	Cr (VI)	Maximum adsorption at pH 3.	Aoyama et al., 2000
Activated carbon (agricultural waste)	Hg (II), Pb (II), Cd (II), Ni (II), Cu (II)	Adsorption increase with increase in pH from 2-6	Kadirvelu et al., 2000
Fe – oxide impregnated activated carbon	As (III), As (VI)		Reed et al., 2000
Pyrolusite	Cd (II)	Temp 30°C, pH 7 Conc. 1-100mg/l	Koyanaka et al., 2000
Iron oxide coated sand	Cu (II)	% Removal 74.9% conc. 5mg/l time 20min, adsorbent 30g/l	Kwak et al., 2000

Hazelnut shell	Cr (VI)		Cimino et al., 2000
Coconut husk	Hg	99.4% adsorption pH 6	Sreedhar and Anirudhan, 2000
Granular activated carbon	Cd (II), Cu (II)	Adsorption increases with pH	Gabaldon et al., 2000
Coniferous leaves	Cr (VI)	Adsorption of Cr(III) increases with increase in pH	Aoyama et al., 2000
Recycled iron material	Pb		Smith and Amini, 2000
Pyrite	Cu (II)	Oxidation is accompanied by the reduction of Cu (II) to Cu (I).	Weisener and Gerson, 2000
Fly ash	Ni (II)	The removal of Ni (II) is 96%.	Ricou Hoeffler et al., 2000

Peat	Zn and Cd	Peat columns are able to retain the main interferent on adsorption of Zn and Cd ions in solution.	Petroni et al., 2000
Manganese oxide	As ions	As ion concentration was decreased to 2.3mg/l from 10mg/l in 20minutes at pH 4.5-5.0	Kasai et al., 2000
Serpentine	Cd (II), Cu (II), Fe (III), Pb (II) and Ni (II)	99% heavy metal removal	Guo and Yuan, 2000
Sawdust	Cu	Provide strong evidence to support the hypothesis of adsorption mechanism.	Yu et al., 2000
<i>Avena monida</i> (Oat) biomass	Cr (VI)	Cr (VI) is reduced to Cr (III) in polluted water	Gardea-Torresdey et al., 2000

Anaerobically digested sludge	Cd (II), Cu (II), Ni (II) and Zn (II)	Affinity of the sludge was Cu (II)>Cd (II)>Zn (II)>Ni (II)	Artola et al., 2000
Cow dung cake	Cr (VI)	Cr (VI) removal is 90%.	Das et al., 2000
Dried animal bones	Zn		Banat et al., 2000
Red mud	As	Follows 1st Order rate expression and obeys Langmuir model .The adsorption of As (III) was exothermic and As (V) was endothermic.	Altundogan et al., 2000
Tyre Rubber	Cu (II)		Al-Asheh and Banat, 2000
Transcarpathian Clinoptilolite	Cd (II)		Vasylechko et al., 2000
Acidic Manganese chloride	Cu, Ni, Co, Pb and Fe		Diniz et al., 2000

Tea leaves	Ni (II) and Cr (III)	Maximum adsorptions were 7.97 and 5.91 mg/g.	Nishioka et al., 2000
Effloresced coal	Pb (II), Cu (II), Zn (II) and Ni (II)	Removal rate was 97% at pH.4 and 20°C.	Mei J., 2000
Lignite-based Cabon	Ni (II) and Cu (II)		Samra S.E., 2000
Barks of eucalyptus and <i>Cassia fistula</i>	Cr and Cu	Eucalyptus bark is more efficient in removal of Cr and Cu then Cassia fistula	Tiwari et al., 2000
Rice straw	Cr (VI)		Samanta et al., 2000
Polyhydroxyethyl-methacrylate	Heavy metal ions	Maximum adsorption ratio was as high as 99%	Arpa et al., 2001

Bone char	Cd, Cu and Zn ions	Sorptions of Cd and Zn ions onto bone char are primarily film-pore diffusion controlled.	Cheung et al., 2001
Nitrified lignite	Cr		Wang et al., 2001
Red mud	Pb and Cr		Gupta et al., 2001
Aluminium based coagulant	As		Gregor, J., 2001
Chitosan	Cr (VI)		Tang et al., 2001
<i>Aspergillus niger</i> biomass	Pb (II)		Jianlong et al., 2001

Poly (hydroxyethyl methacrylate) adsorbents with Thiazolidine Groups	Hg (II)	The maximum desorption ratio was as high as 99%.	Arpa et al., 2002
Methacrylamidocysteine containing Porous Poly (hydroxyethylmethacrylate) Chelating Beads	Heavy metal ions	Maximum adsorption capacity is observed for 1058.2 mg/g for Cd (II).	Denizli et al., 2002
Solar thermal and Chemo thermal Activated Carbon	Pb (II) and Cr (VI)		Nagar and Singh, 2002
Activated Carbon	Au-CN species		Mc Grath et al., 2002
Geothite-coated sand	Cd		Lai et al., 2002
Bone Charcoal	Mo ions		Faghihian et al., 2002
Iron Coated Sand	As		Petrusevski et al, 2002

Fly Ash of Poultry Litter	Cr (III)	Kelleher et al., 2002
Amino-Functionlized MCM-41 and SBA-1	Chromate and Arsenate	Yoshitake et al., 2002
Kaolinite	Pb and Cd	Coles and Yong, 2002
Sawdust	Heavy metals	Shukla et al., 2002
ACCs	Cu, Ni and Pb	Faur-Brasquet et al., 2002
Sludge Ash	Ni (II)	Weng, C.H, 2002
MgO (100)	Metal ions	Campbell and Starr. , 2002
Poly (N-vinyl formamide/ Acrylonitrile) Chelating Fibers	Heavy Metal Ions	Lin et al., 2002

Activated Carbons	Hg (II)	Kannan and Rajakumar, 2003
Aquatic Plant (<i>Myriophyllum spicatum</i>)	Heavy Metal	Keskinkan et al., 2003
Modified Activated Carbons	Cu, Zn, Ni and Cd	Saha et al., 2003
Freshwater alga <i>Chlorella kesslerii</i>	Pb	Slaveykova and Wilkinson, 2003
Olive Mill Residues	Cu	Veglio et al., 2003
Orange Waste	Arsenate and Arsenite Anions	Ghimire et al., 2003
Chitosan	Hg (II)	Jeon and Holl, 2003
Bentonite	Ni (II)	Tahir and Rauf, 2003
Ferrous Saponite	Cr (VI)	Parthasarathy et al., 2003

Humic Acids Extracted from Brown Coals	Metal Ions			Martyniuk and Wickowska, 2003
Activated Carbon from Almond Husks	Zn (II)	92% Zn (II) removal		Hasar et al., 2003
Natural and Modified Radiata Bark Pine	Copper			Montes et al., 2003
Cellulose Graft Copolymers	Heavy Metal Ions			Guclu et al., 2003
Savanna Acid Soil	Copper	65% Cu sorbed	pH \geq 3.0,	Agbenin, J. O, 2003
Recycled-wool-based Non woven Material	Pb (II)			Radetic et al., 2003
SO ₂ Treated Activated Carbon	Cd (II)			Macias-Garcia et al., 2003
Chitosan	Metal Ions			Navarro et al., 2003
Concrete Particles	Silver			Begum, S., 2003
Thai Kaolin and Ballclay	Heavy Metal		Adsorption by kaolin was: Cr > Zn > Cu \approx Cd \approx Ni > Pb by ballclay was: Cr > Zn > Cu > Cd \approx Pb > Ni.	Chantawong and Harvey., 2003

Zeolites synthesized from Fly ash	Heavy Metals	Adsorption capacity of zeolites synthesized is higher than that of fly ash.	Yanxin et al., 2003
Fungus <i>Penicillium canescens</i>	Heavy Metal Ions	Maximum adsorption capacities under non-competitive conditions were 26.4 mg/g for As (III), 54.8 mg/g for Hg (II), 102.7 mg/g for Cd (II) and 213.2 mg/g for Pb (II), respectively.	Say et al., 2003
Synthetic Zeolites	Zn (II)		Badillo-Almaraz et al., 2003
Bagasse Fly Ash	Cd and Ni		Gupta et al., 2003
Natural Condensed Tannin	Lead		Zhan and Zhao, 2003
Sea Nodule	Lead		Bhattacharjee et al., 2003
Chitosan	Lead		Ng et al., 2003
Chemically-treated Chicken Feathers	Copper and Zinc Ions		Al-Asheh and Banat, 2003
Grafted Silica	Cu (II) and Pb (II)		Chiron et al., 2003

Calcined Mg-Al-CO ₃ Hydrotalcite	Cr (VI)		Lazaridis and Asouhidou, 2003
Neutralized Red Mud	Arsenate		Genc et al., 2003
Low-cost Adsorbents	Heavy Metal Ions		Wang et al., 2003
Sheep Manure	Cu (II) and Cd (II)	Maximum uptakes for 100 mg/l Cu (II) and 100 mg/l Cd (II) ions were found to be 17.8 mg g and 10.8 mg g, respectively.	Kandah et al., 2003
Organosolv Lignin	Copper (II)		Acemiolu et al., 2003
Sepiolite	Cu (II) and Zn (II)		Vico, L. I. 2003
Goethite	Phosphate and Arsenate		Gao and Mucci, 2003
Functionalized Silica	Heavy Metal Ions		Bois et al., 2003
Kaolinite	As (V)		Cornu et al., 2003
Aniline propyl silica Xerogel	Cu (II)		Pavan et al., 2003
Activated Carbon from Furfural	Hg (II)		Yardim et al., 2003

Sewage Sludge Ash	Cu (II)		Pan et al., 2003
Clinoptilolite	Cu (II), Fe (III) and Cr (III)		Inglezakis et al., 2003
Goethite	Cu (II), Ni (II), and Cd (II)		Buerge-Weirich and Behra , 2003
<i>Penicillium chrysogenum</i> mycelium	Ni (II)	Adsorption capacity for Ni (II) <i>Penicillium chrysogenum</i> mycelium (the surface-imprinted adsorbent) was 40-45 mg/g (using 200 mg Ni (II)/ l), two times of the mycelium adsorbent.	Su and Wang, 2003
Gibbsite	As (III)		Weerasooriya et al., 2003
Alumina or Chitosan	Heavy metals		Cervera et al., 2003

Mineral Matrix of Tropical Soils	Heavy Metals	Ultisol and Alfisol soils showed the highest maximum adsorption values, in the order of 50.76 and 64.52 mmol kg ⁻¹ , whereas some Oxisols showed the lowest values, in the order of 23.92 and 30.86 mmol /kg	Fontes and Gomes, 2003
Montmorillonite-Al hydroxide	Zn (II)		Janssen et al., 2003
Low-Rank Coal (leonardite)	Zn	Effective removal of Zn (II) was demonstrated at pH values of 5-6.	Sole and Casas, 2003
Goethite	Hg (II) and Cd (II)		Backstrom et al., 2003
Indigenous Low-cost Material	Cr (VI)		Sharma, Y. C., 2003

Gellan Gum Gel Beads	Heavy Metal		Lazaro et al., 2003
Hydrolyzed Polyacrylonitrile Fibers	Cu (II)		Deng et al., 2003
<i>Pseudomonas Putida</i>	Cd, Cu, Pb and Zn	80% removal for all metals	Pardo et al., 2003
<i>Rhizopus arrhizus</i>	Cr (VI), Cu (II), and Cd (II) ions		Sa et al., 2003
Loess with high carbonate content	Cu		Jinren, 2003
Palm Fruit Bunch and Maize Cob	Fe and Mn		Nassar et al., 2003
Activated and Non-activated Oak Shells	Cu (II)	Cu (II) uptake increased with decreasing sorbent concentration or with an increase in Cu (II) concentration or solution pH.	Al-Asheh et al., 2003
Micaceous Mineral of Kenyan Origin	Cu (II)	Adsorption capacity of 0.850 g/g for Cu (II).	Attahiru et al., 2003

Powdered Marble Wastes	Cu (II)	100% Cu (II) was attained	Ghazy et al., 2003
Clinoptilolite Mineral	Lead, Barium		Cakicioglu-Ozkan and Ulku, 2003
Sugarcane Bagasse Pith	Cd (II)		Krishnan and Anirudhan, 2003
Vineyard soils of Geneva	Cu (II)		Celardin et al., 2003
Peat	Metal Ions		Ko et al., 2003
Chicken Feathers	Heavy Metals		Al-Asheh et al., 2003
Na-montmorillonite	Heavy Metals	.	Abollino et al., 2003
Natural Materials	Pb (II)		Abdel-Halim et al., 2003
Calcium Alginate Beads Containing Humic Acid	Cr		Pandey et al., 2003
High-performance Activated Carbons	Cr		Hu et al., 2003
Organic Manure	Cu (II)		Bolan et al., 2003
<i>Penicillium chrysogenum</i>	Metal Ions		Tan and Cheng, 2003

Galena (PbS) and Sphalerite (ZnS)	Arsenite		Arsenite sorbed appreciably only at pH > ~5 for PbS and pH ~4.5 for ZnS, behavior distinct from its adsorption on other substrates	Bostick et al., 2003
2-aminothiazole-modified silica gel	Cu, Ni, and Zn	Adsorption capacities for each metal ion were (mmol/g): Cu (II) =120, Ni (II)=110 and Zn (II)=090		Roldan et al., 2003
A 1.10 Phenanthroline-grafted Brazilian Bentonite	Cu (II)			De Leon et al., 2003
Caustic Waste Yeast Biomass	Treated Baker's	Cu (II)		Goksungur et al., 2003

Activated Carbon	Pb (II), Cd (II), and Cr (VI)	Rivera-Utrilla et al., 2003
<i>Pseudomonas Putida</i> 5-x Isolated from Electroplating Effluent	Cu (II)	Wang et al., 2003
Turbid River water	Cu and Ni	Herzl et al., 2003
Regenerated Sludge from a Water Treatment Plant	Cu (II) and Pb (II)	Wu et al., 2003
Chitosan	Zn (II)	Zhiguang et al., 2003
Sand	Heavy Metals	Awan et al., 2003
Tea Leaves and Coffee Beans	Mercury	Kiyohara et al., 2003
Low Cost Materials	Iron and Manganese	Nassar et al., 2003
Iron-Conditioned Zeolite	Arsenic	Onyango et al., 2003
Sawdust Carbon	Arsenic (III)	Nagarnaik et al., 2003
Activated Carbon from Acidic Media: Nitrate and Sulfate Media	Silver	Jia and Demopoulous., 2003
Iron Oxide-Coated Sand	Arsenic	Thirunavukkarasu and Viraraghavan 2003
Bone Charcoal	Cu and Zn	Wilson and Pulford, 2003

Low Cost and Waste Material	Cu (II) and Cd (II)	Bentonite and compost presented the highest removal efficiencies, reaching 99% for copper when cadmium is also present, for initial solution concentrations of up to 100 mg/l	Ulmanu et al., 2003
Sulfate-modified Iron Oxide-coated Sand (SMIOCS)	Arsenic (III)		Vaishya and Gupta, 2003
Mulloorina Illite and Related Clay Minerals	Cd (II)		Lackovic et al., 2003
Silica-dithizone	Hg (II)		Cestari et al, 2004
Activated Neutralised Red Mud	Arsenic		Genc-Fuhrman et al, 2004
<i>Chryseomonas luteola</i> TEM05	Cr and Al		Ozdemir and Baysal, 2004

Natural Zeolite	Zn, Cu and Pb	Peri et al, 2004
Geothite	Heavy Metal Cations	Kosmulski and Mczka, 2004
<i>Ceratophyllum demersum</i>	Heavy Metal	Keskinkan et al, 2004
Ecklonia maxima	Heavy Metal	Feng and Aldrich, 2004
Streptomyces coelicolor A3 (2)	Ni (II) and Cu (II)	Ozturk et al, 2004
Tree Fern	Cd (II)	Ho and Wang, 2004
Brown, Green and Red Seaweeds	Cd	Hashim and Chu, 2004
Wood Saw dust	Heavy metal ions	Sciban and Klasnja, 2004
Chinese Reed (<i>Miscanthus sinensis</i>)	Cr (III)	Namasiyam and Holl, 2004
<i>Chlorella vulgaris</i>	Cu	Chu and Hashim, 2004
Bone char	Metal ions	Choy et al, 2004
Bagasse Fly Ash	Pb and Cr	Gupta and Ali, 2004
Savanna Alfisol	Cu and Zn	Agbenin and Olojo, 2004

Treated Sawdust	Cr	Garg et al, 2004
Zn(IV) substituted ZnAl/MgAl-layered Double Hydroxide	Cr (VI) and Se (II)	Das et al, 2004
Humic substance	Cu (II)	Alvarez-Puebla et al, 2004
Activated Rice Husk and Activated Alumina	Cr (VI)	Bishnoi et al, 2004
Hazelnut shell	Cr (VI)	Kobyasova, M., 2004
Alumina particles	Ni (II)	Hong et al, 2004
<i>Fontinalis antipyretica</i>	Cd (II) and Zn (II)	Martin et al, 2004
Fe-modified Steam Exploded Wheat Straw	Cr (VI)	Chun et al, 2004
Alginate coated Loofa Sponge Disc	Cd	Iqbal, M., 2004
Peat	Cu	Petroni and Pires, 2004
Poly acrylonitrile-immobilized dead cells of <i>Saccharomyces Cerevisiae</i>	Cu (II)	Godjevargova and Mihova, 2004
Montmorillonites	Cu	Ding and Frost, 2004
Herbaceous Peat	Cu (II)	Gundogan et al, 2004

Mangeneses Dioxide Complex	Co, Ni, Cu, and Zn	Kanungo et al, 2004
Bone char	Metal ions	Ko et al, 2004
Geothite	Cadmium and Phosphate	Wang and Xing, 2004
Chitosan	Cu	Wan et al, 2004
Moroccan Stevensite	Metal ions	Benhammon et al, 2005
Moroccan Stevensite	Hg (II) and Cr (VI)	Benhammou et al., 2005
Amberlite IR-120 Synthetic resin	Cu, Zn, Ni, Pb and Cd ions	Demirbas et al., 2005
Sea Nodule Residues	Pb (II)	Agrawal et al., 2005

Black gram husk (BGH)	Pb, Cd, Cu, Ni, and Zn	The maximum amount of heavy metals (q_{\max}) adsorbed at equilibrium was 49.97, 39.99, 33.81, 25.73 and 19.56 mg/g BGH biomass for Pb, Cd, Zn, Cu and Ni, respectively	Saeed et al., 2005
Bentonite	Cd (II) and Zn (II)		Lacin et al., 2005
Montmorillonite	Hg (II)		Green-Ruiz, C., 2005
H ₃ PO ₄ -activated Rubber Wood Sawdust	Cu (II)		Kalavathy et al., 2005
Mulch	Heavy Metals		Jang et al., 2005

Activated Carbon Prepared from Waste Apricot by Chemical Activation	Ni (II)		Erdogan et al., 2005
Cu-ZSM-5 Zeolite	Cu (II)		Kazansky and Pidko, 2005
Polyacrylamide-bentonite and Zeolite Composites	Pb (II)		Ulusoy and Simsek, 2005
Calcite	Fluoride		Turner et al., 2005
Keratin Powder Prepared from Algerian Sheep Hooves	Hg (II)		Touaibia and Benayada, 2005
Chemically Modified Activated Carbons	Cr (VI)		Zhao et al., 2005
Natural Goethite	Pb (II) and Zn (II)		Abdus-Salam and Adekola, 2005
Peat and Solvent-extracted Peat	Fe (II), Pb (II)		Minihan et al., 2005
Chitosan Flakes	Ni (II)	Adsorption being pH dependent.	Zamin et al., 2005
Modified Sugarcane Bagasse	Cr (VI)		Garg and Sud, 2005
Activated Carbons Prepared from Coconut Shells by Chemical Activation with KOH and ZnCl ₂	Cr		Bendezu et al., 2005
Sawdust	Cu (II)		Larous et al., 2005
Kaolinite	Pb and Cd		Hepinstall et al., 2005

Activated Alumina and Activated Carbon	As (III)		Manjare et al., 2005
Chitosan Functionalized with 2[-bis-(pyridylmethyl)amino methyl]-4-methyl-6-formylphenol	Cu (II), Cd (II), and Ni (II)		Justi et al., 2005
Granular Activated Carbon	Iron and Manganese		Jusoh et al., 2005
Bacterial Biofilm	Zn (II)		Toner et al., 2005
Alumina	Molybdate and Nickel		Al-Dalama et al., 2005
Used Black Tea Leaves	Cr (VI)	Maximum Cr (VI) adsorption achieved at initial Cr (VI) concentration < 150 mg / l; initial pH of solution 1.54-2; processing temperature < 50°C	Hossain et al., 2005
Activated Carbon	Cr (III)		Lyubchik et al., 2005
Clays	Pb (II)		Gupta et al., 2005
Bentonite	Zn (II)		Kaya and Oren, 2005
Crab Shells	Ni (II)		Pradhan et al., 2005

Treated Granular Activated Carbon	Pb (II)			Goel et al., 2005
Corncob Particles	Cu (II) and Cd (II)			Shen and Duvnjak, 2005
Palm Kernel Fibre	Pb (II)			Ho and Ofomaja, 2005
Pretreated Biomass of <i>Neurospora crassa</i>	Pb (II) and Cu (II)			Kiran et al., 2005
Maghemite Nanoparticles	Cr (VI)			Hu et al., 2005
Iron Oxide-coated Cement (IOCC)	As (V)			Kundu and Gupta, 2005
Rice Bran	Cr (VI)			Singh et al., 2005
Coir and Dye Loaded Coir Fibres	Pb (II)			Shukla and Pai., 2005
Coconut fiber and sawdust waste biomass containing chelating agents	As (V), Pb (II) and Hg (II)	As (V) is adsorbed more	Maximum adsorption occurred at pH 2 and 12 whereas minimum adsorption occurred at pH 6-8.	Igwe et al., 2005
Maize Cob and Husk	Zn (II), Cd (II), Pb (II) ions	495.9 mg/g for Zn (II), 456.7 mg/g for Pb (II), 493.7mg/g for Cd (II)		Igwe et al., 2005
Hydroxylapatite and Bone-char	As (v)			Sneddon et al., 2005
Activated Carbon from Oat Hulls	As (V)			Chuang et al., 2005
Low-rank Coal (Leonardite)	Cd (II) and Pb (II)			Lao et al., 2005

<i>Paenibacillus polymyxa</i> Cells and their (EPS) Exopolysaccharide	Cu (II)	Maximum biosorption value (q) of 1602 mg/g observed with purified EPS at 0.1 mg/ ml particularly promising for use in field applications.	Acosta et al., 2005
Polymerized Banana Stem	Pb (II)		Noeline et al., 2005
Nipa Palm Biomass	Pb (II) and Cu (II)	Desorption increases with increase in contact time, reaching 75.3 and 63.7% in acid reagent, 18.9 and 14.06% in basic reagent and 3.35 and 2.44% in distilled water for Pb (II) and Cu (II), respectively, at a contact time of 140 min.	Wankasi et al., 2005
Protonated Macroalga <i>Sargassum muticum</i>	Cd (II)		Lodeiro et al., 2005

Bead Cellulose Loaded with Iron Oxyhydroxide	Arsenic		Guo and Chen, 2005
Cellulose/Chitin Beads	Pb (II)		Zhou et al., 2005
Aminated Chitosan Bead	Hg (II)		Jeon and Park, 2005
4-vinyl pyridine grafted poly (ethylene terephthalate) fibers	Cr (VI)	Maximum adsorption capacity was found to be 263.16 mg/ g	Yigitoglu and Arslan, 2005
Phosphate Rock	Cu (II)		Sarioglu et al., 2005
Natural Kaolin	Cu (II), Zn (II) and Co (II)		Ceylan et al., 2005
Modified Jute Fibres	Cu (II), Ni (II) and Zn (II)		Shukla and Pai, 2005
Chemically Modified Australian Coals	Cd (II)		Burns et al., 2005
Surface Soils of Nuclear Power Plant Sites in India	Zn (II)		Dahiya et al., 2005
Natural and Oxidized Corncob	Cd (II)		Leyva-Ramos et al., 2005
Mn Oxide-Coated Granular Activated Carbon	Cu (II) and Cd (II)		Fan and Anderson, 2005
Zeolite and Sepiolite	Pb (II)		Turan et al., 2005

Biomass of the Marine Macroalga <i>Cystoseira baccata</i>	Hg (II)	Herrero et al., 2005
Amine-Modified Zeolite	Pb and Cd	Wingenfelder et al., 2005
Amazon Soils	Hg (II)	Miretzky et al., 2005
Activated Carbon	Pb (II)	Zhang et al., 2005
Bone Char	Cd (II), Cu (II), and Zn (II)	Choy and McKay , 2005
Immobilized <i>Pinus sylvestris</i> Sawdust	Pb (II)	Taty-Costodes et al., 2005
Hydrous Al (III) Floc in the Presence of a Modified Form of Polyethylenimine	Cd (II)	McCullagh and Saunders, 2005
Kaolinite	Cu (II)	Peacock and Sherman, 2005
Iron Oxide-coated Sand	As (III)	Gupta et al., 2005
Cross-linked Chitosan	Cr	Rojas et al., 2005
PEI-Modified Biomass	Cu (II), Pb (II) and Ni (II)	Deng and Ting, 2005
Modified Pine Tree Materials	Ni (II)	Argun et al., 2005
Treated Granular Activated Carbon	Pb (II)	Goel et al., 2005

Shales belonging to the Proterozoic Vindhyan basin, central India, and a black cotton soil, Mumbai, India	Pb (II) and Cd (II)		Paikaray et al., 2005
Sawdust	Ni (II)		Shukla et al., 2005
Agricultural Waste 'rice Polish'	Cd (II)		Singh et al., 2005
Zero-valent Iron	As		Bang et al., 2005
Commercial activated carbon (CAC) and chemically prepared activated carbons (CPACs) from raw materials such as straw, saw dust and dates nut	Cd (II)	Straw carbon showed the maximum adsorption capacity towards Cd (II)	Kannan and Rengasamy, 2005
Chitosan-based Polymeric Surfactants	Cr (VI)		Lee et al., 2005
Decaying Tamrix Leaves	Pb (II)		Zaggout, F.R., 2005
Activated Carbons	Cr (VI)		Khezami and Capart, 2005
Crosslinked Amphoteric Starch Containing the Carboxymethyl Group	Pb (II)		Xu et al., 2005
Bone Char	Cu, Cd, Zn		Cheung et al., 2005

Vermiculite	Cd (II) and Pb (II)			Abate and Masini, 2005
Activated Carbon	Cd (II) and Zn (II)			Leyva-Ramos et al., 2005
Peanut Hulls through Esterification Using Citric Acid	Co (II) and Ni (II)	Maximum adsorption capacities, for Co (II) and Ni (II) were 28.7 mg/g ; 270.3 mg/g and 5 mg/g ;175.4 mg/g on native and peanut hulls citrate, respectively.	The optimum pH for the adsorption of cobalt (II) ions onto the peanut hulls citrate was 7.0.	Hashem et al., 2005
Iron Complexed Protein Waste	Chromium (VI)			Fathima et al., 2005
Zr-loaded Lysine Diacetic Acid Chelating Resin	As (V) and As (III)			Balaji et al., 2005
Activated Carbon	Cu (II) and Pb (II)			Machida et al., 2005
Palm Kernel Fibre	Pb (II)			Ho and Ofomaja, 2005
Chemically Modified Thin Chitosan Membranes	Cu (II)			Cestari et al., 2005

Natural Bentonite	Pb (II), Ni (II)		Donat et al., 2005
Polarized Activated Carbons	Copper, Silver, and Zinc		Goldin et al., 2005
Polarized Activated Carbon Modified by Quercetin	Copper and Calcium Cations		Goldin et al., 2005
Tree Fern	Pb (II)		Ho, Yuh-Shan, 2005
Iron Oxide-coated Sand	As (iii)		Gupta et al., 2005
Collagen Fiber Immobilized Bayberry Tannin	Pt (II) and Pd (II)		Wang et al., 2005
Rhizopus arrhizus	Zn (II)		Preetha and Viruthagiri, 2005
Maize Cob	Cd, Pb and Zn	% Sorption is 71% for Zn (II), 32% for Cd (II), and 30% for Pb (II)	Abia and Igwe, 2005
Turkish Brown Coals	Cr (III)		Gode and Pehlivan, 2005
Dye Loaded Groundnut Shells and Sawdust	Cu (II), Ni (II) and Zn (II)		Shukla and Pai, 2005
Acidic Polysaccharide Gels	Pb (II)		Dhakar et al., 2005
Chitosan-Cellulose Hydrogel Beads	Copper		Li and Bai, 2005
Siderite	Lead		Erdem and Özverdi, 2005
Solvent-Impregnated Resins Containing Cyanex 272	Zn		Shiau et al., 2005

<i>Agave lechuguilla</i> Biomass	Cr (VI)		Romero-Gonzalez et al., 2005
Carbonaceous Adsorbents Prepared from Rubber of Tyre Wastes	Mercury		Manchón-Vizuite et al., 2005
Lewatit-anion Exchange Resins	Cr (VI)		Gode and Pehlivan, 2005
Caladium Bicolor (wild Cocoyam)	Pb (II) and Cd (II)	Sorption capacity obtained were 49.53 and 65.50 mM/g for Pb (II) and Cd (II)	Horsfall Jr. and Spiff, 2005
Carboxylate-functionalized Polyacrylamide Grafted Lignocellulosics	Co (II)		Shibi and Anirudhan, 2005
Carbon Aerogel	Lead, Mercury and Nickel		Goel et al., 2005
Bentonite	Cu (II)		Al-Qunaibit et al., 2005
Kaolinite	As (V)		Quaghebeur et al., 2005
Immature Coal (leonardite)	Ni (II) and Cu (II)		Zeledon-Toruno et al., 2005
Carrot Residues	Cr (III), Cu (II), Zn (II)		Nasernejad et al., 2005
Iron (III) Hydroxide-Loaded Sugar Beet Pulp	Cr (VI)		Altundogan, H.S, 2005
Active Carbon	Pb (II)		Qadeer et al., 2005

Various Cereals from Korea	Cd (II) and Pb(II)	Park et al., 2005
Activated Eucalyptus Bark	Cr (VI)	Sarin et al., 2006
Agricultural Waste Maize Bran	Pb (II)	Singh et al., 2006
Palm Shell Activated Carbon	Pb (II)	Issabayeva et al., 2006
Composite Sewage Sludge/industrial Sludge-based Adsorbents	Cu (II)	Seredych and Bandosz, 2006
Graphene Layer of Carbonaceous Materials	Pb (II)	Machida et al., 2006
Phenolated Wood Resin	Cr (III), Ni (II), Zn (II), Co (II)	Kara et al., 2006
Clinoptilolite	Ag (I)	Akgul et al., 2006
Clay Mineral	Cd (II), Zn (II), Mg (II) and Cr (VI)	Fonseca et al., 2006
Manganese Oxide Coated Sand	Cu (II) and Pb (II)	Han et al., 2006
Pyrite and synthetic iron sulphide	Cu (II), Cd (II) and Pb (II)	Ozverdi and Erdem, 2006
Immobilized Pseudomonas Aeruginosa PU21 Beads	Pb (II)	Lin and Lai, 2006

Hydrous Manganese Dioxide	Cd (II)	Tripathy et al., 2006
Husk of <i>Lathyrus sativus</i>	Cd (II)	Panda et al., 2006
Iron Oxide-coated Fungal Biomass	As (III), As (V)	Pokhrel and Viraraghavan, 2006
Montmorillonite and Kaolinite	Sr	Basçetin and Atun, 2006
<i>Oryza sativa</i> L. Husk and Chitosan	Pb (II)	Zulkali et al., 2006
Highly Mineralized Peat	Cd (II)	Gabaldón et al., 2006
Kaolinite Clay	Pb (II), Cd (II)	Adebowale et al., 2006
Sugar Beet Pulp and Fly Ash	Zn (II) and Cu (II)	Pehlivan et al., 2006
Activated Carbon from Agricultural Waste Material and Fabric Cloth	Cr (III)	Mohan et al., 2006
Waste of Tea Factory	Ni (II)	Malkoc and Nuhoglu, 2006
Heteroatoms in Activated Carbon	Cr (VI)	Valix et al., 2006
Iron and Manganese	Cu (II)	Mohan and Chander, 2006
Solid Humic Acid from the Azraq Area, Jordan	Cu (II) and Ni (II)	El-Eswed and Khalili, 2006
Activated Carbo-aluminosilicate Material from Oil Shale	Cr (VI)	Shawabkeh, R.A., 2006
Chitosan-Coated Perlite Beads	Cd (II)	Hasan et al., 2006

Acid Soils	Cu (II) and Zn (II)		Arias et al., 2006
Goethite and Birnessite	Cu (II)		Huerta-Diaz, M.A., 2006
Activated Carbon from Sugar Industrial Waste	Cr (III)		Fahim et al., 2006
Microwave Stabilized Heavy Metal Sludge	Cu (II)		Hsieh et al., 2006
Chemically-modified Biomass of Marine Brown Algae <i>Laminaria japonica</i>	Pb (II)		Luo et al., 2006
Natural Bentonite Clay	Co (II)		Shahwan et al., 2006
Arable and Forest Soils	Cd (II)		Palágyi et al., 2006
Sorel's Cement	Cr (VI)	Adsorption capacity 21.4 mg Cr (VI) /g of Sorel's Cement	Hassan et al., 2006
Lignocellulose Adsorption Medium (LAM)	Arsenic		Kim et al., 2006
Activated Carbon	Cr (VI)		Yavuz et al., 2006

Tamarind hull-based adsorbent	Cr (VI)		Verma et al., 2006
Kaolinite, montmorillonite, and their modified derivatives	Cu (II)		Bhattacharyya and Gupta, 2006
Restricted Phyllosilicate Clay	Pb (II)		Giannakopoulos et al, 2006
Coconut Copra Meal	Cd (II)		Ho and Ofomaja, 2006
Peach and Apricot Stones	Pb (II)	Pb (II) adsorption 93% for Apricot and 97.64% for Peach.	Rashed, M.N., 2006
Grape Stalk Wastes Encapsulated in Calcium Alginate Beads	Cr (VI)		Fiol et al., 2006
Thin Vanillin-Modified Chitosan Membranes	Cu (II)		Cestari et al., 2006
<i>Tectona grandis</i> L.f. (teak Leaves Powder)	Cu (II)		King et al., 2006

Iron Oxide-coated Cement (IOCC)	As		Kundu and Gupta, 2006
Haro River Sand	Cd (II)		Ahmed et al., 2006
Particulate Organic Matter in Soil	Pb, Cu, and Cd		Guo et al., 2006
Acacia Nilotica Bark	Cr (VI)		Rani et al., 2006
Industrial Solid Waste Fe (iii)/Cr (iii) Hydroxide	Mo		Namasivayam and Prathap, 2006
Chemically Modified and Unmodified Agricultural Adsorbents	Pb (II) and Ni (II)		Abia and Asuquo, 2006
Kaolinite	Cd (II)		Harris et al., 2006
<i>Tamarindus indica</i> Seeds	Cr (II)		Agarwal et al., 2006
Wheat Bran	Cd (II)		Singh et al., 2006
<i>Spirulina platensis</i>	Cr (III)		Li et al., 2006
Cross-linked Starch Phosphate Carbamate	Pb (II)	Maximum adsorption capacity evaluated from the Langmuir isotherm towards Pb (II) is 2.01 mmol/g.	Guo et al., 2006
ZnCl ₂ Activated Coir Pith Carbon	Molybdate		Namasivayam and Sangeetha, 2006
Manganese Nodule Leached Residue Obtained from NH ₃ -SO ₂ Leaching	Cr (VI)		Mallick et al., 2006
Kraft Lignin	Cu (II) and Cd (II)		Mohan et al., 2006
Manganese Oxide Coated Zeolite	Cu (II) and Pb (II)		Zou et al., 2006

Natural and Crosslinked Chitosan membranes	Hg (II)	Vieira and Beppu, 2006
Natural Clino-pyrrhotite	Cr (VI) and Cr (III)	Lu et al., 2006
Cu (ii)-, Ni (ii)-, or Co (ii)-doped Goethite	As (V)	Mohapatra et al., 2006
Kaolinite-based Clays	Cd (II)	Hizal and Apak, 2006
Dried Activated Sludge	Cu (II) and Pb (II)	Wang et al., 2006
Calcite	Cu (II), Zn (II), and Pb (II)	Elzinga et al., 2006
Kaolinite	Cu (II)	Li and Dai, 2006
Waste Acorn of <i>Quercus ithaburens</i>	Cr (VI)	Malkoc et al., 2006
Pyrite	Cd (II)	Borah and Senapati, 2006
Carbon Sorbent Derived from Fruit Shell of <i>Terminalia Catappa</i>	Hg (II)	Inbaraj and Sulochana, 2006
Seaweed biomass	Cd (II) and Pb (II)	Kumar and Kaladharan, 2006
Tea Factory Waste	Cr (VI)	Malkoc and Nuhoglu, 2006
Eucalyptus Bark	Cr	Sarin and Pant, 2006
<i>Oryza sativa</i> L. Husk	Pb (II)	Zulkali et al., 2006

Cassava (manihot Sculenta Cranz.)	Cr (VI)	Horsfall Jr. et al., 2006
Coir Pith	Co (II), Cr (III) and Ni (II)	Parab et al., 2006
Green Coconut Shell Powder	Cd (II)	Pino et al., 2006
Li/ Al Layered Double Hydroxide	Cr (VI)	Wang et al., 2006
Kaolinite and Montmorillonite	Pb (II)	Bhattacharyya and Gupta, 2006
Spirogyra Species	Cu (II)	Gupta et al., 2006
Treated Rice Husk	Cd (II)	Kumar and Bandyopadhyay, 2006
Ceiba Pentandra Hulls	Cu (II), Cd (II)	Rao et al., 2006
Palm Kernel Fiber	Pb (II)	Ho and Ofomaja, 2006
Schwertmannite and Goethite	Cu (II)	Jönsson et al., 2006
Polymer-grafted Banana (Musa paradisiaca) Stalk	Pb (II) and Cd (II)	Shibi and Anirudhan, 2006
Magnetic Chitosan Nanoparticles	Co (II)	Yang-Chang et al., 2006
Brown Coals	Cr (VI)	Gode and Pehlivan, 2006
Heavy metal precipitant N,N-bis-(dithiocarboxy)piperazine	Cu (II)	Fu et al., 2006
Bagasse Fly Ash	Cd (II) and Ni (II)	Srivastava et al., 2006
Glycidyl methacrylate chelating resin containing Fe ₂ O ₃ particles	Cu (II)	Donia et al., 2006
Methacrylic Acid/acrylamide Monomer Mixture Grafted Poly (ethylene Terephthalate) Fiber	Cu (II), Ni (II) and Co (II)	Coskun et al., 2006

Activated Hazelnut Shell Ash and Activated Bentonite	Cr (VI)	Bayrak et al., 2006
Chitosan and Chitosan/PVA Beads	Cu (II)	Ho, Yuh-Shan, 2006
Activated Carbon	Cu (II)	Boari et al., 2006
Zeolites	Zn (II)	Ören and Kaya, 2006
Fe (iii)/Cr (iii) Hydroxide	Selenite	Namasivayam and Prathap, 2006
Modified Sodium Alginate	Cd (II)	Hashem and Elhmmali, 2006
ZnCl ₂ Activated Coir Pith Carbon	Cr (VI)	Namasivayam and Sangeetha, 2006
Filamentous Algae Spirogyra Species	Hg (II)	Rezaee et al., 2006
Wine-Processing Waste Sludge	Pb (II)	Yuan-Shen et al., 2006
Mesoporous Silicate MCM-41	Cd (II) and Pb (II)	Oshima et al., 2006
Modified and Unmodified Maize Husk	Co (II), Fe (II) and Cu (II)	Igwe et al., 2006
Arbuscular Mycorrhizal Maize (Zea mays L.)	Zn, Cd, P	Shen et al., 2006
Fungi Biomass	Cr (VI)	Louhab et al., 2006
Chitosan Sorbent	As	Chen and Chung, 2006
Chitosan Coated Montmorillonite	Cr (VI)	Fan et al., 2006
Vegetable Biomass	Pb, Fe	Bun-ei et al., 2006

Granular Activated Carbon and Natural Zeolite	Zn (II)	Meshko et al., 2006
Bagasse Fly Ash	Cd (II) and Zn (II)	Srivastava et al., 2006
<i>Agave lechuguilla</i> Biomass	Cr (III)	Romero-González et al., 2006
Cassava (<i>Manihot sculenta</i> Cranz) Tuber Bark Waste	Cd (II), Cu (II), Zn (II)	Horsfall et al., 2006
ZnO Loading to Activated Carbon	Pb (II)	Kikuchi et al., 2006
Clays and Modified Clays	Boron	Karahan et al., 2006
Kaolinite-based Clay Minerals Individually and in the Presence of Humic Acid	Cu (II) and Pb (II)	Hizal and Apak, 2006
Clays	Ni (II)	Gupta and Bhattacharyya, 2006
Anaerobic Granular Biomass	Pb (II), Cd (II), Cu (II) and Ni (II)	Hawari and Mulligan, 2006
Activated Carbon from Alkaline Impregnated Hazelnut Shell	Cu (II)	Sayan, E., 2006
Tannic Acid Immobilised Activated Carbon	Cu (II), Cd (II), Zn (II), Mn (II) and Fe (III)	Uçer et al., 2006
Modified Coir Fibres	Ni (II), Zn (II) and Fe (II)	Shukla et al., 2006
Coir Based Adsorbent	Ni (II)	Nityanandi et al., 2006
Waste Tea and Coffee adsorbents	Cu (II), Zn (II), Cd (II), Pb (II)	Utomo et al., 2006
Purified Carbon Nanotubes	Zn (II)	Lu and Chiu, 2006
Montmorillonite	Cu (II)	Qin and Shan, 2006

Poly (ethylene terephthalate)-g-Acrylamide Fibers	Pb (II)	Adsorption capacity was found as 39.57 mg/g fiber for Pb (II) for the copolymer with a graft yield of 15.7%. Quantitative desorption of Pb (II) from reactive fibers were found to be 96% by 5 M HNO ₃	Coskun and Soykan, 2006
Live and Pretreated Biomass of <i>Aspergillus flavus</i>	Cr (VI)		Deepa et al., 2006
Chelating Cellulose	Cu (II)		Connell et al., 2006
Cellulosic-adsorbent Resin	Cu (II)		Bao-Xiu et al., 2006
Diatom Surface	Cd (II) and Pb (II)		Gelabert et al., 2006
Pretreated <i>Aspergillus Niger</i>	Cu (II) and Pb (II)		Dursun et al., 2006

Multi-amine-grafted Mesoporous Silicas	Pb (II), Cu (II), Cd (II), Zn (II), Hg (II)		The fresh dry samples were found to show much higher adsorption capacity than the aged ones	Zhang et al., 2007
Chitosan-Coated Perlite Beads	Co (II)		A first order reversible rate equation is used to understand the kinetics of metal removal and to calculate the rate constants at different initial concentrations	Kalyani et al., 2007
Natural and Acid Activated Kaolinite and Montmorillonite	Co (II)		Acid activation enhances the adsorption capacity of kaolinite and montmorillonite.	Bhattacharyya and Gupta, 2007
Sugarcane Bagasse	Cd (II)			Ibrahim et al., 2007
Chemically Treated Newspaper Pulp	Zn (II)	Zn (II) loading was 9.20 mg/g for 10.31 mg/l initial zinc concentration at pH 5.80	Zn (II) loading on TNP was dependent on initial zinc concentration	Chakravarty et al., 2007
Degreased Coffee Beans (DCB)	Cu (II), Zn (II), Pb (II), Fe (III), Cd (II)	90% desorption of Cd (II) was achieved	DCB behaves as a cation exchanger.	Kaikake et al., 2007

Turkish Brown Coals	Cr (VI)	Maximum adsorption capacity of 11.2 mM of Cr (VI)/g for Ilgin (BC ₁), 12.4 mM of Cr (VI)/g for Beyşehir (BC ₂), 7.4 mM of Cr (VI)/g for Ermenek (BC ₃) and 6.8 mM of Cr (VI)/g for activated carbon (AQ-30) was achieved at pH of 3.0	The adsorption reached equilibrium in 80 min	Arslan and Pehlivan, 2007
Synthetic Nanocrystalline Mackinawite (FeS)	Hg (II)			Jeong et al., 2007
Red mud and its mixtures with haematite, china clay and fly ash	As (III)		As (III) removal by adsorbents is diffusion controlled	Singh et al., 2007
Unmodified and EDTA-modified Maize Husk	Cd (II), Pb (II) and Zn (II)		Sorption process was found to be physiosorption process	Igwe and Abia, 2007
Granular Ferric Hydroxide	As (v)			Xie et al., 2007
Activated Carbon (Chemviron C-1300)	Cu (II)			Kalpakli and Koyuncu, 2007

Table. 1.7. Summary of various adsorbents used for the removal of organic pollutants from wastewater (2000 -2007)

Adsorbent	Organic pollutant removed	Adsorption / Desorption	Conditions	Reference
Coated Activated Carbon	Nitrobenzene, Benzoic acid, Phenol and Aniline			Koh and Nakajima, 2000
Carbon from Palm seed coat	o -Cresol	95% removal of o-Cresol. Adsorption capacity of 19.58 mg/g		Rengaraj et al., 2000
Bagasse fly ash	2,2-Bis (4chlorophenyl)-1,1-dichloroethane and 2,2-Bis (4-chlorophenyl)-1,1-dichloroethene	< 93% removal	pH-7	Gupta and Ali, 2001
Kaolinite	Sodium Oleate		Adsorption on Kaolinite is found to follow two step-first order kinetic rate equation with two different (K_1 and K_2) rates constants.	Xu et al., 2001
Natural porous coal	Aromatic compounds			Tarasevich, Y.I., 2001

Saw dust	p-nitrophenol	Intraparticle diffusion had a hindering effect on the adsorption	Dutta et al., 2001
Rice Bran	Organochlorine compound and Benzene		Atsuko et al., 2001
Organo-minerals	Phenols, benzene and toluene		Koh and Doxon, 2001
Activated Carbon	p-Cresol & p-Nitrophenol		Nouri et al., 2002
Activated Carbon	Organic contaminants		Schmotzer et al., 2002
HDTMA Modified Kaolinite and Halloysite	Naphthalene		Lee and Kim, 2002
Activated Carbon	Aromatic Compound		Haghseresht et al., 2002
TiO ₂ Photocatalysis	2-chlorophenol		Ilisz et al., 2002

Activated Carbon	Dissolved Organic Matter		Li et al., 2002
Activated Carbon Fibres	Trace Volatile Organic Compounds	ACFs with specific surface areas of 640 m ² /g and 1460 m ² /g were used to adsorb trace VOCs in N ₂ streams at atmospheric pressure at or near room temperature	Huang et al., 2002
Granular Activated Carbon	Chlorobenzene	High adsorption capacity on GAC up to about 450 mg/g	Lorbeer et al., 2002
Spherical Activated Carbons from Oil Agglomerated Bituminous Coals	Organic Impurities		Gryglewicz et al., 2002
Activated Carbon	Organic Contaminants		Schmotzer et al., 2002
Activated Carbons	Aromatic Compounds		Haghseresht et al., 2002
Carbonaceous Materials from Wood Chips	Bisphenol A		Nakanishi et al., 2002

Carbon Blacks	Ionic Surfactant	González-García et al.,2002
Activated Carbon	Phenol	Polaert et al., 2002
Activated Carbon Preloaded with Humic Substances	Trichloroethylene	Kilduff and Karanfil, 2002
Bentonite and Perlite	P-chlorophenol	Koumanova and Peeva-Antova, 2002
Goethite and Kaolinite	Anthracene	Angove et al., 2002
Rubber Seed Coat	Phenol	Rengaraj et al, 2002
Organobentonite	Phenol	Yun-Hwei Shen, 2002
Montmorillonites	Dinitrophenol	Sheng et al., 2002
Activated Carbon	Nitrophenol	Chern and Chien, 2002

Activated Carbon	Benzene and Methylethylketone	Huang et al., 2002
Rice Bran	Chloroform	Adachi et al., 2002
Silica supported cyclodextrin Derivatives	Organic Pollutants	Phan et al., 2002
Activated Carbons Produced from Waste Tyre Rubber	Organic Compounds	Miguel et al., 2002
Rice Husk Ash of Kenyan Origin	Phenolic compounds	Mbui et al., 2002
Phenolic Hydroxyl Modified Polystyrene	Phenolic Compounds	Li et al., 2002
Activated Carbons	Phenol	Fernandez et al., 2003
Modified Hydrotalcites	2,4-dichlorophenol	Klumpp et al., 2003
Coal	Sodium Dodecyl Benzenesulfonate	Mishra et al., 2003

Activated Carbon	2-Naphthalene sulfonate		Chang et al., 2003
Natural Clinoptilolite	1, 2-Dichloroethane		Pilchowski and Chmielewska, 2003
Activated Carbon from Peanut Shells	Organic Compounds (Acetone, pyridine, phenol, iodine, Methylene Blue, Congo Red, Reactive Navy and tannic acid)	A useful correlation for the calculation of the affinity coefficient as a function of relative parachor is presented.	Gonzo, E.E., 2003
Hypercrosslinked Polymeric Adsorbent with Sulphonic Groups	p-toluidine, p-aminophenol and phenol		Wang et al., 2003
Activated Carbon	Chlorinated Organic Compounds		Bembnowska et al., 2003
Activated Bentonites	Phenol		Al-Asheh et al., 2003
Adsorbent from Elutrilite	4-Chloro-2-Methylphenoxy-Acetic Acid		Mahramanlioglu, M., 2003
Sol-Gel Derived Zirconium Oxide Adsorbent Powder	Phenol and p-Chlorophenol		Akarsu et al., 2003
Polymer-Based Active Carbons	Phenol and 2,3,4-Trichlorophenol		László et al., 2003

Activated Carbons	Polycyclic Aromatic Hydrocarbon		Mastral et al., 2003
Granular Activated Carbons	Acetone, Methyl Ethyl Ketone, 1,1,1-Trichloroethane, and Trichloroethylene		Pires et al., 2003
Pyrolyzed oil shale residue	Phenol	Chemically activated oil shale, pretreated with ZnCl_2 , gave the highest uptake of phenol.	Al-Asheh et al., 2003
Low-cost Coir Pith Carbon	2-chlorophenol		Namasivayam and Kavitha, 2003
Granular Activated Carbons	Resorcinol and Catechol		Kumar et al., 2003
Iron Oxides	Residual Organic Matter		Choo and Kang, 2003
Activated Carbon	Benzoic Acid and P-nitrophenol		Chern and Chien, 2003
Activated Carbon from Apricot Stones	p-chlorophenol		Koumanova et al., 2003

Iron Oxides	Residual Organic Matter		Choo and Kang, 2003
Rayon-based Activated Carbon Fibers	Formaldehyde		Rong et al., 2003
Bentonites Modified with Single or Dual Quaternary Ammonium Cations	Organic Compounds	The adsorption affinity on dual-modified bentonites was generally lower than that on single-modified bentonites	Gönülşen et al., 2003
Activated and Non-activated Oak Shells	Phenol and Dyes	Interaction amongst the different operating variables played a role in the uptake of phenol or Methylene Blue dye by the adsorbent considered.	Al-Asheh et al., 2003
Organomontmorillonites	Toluene		Muminov and Gulyamova, 2003
Sewage Sludge	Organic Water Pollutants		Otero et al., 2003
Activated Carbon Fibre-based Monoliths	Volatile Organic Compounds		Fuertes et al., 2003
Synthetic Rubber	Ethoxylated Nonyl Phenol		El-Feky and Shalaby, 2003

Dry Soil	Volatile Chlorinated Organic Compounds	Kobayashi et al., 2004
Activated Carbons Derived from Solid Wastes	Phenol and Reactive Dye	Nakagawa et al., 2004
Granular Activated Carbon	Phenolphthalein	Tansel and Nagarajan, 2004
Polymeric Adsorbents	Phenol	Li et al., 2004
Activated Carbon.I	Volatile Organic Compound	Lordgooei and Kim, 2004
Activated Carbon.II	Volatile Organic Compound	Lordgooei and Kim, 2004
Untreated and Treated Activated Carbon	p-Nitrophenol	Nouri, S., 2004
Hydrotalcite	2,4-Dichlorophenol	Yapar et al., 2004
Organoclays	Phenanthrene	El-Nahhal and Safi, 2004
Ozone-adsorbed High Silica Zeolites	Trichloroethene	Fujita et al., 2004
Electro-activated Carbon Granules	Phenol	Lounici et al., 2004

Raw and Activated Date Pits	Phenol			Banat et al., 2004
Activated Carbon	Phenolic Compounds			Dabrowski et al., 2005
Zeolite	Naphthalene			Ho, Y.S, 2005
Alumina	Anionic Surfactant			Adak et al., 2005
Activated Carbons Prepared from Tectona grandis Sawdust by ZnCl ₂ Activation	Phenol			Mohanty et al., 2005
Silica-Polycation-Immobilized Micelles	Organic Pollutants			Mishaal and Dubin, 2005
Peanut Shell Acid-activated Carbon	Phenol			Gonzo and Gonzo, 2005
PDMDAAC-modified Bentonites	p-Nitrophenol	p-Nitrophenol removal rate is 81.4%	Adsorption process was pH-dependent	Peng et al., 2005

Activated Carbon Fibre Cloths	Toluene		Lorimier et al., 2005
Anaerobic Granular Sludge	Pentachlorophenol		Dong-Sheng et al., 2005
Carbonised Beet Pulp	Phenol		Dursun et al., 2005
Bifunctional Polymeric Adsorbent with Sulfonic Groups	Aniline		Jianguo et al., 2005
Nonionic Polymeric Resins	Phenol and Salicylic Acid		Otero et al., 2005
Sediments in the Yellow River	Bisphenol A	Adsorption is related to both the total organic carbon and dissolved organic carbon of sediments	Sun et al., 2005
Activated Carbon	Phenol and Aniline		Krisztina László, 2005

Organoclays Constructed for Soil Bioremediation	2,4- Dichlorophenol		Witthuhn et al., 2005
Chitin	Phenol		Dursun and Kalayci, 2005
Aminated Hypercrosslinked Polymers	Resorcinol and Catechol		Sun et al., 2005
Organically Modified Bentonites	Benzoic Acid and Hydroquinone		Yildiz et al., 2005
Tamarind Nutshell Activated Carbon	Phenol		Goud et al., 2005
Fly Ash and Sepiolite	Phenolic and Lignin Compounds	pH plays an important role in the adsorption process. The efficiency of adsorption decreases with increasing adsorption temperature	Ugurlu et al., 2005

Different Adsorbents	2,4-Dichlorophenol	Zhenghao et al., 2005
Dealuminated Clinoptilolites	Benzene, Toluene, and p-Xylene	Hernández et al., 2005
Soil	Naphthalene Derivatives	Novosad et al., 2005
Polymeric Adsorbents and Activated Charcoal	Salicylic Acid	Otero et al., 2005
Granular Activated Carbon	Trinitrotoluene	Marinovic et al., 2005
Activated Charcoal	p-Dihydroxybenzene	Halhouli et al., 2005
Technical Hydrolysis Lignin	2-Nitrophenol	Allen et al., 2005
Agroalimentary By-product	Organic Pollutants	Delval et al., 2006
Activated Carbons Prepared from Cork	Phenolic Compounds	Mourão et al., 2006
Xad-4 Resin	4-chlorophenol	Bilgili, M.S., 2006

SDS-modified alumina	Phenol	Adak and Pal, 2006
Brown Alga Sargassum muticum	Phenolic Compounds	Rubín et al., 2006
Sepiolite	Cationic Polyacrylamide	Tekin et al., 2006
Ammonia-treated Activated Carbon	Phenol	Przepiórski, J., 2006
Hydrophobic Zeolite	Bisphenol-A	Tsai et al., 2006
Agricultural Soils	Phenanthrene	Amellal et al., 2006
Lignite	Phenol	Polat et al., 2006
Neutralized Red Mud	Phenol	Tor et al., 2006
Activated Carbon Fixed-bed	P-Nitrophenol	Sabio et al., 2006
Chitosan	Phenol	Yan, Jin-long, 2006
Hyperscrosslinked Resins	Chlorophenol	Wang and Fin., 2006
Dolomitic Sorbents	Pentachlorophenol	Marouf et al., 2006

Surface Modification of an Engineered Activated Carbon	2,4-dichlorophenoxy Acetic Acid and Benazolin	Chingombe et al., 2006
Wood Chars	Pyrene	Wang et al., 2006
<i>Pinus Pinaster</i> Bark Packed Bed	Phenol	Vázquez et al., 2006
Activated Carbon	Phenol	Özkaya, B., 2006
Amberlite IRA-420	Phenol	Carmona et al., 2006
Activated Carbons and Multi-walled Carbon Nanotubes	Benzene	Gauden et al., 2006
Vermiculite	Aliphatic Diamines	da Fonseca et al., 2006
Activated Carbon Cloth	Phenol and 2,4-Dinitrophenol	Vasiljevic et al., 2006
Bagasse Fly Ash and Activated Carbon	Phenol	Srivastava et al., 2006
Activated Carbon Fiber	Pentachlorophenol	Diaz-Flores et al., 2006

Tar Sands and Titania	Phenol		Zeatoun, L, 2007
Hexamethonium Exchanged Bentonite (HM)	Phenol	At low phenol concentrations , adsorption capacity of phenol on 30HM-Bent is higher than that on 60TMA-Bent, while it is lower at high phenol concentrations	Xu and Zhu, 2007
Activated Clay	2,4,6- trichlorophenol		Hameed, B.H., 2007

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Chapter – 2

Adsorption of Copper from aqueous solution on *Brassica cumpestris* (Mustard oil cake)

We never know the worth of water till the well is dry.

Thomas Fuller

2.1. Introduction:

Industrialisation has a tremendous impact on the concentration and distribution of heavy metals in the atmosphere, on the land and in the water bodies. The extent of this widespread but generally diffuse contamination has caused concern about its possible effects on the plants, animals and human beings. Among these contaminants Cu (II) is a metal of concern. Cu (II) is generally considered to be non-toxic for man but at concentration level exceeding 5 mg/l impart colour and undesirable taste to water. The World Health Organisation's guideline for drinking water based on its staining properties is 1mg/l (W.H.O.Guidelines, 1984). Beyond the permissible level (5 mg/l) Cu (II) causes acute and chronic disorders in human beings such as gastrointestinal catarrh, cramps in the calves, hemochromatosis and skin dermatitis brasschills, usually accompanied by high fever (Comp, T.R., 1964 and Mukherjee, A.G., 1986). Industries discharging Cu (II) in the wastewater are electroplating industries, pulp and paper mills, fertiliser plants, steel work foundries, petroleum refineries, aircraft plating and finishing, motor vehicles, non-ferrous metal works (Forstner and Wittman, 1981; Dalang et al., 1984; Jenkins, D.W., 1976).

Processes generally used for the removal of Cu (II) from wastewater include precipitation, evaporation, reverse osmosis and ion exchange. But most of these processes are economically non feasible for small scale industries to treat the waste effluents. The adsorption process has been found to be economically appealing for the removal of heavy metals from wastewater. For the treatment of Cu (II) rich effluents at the solid-solution interface, several adsorbents have been used earlier (Gupta,V. ,1998; Samra, S.E., 2000; Yavuz, et al., 2003; Ho and Mc Kay, 2002; Villaescusa et al.,2004; Peri et al., 2004; Banat et al., 2002). The adsorption behaviour of fruit peel of orange, sawdust, kyanite and rice husk for the removal and recovery of Hg (II), Cr (VI), Ni (II), Cu (II), Cd (II), Pb (II), Zn (II) and Mg (II) from rivers and industrial wastewater have

been studied earlier in this laboratory (Ajmal et al., 2001; Ajmal et al., 1998; Ajmal et al., 1995; Ajmal et al., 2001; Ajmal et al., 2003)

In the present study, a new adsorbent mustard oil cake (MOC) prepared from the seeds of *Brassica cumpestris* (mustard) is used. MOC is a valuable byproduct left after the extraction of oil from the mustard seeds. It contains significant amount of proteins, of value as animal feed if edible and as nitrogenous manures otherwise. The chemical composition of mustard oil cake shows: nitrogen-4.5% and phosphorous pentaoxide – 1.5% (Gaur, 1981).

2.2. Material and methods:

2.2.1. Adsorbent:

Oil was extracted from the *Brassica cumpestris* (mustard) seeds and waste matter left after extraction is known as mustard oil cake (MOC). The mustard oil cake was treated with hot DDW in order to remove the oil and finally dried in an air oven at 60 - 65 °C for 24 hrs. After drying the adsorbent was sieved through 40-60 (BSS) mesh size and used as such.

2.2.2. Adsorbate solution:

Stock solution of Cu (II) was prepared (1000 mg/l) by dissolving the desired quantity of copper nitrate trihydrate (AR grade) in DDW. Solutions of other metal ions were prepared (1000 mg/l) by dissolving their chlorides or nitrates.

2.2.3. Adsorption studies:

Adsorption studies were carried out by batch process. 0.5 g adsorbent was placed in a conical flask in which 50 ml solution of metal ion of desired concentration was added and the mixture was shaken in shaker. The mixture was then filtered and final concentration of Cu (II) in the solution was determined in the filtrate with the help of AAS (GBC 902). The instrument was calibrated with standard Cu (II) solutions under the following specifications.

Wavelength – 324.7 nm

Slit width – 0.5 nm

Lamp current – 3 mA

Flame – Air – acetylene (Oxidising)

Mode – Double beam

The amount of Cu (II) adsorbed was calculated by subtracting final concentration from initial concentration. The % removal of adsorbate and equilibrium adsorption capacity (q_e), were calculated using the following relationships

$$\% \text{ Removal} = [(C_o - C_e) / C_o] * 100 \quad \text{_____} (1)$$

$$\text{Adsorption Capacity } (q_e) (\text{mg/g}) = [(C_o - C_e)] * V / W \quad \text{___} (2)$$

All the experiments were carried out in triplicate and mean concentration was calculated. The R.S.D for each sample was calculated. The values of R.S.D. (on percent basis) in all the experiments were found to be in the range 0.548%-1.252%.

2.2.4. Effect of pH:

The effect of pH on the adsorption of Cu (II) was studied as follows: 100 ml of Cu (II) solution was taken in a beaker. The pH of solution was adjusted by adding dilute solution of hydrochloric acid or sodium hydroxide. The concentration of Cu (II) in this solution was then determined (initial concentration). 50 ml of this solution was taken in a conical flask and treated with 0.5 g of adsorbent and after equilibrium the final concentration of Cu (II) was determined.

2.2.5. Effect of time:

A series of 250 ml conical flask, each having 0.5 g adsorbent and 50 ml solution (of known Cu (II) concentrations) were shaken in a shaker incubator and at the predetermined intervals the solution of the specified flask was taken out and filtered. The concentration of Cu (II) in the filtrate was determined by AAS. The amount of Cu (II) adsorbed in each case was then determined.

2.2,6. Effect of adsorbent dose:

A series of 250 ml conical flasks each containing 50 ml of Cu (II) solution of 50 mg/l concentration were treated at 20°C with varying amount of adsorbent (0.1 to 1.0 g) at pH 4. The flasks were shaken in a shaker incubator and after equilibrium the solutions were filtered. The amount of Cu (II) in the filtrate was then determined by AAS. The amount of Cu (II) adsorbed in each case was then calculated as described above. The same procedure was repeated at 30 and 40°C.

2.2,7. Breakthrough Capacity:

0.5 g of adsorbent was taken in a glass column (0.6 cm internal diameter) with glass wool support. One litre of Cu (II) solution with 50 mg/l initial concentration (C_0) was then passed through the column with a flow rate of 1ml/min. The effluent was collected in 50 ml fractions and the amount of Cu (II), (C) was determined in each fraction with the help of AAS. The breakthrough curve was obtained by plotting C/C_0 vs volume of the effluent.

2.2,8. Desorption Studies:

Desorption of Cu (II) was carried out as follows: 0.5 g of adsorbent was treated with 50 ml Cu (II) solution (50 mg/l) in a conical flask. The solution was filtered after 24 hrs. The adsorbent was then washed several times with DDW to remove excess of Cu (II). It was then treated with 50 ml of 0.1 M sodium chloride solution and then filtered after 24 hrs. The filtrate was analysed for Cu (II) desorbed. The same procedure was repeated with potassium sulphate and hydrochloric acid solutions.

2.2,9. Regeneration Studies:

0.5 g of adsorbent was treated with 50 ml Cu (II) solution (50 mg/l) in a conical flask and after equilibrium it was filtered. The adsorbent was then treated with 50

ml hydrochloric acid solution (0.05 M) for 24 hrs. It was filtered and filtrate was analysed for Cu (II) desorbed. The adsorbent was washed several times with DDW in order to remove excess acid. It was again treated with 50 ml of Cu (II) solution and the above procedure was repeated a number of times (five times or cycles). The same procedure was repeated with 0.1 M hydrochloric acid solution

2.3. Results and Discussion:

The adsorption behaviour of different metal ions on mustard oil cake (MOC) is shown in Table. 2.1. The adsorption or metal uptake (mmols /g) of Cu (II) was found to be maximum followed by Zn (II), Cr (VI), Mn (II), Cd (II), Ni (II) and Pb (II).

2.3.1. Effect of time and initial concentration:

The effect of time and amount adsorbed (x/m) by MOC is presented in **Figure. 2.1**. The adsorption of Cu (II) has been shown to increase with time and attains a maximum value at 20 mins and then remains almost constant for 50 mg/l initial Cu (II) concentration, but below this concentration the maximum adsorption occurs much earlier. When initial Cu (II) concentration is increased from 5 mg/l to 50 mg/l, the amount adsorbed increases from 8.8 to 96 mg/l showing that adsorption of Cu (II) depends upon the initial concentration because amount of Cu (II) adsorbed increases by increasing the initial concentration.

2.3.2. Effect of pH:

The effect of pH on the adsorption of Cu (II) on MOC is shown in Figure. 2.2. The percentage adsorption varies from 44% to 94% when pH is increased from 2 to 10 at 50 mg/l initial concentration. The maximum percentage adsorption is observed between pH 3 - 4. At this pH, there are two species of Cu (II) present in the solution (Ajmal et al., 1998)

(i) Cu (II) (large quantity)

(ii) Cu OH (small quantity)

The maximum adsorption at pH 3 - 4 indicates that Cu (II) ions are predominantly adsorbed on MOC (since Cu (II) ions are present in large quantity in this pH range) either by ion exchange or by hydrogen bonding. The % adsorption increases slowly

with increasing pH and becomes constant above pH 6 due to the precipitation of Cu (II) as Cu (OH)₂.

2.3.3. Adsorption isotherms:

The adsorption isotherm data were analysed with Langmuir and Freundlich isotherms (Ajmal et al., 2001). The Langmuir isotherm is based on the theoretical principle that only a single adsorption layer exists on an adsorbent surface. Linearised form of Langmuir equation may be represented as:

$$1/(x/m) = 1/(\theta^\circ \cdot b) \cdot 1/C_e + 1/\theta^\circ \quad \text{_____} \quad (3)$$

The values of θ° and b were calculated from the slope and intercept of the linear plots of $1/(x/m)$ vs $1/C_e$ (**Table. 2.2**).

This essential feature of the Langmuir isotherm can be expressed in terms of dimensionless constant separation or equilibrium parameter (R_L), which is defined as:

$$R_L = 1/(1+bC_o) \quad \text{_____} \quad (4)$$

The values of R_L reported in Table. 2.2 at different temperatures are less than unity ($R_L < 1$) showing favourable adsorption of Cu (II) on MOC (Poots et al., 1978).

The Freundlich isotherm based on adsorption on a heterogeneous surface may be represented as:

$$\log x/m = \log K_f + 1/n \log C_e \quad \text{_____} \quad (5)$$

The values of K_f and n were calculated from the intercept and slope of the Freundlich plots. These values are reported in Table. 2.2. The values of n between 1 and 10 represent beneficial adsorption. (Kadirvelu et al., 2001)

2.3.4. Effect of temperature:

The temperature range used in this study was 20 to 40 °C. The values of equilibrium constant (K_c) at 20, 30 and 40 °C were calculated from the following relation (Namasivayam and Ranganathan, 1995)

$$K_c = C_{Ac} / C_e \quad \text{_____} (6)$$

$$\Delta G^\circ = - RT \ln K_c \quad \text{_____} (7)$$

$$\log K_c = \Delta S^\circ / 2.303R - \Delta H^\circ / 2.303RT \quad \text{___} (8)$$

ΔS° and ΔH° were calculated from the slope and intercept of linear plot of $\log K_c$ vs $1/T$ (**Figure. 2.3**). **Table. 2.3** shows the values of K_c , ΔH° , ΔS° and ΔG° . The positive value of ΔH° indicates that the process is endothermic. The negative values of ΔG° show that process is spontaneous. The values of ΔG° decreases with increase in temperature showing that spontaneity increases with increase in temperature. The positive value of ΔS° suggests an increase in randomness at the solid – liquid interface during adsorption.

2.3.5. Adsorption kinetics:

The rate constants were calculated by using Lagergren first order and pseudo-second order kinetics equations. Lagergren first order expression is given by equation

$$\log (q_e - q) = \log q_e - K_1 / 2.303 \cdot t \quad \text{_____} (9)$$

The linear plot of $\log (q_e - q)$ vs t is observed (**Figure. 2.4**). The regression coefficient (R^2) in this case is 0.9971. The value of rate constant K_1 as determined from the slope of

the line was 0.357 1/min. The pseudo-second order adsorption kinetics rate equation is given as

$$t/q = 1/K_2q_e^2 + 1/q_e \cdot t \quad (10)$$

The value of K_2 was calculated from the slope of the linear plot of t/q vs t (**Figure. 2.5**). A comparison of the experimental sorption capacities and calculated values obtained from equation 5 and 6 shows that $q_{e \text{ (theor)}}$ value calculated from the pseudo-first order kinetics model (42.6 mg/g) differed largely from $q_{e \text{ (exp)}}$ value (48.0 mg/g). In pseudo-second-order kinetics the calculated $q_{e \text{ (theor)}}$ value (48.0 mg/g) was found to be very close to $q_{e \text{ (exp)}}$ value (48.0 mg/g) and also the high value (0.9998) of the correlation coefficient (R^2) confirmed the applicability of the pseudo-second order kinetics.

2.3.6. Breakthrough Capacity:

The breakthrough curve for 50 mg /l initial Cu (II) concentration and a flow rate of 1 ml/min with 0.5 g adsorbent is shown in **Figure. 2.6**. The breakthrough curve showed that 150 ml of the solution (corresponding to 2.5 mg Cu (II)) could be passed through the column without detecting Cu (II) in the effluent. The breakthrough and exhaustive capacities were determined as 15 and 70 mg/g respectively.

2.3.7. Desorption studies:

In order to make the adsorption process more economical it is important to desorb and regenerate the spent adsorbent. The desorption studies were carried out by batch process using NaCl, K_2SO_4 and HCl solutions of different concentrations. The results are reported in **Table. 2.4**. Desorption of Cu (II) with NaCl or K_2SO_4 is negligible showing that Cu (II) is strongly adsorbed on MOC. This is important because Cu (II) adsorbed by MOC will not be exchanged by NaCl or K_2SO_4 if MOC is to be used to sequester Cu (II) in soil since appreciable amount of these salts are usually present in the soil. However, desorption up to the extent of 67% could be achieved when 0.1 M hydrochloric acid solution was used as eluent. Desorption of metal ions with acid solution indicates that adsorption of Cu (II) is via ion exchange process.

Attempts were made to regenerate the spent adsorbent with 0.05 M and 0.1 M hydrochloric acid solutions. The results were almost similar. **Figure. 2.7** show that % adsorption decreases from 86 to 64% after first regeneration and recovery of Cu (II) is 67.4%. The % adsorption then remains almost constant (64 - 60%) in the subsequent cycles. The remarkable decreases in the first regeneration cycle indicates that perhaps certain adsorption sites or functional groups are decomposed or destroyed by hydrochloric acid and hence it is expected that Cu (II) is weakly adsorbed in the second, third and fourth cycle. However, 60% adsorption could be achieved up to fourth regeneration cycle.

2.4. Conclusions:

The mustard oil cake (MOC) is a low cost material abundantly available in India. It is used as manure in agriculture to provide nitrogen and phosphorous (essential plant nutrients). Its adsorption properties could be utilised to sequester Cu (II) ions in the soil. The order of adsorption of various heavy metals on MOC is Cu (II) > Zn (II) > Cr (VI) > Mn (II) > Cd (II) > Ni (II) > Pb (II).

The adsorption of Cu (II) is pH dependent and maximum adsorption occurs at pH 3 - 4. The adsorption follows pseudo-first and pseudo-second order kinetics but pseudo-second order kinetics equation is better obeyed. The adsorption process is endothermic and spontaneous in nature. Breakthrough capacity shows that 50 ml of water (corresponding to 2.5 mg of Cu (II)) can be treated without detecting Cu (II) in the effluent. The Cu (II) ions are strongly adsorbed on MOC and cannot be recovered with various neutral salt solutions like NaCl, K₂SO₄ etc. The recovery of Cu (II) can be made to some extent with dilute hydrochloric acid solution but treatment of MOC with hydrochloric acid remarkably reduces the capacity of adsorbent.

Table 2.1. Adsorption of different metal ions onto Mustard oil cake (MOC)

S No.	Metal ions	Adsorption (mmols/g)
1	Zn (II)	0.691
2	Mn (II)	0.582
3	Cu (II)	0.717
4	Cr (VI)	0.675
5	Cd (II)	0.396
6	Pb (II)	0.183
7	Ni (II)	0.357

Table 2.2. Langmuir and Freundlich constants at different temperature for the adsorption of Cu (II) onto MOC

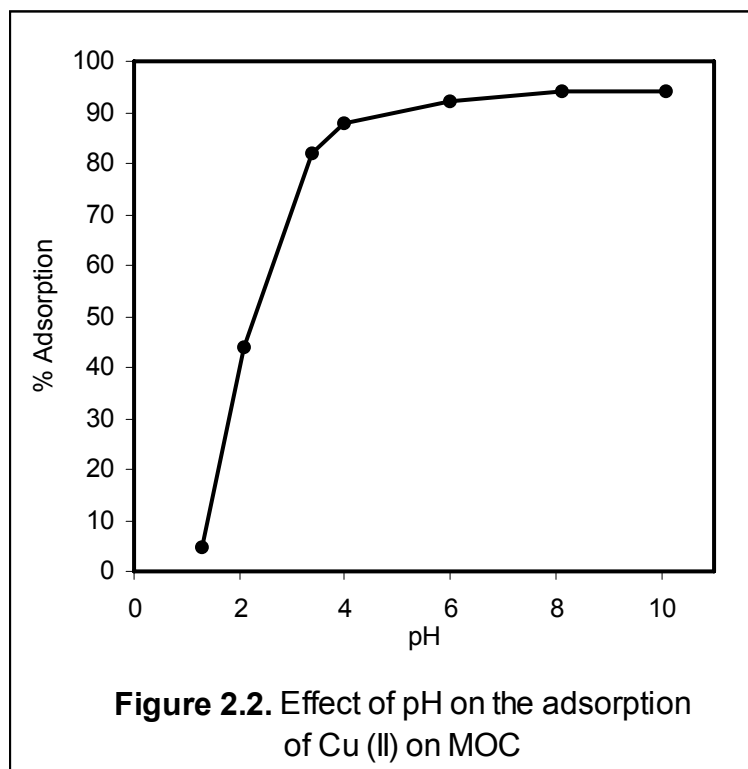
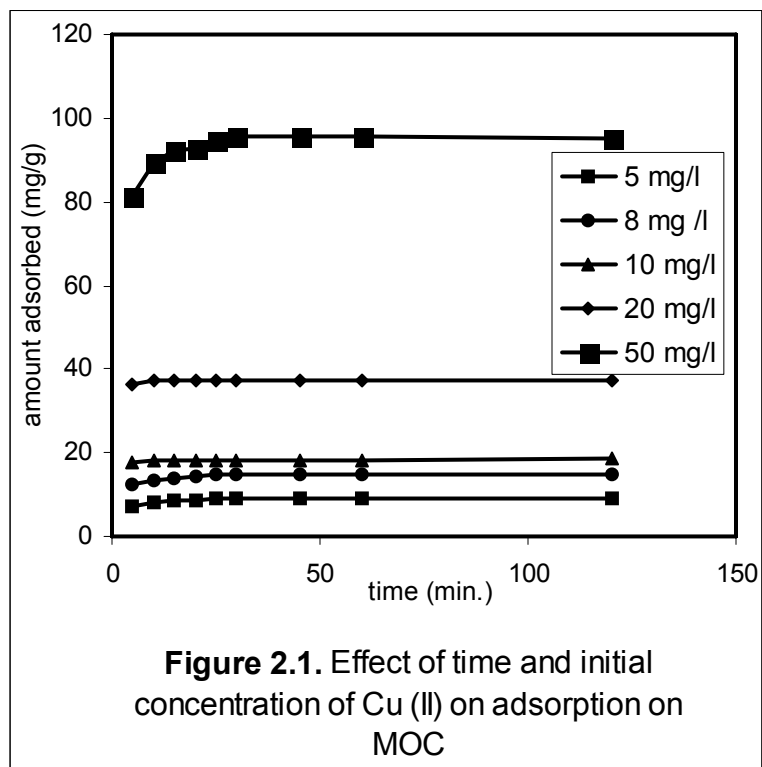
Temperature (°C)	Langmuir isotherms				Freundlich isotherms				
	$\theta^{\circ}.b$ (l/g)	θ° (mg/g)	b (l/mg)	R^2	R_L	$\log K_f$	K_f (mg/g)	n	R^2
20	63.350	454.54	0.139	0.9901	0.887	1.8512	70.99	1.82	0.9933
30	78.125	434.78	0.179	0.9842	0.848	1.9515	89.43	2.09	0.9988
40	74.620	714.28	0.104	0.9853	0.905	1.9539	89.92	1.69	0.9692

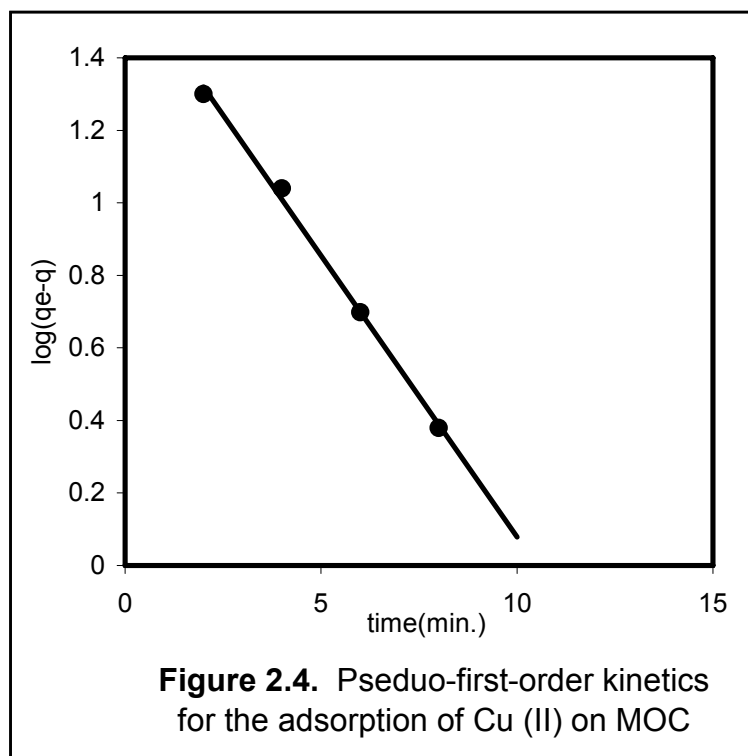
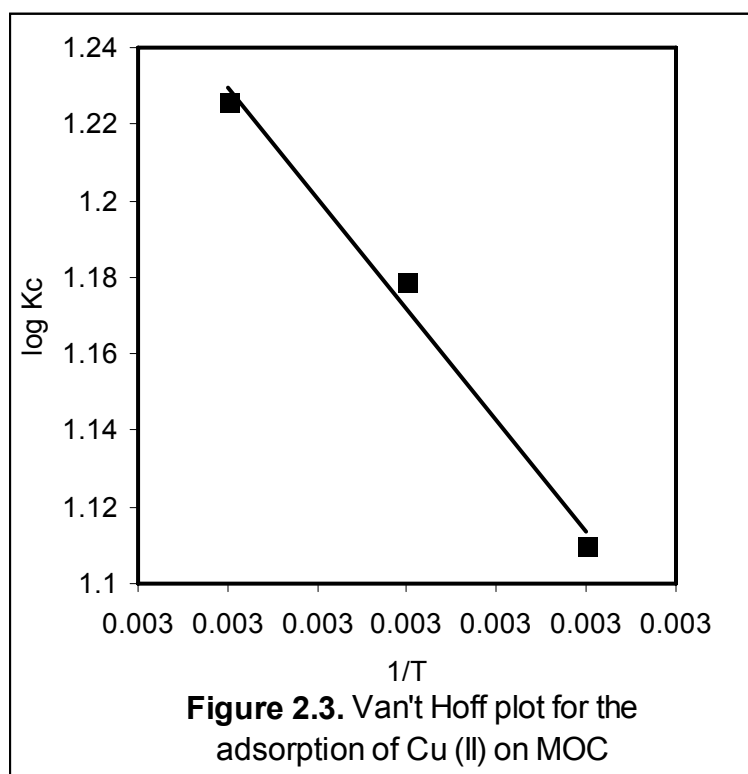
Table 2.3. Thermodynamics parameters at different temperature for the adsorption of Cu (II) on MOC

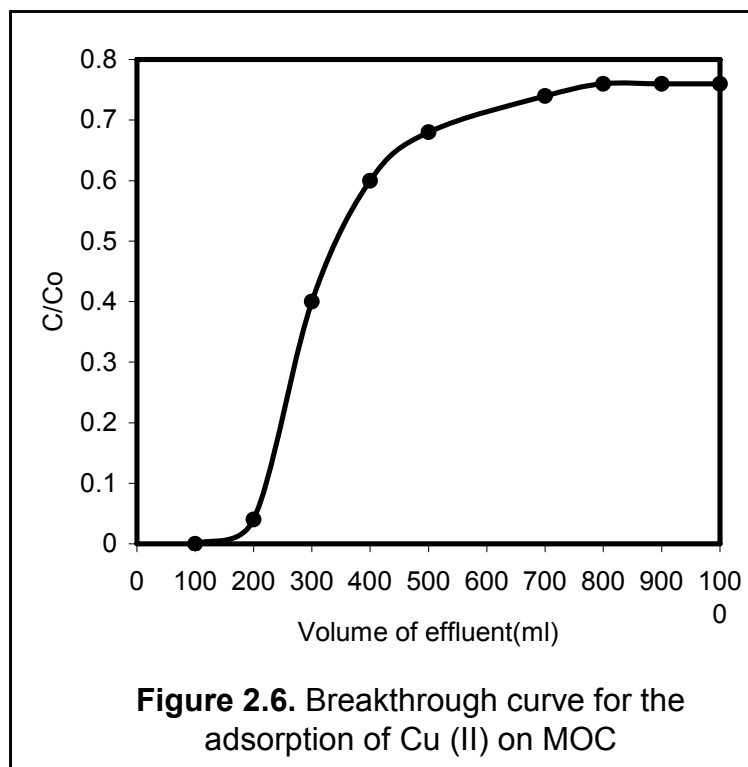
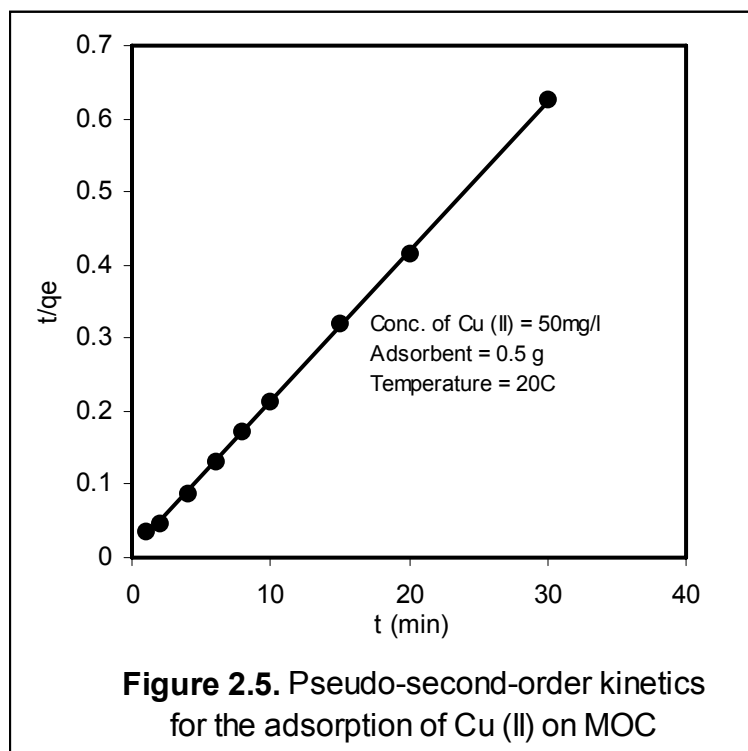
Temperature (°C)	K _c	ΔG° (KJ/mole)	ΔH° (KJ/mole)	ΔS° (KJ/mole-K)
20	12.88	- 6.247		
30	15.13	- 6.842	11.105	0.059
40	16.85	- 7.337		

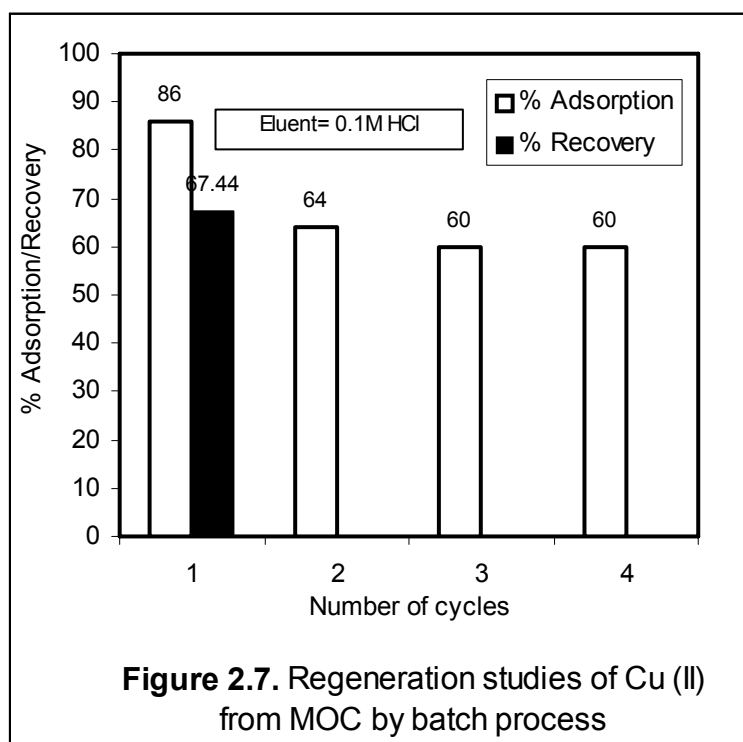
Table 2.4. Desorption of Cu (II) from MOC by various eluents

SNo.	Amount of Cu (II) adsorbed (mg)/0.5g adsorbent	Amount of Cu (II) recovered (mg)	% Recovery	Eluent used
1	45	1.1	2.2	0.1M NaCl
2	42.8	1.2	2.8	1.0M NaCl
3	42.1	2.0	4.0	0.1M K ₂ SO ₄
4	44.2	28	63.3	0.05M HCl
5	43	29	67.4	0.1M HCl









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Chapter – 3

Adsorption studies on *Parthenium hysterophorous* weed: Removal and recovery of Cd (II) from wastewater

For the first time in the history of the world, every human being is now subjected to contact with dangerous chemicals, from the moment of conception until death.

Rachel Carson (1907-1964)

3.1. Introduction:

Heavy metals are essential in small amounts for the normal development of animals and plants but most of them are toxic at higher concentrations. Heavy metals are generally introduced into the environment through natural phenomena and human activities (Abollino et al., 2003). The contamination of the existing water resources is increasing day by day with increasing industrialisation. The disposal of wastewater containing heavy metals is always a challenging task for environmentalists. Various methods available for the removal of heavy metals from industrial wastewater are precipitation, ion-exchange, electrochemical reduction, evaporation and reverse osmosis but these methods involve large liquid surface area and long detention period (Rao et al., 2002). Adsorption on activated carbon is the promising process considered during the past few decades for the removal of trace pollutants but it is costly and requires high cost to regenerate. Therefore, there is a need for the development of low cost and easily available materials, which can adsorb heavy metals.

Cd (II) has been classified as a toxic heavy metal that can cause serious damage to kidney and bones. It also causes high blood pressure, skeletal deformity and muscular cramps (Banat et al., 2003). The World Health Organisation has recommended a maximum permissible limit of 0.005mg/l Cd (II) in drinking water. Numerous low cost adsorbents (Ho and Wang, 2004; Hashim and Chu, 2004; Lackovic et al., 2004; Ramiro et al., 2004) have already been explored for the removal of Cd (II) from aqueous solutions.

In the present study, the sorption behavior of Cd (II) ions on parthenium was examined. *Parthenium hysterophorous*, popularly known as congress weed, star weed, carrot weed, gajar ghas or ramphool, is the most feared weed species (Rao, 1956). It is one of the ten worst weeds in the world. Parthenium is herbaceous annual or ephemeral plant, reaching a height of 2 meter and flowering within 4-6 weeks of germination. The adverse effects of Parthenium on humans as well as on animals have been well

documented. It is known to cause asthma, bronchitis, dermatitis and hay fever in man and livestock. The chemical analysis has indicated that all the plant parts including pollen contain toxins. The major component of these toxins being parthenin and other phenolic acids such as caffeic acid, vanillic acid, anisic acid, chlorogenic acid, parahydroxy benzoic acid, and para anisic acid which are lethal to humans and animals. This weed is generally uprooted and destroyed by burning in air without any use.

The adsorption properties of this natural material have been explored, which can be utilised for the removal of Cd (II) ions from water. The dead biomass of parthenium in powder form may also be utilised to sequester Cd (II) ions in the soil. This technique may help to some extent in reducing the uptake of Cd (II) ions by agricultural crops.

3.2. Material and methods:

3.2.1. Preparation of Adsorbent:

Parthenium plants were collected from the university campus. They were washed with DDW to remove dust and dirt etc, dried in an open-air oven at 60 -70°C. The dried biomass was then crushed and sieved. The particles of 50 -100 (BSS) mesh size were collected and kept in sealed bottles for study.

3.2.2. Adsorbate solution:

Stock solution of Cd (II) was prepared (1000 mg/l) by dissolving the desired quantity of Cd (NO₃)₂.H₂O (AR grade) in DDW.

3.2.3. Adsorption studies:

Batch process was employed for adsorption studies. 0.5g adsorbent was placed in a conical flask having 50 ml Cd (II) solution and the mixture was shaken in a shaker incubator at 100 rpm. The mixture was then filtered at predetermined time interval and the final concentration of metal ions was determined in the filtrate by AAS (GBC 902). The instrument was calibrated with standard Cd (II) solutions under the following specifications.

Wavelength – 228.6 nm

Slit width – 0.5 nm

Lamp current – 3 mA

Flame – Air – acetylene (Oxidising)

Mode – Double beam

Amount of Cd (II) adsorbed was then calculated by subtracting final concentration from initial concentration. Adsorption studies were carried out by varying the adsorbate concentration (10 to 100 mg/l), the agitation time (5 to 60 mints.), adsorbent amount (0.1 to 1.0 g) and adsorption temperature (20, 30 and 40°C). A series of experiments

with pH of the initial Cd (II) solution varying between 2 and 10 (by adding 0.1M HCl and 0.1 M NaOH solutions) were also carried out using 0.5 g adsorbent at 20°C. Adsorption isotherms were studied by varying the initial Cd (II) concentration from 10 to 100 mg/l while weight of adsorbent in each experiment was kept constant at (0.5 g). Each experiment was repeated three times and results were reported as average of them.

3.2.4. Desorption studies:

Batch process was used for desorption studies with varying amount of adsorbent (0.25 –1.0 g). The desired amount of adsorbent was taken in a conical flask and treated with 50 ml of Cd (II) solution (50 mg/l). After adsorption, the solution was filtered and adsorbent was washed several times with DDW to remove any excess of Cd (II). It was then treated with 50 ml of 0.1M HCl solution. The amount of Cd (II) desorbed was then determined as usual. The same procedure was repeated with different adsorbent doses. Attempts were also made to desorb Cd (II) with 0.1M NaCl in the same way.

3.2.5. Breakthrough capacity:

A 0.5 g of adsorbent was taken in a glass column (0.6 cm internal diameter) with glass wool support. One litre of Cd (II) solution of 50 mg/l strength was then passed through the column with a flow rate of 1ml/min. The effluent was collected in 40 ml fractions and Cd (II) was then determined in each fraction by AAS.

3. 3. Results and Discussion:

3.3,1. Effect of concentration:

Parthenium is an effective adsorbent over a wide range of Cd (II) concentration. When the initial Cd (II) concentration is increased from 10 mg/l to 100 mg/l, the adsorption remains maximum (99.5%) and decreases to 97% only when initial concentration is further increased to 150 mg/l (**Figure. 3.1**). The adsorbent can be utilised effectively for the removal of Cd (II) from water at lower as well as higher initial concentration of Cd (II).

3.3,2. Effect of contact time:

The effect of contact time on the adsorption of Cd (II) at 50 mg/l initial Cd (II) concentration is shown in **Figure. 3.2**. The rate of adsorption is very fast initially and maximum removal of Cd (II) occurs within 20 mins. The adsorption rate then decreases during the next 40 mins. The initial fast sorption may be due to the transfer of metal ions from bulk to the adsorbent surface. The active sites in the system is a fixed number and each active site can adsorb only one ion in a monolayer therefore metal uptake by the sorbent surface is rapid initially and then decreases as the availability of active sites decreases thus slowing down the transfer of metal ion from bulk solution to adsorbent surface. The rate of metal removal is of great significance for developing adsorbent based water technology (Saeed et al., 2005). The ability of parthenium to adsorb maximum amount of Cd (II) within 20 mins indicates that parthenium is an effective adsorbent for the removal of Cd (II) from wastewater.

3.3,3. Effect of pH:

Adsorption of Cd (II) at pH 2 is 66% and increases with increase in pH attaining maximum value in the pH range 3 - 4 (**Figure. 3.3**). In acidic medium (pH 2) hydrogen ions compete with metal ions (Saeed et al., 2005) as a result, active sites (negatively charged) become protonated resulting the prevention of metal ions adsorption on the

surface of adsorbent. However, with increase in pH, more and more negatively charged surface of the adsorbent becomes available and hence uptake of metal ions increases. Adsorption of Cd (II) thus increases significantly as pH is increased (99.16% at pH 4). It is known that with the increase in pH, the solubility of metals decreases resulting in their precipitation as hydroxides. The precipitation of Cd (II) as hydroxide was found to occur at pH 9.2 (Namasivayam and Ranganathan, 1995) therefore all adsorption studies were carried out at or below pH 5, which is much below the precipitation pH of Cd (II).

3.3.4. Effect of adsorbent doses:

The adsorption density and percentage adsorption of Cd (II) on parthenium at pH 4.5 is shown in **Figure. 3.4**. The initial Cd (II) concentration was taken as 50 mg/l and the adsorbent dose was varied from 0.1 to 1.0 g at constant temperature (20°C). The percentage adsorption increases from 92.2 to 99% but adsorption density decreases from 23.05 to 3.53 mg/g when adsorbent dose is increased. The decrease in the adsorption density is due to the fact that some of the adsorption sites remain unsaturated when adsorbent dose is increased. On the other hand, more and more Cd (II) is adsorbed as the number of available adsorption sites are increased (Foster and Sharma, 1993) resulting in the overall increase in the removal efficiency.

3.3.5. Adsorption kinetics:

The rate constants were calculated by using pseudo-first order and pseudo-second order kinetic models (Banat et al., 2003). The first order expression is given as

$$\log (q_e - q) = \log q_e - K_1 / 2.303 \cdot t \quad \text{_____} (1)$$

The values of K_1 were calculated from slope of the linear plot of $\log (q_e - q)$ vs t at various concentrations (**Figure. 3.5**). The values of regression coefficient (R^2) and rate constants at various concentrations are reported in **Table. 3.1**.

The pseudo- second order kinetic rate equation is given as

$$t / q = 1 / h + 1/ q_e. t \quad \text{_____} (2)$$

The values of h were calculated from the intercept of the linear plots of t/q vs t at various initial Cd (II) concentrations (**Figure.3.6**). **Table. 3.1** provide the values of K_1 and K_2 , $h = K_2.q_e^2$ calculated equilibrium sorption capacity, $q_{e (theo)}$ and experimental equilibrium sorption capacity $q_{e (exp)}$ at various initial Cd (II) concentrations. The $q_{e (theo)}$ values calculated from pseudo-first order kinetic model differed appreciably (not reported in the table) from the experimental values. However, in pseudo-second order kinetic model the calculated $q_{e (theo)}$ are very close to experimental $q_{e (exp)}$ values at various initial Cd (II) concentrations. Further, the values of correlation coefficients (R^2) of pseudo-first order model were slightly lower than pseudo-second order model indicating that pseudo-second order model is better obeyed than pseudo-first order model.

3.3.6. Effect of temperature:

The temperature range used in this study was from 20°C to 40°C. Thermodynamics parameters such as ΔG° , ΔH° and ΔS° were calculated from the following equation (Namasivayam and Ranganathan, 1995)

$$K_c = C_{Ac} / C_e \quad \text{_____} (3)$$

$$\Delta G^\circ = - RT \ln K_c \quad \text{_____} (4)$$

$$\log K_c = \Delta S^\circ / 2.303R - \Delta H^\circ / 2.303RT \quad \text{_____} (5)$$

ΔH° and ΔS° were calculated from the slope and intercept of Van't Hoff plot of $\log K_c$ vs $1 / T$ (**Figure. 3.7**). **Table. 3.2** shows the values of ΔH° , ΔS° and ΔG° . Positive value of ΔH° indicates the endothermic nature of adsorption. ΔG° is negative and decreases further with increase in temperature indicating that adsorption of Cd (II) on parthenium is spontaneous and spontaneity increases with increase in temperature. Positive value of

ΔS° suggests randomness at the solid/solution interface during adsorption (Namasivayam and Ranganathan, 1995).

3.3,7. Adsorption isotherms:

Langmuir and Freundlich adsorption models were used to analyse the adsorption data at various temperatures. Langmuir model may be described as

$$1/q_e = 1/\theta^\circ \cdot b \cdot 1/C_e + 1/\theta^\circ \quad \text{_____} (6)$$

The plot of $1/q_e$ vs $1/C_e$ is linear showing that adsorption of Cd (II) follows Langmuir isotherm (**Figure. 3.8**). The experimental value of θ° is 27 mg/g that is very close to the calculated value ($\theta^\circ = 23$ mg/g). The value of b is 0.898 l/mg. The correlation coefficient (R^2) is 0.9973. The value of θ° and b for various non-conventional adsorbents used for the removal of Cd (II) ions from water are listed in **Table. 3.3**. The higher value of b (0.898) for parthenium indicates that it has higher affinity to adsorb Cd (II) ions.

The essential feature of Langmuir model can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter (R_L) given by relation

$$R_L = 1 / (1 + b \cdot C_0) \quad \text{_____} (7)$$

The values of R_L lie between 0.1 and 0.01 for the initial Cd (II) concentration range from 10 to 100 mg/l indicating the favourable adsorption (for favourable adsorption the value of R_L should lie between 0 and 1 (Poots et al., 1978)).

The Freundlich adsorption isotherm was also applied for the adsorption of Cd (II). The Freundlich equation is given as

$$\log q_e = \log K_f + 1/n \log C_e \quad \text{_____} (8)$$

Linear plot of $\log q_e$ vs $\log C_e$ follows Freundlich isotherm (**Figure. 3.9**). Value of K_f and n calculated from the slope and intercept is 10.275 and 3.8 respectively. The R^2 value in this case is 0.9841 showing that Langmuir model is better obeyed than Freundlich model. The higher value of K_f (10.275) indicates the higher adsorption efficiency of parthenium for Cd (II) ions.

3.3.8. Desorption studies:

Desorption studies shows that appreciable amount of Cd (II) could be recovered with 0.1M HCl solution (**Table. 3.4**). The percent recovery increases with increase in adsorbent dose and reaches to maximum (82 %) when 0.75 g of adsorbent is used. However, the desorption is negligible with 0.1M NaCl (**Table. 3.5**).

3.3.9. Breakthrough capacity:

The breakthrough curve (**Figure. 3.10**) indicates that 280 ml of the Cd (II) solution containing 50 mg/l could be passed through the column without detecting Cd (II) in the effluent. The breakthrough and exhaustive capacities were determined as 28 and 60 mg/g, respectively.

3.4. Conclusions:

Parthenium hysterophorous is a problem-creating weed. These plants are uprooted and burnt in order to prevent various diseases. Instead of burning, these plants may be dried and the dried mass of parthenium in the form of powder may be added in soil to sequester Cd (II) ions since it can remove up to 99.7% Cd (II) ions over a wide range of Cd (II) concentration (10 -150 mg/l).

The kinetic data shows that pseudo-second order kinetic model is better obeyed than pseudo-first order model since second order model provide high degree of correlation with the experimental data at various initial concentrations. The Langmuir and Freundlich isotherms indicate favourable adsorption and these data would be useful for designing of water treatment plants.

The breakthrough capacity reveals that 280 ml solution containing 50 mg/l Cd (II) can be treated without detecting it in the effluent.

The recovery of Cd (II) ions in the solution by 0.1M HCl is much higher (82 %) as compared to 0.1M NaCl (2 %) showing that adsorption occurs most probably via ion exchange. The material can be utilised to recover Cd (II) ions from wastewater.

Table. 3.1. Pseudo-first order and Pseudo-second order kinetics constants for adsorption of Cd (II) on Parthenium

Concentration (mg /l)	<i>Pseudo-first order kinetics</i>		<i>Pseudo-second order kinetics</i>				
	K_1	R^2	q_e	q_e	K_2	R^2	h
	(1/ min)		(theo.) (mg /g)	(exp.) (mg /g)	(g /mg- min)		(mg/g-min)
25	0.2195	0.9804	2.479	2.479	36.160	1.00	222.22
50	0.1592	0.9836	4.957	4.957	17.695	1.00	434.78
75	0.0526	0.9883	7.422	7.418	4.040	1.00	222.22
100	0.0862	0.9975	9.890	9.900	2.044	1.00	200.00

Table. 3.2. Thermodynamics parameters at different temperature for the adsorption of Cd (II) on Parthenium

Temperature (°C)	ΔS° (KJ/ mol-K)	ΔH° (KJ/mol)	ΔG° (KJ/mol)
20			-6.0103
30	0.0961	22.147	-6.9713
40			-7.9323

Table. 3. 3. Uptake capacities for Cd (II) of various adsorbents

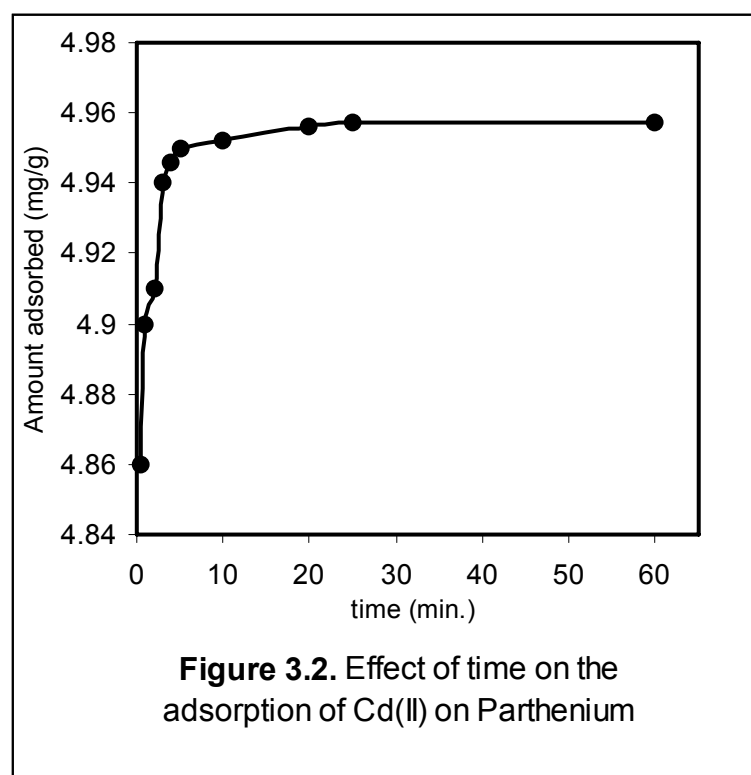
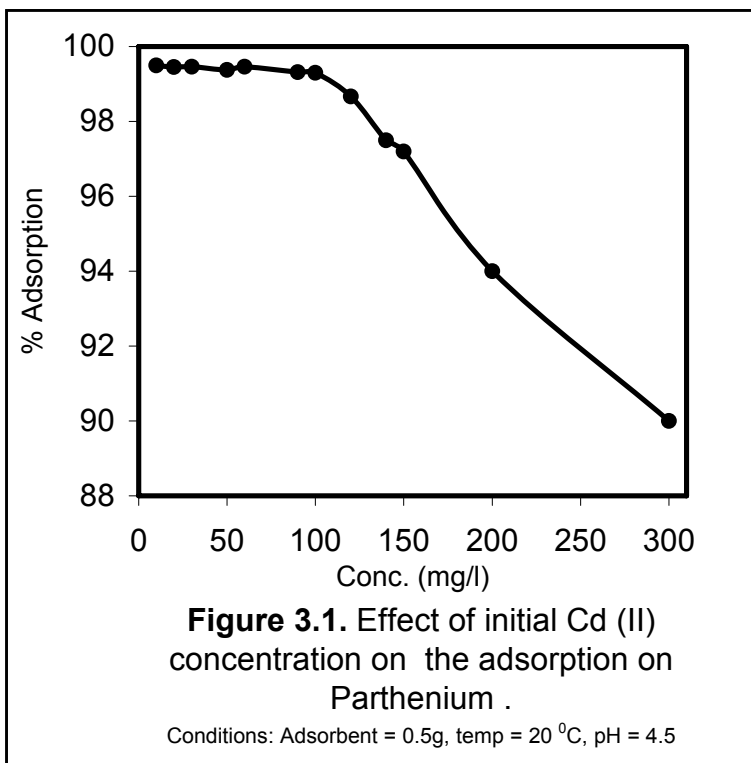
Adsorbent	θ° (mg/g)	b (l/mg)	Reference
Goethite	2.56	0.3600	Johnson, 1990
Waste Fe (III)/Cr(III)	39.00	0.1790	Namasivayam et al, 1995
Hydroxide Pretreated fungal Biomass	62.90	0.1070	Qiming et al, 1999
Date pits	6.50	0.0396	Banat et al, 2003
Date pits (carbonized At 500 ⁰ C)	3.00	0.0847	Banat et al, 2003
Date pits (carbonized At 900 ⁰ C)	1.80	0.0905	Banat et al, 2003
Rice Husk	103.09	0.0060	Ajmal et al, 2003
Untreated Juniper Fiber	9.180	0.03	Han et al, 2004
Black gram husk	39.99	0.3730	Iqbal et al, 2005
Parthenium	27.00	0.8980	present study

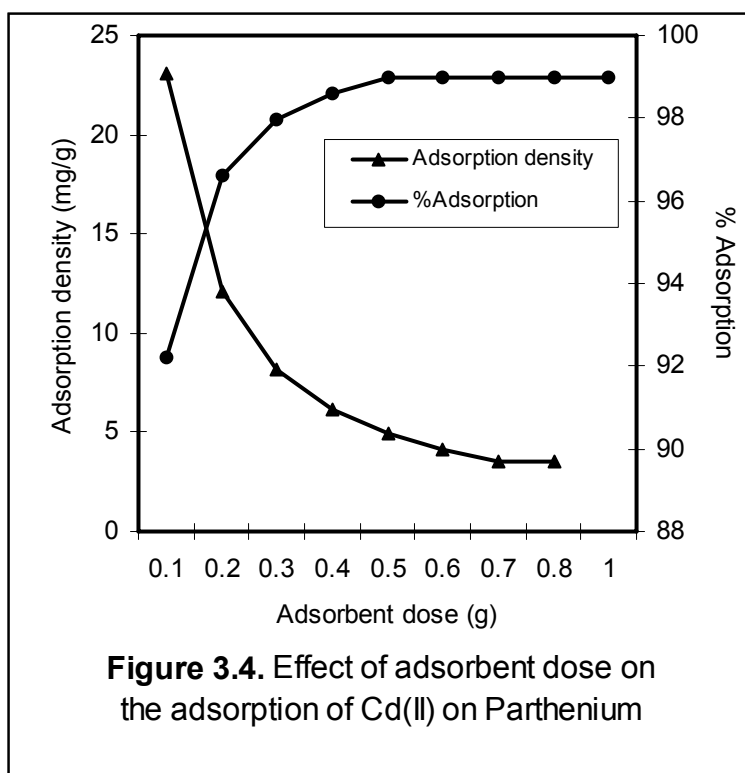
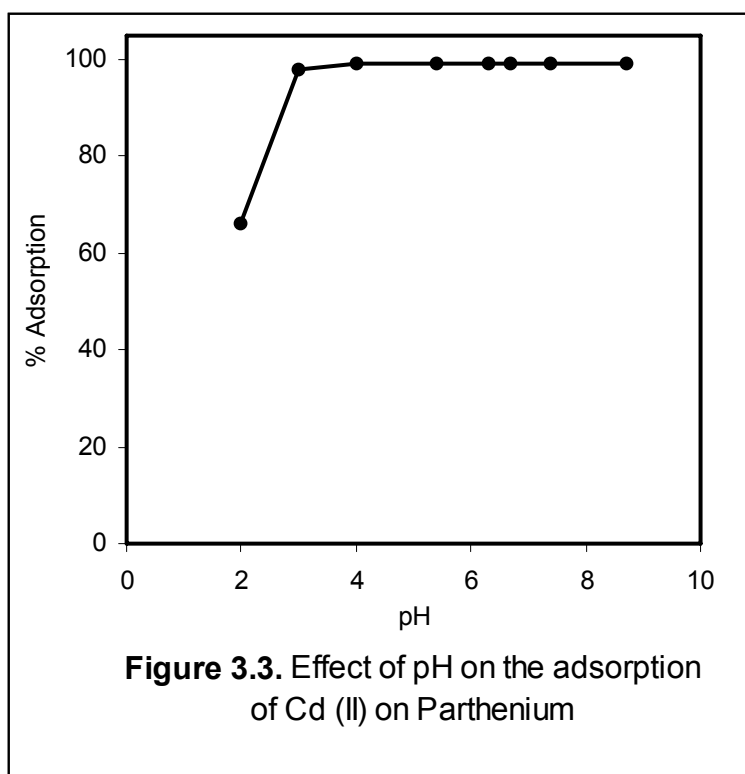
Table. 3.4. Desorption of Cd (II) by 0.1 M HCl

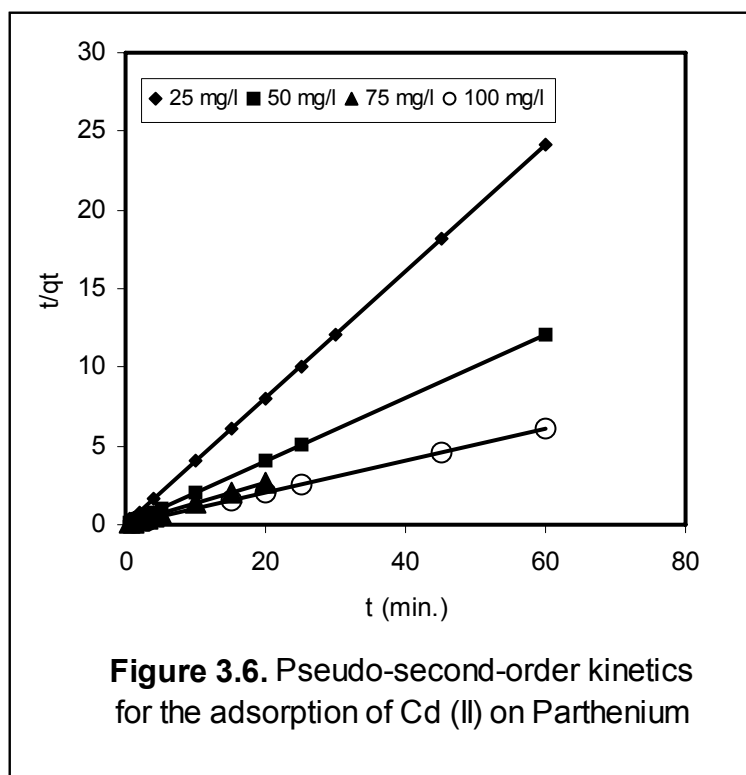
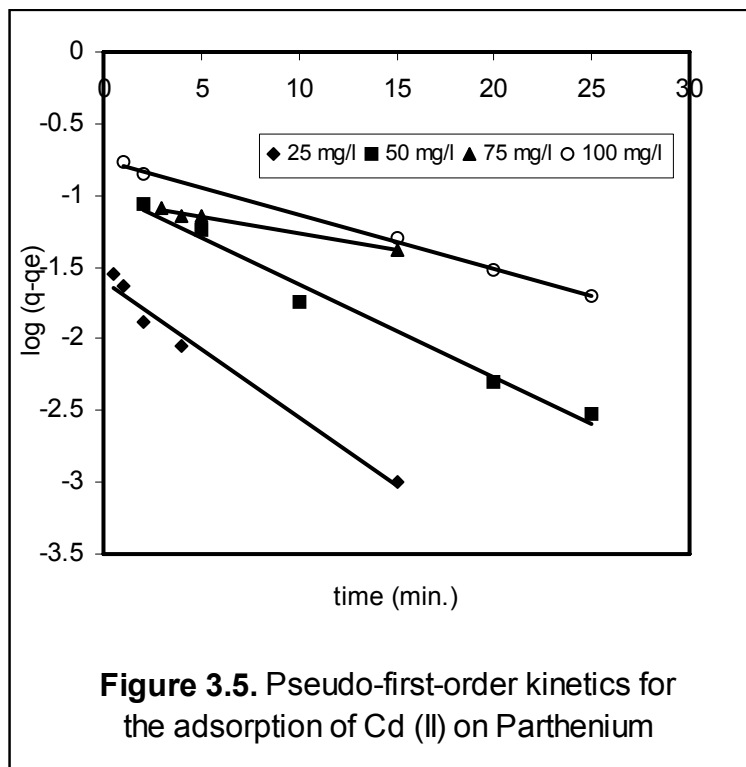
S.No.	Amount of adsorbent (g)	Cd (II) adsorbed (mg/l)	Cd (II) recovered (mg/l)	Recovery (%)
1	0.25	49.1	33	67
2	0.50	49.6	38	76
3	0.75	49.6	41	82
4	1.00	49.6	41	82

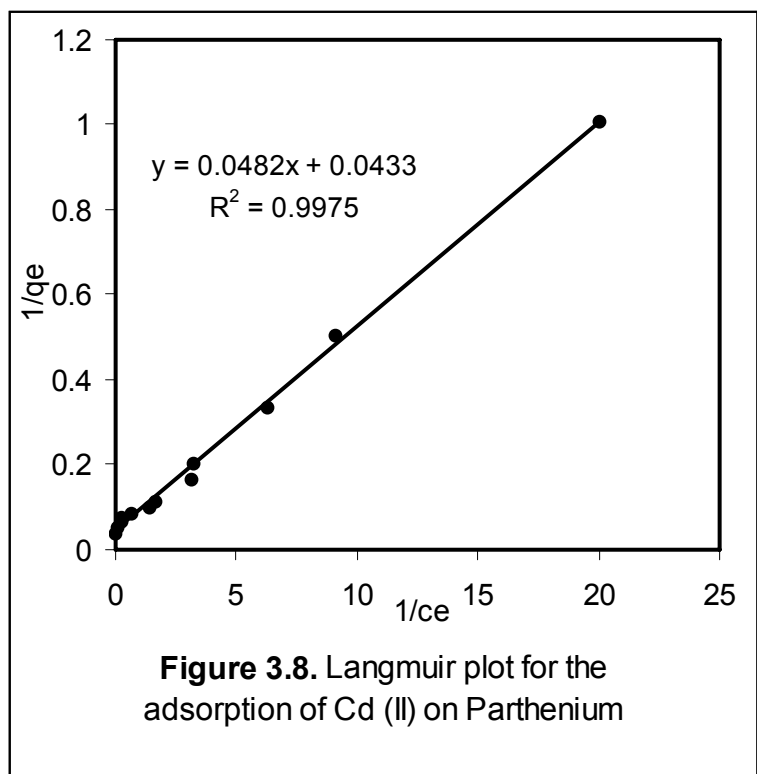
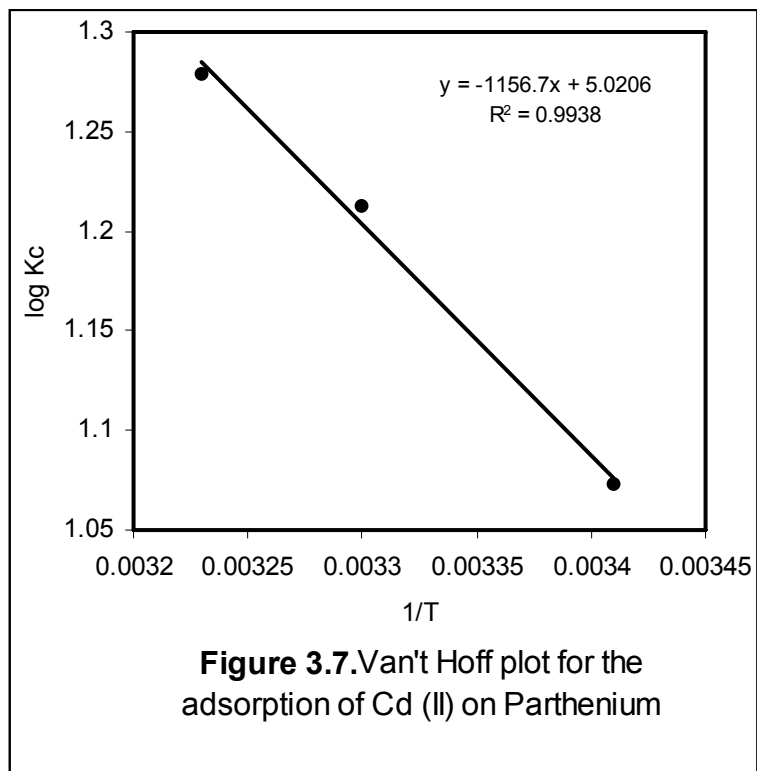
Table. 3.5. Desorption of Cd (II) by 0.1 M NaCl

S.No.	Amount of adsorbent (g)	Cd (II) adsorbed (mg/l)	Cd (II) recovered (mg/l)	Recovery (%)
1	0.50	49.64	1.00	2.01
2	0.75	49.80	0.76	1.52









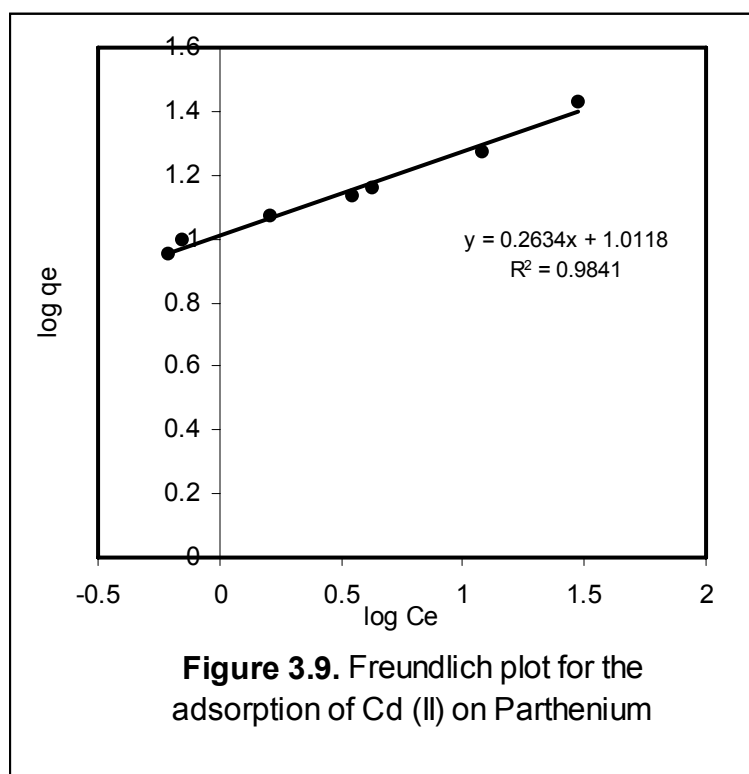


Figure 3.9. Freundlich plot for the adsorption of Cd (II) on Parthenium

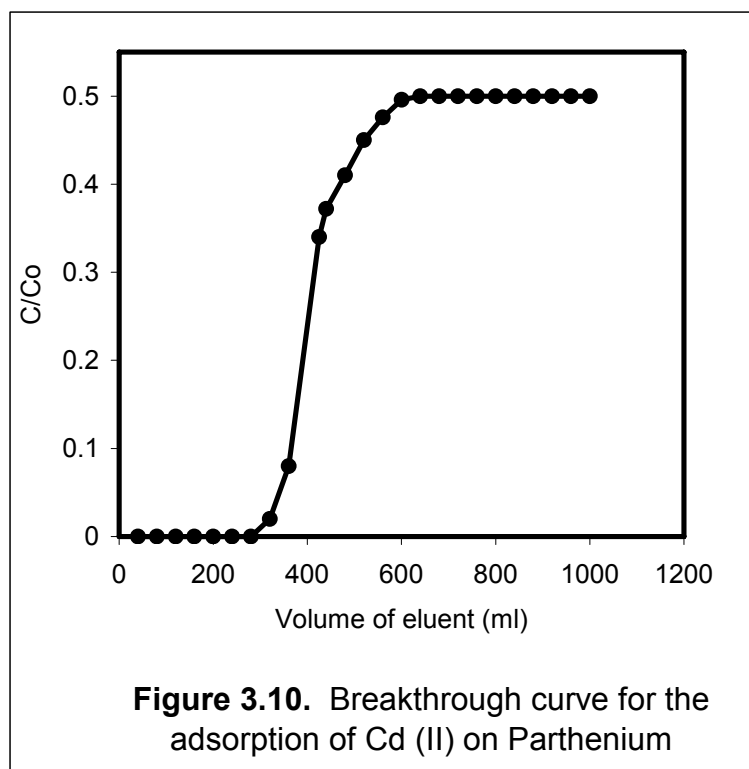


Figure 3.10. Breakthrough curve for the adsorption of Cd (II) on Parthenium

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Chapter – 4

Thermodynamics and kinetics studies of the biosorption of Cu (II) and Cd (II) ions from aqueous media by Neem Oil Cake (NOC)

*In the end, we will conserve only what we love,
we will love only what we understand,
and we will understand only what we are taught.*

Baba Dioum,
Senegalese conservationist

4.1. Introduction:

Toxication of water bodies through the discharge of industrial effluents is a world wide environmental problem. Industrial wastewater often contains considerable amount of heavy metals and organic pollutants that would endanger public health and the environment if discharged without adequate treatment. The heavy metals are of special concern because they are non-degradable and therefore persistent (Namasivayam and Ranganathan, 1995).

Cu (II) and Cd (II) are two most important toxic heavy metals. Cd (II) is more toxic of the two, it make its way to water bodies through wastewater from metal plating industries, industries of Cd-Ni batteries, phosphate fertilizer, mining, pigments, stabilizers and alloys (Low and Lee, 1991). While Cu (II) in low concentration (< 5 mg/l) is generally considered to be toxic for man (Ajmal et al., 2005). Industries discharging Cu (II) in the wastewater are electroplating industries, pulp and paper mills, fertilizer plants, steel work foundries, petroleum refineries, aircraft plating and finishing, motor vehicles and non-ferrous metal works (Forstner and Wittman, 1981; Dalang et al., 1984; Jenkins, D.W., 1976).

Cd (II) poisoning in humans causes high blood pressure, kidney damage and destruction of testicular tissue and RBCs (Encyclopedia of Environmental science, 1980). In small amounts Cd (II) is associated with hypertensive diseases (Schroeder, H.A., 1965) and is considered as carcinogenic to man (International Agency for research on Cancer, 1976). The permissible limits of Cd (II) for the discharge in wastewater and drinking water are 0.1 mg/l (Coupal and Lalancette, 1976) and 0.05 mg/l (Low and Lee, 1991) respectively. While, Cu (II) causes gastrointestinal catarrh, cramps in calves, hemochromatosis and skin dermatitis brasschills, usually accompanied by high fever (Comp, T.R., 1964; Mukherjee, A.G, 1986). The permissible limit of Cu (II) for drinking water following WHO's guidelines is 1mg/l (W.H.O, Geneva, 1984).

Many chemical methods such as precipitation, electro floatation, ion-exchange and reverse osmosis have been used for the removal of heavy metals. Though these processes have high removal efficiency but they are economically non- feasible. The adsorption process has been found to be economically appealing for the removal of heavy metals with better removal efficiency from wastewater.

Activated carbon (A.C) is one of the most common conventional adsorbent used to sequester heavy metals from wastewater but it is expensive due to the regeneration cost and losses in the application process (Gulnaz et al., 2005). Several adsorbents have been used earlier for the treatment of Cu (II) and Cd (II) rich effluents at the solid-liquid interface (Gupta, V.K., 1998; Samra, S.E., 2000; Yavuz et al., 2003; Ho and Mc Kay, 2002; Villaescusa, et al., 2004; Peri, et al., 2004; Banat, et al., 2002; Huang, et al., 1996; Zamzow and Eichbaum, 1990; Ouki and Kavanagh, 1997; Gosset, et al., 1986; Lee and Davis, 2001).

Neem (*Azadirachta indica*) is a fast growing, usually evergreen plant, which reaches a height of 15-20 m and a trunk girth of 1.5 - 3.5m. Neem has been widely explored for solving various problems related to agriculture, public health, population control and environmental pollution (National Research Council, 1992). Neem has been recognized as a natural air purifier and it has been suggested that the planting of neem trees on roadside is an effective way to regulate traffic related pollution (Schmutterer, H, 1995).

Oil cakes in general, have low C/N ratio therefore their degradation is rapid (Gaur et al., 1981). This is an additional advantage that spent oil cakes are degraded rapidly and hence their disposal is easy in comparison to other biosorbents. The adsorption properties of mustard oil cake (MOC) for the adsorption of Cu (II) have been reported (Ajmal et al., 2005). The adsorption properties of Cu (II) and Cd (II) by neem oil cake (NOC), a byproduct of neem fruit have been explored. The composition of NOC shows N₂ – 5.2 %, P₂O₅ – 1 %, K₂O – 1.4 % (Gaur et al., 1981).

4.2. Material and Methods:

4.2,1. Adsorbent:

Oil is extracted from the fruit of neem (*Azadirachta indica*) and waste matter left after extraction is known as neem oil cake (NOC). The NOC was treated with hot DDW in order to remove the traces of oil and finally dried in open-air oven at 60-65°C for 24 hrs. After drying, the adsorbent was sieved through 50 -100 (BSS) mesh size and used as such.

4.2,2. Adsorbate solution:

Single component stock solutions of Cu (II) and Cd (II) were prepared (1000mg/l) by dissolving the desired quantity of their nitrate salts (AR grade) in DDW.

4.2,3. Adsorption studies:

Adsorption studies were carried out by batch process. 0.5 g adsorbent was placed in a conical flask with 50 ml solution of metal ion of desired concentration. The mixture was shaken in temperature controlled shaker incubator for 2 hrs at 120 rpm. The mixture was then filtered using Whatman filter paper number- 41 and final concentration of metal ion was determined in the filtrate by AAS (GBC 902). The instrument was calibrated with standard Cu (II) and Cd (II) solutions under the following specifications.

Metal	– Cu (II)
Wavelength	– 324.7 nm
Slit width	– 0.5 nm
Lamp current	– 3 mA
Flame	– Air – acetylene (Oxidising)
Mode	– Double beam

Metal	– Cd (II)
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Wavelength – 228.8 nm
Slit width – 0.5 nm
Lamp current – 3 mA
Flame – Air – acetylene (Oxidising)
Mode – Double beam

The amount of metal ions adsorbed was calculated by subtracting final concentration from initial concentration. All the experiments were carried out in triplicate and mean concentration was calculated.

4.2.4. Effect of pH:

The effect of pH on the adsorption of Cu (II) and Cd (II) was studied by batch process as described in chapter-2.

4.2.5. Effect of contact time:

A series of 250 ml conical flasks, each having 0.5g adsorbent and 50 ml solution (of known metal concentration) were shaken in temperature controlled shaker incubator at 120 rpm and at the predetermined intervals, the solution of the specified flask was taken out and filtered. The concentration of metal in the filtrate was determined by AAS. The amount of metal adsorbed in each case was then determined.

4.2.6. Effect of adsorbent dose:

A series of 250 ml conical flasks each containing 50 ml of metal solution (50 mg/l) were treated at different temperatures with varying amount of adsorbent (0.1- 0.8 g). The flasks were shaken in temperature controlled shaker incubator at 120 rpm and after equilibrium the solutions were filtered. The amount of metal ions in the filtrate was then determined by AAS. The amount of metal adsorbed in each case was calculated.

4.2.7. Quality assurance and quality control:

To make sure that no metal ions were released to the solution from the adsorbent, an equilibrium test was performed using adsorbent (NOC) in DDW. For assuring quality in the adsorption studies DDW blank and two duplicates were included in the experiments.

To ensure accuracy after each set of five samples, a standard was analysed to ensure that drift had not occurred. All useable data were bracketed by standards that were off by not more than $\pm 10\%$ of the actual value.

The samples were analysed in triplicate by AAS. Average of the values obtained gives mean concentration of the sample. The percent relative standard deviation (R.S.D) for samples was calculated by dividing standard deviation of the sample with the average of the sample multiplied by 100. If the value of percent R.S.D for any sample was greater than 10% the data were declared unusable.

4.3. Results and Discussion:

4.3.1. Effect of Initial concentration:

Initial metal concentration provides important driving force to overcome all mass transfer resistances of the metal between the aqueous and solid phase (Aksu and Akpinar, 2001). The increase in the initial concentration of Cu (II) and Cd (II) solutions at room temperature (32°C) increases the adsorption capacity. **Table. 4.1** summarises the results of the adsorption capacity accuracy test.

4.3, 2. Effect of pH:

The percentage adsorption of Cu (II) and Cd (II) on NOC increases by increase in pH, attaining maximum at pH 4.4 and 4.5 for Cu (II) and Cd (II) (**Figure. 4.1**). Availability of negatively charged groups on the adsorbent surface is necessary for the sorption of metals to proceed (Ajmal et al., 2006), at pH 2 the adsorption is less as there is a net positive charge in the adsorption system due to H^+ and H_3O^+ . In such system H^+ compete with metal ions (Luef et al., 1991) resulting in active sites to become protonated to the virtual exclusion of metal binding on the adsorbent surface (Low et al., 1993). This means that at higher H^+ concentration, the adsorbent surface becomes more positively charged thus reducing the attraction between adsorbent and metal cations (Aldov et al., 1995). In contrast, as the pH increases, more negatively charged surface becomes available thus facilitating greater metal uptake (Saeed, et al., 2002). Thus, metal adsorption tends to increase significantly by increasing pH. Hence solution of Cu (II) and Cd (II) at pH values 4.4 and 4.5 shows 92% and 95.3% adsorption respectively. With further increase in pH, the solubility of metals decreases resulting in their precipitation as hydroxide with no significant increase in adsorption percentage.

4.3.3. Effect of adsorbent doses:

The adsorption capacity (mg/g) and percentage (%) adsorption of Cu (II) and Cd (II) by varying the dose of NOC at different temperatures are shown in **Figures**.

4.2 and 4.3. The % adsorption increases while adsorption density decreases as the adsorbent dose of NOC is increased. An increase in temperature also increases the % adsorption. It may be concluded that by increasing the adsorbent dose, the removal efficiency of NOC increases. The decrease in adsorption density may be due to the fact that some adsorption sites may remain unsaturated during the adsorption process where as the number of sites available for adsorption increases by increasing the adsorbent doses and that results in the increase in removal efficiency (Chang et al., 1997).

4.3.4. Adsorption isotherms:

Adsorption data for wide range of adsorbate concentration are most conveniently described by adsorption isotherms, such as the Langmuir and Freundlich isotherms.

The Langmuir isotherm is given by equation:

$$C_e/q_e = 1/b \cdot q_m + 1/q_m \cdot C_e \quad \text{_____} (1)$$

The values of Langmuir constants b and q_m were calculated from the slope and intercept of the linear plot of C_e/q_e vs C_e (**Figures. 4.4 and 4.5**). The coefficient b in Langmuir equation is a measure of the stability of the complex formed between metal ions and adsorbent under specified experimental conditions (Sharma and Foster, 1993). q_m is calculated for various adsorbents used for the removal of Cu (II) and Cd (II) and compared with the present study (**Table. 4.2**).

The essential feature of the Langmuir isotherm can be expressed in terms of dimensionless constant separation or equilibrium parameter (R_L), which is defined as:

$$R_L = 1 / 1 + bC_0 \quad \text{_____} (2)$$

The average value of R_L calculated from different initial concentrations are reported in **Table. 4.3**. The R_L values for Cu (II) and Cd (II) are in between 0 and 1 showing favourable adsorption of both Cu (II) and Cd (II) on NOC (Say et al. 2001).

Freundlich isotherm is given by equation:

$$\log q_e = \log K_f + 1/n \log C_e \quad \text{_____} \quad (3)$$

The values of K_f and n were calculated from the intercept and slope of the Freundlich plots (**Figures. 4.6** and **4.7**) and are shown in **Table. 4.3**. The constant n is a measure of deviation from linearity of the adsorption. The values of $n > 1$ for Cu (II) and Cd (II) indicating favourable adsorption of Cu (II) and Cd (II) on NOC at different concentrations (Poots et al., 1978).

In order to compare quantitatively the applicability of different models (Langmuir, Freundlich and kinetics models) in fitting to data, the percent relative deviation (P), given by the following equation was calculated:

$$P = 100 / N \sum \{ [q_e (\text{exp}) - q_e (\text{theo})] / q_e (\text{exp}) \} \quad \text{_____} \quad (4)$$

It is found that lower the value of percentage deviation (P), better is the fit. It is generally accepted that when P value is less than 5, the fit is considered to be excellent (Ozcan et al., 2005). The values of P for Langmuir and Freundlich plot of Cu (II) and Cd (II) indicate that both the models are better obeyed which is also evident from regression coefficient values (**Table. 4.3**).

4.3.5. Thermodynamics studies:

The thermodynamics parameters like ΔH° and ΔS° were obtained from the Van't Hoff equation.

$$\log K_c = \Delta S^\circ / 2.303 R - \Delta H^\circ / 2.303 RT \quad (5)$$

Where, ΔS° and ΔH° were calculated from the slope and intercept of linear plots of $\log K_c$ vs $1/T$ (**Figures. 4.8 and 4.9**) for Cu (II) and Cd (II).

Equilibrium constant (K_c) was calculated from the following relationship (Namasivayam and Ranganathan 1995).

$$K_c = C_{Ae} / C_e \quad (6)$$

Free energy change (ΔG°) was calculated from the relation

$$\Delta G^\circ = -RT \ln K_c \quad (7)$$

The positive values of ΔH° for Cu (II) and Cd (II) (**Table. 4.4**) suggest endothermic nature of adsorption. The increase in adsorption of Cu (II) and Cd (II) with temperature might have been due to dissolution of the adsorbing species, change in the pore size and enhanced rate of intra-particle diffusion (Ayranci and Duman, 2005). The values of ΔG° decreases with increase in temperature, which indicates that the process is spontaneous and spontaneity increases with increase in temperature. The positive value of ΔS° shows increase in randomness at the solid / solution interface during the adsorption of Cu (II) and Cd (II) on NOC (Ajmal et al., 2005).

To distinguish between the physical and chemical adsorption on NOC, Dubinin-Redushkevich (D-R) isotherm based on the heterogeneous nature of the adsorbent surface is applied (Panday et al., 1985). The linear form of (D-R) isotherm equation is (Benhammon et al., 2005):

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad \text{_____} \quad (8)$$

Where β Activity coefficient constant (mol^2/J^2)

q_m Maximum adsorption (moles / g)

q_e Adsorption capacity (moles / g)

ε Polanyi potential

Polanyi potential (ε) can be calculated from the relation

$$\varepsilon = RT \ln (1 + 1/C_e) \quad \text{_____} \quad (9)$$

Where T Absolute temperature (K)

R Gas constant (J /mole-K)

C_e Concentration at equilibrium (mole/ l)

Hence, by plotting $\ln q_e$ vs ε^2 , the values of q_m from the intercept and β from the slope are generated (**Figures. 4.10** and **4.11**).

The constant β gives an idea about the mean free energy (E_a)(KJ/ mole) of adsorption of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated using the relationship (Dubinin and Radushkevich, 1947)

$$E_a = 1 / (-2 \beta)^{1/2} \quad \text{_____} \quad (10)$$

The magnitude of E_a for the adsorption of Cu (II) and Cd (II) on NOC lies between 8.3 - 8.7 and 7.17 - 11.4 KJ/mole respectively indicating that the adsorption process is chemical in nature.

4.3.6. Kinetics of Adsorption:

A quantitative understanding of the adsorption is possible with the help of kinetics model. The pseudo-first-order kinetics model as expressed by Lagergren (Ajmal et al., 2001) can be written as:

$$\log (q_e - q_t) = \log q_e - K_1 / 2.303 * t \quad \text{_____} \quad (11)$$

A plot of $\log (q_e - q_t)$ vs t gives straight line and confirms the applicability of the pseudo-first-order rate equation (**Figures. 4.12 and 4.13**).

Pseudo-second-order adsorption rate equation may be expressed as:

$$t / q_t = 1 / K_2 q_e + 1 / q_e * t \quad \text{_____} \quad (12)$$

A plot of t/q_t vs t produces straight line and indicates the applicability of pseudo-second-order model (**Figures. 4.14 and 4.15**).

The results have been analysed using equations (11) and (12). The experimental data are fitted well in both the equations. The values of $q_{e \text{ (theo)}}$ calculated from these models are compared with experimental values $q_{e \text{ (exp)}}$ in **Table. 4.5**. It is found that values of $q_{e \text{ (theo)}}$ calculated from the pseudo-first-order kinetics model differed appreciably from the experimental values $q_{e \text{ (exp)}}$. The percent deviation (P) is also very high. On the other hand, values of $q_{e \text{ (theo)}}$ are found to be very close to $q_{e \text{ (exp)}}$ when pseudo-second-order rate equation was applied. The percent deviation (P) is well with in the range except Cu (II) at higher concentration (when 100 mg/l Cu (II) solution was used) and also the values of correlation coefficients (R^2) are very high as compared to pseudo-first-order rate model. It is therefore confirmed that adsorption of Cu (II) (at lower concentration range up to 75mg/l) and Cd (II) follows pseudo-second-order rate equation.

4.4. Conclusions:

Neem oil cake (NOC) is a biodegradable low cost biosorbent available abundantly in India. It is used as a bio-pesticide for organic farming. The advantage of using oil cake as an adsorbent is that its decomposition is faster than other bulky organic biomass due to low C/N ratio. The adsorption of Cu (II) and Cd (II) is maximum at pH 4.4 and 4.5 respectively. Increase in adsorption dose increases removal efficiency of Cu (II) and Cd (II) while decreases the adsorption density. Removal efficiency also increases by increasing temperature.

The magnitude of the mean free energy indicates that adsorption of Cu (II) and Cd (II) occurs via chemisorption. The values of % deviation (P) and Regression coefficient (R^2) shows that both Langmuir and Freundlich models are well obeyed. The kinetics models for the adsorption of Cu (II) and Cd (II) on NOC confirms better applicability of Pseudo-second-order rate equation as evident by percent deviation (P) and regression coefficient values.

Table 4.1. Reproducibility test for Adsorption capacity of Cu (II) and Cd (II) on NOC

Initial Conc. C_o (mg/l)	Cu (II)				Cd (II)			
	Average final Conc. C_e (mg/l)	Average Adsorption Capacity q_e (mg/g)	Standard Deviation of q_e	RSD	Average final Conc. C_e (mg/l)	Average Adsorption Capacity q_e (mg/g)	Standard Deviation of q_e	RSD
10	0.167	0.9833	0.0047	0.478	0.267	0.9733	0.00057	0.0595
20	0.6	1.94	0.01	0.515	0.32	1.968	0.001	0.0508
30	1.267	2.873	0.0115	0.4003	0.65	2.935	0.001	0.0341
40	1.967	3.803	0.0153	0.4023	0.80	3.92	0	0
60	4.567	5.543	0.0153	0.2760	1.63	5.8367	0.00057	0.0992
70	5.033	6.4967	0.0058	0.0893	4.2	6.58	0.01	0.1198
80	6.1	7.39	0.01	0.135	3.03	7.697	0.01155	0.1500
90	12	7.8	0.01	0.128	6.5	8.35	0.01	0.1198
100	13.1	8.69	0.01	0.115	6.5	9.35	0.01732	0.1852

Table. 4.2. Adsorption capacities (mg/g) of various adsorbents for Cu (II) and Cd (II)

Adsorbents	Cu (II)	Cd (II)	References
Date pits	-	6.50	Banat et al., 2003
Chitosan	16.80	8.54	Huang et al., 1996
Clinoptilolite	1.64	2.40	Zamzow and Eichbaum, 1990
Montmorillonite	-	0.72	Srivastava et al., 1989
Flyash- wollastonite	1.18	-	Panday et al., 1986
Tannic acid modified Activated carbon	2.73	2.46	Ucer et al., 2006
Oligotrophic Peat	6.41	-	Chen et al., 1990
Bentonite	-	11.41	Panday et al., 1986
Chabazite	5.10	6.70	Ouki and Kavanagh, 1997
NOC	9.398	11.82	[Present study]

Table 4.3. Langmuir and Freundlich constants for the adsorption of Cu (II) and Cd (II) on NOC

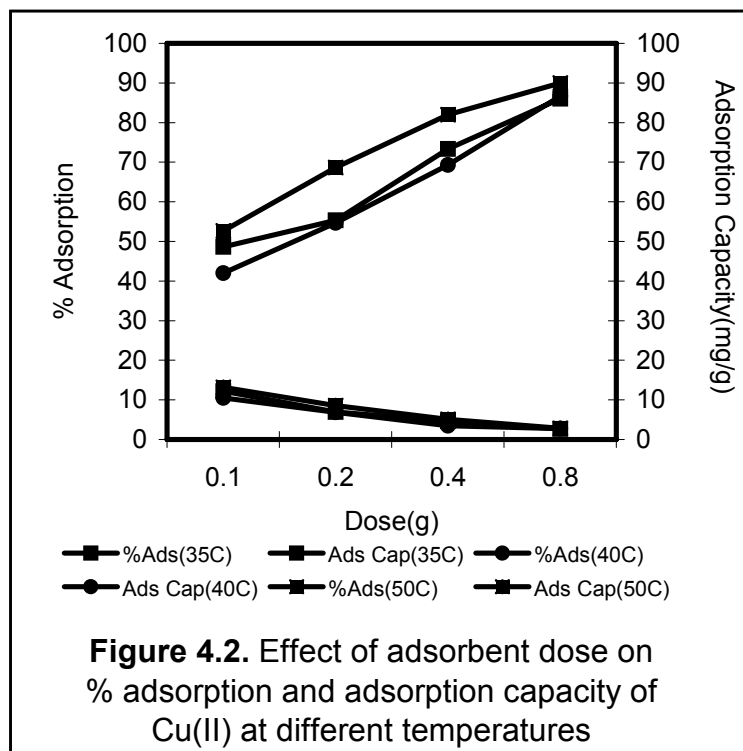
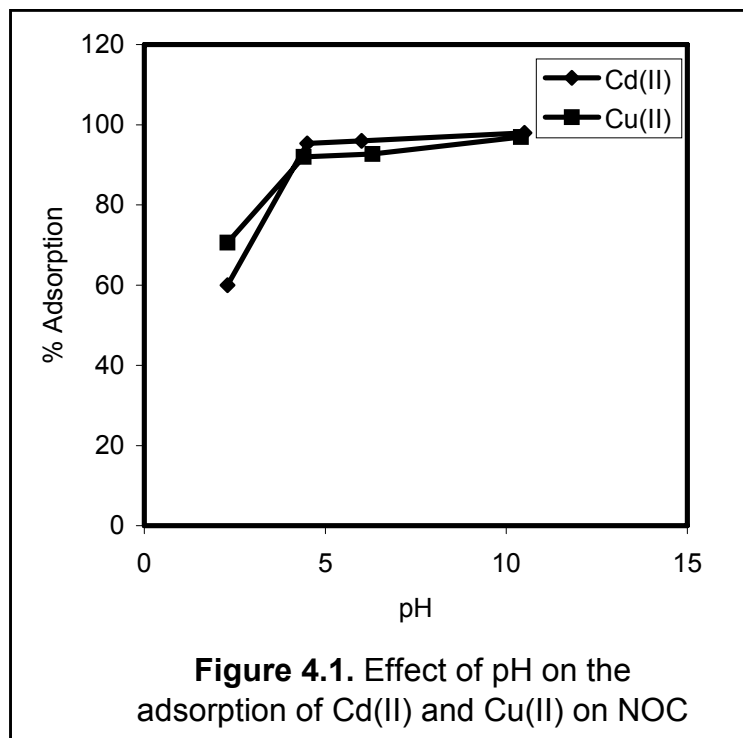
Metal ions	Langmuir constants						Freundlich constants			
	q_m (mg/g)	b (l/mg)	$b.q_m$ (l/g)	R^2	R_L	P	K_f (mg/g)	n	R^2	P
Cu (II)	9.398	0.095	5.22	0.9859	0.9015	0.26	5.11	1.33	0.9977	4.8
Cd (II)	11.82	0.4063	3.818	0.9905	0.469	5.8	2.45	1.92	0.9932	0.05

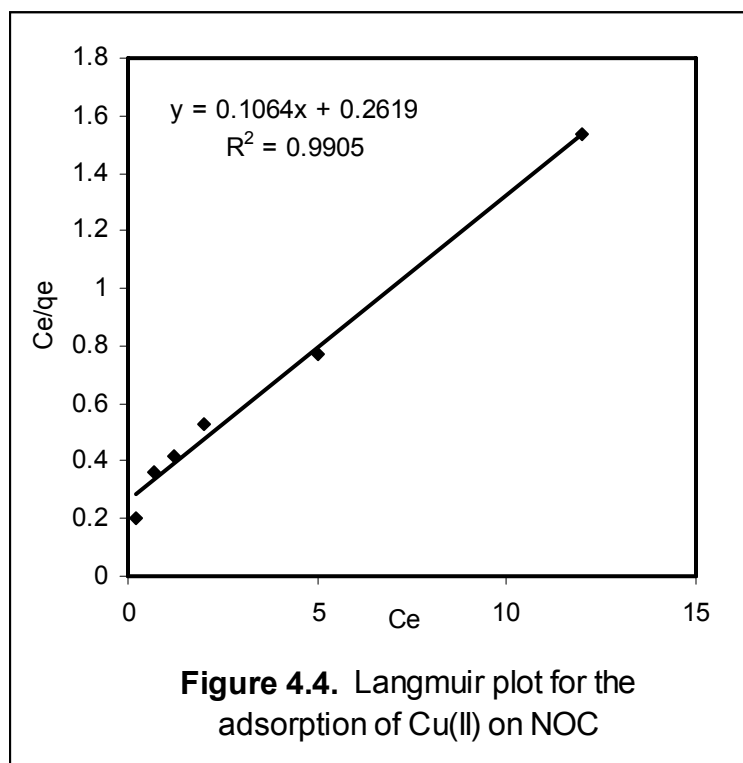
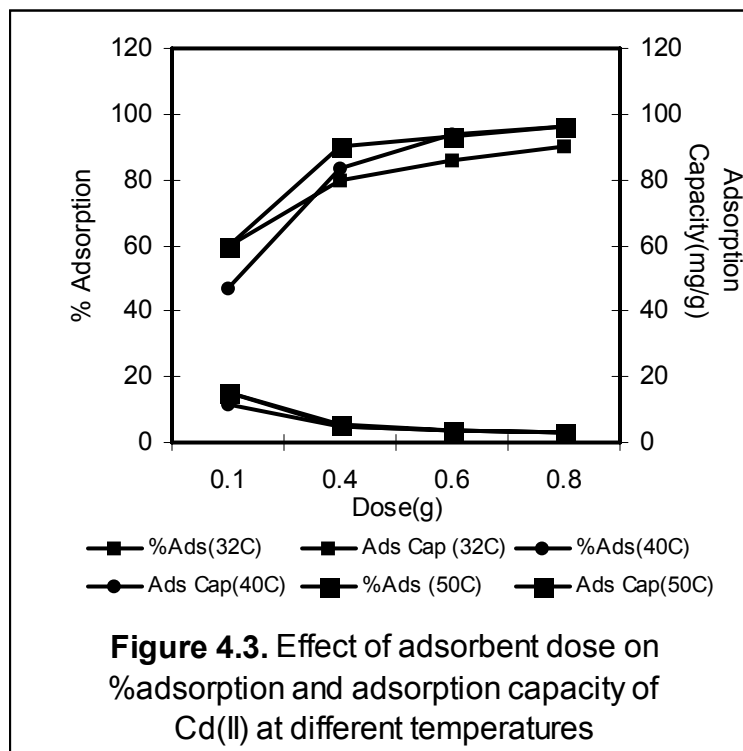
Table 4.4. Thermodynamic parameters for the adsorption of Cu (II) and Cd (II) on NOC at different temperatures

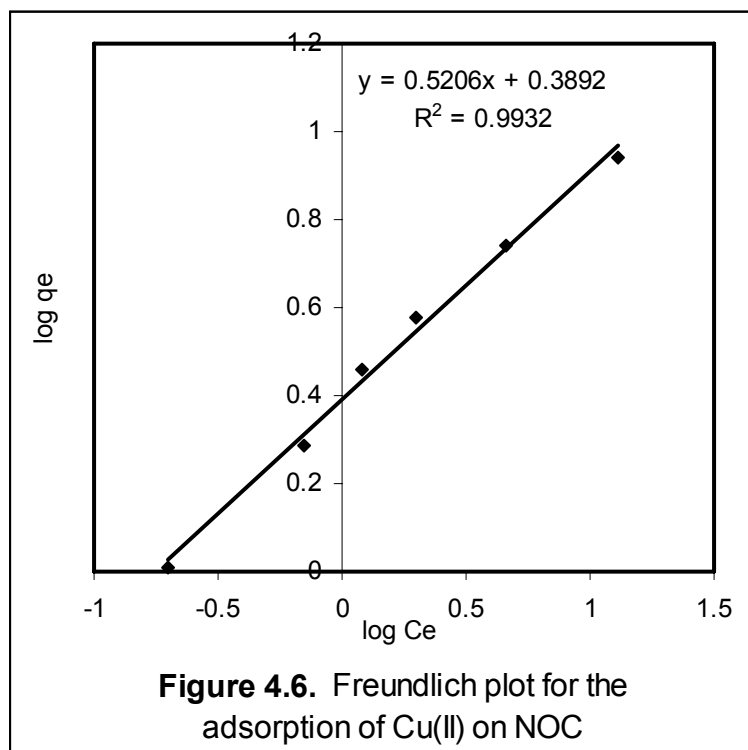
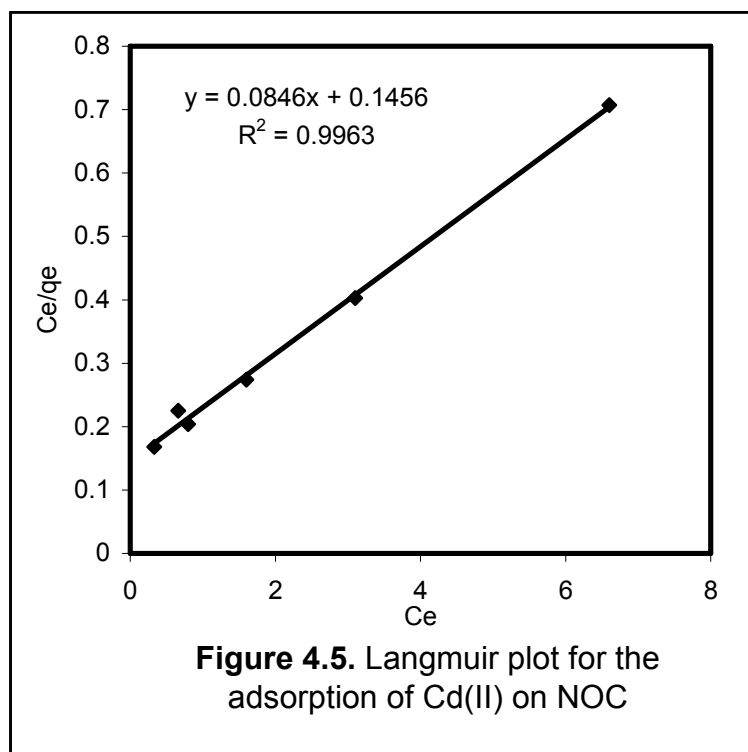
Metal ions	Temp. (°C)	K_c	ΔG° (KJ/mole)	ΔH° (KJ/mole)	ΔS° (KJ/mole-K)	E_a (KJ/mole)
Cu (II)	35	0.469	-3.07			8.7
	40	0.678	-4.035	56.374	0.193	8.9
	50	0.923	-5.965			8.3
Cd (II)	32	0.057	-0.28			9.8
	40	0.299	-1.808	57.975	0.191	11.4
	50	0.602	-5.319			7.17

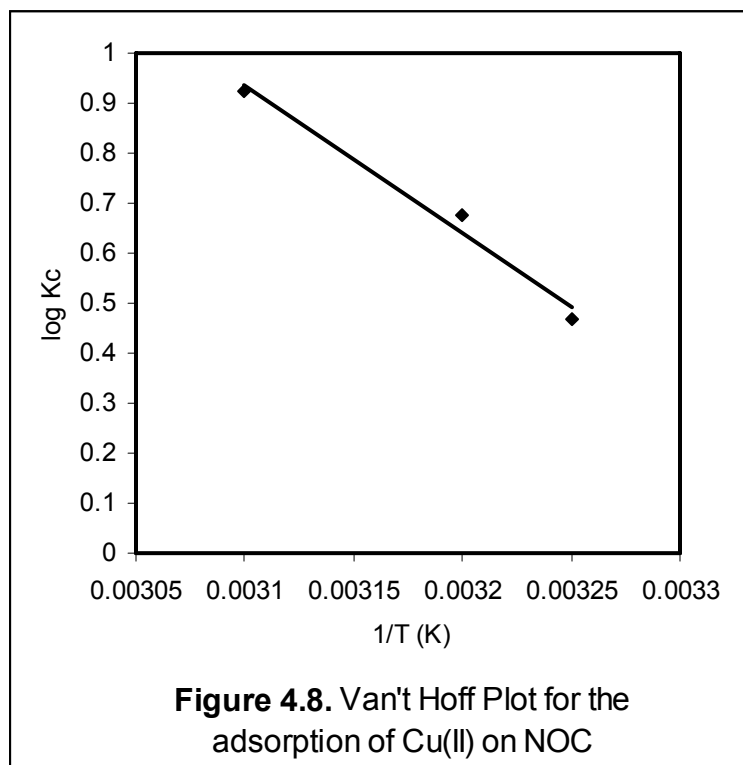
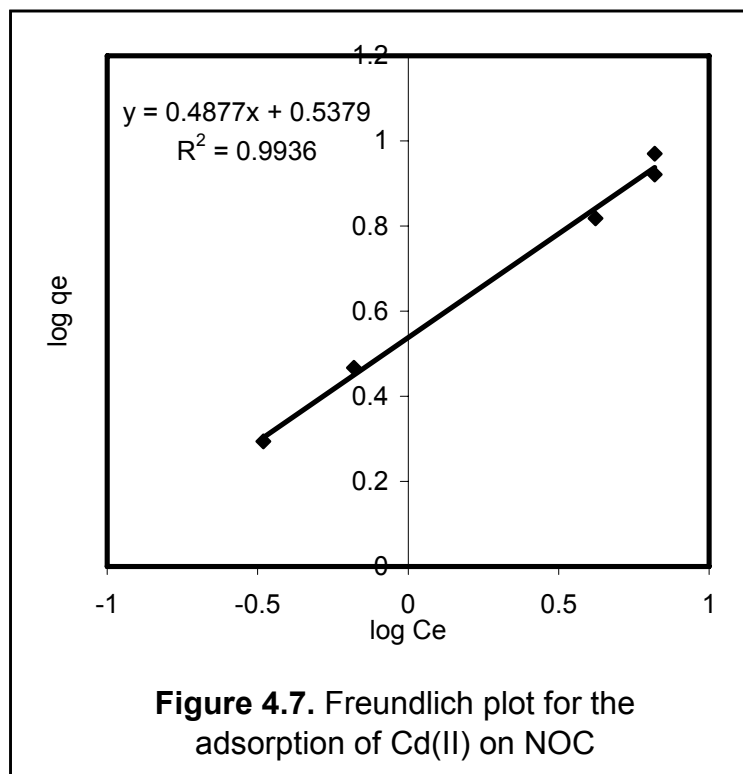
Table 4.5. Pseudo-first order and Pseudo-second order kinetics constants for the adsorption of Cu (II) and Cd (II) on NOC

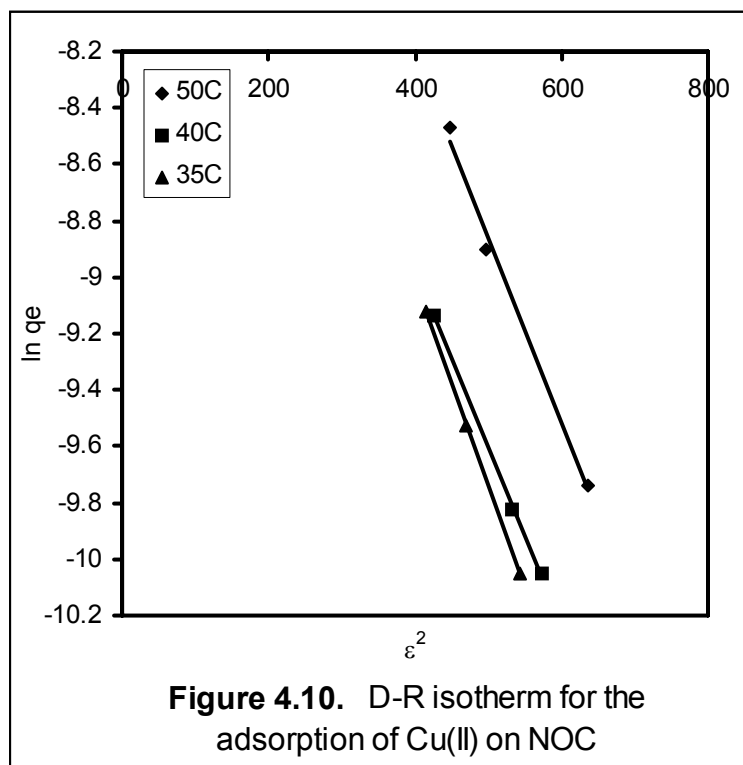
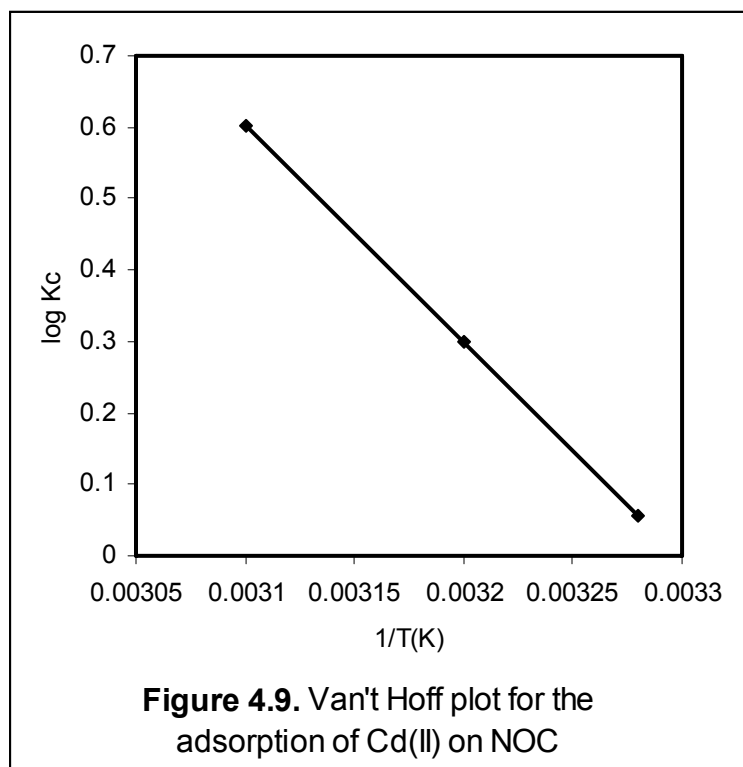
Metal ions	Conc (mg/l)	Pseudo-first order kinetics					Pseudo-second order kinetics				
		K_1 (1/min)	q_e (theo) (mg/g)	q_e (exp) (mg/g)	R^2	P	K_2 (g/mg-min)	q_e (theo) (mg/g)	q_e (exp) (mg/g)	R^2	P
Cu (II)	25	0.9373	0.86	2.37	0.9843	63.7	2.26	2.32	2.37	0.9998	2.1
	50	0.7512	8.62	4.91	0.9941	75.6	0.343	4.97	4.91	0.9998	1.32
	75	0.1098	2.14	7.2	0.9947	70.3	0.162	7.3	7.2	0.9999	1.39
	100	0.0196	6.35	8.4	0.9959	24.4	0.122	6.26	8.4	0.9923	25.5
Cd (II)	5	0.456	0.039	0.49	0.9895	91	50.24	0.49	0.49	1	0
	15	1.296	0.196	1.47	0.9841	86.7	39.2	1.47	1.47	1	0
	25	0.818	1.121	2.41	0.9005	53.5	0.469	2.38	2.41	0.9907	1.24
	50	0.151	1.062	4.95	0.9976	78.5	0.568	4.97	4.95	1	0.56

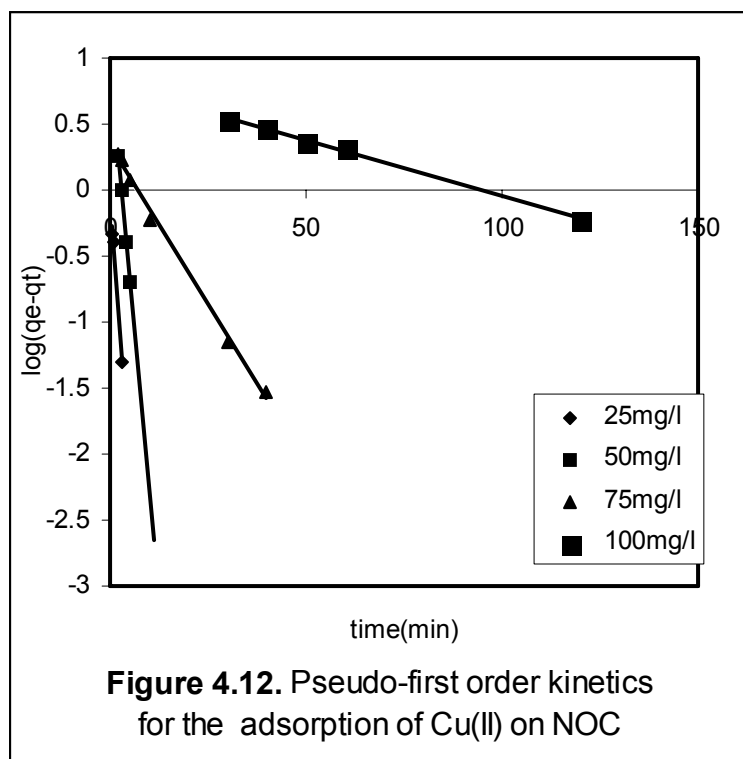
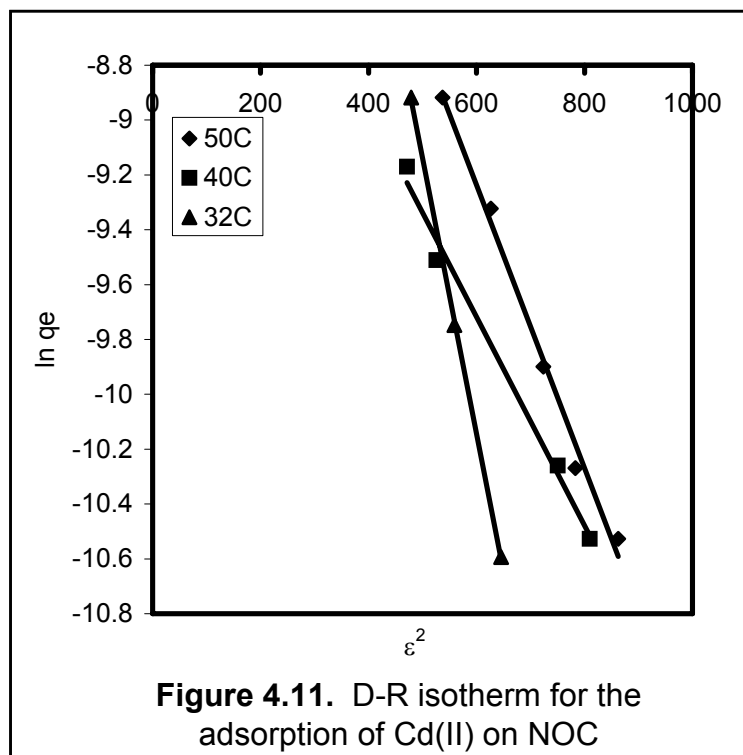


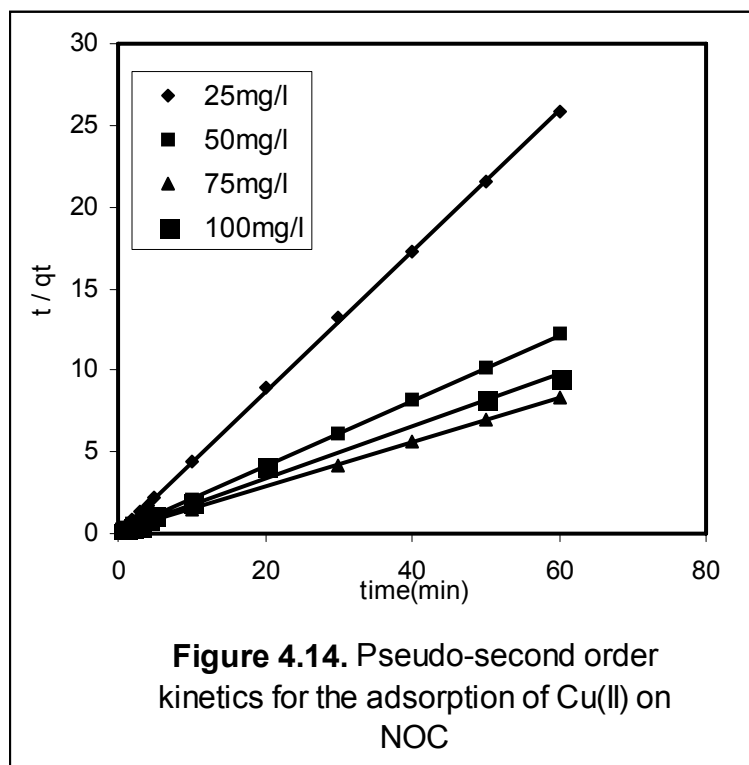
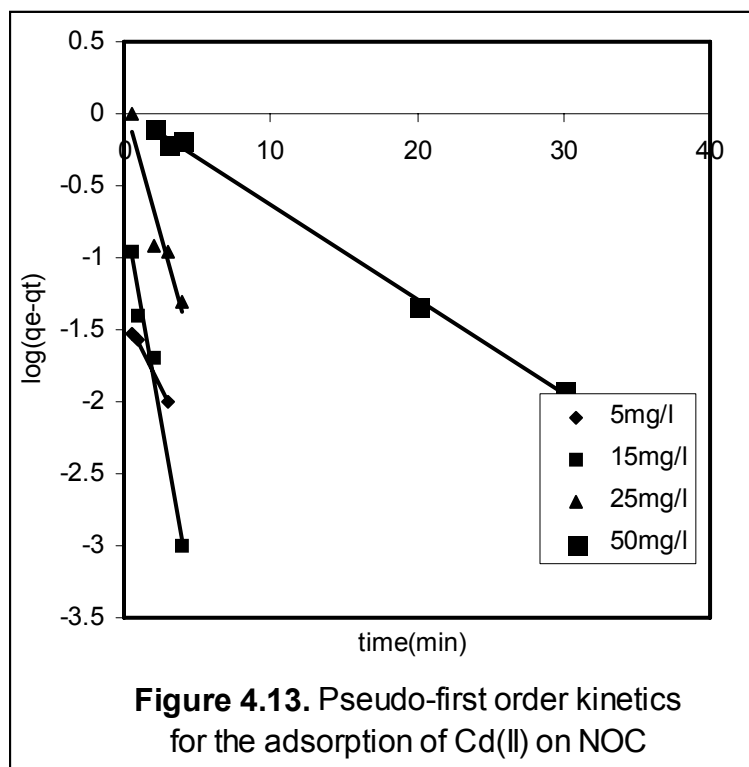


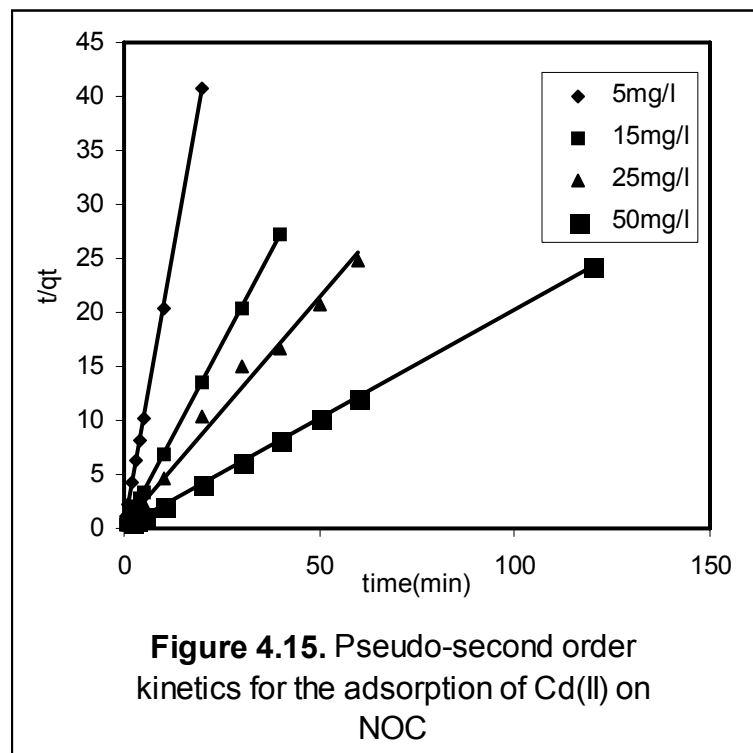












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Chapter – 5

Removal and recovery of Cu (II), Cd (II) and Pb (II) ions from single and multimetal systems by batch and column operation on Neem Oil Cake (NOC)

All substances are poisons; there is none which is not a poison. The right dose differentiates a poison and a remedy

Paracelsus (1493 – 1541)

5.1. Introduction:

Industrial effluents are loaded with toxic heavy metals beyond permissible limit, causing hazardous effects to biota. The toxicity of these pollutants has led to enforce stringent standards on the maximum allowable limits for their disposal into open landscapes and water bodies (UNEP, 1989). Heavy metals are non-degradable and tend to accumulate in human body causing various disorders (Namasivayam and Ranganathan, 1995). Textile, electroplating, painting, dyeing, surface treatment industries, etc. are the main source of heavy metal pollution (Vijayarghavan et al., 2005).

Many conventional techniques have been used to reduce the concentration of heavy metals present in wastewater. Chemical precipitation and filtration, chemical oxidation and reduction, electrochemical treatment, reverse osmosis, solvent extraction and evaporation all shows several disadvantages, such as high cost, incomplete metal removal, low selectivity, high energy requirements and generation of toxic slurries that are difficult to be eliminated (Volesky, B., 2001). Ion-exchange is a highly popular method and has been widely practiced in industrial wastewater treatment process, but the application of such process is often restricted because it cannot guarantee the metal concentration limits required by regulatory standards, especially when metal concentration in the effluents are below 100 mg/l (Wilde and Beneman, 1993; Volesky and Holan, 1995)

Adsorption is a well established technique for the removal of heavy metals present in traces. The practical applicability of heavy metal adsorption is most effectively carried out in packed bed column, as it efficiently utilises the sorbent capacity and results in a better quality of effluent (Volesky and Prasetyo, 1994). Numerous studies have reported adsorption of metals by materials of diverse biological origin, these have remained limited to single species of heavy metal ions and very little information is available for binary and multimetal adsorption systems (Al-Asheh, et al., 2000; Sag, et al., 2001). Wastewater streams however, contain multiple metals, which are likely to cause

interactive effects depending on the number of metals competing for binding sites, the combination of these metals, initial concentrations, the equilibrium steady state concentration of different metal ion species, limitations presented by the binding sites and the nature and quality of biosorbent (Chong and Volesky, 1995; Aksu, and Acikel, 1999). Among the multimetal biosorption systems investigated, few are the removal of Ni and Cr by *Cyanobacterium microcystis* (Singh et al., 2001), Ni and Cu by Sphagnum moss peat (Holan et al., 1993), Cu and Cd by bacterium *Arthrobacter* (Pagnanelli et al., 2001), Cd, Pb and Zn by bacterium *Alteromonas* (Loaec et al., 1997), Cd, Cu, Ni, Zn by BGH (Saeed et al., 2005).

This study has demonstrated the adsorption properties of Neem oil cake (NOC), the residue left after the extraction of oil from neem fruit. Neem (*Azadirachta indica*) is an evergreen tree endemic to the Indian subcontinent. It is used in ayurvedic, unani and folklore traditional medicines, in the treatment of wide range of ailments. Formulations made of neem oil find wide usage as a bio-pesticide for organic farming (Therapeutic Goods Administration (TGA), Australia; Schmutterer, H., 2002). The C/N ratio in NOC is very less that means after its use as an adsorbent it will take no time to decompose (Gaur et al., 1983). This is an additional advantage of NOC that makes it an ecofriendly adsorbent. In this work, adsorption and desorption efficiency of NOC for single metal system of Pb (II) and multimetal system of Pb (II), Cd (II) and Cu (II) in DDW and tap water are studied by applying batch and column processes.

5.2. Material and methods:

5.2,1. Adsorbent:

Oil was extracted from the fruit of neem (*Azadirachta indica*) and waste matter left after extraction is known as neem oil cake (NOC). The NOC was treated with hot DDW in order to remove the traces of oil and finally dried in open-air oven at 60-65°C for 24 hrs. After drying, the adsorbent was sieved through 50 -100 (BSS) mesh size and used as such.

5.2,2. Adsorbate solution:

Single component stock solutions of Cu (II), Cd (II) and Pb (II) were prepared (1000 mg/l) by dissolving the desired quantity of their nitrate salts (AR grade) in DDW.

5.2,3. Adsorption studies:

Adsorption studies were carried out by batch and column processes. In batch process, 0.5 g adsorbent was placed in conical flask in which 50 ml solution of metal ion of desired concentration was added and the mixture was shaken in temperature controlled shaker incubator for 24 hrs at 120 rpm. The mixture was then filtered using Whatman filter paper number- 41 and final concentration of metal ion was determined in the filtrate by AAS (GBC 902). The instrument was calibrated with standard Cu (II), Cd (II) and Pb (II) solutions under the following specifications

Metal – Cu (II)
Wavelength – 324.7 nm
Slit width – 0.5 nm
Lamp current – 3 mA
Flame – Air – acetylene (Oxidising)
Mode – Double beam

Metal – Cd (II)
Wavelength – 228.8 nm

Slit width – 0.5 nm

Lamp current – 3 mA

Flame – Air – acetylene (Oxidising)

Mode – Double beam

Metal – Pb (II)

Wavelength – 217 nm

Slit width – 1 nm

Lamp current – 4 mA

Flame – Air – acetylene (Oxidising)

Mode – Double beam (with background correction)

5.2.4. Effect of pH:

The effect of pH on the adsorption of Pb (II) was studied by batch process as described in chapter-2.

5.2.5. Effect of contact time:

A series of 250 ml conical flasks, each having 0.5 g adsorbent and 50 ml solution (of known Pb (II) concentration) were shaken in temperature controlled shaker incubator at 120 rpm and at the predetermined intervals, the solution of the specified flask was taken out and filtered. The concentration of Pb (II) in the filtrate was determined by AAS. The amount of Pb (II) adsorbed in each case was then determined.

5.2.6. Effect of adsorbent dose:

A series of 250 ml conical flasks each containing 50 ml of metal solution (of known metal concentration) were treated at different temperatures with varying amount of adsorbent (0.1 - 0.8 g). The flasks were shaken in temperature controlled shaker incubator at 120 rpm and after equilibrium the solutions were filtered. The amount of Pb (II) in filtrate was then determined by AAS.

5.2,7. Breakthrough capacity:

0.5g of adsorbent was taken in glass column (0.6 cm internal diameter) with glass wool support. 1000 ml of metal solution with 50 mg/l initial concentration (C_0) was passed through the column with a flow rate of 1 ml/min. The effluent was collected in 50 ml fractions and the amount of metal (C) was determined in each fraction by AAS. The breakthrough curve of each metal was obtained by plotting C/C_0 vs volume of the effluent. In order to see the desorption behaviour, the exhausted column was washed several times with DDW to remove excess of metal ions from the column, then 0.1M HCl was passed separately through each column containing adsorbed Cu (II), Cd (II) and Pb (II). The metal ions eluted were collected in 10 ml fractions. The flow rate was maintained at 1ml/min in each case.

5.2,8. Desorption studies:

Desorption studies were carried out by both batch and column processes. In batch process, 50 ml solution of each Cu (II), Cd (II) and Pb (II) was treated separately with 0.5 g of adsorbent in temperature controlled shaker incubator at 120 rpm for 24 hrs. Similarly, 50 ml of the mixture of metal ions (containing 20 mg/l each of Cu (II), Cd (II) and Pb (II))(Ratio 1: 1:1) in DDW and the mixture of Cu (II), Cd (II) and Pb (II) (20 mg/l each) (Ratio 1:1:1) in tap water were treated in the same way with the adsorbent. The adsorbent in each flask was washed several times with DDW to remove excess of metal ions. The experiment was carried out in duplicate. The adsorbent after washing was treated with 50 ml of water and kept for 24 hrs. It was then analysed for any leaching of metal ions and it was found that no metal ions were released from the adsorbent. The adsorbent in another flask was treated with 50 ml 0.1M HCl. The flasks were shaken in temperature controlled shaker incubator at 120 rpm (to desorb Cu (II), Cd (II) and Pb (II)) for 24 hrs. The solutions were then filtered using Whatman filter paper number- 41. The filtrates were analysed for metals desorbed.

In column process, 0.5g of adsorbent was taken in glass column (0.6 cm internal diameter) with glass wool support. 50 ml solution of Cu (II), Cd (II) and

Pb (II) (50 mg/l each), 50 ml mixture of Cu (II), Cd (II) and Pb (II) containing 20 mg/l each (Ratio 1:1:1) in DDW and mixture of Cu (II), Cd (II) and Pb (II) containing 20 mg/l each (Ratio 1:1:1) in tap water were passed through each column at 1ml/min flow rate. The adsorbent in each column was washed several times by DDW in order to remove traces of metal ions remained unadsorbed. 0.1M HCl solution was then passed separately through each column as an eluent. The effluent was collected in 10 ml fractions in each case with a flow rate of 1ml/ min and the metal ions desorbed were determined in each fraction.

5.2.9. Quality assurance and quality control:

To make sure that no metal ions were released to the solution from the adsorbent, an equilibrium test was performed using adsorbent (NOC) in DDW. For assuring quality in the adsorption studies, DDW blank and two duplicates were included in the experiments. To ensure accuracy after each set of five samples, a standard was analysed to ensure that drift had not occurred.

The samples were analysed in triplicate by AAS. Average of the values obtained gives mean concentration of the sample. The percent relative standard deviation (R.S.D) for samples was calculated by dividing standard deviation of the sample with the average of the sample multiplied by 100. If the value of percent R.S.D for any sample was greater than 10% the data were declared unusable.

5.3. Results and Discussion:

5.3,1. Effect of Initial concentration:

Initial metal concentration provides important driving force to overcome all mass transfer resistances of the metal between the aqueous and solid phase (Aksu and Akpinar, 2001). The increase in the initial concentration of Pb (II) solution at room temperature (32°C) increases the adsorption capacity. Table. 5.1 summarizes the results of the adsorption capacity accuracy test.

5.3,2. Effect of pH:

The percentage adsorption of Pb (II) on NOC increases with increase in pH, attaining optimum at pH 4 (**Figure. 5.1**). Availability of negatively charged groups on the adsorbent surface is necessary for the sorption of metals to proceed (Luef et al., 1991). At pH 2, the adsorption is likely as there is a net positive charge in the adsorption system due to H^+ and H_3O^+ . In such system H^+ compete with metal ions (low et al., 1993) resulting in active sites to become protonated to the virtual exclusion of metal binding on the adsorbent surface (Aldov et al., 1995). This means that at higher H^+ concentration, the adsorbent surface becomes more positively charged thus reducing the attraction between adsorbent and metal cations (Saeed et al., 2002) in contrast, as the pH increases, more negatively charged surface becomes available thus facilitating greater metal uptake (Chang et al., 1997). The metal adsorption noted to increase significantly by increasing pH, thus Pb (II) with 50 mg/l (initial concentration) at pH 4 shows 98 % (maximum) adsorption. With further increase in pH, the solubility of metals decreases resulting in their precipitation as hydroxide with no significant increase in percentage adsorption.

5.3,3. Effect of adsorbent doses:

The adsorption capacity (mg/g) and percentage (%) adsorption of Pb (II) by varying the dose of NOC at different temperatures is shown in **Figures. 5.2a, 5.2b** and **5.2c**. The %

adsorption increases as the adsorbent dose of NOC is increased for Pb (II). However, increase in temperature has no significant effect on % adsorption. It may be concluded that by increasing the adsorbent dose, the removal efficiency of NOC increases, while adsorption density/capacity decreases. The decrease in adsorption density may be due to the fact that some adsorption sites may remain unsaturated during the adsorption process whereas the number of sites available for adsorption increases by increasing the adsorbent doses and that results in the increase in removal efficiency (Sharma and Foster, 1993).

5.3.4. Adsorption Isotherms:

The adsorption isotherms are well described by Langmuir and Freundlich isotherms for a wide range of adsorbate concentration.

The Langmuir isotherm is given by equation

$$C_e/q_e = 1/b \cdot q_m + 1/q_m \cdot C_e \quad \text{_____} (1)$$

The values of Langmuir constants b and q_m were calculated from the slope and intercept of the linear plot of C_e/q_e vs C_e (**Figure. 5.3**). The coefficient b in Langmuir equation is a measure of the stability of the complex formed between metal ions and adsorbent under specified experimental conditions (Ayranci and Duman, 2005).

The essential feature of the Langmuir isotherm can be expressed in terms of dimensionless constant separation or equilibrium parameter (R_L), which is defined as

$$R_L = 1/1 + bC_o \quad \text{_____} (2)$$

The value of R_L calculated from different initial concentrations of Pb (II), Cu (II) and Cd (II) are 0.521, 0.9015 and 0.4690 respectively. The values are in between 0 and 1 showing favourable adsorption on NOC (Poots et al., 1978).

Freundlich isotherm is given by equation

$$\log q_e = \log K_f + 1/n \log C_e \quad \text{_____} (3)$$

The values of K_f and n were calculated from the intercept and slope of the Freundlich plot (**Figure. 5.4**). (**Table. 5.2**) K_f expresses the adsorption capacity of adsorbent. The heterogeneity factor n is a measure of deviation from linearity of the adsorption. The value of $n > 1$ for Pb (II) (**Table. 5.2**) indicates favourable adsorption by NOC at different concentrations (Ozcan et al., 2005). The higher value of regression coefficient (R^2) in case of Freundlich model indicates better applicability of the model.

5.3.5. Thermodynamics studies:

The thermodynamics parameters such as ΔH° and ΔS° were obtained from the Van't Hoff equation

$$\log K_c = \Delta S^\circ / 2.303 R - \Delta H^\circ / 2.303 RT \quad \text{_____} (4)$$

ΔS° and ΔH° were calculated from the slope and intercept of linear plots of $\log K_c$ vs $1/T$ (**Figure. 5.5**) for Pb (II). K_c calculated from the following relationship (Namasivayam and Ranganathan, 1995)

$$K_c = C_{Ae} / C_e \quad \text{_____} (5)$$

ΔG° was then calculated from the equation

$$\Delta G^\circ = - RT \ln K_c \quad \text{_____} (6)$$

The positive values of ΔH° (**Table. 5.3**) suggest endothermic nature of adsorption of Pb (II) on NOC. The value of ΔG° for the process decreases with increase in temperature, which indicates that the process is spontaneous. The positive value of ΔS° shows the increase in randomness at the solid / solution interface during the adsorption of Pb (II) on NOC.

5.3.6. Kinetics studies:

A quantitative understanding of the adsorption is possible with the help of kinetics models. A pseudo-first-order kinetics model as expressed by Lagergren (Ajmal et al., 2001) can be written as:

$$\log (q_e - q_t) = \log q_e - K_1 / 2.303 \cdot t \quad \text{_____} \quad (7)$$

A plot of $\log (q_e - q_t)$ vs t gives straight line and confirms the applicability of the pseudo-first-order rate equation (**Figure. 5.6**).

Pseudo-second-order adsorption rate equation may be expressed as:

$$t / q_t = 1 / K_2 q_e + 1 / q_e \cdot t \quad \text{_____} \quad (8)$$

A plot of t/q_t vs t produces straight line and indicates the applicability of pseudo-second-order model (**Figure. 5.7**).

In order to compare quantitatively the applicability of kinetics models in fitting to data, the percent relative deviation (P), given by the following equation was calculated

$$P = 100 / N \sum \{ [q_{e \text{ (exp)}} - q_{e \text{ (theo)}}] / q_{e \text{ (exp)}} \} \quad \text{_____} \quad (9)$$

It is found that lower the value of percentage deviation (P), better is the fit. It is generally accepted that when P value is less than 5, the fit is considered to be excellent (Ayranci and Duman, 2005). The results have been analysed using equation (8) and (9). The experimental data fitted well in both the equations. The values of $q_{e \text{ (theo)}}$ calculated from these models are compared with experimental values $q_{e \text{ (exp)}}$ in **Table. 5.4**. It is found that values of $q_{e \text{ (theo)}}$ calculated from the pseudo-first-order kinetics model differed appreciably from the experimental values $q_{e \text{ (exp)}}$. The value of P is also very high. On the

other hand, values of q_e (theo) are found to be very close to q_e (exp) when pseudo-second-order rate equation was applied. The value of P is well within the range and also the values of correlation coefficients (R^2) are very high as compared to pseudo-first-order rate model. It is therefore confirmed that adsorption of Pb (II) follows pseudo-second-order rate equation.

5.3.7. Removal and recovery:

In order to explore the practical utility of the adsorbent, removal and recovery of Cu (II), Cd (II) and Pb (II) was carried out by batch and column processes using single metal system, multimetal system in DDW and multimetal system prepared in tap water since wastewater contains other ions also similar to tap water (like Ca^{2+} , Mg^{2+} , HCO_3^- , SO_4^{2-} , Cl^- etc.) and results are compared in **Table. 5.5**. It is found that in single metal system adsorption of Cu (II) by column process is higher than batch process, adsorption of Cd (II) is comparable when batch and column processes are used while adsorption of Pb (II) is higher by batch process. The removal of Cu (II), Cd (II) and Pb (II) by batch or column process is not very much affected when multimetal system in DDW and tap water are used, showing that removal efficiency of these metals remains the same even in the presence of other ions present in tap water. However, the recovery of Cu (II), Cd (II) and Pb (II) is poor by batch process (**Table. 5.5**) as compared to column process. The % recovery of Pb (II) is slightly decreased in multimetal system in DDW (Pb (II) = 71%) and tap water (Pb (II) = 83%). Elution of Cd (II), Pb (II) and Cu (II) in multimetal systems in DDW and tap water from NOC are shown in **Figures. 5.8 and 5.9**. It is important to note that maximum elution of all the metals occur within 10 ml fraction of the effluent, showing that metal ions can be preconcentrated effectively using NOC as adsorbent.

The amount of adsorbent required for complete removal of heavy metal ions can be found out by determining the breakthrough capacity. The breakthrough capacities of Cu (II), Cd (II) and Pb (II) are found to be 10, 15 and 30 mg/g (**Figures. 5.10, 5.11 and 5.12**). When column became saturated with metal ions (or exhausted), the desorption studies were carried out by passing 0.1M HCl solution through each column. **Figure.**

5.13 indicates that 2.5, 2.485, 1.6 and 0 mgs of Cu (II) was adsorbed consecutively from each 50 ml fraction of Cu (II) (50 mg/l) when passed through the column. This indicates that total 6.58 mg of Cu (II) was adsorbed from 200 ml of Cu (II) solution before the column exhausted. 0.1M HCl solution was then passed through this column. Eight fractions of 10 ml each were collected consecutively. The Cu (II) recovered from 80 ml effluent was 6.71 mg (100% recovery of Cu (II)). Similarly **Figure. 5.14** indicates that 2.5, 2.5, 2.5, 2.5, 2.5, 2.5, 2.45, 2.05, 1.45 and 0.9 mg of Pb (II) was adsorbed consecutively from each 50 ml fraction of Pb (II) solution before the column exhausted. This indicates that 21.85 mg of Pb (II) was adsorbed from 500 ml of Pb (II) solution. 0.1M HCl solution was passed through this column. Eight fractions of 10 ml each were collected consecutively. The Pb (II) recovered from 80 ml effluent was 12.44 mg (57 % recovery of Pb (II)).

It can be inferred from above findings that wastewater containing small quantities of Cu (II), Cd (II) and Pb (II) can be treated effectively using NOC as adsorbent. The column operation is more effective because spent or exhausted adsorbent can be regenerated easily by 0.1M HCl and at the same time these metal ions can be recovered in small volume of effluent. This may help in easy disposal of extracted/ preconcentrated metal solution.

5.4. Conclusion:

Neem oil cake (NOC) is used as bio-pesticide and bio-fertiliser in organic farming. The advantage of using NOC as biosorbent is that its decomposition is fast as compared to other bulky organic sorbents because of its low C/N ratio. NOC is highly selective for Pb (II) and shows 98% adsorption of Pb (II) at pH 4. The adsorption studies indicate that Freundlich model is better obeyed. Thermodynamics parameters (ΔH° and ΔG°) suggest that adsorption process is endothermic and spontaneous. The kinetics data are best fitted in second-order rate equation as evident from the values of % deviation (P) and regression coefficients (R^2). The breakthrough capacities for Cu (II), Cd (II) and Pb (II) are found to be 10, 15 and 30 mg/g respectively. The analytical applications could be demonstrated by using NOC for the removal and recovery of Cu (II), Cd (II) and Pb (II) from single and multimetal solution systems. It has been found that removal and recovery of Cu (II), Cd (II) and Pb (II) is better by column operation as compared to batch process in single metal and multimetal systems. The maximum efficiency of NOC has been demonstrated by eluting Cu (II) and Pb (II) from exhausted columns (i.e. beyond exhaustive capacity) and it has been found that 100% Cu (II) could be recovered while recovery of Pb (II) is 57% when 0.1M HCl was used as eluent. NOC therefore is an effective biosorbent and can be utilised for the removal and recovery of Cu (II), Cd (II) and Pb (II) from water and wastewater. The regeneration of the adsorbent and maximum recovery of these ions in small volume of effluent makes the adsorbent more economical and easy disposal of the preconcentrated metal ions.

Table. 5.1. Reproducibility test for adsorption capacity of Pb (II) on NOC

Initial Conc. (C _o) (mg/l)	Average final Conc. (C _e) (mg/l)	Average Adsorption Capacity (q _e) (mg/g)	Standard Deviation of q _e	Relative standard deviation of q _e
10	0.1667	0.9833	0.0058	0.590
20	0.4333	1.9567	0.0058	0.296
30	0.6333	2.9367	0.0058	0.197
40	0.7667	3.9233	0.0153	0.390
50	0.7667	4.9233	0.0058	0.118
60	0.8000	5.9200	0.0082	0.138
70	0.8000	6.9200	0.0082	0.118
90	0.8333	8.9167	0.0115	0.129
100	0.8667	9.9133	0.0153	0.154

Table. 5.2. Langmuir and Freundlich constants for the adsorption of Pb (II) on NOC

Langmuir constants					Freundlich constants		
q _m (mg/g)	b (l/mg)	b.q _m (l/g)	R ²	R _L	K _f (mg/g)	n	R ²
54.94	0.095	5.219	0.9859	0.521	8.035	1.49	0.9992

Table. 5.3. Thermodynamics parameters for the adsorption of Pb (II) on NOC at different temperatures

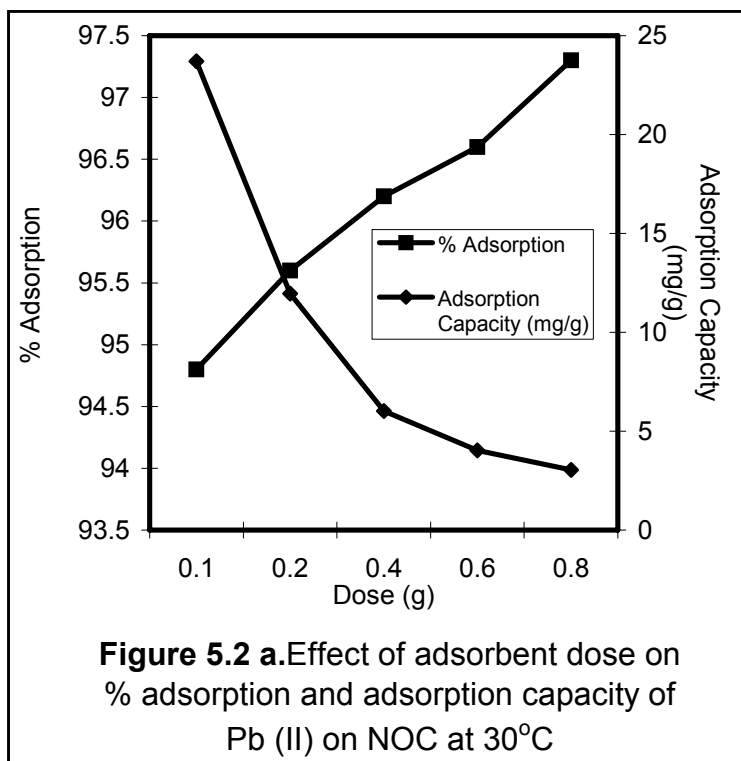
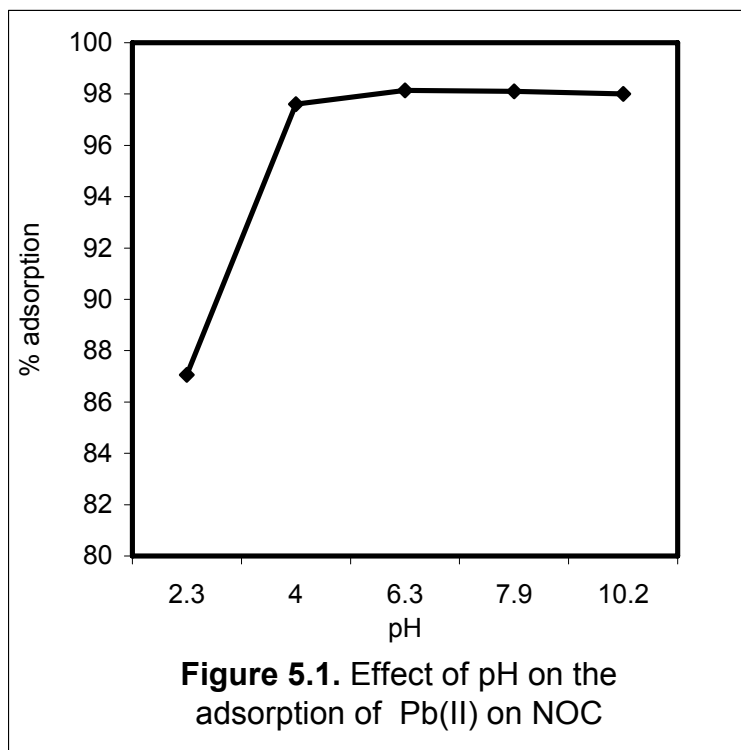
Temp. (°C)	K _c	ΔG° (KJ/mole)	ΔH° (KJ/mole)	ΔS° (KJ/mole-K)
30	1.261	-7.277		
40	1.38	-8.367	25.75	0.109
50	1.53	-9.457		

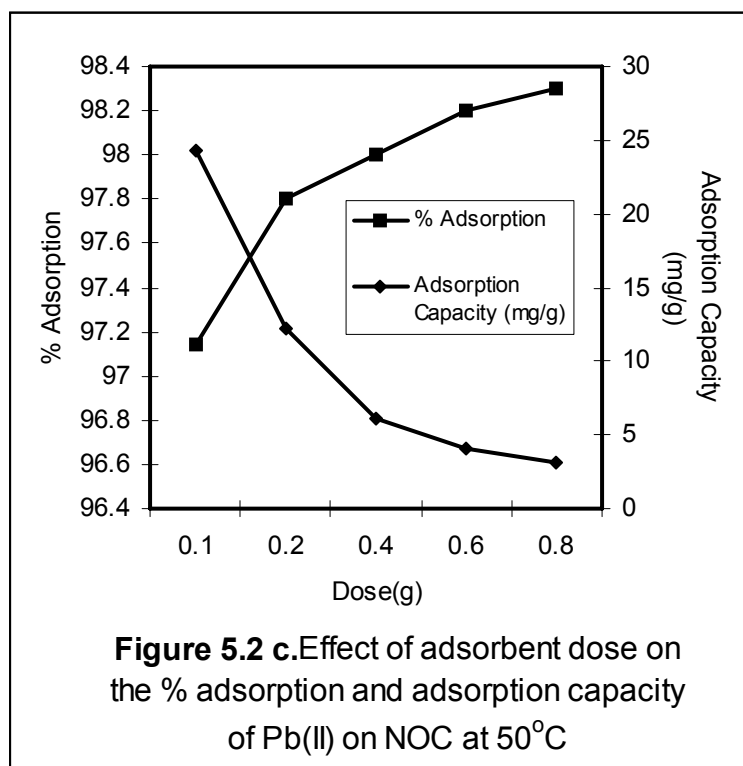
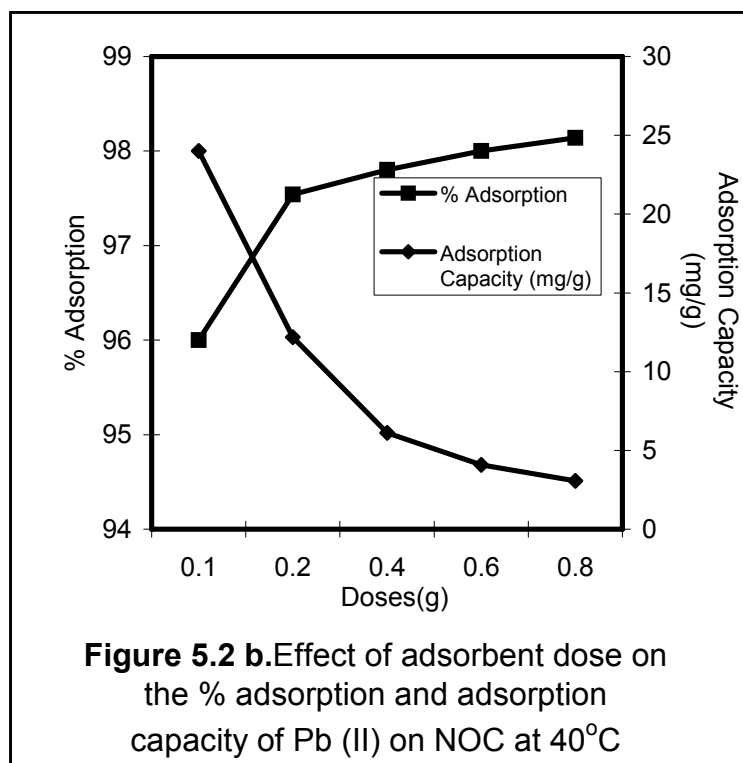
Table. 5.4. Pseudo-first order and Pseudo-second order kinetics constants for the adsorption of Pb (II) on NOC

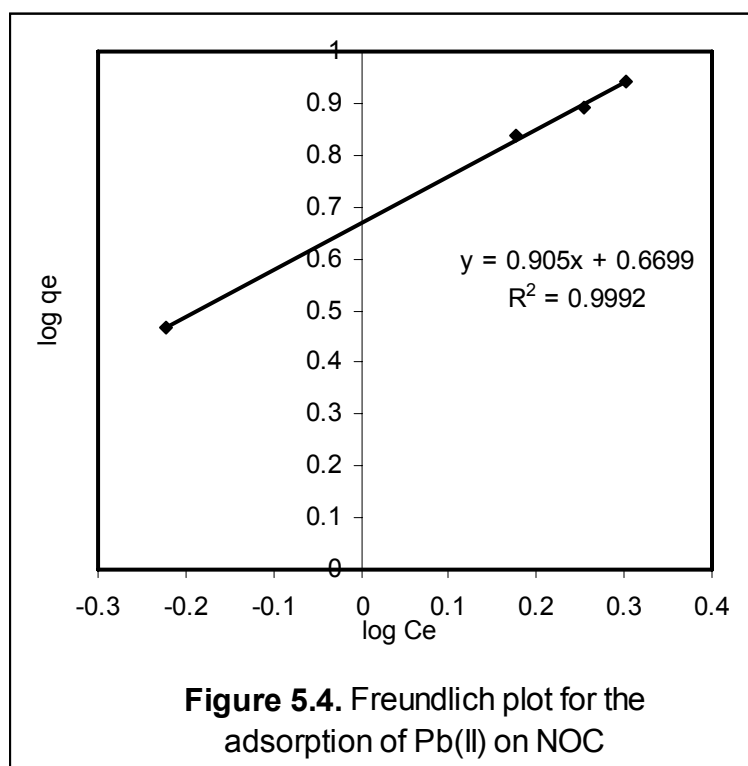
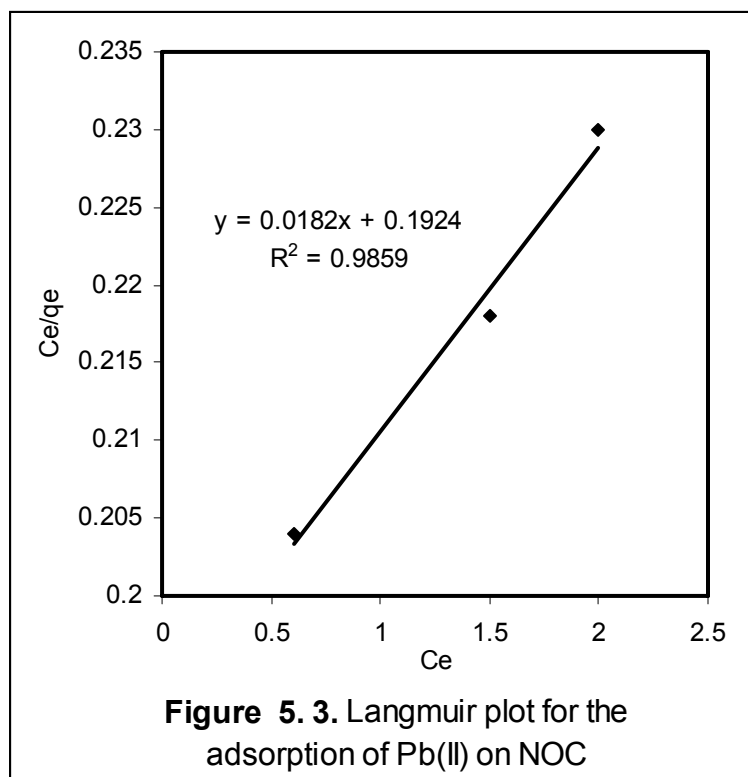
Concent ration (mg/l)	Pseudo-first order kinetics					Pseudo-second order kinetics				
	K ₁ (1/min)	q _e (theo) (mg/g)	q _e (exp) (mg/g)	R ²	P	K ₂ (g/mg- min)	q _e (theo) (mg/g)	q _e (exp) (mg/g)	R ²	P
50	1.055	1.105	4.99	0.9943	77.8	4.715	4.99	4.99	1	0
75	1.191	3.89	7.42	0.994	47.6	2.082	7.42	7.42	1	0
100	0.062	0.221	9.94	0.9624	97.8	0.863	9.95	9.94	1	0.1

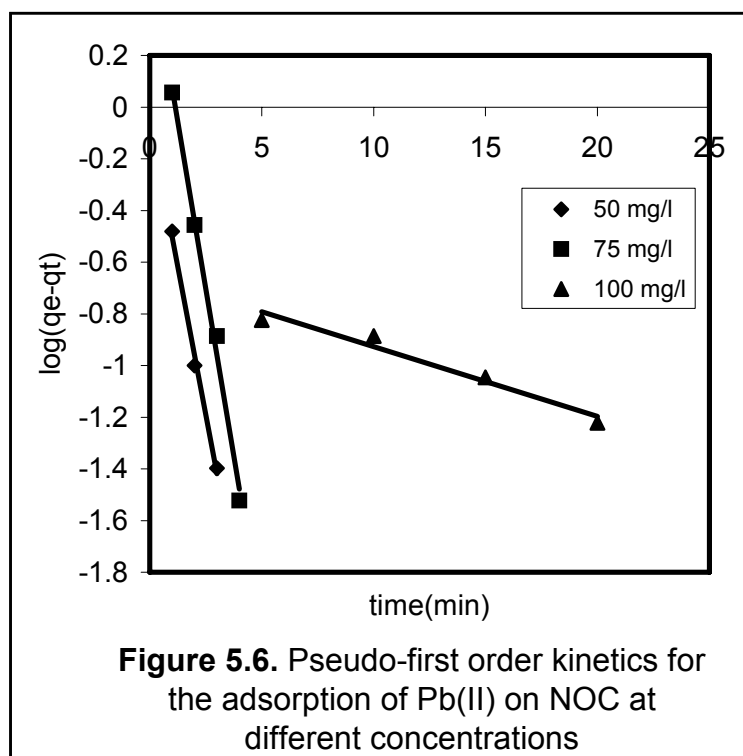
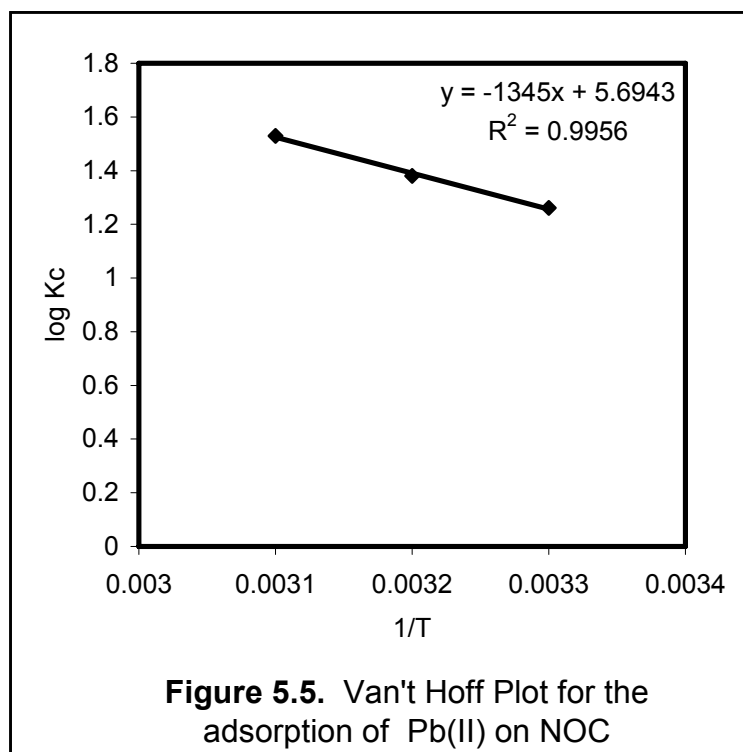
Table. 5.5. Adsorption and desorption of Cu (II), Cd (II) and Pb (II) in single and multimetal systems on NOC by batch and column process

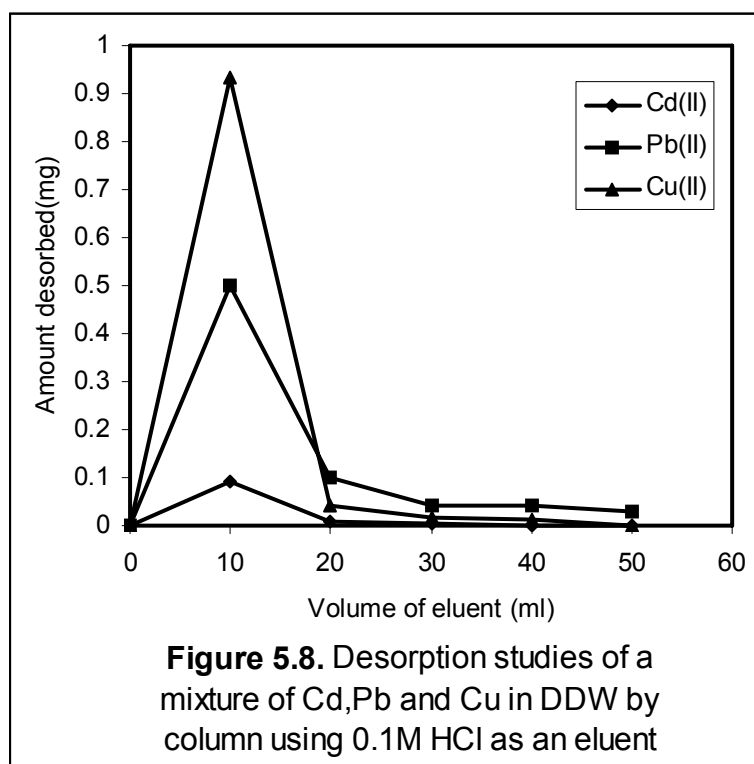
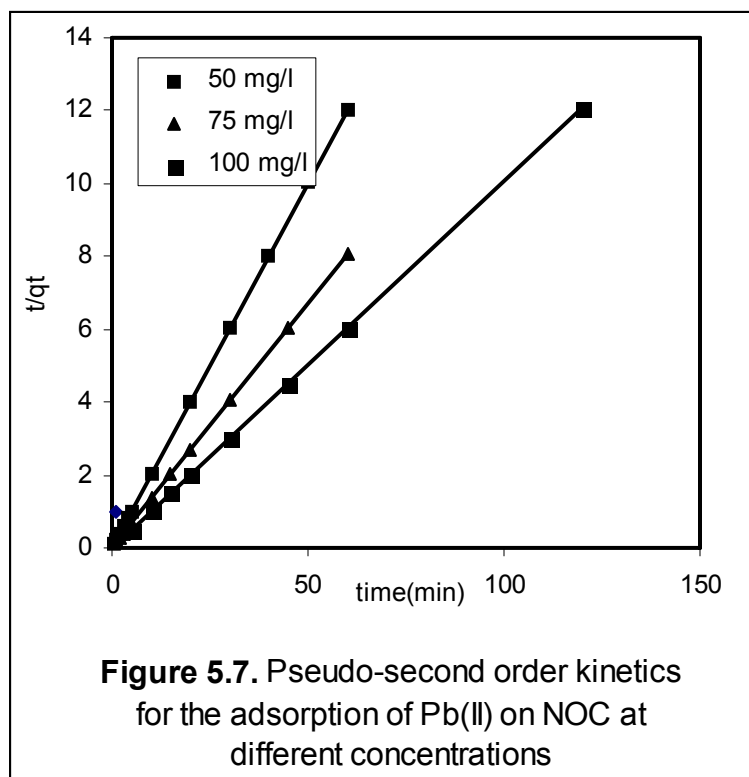
Metal solutions			Batch process (Amount of adsorbent = 0.5g)		Column operation (Amount of adsorbent = 0.5g)	
	Metal	Amount loaded (mg)	% Adsorption	% Recovery	% Adsorption	% Recovery
Single metal system solution	Cu (II)	2.5	92	36.2	100	100
	Cd (II)	2.5	98	8.2	95.2	95.7
	Pb (II)	2.5	95.7	55.5	88.4	94.1
Multimetal system in DDW	Cu (II)	1.0	90	38.84	100	100
	Cd (II)	1.0	99.5	49.75	99.3	100
	Pb (II)	1.0	99.3	39.61	100	71
Multimetal system in tap water	Cu (II)	1.0	85	23.5	100	99
	Cd (II)	1.0	96.3	48.1	99.8	91.6
	Pb (II)	1.0	99.5	64.8	100	83

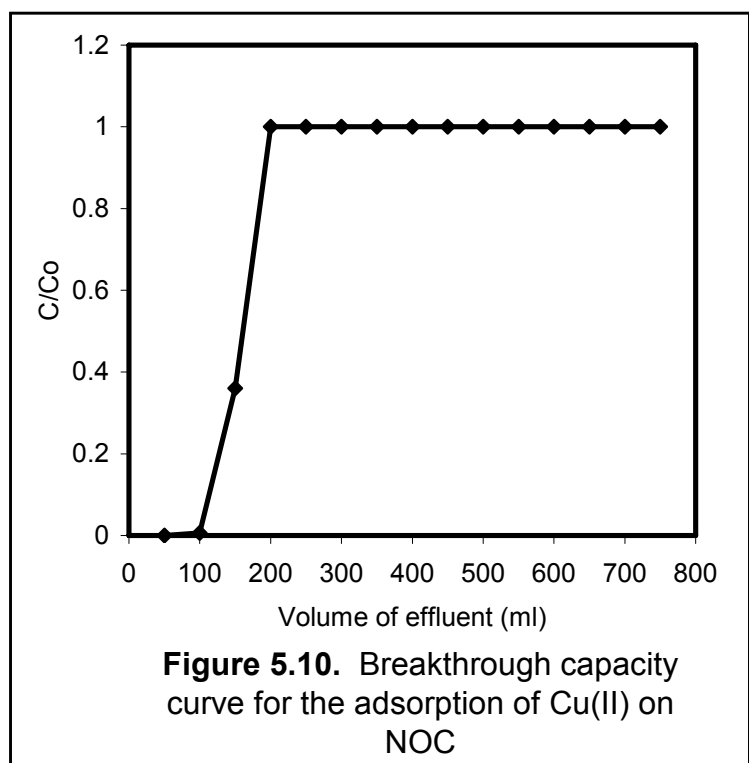
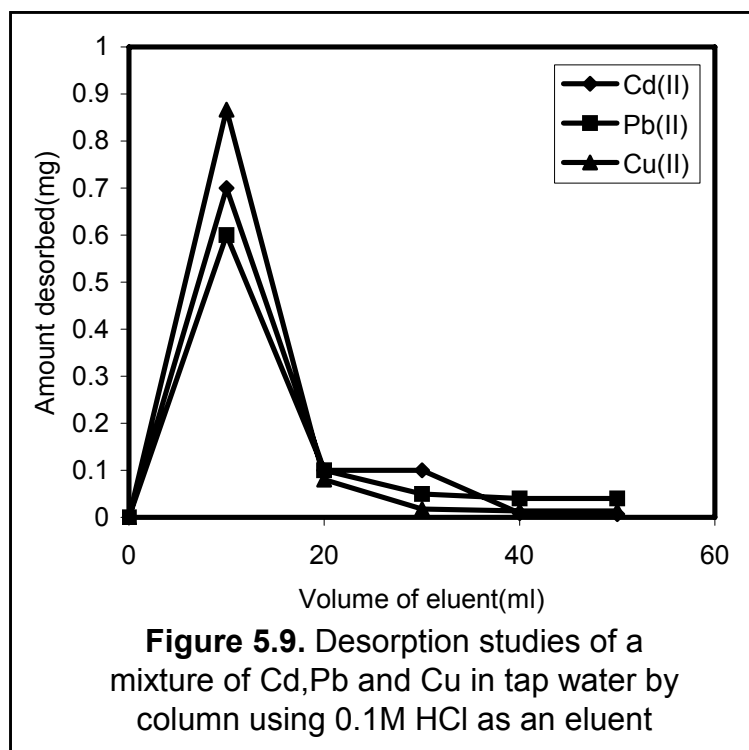


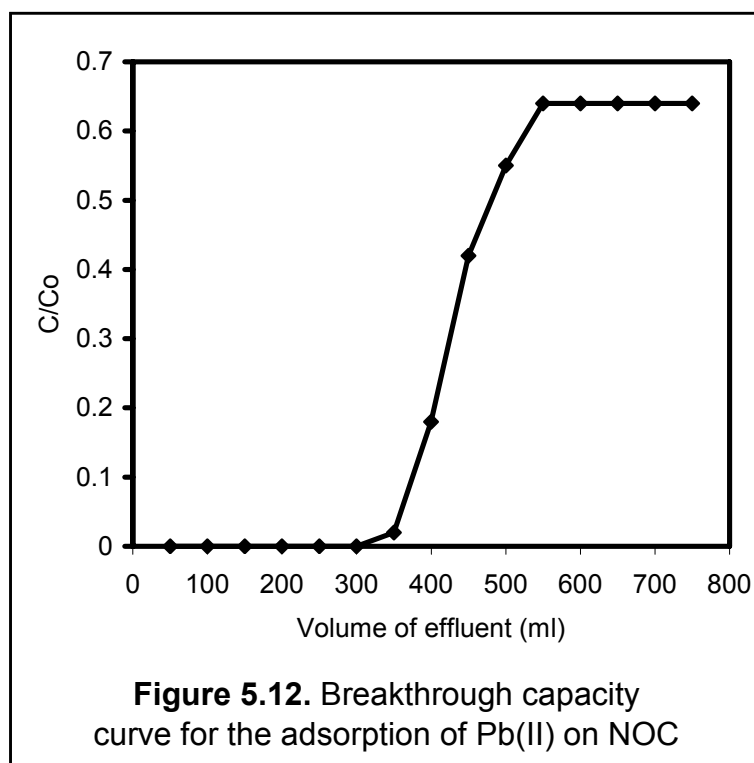
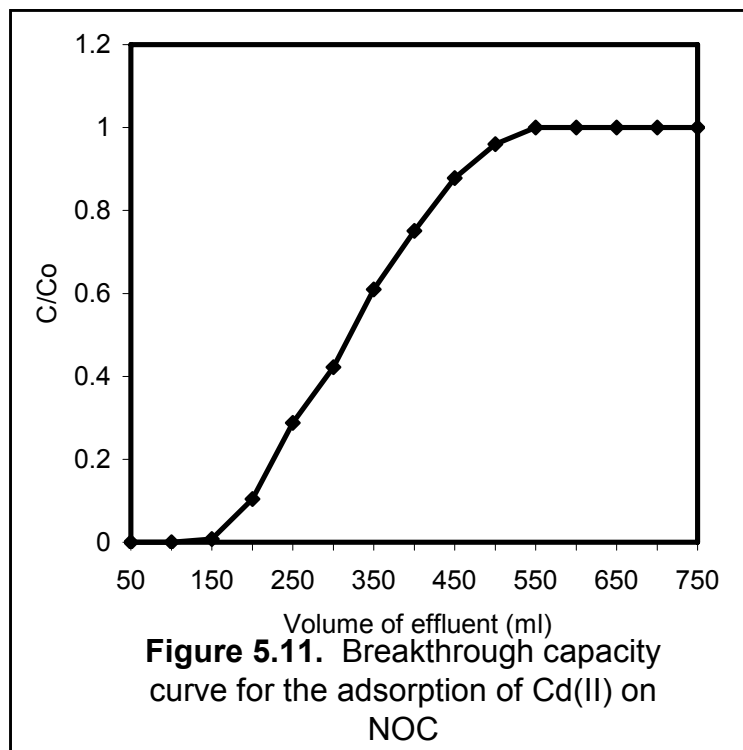


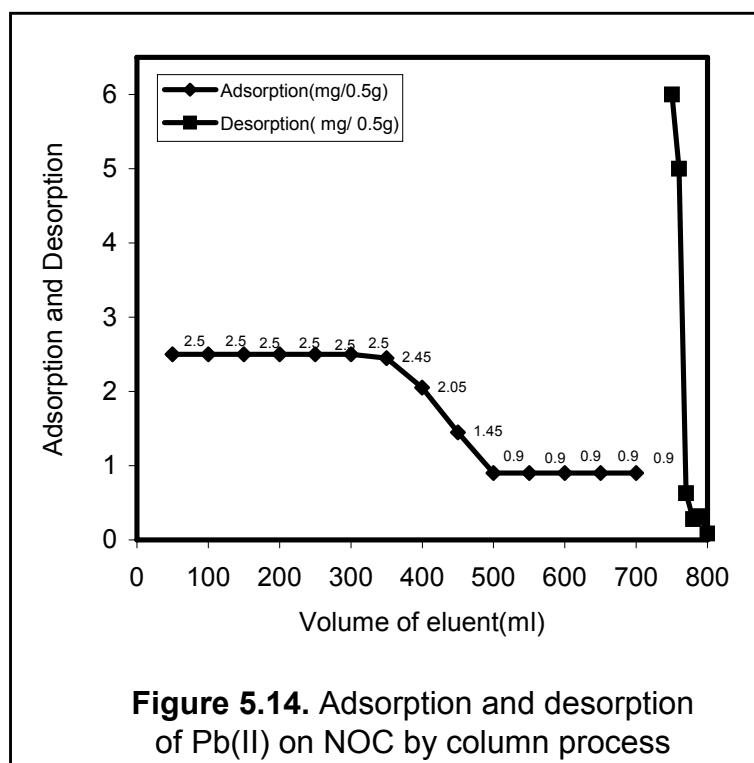
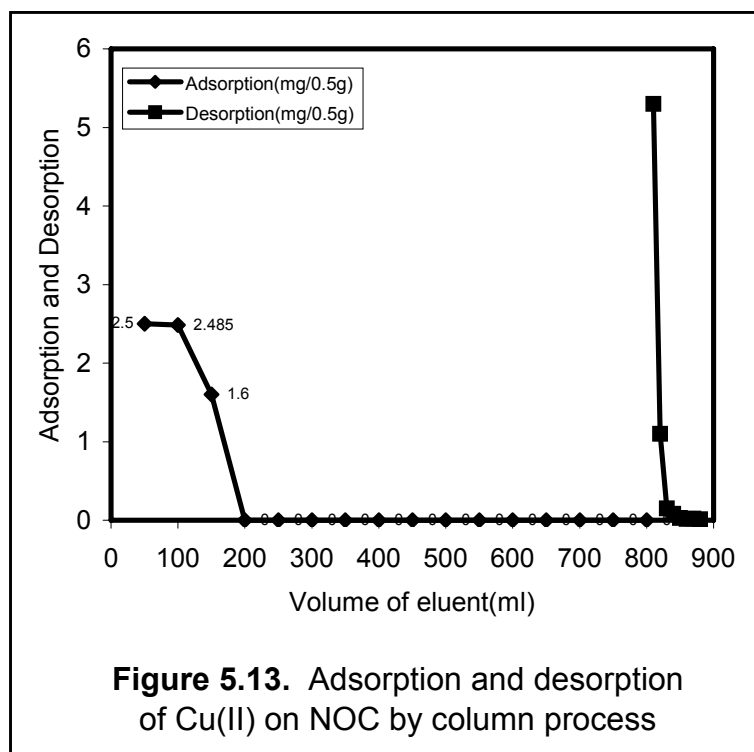












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Chapter – 6

Effect of SDS (Sodium dodecyl sulphate) on the adsorption of bivalent heavy metals on activated carbon prepared from Mustard Oil Cake (AMOC): Thermodynamics and Kinetics study

*Earth provides enough to satisfy every man's need,
but not every man's greed.*

Mahatma Gandhi

6.1. Introduction:

The extent of heavy metal adsorption is a critical component in the evaluation of fate of natural water systems. Heavy metals discharged from civil and industrial wastewater streams have become an ecotoxicological hazard of prime interest. Heavy metals represent a major problem for the environment since they are non-biodegradable and have the tendency to accumulate in vital organs of humans and animals, thereby posing a threat to flora and fauna.

Various techniques have been employed for the treatment of heavy metals such as chemical precipitation, electrolysis, ion exchange, reverse osmosis and adsorption (Netzer and Hughes, 1984; Karabulut et al., 2000; Brown et al., 2000; Kandah, 2004; Axtell et al., 2003). Surfactant based separation processes (Christian and Scamehorn, 1989) such as micellar enhanced ultra filtration (MEUF) has shown to be an effective alternative in removing the multivalent metal ions from waste streams (Tounissou et al., 1996). A disadvantage of MEUF is the relatively large concentration of surfactant that must be used for ion effective separation. Often the economic viability of the MEUF process is strongly dependent on the ability to recover or recycle a substantial expense to the separation (Fillipi et al., 1997) or makes the processed effluent environmentally unacceptable.

Adsorption technique using a number of organic, inorganic, natural, synthetic, activated or modified adsorbents is the most widely employed procedure in the wastewater treatment. Low cost alternatives or cheaper and effective adsorbents are still needed. Use of oil cakes as an adsorbent for the removal of heavy metals is an effective alternative (Ajmal et al., 2005; Konstantinou et al., 2007; Rao and Khan, 2007) as they are cheaper than other materials such as activated carbon and zeolite and are abundantly available. The other advantage of using oil cakes as an adsorbent is the low C/N ratio therefore their degradation is rapid (Gaur et al., 1981).

The aim of this work is to study the effect of Sodium dodecyl sulfate (SDS) on the adsorption of Zn (II) and Ni (II) on activated mustard oil cake (AMOC). Surfactants, surface-active agents can be synthetic but are also naturally produced by plants, animals and many different microorganisms. These molecules reduce surface and interfacial tensions in both aqueous and hydrocarbon mixtures.

6.2. Material and Methods:

6.2,1. Adsorbent:

Mustard Oil Cake (MOC) was burnt in a furnace at 700 °C for about 15 mins in absence of air in order to remove organic matter. The carbon obtained by burning MOC was named as AMOC. It was crushed to a desired mesh size (150 -200 BSS), washed several times with DDW in order to remove dirt and dust and then dried at 65 °C for 24 hrs in an oven.

6.2,2. Adsorbate solution:

Single component stock solutions of Ni (II) and Zn (II) were prepared (1000 mg/l) by dissolving the desired quantity of its nitrate salt (AR grade) in DDW. Stock solution of anionic surfactant (0.1M) Sodium dodecyl sulfate (SDS) ($C_{12}H_{25}OSO_3Na$) was prepared by dissolving the desired quantity of SDS (AR grade) in DDW.

6.2,3. Surfactant Characters:

The CMC of SDS is 8 mM (Lin et al., 1990). In aqueous solution without electrolysis, the reported micelles aggregation number for SDS is 64 (Attwood and Florence, 1983) that gives the micelles equivalent molecular weight of $\cong 18$ kDa.

6.2,4. Adsorption studies:

Adsorption studies were carried out by batch process. 0.25 g adsorbent was placed in conical flask with 25 ml solution of metal ion of desired concentration. The mixture was shaken in temperature controlled shaker incubator for 24 hrs at 120 rpm. The mixture was then filtered using Whatman filter paper number- 41 and final concentration of metal ions was determined in the filtrate by AAS (GBC 902). The % removal of adsorbate and equilibrium adsorption capacity (q_e), were calculated using the following relationships

$$\% \text{ Removal} = [(C_o - C_e) / C_o] * 100 \quad \text{_____} \quad (1)$$

$$\text{Adsorption Capacity } (q_e) (\text{mg/g}) = [(C_o - C_e)] * V / W \quad \text{___} \quad (2)$$

6.2.4. Effect of pH:

The effect of pH for the adsorption of metal ions in presence of 0.1 M SDS on AMOC was studied by batch process as follows: 50ml of Cu (II) solution (50 mg/l initial concentration) was taken in a beaker. The pH of solution was adjusted by adding dilute solution of HCl and NaOH. The concentration of metal ions in this solution was then determined (initial concentration). 25 ml of this solution was taken in conical flask and treated with 0.25 g adsorbent and after equilibrium, the final concentration of metal ions was determined.

6.2.5. Effect of contact time:

A series of 100ml conical flasks, each having 0.25 g adsorbent and 25 ml solution of 50 mg/l initial concentration of Cu (II) were shaken in temperature controlled shaker incubator at 120 rpm and at the predetermined intervals, the solution of the specified flask was taken out and filtered. The concentration of metal ions in the filtrate was determined by AAS. The amount of metal adsorbed in each case was then determined.

6.2.6. Effect of adsorbent dose:

A series of 100 ml conical flasks each containing 25 ml of Cu (II) solution (50 mg/l) were treated with varying amount of adsorbent (0.1-1.0 g). The flasks were shaken in shaker incubator at 120 rpm and after equilibrium the solutions were filtered. The amount of metal ions in filtrate was then determined by AAS. The amount of metal adsorbed in each case was then calculated.

6.2.7. Quality assurance and quality control:

To make sure that no metal ions were released to the solution from the adsorbent, an equilibrium test was performed using adsorbent AMOC in DDW. For assuring quality in

the adsorption studies DDW blank and two duplicates were included in the experiment. To ensure accuracy after each set of five samples, a standard was run to ensure that drift had not occurred.

The samples were analysed in triplicate by AAS. Average of the values obtained gives mean concentration of the sample. In order to compare quantitatively the applicability of different models in fitting to data, the percent relative deviation (P), was calculated by equation:

$$P = 100 / N \sum \{ [q_{e(\text{exp})} - q_{e(\text{theo})}] / q_{e(\text{exp})} \} \quad \text{_____} \quad (3)$$

It is generally accepted that when P value is less than 5, the fit is considered to be excellent (Ozcan et al., 2005).

6.3. Results and Discussion:

6.3.1. Effect of SDS concentration:

The adsorption of Zn (II) and Ni (II) (initial concentration 50 mg/l) on AMOC in absence of SDS is 85.6 % and 60.4 % respectively. The percentage adsorption increases in presence of SDS below its critical micelle concentration (CMC) value (8 mM), above CMC value of SDS the percentage adsorption decreases. The percentage adsorption of Zn (II) and Ni (II) on AMOC is 96 % (maximum) and 85.8 % (maximum) respectively at 2 mM SDS concentration. Further increase in the concentration of SDS decreases the percentage adsorption (**Figure. 6.1**). Therefore below CMC value, metal cations are preferentially adsorbed as compared to large negatively charged SDS ions. A decrease in adsorption above CMC may be due to slow transfer of micelles-metal complex from bulk to the surface of the adsorbent. The physico-chemical properties of surfactants vary markedly above and below the CMC values. Below the CMC values, the physico-chemical properties of ionic surfactants (SDS) resemble those of a strong electrolyte (Schramm et al., 2003). Above CMC, surfactant molecules form dynamic aggregation (micelles). These micelles possess a hydrophobic interior and hydrophilic exterior, causing them to behave like dispersed oil drops. The interaction between the micelles and ionic species is mainly through hydrogen bonding and electrostatic forces. (Shimamoto and Mima, 1979). Therefore, further studies were carried out at 2 mM concentration of SDS.

6.3.2. Effect of Concentration of metal ions:

The adsorption isotherms (**Figures. 6.2 and 6.3**) are regular, smooth, positive and concave towards concentration axis. The adsorption capacities of Zn (II) and Ni (II) on AMOC at lower equilibrium concentration in presence and absence of SDS are almost equal (**Figures. 6.2 and 6.3**). The increase in the concentration of Zn (II) and Ni (II) in presence of SDS leads to drastic increase in the adsorption capacity. The discharge of wastewater from commercial and domestic sectors may cause the contamination of

natural water by heavy metals, surfactants, and other substances. It is, therefore necessary to examine the interference of other metal ions/ surfactants etc., for the removal of Zn (II) and Ni (II). The effect of ionic interaction on the adsorption may be interpreted, using the ratio of the adsorption capacity of the ion in multicomponent system (q_M) to that in a single component system (q_o) (Tan et al., 1985) such that

$q_M / q_o > 1$ adsorption is promoted by the presence of other metal ions/surfactants.

$q_M / q_o = 1$ no observable net interaction effect.

$q_M / q_o < 1$ adsorption is suppressed by the presence of other metal ions/surfactants

The values of q_M / q_o for Zn (II) and Ni (II) are greater than unity therefore it can be concluded that adsorption is promoted in the presence of SDS as evident from the **Figures. 6.2 and 6.3.**

6.3.3. Effect of pH:

The adsorption of Zn (II) is negligible at pH 2 (**Figure. 6.4**). When pH of the solution is increased the adsorption of Zn (II) increases and reaches to a maximum value at pH 4 and then remains constant up to pH 9. This is the general trend observed in many cases. At lower pH, H^+ ions compete with metal ions (high H^+ ions concentration) hindering the adsorption of metal ions. When pH is increased (H^+ ions concentration is lowered), more negatively charged surface becomes available for the adsorption of metal ions hence metal uptake on the adsorbent surface is increased. At higher pH value (pH 6 and above) Zn (II) is adsorbed in the form of hydroxide and continues up to pH 9. When SDS is added in the solution its effect is not seen up to pH 6 most probably because SDS is a strong electrolyte and its ionisation is not affected by varying pH. However, above pH 6 perhaps it prevents the adsorption of $Zn(OH)_2$ and hence the adsorption of Zn (II) is lowered. A similar explanation may be given for the adsorption of Ni (II) (**Figure. 6.5**).

6.3,4. Effect of adsorbent doses:

The adsorption capacity (mg/g) and percentage adsorption of Zn (II) and Ni (II) by varying the dose of AMOC are shown in **Figures. 6.6 and 6.7**. The percentage adsorption increases while adsorption capacity decreases as the dose of AMOC is increased. It may be concluded that by increasing the adsorbent dose, the removal efficiency of AMOC increases. The decrease in adsorption capacity may be due to the fact that some adsorption sites may remain unsaturated during the adsorption process where as the number of sites available for adsorption increases by increasing the adsorbent doses and that results in the increase in removal efficiency (Sharma and Foster, 1993). The effect of SDS is more pronounced in case of Ni (II) as compared to Zn (II) (**Figure. 6.7**).

6.3,5. Effect of Contact time:

The adsorption increases with increase in contact time. The metal uptake (qt) vs contact time (t) curves for Zn (II) and Ni (II) in presence and absence of SDS shown in **Figures. 6.8 and 6.9**. The Zn (II) uptake on AMOC in presence and absence of SDS is 39 mg/g and 28 mg/g respectively within 15 mins contact time, reaching to 45.8 mg/g and 40 mg/g at equilibrium (**Figure. 6.8**). It is also observed that adsorption of Zn (II) in presence of SDS is fast and equilibrium is reached within 50 mins when compared to the adsorption in absence of SDS. The Ni (II) uptake on AMOC in presence and absence of SDS is 31.6 mg/g and 27.4 mg/g with in 15 mins contact time, reaching to 47.2 mg/g and 31 mg/g at equilibrium (**Figure. 6.9**). The maximum adsorption of Ni (II) in presence of SDS is observed within 50 mins. However, the initial rapid adsorption subsequently gives way to a very slow approach to equilibrium. The curves are single, smooth and continuous leading to saturation, suggesting possible monolayer coverage of metal ions on the surface of the adsorbent.

6.3,5. Adsorption isotherms:

Adsorption data for wide rang of adsorbate concentration are most conveniently described by adsorption isotherms, such as Langmuir and Freundlich isotherms.

The Langmuir isotherm is given by equation:

$$C_e/q_e = 1 / bq_m + 1 / q_m \cdot C_e \quad (4)$$

The values of Langmuir constants b and q_m were calculated from the slope and intercept of the linear plot of C_e/q_e vs C_e (**Figures. 6.10 and 6.11**). The coefficient b in Langmuir equation is a measure of the stability of the complex formed between metal ions and adsorbent under specified experimental conditions (Sharma and Foster, 1993). The $q_{m \text{ (exp)}}$ and $q_{m \text{ (theo)}}$ values for the adsorption of Zn (II) and Ni (II) in absence of SDS are very close (**Table. 6.1**). The values of stability coefficient (b) of Zn (II) and Ni (II) in absence of SDS are higher than in presence of SDS showing more stable complex formation in absence of SDS.

The essential feature of the Langmuir isotherm can be expressed in terms of dimensionless constant separation or equilibrium parameter (R_L), which is defined as:

$$R_L = 1 / 1 + bC_o \quad (5)$$

The R_L values calculated for Zn (II) and Ni (II) in presence and absence of SDS are in between 0 and 1 showing favourable adsorption on AMOC (**Table. 6.1**) (Say et al., 2001)

Freundlich isotherm is given by equation:

$$\log q_e = \log K_f + 1 / n \log C_e \quad (6)$$

Where K_f and n are known as Freundlich constants.

The values of K_f and n calculated from intercept and slope of the Freundlich plots (**Figures. 6.12 and 6.13**) are shown in **Table. 6.1**. The values of K_f are higher for Zn (II)

and Ni (II) in presence of SDS. The constant n is a measure of deviation from linearity of the adsorption. The values of n are greater than 1 in all cases indicating favourable adsorption on AMOC (Poots et al.,1978).

6.3.6. Thermodynamics studies:

The thermodynamics parameters like ΔH° and ΔS° were obtained from the Van't Hoff equation.

$$\log K_c = \Delta S^\circ / 2.303 R - \Delta H^\circ / 2.303 RT \quad \text{_____} (7)$$

Where ΔS° and ΔH° were calculated from slope and intercept of linear plots of $\log K_c$ vs $1/T$ for Zn (II) and Ni (II) in presence and absence of SDS. Equilibrium constant (K_c) was calculated from following relationship (Namasivayam and Ranganathan, 1995)

$$K_c = C_{Ae} / C_e \quad \text{_____} (8)$$

Free energy change (ΔG°) was calculated from the relation

$$\Delta G^\circ = - RT \ln K_c \quad \text{_____} (9)$$

The positive values of ΔH° for the adsorption of Zn (II) and Ni (II) on AMOC in presence and absence of SDS (**Table. 6.2**) suggest endothermic nature of adsorption. The increase in adsorption of Zn (II) and Ni (II) in presence and absence of SDS with temperature might have been due to dissolution of the adsorbing species, change in the pore size and enhanced rate of interparticle diffusion (Ayranci and Duman, 2005). The free energy change (ΔG°) of the process is spontaneous and spontaneity increases with increase in temperature. The positive value of entropy change (ΔS°) shows the increase in randomness at the solid / solution interface during the adsorption of Zn (II) and Ni (II) in presence and absence of SDS on AMOC (Ajmal et al., 2005)

To distinguish between the physical and chemical adsorption on AMOC, Dubnin-Redushkevich (D-R) isotherm based on the heterogeneous nature of the adsorbent surface is applied. The linear form of (D-R) isotherm equation is (Benhammon et al., 2005; Pandey et al., 1985)

$$\ln C_{ad} = \ln q_m - \beta \varepsilon^2 \quad (10)$$

Where β Activity coefficient constant ($\text{mol}^2 / \text{J}^2$)

q_m Maximum adsorption (moles / g)

C_{ad} Adsorption capacity (moles/g)

ε Polanyi potential

Polanyi potential (ε) can be calculated from the relation

$$\varepsilon = RT \ln (1 + 1/C_e) \quad (11)$$

Where T Absolute temperature (K)

R Gas constant (KJ/ mole-K)

C_e Concentration at equilibrium (mole/l)

Hence, by plotting $\ln C_{ad}$ vs ε^2 , the values of q_m from the intercept and β from the slope are generated.

The mean free energy for the adsorption E_a can be calculated from the following equation:

$$E_a = 1 / (-2 \beta)^{1/2} \quad (12)$$

The magnitudes of E_a for the adsorption of Zn (II) and Ni (II) in presence and absence of SDS lies in between 12.5 and 14.7 KJ/mole respectively (**Table. 6.3**) which are in the

energy range of an ion exchange reaction, i.e., 8-16 KJ/mole. (Helfferich, F., 1962). This indicates and support the idea that adsorption of Zn (II) and Ni (II) in presence and absence of SDS on AMOC is chemical adsorption and may proceed through ion exchange process. It has been observed that addition of SDS to Ni (II) decreases the energy of activation from 14.7 to 12.5 KJ/mole. While no such effect of addition of SDS is observed in case of Zn (II).

6.3.6. Kinetics of Adsorption:

The rate constants were calculated by pseudo-first-order and pseudo-second-order models (Banat et al., 2003). The pseudo-first-order kinetics model as expressed by Lagergren (Ajmal et al., 2001) is given as

$$\log (q_e - q_t) = \log q_e - K_1 / 2.303 * t \quad (13)$$

The values of rate constant K_1 for Zn (II) and Ni (II) in presence and absence of SDS were calculated from slope the linear plot of $\log (q_e - q_t)$ vs t (**Figures. 6.14** and **6.15**). The values of regression coefficient (R^2) and rate constant (K_1) are reported in **Table. 6.4**.

The Pseudo-second-order kinetics rate expression is given as

$$t / q_t = 1 / K_2 q_e + 1 / q_e * t \quad (14)$$

The values of rate constant K_2 for Zn (II) and Ni (II) in presence and absence of SDS were calculated from the slope of the linear plot of t/q_t vs t (**Figures 6.16** and **6.17**) are reported in **Table. 6.4**.

The values of rate constants K_1 and K_2 for the adsorption of Zn (II) and Ni (II) are higher in absence of SDS. The q_e (theo) and q_e (exp) values for pseudo-first-order kinetics model differed appreciably. The percentage deviation (P) is also very high. In pseudo-second-order kinetics model the values of q_e (theo) and q_e (exp) are found to be very close in case

of Zn (II) in presence of SDS and Ni (II) in absence of SDS. The percentage deviation (P) values are well within the range and also the values of correlation coefficients (R^2) are very high as compared to pseudo-first-order model. It is therefore confirmed the adsorption of Zn (II) in presence of SDS and Ni (II) in absence of SDS follow pseudo-second-order rate equation.

The nature of adsorption was also verified using Reichenberg equation (Reichenberg, 1958):

$$F = 1 - \frac{6}{\pi^2} e^{-\beta t} \quad (15)$$

The nature of βt is mathematical function of R and can be calculated as

$$\beta t = -0.4977 - \ln (1-F) \quad (16)$$

Where, $F = q_t / q_e \quad (17)$

The linearity test of βt vs time (t) plots is employed to distinguish between film and particle diffusion controlled rates of adsorption. The adsorption plots of Zn (II) and Ni (II) on AMOC in presence of SDS (**Figures. 6.18** and **6.19**) are linear but do not pass through the origin thereby indicating that the pore diffusion is not only the rate limiting process but some other processes like film diffusion is also involved.

6.4. Conclusions:

AMOC is an ecofriendly adsorbent. Addition of SDS to Zn (II) and Ni (II) solutions leads to drastic increase in the adsorption capacity. Adsorption process for Zn (II) and Ni (II) is chemical in nature as evident from the values of mean free energy. The adsorption of both Zn (II) and Ni (II) in presence and absence of SDS follows second order kinetics rate equation. The adsorption of Zn (II) and Ni (II) in presence of SDS indicates that film diffusion is also involved. The presence of SDS reduces the hindrance in the film diffusion process and makes easy transfer of Zn (II) and Ni (II) from bulk to the adsorbent surface. This property can be effectively utilised for the removal of Zn (II) and Ni (II) from wastewater discharged from commercial and domestic sectors containing surface active agents like SDS.

Table. 6.1. Langmuir and Freundlich constants for the adsorption of Ni (II) and Zn (II) in absence and presence of SDS on AMOC

Metal ions	Langmuir constants						Freundlich constants		
	qm (theo) (mg/g)	qm (exp) (mg/g)	b (l/mg)	R ²	R _L	P	K _f (mg/g)	n	R ²
Ni (II)	4.69	4.63	0.466	0.9961	0.021-0.300	1.29	1.622	2.487	0.9738
Ni (II) + SDS	7.16	10.8	0.279	0.9919	0.018-0.417	33.7	1.995	2.728	0.9738
Zn (II)	5.06	4.92	0.437	0.9858	0.022-0.186	2.84	2.340	3.020	0.9911
Zn (II) + SDS	10.13	9.6	0.142	0.9915	0.034-0.585	5.52	2.485	3.334	0.9832

Table. 6.2. Thermodynamics parameters for the adsorption of Zn (II) and Ni (II) in absence and presence of SDS on AMOC

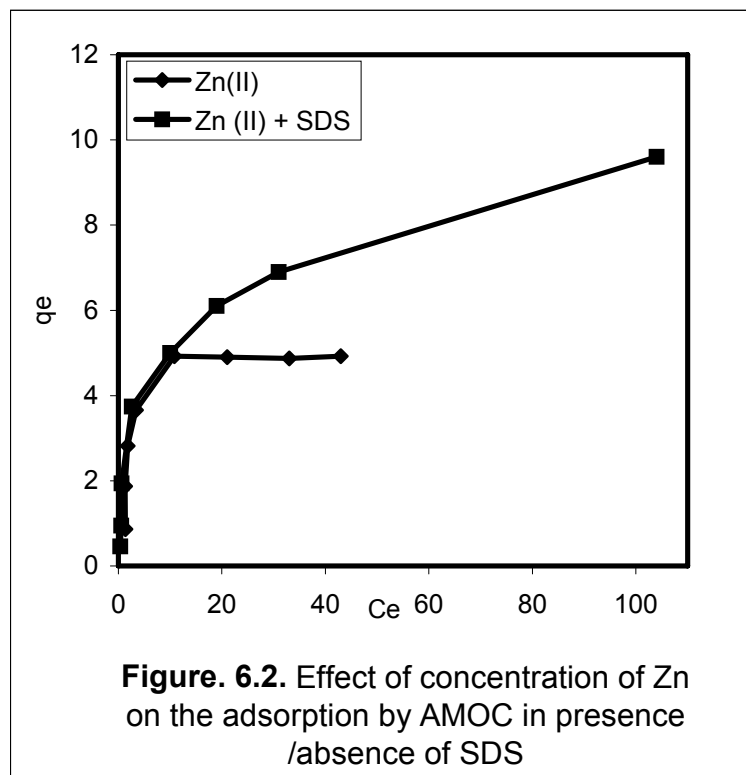
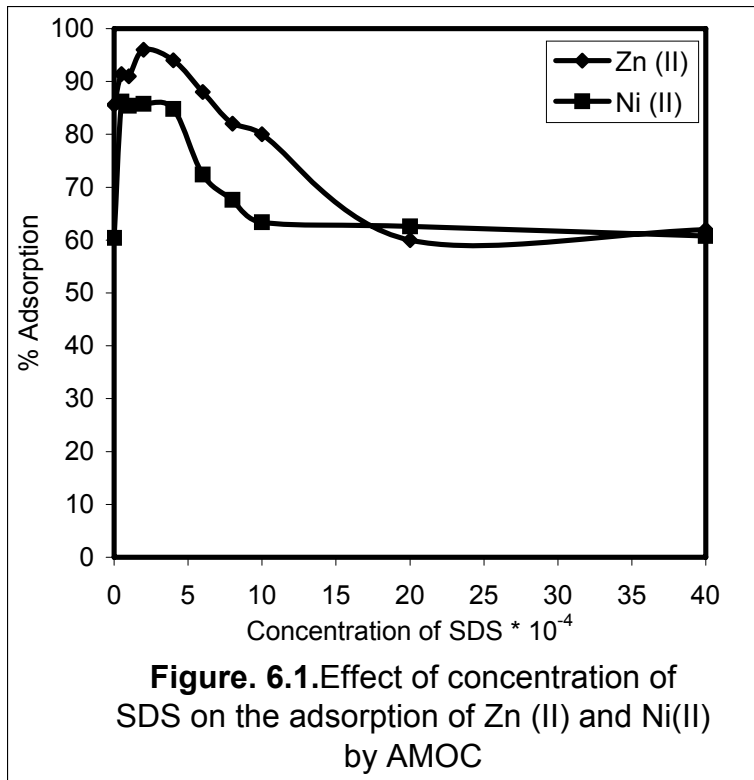
Temperature (°C)	K _c	ΔG° (KJ/ mole)	ΔS° (KJ/mole)	ΔH° (KJ/ mole-K)
Zn (II)				
25	30.25	-8.446		
45	49	-10.289	0.0944	19.708
55	61.5	-11.232		
Zn (II)+ SDS				
25	6.936	-4.799		
35	11.195	-6.184	0.2004	55.212
55	49	-10.613		
Ni (II)				
25	4.102	-3.495		
45	5.25	-4.383	0.0841	21.764
55	9.638	-6.179		
Ni (II) + SDS				
25				
35	3.630	-3.193		
55	5.024	-4.133	0.2442	70.227
	14.625	-7.316		

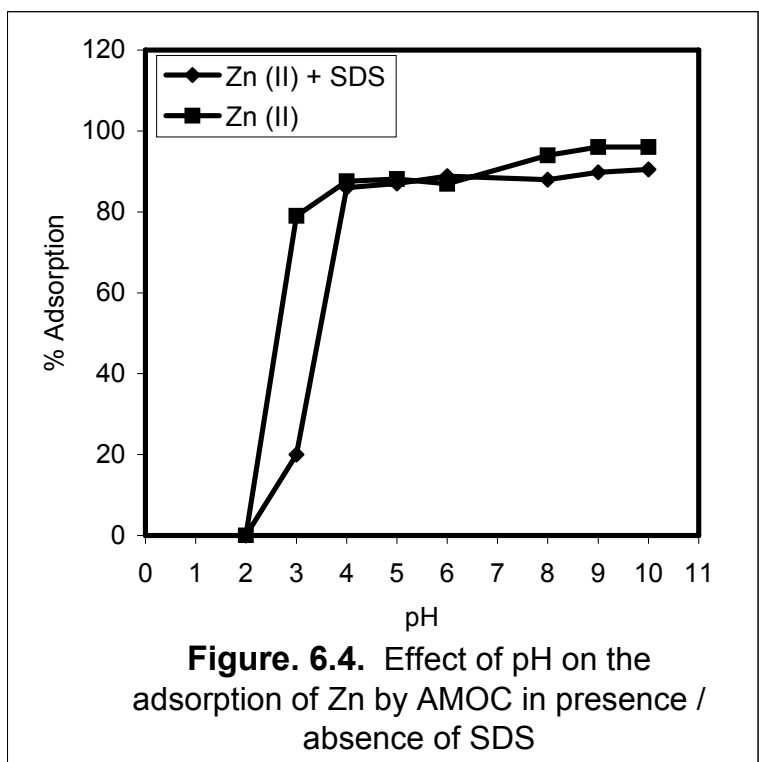
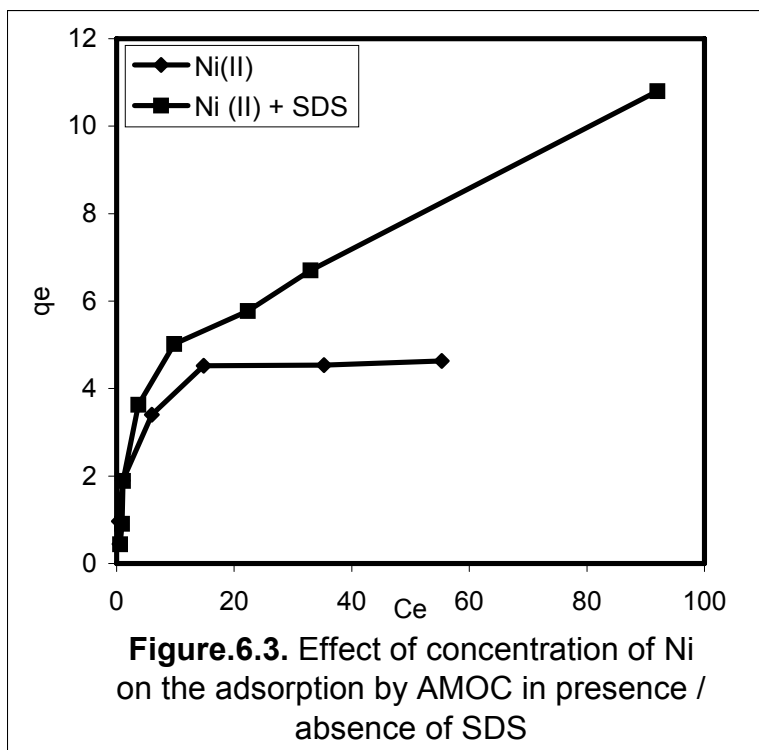
Table. 6.3. Dubinin-Radushkevsk (D-R) parameters for the adsorption of Ni (II) and Zn (II) on AMOC absence and presence SDS at 25°C

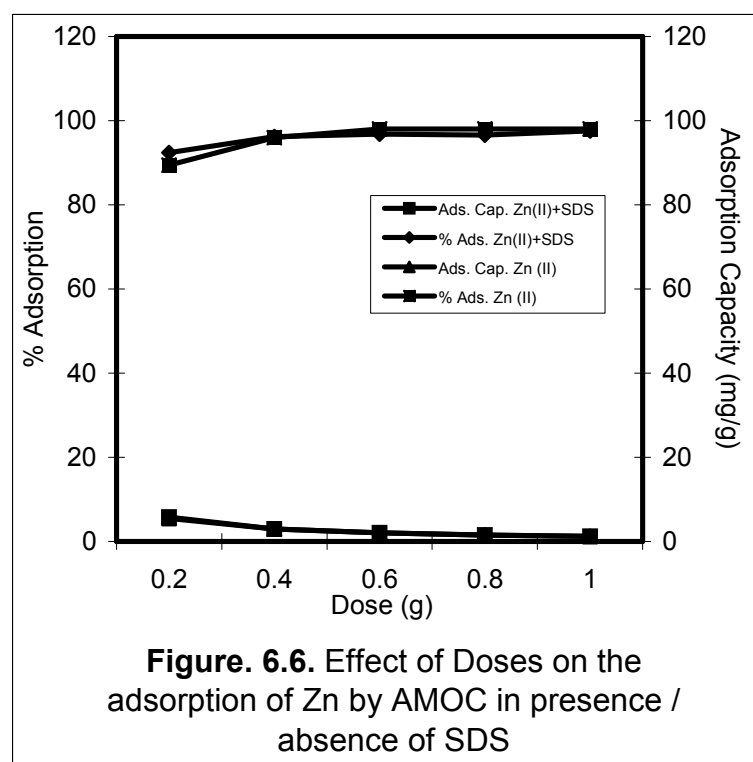
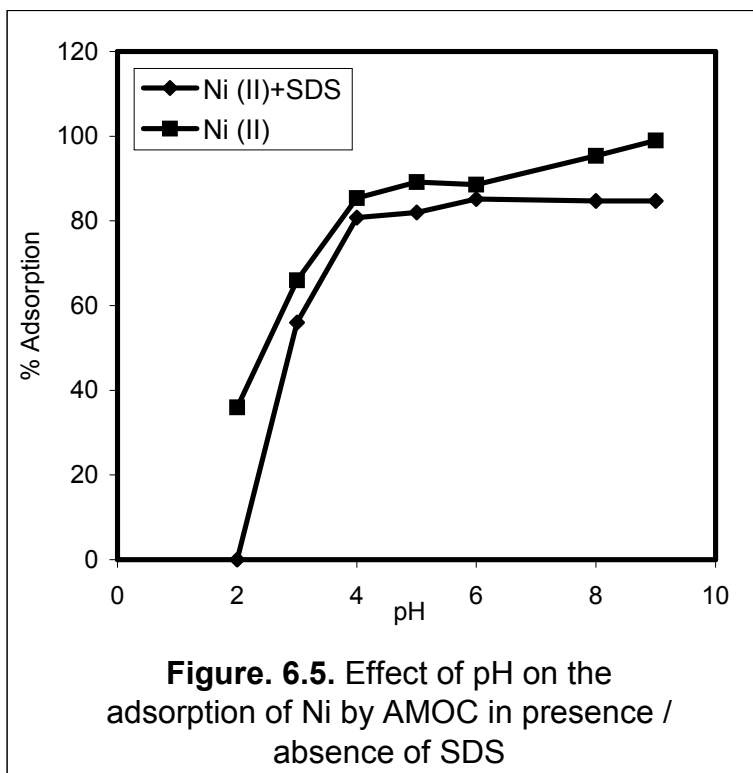
Metal ions	β (mol/ KJ) ²	ln q _m	q _m (mol/g)	E _a (KJ/mol)	R ²
Ni (II)	-0.0023	-8.5556	0.0002	14.7	0.9801
Ni (II) +SDS	-0.0032	-7.9871	0.0003	12.5	0.9956
Zn (II)	-0.0026	-8.2729	0.0002	13.8	0.9915
Zn (II) +SDS	-0.0027	-8.1406	0.0003	13.6	0.9922

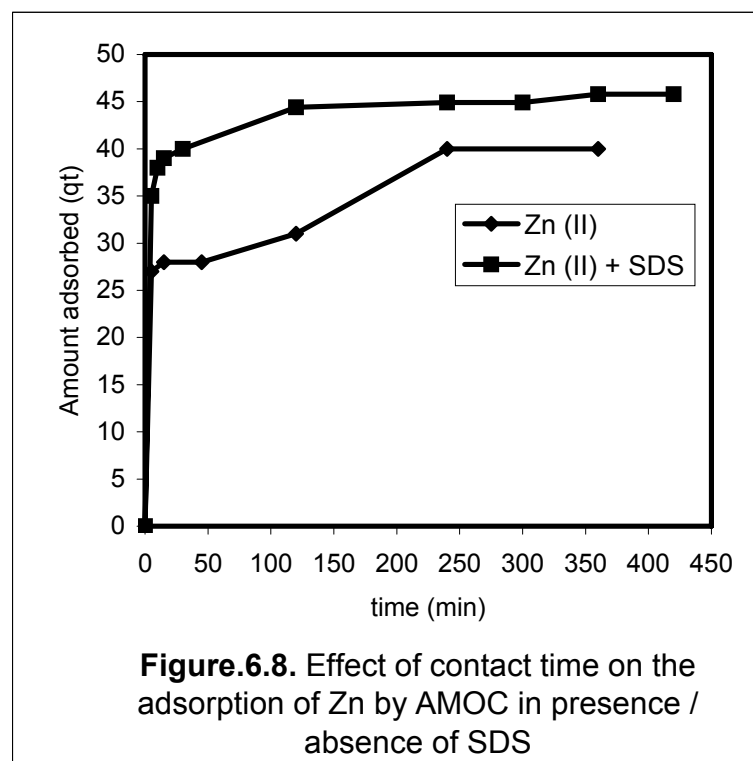
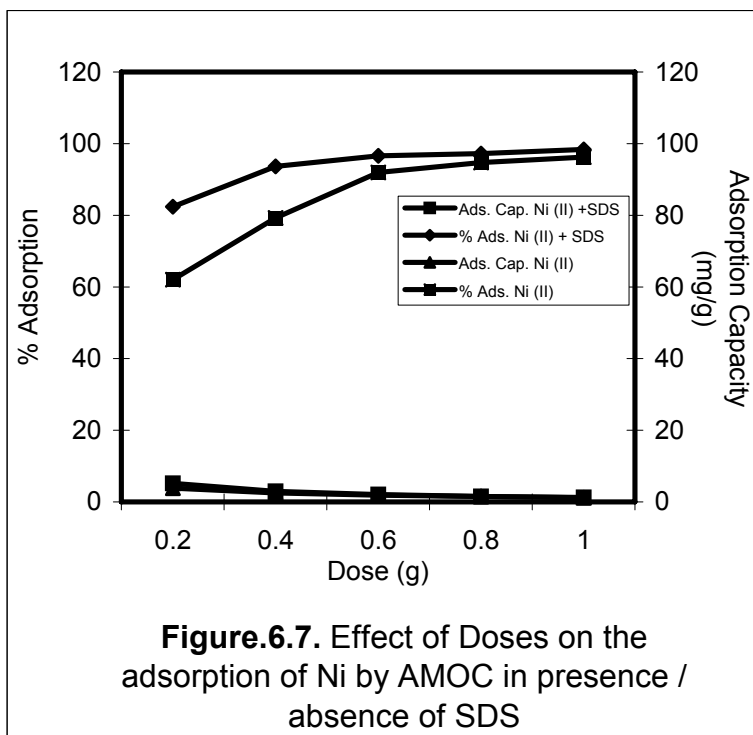
Table. 6.4. Pseudo-first order and pseudo-second order kinetics constants for the adsorption of Ni (II) and Zn (II) absence and presence SDS on AMOC

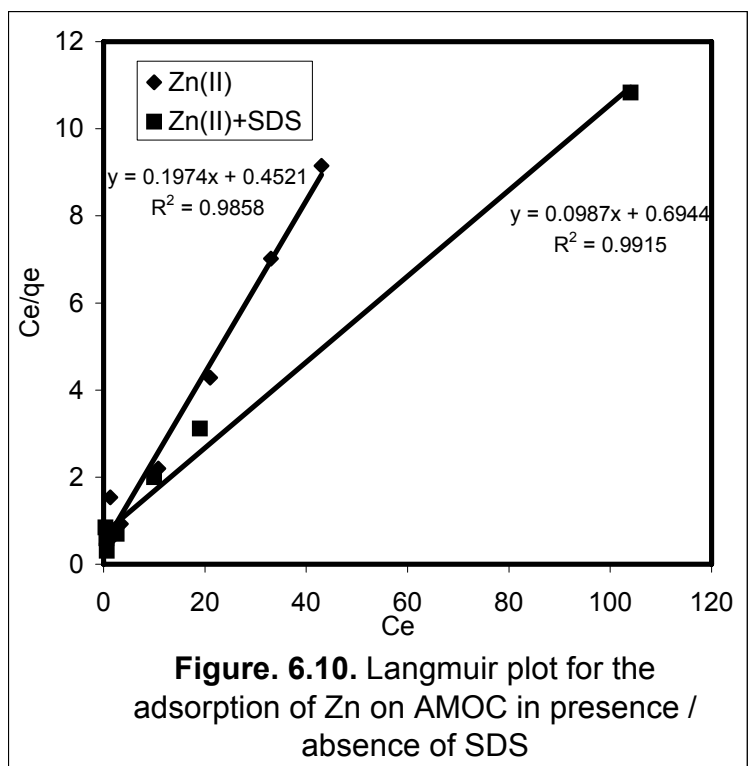
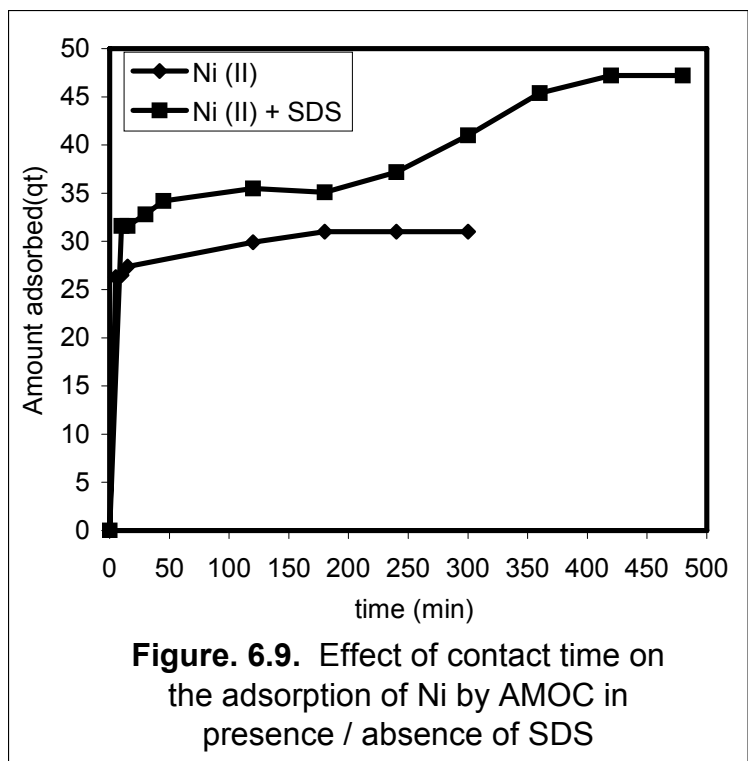
Metal ions	Pseudo-first order kinetics					Pseudo-second order kinetics				
	K ₁ (1/min)	q _e (theo) (mg/g)	q _e (exp) (mg/g)	R ²	P	K ₂ (g/mg-min)	q _e (theo) (mg/g)	q _e (exp) (mg/g)	R ²	P
Ni (II)	0.0124	4.79	31	0.9891	84.5	0.0052	31.5	31	0.9959	1.613
Ni (II) + SDS	0.0032	16.13	47.2	0.9959	65.8	0.0036	39.52	47.2	0.9925	16.27
Zn (II)	0.0212	13.70	40	0.6592	65.8	0.0490	28.73	40	0.9984	28.17
Zn(II) + SDS	0.0081	8.59	45.8	0.9585	81.2	0.0052	45.45	45.8	0.9993	0.76

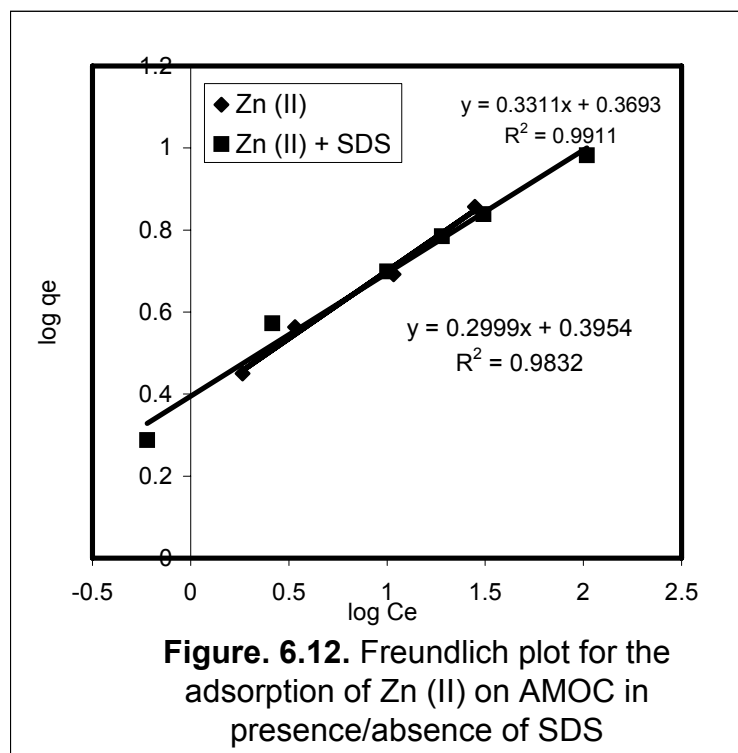
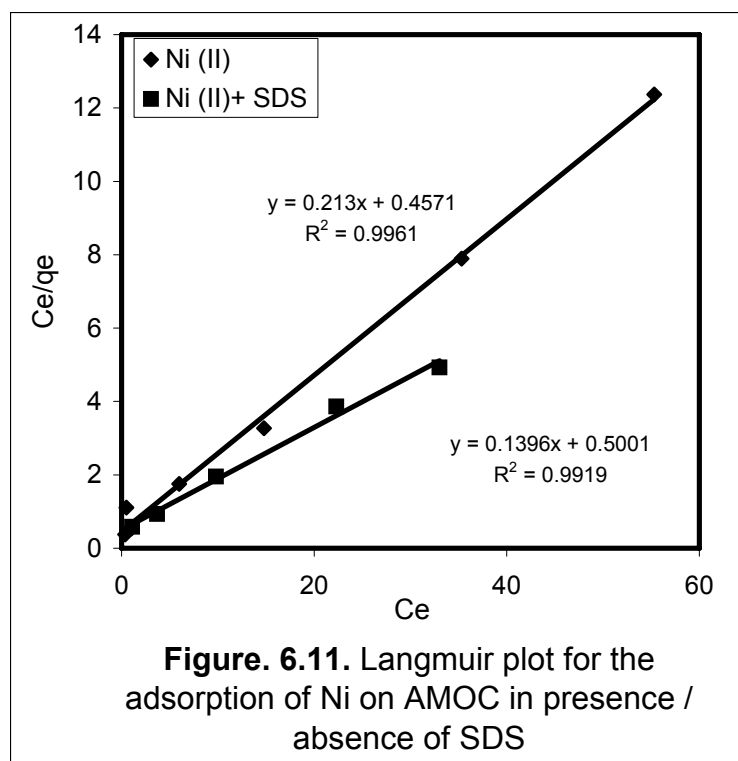


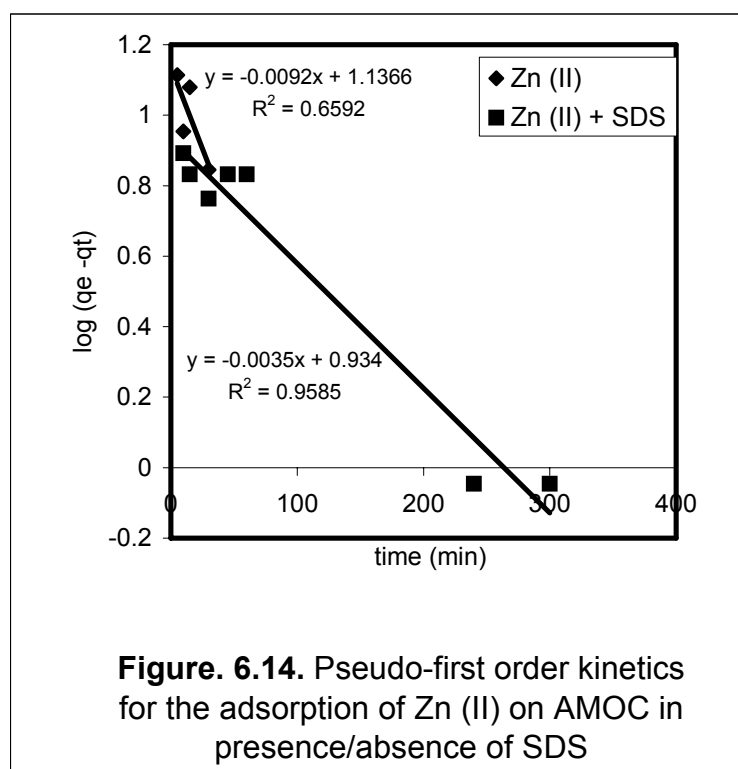
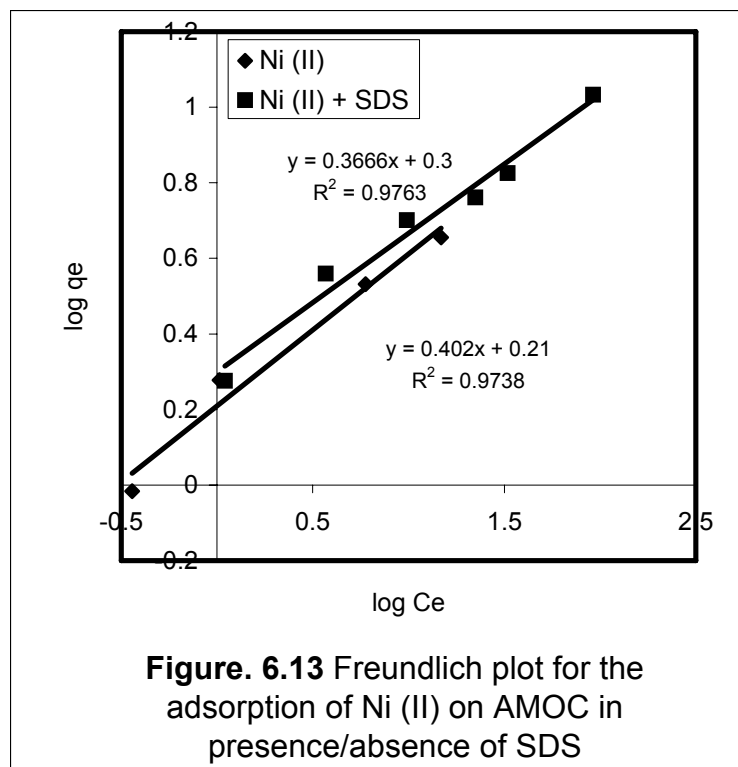


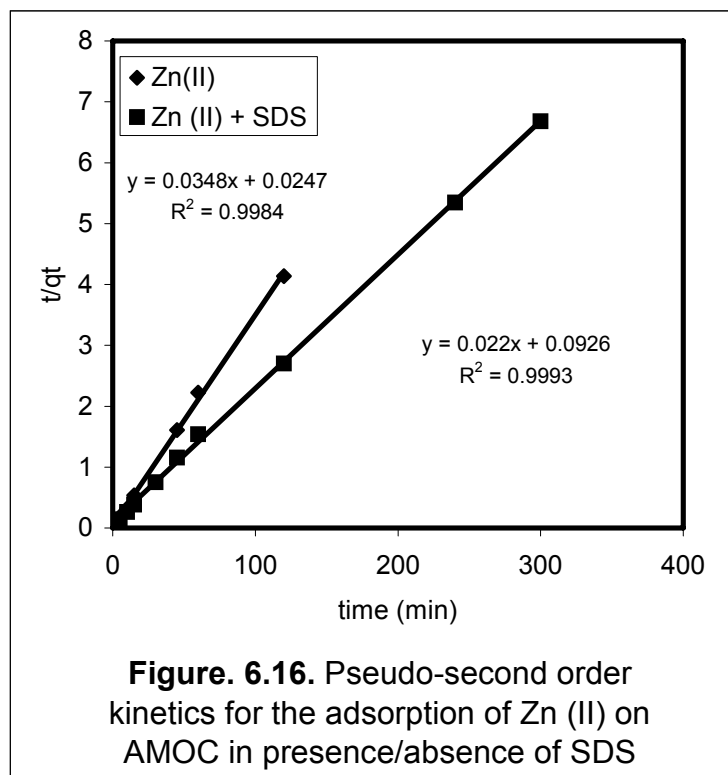
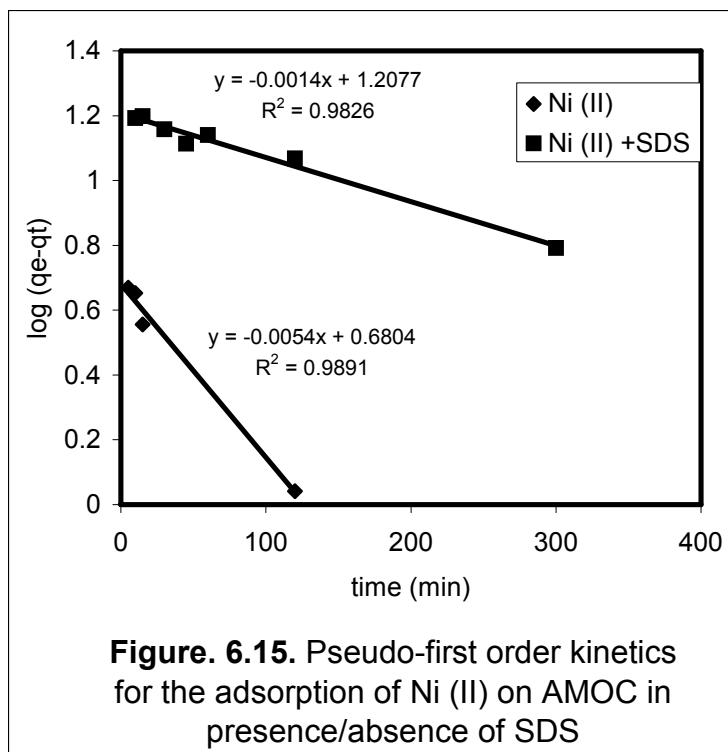












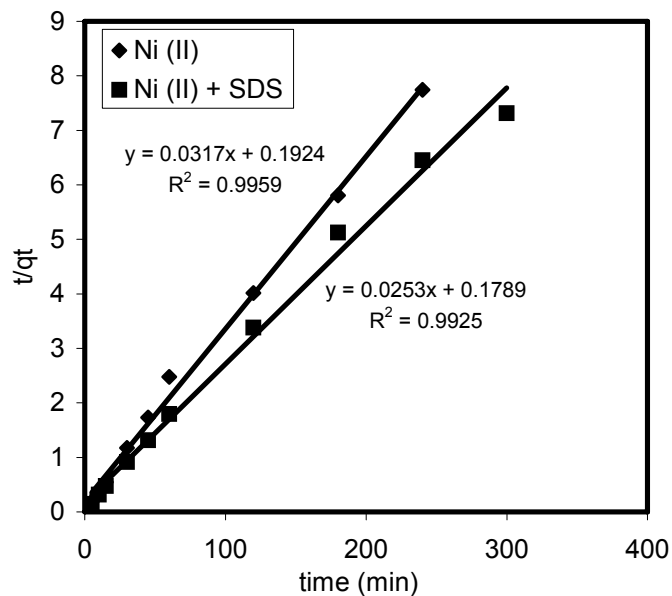


Figure. 6.17. Pseudo-second order kinetics for the adsorption of Ni (II) on AMOC in presence/absence of SDS

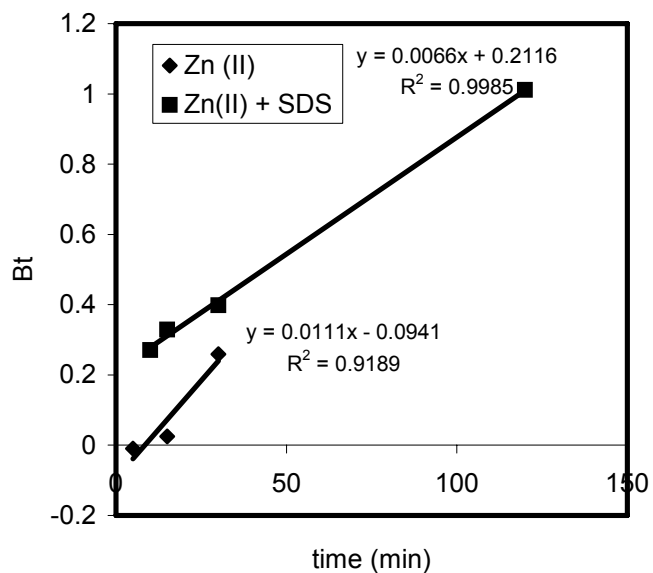


Figure. 6.18. Reichenberg plot for the adsorption of Zn (II) on AMOC in presence/absence of SDS

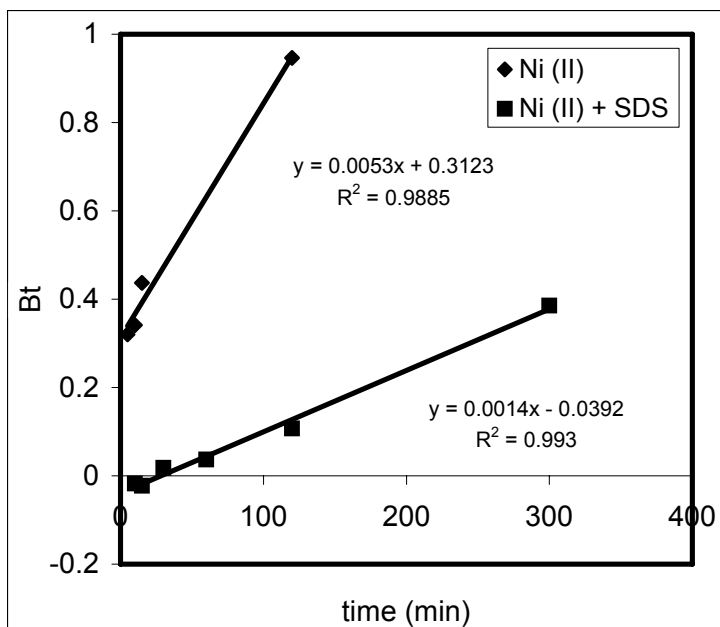


Figure. 6.19. Reichenberg plot for the adsorption of Ni (II) on AMOC in presence /absence of SDS

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Chapter – 7

Adsorption of Cu (II) on activated carbon prepared from Mustard Oil Cake (AMOC): Effect of surfactant (Sodium dodecyl sulphate) on the removal and recovery of Cu (II), Ni (II) and Zn (II) from wastewater

Water is the driver of nature

Leonardo da Vinci

7.1. Introduction:

Heavy metal ions such as Cu (II), Ni (II) and Zn (II) are detected in waste streams from mining operations, tanneries, electronics, electroplating and petrochemical industries (Patterson and Passino, 1987). Heavy metals are harmful on human physiology and other biological systems. They are non-biodegradable and tend to accumulate in the living organisms causing various diseases and disorders. Safe and effective disposal of heavy metals bearing wastewater is a difficult task due, in part, to the fact that cost effective treatment alternates are not available (Weng and Huang, 1994). Various methods exist for the removal of toxic heavy metal ions from aqueous solutions are Ion exchange, chemical precipitation, reverse osmosis, evaporation, membrane filtration etc. Though these methods are very effective for the removal of heavy metals, but the drawbacks of these methods is their high capital and operational cost or the disposal of the residual metal sludge, and are not suitable for small scale industries.

Adsorption is by far the most versatile and widely used process. Activated carbon (A.C) is one of the most common conventional adsorbent for the reclamation of municipal and industrial wastewaters for potable use since last three decades (Fornwalt and Hutchins, 1966). High surface area, micro porous character and chemical nature of activated carbon surface have made them potential adsorbents. In spite of its large use in water and waste industries, A.C is an expensive material and therefore the production of its low cost alternatives has been the focus of researchers in the area for many years. Efforts made in this direction for the removal of heavy metals from aqueous solutions including natural and industrial wastewaters are well documented (Pollard et al., 1992). Studies on the adsorption of heavy metals by activated carbons prepared from various low cost materials have been reported in the literature. These include activated carbon prepared from peat, coconut shell, coal (Paajanen et al., 1997), anthracite (Petrov, et al., 1992), hazelnut shell activated carbon (Cimino et al., 2000).

The adsorption properties of Mustard Oil Cake (MOC) for the removal of Cu (II) were studied earlier (Ajmal et al., 2005). Encouraging results have prompted us to prepare activated carbon (AC) from Mustard Oil Cake, which has been used for the removal and recovery of Cu (II), Zn (II) and Ni (II) from wastewater. Mustard Oil Cake is available in abundance in Northern India. It is a waste product obtained after the extraction of mustard oil from mustard seeds. Mustard is the major source of edible oil in this region.

The effect of Sodium dodecyl sulphate (SDS) has also been studied for the removal and recovery of these metal ions. Use of oil cakes have an upper hand over other non-conventional adsorbents as these adsorbents have low C/N ratio that is an indication of its rapid degradation (Gaur et al., 1981).

7.2. Material and Methods:

7.2.1. Adsorbent:

Mustard Oil Cake (MOC) was burnt in a furnace at 700 °C for about 15 mins in absence of air in order to remove organic matter. The activated carbon obtained by burning MOC was named as AMOC. AMOC was crushed to a desired mesh size (150-200 BSS). In order to remove dirt and dust crushed AMOC was washed several times with DDW. It was dried at 65 °C for 24 hrs in an oven.

7.2.2. Adsorbate solution:

Single component stock solutions of Cu (II), Ni (II) and Zn (II) were prepared (1000 mg/l) by dissolving the desired quantity of their nitrate salts (AR grade) in DDW. Stock solution of anionic surfactant (0.1M) Sodium dodecyl sulfate (SDS) ($C_{12}H_{25}OSO_3Na$) was prepared by dissolving the desired quantity of SDS (AR grade) in DDW.

7.2.3. Adsorption and Desorption studies:

Adsorption studies were carried out by batch process. 0.25 g adsorbent was placed in conical flask with 25 ml solution of metal ion of desired concentration. The mixture was shaken in temperature controlled shaker incubator for 24 hrs at 120 rpm. The mixture was then filtered using Whatman filter paper number- 41 and final concentration of metal ion was determined in the filtrate by AAS (GBC 902). The instrument was calibrated with standard Cu (II), Ni (II) and Zn (II) solutions under the following specifications.

Metal	– Cu (II)
Wave length	– 324.7 nm
Slit width	– 0.5 nm
Lamp current	– 3 mA
Flame	– Air – acetylene (Oxidising)
Mode	– Double beam

Metal – Ni (II)
Wave length – 341.5 nm
Slit width – 0.2 nm
Lamp current – 4 mA
Flame – Air – acetylene (Oxidising)
Mode – Double beam

Metal – Zn (II)
Wave length – 213.9 nm
Slit width – 0.5 nm
Lamp current – 5 mA
Flame – Air – acetylene (Oxidising)
Mode – Double beam (with background correction)

The % removal of adsorbate and equilibrium adsorption capacity (q_e), were calculated using the following relationships.

$$\% \text{ Removal} = [(C_o - C_e) / C_o] * 100 \quad (1)$$

$$\text{Adsorption Capacity } (q_e)(\text{mg/g}) = [(C_o - C_e)] * V / W \quad (2)$$

Desorption studies were carried out by batch process. 50ml solution of Ni (II), Zn (II) and Cu (II) each of 50 mg/l concentration in presence and absence of SDS (2 mM) was treated separately with 0.5g of adsorbent in temperature controlled shaker incubator at 120 rpm for 24 hrs. The adsorbent in each flask was washed several times with DDW to remove excess of metal ions. The adsorbent after washing was treated with 50 ml of water and kept for 24 hrs. It was then analysed for any leaching of metal ions. The adsorbent in other flasks were treated with 50 ml of various eluents. The flasks were shaken in temperature controlled shaker incubator at 120 rpm for 24 hrs. The solutions were then filtered by using Whatman filter paper number- 41. The filtrates were analysed for metals desorbed.

7.2,4. Effect of pH:

The effect of pH for the adsorption of Cu (II) on AMOC was studied by batch process as follows: 50ml of Cu (II) solution (50 mg/l initial concentration) was taken in a beaker. The pH of solution was adjusted by adding dilute solution of HCl and NaOH. The concentration of metal ions in this solution was then determined (initial concentration). 25 ml of this solution was taken in conical flask and treated with 0.25 g adsorbent and after equilibrium, the final concentration of metal ions was determined.

7.2,5. Effect of contact time:

A series of 100 ml conical flasks, each having 0.25 g adsorbent and 25 ml solution of 50 mg/l initial concentration of Cu (II) were shaken in temperature controlled shaker incubator at 120 rpm and at the predetermined intervals, the solution of the specified flask was taken out and filtered. The concentration of metal ions in the filtrate was determined by AAS. The amount of metal adsorbed in each case was then determined.

7.2,6. Effect of adsorbent dose:

A series of 100 ml conical flasks each containing 25 ml of Cu (II) solution (50mg/l) were treated with varying amount of adsorbent (0.1-1.0 g). The flasks were shaken in shaker incubator at 120 rpm and after equilibrium the solutions were filtered. The amount of metal ions in filtrate was then determined by AAS. The amount of metal adsorbed in each case was then calculated.

7.3. Result and Discussions:

Adsorption of Cu (II) Zn (II) and Ni (II) on AMOC are shown in **Table. 7.1**. The adsorption follows the order Cu (II)> Zn (II)> Ni (II). The percentage adsorption of Ni (II) and Zn (II) increases by adding SDS below critical micelle concentration (2mM). While adsorption of Cu (II) decreases slightly in presence of SDS below critical micelle concentration (2mM).

7.3,1. Effect of pH:

The effect of pH on the adsorption of Cu (II) on AMOC is presented in **Figure.7. 1**. The percentage adsorption varies from 23.4% to 93%. When pH is increased from 1 to 6 at 50 mg/l initial Cu (II) concentration, the maximum percentage adsorption is observed at pH 6. At this pH, there are two species of Cu (II) present in the solution Cu (II) (large quantity) and Cu OH (small quantity) (Ajmal et al., 1998). Therefore at pH.6, Cu (II) ions are predominantly adsorbed since Cu (II) ions are present in large quantity at this pH. The percentage adsorption increases slowly with increasing pH and becomes almost constant above pH 6 due to precipitation of Cu (II) as Cu (OH)₂.

7.3,2. Effect of adsorbent doses:

The adsorption capacity (mg/g) and percentage adsorption of Cu (II) by varying the dose of AMOC is shown in **Figure. 7.2**.The percentage adsorption increases while adsorption capacity decreases as the dose of AMOC is increased. It may be concluded that by increasing the adsorbent dose, the removal efficiency of AMOC increases. The decrease in adsorption capacity may be due to the fact that some adsorption sites may remain unsaturated during the adsorption process where as the number of sites available for adsorption increases by increasing the adsorbent doses and that results in the increase in removal efficiency (Sharma and Foster, 1993).

7.3.3. Adsorption isotherms:

Adsorption data for wide range of adsorbate concentration are described by Langmuir and Freundlich isotherms.

The Langmuir equation is:

$$C_e/q_e = 1/b.q_m + 1/q_m \cdot C_e \quad \text{_____}(3)$$

The values of Langmuir constants b and q_m were calculated from the slope and intercept of the linear plot of C_e/q_e vs C_e (**Figure. 7.3**). The coefficient b in Langmuir equation is a measure of the stability of the complex formed between metal ions and adsorbent under specified experimental conditions (Sharma and Foster, 1993). It was found that experimental values of q_m (exp) were differed appreciably. Also the values of regression coefficient R^2 is very low (**Table. 7.2**). This indicates that Langmuir model is not obeyed by the system.

Freundlich isotherm is given by equation:

$$\log q_e = \log K_f + 1/n \log C_e \quad \text{_____}(4)$$

The values of K_f and n were calculated from the intercept and slope of the Freundlich plots (**Figure. 7.4**) are shown in **Table. 7.2**. K_f indicates the adsorption capacity of adsorbent. The constant n is a measure of deviation from linearity of the adsorption. It can be concluded from the data that Freundlich model is better obeyed for the adsorption of Cu (II) on AMOC.

7.3.5. Thermodynamics studies:

The thermodynamics parameters like ΔH° and ΔS° were obtained from the Van't Hoff equation.

$$\log K_c = \Delta S^\circ / 2.303 R - \Delta H^\circ / 2.303 RT \quad \text{_____}(5)$$

Where, ΔS° and ΔH° were calculated from the slope and intercept of linear plots of $\log K_c$ vs $1/T$ for Cu (II). Equilibrium constant (K_c) was calculated from the following relationship (Namasivayam and Ranganathan, 1995)

$$K_c = C_{Ae} / C_e \quad \text{_____} \quad (6)$$

ΔG° was calculated from the relation

$$\Delta G^\circ = -RT \ln K_c \quad \text{_____} \quad (7)$$

The positive values of ΔH° (**Table. 7.3**) suggest endothermic nature of adsorption. The increase in adsorption of Cu (II) with increase in temperature might have been due to dissolution of the adsorbing species, change in the pore size and enhanced rate of intraparticle diffusion (Ayranci and Duman, 2005). The values of ΔG° decreases with increase in temperature, which indicates that the process is spontaneous. The positive value of ΔS° shows the increase in randomness at the solid / solution interface during the adsorption of Cu (II) on AMOC (Ajmal et al., 2005)

7.3.6. Kinetics of Adsorption:

The rate constants were calculated by pseudo-first-order and pseudo-second-order models (Banat et al., 2005). The pseudo-first-order kinetics model as expressed by Lagergren is given as:

$$\log (q_e - q_t) = \log q_e - K_1 / 2.303 * t \quad \text{_____} \quad (11)$$

The values of rate constant K_1 was calculated from slope of the linear plot of $\log (q_e - q_t)$ vs t (**Figure. 7.5**). The values of regression coefficient (R^2) and rate constant (K_1) are reported in **Table. 7.4**.

The Pseudo-second-order kinetics rate expression is given as:

$$t / q_t = 1 / K_2 q_e + 1 / q_e * t \quad (12)$$

The values of rate constant K_2 were calculated from the slope of the linear plot of t/q_t vs t (**Figure 7. 6**) and are reported in **Table. 7.4**.

The values q_e (theo) and q_e (exp) for pseudo-first-order kinetics model differed appreciably. For pseudo-second-order kinetics model values of q_e (theo) and q_e (exp) are found to be very close. The value of correlation coefficients (R^2) is higher as compared to pseudo-first-order model. It is therefore confirmed the adsorption of Cu (II) on AMOC follows pseudo-second-order rate equation.

The nature of adsorption was also verified using Reichenberg equation (Reichenberg, D., 1953)

$$F = 1 - 6 / \pi^2 e^{-\beta t} \quad (13)$$

The nature of βt is a mathematical function of R and can be calculated as:

$$\beta t = -0.4977 - \ln (1-F) \quad (14)$$

Where, $F = q_t / q_e \quad (15)$

The plot of βt vs t for the adsorption of Cu (II) on AMOC is linear (**Figure. 7. 7**) and does not pass through the origin indicating that pore diffusion is not the only rate limiting step but other process like film diffusion may be also involved.

7.3.7. Desorption studies:

In order to make the process economically feasible, it is important to desorb and regenerate the spent adsorbent. The desorption studies were carried out by batch

process using HCl, KCl, NaOH, NaCl and H₂O solutions of different concentration as eluents. The results are reported in **Table. 7.5**. Desorption of Ni (II), Zn (II) and Cu (II) in presence and absence of SDS by water is almost negligible. The percentage recovery of Ni (II), Zn (II), Cu (II) in presence and absence of SDS is approximately 10 -12 % when different concentrations of KCl, NaOH and NaCl are used as eluents showing strong adsorption on AMOC. This is important because metal ions adsorbed by AMOC will not be desorbed by KCl, NaOH, and NaCl if AMOC is used to sequester metal ions in soil since appreciable amount of these salts is usually present in the soil. The percentage recovery of Cu (II) by 0.1M HCl solution in presence of SDS is very high (80.49 %). The recovery of Ni (II) by 0.1 M HCl in presence of SDS is 78.97 %. While the recovery of Zn (II) is 75 % by 0.1 M HCl in absence of SDS. Lowering the concentration of HCl to 0.05 M has no effect on the recovery of Ni (II) and Zn (II) in presence and absence of SDS from AMOC (**Table. 7.5**). The desorption of metal ions with acidic solution indicates that adsorption is via ion exchange process.

7.4. Conclusions:

Activated carbon (AC) prepared from Mustard Oil Cake (MOC) is an effective adsorbent for the removal and recovery of Cu (II), Ni (II) and Zn (II). Uptake of Ni (II) and Zn (II) increases by 5.54 % and 16.67 % respectively in presence of SDS. While the uptake of Cu (II) decreases slightly (8.89%) in presence of SDS. Cu (II), Ni (II) and Zn (II) are not eluted with water as well as SDS. The recovery of Cu (II) is excellent (80%) when 0.1 M HCl is used in presence of SDS followed by Ni (78.97%). Adsorption of Zn (II) is strong in presence of SDS hence its recovery is poor (41 %). However 75 % of Zn (II) can be recovered when 0.1M HCl is used in absence of SDS.

Table. 7.1. Adsorption of metal ions in presence and absence of SDS on AMOC

Metal ions	Concentration of Metal ions (mg/l)	% Adsorption in absence of SDS	% Adsorption in presence of SDS
Zn (II)	50	80	96
Ni (II)	50	78.8	83.6
Cu (II)	50	90	82

Table. 7.2. Langmuir and Freundlich constants for the adsorption of Cu (II) on AMOC

Langmuir constants				Freundlich constants		
q_m (theo) (mg/g)	q_m (exp) (mg/g)	b (l/mg)	R^2	K_f (mg/g)	n	R^2
33.11	7.3	0.0099	0.629	0.064	0.684	0.9961

Table. 7.3. Thermodynamics Parameters for the adsorption of Cu (II) on AMOC

Temperature (°C)	Kc	ΔG° (KJ/ mole)	ΔS° (KJ/mole-K)	ΔH° (KJ/mole)
25	18.23	-7.192		
45	40.67	-9.795	0.111	25.9
55	44.45	-10.346		

Table. 7.4. Pseudo-first order and Pseudo-second order kinetics constants for the adsorption of Cu (II) on AMOC

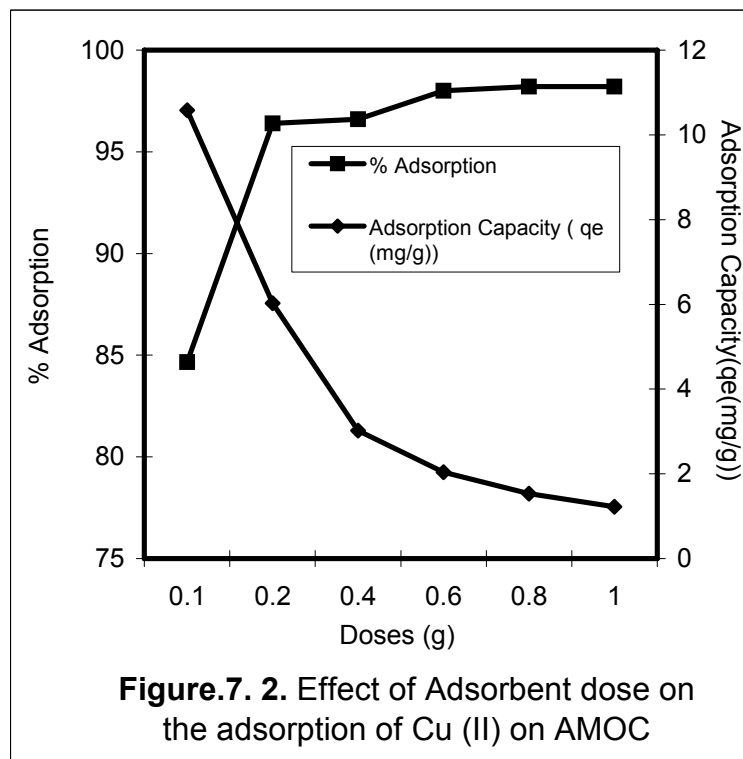
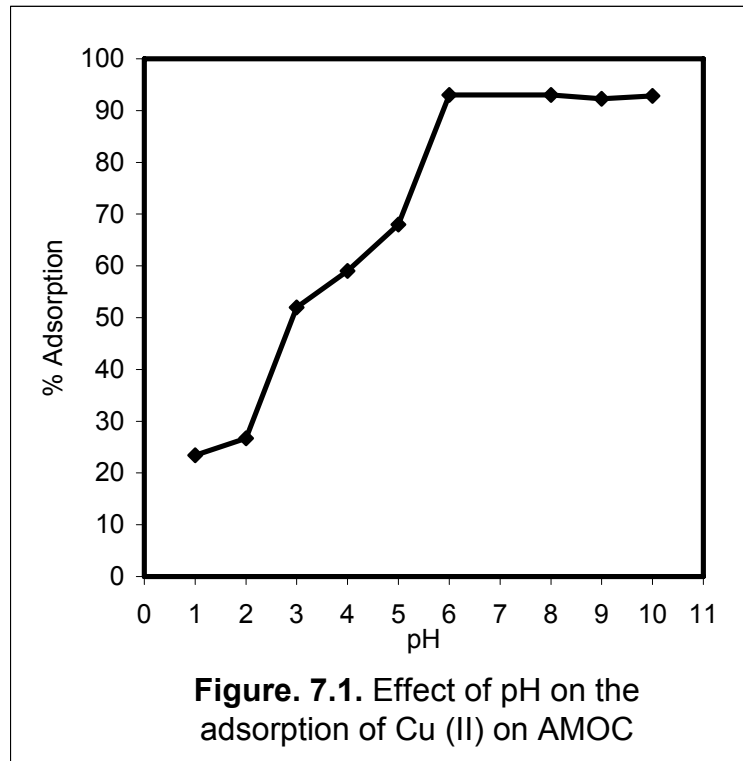
Pseudo-first order kinetics					Pseudo-second order kinetics				
K_1 (1/min)	q_e (theo) (mg/g)	q_e (exp) (mg/g)	R^2	P	K_2 (g/mg- min)	q_e (theo) (mg/g)	q_e (exp) (mg/ g)	R^2	P
0.0212	8.203	45	0.9964	81.8	0.0091	41.32	45	0.9994	8.18

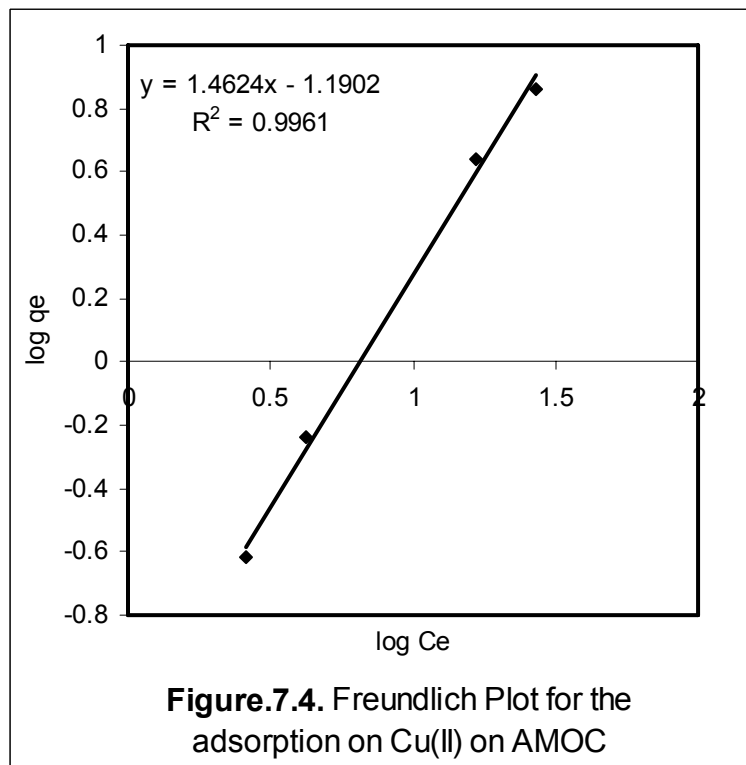
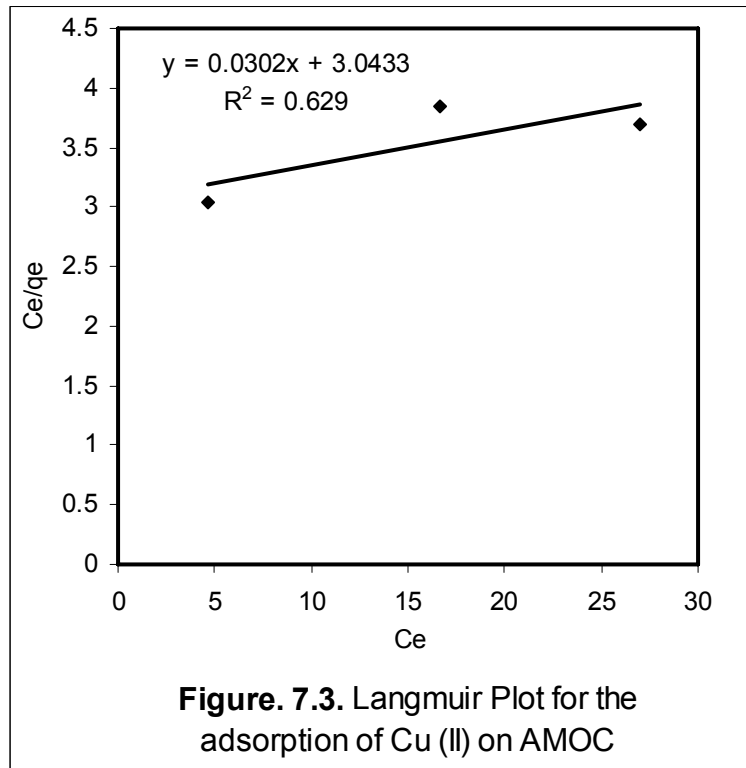
Table. 7.5. Recovery of Ni (II), Zn (II) Cu (II) with and without SDS from AMOC by batch process

Eluents used	Metal ions	Amount loaded (mg)	Amount adsorbed (mg)	%Adsorption	Amount recovered (mg)	%Recovery
H₂O	Ni (II)	2.5	1.97	78.8	0.015	0.75
	Ni (II)	2.5	2.09	83.6	0	0
	+ SDS					
	Zn (II)	2.5	2	80	0.02	0.88
	Zn (II)	2.5	2.4	96	0.01	0.42
	+ SDS					
	Cu (II)	2.5	2.25	90	0.02	0.88
0.1M HCl	Cu (II)	2.5	2.05	82	0.03	1.46
	+ SDS					
	Ni (II)	2.5	1.97	78.8	1.3	65.9
	Ni (II)	2.5	2.09	83.6	1.65	78.97
	+ SDS					
	Zn (II)	2.5	2	80	1.5	75
	Zn (II)	2.5	2.4	96	1	41.67
0.05 M HCl	+ SDS					
	Cu (II)	2.5	2.25	90	1.35	60
	Cu (II)	2.5	2.05	82	1.65	80.49
	+ SDS					
	Ni (II)	2.5	1.97	78.8	1.3	65.9
	Ni (II)	2.5	2.09	83.6	1.55	74.16
	+ SDS					
0.05 M KCl	Zn (II)	2.5	2	80	1.5	75
	Zn (II)	2.5	2.4	96	1	41.67
	+ SDS					
	Cu (II)	2.5	2.25	90	1.05	46.7
	Cu (II)	2.5	2.05	82	1.15	56.1
	+ SDS					
	Ni (II)	2.5	1.97	78.8	0.14	7.11
	Ni (II)	2.5	2.09	83.6	0.125	5.98
	+ SDS					
	Zn (II)	2.5	2	80	0.05	2.5
	Zn (II)	2.5	2.4	96	0.04	1.67
	+ SDS					
	Cu (II)	2.5	2.25	90	0.05	2.22
	Cu (II)	2.5	2.05	82	0.045	2.19
	+ SDS					

Contd.

Solvents	Metal ions	Amount loaded (mg)	Amount adsorbed (mg)	%Adsorption	Amount recovered (mg)	%Recovery
0.1M KCl	Ni (II)	2.5	1.97	78.8	0.17	8.63
	Ni (II) + SDS	2.5	2.09	83.6	0.17	8.63
	Zn (II)	2.5	2	80	0.1	5
	Zn (II) + SDS	2.5	2.4	96	0.05	2.08
	Cu (II)	2.5	2.25	90	0.055	2.44
	Cu (II) + SDS	2.5	2.05	82	0.055	2.68
0.05M NaOH	Ni (II)	2.5	1.97	78.8	0	0
	Ni (II) + SDS	2.5	2.09	83.6	0	0
	Zn (II)	2.5	2	80	0.25	12.5
	Zn (II) + SDS	2.5	2.4	96	0.1	4.17
	Cu (II)	2.5	2.25	90	0.06	2.67
	Cu (II) + SDS	2.5	2.05	82	0.1	4.88
0.1M NaCl	Ni (II)	2.5	1.97	78.8	0.135	6.85
	Ni (II) + SDS	2.5	2.09	83.6	0.14	6.7
	Zn (II)	2.5	2	80	0.05	2.5
	Zn (II) + SDS	2.5	2.4	96	0.04	1.67
	Cu (II)	2.5	2.25	90	0.075	3.33
	Cu (II) + SDS	2.5	2.05	82	0.08	3.9





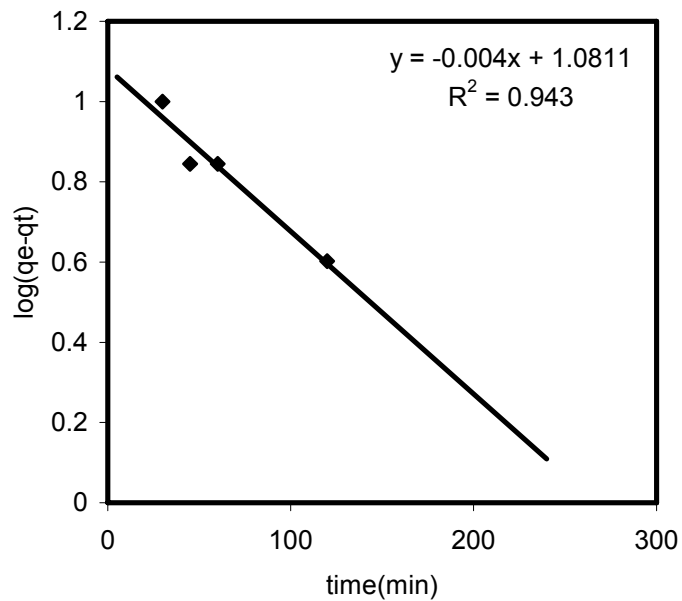


Figure. 7.5. Pseudo-first order Kinetics for the adsorption of Cu(II) on AMOC

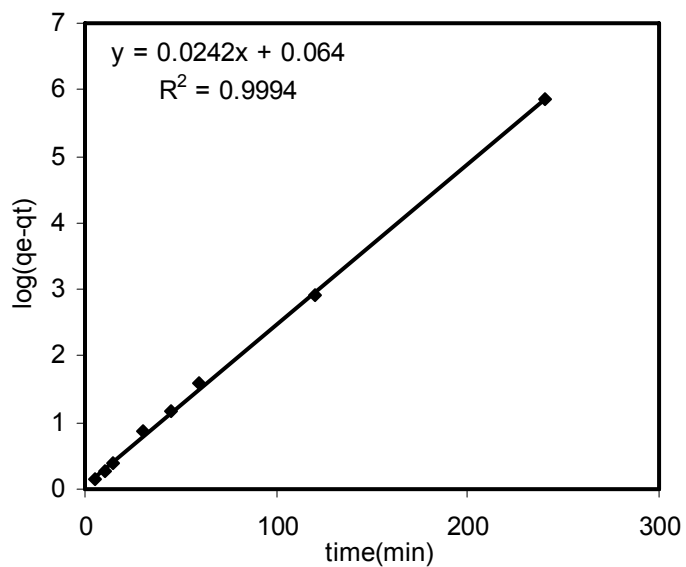
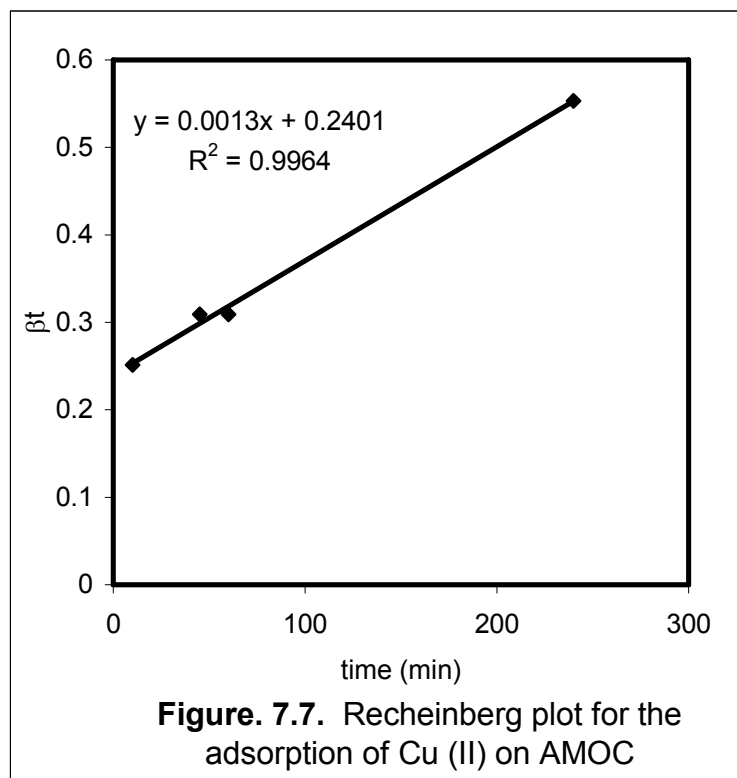


Figure. 7.6. Pseudo-second order kinetics for the adsorption of Cu(II) on AMOC



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Chapter – 8

Adsorption of some toxic organic pollutants on natural minerals. A comparative study with activated carbon. Removal and recovery of β -Naphthol from aqueous solution

*So let's leave some blue up above us
Let's leave some green on the ground
It's only ours to borrow, let's save some for tomorrow
Leave it and pass it on down*

Song Lyric by Alabama

8.1. Introduction:

Detection, determination and removal of organic pollutants from contaminated ground and surface water have recently created a growing interest. Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) were the methods used earlier to quantify organic pollutants in water but they failed to quantify the organic compounds when present in traces. The development of new analytical techniques like High Performance Liquid Chromatography (HPLC) and Gas Liquid Chromatography (GLC) have contributed largely to the identification and quantification of various organic compounds present in water and has led to the discovery of certain organic pollutants, which despite their low concentration cause damaging effect.

Increasing interest is taking place at present in developing and implementing various techniques for the removal of individual organic compounds from aqueous solution. A number of methods have been applied for the purification of water contaminated by organics often with limited success such as aeration, biological degradation, coagulation, electrochemical treatment, oxidation and photocatalytic decomposition (Fuqiang et al., 2004).

Adsorption is simple and relatively economical method, which is widely used in the removal of individual organic pollutants from wastewater. Commercially available activated carbons possess high adsorption efficiency owing to their high surface area and well defined microporous structure but they are expensive and their use requires elaborate regeneration and reactivation procedures. The gradual loss of activated carbon during regeneration can affect the economic viability of the process. Synthetic adsorbents are also relatively expensive hence, the use of natural adsorbents in an active research area has an upper hand. Natural adsorbents like montmorillonite, clinoptilolite and hydrotalcite have recently been used for the removal of phenol from aqueous solution (Yapar and Yilmaz, 2004). Phenols and its derivatives belong to a

group of common environmental contaminants. They are very toxic, and many are known or suspected human carcinogens (USEPA, 1988; Slein and Sansone, 1980; USEPA, 1990). Excessive intake of phenols for long term may lead to loss of appetite, headache, rapid fatigue and severe chronic insomnia in human beings. Phenolic compounds are present in waste effluents discharged from paint, solvent, petroleum, petrochemical, pharmaceutical, plastic, pesticide, iron and steel, paper and pulp industries. Large scale gasification and carbonisation plants generate huge quantities of high strength phenolic wastewater (Dutta, et al., 1998). World Health Organization (WHO) recommends the permissible phenolic concentration of 0.001 mg/l in potable water (WHO, 1963).

In earlier work, the adsorption behavior of some aromatic amines on pyrolusite (Rao et al., 2001) have been reported. The use of kyanite for the removal and recovery of heavy metals from electroplating wastewater have been reported (Ajmal et al., 2001). In this work, the adsorption behaviour of Phenol, Chlorophenol and β -Naphthol on kyanite and pyrolusite have been reported and compared it with activated carbon. Adsorption of β -Naphthol is considerable hence it has been chosen for detailed study.

8.2. Material and methods:

8.2,1. Adsorbents:

Pyrolusite, Kyanite and Activated Carbon were used as adsorbents. The adsorbents were crushed and sieved to a desired particle size (50 -100 BSS), washed several times with DDW in order to remove dirt and finally dried in an oven at 60°C for 24 hrs.

8.2,2. Reagents and samples:

Stock solution of Chlorophenol, Phenol and β - Naphthol (1000 mg/l) (AR Grade) were prepared in methanol (HPLC grade). All other reagents and solvents used were also of HPLC grade.

8.2,3. Apparatus:

The samples were analyzed by HPLC equipped with Shimadzu spectrophotometric detector model SPD 6AV, pump LC 6A and system controller SCL 6B. Peak area and retention time was calculated with Shimadzu chromatopack C-R6A data processor (Shimadzu Scientific Instrument Inc. Japan).

The samples and reagents used were filtered and degasified in an ultrasonic shaker (Elma, Germany) for 10 mins.

8.2,4. Sample analysis:

The analysis of Chlorophenol, Phenol and β - Naphthol was carried out on 0.6 Φ X 15 cm shimpack CLC ODS (Shimadzu, Japan) column at ambient temperature. Using methanol (HPLC grade) and 0.1 M NaClO₄ mixture (80:20) as mobile phase with flow rate of 0.5 ml/min. Samples were injected through a micro syringe (20 μ l capacity) in the sample loop (200 μ l). The effluents were monitored at 270 nm (Phenol), 274 nm

(Chlorophenol) and 256 nm (β - Naphthol) by Ultra Violet (U.V) Detector. Calibration curves for each compound were drawn by plotting peak area vs concentration (μg).

8.2,5. Adsorption Studies:

Adsorption studies were carried out by batch process. 0.5 g of adsorbent with 50 ml of adsorbate of desired concentration was shaken in a temperature controlled shaker incubator at 150 rpm for 24 hrs. The mixture was then filtered (Whatman No.41 filter paper) and final concentration of adsorbate in the filtrate was determined by HPLC.

The % removal of adsorbate and equilibrium adsorption capacity (q_e), were calculated using the following relationships

$$\% \text{ Removal} = [(C_o - C_e) / C_o] * 100 \quad \text{_____} \quad (1)$$

$$\text{Adsorption Capacity } (q_e) \text{ (mg/g)} = [(C_o - C_e)] * V / W \quad \text{___} \quad (2)$$

8.2,6. Effect of pH:

The effect of pH on the adsorption of β - Naphthol was studied as described in chapter-2.

8.2,7. Desorption Studies:

Batch process was used for desorption. 0.5 g of adsorbent with 50 ml adsorbate of desired concentration was shaken in shaker incubator at 150 rpm. The unadsorbed adsorbate in the filtrate was determined by HPLC. The adsorbent was washed several times with DDW. It was then transferred to another stopper cork flask and was treated with 50 ml solvent for 24 hrs in shaker at 150 rpm. The desorbed matter was then determined by HPLC.

8.3. Results and Discussion:

The adsorption of Phenol, Chlorophenol and β -Naphthol (initial concentration 50 mg/l) on pyrolusite, kyanite and activated carbon is given in **Table. 8.1**. Phenol and Chlorophenol are not adsorbed on kyanite and pyrolusite. β -Naphthol is adsorbed to some extent. The adsorption of β -Naphthol is higher on pyrolusite as compared to kyanite. Therefore, β -Naphthol is chosen for detailed study. However, all these compounds are completely adsorbed on activated carbon. Phenol, Chlorophenol and β -Naphthol are eluted with a mixture of methanol and 0.1 M NaClO_4 (80: 20). The peaks are sharp without any tailing. The chromatogram of β -Naphthol and calibration curve are shown in **Figures. 8.1** and **8.2** respectively. The calibration curve of β -Naphthol (**Figure. 8.2**) indicates that a minimum 4 μg of β -Naphthol can be determined accurately by HPLC.

8.3.1. Effect of Concentration:

The adsorption of β -Naphthol with varying concentration on Kyanite, pyrolusite and activated carbon is shown in **Table. 8.2**. Adsorption of β -Naphthol on activated carbon is very high (100%) over a wide range of concentration (20 – 200 mg/l). Adsorption on kyanite does not follow any trend when concentration is increased. Maximum adsorption (42.5%) occurs at 80 mg/l initial concentration of β -Naphthol at pH 7.1. Adsorption on pyrolusite increases initially and reaches to a maximum value (62%) when initial concentration of β -Naphthol is increased from 20 to 50mg/l at pH 7.1 and then decreases to a minimum value (20%) when concentration is increased beyond 50 mg/l.

The adsorption of β -Naphthol on kyanite and pyrolusite was also studied in acidic medium with varying concentrations of β -Naphthol. Adsorption on kyanite at pH 3 again indicates that no proper trend is followed (Table. 8.2). The only inference that can be drawn from this study is that adsorption of β -Naphthol on kyanite increases from 24 – 79 % when pH is reduced from 7.1 to 3 at 50 mg/l initial concentration.

Adsorption on pyrolusite at pH 4 indicates that adsorption increases from 37.5 to 90 % when concentration of β - Naphthol is increased from 20 to 50 mg/l and then starts decreasing reaching to a minimum value (61%) when initial concentration reaches to 100 mg/l.

It can be concluded that adsorption of β - Naphthol on both kyanite and pyrolusite is increased when pH is reduced from 7.1 to 3-4. The removal efficiency of pyrolusite is high (90%) at pH 4 and 50 mg/l initial concentration of β - Naphthol.

8.3.2. Effect of pH:

The effect of solution pH on the adsorption of β - Naphthol on kyanite and pyrolusite is shown in **Figure. 8.3**. The adsorption of β - Naphthol onto kyanite and pyrolusite is maximum at pH 3 and 4 respectively. Further increase in pH decreases the adsorption. This may be due to the amphoteric nature of these natural minerals. β - Naphthol perhaps, is adsorbed on the surface in its molecular form because in acidic medium β - Naphthol is not dissociated. In acidic medium, the H^+ ions are preferentially adsorbed and charge on these adsorbents is neutralised but when pH is increased, the surfaces of these adsorbents start acquiring negative charge and at the same time β - Naphthol starts dissociating. Thus, naphtholate ions generated at higher pH are repelled by negative charge on the adsorbent surface. This results in the decrease in adsorption of β - Naphthol with increase in pH. However, the adsorption of β - Naphthol on activated carbon is 100% with no significant influence of pH.

8.3.3. Kinetics of Adsorption:

The main objective of the kinetics studies is to determine equilibrium contact time. Various kinetic models including the Pseudo-first-order, Pseudo-second-order and Elovich equation have been applied for the experimental data to predict the adsorption kinetics.

The Pseudo-first-order rate equation can be written as follows (Rinkus and Reed, 1997)

$$\log (q_e - q_t) = \log q_e - K_1 / 2.303 \cdot t \quad \text{_____} \quad (3)$$

The plots between $\log (q_e - q_t)$ vs t are linear. The values of K_1 and q_e can be calculated from the slope and intercept (**Figures. 8.4 and 8.5**). **Table. 8.3** show that values of K_1 increases with increase in concentration of β - Naphthol on both the adsorbents. However, Pseudo-first-order model fails to fit since values of q_e calculated for the above equation ($q_{e \text{ (theo)}}$) differ largely from the experimental values ($q_{e \text{ (exp)}}$).

The Pseudo-second-order kinetics model is expressed as follows (Ajmal et al., 2001)

$$t / q_t = 1 / K_2 \cdot q_e^2 + 1 / q_e \cdot t \quad \text{_____} \quad (4)$$

The values of K_2 and q_e were calculated from the plots t/q_t vs t (**Figures. 8.6 and 8.7**). The $q_{e \text{ (theo)}}$ value agrees with $q_{e \text{ (exp)}}$ values, at 50 mg/l initial concentration for kyanite and 40 mg/l initial concentration for pyrolusite. The correlation coefficient values at the respective concentrations for kyanite and pyrolusite are high (**Table. 8.3**), showing that Pseudo-second-order kinetics model is better obeyed at lower concentration of β -Naphthol.

The Elovich equation (Ho and Mc Kay, 1998), applicable for chemisorption on energetically heterogeneous solid surface is given by:

$$q_t = \beta \ln (\alpha \beta) + \beta \ln t \quad \text{_____} \quad (5)$$

Where, α and β – Elovich coefficients, represent the initial adsorption ($\text{g-min}^2/\text{mg}$) and the desorption coefficient (mg/g-min) respectively (**Table. 8.3**). These values are calculated from the plot q_t vs $\ln t$ (**Figures. 8.8 and 8.9**).

The nature of adsorption on kyanite and pyrolusite was also verified using Reichenberg equation (Reichenberg, D., 1953)

$$F = 1 - 6 / \pi^2 e^{-\beta t} \quad (6)$$

The nature of βt is a mathematical function of R and can be calculated as

$$\beta t = -0.4977 - \ln (1-F) \quad (7)$$

Where, $F = q_t/q_e \quad (8)$

The plot of βt vs t is shown in Figures. 8.10 and 8.11. The plots are linear and do not pass through the origin thereby indicating that pore diffusion is not the only rate limiting step but some other processes like film diffusion may also involved.

8.3.4. Adsorption Isotherms:

Langmuir and Freundlich adsorption models were used to analyse the adsorption data for the adsorption of β - Naphthol on kyanite and pyrolusite. Langmuir model may be defined as:

$$C_e/q_e = 1 / b.q_m + 1 / q_m * C_e \quad (9)$$

Plots of C_e/q_e vs C_e are linear with slope $1/q_m$ and intercept of $1/b.q_m$ (**Figures. 8.12, 8.13, 8.14, and 8.15**).

The adsorption energies for the adsorption of β -Naphthol on kyanite and pyrolusite are maximum in acidic medium (pH 3 – 4) indicating higher affinity for the adsorption of β - Naphthol (**Table. 8.4**). The q_m (theo) values are very near to q_m (exp) for the adsorption of β - Naphthol on pyrolusite at pH 7.1 and 4, predicting monolayer adsorption (**Table. 8.4**). These results indicate that the affinity of β - Naphthol on kyanite is more at pH 3 but on the other hand affinity on pyrolusite is high at pH 4 and 7.1 indicating that pyrolusite can be used for the removal of traces of β - Naphthol from wastewater over a wide range of pH as compared to kyanite.

The essential feature of Langmuir model can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter (R_L) given by relation:

$$R_L = 1 / (1 + bC_0) \quad (10)$$

If $0 < R_L < 1$ favourable adsorption, $R_L > 1$ unfavourable adsorption, $R_L = 1$ linear adsorption, $R_L = 0$ irreversible adsorption. The values of R_L for the adsorption β - Naphthol on kyanite and pyrolusite are as follows:

Kyanite : R_L (0.1577 - 0.4304) : pH 3
 Kyanite : R_L (0.1041 - 0.2460) : pH 7.1
 Pyrolusite: R_L (0.02 - 0.1310) : pH 3
 Pyrolusite: R_L (0.0176 - 0.0585) : pH 7.1

All the values of R_L are in the range $0 < R_L < 1$ showing favourable adsorption of β - Naphthol.

Freundlich adsorption model is given as:

$$\log q_e = \log K_f + 1/n \log C_e \quad (11)$$

Linear plots of $\log q_e$ vs $\log C_e$ indicates that Freundlich isotherm is followed. (**Figures. 8.16, 8.17, 8.18 and 8.19**). The values of K_f and n calculated from the slope and intercept are given in **Table. 8.4**. The values of K_f on kyanite and pyrolusite are higher in acidic solution (pH 3 – 4), indicating the higher adsorption efficiency.

8.3.5. Desorption studies:

The desorption of β - Naphthol on kyanite, pyrolusite and activated carbon using different solvents is summarised in **Table. 8.5**. There is no recovery of β - Naphthol from activated carbon illustrating that it cannot be regenerated under normal conditions. The maximum recovery of β - Naphthol from kyanite is 39.4 % with acetonitrile (**Table. 8.5**). The order

of recovery of β - Naphthol by different solvents from kyanite is 39.4 % (acetonitrile) > 23.2 % (0.1M HCl) > 12.16 % (hexane: propanol (99:1)) > 10.71 % (butanol) > 3.21 % (propanol). This behaviour shows that β - Naphthol is very strongly adsorbed on kyanite and β - Naphthol cannot be recovered completely by any of these solvents. However, excellent results are obtained when hexane and hexane: propanol mixture (99:1) are used as eluent for the recovery of β - Naphthol from pyrolusite (**Table. 8.5**).

8.4. Conclusion:

Adsorption of β - Naphthol on activated carbon is maximum (100%) followed by pyrolusite and kyanite but at the same time β - Naphthol could not be recovered from activated carbon. However, a small quantity of adsorbed β - Naphthol could be recovered from kyanite. Pyrolusite is found to be superior over activated carbon and kyanite in this respect since after adsorption 100 % β - Naphthol could be recovered successfully using hexane and butanol mixture as eluent. Pyrolusite therefore, could be utilised for the recovery or preconcentration of traces of β - Naphthol present in water and wastewater prior to its determination.

Table. 8 1. Adsorption of some organic pollutants on Kyanite, Pyrolusite and Activated Carbon

S.No.	Organic Pollutants	% Adsorption		
		Kyanite	Pyrolusite	Activated Carbon
1.	Chlorophenol	0	0	100
2.	Phenol	0	0	100
3.	β - Napthol	24	62	100

Table. 8.2. Effect of concentration on the adsorption of β - Napthol on Kyanite, Pyrolusite and Activated Carbon

Initial concentration (mg/l)	% Adsorption				
	Activated Carbon	Kyanite (pH 7.1)	Kyanite (pH 3)	Pyrolusite (pH 7.1)	Pyrolusite (pH 4)
20	100	2.5	12	25	37.5
40	100	18.5	43.75	60	61.25
50	100	24	79	62	90
60	100	12.5	65	40	72
80	100	42.5	66.6	30.8	62.5
100	100	8.5	58.6	20	61
200	100	-	-	-	-

Table. 8.3. Pseudo-first-order kinetics, Pseudo-second-order kinetics and Elovich equation parameters for the adsorption of β - Naphthol on Kyanite (pH 3) and Pyrolusite (pH 4)

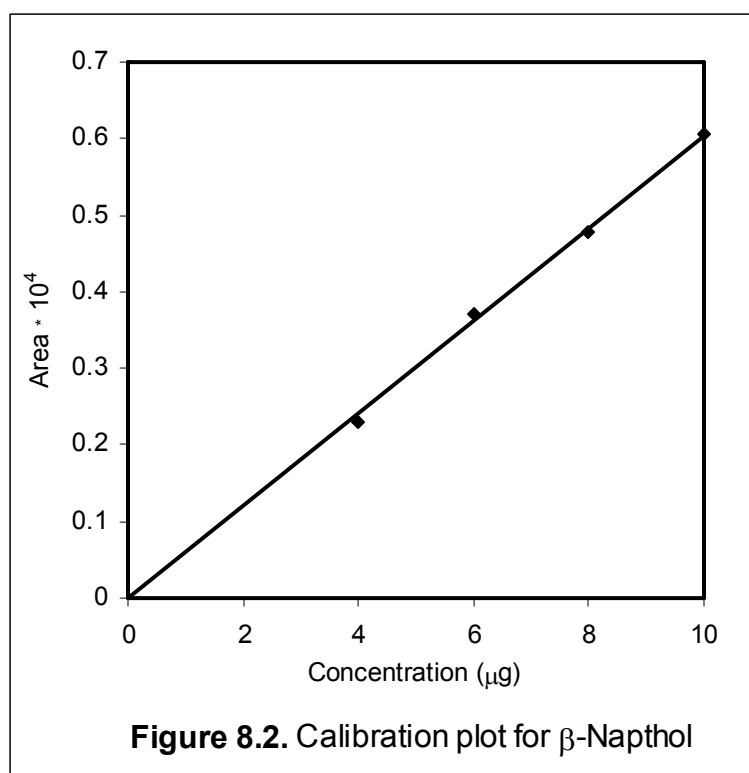
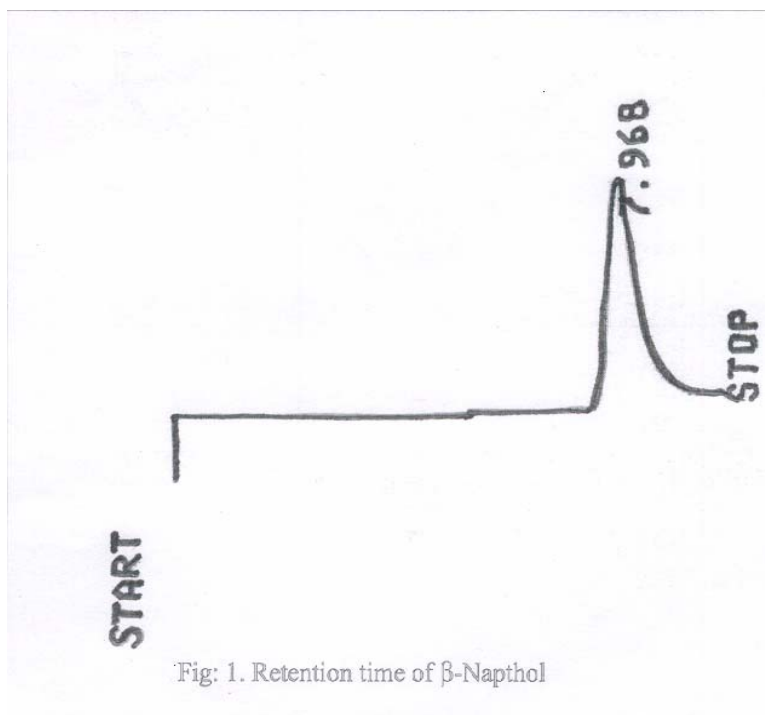
Kinetics Parameters	Kyanite (pH 3)		Pyrolusite (pH 4)	
	Concentrations		Concentrations	
	50 mg/l	60 mg/l	40 mg/l	50 mg/l
Ist Order				
K_1 (1/min)	0.0108	0.0437	0.0083	0.0373
R^2	0.9989	0.9964	0.9999	0.9973
q_e (theo) (mg/g)	15.149	35.514	10.437	16.014
q_e (exp) (mg/g)	41	44.4	23.8	10.8
IInd Order				
K_2 (g /mg-min)	0.021	0.0024	0.0048	0.0290
R^2	0.9877	0.9860	0.996	0.9983
q_e (theo) (mg/g)	41.32	49.02	23.8	32.258
q_e (exp) (mg/g)	41	44.4	23.8	10.8
Elovich Eq.				
α (g-min ² /mg)	0.3808	0.2559	0.2127	20.577
β (mg/g-min)	6.6844	8.997	5.2314	3.9393
R^2	0.9999	0.999	0.9996	0.993

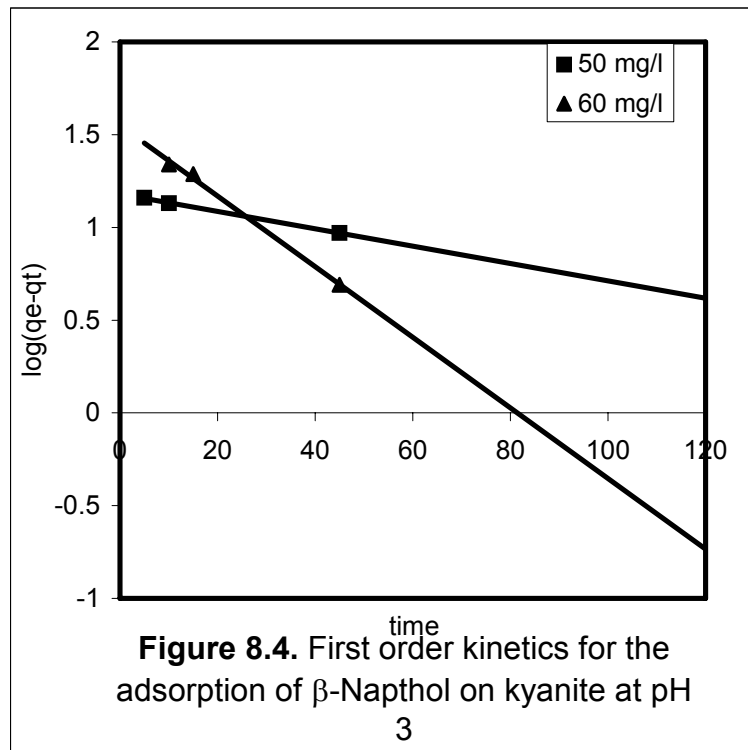
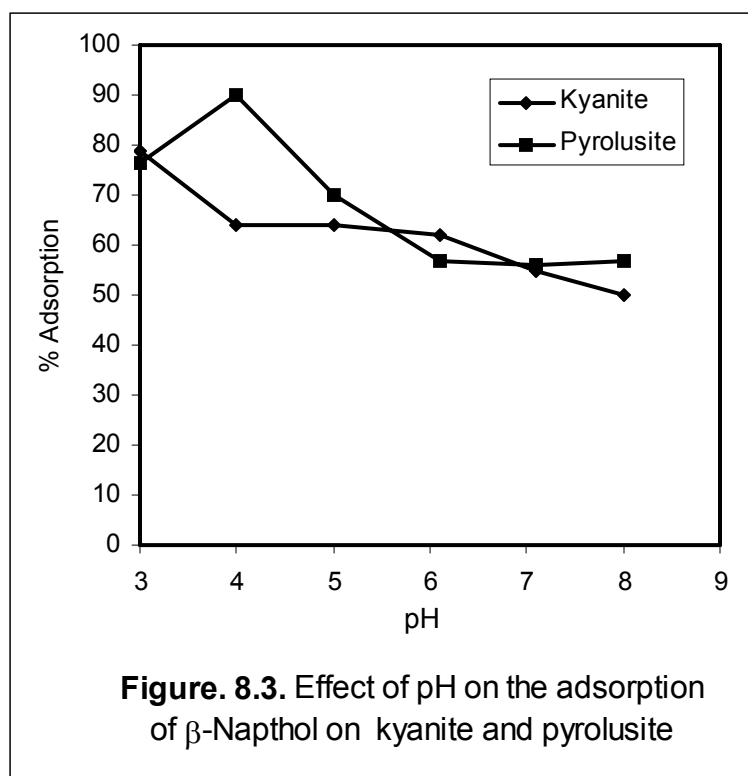
Table. 8.4. Adsorption isotherms parameters for the adsorption of β - Naphthol on Kyanite and Pyrolusite

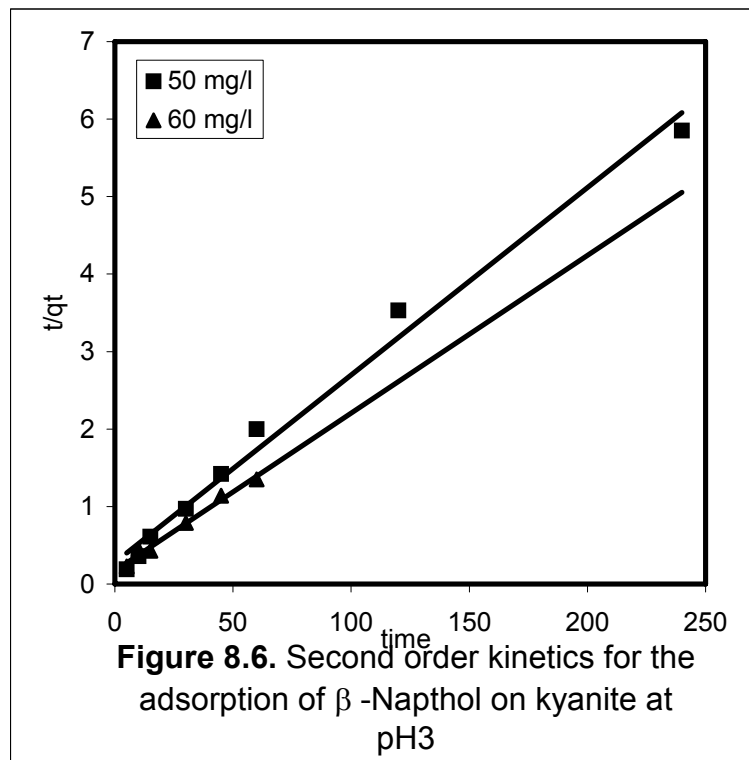
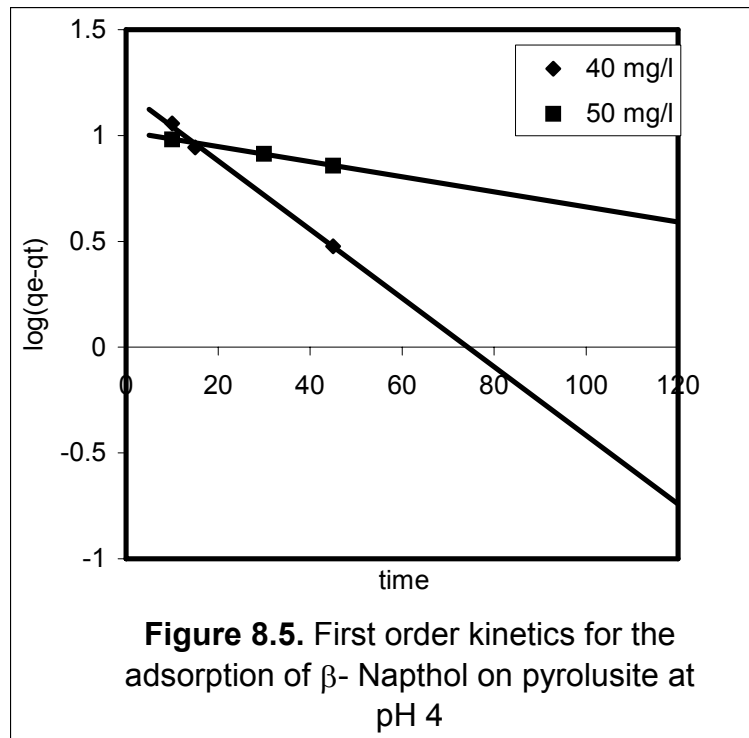
Adsorption Isotherms	Kyanite (pH 7.1)	Kyanite (pH 3)	Pyrolusite (pH 7.1)	Pyrolusite (pH 4)
Langmuir				
b (l/mg)	0.094	0.126	1.006	1.327
q_m (theo) (mg/g)	0.941	6.978	2.499	5.131
q_m (exp) (mg/g)	0.75	5.86	2.5	5.0
R^2	0.9937	0.9998	0.9995	0.9877
R_L	0.2460	0.4304	0.0585	0.1310
	0.1685	0.2305	0.0268	0.0430
	0.1041	0.1577	0.0176	0.0245
Freundlich				
K_f (mg/g)	0.0002	0.0962	0.0151	0.1575
n	0.5148	0.2938	0.7554	0.9945
R^2	0.8997	0.9873	0.9097	0.9949

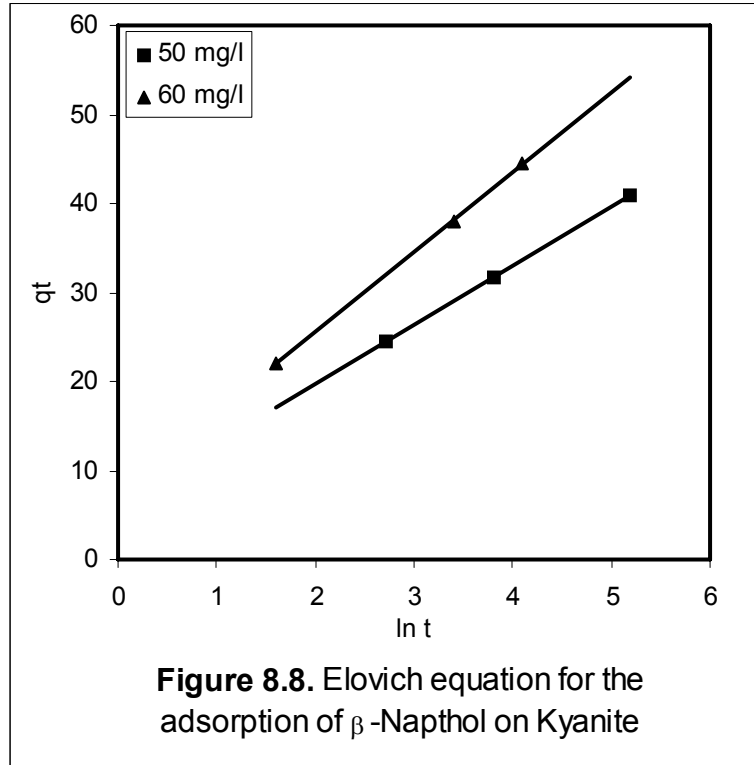
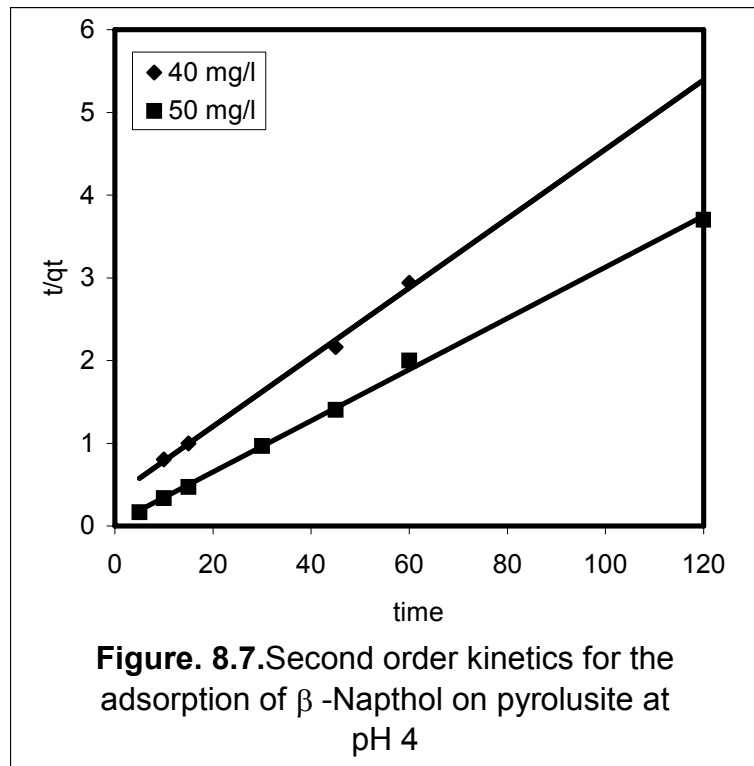
Table. 8.5. Recovery of β -Naphthol from Activated Carbon (A.C), Kyanite and Pyrolusite by batch process

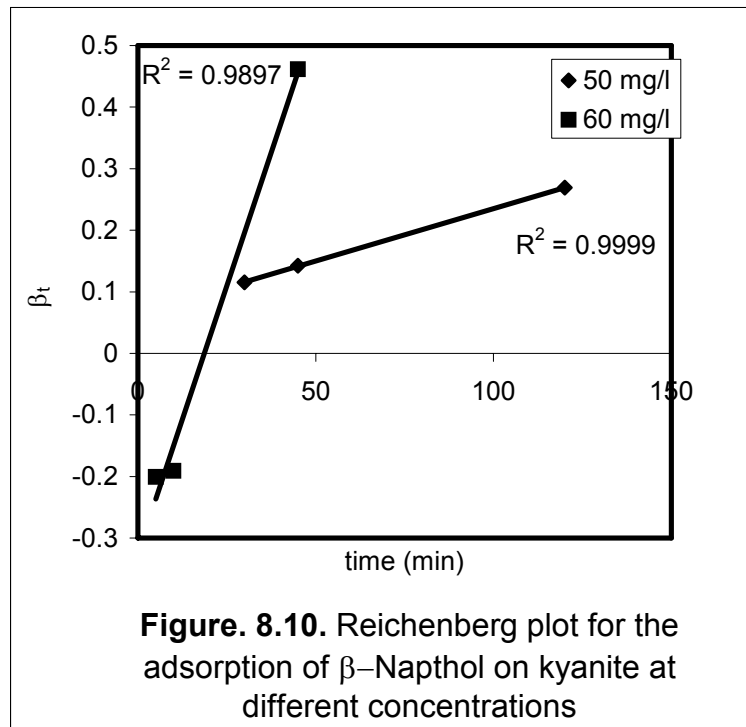
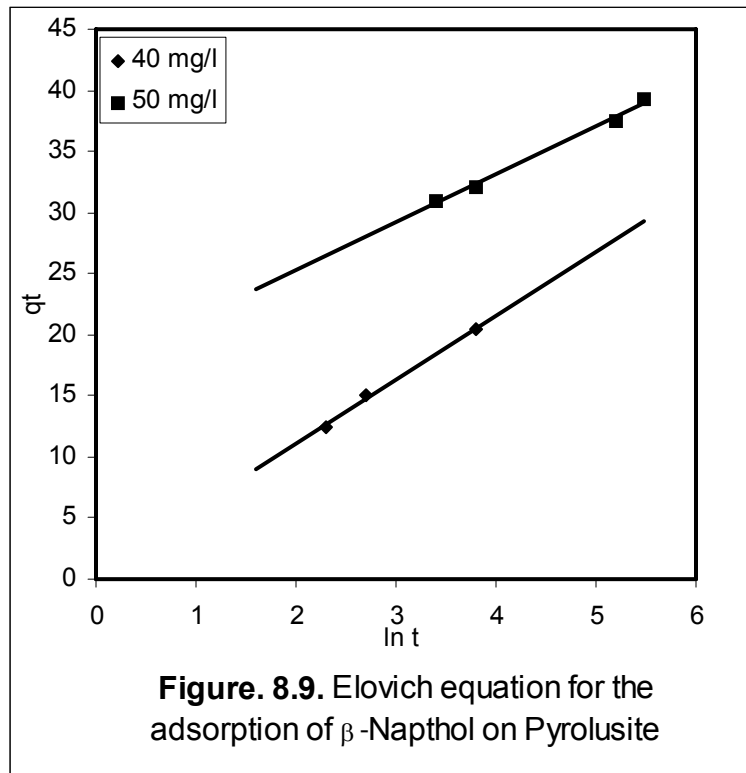
Solvent	Amount of β -Naphthol loaded (mg)	Activated Carbon		Pyrolusite		Kyanite	
		Amount adsorbed (mg)	Amount recovered (mg)	Amount adsorbed (mg)	Amount recovered (mg)	Amount adsorbed (mg)	Amount recovered (mg)
Hexane	2.5	2.5	0.00	1.87	1.87	1.85	0.00
Hexane	0.25	-	-	0.2075	0.14	-	-
Hexane: Propanol (99:1)	2.5	2.5	0.00	1.87	1.86	1.85	0.225
Butanol	2.5	2.5	0.00	1.92	0.00	1.86	0.199
Acetonitrile	2.5	2.5	0.00	1.87	0.45	1.82	0.717
Water	2.5	2.5	0.00	1.87	0.00	1.85	0.00
Propanol	2.5	2.5	0.00	1.87	0.00	1.87	0.060
0.05M NaOH	2.5	2.5	0.00	1.87	0.00	1.85	0.00
0.1M HCl	2.5	2.5	0.00	1.87	0.00	1.85	0.429
Methyl isobutyl ketone (MIBK)	2.5	2.5	0.00	1.88	0.00	1.86	0.00

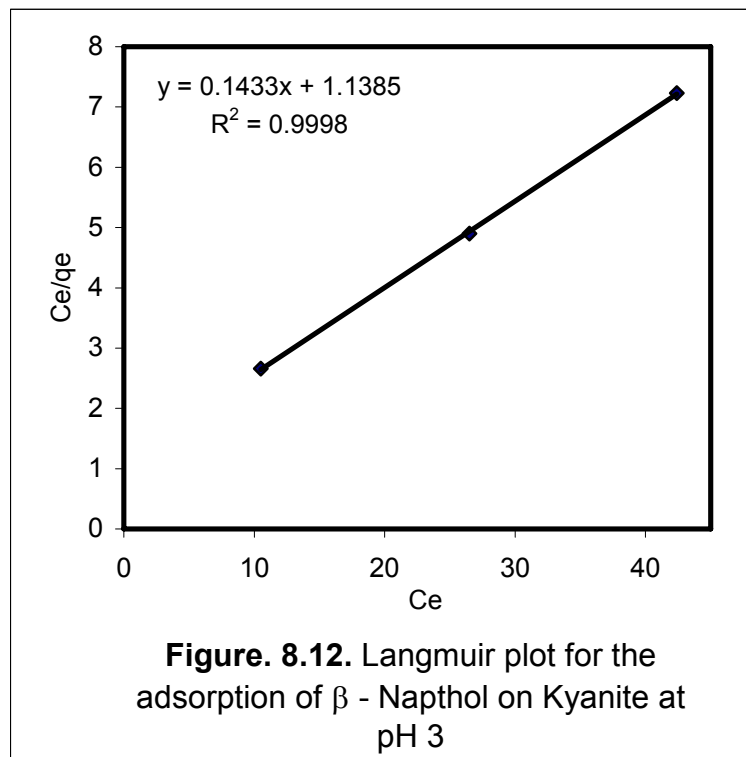
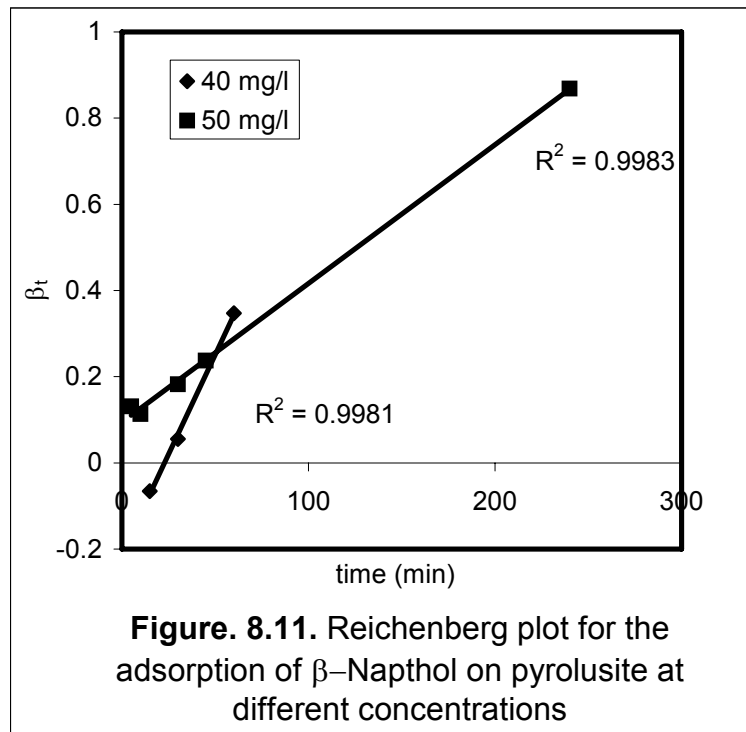












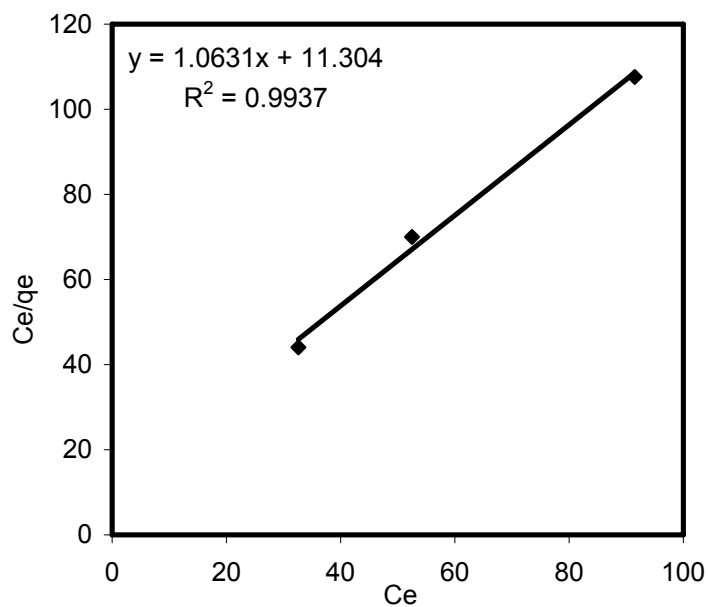


Figure. 8.13. Langmuir Plot for the adsorption of β – Naphthol on Kyanite at pH 7.1

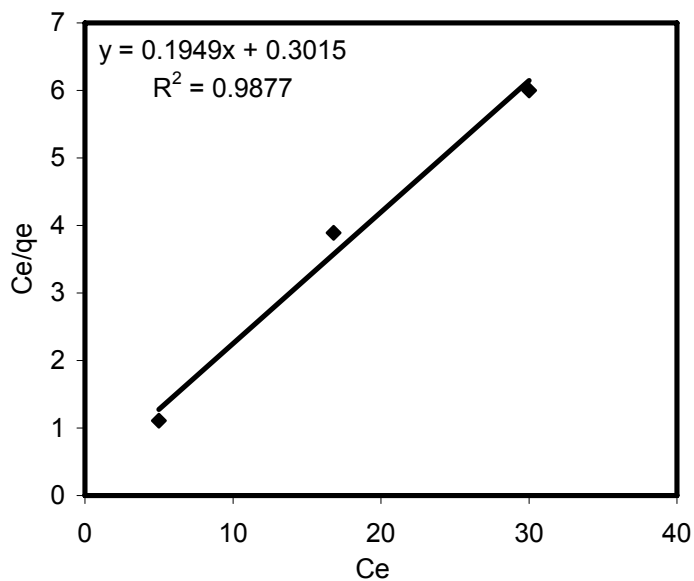
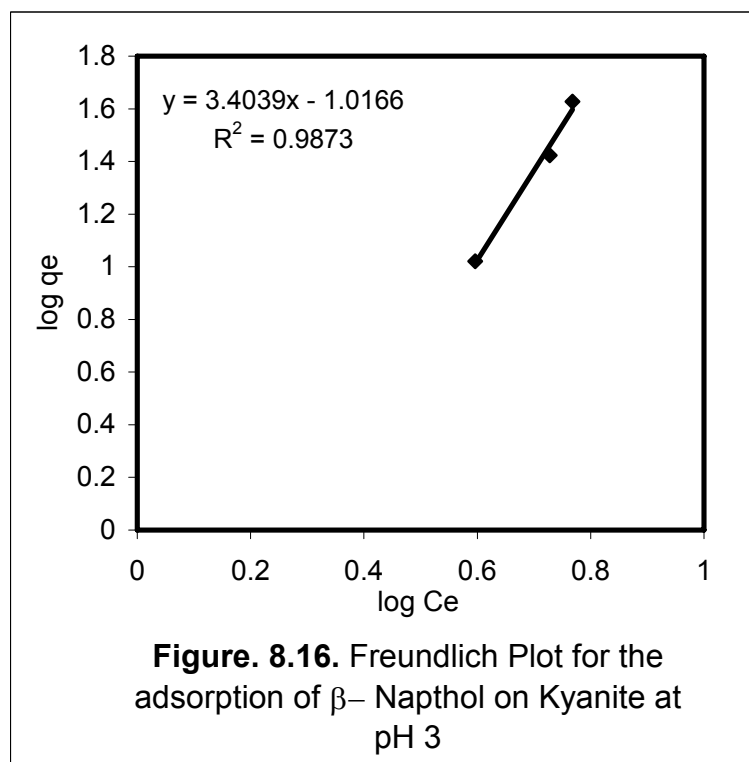
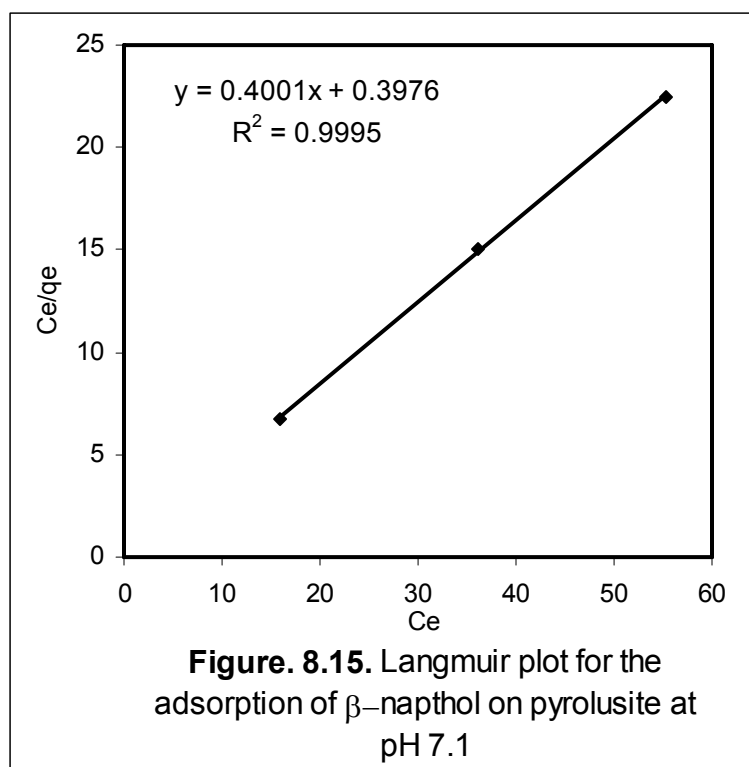
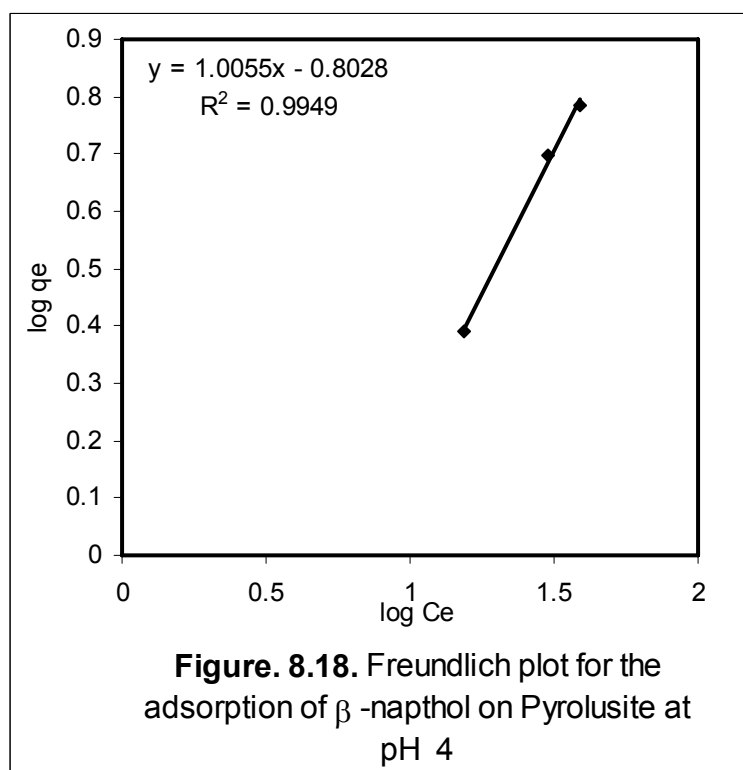
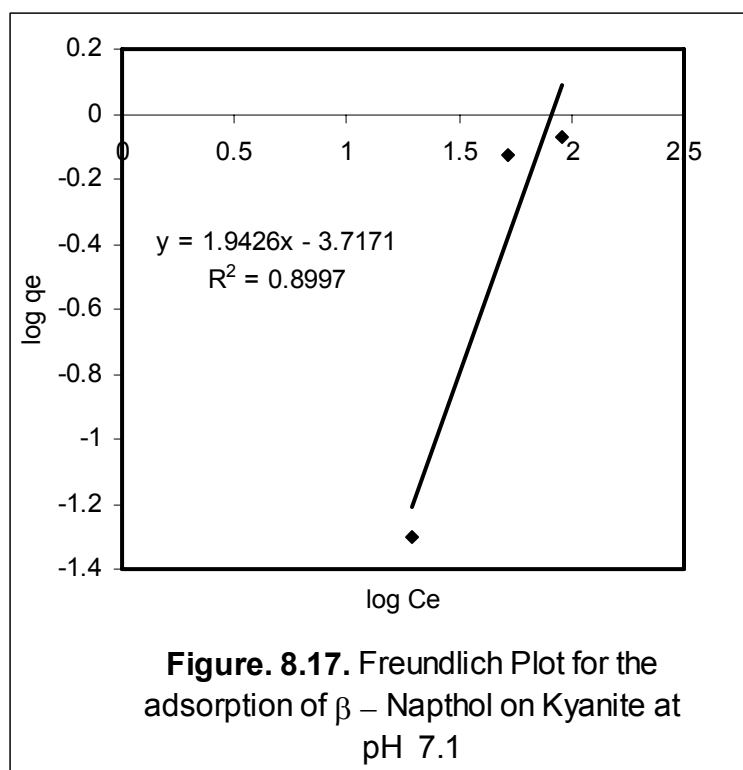
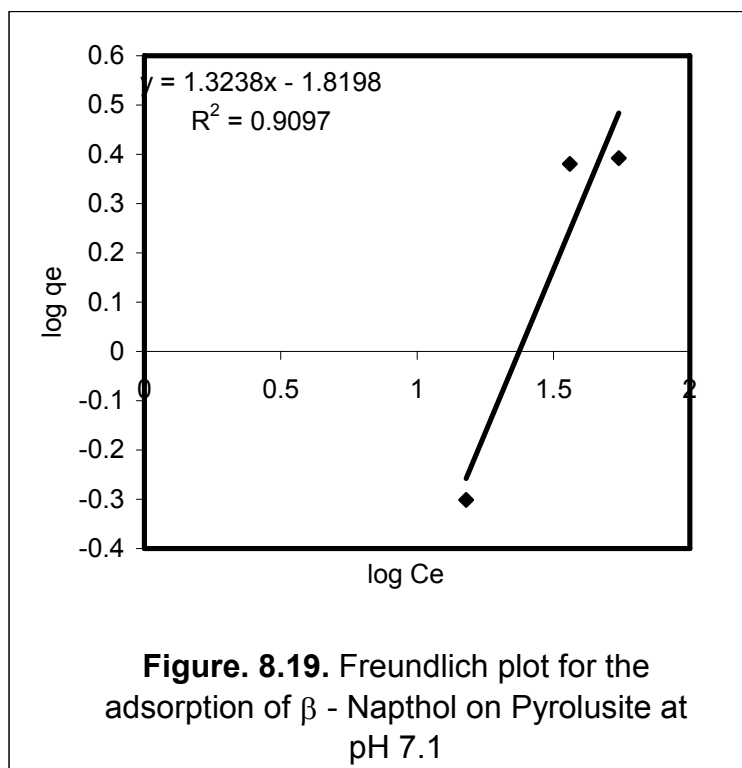


Figure. 8.14. Langmuir plot for the adsorption of β – Naphthol on Pyrolusite at pH 4







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