ADSORPTIVE REMOVAL OF 2,4-DICHLOROPHENOL FROM AQUEOUS SOLUTION USING APRICOT STONES BASED ACTIVATED CARBON

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
AAKARSHA SRIVASTAVA

DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE -247 667 (INDIA)
JUNE, 2011

CANDIDATE'S DECLARATION

I hereby declare that the work presented in this thesis entitled **"Adsorptive removal of 2,4-Dichlorophenol from aqueous solution using Apricot Stones based Activated carbon"** in partial fulfillment of the requirements for the award of the degree of Master of Technology with specialization in Industrial Pollution Abatement to the Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee. It is an authentic record of my original work carried out under the guidance of Dr.(Mrs.) Shashi Kumar, Associate Professor, Department of Chemical Engineering, IIT Roorkee.

The matter embodied in this report has not been submitted for the award of any other degree or any other Institute/University.

Place: Roorkee
Date: 29 June 2011

Akarsha Srivastava
M.Tech.2nd Year (IPA)
Enrollment No. 09515002

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

Shashi
29\6\11

Dr.(Mrs.) Shashi Kumar
Associate Professor
Department of Chemical Engineering
Indian Institute of technology, Roorkee

ACKNOWLEDGEMENT

Nothing worth more than praising and acknowledgement at the way outset, the eternal and immense benevolence of the almighty god who endowed with the power of intellect and convergence. It is his will which has enabled me to accomplish my work which otherwise would not have been possible.

It is with a deep sense of gratitude that I profoundly acknowledge my indebtness to my supervisor, **Dr.(Mrs.) Shashi Kumar,** Associate Professor, Chemical Engineering Department for her perceptive suggestions and comments that helped me to remain motivated and enthused in compliling this work. Her infallible supervision and guidance has made this work a more rewarding experience for me. My special thanks are due to **Dr. Surendra Kumar,** Professor, Chemical Engineering Department for his inspiring guidance. I would also like to thank and acknowledge the efforts by **Md. Zafar**, Research scholar, chemical engineering department.

I would like to thank **Dr. I D Mall**, Head of the Chemical Engineering Department for providing various facilities during the course of this project work . I would like to thank all the teaching and non teaching staff members who have contributed directly or indirectly in successful completion of my project work.

Last but not the least, it is all owed to the blessings of my parents and friends which helped me to complete the work in due time.

Akarsha Srivastava
M.Tech.2nd Year (IPA)

ABSTRACT

The activated carbon was prepared from carbonaceous agricultural waste Apricot Stones by chemical activation using concentrated H_2SO_4 at 130±5 °C. The prepared activated carbon was characterized and was found as an effective adsorbent material. In order to test the efficacy of Apricot Stones based activated carbon (ASAC), batch experiments were performed to carry out the adsorption studies on ASAC for the removal of highly toxic pollutant 2,4-Dichlorophenol from aqueous solution. For ASAC, the predictive capabilities of two types of kinetic models and six types of adsorption equilibrium isotherm models were examined. The effect of pH of solution, adsorbent dose, temperature and initial 2,4-dichlorophenol concentration on adsorption behaviour was investigated, as well. Thermodynamic study showed that adsorption of 2,4-DCP on ASAC was spontaneous. The change in entropy (ΔS^0) and heat of adsorption (ΔH^0) of apricot stones was estimated as 14.99 J/mol/k and 4.020 kJ/mol, respectively. The adsorption on ASAC was found to follow pseudo-second order kinetics and showed better fit with correlation co-efficient as 0.99. Freudlich, Redlich-Peterson and Fritz-Schlunder models were appropriate for the current experimental data.

Keywords: Apricot Stones; Activated carbon; 2-4-Dichlorophenol; Adsorption isotherms; Adsorption kinetics; Chemical Activation.

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NOMENCLATURE

a	Constant in Toth isotherm $(mg/l)^n$
A_F	Accuracy factor (-)
b	Langmuir isotherm constant , Redlich-Peterson isotherm exponent
B_F	Bias factor (-)
C_e	Concentration of adsorbate in solution at equilibrium (mg/l)
C_t	Concentration of adsorbate in solution at any time (mg/l)
k	Radke – Prausnitz isotherm constant $(mg/g)(1/mg)^{1/n}$
k_1	Adsorption rate constant of pseudo-first order kinetics (min^{-1})
k_2	Adsorption rate constant of pseudo-second order kinetics $(g\ mg^{-1}\ min^{-1})$
K	Radke – Prausnitz isotherm constant(1/g)
K_F	Freundlich isotherm constant (mg/g) $(1/mg)^{1/n}$
K_1	Redlich –Peterson isotherm constant (1/g)
K_2	Redlich –Peterson isotherm constant $(1/mg)^b$
m	Weight of adsorbent dose (g)
n	Constant in Freundlich, Toth and Radke-Prausnitz isotherm
N	Number of data points in experimental run (-)
ND	Normalized deviation (-)
NSD	Normalized standard deviation (-)
$q_{e,exp}$	Experimental value of q_e (mg/g)
$q_{e,pred}$	Predicted value of q_e (mg/g)
q_e	Amount of adsorbate adsorbed per gram of adsorbent (adsorbate loading) at equilibrium (mg/g)
q_e^{∞}	Toth isotherm constant (mg/g)
q_t	Amount of adsorbate adsorbed per gram of adsorbent (adsorbate loading) at any time t (mg/g).
Q_0	Langmuir isotherm constant (mg/g)
t	Time (min)

V	Volume of adsorbate solution (l)

Greek symbols

α_1	Fritz-Schlunder isotherm constant $(mg/g)/(mg/l)^{\beta 1}$
α_2	Fritz-Schlunder isotherm constant $(mg/l)^{-\beta 2}$
β_1, β_2	Fritz-Schlunder isotherm constant

1.1 INTRODUCTION

Water pollution is a major cause of concern in most of the countries such as India and other developing nations. Speedy industrialization has provided much comfort to human beings; however, its adverse effects have emerged in the shape of environmental deterioration. Industries discharging pollutants into the environment include oil refineries, tanneries, textile plants, food, pharmaceutical, paint, coal processing industries and many more. Many of these pollutants from industrial and municipal waste are toxic, persistent, and not readily biodegradable. Priority Pollutants refer to a list of specific pollutants that includes heavy metals, specific organic chemicals, pesticides, polycyclic aromatic hydrocarbons and others, which are being discharged brazenly from the industries. The priority pollutants are a subset of "toxic pollutants" as defined in the Clean Water Act (USA). These pollutants were assigned a high priority for development of water quality criteria and effluent limitation guidelines because they are frequently found in wastewater. With ever-increasing concern for public health and environmental quality, many regulatory agencies have set up a rigid limit for the acceptable level of these priority pollutants in the environment. Hence, it becomes the responsibility of the industrialists, engineers and administration to curb the discharge of the pollutants from waste water.

1.2 TREATMENT TECHNIQUES FOR PRIORITY POLLUTANTS

The treatment processes of different types of effluents to be used must guarantee the elimination or recuperation of the pollutant in order to reach the strict authorized levels for the discharge of these effluents. The levels of pollutants allowed in discharge waters, are directly related with the type of present pollutant in the effluent. The most widely used methods for removing inorganic and organic chemicals from wastewaters include ion exchange, chemical precipitation, reverse osmosis, evaporation, membrane filtration and adsorption. Most of these methods suffer from some drawbacks, such as high capital and operational cost or the disposal of the residual metal sludge, and are not suitable for small-scale industries [Kobya et.al, 2005]. In general, the elimination of organic pollutants in aqueous solution needs one or various basic treatment technique: chemical oxidation, air desorption, liquid-liquid extraction, adsorption, inverse osmosis, ultrafiltration and biological treatment. Depending on the present compound in solution the methods to use can be destructive as for example, chemical oxidation, incineration or degradation, which only allow the efficient elimination of the pollutant from an aqueous form; and the non-destructive methods, among which is liquid-liquid extraction and absorption, that allow the recuperation of the pollutant. On the other hand, the application of one or other of the methods depends on the concentration of the effluent.

Table 1.1 Black List of Chemicals Substances Selected by the E.U.

GROUP	INCLUDED SUBSTANCES
Chloride Hydrocarbons	Aldrin, dieldrin, chlorobenzene, dichlorobenzene, chloronaphthalene, chloroprene, chloropropene, endosulfane, endrin, hexachlorobenzene, hexachlorobutadiene, Hexachlorocyclo-hexane, hexachloroethane, PCBs, tetrachlorobenzene, trichlorobenzene.
Chlorophenol	Monochlorophenol, 2, 4-dichlorophenol, 2-amino-4-chlorophenol, pentachlorophenol, 4-chloro-3-methylphenol, trichlorophenol.
Pesticides	Cyanide chloride, 2,4-dichlorophenoxyacetic acid and derivatives, 2,4,5 trichlorophenoxyacetic acid and derivatives, DDT, demeton, dichloroprope, dichlorvos, dimethoate, disulfoton, phenitrothion, phenthyon, linuron, malathion, MCPA, mecoprope, monolinuron, omethoate, parathion, phoxime, propanyl, pirazone, simacine, triazofos, trichlorofon, trifularin and derivatives.
Chloroanilines and nitrobenzenes	Monochloroanilines, 1-chloro-2,4dinitrobenzene, dichloroaniline, 4-chloro-2-nitrobenzene, chloronitrobenzene, chloro-nitrotoluene,dichloronitrobenzene.
PolycyclicAromatic Hydrocarbons	Antracene, biphenyl, naphthalene, PAHs
Inorganic substances	Arsenic and its compounds, cadmium and its compounds, mercury and its compounds.
Solvents	Benzene, carbon tetrachloride, chloroform, dichloroethane, dichloroethylene, dichloromethane, dichloropropane, dichloropropanol, dichloropropene, ethyl benzene, toluene,

	tetrachloroethylene, trichloroethane, trichloroethylene.
Other	Benzidine, chloroacetic acid, chloroethanol, dibromo-methane, dichlorobenzidine, dichloro-diisopropyl-ether, diethylamine, dimethylamine, isopropyl benzene, Tributylphosphate, trichlorotrifluoroethane, vinyl chloride, xilene.

1.3 CHLOROPHENOLS: HAZARDOUS INDUSTRIAL AND MUNICIPAL WASTE

Chlorinated organic compounds, specifically chlorophenols, are among priority water pollutants whose ecological risks and toxicity to aquatic flora and fauna are biomagnified through various food chains [Tutem et al, 1998]. Chlorophenols are present in drinking-water as a result of the chlorination of phenols, as by-products of the reaction of hypochlorite with phenolic acids, as biocides or as degradation products of phenoxy herbicides. Those most likely to occur in drinking-water as by-products of chlorination are 2-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol. The taste thresholds for chlorophenols in drinking-water are low. I can be found in the environment in degraded herbicides, sawmills, wood waste incinerators, an hazardous waste sites (Syracuse Research Corp., 1992; World Health Organization, 1989), coa conversion processes, coking plants, petroleum refineries, fiberglass manufacturing and severa chemical industries, as pharmaceuticals, resin and dye manufactures. Chlorophenols constitute significant category of pollutants and are also major components of paper pulp bleach plant effluents [Sathishkumar et al, 2009]. The present study focuses on the removal of 2,4-dichlorophenol from aqueous solutions, it being a potentially hazardous industrial and municipal pollutant.

1.4 2,4-DICHLOROPHENOL : SOURCES, USES AND EFFECTS

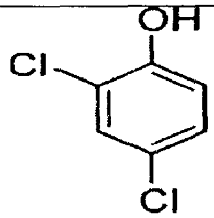
2,4-DCP is widespread in the environment and has even been detected in atmospheric emissions from the combustion of municipal solid waste, hazardous waste, coal, wood and herbicides. Nevertheless, the main release of 2,4-DCP has been found in surface waters: it was detected in several different industrial waste discharges including some from sewage treatment plants and drinking water treatment plants [Laurenti et.al, 2003]. They are toxic compounds, but the toxic property accounts for many of their uses. They are used as bactericides, fungicides and preservatives. 2-4-Dichlorophenol is used primarily as intermediate in the preparation of the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) a herbicide found as a component of the infamous 'Agent Orange' used as a defoliant in the Vietnam war. It serves as an ingredient of antiseptics; starting material for higher chlorophenols; intermediate for production of Sesone, Nitrofen, Nemacide; antihelminthic drug; mothproofing; seed disinfectants; 2-4-Dichlorophenol is also reacted with benzene sulfonyl chloride to produce miticide or further chlorinated to pentachlorophenol, a wood preservative.

Its presence is quite pronounced with a medicinal taste and objectionable when, get mixed with drinking water. It is a typical organic pollutant with malodor, peculiar smell and highly poisonous. It is not only harmful to the environment, but also very dangerous to the human beings, animals and crops. Excessive exposure to 2,4-dichlorophenol may affect the digestive system, eye, immune system, skin, and throat. DCP can cause death, respiratory failure, bone marrow atrophy, and skin damage in animals. The mechanism by which 2,4-DCP causes death is uncertain, but this and other chlorinated phenols are known to uncouple oxidative phosphorylation [Exon, 1984]. Most production of adenosine triphosphate, the carrier of free energy in cells, occurs through oxidative phosphorylation. Potentially exposed workers, their supervisors, and health and safety staff should be aware of the hazards associated with exposure to 2-4 DCP, especially when the chemical is in the liquid state. Detailed recommendations for appropriate protective clothing for dermal protection and respirators for inhalation protection are specified in the EPA/OSHA chemical advisory. Workers who made pesticides or were exposed to chlorophenols developed acne and mild liver injuries. Further four cases of death have also been reported: a man who accidentally splashed pure 2,4-DCP on his right arm and leg and three workers who were sprayed with 2,4-DCP in the containing steam [Laurenti et.al, 2003].

The Ministry of Environment and Forests (MOEF), Government of India and Environmental Protection Agency (EPA), USA, have listed chlorophenols on the priority pollutants list. The MOEF has set a maximum concentration level of 1.0 mg/l of phenolic compounds in the industrial effluents for safe discharge into surface water. World Health Organization (WHO) recommends the permissible concentration of 0.001 mg/l in potable water.

However, higher concentrations than those mentioned were frequently found in contaminated environments, where the reported levels of 2,4-dichlorophenol ranged from 150 µg/L to 200 mg/L and even more [Angelini et.al, 2011].

Table 1.2 Properties of 2,4 -Dichlorophenol

S. NO.	PROPERTY	VALUE
1	Molecular Formula	$C_6H_4Cl_2O$
2	Apparent Color	Colorless crystals ; hexagonal needles from benzene ; white solid
3	Odor	Strong medicinal
4	Boiling Point	210 °C
5	Melting Point	45 °C
6	Molecular Weight	163.00
7	Density	1.383 at 25 °C
8	pKa	7.8
9	pH	6
10	Vapor Pressure	0.075 mm Hg at 25 °C
11	Taste threshold	0.3 µg/litre
12	Odor threshold	40 µg/litre
13	Industrial effluent limit	Limit set by MOEF is 1.0 mg/l
		Limit set by (WHO) is 0.001 mg/l
14	Structure	

1.5 ADSORPTION AS THE PREFERRED REMOVAL TECHNIQUE AMONG OTHER RECUPERATIVE METHODS

Physical, chemical and biological methods, including incineration, adsorption on activated carbon, chemical or enzymatic oxidation, solvent extraction, microbial degradation, incubation in the presence of microorganisms, etc., have been proposed for removing or degrading several chlorophenols from waste waters. Adsorption has been found to be superior compared to other techniques for water reuse in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances [Ahmaruzzaman, 2008]. Activated carbon adsorption is especially known for its power in adsorbing organic compounds due to carbon's particular affinity for organics emanating from its non-polar nature. 2,4-dichlorophenol due to the polarity of the DCP molecule gives rise to stronger attraction to the sorbent surface. Even a quick overview of the literature reveals successful applications of this method in the treatment of pesticide wastes, hazardous industrial wastes, municipal wastewaters, petroleum refinery wastewaters, textile wastewaters, and municipal drinking water.

1.6 ADSORPTION FUNDAMENTALS

Adsorption is the process by which a solid adsorbent can attract a component in water to its surface and form an attachment via physical or chemical bond, thus removing the component from the fluid phase. The adsorption is called physical when relatively weak intermolecular forces cause the attachment and, chemical when chemical bonding like forces causes this attachment.

1.6.1 Adsorption Mechanism

For a solid liquid adsorption process, the solute transfer is usually characterized by either external mass transfer (boundary layer diffusion) or intraparticle diffusion or both. The adsorption dynamics can be described by the following three consecutive steps:

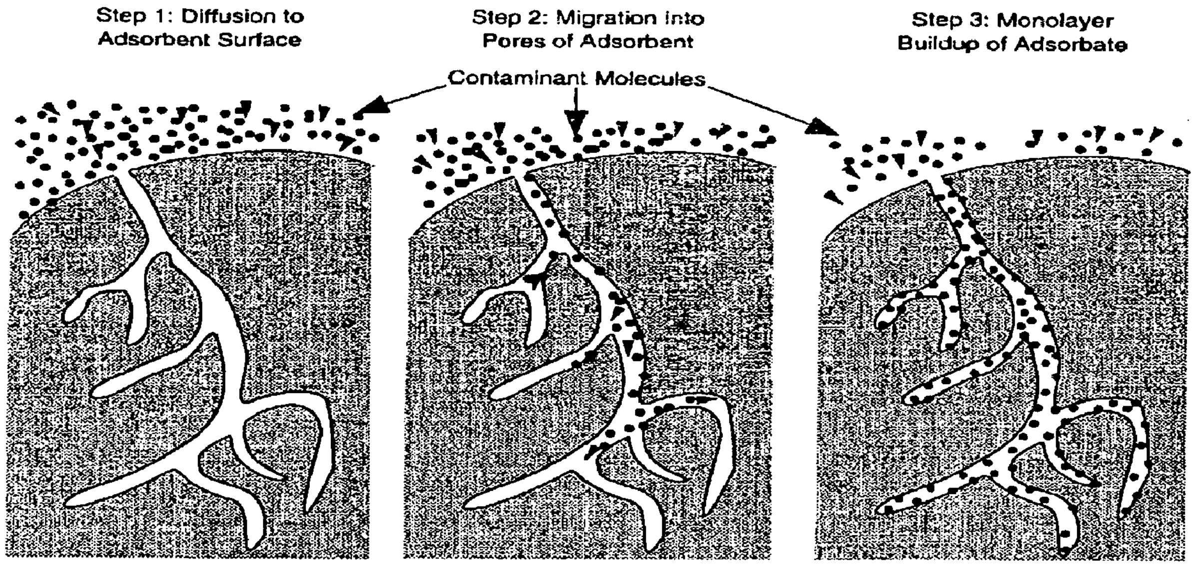


Figure 1.1 Depicting Adsorption mechanism

1) Transport of solute from bulk solution through liquid film to adsorbent exterior surface;
2) Solute diffusion into pore of adsorbent except for a small quantity of sorption on external surface; parallel to this is intra-particle transport mechanism of surface diffusion; and
3) Adsorption of solute on interior surfaces of the pores and capillary spaces of adsorbent.

The last step is an equilibrium reaction. Of the three steps, the third step is rapid and negligible. The overall rate of adsorption will be controlled by the slowest step that would be either film diffusion or pore diffusion controlled.

1.6.2 Kinetic Models

1.6.2.1 Lagergren Pseudo-First Order Kinetics:

This pseudo first order equation is based on the assumption that the rate of change of solute uptake with time is directly proportional to the difference in saturation concentration and the amount of solid adsorbed with time.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad \text{.........Eq.1}$$

The integrated form of Eq. (1) with the boundary conditions, q_t (t = 0) = 0 becomes

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad \text{.............Eq.2}$$

where k_1 is pseudo-first order adsorption rate constant (min^{-1}), q_e is the amount of solute adsorbed at equilibrium and q_t is the amount of solute adsorbed at time *t*. The adsorption process is said to follow this model if the curves are linear. The values of q_e and k_1 were calculated from a plot of ln $(q_e - q_t)$ versus t.

1.6.2.2 The Pseudo-Second Order Kinetics:

The pseudo-second order kinetics model is expressed as:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \qquad \text{.........Eq. 3}$$

Where, k_2 is the pseudo-second order adsorption rate constant (g mg^{-1} min^{-1}). Integrating Eq.3 and noting that $q_t = 0$ at $t=0$, the obtained equation can be rearranged into a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad \text{..........Eq.4}$$

The values of q_e and k_2 can be obtained by a linear plot of t/q_t vs. t. If the plot is linear, then the adsorption mechanism follows the pseudo 2nd order model.

1.6.2.3 Boyd Model

It is well established that when a solute in solution adsorbs on porous adsorbents, three types of mechanisms are involved which are:

1. Film diffusion, which involves the movement of adsorbate molecules from the bulk of the solution towards the external surface of the adsorbent.
2. Particle diffusion, where the adsorbate molecules move in the interior of the adsorbent particles.
3. Sorption of the adsorbate molecules on the interior of the porous adsorbent.

The sorption stage is usually fast and can be considered negligible. Therefore, it is essential to distinguish between film diffusion and particle diffusion mechanisms since this information is required for design purposes. In order to identify the slowest steps in the adsorption process, the Boyd kinetic equation was applied and it is represented as:

$$F = 1 - \frac{6}{\pi^2}\exp(-Bt) \qquad \text{.........Eq.5}$$

where F is the fractional approach to equilibrium at time t and B is given as:

$$B = \frac{\pi^2 D_i}{r_0^2} \qquad \text{..........Eq.6}$$

D_i is the effective diffusion coefficient of solute in the adsorbent phase and r_o is the radius of the adsorbent particles. Equation (5) can be re-arranged while taking natural logarithm to obtain the equation

$$Bt = -0.4977 - \ln(1 - F) \qquad \text{........Eq.7}$$

The values of Bt can be evaluated for different time intervals using Eq. (7). A plot of $-0.4977 - \ln(1 - F)$ against time t can be employed to test the linearity of the experimental values. If the plots are linear and pass through the origin, then the slowest (rate controlling) step in the adsorption process is the internal diffusion, and vice versa [Boyd et al, 1947].

1.6.2.4 Bangham's Equation

Kinetic data can further be used to check whether pore diffusion is the only rate-controlling step or not in the adsorption system using Bangham's equation :

$$\log\log\left(\frac{c_0'}{c_0' - q'm'}\right) = \log\left(\frac{k_0 m'}{2.303V}\right) + \alpha\log t \qquad \text{...........Eq.8}$$

[where C_0' is the initial concentration of adsorbate in solution (mmol/l), V is the volume of solution (ml), m' is the weight of sorbent used per liter of solution (g/l), q' is the amount of adsorbate retained at time t (mmol/g), α(<1) and k_0 are constants] was tested for its applicability to 2,4-Dichlorophenol adsorption [Tutem E. et al,1998].

1.6.3 Adsorption Isotherms

Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its concentration at constant temperature. The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials. An adsorption equilibrium isotherm relates the adsorbate loading on the adsorbent (q_e) and liquid phase concentration of adsorbate (C_e) at equilibrium condition keeping temperature constant. The equilibrium adsorption isotherm is fundamentally very crucial in the design of adsorption systems.

1.6.3.1 Langmuir Isotherm Model

It applies to adsorption on completely homogenous surfaces with negligible interaction between adsorbed molecules.

$$q_e = \frac{Q_0 b C_e}{1 + bC_e} \qquad \text{..........Eq.9}$$

where C_e is the concentration of 2,4-DCP solution (mg/l) at equilibrium, q_e is the maximum 2,4-DCP uptake (mg/g) and b is the Langmuir equilibrium constant related to the free energy of adsorption and is the measure of adsorption affinity or heterogeneity. Q_0 is the maximum amount of *p*-cresol per gram of activated carbon to form a complete monolayer on the surface.

1.6.3.2 Freundlich Model

It is an empirical model and is described by the equation

$$q_e = K_F C_e^{1/n} \qquad \text{.........Eq.10}$$

K_F is the measure of the adsorption capacity and n is a measure of the adsorption intensity. Model assumes logarithmic decrease in heat of adsorption in the surface coverage. The disadvantage is that it does not follow Henry's law at concentration approaching zero.

1.6.3.3 Redlich–Peterson Model

It is a three parameter model which combines elements of the Langmuir and Freundlich isotherm in a single equation as given below:

$$q_e = \frac{K_1 C_e}{1 + K_2 C_e^b} \qquad \text{........Eq.11}$$

Where, K_1 and K_2 are Redlich–Peterson isotherm constants and b is Redlich–Peterson isotherm exponent which lies between 0 and 1 [Carvalho et.al, 2007]. This model is also valid for wide range of concentration. For b = 1, the equation is converted to the Langmuir isotherm, for $K_2C_e^b$ $\gg$ 1.0, it reduces to Freundlich model and for $K_2C_e^b$ $\ll$ 1.0, it reduces to Henry's law.

1.6.3.4 Toth Model

Another well known three-parameter model was proposed by Toth. The Toth equation reduces to Henry's law at very low concentrations and contains three adjustable parameters. The mathematical expression of the Toth isotherm equation, with q_e^∞, a and n as its three parameters, can be given by ;

$$q_e = \frac{q_e^\infty C_e}{\left[a + C_e^n\right]^{1/n}} \qquad \text{............Eq.12}$$

1.6.3.5 Radke- Prausnitz Isotherm Model

It represents the Langmuir model for α = 1 and Henry's model for α = 0. Having parameters 3 parameters K,k and n it is as follows :

$$\frac{1}{q_e} = \frac{1}{KC_e} + \frac{1}{kC_e^{1/n}} \qquad \text{..........Eq.13}$$

1.6.3.6 Fritz –Schlunder Model

The Fritz-Schlunder isother is a four parameter model which further minimize the error in two parameter models and hence give better representation of data and is formulated as :

$$q_e = \frac{\alpha_1 C_e^{\beta_1}}{1 + \alpha_2 C_e^{\beta_2}} \qquad \text{.........Eq.14}$$

1.6.3.7 *Bet Isotherm*

Often molecules do form multilayers, that is, some are adsorbed on already adsorbed molecules and the Langmuir isotherm is not valid. The derivation of the formula is more complicated than Langmuir's. We obtain:

$$\frac{x}{v(1-x)} = \frac{1}{v_{mon}c} + \frac{x(c-1)}{v_{mon}c} \qquad \text{..........Eq.15}$$

x is the pressure divided by the vapor pressure for the adsorbate at that temperature (usually denoted P / P^0), v is the STP volume of adsorbed adsorbate, v_{mon} is the STP volume of the amount of adsorbate required to form a monolayer and c is the equilibrium constant K we used in Langmuir isotherm multiplied by the vapor pressure of the adsorbate. The Langmuir isotherm is usually better for chemisorption and the BET isotherm works better for physisorption for non-microporous surfaces.

1.6.3.8 Dubinin–Redushkevich (D–R) Model

This adsorption isotherm is given as:

$$q_e = q_m \exp(-Be^2) \qquad \text{.........Eq.16}$$

where q_m (mol/g) is the theoretical monolayer saturation capacity of the adsorbent and e (known as Polanyi potential) is given as:

$$e = RT\ln\left(1 + \frac{1}{C_e}\right) \qquad \text{..........Eq.17}$$

The constant B (mol^2/J^2) given by the following equation, the mean free energy E (J/mol) of adsorption per molecule of adsorbate, when it is transferred to the surface of the solid from infinity in the solution, is:

$$E = \frac{1}{\sqrt{2B}} \qquad \text{..........Eq.18}$$

The linear form of D–R equation is:

$$\ln q_e = \ln q_m - Be^2 \qquad \text{..........Eq.19}$$

A plot of ln q_e versus e^2 should yield a straight line.

1.6.3.9 Temkin Model

The Temkin adsorption isotherm is expressed as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \qquad \text{.........Eq.20}$$

where B_1 = RT/b; R is the universal gas constant (8.314 J/mol K) and T is the absolute temperature (K). Temkin isotherm takes into account the adsorbing species–adsorbent interactions. A plot of q_e versus lnC_e yields a straight line from which the isotherm constants B_1 and K_T (L/mg) can be determined. K_T is the equilibrium binding constant corresponding to the maximum binding energy and constant B_1 is related to the heat of adsorption. From the values of K_T it may be observed that the binding energy is better for FE than AC as evinced by the Freundlich model, whereas the heat of adsorption is more for AC than FE.

1.6.3.10 Sips Adsorption Isotherm

The Sips isotherm, at low sorbate concentrations, reduces to the Freundlich isotherm. At high sorbate concentrations, Sips model predicts monolayer sorption capacity, which is a distinctiveness of the Langmuir isotherm

$$q_e = \frac{q_m (K_s C_e)^\gamma}{1 + (K_s C_e)^\gamma} \qquad \text{...........Eq.21}$$

Table 1.3 Comparison of different Isotherms

ISOTHERMS	SIGNIFICANCE
Langmuir	• monolayer adsorption, • no interaction b/w molecules • for low concentrations • same activity of surface
Freundlich	Heterogeneous surface, wide concentration applicabality
Redlich-Peterson	Combination of Langmuir and Freundlich
Toth	Heterogenous surface
Radke–Prausnitz	Heterogenous surface

Fritz–Schlunder	Heterogenous surface
BET isotherm	Multilayer adsorption
Dubinin-Redushkevich	Monolayer adsorption
Temkin	Adsorbate-adsorbate interactions
Harkins–Jura	Multilayer adsorption

1.7 ADSORBENTS

Most industrial adsorbents fall into one of three classes:

- Oxygen-containing compounds – Are typically hydrophilic and polar, including materials such as silica gel and zeolites.
- Carbon-based compounds – Are typically hydrophobic and non-polar, including materials such as activated carbon and graphite.
- Polymer-based compounds - Are polar or non-polar functional groups in a porous polymer matrix.

1.7.1. Raw Sources For Adsorbents : Classification

Table 1.4 Natural materials for activated carbon preparation

TYPES	EXAMPLES	PROPERTIES
Clay	smectites, mica (illite), kaolinite, serpentine, pylophyllite, vermiculite and sepiolite	➢ negative charge on the structure of minerals, ➢ low cost ➢ potential for ion-exchange, ➢ high-surface-area and high porosity

Siliceous materials	silica beads, glasses,alunite, perlite and dolomite.	➢ Presence of acidic silanol groups, ➢ hydrophilic, mechanical stability
Zeolite	clinoptilolite	➢ negatively charged lattice ➢ High ion-exchange capacity

Table 1.5 List of Bioadsorbents

TYPES	EXAMPLES	PROPERTIES
Chitin and chitosan	biopolymers such as mucopoly saccharide extracted from crustaceans (crab, krill, and crayfish)	➢ high contents of amino and hydroxyl functional groups ➢ chemical stability,high reactivity, excellent chelation behavior and high selectivity toward pollutants
Peat	Raw peat contains lignin,cellulose, fulvic and humic acid as major constituents	➢ polar functional groups ➢ low mechanical strength, ➢ a high affinity for water, poor chemical stability
Biomass	white-rot fungi and other microbial cultures	➢ high potential as an adsorbent

Table 1.6 Waste materials from Industry and Agriculture

TYPES	EXAMPLES	PROPERTIES
Activated carbons from solid wastes and coal-based adsorbents	wood, coconut shell, lignite or coal	➢ porous material and is known to have micro porosity and thus high-surface-area.
Agricultural solid wastes	sawdust, rice husk, and bark	➢ polyphenolic groups
Industrial by-products/waste materials	Fly ash, Sludge, red mud	➢ It contains insoluble metal hydroxides and other salts. ➢ Its properties are extremely variable and depend strongly on its origin

1.7.2 Activated Carbon

Activated carbon is a highly porous, amorphous solid consisting of microcrystallites with a graphite lattice, usually prepared in small pellets or a powder. It is non-polar and cheap. One of its main drawbacks is that it is combustible. Activated carbon can be manufactured from carbonaceous material, including coal (bituminous, subbituminous, and lignite), peat, wood, or nutshells (e.g., coconut).

1.7.2.1 Manufacturing Process : Carbonisation And Activation

The manufacturing process consists of two phases, carbonization and activation. The carbonization process includes drying and then heating to separate by-products, including tars and other hydrocarbons, from the raw material, as well as to drive off any gases generated. The carbonization process is completed by heating the material at 400–600 °C (750–1,100 °F) in an oxygen-deficient atmosphere that cannot support combustion.

The carbonized particles are "activated" by exposing them to an oxidizing agent, usually steam or carbon dioxide at high temperature. This agent burns off the pore blocking structures created during the carbonization phase and so, they develop a porous, three-dimensional graphite lattice structure. The size of the pores developed during activation is a function of the time that they spend in this stage. Longer exposure times result in larger pore sizes. The most popular aqueous phase carbons are bituminous based because of their hardness, abrasion resistance, pore size distribution, and low cost, but their effectiveness needs to be tested in each application to determine the optimal product.

The strong market position held by AC relates to their unique properties and low cost compared with that of possible competitive inorganic adsorbents like zeolites. The growth of the activated carbon market in the last two decades in the most industrialized region will very probably continue in the near future as more developing areas of the world will realize the importance of controlling water and air pollution. This demand can be satisfied considering the large number of raw material available for the production of AC, the variety of activation processes described, and the available forms of AC. Thus, the continuous research has to be implementing to develop the high quality of AC for specific uses. Following are the properties which are required for efficient Activated Carbon.

The factors are:

- i. High carbon content.
- ii. Low in inorganic content (i.e low ash).
- iii. High density and sufficient volatile content.
- iv. Potential extent of activation.
- v. Inexpensive material.

CHAPTER 2 LITERATURE REVIEW

An exhaustive study has been done to explore the various types of non-conventional low-cost adsorbents used for the removal of chlorophenols from the wastewater and an attempt is made to cover a wide range research work regarding inexpensive, locally available and effective materials that can be used in place of commercial activated carbon for the removal of chlorophenols from aqueous solution. Undoubtedly, low-cost adsorbents offer a lot of promising benefits for commercial purposes in the future. In particular, from the recent literature reviewed, several adsorbents have demonstrated good removal capabilities for certain chlorophenols in comparison to the activated carbon. The present literature review has been initiated to search for pertinent methodologies, theoretical and technical, to conduct the batch adsorption equilibria of the apricot stones based activated carbon systems. This literature review is conducted to determine the current state of knowledge of the theoretical and technical aspects of adsorption.

This Literature review covers the following topics:

1. Non-conventional low cost adsorbents
2. Characterization of the adsorbent
3. 2,4-dichlorophenol removal using other meth
4. Adsorption Study-
    - Adsorbates
    - Experimental Procedures

5. Kinetics and Equilibrium Adsorption Isotherm
6. Thermodynamics of Adsorption Process

2.1 NON-CONVENTIONAL LOW COST ADSORBENTS

Demirbas et al., [2008] dealt with the adsorption abilities of apricot stone activated carbon (ASC) for removal of astrazon yellow 7GL dye from synthetic aqueous solutions. The rate limiting step of the basic dye onto the adsorbent was determined from the adsorption kinetic results. The thermodynamic parameters were also calculated from the adsorption equilibrium measurements. The adsorbent was characterized by FTIR, BET and SEM, respectively. The maximum dye adsorption capacity on ASC at 50 °C was 221.23 mg/g. Thermodynamics parameters were also evaluated. The values of enthalpy and entropy were 49.87 kJ/mol and 31.93 J/mol K, respectively, indicating that this process was spontaneous and endothermic. The experimental studies indicated that ASC had the potential to act as an alternative adsorbent to remove the basic dye from aqueous solutions.

In this study, **Gergova and Eser, [1996]** investigated the differences in the porous structure of activated carbons produced from a single precursor, apricot stones, employing two different methods, a two-step physical activation and one-step pyrolysis/activation. In both cases, steam was used as the activation agent. Apricot stones are abundant waste materials from the canning industry. Their hardness along with the low ash and sulfur contents make them good precursors for activated carbon production. The steam activation of apricot stones produces carbons with well-developed porosity. In order to achieve good porosity development and high surface area, one should use relatively low temperature and long reaction time for one-step carbons and higher temperatures and shorter activation times for two-step carbons.

Debirmas et al., [2005] used Apricot stones as the activated carbon precursor. They were carbonised and activated after treatment with sulphuric acid (1:1) at 200 °C for 24 h. The ability of the activated carbon to remove Ni(II), Co(II), Cd(II), Cu(II), Pb(II), Cr(III) and Cr(VI) ions from aqueous solutions. Chemical activation utilizes chemicals, such as H_2SO_4, H_3PO_4, $ZnCl_2$, KOH and $CaCl_2$, that have dehydration and oxidation characteristics. Carbonisation and activation are usually carried out simultaneously in the chemical activation process. Batch experiments were conducted to assess the effect of pH on ASAC. Adsorptions of the metal ions were found to be highly pH dependent and the results indicated that the optimum pH for removal was 1 for Cr(VI) while that for the rest of the metal ions varied from 3 to 6.

In this work, **Kazemipour et al., [2008]** carried out adsorption of copper (Cu), zinc (Zn), lead (Pb), and cadmium (Cd) that exist in industrial wastewater onto the carbon produced from nutshells of walnut, hazelnut, pistachio, almond, and apricot stone. All the agricultural shell or stone used were ground, sieved to a defined size range, and carbonized in an oven. Time and temperature of heating were optimized at 15 min and 800 °C, respectively, to reach maximum removal efficiency. Almond, walnut, hazelnut, pistachio shells and apricot stones were used as starting materials. These natural raw materials appear to be very suitable starting materials for activated carbons because of their low ash content (0.31–0.78%). Removal of heavy metals from wastewater by agricultural wastes is a green chemistry method for managing our environment cleanliness.

Kinetic studies of phenol adsorption on activated carbon (AC) produced fromwaste dates' stone (DS) were performed using four different AC particle sizes (1.47, 0.8, 0.45 and 0.225mm) and initial concentration of phenol of 200 and 400 ppm by **Alhamed, [2009].** It was shown that the adsorption kinetics of phenol on activated carbon (AC) produced from waste dates' stone is very well represented by the pseudo-second order model. Breakthrough curves for phenol removal using a packed bed of activated carbon produced from dates' stones were very well predicted using an axial dispersion model. BET surface area was found to be 951 m^2/g.

Activated carbons were obtained by carbonization of orange skin waste and partial gasification with CO_2 by **Rosas et al., [2010].** The orange skin contains a significant amount of inorganic matter mainly potassium, calcium and phosphorus. CO_2 gasification is catalyzed by potassium and calcium, resulting in carbons with a microporous structure. Thermal treatment up to 900 °C applied to orange skin-derived activated carbons yields carbons with a highly developed porous structure, and a significant contribution of mesopores, due to the activation effect of potassium compounds. This porous structure is initially blocked by the inorganic matter that is removed by a subsequent acid wash, opening the porous structure of the final carbon; an activated carbon with a very wide porous structure and a specific surface area of around 1200 m^2/g was obtained. The activated carbon with high potassium content shows relatively high NO adsorption capacities in the presence of oxygen at 120°C, probably due to the catalytic effect of potassium on the oxidation of NO.

Preparation and characterization of activated carbons from oil-palm stones by carbon dioxide activation were studied in this paper by **Lua and Guo, [2001]**. These oil-palm stones are agricultural by-products from palm-oil mills in several tropical countries. Ultimate and proximate analyses, pycnometry, mercury porosimetry, surface area and porosimetry as well as transmission electron microscopy were carried out for evaluating the textural properties of the activated carbons. It was found that the activation temperature and hold time had significant influences on the surface area and pore size distribution of the activated carbon. The optimum conditions for preparing these activated carbons from chars pyrolyzed at 600 °C to derive the highest specific surface areas were found to be an activation temperature of 900 °C and a hold time of 30 min.

Herein, **Mohan and Pittman, [2006]** provided the first review article that provides readers an overview of the sorption capacities of commercial developed carbons and other low cost sorbents for chromium remediation. After an overview of chromium contamination is provided, more than 300 papers on chromium remediation using adsorption were discussed to provide recent information about the most widely used adsorbents applied for chromium remediation. Particular attention is paid to comparing the sorption efficiency and capacities of commercially available activated carbons to other low cost alternatives.

Adsorption techniques are widely used to remove certain classes of pollutants from wastewater. Phenolic compounds represent one of the problematic groups. Although commercial activated carbon is a preferred adsorbent for phenol removal, its widespread use is restricted due to the high cost. As such, alternative nonconventional adsorbents have been investigated. The natural materials, waste materials from industry and agriculture and bioadsorbents can be employed as inexpensive adsorbents. The review (i) presents a critical analysis of these materials; (ii) describes their characteristics, advantages and limitations; and (iii) discusses the various mechanisms involved. There are several issues and drawbacks concerned on the adsorption of phenolic compounds that have been discussed in this review article by **Ahmaruzzaman, [2008].**

2.2 CHARACTERIZATION OF THE ADSORBENT

Shalaby et al., [2006] prepared activated carbons from apricot stones by one-step steam pyrolysis activation process and characterized for their pore structures. The activated carbons were evaluated for their chemical (elemental composition), surface (BET surface area, mercury porosimetry), and adsorption (iodine number) properties. Carbonization behavior of the apricot stones was investigated by thermogravimetric analysis. Scanning electron microscopy (SEM) was used to follow the changes in the carbon texture upon activation. The experimental results revealed that carbons obtained by the same conditions of activation show differences in their pore structures and adsorption characteristics due to their sulfur contents. The highest BET surface area carbon (1092 m^2/g) was obtained from the low sulfur content (0.04%) apricot stone with a particle size range of 1−3.35 mm at the activation conditions of 800 °C for 4 h.

Almaza′n-Almaza′n et al., [2007] developed a new method for the preparation of activated carbons from poly(ethyleneterephthalate) (PET). It is based on the basic hydrolysis of the PET wastes followed by heat treatment of the solid residue (terephthalate salt + base excess) under inert atmosphere. In this way, carbonisation and activation are combined on a single-step process which increases the carbon yield and reduces the evolution of volatile compounds and the temperature of treatment in comparison to the common PET carbonisation – CO_2 activation method. The so prepared activated carbon samples present high adsorption capacity and a relatively homogenous and narrow microporosity which enlarges with treatment time, according to the data obtained from adsorption of different gases and organic vapours and by molecular simulation of adsorption. In fact, the textural characteristics of these samples are improved in relation to those produced by CO_2 activation for the same time of treatment (besides the latter ones need to be activated at higher temperature).

2.3 2,4-DICHLOROPHENOL REMOVAL USING OTHER METHODS

Yinchun et al., [2009] used Catalytic degradation for simulated 2,4-dichlorophenol wastewater are investigated by using self-synthesized Fe/activated carbon (AC) catalysts and hydrogen peroxide oxidation agent. Effects of the most relevant operating conditions (pH, catalysts concentration, 2,4-dichlorophenol concentration, H_2O_2 concentration and reaction temperature) were discussed. The reaction kinetics studies illustrate that the degradation of 2,4-dichlorophenol nearly follows the first-order reaction, and the reaction apparent kinetics equation is $-r = -\,\mathrm{d}C/\mathrm{d}t = 0.0061\ \exp^{(-6.650\times 104/MT).}$ The reaction rate is 0.00626 min^{-1} at 30 °C, and the apparent reaction activity energy is 66.50 kJ / mol.

Uysal and Tu¨rkman, [2005] studied the effect of biosurfactant on biodegradability of 2,4-dichlorophenol (2,4-DCP) was investigated by activated sludge bioreactor. In 2,4-DCP treatability experiments, acclimated culture was used in the presence of readily degradable substrate (glucose). JBR 425 rhamnolipid was used as biosurfactant. A test reactor with added biosurfactant and control reactor (without biosurfactant) were used in parallel tests. 2,4-DCP removal efficiency for control and test reactor ranged between 97.4–97.7 and 99.7–99.8%, respectively, when the influent concentration of 2,4-DCP ranged between 30 and 100 mg/l. The removal efficiency of 2,4-DCP decreased up to 24.2% and 32.9% in the control and test reactor, respectively, when the concentration of 2,4-DCP was increased from 100 to 150 mg/l. As a result, application of biosurfactant caused some increase in biodegradation rate of 2,4-DCP.

Elkarmi et al., [2009] The aims of this work were to isolate a microorganism from the wastewater of pharmaceutical industries, to examine the difference in its growth utilization of 2,4-dichlorophenol as the sole carbon source pre and post-exposure to UV-irradiation and to investigate its efficiency of biodegradation at different temperatures and pH values using a laboratory benchtop bioreactor. The biodegradability was tested at temperatures of 25, 30, 35 and 40°C and at pH values of 6.5, 7.0 and 8.0. The results indicated that the isolated microorganism was *Pseudomonas alcaligenes*, the maximum concentration of 2,4-dichlorophenol which bacteria can grow on before UV-irradiation was 220 and 380 mg/l after

UV-irradiation. UV-irradiation can be successfully used for the improvement of *P. alcaligenes* biodegradability and that the best 2,4-dichlorophenol biodegradation was at 35 °C and pH 7.

Table 2.1 2-4-Dichlorophenol removal using other low cost Adsorbents

Sn0	**Authors**	**Adsorbent**	**Operating conditions**				**Langmuir constant**
			pH	**Initial Concn mg/l**	**Dosage g/l**	**Temperature ^{0}C**	**Q_{max}**
1	Sathish kumar et al.	Maize Cob	2	10-40	02	30	17.94
2	Shaarani and Hameed	oil palm empty fruit bunch	2	25-250	02	30	232.56
3	Wang et al.	Polygonum orientale Linn	Acidic	150-250	02	25	244.00
4	Calace et al.	Paper Mill Sludge	4.8-8.0	0.5-800	100	20	4.49
5	Bhatnagar and Minocha	Pomegranate peel	5.5-6.5	50-100	10	25	65.70
6	Sathish kumar et al.	Banana pith	2	0-300	02	35	45.30
7	Present study	Apricot Stones	2	100-500	10	30	108.00

2.4 ADSORPTION STUDY

Shaarani and Hameed, [2010] studied the potential feasibility of activated carbon derived from oil palm empty fruit bunch (EFB) for the removal of 2,4-dichlorophenol (2,4-DCP) from aqueous solution was studied. The activated carbon was prepared via chemical activation with phosphoric acid. The effect of contact time, initial concentration (25–250 mg/L), temperature (30–50 °C) and pH (2–12) were investigated. The experimental data were analyzed by the Langmuir and Freundlich isotherm models. The equilibrium data were best represented by Langmuir isotherm model, with a maximum monolayer adsorption capacity of 232.56 mg/g at 30 °C. The adsorption kinetics was well described by the pseudo-second-order kinetic model. The empty fruit bunch based activated carbon (EFBAC) was shown to be a promising material for adsorption of 2,4-DCP from aqueous solutions.

Tay et al., [2009] found lignocellulosic materials to be good and cheap precursors for the production of activated carbon. In this study, activated carbons were prepared from the pyrolysis of soybean oil cake at 600 and 800 °C by chemical activation with K_2CO_3 and KOH. The influence of temperature and type of chemical reagents on the porosity development was investigated and discussed. K_2CO_3 was found more effective than KOH as a chemical reagent under identical conditions in terms of both porosity development and yields of the activated carbons. The maximum surface area (1352.86 m^2g^{-1}) was obtained at 800 °C with K_2CO_3 activation which lies in the range of commercial activated carbons. Elemental analyses of the activated carbons indicate insignificant sulphur content for all activated carbons. The ash and sulphur contents of the activated carbons obtained with chemical activation by K_2CO_3 were lower than those by chemical activation with KOH.

Akhtar et al., [2006] studied the sorption potential of chemically and thermally treated rice husk (RHT) for the removal of 2,4-dichlorophenol (DCP) from aqueous solutions has been investigated The pore area and average pore diameter of RHT by BET method are calculated to be 17 ± 0.6 m^2g^{-1} and 51.3 ± 1.5 nm, respectively. Maximum sorption ($98 \pm 1.2\%$) was achieved for RHT from 6.1×10^{-5} moldm^{-3} of sorbate solution using 0.1 g of rice husk for 10 min agitation time at pH 6 and 303 K, which is comparable to activated carbon commercial (ACC)

96.6 ± 1.2%, but significantly higher than chemically treated rice husk (RHCT) 65 ± 1.6% and rice husk untreated (RHUT) 41 ± 2.3%. The sorption data obtained at optimized conditions was subjected to Freundlich, Langmuir and Dubinin–Radushkevich (D–R) isotherms. Sorption intensity $1/n$ (0.31 ± 0.01) and sorption capacity multilayer Cm (12.0 ± 1.6 mmol g^{-1}) have been evaluated using Freundlich sorption isotherm, whereas the values of sorption capacity monolayer Q (0.96 ± 0.03 mmol g^{-1}) and binding energy, b, (4.5 ± 1.0) × 104 dm^3 mol^{-1} have been estimated by Langmuir isotherm. The Langmuir constant, b, was also used to calculate the dimensionless factor, R_L, in the concentration range $(0.6–6.1) \times 10^{-4}$ mol dm^{-3}, suggesting greater sorption at low concentration. D–R sorption isotherm was employed to calculate sorption capacity Xm (2.5 ± 0.07 mmolg^{-1}) and sorption energy E (14.7 ± 0.13 kJ mol^{-1}). Lagergren and Morris–Weber equations were employed to study kinetics of sorption process using 0.2 g of RHT, 25 cm^3 of 0.61 × 10–4 mol dm^{-3} sorbate concentration at pH 6, giving values of first-order rate constant, k, and rate constant of intraparticle transport, R_{id}, (0.48 ± 0.04 min^{-1} and 6.8 ± 0.8 nmolg^{-1} $min^{-1/2}$, respectively) at 0.61×10^{-4} mol dm^{-3} solution concentration of DCP, 0.1 g RHT, pH 6 and 2–10 min of agitation time. For thermodynamic studies, sorption potential was examined over temperature range 283–323K by employing 6.1×10^{-4} mol dm^{-3} solution concentration of DCP, 0.1 g RHT at pH 6 and 10 min of agitation time and values of ΔH° (−25 ± 1 kJmol^{-1}), ΔS° (−61 ± 4 J mol^{-1} K^{-1}) and $\Delta G°_{303K}$ (−7.1 ± 0.09 kJ mol^{-1}) were computed. The negative values of enthalpy, entropy, and free energy suggest that the sorption is exothermic, stable, and spontaneous in nature.

In this paper, **Calace et al., [2002]** studied the sorption capacity of paper mill sludges for phenols. Phenol, 2-chlorophenol (2-CP), 3-chlorophenol (3-CP), 4-chlorophenol (4-CP), 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), 2,4-dichlorophenol (2,4-DCP), 3,4-dichlorophenol (3,4-DCP) 3,5-dichlorophenol (3,5-DCP) and 2,4,5-trichlorophenol (2,4,5-TCP) were chosen for the sorption tests. Kinetic experiments showed that substituted-phenol sorption on paper mill sludge was rapid (equilibrium was reached after 3 h); conversely, the time taken by the phenol to reach equilibrium conditions was 260 h. Experimental data showed that particle diffusion was involved in the sorption process but was not the only rate-limiting mechanism; several other oxygen containing functional groups. It was noted that pore size distribution alone was not the only contributing factor for the uptake of atrazine onto the activated carbons. The sorption data were fitted well using the Freundlich isotherm. The free energy change showed that sorption of atrazine on activated carbons is a spontaneous process. A pseudo-second order kinetic model was used for analysing the kinetic data, and it was concluded through Boyd Model that adsorption of atrazine was controlled by a film diffusion mechanism.

The modelling study on simultaneous adsorption of phenol and resorcinol onto granular activated carbon (GAC) in multicomponent solution was carried out at 303K by **Kumar et al., [2011].** Three equilibrium isotherm models for multicomponent adsorption studies were considered. In order to determine the parameters of multicomponent adsorption isotherms, individual adsorption studies of phenol and resorcinol on GAC were also carried out. The experimental data of single and multicomponent adsorption were fitted to these models. The parameters of multicomponent models were estimated using error minimization technique on MATLAB R2007a. The adsorption of phenol and resorcinol onto GAC has been studied using single and binary component systems in aqueous solutions at 303 K. The simultaneous adsorption of phenol and resorcinol on GAC shows that extended Freundlich model gives a best fit with experimental observations.

2.6 THERMODYNAMIC STUDY

Sathishkumar et al., [2008] observed that Acidic pH was favourable for the adsorption of 2,4-DCP. Studies on pH effect and desorption showed that chemisorption seemed to play a major role in the adsorption process. Thermodynamic study showed that adsorption of 2,4-DCP on palm pith carbon was more favoured. The change in entropy (ΔS°) and heat of adsorption (ΔH°) of palm pith carbon was estimated as 30.72 J/mol/k and 7.16 kJ/mol, respectively. The high positive value of change in Gibbs free energy indicated the feasible and spontaneous adsorption of 2,4-DCP on palm pith carbon. Kinetics and Thermodynamics model were discussed at length.

The present study by **Sathishkumar et al., [2009]** deals with the adsorption potential of thermally activated carbon developed from maize cob for the removal of 2,4-dichlorophenol (2,4-DCP) from aqueous solutions. Studies were conducted to delineate the effects of contact time, 2,4-DCP initial concentration, pH and temperature. The kinetics of 2,4-DCP adsorption from a solution onto an adsorbent was explored experimentally. Bangham's and intraparticle diffusion modelwere also used. Non-linear form of Langmuir isotherm model was applied and the data correlate well and the maximum adsorption capacity was found to be 17.94 mg/g for the particle size of 250–500 μm. Acidic pH was favorable for the adsorption of 2,4-DCP. Studies on pH effect and desorption. Thermodynamic study showed that adsorption of 2,4-DCP on maize cob carbon is more favored. The change in entropy (ΔS°) and heat of adsorption (ΔH°) of maize cob carbon were estimated as 26.91 J/(K mol) and 6.78 kJ/mol, respectively.

Kinetic analysis by **TuèTem et al., [1998]** showed that the adsorption reaction could be approximated by a first-order rate equation for which pore-diffusion was the essential rate-controlling step. Adsorption was endothermic and basically of a physical character. Equilibrium modelling by linearized adsorption isotherms revealed that a Langmuir equation could well represent the observed data. The entropy change of adsorption was more positive for DCP due to its higher polarity. The saturation capacity of the sorbent for both chlorophenols were determined by dynamic column tests, this experimental capacity being lower than the theoretical monolayer capacity envisaged by the Langmuir equation. Adsorption was completely reversible as the retained DCP could be completely desorbed from the column with distilled water as eluant. The results were evaluated within the scope of utilization of cost effective unconventional sorbents to remove chlorinated organics as possible substitutes for activated carbon.

3.1 OBJECTIVE OF THE THESIS

1. Development of activated carbon from apricot stones, an agricultural waste.
2. Detailed Characterization of the adsorbent to be carried out including SEM, XRD, BET, FTIR and TGA.
3. Determine the adsorption efficiency of the activated carbon for the toxic pollutant i.e. 2,4-dichlorophenol.
4. Examine the effect of various parameters on the adsorption of 2,4-dichlorophenol over apricot stones based activated carbon i.e., effect of pH, adsorbent dosage, adsorbate concentration and temperature.
5. Explore the thermodynamics of the adsorption system involving the determination of $\Delta G°$, $\Delta S°$ and $\Delta H°$.
6. Fit the various rate equation models to search for the appropriate kinetics for the process and find whether Film or Particle diffusion prevails predominantly in the mechanism.
7. To befit the various Isotherm model and determine the Parameters in the equations to select the the isotherm which conforms to the present adsorption system.

4.1 MATERIALS PROCUREMENT AND CALIBRATION

2-4-Dichlorophenol of analytical reagent grade (purity > 99%) was supplied by S.D. Fine Chemicals Limited, Mumbai (India). All the reagents were of analytical grade and procured from Merck. The adsorbate solution of 2-4-Dichlorophenol was simulated in the laboratory by preparing its aqueous solution whose initial concentration was kept in the range of 100-500 mg/l. The calibration of the adsorbate solution and the concentration detection was carried out in a UV visible Spectrophotometer (HACH, Germany) at a maximum wavelength of 283 nm. Calibration curve was obtained between known values of concentration of adsorbate and its corresponding absorbance as shown in Figure 4.1.

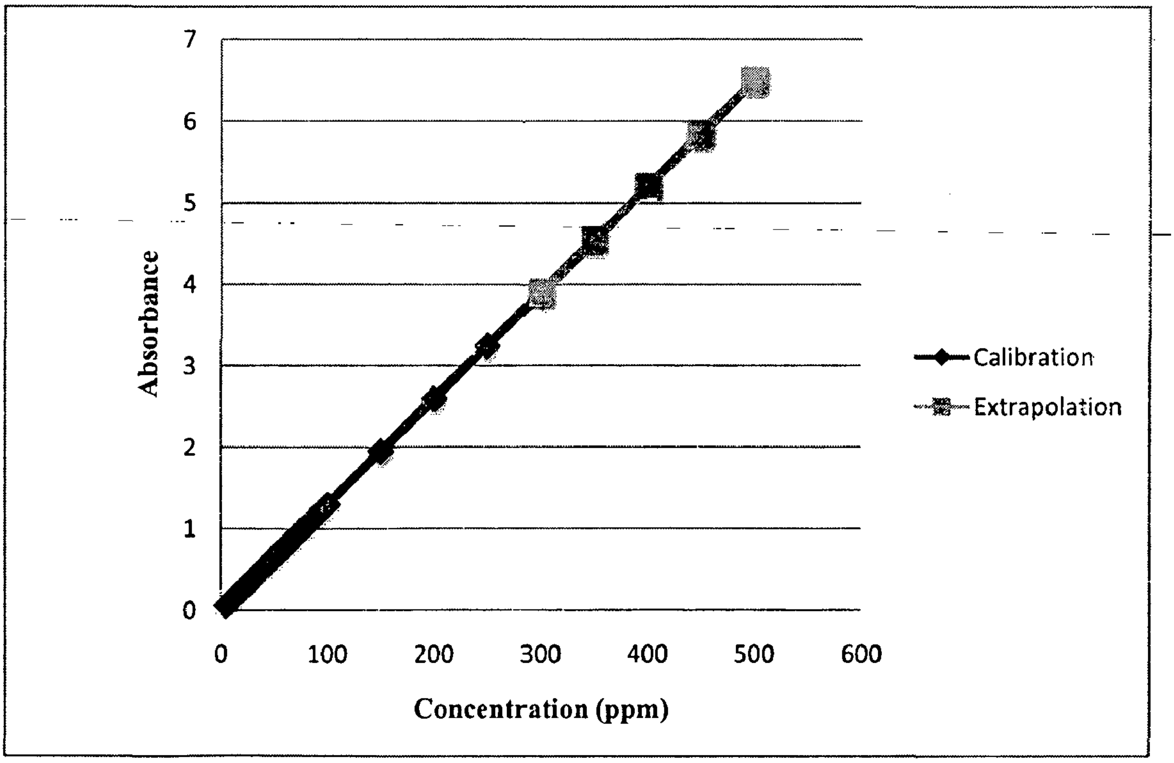


Figure 4.1 Calibration curve for 2,4-dichlorophenol

4.2 ACTIVATED CARBON PREPARATION AND CHARACTERIZATION

The hard shelled Apricot stones, a waste product from canning industry and an agricultural waste, were selected for the activated carbon preparation due to its high carbon content and relatively low ash and sulfur content, which makes it appropriate material for purification processes. 200 g of ASAC, the precursor, was washed thoroughly with distilled water, dried for 24 hrs, crushed and sieved. To ensure that there is no moisture left, the precursor was oven dried for 2 hrs at 100°C. Then followed the impregnation of ASAC by concentrated H_2SO_4 in a 1:1 weight ratio. Subsequently, this mixture was left in an air oven at 100 °C for 24 hrs. It was further subjected to activation in the electric furnace at 250°C for 4 hours. After the produced activated carbon was cooled to room temperature, the samples were washed with hot distilled water to remove free acids. It was soaked in 1% $NaHCO_3$ until the pH of the activated carbon reached 6, dried at 100 °C, pulverized and sieved by a 600 μm sieve.

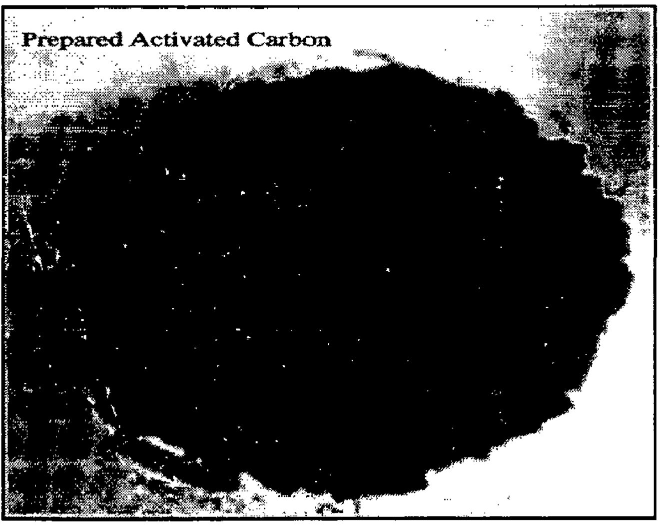


Figure 4.2 Image of Prepared Activated Carbon after activation.

Characterization of activated carbon is important to their applications in adsorption and separation process. Activated carbons were characterized by selected physical and chemical properties. The Surface area for the samples were measured using a Micromeritics, Chemisorb 2720 surface area analyser that uses a nitrogen adsorption–desorption method. The samples were initially outgassed on the degas port of the analyser at 393 K for 24 h before adsorption isotherms were generated by dosing nitrogen (at 77 K) on the carbon. The surface of adsorbent was characterized by scanning electron microscopy. X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-YA diffractometer with Ni-filtered Cu Ka radiation as the X-ray source. The infrared spectrum was recorded using a Fourier transform infrared (FTIR) spectrometer (Nicolet 6700) between wave numbers of 400–4000 cm−1 using a KBr beamsplitter and a deuterated L-alanine doped triglycine sulfate (DLaTGS) detector with a KBr window. The thermogravimetric carbonization experiments for ASAC were also conducted using samples of approximately 10 mg and average particle size of 0.25 mm were heated at 10 °C/min from room temperature to 900 °C under nitrogen flow. The flow of nitrogen was fixed at 10 ml/min throughout the measurements.

4.3 EXPERIMENTAL PROCEDURE

A stock solution of known initial concentration for 2,4-Dichlorophenol was prepared by dissolving an appropriate amount in distilled water. Batch adsorption experiments were performed by shaking 50 ml of aqueous 2,4-Dichlorophenol solution sample with known initial concentration, ph and known adsorbent dose in a 250 ml stoppered conical flask. This mixture was shaken on a reciprocating type horizontal shaker (Metrex Scientific Instruments(P) Ltd, New Delhi) with temperature control. The shaker was set at a temperature of 303 ± 1 K at a speed of 150 rpm. Initial solution concentrations of between 100 and 500 mg L^{-1} were prepared by diluting the stock solution with the measured amount of distilled water. The pH of solutions were adjusted using 0.01 M sulphuric acid or sodium hydroxide solutions. Adsorbent were weighed accurately on aluminium foils using an analytical balance. The adsorbents were transferred carefully into the conical flasks. The sample flask was taken out from the shaker at appropriate intervals of time and then filtered through a filter paper (Whatman No. 42).The filtrate was kept in a refrigerator prior to its analysis. Finally, the 2,4-DCP concentration in each flask was determined using a UV/visible spectrophotometer at a maximum wavelength of 283 nm. This procedure was followed in adsorption kinetics, equilibrium and isotherm studies at various operating conditions as discussed below.

Initially, experiments were held to determine the optimum adsorbent dose varying the quantities from 2 to 14 g/l keeping the initial concentration and pH fixed at 100 mg/l and 2 respectively. The samples were withdrawn at pre-specified time intervals (one at a time) and filtered. The filtrates were stored in a refrigerator. The filtrate samples were taken at different time intervals and the concentrations C_t were estimated. For ASAC, equilibrium condition was established after 24 h. At equilibrium the samples were taken and the equilibrium concentration C_e was calculated for each run. The amount of adsorption of 2,4-DCP per gram adsorbent, q_t (mg/g) at any time *t* was calculated by:

$$q_t = \left[(C_0 - C_t)V\right]/m \qquad \text{........Eq.22}$$

Where, C_0 and C_t are the concentration of *p*-cresol at the initial and time *t*, respectively, *V* is the volume of adsorbate solution, and *m* is the mass of adsorbent dose used in the run. At equilibrium condition, the amount of adsorption per gm of adsorbent q_e (mg/g), was calculated by:

$$q_e = \left[(C_0 - C_e)V\right]/m \qquad \text{..........Eq.23}$$

In industrial liquid effluents, the concentration of 2,4-DCP from 100 to 250 mg/l and sometime even more than 250 mg/l [Calace et al. 2002]. Therefore, initial concentration range is kept in between 100–500 mg/l. The experiments for adsorption kinetics and equilibrium studies were conducted at 30 °C by using six initial *p*-cresol concentrations: 100, 200, 250, 300, 400 and 500 mg/l. In each flask, a fixed adsorbent dose of 10 g/l was added. The pH was maintained at 2 by adding HCl or NaOH as required.

The experiments to enquire the effect of ph were also conducted in the same way. Keeping constant the adsorbent dose at 10 g/l, initial concentration at 100 mg/l and temperature at 30°C, the pH values were variegated from 2-8 to study the change in adsorption uptake and find the optimum pH value.

We were also interested in learning how the change in temperaute affects the adsorption phenomenon. The thermo- stated rotary shaker wasset at 20, 30 and 40°C subsequently with all the other parameters fixed i.e. pH at 2, 10 g/l adsorbent dosage and initial concentration as 100 mg/l.

4.4 KINETIC EXPERIMENTS

To enquire the kinetics of the adsorption process, experiments were conducted at six initial concentrations (100, 200, 250, 300, 400, 500 mg/l), keeping pH of solution constant at 2, temperature at 30 °C and adsorbent dose at 10 g/l. The most widely applied kinetic models for adsorption on activated carbon are pseudo-first order and pseudo-second order kinetic models. In this study, the predictive capabilities of four types of kinetic models regarding adsorption of 2,4-Dichlorophenol on ASAC are examined.

The goodness of the fit of the experimental data to the proposed kinetic models is generally attested by correlation coefficient R^2 and normalized deviations. The percentage deviation between experimental and predicted values for each model has been calculated by following two equations

$$\text{Normalized deviation} = \frac{100}{N} \times \left(\sum \left| \frac{(q_{e,\exp} - q_{e,pred})}{q_{e,\exp}} \right| \right) \qquad \text{.........Eq.24}$$

$$\text{Normalized standard deviation } \Delta q_e \,\% = 100 \sqrt{\frac{\sum \left[q_{e,\exp} - q_{e,pred} \big/ q_{e,\exp} \right]^2}{N}} \qquad \text{.........Eq.25}$$

Where, $q_{e,\exp}$ is the experimental q_e and $q_{e,\text{pred}}$ is the corresponding predicted q_e according to the equation under study with best fitted parameters, N is the number of measurements. It is clear that lower the values of normalized deviations, the better is the fit of experimental data.

4.5 SORPTION STUDIES

In order to determine 2,4-dichlorophenol adsorption isotherm, experiments were conducted at 30 °C and initial concentration of 100 mg/l. Adsorbent dose was varied from 2 to 14 g/l for the prepared activated carbon. For each run the value C_e was different. These experimental data are fitted to six isotherm models Langmuir, Freundlich, Redlich-Peterson, Toth, Radke-Prausnitz and Fritz-Schlunder Isotherm models (Eqn.9-14). The parameters of two parameter models are easily obtained using the linear least square method. However, for models with more than two parameters, model parameters are estimated by a non-linear least square method. For this purpose, curve fitting tool of MATLAB v9.1 has been used. Model parameters are estimated for both AC and PAC. The values of correlation coefficient (R^2) are tabulated with the values of isotherm parameters. The normalized deviation and normalized standard deviation between experimental and predicted values for each isotherm model are calculated by Eqs. (31) and (30). One way to assess the goodness of fit of experimental data to isotherm model equations, is to check the correlation coefficients.

4.6 MODEL VALIDATION

In order to evaluate the goodness of the fit of experimental data and the prediction accuracy of the models utilized in the present work, the following statistical indices are employed for the 2,4-dichlorophenol adsorption system.

$$B_F = 10^{\left(\sum \log_{10}\left(\frac{q_{e,cal}}{q_{e,\exp}}\right)\Big/N\right)} \qquad \text{.........Eq.26}$$

$$A_F = 10^{\left(\sum \left|\log_{10}\left(q_{e,cal}\big/q_{e,\exp}\right)\right|\Big/N\right)} \qquad \text{..........Eq.27}$$

$$RMSE = \sqrt{\frac{\sum \left(q_{e.\exp} - q_{e,cal}\right)^2}{N}} \qquad \text{...........Eq.28}$$

$$SEP = \frac{RMSE}{\sum q_{e,\exp}\Big/N} \times 100 \qquad \text{..........Eq.29}$$

$$NSD = \sqrt{\frac{\sum \left[\left(q_{e,\exp} - q_{e,cal}\right)\Big/q_{e,\exp}\right]^2}{N}} \times 100 \qquad \text{..........Eq.30}$$

$$ND = \sum \left|\frac{q_{e,\exp} - q_{e,cal}}{q_{e,\exp}}\right| \times \frac{100}{N} \qquad \text{........Eq.31}$$

where $q_{e,exp}$ is experimental value of q_e, $q_{e,cal}$ is the predicted value of q_e by models, N indicates the number of data points in the experimental run.

CHAPTER 5 RESULTS AND DISCUSSION

5.1 CHARACTERIZATION

The characteristics of the apricot carbon are shown in Table 5.1. The surface area of apricotcarbon was 385 m^2/g and was comparable to various low-cost adsorbents namely, oil palm stone [Lua and Guo, 2001] (356m^2/g), maize cob carbon [Satishkumar et.al, 2009] (468 m^2/g). Figure 5.3(a, b, c and d) shows the SEM images of the apricot stone based activated carbon (ASAC). It revealed the surface texture and porosity of the carbon prepared and uniform pore size distribution can also be noticed. The profiles in XRD (Figure 5.2) obtained show that the main oxidized metal compound corresponds to CuO. The signals of Cu_2O and Cu are also present in the spectra, specially the last one. FTIR analysis (Figure5.4) Inorganic nitrates have very characteristic spectra. There are three characteristic bands at around 1780 cm^{-1}, 1380 cm^{-1} and 830 cm^{-1}. The 1380 cm^{-1} band is the strongest and is relatively broad while the other two absorptions are weaker and very narrow. There may also be the typical water bands around 3400 cm^{-1} and 1640 cm^{-1}. TGA analysis (Figure 5.1) shows the degradation in weight of the sample with respect to increasing temperature. The study revealed that the moisture content was reported as 16.4% and it might have reduced the efficiency of the carbon prepared. Ash content was low as much as 5.6%. It is known that higher moisture content of the adsorbent dilutes the action of carbon.

Table 5.1 Properties of Prepared ASAC as compared to Commercial Activated Carbon

Properties	**Apricot Stones based activated carbon ASAC**	**Commercial grade activated carbon AC**
BET surface area(m^2/g)	385.0	686.0
Bulk density (g/ml)	0.451	0.977
pH (1% solution)	6.000	7.200
Average particle size(mm)	0.480	0.536
Moisture content (%)	16.400	5.500
Ash content (%)	5.600	3.100

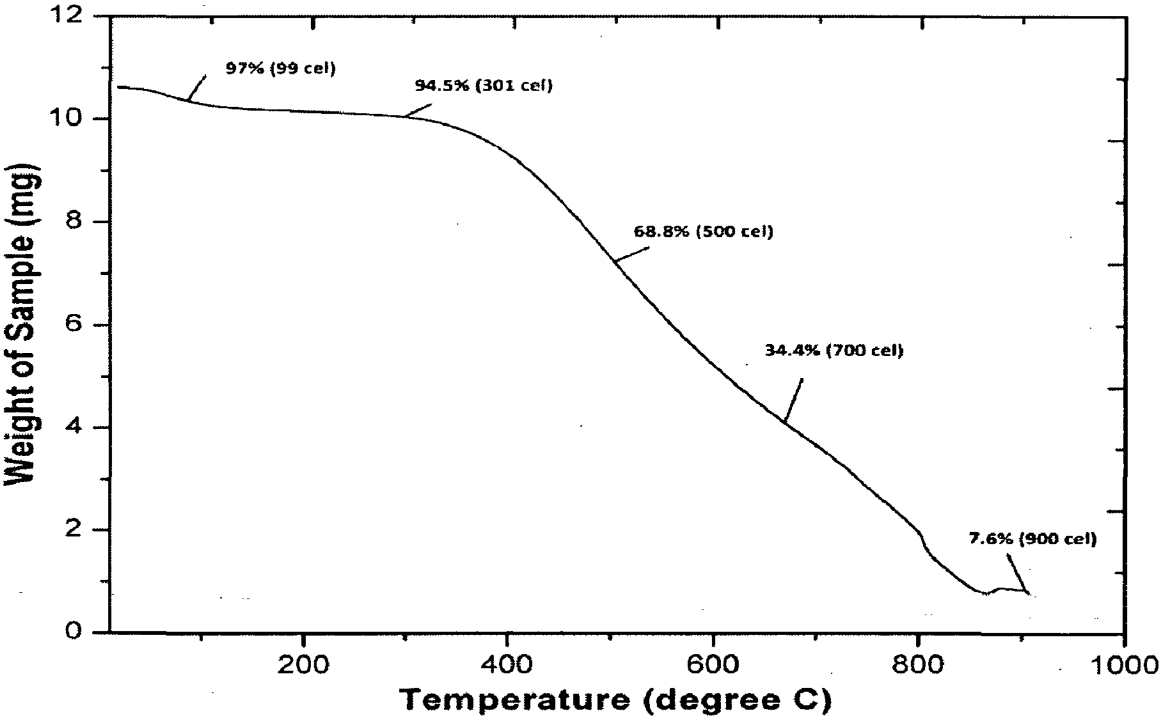


Figure 5.1 Thermogravimetric analysis of the adsorbent (ASAC)

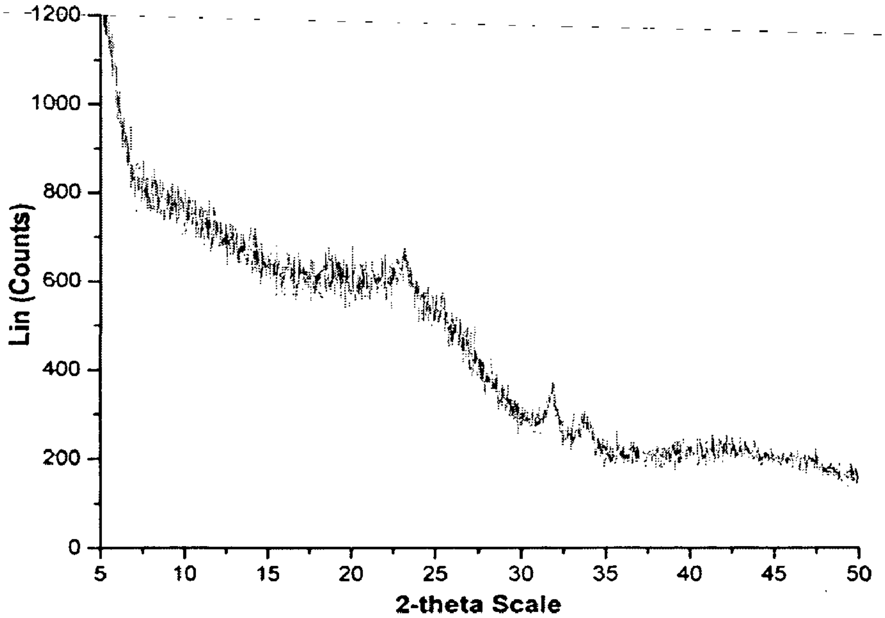


Figure 5.2 X-ray diffraction pattern for apricot stones based activated carbon.

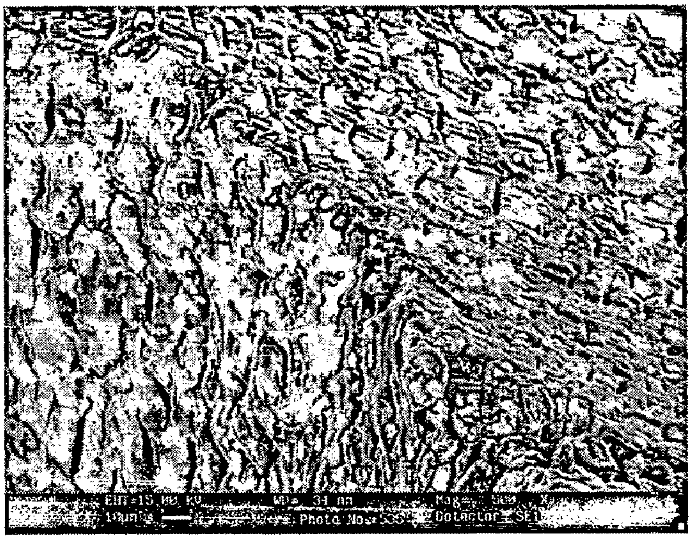


Figure 5.3 (a): SEM image(500X)

Figure 5.4 (b): SEM image(1000X)

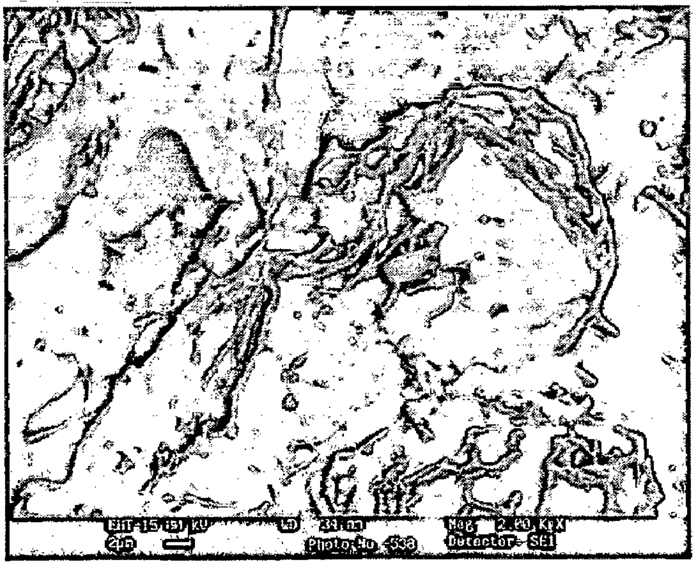


Figure 5.3 (c): SEM image(5000X)

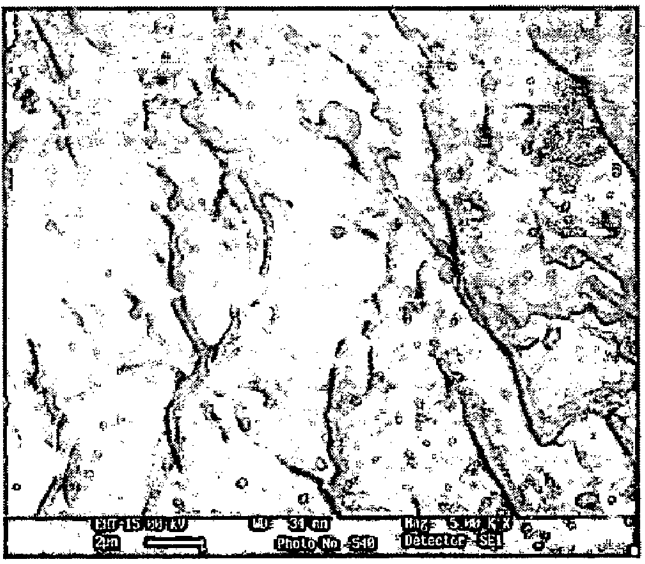


Figure 5.3 (d): SEM image(10000X)

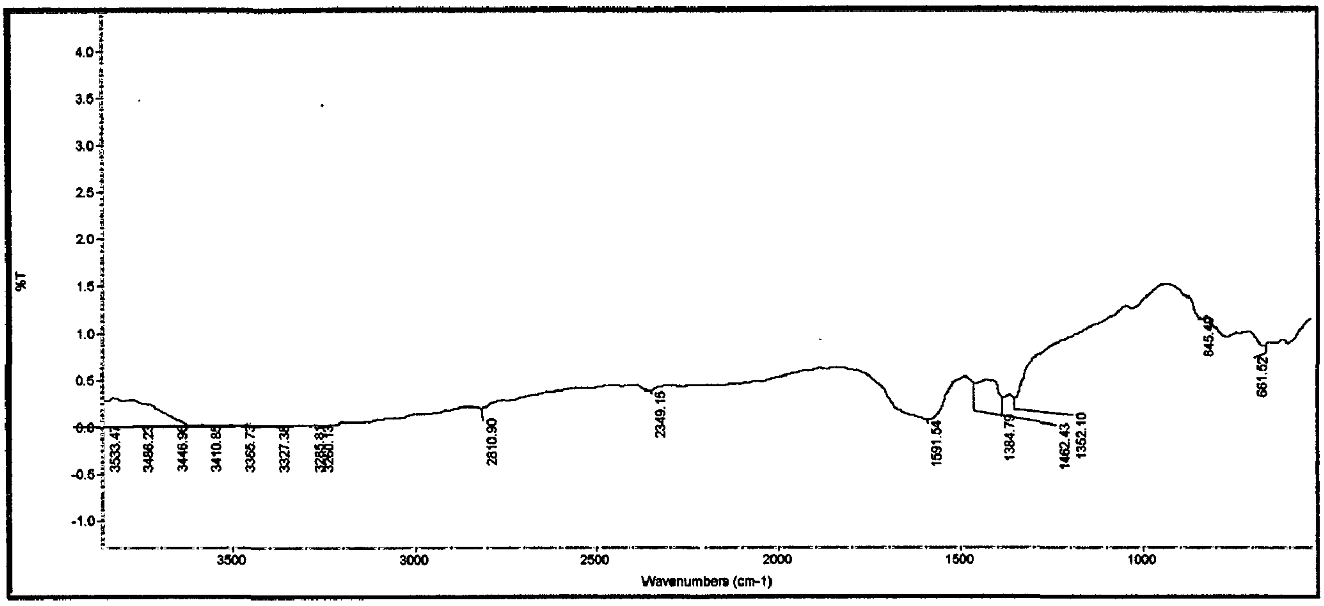


Figure 5.4 (a) FTIR spectra of the prepared activated carbon before adsorption

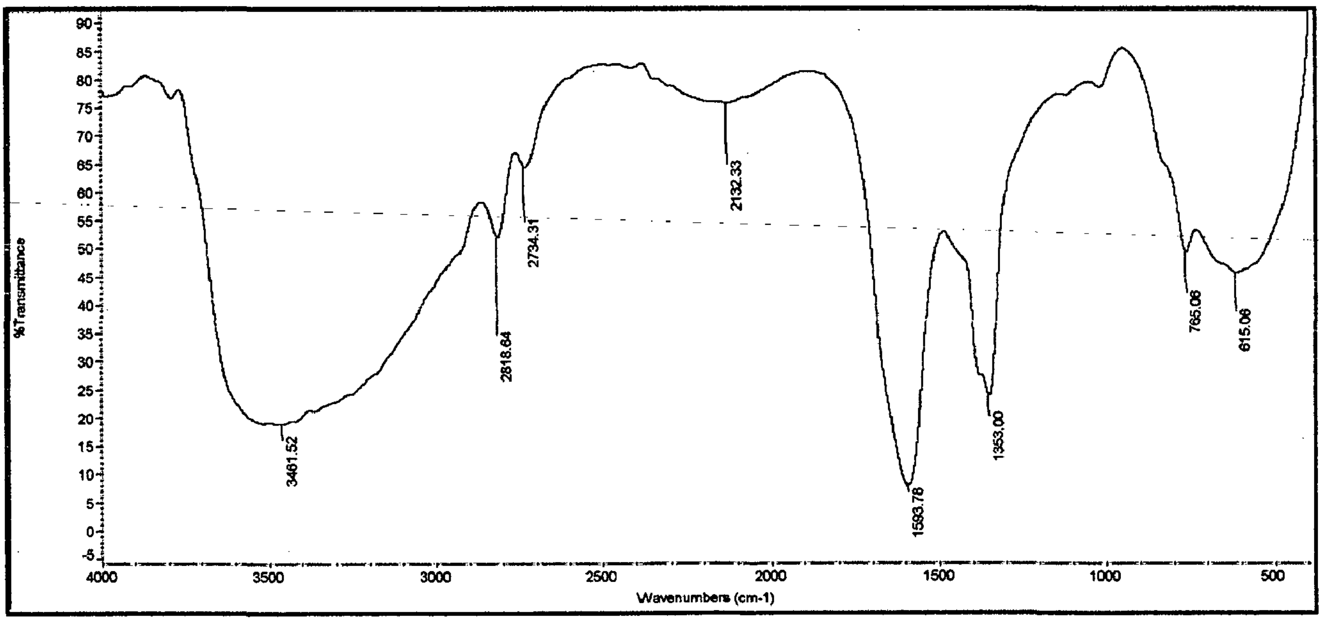


Figure 5.4 (b) FTIR spectra of the prepared activated carbon after adsorption

5.2 EFFECT OF PH

pH of the solution influences the surface charge of the adsorbent and degree of ionization of the adsorbate which in turn affects the rate of adsorption. The conclusions made in this respect in view of the affect of pH are summarized in Table 5.2. The percent removal decreased with increase in pH (Figure 5.5) as reported by other authors also [Sathishkumar et al. 2009)] [Singh K.P. et.al, 2008]. The optimum pH was found out to be 2 as there was highest adsorption observed at this pH. The percent removal decreased from 90% to 67.84% as the pH was increased from 2-8. The pKa value of 2,4-dichlorophenol is 7.85. Therefore, at pH greater than 7.85 2,4-dichlorophenol molecules are mainly in ionic form and much less in molecular form. At this state also high electrostatic repulsion between identical charge lowers the adsorption uptake of 2,4-dichlorophenol.

Table 5.2 Parameters calculated when pH varies from 2-8

pH	**Adsorption Parameters**		
	C_e(mg/l)	**Q_e(mg/g)**	**% Removal**
2	0.1300	9.00000	90.0000
3	0.1470	8.86923	88.6923
4	0.1660	8.72308	87.2308
5	0.2108	8.37846	83.7846
6	0.3380	7.40000	74.0000
7	0.3987	6.93308	69.3308
8	0.4180	6.78462	67.8462

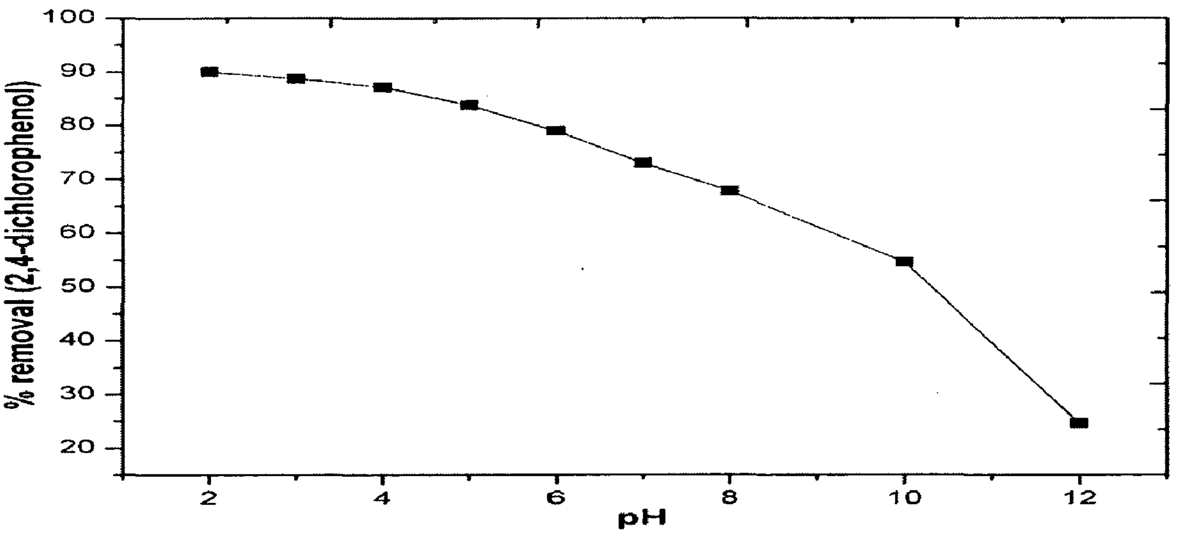


Figure 5.5 Effect of pH (dose 10g/l, initial conc. 100 ppm and temperature 30°C)

5.3 EFFECT OF ADSORBATE INITIAL CONCENTRATION

The experimentation consisted of varying the initial concentration from 100 to 500 mg/l (100, 200, 250, 300, 400, 500 mg/l), keeping the adsorbent dosage at 10 g/l, pH at 2 and temperature at 30°C constant. Time to reach equilibrium was estimated to be 24 hrs. Results have been plotted taking into account two parameters to adjudge the adsorption capacity i.e. Adsorption uptake and % Removal. Figure 5.6 depicts the change in adsorption uptake (Q_t) with respect to time for varied concentrations. The observation made out were: On changing the initial concentration from 100 to 500 mg/l, the amount of 2,4-Dichlorophenol adsorbed increased from 9 to 34.37 mg/g. Rate of adsorption is faster for the initial time period. 75% of the adsorption takes place within 7 hrs. This behavior is observed as initially there are vacant sites available for the adsorbate molecules to adsorb upon which by the time decreases. With the decrease in adsorbate concentration in the solution, the diffusion rate becomes constantly lower and consequently, the diffusion process reaches equilibrium. Percent removal decreased from 90% to 77.05% with increasing Initial Concentration for the fixed adsorbent dose 10 g/l. For concentration below 100 mg/l, ASAC proved out to be an excellent adsorbent and satisfactory for the concentrations greater than 100 mg/l. The decrease in percent removal with the increase in initial concentration attributes to the fact that the same amount of adsorbent had been used for each sample. At higher concentrations the surface becomes saturated and hence no scope for further adsorption.

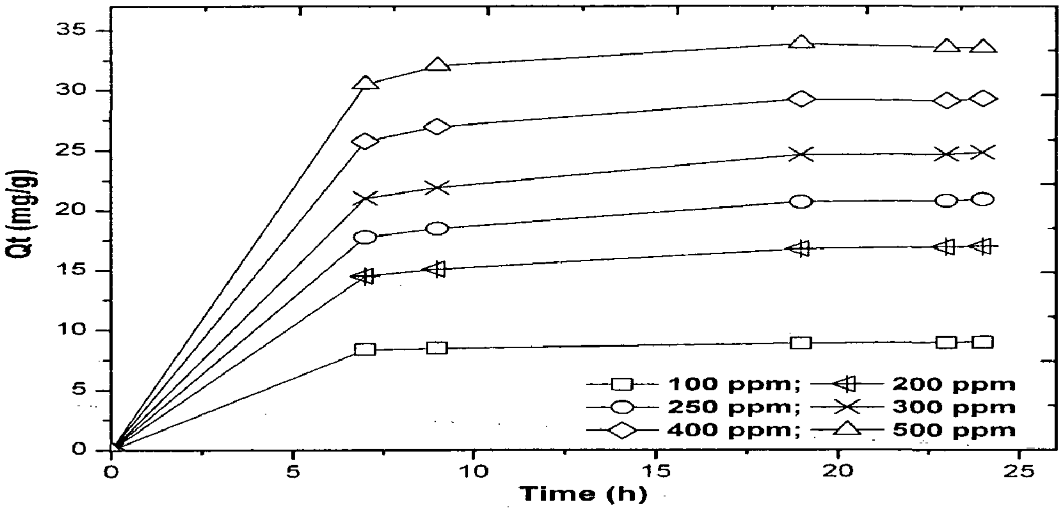


Figure 5.6 Effect of Initial Concentration (pH=2, Temp=30°C and Dose=10 g/l)

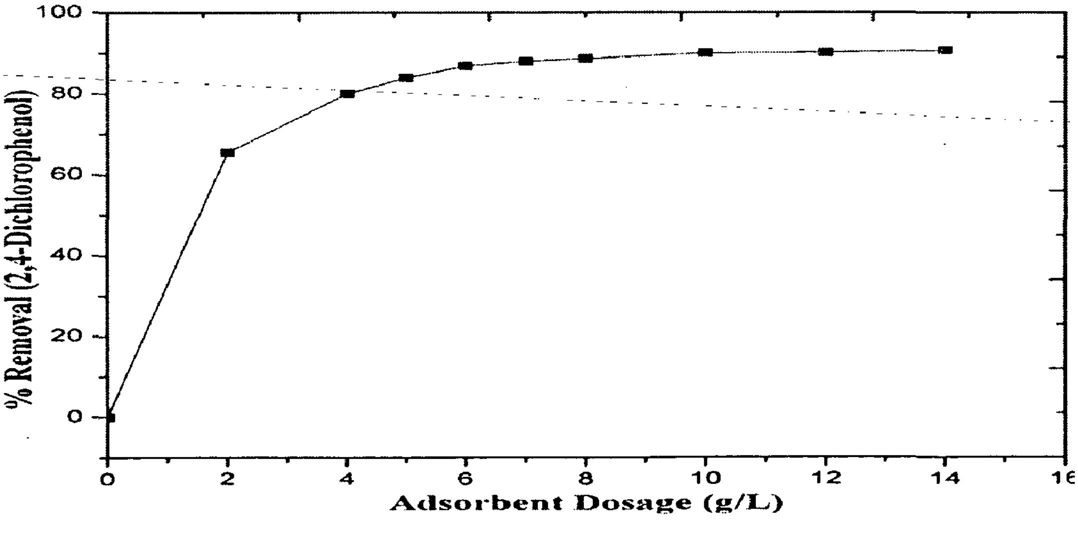


Figure 5.7 Effect of adsorbent dosage(pH=2, C_0 = 100 mg/l and Temperature= 30°C)

5.4 EFFECT OF ADSORBENT DOSAGE

The adsorbent dose used for the adsorption process is decided by studying the effect of variation in dosage on percent removal. The study was done taking thirteen 250 ml flasks having different dosages of adsorbent i.e. 2-14 g/l, adsorbate solution concentration as 100 mg/l, pH at 2 and temperature at 30°C. The percentage adsorbate removal increased from 65.53% to 90.67% with an increase in adsorbent concentration from 2 to 14 g/l (Figure 5.7).

5.5 EFFECT OF TEMPERATURE

The effect of temperature on the adsorption uptake was studied at 20, 30 and 40 °C to observe the thermodynamic parameters. The other variables were fixed at their optimum value (pH 2, Dosage 10 g/l, Initial Concentration 100 mg/l). Increase of temperature slightly increased the removal of 2,4-DCP. The rate of diffusion of the adsorbate molecules increases across the external boundary layer and in the internal pores of the adsorbent particle by increasing the temperature. It happens due to the decrease in the viscosity of the solution.

Thermodynamic parameters such as change in free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) associated to the adsorption process were determined using the following equations.

$$\Delta G^0 = -RT \ln K_0 \qquad (32)$$

Where, R is the universal gas constant (8.314 JK−1 mol−1) and T is the temperature in Kelvin. K_0 can be evaluated using a method described by [Chingombe et.al, 2006]

$$K_0 = \frac{a_S}{a_e} = \frac{v_e C_S}{v_e C_e} \qquad (33)$$

Where, a_s and a_e are the activities of the adsorbed solute and the solute in solution at equilibrium, respectively while v_s and v_e represents the activity coefficients of the adsorbed solute and the solute present in solution, respectively. Table lists the values for $\Delta G°$ for different temperatures

(Table 5.3). The negative values of ΔG° indicate the spontaneous nature of adsorption for 2,4-DCP at 20, 30, and 40°C for the equilibrium constant values of K_0(1.072, 1.16, and 1.223).

Table 5.3 Calculated values of ΔG° for different temperatures

Temperature K	ΔG° (kJ/mol)
293	-169.37
303	-373.89
313	-523.86

According to van't Hoff equation,

$$\log_{10} K_0 = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \tag{34}$$

$\Delta H°$ and $\Delta S°$ can be obtained from the slope and intercept of the Van't Hoff plot of ln K_0 versus 1/T. Positive values of $\Delta H°$ (4.020 kJ/mol) show the endothermic nature of adsorption. The positive values of ΔS^0 (14.9 J/(K mol)) suggest the increased randomness at the solid/solution interface during the adsorption of 2,4-DCP on apricot stones carbon. [Sathishkumar et al., 2007] reported the change in entropy (ΔS^0) and heat of adsorption (ΔH^0) for 2,4-Dichlorophenol adsorption on maize cob carbon as 26.91 J/(K mol) and 6.78 kJ/mol respectively.

5.6 KINETIC STUDY

5.6.1 Pseudo-First-Order Model

The adsorption process is said to follow this model if the curves are linear. The values of q_e and k_1 were calculated from a plot of ln (q_e- q_t) versus t (Eq.2). k_1 was calculated as 0.003 min^{-1} and R^2 as 0.943. Table 5.4 shows all the parameter calculated for pseudo first order model including the values of k, q_e predicted, R^2 and normal standard deviation for various concentrations. It can very firmly be concluded that this model did not fit the experimental data as the curves were not linear and normal standard deviation (eqn.25) came out to be 46.93%.

Table 5.4 Pseudo 1st Order Kinetics parameters and Standard Deviation

S.No.	Concentration of 2,4-Dichlorophenol (mg/l)	Pseudo 1st Order Kinetics				
		K_1 (min^{-1})	q_e predicted (mg/g)	q_e experimental (mg/g)	R^2	Normalized standard deviation Δq_e(%)
1	100	0.003	5.6700	9.98729	0.943	46.93
2	200	0.003	1.2943	17.10769	0.988	
3	250	0.003	16.1500	21.06923	0.983	
4	300	0.003	19.1060	25.03077	0.975	
5	400	0.002	18.2100	29.70000	0.923	
6	500	0.001	21.0100	38.52308	0.679	

5.6.2 .Pseudo-Second-Order Model

The values of q_e and k_2 can be obtained by a linear plot of t/qt vs. t (Eq.4). If the plot is linear, then the adsorption mechanism follows the pseudo 2nd order model. Fig 5.8 reveals the linear nature of the curves for concentration range 100-500 ppm. k_2 was reported as 0.002 g mg^{-1} min^{-1} and correlation coefficient was as high as 0.999 which shows the high predictive capability of the 2nd order model for the experimental data. Table 5.5 shows all the parameter calculated for pseudo first order model including the values of k, q_e predicted, R^2 and normal standard deviation for various concentrations. The normal standard deviation calculated by (Eq.25) was found as 8.82%. The goodness of the fit of the experimental data to the proposed kinetic models is generally attested by correlation coefficient R^2 and normalized deviations both of which confirmed the adsorption mechanism follows 2nd order kinetics.

Table 5.5 Pseudo 2nd Order Kinetics Parameters and Standard Deviation

S.No.	Concentration of 2,4-Dichlorophenol (mg/l)	Pseudo 2nd Order Kinetics				
		K_2 (g mg^{-1} min^{-1})	q_e predicted (mg/g)	q_e experimental (mg/g)	R^2	Normalized standard deviation Δq_e(%)
1	100	0.002118	9.35	9.98729	0.999	8.82
2	200	0.000462	18.52	17.10769	0.999	
3	250	0.000349	23.26	21.06923	0.999	
4	300	0.000284	27.78	25.03077	0.999	
5	400	0.000341	32.26	29.70000	0.999	
6	500	0.000430	35.71	38.52308	0.999	

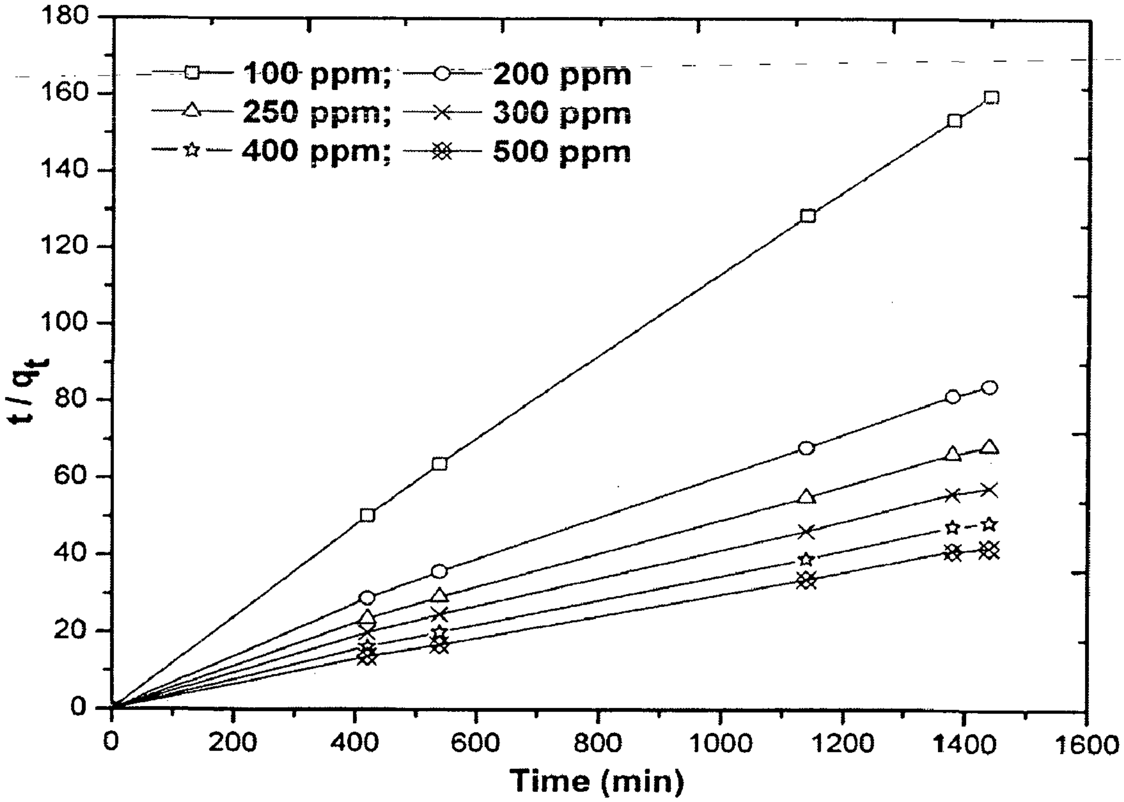


Figure 5.8 2^{nd} order kinetics plot for various concentrations, $R^2 = 0.999$

5.6.3 Boyd Model

The boyd model graph was plotted between $(-0.4977 - \ln(1-F))$ and t, to further investigate whether film diffusion or particle diffusion is the rate determing step (Eq.7). The plots for 2,4-dichlorophenol on ASAC are shown in Figure 5.9. Data has been plotted for various initial concentration ranges. The plots do not pass through the origin, suggesting that the adsorption process is controlled by film diffusion.

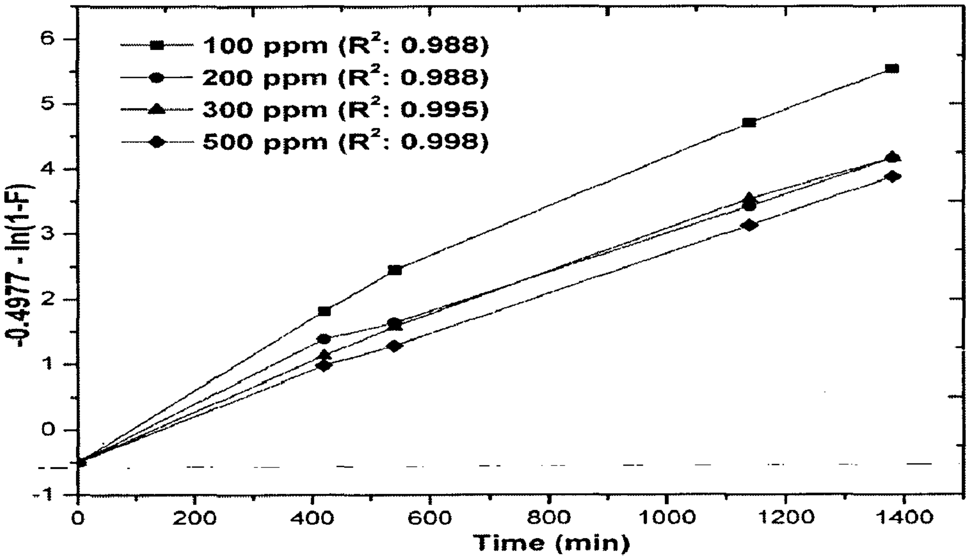


Figure 5.9 Boyd Model for 2,4-dichlorophenol adsorption

5.6.4 Bangham Equation

Kinetic data was further used to check whether pore diffusion or film diffusion is the rate-controlling step in the adsorption system. Linear curves for the (Eq.8) show that particle diffusion prevails and vice versa. The double logarithmic plot according to equation 3 yielded non-linear curves (see Figure 5.10) showing that the diffusion of adsorbate molecules from the bulk of the solution towards the external surface of the adsorbent basically controls the adsorption process. Boyd Model also brought forth the similar results.

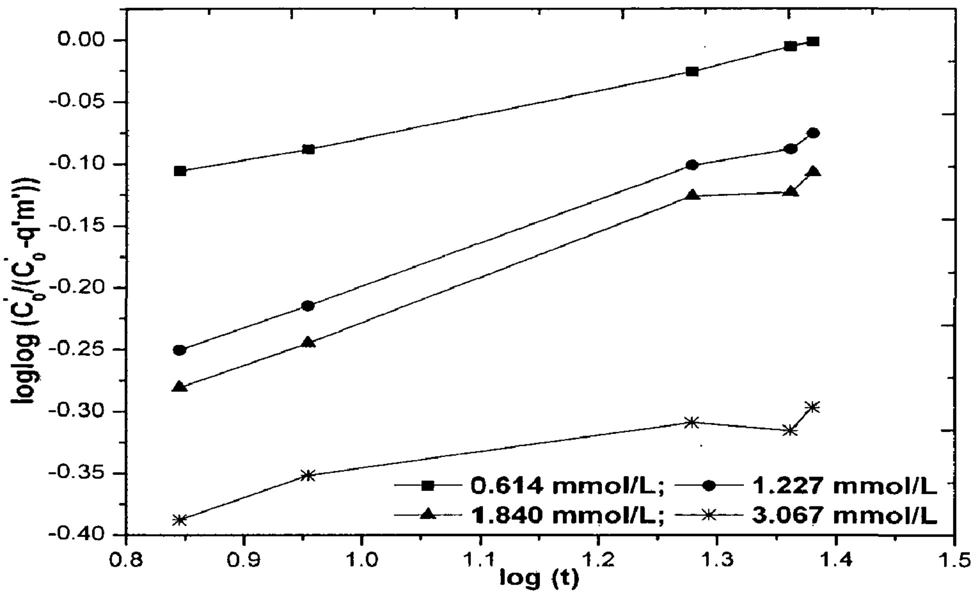


Figure 5.10 Bangham equation plot for 2,4-dichlorophenol adsorption

5.7 SORPTION STUDIES

In this study, the sorption data was correlated using six isotherms and their predictive capabilities were determined. Langmuir, and Freundlich are two parameter models, Redlich–Peterson, Toth and Radke–Prausnitz are three parameter models, and Fritz–Schlunder model is four parameter model, all of them studied and fitted for the equilibrium data to determine the parameters through non-linear curve fitting tool (Matlab).

Table 5.6 Isotherm model parameters and R^2 calculation

Adsorbent	Isotherm Model									
	Freundlich			Langmuir			Redlich–Peterson			
	$q_e = K_F C_e^{1/n}$			$q_e = \frac{Q_0 b C_e}{1 + bC_e}$			$q_e = \frac{K_1 C_e}{1 + K_2 C_e^b}$			
	K_F	1/n	R^2	Q_0	b	R^2	K_1	K_2	b	R^2
ASAC	24.84	0.3122	0.9787	108	0.236	0.9601	0.9917	9.99	0.6845	0.9727

Table 5.7 Isotherm model parameters and R^2 calculation for Toth, Padke-Prausnitz and Fritz Schlunder Isotherms

Adsorbent	Isotherm Model												
	Toth				Radke- Prausnitz				Fritz –Schlunder				
	$q_e = \frac{q_e^{\infty} C_e}{[a + C_e^n]^{1/n}}$				$\frac{1}{q_e} = \frac{1}{KC_e} + \frac{1}{kC_e^{1/n}}$				$q_e = \frac{\alpha_1 C_e^{\beta_1}}{1 + \alpha_2 C_e^{\beta_2}}$				
	q_e^{∞}	A	N	R^2	K	K	$1/n$	R^2	α_1	α_2	β_1	β_2	R^2
ASAC	53.33	4.007	4.382	0.961	0.01478	0.2933	0.655	0.9726	1.042	6.15	5.646	6.48	0.9812

Table 5.8 Model Validation for the Adsorption Isotherms

S.No.	**Adsorption isotherm model**	**ASAC**					
		Normalized deviation	**Normalized standard deviation**	**RMSE**	**SEP**	**AF**	**BF**
1	Langmuir	9.85	11.82	1.49	11.76	1.10	0.98
2	Freundlich	8.08	9.91	0.92	7.26	0.99	1.00
3	Redlich–Peterson	7.13	7.79	1.25	9.87	1.07	0.94
4	Toth	9.45	12.02	1.4	11.05	1.10	0.99
5	Radke–Prausnitz	10.18	11.25	1.56	12.31	1.11	0.97
6	Fritz–Schlunder	10.02	14.11	1.12	8.84	1.10	1.02

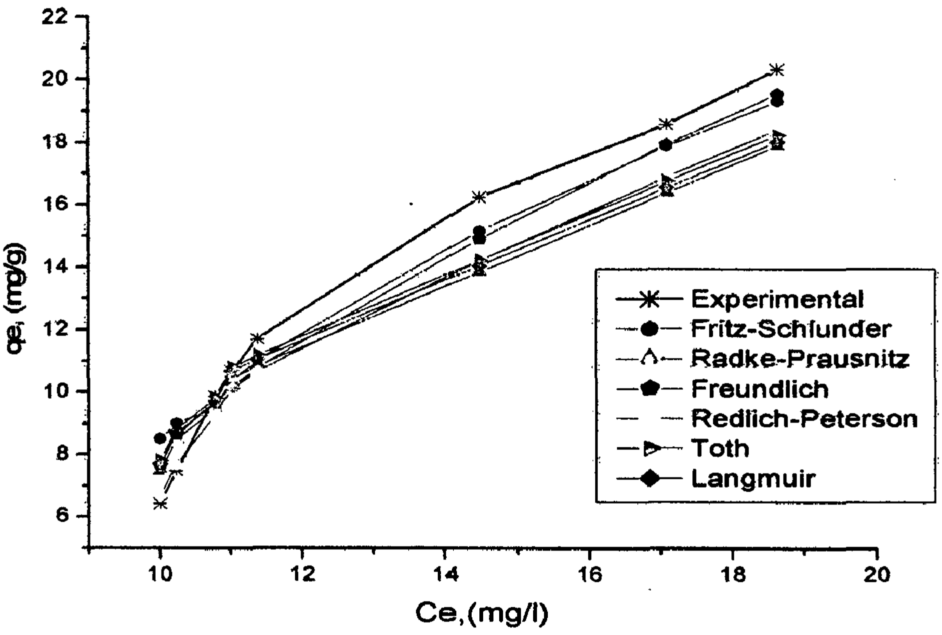


Figure 5.11: Equilibrium isotherm shown for experimental and predicted data.

In the present investigation, the values of R_L have been found to be below 1.0 for 2,4-dichlorophenol on ASAC, showing that the adsorption is very much favourable under prevailing operating conditions. In view of the results obtained, it is deduced that Fritz-Schlunder , Freundlich and Redlich-Peterson isotherm model fit the data reasonably well(on the basis of table 5.6, 5.7, 5.8). Toth and Langmuir isotherm did not fit well and it can be inferred that they were not the appropriate model for the current study. As Langmuir isotherm applies for monolayer adsorption and is appropriate for low concentrations hence it was not suitable for the present study.

CHAPTER 6 CONCLUSION

The results of the present study evince that ASAC has great potential as an economical and efficient adsorbent to remediate 2,4-DCP ions from aqueous solutions. With its BET surface area as 385 m^2/g. Freudlich, Redlich-Peterson and Fritz-Schlunder models were appropriate for the current experimental data. Toth and Langmuir isotherm did not fit well The equilibrium data followed the 2nd order kinetics with K_2 ranging between 0.0002-0.002 g mg^{-1} min^{-1}, and the thermodynamic parameters showed that adsorption was spontaneous and endothermic as ΔH values are positive. The kinetic data fitted well by a pseudo-second order kinetic model and the film diffusion was confirmed as the slowest step in the sorption process. Positive values of ΔH° (4.020 kJ/mol) show the endothermic nature of adsorption. The percent removal decreased from 90% to 67.84% as the ph was increased from 2-8. Percent removal decreased from 90% to 77.05% with increasing Initial Concentration for the fixed adsorbent dose 10 g/l. The percentage adsorbate removal increased from 65.53% to 90.67% with an increase in adsorbent concentration from 2 to 14 g/l.

Further Work recommended:

The activated carbon in this study was developed by utilizing the agricultural waste, apricot stones. It can also be modified to increase the sorption capacity of the activated carbon. With the application of surface modifiers the adsorption uptake by the activated carbon can be enhanced significantly. The removal process here involved Batch adsorption, for further work continuous operation studies can be done on a packed bed Column.

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96.6 ± 1.2%, but significantly higher than chemically treated rice husk (RHCT) 65 ± 1.6% and rice husk untreated (RHUT) 41 ± 2.3%. The sorption data obtained at optimized conditions was subjected to Freundlich, Langmuir and Dubinin–Radushkevich (D–R) isotherms. Sorption intensity $1/n$ (0.31 ± 0.01) and sorption capacity multilayer Cm (12.0 ± 1.6 mmol g^{-1}) have been evaluated using Freundlich sorption isotherm, whereas the values of sorption capacity monolayer Q (0.96 ± 0.03 mmol g^{-1}) and binding energy, b, (4.5 ± 1.0) × 104 dm^3 mol^{-1} have been estimated by Langmuir isotherm. The Langmuir constant, b, was also used to calculate the dimensionless factor, R_L, in the concentration range $(0.6–6.1) \times 10^{-4}$ mol dm^{-3}, suggesting greater sorption at low concentration. D–R sorption isotherm was employed to calculate sorption capacity Xm (2.5 ± 0.07 mmolg^{-1}) and sorption energy E (14.7 ± 0.13 kJ mol^{-1}). Lagergren and Morris–Weber equations were employed to study kinetics of sorption process using 0.2 g of RHT, 25 cm^3 of 0.61 × 10–4 mol dm^{-3} sorbate concentration at pH 6, giving values of first-order rate constant, k, and rate constant of intraparticle transport, R_{id}, (0.48 ± 0.04 min^{-1} and 6.8 ± 0.8 nmolg^{-1} $min^{-1/2}$, respectively) at 0.61×10^{-4} mol dm^{-3} solution concentration of DCP, 0.1 g RHT, pH 6 and 2–10 min of agitation time. For thermodynamic studies, sorption potential was examined over temperature range 283–323K by employing 6.1×10^{-4} mol dm^{-3} solution concentration of DCP, 0.1 g RHT at pH 6 and 10 min of agitation time and values of $\Delta H°$ (−25 ± 1 kJmol^{-1}), $\Delta S°$ (−61 ± 4 J mol^{-1} K^{-1}) and $\Delta G°_{303K}$ (−7.1 ± 0.09 kJ mol^{-1}) were computed. The negative values of enthalpy, entropy, and free energy suggest that the sorption is exothermic, stable, and spontaneous in nature.

In this paper, **Calace et al., [2002]** studied the sorption capacity of paper mill sludges for phenols. Phenol, 2-chlorophenol (2-CP), 3-chlorophenol (3-CP), 4-chlorophenol (4-CP), 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), 2,4-dichlorophenol (2,4-DCP), 3,4-dichlorophenol (3,4-DCP) 3,5-dichlorophenol (3,5-DCP) and 2,4,5-trichlorophenol (2,4,5-TCP) were chosen for the sorption tests. Kinetic experiments showed that substituted-phenol sorption on paper mill sludge was rapid (equilibrium was reached after 3 h); conversely, the time taken by the phenol to reach equilibrium conditions was 260 h. Experimental data showed that particle diffusion was involved in the sorption process but was not the only rate-limiting mechanism; several other mechanisms were involved. The adsorption isotherms showed the following order of retention capacity of papermill sludge: 2-NP=4-NP<<2-CP<phenol<4-CP43-CP<2,4 DCP<3,4 DCP=2,4,5 TCP<3,5 DCP. In all cases the experimental data showed a good fit with the Hill equation, which is mathematically equivalent to the Langmuir–Freundlich model obtained by assuming that the surface is homogeneous, and that the adsorption is a cooperative process influenced by adsorbate–adsorbate interactions.

2.5 KINETICS AND EQUILIBRIUM ADSORPTION ISOTHERM

The activated carbon was prepared from carbonaceous agriculture waste *Parthenium hysterophorous* by chemical activation using concentrated H2SO4 at 130±5 °C by **Singh et al., [2008]**. The prepared activated carbon was characterized and was found as an effective adsorbent material. In order to test the efficacy of parthenium based activated carbon (PAC), batch experiments were performed to carry out the adsorption studies on PAC for the removal of highly toxic pollutant *p*-cresol from aqueous solution. The *p*-cresol adsorption studies were also carried out on commercial grade activated carbon (AC) to facilitate comparison between the adsorption capabilities of PAC and AC. For PAC and AC, the predictive capabilities of two types of kinetic models and six types of adsorption equilibrium isotherm models were examined. The effect of pH of solution, adsorbent dose and initial *p*-cresol concentration on adsorption behaviour was investigated, as well. The adsorption on PAC and on AC was found to follow pseudo-first order kinetics with rate constant 0.0016 min^{-1} and 0.0050 min^{-1}, respectively. The highest adsorptive capacity of PAC and AC for *p*-cresol solution was attained at pH 6.0. Further, as an adsorbent PAC was found to be as good as AC for removal of *p*-cresol upto a concentration of 500 mg/l in aqueous solution. Freundlich, Redlich–Peterson, and Fritz–Schlunder models were found to be appropriate isotherm models for PAC while Toth, Radke–Prausnitz and Fritz–Schlunder were suitable models for AC to remove *p*-cresol from aqueous solution.

The sorption of atrazine from water has been studied by **Chingombe et al., [2006]** using a conventional activated carbon, F400, an annealed carbon sample, F400AN, and an aminated carbon sample, $F400NH_2$. Characterisation of the carbon samples showed that sample $F400NH_2$ had the highest proportion of micropores, but had the lowest values of point of zero charge (PZC) and iso-electric point (IEP). This was attributed to the existence of a high proportion of oxygen containing functional groups. It was noted that pore size distribution alone was not the only contributing factor for the uptake of atrazine onto the activated carbons. The sorption data were fitted well using the Freundlich isotherm. The free energy change showed that sorption of atrazine on activated carbons is a spontaneous process. A pseudo-second order kinetic model was used for analysing the kinetic data, and it was concluded through Boyd Model that adsorption of atrazine was controlled by a film diffusion mechanism.

The modelling study on simultaneous adsorption of phenol and resorcinol onto granular activated carbon (GAC) in multicomponent solution was carried out at 303K by **Kumar et al., [2011].** Three equilibrium isotherm models for multicomponent adsorption studies were considered. In order to determine the parameters of multicomponent adsorption isotherms, individual adsorption studies of phenol and resorcinol on GAC were also carried out. The experimental data of single and multicomponent adsorption were fitted to these models. The parameters of multicomponent models were estimated using error minimization technique on MATLAB R2007a. The adsorption of phenol and resorcinol onto GAC has been studied using single and binary component systems in aqueous solutions at 303 K. The simultaneous adsorption of phenol and resorcinol on GAC shows that extended Freundlich model gives a best fit with experimental observations.

2.6 THERMODYNAMIC STUDY

Sathishkumar et al., [2008] observed that Acidic pH was favourable for the adsorption of 2,4-DCP. Studies on pH effect and desorption showed that chemisorption seemed to play a major role in the adsorption process. Thermodynamic study showed that adsorption of 2,4-DCP on palm pith carbon was more favoured. The change in entropy (ΔS°) and heat of adsorption (ΔH°) of palm pith carbon was estimated as 30.72 J/mol/k and 7.16 kJ/mol, respectively. The high positive value of change in Gibbs free energy indicated the feasible and spontaneous adsorption of 2,4-DCP on palm pith carbon. Kinetics and Thermodynamics model were discussed at length.