# REMOVAL OF LEAD FROM WASTE WATER BY ADSORPTION

## A DISSERTATION

*Submitted in partial fulfillment of the requirements for the award of the degree of*

**MASTER OF TECHNOLOGY**

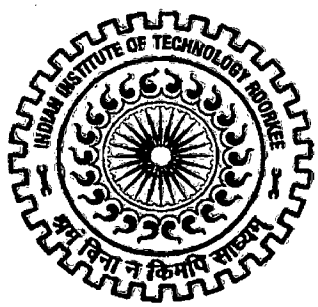
**in**

**CHEMICAL ENGINEERING**

**(With Specialization in Industrial Pollution Abatement)**

**By**

**RAMAMOHANA RAO LATCHIREDDI**


**DEPARTMENT OF CHEMICAL ENGINEERING**
**INDIAN INSTITUTE OF TECHNOLOGY ROORKEE**
**ROORKEE - 247 667 (INDIA)**
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# CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in the dissertation entitled **"REMOVAL OF LEAD FROM WASTE WATER BY ADSORPTION"** in the partial fulfillment of the requirements of the award of the degree of Master of Technology in Chemical Engineering with specialization in **Industrial Pollution Abatement**, submitted in the **Department of Chemical Engineering** of **Indian Institute of Technology Roorkee**, under the kind guidance of **Dr. SHRI CHAND**, Professor and Head ,Chemical Engineering Department, Indian Institute of Technology Roorkee, Roorkee.

The matter embodied in this dissertation has not been submitted by me for the award of any other degree of this or any other Institute.

Date: 25th June, 2007.
Place: Roorkee.

L. Ramamohana Rao
**(RAMAMOHANA RAO LATCHIREDDI)**

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## CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge and belief.

25/6/07

**(Dr. SHRI CHAND)**
Professor & Head,
Department of Chemical Engineering,
Indian Institute of Technology Roorkee,
Roorkee – 247 667 (India).

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Date: 25th June 2007 **( RAMAMOHANA RAO LATCHIREDDI )**

# ABSTRACT

The pollution of water resources due to indiscriminate disposal of heavy metals has been causing worldwide concern for the last few decades. Unlike organic pollutants, the majority of which are susceptible to bio-degradation, heavy metals are non-degradable to harmless end products. They are toxic to aquatic flora and fauna even in relatively low concentrations. Metals, which are significantly toxic to human beings and ecological environments, include arsenic (As), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), manganese (Mn), cadmium (Cd), nickel (Ni), zinc (Zn) and iron (Fe), etc.

Lead, an element which has been used by man for years, can be regarded as a longstanding environmental contaminant. All the chemicals/compounds containing lead are considered as cumulative poisons that usually affect the gastrointestinal track, nervous system and sometimes both. The chief sources of lead in water are the effluents of processing industries. Apart from this lead is also used in storage batteries, insecticides, plastic water pipes, food, beverages, ointments and medicinal concoctions for flavoring and sweetening. Lead poisoning causes damage to liver, kidney and reduction in hemoglobin formation, mental retardation, infertility and abnormalities in pregnant women etc.

There are several methods for removing toxic/heavy metals from aqueous solutions, such as chemical precipitation, membrane filtration, ion exchange, biosorption and adsorption. Removal of lead from contaminated water bodies has been attempted by several researchers employing a wide variety of techniques. Majority of these are adsorption on various surfaces like activated carbon, peat, goethite mineral, hydrated iron etc.

In the present study laboratory scale experiments have been carried out using the Coconut Jute Activated Carbon (CJAC) and Commercial Activated Carbon (CAC) as adsorbents for the removal of Lead. The present study has been undertaken with the objective to

investigate the suitability of CJAC as a low cost adsorbent for the removal of Lead as replacement of CAC. Batch experiments were carried out to determine the effect of various factors such as contact time, initial concentration, pH, adsorbent dose, adsorbent particle size and temperature on adsorption process.

Kinetic study shows that adsorption of Pb(II) on CJAC and CAC follows the Pseudo-second order kinetics. Langmuir isotherm best-fitted the isotherm data for Pb(II) adsorption on CJAC and CAC at almost all temperatures. However, the error analysis values and the non-linear correlation coefficients, $R^2$, are comparable for Langmuir, Temkin isotherms (for CJAC) and Langmuir, Temkin, Redlich-Peterson (for CAC). Adsorption rate increases with increase in temperature for both the adsorbents, showing the endothermic nature of adsorption. From thermodynamic study $\Delta G^0$, $\Delta H^0$ and $\Delta S^0$ values are also calculated for both adsorbents.

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# NOMENCLATURE

| | |
|---|---|
| $C_o$ | Initial concentration of effluent (mg/l) |
| $C_e$ | Concentration of adsorbate solution at equilibrium (mg/l) |
| K | Adsorption rate constant (1/min) |
| $K_A$ | Langmuir isotherm constant, (l/mg) |
| $K_T$ | Temkin isotherm constant, (l/mg) |
| $K_F$ | Freundlich isotherm constant, $((mg/g)/(mg/l)^{1/n})$ |
| $1/n$ | Heterogeneity factor, dimensionless |
| $Q_t$ , $q_t$ | Amount of adsorbate adsorbed per unit amount of adsorbent at time t, (mg/g) |
| $Q_e$ , $q_e$ | Amount of adsorbate adsorbed per unit amount of adsorbent at equilibrium, (mg/g) |
| $R_L$ | Separation Factor |
| $k_f$ | First order rate constant, (1/min) |
| $k_s$ | Second order rate constant, (g/mg min) |
| $K_{id}$ | The intra-particle diffusion rate constant |
| $\Delta G°$ | Gibbs free energy, (KJ/mol) |
| $\Delta H°$ | Enthalpy, (KJ/mol) |
| $\Delta S°$ | Entropy, (J/ mol K ) |
| R | Universal gas constant, 8.314 J/mol K |
| SSE | Sum of the Squares of the Errors |
| SAE | Sum of the Absolute Errors |
| ARE | Average Relative Error |
| HYBRID | Hybrid Fractional Error Function |
| MPSD | Marquardt's Percent Standard Deviation |
| CJAC | Coconut Jute Activated Carbon |
| CAC | Commercial Activated Carbon |

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# CHAPTER-1
# INTRODUCTION

Heavy metals can be defined in variety of ways, on the basis of their physical, chemical and biological properties. Metals with specific gravity of about $5g/cm^3$ or greater are generally defined as heavy metals and these include metals from group II A, III B, IV B, V B and VI B of the periodic table. Lead symbolized Pb is located in group IV of the periodic table, it has an atomic weight and number of 207.19 g and *82,* respectively. It has a melting point of 327°C and a density of 11 .$4g/cm^3$ ($11.4t/m^3$) and a remarkably high corrosion resistance to most acids, including sulphuric ($H_2S0_4$) and hydrochloric (HCl) acids with the exception of nitric acid ($HN0_3$). This corrosion resistance can be attributed to its ability to form a wide variety of oxides ranging from $Pb_2O$ to $PbO_2$ thereby forming a protective film on the exposed surface.

Lead is a normal constituent of the earth's crust, with trace amounts found naturally in soil, plants, and water. If left undisturbed, lead is practically immobile. However, once mined and transformed into man-made products, which are dispersed throughout the environment, lead becomes highly toxic. Solely as a result of man's actions, lead has become the most widely scattered toxic metal in the world. Unfortunately for people, lead has a long environmental persistence and never looses its toxic potential, if ingested.

It is believed that mankind has used lead for over 6000 years. Lead mining probably predated the Bronze or Iron Ages, with the earliest recorded lead mine in Turkey about 6500 BC. The oldest artifact of smelted lead is a necklace found in the ancient city site in Anatolia. The estimated age of this necklace is 6,000 to 8,000 years ago. There were many reasons for lead's use other than its abundance and ease in obtaining it. Some of the properties which make it commercially attractive include: easy workability, low melting point, ability to form carbon metal compounds, hold pigments well, very easily recycled, stands up well to the outside weather elements, a high degree of corrosion resistance, it is inexpensive, etc. There are also several habits and customs of cultures that contributed to human exposure, such as using lead in medicines and cosmetics.

The Romans conducted lead mining on a massive scale and had several huge lead mine and smelter sites. Lead was in big demand and was a byproduct of refining silver and gold ore. One smelter site located in Spain required tens of thousands of slaves to operate. Another large site was in Greece and the emissions from these two sites would raise high into the atmosphere and get picked up by the world's air currents. Some lead would fall back to earth in the snow and recently, scientists measured lead particles deposited in Greenland's ice to determine the history of lead production. The massive mining and smelting of lead went on for hundreds of years and the production of Roman lead was not surpassed till the period of the Industrial Revolution.

Lead's toxicity was recognized and recorded as early as 2000 BC and the widespread use of lead has been a cause of endemic chronic plumbism in several societies throughout history. The Greek philosopher Nikander of Colophon in 250 BC reported on the colic and anemia resulting from lead poisoning. Hippocrates related gout to the food and wine, though the association between gout and lead poisoning was not recognized during this period (450-380 BC). Later during the Roman period, gout was prevalent among the upper classes of Roman society and is believed to be a result of the enormous lead intake.

Lead is not biodegradable. It persists in the soil, in the air, in drinking water, and in homes. It crosses all social, economical and geographical lines. It never disappears, it only accumulates where it is deposited and can poison generations of children and adults unless properly removed. At high levels, lead poisoning causes coma, convulsions and death. At low levels, levels far below those that present obvious symptoms, lead poisoning in childhood causes reductions in IQ and attention span, reading and learning disabilities, hyperactivity, impaired growth, behavioral problems, and hearing loss. These effects are long-term and may be irreversible.

**1.1) Lead In Periodic Table:**

TABLE-1.1: LEAD IN PERIODIC TABLE

| | |
|---|---|
| Symbol | Pb |
| Atomic Number | 82 |
| Atomic Weight | 207.2 |
| Element Classification | Other Metal |
| Discovered by | Known to the ancients |
| Discovery Date | Unknown |
| Name Origin | Anglo-Saxon: lead; symbol from Latin: Plumbum |
| Density (g/cc) | 11.35 |
| Melting Point (°K) | 600.65 |
| Boiling Point (°K) | 2013 |
| Appearance | Very soft, highly malleable and ductile, blue-white shiny metal |
| Atomic Radius (pm) | 175 |
| Atomic Volume (cc/mol) | 18.3 |
| Covalent Radius (pm) | 147 |
| Ionic Radius | 84 (+4e) 120 (+2e) |
| Specific Heat (@20°C J/g mol) | 0.159 |
| Fusion Heat (kJ/mol) | 4.77 |
| Evaporation Heat (kJ/mol) | 177.8 |
| Debye Temperature (°K) | 88.00 |
| Pauling Negativity Number | 1.8 |
| First Ionizing Energy (kJ/mol) | 715.2 |
| Oxidation States | 4,2 |
| Electronic Configuration | [Xe] $4f^{14}$ $5d^{10}$ $6s^2$ $6p^2$ |
| Lattice Structure | Face Centred Cubic(FCC) Lattice |
| Lattice Constant (Å) | 4.950 |

**1.2) Sources of Lead:**

Lead is a naturally occurring bluish-gray metal found in small amounts in the earth's crust. It has no characteristic taste or smell. Metallic lead does not dissolve in water and does not burn. Some natural and man-made substances contain lead, but do not look like lead in its metallic form. Some of these substances can burn. It is very soft, highly malleable, ductile, and a relatively poor conductor of electricity. It is very resistant to corrosion but tarnishes upon exposure to air. Lead pipes bearing the insignia of Roman emperors, used as drains from the baths, are still in service. Alloys include pewter and solder.Lead isotopes are the end products of each of the three series of naturally occurring radioactive elements. Lead is available in several forms including foil, granules, ingots, powder, rod, shot, sheet, and wire.

Lead has many different uses. Its most important use is in the production of some types of batteries. Other uses include the production of ammunition, in some kinds of metal products (such as sheet lead, solder, and pipes) and in ceramic glazes. Some chemicals containing lead, such as tetraethyl lead and tetraethyl lead are used as gasoline additives. However, the use of these lead containing chemicals in gasoline is much less than it used to be because the last producer of these additives in the United States stopped making them in early 1991. Other chemicals containing lead are used in paint. The amount of lead added to paints and ceramic products, gasoline additives, and solder has also been reduced in recent years because of lead's harmful effects in humans and animals. However, the use of lead in ammunition and roofing has actually increased in recent years. Lead is also used for radiation shields for protection against X-rays and in a large variety of medical (electronic ceramic parts of ultrasound machines, intravenous pumps, fetal monitors, and other surgical equipment), scientific (circuit boards for computers and other electronic circuitry), and military equipment (jet turbine engine blades, military tracking systems).

Most lead used by industry comes from mined ores ("primary") or from recycled scrap metal or batteries ("secondary"). Human activities have spread lead and substances that contain lead to all parts of the environment. For example, lead is in air, drinking water, rivers, lakes, oceans, dust, and soil. Lead is also in plants and animals that humans may eat. Lead occurs naturally in the environment. However, most of the lead dispersed throughout the environment comes from human activities. Before the use of leaded gasoline was limited, most of the lead released into the U.S. environment came from car exhaust. Since the EPA has limited the use of leaded gasoline,

the amount of lead released into the air has decreased. In 1979, cars released 94.6 million kilograms (kg) of lead into the air in the United States. In contrast, in 1989 cars released only 2.2 million kg to the air. Other sources of lead released to the air include burning fuel, such as coal or oil, industrial processes, and burning solid waste.

**Lead Sources in India:**

Lead is a widespread constituent of the earth's crust. It has always been present in soils in rivers, lakes and seas, in the air, following the burning of wood and coal, and in plants, both edible and inedible. Throughout history, lead has been well known and extensively used by mankind and so, over a period of centuries, it has been dispersed by man into the environment. There are many reasons for the vast commercial utilization of lead. Some of the important properties include low melting points, easy workability, ability to form carbon metal compounds, favorable oxidation-reduction potential useful for electrochemical application, formation of crystal desirable in pigment, relatively low cost and easy recyclability. At present one of the major uses of lead is in the Lead Acid Storage manufacturing industries which account for about 50% of the refined lead consumption, while production of tetraethyl lead as an automobile additive to reduce engine knock accounts for almost 10% of the consumption.

India was centuries ahead of Western Europe in the industrial production of lead. This has been reaffirmed by excavation work carried out by the British Museum, Baroda University and Hindustan Zinc Limited. Zawar mines are the "earliest dated Lead-zinc mines in the world". The commercial exploitation of Zawar mines was resumed in the 20$^{th}$ century by Metal Corporation of India (MCI). MCI had also put up a lead smelter in Tundoo, Bihar in the year 1942 to treat lead concentrate. Hindustan Zinc Limited (HZL) was incorporated in 1966. Starting with one mine producing 500 TPD lead zinc ore and a 3600 TPA Lead Smelter in 1966, HZL has come a long way and today operates nearly six lead zinc mines. India's total identified lead ore reserves are estimated to be around 383 million tonnes (as of 1989) with Rajasthan having a major share. Andhra Pradesh, Gujarat, Orissa, Bihar and West Bengal also have some reserves. Total production of lead concentrates in India was 17,000 tonnes in 1980 and 89,000 tonnes in 1989. India has a very small share in world market for refined lead production which was only 0.5% in 1986. Production of primary lead metal follows the sinister roast, blast furnace reduction fire refining process using sulphide lead concentrates.

**The sources of lead in India from the viewpoint of health hazards may be in the following order of importance:**

1. Lead-battery recycling plants
2. Lead smelting as in silver refining for jewelry & articles works.
3. Lead based pigments & paints
4. Printing press
5. Ceramic pottery glazes
6. Lead containing cosmetics & folk medicines

Every country is developing recycling activities. In 1995, European industry was recycling over 10 million vehicles and 45-48 million lead-acid batteries. In 1997, Western world average lead ratio between production of refined lead & lead alloys from scrap 2,929 mt. and refined lead production 4,956 mt amounted to 59% and for USA to 76%. These activities are increasing in Asia.

**Priority Areas for Investigation in India**

1. Lead battery recycling activities
2. Lead smelting for silver purification for jewellery & articles
3. Childhood lead poisoning from lead based pigments & paints, soil etc. 1-6 years

**1.3) Exposure of Lead:**

People living near hazardous waste sites can be exposed to lead and chemicals that contain lead by breathing air, drinking water, eating foods, or swallowing or touching dust or dirt that contains lead. For people who do not live near hazardous waste sites, most exposure to lead occurs by eating foods that contain lead, occupationally in brass/bronze foundries, or in areas where leaded paints exist. Foods such as fruits, vegetables, meats grains, seafood, soft drinks, and wine may have lead in them. Cigarettes also contain small amounts of lead. In general, very little lead is in drinking water. More than 99% of all drinking water contains less than 0.005 part of lead per million parts of water (ppm).Acidic water can make the lead found in lead pipes, solder, and brass faucets enter water.

Sources of lead in drinking water include lead that can come out of lead pipes, faucets, and solder used in plumbing. Lead-containing plumbing may be found in public drinking water systems, in houses, apartment buildings, and public buildings. Sources of lead in surface water or sediment include deposits of lead-containing dust from the atmosphere, waste water from industries that handle lead (primarily iron and steel industries and lead producers), and urban runoff.

Sources of lead in food and beverages include deposition of lead-containing dust from the atmosphere on crops and during food processing and uptake of lead from soil by plants. Lead may also enter foods when foods are put into improperly glazed pottery and ceramic dishes and leaded-crystal glassware. Illegal whiskey made using stills that contain lead-soldered parts (such as truck radiators) may also contain lead. The potential for exposure to lead in canned food from lead-soldered containers is greatly reduced because the content of lead in canned foods has decreased 87% from 1980 to 1988. Lead may also be released from soldered joints in kettles used to boil water for beverages. Sources of lead in dust and soil include deposition of atmospheric lead and weathering and deterioration of lead-based paint. Lead in dust may also come from windblown soil. Disposal of lead in municipal and hazardous waste dump sites also adds lead to soil.

We may swallow a lot of lead by eating food and drinking liquids that contain it. Most of the lead that enters your body comes through swallowing, even though very little of the amount you swallow actually enters your blood and other parts of your body. The amount that gets into your body from your stomach partially depends on when you ate your last meal. It also depends on how old you are and how well the lead particles you ate dissolved in your stomach juices. Experiments in adult volunteers showed that the amount of lead that got into the body from the stomach was only about 6% in adults who had just eaten. In adults who had not eaten for a day, about 60-80% of the lead from the stomach got into their blood. On the other hand, 50% of the lead swallowed by children enters the blood and other body parts even if their stomachs are full.

Frequent skin contact with lead in the form of lead-containing dusts and soil can result in children swallowing lead through hand-to-mouth behavior. In adults, only a small portion of the lead will pass through your skin and enter your body if it is not washed off after skin contact.

More lead can pass through your skin if it is damaged. Certain types of lead compounds, however, may penetrate your skin.

**1.4) Health Hazard Information:**

Lead poisoning is the number one environmental disease among children in developing countries. The full impact of lead poisoning on the health of children and adults is becoming clearer to most countries, and many governments have begun to take action. Significant health and economic benefits have been realized by those countries which have developed lead prevention programs.

Exposure to lead can occur from breathing contaminated workplace air or house dust or eating lead-based paint chips or contaminated dirt. Lead is a very toxic element, causing a variety of effects at low dose levels. Brain damage, kidney damage, and gastrointestinal distress are seen from acute (short-term) exposure to high levels of lead in humans. Chronic (long-term) exposure to lead in humans results in effects on the blood, central nervous system (CNS), blood pressure, kidneys, and Vitamin D metabolism. Children are particularly sensitive to the chronic effects of lead, with slowed cognitive development, reduced growth and other effects reported. Reproductive effects, such as decreased sperm count in men and spontaneous abortions in women, have been associated with high lead exposure. The developing fetus is at particular risk from maternal lead exposure, with low birth weight and slowed postnatal neurobehavioral development noted. Human studies are inconclusive regarding lead exposure and cancer.

**Acute Effects:**

1) Death from lead poisoning may occur in children who have blood lead levels greater than 125 μg/dL and brain and kidney damage have been reported at blood lead levels of approximately 100 μg/dL in adults and 80 μg/dL in children.

2) Gastrointestinal symptoms, such as colic, have also been noted in acute exposures at blood lead levels of approximately 60 μg/dL in adults and children.

Short-term (acute) animal tests in rats have shown lead to have moderate to high acute toxicity.

**Chronic Effects (Noncancer):**

1) Chronic exposure to lead in humans can affect the blood. Anemia has been reported in adults at blood lead levels of 50 to 80 μg/dL, and in children at blood lead levels of 40 to 70 μg/dL.

2) Lead also affects the nervous system. Neurological symptoms have been reported in workers with blood lead levels of 40 to 60 μg/dL, and slowed nerve conduction in peripheral nerves in adults occurs at blood lead levels of 30 to 40 μg/dL.

3) Children are particularly sensitive to the neurotoxic effects of lead. There is evidence that blood lead levels of 10 to 30 μg/dL, or lower, may affect the hearing threshold and growth in children.

4) Other effects from chronic lead exposure in humans include effects on blood pressure and kidney function, and interference with vitamin D metabolism.

5) Animal studies have reported effects similar to those found in humans, with effects on the blood, kidneys, and nervous, immune, and cardiovascular systems noted.

**Reproductive/Developmental Effects:**

1) Studies on male workers have reported severe depression of sperm count and decreased function of the prostate and/or seminal vesicles at blood lead levels of 40 to 50 μg/dL. These effects may be seen from acute as well as chronic exposures.

2) Occupational exposure to high levels of lead has been associated with a high likelihood of spontaneous abortion in pregnant women. However, the lowest blood lead levels at which this occurs has not been established. These effects may be seen from acute as well as chronic exposures.

3) Exposure to lead during pregnancy produces toxic effects on the human fetus, including increased risk of preterm delivery, low birthweight, and impaired mental development. These effects have been noted at maternal blood lead levels of 10 to 15 μg/dL, and possibly lower. Decreased IQ scores have been noted in children at blood lead levels of approximately 10 to 50 μg/dL.

4) Human studies are inconclusive regarding the association between lead exposure and other birth defects, while animal studies have shown a relationship between high lead exposure and birth defects.

**Cancer Risk:**

1) Human studies are inconclusive regarding lead exposure and an increased cancer risk. Four major human studies of workers exposed to lead have been carried out; two studies did not find an association between lead exposure and cancer, one study found an increased incidence of respiratory tract and kidney cancers, and the fourth study found excesses for lung and stomach cancers. However, all of these studies are limited in usefulness because the route(s) of exposure and levels of lead to which the workers were exposed were not reported. In addition, exposure to other chemicals probably occurred.

2) Animal studies have reported kidney tumors in rats and mice exposed to lead via the oral route.

**1.5) Environmental Levels and Standards:**

Environmental impacts from industries in general consist of degradation of Eco-system, pollution of air and water, and socio-economic change. Production of lead can also have similar impact. In India, permissible limit of lead in effluent discharged from industries as per standard laid down by Central and State Pollution Control Boards is 0.1 milligram/litre. Portable water having concentration about O.l mg/litre is considered unsafe and should be rejected for human consumption. WHO has set 0.05 mg/litre as a guideline value for lead in drinking water.

TABLE 1.2: PERMISSIBLE LEAD LEVELS FROM DIFFERENT INDUSTRIAL EFFLUENT

| S.No | INDUSTRY NAME | PERMISSIBLE LEAD LEVEL(mg/l) |
|---|---|---|
| 1 | Battery Manufacturing | 0.1 |
| 2 | Dry Cell Manufacturing | 10 |
| 3 | Glass Industry | 20 |
| 4 | Inorganic Chemical Industry | 0.1 |
| 5 | Organic Chemical Industry | 0.1 |
| 6 | Paint Industry | 0.1 |
| 7 | Pharmaceuticals Industry | 0.1 |

# CHAPTER-2

# GENERAL PROCESSES FOR LEAD REMOVAL

Many methods have been developed to remove lead from industrial effluents, including precipitation, co-precipitation, electrodialysis, electrocoagulation, cementation, membrane separation, solvent extraction, ionexchange, adsorption, biosorption, reverse osmosis and membrane separation.

## 2.1) Chemical Precipitation:

Chemical precipitation is a method of wastewater treatment. Wastewater treatment chemicals are added to form particles which settle and remove contaminants. The treated water is then decanted and appropriately disposed of or reused. The resultant sludge can be dewatered to reduce volume and must be appropriately disposed of. Chemical precipitation can be used to remove metals, fats, oils and greases (FOG), suspended solids and some organics. It can also to be used to remove phosphorus, fluoride, ferrocyanide and other inorganics.

It can be used on a small or large scale. A beaker full of waste, a 50,000 tank, a 1,000,000 gallon lagoon or a lake can be batch treated with chemicals. Chemical precipitation can be used in a continuous treatment system on flows ranging from a trickle to 1 gallon/minute, 1,000 gallons/minute and more.

Chemical precipitation can be accomplished with very little equipment. For example, a 55 gallon drum and a mixing paddle can be used by a small discharger to treat wastewater with little capital investment. For larger volumes, a tank with a mixer and chemical feed pumps will suffice. For even larger volumes a continuous system with metering pumps, mixing tanks, a clarifier and control instrumentation can be employed.

## 2.2) Ion Exchange:

Ion exchange is a reversible chemical reaction wherein an ion (an atom or molecule that has lost or gained an electron and thus acquired an electrical charge) from solution is exchanged for a similarly charged ion attached to an immobile solid particle. These solid ion exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. The synthetic organic resins are the predominant type used today because their characteristics can be tailored to specific applications.

An organic ion exchange resin is composed of high-molecular-weight polyelectrolytes that can exchange their mobile ions for ions of similar charge from the surrounding medium. Each resin has a distinct number of mobile ion sites that set the maximum quantity of exchanges per unit of resin.

Most plating process water is used to cleanse the surface of the parts after each process bath. To maintain quality standards, the level of dissolved solids in the rinse water must be regulated. Fresh water added to the rinse tank accomplishes this purpose, and the overflow water is treated to remove pollutants and then discharged. As the metal salts, acids, and bases used in metal finishing are primarily inorganic compounds, they are ionized in water and could be removed by contact with ion exchange resins. In a water deionization process, the resins exchange hydrogen ions (H+) for the positively charged ions (such as nickel. copper, and sodium) and hydroxyl ions (OH-) for negatively charged sulfates, chromates and chlorides. Because the quantity of H+ and OH ions is balanced, the result of the ion exchange treatment is relatively pure, neutral water.

### Resin Types:

Ion exchange resins are classified as cation exchangers, which have positively charged mobile ions available for exchange, and anion exchangers, whose exchangeable ions are negatively charged. Both anion and cation resins are produced from the same basic organic polymers. They differ in the ionizable group attached to the hydrocarbon network. It is this functional group that determines the chemical behavior of the resin. Resins can be broadly classified as strong or weak acid cation exchangers or strong or weak base anion exchangers.

**Strong Acid Cation Resins** Strong acid resins are so named because their chemical behavior is similar to that of a strong acid. The resins are highly ionized in both the acid ($R\text{-}SO_3H$) and salt ($R\text{-}SO_3Na$) form. They can convert a metal salt to the corresponding acid by the reaction:

$$2(R\text{-}SO_3H) + NiCl_2 \text{ --> } (R\text{-}SO_4), Ni + 2HCl$$

**Weak Acid Cation Resins** In a weak acid resin the ionizable group is a carboxylic acid (COOH) as opposed to the sulfonic acid group ($SO_3H$) used in strong acid resins. These resins behave similarly to weak organic acids that are weakly dissociated.

**Strong Base Anion Resins** Like strong acid resins strong base resins are highly ionized and can be used over the entire pH range. These resins are used in the hydroxide (OH) form for water deionization. They will react with anions in solution and can convert an acid solution to pure water: $R\text{--}NH_3OH + HCl \text{ -> } R\text{-}NH_3Cl + HOH$

**Weak Base Anion Resins** Weak base resins are like weak acid resins in that the degree of ionization is strongly influenced by pH. Consequently, weak base resins exhibit minimum exchange capacity above a pH of 7.0. These resins merely sorb strong acids: they cannot split salts.

**Heavy-Metal-Selective Chelating Resins** Chelating resins behave similarly to weak acid cation resins but exhibit a high degree of selectivity for heavy metal cations. Chelating resins are analogous to chelating compounds found in metal finishing wastewater; that is, they tend to form stable complexes with the heavy metals. In fact the functional group used in these resins is an EDTA compound. The resin structure in the sodium form is expressed as R-EDTA-Na.

For removal of lead from wastewaters we can use natural and pretreatment zeolites. The structures of zeolites consist of a three-dimensional framework of $SiO_4$ and $AlO_4$ tetrahedral. The aluminum ion is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms, and the isomorphous replacement of $Al^{+3}$ for $Si^{+4}$ raises a negative charge in the lattice. The net negative charge is balanced by the exchangeable cation (sodium, potassium and calcium). These cations are exchangeable with certain cations in solutions such as lead. The fact that zeolite exchangeable ions are relatively innocuous (sodium, calcium and potassium ions)

makes them particularly suitable for removing undesirable heavy metal ions from industrial effluent waters.

**2.3) Adsorption:**

Adsorption, the binding of molecules or particles to a surface, must be distinguished from absorption, the filling of pores in a solid. The binding to the surface is usually weak and reversible. Just about anything including the fluid that dissolves or suspends the material of interest is bound, but compounds with color and those that have taste or odor tend to bind strongly. Compounds that contain chromogenic groups (atomic arrangements that vibrate at frequencies in the visible spectrum) very often are strongly adsorbed on activated carbon. Decolorization can be wonderfully efficient by adsorption and with negligible loss of other materials.

The most common industrial adsorbents are activated carbon, silica gel, and alumina, because they present enormous surface areas per unit weight. Activated carbon is produced by roasting organic material to decompose it to granules of carbon - coconut shell, wood, and bone are common sources. Silica gel is a matrix of hydrated silicon dioxide. Alumina is mined or precipitated aluminum oxide and hydroxide. Although activated carbon is a magnificent material for adsorption, its black color persists and adds a grey tinge if even trace amounts are left after treatment; however filter materials with fine pores remove carbon quite well.

A surface already heavily contaminated by adsorbates is not likely to have much capacity for additional binding. Freshly prepared activated carbon has a clean surface. Charcoal made from roasting wood differs from activated carbon in that its surface is contaminated by other products, but further heating will drive off these compounds to produce a surface with high adsorptive capacity. Although the carbon atoms and linked carbons are most important for adsorption, the mineral structure contributes to shape and to mechanical strength. Spent activated carbon is regenerated by roasting, but the thermal expansion and contraction eventually disintegrate the structure so some carbon is lost or oxidized. Temperature effects on adsorption are profound, and measurements are usually at a constant temperature. Graphs of the data are called *isotherms*. Most steps using adsorbents have little variation in temperature.

## 2.4) Electrodialysis:

Electro dialysis (ED) is a possible technique for treatment of the wastewater. The principle of ED involves removal of ionic components (like $Pb^{2+}$) from an aqueous solution through ion-exchange membranes using an electrical driving force. The wastewater to be treated is pumped through a membrane stack which consists of alternately placed anionic and cationic selective membranes separated by gasket frames and spacers. The membranes are fixed between two end plates that contain the electrodes producing the electric field. In order to transfer the electric current and to remove gases produced by electrode reactions, the electrode chambers are rinsed with an electrolyte solution.

## 2.5) Solvent Extraction:

Solvent extraction is accomplished by contacting soil with a solvent, separating the soil and solvent, and regenerating the solvent for reuse. To be successful, the extraction solvent should have a high solubility for the contaminant and low solubility in the waste matrix. Typical solvents include liquefied gas (propane or butane), supercritical carbon dioxide fluid, triethylamine, or proprietary organic fluids. The extraction solvent is well mixed with the contaminated matrix to allow contaminants to transfer to the solvent. The clean matrix and solvent are then separated by physical methods, such as gravity decanting or centrifuging. Distillation regenerates the solvent, which is then returned for reuse in the extraction process.

Extraction typically is mass transfer limited, so thorough mixing of the solvent and contaminated matrix is required. Some solvent extraction systems require the addition of water if the waste is a dry, nonflowing solid. In other systems, extraction fluid is added to make the waste flow.

The extraction solvent typically is purified by distillation. In systems that use pressurized solvents, such as liquefied gas or supercritical carbon dioxide, vaporization occurs by pressure release, which causes the solvent to boil. With higher-boiling solvents, distillation tanks or towers may be used to separate the extraction solvent from the organic contaminants.

## 2.6) Reverse Osmosis:

To understand "reverse osmosis," it is probably best to start with normal osmosis. According to Merriam-Webster's Collegiate Dictionary, osmosis is the "movement of a solvent through a semipermeable membrane (as of a living cell) into a solution of higher solute concentration that tends to equalize the concentrations of solute on the two sides of the membrane." That's a mouthful.

A semipermeable membrane is a membrane that will pass some atoms or molecules but not others. Saran wrap is a membrane, but it is impermeable to almost everything we commonly throw at it. The best common example of a semipermeable membrane would be the lining of your intestines, or a cell wall. Gore-tex is another common semipermeable membrane. Gore-tex fabric contains an extremely thin plastic film into which billions of small pores have been cut. The pores are big enough to let water vapor through, but small enough to prevent liquid water from passing.

The membrane allows passage of water molecules but not salt molecules. One way to understand osmotic pressure would be to think of the water molecules on both sides of the membrane. They are in constant Brownian motion. On the salty side, some of the pores get plugged with salt atoms, but on the pure-water side that does not happen. Therefore, more water passes from the pure-water side to the salty side, as there are more pores on the pure-water side for the water molecules to pass through. The water on the salty side rises until one of two things occurs:

- The salt concentration becomes the same on both sides of the membrane (which isn't going to happen in this case since there is pure water on one side and salty water on the other).
- The water pressure rises as the height of the column of salty water rises, until it is equal to the osmotic pressure. At that point, osmosis will stop.

Osmosis, by the way, is why drinking salty water (like ocean water) will kill you. When you put salty water in your stomach, osmotic pressure begins drawing water out of your body to try to dilute the salt in your stomach. Eventually, you dehydrate and die.

In reverse osmosis, the idea is to use the membrane to act like an extremely fine filter to create drinkable water from salty or metal ion(like $Pb^{2+}$) contaminated water. The salty or metal ion contaminated water is put on one side of the membrane and pressure is applied to stop, and then reverse, the osmotic process. It generally takes a lot of pressure and is fairly slow, but it works.

**2.7) Membrane Separation:**

In membrane separation, spent metal removal (like lead) fluids are pumped from a process tank at a moderate pressure (typically 30 to 50 psig) and rapid flow to a series of membranes. This flow is typically between 750 to 1,100 gallons per square foot of membrane per day and is referred to as the feed rate. Large molecules and virtually all petroleum products are blocked at the membrane surface. The compounds that do not pass through the membrane are referred to as the reject. The water-like solutions that pass through the membrane are referred to as the "permeate". The rate at which the permeate flows through the membrane is called the flux rate.

Membranes come in two basic sizes:

**A) Micro filtration** Membranes with a pore size of 0.1 – 10 μm perform micro filtration. Microfiltration membranes remove all bacteria. Only part of the viral contamination is caught up in the process, even though viruses are smaller than the pores of a micro filtration membrane. This is because viruses can attach themselves to bacterial biofilm.Micro filtration can be implemented in many different water treatment processes when particles with a diameter greater than 0.1mm need to be removed from a liquid.

**B) Ultra filtration:** For complete removal of viruses, ultra filtration is required. The pores of ultra filtration membranes can remove particles of 0.001 – 0.1 μm from fluids.

Advantages and Disadvantages of membrane separation:

**Advantages:**

a) Membrane separation consistently separates a wide variety of emulsion, surfactant, and chelating chemistries and various mixtures.
b) It requires no specific chemical knowledge.

c) Complex instrumentation is not required.

d) The method does not require constant attention.

e) The basic concept is simple to understand.

**Disadvantages:**

a) Membranes are expensive.

b) Certain solvents can quickly and permanently destroy the membrane.

c) Certain colloidal solids, especially graphite and residues from vibratory deburring operations, can permanently foul the membrane surface.

d) The energy cost is higher than chemical treatment, although less than evaporation.

e) Oil emulsions are not "chemically separated," so secondary oil recovery can be difficult.

f) Synthetics are not effectively treated by this method.

### 2.8) Gamma Irradiation:

Removal of heavy metals ions like lead ions from waste water using gamma irradiation has been investigated. These metal ions are reduced by hydrated electrons and hydrogen atoms to lower or zero valence state and eventually precipitated out of solution.Ethonol is applied as a relatively non-toxic additive to scavenge OH radicals, to enhance reduction and inhibit oxidation.

### 2.9) Cementation:

Cementation is the term used to describe the electrochemical precipitation of a metal (like lead), usually from an aqueous solution of its salts, by a more electropositive metal. The process has been used in industry for a long time, not only in hydrometallurgy but also in the purification of process streams and wastewater. The cementation treatment process has several advantages. These include simple control requirement, low energy consumption and recovery of valuable or toxic metals in a harmless and reusable form. The main disadvantage is electropositive metal consumption, especially when iron or zinc are used at low pH values.

## 2.10) Biological:

Biological treatment transforms, stabilizes and/or removes lead by means of microorganisms. Microorganisms, primarily certain specific bacteria, accomplish this by oxidation/reduction, mineralization, detoxification or methylation. Critical factors include energy and carbon source; aerobic, anoxic or anaerobic conditions; temperature; pH.

Although some of these treatment methods treatment methods can be successfully used for treating most wastewaters, others are quite limited in use. The application of chemical precipitation to dilute solutions (low concentration) can be difficult unless the addition of flocculating agents such as lime, caustic and sodium carbonate is employed. However a bulky sludge is produced and the disposal constitutes a problem. Ion exchange and activated carbon adsorption are quite expensive and require recharge of resin or spent activated carbon as well as the disposal of substantial volume of used regeneration solution. In addition to the fact that membrane technology is expensive, membranes are susceptible to attack by microorganisms, likewise other methods mentioned require elaborate and considerably high operation costs.

# CHAPTER-3

# ADSORPTION FUNDAMENTALS

## 3.1) General:

Adsorption is a surface phenomenon. The adsorption operations exploit the ability of certain solids preferentially to concentrate specific substances from solution onto their surfaces. The solute accumulated is called the adsorbate or solute and the adsorbing substance is the adsorbent. In the water purification, adsorbents are used to remove organic impurities, particularly those that are non-biodegradable or associated with taste, colour, and odour. Although adsorption is applied in low concentration, recent physical-chemical processes use adsorption as a primary technique to remove soluble organics from the wastewater. The adsorption is called physical adsorption when the bonding forces are relatively weak intermolecular forces like van der Waal's forces and, chemical when the bonding forces are strong like chemical bonding. During adsorption, the solid adsorbent becomes saturated or nearly saturated with the adsorbate. To recover the adsorbate and allow the adsorbent to be reused, it is regenerated by desorbing the adsorbed substances (i.e. the adsorbates).

### 3.1.1 Physical Adsorption vs. Chemisorption

Adsorption processes can be classified as physical adsorption (van der Waals adsorption) and chemisorption (activated adsorption) depending on the type of forces between the adsorbate and the adsorbent. In physical adsorption, the individuality of the adsorbate and the adsorbent are preserved. In chemisorption, there is a transfer or sharing of electron, or breakage of the adsorbate into atoms or radicals, which are bound separately.

Physical adsorption of a gas occurs when the inter-molecular attractive forces between molecules of the solid adsorbent and the gas are greater than those between molecules of the gas itself. In effect, the resulting adsorption is like condensation, which is exothermic and thus is accompanied by the release of heat, similar in magnitude to the heat of condensation. Physical adsorption occurs quickly and may be monomolecular (unimolecular) layer or monolayer, or two, three or more layers thick (multi-molecular). As physical adsorption takes place, it begins as a monolayer. It can then become multi-layer, and then, if the pores are close to the size of the molecules, more adsorption occurs until the pores are filled with adsorbate. Accordingly, the

maximum capacity of a porous adsorbent can be more related to the pore volume than to the surface area.

In contrast, chemisorption is monolayer, involves the formation of chemical bonds between the adsorbate and adsorbent, often with a release of heat much larger than the heat of condensation. Chemisorption from a gas generally takes place only at temperatures greater than 200 °C, and may be slow and irreversible.

Most commercial adsorbents rely on physical adsorption; while catalysis relies on chemisorption. A comparison between physical adsorption and chemical adsorption is given in Table 3.1.

**Table 3 .1. Comparison of Physical and Chemical Adsorption**

| Sl. No. | Physical Adsorption | Chemical Adsorption |
|---|---|---|
| 1. | Van der Wall's adsorption | Activated adsorption |
| 2. | Heat of adsorption = 5 kcal/mol | Heat of adsorption = 20-100 kcal/mol |
| 3. | Adsorption occurs only at temperature less than the boiling point of the adsorbate | Adsorption can occur even at higher temperature |
| 4. | No activation energy is involved in the adsorption process | Activation energy may be involved |
| 5. | Adsorption occurs in mono and multi layers | Adsorption occurs almost in mono layer |
| 6. | Quantity adsorbed per unit mass is high i.e. entire surface is participating | Quantity adsorbed per unit mass is low i.e. only active surface sites are important |
| 7. | Rate of adsorption controlled by mass transfer resistance | Rate of adsorption controlled by resistance reaction |

### 3.1.2 Intra-particle Diffusion Process

The rate of adsorption is determined by the rate of transfer of the adsorbate from the bulk solution to the adsorption sites within the particles. This can be broken conceptually into a series of consecutive steps.

1. Diffusion of adsorbate across a stationary solvent film surrounding each adsorbent
2. Diffusion through the macro pore
3. Diffusion through micro pore
4. Adsorption at an appropriate site

It is assumed that the fourth step occurs very rapidly in comparison to the second step. If the system is agitated vigorously, the exterior diffusion film around the adsorbent will be very thin, offering negligible resistance to diffusion. So, it can be assumed that the main resistance to adsorption shall lie in the pore diffusion step. Weber and Morris while referring to the rate limiting step of organic materials uptake by granulated activated carbon in the rapidly mixed batch system propose the term "intra-particle transport" which comprises of surface diffusion and molecular diffusion. Several researchers have shown that surface diffusion is the dominant mechanism and is the rate-determining step. A functional relationship common to most of the treatments of intra-particle transport is that the uptake varies almost proportionally with the square root of time.

### 3.1.3 Stages in Adsorption Process

Adsorption is thought to occur in three stages, as the adsorbate concentration increases.

Stage I: First, a single layer of molecules builds up over the surface of the solid. This monolayer may be chemisorbed and is associated with a change in free energy that is a characteristic of the forces that hold it.

Stage II: As the fluid concentration is further increased, second, third etc., layers are formed by physical adsorption; the number of layers which can form are limited by the size of the pores.

Stage III: Finally, for adsorption from the gas phase, capillary condensation may occur in which capillaries become filled with condensed adsorbate, when its partial pressure reaches a critical value relative to the size of the pore.

### 3.2) Adsorption Isotherms:

When a solution is contacted with a solid adsorbent, molecules of adsorbate get transferred from the fluid to the solid until the concentration of adsorbate in solution as well as in the solid phase are in equilibrium. At equilibrium, equal amounts of solute eventually are being adsorbed and desorbed simultaneously. This is called adsorption equilibrium. The equilibrium data at a given temperature are represented by adsorption isotherm and the study of adsorption is important in a number of chemical processes ranging from the design of heterogeneous chemical reactors to purification of compounds by adsorption.

Many theoretical and empirical models have been developed to represent the various types of adsorption isotherms. Langmuir, Freundlich, Temkin, Redlich-Peterson (R-P) etc. are most commonly used adsorption isotherm models for describing the dynamic equilibrium. The isotherm equations used for the study are described follows:

#### 3.2.1 Langmuir Isotherm

This equation based on the assumptions that:

1. Only monolayer adsorption is possible.
2. Adsorbent surface is uniform in terms of energy of adsorption.
3. Adsorbed molecules do not interact with each other.
4. Adsorbed molecules do not migrate on the adsorbent surface

The adsorption isotherm derived by Langmuir for the adsorption of a solute from a liquid solution is

$$Q_e = \frac{Q_m K_A C_e}{1 + K_A C_e} \qquad (3.1)$$

where,

$Q_e$ = Amount of adsorbate adsorbed per unit amount of adsorbent at equilibrium.

$Q_m$ = Amount of adsorbate adsorbed per unit amount of adsorbent required for monolayer adsorption (limiting adsorbing capacity).

$K_A$ = Constant related to enthalpy of adsorption.

$C_e$ = Concentration of adsorbate solution at equilibrium.

The Langmuir isotherm can be rearranged to the following linear forms:

$$\frac{C_e}{Q_e} = \frac{1}{K_A Q_m} + \frac{C_e}{Q_m} \tag{3.2}$$

or

$$\frac{1}{Q_e} = \left(\frac{1}{K_A Q_m}\right)\left(\frac{1}{C_e}\right) + \left(\frac{1}{Q_m}\right) \tag{3.3}$$

### 3.2.2 Freundlich Isotherm

The heat of adsorption in many instances decreases in magnitude with increasing extent of adsorption. This decline in heat of adsorption is logarithmic, implying that adsorption sites are distributed exponentially with respect to adsorption energy. This isotherm does not indicate an adsorption limit when coverage is sufficient to fill a monolayer .The equation that describes such isotherm is the Freundlich Isotherm, given as

$$Q_e = K_F C_e^{\frac{1}{n}} \tag{3.4}$$

where ,

$K_F$ and n are the constants

$C_e$ = the concentration of adsorbate solution at equilibrium

by taking logarithm on both sides, this equation is converted into a linear form:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{3.5}$$

Thus a plot between ln $Q_e$ and ln $C_e$ is a straight line. The Freundlich equation is most useful for dilute solutions over small concentration ranges. It is frequently applied to the adsorption of impurities from a liquid solution on to the activated carbon. A high $K_F$ and high 'n' value is an indication of high adsorption through out the concentration range. A low $K_F$ and high 'n' indicates a low adsorption through out the concentration range. A low 'n' value indicates high adsorption at strong solute concentration.

### 3.2.3 Temkin Isotherm

It is given as

$$q_e = \frac{RT}{b}\ln(K_T C_e) \tag{3.10}$$

which can be linearized as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \tag{3.11}$$

where $B_1 = \frac{RT}{b}$

Temkin isotherm contains a factor that explicitly takes into the account of adsorbing species-adsorbent interactions. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. A plot of $q_e$ versus $\ln C_e$ enables the determination of the isotherm constants $B_1$ and $K_T$ from the slope and the intercept, respectively. $K_T$ is the equilibrium binding constant (l/mol) corresponding to the maximum binding energy and constant $B_1$ is related to the heat of adsorption.

### 3.2.4 Redlich-Peterson isotherm

Redlich and Peterson (1959) model combines elements from both the Langmuir and Freundlich equation and the mechanism of adsorption is a hybrid and does not follow ideal monolayer adsorption. The Redlich-Peterson isotherm has a linear dependence on concentration in the numerator and an exponential function in the denominator. The R–P equation is a combination of the Langmuir and Freundlich models. It approaches the Freundlich model at high concentration and is in accord with the low concentration limit of the Langmuir equation. Furthermore, the R–P equation incorporates three parameters into an empirical isotherm, and therefore, can be applied either in homogenous or heterogeneous systems due to the high versatility of the equation.

It can be described as follows:

$$Q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}} \tag{3.12}$$

Where $K_R$ is R–P isotherm constant (L/g), $a_R$ is R–P isotherm constant (L/mg) and β i the exponent which lies between 1 and 0, where β=1

$$Q_e = \frac{K_R C_e}{1 + a_R C_e} \tag{3.13}$$

It becomes a Langmuir equation. Where β=0

$$Q_e = \frac{K_R C_e}{1 + a_R} \tag{3.14}$$

i.e. the Henry's Law equation

Eq. (3.12) can be converted to a linear form by taking logarithms:

$$\ln\left(K_R \frac{C_e}{Q_e} - 1\right) = \ln a_R + \beta \ln C_e \tag{3.15}$$

Plotting the left-hand side of equation (3.15) against ln $C_e$ to obtain the isotherm constants is not applicable because of the three unknowns, $a_R$, $K_R$ andβ. Therefore, a minimization procedure was adopted to solve equation (3.15) by maximizing the correlation coefficient between the theoretical data for $Q_e$ predicted from equation (3.15) and experimental data. Therefore, the parameters of the equations were determined by minimizing the distance between the experimental data points and the theoretical model predictions with any suitable computer programme.

4. Contact time
5. Degree of agitation
6. Nature of adsorbent

### 3.4.1 Initial Concentration

The initial concentration of pollutant has remarkable effect on its removal by adsorption. The amount of adsorbed material increases with the increasing adsorbate concentration as the resistance to the uptake of the adsorbate from solution decreases with increasing solute concentration. Percent removal increases with decreasing concentrations.

### 3.4.2 Temperature

Temperature is one of the most important controlling parameter in adsorption. Adsorption is normally exothermic in nature and the extent and rate of adsorption in most cases decreases with increasing temperature of the system. Some of the adsorption studies show increased adsorption with increasing temperature. This increase in adsorption is mainly due to increase in number of adsorption sites caused by breaking of some of the internal bonds near the edge of the active surface sites of the adsorbents.

### 3.4.3 pH

Adsorption from solution is strongly influenced by pH of the solution. The adsorption of cations increases while that of the anions decreases with increase in pH. The hydrogen ion and hydroxyl ions are adsorbed quite strongly and therefore the adsorption of other ions is affected by pH of solution. Change in pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface active sites. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of adsorption process. It is an evident observation that the surface adsorbs anions favorably at lower pH due to presence of $H^+$ ions, whereas the surface is active for the adsorption of cations at higher pH due to the deposition of $OH^-$ ions.

### 3.4.4 Contact Time

The studies on the effect of contact time between adsorbent and adsorbate have significant importance. In physical adsorption, most of the adsorbate species are adsorbed on the adsorbent surface with in short contact time. The uptake of adsorbate is fast in the initial stages of the contact period and becomes slow near equilibrium. Strong chemical binding of adsorbate with adsorbent requires a longer contact time for the attainment of equilibrium. Available adsorption results reveal that the uptake of heavy metals is fast at the initial stages of the contact period, and there after it becomes slow near equilibrium.

### 3.4.5 Degree of Agitation

Agitation in batch adsorbers is most important to ensure proper contact between the adsorbent and the solution. At lower agitation speed, the stationary fluid film around the particle is thicker and the process is mass transfer controlled. With the increase in agitation this film decreases in thickness and the resistance to mass transfer due to this film reduces and after a certain point the process becomes intra particle diffusion controlled. Whatever is the extent of agitation the solution inside the process remain unaffected and hence for intraparticle mass transfer controlled process agitation has no effect on the rate on the adsorption.

### 3.4.6 Nature of Adsorbent

Many solids are used as adsorbents to remove the impurities from fluids. Commercial adsorbents generally have large surface area per unit mass. Most of the surface area is provided by a network of small pores inside the particles. Common industrial adsorbents for fluids include activated carbon, silica gel, activated alumina, molecular sieves etc. Adsorption capacity is directly proportional to the exposed surface. For the non-porous adsorbents, the adsorption capacity is directly proportional to the particle size diameter whereas for porous materials it is practically independent of particle size.

Activated carbon is the most widely used adsorbent for water purification. In the manufacture of activated carbon, organic materials such as coal nutshells, bagasse is first pyrolysed to a carbonaceous residue. Larger channels or pores with diameter 1000 Å are called macro pores. Most of the surface area for adsorption is provided by micropores, which are arbitrarily defined as pores with diameter from 10-1000 Å.

**Table.3.2: Various commercial adsorbents**

| Adsorbent | Properties& method of preparation | Application |
|---|---|---|
| Silica gel | Hard, granular and very porous product made from gel precipitated by sodium silicate. | Drying of gases, refrigerants, organic solvents.<br>Desiccant in packing and double glazing.<br>Due point control of natural gas. |
| Activated alumina | Hard, hydrated aluminum hydroxide which is activated by heating to drive moisture. | Dry of gases, organic solvents, transformer oils.<br>Desiccant in packing and double glazing.<br>Removal of HCl from hydrogen. |
| Carbon | Activated carbon is the residue obtained from various carbonaceous material like coal,wood,paper mills sludge, agro waste. | Nitrogen from air.<br>Recovery of certain vapors.<br>Purification of helium.<br>Water purification. |
| Polymeric and Resin | These are hydrophobic adsorbents which are obtained from pyrolysis and activation of polymeric compounds. | Separation of fatty acids from water and toluene.<br>Separation of aromatics from aliphatics.<br>Removal of colour from syrups. |
| Fuller's Earth | These are natural clays The clay is heated and dried during which it develops a porous structure. | Treatment of edible oils.<br>Removal of organic pigments.<br>Refining of mineral oils. |
| Zeolites | It is insoluble and chemically stable aluminum silicate mineral that was formed from the glass component of volcanic ash. | Removing water from azeotropes.<br>Sweetening sour gases and liquids.<br>Purification of hydrogen.<br>Separation of ammonia and hydrogen.<br>Recovery of carbon dioxide.<br>Separation of xylene and ethyl benzene. |

**Table.3.3: Typical non conventional adsorbents**

| Adsorbent | Application |
|---|---|
| Coal fly ash | Heavy metals, organic compounds, COD of waste water, phosphate, phenolic compounds. |
| Bagasse fly ash | Sugar and distillery effluents, heavy metals, chlorinated phenols. |
| Peat | Heavy metals, cyanide, phosphate, oil in water, color and dyes. |
| Lignite | Ammonia dyes. |
| Activated carbon from lignin sludge, bark, rice husk. | Color, heavy metals, dyes, distillery waste. |
| Coconut husk, peanut skin, bagasse pitch. | Heavy metals, dyes. |
| Hardwood, softwood, saw dust. | Heavy metals, dyes, COD. |
| Waste rubber. | Heavy metals. |
| Hematite, slag. | Heavy metals. |
| Tannery hair | TOC, soluble organic dyes, virus. |
| China clay, wollastonite. | Dyes, oxalic acid and Fluorides. |

# CHAPTER-4

# LITERATURE REVIEW

**General**

Several investigations have been worked on the removal of lead by using different adsorbents. These are reported below.

The phenomena of lead, copper and cobalt adsorption by activated carbon from aqueous solution was studied in detail by **A.Netzer et.al. (1982)**.Laboratory studies were conducted to evaluate and optimize the various process variables (i.e. carbon type, solution pH, equilibrium time and carbon dose). A quantitative determination of the adsorptive capacity of activated carbon to remove these metals was also determined. Solution pH was found to be the most important parameter affecting the adsorption. Of the ten commercially available activated carbons evaluated in these experiments, Barney Cheney NL 1266 was found to adsorb the largest percentage of lead, copper and cobalt.

Waste Biogas Residual Slurry as an Adsorbent for the Removal of Pb (II) from aqueous solution and Radiator Manufacturing Industry Wastewater was studied by **C.Namasivayam et.al. (1995)**. Waste biogas residual slurry (BRS) was used for the adsorption of Pb (II) from aqueous solution, over a range of initial metal ion concentrations, agitation times, adsorbent doses and initial pH values. The amount of Pb (II) adsorbed increased with increases in the initial concentration of Pb (II). The applicability of the Lagergren rate equation was also investigated. The process of uptake of Pb (II) by BRS followed the Langmuir isotherm model and the adsorption capacity was 28 mg/g.

The adsorption of aqueous Pb (II), EDTA, and Pb( II )-EDTA complexes onto TiO2 were studied at both stoichiometric and non- stoichiometric Pb( II ) /EDTA concentrations by **Muhammad S. Vohra et.al.(1997)**. Inner-sphere complexation was considered to occur between Pb (II), EDTA, Pb(II)-EDTA, and the TiO2 surface sites. Surface complexes used in the modeling included Ti-O-Pb/, Ti-EDTAH20, Ti-EDTA-Pb0, and Ti-O-Pb-EDTA. The cationic-type complexation, Ti-O-Pb-EDTA, was postulated to explain and model the anomalous EDTA adsorption as noted for Pb( II ) .

The sorption of lead ions from aqueous solution onto peat has been studied by **Y. S. Ho et.al.(1998)**. Kinetic studies have been carried out using an agitated batch and the effect of varying process parameters has been investigated; these include initial lead ion concentration, peat particle size, solution temperature and agitation speed. The data were analyzed using a pseudo-first order Lagergren equation and the data were correlated using a two-step first order reaction mechanism.

Removal of Cu, Zn and Pb by fly ash and fly ash/lime mixing was studied by **P.Ricou et.al.(1999).** In the first part of the study, isotherms at different pH were carried out at room temperature. Results show increasing removal with increasing pH. In the second part, experimental design methodology was used. The objectives were to determine the influential parameters among the seven studied for adsorption of copper, zinc and lead, then to study their interactions. Results indicate greater removal by using 100 $g.l^{-1}$ of adsorbent with 20% mass of lime at pH 5. However, the preparation of the adsorbent must be modified to increase the role of lime in the removal mechanism.

Red mud, an aluminium industry waste, has been converted into an inexpensive and efficient adsorbent and used for the removal of lead and chromium from aqueous solutions and this investigation was done by **Vinod K. Gupta et.al.(2000).** Effect of various factors on the removal of these metal ions from water (e.g. pH, adsorbent dose, adsorbate concentration, temperature, particle size, etc.) has been studied and discussed. The material exhibits good adsorption capacity and the data follow both Freundlich and Langmuir models. Thermodynamic parameters indicate the feasibility of the process. Kinetic studies have been performed to understand the mechanism of adsorption. Dynamic modelling of lead and chromium removal on red mud has been undertaken and found to follow first-order kinetics.

An evaluation of the application of electric furnace slag (EFS) as an adsorbent to remove Pb2+ and Cu2+ from industrial effluents was investigated by **L.Kurkovic et.al.(2000)** .In the batch experiments, parameters studied include the effect of initial concentration of lead and copper ions, temperature, and contact time. Over the temperature range studied (293–313 K) the results of adsorption experiments could be fitted by using both Langmuir and Freundlich models and thermodynamic values of corresponding to each adsorption process were calculated.

In this work, sorption of lead on sawdust (SD) has been studied by **BinYu et.al.(2001)** using batch techniques. The equilibrium sorption level for lead is a function of the solution pH, contact time, sorbent and sorbate concentration. The equilibrium adsorption capacity of sawdust for lead was measured and extrapolated using linear Freundlich and Langmuir isotherms and compared with that for copper. Metal ions which are bounded to the sawdust could be stripped by acidic solution so that the sawdust can be recycled.

This paper discusses the sorption performance of novel materials for the removal of lead(II) and copper(II) from near-neutral aqueous solutions by **D.J. Malik et.al.(2001)**. Active carbons with surface heteroatoms of oxygen and phosphorus have been prepared. The surface functional groups display weakly acidic ion exchange characteristics. The optimum solution pH for maximum metal sorption is related to the pK values of the surface functional groups. The weakly acidic carboxyl groups of structural polysaccharides present within the algal matrix display high sorption capacity for both metals. The negative surface charge of algal particles results in electrostatic interactions as well as coordination between metal species and the adsorbent surface. The surface functional groups in algae unlike those in oxidized active carbons may be represented by discrete acid-dissociation constant values.

Carbon nanotubes (CTNs) show exceptional adsorption capability and high adsorption efficiency for lead removal from water. This was studied by **Yan-Hui Li et.al.(2002)**. The adsorption is significantly influenced by the pH value of the solution and the nanotube surface status, which can be controlled by their treatment processing. The adsorption isotherms are well described by both Langmuir and Freundlich models. Our results suggest that CNTs can be good $Pb^{2+}$ adsorbers and have great potential applications in environmental protection.

The adsorption capacity of some natural materials for lead such as animal bone powder, active carbon, Nile rose plant powder, commercial carbon and ceramics was studied by **S.H. Abdel-Halim et.al.(2002)**.The adsorption process was affected by various parameters such as contact time, pH and concentration of lead solution. The lead uptake percent reaches equilibrium state after 15, 30, 45 and 120 min for bone powder, active carbon, plant powder and commercial carbon, respectively. The uptake percent of lead increased by increasing pH value.The percent removal of lead was 100% by bone powder, 90% by active carbon, 80% by plant powder and 50% by commercial carbon. There was no removal of lead by ceramics. This may be due to the presence of high percent of lead in the constituent of ceramics (372 mg/g).

The removal of heavy metals from plating factory wastewater with economical materials was investigated by **Hideyuki Katsumata et.al.(2003),** montmorillonite, kaolin, tobermorite, magnetite, silica gel and alumina were used as the economical adsorbents to wastewater containing Cd(II), Cr(VI), Cu(II) and Pb(II). This removal method of heavy metals proved highly effective as removal efficiency tended to increase with increasing pH and decrease with increasing metal concentration. The proposed method was successfully applied to the removal of Cd(II), Cr(VI) and Cu(II) in rinsing wastewater from plating factory in Nagoya City, Aichi Prefecture, Japan.

The adsorption of lead on a new adsorbent synthesized from natural condensed tannin has been investigated by **Xin-Min Zhan et.al.(2003)**using a series of batch adsorption experiments. The study on the adsorption mechanism indicates that the adsorbent performed in aqueous solutions as an ionic exchanger whose end group was sodium ion (Na+). One lead (II) ion (Pb2+) was adsorbed onto the adsorbent by taking the place of two Na+ ions. To a significant extent, pH influenced the extraction of lead from aqueous solutions. The lead removal efficiency was up to 71%, 87% and 91% with initial solution pH at 3.0, 3.6 and 4.2, respectively. The Langmuir equation fitted the adsorption isotherm data well. The maximum adsorption capacity of lead calculated was 57.5, 76.9.

Adsorption of water soluble lead on polymetallic sea nodule has been studied by **S. Bhattacharjee et.al.(2003)**. Complete decontamination of lead is possible by appropriate sea nodule dosing. Adsorption is also dependent on pH and best adsorption is achieved at pH 6. Both Freundlich and Langmuir isotherms may reasonably explain adsorption of lead on sea nodule.

Fixation of heavy metal ions (Cd(II) and Pb(II)) onto sawdust of Pinus sylvestris is presented in this paper. Batch experiments were conducted to study the main parameters such as adsorbent concentration, initial adsorbate concentration, contact time, kinetic, pH solution, and stirring velocity on the sorption of Cd(II) and Pb(II) by sawdust of P. sylvestris. Kinetic aspects are studied in order to develop a model which can describe the process of adsorption on sawdust. The capacity of the metal ions to bind onto the biomass was 96% for Cd(II), and 98% for Pb(II). The sorption followed a pseudo-second-order kinetics.

An inexpensive and effective adsorbent was developed from bagasse fly ash, obtained from a sugar industry, for the dynamic uptake of lead and chromium. This investigation was done by **V.K. Gupta et.al.(2003)**. Lead and chromium are sorbed by the developed adsorbent up to 96–98%. The removal of these two metal ions up to 95–96% was achieved by column experiments at a flow rate of 0.5 ml min−1. The adsorption was found to be exothermic in nature. The adsorbent was successfully tried for the removal of lead and chromium from wastewater in our laboratory. The developed system for the removal of two ions is very useful, economic, rapid, and reproducible.

An uptake of zinc (Zn), copper (Cu), and lead (Pb) from aqueous solutions by ion exchange on natural zeolitic tuff has been studied by **J. Peri et.al.(2003)**.The Croatian zeolite clinoptilolite from the Donje Jesenje deposit has been used as a natural ion exchanger. The efficiency of removal is higher for Pb and Cu than for Zn ions. The adsorption isotherm equations; Langmuir–Freundlich, Redlich–Petersen, Toth, Dubinin–Radushkevich,modified Dubinin–Radushkevich, and Lineweawer–Burk were derived from the basic empirical equations, and used for calculation of ion exchange parameters.

In this paper, the ability of siderite to remove Pb2+ from aqueous solution by adsorption has been investigated by **Mehmet Erdem et.al.(2004)** through batch experiments. The Pb2+ adsorption property of the siderite was evaluated as a function of pH, siderite dosage, initial Pb2+ concentration, and temperature. Maximum Pb2+ adsorption yield was obtained to be 99.6% for initial Pb2+ concentration of 50 mg/l at 25 °C and pH 2.97 for 180 min in the presence of 10 g/l siderite. Adsorption data obtained at 25, 30 and 35 °C showed that the adsorption process fitted first-order adsorption rate expression and Langmuir and Freundlich adsorption models. Adsorption capacities of siderite at 25, 30 and 35 °C were found to be 10.32, 12.45 and 14.06 mg Pb2+/g siderite, respectively. Adsorption enthalpy and activation energy values were calculated to be 49.73 and 32.49 kJ/g mol from the isotherm and kinetic data, respectively.

Removal of heavy metals when present singly or in binary and ternary systems by the milling agrowaste of Cicer arientinum (chickpea var. black gram) as the biosorbent has been studied by **Asma Saeed et.al.(2004)**. The biosorbent removed heavy metal ions efficiently from aqueous solutions with the selectivity order of Pb >Cd > Zn >Cu > Ni. The biosorption of metal ions by black gram husk (BGH) increased as the initial metal concentration increased. Biosorption

equilibrium was established within 30 min, which was well described by the Langmuir and Freundlich adsorption isotherms.

In an attempt to reuse food waste for useful purposes, **Toshimitsu Tokimoto et.al.(2004)** investigated the possibility of using coffee grounds to remove lead ions from drinking water. They studied the lead ion adsorption characteristics of coffee beans and grounds by measuring their fat and protein content, adsorption isotherms for lead ions, and adsorption rates for lead ions. The number of lead ions adsorbed by coffee grounds did not depend on the kind of coffee beans or the temperature at which adsorption tests were performed. The rate of lead ion adsorption by coffee grounds was directly proportional to the amount of coffee grounds added to the solution. When coffee grounds were degreased or boiled, the number of lead ions decreased. When proteins contained in coffee grounds were denatured, the lead ion adsorption was considerably reduced. The lead ion adsorption capacity of coffee grounds decreased with increased concentration of perchloric acid used for treating them and disappeared with 10% perchloric acid.

Different morphologies of carbon nanotubes effect on the lead removal from aqueous solution was studied by **Yan-Hui Li et.al.(2005)**.Four kinds of CNTs with different morphologies were produced by chemical vapor deposition method. After oxidation with nitric acid, their specific surface area, particle size distribution and functional groups on the surfaces were characterized. Adsorption isothermal experiment shows that the CNTs with more defects, which can be easily, introduced more functional groups on their surfaces prepared at 650°C, have higher lead adsorption capability from aqueous solution and are promising adsorbents in wastewater treatment.

The sorption of lead ion onto palm kernel fiber was studied by **Yuh-Shan Ho et.al.(2005)** performing batch kinetic sorption experiments. The batch sorption model, based on a pseudo-second-order mechanism, was applied to predict the rate constant of sorption, the equilibrium capacity and the initial sorption rate with the effects of the initial solution pH and fiber dose. Equilibrium concentrations were evaluated with the equilibrium capacity obtained from the pseudo-second-order rate equation. In addition, pseudo-isotherms were also obtained by changing fiber doses using the equilibrium concentration and equilibrium capacity obtained based on the pseudo-second-order constants.

Maize bran is a low cost biosorbent that has been used for the removal of lead (II) from an aqueous solution and it was studied by **K.K. Singh et.al.(2005)**. The effects of various parameters such as contact time, adsorbate concentration, pH of the medium and temperature were examined. Optimum removal at 20°C was found to be 98.4% at pH 6.5, with an initial Pb (II) concentration of 100 mg /1. Dynamics of the sorption process and mass transfer of Pb (II) to maize bran were investigated and the values of rate constant of adsorption, rate constant of intraparticle diffusion and the mass transfer coefficients were calculated. Different thermodynamic parameters viz., changes in standard free energy, enthalpy and entropy were evaluated and it was found that the reaction was spontaneous and exothermic in nature. The adsorption data fitted the Langmuir isotherm. A generalized empirical model was proposed for the kinetics at different initial concentrations. The data were subjected to multiple regression analysis and a model was developed to predict the removal of Pb (II) from an aqueous solution.

The performance of a commercially available palm shell based activated carbon to remove lead ions from aqueous solutions by adsorption was evaluated by **Gulnaziya Issabayeva et.al.(2005)**. The adsorption experiments were carried out at pH 3.0 and 5.0. The effect of malonic and boric acid presence on the adsorption of lead ions was also studied. Palm shell activated carbon showed high adsorption capacity for lead ions, especially at pH 5 with an ultimate uptake of 95.2 mg/g. This high uptake showed palm shell activated carbon as amongst the best adsorbents for lead ions. Boric acid presence did not affect significantly lead uptake, whereas malonic acid decreased it. The diffuse layer surface complexation model was applied to predict the extent of adsorption. The model prediction was found to be in concordance with the experimental values.

The removal of lead ions from aqueous solution was studied by **M. Mouflih et.al.(2005)** in batch experiments using natural phosphate (NP). The effects of initial concentration of lead and initial pH of solution were investigated and the mechanism for removal of lead has been suggested. The data obtained from sorption isotherms at different temperatures conformed to the linear form of the Langmuir adsorption equation. The influence of NO3− and Cl− anions has been evaluated. The effect of varying levels of Cl− has significant influence on the sorption capacity of Pb2+, while NO3− did not. The abundance of natural phosphate, its low price and non-aggressive

nature towards the environment are advantages for its utilization in point of view of wastewater and wastes clean up.

The capacity of hydroxyapatite (HAp) to remove lead from aqueous solution was investigated by **Baillez Sandrine et.al.(2006)** under different conditions, namely initial metal ion concentration and reaction time. The sorption of lead from solutions containing initial concentrations from 0 to 8000 mg/L was studied for three different HAp powders. Soluble Pb and Ca monitoring during the experiment allows characterizing the mechanism of lead uptake. Dissolution of calcium is followed by the formation of a solid solution with a Ca/P ratio decreasing continuously. Langmuir–Freundlich classical adsorption isotherms modeled adsorption data. The adsorption capacities calculated from this equation vary from 330 to 450 mg Pb/g HAp for the different solids. Modeling of the sorption process allows to determine theoretical saturation times and residual lead concentrations at equilibrium.

In the present study, the ability of natural zeolite clinoptilolite and bentonite (clay) to remove Pb(II) from aqueous solutions has been investigated by **Vassilis J. Inglezakis et.al.(2006)** in batch reactors with a maximum contact time of 120 min. Adsorption tests of Pb(II) were carried out using a solution concentration of 1,036 ppm at initial pH = 4, and solid to liquid ratio of 2 g/100 ml. The effects of agitation speed (0, 100, 200, 500 rpm), temperature (28°C, 45°C, 60°C) and particle size (2.5–5.0 mm, dust) of the minerals were examined. The effect of acidity of the aqueous solution was also examined. Bentonite was found to be more effective for the removal of Pb(II) than clinoptilolite, under the experimental conditions used. The removal of Pb(II) using bentonite reached 100% at ambient temperature and mild agitation (100 rpm), while it was approximately 90% at 60°C without agitation.

The removal of heavy metals from wastewater using olive cake as an adsorbent was investigated by **Sabriye Doyurum et.al.(2006)**.The effect of the contact time, pH, temperature, and concentration of adsorbate on adsorption performance of olive cake for Pb(II) and Cd(II) ions were examined by batch method. Adsorption of Pb(II) and Cd(II) in aqueous solution onto olive cake was studied in single component. After establishing the optimum conditions, elution of these ions from the adsorbent surface was also examined. The optimum sorption conditions were determined for two elements. Maximum desorption of the Pb(II) and Cd(II) ions were found to be 95.92 and 53.97% by 0.5M HNO3 and 0.2M HCl, respectively. The morphological analysis of the olive cake was performed by the scanning electron microscopy (SEM).

An indigenously prepared, steam activated and chemically modified carbon from husk and pods of Moringa oleifera (M.oleifera), an agricultural waste, was comparatively examined as an adsorbent for the removal of lead from aqueous solutions by **Muhammad Nadeem et.al.(2006)**. Studies were conducted as a function of contact time, initial metal concentration, dose of adsorbent, agitation speed, particle size, and pH. Maximum uptake capacities were found to be, 98.89, 96.58, 91.8, 88.63, 79.43% for cetyltrimethyl ammonium bromide (CTAB), phosphoric, sulfuric, hydrochloric acid treated and untreated carbon adsorbents respectively. Bangham, Pseudo-first and second order, Intra Particle Diffusion equations were implemented to express the sorption mechanism by utilized adsorbents. The results of adsorption were fitted to both the Langmuir and Freundlich models.

The biosorption of lead ions from aqueous solution by Syzygium cumini L. was studied by **P.King et.al.(2006)** in a batch adsorption system as a function of pH, contactn time, lead ion concentration, adsorbent concentration and adsorbent size. The biosorption capacities and rates of lead ions onto S. cumini L. were evaluated. The Langmuir, Freundlich, Redlich–Peterson and Temkin adsorption models were applied to describe the isotherms and isotherm constants. Biosorption isothermal data could be well interpreted by the Langmuir model followed by Temkin model with maximum adsorption capacity of 32.47 mg/g of lead ion on S. cumini L. leaves biomass. The kinetic experimental data were properly correlated with the second-order kinetic model.

The use of natural palygorskite clay for the removal of Pb (II) from aqueous solutions for different contact times, pHs of suspension, and amounts and particle sizes of palygorskite clay were investigated by **Hao Chen et.al.(2006)**.The variations of the pH value of Pb (II) solutions on natural palygorskite in the adsorption process were determined. Batch adsorption kinetic experiments revealed that the adsorption of Pb (II) onto palygorskite clay involved fast and slow processes. It was found that the adsorption mechanisms in the lead/palygorskite system follow pseudo-second-order kinetics with a significant contribution from film diffusion. SEM observations demonstrated that an important interaction at the lead–granule interface occurred during the adsorption process. The adsorption isotherms were described by means of the Langmuir and Freundlich isotherms and the Langmuir model represents the adsorption process better than the Freundlich model. The maximum adsorption capacity of Pb(II) onto natural palygorskite was 104.28 mg /g.

The ability of low-cost activated carbon prepared from Ceiba pentandra hulls, an agricultural waste material, for the removal of lead and zinc from aqueous solutions has been investigated by **M. Madhava Rao et.al.(2007)**. In the batch tests experimental parameters were studied, including solution pH, contact time, adsorbent dose and initial metal ions concentration. The adsorbent exhibited good sorption potential at pH 6.0. Maximum removal of lead (99.5%) and of zinc (99.1%) with 10 g/l of sorbent was observed at 50 mg/L sorbate concentration. Removals of about 60–70% occurred in 10 min, and equilibrium was attained at around 50 min for both metals. The desorption studies were carried out using dilute HCl, and the effect of HCl concentration on desorption was studied. Maximum desorptions of 85% for lead and 78% for zinc were attained with 0.15 M HCl.

Adsorption of copper and lead ions onto tea waste from aqueous solutions was studied by **B.M.W.P.K. Amarasinghe et.al.(2007)** to enable comparison with alternative commonly available absorbents. Batch experiments were conducted to determine the factors affecting adsorption and kinetics of the process. Fixed bed column experiments were performed to study practical applicability and breakthrough curves were obtained. Tea waste is capable of binding appreciable amounts of Pb and Cu from aqueous solutions. The adsorption capacity was highest at solution pH range 5–6. The adsorbent to solution ratio and the metal ion concentration in the solution affect the degree of metal ion removal. The equilibrium data were satisfactorily fitted to Langmuir and Freundlich isotherms. Highest metal uptake of 48 and 65 mg/g were observed for Cu and Pb, respectively. Pb showed higher affinity and adsorption rate compared to Cu under all the experimental conditions. Kinetic studies revealed that Pb and Cu uptake was fast with 90% or more of the adsorption occurring within first 15–20 min of contact time.

The equilibrium and kinetic properties of $Pb^{2+}$ ion adsorption by retorted shale (RS) have been investigated by P.M. Pimentel et.al.(2007) during a series of batch adsorption experiments. The effects of pH, contact time and adsorbate initial concentrations were evaluated. The pseudo-second-order model was used to predict the rate constants of adsorption system. Langmuir and Freundlich models were used to fit the equilibrium data, which showed that Langmuir best-fitted these data. Thermodynamic parameters of adsorption indicate spontaneous and endothermic nature of the process.

This paper presents the results of research on heavy metals removal from water by filtration using low cost coarse media which could be used as an alternative approach to remove heavy metals from water or selected wastewater and this was studied by **Hamidi A. Aziz et.al.(2007)**. A series of batch studies were conducted using different particle media (particle size 2.36–4.75 mm) shaken with different heavy metal solutions at various pH values to see the removal behaviour for each metal. Each solution of cadmium (Cd), lead (Pb), zinc (Zn), nickel (Ni), copper (Cu) and chromium (Cr(III)) with a concentration of 2 mg/L was shaken with the media. At a final pH of 8.5, limestone has significantly removed more than 90% of most metals followed by 80% and 65% removals using crushed bricks and gravel, respectively.

The adsorption of lead onto formaldehyde or sulphuric acid treated acorn waste was studied by **Ahmet Ornek et.al.(2007)** using a batch sorber. The aim of this study was to understand the mechanisms that govern lead removal and find a suitable equilibrium isotherm and kinetic model for the lead removal in a batch reactor. The experimental isotherm data were analyzed using the Langmuir, Freundlich and Temkin equations. The equilibrium data fit well the Langmuir isotherm. The experimental data were analyzed using four adsorption kinetic models – the pseudo first- and second-order equations, intraparticle diffusion equation and the Elovich equation – to determine the best fit equation for the adsorption of lead ions onto formaldehyde or sulphuric acid treated acorn waste. The rate constants, equilibrium capacities and related correlation coefficients for each kinetic model were calculated and discussed. Also, predicted qt values from the kinetic equations were compared with the experimental data. Results show that the pseudo second-order equation provides the best correlation for the adsorption process, whereas the Elovich equation also fits the experimental data well.

# CHAPTER-5

# EXPERIMENTAL PROGRAMME

Experimental details of the study have been presented in this chapter. These details include characterization of adsorbents and batch adsorption studies.

## 5.1) Objective of present study:

The objective of this study is to investigate some useful information regarding the use of adsorption for the removal of lead from waste water. Here I have used Coconut Jute Activated Carbon (CJAC) and Commercial Activated Carbon (CAC) as adsorbents. The entire study deals with various parameters dealing with adsorption and adsorption kinetics.

- 1000mg/l of stock solution is to be prepared by dissolving 1.6g of lead nitrate ($Pb(NO_3)_2$) in 1000ml of distilled water, from this stock solution solutions of desired concentrations (20-100 mg/l) were prepared.
- Lead concentration is to be estimated by UV/VIS spectrophotometer (Perkin Elmer 35) using PAR reagent ( 2,4-pyridyl azoresorcinol) at 580 nm.
- The Physico-Chemical characteristics of adsorbents are to be found by various methods like Proximate Analysis, Density, Particle Size Analysis, Surface area measurement, Scanning Electron Micrograph (SEM) etc.,
- Study the effect of various batch parameters like optimum pH, contact time, adsorbent dose, temperature, concentration on the removal of lead.
- Study of the kinetics of adsorption.
- Studies of the isotherms are to be used to find the adsorption capacity of the adsorbent.
- Study of thermodynamic adsorption parameters, $\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$.

## 5.2) Preparation of the adsorbents:

The adsorbent coconut jute activated carbon was prepared by the coconut jute. Coconut jute is a light fluffy material. India, the third largest producer of coconuts in the world, produces about 12.8 billion coconuts a year. It is estimated that the production of coconut jute in India is about 0.5 million tons per year.Coconut jute is not easily biodegradable. Preparation of activated

carbons from this cheap and abundant biomass will eliminate the costly problem of solid waste disposal while at the same time deriving economic benefits from such value-added products.

First coconut jute was washed with the distilled water and dried in sunlight. Then the dried material was washed with concentration sulfuric acid (for 1 part of material 1.8 parts of acid) and kept at atmospheric temperature for about 5 hours with occasional stirring. The product, acid-carbonized coconut jute was washed several times with distilled water and with 5% sodium bicarbonate solution for the removal of remaining amount of acid, followed by again distilled water and kept in muffle furnace at 600°C for 1 hr .It was sieved to different particle sizes, 100 to 450 μm, and finally kept in bottles. The particle size 100 μm was used in the following batch adsorption experiments.

The commercial activated carbon LR grade was supplied by S.D. Fine-Chem (Boisar, India). It was treated with acid before delivery. These were subsequently pulverized and sieved through 18 to 44 BS mesh to get the activated carbon particles of the desired size range.

**5.3) Characterization of adsorbents:**

The physico-chemical characteristics of the CJAC and CAC were determined using standard procedures as discussed below:

**5.3.1 Proximate Analysis**

Proximate analysis of the CJAC and CAC were carried out using the procedure as per IS 1350:1984.

**5.3.2 Density**

The Bulk density of CJAC and CAC were determined using MAC bulk density meter.

**5.3.3 Energy dispersive spectrum (EDS)**

Energy dispersive x-ray spectroscopy (EDS) is a chemical microanalysis technique performed in conjunction with a Scanning Electron Micrograph (SEM) for analysis of CJAC and CAC.

**5.3.4 Scanning Electron Micrograph (SEM)**

SEM analysis of CJAC and CAC were carried out before and after the adsorption of lead from waste water by using LEO 435 VP Scanning electron microscope.

### 5.4) Adsorbate:

Synthetic wastewater solutions of Lead of desired concentrations (20–100 mg/l) were prepared by dissolving accurately weighed quantity of lead nitrate ($Pb(NO3)_2$) of AR grade in distilled water.

#### 5.4.1 Analytical measurement

Concentration of lead was estimated spectrophotometrically by using PAR reagent ( 2,4-pyridyl azoresorcinol) monitoring the absorbance characteristic wavelength using UV/VIS spectrophotometer (Perkin Elmer 35). To the sample add PAR reagent drop wise which is acting as complexing agent and it turns the sample to pink colour.The intensity of the colour is proportional to the lead concentration in the solution. A standard solution of Lead was taken and the absorbance was determined at different wavelengths to obtain a plot of absorbance versus wavelength. The wavelength corresponding to maximum absorbance ($\lambda_{max}$) was determined from this plot. The $\lambda_{max}$ for Lead was found to be 580 nm. Calibration curve was plotted between the absorbance and the concentration of Lead solution. The linearity of calibration curve (Fig. 5.1) indicated the applicability of the Lambert-Beer's Law.

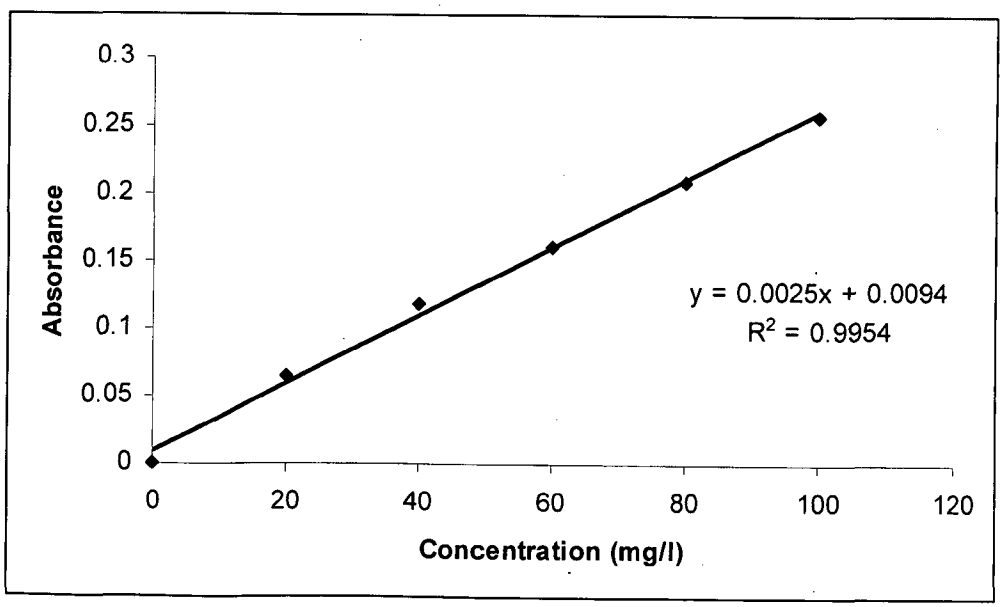


Fig. 5.1: Calibration Graph of Lead (II)

## 5.5) Experimental Programme:

The experimental programme was performed by Batch adsorption studies.

### 5.5.1 Batch Adsorption Experiments

To study the effect of important parameters like initial pH ( $pH_0$ ), adsorbent dose ( $m$ ), initial concentration ( $C_0$ ), contact time ( $t$ ), adsorbent size(s) and temperature (T) on the adsorptive removal of lead by CJAC and CAC, batch experiments were conducted at 30 ± 1 °C. For each experimental run, 100 ml of lead solution of known $C_0$, $pH_0$ ,known adsorbent size and known amount of the adsorbent were taken in a 250 ml stoppered conical flask. This mixture was agitated in a temperature-controlled shaking water bath at a constant speed at 30 ± 1 °C. Samples were withdrawn at appropriate time intervals. After filtration Pb(II) remaining in solution was analyzed spectrophotometrically using UV/VIS spectrophotometer at 580 nm, using PAR reagent ( 2,4-pyridyl azoresorcinol). The effect of $pH_0$ on lead removal was studied over a $pH_0$ range of 2 to 8. $pH_0$ was adjusted by the addition of dilute aqueous solutions of $HNO_3$ or NaOH (0.10 M). For the optimum amount of $m$, a 100 ml dye solution was contacted with different amounts of CJAC and CAC till equilibrium was attained. To see the effect of temperature for the adsorption of lead from solution by CJAC and CAC, experiments were also conducted at 35°C, 50°C and 60°C.The kinetics of adsorption was determined by analyzing adsorptive uptake of the Lead from the aqueous solution at different time intervals. For adsorption isotherms, lead solutions of different concentrations were agitated with the known amount of adsorbent till the equilibrium was achieved. The residual lead concentration of the solution was then determined. Blank experimental runs, with only the adsorbent in 100 ml of distilled water, were conducted simultaneously at similar conditions to account for any colour leached by the adsorbents and adsorbed by glass containers. Batch tests were carried out to compare the adsorptive capacity and intensity of CJAC and CAC.

The percentage removal of lead and equilibrium adsorption uptake in solid phase, $q_e$ (mg/g), was calculated using the following relationships:

$$\text{Percentage metal ions removal} = 100(C_0 - Ce)/ C_0 \quad (4.1)$$

$$\text{Amount of adsorbed metal ions per g of solid, } q_e = (C_0 - Ce)V/w \quad (4.2)$$

where, $C_0$ is the initial metal ion concentration (mg/l), Ce is the equilibrium phosphate concentration (mg/l), V is the volume of the solution (l) and w is the mass of the adsorbent (g).

# CHAPTER-6

# RESULTS AND DISCUSSION

## 6.1) General:

The detailed discussion on the results of the experiments conducted is given in this chapter. These results include

- Characterization of Coconut Jute Activated Carbon (CJAC) and Commercial Activated Carbon (CAC).
- Batch adsorption studies.

## 6.2) Characterization of Coconut Jute Activated Carbon (CJAC) and Commercial Activated Carbon (CAC):

Characteristics of CJAC and CAC included proximate analysis was carried out for the physico-chemical characteristics. The physico-chemical characteristics of CJAC and CAC are given in Table C–1 and C-2 respectively. Due to presence of high carbon content, CJAC and CAC may be treated as organic in nature. The organic nature of AC imparts porosity to it. Compared to CJAC CAC has more carbon content.

For structural and morphological characteristics, scanning electron micrograph (SEM) analysis and Energy dispersive spectrum were carried out. Scanning electron micrograph photographs of CJAC and CAC before and after adsorption are shown in Figs. B-1, B-2 and Figs. B-3, B-4 respectively. These photographs reveal their surface texture and porosity. This photomicrograph shows fibrous structure of CJAC and CAC. However, the surface of the CJAC and CAC becomes smooth after adsorption of lead as shown in Fig. B-2 and B-4 respectively.

The EDS x-ray detector measures the number of emitted x-rays versus their energy. The energy of the x-ray is characteristic of the element from which the x-ray was emitted. A spectrum of the energy versus relative counts of the detected x-rays is obtained and evaluated for

qualitative and quantitative determinations of the elements present in the sampled volume. Figs.B-5, B-6 and B-7, B-8 shows the energy dispersive spectrum for the CJAC and CAC before and after adsorption respectively. Fig.B-5 , B-7 reveals that the CJAC and CAC contains high carbon besides silica, sodium, sulphur etc., In Fig.B-6,B-8 there was peak of lead due to adsorption of lead on CJAC and CAC.

**6.3) Batch adsorption study:**

Batch operations were performed to study the effect of different parameters. Batch adsorption experiments were carried out in 250 ml Stoppard conical flask for removal of lead from synthetic solutions of known concentrations by using CJAC and CAC. The effect of various operating parameters, viz. pH, adsorbent dose, initial concentration, contact time, adsorbent size and temperature are studied and presented here.

**6.3.1. Effect of initial pH ($pH_0$ )**

pH is one of the most important environmental factors influencing not only site dissociation, but also the solution chemistry of the heavy metals: hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, and precipitation are strongly influenced by pH and, on the other hand, strongly influence the speciation and adsorption availability of heavy metals.

Adsorption of lead on CJAC and CAC was studied at varying pH values to optimize the removal and shown in Fig. B-9 and Fig.B-10, respectively. It is apparent that uptake is quite low at low pH, however with in increase in pH, a significant enhancement in adsorption was recorded. The optimum pH for CJAC-Pb and CAC-Pb systems was found to be 5 and 4.2 with removal about 68% and 79% metal from solution with initial lead concentration of 20 mg/l respectively. At lower pH values the electrostatic forces of repulsion between adsorbents (CJAC

and CAC) and adsorbate ($Pb^{2+}$) is prominent.So the efficiency of metal removal is low at lower pH. At pH above 6.0(for CJAC), 5(for CAC), there is a possibility of $Pb^{2+}$ precipitation as $Pb(OH)_2$ on the surface of the adsorbents by nucleation. So the lead removal efficiency is low. Between pH 2 and 5 (for CJAC), 2.0 and 4.2(for CAC) the percentage removal increases sharp. This might be due to the fact that metal ions start replacing hydrogen ions from adsorbent surface.



### 6.3.2. Effect of adsorbent dosage (m)

The effect of m on the removal of lead by CJAC and CAC at initial concentration = 20 mg/l is shown in Figs. B-11 and B-12, respectively. It can be seen that the lead removal increases up to a certain limit and then it remains almost constant. Optimum m was found to be 1g/l for CJAC and 1g/l for CAC. An increase in the adsorption with the adsorbent dose can be attributed to greater surface area and the availability of more adsorption sites.

### 6.3.3 Effect of initial lead concentration ($C_0$)

The effect of $C_0$ on the removal of lead by CJAC and CAC is shown in Figs. B-13, B-14 and B-15,B-16 respectively. It is evident from the Figures, that the amount of lead adsorbed per unit mass of adsorbent ($q_e$) increased with the increase in $C_0$ (Figs.B-13and B-15), although percentage lead removal decreased with the increase in $C_0$ (Figs. B-14 and B-16). $q_e$ increased with the increase in $C_0$ as the resistance to the uptake of lead from the solution decreases with the increase in lead concentration. The rate of adsorption also increases with the increase in $C_0$ due to increase in the driving force.

### 6.3.4 Effect of contact time ($t$)

The effect of contact time on the removal of lead by CJAC and CAC at $C_0$ =20, 40, 60, 80 and 100 mg/l is given in Figs. B-14 and B-16, respectively. The contact time curves show rapid adsorption of lead in the first 30 min, thereafter, the adsorption rate decreases gradually and the adsorption reaches equilibrium in 4 h for CJAC and CAC (optimum contact time).Aggregation of lead molecules with the increase in contact time makes it almost impossible to diffuse deeper into

the adsorbent structure at highest energy sites. This aggregation negates the influence of contact time as the mesopores get filled up and start offering resistance to diffusion of aggregated lead molecules in the adsorbents. This is the reason why an insignificant enhancement in adsorption after optimum time. Hence further experiments were conducted for optimum contact time only. The curves are single, smooth and continuous leading to saturation. The adsorption curves of contact time indicate the possible mono-layer coverage of lead ions on the surface of CJAC and CAC.

### 6.3.5 Effect of particle size(s)

The effect of particle size on uptake of lead was studied with different adsorbent sizes from 100 to 300μm. Fig.B-17 (for CJAC) and Fig.B-18 (for CAC) shows that the percent removal of lead increases from 38 to 69% (for CJAC) and 43 to 79% (for CAC) as the particle size decreases from 300 to 100μm for an initial concentration of 20 mg/l lead solution. The extent of the adsorption process increases with increased specific surface area. The specific surface available for adsorption will be greater for smaller particles and hence percent removal increases as particle size decreases. For larger particles the diffusional resistance to mass transport is higher and most of the internal surface of the particle may not be utilized for adsorption. Consequently the amount of lead adsorbed is small.

### 6.3.6 Effect of temperature (T)

Temperature has a pronounced effect on the adsorption capacity of the adsorbents. Figs. B-19-B-20 and B-21-B-22 show the plots of adsorption isotherms, for Pb-CJAC and Pb-CAC systems at 303, 323 and 343 K, respectively. It shows that the adsorptivity of lead increases with the increase in temperature. This increase shows that the adsorption process may be by chemisorption. Since sorption is an exothermic process, it would be expected that an increase in temperature of the adsorbate-adsorbent system would result in decreased sorption capacity. However, if the adsorption process is controlled by the diffusion process (intraparticle transport-pore diffusion), the sorption capacity will show an increase with an increase in temperatures. This is basically due to the fact that the diffusion process is an endothermic process. With an increase in temperature, the mobility of the lead ions increases and the retarding forces acting on the diffusing ions decrease, thereby increasing the sorptive capacity of adsorbent.

## 6.4) Adsorption Kinetics Study:

There are various models available to explain the kinetics of adsorption. In order to investigate the adsorption process of Pb (II) on CJAC and CAC, four kinetics models viz. pseudo- first-order model, pseudo-second-order model, intraparticle diffusion model and Bangham's model were used.

### 6.4.1 Pseudo-first-order model:

Lagergren rate equation is one of the most widely used sorption rate equations for the adsorption.

The pseudo-first-order equation is

$$\frac{dQ}{dt} = k_f (Q_e - Q_t) \tag{6.1}$$

where $Q_t$ is the amount of adsorbate adsorbed at time t (mg/g), $Q_e$ is the adsorption capacity in equilibrium (mg/g), $k_f$ is the rate constant of pseudo-first-order model ($min^{-1}$), and t is the time (minute). After definite integration by applying initial conditions at t=0, $Q_t$=0 and at t=t, $Q_t$=$Q_t$, the equation becomes:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_f}{2.303} t \tag{6.2}$$

The values of adsorption rate constant ($k_f$) for lead ions adsorption on CJAC and CAC at $C_0$=20, 40, 60, 80 and 100 mg/l were determined from the plot of log ($Q_e$ – $Q_t$) against t (Figs. B-23 and B-24). The $k_f$ values are given in Table C-3.

### *6.4.2* Pseudo-second-order model:

The pseudo-second-order model is represented as:

$$\frac{dq_t}{dt} = k_S (q_e - q_t)^2 \tag{6.3}$$

Where, $k_S$ is the pseudo-second-order rate constant (g/mg/min). Integrating Eq (6.3) and noting that $q_t$=0 at t=0, the following equation is obtained:

$$\frac{t}{q_t} = \frac{1}{k_S q_e^2} + \frac{1}{q_e} t \tag{6.4}$$

The initial sorption rate, h (mg/g/min), at t $\rightarrow$ 0 is defined as

$$h = k_S q_e^2$$

Figs. B-25 and B-26 shows the plot of $t/q_t$ versus $t$ for CJAC and CAC, respectively, at $C_0$=20, 40, 60, 80 and 100 mg/l. The $q_e$ is obtained from the slope of the plot and the h value is obtained from the intercept. Since $q_e$ is known from the slope, $k_S$ can be determined from the h value. The $k_S$ and h values as calculated from the Figures are listed in Table C-4 for both the adsorbents. The calculated correlation coefficients are also closer to unity and also $q_{e,\,calc}$ and $q_{e,\,expt}$ values are almost same for pseudo-second-order kinetics than that for the pseudo first-order kinetic model. Therefore the sorption can be approximated more appropriately by the pseudo-second-order kinetic model. It can be seen that the CAC has higher $h$ and $q_e$ values for lead ions adsorption.

**6.4.3 Weber-Morris intra-particle diffusion model:**

The adsorbate transport from the solution phase to the surface of the adsorbent particles occurs in several steps. The overall adsorption process may be controlled either by one or more steps, e.g. film or external diffusion, pore diffusion, surface diffusion and adsorption on the pore surface, or a combination of more than one step. In a rapidly stirred batch adsorption, the diffusive mass transfer can be related by an apparent diffusion coefficient, which will fit the experimental sorption-rate data. Generally, a process is diffusion controlled if its rate is dependent upon the rate at which components diffuse towards one another. The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model.

$$q_t = k_{id} t^{1/2} + I \qquad (6.5)$$

Where, is the intra-particle diffusion rate constant (mg/g min1/2) and is the intercept (mg/g). Plot of $q_t$ versus $t^{1/2}$ should be a straight line with a slope and intercept when adsorption mechanism follows the intra-particle diffusion process. If the Weber-Morris plot of $q_t$ versus $t^{1/2}$ satisfies the linear relationship with the experimental data, then the sorption process is found be controlled by intra-particle diffusion only. However, if the data exhibit multi-linear plots, then two or more steps influence the sorption process. Fig. B-27 and Fig.B-28 represents plot of $q_t$ versus $t^{1/2}$ at =20, 40,60,80 and 100 mg/l for lead adsorption on CJAC and CAC, respectively. In Fig.B-27, B-28 the data points are related by two straight lines—the first straight portion depicting macropore diffusion and the second representing meso-pore diffusion. These show only the pore diffusion data. The deviation of straight lines from the origin may be due to difference in rate of mass transfer in the initial and final stages of adsorption. Further, such

deviation of straight line from the origin indicates that the pore diffusion is not the sole rate-controlling step. The adsorption data for $q_t$ versus $t^{1/2}$ for the initial period show curvature, usually attributed to boundary layer diffusion effects or external mass transfer effects. The values of rate parameters ($k_{id}$,I and $k_{id}$,II) are given in Table C-5.The values of the correlation coefficients are also given in Table C-5.

**6.4.4. Bangham's model:**

The rate constants, Kr for the sorption of lead were calculated using the simplest form of Bangham equation :

$dQ/dt = Q_t/(mt)$ (6.6)

The integral form of the equation can be written as:

$Q_t = K_r t^{1/m}$ (6.7)

Assessment of the rate constants is possible by simple linear transformation of the equation:

$\log Q_t = \log K_r + (1/m) \log t$ (6.8)

As can be observed from the Fig.B-29, B-30, the linearity of the obtained plots indicate the applicability of the of the 1/m th order kinetics for the system under observation. The adsorption rate constants were calculated from the intercepts and slopes of the straight lines and are reported in Table C-6.

**6.5) Adsorption Equilibrium Study:**

To optimize the design of an adsorption system for the adsorption of adsorbates, it is important to establish the most appropriate correlation for the equilibrium curves. Various isotherm equations have been used to describe the equilibrium characteristics of adsorption. Some of these equations are Freundlich, Langmuir, Temkin and Redlich Peterson equations.

**6.5.1 Freundlich and Langmuir Isotherms**

Linearised form of Freundlich and Langmuir isotherm equations are given as

$$\ln Q_e = \ln K_F + \frac{1}{n}\ln C_e \quad \text{(Linear form)} \qquad (6.9)$$

$$\frac{C_e}{Q_e} = \frac{1}{K_A Q_m} + \frac{C_e}{Q_m} \quad \text{(Linear form)} \qquad (6.10)$$

Fig.B-31, B-32 shows the Freundlich isotherm plots (lnQe versus lnCe) for adsorption of lead on CJAC, CAC at 303, 323 and 343 K, respectively. Langmuir isotherm plot ($C_e/Q_e$ versus $C_e$ )

shown in Fig.B-33,B-34 for adsorption onto CJAC,CAC respectively. Freundlich and Langmuir isotherm parameters for both adsorbents along with linear and non-linear correlation coefficients are given in Table C-7, C-8, C-9 and C-10. At all temperatures, Langmuir isotherm represents a better fit of the experimental data than Freundlich isotherm. This suggests adsorption of lead ions by CJAC and CAC are apparently with monolayer coverage of adsorbed molecules. The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless factor, $R_L$, which describes the type of pattern and is defined as $R_L=1/(1+K_AC_0)$ indicates the nature of adsorption as

| | | |
|---|---|---|
| If | $R_L > 1$ | Unfavorable |
| | $R_L = 1$ | Linear |
| | $0 < R_L < 1$ | Favorable |
| | $R_L = 0$ | Irreversible |

The value of $R_L$ is found to be less than 1 for adsorption of lead ions on CJAC and CAC, so adsorption using CJAC and CAC is favorable.

### 6.5.2 Temkin Isotherm

It is given as

$$q_e = \frac{RT}{b}\ln(K_T C_e) \tag{6.11}$$

which can be linearized as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \tag{6.12}$$

where $B_1 = \frac{RT}{b}$

Temkin isotherm contains a factor that explicitly takes into the account adsorbing species-adsorbent interactions. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. A plot of $q_e$ versus $\ln C_e$ enables the determination of the isotherm constants $B_1$ and $K_T$ from the slope and the intercept, respectively. $K_T$ is the equilibrium binding constant (l/mol) corresponding to the maximum binding energy, constant $B_1$ is related to the heat of adsorption and R is gas constant (8.314 J/mol K). Fig.B-35,B-36 shows the Temkin isotherm

plots for both adsorbents. The Temkin isotherm parameters listed in Table C-11,C-12. It shows better fit than Langmuir isotherm.

### 6.5.3 Redlich-Peterson Isotherm

Redlich and Peterson (1959) model combines elements from both the Langmuir and Freundlich equation and the mechanism of adsorption is a hybrid and does not follow ideal monolayer adsorption. The Redlich Peterson isotherm has a linear dependence on concentration in the numerator and an exponential function in the denominator. The R-P equation is the combination of Langmuir and Freundlich models. It approaches Freundlich model at high concentration and is accord with the low concentration limit of Langmuir equation. Further more, the R-P equation incorporates three parameters into an empirical isotherm, and therefore can be applied either in homogeneous or heterogeneous system due to high versatility of the equation.

It can be described as follows:

$$Q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}} \tag{6.13}$$

where $K_R$ is R-P isotherm constant (l/g), $a_R$ is R-P isotherm constant (l/mg) and $\beta$ is the exponent which lies between 1 and 0, where $\beta=1$

$$Q_e = \frac{K_R C_e}{1 + a_R C_e} \tag{6.14}$$

It becomes Langmuir equation. Where $\beta=0$

$$Q_e = \frac{K_R C_e}{1 + a_R} \tag{6.15}$$

i.e. the Henry's law equation.

Above Eq. can be converted into al linear form by taking logarithms:

$$\ln(K_R \frac{C_e}{Q_e} - 1) = \ln a_R + \beta \ln C_e \tag{6.16}$$

Plotting the left hand side of above eq. against $\ln C_e$ to obtain isotherm constant is not applicable because of three unknowns, $a_R$, $K_R$ and $\beta$. Therefore a minimization procedure was adopted to solve the equation by maximizing the correlation coefficient between theoretical data for $Q_e$ predicted from equation and experimental data. Therefore, the parameters of equations were determined by minimizing the distance between the experimental data points and the theoretical model predictions with solver add-in function of Microsoft excel. The Fig.B-37, B-38

shows the R-P isotherm plots for both adsorbents. The R-P isotherm parameters listed in Table C-13,C-14. The R-P isotherm parameters and the correlation coefficients are significantly higher than both the Langmuir and Freundlich values for Pb (II) adsorption on CJAC and CAC. The Redlich-Peterson is the certainly best fit isotherm equation of the four isotherm studied so far.

**6.6 Error Analysis:**

The use of $R^2$ is limited to solving linear forms of isotherm equation, which measure the difference between experimental data and theoretical data in linear plots only, but not the errors in isotherm curves. Purely, from a comparison of the correlation coefficients ($R^2$ values) for the linearized models, it can be seen that higher weightage is given to the higher $C_e$ value data points, thus giving a better fit correlation to the higher $C_e$ value date points. Due to the inherent bias resulting from linearization, error functions of non-linear regression basin are employed to evaluate the isotherm constants and compare them with the less accurate linearized analysis values. Five different error functions of non-linear regression basin were employed in this study to find out the best-fit isotherm model to the experimental equilibrium data.

**6.6.1 The Sum of the Squares of the Errors (SSE)**

This error function, SSE is given as

$$SSE = \sum_{i=1}^{n} \left(q_{e,calc} - q_{e,\exp}\right)_i^2 \qquad (6.17)$$

Here, $q_{e,cal}$ and $q_{e,\exp}$ are, respectively, the calculated and the experimental value of the equilibrium adsorbate solid concentration in the solid phase (mg/g) and $n$ is the number of data points. This most commonly used error function, SSE has one major drawback in that it will result in the calculated isotherm parameters providing a better fit at the higher end of the liquid phase concentration range. This is because of the magnitude of the errors, which increase as the concentration increases. The values of SSE are given in Tables C-15 and C-16, both for CJAC and CAC, respectively.

### 6.6.2 The Average Relative Error (ARE)

ARE is given as

$$ARE = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{(q_{e,\exp} - q_{e,calc})}{q_{e,\exp}}\right|_i \tag{6.18}$$

This error function attempts to minimize the fractional error distribution across the entire concentration range. The values of ARE are given in Tables C-15 and C-16, both for CJAC and CAC, respectively.

### 6.6.3 The Hybrid Fractional Error Function (HYBRID)

HYBRID is given as

$$HYBRID = \frac{100}{n-p}\sum_{i=1}^{n}\left[\frac{(q_{e,\exp} - q_{e,calc})}{q_{e,\exp}}\right]_i \tag{6.19}$$

This error function was developed to improve the fit of the ARE method at low concentration values. Instead of n as used in ARE, the sum of the fractional errors is divided by (n-p) where p is the number of parameters in the isotherm equation. The values of HYBRID error functions are given in Tables C-15 and C-16, both for CJAC and CAC, respectively.

### 6.6.4 Marquardt's Percent Standard Deviation (MPSD)

MPSD has been used by a number of researchers in the field to test the adequacy and accuracy of the model fit with the experimental data. It has some similarity to the geometric mean error distribution, but was modified by incorporating the number of degrees of freedom. This error function is given as

$$100\sqrt{\frac{1}{n-p}\sum_{i=1}^{n}\left(\frac{(q_{e,meas} - q_{e,calc})}{q_{e,meas}}\right)_i^2} \tag{6.19}$$

The values of MPSD error functions are given in Tables C-15 and C-16, both for CJAC and CAC, respectively.

### 6.6.5 The Sum of the Absolute Errors (SAE)

SAE is given as

$$SAE = \sum_{i=1}^{n}\left|q_{e,calc} - q_{e,\exp}\right|_i \tag{6.20}$$

The isotherm parameters determined by this method provide a better fit as the magnitude of the errors increase, biasing the fit towards the high concentration data. The values of SAE are given in Tables C-15 and C-16, both for CJAC and CAC, respectively.

### 6.6.6 Choosing best-fit isotherm based on error analysis

The values of the five error functions are presented in Tables C-15 and C-16. By comparing the results of the values of the error functions, it is found that Temkin and Langmuir isotherms are best-fitted the isotherm data for Pb(II) adsorption on CJAC at almost all temperatures and Langmuir, Temkin and Redlich-Peterson isotherms are best-fitted for Pb(II) on CAC at almost all temperatures .

## 6.7) Thermodynamic study:

The Gibbs free energy change of the adsorption process is related to the equilibrium constant by the classic Van't Hoff equation

$$\Delta G^0 = -RT \ln K \tag{6.21}$$

According to thermodynamics, the Gibbs free energy change is also related to the entropy change and heat of adsorption at constant temperature by the following equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{6.22}$$

Combining above two equations, we get

$$\ln K = \frac{-\Delta G^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R}\frac{1}{T} \tag{6.23}$$

where $\Delta G^0$ is the free energy change (kJ/mol), $\Delta H^0$ is the change in enthalpy (kJ/mol), $\Delta S^0$ is the entropy change (J/mol K), $T$ is the absolute temperature (K) and R is the universal gas constant (8.314 J/mol K) and K is the thermodynamic equilibrium constant.

Thermodynamic parameters are calculated from the variation of the thermodynamic equilibrium constant K (or the thermodynamic distribution coefficient)
with changes in temperature. K for the adsorption reaction can be defined:

$$K = \frac{a_s}{a_e} = \frac{\nu_s}{\nu_e}\frac{C_s}{C_e} \tag{6.24}$$

where $a_s$ is the activity of the adsorbed solute, $a_e$ the activity of the solute in the equilibrium solution, $C_s$, the surface concentration of adsorbate and $C_e$ is the concentration of adsorbate in

equilibrium suspension $v_s$, the activity coefficient of the adsorbed solute, and $v_e$ the activity coefficient of the solute in the equilibrium solution. As the concentration of the solute in the solution approaches zero, the activity coefficient v approaches unity. Equation (6.24) may then be written as:

$$\lim_{Ce--0} \frac{C_s}{C_e} = \frac{a_s}{a_e} = K \qquad (6.25)$$

Values of K are obtained by plotting In ($C_s/C_e$,) versus $C_e$, and extrapolating to zero $C_e$. From Fig.B-39 (for CJAC), B-40(CAC) K values are obtained at different temperatures. The increase in $K$ with increase in temperature indicates the endothermic nature of the process.

The $\Delta G^0$ is calculate from the equation 6.21 for different temperatures. The negative values of $\Delta G^0$ indicate the process to be feasible and adsorption to be spontaneous. And $\Delta H^0$ and $\Delta S^0$ were calculated using the equation 6.23. A plot of ln$K$ vs $1/T$ was found to be linear in Fig.B-41. $\Delta H^0$ and $\Delta S^0$ are determined from the slope and intercept of the plot.

The positive $\Delta H^0$ value confirms the endothermic nature of the overall-sorption process. The adsorption process in the solid-liquid system is a combination of two processes: (a) the desorption of the molecules of solvent (water) previously adsorbed and (b) the adsorption of adsorbate species. Basically adsorption process is exothermic in nature, in this study it is endothermic may be due to the desolvation of the adsorbing species(lead ions), the changes in the size of pores, and the enhanced rate of intraparticle diffusion of adsorbate. The value of $\Delta H^0$ was less than 20 KJ/mol, so the adsorption is physical adsorption.

The positive value of $\Delta S^0$ suggests increased randomness at the solid/solution interface with some structural changes in the adsorbate and adsorbent and an affinity of CJAC and CAC towards lead ions. Also, positive $\Delta S^0$ value corresponds to an increase in the degree of freedom of the adsorbed species. All the thermodynamic parameters are given in the Table C-17.

# CHAPTER-7

# CONCLUSION AND RECOMMENDATIONS

## 7.1 Conclusions:

The following major conclusions can be drawn from the present work .

1. Bulk density of coconut jute activated carbon was found to be 318.90 Kg/m$^3$, fixed carbon percentage is 0.571 and bulk density of commercial activated carbon was found to be 268.70, fixed carbon is 0.711, which shows excellent adsorptive characteristics of activated carbon for the removal of Pb (II) from waste water.
2. SEM of CAC shows fibrous structure with large pore size with strands in each fibre. Number of pores in CJAC is lesser than that in CAC. Surface of the CJAC and CAC becomes smooth after adsorption of Pb(II).
3. Percent removal of Pb(II) increases with the increase in adsorbent dose for both CJAC and CAC up to a certain limit and then remains almost constant. However, Percent removal decreases with increase in Pb(II) concentration for both the adsorbents.
4. Adsorption of Pb(II) on CJAC and CAC is maximum in acidic pH range. Adsorption of Pb (II) increases with increase in pH and reaches to maximum value at 5 (for CJAC), 4.2 (for CAC) and then percent removal slightly decreases after this pH region.
5. Effect of initial Pb(II) concentration on removal by CJAC and CAC shows that for any contact time the percent removal decreases with increase in initial concentration of Pb(II).Amount adsorbed per amount of adsorbent ($q_t$ ) increased with the increase in initial Pb(II) concentration .
6. Increase in temperature slightly increases the amount adsorbed for both adsorbents indicating endothermic in nature.
7. The percent removal of Pb (II) increases (for both adsorbents) as the particle size decreases because of specific surface available for adsorption will be greater for smaller particles.

8. Kinetic study shows that adsorption of Pb(II) on CJAC and CAC follows the second order kinetics for both adsorbents.
9. Weber-Morris plot reveals that the intraparticle transport (pore diffusion) is not the only rate-controlling step.
10. Langmuir isotherm best-fitted the isotherm data for Pb(II) adsorption on CJAC and CAC at almost all temperatures, However, the non-linear correlation coefficients, $R^2$ and the error analysis values are nearly similar for the Temkin and Langmuir isotherms(for CJAC) and Langmuir,Temkin and Redlich-Peterson(for CAC).Hence we can use Temkin or Langmuir for Pb(II) adsorption on CJAC and Temkin,Langmuir or Redlich-Peterson on CAC.
11. Adsorption capacity of CJAC and CAC for Pb(II) removal increases with increase in temperature for both the adsorbents, showing the endothermic nature of adsorption. The energy of adsorption reveals that it is a transitional state adsorption.
12. The increase in $K$ with increase in temperature indicates the endothermic nature of the process. The negative values of $\Delta G^0$ indicate the process to be feasible and adsorption to be spontaneous. And $\Delta H^0$ and $\Delta S^0$ are 2.5441 KJ/mol and 17.6350 J/K mol(for CJAC), 3.4611 KJ/mol and 23.7780 J/ K mol (for CAC) respectively.
13. Lead removal efficiency for CJAC is less than CAC (the difference is not very high). But CJCA was prepared by cheap coconut jute which is abundantly available in India . So the low cost coconut jute can be used as a potential adsorbent for the removal of Pb(II) from wastewater in developing countries like India.

## 7.2 Recommendations :

1) Coconut Jute Activated Carbon should be characterized for physical-chemical parameters and surface characteristics to arrive at average values for use in design.
2) Costing of the adsorption based on industrial scale treatment system should be carried out to popularize the adsorption technique with coconut jute activated carbon.
3) Further pilot scale studies are required to evaluate the suitability of coconut jute activated carbon for the adsorptive removal on plant scale.

4) To further improve adsorption properties of coconut jute activated carbon, it should be gone through some treatment processes which improves adsorption property.
5) Under continuous study, fixed bed column study should be carried out to get effect of different parameters on removal of metal ion from waste water.
6) Equilibrium adsorption data should be obtained for mixed metal ions concentrations encountered in industries.
7) Many more combination of different adsorbents could be tried to get much better result.
8) It could also be tested for removal of other heavy metals.

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# APPENDIX – A

**Table A-1: Calibration curve for lead**

| Concentration of lead (mg/l) | Absorbance |
|---|---|
| 0 | 0 |
| 20 | 0.0652 |
| 40 | 0.1183 |
| 60 | 0.1610 |
| 80 | 0.2090 |
| 100 | 0.2570 |

**Table A-2: Effect of pH on the removal of lead using CJAC**
(T=303 K, Dose=1g/l, t=4 hr, $C_o$=20 mg/l)

| pH | % Removal |
|---|---|
| 2 | 34.85 |
| 3 | 55.76 |
| 4 | 60.83 |
| 5 | 68.275 |
| 6 | 56.865 |
| 7 | 52.16 |
| 8 | 47.34 |

**Table A-3: Effect of pH on the removal of lead using CAC**
(T=303 K, Dose=1g/l, t=4 hr, $C_o$=20 mg/l)

| pH | % Removal |
|---|---|
| 2 | 42.56 |
| 3 | 59.34 |
| 4 | 78.33 |
| 5 | 72.33 |
| 6 | 58.89 |
| 7 | 52.54 |
| 8 | 35.55 |

**Table A-4: Effect of Adsorbent dose on removal of lead using CJAC**
(T=303 K, t=4 hr, $C_o$=20 mg/l, pH=5)

| Adsorbent Dose ( mg) | % Removal |
|---|---|
| 10 | 16.41 |
| 20 | 27.34 |
| 30 | 42.95 |
| 60 | 65.14 |
| 80 | 66.67 |
| 100 | 68.83 |
| 150 | 69.01 |

**Table A-5: Effect of Adsorbent dose on removal of lead using CAC**
(T=303 K, t=4 hr, $C_o$=20 mg/l, pH=4.2)

| Adsorbent Dose ( mg) | % Removal |
|---|---|
| 10 | 27.52 |
| 20 | 40.07 |
| 30 | 55.32 |
| 60 | 61.67 |
| 80 | 78.49 |
| 100 | 79.17 |
| 150 | 79.54 |

**Table A-6: Effect of Contact time and initial concentration of lead removal of using CJAC** (T=303 K, pH=5, Dose= 1 g/l)

| Time(min) | % Removal ( 20 mg/l) | % Removal ( 40 mg/l) | % Removal ( 60 mg/l) | % Removal ( 80 mg/l) | % Removal ( 100 mg/l) |
|---|---|---|---|---|---|
| 10 | 31.875 | 18.750 | 15.000 | 13.750 | 9.500 |
| 20 | 37.250 | 25.875 | 20.830 | 17.250 | 17.250 |
| 30 | 53.625 | 51.875 | 46.500 | 36.250 | 29.450 |
| 60 | 58.750 | 54.750 | 46.670 | 38.750 | 32.250 |
| 120 | 65.500 | 56.250 | 48.170 | 39.657 | 33.250 |
| 180 | 67.750 | 58.125 | 49.160 | 41.250 | 36.250 |
| 240 | 68.125 | 58.625 | 49.830 | 42.250 | 37.250 |

**Table A-7: Effect of Contact time and initial concentration of lead removal of using CAC** (T=303 K, pH=4.2, Dose= 1 g/l)

| Time(min) | % Removal ( 20 mg/l) | % Removal ( 40 mg/l) | % Removal ( 60 mg/l) | % Removal ( 80 mg/l) | % Removal ( 100 mg/l) |
|---|---|---|---|---|---|
| 10 | 32.540 | 28.75 | 24.250 | 23.750 | 19.000 |
| 20 | 46.620 | 36.875 | 30.560 | 27.350 | 21.880 |
| 30 | 55.470 | 60.875 | 58.460 | 46.250 | 37.000 |
| 60 | 59.160 | 64.920 | 60.061 | 48.750 | 39.000 |
| 120 | 67.530 | 65.750 | 61.750 | 49.550 | 39.640 |
| 180 | 78.330 | 68.125 | 62.150 | 51.650 | 41.321 |
| 240 | 79.160 | 68.575 | 62.750 | 51.950 | 41.560 |

**Table A-8: Effect of particle size on removal of lead using CJAC**
(T=303 K, pH=5, Dose=1 g/l, t=4 hr, $C_o$=20 mg/l)

| Particle Size (μm) | % Removal |
|---|---|
| 100 | 69.14 |
| 125 | 66.57 |
| 150 | 61.05 |
| 250 | 55.09 |
| 300 | 38.17 |

**Table A-9: Effect of particle size on removal of lead using CAC**
(T=303 K, pH=4.2, Dose=1 g/l, t=4 hr, $C_o$=20 mg/l)

| Particle Size (μm) | % Removal |
|---|---|
| 100 | 79.53 |
| 125 | 69.82 |
| 150 | 63.79 |
| 250 | 49.07 |
| 300 | 43.14 |

**Table A-10: Lagergren plot for the removal of lead for different initial concentrations using CJAC**

( pH=5, T=303 K, Dose=1g/l)

| Time(min) | log ($q_e$-$q_t$) ( 20 mg/l) | log ($q_e$-$q_t$) ( 40 mg/l) | log ($q_e$-$q_t$) ( 60 mg/l) | log ($q_e$-$q_t$) ( 80 mg/l) | log ($q_e$-$q_t$) ( 100 mg/l) |
|---|---|---|---|---|---|
| 10 | 0.8603 | 1.2028 | 1.3201 | 1.3579 | 1.4433 |
| 20 | 0.7906 | 1.1173 | 1.2405 | 1.3010 | 1.3010 |
| 30 | 0.4624 | 0.4314 | 0.3010 | 0.6812 | 0.8948 |
| 60 | 0.2730 | 0.1903 | 0.2787 | 0.4472 | 0.6989 |
| 120 | -0.2798 | -0.0223 | 0.0000 | 0.3010 | 0.6020 |
| 180 | -1.1249 | -0.6989 | -0.3979 | -0.0969 | 0.0000 |
| 240 | - | - | - | - | |

**Table A-11: Lagergren plot for the removal of lead for different initial concentrations using CAC**

( pH=4.2, T=303 K, Dose=1g/l)

| Time(min) | log ($q_e$-$q_t$) ( 20 mg/l) | log ($q_e$-$q_t$) ( 40 mg/l) | log ($q_e$-$q_t$) ( 60 mg/l) | log ($q_e$-$q_t$) ( 80 mg/l) | log ($q_e$-$q_t$) ( 100 mg/l) |
|---|---|---|---|---|---|
| 10 | 0.9696 | 1.2022 | 1.3636 | 1.3533 | 1.4425 |
| 20 | 0.8134 | 1.1031 | 1.2859 | 1.2940 | 1.2576 |
| 30 | 0.6756 | 0.4885 | 0.4106 | 0.6589 | 0.8261 |
| 60 | 0.6020 | 0.1649 | 0.2079 | 0.4082 | 0.6608 |
| 120 | 0.3666 | 0.0531 | -0.2218 | 0.2833 | 0.4624 |
| 180 | -0.7799 | -0.7447 | -0.4437 | -0.6198 | -0.2218 |
| 240 | - | - | - | - | - |

**Table A-12: Pseudo second order kinetic plot for the removal of lead for different initial concentrations using CJAC** (pH=5, T=303 K, Dose=1 g/l)

| Time(min) | $t/q_t$(min.g/mg) ( 20 mg/l) | $t/q_t$(min.g/mg) ( 40 mg/l) | $t/q_t$(min.g/mg) ( 60 mg/l) | $t/q_t$(min.g/mg) ( 80 mg/l) | $t/q_t$(min.g/mg) ( 100 mg/l) |
|---|---|---|---|---|---|
| 10 | 1.5686 | 1.3333 | 1.1111 | 0.9091 | 1.0526 |
| 20 | 2.6846 | 1.9324 | 1.6000 | 1.4493 | 1.1594 |
| 30 | 2.7972 | 1.4458 | 1.0753 | 1.0345 | 1.0204 |
| 60 | 5.1064 | 2.7397 | 2.1428 | 1.9355 | 1.8605 |
| 120 | 9.1603 | 5.3333 | 4.1522 | 3.7736 | 3.6090 |
| 180 | 13.2841 | 7.7419 | 6.1017 | 5.4545 | 4.9655 |
| 240 | 17.6147 | 10.2345 | 8.0267 | 7.1006 | 6.4429 |

**Table A-13: Pseudo second order kinetic plot for the removal of lead for different initial concentrations using CAC** (pH=4.2, T=303 K, Dose=1 g/l)

| Time(min) | $t/q_t$(min.g/mg) ( 20 mg/l) | $t/q_t$(min.g/mg) ( 40 mg/l) | $t/q_t$(min.g/mg) ( 60 mg/l) | $t/q_t$(min.g/mg) ( 80 mg/l) | $t/q_t$(min.g/mg) ( 100 mg/l) |
|---|---|---|---|---|---|
| 10 | 1.5366 | 0.8696 | 0.6873 | 0.5263 | 0.5333 |
| 20 | 2.1450 | 1.3559 | 1.0907 | 0.9141 | 0.7055 |
| 30 | 2.7042 | 1.2320 | 0.8553 | 0.8108 | 0.7547 |
| 60 | 5.0710 | 2.3105 | 1.6650 | 1.5385 | 1.4330 |
| 120 | 8.8849 | 4.5627 | 3.2389 | 3.0272 | 2.7554 |
| 180 | 4.4898 | 6.6055 | 4.8270 | 4.3562 | 3.9258 |
| 240 | 15.1592 | 8.7495 | 6.3745 | 5.7748 | 5.1668 |

**Table A-14: Weber Morris plot for the removal of lead for different initial concentrations using CJAC**

( pH=5, T=303 K, Dose=1 g/l).

| $t^{1/2}(min^{1/2})$ | $q_t$(mg/g) ( 20 mg/l) | $q_t$(mg/g) ( 40 mg/l) | $q_t$(mg/g) ( 60 mg/l) | $q_t$(mg/g) ( 80 mg/l) | $q_t$(mg/g) ( 100 mg/l) |
|---|---|---|---|---|---|
| 3.1623 | 6.3750 | 7.5000 | 9.0000 | 11.0000 | 9.5000 |
| 4.4721 | 7.4500 | 10.3500 | 12.5000 | 13.8000 | 17.2500 |
| 5.4772 | 10.7250 | 20.7500 | 27.9000 | 29.0000 | 29.4000 |
| 7.7460 | 11.7500 | 21.9000 | 28.0000 | 31.0000 | 32.2500 |
| 10.9544 | 13.1000 | 22.5000 | 28.9000 | 31.8000 | 33.2500 |
| 13.4164 | 13.5500 | 23.2500 | 29.5000 | 33.0000 | 36.2500 |
| 15.4919 | 13.6250 | 23.4500 | 29.9000 | 33.8000 | 37.2500 |

**Table A-15: Weber Morris plot for the removal of lead for different initial concentrations using CAC**

( pH=4.2, T=303 K, Dose=1 g/l).

| $t^{1/2}(min^{1/2})$ | $q_t$(mg/g) ( 20 mg/l) | $q_t$(mg/g) ( 40 mg/l) | $q_t$(mg/g) ( 60 mg/l) | $q_t$(mg/g) ( 80 mg/l) | $q_t$(mg/g) ( 100 mg/l) |
|---|---|---|---|---|---|
| 3.1623 | 6.5080 | 11.5000 | 14.4500 | 19.0000 | 18.7500 |
| 4.4721 | 9.3240 | 14.7500 | 18.3360 | 21.8800 | 28.3500 |
| 5.4772 | 11.0940 | 24.3500 | 35.0760 | 37.0000 | 39.7500 |
| 7.7460 | 11.8320 | 25.9680 | 36.0360 | 39.0000 | 41.8700 |
| 10.9544 | 13.5060 | 26.3000 | 37.0500 | 39.6400 | 43.5500 |
| 13.4164 | 15.6660 | 27.2500 | 37.2900 | 41.3200 | 45.8500 |
| 15.4919 | 15.8320 | 27.4300 | 37.6500 | 41.5600 | 46.4500 |

**Table A-16: Bangham's plot for the removal of lead for different initial concentrations using CJAC**

( pH=5, T=303 K, Dose=1 g/l).

| log t | log $q_t$ ( 20 mg/l) | log $q_t$ ( 40 mg/l) | log $q_t$ ( 60 mg/l) | log $q_t$ ( 80 mg/l) | log $q_t$ ( 100 mg/l) |
|---|---|---|---|---|---|
| 1 | 0.8045 | 0.8751 | 0.9542 | 1.0414 | 0.9777 |
| 1.3010 | 0.8721 | 1.0149 | 1.0969 | 1.1399 | 1.2368 |
| 1.4771 | 1.0304 | 1.3170 | 1.4456 | 1.4624 | 1.4683 |
| 1.7782 | 1.0700 | 1.3404 | 1.4471 | 1.4914 | 1.5088 |
| 2.0792 | 1.1173 | 1.3522 | 1.4609 | 1.5024 | 1.5218 |
| 2.2553 | 1.1319 | 1.3664 | 1.4698 | 1.5185 | 1.5593 |
| 2.3802 | 1.1343 | 1.3701 | 1.4757 | 1.5289 | 1.5711 |

**Table A-17: Bangham's plot for the removal of lead for different initial concentrations using CAC**

( pH=4.2, T=303 K, Dose=1 g/l).

| log t | log $q_t$ ( 20 mg/l) | log $q_t$ ( 40 mg/l) | log $q_t$ ( 60 mg/l) | log $q_t$ ( 80 mg/l) | log $q_t$ ( 100 mg/l) |
|---|---|---|---|---|---|
| 1 | 0.8134 | 1.0607 | 1.1598 | 1.2787 | 1.2730 |
| 1.3010 | 0.9696 | 1.1688 | 1.2633 | 1.3400 | 1.4525 |
| 1.4771 | 1.0451 | 1.3865 | 1.5450 | 1.5682 | 1.5993 |
| 1.7782 | 1.0730 | 1.4144 | 1.5567 | 1.5911 | 1.6219 |
| 2.0792 | 1.1305 | 1.4199 | 1.5688 | 1.5981 | 1.6389 |
| 2.2553 | 1.1949 | 1.4354 | 1.5716 | 1.6162 | 1.6613 |
| 2.3802 | 1.1995 | 1.4382 | 1.5758 | 1.6187 | 1.6669 |

**Table A-18: Effect of temperature on removal of lead by CJAC**
(pH=5, Dose=1 g/l, t=4 hr, $C_o$=20 mg/l)

| Time (min) | 303 K | 323 K | 343 K |
|---|---|---|---|
| | $Q_t$ (mg/g) | $Q_t$ (mg/g) | $Q_t$ (mg/g) |
| 10 | 6.3750 | 6.5750 | 6.7750 |
| 20 | 7.4500 | 7.7850 | 7.9850 |
| 30 | 10.7250 | 10.3728 | 10.5728 |
| 60 | 11.7500 | 12.0500 | 12.2500 |
| 120 | 13.1000 | 13.4300 | 13.8300 |
| 180 | 13.5000 | 13.9500 | 14.3500 |
| 240 | 13.6250 | 14.0250 | 14.4250 |

**Table A-19: Effect of temperature on removal of lead by CAC**
(pH= 4.2, Dose=**1** g/l, t=4 hr, $C_o$=20 mg/l)

| Time (min) | 303 K | 323 K | 343 K |
|---|---|---|---|
| | $Q_t$ (mg/g) | $Q_t$ (mg/g) | $Q_t$ (mg/g) |
| 10 | 6.5080 | 6.3080 | 6.5080 |
| 20 | 9.3240 | 9.5920 | 9.7920 |
| 30 | 11.0940 | 11.4500 | 11.6500 |
| 60 | 11.8320 | 12.0320 | 12.2320 |
| 120 | 13.5060 | 13.9060 | 14.3060 |
| 180 | 15.6660 | 16.0660 | 16.4660 |
| 240 | 15.8320 | 16.2320 | 16.6320 |

**Table A-20: Freundlich isotherm for the removal of lead at different temperatures using CJAC**

( pH=5, t= 4 hr, Dose=1 gm/l).

| Initial Concentration (mg/l) | 303 K | | 323 K | | 343 K | |
|---|---|---|---|---|---|---|
| | ln $Q_e$ | ln $C_e$ | ln $Q_e$ | ln $C_e$ | ln $Q_e$ | ln $C_e$ |
| 20 | 2.6119 | 1.8524 | 2.6408 | 1.7876 | 2.6690 | 1.7183 |
| 40 | 3.1549 | 2.8064 | 3.1884 | 2.7568 | 3.2209 | 2.7047 |
| 60 | 3.3978 | 3.4045 | 3.4371 | 3.3639 | 3.4750 | 3.3215 |
| 80 | 3.5205 | 3.8329 | 3.5667 | 3.7977 | 3.6109 | 3.7612 |
| 100 | 3.6176 | 4.1391 | 3.6699 | 4.1068 | 3.7196 | 4.0733 |

**Table A-21: Freundlich isotherm for the removal of lead at different temperatures using CAC**

( pH=4.2, t= 4 hr, Dose=1 gm/l).

| Initial Concentration (mg/l) | 303 K | | 323 K | | 343 K | |
|---|---|---|---|---|---|---|
| | ln $Q_e$ | ln $C_e$ | ln $Q_e$ | ln $C_e$ | ln $Q_e$ | ln $C_e$ |
| 20 | 2.7620 | 1.4274 | 2.7870 | 1.3265 | 2.8113 | 1.2143 |
| 40 | 3.3116 | 2.5313 | 3.3439 | 2.4655 | 3.3683 | 2.3952 |
| 60 | 3.6283 | 3.1068 | 3.6597 | 3.0516 | 3.6901 | 2.9930 |
| 80 | 3.7271 | 3.6491 | 3.7655 | 3.6059 | 3.8013 | 3.5622 |
| 100 | 3.8384 | 3.9806 | 3.8805 | 3.9425 | 3.9210 | 3.9030 |

**Table A-22: Langmuir isotherm for the removal of lead at different temperatures using CJAC**

( pH=5, t= 4 hr, Dose=1 gm/l).

| Initial Concentration (mg/l) | 303 K | | 323 K | | 343 K | |
|---|---|---|---|---|---|---|
| | $C_e$ | $C_e/Q_e$ | $C_e$ | $C_e/Q_e$ | $C_e$ | $C_e/Q_e$ |
| 20 | 6.3750 | 0.4679 | 5.9750 | 0.4260 | 5.5750 | 0.3865 |
| 40 | 16.5500 | 0.7057 | 15.7500 | 0.6495 | 14.9500 | 0.5968 |
| 60 | 30.1000 | 1.0067 | 28.9020 | 0.9294 | 27.7020 | 0.8577 |
| 80 | 46.2000 | 1.3669 | 44.6000 | 1.2599 | 43.0000 | 1.1622 |
| 100 | 62.7500 | 1.6846 | 60.7500 | 1.5478 | 58.7500 | 1.4242 |

**Table A-23: Langmuir isotherm for the removal of lead at different temperatures using CAC**

( pH=4.2, t= 4 hr, Dose=1 gm/l).

| Initial Concentration (mg/l) | 303 K | | 323 K | | 343 K | |
|---|---|---|---|---|---|---|
| | $C_e$ | $C_e/Q_e$ | $C_e$ | $C_e/Q_e$ | $C_e$ | $C_e/Q_e$ |
| 20 | 4.1680 | 0.2633 | 3.7680 | 0.2321 | 3.3680 | 0.2025 |
| 40 | 12.5700 | 0.4583 | 11.7700 | 0.4155 | 10.9700 | 0.3779 |
| 60 | 22.3500 | 0.5936 | 21.1500 | 0.5444 | 19.9500 | 0.4981 |
| 80 | 38.4400 | 0.9249 | 36.8160 | 0.8525 | 35.2400 | 0.7873 |
| 100 | 53.5500 | 1.1528 | 51.5500 | 1.0640 | 49.5500 | 0.9822 |

**Table A-24: Temkin isotherm for the removal of lead at different temperatures using CJAC**
( pH=5, t= 4 hr, Dose=1 gm/l).

| Initial Concentration (mg/l) | 303 K | | 323 K | | 343 K | |
|---|---|---|---|---|---|---|
| | Qe | ln Ce | Qe | ln Ce | Qe | ln Ce |
| 20 | 13.6250 | 1.8524 | 14.0250 | 1.7876 | 14.4250 | 1.7183 |
| 40 | 23.4500 | 2.5064 | 24.2500 | 2.7568 | 25.0500 | 2.7047 |
| 60 | 29.9000 | 3.4045 | 31.0980 | 3.3639 | 32.2980 | 3.3215 |
| 80 | 33.8000 | 3.8329 | 35.4000 | 3.7977 | 37.0000 | 3.7612 |
| 100 | 37.2500 | 4.1391 | 39.2500 | 4.1068 | 41.2500 | 4.0733 |

**Table A-25: Temkin isotherm for the removal of lead at different temperatures using CAC**
( pH=4.2, t= 4 hr, Dose=1 gm/l).

| Initial Concentration (mg/l) | 303 K | | 323 K | | 343 K | |
|---|---|---|---|---|---|---|
| | Qe | ln Ce | Qe | ln Ce | Qe | ln Ce |
| 20 | 15.8320 | 1.4274 | 16.2320 | 1.3265 | 16.6320 | 1.2143 |
| 40 | 27.4300 | 2.5313 | 28.3300 | 2.4655 | 29.0300 | 2.3952 |
| 60 | 37.6500 | 3.1068 | 38.5500 | 3.0516 | 40.0500 | 2.9930 |
| 80 | 41.5600 | 3.6491 | 43.1840 | 3.6059 | 44.7600 | 3.5622 |
| 100 | 46.4500 | 3.9806 | 48.4500 | 3.9425 | 50.4500 | 3.9030 |

**Table A-26: Redlich -Peterson isotherm for the removal of lead at different temperatures using CJAC**

( pH=5, t= 4 hr, Dose=1 gm/l).

**Here, W= ln((KR*(Ce/Qe)-1)**

| Initial Concentration (mg/l) | 303 K | | 323 K | | 343 K | |
|---|---|---|---|---|---|---|
| | ln Ce | W | ln Ce | W | ln Ce | W |
| 20 | 1.8524 | 0.3299 | 1.7876 | 0.4003 | 1.7183 | 0.5450 |
| 40 | 2.5064 | 0.9579 | 2.7568 | 1.0294 | 2.7047 | 1.1655 |
| 60 | 3.4045 | 1.4217 | 3.3639 | 1.4899 | 3.3215 | 1.6187 |
| 80 | 3.8329 | 1.7892 | 3.7977 | 1.8516 | 3.7612 | 1.9731 |
| 100 | 4.1391 | 2.0292 | 4.1068 | 2.0862 | 4.0733 | 2.2017 |

**Table A-27: Redlich -Peterson isotherm for the removal of lead at different temperatures using CAC**

( pH=4.2, t= 4 hr, Dose=1 gm/l).

**Here, W= ln((KR*(Ce/Qe)-1)**

| Initial Concentration (mg/l) | 303 K | | 323 K | | 343 K | |
|---|---|---|---|---|---|---|
| | ln Ce | W | ln Ce | W | ln Ce | W |
| 20 | 1.4274 | -0.2625 | 1.3265 | -0.1381 | 1.2143 | 0.0249 |
| 40 | 2.5313 | 0.7321 | 2.4655 | 0.8589 | 2.3952 | 1.0222 |
| 60 | 3.1068 | 1.0950 | 3.0516 | 1.2202 | 2.9930 | 1.3817 |
| 80 | 3.6491 | 1.6516 | 3.6059 | 1.7701 | 3.5622 | 1.9277 |
| 100 | 3.9806 | 1.9091 | 3.9425 | 2.0249 | 3.9030 | 2.1773 |

# APPENDIX – B

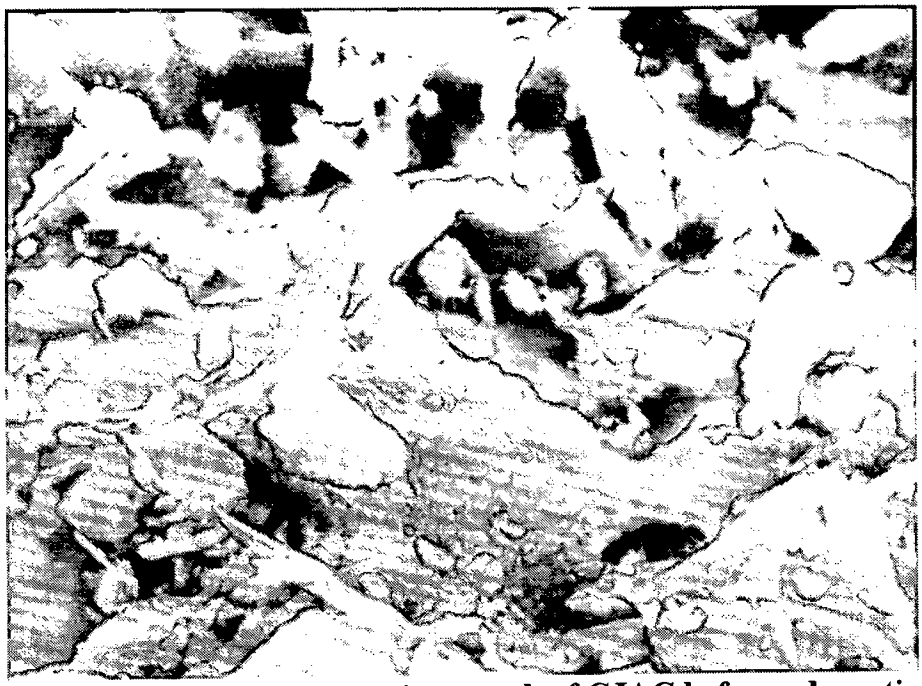

**Fig B -1: Scanning electron micrograph of CJAC before adsorption at 1000 X magnification**

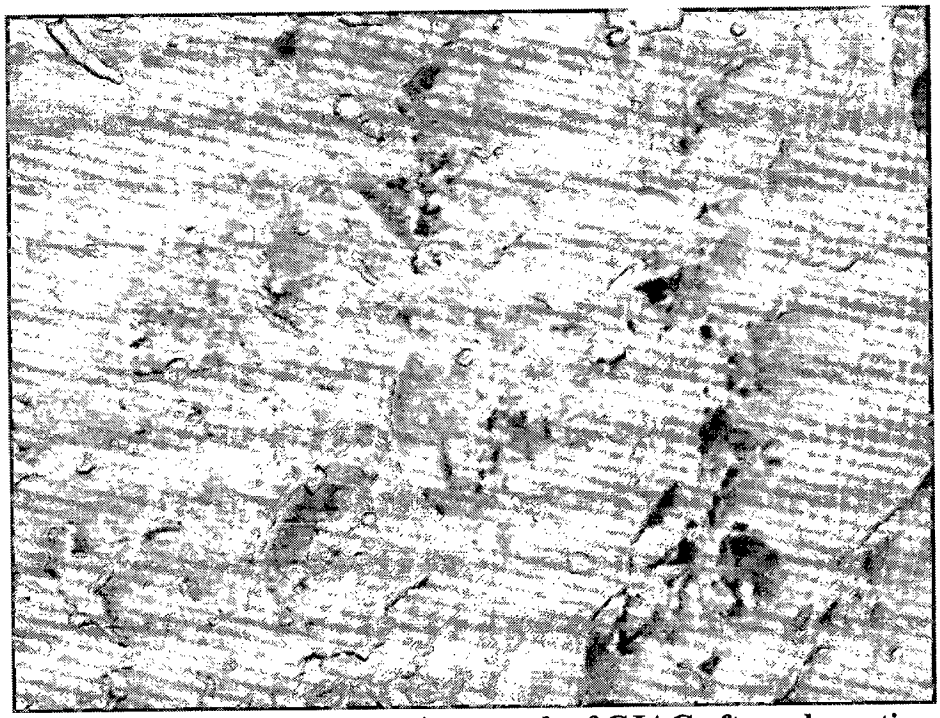

**Fig B - 2: Scanning electron micrograph of CJAC after adsorption at 1000 X magnification**

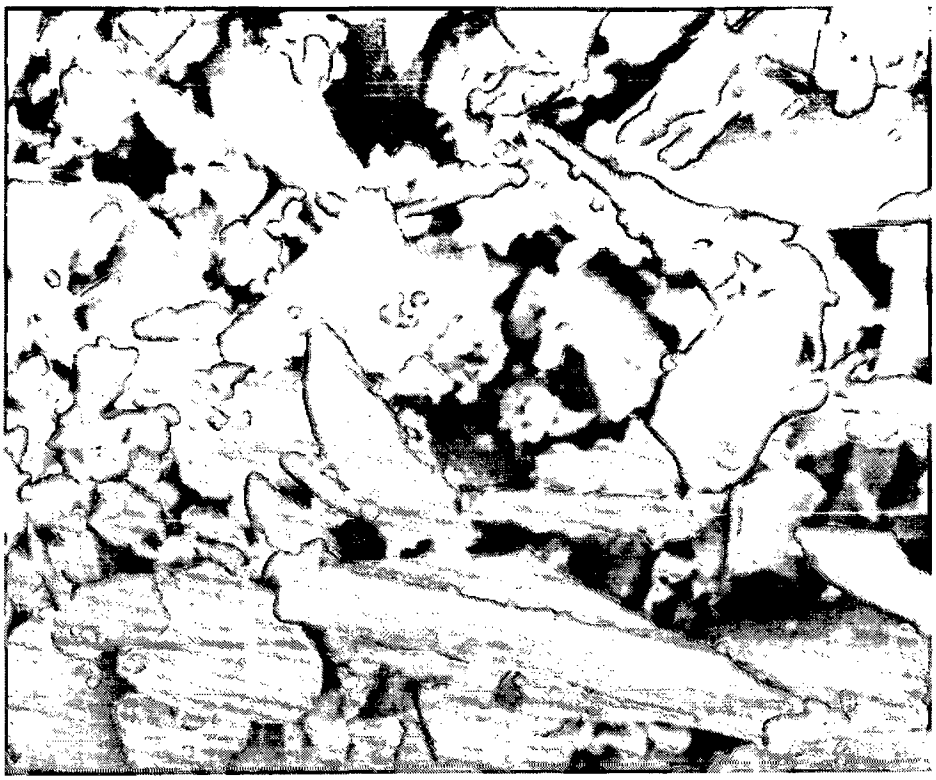

**Fig B-3: Scanning electron micrograph of CAC before adsorption at 1000 X magnification**

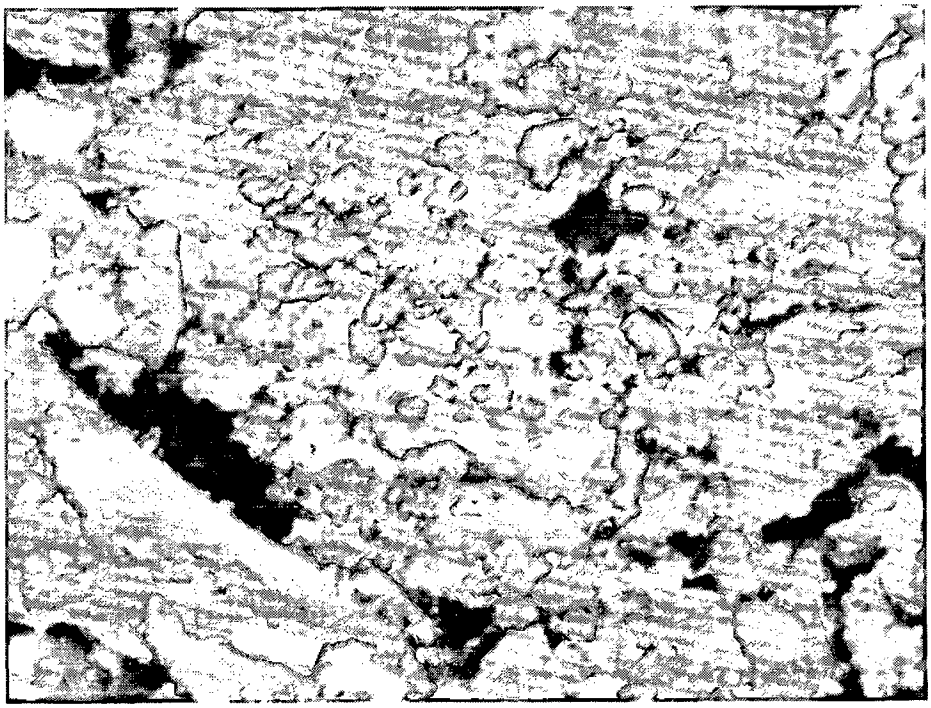

**Fig B - 4: Scanning electron micrograph of CAC after adsorption at 1000 X magnification**

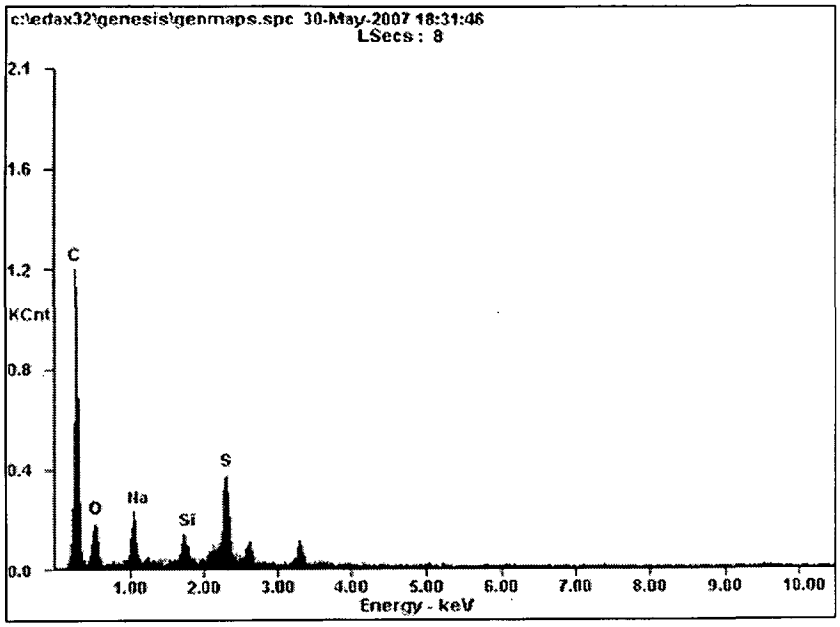


**Fig.B - 5: EDS pattern for CJAC before adsorption**

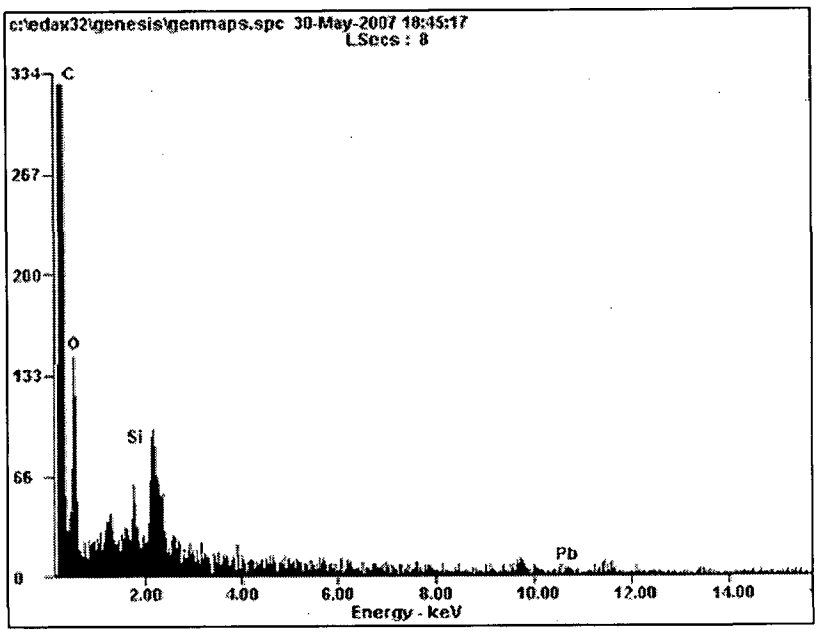


**Fig.B - 6: EDS pattern for CJAC after adsorption**

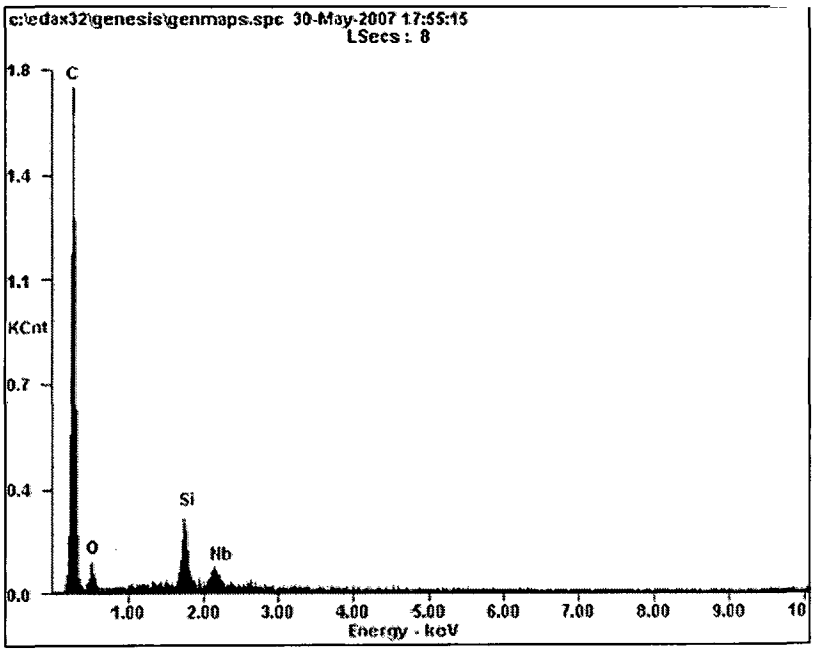


**Fig.B - 7: EDS pattern for CAC before adsorption**

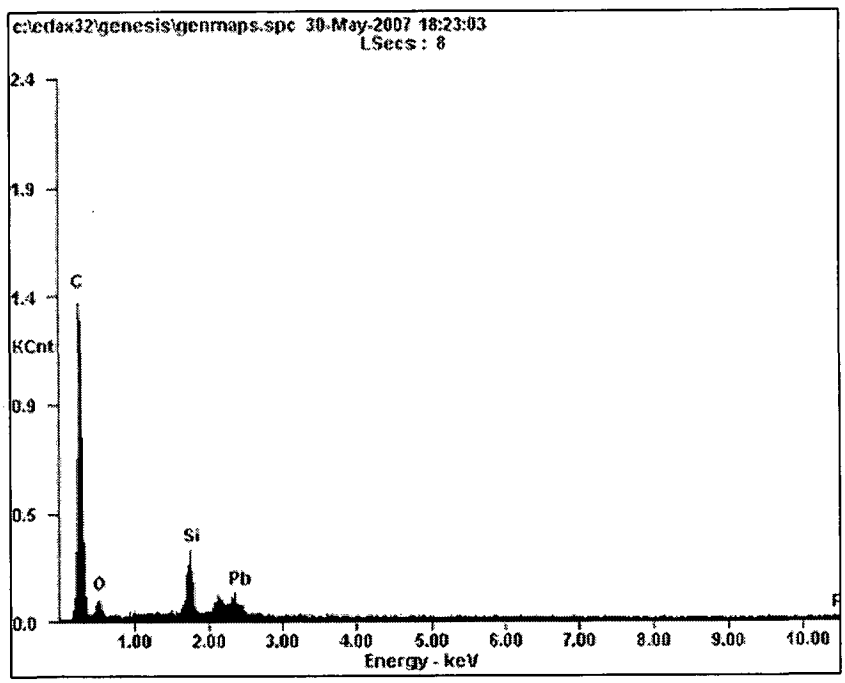


**Fig.B- 8: EDS pattern for CAC after adsorption**

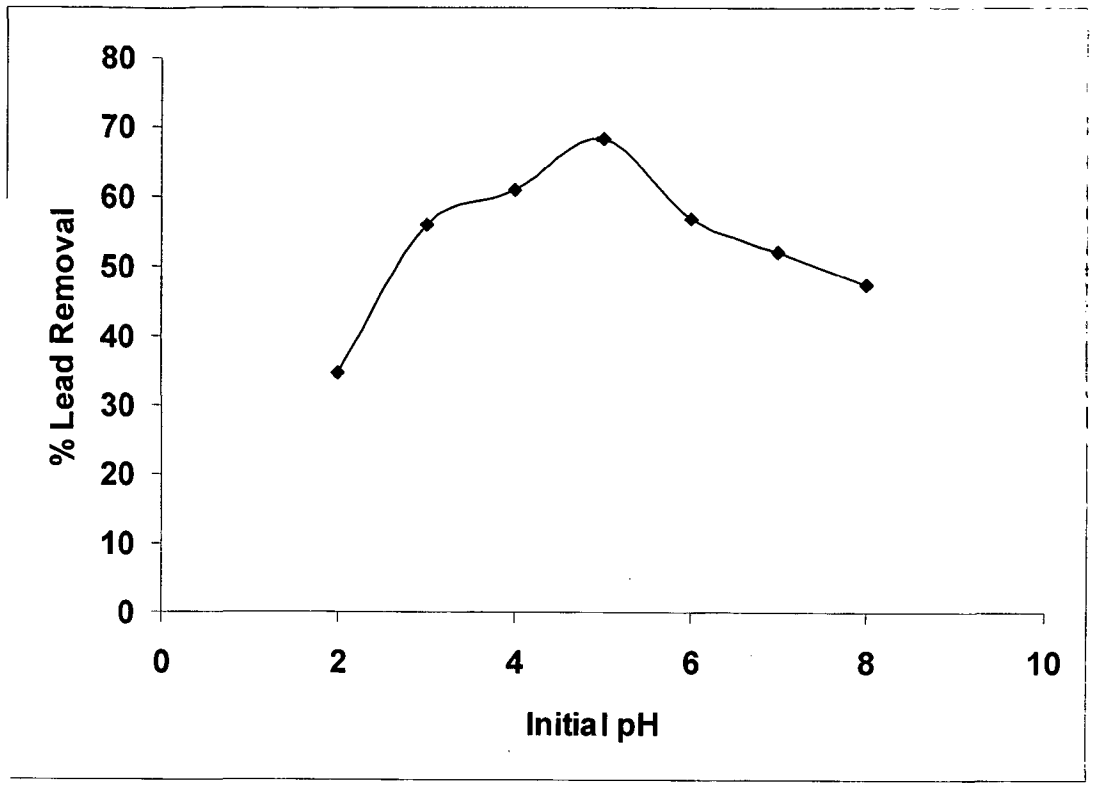


**Fig. B - 9: Effect of $pH_0$ on the adsorption of Pb(II) using CJAC as an adsorben**
(T = 303K, $t$ =4 h, $C_0$ = 20 mg /l, CJAC dose =1 g /l).

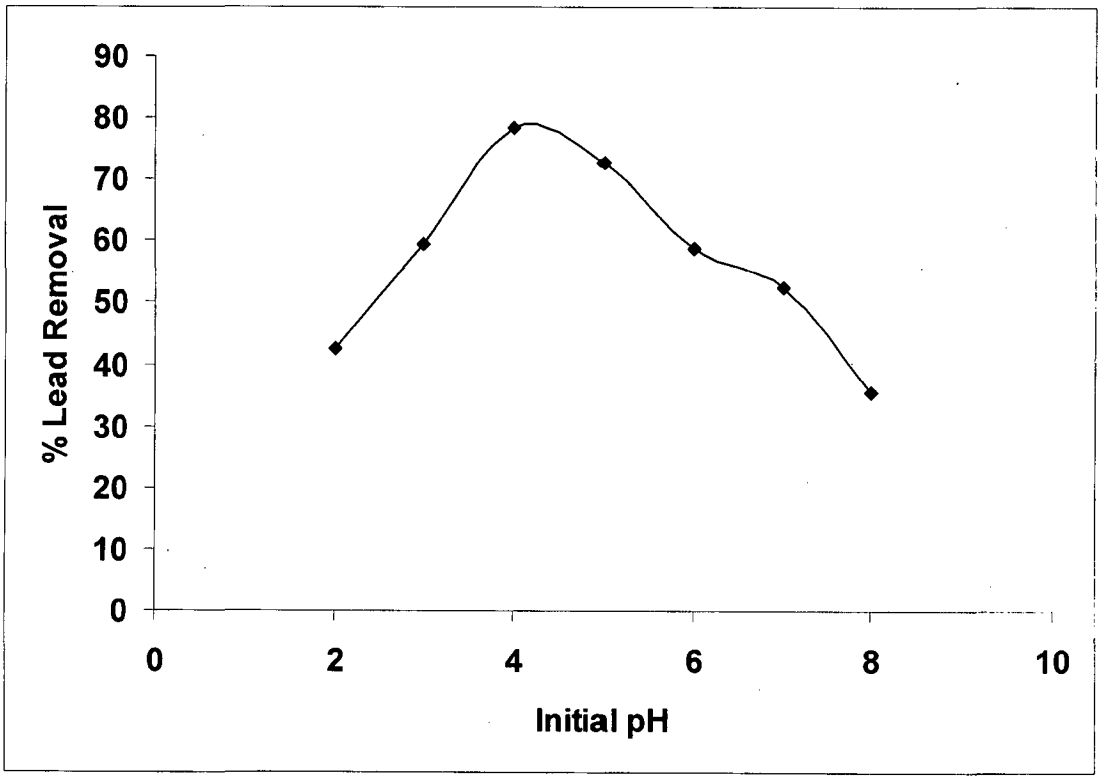


**Fig. B - 10: Effect of $pH_0$ on the adsorption of Pb(II) using CAC as an adsorbent**
(T = 303K, $t$ =4 h, $C_0$ = 20 mg /l, CAC dose =1 g /l).

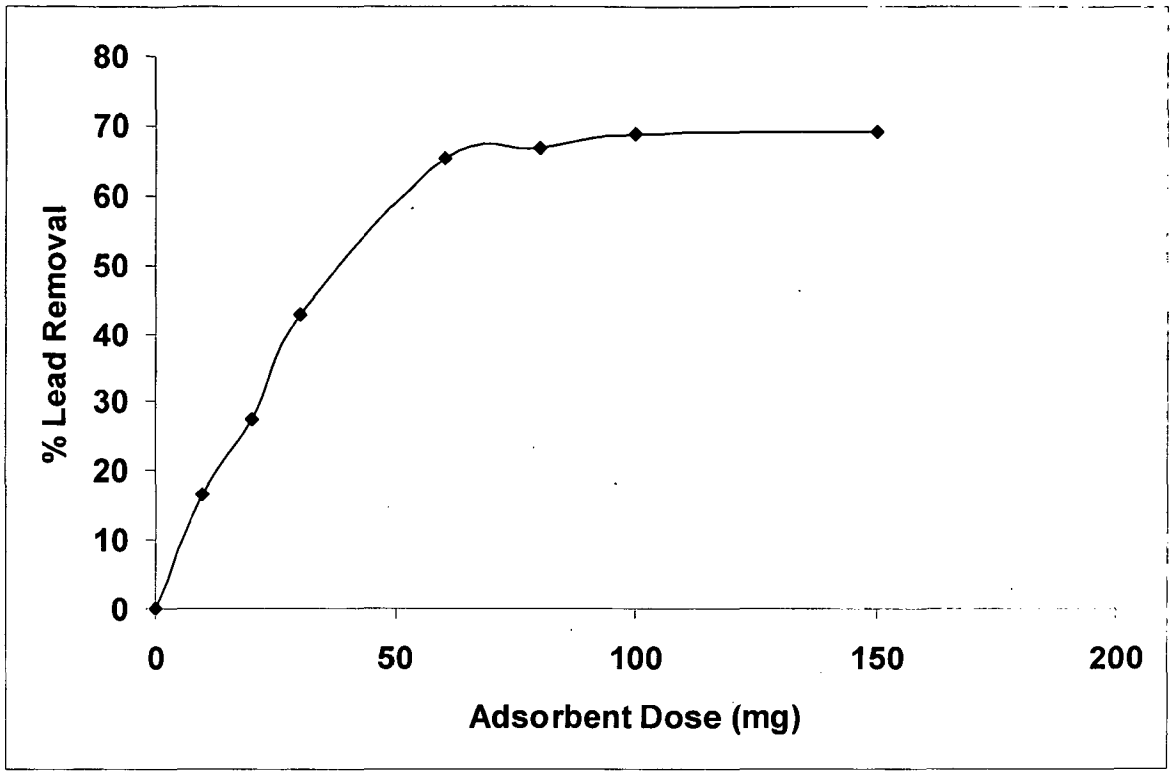


**Fig. B - 11: Effect of adsorbent dose on the adsorption of Pb(II) using CJAC as an adsorbent**

(T = 303K, $t$ =4 h, $C_0$ = 20 mg /l,pH=5, CJAC dose =1 g /l).

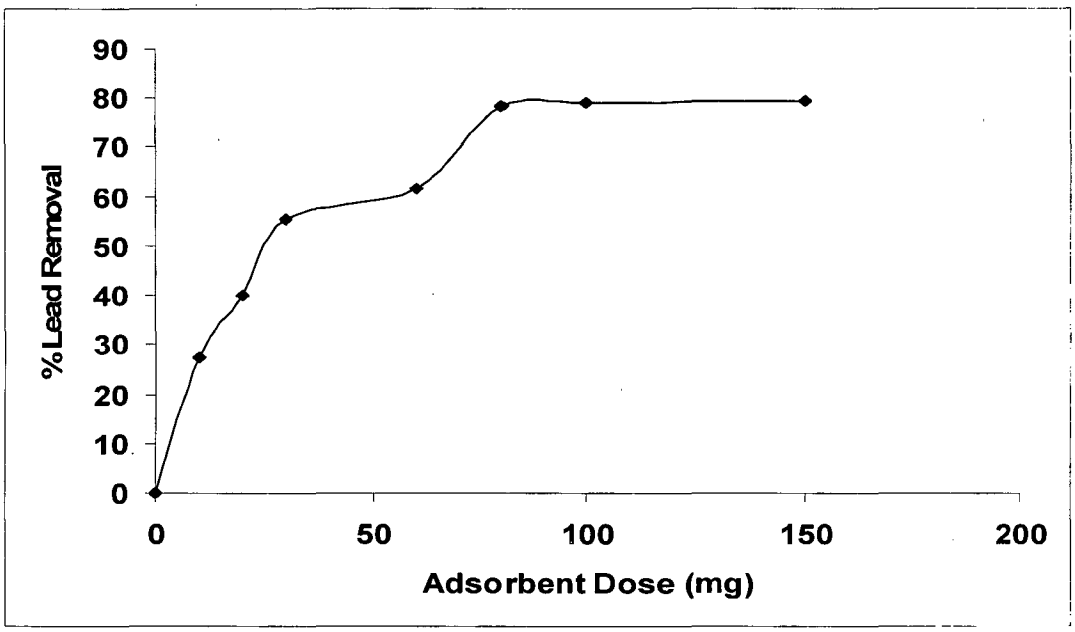


**Fig. B - 12: Effect of adsorbent dose on the adsorption of Pb(II) using CAC as an adsorbent**

(T = 303K, $t$ =4 h, $C_0$ = 20 mg /l,pH=4.2, CAC dose =1 g /l).

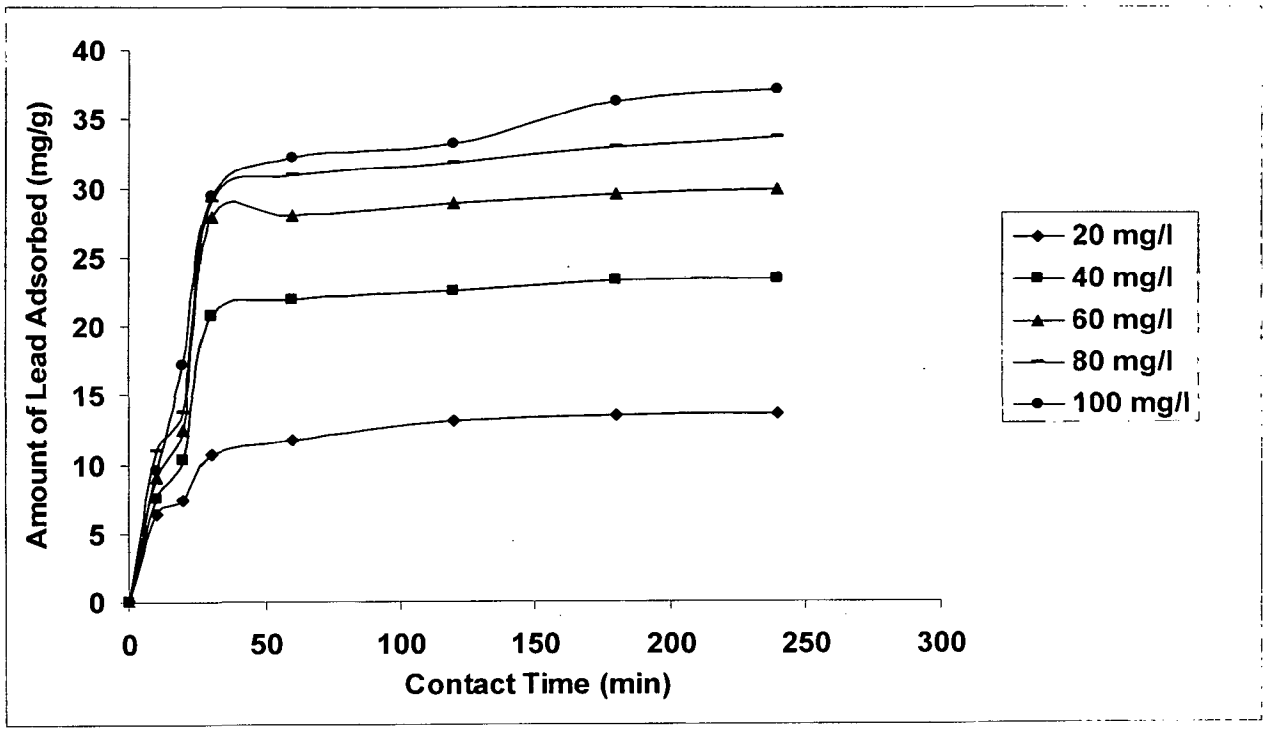


**Fig. B - 13: Effect of contact time and intial concentration on the adsorption of Pb(II) using CJAC as an adsorbent**

(T = 303K, $t$ =4 h, $C_0$ = 20 mg /l, pH=5,CJAC dose =1 g /l).

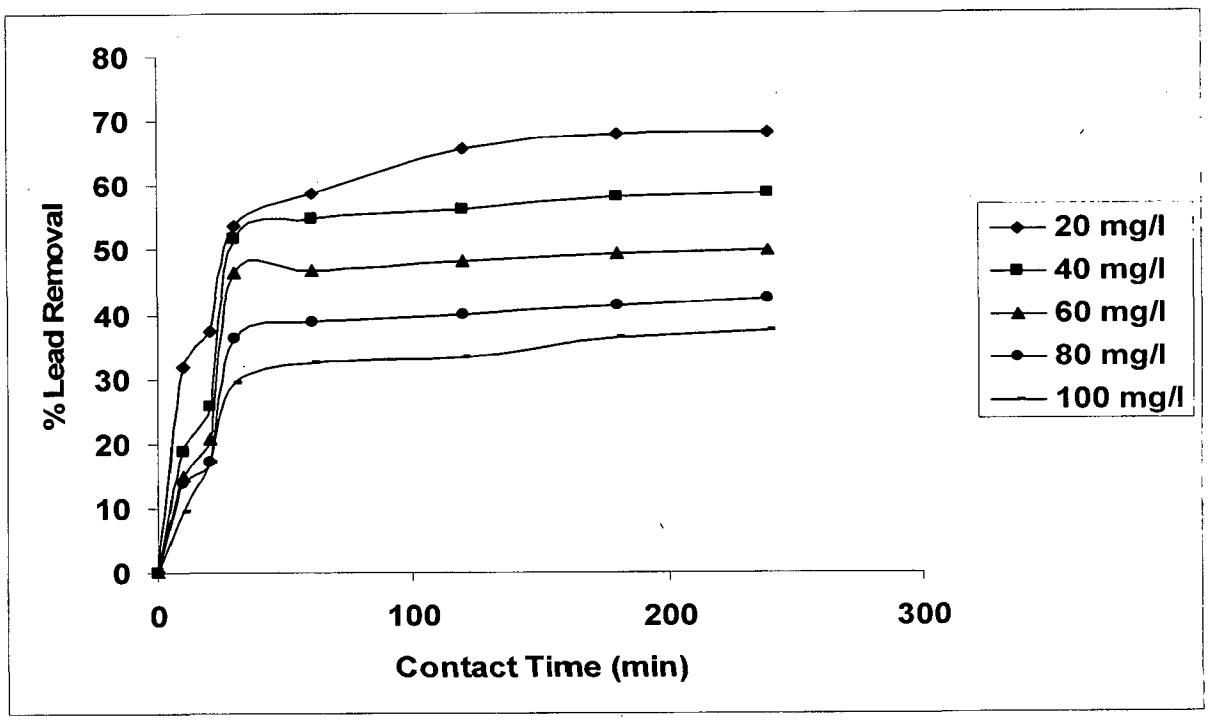


**Fig. B - 14: Effect of contact time and intial concentration on the adsorption of Pb(II) using CJAC as an adsorbent**

(T = 303K, $t$ =4 h, $C_0$ = 20 mg /l, pH=5,CJAC dose =1 g /l).

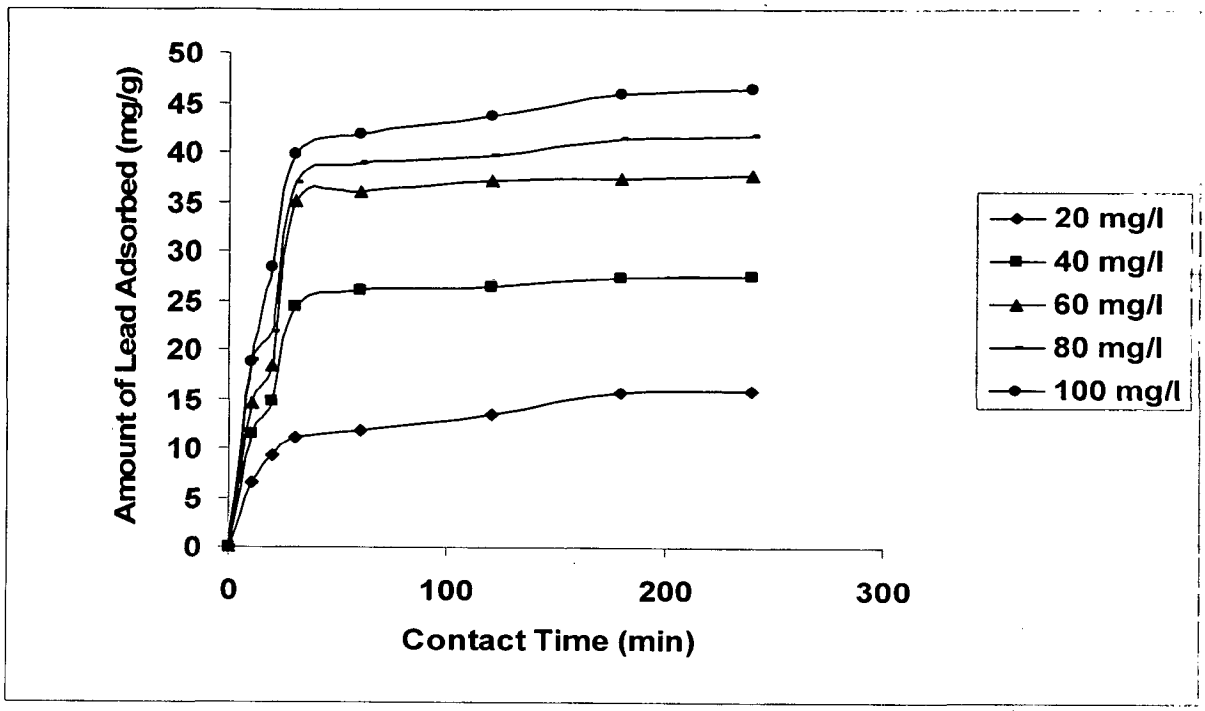


**Fig. B - 15: Effect of contact time and intial concentration on the adsorption of Pb(II) using CAC as an adsorbent**

(T = 303K, $t$ =4 h, $C_0$ = 20 mg /l,pH=4.2, CAC dose =1 g /l).

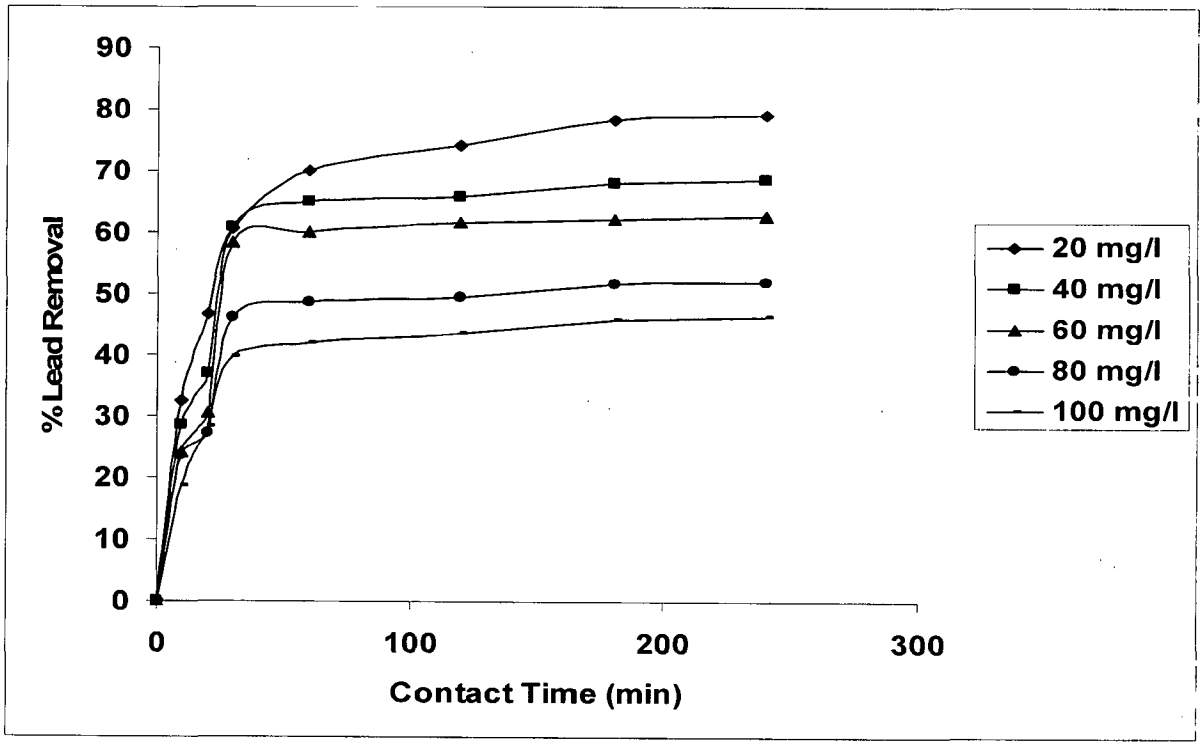


**Fig. B - 16: Effect of contact time and intial concentration on the adsorption of Pb(II) using CAC as an adsorbent**

(T = 303K, $t$ =4 h, $C_0$ = 20 mg /l,pH=4.2, CAC dose =1 g /l).

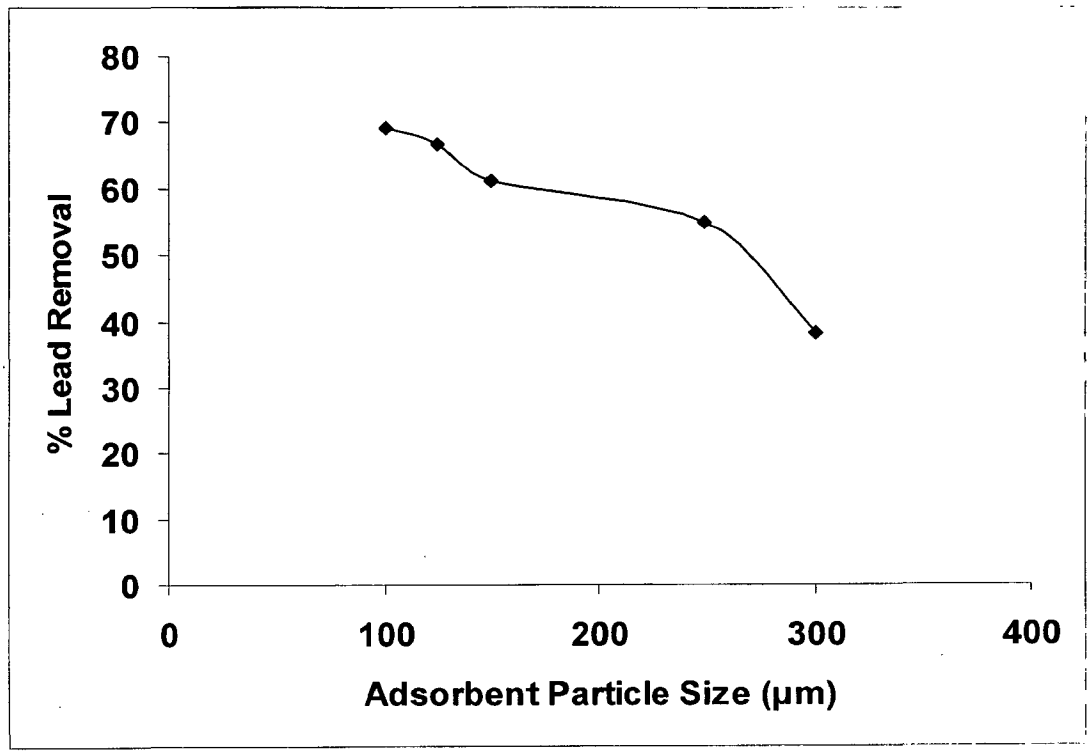


**Fig. B - 17: Effect of particle size on the adsorption of Pb(II) using CJAC as an adsorbent** (T = 303K, $t$ =4 h, $C_0$ = 20 mg /l, pH=5,CJAC dose =1 g /l).

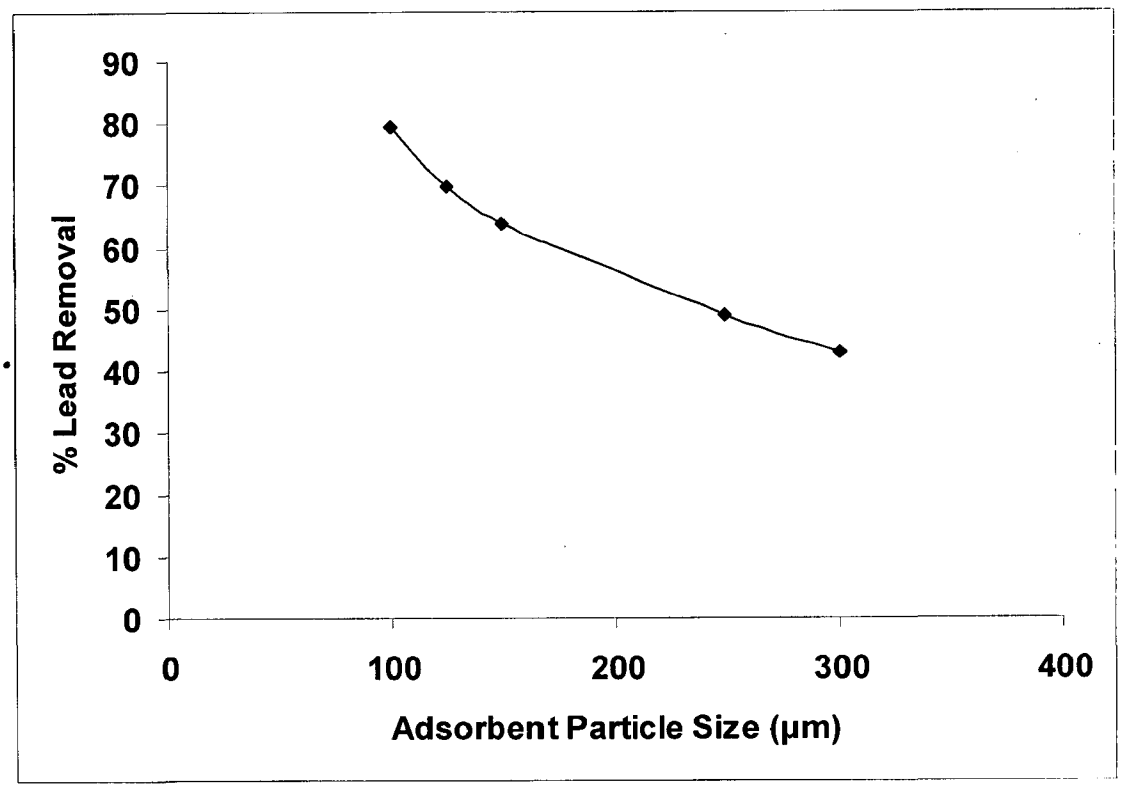


**Fig. B - 18: Effect of particle size on the adsorption of Pb(II) using CAC as an adsorbent** (T = 303K, $t$ =4 h, $C_0$ = 20 mg /l, pH=4.2,CAC dose =1 g /l).

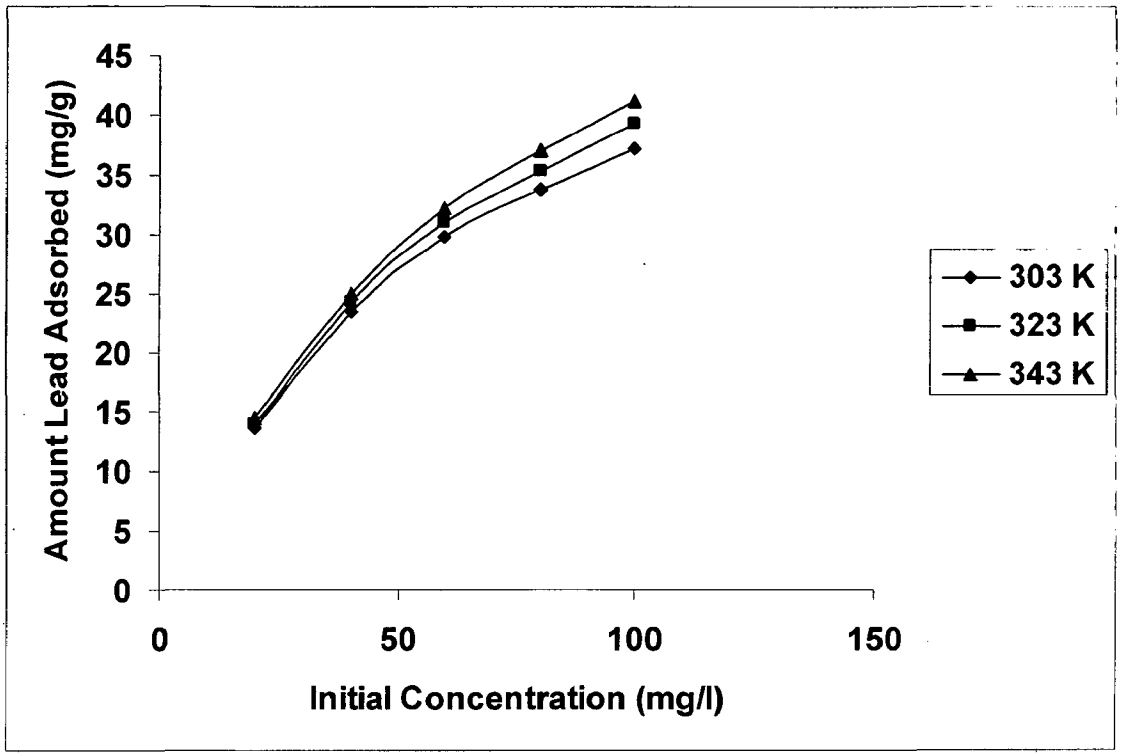


**Fig. B - 19: Effect of temperature on removal of Pb(II) by using CJAC** ($t$ = 4 h, pH=5, dose=1g/l).

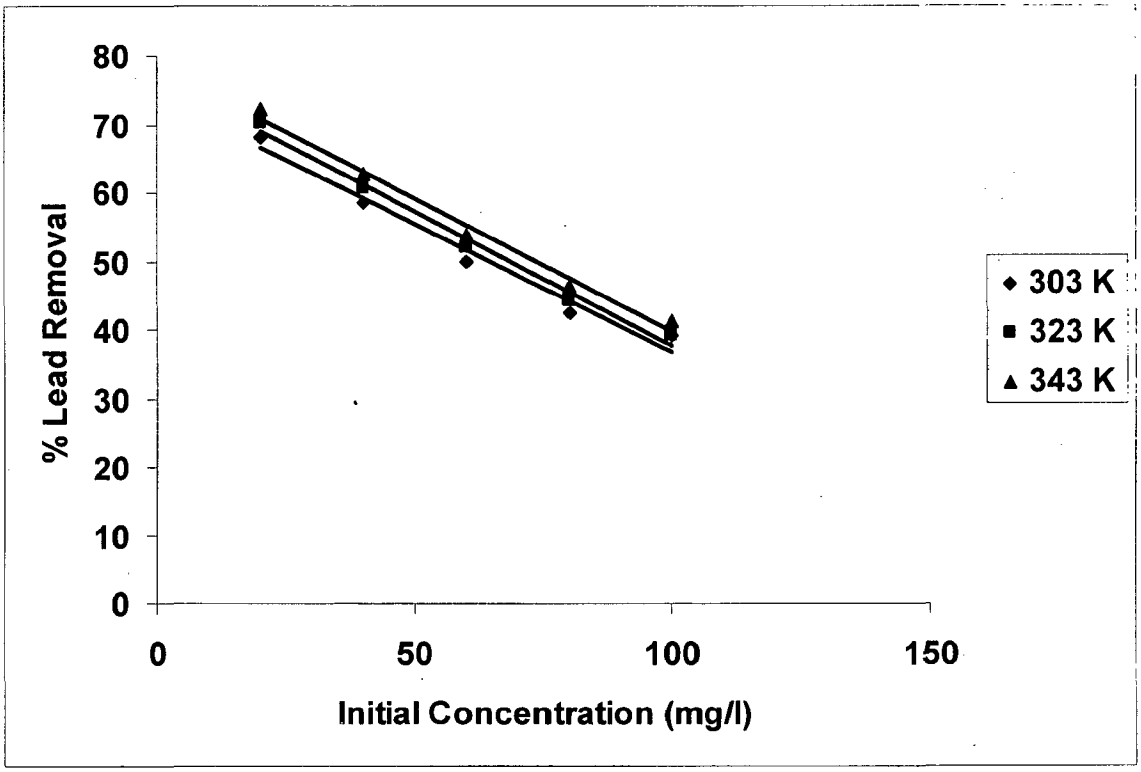


**Fig. B - 20: Effect of temperature on removal of Pb(II) by using CJAC** ($t$ = 4 h, pH=5, dose=1g/l).

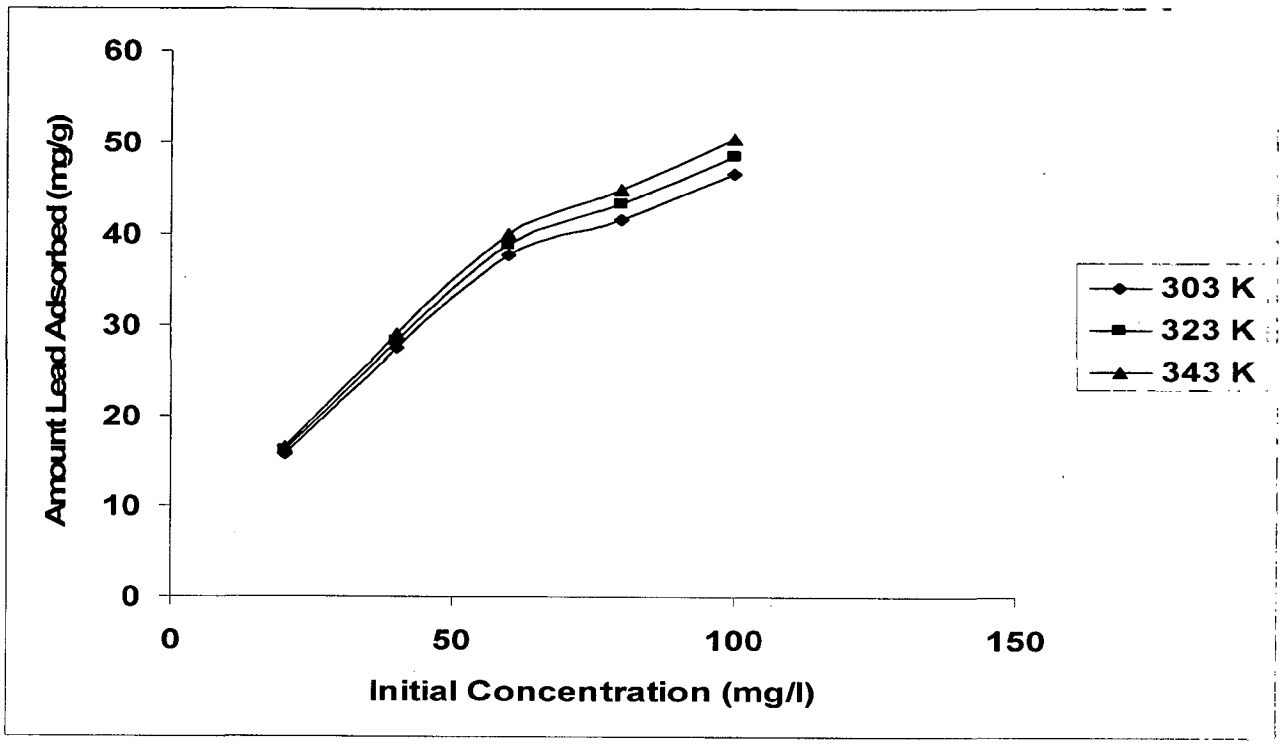


**Fig. B - 21: Effect of temperature on removal of Pb(II) by using CAC**
($t$ = 4 h, pH=4.2, dose=1g/l).

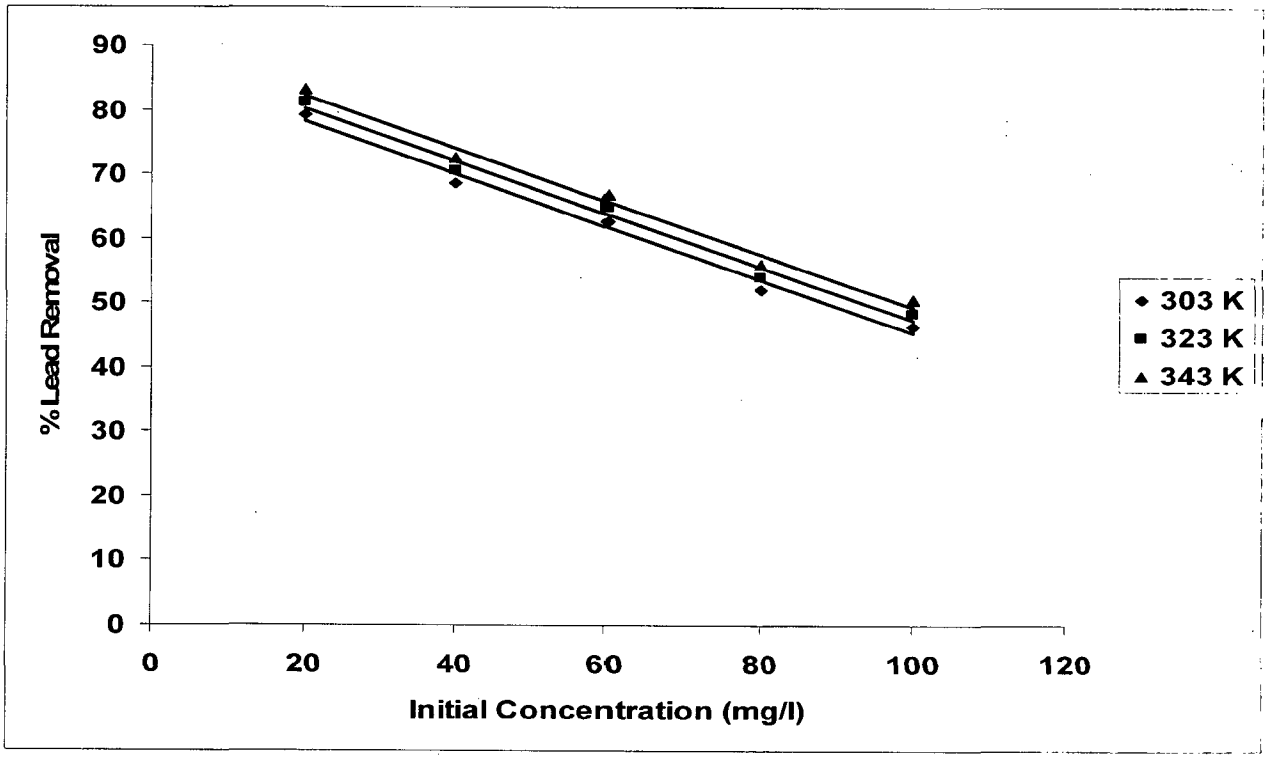


**Fig. B - 22: Effect of temperature on removal of Pb(II) by using CAC**
($t$ = 4 h, pH=4.2, dose=1g/l).

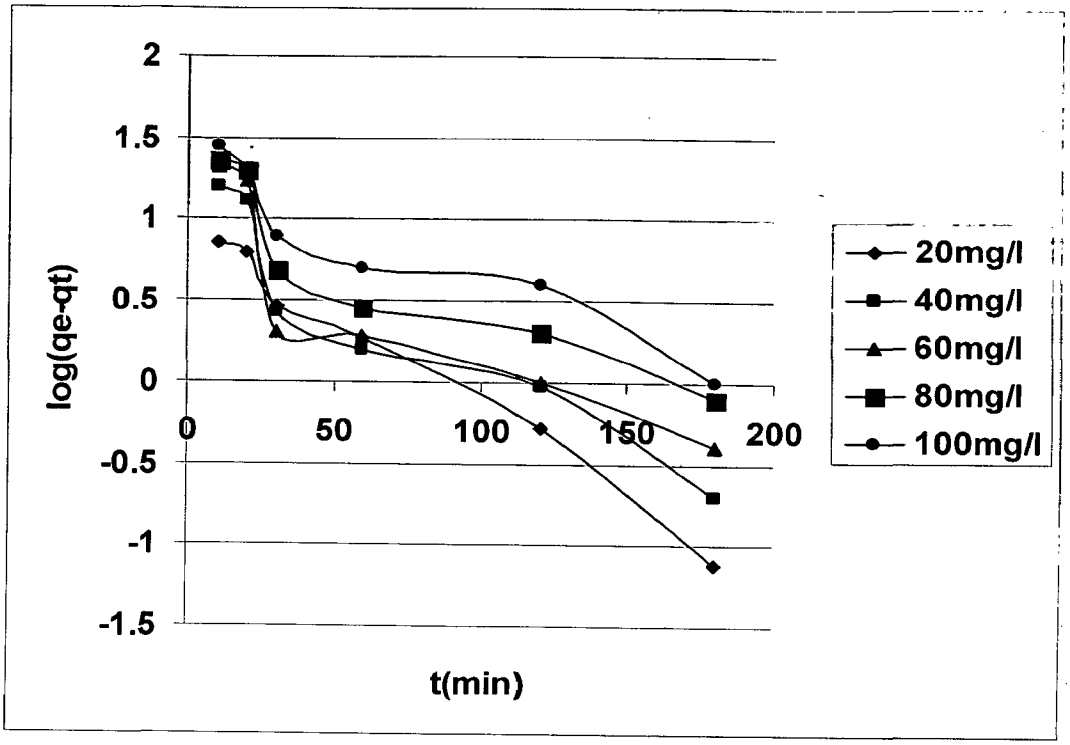


**Fig. B - 23: Pseudo - First Order Kinetics for the removal of Pb(II) for CJAC** (T= 303 K, dose =1 g/l, pH=5, t=4h).

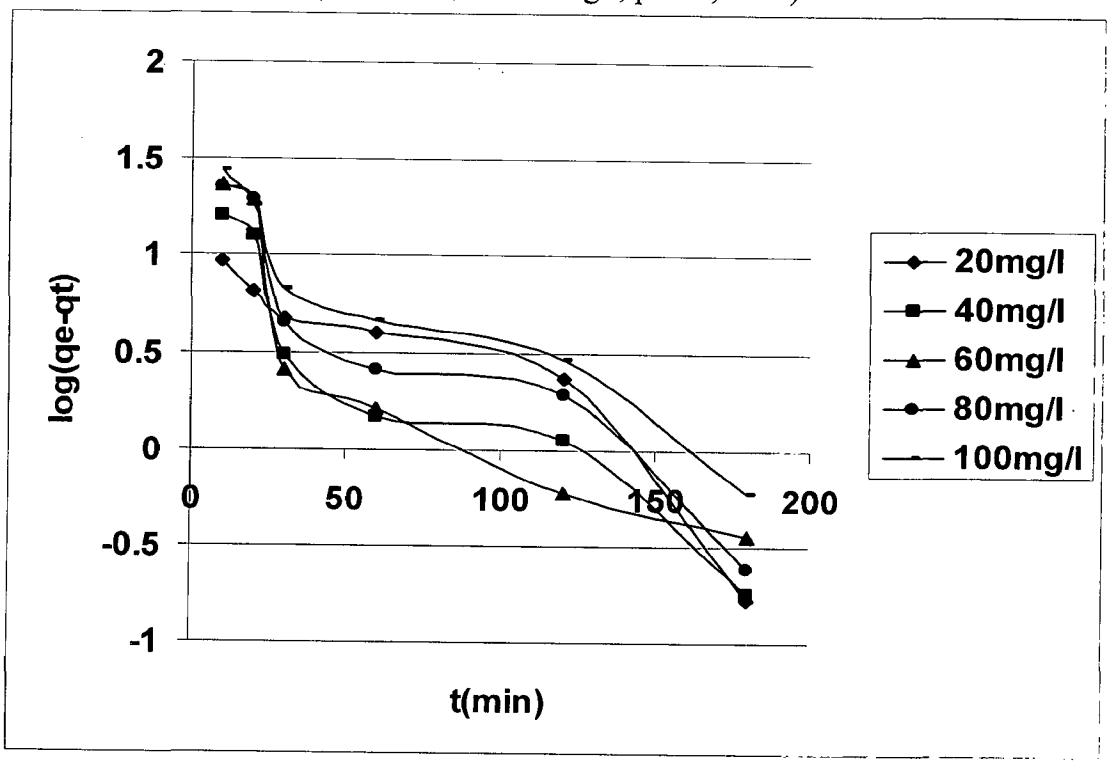


**Fig. B - 24: Pseudo - First Order Kinetics for the removal of Pb(II) for CAC** (T= 303 K, dose =1 g/l, pH=4.2, t=4h).

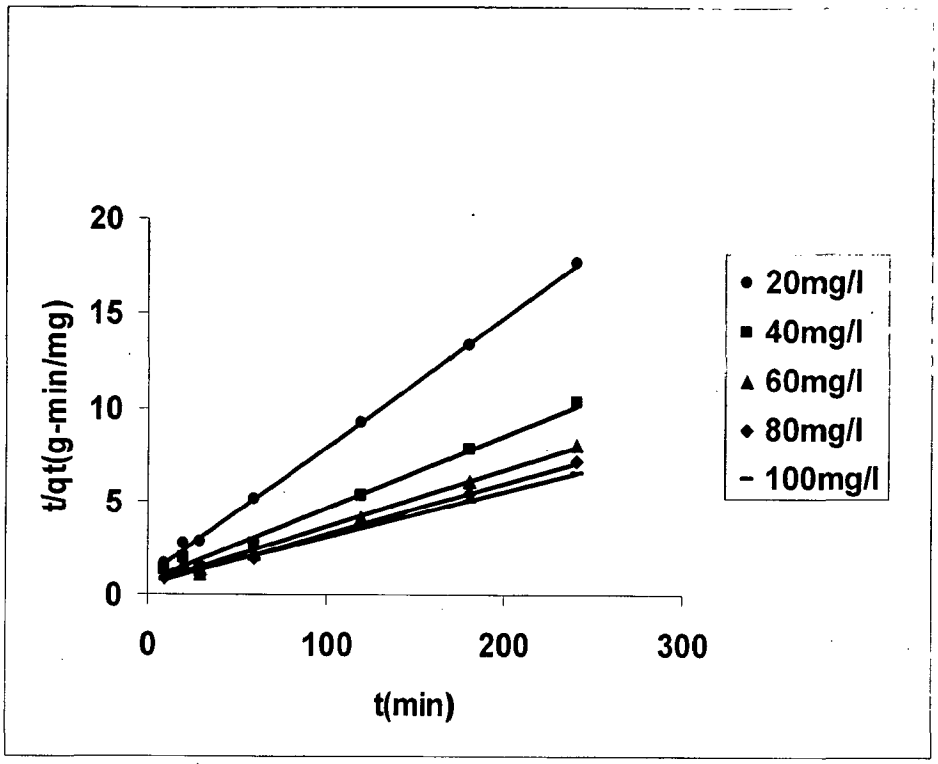


**Fig. B - 25: Pseudo - Second Order Kinetics for the removal of Pb(II) for CJAC** (T= 303 K, dose =1 g/l, pH=5, t=4h).

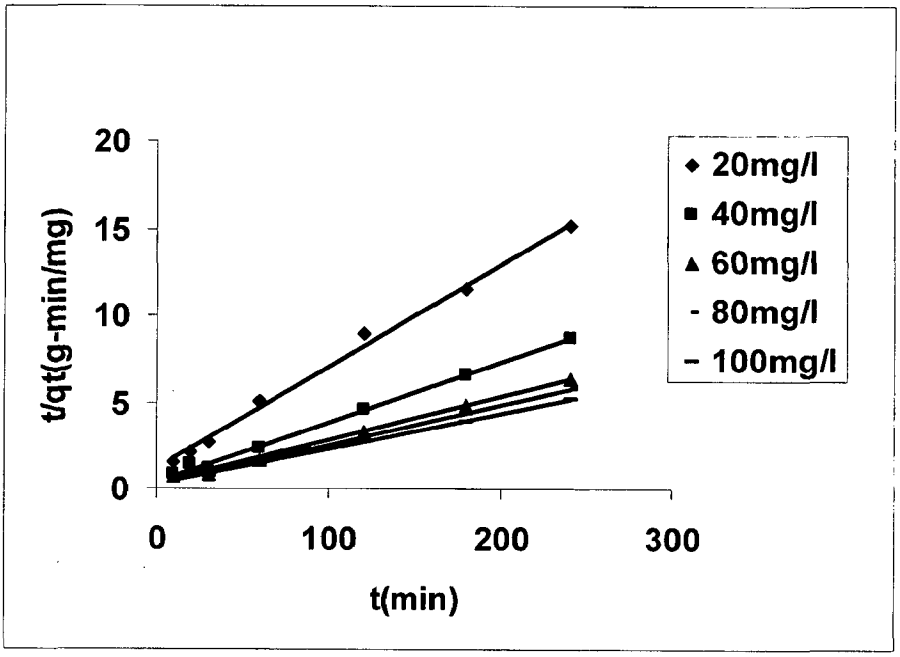


**Fig. B - 26: Pseudo - Second Order Kinetics for the removal of Pb(II) for CAC** (T= 303 K, dose =1 g/l, pH=4.2, t=4h).

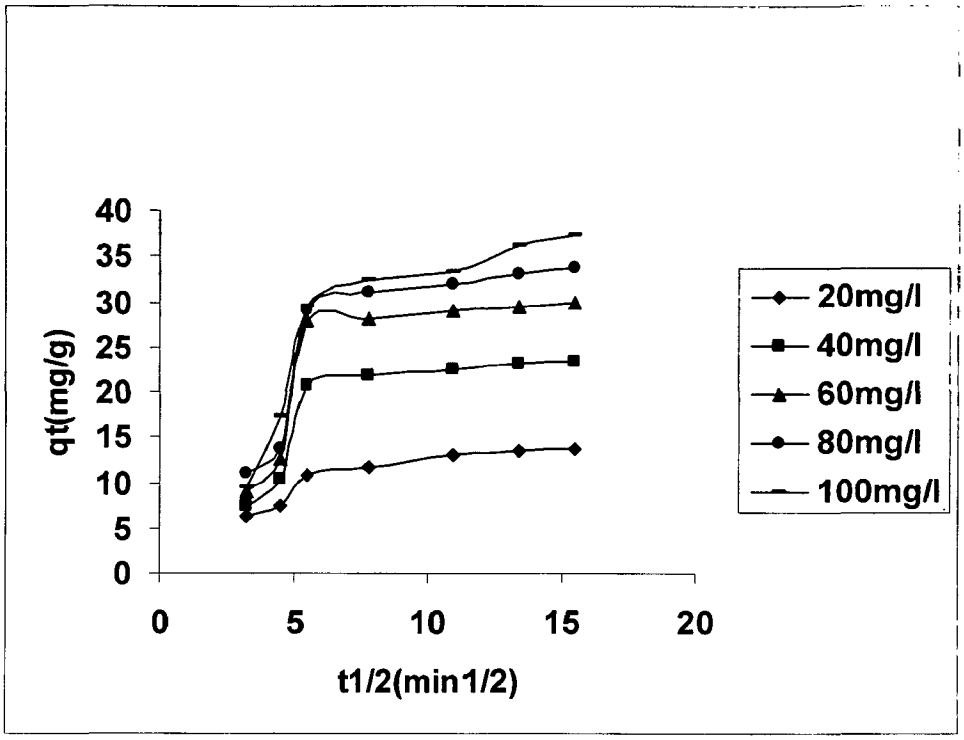


**Fig. B - 27: Intra-particle diffusion model for the removal of Pb(II) for CJAC** (T= 303 K, dose =1 g/l, pH=5, t=4h).

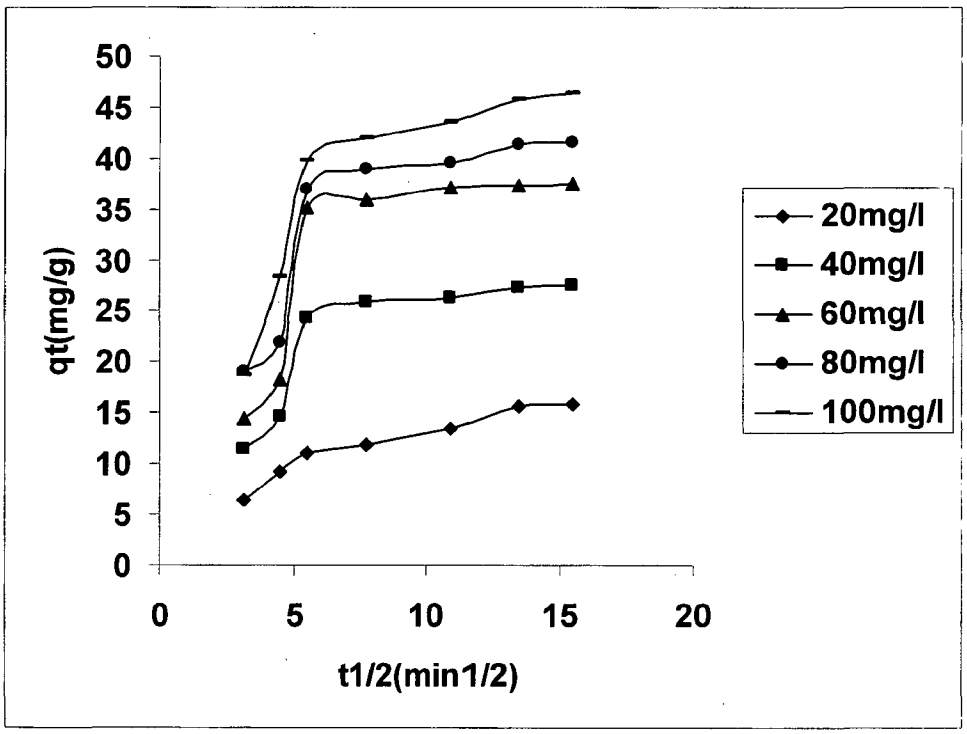


**Fig. B - 28: Intra-particle diffusion model for the removal of Pb(II) for CAC** (T= 303 K, dose =1 g/l, pH=4.2, t=4h).

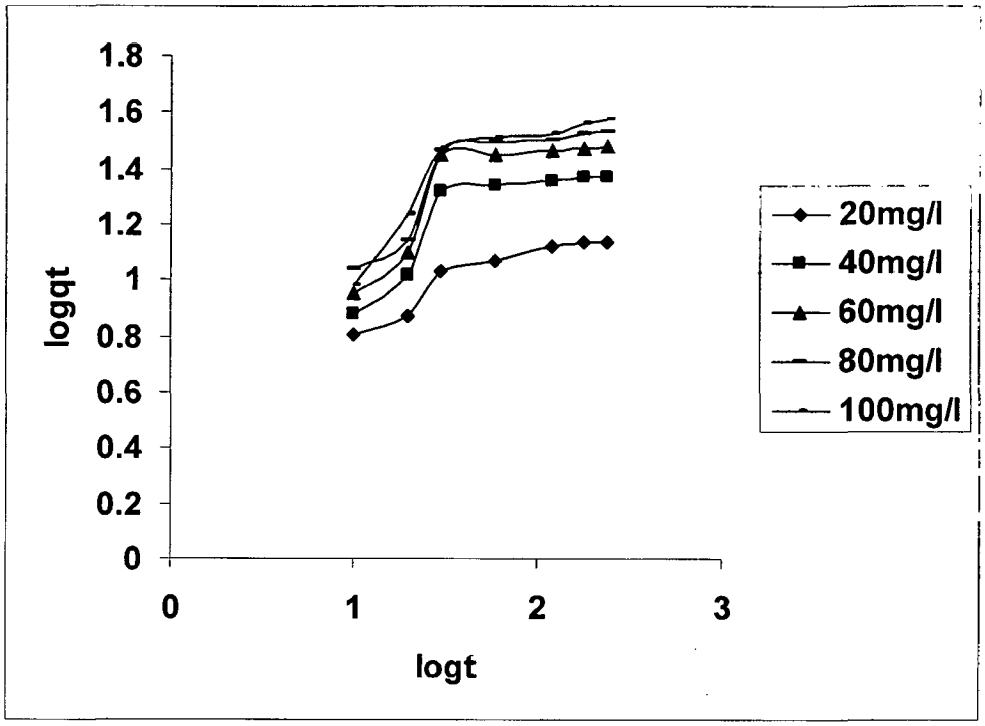


**Fig. B - 29: Bangham's model for the removal of Pb(II) for CJAC**
(T= 303 K, dose =1 g/l, pH=5, t=4h).

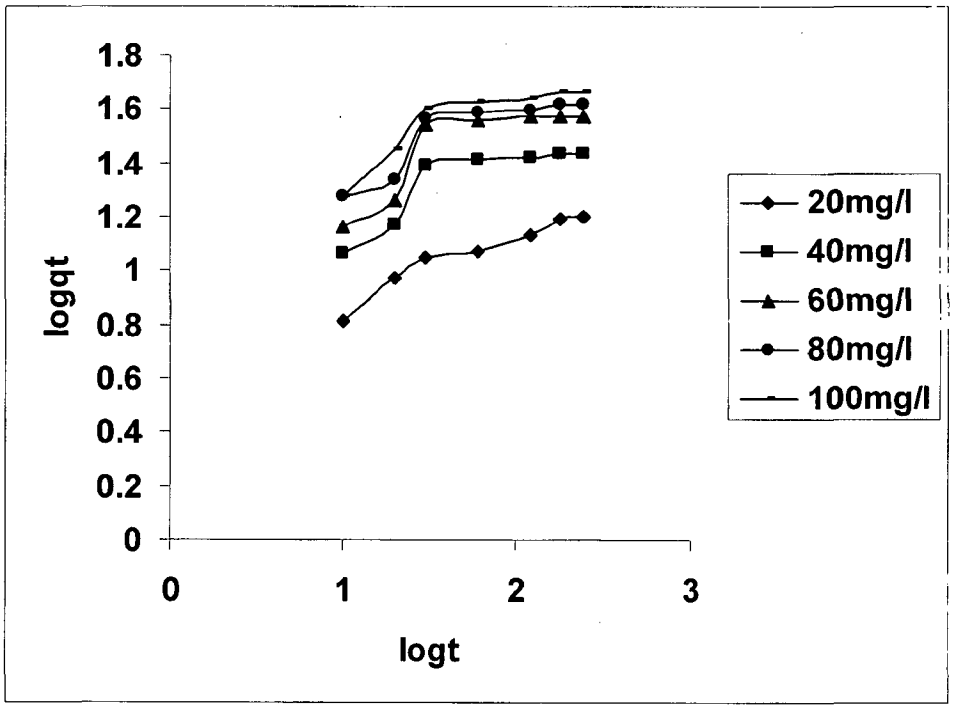


**Fig. B - 30: Bangham's model for the removal of Pb(II) for CAC**
(T= 303 K, dose =1 g/l, pH=4.2, t=4h).

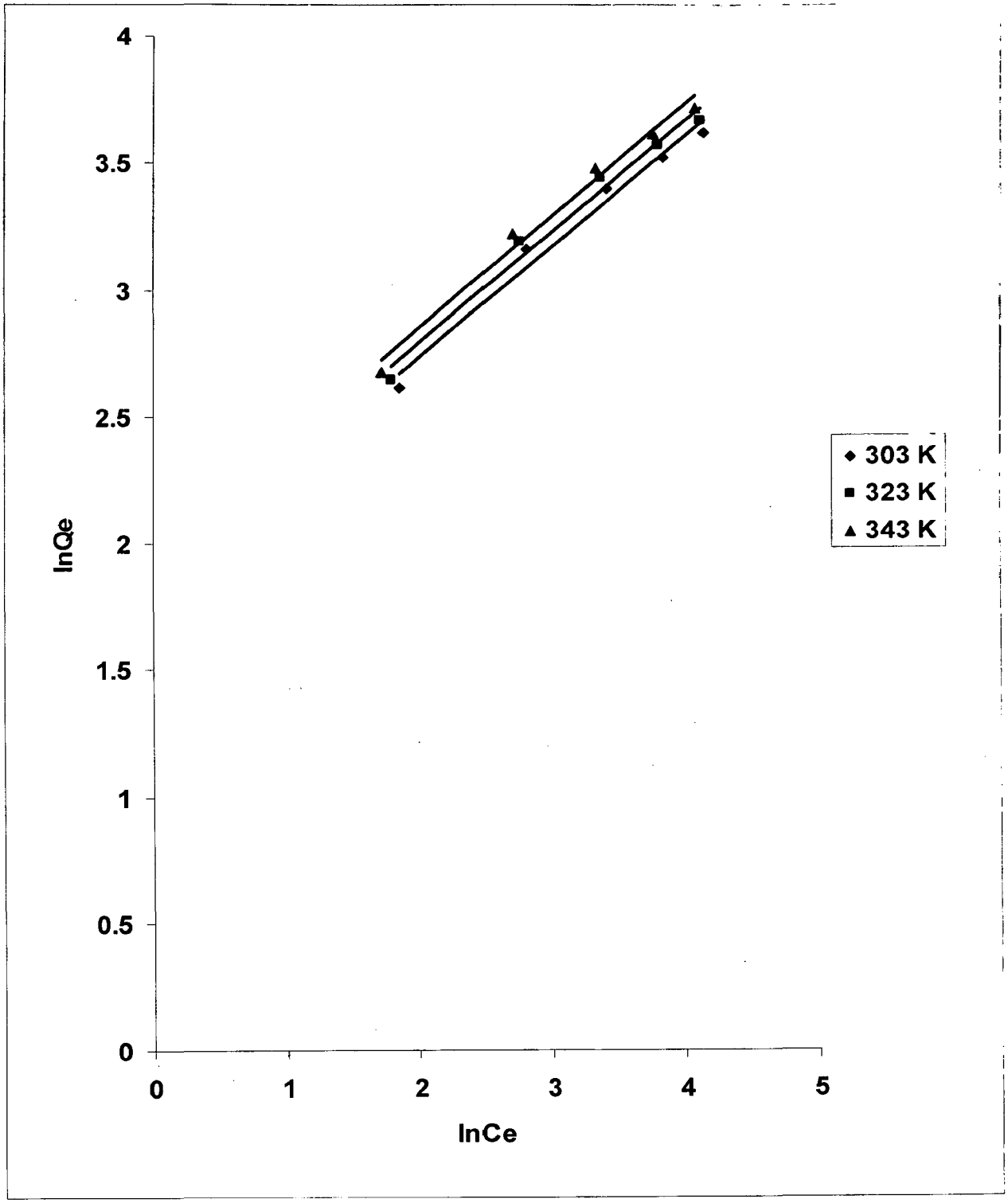


**Fig. B - 31: Freundlich isotherm plots for the removal of Pb(II) for CJAC**

(t=4 h, dose = 1 g/l, pH=5, $C_0$ = 20, 40,60,80 and 100 mg/l).

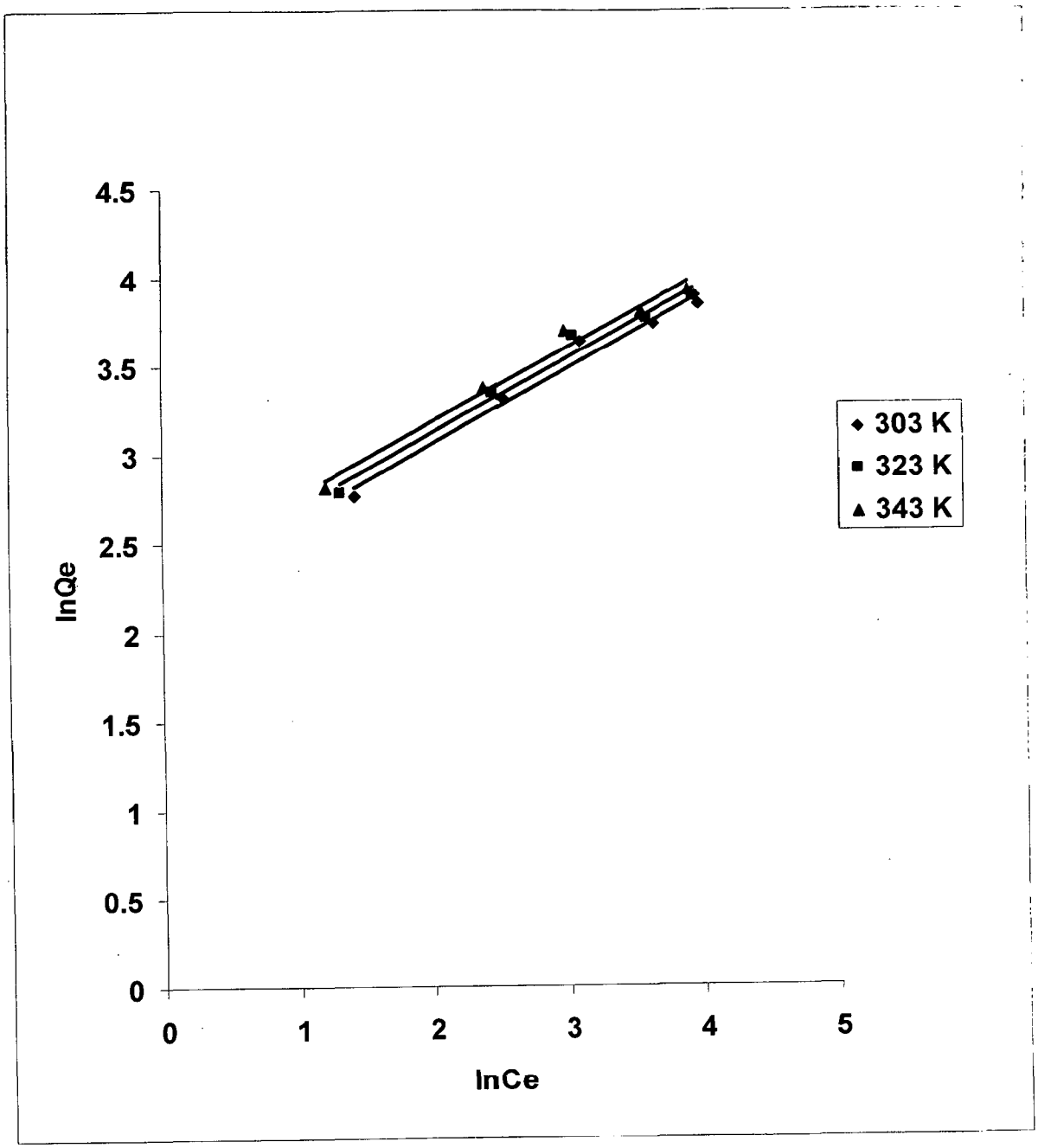


**Fig. B - 32: Freundlich isotherm plots for the removal of Pb(II) for CAC**

(t=4 h, dose = 1 g/l, pH=4.2, $C_0$ = 20, 40,60,80 and 100 mg/l).

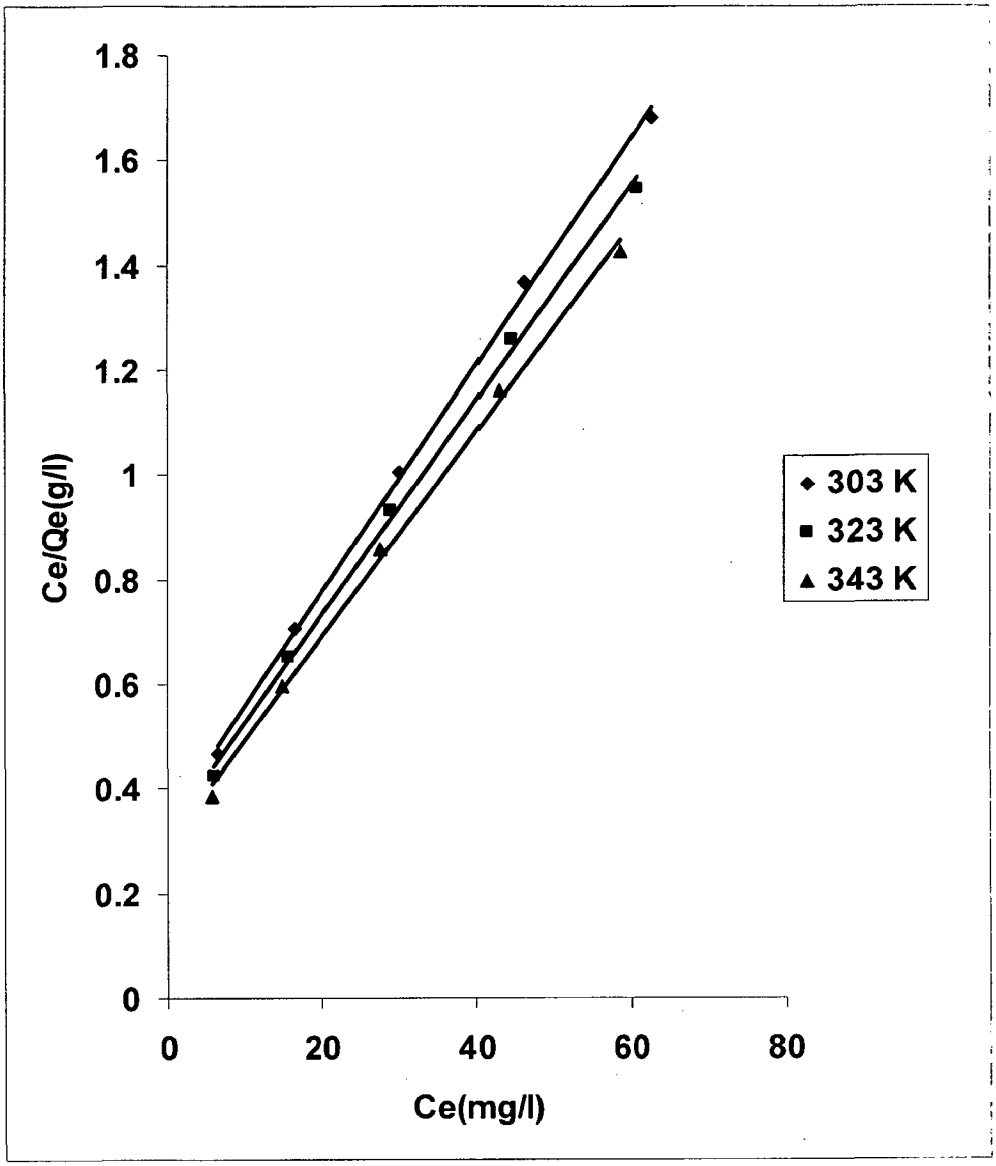


**Fig. B - 33: Langmuir isotherm plots for the removal of Pb(II) for CJAC**

(t=4 h, dose = 1 g/l, pH=5, $C_0$ = 20, 40,60,80 and 100 mg/l).

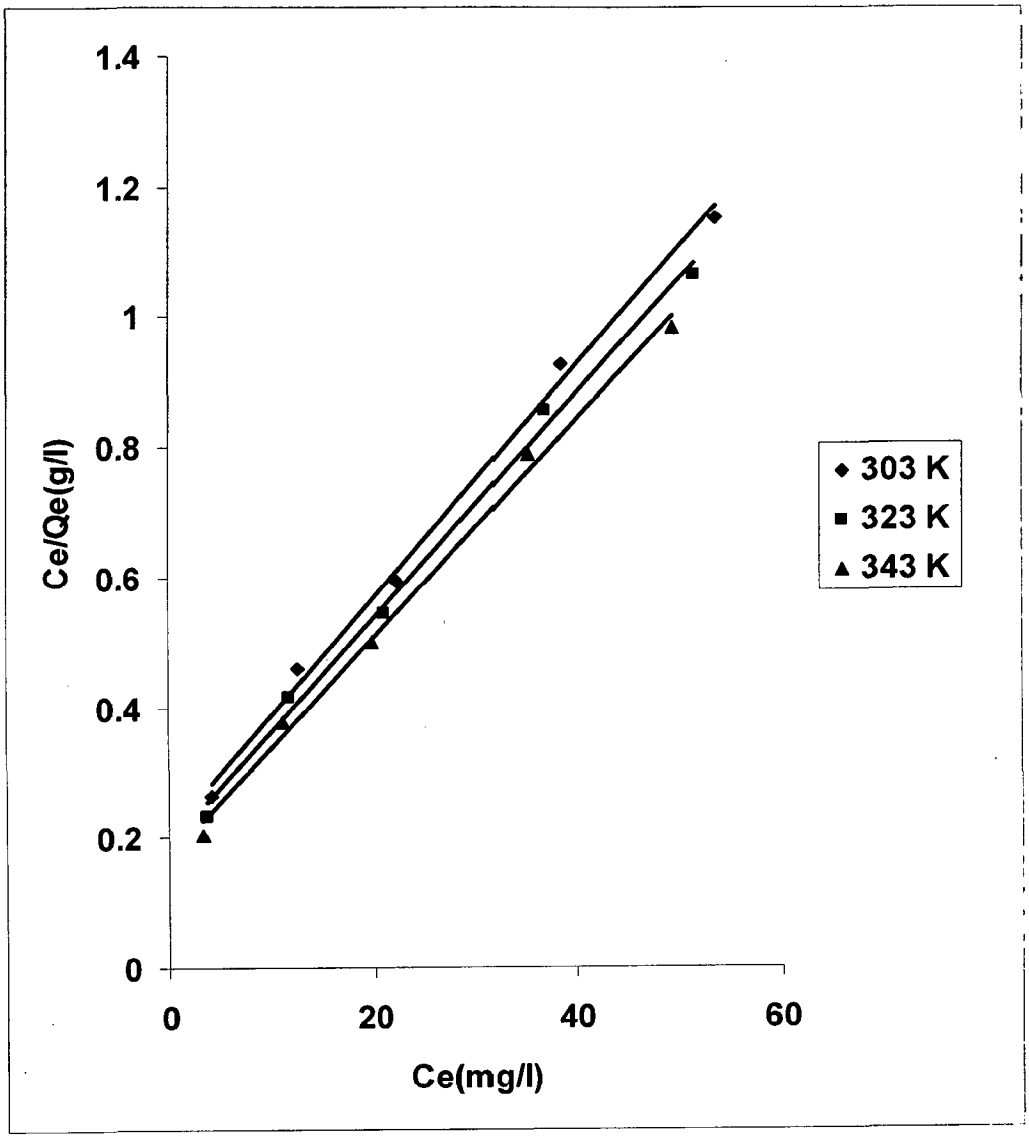


**Fig. B - 34: Langmuir isotherm plots for the removal of Pb(II) for CAC**

(t=4 h, dose = 1 g/l, pH=4.2, $C_0$ = 20, 40,60,80 and 100 mg/l).

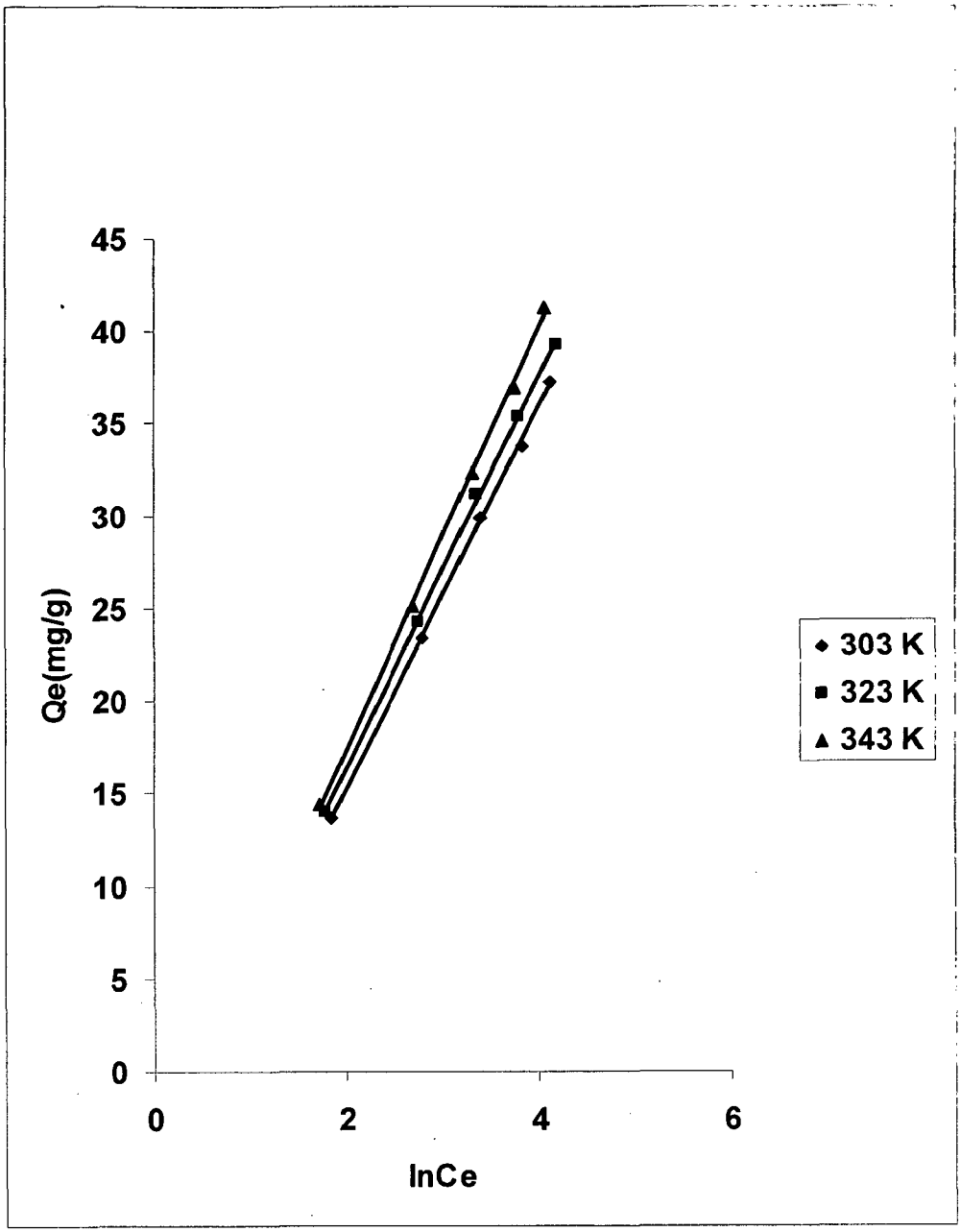


**Fig. B - 35: Temkin isotherm plots for the removal of Pb(II) for CJAC**

(t=4 h, dose = 1 g/l, pH=5, $C_0$ = 20, 40,60,80 and 100 mg/l).

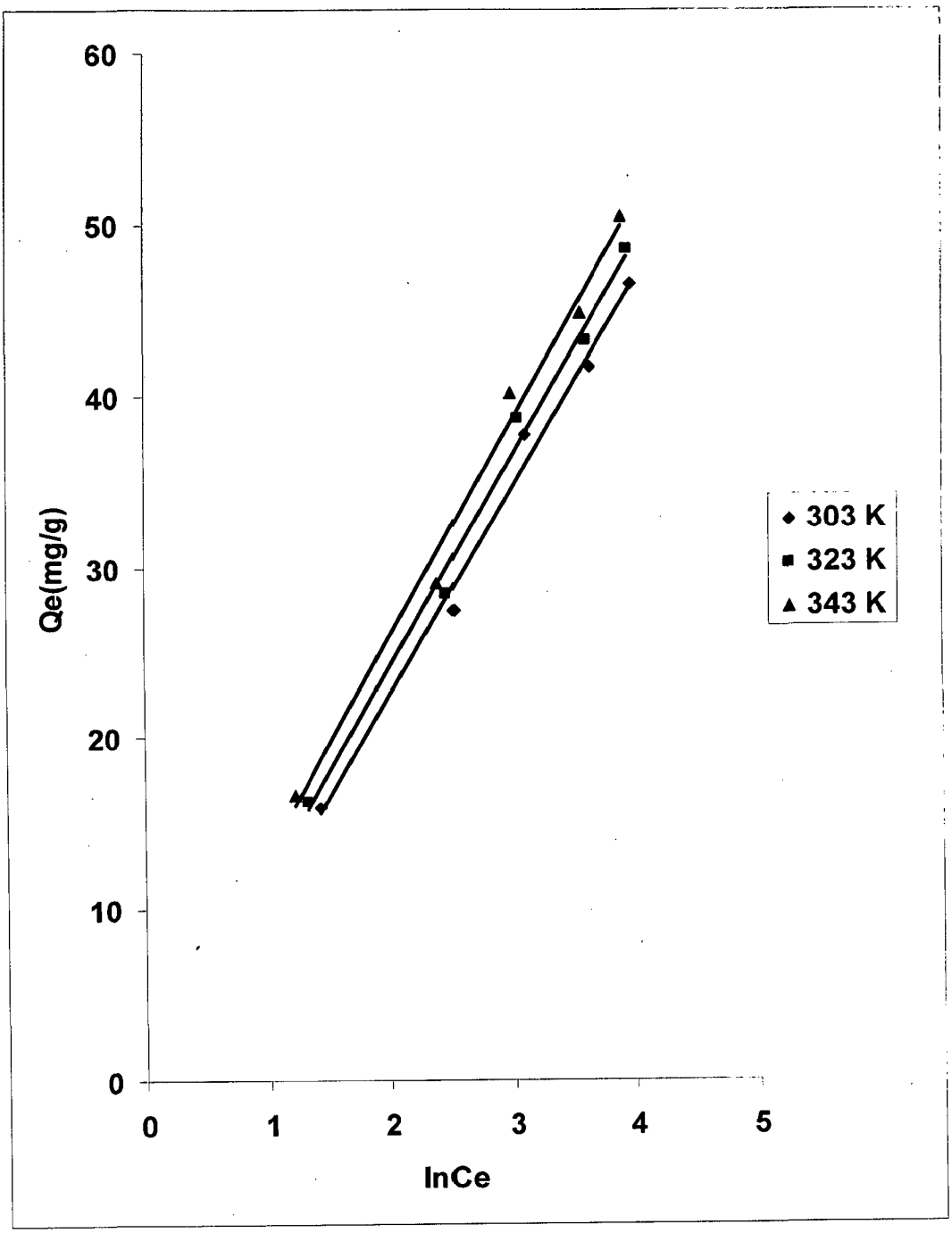


**Fig. B - 36: Temkin isotherm plots for the removal of Pb(II) for CAC**

(t=4 h, dose = 1 g/l, pH=4.2, $C_0$ = 20, 40,60,80 and 100 mg/l).

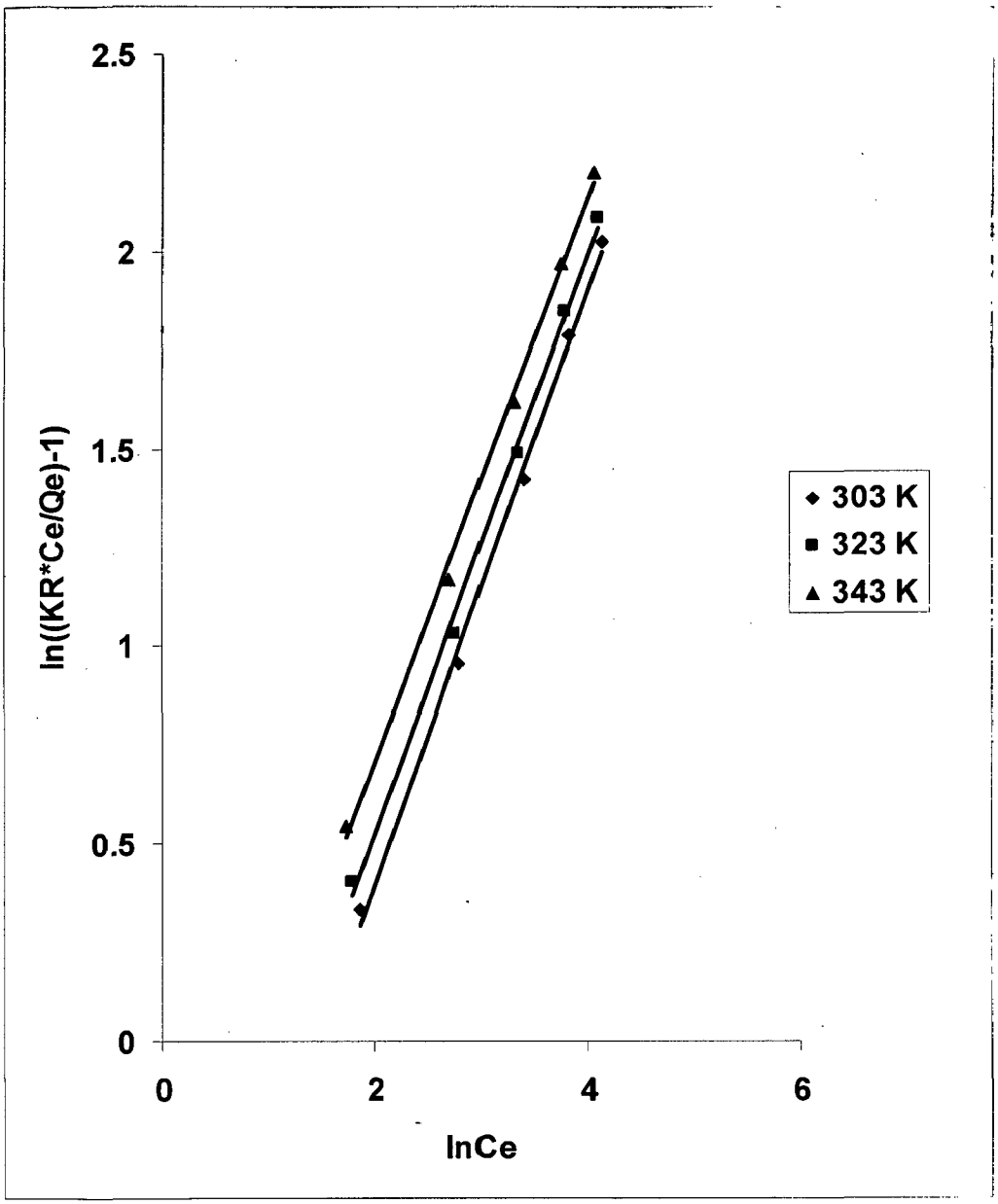


**Fig. B - 37: Redlich-Peterson isotherm plots for the removal of Pb(II) for CJAC**

(t=4 h, dose = 1 g/l, pH=5, $C_0$ = 20, 40,60,80 and 100 mg/l).

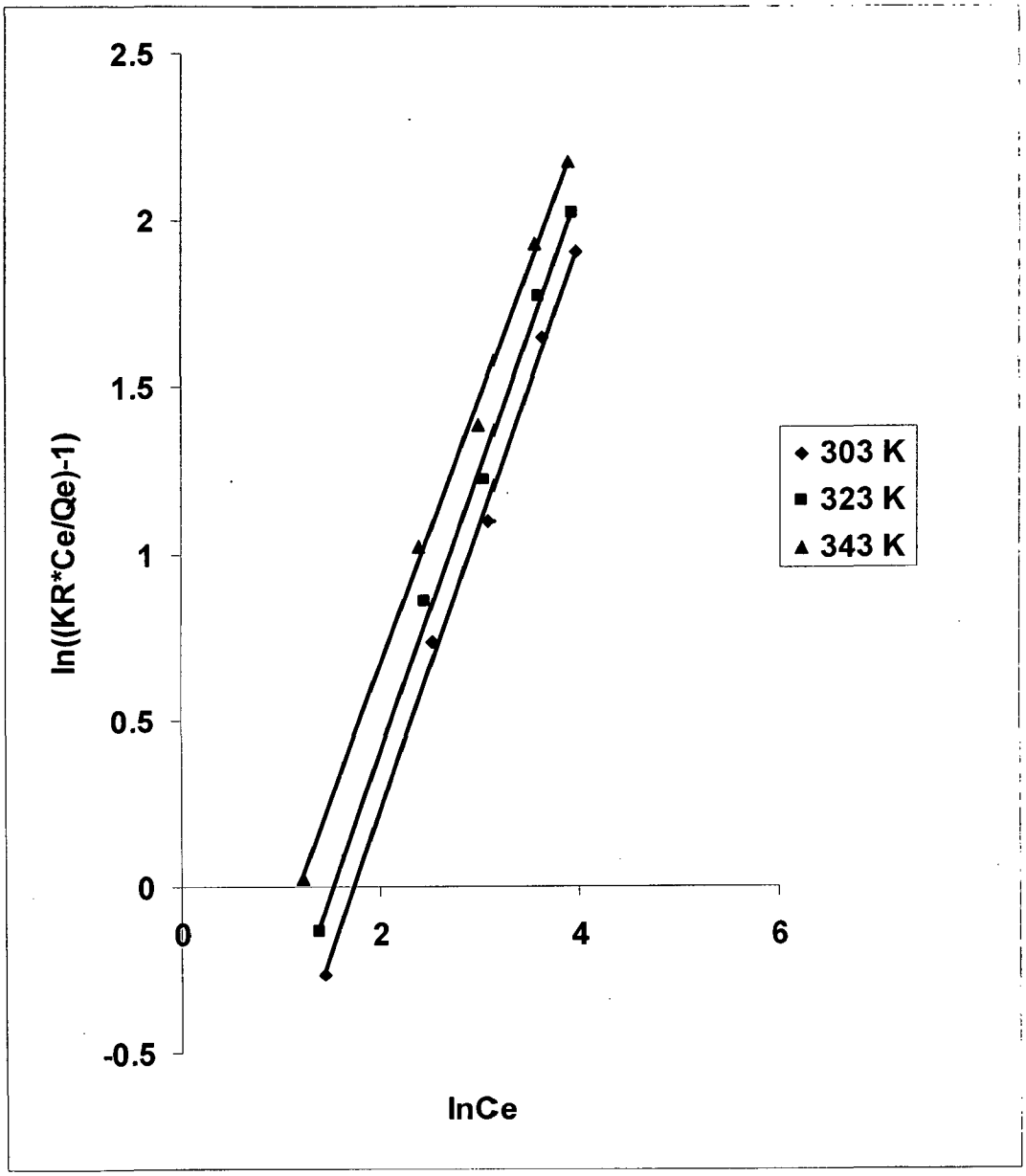


**Fig. B - 38: Redlich-Peterson isotherm plots for the removal of Pb(II) for CAC**

(t=4 h, dose = 1 g/l, pH=4.2, $C_0$ = 20, 40,60,80 and 100 mg/l).

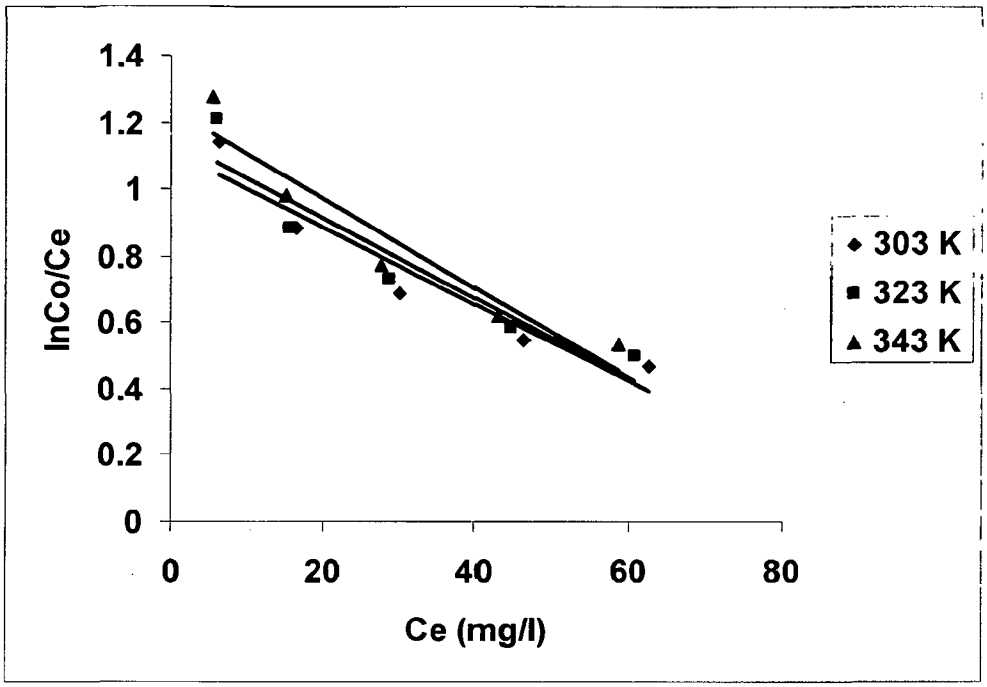


**Fig. B - 39: Thermodynamic equilibrium constant values at different temperatures for CJAC**
(t=4 h, dose = 1 g/l, pH=5).

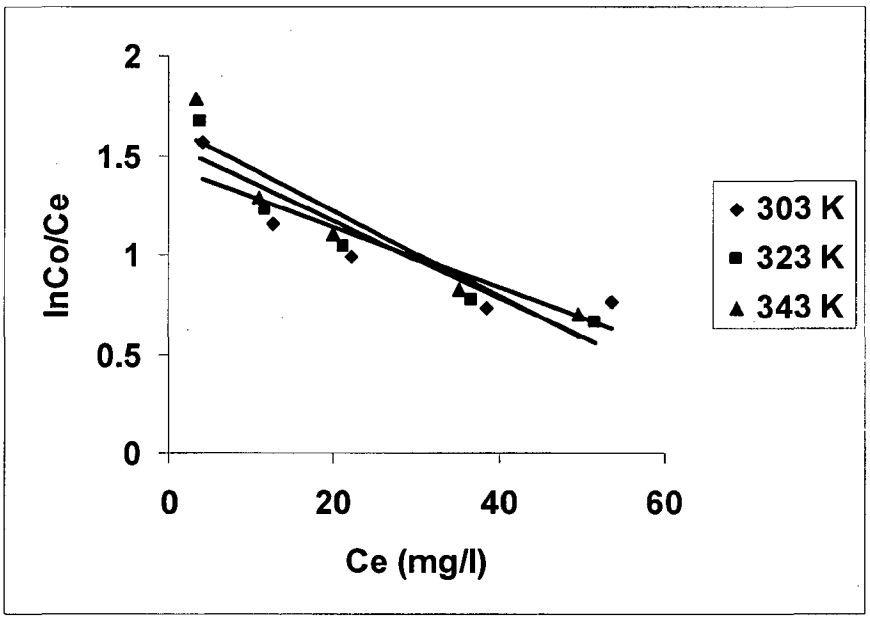


**Fig. B - 40: Thermodynamic equilibrium constant values at different temperatures for CAC**
(t=4 h, dose = 1 g/l, pH=4.2).

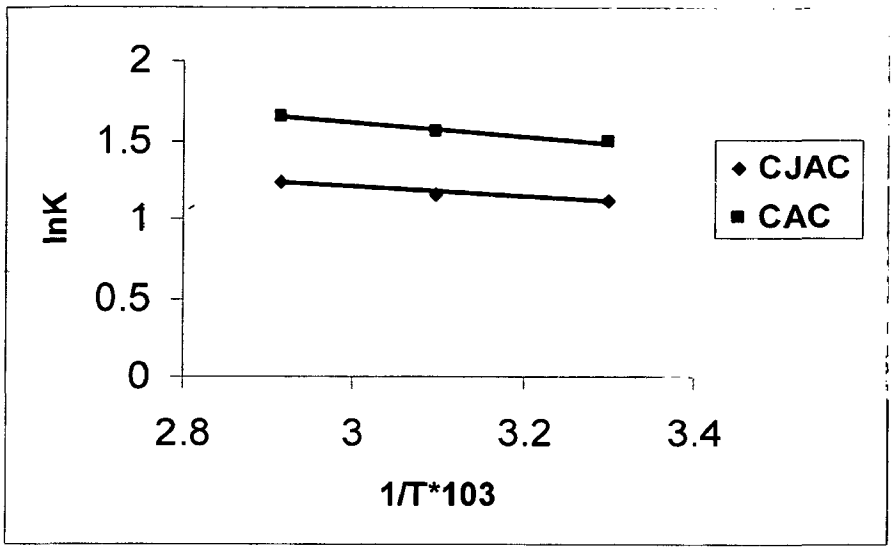


**Fig. B- 41: Vant Hoff's plot**

# APPENDIX – C

**Table C - 1: Characteristics of Coconut Jute Activated Carbon**

| Proximate Analysis | | Physical Properties |
|---|---|---|
| Moisture Percentage | 0.188 | Bulk density ($Kg/m^3$) |
| Ash Percentage | 0.032 | 318.90 |
| Volatile matter Percentage | 0.209 | |
| Fixed carbon Percentage | 0.571 | |

**Table C - 2: Characteristics of Commercial Activated Carbon**

| Proximate Analysis | | Physical Properties |
|---|---|---|
| Moisture Percentage | 0.082 | Bulk density ($Kg/m^3$) |
| Ash Percentage | 0.164 | 268.70 |
| Volatile matter Percentage | 0.043 | |
| Fixed carbon Percentage | 0.711 | |

**Kinetic parameters for the removal of Pb(II) from waste water by CJAC ( $pH_0$ = 5, T = 303 K, $C_0$ = 20, 40,60,80 and 100 mg/l, dose = 1 g/l) and CAC ($pH_0$=4.2,T=303 K, $C_0$= 20,40,60,80 and 100 mg/l, dose = 1 mg/l).**

**Table C - 3: Pseudo-first-order model**

| Pseudo-first-order model | | | | | |
|---|---|---|---|---|---|
| CJAC | Initial Concentration (mg/l) | $k_f$ ($min^{-1}$) | $q_e$ (mg/g) | | $R^2$ |
| | | | $q_e$ (Cal) | $q_e$ (Exp) | |
| | 20 | 0.0258 | 8.8145 | 13.6250 | 0.9844 |
| | 40 | 0.0233 | 11.8522 | 23.4500 | 0.8759 |
| | 60 | 0.0205 | 12.0642 | 29.9000 | 0.7571 |
| | 80 | 0.0179 | 16.1622 | 33.8000 | 0.8201 |
| | 100 | 0.0168 | 21.7220 | 37.2500 | 0.8864 |
| CAC | 20 | 0.0205 | 11.5931 | 15.8320 | 0.8892 |
| | 40 | 0.0235 | 12.2885 | 27.4300 | 0.8808 |
| | 60 | 0.0230 | 13.6500 | 37.6500 | 0.7917 |
| | 80 | 0.0237 | 19.1778 | 41.5600 | 0.8874 |
| | 100 | 0.0196 | 21.5179 | 46.4500 | 0.9103 |

**Table C - 4 : Pseudo-second order model**

| Adsorbent | Conc(mg/l) | $q_{e,exp}$(mg/g) | $q_{e,cal}$(mg/g) | h(mg/g.min) | $k_s$(g/mg.min) | $R^2$ |
|---|---|---|---|---|---|---|
| CJAC | | | | | | |
| | 20 | 13.625 | 14.6627 | 1.0081 | 0.0047 | 0.9983 |
| | 40 | 23.45 | 26.1780 | 1.3428 | 0.0019 | 0.9843 |
| | 60 | 29.9 | 33.5570 | 1.6377 | 0.0014 | 0.9773 |
| | 80 | 33.8 | 37.3734 | 1.8241 | 0.0013 | 0.9818 |
| | 100 | 37.25 | 40.9836 | 1.7504 | 0.0010 | 0.9860 |
| CAC | | | | | | |
| | 20 | 15.832 | 16.5837 | 0.9199 | 0.0033 | 0.9910 |
| | 40 | 27.43 | 29.4118 | 2.2717 | 0.0026 | 0.9943 |
| | 60 | 37.65 | 40.9836 | 2.8281 | 0.0017 | 0.9885 |
| | 80 | 41.56 | 44.2478 | 3.5373 | 0.0018 | 0.9942 |
| | 100 | 46.45 | 49.0196 | 3.9385 | 0.0016 | 0.9974 |

**Table C - 5 : Weber-Morris Intra-particle diffusion model**

| Adsorbent | Conc (mg/l) | $k_{id,I}$(mg/g .$min^{1/2}$) | C,I (mg/g) | $R^2$,I | $k_{id}$,II(mg/g .$min^{1/2}$) | C,II (mg/g) | $R^2$,II |
|---|---|---|---|---|---|---|---|
| **CJAC** | | | | | | | |
| | 20 | 1.8269 | 0.1989 | 0.8759 | 0.2452 | 10.0880 | 0.8849 |
| | 40 | 5.5486 | -11.3840 | 0.8529 | 0.2111 | 20.2630 | 0.9760 |
| | 60 | 7.8934 | -18.0320 | 0.8304 | 0.2470 | 26.1350 | 0.9940 |
| | 80 | 7.4974 | -14.8340 | 0.8073 | 0.3694 | 28.0030 | 0.9811 |
| | 100 | 8.4642 | -18.2760 | 0.9594 | 0.6914 | 26.5210 | 0.9377 |
| **CAC** | | | | | | | |
| | 20 | 1.9894 | 0.2805 | 0.9970 | 0.5570 | 7.5790 | 0.9493 |
| | 40 | 5.3995 | -6.7319 | 0.8800 | 0.2061 | 24.284 | 0.9288 |
| | 60 | 8.6167 | -15.0390 | 0.8328 | 0.2018 | 34.6040 | 0.9447 |
| | 80 | 7.5004 | -6.8208 | 0.8108 | 0.3627 | 36.0630 | 0.9279 |
| | 100 | 8.9857 | -10.3220 | 0.9844 | 0.6259 | 36.9800 | 0.9733 |

**Table C - 6: Bangham's model**

| Adsorbent | Conc (mg/l) | $k_r$(mg/g.min) | 1/m | $R^2$ |
|---|---|---|---|---|
| **CJAC** | | | | |
| | 20 | 3.9700 | 0.2419 | 0.8844 |
| | 40 | 4.3924 | 0.3371 | 0.7423 |
| | 60 | 5.2264 | 0.3523 | 0.7084 |
| | 80 | 6.0940 | 0.3415 | 0.7532 |
| | 100 | 5.5706 | 0.3763 | 0.7811 |
| **CAC** | | | | |
| | 20 | 4.0973 | 0.2557 | 0.9345 |
| | 40 | 7.5910 | 0.2577 | 0.7605 |
| | 60 | 9.1432 | 0.2863 | 0.7166 |
| | 80 | 12.3481 | 0.2420 | 0.7621 |
| | 100 | 13.2404 | 0.2494 | 0.7824 |

**Isotherm parameters for the removal of Pb(II) from waste water by CJAC ( $pH_0$ = 5, T = 303 K, 323 K, 343 K ,dose = 1 g/l) and CAC ($pH_0$=4.2,T=303 K,323 K ,343 K, dose = 1 mg/l).**

**Table C - 7: Langmuir Constants (CJAC)**

| Adsorbent | Constant | T=303 K | T=323 K | T=343 K |
|---|---|---|---|---|
| CJAC | | | | |
| | $K_L$(l/mg) | 0.0631 | 0.0641 | 0.0656 |
| | $q_m$(mg/g) | 46.0829 | 48.5437 | 51.0204 |
| | $R_L$ | 0.4421 | 0.4382 | 0.4395 |
| | $R^2$(linear) | 0.9988 | 0.9981 | 0.9974 |
| | $R^2$(non-linear) | 0.9994 | 0.9991 | 0.9987 |

**Table C - 8: Langmuir Constants (CAC)**

| Adsorbent | Constant | T=303 K | T=323 K | T=343 K |
|---|---|---|---|---|
| CAC | | | | |
| | $K_L$(l/mg) | 0.0806 | 0.0926 | 0.0989 |
| | $q_m$(mg/g) | 55.5555 | 57.4713 | 59.5238 |
| | $R_L$ | 0.3655 | 0.3506 | 0.3358 |
| | $R^2$(linear) | 0.9957 | 0.9953 | 0.9943 |
| | $R^2$(non-linear) | 0.9978 | 0.9976 | 0.9972 |

**Table C - 9: Freundlich Constants (CJAC)**

| Adsorbent | Constant | T=303 K | T=323 K | T=343 K |
|---|---|---|---|---|
| CJAC | | | | |
| | $K_F((mg/g)/(mg/l)^{1/n})$ | 6.6.3949 | 6.7087 | 7.0696 |
| | n | 2.2826 | 2.2635 | 2.2527 |
| | 1/n | 0.4381 | 0.4418 | 0.4439 |
| | $R^2$(linear) | 0.9794 | 0.9822 | 0.9846 |
| | $R^2$(non-linear) | 0.9896 | 0.9911 | 0.9823 |

**Table C - 10: Freundlich Constants (CAC)**

| Adsorbent | Constant | T=303 K | T=323 K | T=343 K |
|---|---|---|---|---|
| CAC | | | | |
| | $K_F((mg/g)/(mg/l)^{1/n})$ | 9.0739 | 9.7406 | 10.4793 |
| | n | 2.3552 | 2.3769 | 2.4067 |
| | 1/n | 0.4246 | 0.4207 | 0.4155 |
| | $R^2$(linear) | 0.9757 | 0.9782 | 0.9810 |
| | $R^2$(non-linear) | 0.9878 | 0.9892 | 0.9904 |

**Table C-11: Tempkin Constants ( CJAC)**

| Adsorbent | Constant | 303 K | 323 K | 343 K |
|---|---|---|---|---|
| CJAC | | | | |
| | B | 10.2950 | 10.8190 | 9.1554 |
| | $K_T$(l/mg) | 0.5911 | 0.6065 | 1.3093 |
| | $R^2$(linear) | 0.9996 | 0.9996 | 0.9806 |
| | $R^2$(non-linear) | 0.9998 | 0.9998 | 0.9995 |

**Table C - 12: Tempkin Constants ( CAC)**

| Adsorbent | Constant | 303 K | 323 K | 343 K |
|---|---|---|---|---|
| CAC | | | | |
| | B | 12.0660 | 12.3550 | 12.6140 |
| | $K_T$(l/mg) | 0.8702 | 0.9516 | 1.0565 |
| | $R^2$(linear) | 0.9897 | 0.9919 | 0.9897 |
| | $R^2$(non-linear) | 0.9948 | 0.9949 | 0.9948 |

**Table C - 13: Redlich-Peterson Constants (CJAC)**

| Adsorbent | Constant | 303 K | 323 K | 343 K |
|---|---|---|---|---|
| CJAC | | | | |
| | $a_R$(l/mg) | 0.3363 | 0.3864 | 0.4951 |
| | $K_R$(l/mg) | 5.1100 | 5.8500 | 7.0500 |
| | β | 0.7469 | 0.7338 | 0.7073 |
| | $R^2$(linear) | 0.9969 | 0.9976 | 0.9974 |
| | $R^2$(non-linear) | 0.9985 | 0.9986 | 0.9987 |

**Table C - 14: Redlich-Peterson Constants (CAC)**

| Adsorbent | Constant | 303 K | 323 K | 343 K |
|---|---|---|---|---|
| CAC | | | | |
| | $a_R$(l/mg) | 0.2317 | 0.2949 | 0.3924 |
| | $K_R$(l/mg) | 6.7200 | 8.0600 | 10.0010 |
| | β | 0.8463 | 0.8227 | 0.7969 |
| | $R^2$(linear) | 0.9970 | 0.9972 | 0.9973 |
| | $R^2$(non-linear) | 0.9985 | 0.9986 | 0.9986 |

**Values of five different error analyses of isotherm models for adsorption of Pb(II).**

**Table C - 15: Error Analysis for CJAC**

| 303 K | | | | | |
|---|---|---|---|---|---|
| | **SSE** | **HYBRID** | **MPSD** | **ARE** | **SAE** |
| **Freundlich** | 9.3658 | -0.0931 | 4.3414 | 4.8132 | 6.2803 |
| **Langmuir** | 0.7292 | 0.1912 | 1.4015 | 1.4152 | 1.7562 |
| **R-P** | 2.3533 | 0.0019 | 2.0909 | 2.3818 | 3.2286 |
| **Temkin** | 0.1351 | -0.0114 | 0.4476 | 0.4220 | 0.6225 |
| **323 K** | | | | | |
| | **SSE** | **HYBRID** | **MPSD** | **ARE** | **SAE** |
| **Freundlich** | 9.0917 | -0.0863 | 4.1163 | 4.5725 | 6.2111 |
| **Langmuir** | 1.2496 | 0.3146 | 1.8706 | 1.8555 | 2.3367 |
| **R-P** | 2.0861 | -0.0731 | 1.9505 | 2.2397 | 3.0963 |
| **Temkin** | 0.1791 | 0.0226 | 0.5372 | 0.6196 | 0.8818 |
| **343 K** | | | | | |
| | **SSE** | **HYBRID** | **MPSD** | **ARE** | **SAE** |
| **Freundlich** | 8.7638 | -0.0643 | 3.9028 | 4.3385 | 6.1191 |
| **Langmuir** | 1.9948 | 0.3623 | 2.3520 | 2.3252 | 2.9944 |
| **R-P** | 2.3975 | 0.0003 | 1.9780 | 2.2538 | 3.2836 |
| **Temkin** | 21.56 | -4.6832 | 10.5326 | 8.1067 | 8.1205 |

**Table C - 16: Error Analysis for CAC**

| 303 K | | | | | |
|---|---|---|---|---|---|
| | **SSE** | **HYBRID** | **MPSD** | **ARE** | **SAE** |
| **Freundlich** | 25.7860 | -0.8266 | 5.9184 | 6.2935 | 10.0320 |
| **Langmuir** | 6.4960 | 0.3502 | 3.6970 | 3.9019 | 5.5365 |
| **R-P** | 5.7629 | -0.0439 | 2.5531 | 2.3235 | 4.0381 |
| **Temkin** | 6.1671 | -0.0334 | 2.8840 | 2.8090 | 4.4519 |
| **323 K** | | | | | |
| | **SSE** | **HYBRID** | **MPSD** | **ARE** | **SAE** |
| **Freundlich** | 21.6030 | -0.2149 | 4.6092 | 5.0066 | 8.9456 |
| **Langmuir** | 16.8420 | -1.9063 | 5.0109 | 5.1100 | 7.8228 |
| **R-P** | 4.7483 | -0.1060 | 2.2643 | 2.1075 | 3.7593 |
| **Temkin** | 5.3396 | 0.0304 | 2.7915 | 2.8859 | 4.5415 |
| **343 K** | | | | | |
| | **SSE** | **HYBRID** | **MPSD** | **ARE** | **SAE** |
| **Freundlich** | 23.0630 | -0.1081 | 4.5444 | 4.7888 | 8.9804 |
| **Langmuir** | 10.4310 | 0.5600 | 4.9820 | 4.7971 | 6.7575 |
| **R-P** | 6.6281 | -0.0458 | 2.5783 | 2.3453 | 4.3337 |
| **Temkin** | 7.4915 | 0.0532 | 3.3059 | 3.4337 | 5.4884 |

**Table C - 17: Thermodynamic parameters for adsorption of Pb(II) by CJAC and CAC**

| Adsorbent | $-\Delta G^0$ (kJ/mol K) | | | $\Delta H^0$ (kJ/mol) | $\Delta S^0$ (J/mol K) |
|---|---|---|---|---|---|
| | 303 K | 323 K | 343K | | |
| CJAC | 2.8209 | 3.0971 | 3.5327 | 2.5441 | 17.6350 |
| CAC | 3.754 | 4.1949 | 3.4611 | 3.4611 | 23.7780 |