REMOVAL OF 2-4 DICHLOROPHENOL USING VARIOUS ADSORBENTS

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

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CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in the dissertation entitled "**REMOVAL OF 2-4DICHLOROPHENOL USING VARIOUS ADSORBENTS** " 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: 30June, 2008.
Place: Roorkee.

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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.

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This is consummated and symbolized not only my efforts but also guidance and vital inputs of different people at crucial junctures in the course of this undertaking to whom I would like to express my gratitude.

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ABSTRACT

2,4 dichlorophenol as one type of the most hazardous materials they are, mutagenic and resistant to biodegradation, and thus have to be decomposed before discharging into receiving waters, in order to avoid the biomagnified toxicity to aquatic flora and fauna through various food chains. Many efforts have been made for the physico-chemical and/or biological treatments of 2,4dichlorophenol rich waste waters

Chlorophenols are organic chemicals formed from phenol by substitution in the phenol ring with one or more atoms of chlorine Among all the dichlorophenols $C_6H_4Cl_2O$ it is 2,4 dichlorophenol that is produced in greater quandity.2,4 dichlorophenols used in the manufacture of 2,4 dichlorophenoxy propionic acid (2,4DP), 2,4 dichlorophenoxy acetic acid (2,4D). Industrially 2,4dicholorophenol is obtained by chlorinating phenol, p-chlorophenol, o-chlorophenol or mixture of these compounds in cast iron reactors. The chlorinating agent may be chlorine or surfuryl chloride in combination with Lewis acid

There are several methods for removing toxic 2,4dichlorophenols from aqueous solutions, such as adsorption, membrane filtration, solvent extraction, chemical oxidation , biological teratmnet.Removal of 2,4dichlorophenol 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, agricultural waste

In the present study laboratory scale experiments have been carried out using the Coconut shell activated carbon (CSAC) and Commercial activated carbon (CAC), Bagasse fly ash (BFA), Rice husk ash (RHA) and mixed activated carbon (MAC) as adsorbents for the removal of 2,4dichlorophenol. The present study has been undertaken with the objective to investigate the suitability of BFA, RHA, CSAC and MAC as a low cost adsorbent for the removal of 2,4dichlorophenols 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 2,4dichlorophenols on CSAC and CAC,BFA, RHA and MAC, follows the Pseudo- second order kinetics. Langmuir isotherm best-fitted the isotherm data for 2,4dichlorophenol adsorption on CSAC, CAC, MAC, RHA and BFA at almost all temperatures. However, the error analysis values and the non-linear correlation coefficients, R^2, are comparable for Langmuir, Temkin and Freundlich isotherm. Adsorption increases with increase in temperature for all the adsorbents, showing the endothermic nature of adsorption. From thermodynamic study ΔG^0, ΔH^0 and ΔS^0 values are also calculated for CSAC,CAC, MAC, RHA and BFA adsorbents The order of removal of 2,4dichlorophenol CAC>BFA.>RHA>MAC>CSAC. Due to less surface area and the least number pores of coconut shell activated carbon (CSAC) the amount of removal is low among all the adsorbent s apart from that all the adsorbent s proved to be effective CAC was adjudged to be the best adsorbent with 93% removal of 2,4 dcp at pH 4 and 30^{0}C temperature and 8 g/l adsorbent dose. This was followed by BFA(86%) MAC(83.4%) and RHA (83%) at nearly similar conditions

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CHAPTER-1
INTRODUCTION

The uses of commercial dichlorophenols, These compounds are biocides, a property that accounts for many of their uses. Chlorophenols, particularly tetra-, and to a lesser extent, trichlorophenols, have been used as bactericides, algicides, molluscicides, acaricides, fungicities, and mould inhibitors, and for less specific uses, such as general antiseptics and disinfectants. Dichlorophenols are also used as intermediates in the production of certain herbicides, dyes, and drugs. Large quantities of higher chlorophenols are used in wood preservation . most chlorophenol-treated wood was preserved by pressure treatment with pentachlorophenol. Substantial amounts of the sodium salts of T_4CP and lesser amounts of $NaT_3CP$and NaPCP have been used tò protect fresh-cut logs and lumber. These compounds, which are readily soluble in water, are used to surface-treat lumber by dipping or spraying to protect against sapstain or mould. Some plywood mills also use T_4CP to reduce decay and mould, and insect attack. The preservative is usually added to the glue dichlorophenol-treatment was widely used in agriculture, to prevent wood decay in buildings, food containers, and horticultural timbers. Large amounts of 2,4-DCP are consumed in the manufacture of the phenoxy herbicide 2,4-D , and also as a precursor for the production of the pesticides Sesone, Nitrofen, Nemacide, an Genite-EM-923.

1.1 CHLOROPHENOLS

Chlorophenols (CPs) are organic chemicals formed from phenol by substitution in the phenol ring with one or more atoms of chlorine. Nineteen congeners are possible, ranging from monochlorophenols to the fully chlorinated pentachlorophenol (PCP). Chlorophenols,particularly trichlorophenols (T_3CP), tetrachloro-phenols (T_4CP) and PCP,are also available as sodium or potassium salts. Chlorophenols are solids at room temperature, except for 2-MCP,which is a liquid. The aqueous solubility of chlorophenols is low, but the sodium or potassium salts of chlorophenols are up to four more soluble in water than the parent compounds. The acidity of chlorophenols increases as the number of chlorine substitutions increases.

A large number of sampling and analytical methods have been developed for the determination of chlorophenols in different media. Sensitive methods, such as gas chromatography, high-performance liquid chromatography, and mass spectrometry are increasingly used.

The compounds 2-MCP, 4-MCP, 2,4-DCP, 2,3,4-T_3CP, 2,4,6-T_3CP, 2,3,4,6-T_4CP, and PCP have been made by direct stepwise chlorination of phenol or lower chlorinated phenols at a high temperature; a catalyst is necessary if the last two chlorophenols are being produced. Alternatively, some chlorophenols (2,5-DCP, 3,4-DCP,2,4,5-T_3CP, 2,3,4,5-T_4CP and PCP) can be produced by the alkaline hydrolysis of the appropriate chlorobenzene.

Patterns of losses to the environment appear similar in most industrialized countries. The majority of chlorophenol wastes are released in spills and leaching from treated lumber (PCP, NaPCP, NaT_4CP), and as contaminants or breakdown products of agricultural pesticides (2,4-DCP, 2,4,5-T_3CP). Substantial amounts of wastes (NaT_4CP, NaPCP) are released from sawmills, planer mills, and the incineration of wood wastes. Significant amounts of chlorophenols can be formed and subsequently released into the environment from the chlorine bleaching process in pulp and paper-mills, the chlorination of waste-water and drinking-water, and the incineration of municipal waste. A significant amount of wastes is discharged from manufacturing sites. Losses during storage and transport are negligible. No estimates are available of the quantities of chlorophenols released as a result of the disinfection of waste-waters with chlorine, volatilization, or domestic uses of products containing these compounds.

2,4dichlorophenols are mainly produced in chemical industries, such as petroleum refineries, plastics, pharmaceuticals, pesticide, and wood preservation. As one type of the most hazardous materials they are carcinogenic, mutagenic and resistant to biodegradation, and thus have to be decomposed before discharging into receiving waters, in order to avoid the biomagnified toxicity to aquatic flora and fauna through various food chains. Many efforts have been made for the physicochemical and/or biological treatments of chlorophenol-rich waste waters. For instance, they could be removed effectively through adsorption process by using a variety of adsorbents. Among various adsorbents, activated carbon is most commonly used in wastewater treatment, attributed to its vast surface area and great affinity for organics

EFFECTS ON HUMAN HEALTH

Its toxicity may result from a general inhibition of enzyme activity. It has been found to bind strongly to mitochondrial proteins and to exert direct inhibition on the electron transport system in mitochondrial respiration Free 2,4-DCP did not accumulate in tissues (the quantities of free compound 60 minutes after the injection was only about 1% of the injected amount). It was rapidly metabolised by conjugation to its glucuronate conjugates or ring methoxylation (formation of dichloromethoxyphenol). Glucuronide conjugates were the major metabolites found in kidneys, liver, brain and plasma; no glucuronide conjugates were detected in fat.

Acute toxicology

Acute oral toxicity

The L.D. 50 values obtained were 1276 mg/kg . for males and 1352 mg/kg . for females . All displayed signs of toxicity 10-15 minutes after dosing. Clinical signs were : ataxia, loss of righting reflex, slights tremors, salivation, labored breathing and depression. All death occurred within 6-24 hours after dosing. At necropsy, no gross abnormalities were noted in dead animals nor in survivors.(* test conducted on rats)

The skin irritation tests with 2,4-dichlorophenol reports the substance to be "corrosive" to skin and risk of serious damage to the eyes is expected.

The genetic toxicity is assessed by *in vitro* and *in vivo* studies. *In vitro*, most of the test results were negative. An *in vivo* micronucleus test, an unscheduled DNA synthesis test and two sister chromatid exchange assays were all negative. It is concluded that the material is not genotoxic as the results of the *in vivo* tests are negative.

The carcinogenicity of 2,4-DCP was assessed in 4 different studies which reveals that there is no evidence of carcinogenic activities of 2,4-Dichlorophenol.

1.2 ADSORBENTS

Activated carbons are widely used as an adsorbent for the removal of a wide range of pollutants from various matrices because of their high adsorption capacity, fast adsorption kinetics and ease of regeneration. One of the most important uses of activated carbon is a water treatment process. Several researchers have been reported about the adsorption theory and application of those to the solid phase extraction to remove2,4dichlorophenols from water system . Activated carbons are complex and heterogeneous material with unique adsorptive characteristics mainly influenced by the porous structure, surface area and chemical structure of the surface.

The adsorptive capacity of a given carbon is a function of

(i) porous structure,

(ii) the chemical nature of the surface, and

(iii) the pH of the aqueous solution.

Among all the dichlorophenols $C_6H_4Cl_2O$ it is 2,4 dichlorophenol that is produced in greater quantity. 2,4 dichlorophenol is used in the manufacture of 2,4 dichlorophenoxy propionic acid (2,4DP), 2,4 dichlorophenoxy acetic acid (2,4D). Industrially 2,4dichlorophenolis obtained by chlorinating phenol , p-chlorophenol, o-chlorophenol or mixture of these compounds in cast iron reactors. the chlorinating agent may be chlorine or surfuryl chloride in combination with Lewis acid

The synthesis of 2,4-DCP is made by chlorination of phenol with chlorine gas or sulfuryl chloride. The purification and distillation steps ensure a material of 99% minimum purity

Phenol on chlorinating produce

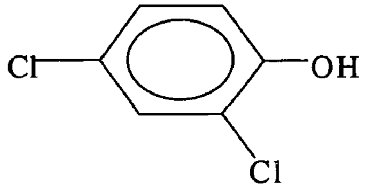
2,4 dichlorophenol - 94%

2,6 dichlorophenol -1.4%

2,4,6 trichlorophenol -1.3%

The remaining is mono chlorophenol around 3.3%

2,4-Dichlorophenol



Chemical name: 2,4-Dichlorophenol (2,4-DCP)

Synonym: 4-Hydroxy-1,3-dichlorobenzene, 2,4-DCP

Molecular formula: $C_6H_4Cl_2O$

Molecular weight: 163.0

Appearance: Colorless Crystals, White or Pale yellow solid

Melting point: 45^0C

Boiling point: 210.0^0C

Specific gravity: 1.383

Vapor pressure: 16 Pa (25^0C),133,000 Pa (53^0C))

Partition coefficient: Log Pow = 3.06 (calculated value)

Biodegradability: Poorly biodegradable (BOD = 0%, 4 weeks) 2)

Solubility: Water 4.5 *g/l* (20^0C)

Organic solvents: Soluble in carbon tetrachloride, ethanol, benzene and ethyl ether1), Soluble in aqueous alkali1)

GENERAL INFORMATION OF SOURCES

The substance 2,4-Dichlorophenol is produced in Europe, Americas, Africa, Asia and Oceania. The production in the (France) was 2000 to 5000 tonnes /year, and the substance is produced at a unique site. Former producer in North America, DOW Agro Sciences, LLC, produce >4500 tonnes/year to < 45000 tons/year for 2,4-DCP and 2,4-Dichlorophenol sodium salt. European production in 1997 was about 18500 tons.

Product is largely an in-process intermediate used primarily as an intermediate for the synthesis of pesticide (2,4-Dichlorophenoxy Acetic Acid (2,4-D)). It has although to be noted that 2,4-DCP can be detected in the environment, together with other products, as a result of the 2,4-D degradation Another source of 2,4-DCP in the environment would be through chlorination of phenol-containing water. Nevertheless, if the 2,4-DCP formation has been demonstrated in laboratory experiments, it has not been established under conditions simulating the natural environment, that 2,4-DCP is a significant product resulting from chlorination of phenol-containing waters

2,4-DCP distribution in the environment should be as follow:

Air:	4.5 %
Water:	37.6 %
Soil:	56.6 %
Sediment:	1.3 %

Environmental Transport, Distribution and Transformation

Dichlorophenols adsorb strongly on acidic soils, and those with a high organic content. Leaching is more significant in basic and mineral soils. Adsorption appears to play an important role in surface waters. Dichlorophenols that are not degraded in the water body are incorporated into the sediments, most likely because they adsorb on sediment particulates. They may persist in sediments for years. Although dichlorophenols are principally water and soil contaminants, some atmospheric movement occurs.

Natural Occurrence

Some dichlorophenols are present in the environment independent of man-made input. Dichlorophenols have been detected in a variety of organisms. 2,4-Dichlorophenol occurs naturally in a *Penicillium* sp., while 2,6-DCP serves as a sex pheromone for several species . A number of related organohalogens are also found in flora and fauna . However, these sources cannot account for the significant amounts of chlorophenols, particularly the higher chlorinated phenols, found in the environment

CHAPTER-2

GENERAL PROCESSES FOR 2,4 DICHLOROPHENOL REMOVAL

Many methods have been developed to remove 2,4dcp from industrial effluents, including, membrane separation, solvent extraction, adsorption, Fenton process and biodegradation

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

Solvent Extraction:

Solvent extraction is accomplished by contacting solute with a solvent, separating the solute 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, non flowing 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.

Membrane Separation:

In membrane separation, spent 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:

1. Membrane separation consistently separates a wide variety of emulsion, surfactant, and chelating chemistries and various mixtures.
2. It requires no specific chemical knowledge.
3. Complex instrumentation is not required.
4. The method does not require constant attention.
5. 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.

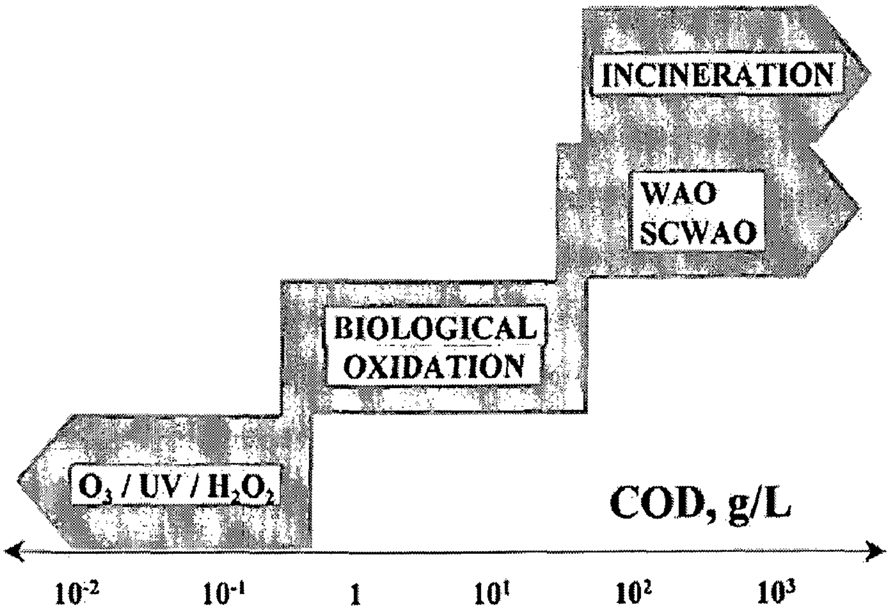
f) Synthetics are not effectively treated by this method.

Biological treatment :

Biological treatment transforms, stabilizes and/or removes 2,4 dichlorophenol 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

Ozone–UV Radiation–HydrogenPeroxide Oxidation Technologies

Processes involving the use of ozone, UV radiation, and hydrogen peroxide, characterized by the generation of short-lived chemical species of high oxidation power, mainly the hydroxyl radical, are classified as advanced oxidation technologies (AOTs). The importance of these processes is due to the high reactivity and redox potential of this free radical that reacts nonselectively with organic matter present in water. These processes present a high degree of flexibility because they can be used individually or in combination depending on the problem to be solved. For instance, for phenols or substances with high UV molar absorption coefficients, ozone or UV radiation can be used alone, respectively, without the need of any additional reagent; such as hydrogen peroxide. Another advantage of these AOTs is that they may be applied under mild experimental conditions



Oxidation process advisable according to COD of water. (WAO, wet air oxidation. SCWAO, supercritical wet air oxidation).

Supercritical Water Oxidation Technology

Supercritical water oxidation (SCWO) is a waste treatment technology that uses supercritical water as a medium for oxidizing organic material. SCWO can also be described as an extension of the subcritical oxidation process, wet air oxidation (WAO) process, or widely known Zimpro process Both processes (SCWO and WAO) involve bringing together organic wastewater, and an oxidant (such as air or oxygen) to elevated temperatures and pressures to bring about chemical oxidations. Generic operational conditions for the two processes are as follows:

WAO: 150–300^{0}C, 10–200 bar

SCWO: >374–675^{0}C, > 220 bar.

Fenton Process

Fenton reagent has been applied to the degradation of a wide range of contaminants, predominantly persistent organic pollutants. The primary benefits of the Fenton reagent are its ability to convert a broad range of pollutants to harmless or biodegradable products, its benign nature (residual reagents do not pose an environmental threat), and the relatively low cost of the reagents. The major drawbacks to utilization of Fenton reagent are interferences from non pollutant species, difficulty in application to the subsurface,

generation of excessive or explosive heat under aggressive conditions, and wasted reagent costs due to inefficient application or inefficient pollutant degradation in the subsurface

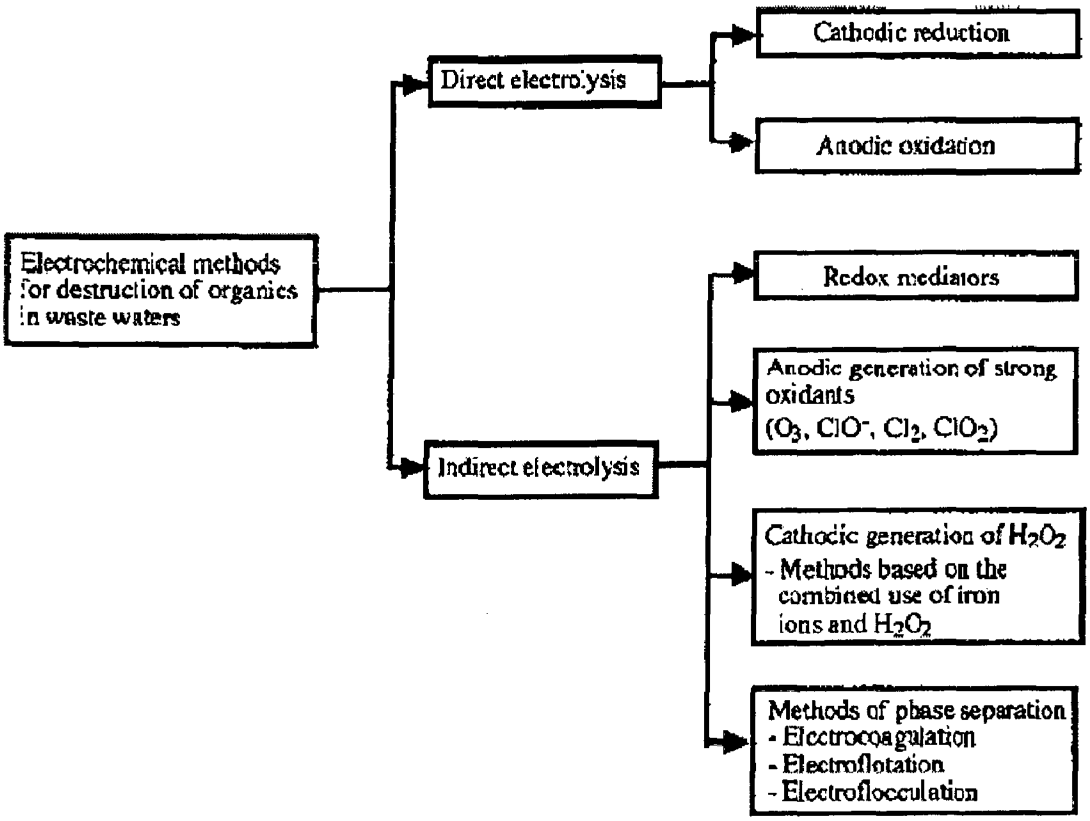
Photo–Fenton

In the presence of light, additional reactions that produce hydroxyl radical or increase the production rate of hydroxyl radical can occur Often called the photo–Fenton system, irradiation of iron-peroxide solutions can result in more effective pollutant degradation than dark Fenton systems.

Electrochemical Methods for Degradation of Organic Pollutants in Aqueous Media

A large variety of electrochemical techniques for the destruction of toxic and organic pollutants for wastewater treatment have been proposed and developed. This process can occur either by a direct electron transfer reaction to (reduction) or from (oxidation) the undesired organic, or by a chemical reaction of the pollutant with previously electro generated species, which remain adsorbed at the electrode surface. Most electrochemical methods are based on indirect (or mediated) electrolysis in which the target pollutant is removed in the solution by active species produced reversibly or irreversibly at the electrode.

Classification of electrochemical methods for the destruction of organics In aqueous wastes



The Electron Beam Process for the Radiolytic Degradation of Pollutants

Several innovative, ultimate disposal technologies are currently being developed for the treatment of water. These advanced oxidation technologies act as sources of free radicals, principally hydroxyl radical (.OH), which oxidatively decompose pollutants. An excellent source of free radicals for water treatment is ionizing radiation. Irradiation of water produces both reducing and oxidizing species, which allow for a versatile approach to the ultimate treatment of a variety of pollutants. Machine-generated electron beams (e-beams) provide reliable and safe radiation sources for treatment of flowing waste streams on a process scale. Process versatility is provided by continuous, rapid treatment potential and a tolerance for feed stocks of varying quality. Additionally, modern e-beams have excellent operational reliability. They are easily automated and many models are portable. Isotope gamma-ray sources have also been used, but are more important as experimental sources for process design and scale-up for e-beam irradiation

Chemical oxidation

Chemical oxidation can be used for the oxidation of nonbiodegardable organics. The most common agents are chlorine ozone and hydrogen peroxide. Chlorine oxidation is extremely effective and it application in the treatment of cyanides and phenol is an established process. In some cases , how ever, it uses can 2,4dcp to the formation of toxic chlorides organic chlorides and the discharge of excess chlorine can be harmful aquatic life and vegetables

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 is 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.

3.3) Adsorption Practices:

Adsorption systems are run either on batch or on continuous basis. Following text gives a brief account of both types of systems as in practice.

3.3.1 Batch Adsorption Systems

In a batch adsorption process the adsorbent is mixed with the solution to be treated in a suitable reaction vessel for the stipulated period of time, until the concentration of adsorbate in solution reaches an equilibrium value. Agitation is generally provided to ensure proper contact of the two phases. After the equilibrium is attained the adsorbent is separated from the liquid through any of the methods available like filtration, centrifugation or settling. The adsorbent can be regenerated and reused depending upon the need.

3.3.2 Continuous Adsorption Systems

The continuous flow processes are usually operated in fixed bed adsorption columns. These systems are capable of treating large volumes of waste wasters and are widely used for treating domestic and industrial wastewaters. They may be operated either in the up flow columns or down flow column. Continuous counter current columns are generally not used for wastewater treatment due to operational problems.

Fluidized beds have higher operating costs hence are not common in use. Wastewater usually contains several compounds which have different properties and which are adsorbed at different rates. Biological reactions occurring in the column may also function as filter bed, retaining solids entering with the feed. As a result of these and other complicating factors, laboratory or pilot plant studies on specific wastewater to be treated should be carried out. The variables to be examined include type of adsorbent, liquid feed rate, solute concentration in feed and height of adsorbent bed.

3.4) Factors Controlling Adsorption:

The amount adsorbed by an adsorbent from the adsorbate solution is influenced by a number of factors such as:

1. Initial concentration
2. Temperature
3. pH
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 2,4DCPs 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. Desiccant in packing and double glazing. 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. Desiccant in packing and double glazing. 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. Recovery of certain vapors. Purification of helium. 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. Separation of aromatics from aliphatics. 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. Removal of organic pigments. 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. Sweetening sour gases and liquids. Purification of hydrogen. Separation of ammonia and hydrogen. Recovery of carbon dioxide. 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.

p.singh et al., (2007) studied Physical and chemical properties of activated carbons prepared from coconut shells The adsorption equilibria and kinetics of phenol and 2,4-dichlorophenol from aqueous solutions on such carbons were then examined at three different temperatures (10, 25 and 40 °C). Adsorption of both phenol and 2,4-dichlorophenol increased with an increase in temperature. The experimental data were analyzed using the Langmuir and Freundlich isotherm models. Both the isotherm models adequately fit the adsorption data for both the phenols. The equilibrium sorption and kinetics model parameters and thermodynamic functions were estimated and discussed. The thermodynamic parameters exhibited the feasibility and spontaneous nature of the adsorption process. The sorption kinetics was studied using the pseudo-first-order and second-order kinetics models. The adsorption kinetics data for both the phenol and 2,4-dichlorophenol fitted better to the second-order model. An attempt was also made to identify the rate-limiting step involved in the adsorption process. Results of mass transfer analysis suggested the endothermic nature of the reaction and change in the mechanism with time and initial concentration of the adsorbate. The results of the study show that the activated carbons derived from coconut shells can be used as potential adsorbent for phenols in water/wastewater

Girgis et al., (1997) studied equilibrium removal of phenol (P),2-chlorophenol (2-CP), 4-nitrophenol (4-NP), 2,4-dichlorophenol (2,4-DCP), and 2,4-dinitrophenol (2,4-DNP) by adsorption onto activated carbon prepared from apricot stone shells by chemical treatment with H_3PO_4. Disubstituted phenols are adsorbed in larger amounts than monosubstituted ones. No clear correlation seems to hold between the amount removed and texture characteristics of the sorbent. Uptake of phenols increases in the order 2-CP < 4-NP < 2,4-DNP < 2,4-DCP, which correlates well with respective increase in molecular dimensions and acidity and decrease in solubility of the sorbates. Abnormality shown by 2,4-DNP as a drop in its removal, is due to strong adsorption at the entrace or inside ie:tain pores thus limiting further diffusion of solute molecules and/or probable molecular sieve effect

Ozgiir and Ferhan (2006) studied the effect of activated carbon type on the extent of adsorbability, desorbability, and bioregenerability in the treatment of 2-chlorophenol. Four different activated carbon types; thermally activated and chemically activated powdered carbons (PAC), and their granular countertypes (CAC) with similar physical characteristics were used. Thermally activated carbons adsorbed 2-chlorophenol much better than chemically activated ones. However, adsorption was more reversible in the case of chemically activated ones. The use of powdered and granular activated carbon countertypes resulted in comparable adsorption and desorption characteristics. For each activated carbon type, 2-chlorophenol exhibited higher adsorbability and lower desorbability than phenol. Biodegradation of 2-chlorophenol took place very slowly when it was used as the sole carbon source in acclimated and non-acclimated activated sludges. Bioregeneration occurred only via desorption due to an initial concentration gradient and no further desorption took place due to low biodegradability. Bioregeneration of activated carbon loaded with 2-chlorophenol was not a suitable option when 2-chlorophenol was the only carbon source. It is suggested to remove 2-chlorophenol via adsorption onto activated carbon rather than applying biological treatment. Also in such cases, the use of thermally activated carbons with higher adsorption and lower desorption capacities is recommended rather than chemically activated carbo

Sponza and Ulukoy (2005) studied the removal of 2,4-dichlorophenol (DCP) in an anaerobic/aerobic sequential reactor system when molasses was used as carbon source. Laboratory scale upflow anaerobic sludge blanket (UASB) reactor/continuous stirred tank reactor (CSTR) were operated at different 2,4-DCP loading rates and constant hydraulic retention times (HRTs) to investigate the COD removal efficiencies, accumulation of volatile fatty acid (VFA) total, methane gas productions and methane percentages. Studies were carried out in continuous mode and the effluent of the UASB reactor was used as feed of the CSTR reactor. 2,4-DCP removal efficiency decreased from 99 to 78.7% when the initial 2,4-DCP concentration and 2,4-DCP loading rates were increased from 5 to 120 mg/l and from 0.006 to 0.144 g/ (1 day), respectively. The maximum COD removal efficiency was achieved as 77% at a 2,4-DCP loading rate of 0.042 g/(l day). When the 2,4-DCP loading rate was increased to 0.12 g/(l day), the maximum measured VFA concentration was 1000 mg CH_3COOH/1 in UASB reactor. In the aerobic reactor, the COD removal efficiencies varied between 60 and 90% depending on UASB reactor treatment efficiencies and to COD concentration coming from the UASB reactor. The effects of sludge retention time (SRT) on the 2,4-DCP and COD removal efficiencies were also investigated in the aerobic reactor. The 2,4-DCP and COD removal efficiencies were observed as 90 and 85%, respectively, at a SRT of 25 days. 86.67% 2,4-DCP removal efficiency was obtained in whole sequential anaerobic/ aerobic (CSTR) reactor system an initial 2,4-DCP concentration of 120 mg/1.

Ahmaruzzaman and Sharma (2005) investigated the possible use of coal, residual coal, and residual coal treated with H_3P0_4 as a means of removal of phenol from wastewater. The study was realized using batch experiments, with synthetic wastewater having phenol concentration of 1000 ppm. Other low-cost adsorbents such as petroleum coke, coke breeze, rice husk, and rice husk char have also been used. The effect of system variables such as pH, contact time, and temperature has been investigated. The suitability of the Freundlich, Langmuir, and Redlich-Peterson adsorption models to the equilibrium data was investigated for each phenol-adsorbent system. The results showed that the equilibrium data for all the phenol-sorbent systems fitted the Redlich-Peterson model best. Kinetic modeling of removal of phenols was done using the Lagergren first-order rate expression. A series of column experiments were performed to determine the breakthrough curves.

Gonzalez et al., (2007) studied the optimized processes in which enzymes, like peroxidases, are used to remove phenolic compounds from polluted wastewater. they described the use of peroxidase isoenzymes from tomato hairy roots, which were able to oxidise 2,4-dichlorophenol (2,4-DCP) and phenol from aqueous solutions. This could be an interesting alternative for the removal of these compounds from contaminated sites. We used different enzyme fractions: total peroxidases (TP), ionically bound to cell wall peroxidases (IBP), basic (BP) and acidic peroxidases (AP). We analyzed the optimum conditions of removal, the effect of Polyethyleneglycol (PEG-3350) on the process and on the enzyme activities, to obtain the maximum efficiency

TP, IBP and BP showed better removal efficiencies than AP, for both contaminants. The addition of different concentrations (10-100 mg $I"^1$) of PEG-3350 to solutions containing 2,4-DCP showed no effect on the removal efficiencies of the isoenzymes. However, PEG (100 mg $I"^1$) increased the removal efficiency of phenol by BP and IBP fractions. On the other hand, peroxidase activities from BP and IBP fractions were 3 and 13 times higher, respectively, than those detected for the same fractions in phenol treated solutions without PEG. The protective effect of PEG, which depends on the contaminant as well as of the enzyme fraction used, would be important to improve the removal efficiency of phenol by some peroxidase isoenzymes

ALAM et al., (2006) were reported the adsorption capacity of activated carbon produced from oil palm empty fruit bunches through removal of 2,4-dichlorophenol from aqueous solution,. The activated carbon was produced by thermal activation of activation time with 30 min at 800°C. The adsorption process conditions were determined with the statistical optimization followed by central composite design. A developed polynomial model for operating conditions of adsorption process indicated that the optimum conditions for maximum adsorption of phenolic compound were: agitation rate of 100 r/min, contact time of 8 h, initial adsorbate concentration of 250 mg/L and pH 4. Adsorption isotherms were conducted to evaluate biosorption process

Emmanuel (2006) studied the adsorption equilibrium isotherms of five phenolic compounds from aqueous solutions onto granular activated carbon (CAC) were studied and modeled. Phenol (Ph), 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (DCP), and 2,4,6-trichlorophenol (TCP) were chosen for the adsorption tests. To predict the adsorption isotherms and to determine the characteristic parameters for process design, seven isotherm models: Langmuir (five linear forms), Freundlich, Elovich, Temkin, Fowler-Guggenheim, Kiselev, and Hill-de Boer models were applied to experimental data. The results reveal that the adsorption isotherm models fitted the data in the order: Fowler-Guggenheim > Hill-de Boer > Temkin > Freundlich > Kiselev > Langmuir isotherms. Adsorption isotherms modeling shows that the interaction of phenolic compounds with activated carbon surface is localized monolayer adsorption, that is adsorbed molecules are adsorbed at definite, localized sites. Each site can accommodate only one molecule. The interaction among adsorbed molecules is repulsive and there is no association between them, adsorption is carried out on energetically different sites and is an exothermic process. Uptake of phenols increases in the order Ph < 2-CP < 4CP<DCP<TCP, which correlates well with respective increase in molecular weight, cross-sectional area, and hydrophobicity and decrease in solubility

Summary of literature review

S No.	Name of the paper	Authors and Year of Publication	Journal	Conclusions Drawn
1.	Liquid-phase adsorption of phenols using activated carbons derived from agricultural waste material	Kunwar P. Singh et.al(2007)	Journal of hazardous materials	• They investigated the adsorption of phenol and 2,4 dichlorophenol on coconut shell activated carbon from aqueous solution • They studied isotherms on three different temperatures of 10,25,40^0C • The adsorption kinetics data for both the phenol and 2,4-dichlorophenol fitted better to the second-order model
2.	Analysis of adsorption characteristics of 2,4dichlorophenol from aqueous solutions by activated carbon fiber	Jian-Ping Wang,et.al(2006)	Journal of hazardous materials	• Investigated the adsorption of 2,4-dichlorophenol (2,4-DCP) by activated carbon fiber (ACF)activated by static air. • The order of isotherms for batch experiment is arranged as Langmuir > Redlich-Peterson > Toth > Freundlich

3.	Treatment of 2,4-dichlorophenol (DCP) in a sequential anaerobic (upflow anaerobic sludge blanket) aerobic (completely stirred tank) reactor system	Delia Teresa Sponza, Aysen Ulukoy(2005)	Process biochemistry	• up flow anaerobic sludge blanket (UASB) reactor/completely stirred tank reacto(CSTR) were operated at different 2,4-DCP loading rates and constant hydraulic retention times (HRTs) to investigate the COD removal efficiencies. • 2,4-DCP removal efficiency decreased from 99 to78.7% when the initial 2,4-DCP concentration and 2,4-DCP loading rates were increased from 5 to 120 mg/l and from 0.006 to 0.144 g/(l day), respectively.
4.	2,4-Dichlorophenol Degradation by an Integrated Process: Photoelectrocatalytic Oxidation and E-Fenton Oxidation	Zhao, et.al(2007)	Journal of hazardous materials	• They studied the integrated process involving photoelectrocatalytic oxidation (PECO) and electro-Fenton (E-Fenton) oxidation. • experimental results demonstrated that 2,4-DCP degradation in aqueous solution was greatly enhanced.they concluded combined reaction becomes less pH sensitive than the typical E-Fenton reaction pH

5.	Photodecomposition of 2,4-Dichlorophenol in Aqueous Solution Catalyzed by Cadmium Sulfide Particles	Young Ku,* Ching-Bin Hsieh (1992)	*Ind. Eng.* Chem. Res.	• The degradation of 2,4-dichlorophenol in the presence of cadmium sulfide suspensions by ultravioletillumination was studied under various solution pH conditions, reaction times, and CdS loadings. • The degradation and demineralization of 2,4dichlorophenol by the photocatalytic process can be described fairly well by a simplified two step consecutive reaction scheme based on carbonbalance.
6.	Enhanced degradation of 2,4-dichlorophenol by ultrasound in a new Fenton like system (Fe/EDTA) at ambient circumstance	Tao Zhou et.al(2008)	ultrasonics	• study investigated the effect of ultrasound (US) enhancement on the degradation of 2,4-DCP in a new Fenton like system • Good correspondences with pseudo-first order were found in each reaction system • Low molecular weight organic acids are identified as the main products, which contribute to the solution self-buffer at aboutpH 6.5 along with the reaction. • In addition, the effect of initials condition, i.e., iron addition, EDTA dosage, DCP concentration and US input power as well as reaction temperature studied

7.	Removal of 2,4-dichlorophenol from wasterwater by vacuum membrane distillation using hydrophobic PPESK hollow hiber membrane	Shou Hai Zhang,et.al(2007)	Chineese chemical letters	• hydrophobic poly (phthalazinone ether sulfone ketone) (PPESK) hollowfiber membrane was used to remove 2,4-DCP from wasterwater by vacuum membrane distillation (VMD) method, andthe results was satisfactory. • Vacuummembrane distillation (VMD) is a thermally driven process. The driving force is maintained by applying vacuum at thedownstream side to keep the pressure at this side below the equilibrium vapor pressure.
8.	Comparison of the removal of 2,4-dichlorophenol and phenolfrom polluted water, by peroxidases from tomato hairy roots, and protective effect ofpolyethylene glycol	Silvia Raquel Milrad et.al(2007)	chemosphere	• Studied the optimized processes in which enzymes, like peroxidases, are used to remove phenolic compoundsfrom polluted wastewater. describe the use of peroxidase isoenzymes from tomato hairy roots, which were able to oxidise2,4-dichlorophenol (2,4-DCP) and phenol from aqueous solutions • From the studies they concluded The optimal H_2O_2 concentrations for 2,4-DCP andphenol removal were 1 and 0.1 mMthe enzyme fractions used total peroxidases (TP), ionically bound to cell wall peroxidases(IBP), basic (BP) and acidic peroxidases (AP). • The addition of different concentrations (10–100 mg l_1) of PEG-3350 to solutions containing 2,4-DCP showed no effect on the removalefficiencies of the isoenzymes. However, PEG (100 mg l_1) increased the removal efficiency of phenol by BP and IBP fractions,PEG(Polyethyleneglycol)

9.	Adsorption Of Phenol And Substituted Chlorophenols From Aqueous Solution By Activated Carbon Prepared From Jackfruit (Artocarpus Heterophyllus) Peel-Kinetics And Equilibrium Studies	Seema Jain; Radha V. Jayaram (2007)	Separation science and technology	• They studied effectiveness of an adsorbent prepared from jackfruit peel, an agricultural waste, for the removal of phenol, 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol from aqueous solutions. • The order of removal was found to be 2,4-dichlorophenol> 4chlorophenol>2chlorophenol>phenol . • The removal of phenols was found to be most effective at lower pH. Kinetic data of the adsorption process could fit a pseudo second order rate equation
10.	Adsorption, desorption and bioregeneration in the treatment of 2-chlorophenol with activated carbon	zgu¨r Aktas¸, Ferhan C¸ (2005)	Journal of Hazardous materias	• They studied the the effect of activated carbon type on the extent of adsorbability, desorbability, and bioregenerability in the treatment of 2-chlorophenol, Four different activated carbon types; thermally activated and chemically activated powdered carbons (PAC), and their granularcountertypes (CAC) with similar physical characteristics were used • From the studies they concluded that Biodegradation of 2-chlorophenol took place very slowly,and suggested to remove 2-chlorophenol via adsorption onto activated carbonrather than applying biological treatment

11.	Adsorption of phenols from wastewater	M.Ahmaruzzaman , D.K. Sharma(2004)	Journal of colloids and interface science	• They investigated possible use of coal, residual coal, and residual coal treated with H_3PO_4 as a means ofremoval of phenol from wastewater • The results showed that theequilibrium data for all the phenol–sorbent systems fitted the Redlich–Peterson model best
12.	Competitive Activated Carbon Adsorption of Phenolic Compounds	E. Knettig, et.al(1986)	Environmental pollution series	• *They studied Competitive adsorption, by activated carbon, Phenols with 2 or 3 chlorinesubstituents (2, 4-dichlorophenol and 2, 4 ,6-trichlor ophenol) were strongly adsorbable and adsorbed preferentially to 2-chlorophenol, phenol and mcresol* • *Thecumulative adsorption capacities for the mixtures containing all phenoliccompounds were lower than those for individual compounds.*
13.	Removal of phenol, phenoxide and chlorophenols from waste-waters by adsorption and electrosorption at high-area carbon felt electrodes	Erol Ayranci *, Brian E. Conway (2001)	Journal of Electroanalytical chemistry	• They studied the behavior of of phenol, sodium phenoxide, 1-, 2- and 3-chlorophenol and 2,6-dichlorophenolwere studied at high-area carbon-felt (C-felt) electrodes • Among the three monochlorophenols, 4-chlorophenol exhibitedthe lowest rate of adsorption with 2-chlorophenol having the highest according to a kinetically first-order treatment of theadsorption data, while 2,6-dichlorophenol was adsorbed at an intermediate rate

	degradation of 2,4-dichlorophenol on a palladium modified gas-diffusionelectrode	JianlongWangb,(2008)	Electrochimica Acta	investigated in a diaphragm electrolysis system, feeding firstly with hydrogen gasthen with air, using the Pd/C gasdiffusionelectrodeandthecarbon/polytetrafluoroethylene (C/PTFE) gas diffusion electrode as a cathode, respectively. • Indicated that the self-made Pd/C gas-diffusion cathode can not only reductively dechlorinate 2,4-dichlorophenols by feeding hydrogen gas, but alsoaccelerate the two-electron reduction of O2 to hydrogen peroxide(H_2O_2) by feeding air.
15.	Removal of phenolic compounds from synthetic wastewater using soybean peroxidase	K. E. TAYLOR et.al(1999)	Journal of Hazardous Materials	• They investigated the e□ciency of using soybean peroxidase (SBP)to remove several di€erent phenolic compounds from unbu€ered synthetic wastewater. pH, SBP dose in theabsence and presence of polyethylene glycol (PEG) were the parameters investigated • The opti-mum pH for di€erent phenolic compounds ranged from 5.5 to 8. • studies showed that PEG only slightlyreduced the amount of SBP required for 95% removal of the substrate. For most of the substrates, anincrease in PEG dose beyond the optimum dose did not significantly change the removal effciency
16	Application of a fluorinated solvent to the conventional ozonation process for the destruction of 2,4-dichlorophenol	Chia-yuan etal(1994)	Environment international vol 21	• They investigated The removal of 2,4-dichlorophenol from aqueous solution with fluorinated solvent, with ozone, and withfluorinated solvent/ozone combined • The results of extraction tests showed that the distribution coeffcientdecreased with increasing initial pH value of the aqueous phase. The experiment results indicated that 2,4-dichlorophenol was removed at a faster rate at low initial pH value

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) Objectives of present study:

The objectives of this study was to explore the use of various adsorbents for the removal of 2,4dichlorophenol from aqueous solution. Coconut shell Activated Carbon (CSAC),Commercial activated carbon (CAC), Bagasse flyash (BFA), Rice husk ash (RHA) and mixed activated carbon (MAC) were as adsorbents. The entire study deals with various parameters dealing with adsorption and adsorption kinetics.

The Physico-Chemical characteristics of adsorbents are such as Proximate analysis, Surface area, Scanning electron micrograph (SEM) etc.,EDS

Studies on the effect of various adsorption batch parameters like pH, contact time, adsorbent dose, temperature, concentration on the removal of 2,4dcp.

Studies of the kinetics of adsorption.

Studies of the adsorption isotherms are were used to estimate the adsorption capacity of the adsorbents.

Study of thermodynamic adsorption parameters, ΔG^o, ΔH^o and ΔS^o.

5.2) Preparation of the adsorbents:

The adsorbent coconut shell activated carbon was prepared by the coconut shell. India, the third largest producer of coconuts in the world, producing about 12.8 billion coconuts a year. It is estimated that the production of coconut shell in India is about 3.4 million tons per year. Coconut shell 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. The coconut shells were dried at 110°C, crushed and sieved to a uniform size range of 1.41-2.0 mm. KOH in the form of pellets was mixed with 20 g of shell particles in a stainless steel beaker; then water was added until the KOH dissolved. The mixtures were dehydrated at 300°C in a furnace for 3 h and subsequently pyrolyzed in a furnace under a nitrogen flow of 5 L/h at temperatures in the range 600-800°C.

5.3) Characterization of adsorbents:

The physico-chemical characteristics of the CSAC, CAC, RHA, BFA, MAC were determined using standard procedures as discussed below:

5.3.1 Proximate Analysis

Proximate analysis of the CSAC, CAC, RHA, BFA, MAC were carried out using the procedure as per IS 1350:1984.

5.3.2 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 the analysis of CSAC, CAC, RHA, BFA, MAC. To estimate the carbon content

5.3.3 Scanning Electron Micrograph (SEM)

SEM analysis of CSAC,CAC, RHA, BFA, and MAC were carried out before and after the adsorption of 2,4 dichlorophenol from aqueous solution by using LEO 435 VP Scanning electron microscope. To observe the adsorbent surface structure

5.4) Adsorbate:

Aqueous solutions of 2,4dichlorophenolof desired concentrations (20–100 mg/l) were prepared by dissolving accurately weighed quantity of 2,4dichlorophenol of AR grade in distilled water.

5.4.1 Analytical measurement

Concentration of 2,4dichlorophenol was estimated spectrophotometrically by monitoring the absorbance characteristic wavelength using UV/VIS spectrophotometer (Perkin Elmer 35). A standard solution of 2,4dichlorophenolwas taken and the absorbance was determined at different wavelengths to obtain a plot of absorbance versus wavelength. The wavelength corresponding to maximum absorbance (λ_{max}) was determined from this plot. The λ_{max} for 2,4dcp was found to be 285 nm. Calibration curve was plotted between the absorbance and the concentration of 2,4dichlorophenol solution. The linearity of calibration curve (Fig. 5.1) indicated the applicability of the Lambert-Beer's Law.

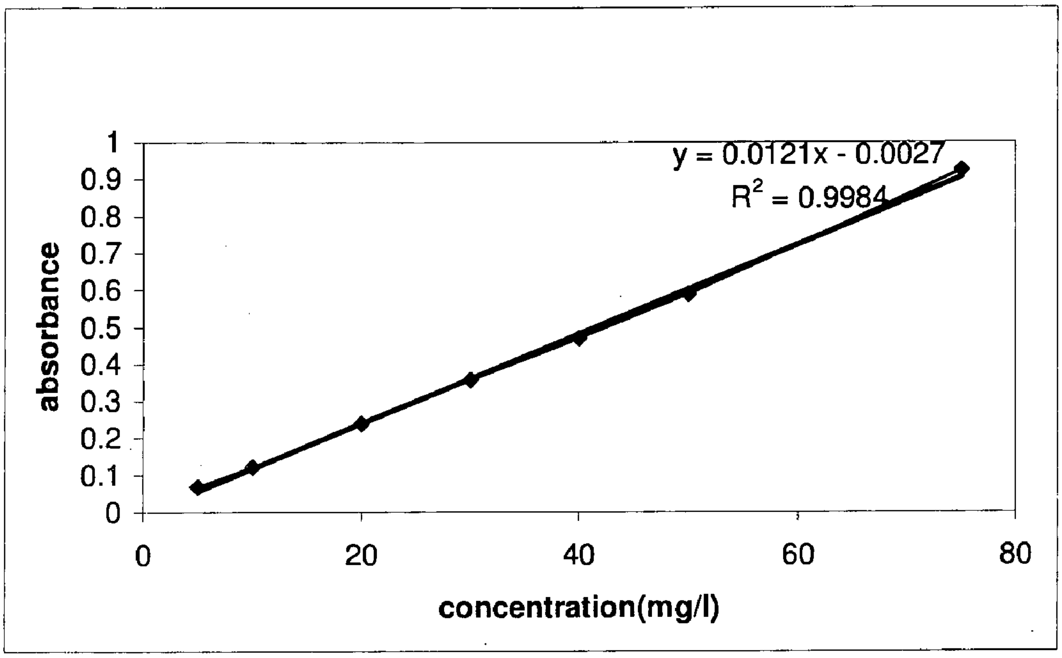


Fig. 5.1: Calibration Graph of 2,4dcp

5.5) Experimental Programme:

The experimental programme was performed as batch studies.

5.5.1 Batch Adsorption Experiments

1000mg/l of stock solution is to be prepared by dissolving 1g of 2,4dcp in 1000ml of distilled water, from this stock solution solutions of desired concentrations (20-100 mg/l) were prepared.

studies 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 24dcp by CSAC, CAC ,BFA, RHA and MAC, batch experiments were conducted at 30 ± 1 °C. For each experimental run, 50 ml of 2,4dichlorophenol solution of known C_0, pH_0, known adsorbent size and known amount of the adsorbent were taken in a 250 ml conical flask. This mixture was agitated in a temperature-controlled incubator at a constant speed at 25 ± 1°C. Samples were withdrawn at appropriate time intervals. After filtration 2,,4dichlorophenol remaining in solution was analyzed spectrophotometrically using UV/VIS spectrophotometer at 285 nm. The effect of pH_0 on 2,4dcp removal was studied over a pH_0 range of 1 to 9. pH_0 was adjusted by the addition of dilute aqueous solutions of HNO_3 or NaOH (0.10 M).. To see the effect of temperature for the adsorption of 2,4dcp from solution by CSAC,CAC, RHA, BFA and MAC, experiments were also conducted at 10°C, 30°C and 50°C.The kinetics of adsorption was determined by analyzing adsorptive uptake of the 2,4dcp from the aqueous solution at different time intervals. For adsorption isotherms, 2,4dcp solutions of different concentrations were agitated with the known amount of adsorbent till the equilibrium was achieved. The residual 2,4dcp concentration of the solution was then determined. Blank experimental runs, with only the adsorbent in 50 ml of distilled water,. Batch tests were carried out to compare the adsorptive capacity of intensity of CSAC, CAC, RHA, BFA and MAC. 2,4dcp concentration is to be estimated by UV/VIS spectrophotometer (Perkin Elmer 35) at 285 nm.

The percentage removal of 2,4dcp and equilibrium adsorption uptake in solid phase, q_e (mg/g), was calculated using the following relationships:

$$\text{Percentage of 2,4dichlorophenol removal} = 100(C_0 - Ce)/ C0 \quad (4.1)$$

$$\text{Amount of adsorbed 2,4dichlorophenol per g of solid, } q_e = (C_0 - Ce)V/w \quad (4.2)$$

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 shell activated carbon (CSAC) Commercial activated carbon (CAC), Rice husk ash(RHA), Bagasse flyash(BFA) and Mixed activated carbon(MAC)
- Batch adsorption studies.

6.2) Characterization of coconut shell activated carbon (CSAC), Commercial activated carbon (CAC), Rice husk ash (RHA), Bagasse flyash (BFA) and Mixed activated carbon (MAC):

Physico-Chemical Characteristics of CSAC, CAC, MAC ,RHA and BFA including proximate analysis. are given in Table C – 1 and C - 2 , C-3, C-4 and C-5 respectively. Due to presence of high carbon content, CSAC, CAC, MAC, BFA may be treated as organic in nature. The carbon content of RHA is very less The organic nature of AC imparts porosity to it. Compared to CSAC, 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 CSAC, CAC, MAC ,RHA and BFA before and after adsorption are shown in Figs. B - 1, B - 2 ,B - 3, B - 4 ,B -5, B-6,B-7 and B-8,resepectively. These photographs reveal their surface texture and porosity.

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 conical flask for removal of 2,4dcp from synthetic solutions of known concentrations by using CSAC, CAC, MAC , RHA and BFA. The effect of various operating parameters, viz. pH, adsorbent dose, initial concentration, contact time, adsorbent size and temperature were studied and presented here.

6.3.1. Effect of initial pH (pH_0)

pH is one of the most important environmental factors: 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 .

Adsorption of 2,4dichlorophenol on CSAC,CAC, MAC ,RHA, BFA was studied at varying pH values to optimize the removal and shown in Fig. B - 9. 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 systems CSAC and CAC, MAC ,RHA and BFA was found to be 4,4,5,3,3 with 2,4dcp removal of about 63% and 96%, 83.4%, 83%, 86% solution with initial 2,4dcp concentration of 50 mg/l.. At lower pH values the electrostatic forces of repulsion between adsorbents (CSAC and CAC, MAC ,RHA, BFA) and adsorbate (2,4dcp) is prominent. For the commercial activated carbon and coconut shell activated carbon the percentage increases sharply from 3 to 6, but in case of rice husk ash, bagasse fly ash , mixed activated carbon its varied between 2 to 5

6.3.2. Effect of adsorbent dosage (m)

The effect of adsorbent dose(intitial concentration 50ppm) on the removal of 2,4dcp by using adsorbents CSAC,CAC, MAC ,RHA and BFA is shown in Figs. B - 10. It can be seen that the removal of 2,4 dcp increases up to a certain limit and then it remains almost constant. Optimum dose was found to be for CSAC, CAC, MAC ,RHA and BFA were 8g/l, 8g/l, 6g/l, 4g/l,12g/l respectively . 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 2,4dcp concentration (C_0)

The effect of C_0 on the percent removal of 2,4dcp by CSAC,CAC, MAC ,RHA and BFA is shown in Figs. B –11a, B-11b, B-11c, B-11d, B-11e respectively. It is evident from the Figures, that the amount of 2,4dcp adsorbed per unit mass of adsorbent (q_e) increased with the increase in C_0(Figs. B - 11a, B-11b, B-11c, B-11d, B-11e), although percentage 2,4dcp removal decreased with the increase in C_0(Figs. B – 11a,B-11b,B-11c, B-11d and B-11e). q_e increased with the increase in C_0 as the resistance to the uptake of 2,4dcp from the solution decreases with the increase in 2,4dcp 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 2,4dcp by CSAC, CAC, MAC ,RHA and BFA at C_0=20, 40, 60, 80 and 100 mg/l is given in Figs. B – 11a, B-11b, B-11c, B-11d and B-11e respectively. The contact time curves show rapid adsorption of 2,4dcp in the first 30 min, thereafter, the adsorption rate decreases gradually and the adsorption reaches equilibrium in 6 h for CSAC, CAC, MAC,RHA, BFA (optimum contact time). Aggregation of 2,4dcp 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 2,4dcp molecules in the adsorbents. This is the reason why an insignificant enhancement is observed 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 of 2,4 dcp. The adsorption curves of contact time indicate the possible mono-layer coverage of 2,4dcp on the surface of CSAC, CAC, MAC ,RHA, BFA.

6.3.5 Effect of particle size(s)

The effect of adsorbent particle size on uptake of 2,4dcp studied with different adsorbent sizes of 400 to 1200μ that the percent removal of 2,4dcp increases from 41 to 69% (for CSAC) for an initial concentration of 50 mg/l of 2,4dcp 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 2,4dcp adsorbed is small.

6.3.6 Effect of temperature (T)

Temperature has a pronounced effect on the adsorption capacity of the adsorbents. Figs. B-17a to B-20c show the plots of adsorption isotherms, for CSAC,CAC, MAC ,RHA and BFA-2,4dcp-systems at 303, 323 and 283 K.. It shows that the adsorptivity of 2,4dcp 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 2,4dcp 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 2,4DCPon CSAC, CAC, MAC ,RHA and BFA., 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 2,4dcp adsorption on CSAC and CAC, MAC ,RHA and BFA. at C_0=20, 40, 60, 80 and 100 mg/l were determined from the plot of log (Q_e – Q_t) against t (fig 14 a to 14 e). The k_f values are given in table 6 and 7

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→0 is defined as

$$h = k_S q_e^2$$

Figs. B-25 and B-26 sho the plot of t/q_t versus t for CSAC, CAC, MAC ,RHAand BFA, 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 6&7 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.

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, k_{id} is the intra-particle diffusion rate constant (mg/g min1/2) and I is the intercept (mg/g). Plot of q_t versus $t^{1/2}$ should be a straight line with a slope k_{id} and I 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. 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 6and 7.The values of the correlation coefficients are also given in Table 6 and Table 7

6.4.4. Bangham's model

The rate constants, Kr for the sorption of 2,4dcp were calculated using the simplest form of

Bangham equation :

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

The integral form of the equation can be written as:

$Qt=Krt^{1/m}$ (6.7)

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

$\log Qt=\log Kr + (1/m)\log t$ (6.8)

As can be observed from the Fig.B-16a to B-16e it shows applicability of the 1/m th order kinetics for the system under observation. The adsorption rate constants calculated from the intercepts and slopes of the straight lines and are reported in Table 6&7

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 and Temkin

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-17b, B-18b,B-19b,B-20bB-21b show the Freundlich isotherm plots (lnQe versus lnCe) for adsorption of 2,4dcp on CSAC, CAC, MAC ,RHA and BFA at 303, 323 and 283 K, respectively. Langmuir isotherm plot (Ce/Qe versus Ce) shown in Fig.B-17a, B-18a,B-19a, B- 20a B-21a for adsorption onto CSAC and CAC, MAC ,RHA and BFA respectively. Freundlich and Langmuir isotherm parameters for both adsorbents along with linear and non-linear correlation coefficients are given in Table C-8a to C-8e and C-9a to C-9e. At all temperatures, Langmuir isotherm represent a better fit of the experimental data than Freundlich isotherm. This suggests adsorption of 2,4dcp by CSAC, CAC, MAC ,RHAand BFA 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 2,4dcp on CSAC, CAC,MAC ,RHA and BFA

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 $B_1 = \dfrac{RT}{b}$

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-17c through B-21c shows the Temkin isotherm plots for both adsorbents. The Temkin isotherm parameters are listed in Tables C-10 through C-10e.

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 data points. Due to the inherent resulting from linearization, error functions of non-linear regression 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-11 through C-15, CSAC and CAC, MAC ,RHA and BFA respectively.

6.6.2 The Average Relative Error (ARE)

ARE is given as

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

This error function attempts to minimize the fractional error distribution across the entire concentration range. The values of ARE are given in Tables Tables C-11 to C-15, CSAC and CAC, MAC ,RHA and BFA, respectively.

6.6.3 The Hybrid Fractional Error Function (HYBRID)

HYBRID is given as

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

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-11 through C-15 for CSAC and CAC, MAC ,RHA and BFA, 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

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

The values of MPSD error functions are given in Tables C-11 through C-15, CSAC CAC, MAC ,RHA and BFA, respectively.

6.6.5 The Sum of the Absolute Errors (SAE)

SAE is given as

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

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 Tables C-11 through C-15, for CSAC CAC, MAC ,RHA and BFA, respectively.

6.6.6 Choosing best-fit isotherm based on error analysis

The values of the five error functions are presented in Tables C-12 through C-15, CSAC, CAC, MAC ,RHA and BFA, respectively. By comparing the results of the values of the error functions, it is found that Langmuir isotherms best-fitted the isotherm data for 2,4dcp adsorption on CSAC at almost all temperatures and Langmuir best-fitted for 2,4dcp on CAC,RHA,BFA.

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

$$\Delta G^0 = -RT \ln K \qquad (6.21)$$

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:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (6.22)$$

Combining above two equations, we get

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

where ΔG^0 is the free energy change (kJ/mol), ΔH^0 is the change in enthalpy (kJ/mol), ΔS^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:

$$K = \frac{a_s}{a_e} = \frac{V_s}{V_e}\frac{C_s}{C_e} \qquad (6.24)$$

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:

$$\lim_{Ce \to 0} \frac{C_s}{C_e} = \frac{a_s}{a_e} = K$$

(6.25)

Values of K are obtained by plotting In (C_s/C_e,) versus C_e, and extrapolating to zero C_e. from values are obtained at different temperatures. The increase in *K* with increase in temperature indicates the endothermic nature of the process.

The ΔG^0 is calculated from the equation 6.21 for different temperatures. The negative values of ΔG^0 indicate the process to be feasible and adsorption to be spontaneous. And ΔH^0 and ΔS^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. ΔH^0 and ΔS^0 are determined from the slope and intercept of the plot.

The positive ΔH^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(2,4dcp), the changes in the size of pores, and the enhanced rate of intraparticle diffusion of adsorbate. The value of ΔH^0 was less than 20 kJ/mol, so the adsorption is physical adsorption.

The positive value of ΔS^0 suggests increased randomness at the solid/solution interface with some structural changes in the adsorbate and adsorbent and an affinity of CAC, MAC ,RHA, BFA, respectively. towards 2,4dcp Also, positive ΔS^0 value corresponds to an increase in the degree of freedom of the adsorbed species. All the thermodynamic parameters are given

CHAPTER-7

CONCLUSION AND RECOMMENDATIONS

7.1 Conclusions:

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

1. SEM of CAC, RHA show structure with large pore size with strands in each .Number of pores in CSAC is lesser than that in CAC, BFA, RHA,. Surface of the CSAC, CAC, BFA, RHA becomes smooth after adsorption of 2,4dcp.
2. Percent removal of 2,4dcp increases with the increase in adsorbent dose for CSAC,CAC,BFA,RHA and MAC up to a certain limit and then remains almost constant. However, percent removal decreases with increase in 2,4dcp concentration for the adsorbents.
3. Adsorption of 2,4dcp on CSAC, CAC, BFA, RHA and MAC is higher in acidic pH range. giving dcp maximum value at 4, 4, 3, 3, 5and then percent removal slightly decreases after this pH region.
4. Effect of initial 2,4dcp concentration on removal by CSAC, CAC,BFA,RHA and MAC show that for any contact time the percent removal decreases with increase in initial concentration .Amount adsorbed per unit of adsorbent (q_t) increased with the increase initial 2,4dcp concentration .
5. Increase in temperature slightly increases the amount adsorbed for CSAC, CAC, BFA, RHA and MAC adsorbents indicating endothermic in nature.
6. The percent removal of 2,4dcp increases CSAC as the particle size decreases because of specific surface available for adsorption will be greater for smaller particles.
7. Kinetic study shows that adsorption of 2,4dcp on follows the second order kinetics for all the adsorbents.
8. Weber-Morris plot reveals that the intraparticle transport (pore diffusion) is not the only rate-controlling step.
9. Langmuir isotherm best-fitted the isotherm data for 2,4dcp adsorption on CSAC, CAC, BFA, RHA and MAC 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 and hence any one of the isotherms could be used for 2,4dcp adsorption on CSAC, CAC, BFA, RHA and MAC.

10. Adsorption capacity of CSAC, CAC, BFA, RHA and MAC for 2,4dcp removal increases with increase in temperature for CSAC,CAC,BFA,RHA,MAC adsorbents, showing the endothermic nature of adsorption. The energy of adsorption reveals that it is a transitional state adsorption.
11. The increase in K with increase in temperature indicates the endothermic nature of the process. The negative values of ΔG^0 indicate the process to be feasible and adsorption to be spontaneous
12. 2,4dcp removal efficiency varies in the order of adsorbents CSAC<MAC<RHA<BFA<CAC (the difference is not very high except CSAC). But RHA,BFA were prepared from agricultural cheap sources which is abundantly available in India . So the low cost RHA,BFA can be used as a potential adsorbent for the removal of 2,4dcpfrom wastewater in developing countries like India.

Recommendations :

1) CSAC, BFA, RHA and MAC 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. Further pilot scale studies are required to evaluate the suitability of CSAC, CAC, BFA, RHA and MAC carbon for the adsorptive removal on plant scale.
3) To further improve adsorption properties of coconut shell activated carbon, it should be gone through some treatment processes which improves adsorption property.
4) Under continuous study, fixed bed column study should be carried out to get effect of different parameters on removal from waste water.

5) Many more combination of different adsorbents could be tried to get much better result CSAC, CAC, BFA, RHA and MAC could also be tested for removal of other chlorophenols.

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. APPENDIX – A

Table A-1: Calibration curve for 2 4dichlorophenol

Concentration of 2,4dcp (mg/l)	Absorbance
5	0.069
10	0.122
20	0.24
30	0.3569
40	0.4691
50	0.5888
75	0.9237

Table A-2a: Effect of pH on the removal of 2,4dichlorophenol using CAC (T=303 K, Dose=8g/l, t=6 hr, C_0=50 mg/l)

pH	% Removal
1	70.75
2	83.23
3	94.97
4	96.45
5	94.9
6	90.9
7	89.23
8	86.45
9	85.2

Table A-2b: Effect of pH on the removal of 2,4dichlorophenol using CSAC (T=303 K, Dose=8g/l, t=6 hr, C_0=50 mg/l)

pH	% Removal
1	40.23
2	48.31
3	55.75
4	63.14
5	50.25
6	45.62
7	42.85
8	41.25
9	39.78

Table A-2c: Effect of pH on the removal of 2,4dichlorophenol using BFA (T=303 K, Dose=12g/l, t=6 hr, C_0=50 mg/l)

pH	% Removal
1	76.73
2	83.63
3	91.87
4	86.85
5	83.83
6	81.12
7	80.42
8	79.84
9	78.25

Table A-2d: Effect of pH on the removal of 2,4dichlorophenol using RHA (T=303 K, Dose=4g/l, t=6hr, C_0=50 mg/l)

pH	% Removal
1	76.73
2	83.63
3	91.87
4	86.85
5	83.83
6	81.12
7	80.42
8	79.84
9	78.25

Table A-2e: Effect of pH on the removal of 2,4dichlorophenol using MAC (T=303 K, Dose=6g/l, t=6 hr, C_0=50 mg/l)

pH	% Removal
1	73.67
2	76.75
3	79.91
4	81.66
5	83.55
6	79.43
7	77.85
8	76.67
9	70.24

Table A-3a: Effect of Adsorbent dose on removal of 2,4dichlorophenol using CAC (T=303 K, t=6 hr, C_o=50 mg/l, pH=4)

Adsorbent Dose (mg)	% Removal
0.2	91.9
0.4	95.85
0.6	91.228
0.8	91.11
1	90.26

Table A-3b: Effect of Adsorbent dose on removal of 2,4dichlorophenol using CSAC (T=303 K, t=6 hr, C_o=50 mg/l, pH=4)

Adsorbent Dose (mg)	% Removal
0.2	50.76
0.4	62.46
0.6	60.03
0.8	60.27
1	59.83

Table A-3c: Effect of Adsorbent dose on removal of 2,4dichlorophenol using BFA (T=303 K, t=6 hr, C_o=50 mg/l, pH=3)

Adsorbent Dose (mg)	% Removal
0.2	61.14
0.4	68.049
0.6	83.14
0.8	82.14
1	82.09

Table A-3d: Effect of Adsorbent dose on removal of 2,4dichlorophenol using RHA (T=303 K, t=6 hr, C_o=50 mg/l, pH=3)

Adsorbent Dose (mg)	% Removal
0.2	78.15
0.4	73.14
0.6	73.256
0.8	71.95
1	70.66

Table A-3e: Effect of Adsorbent dose on removal of 2,4dichlorophenol using MAC (T=303 K, t=4 hr, C_o=50 mg/l, pH=5)

Adsorbent Dose (mg)	% Removal
0.1	80.12
0.2	84.65
0.3	82.32
0.4	82.29
0.5	81.89

Table A-4a: Effect of Contact time and initial concentration of 2,4dichlorophenol removal of using CAC (T=303 K, pH=4, Dose= 8 g/l)

Time(min)	% Removal (20 mg/l)	% Removal (40 mg/l)	% Removal (60 mg/l)	% Removal (80 mg/l)	% Removal (100 mg/l)
0	0	0	0	0	0
20	53.85	70.35	45.92	51	33.8
30	83.75	84.05	69.3	59.3	50.3
60	89	87.35	71	60.1	52.49
120	94	88.775	72.1	61.2125	52.06
180	95.5	92.35	72.7	61.7	53.67
240	97.525	92.9	73.55	62	53.2
360	98	93.025	74	62.5	53.99

Table A-4b: Effect of Contact time and initial concentration of 2,4dichlorophenol removal of using BFA (T=303 K, pH=3, Dose= 12 g/l)

Time(min)	% Removal (20 mg/l)	% Removal (40 mg/l)	% Removal (60 mg/l)	% Removal (80 mg/l)	% Removal (100 mg/l)
0	0	0	0	0	0
20	52.03	59.75	50.9	49.9875	23.18
30	78.3	74.3	64.3	51.8	39.06
60	80.65	76.525	66.65	52.25	40.63
120	83.5	78.5	68	53.6	40.95
180	83.67	80.67	68.8167	54.0125	41.78
240	84.17	81.2	68.133	54.525	42.02
360	84.9	81.9	68.9	54.8625	43.16

Table A-4c: Effect of Contact time and initial concentration of 2,4dichlorophenol removal of using CSAC

(T=303 K, pH=4, Dose= 8 g/l)

Time(min)	% Removal (20 mg/l)	% Removal (40 mg/l)	% Removal (60 mg/l)	% Removal (80 mg/l)	% Removal (100 mg/l)
0	0	0	0	0	0
20	50.55	45.375	30.75	22.1875	20.75
30	65.9	47.72	39.2	30.9625	23.75
60	65.8	48.15	40.75	32.2125	24.26
120	69.65	47.6125	40.8	32.425	25.25
180	70.2	49.1	41.5833	32.6875	26.35
240	72.57	51.725	41.9	33.075	26.48
360	74.35	52.45	432,333	33.225	26.58

Table A-4d: Effect of Contact time and initial concentration of 2,4dichlorophenol removal of using MAC

(T=303 K, pH=5, Dose= 6 g/l)

Time(min)	% Removal (20 mg/l)	% Removal (40 mg/l)	% Removal (60 mg/l)	% Removal (80 mg/l)	% Removal (100 mg/l)
0	0	0	0	0	0
20	45.5	51.525	29.75	38.4625	23.75
30	60.21	72.325	49.1333	45.85	35.75
60	61.8	72.65	51.9667	45.8625	36.15
120	71.1	76.1875	56.2667	45.075	37.47
180	75.25	78.975	57.9834	45.05	37.88
240	80.75	79.425	57.2667	45.0125	38.98
360	81.8	80.85	59.9333	47.3125	39.11

Table A-4e: Effect of Contact time and initial concentration of 2,4dichlorophenol removal of using RHA
(T=303 K, pH=3, Dose= 4 g/l)

Time(min)	% Removal (20 mg/l)	% Removal (40 mg/l)	% Removal (60 mg/l)	% Removal (80 mg/l)	% Removal (100 mg/l)
0	0	0	0	0	0
20	52.625	53.95	34.4167	25.4	35.14
30	66.425	73.275	57.5833	51.6625	46.58
60	68.3	74.625	58.7667	52.525	47.72
120	70.1	75.0125	58.5167	53.0175	47.04
180	75.75	76.9	61.4167	53.25	48.11
240	77.6	78.575	60.6	53.925	48.28
360	83.1	79.15	61.6333	54.4375	48.58

Table A-6a: Lagergren plot for the removal of 2,4dichlorophenol for different initial concentrations using CAC
(pH=4, T=303 K, Dose=4g/l)

Time(min)	log (qe-q_t) (20 mg/l)	log (qe-q_t) (40 mg/l)	log (qe-q_t) (60 mg/l)	log (qe-q_t) (80 mg/l)	log (qe-q_t) (100 mg/l)
0	0	0	0	0	0
20	0.04287	0.05452	0.32351	0.0607	0.40205
30	-0.4483	-0.348	-0.4528	-0.4949	-0.3361
60	-0.6478	-0.5471	-0.6478	-0.6198	-0.727
120	-1	-0.6726	-0.8462	-0.8903	-0.6175
180	-1.2041	-1.4717	-1.011	-1.0969	-1.3979
240	-1.9254	-2.2041	-1.4717	-1.301	-1.0055
360	----	---	----	-----	----

Table A-6b: Lagergren plot for the removal of 2,4dichlorophenol for different initial concentrations using BFA
(pH=3, T=303K, Dose=12g/l)

Time(min)	log (qe-q_t) (20 mg/l)	log (qe-q_t) (40 mg/l)	log (qe-q_t) (60 mg/l)	log (qe-q_t) (80 mg/l)	log (qe-q_t) (100 mg/l)
0	0	0	0	0	0
20	-0.2614	-0.1318	-0.0458	-0.4881	0.22141
30	-0.9586	-0.5963	-0.6383	-0.69	-0.4664
60	-1.1498	-0.7467	-0.9489	-0.759	-0.6761
120	-1.632	-0.9456	-1.3468	-1.0749	-0.7348
180	-1.6883	-1.3872	-2.3802	-1.2467	-0.9393
240	-1.9148	-1.632	-1.4164	-1.6478	-1.0223
360	---	---	---	---	---

Table A-6c: Lagergren plot for the removal of 2,4dichlorophenol for different initial concentrations using CSAC
(pH=4, T=303 K, Dose=8g/l)

Time(min)	log (qe-q_t) (20 mg/l)	log (qe-q_t) (40 mg/l)	log (qe-q_t) (60 mg/l)	log (qe-q_t) (80 mg/l)	log (qe-q_t) (100 mg/l)
0	0	0	0	0	0
20	-0.2255	-0.4513	-0.0286	0.04287	-0.1374
30	-0.6752	-0.6262	-0.5193	-0.6454	-0.4513
60	-0.6701	-0.6676	-0.7299	-0.9946	-0.5376
120	-0.93	-0.6164	-0.7387	-1.0969	-0.7792
180	-0.984	-0.776	-0.9075	-1.2696	-1.5414
240	-1.3516	-1.4407	-1	-1.8239	-1.9031
360	---	---	---	---	---

Table A-6d: Lagergren plot for the removal of 2,4dichlorophenol for different initial concentrations using MAC
(pH=5, T=303 K, Dose=6g/l)

Time(min)	log (qe-q_t) (20 mg/l)	log (qe-q_t) (40 mg/l)	log (qe-q_t) (60 mg/l)	log (qe-q_t) (80 mg/l)	log (qe-q_t) (100 mg/l)
0	0	0	0	0	0
20	0.08279	0.24428	0.35483	-0.0531	0.40824
30	-0.1429	-0.4338	-0.0915	-0.8349	-0.2518
60	-0.1761	-0.4601	-0.2237	-0.8386	-0.3069
120	-0.4477	-0.9553	-0.5607	-0.6502	-0.5633
180	-0.6609	-1.2341	-0.8349	-0.6454	-0.6883
240	-1.4559	-1.5477	-0.699	-0.6383	-1.6642
360	---	---	---	---	---

Table A-6e: Lagergren plot for the removal of 2,4dichlorophenol for different initial concentrations using RHA
(pH=3, T=303 K, Dose=4g/l)

Time(min)	log (qe-q_t) (20 mg/l)	log (qe-q_t) (40 mg/l)	log (qe-q_t) (60 mg/l)	log (qe-q_t) (80 mg/l)	log (qe-q_t) (100 mg/l)
0	0	0	0	0	0
20	0.18291	0.4014	0.61093	0.76399	0.52634
30	-0.079	-0.231	-0.2165	-0.2557	-0.301
60	-0.1308	-0.3444	-0.3665	-0.4174	-0.6676
120	-0.1871	-0.3833	-0.3302	-0.5467	-0.4145
180	-0.4347	-0.6478	-1.4881	-0.6243	-0.93
240	-0.5607	-1.2403	-0.8097	-0.9893	-1.1249
360	---	---	---	---	---

Table A-7a: Pseudo second order kinetic plot for the removal of 2,4dichlorophenol for different initial concentrations using CAC (PH=4, T=303 K, Dose=8 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 (min.g/mg) (100 mg/l)
0	0	0	0	0	0
20	14.856	5.6859	5.8076	3.9216	4.7337
30	14.328	7.1386	5.772	5.059	4.7714
60	26.966	13.738	11.268	9.9834	9.1446
120	51.064	27.035	22.191	19.604	18.44
180	75.393	38.982	33.012	29.173	26.831
240	98.436	51.668	43.508	38.71	36.09
360	146.94	77.399	64.865	57.6	53.343

Table A-7b: Pseudo second order kinetic plot for the removal of 2,4dichlorophenol for different initial concentrations using BFA (PH=3, T=303 K, Dose=12 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 (min.g/mg) (100 mg/l)
0	0	0	0	0	0
20	23.064	10.042	7.8585	6.0015	10.354
30	22.989	12.113	9.3313	8.6873	9.2166
60	44.637	23.522	18.005	17.225	17.721
120	86.228	45.86	35.294	33.582	35.165
180	129.08	66.939	52.313	49.988	51.699
240	171.08	88.67	70.45	66.025	68.539
360	254.42	131.87	104.5	98.428	100.09

Table A-7c: Pseudo second order kinetic plot for the removal of 2,4dichlorophenol for different initial concentrations using CSAC (PH=5, T=283 K, Dose=4 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 (min.g/mg) (100 mg/l)
0	0	0	0	0	0
20	15.826	8.8154	8.6721	9.0141	7.7108
30	18.209	12.573	10.204	9.6891	10.105
60	36.474	24.922	19.632	18.626	19.786
120	68.916	50.407	39.216	37.008	38.02
180	102.56	73.32	57.715	55.067	54.649
240	132.29	92.798	76.372	72.562	72.508
360	193.68	137.27	111.03	108.35	108.35

Table A-7d: Pseudo second order kinetic plot for the removal of 2,4dichlorophenol for different initial concentrations using MAC (pH=5, T=303 K, Dose=6g/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 (min.g/mg) (100 mg/l)
0	0	0	0	0	0
20	13.187	5.8224	8.9636	5.1999	5.0526
30	14.948	6.2219	8.1411	6.5431	5.035
60	29.126	12.388	15.394	13.083	9.9585
120	50.633	23.626	28.436	26.622	19.215
180	71.761	35.076	41.391	39.956	28.511
240	89.164	46.497	55.879	53.319	36.942
360	132.03	69.364	80.089	76.09	55.229

Table A-7e: Pseudo second order kinetic plot for the removal of 2,4dichlorophenol for different initial concentrations using RHA (PH=3, T=303 K, Dose=4 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 (min.g/mg) (100 mg/l)
0	0	0	0	0	0
20	7.601	3.7071	3.8741	3.937	2.2766
30	9.0327	4.0942	3.4732	2.9035	2.5762
60	17.57	8.0402	6.8066	5.7116	5.0293
120	34.237	15.997	13.671	11.317	10.204
180	47.525	23.407	19.539	16.901	14.966
240	61.856	30.544	26.403	22.253	19.884
360	86.643	45.483	38.94	33.065	29.642

Table A-8a: Weber Morris plot for the removal of 2,4dichlorophenol for different initial concentrations using CAC (pH=4, T=303 K, Dose=8 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)
0	0	0	0	0	0
4.47214	1.346	3.518	3.444	5.1	4.225
5.47723	2.094	4.203	5.198	5.93	6.288
7.74597	2.225	4.368	5.325	6.01	6561
10.9545	2.35	4.439	5.408	6.121	6.508
13.4164	2.388	4.618	5.453	6.17	6.709
15.4919	2.438	4.645	5.516	6.2	6.65
18.9737	2.45	4.651	5.55	6.25	6.749

Table A-8b: Weber Morris plot for the removal of 2,4dichlorophenol for different initial concentrations using BFA (pH=3, T=303 K, Dose=12 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)
0	0	0	0	0	0
4.47214	0.867	1.992	2.545	3.333	1.932
5.47723	1.305	2.477	3.215	3.453	3.255
7.74597	1.344	2.551	3.333	3.483	3.386
10.9545	1.392	2.617	3.4	3.573	3.413
13.4164	1.395	2.689	3.441	3.601	3.482
15.4919	1.403	2.707	3.407	3.635	3.502
18.9737	1.415	2.73	3.445	3.658	3.597

Table A-8c: Weber Morris plot for the removal of 2,4dichlorophenol for different initial concentrations using CSAC (pH=4, T=303K, Dose=8g/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)
0	0	0	0	0	0
4.47214	1.264	2.269	2.306	2.219	2.594
5.47723	1.648	2.386	2.94	3.096	2.969
7.74597	1.645	2.408	3.056	3.221	3.033
10.9545	1.741	2.381	3.06	3.243	3.156
13.4164	1.755	2.455	3.119	3.269	3.294
15.4919	1.814	2.586	3.143	3.308	3.31
18.9737	1.859	2.623	3.243	3.323	3.323

Table A-8d: Weber Morris plot for the removal of 2,4dichlorophenol for different initial concentrations using MAC (pH=5, T=303 K, Dose=6 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)
0	0	0	0	0	0
4.47214	1.517	3.435	2.231	3.846	3.958
5.47723	2.007	4.822	3.685	4.585	5.958
7.74597	2.06	4.843	3.898	4.586	6.025
10.9545	2.37	5.079	4.22	4.508	6.245
13.4164	2.508	5.132	4.349	4.505	6.313
15.4919	2.692	5.162	4.295	4.501	6.497
18.9737	2.727	5.19	4.495	4.731	6.518

Table A-8e: Weber Morris plot for the removal of 2,4dichlorophenol for different initial concentrations using RHA (pH=3, T=303 K, Dose=4 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)
0	0	0	0	0	0
4.47214	2.631	5.395	5.163	5.08	8.785
5.47723	3.321	7.328	8.638	10.333	11.645
7.74597	3.415	7.463	8.815	10.505	11.93
10.9545	3.505	7.501	8.778	10.604	11.76
13.4164	3.788	7.69	9.213	10.65	12.028
15.4919	3.88	7.858	9.09	10.785	12.07
18.9737	4.155	7.915	9.245	10.888	12.145

Table A-9a: Bangham's plot for the removal of 2,4dichlorophenol for different initial concentrations using CAC (pH=4, T=303K, Dose=8g/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)
1.301	0.129	0.5463	0.5371	0.7075	0.6258
1.4771	0.3209	0.6235	0.7158	0.7731	0.7985
1.7782	0.3473	0.6402	0.7263	0.7788	0.8169
2.0792	0.3711	0.6473	0.7331	0.7868	0.8134
2.2553	0.378	0.6644	0.7366	0.7902	0.8266
2.3802	0.387	0.6669	0.7416	0.7923	0.8228
2.5563	0.3892	0.6675	0.7443	0.7958	0.8292

Table A9b: Bang ham's plot for the removal of 2,4dichlorophenol for different initial concentrations using BFA (pH=3 T=303 K, Dose=12 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)
1.301	-0.0619	0.2992	0.4057	0.5228	0.286
1.4771	0.1156	0.3939	0.5071	0.5382	0.5125
1.7782	0.1283	0.4067	0.5228	0.5419	0.5296
2.0792	0.1436	0.4178	0.5314	0.553	0.5331
2.2553	0.1445	0.4295	0.5366	0.5564	0.5418
2.3802	0.1471	0.4324	0.5368	0.5605	0.5443
2.5563	0.1507	0.4361	0.5372	0.5632	0.5559

Table A-9cBang ham's plot for the removal of 2,4dichlorophenol for different initial concentrations using CSAC (pH=4 T= 303k Dose=8g/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)
1.301	0.1017	0.3558	0.3628	0.3461	0.4139
1.4771	0.2169	0.3776	0.4683	0.4908	0.4726
1.7782	0.2161	0.3816	0.4851	0.5079	0.4818
2.0792	0.2407	0.3767	0.4857	0.5109	0.4991
2.2553	0.2442	0.39	0.494	0.5144	0.5177
2.3802	0.2586	0.4126	0.4973	0.5195	0.5198
2.5563	0.2692	0.4187	0.5109	0.5215	0.5215

Table A-9d Bangham's plot for the removal of 2,4dichlorophenol for different initial concentrations using MAC (pH=5 T=303k Dose=6 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)
1.301	0.1809	0.5359	0.3485	0.585	0.5974
1.4771	0.3025	0.6832	0.5664	0.6613	0.7751
1.7782	0.3138	0.6851	0.5908	0.6614	0.7799
2.0792	0.3747	0.7057	0.6253	0.6539	0.7955
2.2553	0.3993	0.7102	0.6383	0.6536	0.8002
2.3802	0.43	0.7128	0.6329	0.6533	0.8127
2.5563	0.4356	0.7151	0.6527	0.6749	0.8141

Table A-9eBang ham's plot for the removal of 2,4dichlorophenol for different initial concentrations using RHA (pH=3 T=303 Dose=4g/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)
1.301	0.4201	0.7319	0.7129	0.7058	0.9437
1.4771	0.5212	0.8649	0.9364	1.0142	1.0661
1.7782	0.5333	0.8729	0.9452	1.0213	1.0766
2.0792	0.5446	0.8751	0.9433	1.0254	1.0704
2.2553	0.5784	0.8859	0.9644	1.0273	1.0801
2.3802	0.5888	0.8953	0.9585	1.0328	1.0817
2.5563	0.6185	0.8984	0.9659	1.0369	1.0844

Table A-10a: Effect of temperature on removal of 2,4dichlorophenol by CAC (pH=4, Dose=8 g/l, t=6 hr, C_o=50 mg/l)

Time (min)	283 K	303 K	323 K
	Q_t (mg/g)	Q_t (mg/g)	Q_t (mg/g)
10	1.62375	2.1253	2.15625
20	3.28875	3.444	3.672
30	4.80675	5.186	5.19525
60	5.06325	5.325	5.60625
120	5.1555	5.408	5.718
240	5.17125	5.516	5.7435
360	5.31375	5.550	5.7795

Table A-10b: Effect of temperature on removal of 2,4dichlorophenol by BFA
(pH=3, Dose=12 g/l, t=6 hr, C_o=50 mg/l)

Time (min)	283 K	303 K	323 K
	Q_t (mg/g)	Q_t (mg/g)	Q_t (mg/g)
10	1.265	1.132	1.157
20	2.445	2.455	2.4935
30	2.766	3.215	3.762
60	2.9125	3.333	3.875
120	3.023	3.400	3.960
240	3.085	3.441	3.990
360	3.105	3.845	4.00

Table A-10c: Effect of temperature on removal of 2,4dichlorophenol by CSAC
(pH=4, Dose=8 g/l, t=6 hr, C_o=50 mg/l)

Time (min)	283 K	303 K	323 K
	Q_t (mg/g)	Q_t (mg/g)	Q_t (mg/g)
10	0.87	1.187	1.22925
20	1.82625	2.306	2.979
30	2.3625	2.940	3.46875
60	2.6445	3.056	3.615
120	2.8605	3.060	3.74025
240	2.94375	3.143	3.78
360	3.0375	3.243	3.84975

Table A-10d: Effect of temperature on removal of 2,4dichlorophenol by RHA (pH=3 Dose=4 g/l, t=6 hr, C_o=50 mg/l)

Time (min)	283 K	303 K	323 K
	Q_t (mg/g)	Q_t (mg/g)	Q_t (mg/g)
10	2.3835	2.864	3.012
20	6.831	5.163	5.2065
30	7.5375	8.138	8.1795
60	7.695	8.815	8.898
120	7.86	8.778	9.198
240	7.9995	9.090	9.372
360	8.1015	9.245	9.4875

Table A-10e: Effect of temperature on removal of 2,4dichlorophenol by MAC (pH=5, Dose=6g/l, t=4 hr, C_o=50 mg/l)

Time (min)	283 K	303 K	323 K
	Q_t (mg/g)	Q_t (mg/g)	Q_t (mg/g)
10	1.425	1.967	2.101
20	4.485	4.645	4.852
30	4.965	6.987	7.562
60	5.174	7.625	7.725
120	5.278	7.703	7.83
240	5.388	7.745	7.985
360	5.401	7.980	8.10

Table A-11a: Freundlich isotherm for the removal of 2,4dichlorophenol at different temperatures using CAC (pH=4, t= 6hr, Dose=8 g/l).

Initial Concentration (mg/l)	283 K		303 K		323 K	
	ln Q_e	ln C_e	ln Q_e	ln C_e	ln Q_e	ln C_e
20	0.81093	0.69315	0.87025	-0.1054	0.89609	-0.9163
40	1.40168	2.049	1.53687	1.02604	1.56025	0.62701
60	1.65033	2.90854	1.66771	2.8679	1.76835	2.57338
80	1.75527	3.51809	1.77834	3.4837	1.84245	3.38439
100	1.76747	3.97312	1.82938	3.9122	1.96361	3.90197

Table A-11b: Freundlich isotherm for the removal of 2,4dichlorophenol at different temperatures using BFA (pH=3, t= 6 hr, Dose=12 g/l).

Initial Concentration (mg/l)	283 K		303 K		323 K	
	ln Q_e	ln C_e	ln Q_e	ln C_e	ln Q_e	ln C_e
20	0.27003	1.43508	0.34713	1.10526	0.35767	1.02819
40	1.02245	1.88099	0.99325	1.97962	1.08519	1.49962
60	1.1314	3.12676	1.23547	2.92638	1.38629	2.48491
80	1.22847	3.66356	1.29473	3.58657	1.4061	3.43399
100	1.44692	3.89182	1.49082	3.93183	1.59127	3.71357

Table A-11c: Freundlich isotherm for the removal of 2,4dichlorophenol at different temperatures using CSAC (pH=4, t= 6 hr, Dose=8 g/l).

Initial Concentration (mg/l)	283 K		303 K		323 K	
	$\ln Q_e$	$\ln C_e$	$\ln Q_e$	$\ln C_e$	$\ln Q_e$	$\ln C_e$
20	0.54985	1.81417	0.61519	1.63511	0.66783	1.4816
40	1.0936	2.78006	1.16627	2.65676	1.28785	2.3979
60	1.13943	3.55535	1.30968	3.41313	1.34807	3.37417
80	1.25276	3.95124	1.34077	3.90036	1.39872	3.90399
100	1.32176	4.2485	1.44338	4.19147	1.58658	4.10923

Table A-11d: Freundlich isotherm for the removal of 2,4 dichlorophenol at different temperatures using MAC (pH=5, t= 6 hr, Dose=6 g/l).

Initial Concentration (mg/l)	283 K		303 K		323 K	
	$\ln Q_e$	$\ln C_e$	$\ln Q_e$	$\ln C_e$	$\ln Q_e$	$\ln C_e$
20	0.96317	1.45395	1.00063	1.29198	1.02962	1.06471
40	1.15902	2.48491	1.64673	2.18155	1.56025	1.62701
60	1.6864	3.31745	1.79009	3.36867	1.76835	2.57338
80	1.79176	3.78872	1.84182	3.74123	1.8718	3.713357
100	1.82294	4.14091	1.87457	4.10907	1.9373	4.06044

Table A-11e: Freundlich isotherm for the removal of 2,4 dichlorophenol at different temperatures using RHA (pH=3, t= 6hr, Dose=4 g/l).

Initial Concentration (mg/l)	283 K		303 K		323 K	
	ln C_e	ln Q_e	ln Q_e	ln C_e	ln Q_e	ln C_e
20	1.33237	1.39933	1.44692	1.09861	1.45862	1.02962
40	2.30259	2.0149	2.06876	2.12106	2.10108	1.98787
60	3.3322	2.07944	2.19165	3.17889	2.24601	3.10009
80	3.68888	2.30259	2.33336	3.64936	2.43361	3.54962
100	4.04305	2.37491	2.51729	3.92039	2.55529	3.88568

Table A-12a: Langmuir isotherm for the removal of 2,4dichlorophenol at different temperatures using CAC (pH=4, t= 6 hr, Dose=8 g/l).

Initial Concentration (mg/l)	283 K		303 K		323 K	
	C_e	C_e/Q_e	C_e	C_e/Q_e	C_e	C_e/Q_e
20	2	0.888889	0.9	0.376963	0.4	0.163265
40	7.5	1.846381	2.79	0/6	1.872	0.393277
60	18.33	3519112	17.6	3.320755	13.11	2.236743
80	33.72	5.828868	32.58	5.503378	29.5	4.67638
100	53.15	9.076161	50.01	8.027287	49.5	6.947368

Table A-12b: Langmuir isotherm for the removal of 2,4dichlorophenol at different temperatures using BFA (pH=3, t= 6 hr, Dose=12g/l).

Initial Concentration (mg/l)	283 K		303 K		323 K	
	C_e	C_e/Q_e	C_e	C_e/Q_e	C_e	C_e/Q_e
20	4.2	3.206107	3.02	2.134276	2.796	1.1955245
40	6.56	2.359712	7.24	2.681481	4.48	1.513514
60	22.8	7.354839	18.66	5.424419	12	3
80	39	11.41686	36.11	9.893151	31	7.598039
100	49	11.52941	51	12.49082	41	8.350305

Table A-12c: Langmuir isotherm for the removal of 2,4dichlorophenol at different temperatures using CSAC (pH=4 t= 6 hr, Dose=8g/l).

Initial Concentration (mg/l)	283 K		303 K		323 K	
	C_e	C_e/Q_e	C_e	C_e/Q_e	C_e	C_e/Q_e
20	6.136	0.54985	5.13	2.772973	4.4	2.25641
40	16.12	5.400335	14.25	4.439252	11	3.034483
60	35	11.2	30.36	8.194332	29.2	7.584416
80	52	14.85714	49.42	12.9304	49.6	12.24691
100	70	18.66667	66.12	15.61275	60.9	12.46163

Table A-12d: Langmuir isotherm for the removal of 2,4dichlorophenol at different temperatures using MAC (pH=5, t= 6 hr, Dose=6 g/l).

Initial Concentration (mg/l)	283 K		303 K		323 K	
	C_e	C_e/Q_e	C_e	C_e/Q_e	C_e	C_e/Q_e
20	4.28	1.633588	3.64	1.338235	2.9	1.035714
40	12	2.575107	8.86	1.707129	8.72	1.393277
60	27.59	5.109259	29.04	4.84808	13.11	2.236743
80	44.2	7.366667	42.15	6.681991	41	6.307692
100	62.86	10.15509	60.89	9.341823	58	8.357349

Table A-12e: Langmuir isotherm for the removal of 2,4 dichlorophenol at different temperatures using RHA (pH=3, t= 6 hr, Dose=4 gm/l).

Initial Concentration (mg/l)	283 K		303 K		323 K	
	C_e	C_e/Q_e	C_e	C_e/Q_e	C_e	C_e/Q_e
20	3.79	0.935225	3	0.705882	2.8	0.651163
40	10	1.33333	8.34	1.053696	7.3	0.892966
60	28	3.5	24.02	2.683799	22.2	2.349206
80	40	4	38.45	3.728485	34.8	3.052632
100	57	5.302326	50.42	4.067769	48.7	3.782524

Table A-13a: Temkin isotherm for the removal of 2,4dichlorophenolat different temperatures using CAC (pH=4, t= 6 hr, Dose=8g/l).

Initial Concentration (mg/l)	283 K		303 K		323 K	
	Qe	ln Ce	Qe	ln Ce	Qe	ln Ce
20	2.25	0.69315	2.3875	-0.1054	2.45	-0.9163
40	4.062	2.0149	4.65	1.02604	4.76	0.62701
60	5.2087	2.90854	5.3	2.8679	5.8612	2.57338
80	5.785	3.51809	5.92	3.4837	6.312	3.38439
100	5.856	3.97312	6.23	3.91222	7.125	3.90197

Table A-13b: Temkin isotherm for the removal of 2,4dichlorophenolat different temperatures using BFA (pH=3, t= 6 hr, Dose=12 g/l).

Initial Concentration (mg/l)	283 K		303 K		323 K	
	Qe	ln Ce	Qe	ln Ce	Qe	ln Ce
20	1.31	1.43508	1.415	1.10526	1.43	1.02819
40	2.78	1.88099	2.7	1.97962	2.96	1.49962
60	3.1	3.12676	3.44	2.92638	4	2.48491
80	3.416	3.66356	3.65	3.58657	4.08	3.43399
100	4.25	3.89182	4.083	3.93183	4.91	3.71357

Table A-13c: Temkin isotherm for the removal of 2,4dichlorophenol at different temperatures using CSAC (pH=4, t= 6 hr, Dose=8g/l).

Initial Concentration (mg/l)	283 K		303 K		323 K	
	Qe	ln Ce	Qe	ln Ce	Qe	ln Ce
20	1.733	1.81417	1.85	0.61519	1.95	1.4816
40	2.985	2.78006	3.21	2.65676	3.625	2.3979
60	3.125	3.55535	3.705	3.41313	3.85	3.37417
80	3.5	3.95124	3.822	3.90036	4.05	3.90399
100	3.75	4.2485	4.235	4.19147	4.887	4.10923

Table A-13d: Temkin isotherm for the removal of 2,4dichlorophenol at different temperatures using MAC (pH=5, t= 6 hr, Dose=6 g/l).

Initial Concentration (mg/l)	283 K		303 K		323 K	
	Qe	ln Ce	Qe	ln Ce	Qe	ln Ce
20	2.62	1.45395	2.72	1.29198	2.8	1.06471
40	4.66	2.48491	5.19	2.18155	4.76	0.62701
60	5.4	3.31745	5.99	3.36867	5.862	2.57338
80	6	3.78872	6.308	3.74123	6.5	3.71357
100	6.19	4.14091	6.518	4.10907	6.94	4.06044

Table A-13e: Temkin isotherm for the removal of 2,4dichlorophenol at different temperatures using RHA (pH=3, t= 6hr, Dose=4 g/l).

Initial Concentration (mg/l)	**283 K**		**303 K**		**323 K**	
	Qe	**ln Ce**	**Qe**	**ln Ce**	**Qe**	**ln Ce**
20	4.0525	1.33237	4.25	1.09861	4.3	1.02962
40	7.5	2.30259	7.915	2.12106	8.175	1.98787
60	8	3.3322	8.95	3.17889	9.45	3.10009
80	10	3.68888	10.3125	3.64936	11.4	3.54962
100	10.75	4.04305	12.395	3.92039	12.875	3.88568

APPENDIX – B

Fig B -1: Scanning electron micrograph of CAC before adsorption at 1000 X Magnification

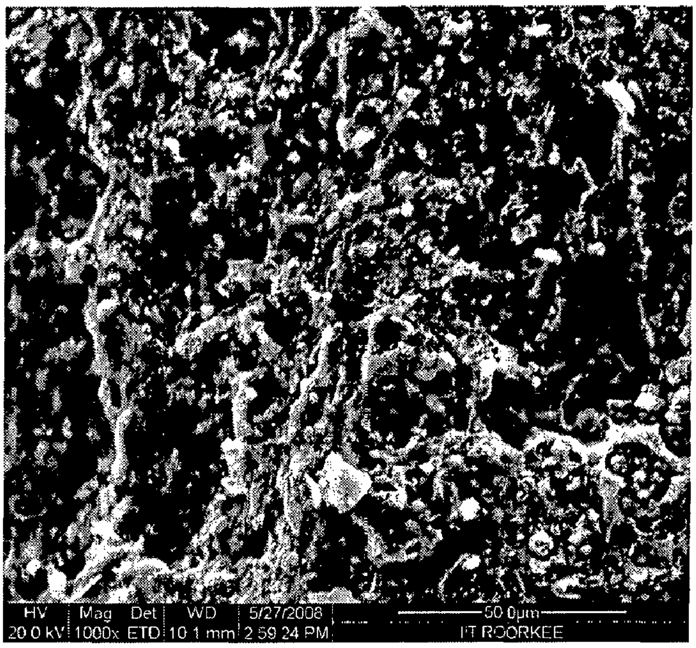


Fig B - 2: Scanning electron micrograph of CAC after adsorption at 1000 X magnification

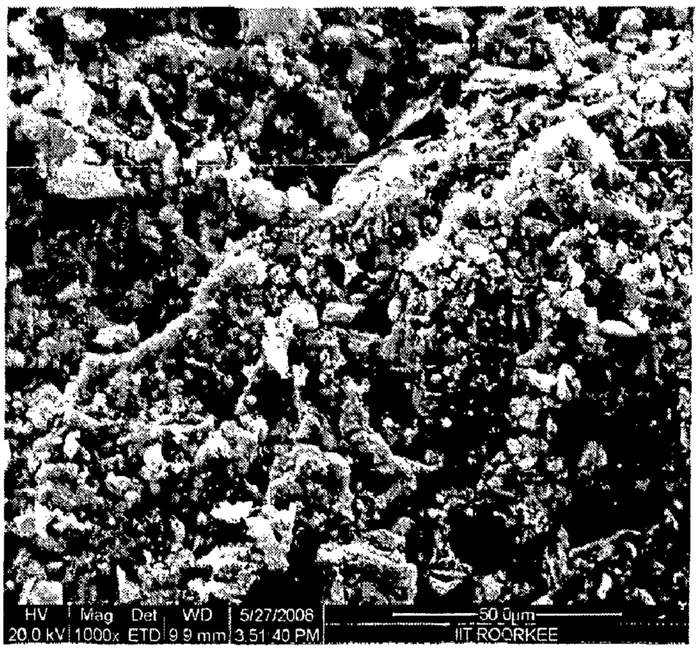


Fig B -3: Scanning electron micrograph of BFA before adsorption at 1000 X Magnification

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

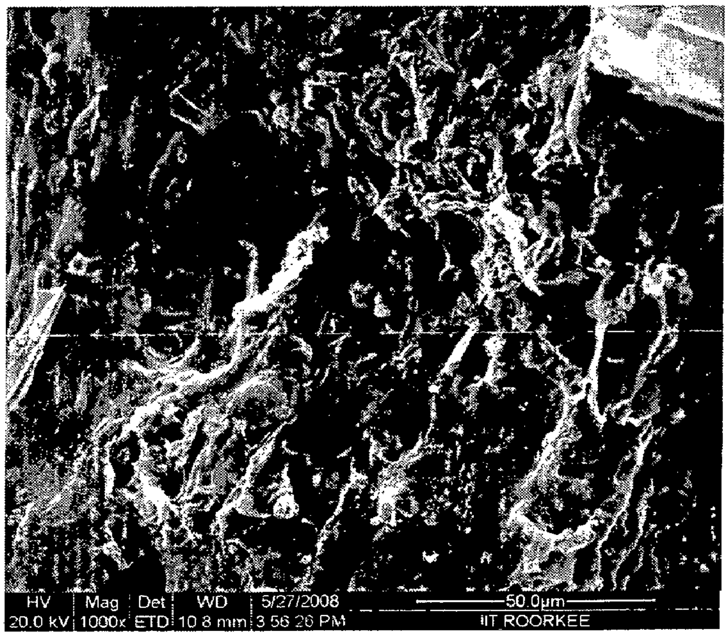


Fig B -5: Scanning electron micrograph of CSAC before adsorption at 2000 X Magnification

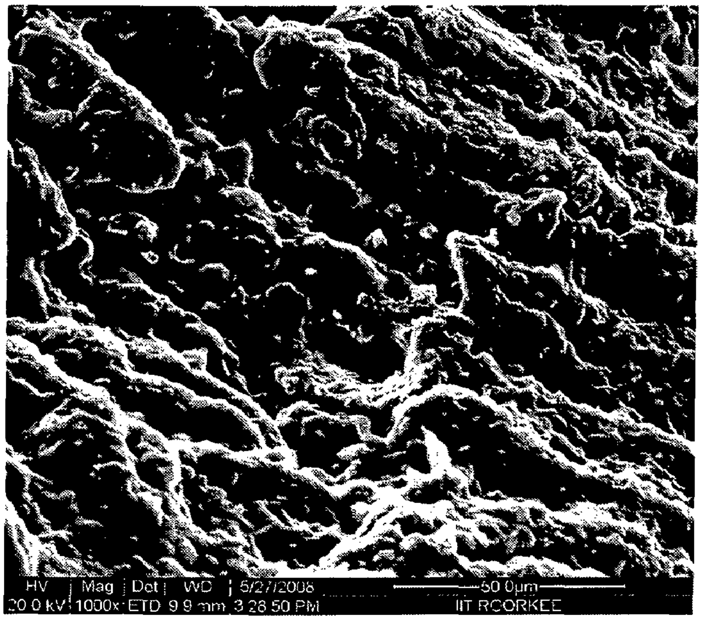


Fig B 6- : Scanning electron micrograph of CSAC after adsorption at 2000 X magnification

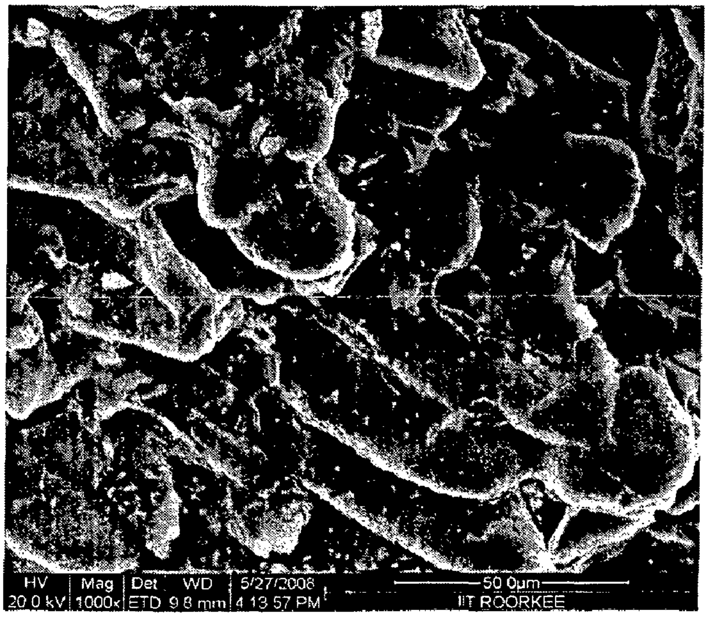


Fig B -7: Scanning electron micrograph of RHA before adsorption at 1000 X Magnification

Fig B - 8: Scanning electron micrograph of RHA after adsorption at 1000 X magnification

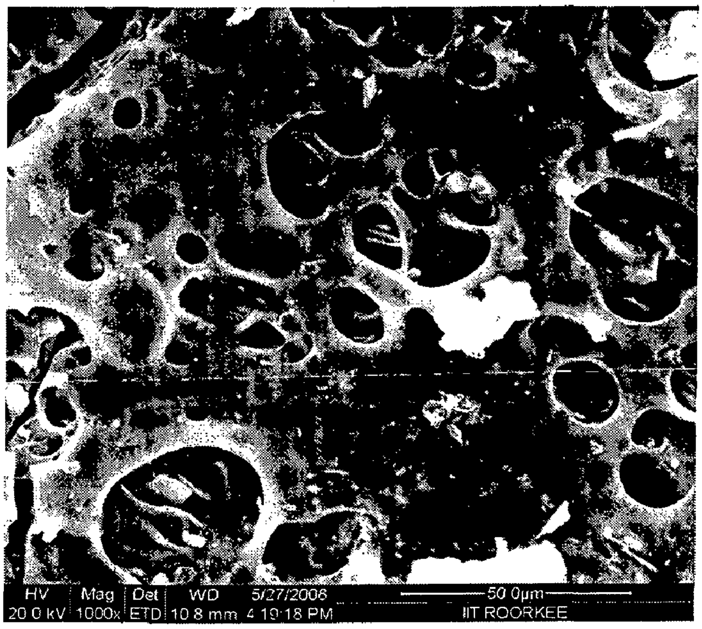
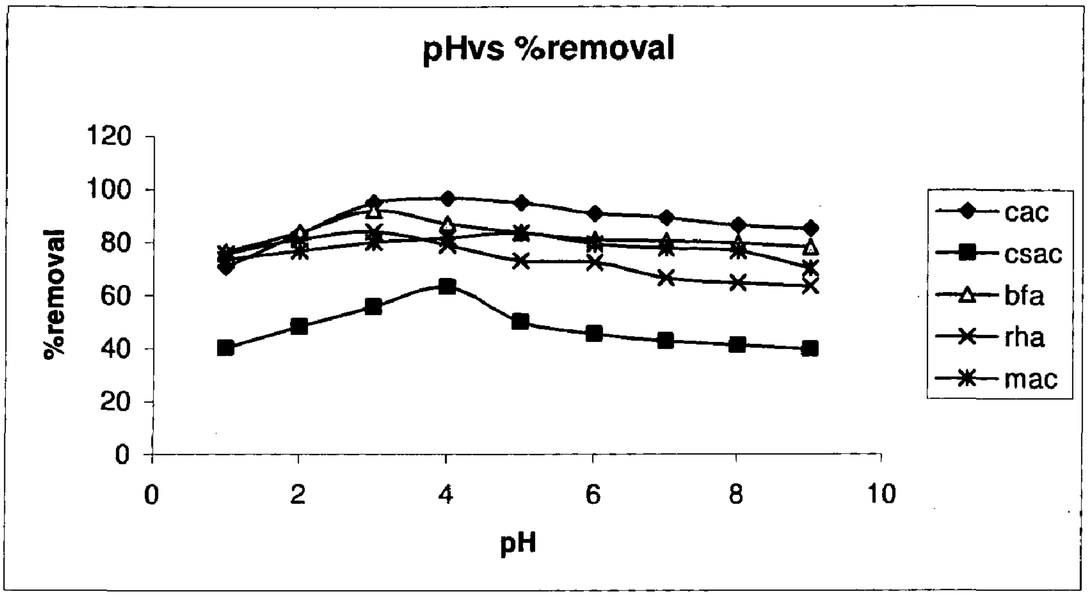
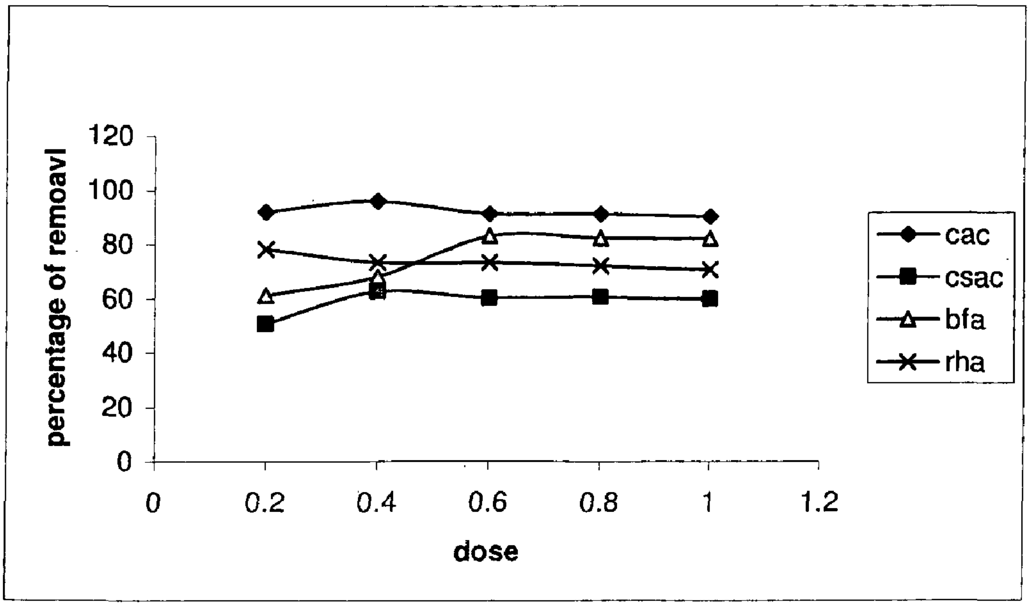


Fig. B – 9.: Effect of pH_0 on the adsorption of 2,4dcp using CSAC,MAC,CSAC,BFA,RHA as an adsorbent (T = 303K, t =6 h, C_0 = 50 mg /l,).



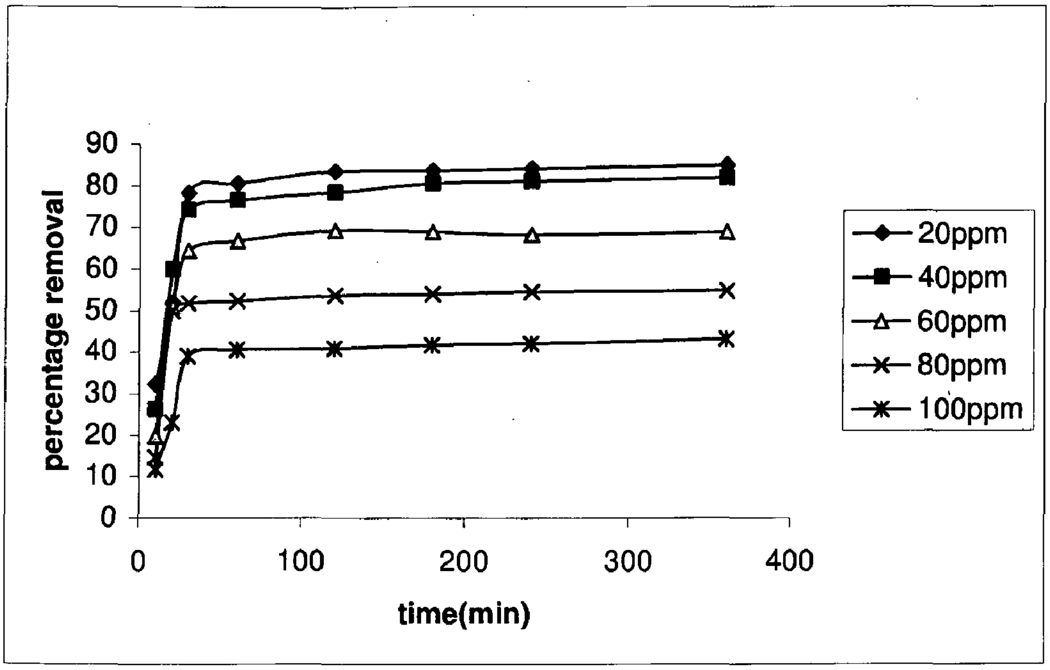
Percentage removal vs pH

Fig. B10 -.: Effect of adsorbent dose on the adsorption of 2,4dcpusing CAC,BFA, CSAC, RHA, MAC as an adsorbent



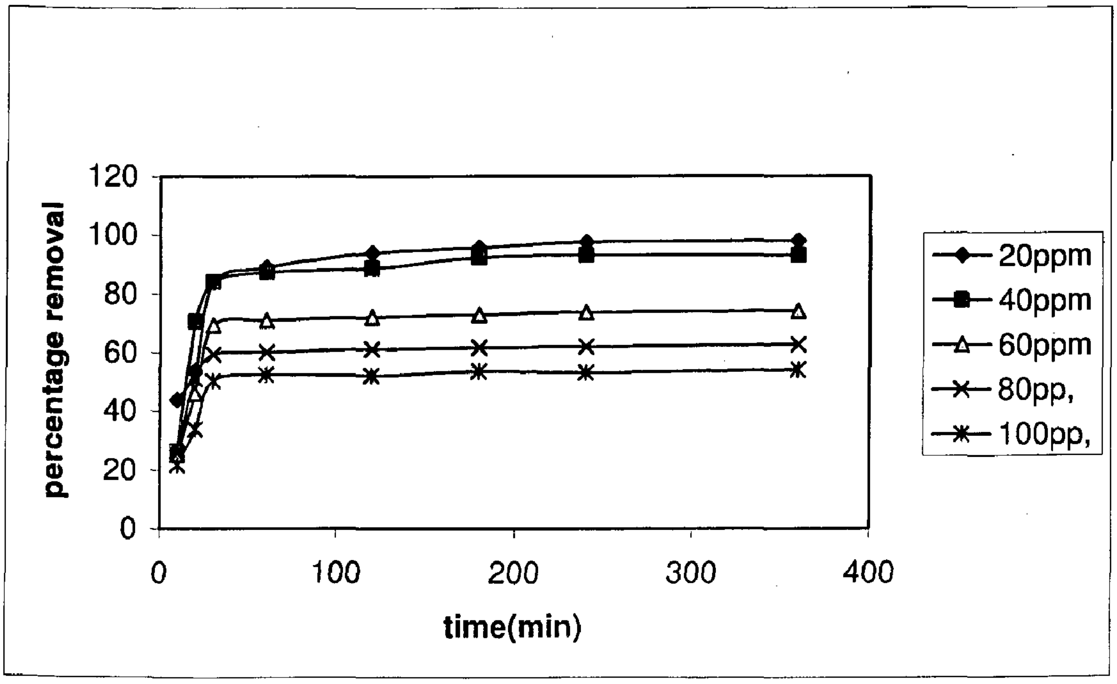
Comparison of all adsorbents

Fig. B 11a.: Effect of contact time and initial concentration on the adsorption of 2,4dcpusing BFA as an adsorbent
(T = 303K, t =6 h, C_0 = 60 mg /l, pH=3,CAC dose =12g /l).



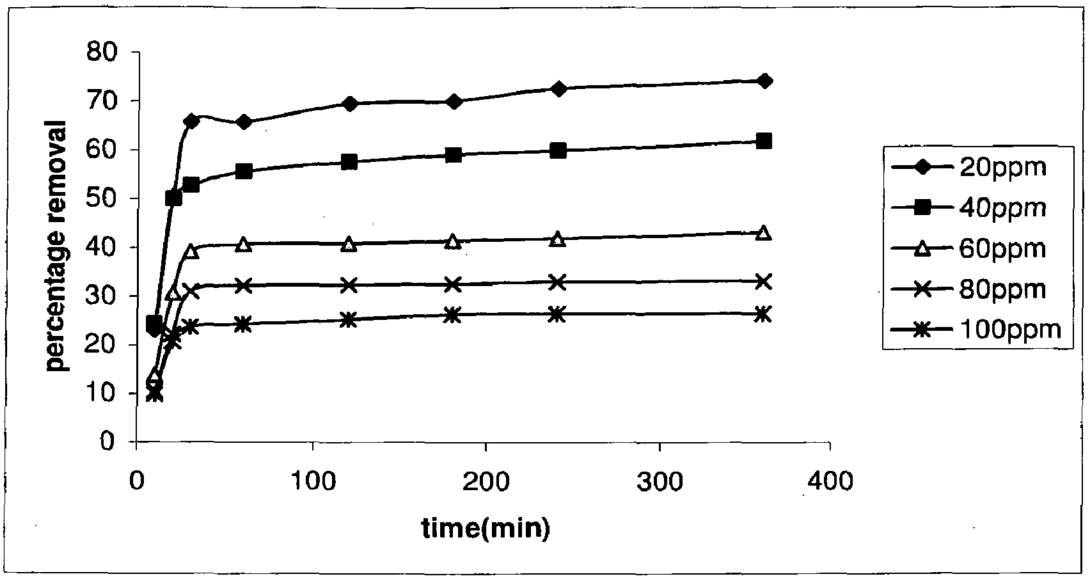
Percentage removal as a function of time and initial concentration

Fig. B 11b.: Effect of contact time and initial concentration on the adsorption of 2,4dcpusing CAC as an adsorbent
(T = 303K, t =6 h, C_0 = 60 mg /l, pH=4,CAC dose =8 g /l)

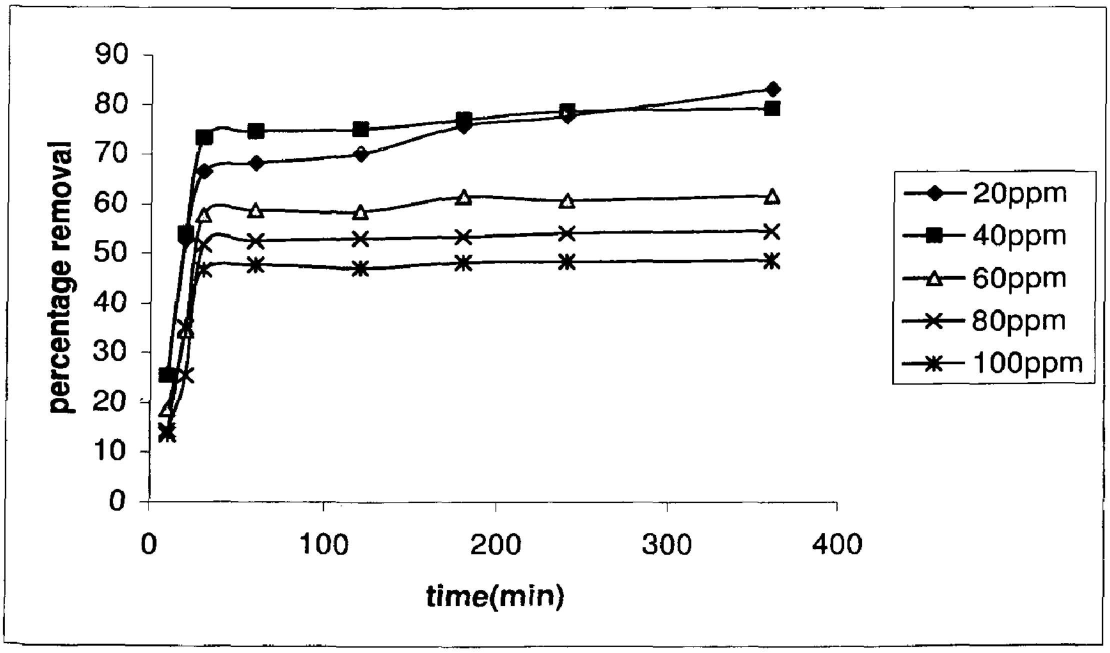


Percentage removal as a function of time and initial concentratin

Fig. B11c .: Effect of contact time and initial concentration on the adsorption of 2,4dcp using CSAC as an adsorbent
(T = 303K, t =6 h, C_0 = 60 mg /l, pH=4,CSAC dose =8 g /l).

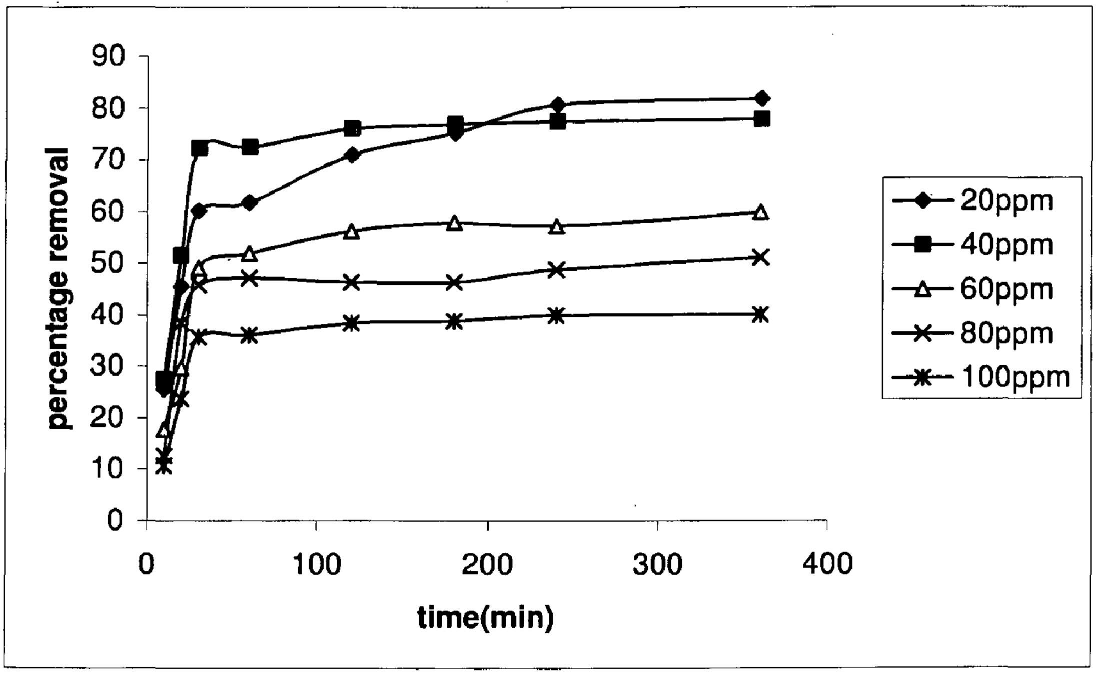


Percentage removal as a function of time and initial concentration
Fig. B 11d.: Effect of contact time and initial concentration on the adsorption of 2,4dcp using RHA as an adsorbent
(T = 303K, t =6 h, C_0 = 60 mg /l, pH=3 RHA dose =4 g /l)



Percentage removal as a function of time and initial concentration

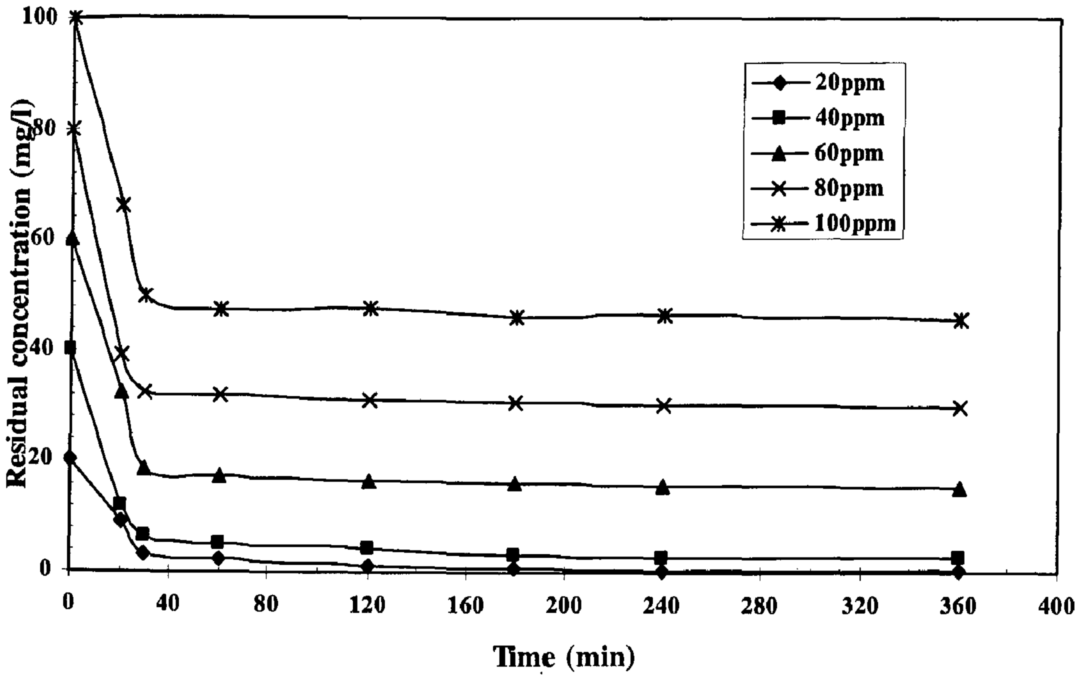
Fig. B11e .: Effect of contact time and initial concentration on the adsorption of 2,4dcp using MAC as an adsorbent
(T = 303K, t =6 h, C_0 = 60 mg /l, pH=5 MAC dose =6 g /l)



Percentage removal as a function of time and initial concentration.

Fig. B12a .: Effect of contact time and residual concentration on the adsorption of 2,4dcpusing CAC an adsorbent

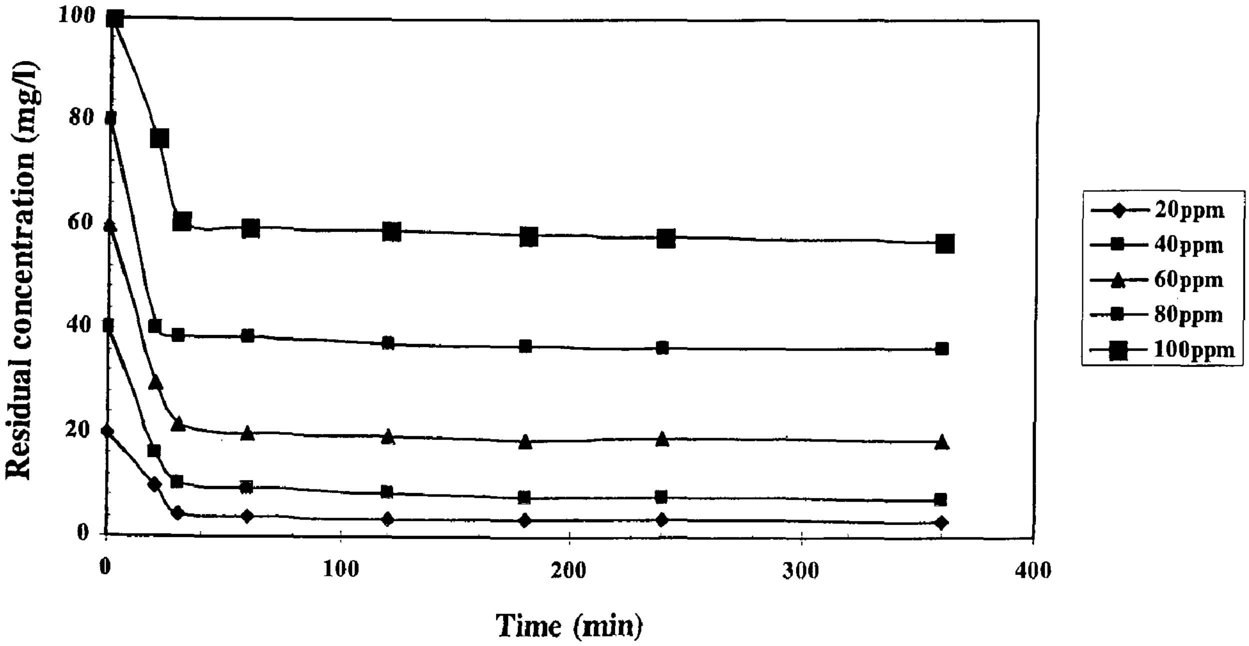
(T = 303K, t =6 h, C_0 = 50 mg /l, pH=4CAC dose =8 g



/l

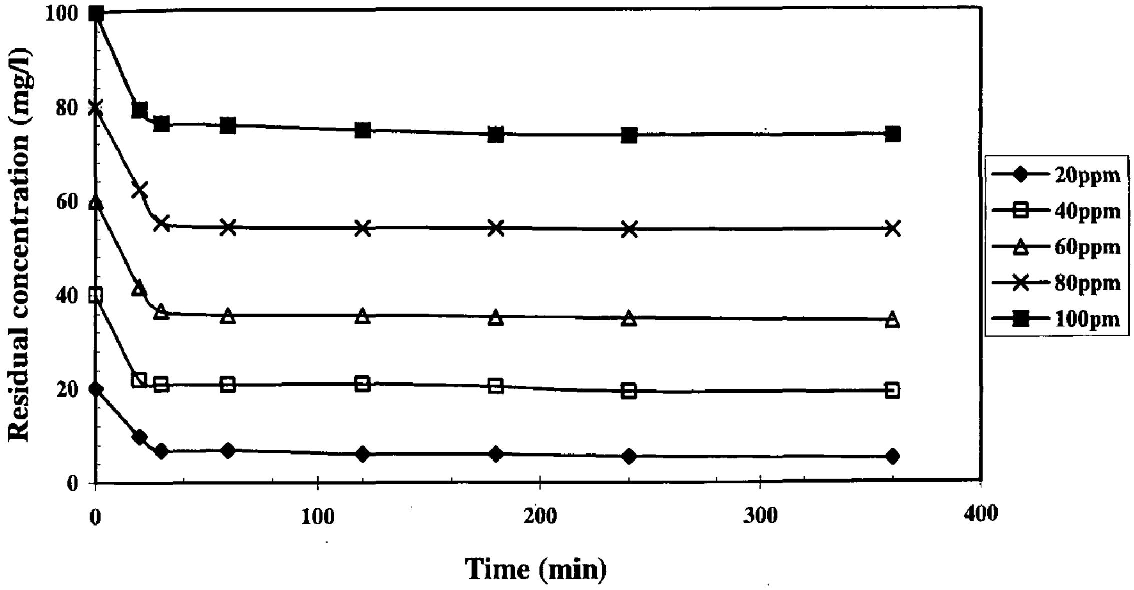
Fig. B12b .: Effect of contact time and residual concentration on the adsorption of 2,4dcpusing BFA as an adsorbent

(T = 303K, t =6 h, C_0 = 60 mg /l, pH=3 CAC dose =12g /l).



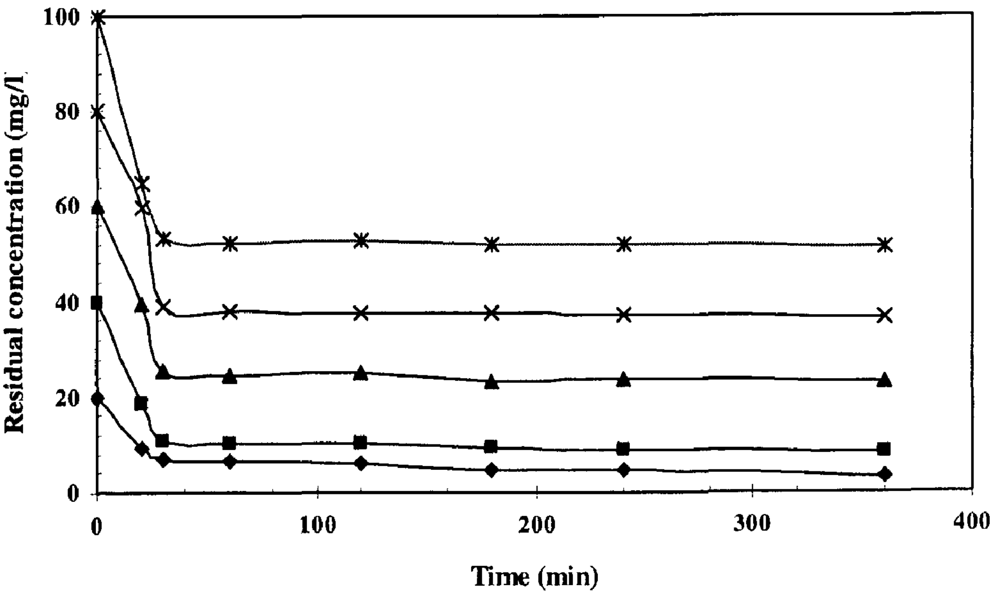
Effect of contact time on removal

Fig. 12c .: Effect of contact time and residual concentration on the adsorption of 2,4dcpusing CSAC as an adsorbent
(T = 303K, *t* =6 h, C_0 = 60 mg /l, pH=4,CSAC dose =8 g /l).



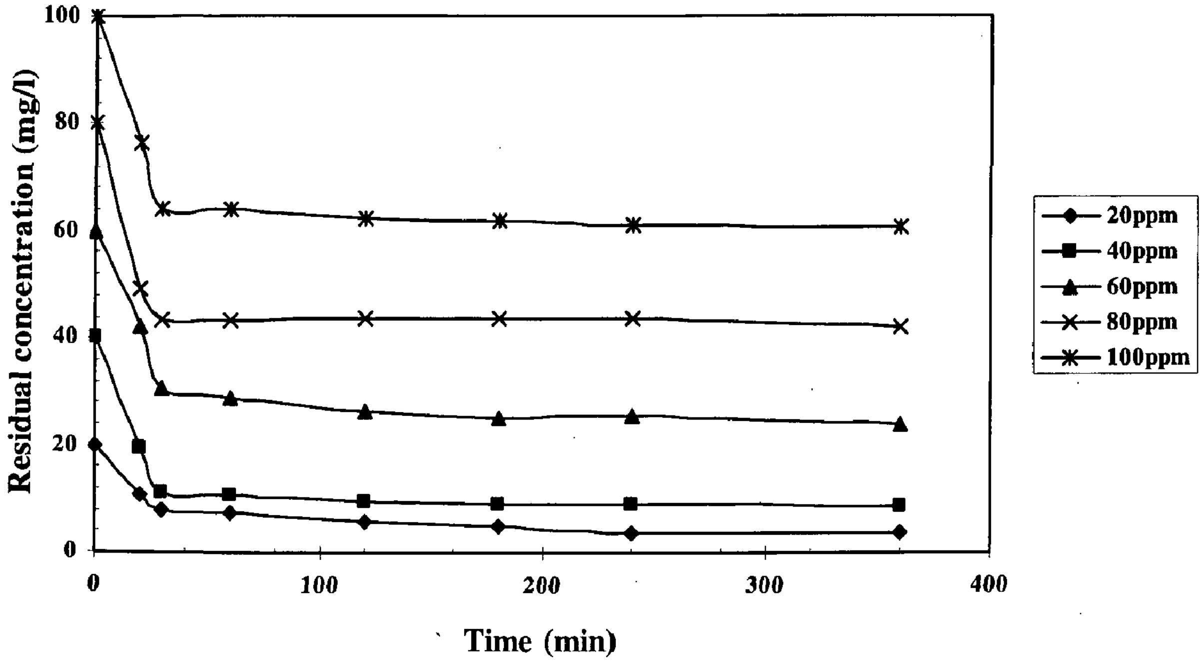
Effect of contact time on removal

Fig. B12d .: Effect of contact time and residual concentration on the adsorption of 2,4dcpusing RHA as an adsorbent
(T = 303K, *t* =6 h, C_0 = 60 mg /l, pH=3RHA dose =4 g /l



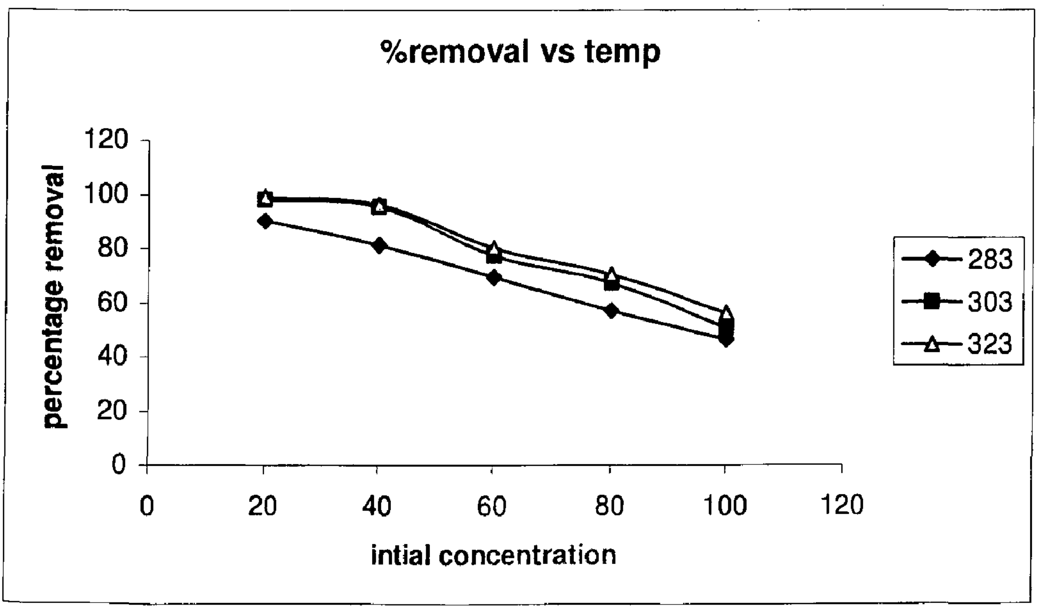
Effect of contact time on removal

Fig. B12e .: Effect of contact time and residual concentration on the adsorption of 2,4dcp using MAC as an adsorbent
(T = 303K, *t* =6 h, C_0 = 60 mg /l, pH= dose=6g/l)



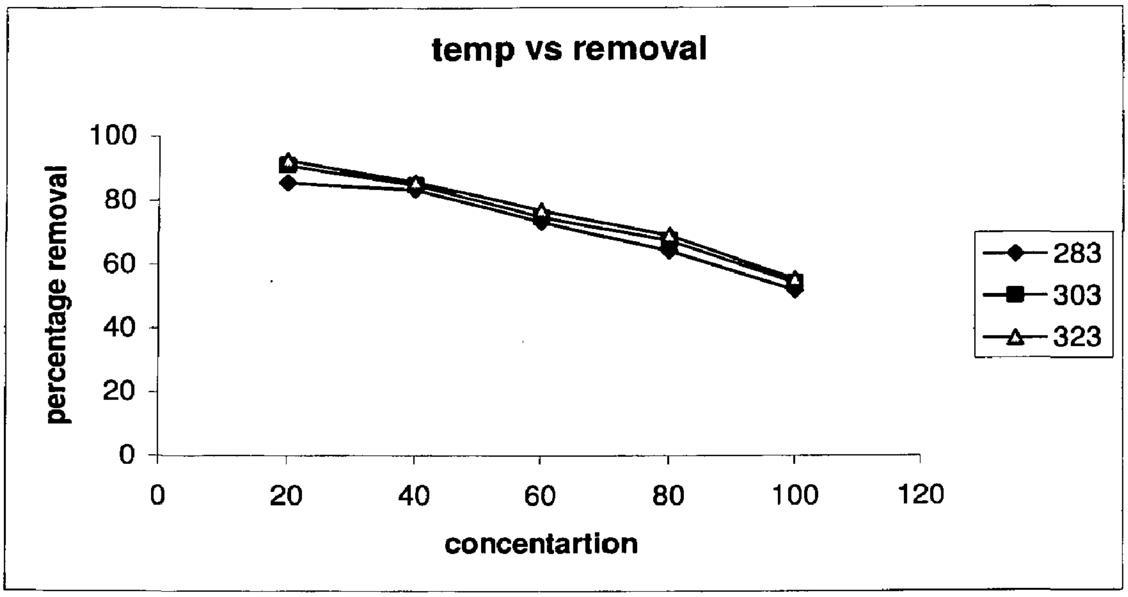
Effect of contact time on removal

Fig. B13a : Effect of temperature on removal of 2,4dcpby using CAC
(*t* = 6 h, pH=5, dose=8g/l).



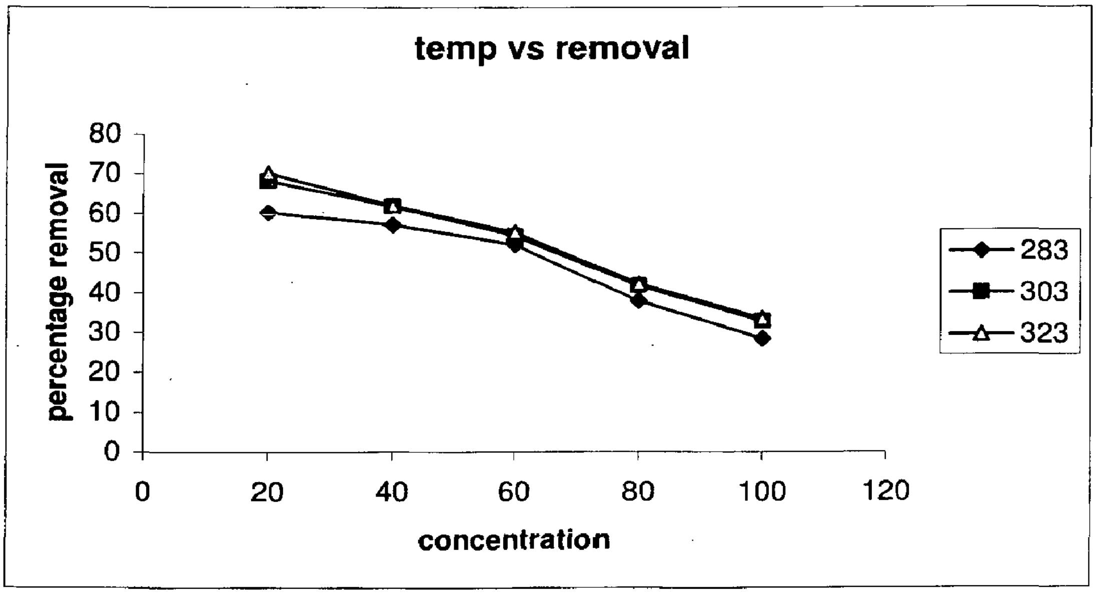
Removal as a function of temperature

Fig. B13b -: Effect of temperature on removal of 2,4dcpby using BFA
(t = 6 h, pH=3, dose=12g/l).



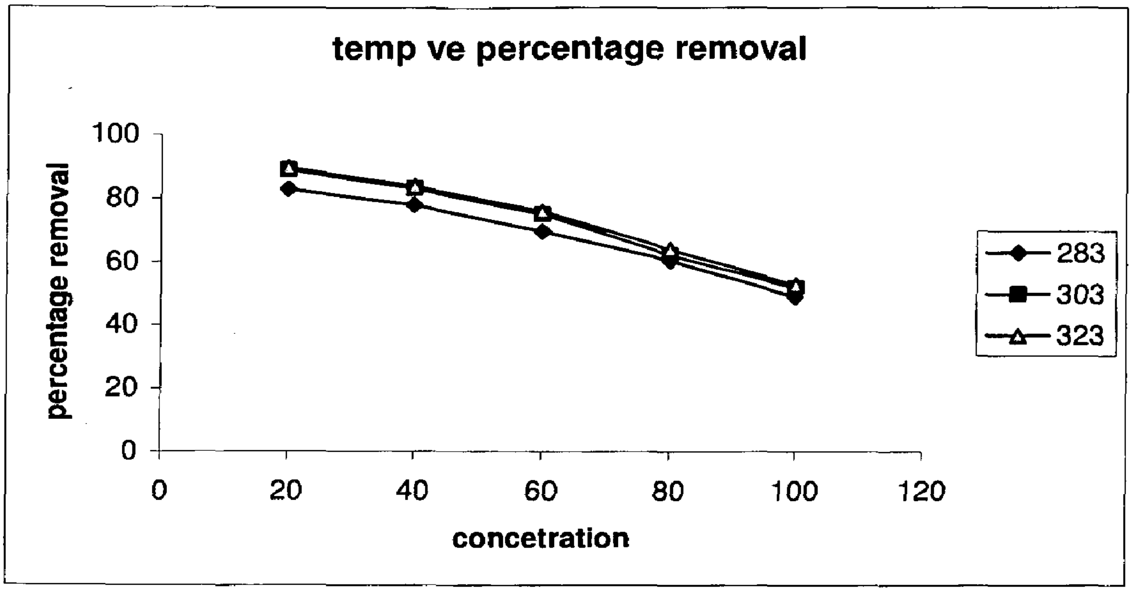
Removal as a function of temperature

Fig. B13c -: Effect of temperature on removal of 2,4dcpby using CSAC
(t = 6 h, pH=4, dose=8 g/l).



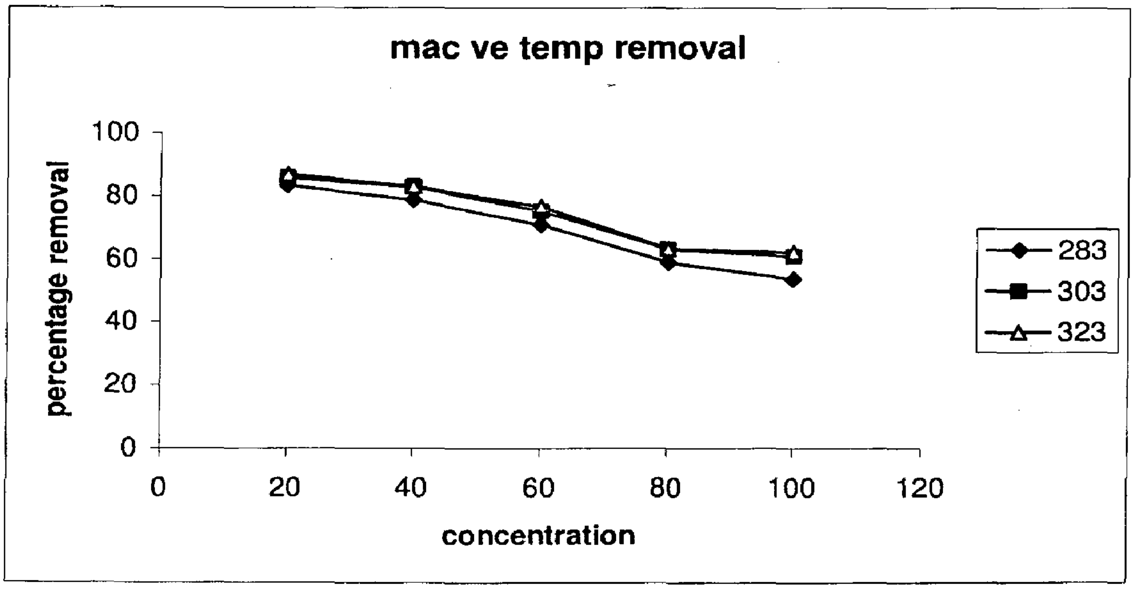
Removal as a function of temperature

Fig. B13d -: Effect of temperature on removal of 2,4dcpby using RHA
(*t* = 6 h, pH=3, dose=4 g/l).



Removal as a function of temperature

Fig. B13e -: Effect of temperature on removal of 2,4dcpby using MAC
(*t* = 6 h, pH=5, dose=6 g/l).



Removal as a function of temperature

Fig. B 14a-: Pseudo - First Order Kinetics for the removal of 2,4dcpfor CAC
(T= 303 K, dose =8 g/l, pH=4, t=6h).

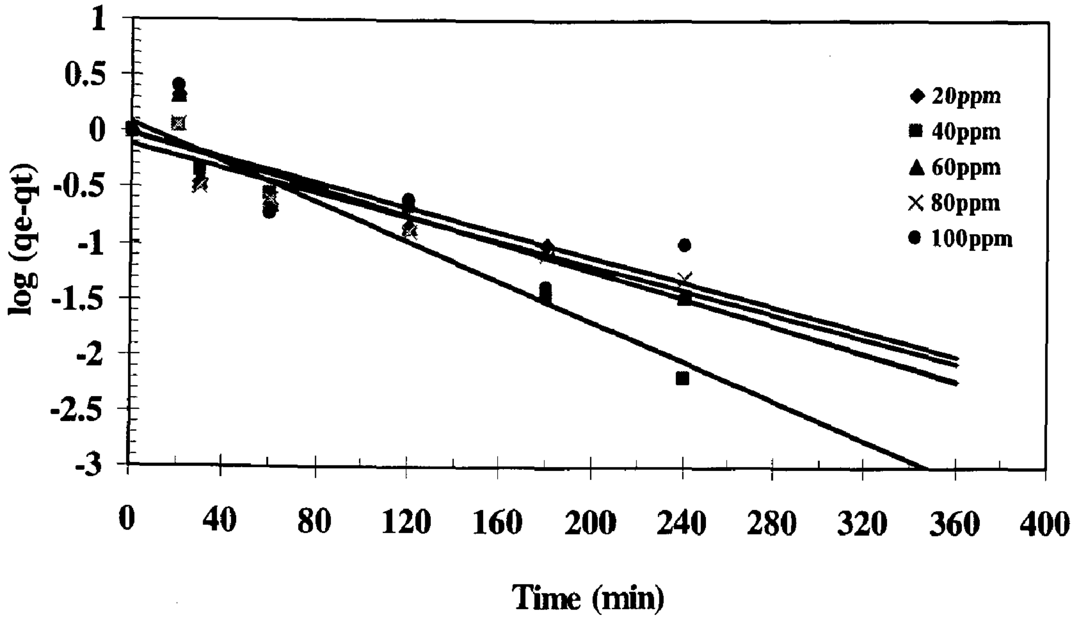


Fig. B14b -: Pseudo - First Order Kinetics for the removal of 2,4dcpfor BFA
(T= 303 K, dose =12 g/l, pH=3, t=6h).

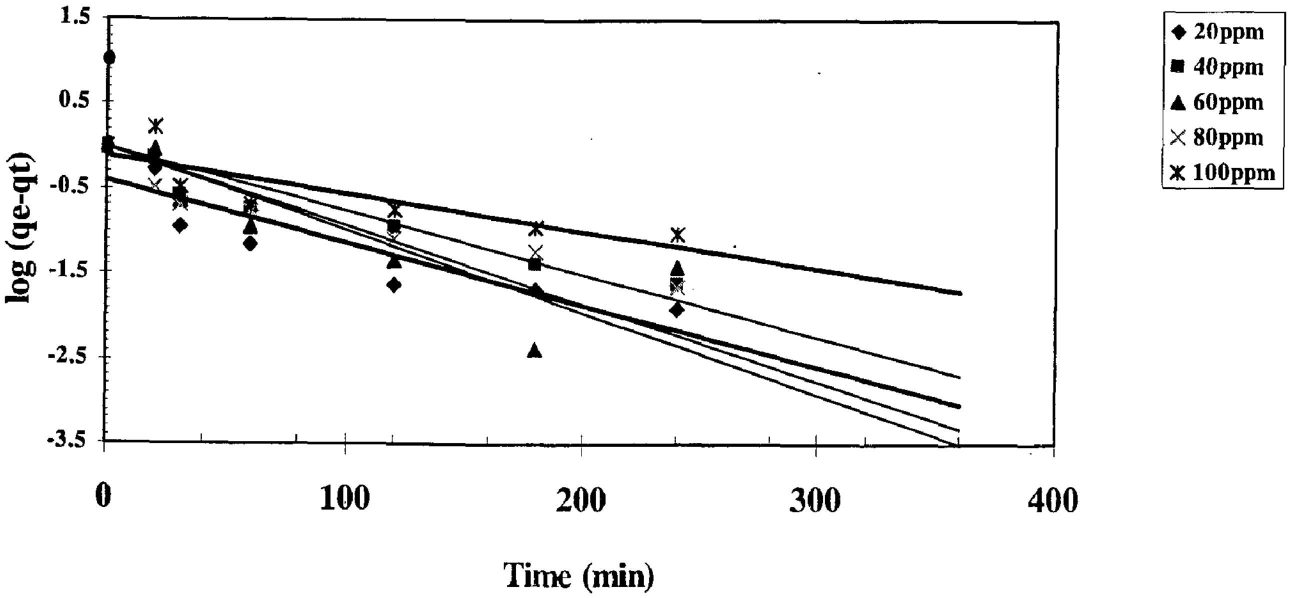


Fig. B14c -: Pseudo - First Order Kinetics for the removal of 2,4dcpfor CSAC
(T= 303 K, dose =8 g/l, pH=4, t=6h).

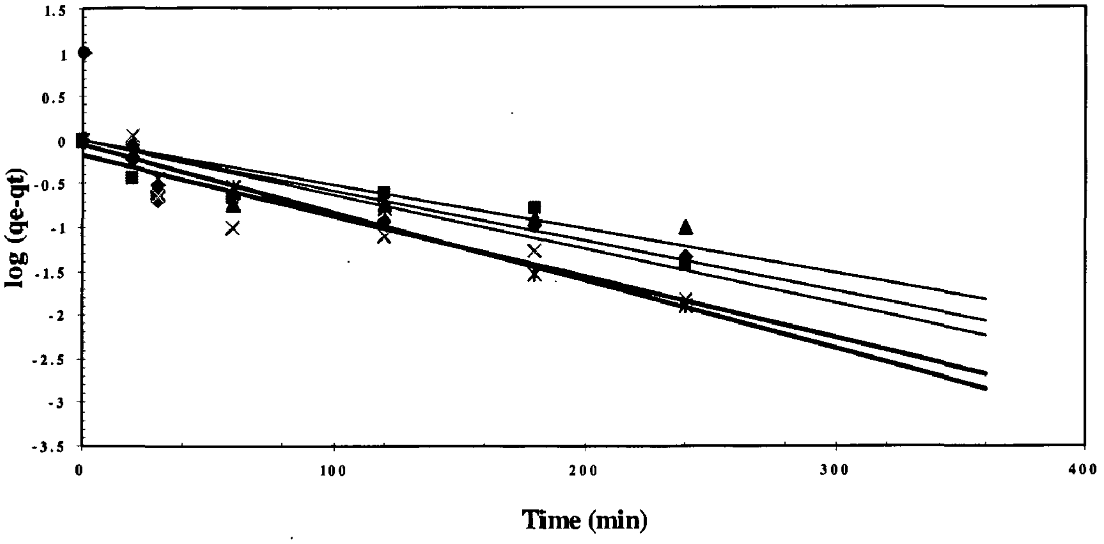


Fig. B14d -: Pseudo - First Order Kinetics for the removal of 2,4dcpfor RHA
(T= 303 K, dose =4 g/l, pH=3, t=6h).

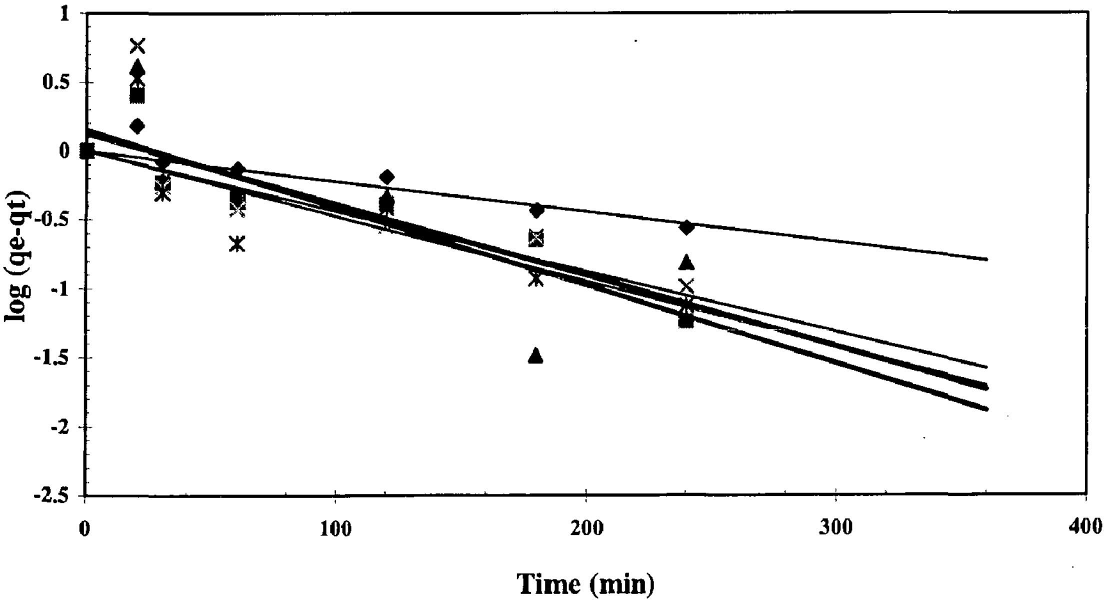


Fig. B14e -: Pseudo - First Order Kinetics for the removal of 2,4dcpfor MAC
(T= 303 K, dose =4 g/l, pH=3, t=6h).

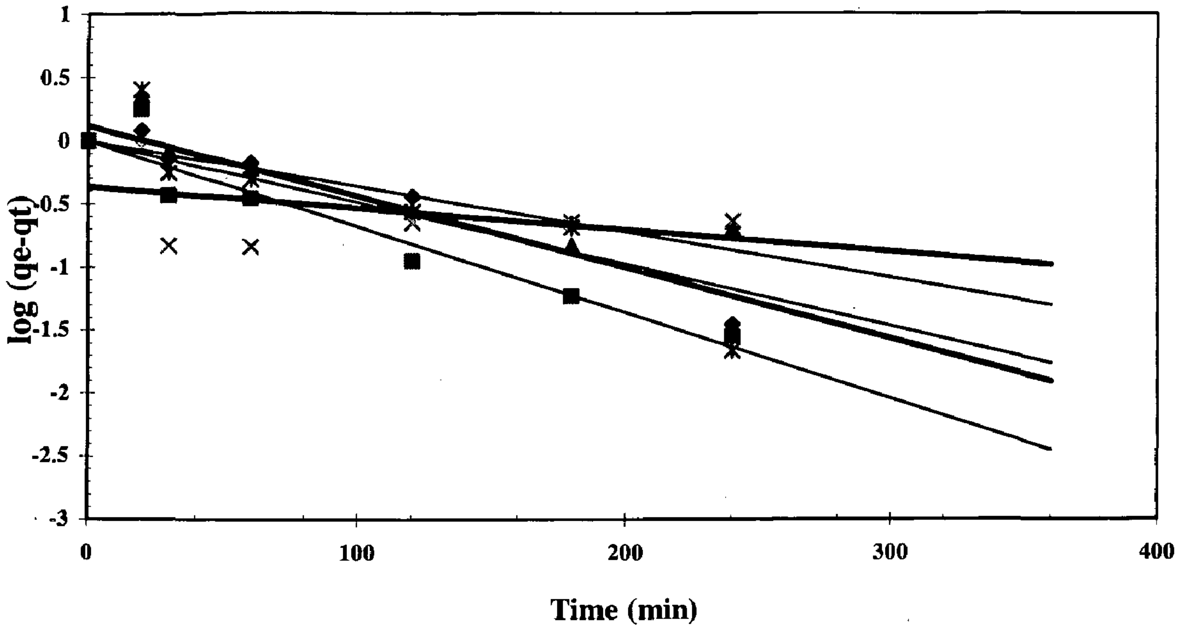


Fig. B15a - : Pseudo - Second Order Kinetics for the removal of 2,4dcpfor CAC
(T= 303 K, dose =4 g/l, pH=4, t=6h).

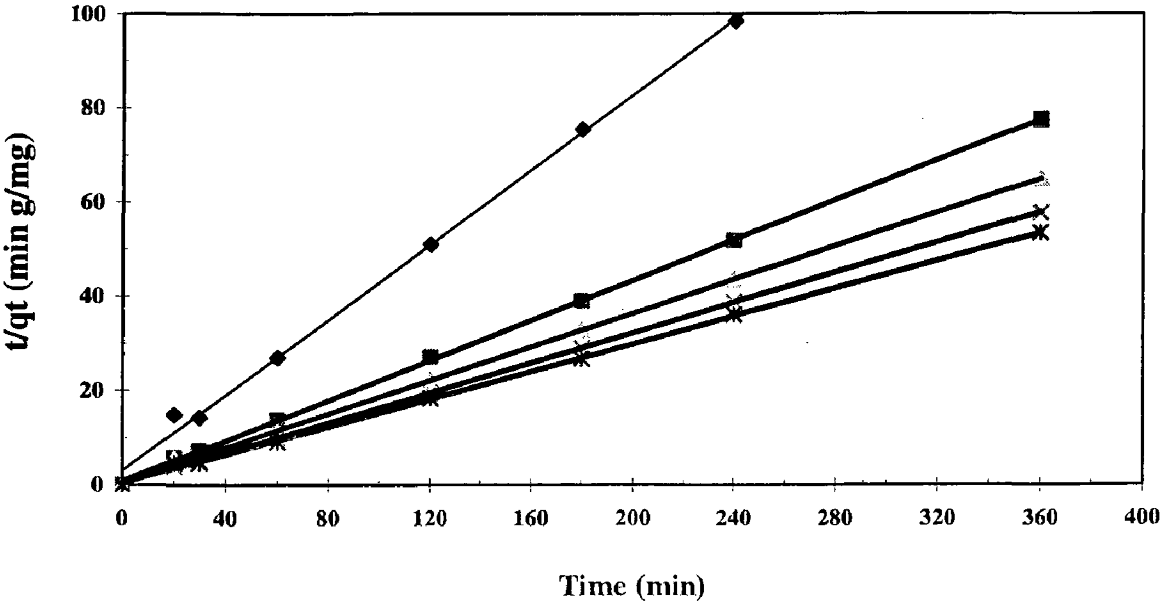


Fig. 8: Pseudo second-order kinetic plots

Fig. B 15b- : Pseudo - Second Order Kinetics for the removal of 2,4DCPfor BFA
(T= 303 K, dose =12 g/l, pH=3, t=6h).

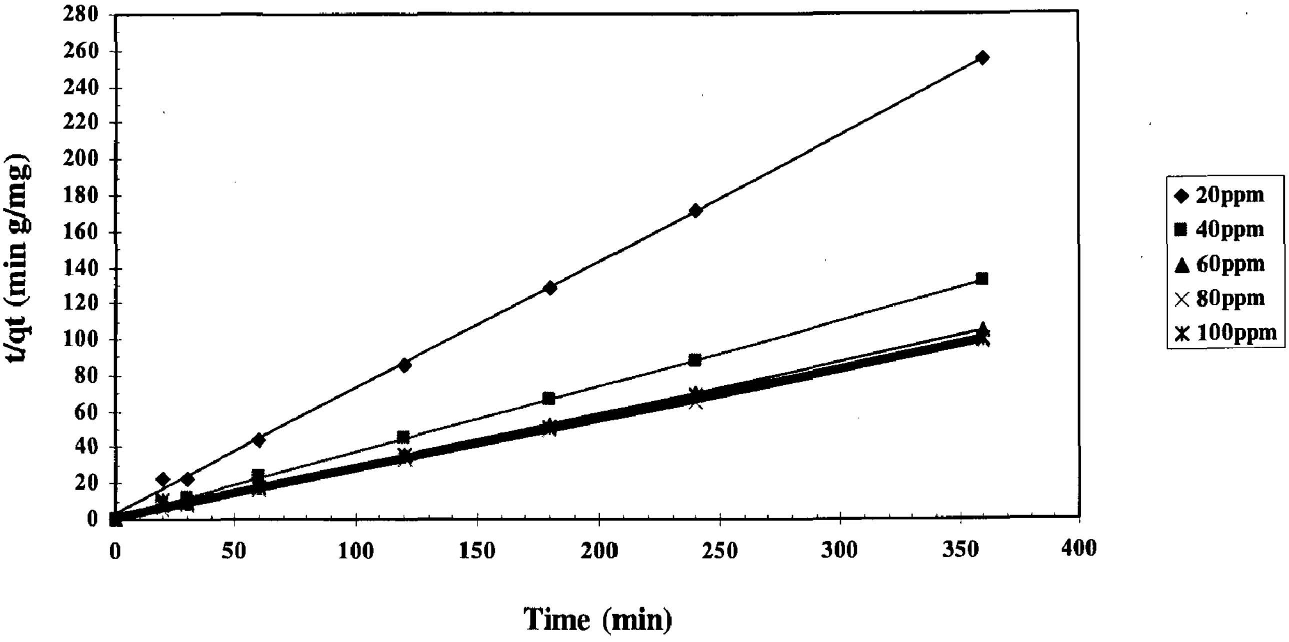
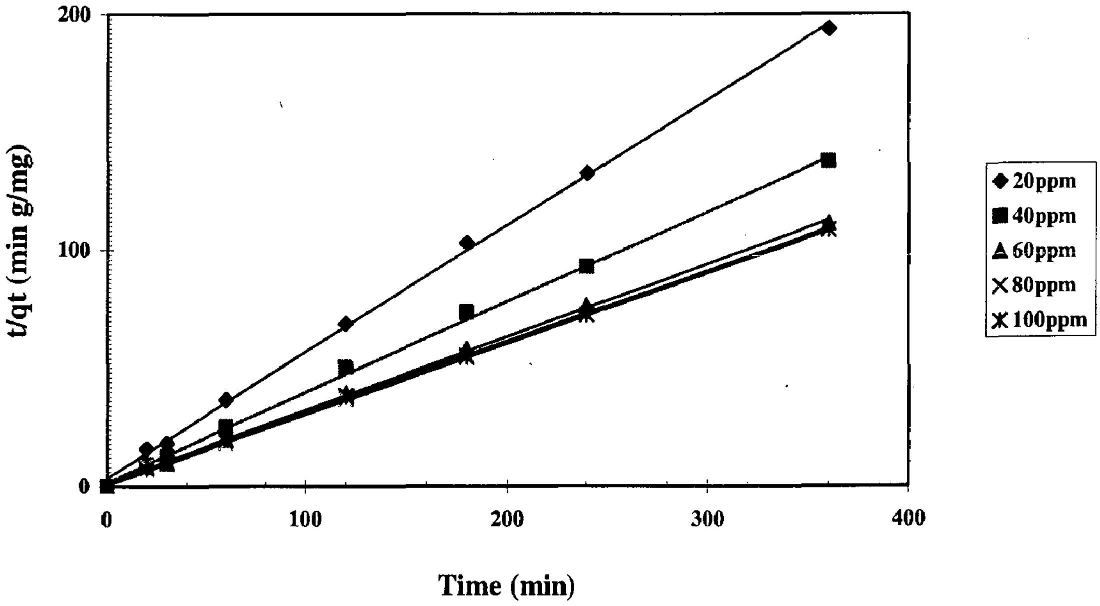


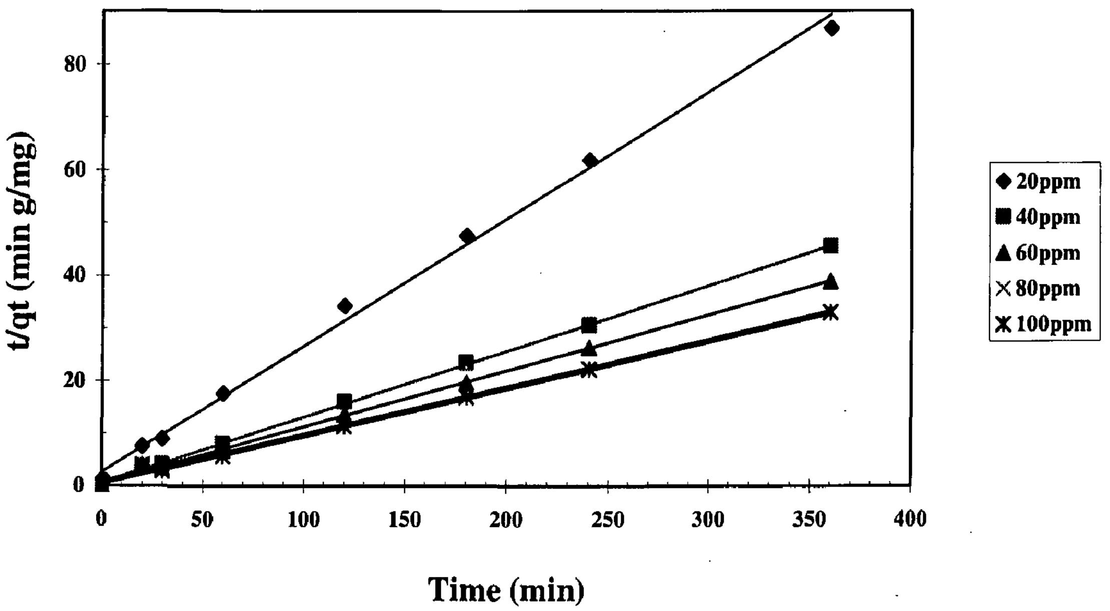
Fig. 8: Pseudo second-order kinetic plots

Fig. B15c - : Pseudo - Second Order Kinetics for the removal of 2,4dcpforCSAC
(T= 303 K, dose =8 g/l, pH=4, t=6h).



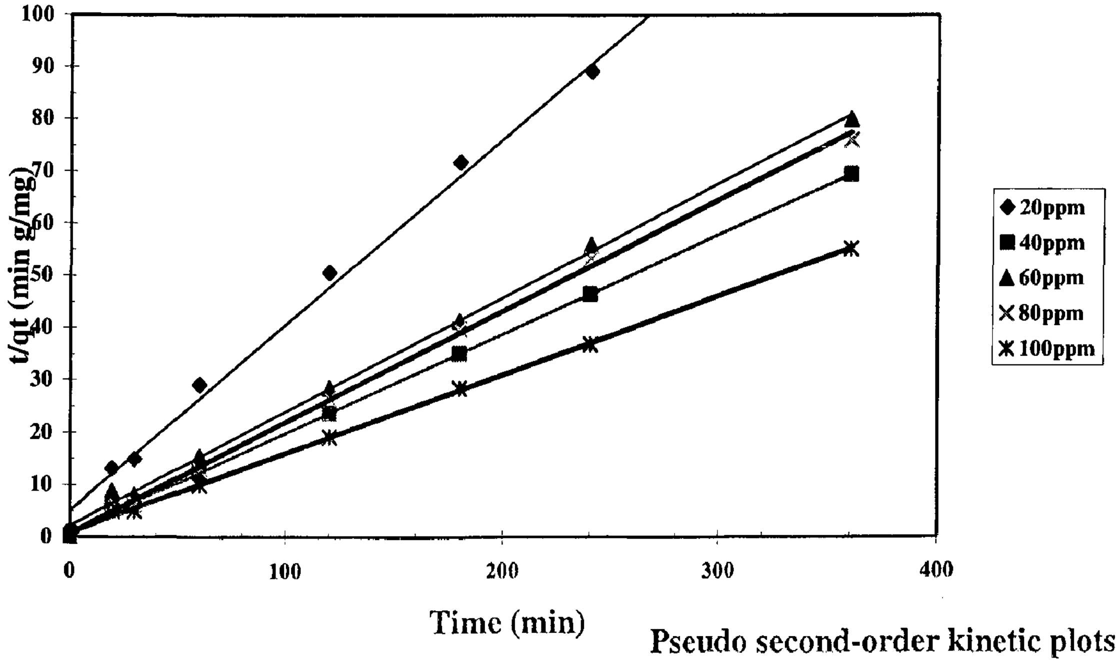
Pseudo second-order kinetic plots

Fig. B15d - : Pseudo - Second Order Kinetics for the removal of 2,4dcpfor RHA
(T= 303 K, dose =4 g/l, pH=3, t=6h).



Pseudo second-order kinetic plots

Fig. B15e - : Pseudo - Second Order Kinetics for the removal of 2,4dcpfor MAC
(T= 303 K, dose =6 g/l, pH=5, t=6h).



Pseudo second-order kinetic plots

Fig. B 16a Bangham's model for the removal of 2,4dcpfor CAC
(T= 303 K, dose =8 g/I, pH=4, t=6h).

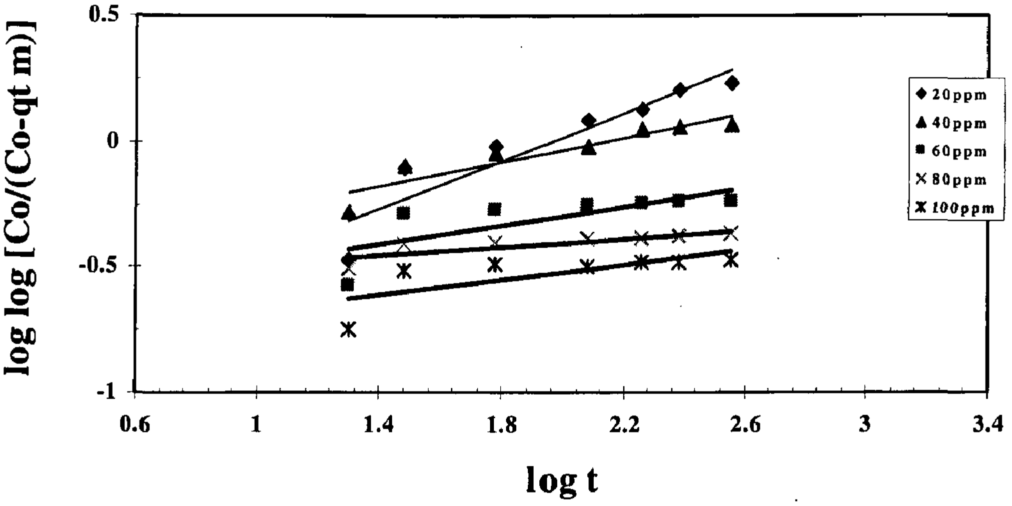


Fig. B16b -: Bangham's model for the removal of 2,4dcpfor BFA
(T= 303 K, dose =12g/l, pH=3, t=6h).

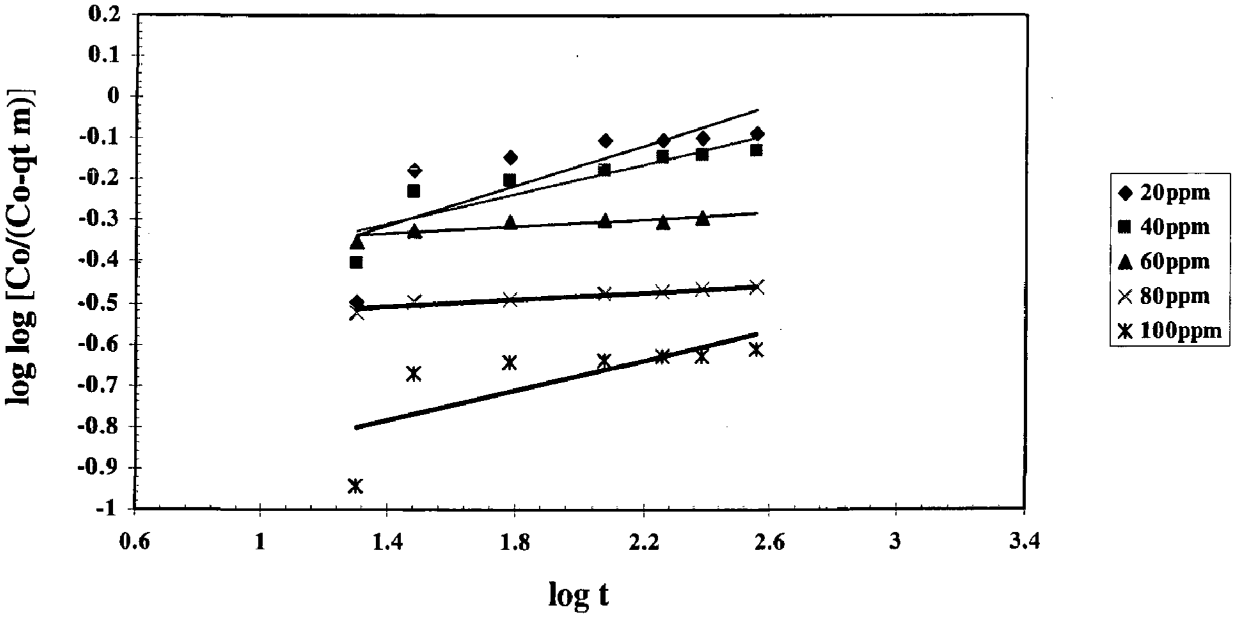


Fig. B16c -: Bangham's model for the removal of 2,4dcpfor CSAC
(T= 303 K, dose =8g/l, pH=4, t=6h).

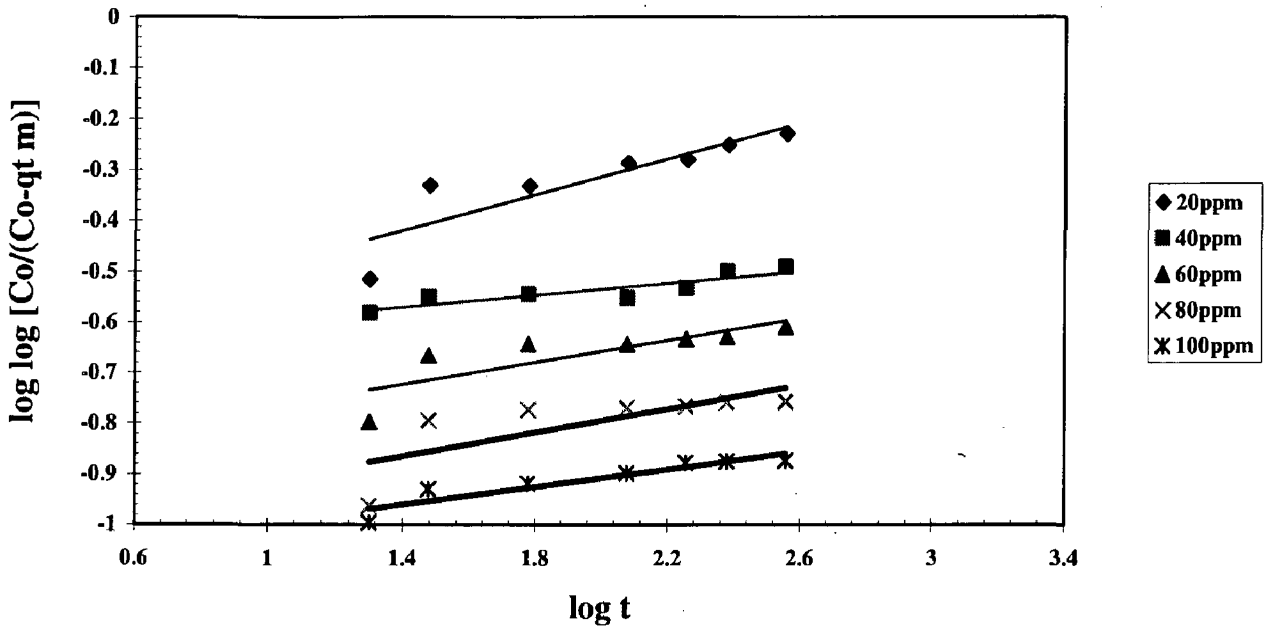


Fig. B16d -: Bangham's model for the removal of 2,4dcpfor RHA
(T= 303 K, dose =4g/l, pH=3, t=6h).

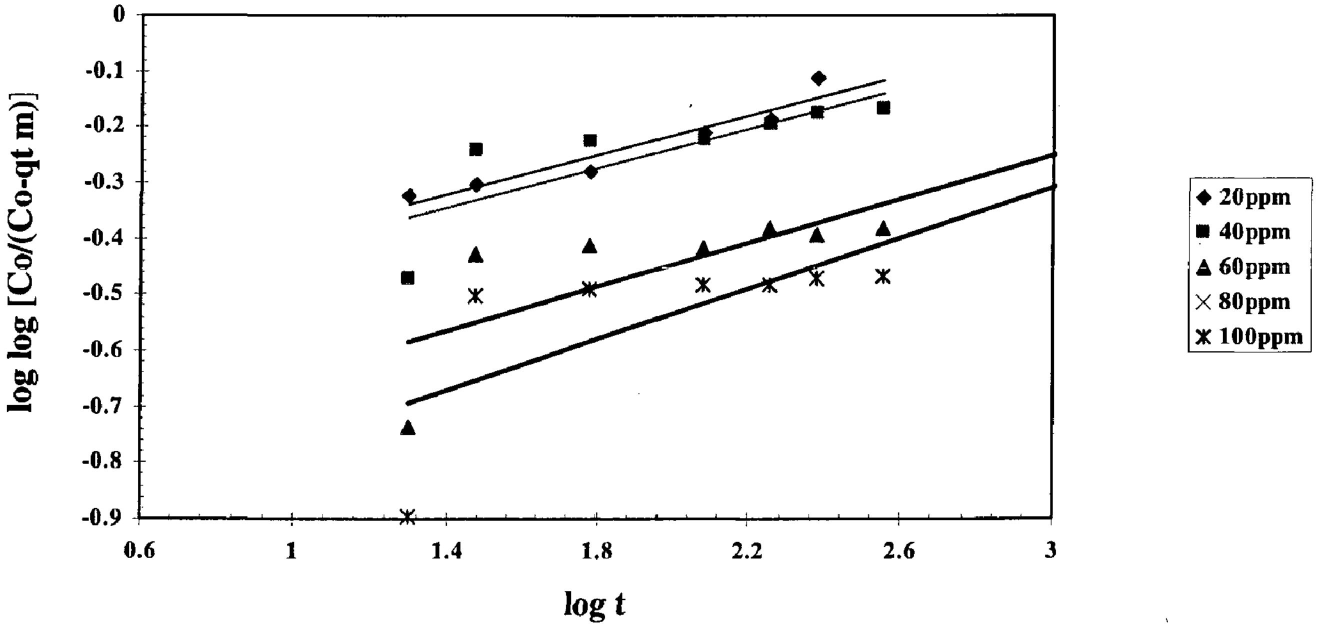


Fig. B16e -: Bangham's model for the removal of 2,4dcpforMAC

(T= 303 K, dose =6g/l, pH=3, t=6h).

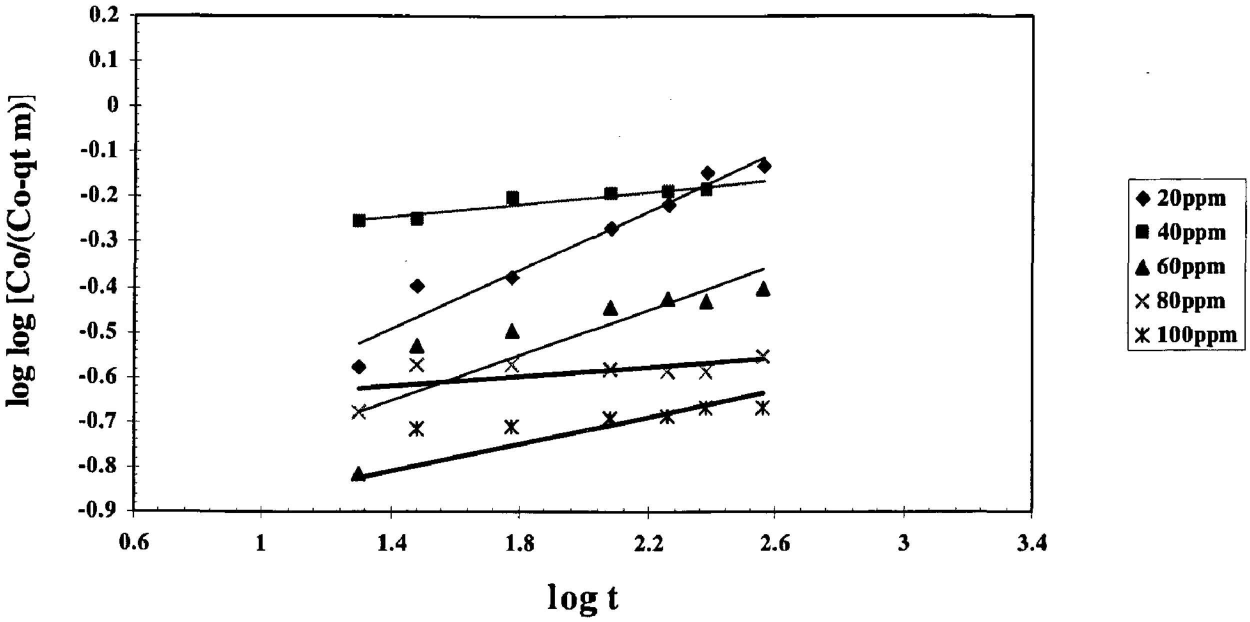


Fig. B17a- : Langmuir isotherm plots for the removal of 2,4dcpfor CAC

(t=6 h, dose = 8 g/l, pH=4, C_0 = 20, 40,60,80 and 100 mg/l).

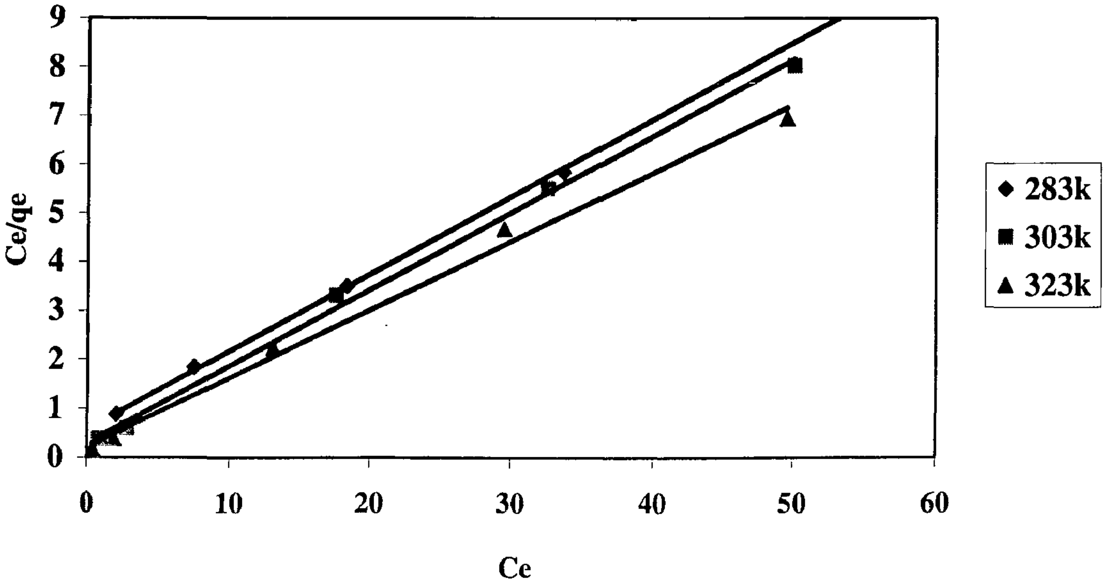


Fig. B17b -: Freundlich isotherm plots for the removal of 2,4dcpfor CAC

(t=4 h, dose = 8 g/l, pH=4.2, C_0 = 20, 40,60,80 and 100 mg/l).

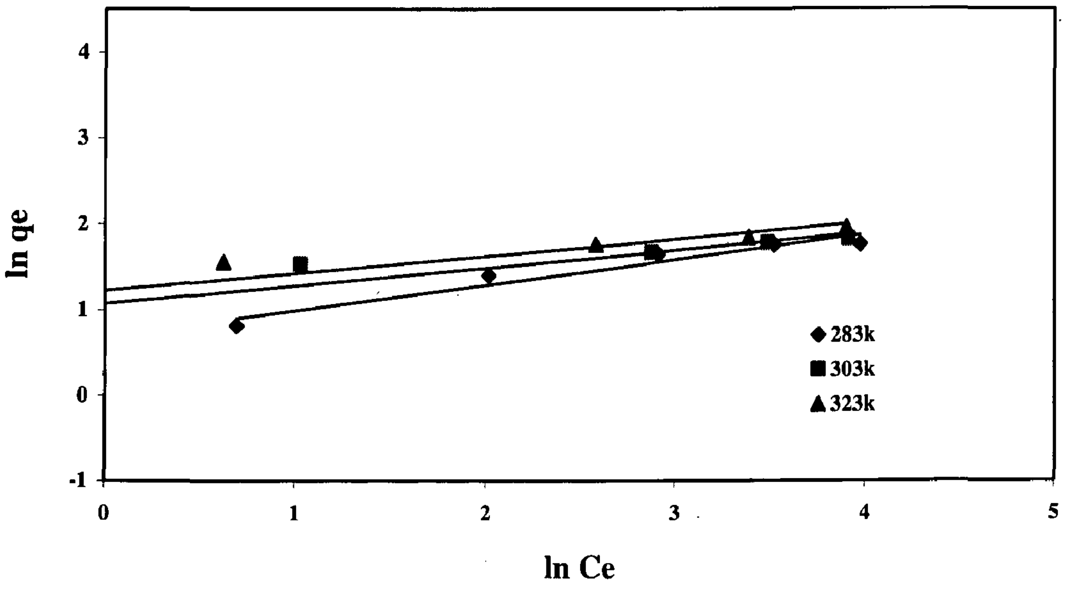


Fig. B17c -: Temkin isotherm plots for the removal of 2,4dcpfor CAC

(t=4 h, dose = 8 g/l, pH=5, C_0 = 20, 40,60,80 and 100 mg/l).

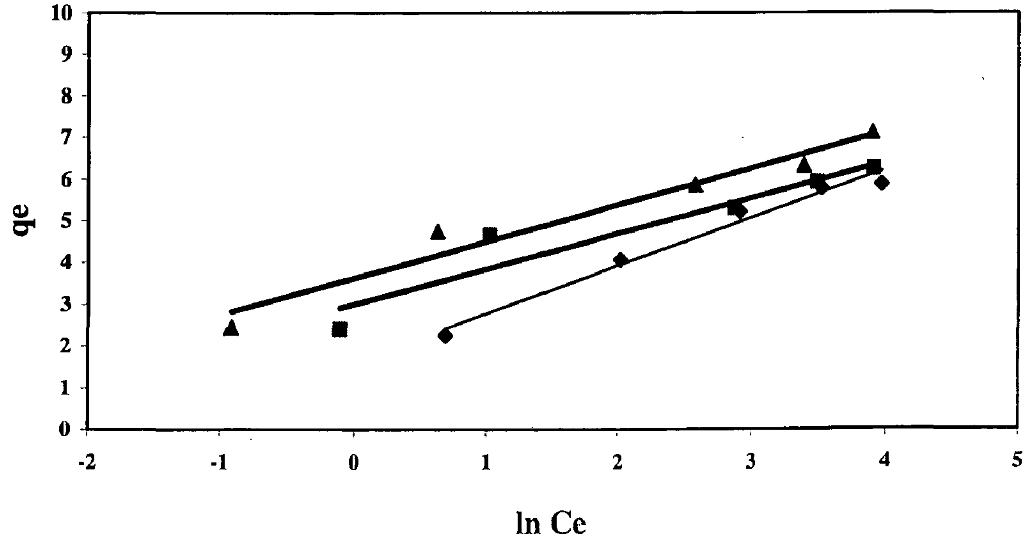


Fig. B 18a - : Langmuir isotherm plots for the removal of 2,4dcpfor BFA

(t=6 h, dose = 12 g/l, pH=436 C_0 = 20, 40,60,80 and 100 mg/l).

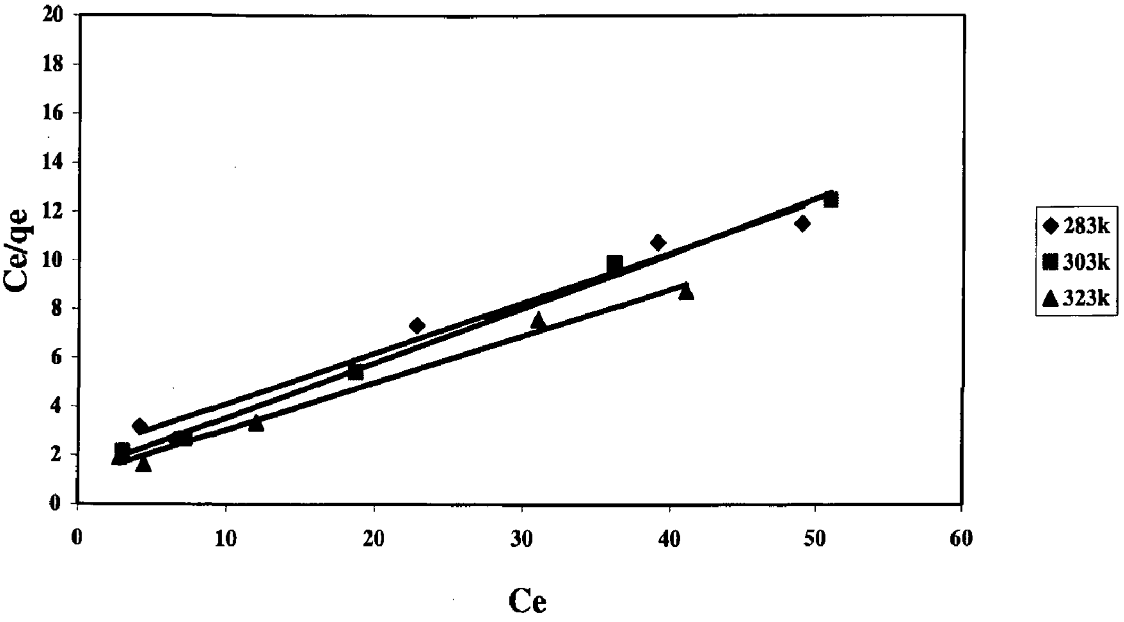


Fig. B18b-: Freundlich isotherm plots for the removal of 2,4dcpfor BFA

(t=6 h, dose = 12 g/l, pH=3, C_0 = 20, 40,60,80 and 100 mg/l).

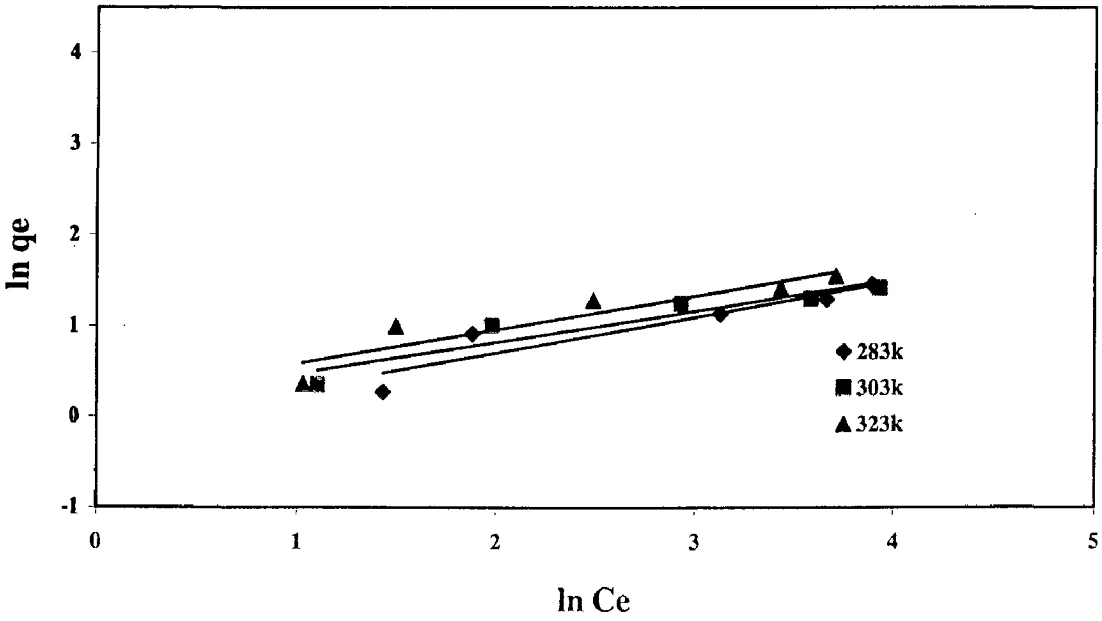


Fig. B18c -: Temkin isotherm plots for the removal of 2,4dcpfor BFA

(t=6 h, dose = 12 g/l, pH=3, C_0 = 20, 40,60,80 and 100 mg/l).

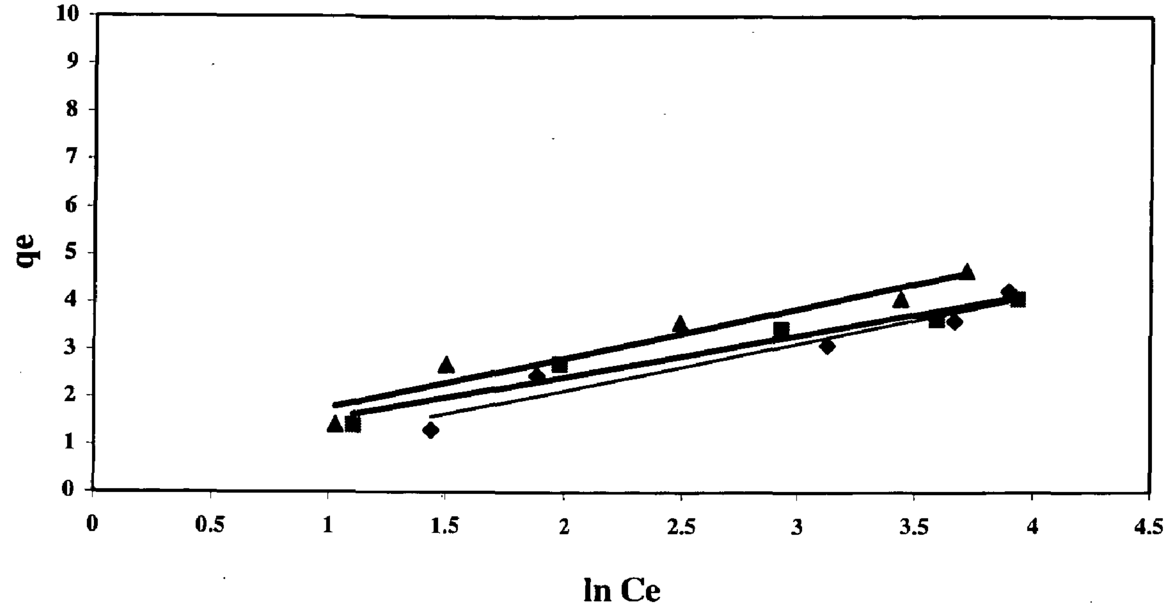


Fig. B19a - : Langmuir isotherm plots for the removal of 2,4dcpforCSAC

(t=6 h, dose = 8 g/l, pH=4, C_0 = 20, 40,60,80 and 100 mg/l).

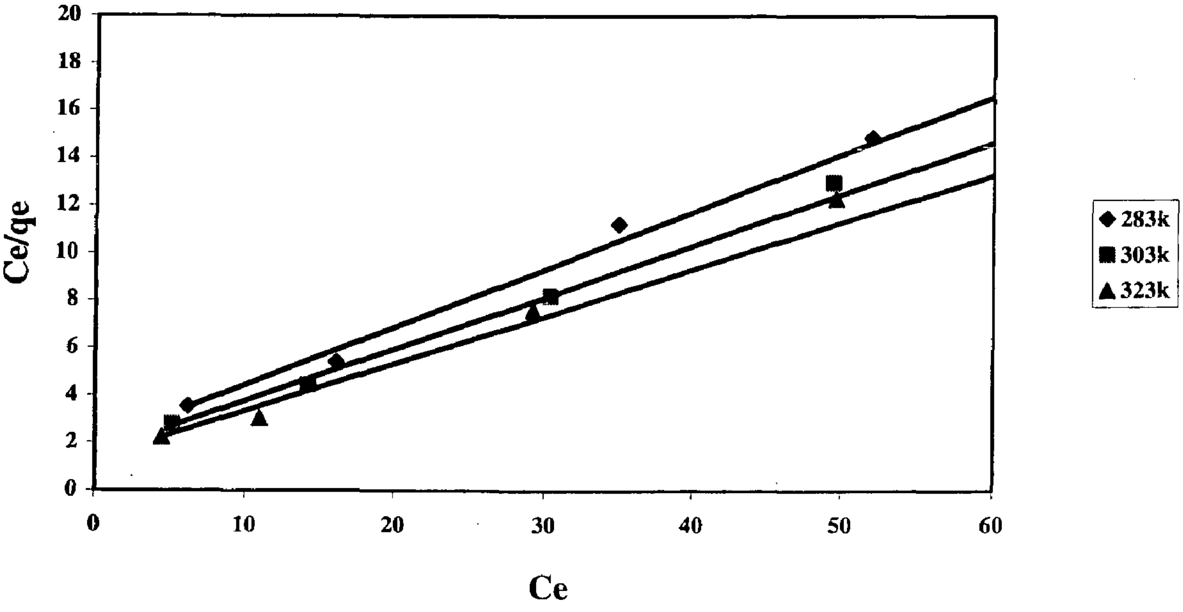


Fig. B19b -: Freundlich isotherm plots for the removal of 2,4dcpfor CSAC

(t=6 h, dose = 8g/l, pH=4. C_0 = 20, 40,60,80 and 100 mg/l)

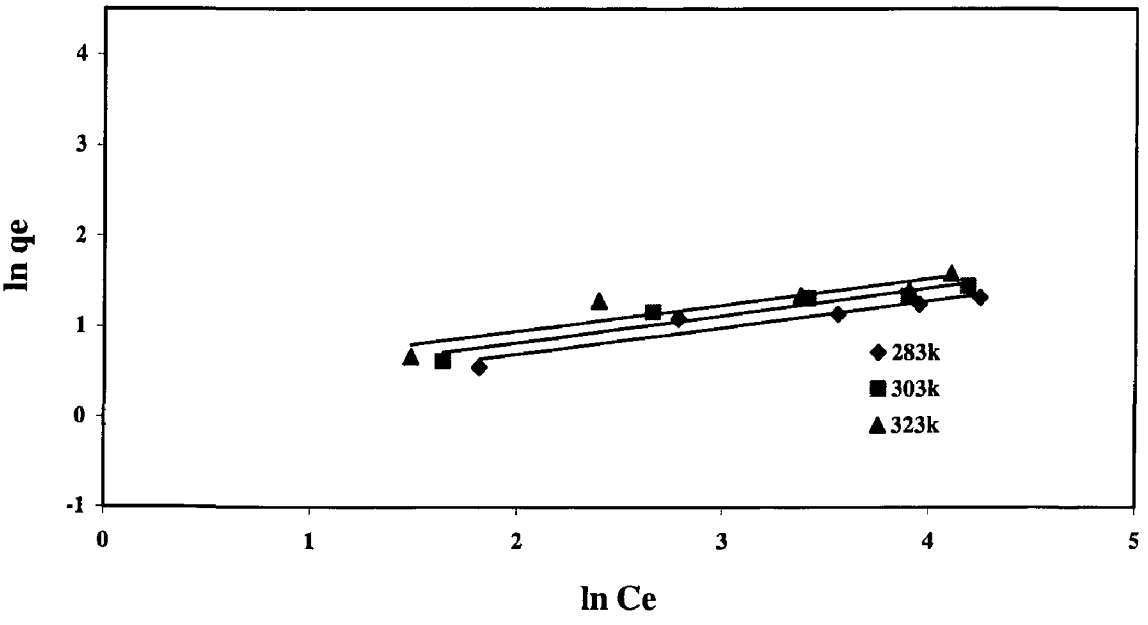


Fig. B19c -: Temkin isotherm plots for the removal of 2,4dcpfor CSAC

(t=6 h, dose = 8 g/l, pH=4, C_0 = 20, 40,60,80 and 100 mg/l).

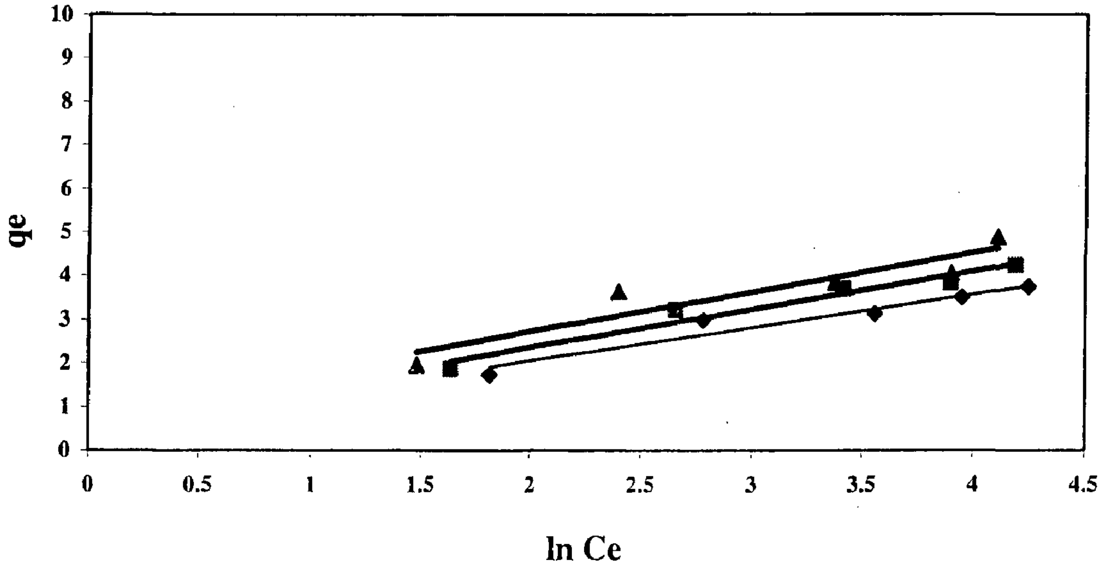


Fig. B20a - : Langmuir isotherm plots for the removal of 2,4dcpfor MAC

(t=6 h, dose = 6 g/l, pH=5, C_0 = 20, 40,60,80 and 100 mg/l).

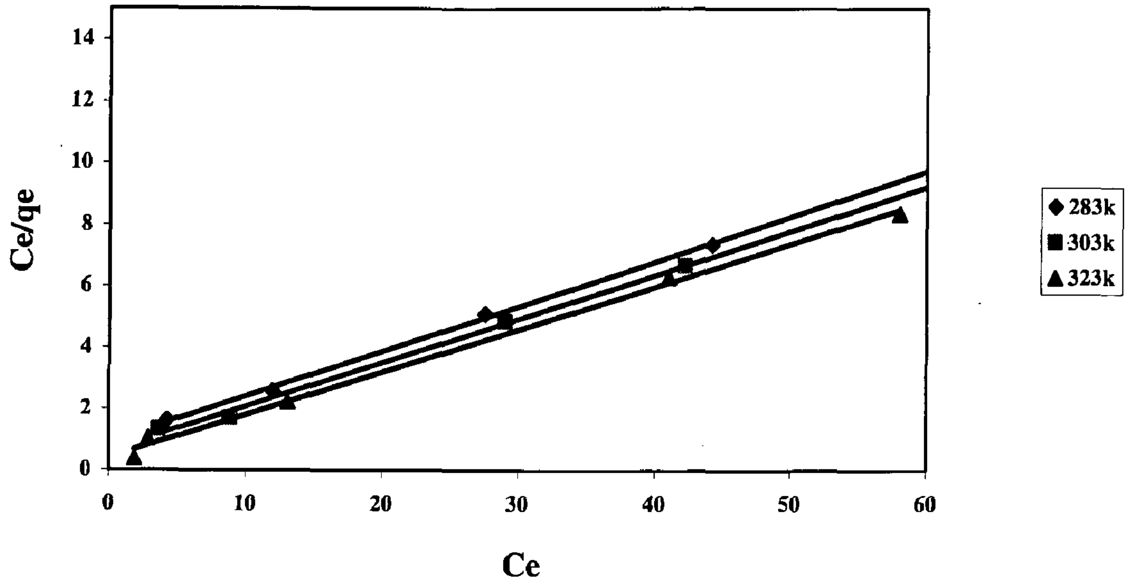


Fig. B20b -: Freundlich isotherm plots for the removal of 2,4dcpfor MAC
(t=6 h, dose = 6g/l, pH=4. C_0 = 20, 40,60,80 and 100 mg/l).

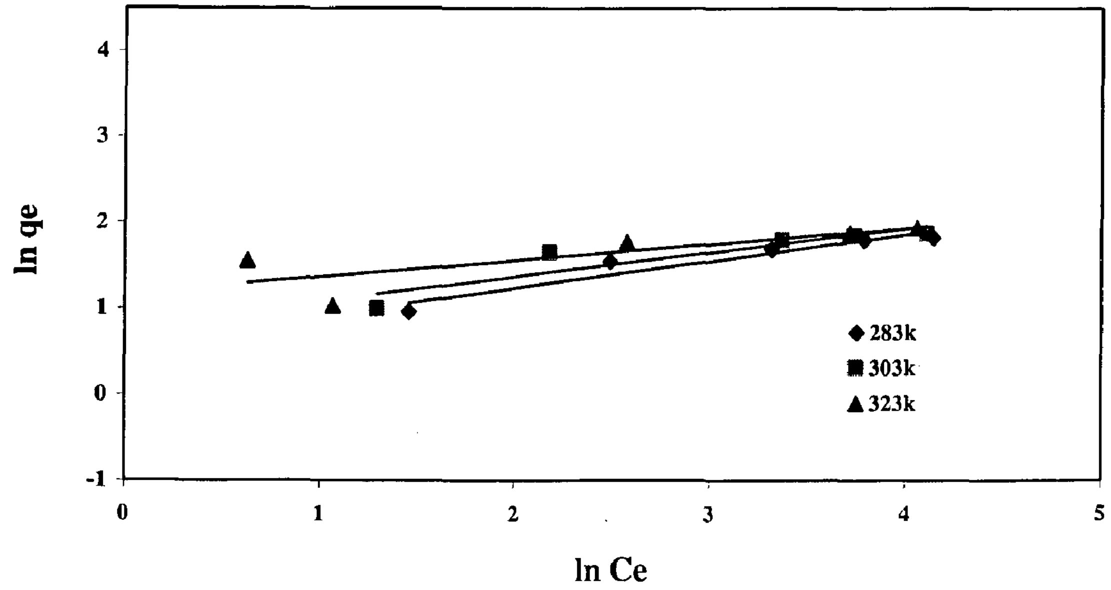


Fig. B20c -: Temkin isotherm plots for the removal of 2,4dcpfor MAC

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

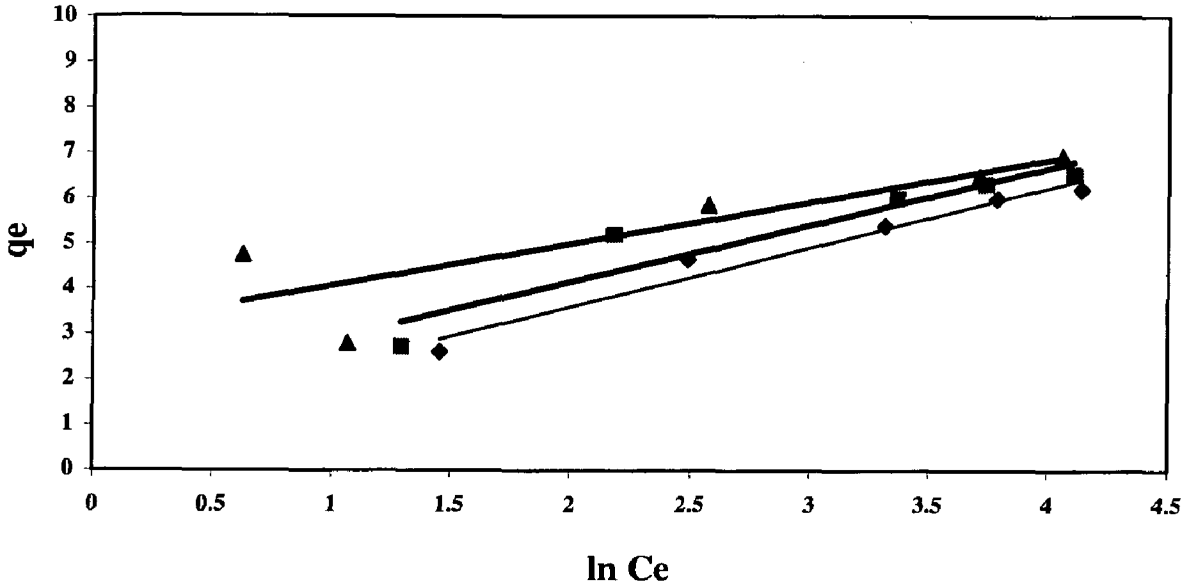


Fig. B21a - : Langmuir isotherm plots for the removal of 2,4dcpforRHA

(t=6 h, dose = 4 g/l, pH=3, C_0 = 20, 40,60,80 and 100 mg/l)

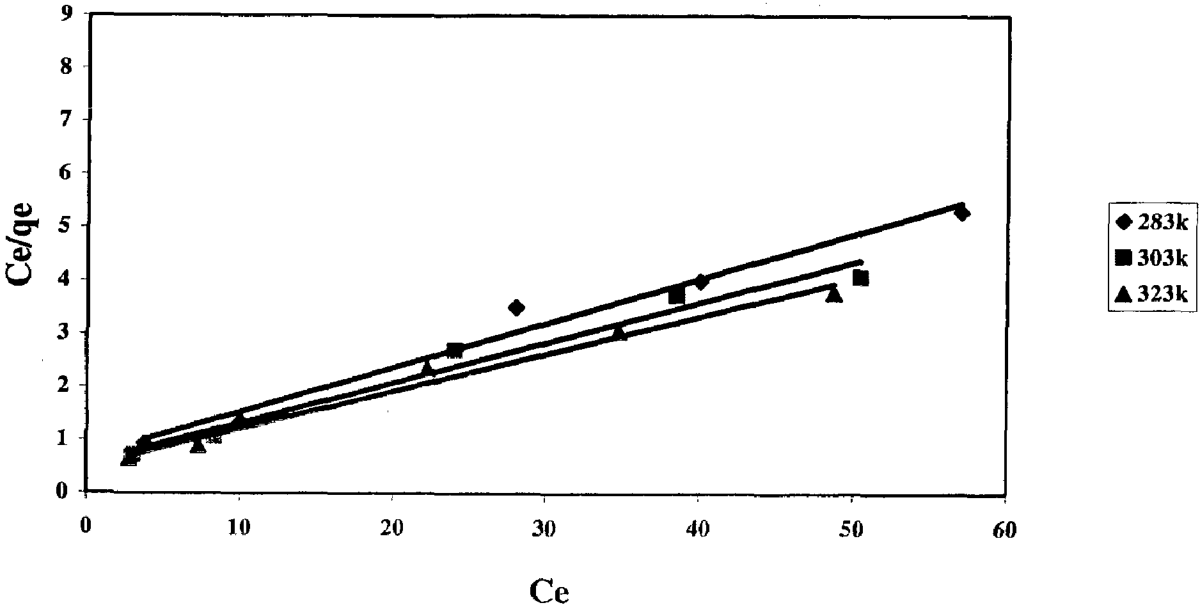
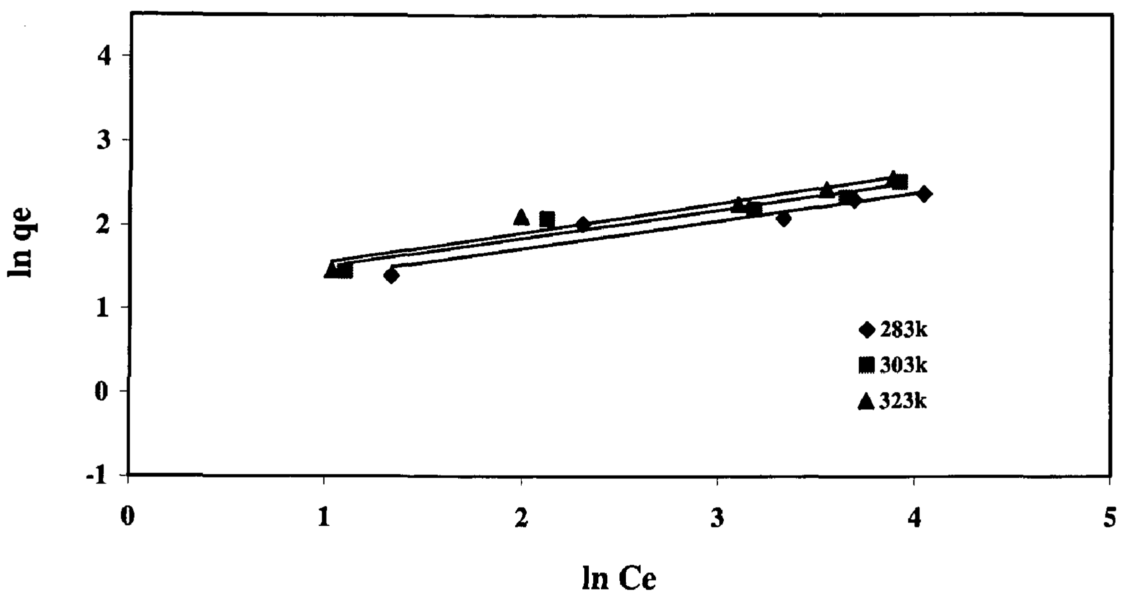


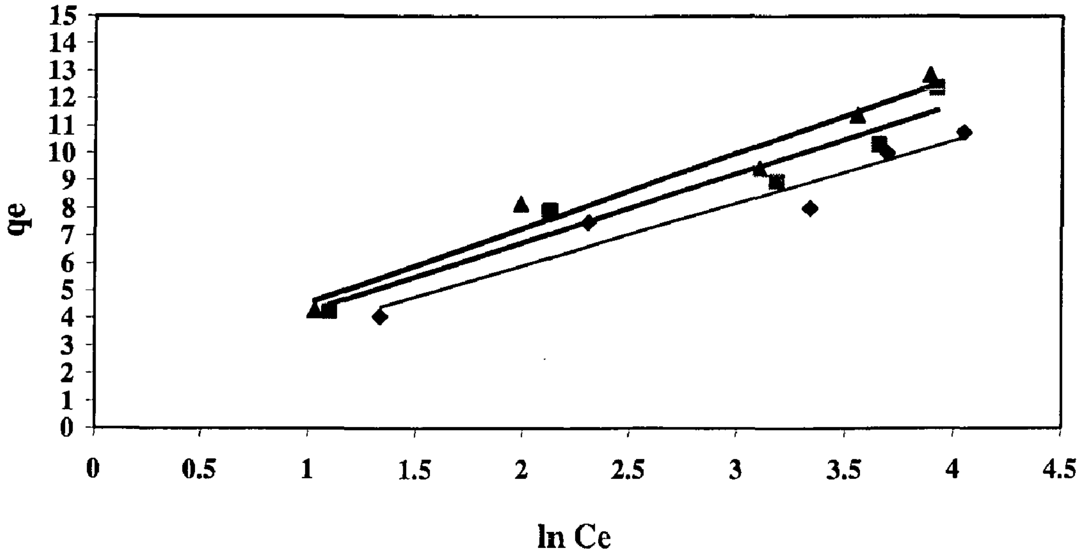
Fig. 21b -: Freundlich isotherm plots for the removal of 2,4dcpfor RHA

(t=6 h, dose = 4 g/l, pH=3, C_0 = 20, 40,60,80 and 100 mg/l)



B21c -: Temkin isotherm plots for the removal of 2,4dcpfor RHA

(t=6 h, dose = 4g/l, pH=, C_0 = 20, 40,60,80 and 100 mg/l).



APPENDIX – C

Table C-1Characteristics of commercial Activated Carbon

Moisture Percentage	4.45
Ash Percentage	51.2
Volatile matter Percentage	3.32
Fixed carbon Percentage	41.03

Table C-2: Characteristics of Bagasse fly ash

Moisture Percentage	4.9
Ash Percentage	27.9
Volatile matter Percentage	14.6

TableC-3 : Characteristics of coconut shell activated carbon

Moisture Percentage	3.3
Ash Percentage	32.4
Volatile matter Percentage	13.23
Fixed carbon Percentage	51.06

TableC-4 : Characteristics of Rice husk ash

Moisture Percentage	1.3
Ash Percentage	80.5
Volatile matter Percentage	7.3
Fixed carbon Percentage	10.9

TableC-5 : Characteristics of mixed activated carbon

Moisture Percentage	4.1
Ash Percentage	42.8
Volatile matter Percentage	16.7
Fixed carbon Percentage	36.4

Table 6

Activated carbon				
Co(mg/l)	q_{expm}(mg/g)	$q_{cal(mg/g)}$	k_f(min^{-1})	R^2non linear
20	2.450	1.5569	.034125	.867
40	4.651	1.5855	.03017	.889
60	5.550	3.0259	.04647	.817
80	6.250	1.458	.03235	.807
100	6.749	4.8534	.0569	.897
	Second order			
	$q_{cal(mg/g)}$	h(mg/g min)	Ks(g/mg min)	R^2non linear
20	1.5569	.3309	0529	.9931
40	4.7015	1.1764	.0532	9992
60	5.611	1.2005	.0382	.9996
80	6.2761	2.5609	.065	.9992
100	6.8194	1.5225	0.0327	.9995
	bangham			
	K_0(g)	alpha		R^2non linear
20	2.6701	.4779		.9262
40	7.1221	.2382		.9243
60	4.7965	.1924		.7456
80	6.2143	0.0834		.8186
100	3.42	.1531		.7371
	Intra particle diffusion model			
	k_{id1}mg/gmin $^{1/2}$)	I_1(mg/g)		R^2non linear
20	.23264	.516094		.82308
40	.2278	2.6850		.8479
60	.4856	1.7854		.7762
80	.2363	4.2836		.7879
100	.6128	2.076		.8047
	k_{id2}g/gmin $^{1/2}$)	I_2mg/g)		R^2non linear
20	.01293	2.2162		.9469
40	.0242	4.232		.8167
60	.01836	5.2115		.9776
80	.01584	5.9522		.996
100	.02546	6.2792		.8153

Bagasse flyash				
Co(mg/l)	q_{expm}(mg/g)	$q_{cal(mg/g)}$	k_f(min^{-1})	R^2non linear
20	1.415	0.771	0.042733	0.826
40	2.730	0.9649	0.029902	0.843
60	3.445	1.5139	0.045498	0.8964
80	3.658	0.3671	0.01332	0.8458
100	3.597	2.4624	0.04364	0.8367
	Second order			
	$q_{cal(mg/g)}$	h(mg/g min)	Ks(g/mg min)	R^2non linear
20	1.4339	0.2977	0.1449	0.9995
40	2.755	0.646	0.0849	0.9998
60	3.4694	1.206	0.1001	0.9998
80	3.666	1.790	0.1332	0.9999
100	3.641	0.5193	0.0392	0.9991
	bangham			
	K_0(g)	alpha		R^2non linear
20	5.1259	0.2426		0.7832
40	6.466	0.1763		0.8741
60	5.8378	0.195		0.7895
80	6.1689	0.044		0.9769
100	2.0945	0.1829		0.7396
	Intra particle diffusion model			
	k_{id1}(mg/gmin $^{1/2}$)	I_1(mg/g)		R^2non linear
20	0.1238	0.4414		0.7854
40	0.1473	1.4706		0.8132
60	0.2048	1.8011		0.823
80	0.0404	3.184271		0.8504
100	0.3785	0.6248		0.789
	k_{id2}g/gmin $^{1/2}$)	I_2mg/g)		R^2non linear
20	0.00303	1.3564		0.9811
40	0.01331	2.4879		0.9239
60	0.0041	3.361		0.7114
80	0.01075	3.454		0.9834
100	0.02215	3.1772		0.9852

Table 7

Coconut shell activated carbon				
Co(mg/l)	q_{expm}(mg/g)	$q_{cal(mg/g)}$	k_f(min^{-1})	R^2non linear
20	1.859	0.6114	0.0190	0.6824
40	2.623	0.3824	0.0103	0.8112
60	3.243	1.3247	0.0347	0.8739
80	3.323	1.9845	0.0521	0.8926
100	3.423	0.8533	0.01925	0.8263
	Second order			
	$q_{cal(mg/g)}$	h(mg/g min)	Ks(g/mg min)	R^2non linear
20	1.87044	0.286	0.0817	0.994
40	2.622	0.533	0.0775	0.992
60	3.248	0.6727	0.0638	0.996
80	3.356	0.85	0.0754	0.997
100	3.3587	0.7734	0.0686	0.998
	bangham			
	K_0(g)	alpha		R^2non linear
20	4.9741	0.1764		0.8754
40	5.1202	0.0593		0.8943
60	3.0832	0.1082		0.8094
80	2.1554	0.1175		0.7455
100	1.9114	0.0869		0.927
	Intra particle diffusion model			
	k_{id1}mg/gmin ^{½})	I_1(mg/g)		R^2non linear
20	0.09648	0.9496		0.73260
40	0.0369	2.1372		0.8263
60	0.1988	1.5945		0.8326
80	0.2635	1.2908		0.8098
100	0.1160	2.1806		0.8207
	k_{id2}g/gmin ^{½})	I_2 (mg/g)		R^2non linear
20	0.01563	1.5623		0.9746
40	0.03171	2.044		0.936
60	0.02219	2.814		0.9899
80	0.01036	3.132		0.9651
100	0.01885	2.993		0.8293

Co(mg/l)	q_{expm}(mg/g)	q_{cal}(mg/g)	k_f(min^{-1})	R^2non linear
20	4.155	1.686	0.01481	0.7960
40	7.915	3.1613	0.03503	0.7889
60	9.245	5.5605	0.04594	0.789
80	10.88	8.1079	0.05518	0.7787
100	12.145	6.2779	0.059369	0.8774
	Second order			
	$q_{cal(mg/g)}$	h(mg/g min)	Ks(g/mg min)	R^2non linear
20	4.1587	0.371	0.0215	0.9997
40	7.988	1.6529	0.0259	0.9997
60	9.3815	1.5858	0.018	0.9992
80	11.114	1.5337	0.0124	0.998
100	12.294	4.0202	0.0269	0.998
	bangham			
	K_0(g)	alpha		R^2non linear
20	4.106	0.2413		0.9435
40	5.845	0.1787		0.8014
60	3.342	0.1961		0.7248
80	2.359	0.2268		0.6834
100	3.8559	0.1016		0.7156
	Intra particle diffusion model			
	k_{id1}mg/gmin $^{1/2}$)	I_1(mg/g)		R^2non linear
20	0.2057	1.9089		0.8061
40	0.5343	3.5765		0.7745
60	0.9394	1.9972		0.7652
80	1.3884	0.4498		0.7517
100	0.8187	5.957		0.7894
	k_{id2}g/gmin $^{1/2}$)	I_2mg/g)		R^2non linear
20	0.07812	2.682		0.9827
40	0.05205	6.975		0.9431
60	0.04848	8.368		0.9342
80	0.03741	10.181		0.9831
100	0.04451	11.34		0.9015
20	2.727	1.2977	0.0120	0.7736
40	5.190	1.939	0.0316	0.7156
60	5.993	3.812	0.0279	0.8337
80	6.308	1.2717	0.0348	0.7058
100	6.518	2.9486	0.0326	0.741

Co(mg/l)	q_{expm}(mg/g)	$q_{cal(mg/g)}$	k_f(min^{-1})	R^2non linear
MAC	Second order			
	$q_{cal(mg/g)}$	h(mg/g min)	Ks(g/mg min)	R^2non linear
20	2.8004	0.1991	0.0254	0.998
40	5.2535	1.1862	0.043	0.997
60	6.06468	0.6153	0.0166	0.998
80	6.2446	2.077	0.053	0.999
100	6.6132	1.1081	0.0253	0.9995
	bangham			
	K_0(g)	alpha		R^2non linear
20	2.5577	0.3301		0.9709
40	5.3785	0.1911		0.7969
60	2.2535	0.2546		0.8389
80	4.637	0.0533		0.6432
100	2.1828	0.1517		0.7728
	Intra particle diffusion model			
	k_{id1}mg/gmin $^{1/2}$)	I_1(mg/g)		R^2non linear
20	0.1474	1.0251		0.7935
40	0.3587	2.2507		0.7455
60	0.58454	0.9137		0.8107
80	0.2505	4.3091		0.7375
100	0.5290	2.1935		0.7554
	k_{id2}g/gmin $^{1/2}$)	I_2mg/g)		R^2non linear
20	0.0461	1.8958		0.9406
40	0.01358	4.9409		0.9725
60	0.0410	5.1820		0.899
80	0.03674	5.5412		0.8251
100	0.0386	5.8510		0.9226

Isotherm parameters for the removal of 2, 4dichlorophenol from aqueous solution by CAC (pH_0 = 4, T = 283 K, 303 K, 323 K ,dose = 8 g/l)

Table C- 8a: Langmuir Constants (CAC)

Adsorbent	Constant	T=283^{0}K	T=303^{0}K	T=323^{0}K
CAC				
	K_L(l/mg)	0.2656	0.5247	.5764
	q_m(mg/g)	6.3101	6.3611	7.14
	R_L	0.070	0.036	0.0335
	R^2(non-linear)	0.9997	0.9998	.97814

Isotherm parameters for the removal of 2, 4dichlorophenol from aqueous solution by BFA (pH_0 = 3, T = 283 K, 303 K, 323 K ,dose = 12g/l)

Table C- 8b: Langmuir Constants (BFA)

Adsorbent	Constant	T=283^{0}K	T=303^{0}K	T=323^{0}K
BFA				
	K_L(l/mg)	0.1132	0.1709	0.182
	q_m(mg/g)	4.620	4.952	5.290
	R_L	0.150	0.104	0.098
	R^2(non-linear)	0.961	0.971	0.967

Isotherm parameters for the removal of 2, 4dichlorophenol from aqueous solution byCSAC (pH_0 = 4, T = 283 K, 303 K, 323 K ,dose = 8g/l)

Table C- 8c: Langmuir Constants (CSAC)

Adsorbent	Constant	T=283^{0}K	T=303^{0}K	T=323^{0}K
CSAC				
	K_L(l/mg)	0.1202	0.1368	0.1437
	q_m(mg/g)	4.1153	4.592	5.053
	R_L	0.1419	0.1278	0.1221
	R^2(non-linear)	0.964	0.973	0.930

Isotherm parameters for the removal of 2, 4dichlorophenol from aqueous solution byRHA (pH_0 =3 , T = 283 K, 303 K, 323 K ,dose = 4g/l)

Table C- 8d: Langmuir Constants (BFA)

Adsorbent	Constant	T=283^{0}K	T=303^{0}K	T=323^{0}K
RHA				
	K_L(l/mg)	0.1217	0.1366	0.1368
	q_m(mg/g)	11.934	13.276	14.198
	R_L	0.1419	0.132	0.127
	R^2(non-linear)	0.964	0.969	0.971

Isotherm parameters for the removal of 2, 4dichlorophenol from aqueous solution by MAC (pH_0 = 5, T = 283 K, 303 K, 323 K ,dose = 6g/l)

Table C- 8e Langmuir Constants (BFA)

Adsorbent	Constant	T=283^{0}K	T=303^{0}K	T=323^{0}K
RHA				
	K_L(l/mg)	0.1541	0.2181	0.341
	q_m(mg/g)	6.8321	7.003	7.17
	R_L	0.1148	0.083	0.054
	R^2(non-linear)	0.984	0.944	0.956

Table C -9a:Freundlich Constants (CAC)

Adsorbent	Constant	T=283^{0}K	T=303^{0}K	T=323^{0}K
CAC				
	K_F((mg/g)/(mg/l)$^{1/n}$)	2.008	2.9195	3.4022
	1/n	0.297	0.2079	3.402
	R^2(non-linear)	0..9678	0.9141	0.9481

Table C -9b:Freundlich Constants (BFA)

Adsorbent	Constant	T=283^{0}K	T=303^{0}K	T=323^{0}K
CAC				
	K_F((mg/g)/(mg/l)$^{1/n}$)	1.0164	1.134	1.3176
	1/n	0.3586	0.3431	0.3656
	R^2(non-linear)	0..9378	0.942	0.922

Table C -9c:Freundlich Constants (CSAC)

Adsorbent	Constant	T=283^{0}K	T=303^{0}K	T=323^{0}K
CSAC				
	K_F((mg/g)/(mg/l)$^{1/n}$)	1.1156	1.2409	1.4151
	1/n	0.2942	0.3036	0.2891
	R^2(non-linear)	.9471	0.953	0.9258

Table C -9d:Freundlich Constants (RHA)

Adsorbent	Constant	T=283^{0}K	T=303^{0}K	T=323^{0}K
RHA				
	$K_F((mg/g)/(mg/l)^{1/n})$	2.892	3.2424	3.363
	1/n	0.334	0.336	0.349
	R^2(non-linear)	0.9521	0.961	0.962

Table C -9e:Freundlich Constants (MAC)

Adsorbent	Constant	T=283^{0}K	T=303^{0}K	T=323^{0}K
MAC				
	$K_F((mg/g)/(mg/l)^{1/n})$	0.1541	0.2181	0.3418
	1/n	0.31163	0.284	0.1882
	R^2(non-linear)	0.957	0.941	0.981

Table C-10a: Tempkin Constants (CAC)

Adsorbent	Constant	303^{0}K	323^{0}K	343^{0}K
CSC				
	B	1.146	0.8487	0.8762
	K_T(l/mg)	4.138	34.24	61.55
	R^2(non-linear)	0.9874	0.965	0.9781

Table C-10b: Tempkin Constants (BFA)

Adsorbent	Constant	303^{0}K	323^{0}K	343^{0}K
BFA				
	B	0.8976	0.8773	1.0609
	K_T(l/mg)	1.66	2.179	2.3259
	R^2(non-linear)	0.961	0.976	0.967

Table C-10c: Tempkin Constants (CSAC)

Adsorbent	Constant	303^{0}K	323^{0}K	343^{0}K
CSAC				
	B	0.7668	0.8719	0.9086
	K_T(l/mg)	1.947	2.011	2.687
	R^2(non-linear)	0.966	0.9753	0.9320

Table C-10d: Tempkin Constants (RHA)

Adsorbent	Constant	303^0K	323^0K	343^0K
RHA				
	B	2.274	2.5038	2.728
	K_T(l/mg)	1.829	2.027	1.964
	R^2(non-linear)	0.964	0.97	0.94

Table C-10e: Tempkin Constants (MAC)

Adsorbent	Constant	303^0K	323^0K	343^0K
MAC				
	B	1.312	1.251	0.9262
	K_T(l/mg)	2.123	3.790	3.81
	R^2(non-linear)	0.981	0.948	0.953

Values of five different error analyses of isotherm models for adsorption of 2,4 dichlorophenol

Table C-11 : Error Analysis for CAC

283 K					
	HYBRID	**MPSD**	**SSE**	**SAE**	**ARE**
Langmuir	4.720	4.5602	0.1202	0.6670	2.176
Freundlich	-0.452	11.582	0.8796	1.8235	5.873
Temkin	-1.07	6.471	0.2271	0.9929	3.306
303 K					
	HYBRID	**MPSD**	**SSE**	**SAE**	**ARE**
Langmuir	0.0284	11.279	0.5071	1.4036	5.064
Freundlich	-8.146	12.089	0.3917	1.1749	4.6012
Temkin	-35.34	32.184	3.8157	4.3256	15.1054
323 K					
	HYBRID	**MPSD**	**SSE**	**SAE**	**ARE**
Langmuir	14.253	29.953	3.028	3.619	13.005
Freundlich	-46.712	52.545	32.74	10.055	13.005
Temkin	-6.109	13.065	0.9292	1.954	6.255

Values of five different error analyses of isotherm models for adsorption of 2,4 dichlorophenol

Table C-12 Error Analysis for BFA

283 K					
	HYBRID	**MPSD**	**SSE**	**SAE**	**ARE**
Langmuir	1.998	20.141	0.976	1.8837	9.652
Freundlich	-3.376	24.360	0.9185	1.6516	10.156
Temkin	-6.249	24.21	0.8034	1.8836	11.001
303 K					
	HYBRID	**MPSD**	**SSE**	**SAE**	**ARE**
Langmuir	1.965	8.430	0.189	.870	4.244
Freundlich	1.1885	15.937	0.478	1.370	7.556
Temkin	-0.2957	12.62	0.243	1.067	6.017
323 K					
	HYBRID	**MPSD**	**SSE**	**SAE**	**ARE**
Langmuir	-1.044	19.12	0.674	1.6556	8.786
Freundlich	-4.56	26.927	1.6132	2.782	13.54
Temkin	-7.71	25.335	0.8758	1.9702	11.00

Values of five different error analyses of isotherm models for adsorption of 2,4 dichlorophenol

Table C-13 Error Analysis for CSAC

303 K					
	HYBRID	**MPSD**	**SSE**	**SAE**	**ARE**
Langmuir	0.2883	4.443	.00709	.4752	2.0117
Freundlich	-0.5284	11.035	0.3569	1.2454	5.6554
Temkin	-1.18459	8.24	0.1626	0.8008	3.9211
283 K					
	HYBRID	**MPSD**	**SSE**	**SAE**	**ARE**
Langmuir	-1.977	7.945	0.1608	0.7687	3.828
Freundlich	-2.780	11.949	0.2973	1.0306	5.501
Temkin	-3.583	10.656	0.2019	0.8372	4.729
323 K					
	HYBRID	**MPSD**	**SSE**	**SAE**	**ARE**
Langmuir	0.4999	12.99	0.7361	1.664	6.026
Freundlich	-2.499	16.84	0.9821	1.722	7.469
Temkin	-3.8026	15.234	0.7817	1.7654	7.5049

Values of five different error analyses of isotherm models for adsorption of 2,4 dichlorophenol

Table C-14: Error Analysis for RHA

283 K					
	HYBRID	**MPSD**	**SSE**	**SAE**	**ARE**
Langmuir	2.5817	12.296	2.5897	2.8213	5.486
Freundlich	-3.9941	13.504	2.6615	3.162	6.356
Temkin	-1.724	11.00	1.885	2.5524	5.1228
303 K					
	HYBRID	**MPSD**	**SSE**	**SAE**	**ARE**
Langmuir	4.426	13.43	3.682	4.167	7.2029
Freundlich	-0.2744	12.213	2.6327	3.159	5.7716
Temkin	108.27	83.788	181.2	28.62	46.319
323 K					
	HYBRID	**MPSD**	**SSE**	**SAE**	**ARE**
Langmuir	2.9650	12.2006	3.228	3.585	36.053
Freundlich	-1.2959	12.8147	2.726	2.973	5.6035
Temkin	-1.677	9.7244	1.8656	2.712	4.7434

Values of five different error analyses of isotherm models for adsorption of 2,4 dichlorophenol

Table C-15 Error Analysis for MAC

283 K					
	HYBRID	**MPSD**	**SSE**	**SAE**	**ARE**
Langmuir	-0.4070	3.7862	0.00772	0.4545	1.5711
Freundlich	-0.8907	11.5892	0.8282	1.726	5.4550
Temkin	-1.4576	8.546	0.3024	0.977	3.455
303 K					
	HYBRID	**MPSD**	**SSE**	**SAE**	**ARE**
Langmuir	4.7928	11.838	0.90756	2.078	6.037
Freundlich	2.195	18.026	2.075	2.892	3.622
Temkin	3.9474	16.573	1.5581	2.4363	7.620
323 K					
	HYBRID	**MPSD**	**SSE**	**SAE**	**ARE**
Langmuir	21.287	30.381	12.693	7.608	16.66
Freundlich	14.37	34.903	6.6732	5.369	14.930
Temkin	16.545	38.394	15.667	8.550	20.541

Table C16 -: Thermodynamic parameters for adsorption CAC

Free Energy Calculations (From Langmuir Constant)

ΔH, KJ/mol	ΔS,K J/mol K	ΔG, KJ/mol
10.00	0.14	-3.391
		-1.094
		-1.21

Free Energy Calculations (From Freundlich Constant)

ΔH, KJ/mol	ΔS,K J/mol K	ΔG, KJ/mol
4.914	0.11	-311.57
		-33.507
		-35.86

Free Energy Calculations (From Temkin Constants)

ΔH, KJ/mol	ΔS,K J/mol K	ΔG, KJ/mol
6.48	0.122	-74.64
		-72.19
		-69.74

Table

C17 -: Thermodynamic parameters for adsorption BFA

Free Energy Calculations (From Langmuir Constant)

ΔH, KJ/mol	ΔS,K J/mol K	ΔG, KJ/mol
14.86	0.14	-4.281
		-7.052
		-9.886

Free Energy Calculations (From Freundlich Constant)

ΔH, KJ/mol	ΔS,K J/mol K	ΔG, KJ/mol
10.096	0.14	-38.14
		-40.75
		-43.16

Free Energy Calculations (From Temkin Constants)

ΔH, KJ/mol	ΔS,K J/mol K	ΔG, KJ/mol
52.15	0.29	-26.68
		-20.84
		-15.01

Table C 18-: Thermodynamic parameters for adsorption CSAC

Free Energy Calculations (From Langmuir Constant)

ΔH, KJ/mol	ΔS,K J/mol K	ΔG, KJ/mol
15.065	0.137	-2.959
		-5.740
		-8.449

Free Energy Calculations (From Freundlich Constant)

ΔH, KJ/mol	ΔS,K J/mol K	ΔG, KJ/mol
10.69	0.143	-384.04
		-412.66
		-44.128

Free Energy Calculations (From Temkin Constants)

ΔH, KJ/mol	ΔS,K J/mol K	ΔG, KJ/mol
65.49	0.277	-30.785
		-25.33
		-19.79

Table C 19-: Thermodynamic parameters for adsorption RHA

Free Energy Calculations (From Langmuir Constant)

ΔH, KJ/mol	ΔS,K J/mol K	ΔG, KJ/mol
3.456	0.094	-9.139
		-7.249
		-5.358

Free Energy Calculations (From Freundlich Constant)

ΔH, KJ/mol	ΔS,K J/mol K	ΔG, KJ/mol
4.966	0.118	-313.47
		-337.10
		-360.73

Free Energy Calculations (From Temkin Constants)

ΔH, KJ/mol	ΔS,K J/mol K	ΔG, KJ/mol
5.906	.0119	-754.33
		-730.40
		-70.646

Table C20 -: Thermodynamic parameters for adsorption MAC

Free Energy Calculations (From Langmuir Constant)

ΔH, KJ/mol	ΔS,K J/mol K	ΔG, KJ/mol
1.817	0.0884	-107.3
		-93.00
		-72.35

Free Energy Calculations (From Freundlich Constant)

ΔH, KJ/mol	ΔS,K J/mol K	ΔG, KJ/mol
4.066	0.123	-327.62
		-352.2
		-376.6

Free Energy Calculations (From Temkin Constants)

ΔH, KJ/mol	ΔS,K J/mol K	ΔG, KJ/mol
8.468	0.130	-724.22
		-698.15
		-672.09