ADSORPTIVE REMOVAL OF TRICHLOROETHYLENE AND TETRACHLOROETHYLENE USING PARTHENIUM 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)

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CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in this dissertation, entitled **ADSORPTIVE REMOVAL OF TRICHLOROETHYLENE AND TETRACHLORO - ETHYLENE USING PARTHENIUM BASED ACTIVATED CARBON,** in partial fulfillment of the requirements for the award of **Master of Technology** in **Chemical Engineering** with specialization in **Industrial Pollution Abatement,** is an authentic record of my own work carried out during the period from June 2010 to June 2011, under the supervision of **Dr.(Mrs.) Shashi**, Associate Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee. The matter embodied in this thesis work has not been submitted for the award of any other degree.

Date - 30.6.11

Place - Roorkee

A. SIREESHA

CERTIFICATE

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

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ABSTRACT

A noxious weed and an agricultural waste material *Parthenium hysterophorous* serves as a source for the preparation of activated carbon (PAC) for our study. The impregnation ratio used for the chemical activation process was 1:1.5:0.4 (PAC: H_2SO_4: $(NH_4)_2S_2O_8$). Characterization of the prepared PAC was done and it was found that it was an effective adsorbent for the removal of organic pollutants. Batch adsorption studies were carried out for the removal of major groundwater pollutants Trichloroethylene (TCE) and Tetrachloroethylene (PCE) from aqueous solutions. For both the adsorbates, predictive capabilities of three types of kinetic models and six types of adsorption equilibrium isotherms were investigated. Optimum adsorption conditions were determined with respect to pH, temperature, adsorbent dose and initial adsorbate concentration for both TCE and PCE. The thermodynamic parameters, ΔG^0, ΔH^0 and ΔS^0, were calculated to better understand the nature of the adsorption process. The adsorption of both the adsorbates was found to be following pseudo-second order kinetics with rate constants 0.00032 g mg^{-1} min^{-1} and 0.0029 g mg^{-1} min^{-1} for TCE and PCE, respectively . Among the six isotherm models examined, Freundlich model gave the best fit for TCE adsorption and Fritz-Schlunder model gave the best fit for PCE adsorption. The negative values of thermodynamic parameters represented the spontaneity, chemical control and exothermic nature of the adsorption process. Under optimum conditions, maximum removal efficiencies of TCE and PCE were found to be 98.64% and 83.75% respectively. From various results, it was established that the prepared PAC was more compatible in the removal of TCE than PCE at similar operating conditions. The study concluded that the prepared PAC is an excellent and effective alternative adsorbent for the removal of TCE and PCE from Industrial wastewater because of its negligible-cost, efficiency and ease of availability.

Keywords:

Activated carbon, Parthenium hysterophorous, Groundwater pollutants, Trichloroethylene, Tetrachloroethylene, Adsorption

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NOMENCLATURE

a_s	Sips isotherm constant (-)
A	Koble-Corrigan parameter ($\mathrm{mol}^{(1-n)}$ L^n/kg)
B	Koble-Corrigan parameter (L^n/ mol^n)
C	intercept for intraparticle diffusion model(-)
C_e	adsorbate concentration in the solution at equilibrium, (mg/L)
C_0	concentration of adsorbate in the solution at time t=0, (mg/L)
C_t	concentration of adsorbate in the solution at time t, (mg/L)
ΔG^0	Gibbs free energy, (kJ/mol)
ΔH^0	enthalpy change, (kJ/mol)
k	Radke-Prausnitz isotherm constant, $(\mathrm{mg/g})(\mathrm{L/mg})^{1/n}$
k_1	Pseudo-first order adsorption rate constant, (1/min)
k_2	Pseudo-second order adsorption rate constant, (g/ mg min)
k_p	intraparticle diffusion rate constant (mg/g $\mathrm{min}^{1/2}$)
K	constant in Radke-Prausnitz isotherm, (1/g)
K_D	distribution coefficient (1/g)
K_F	constant in Freundlich isotherm, $(\mathrm{mg/g})(\mathrm{L/mg})^{1/n}$
m	constant in Sips isotherm (-); mass of adsorbent dose, (g)
n	constant in Freundlich, Langmuir-Freundlich, Koble-Corrigan and Radke-Prausnitz isotherms(-)
N	number of data points in the experimental run(-)
q_e	amount of adsorbate adsorbed per gram of adsorbent at equilibrium condition, (mg/g)
$q_{e,cal}$	estimated value of adsorption uptake by isotherm model, (mg/g)
$q_{e,\exp}$	experimental value of adsorption uptake at equilibrium, (mg/g)
$q_{e,\max}$	maximum amount adsorbed on surface in Langmuir-Freundlich isotherm model, (mg/g)
q_m	Langmuir monolayer saturation capacity in Sips isotherm model, (mol/g)
q_t	amount of adsorption per gram adsorbent at any time t, (mg/g)

R	Universal gas constant, (J/mol K)
R^2	correlation coefficient, (-)
ΔS^0	Entropy, (kJ/mol K)
T	temperature, (K)
V	volume of solution, (L)

Greek letters

α_1	Fritz-Schlunder model parameter, $(mg/g)(mg/L)^{\beta 1}$
α_2	Fritz-Schlunder model parameter, $(mg/g)(mg/L)^{\beta 2}$
β_1, β_2	Fritz-Schlunder equation exponents (-)

Abbreviations

AC	Activated carbon
ARE	average relative error
IUPAC	International union for pure and applied chemistry
NSD	normalised standard deviation
ND	normalised deviation
PCE	Perchloroethylene (tetrachloroethylene)
PAC	Parthenium-based activated carbon
RMSE	root mean square error
SEP	standard error of prediction
TCE	Trichloroethylene

CHAPTER 1
INTRODUCTION

1.1GROUNDWATER CONTAMINANTS

Wastewater is the water that has been adversely affected in quality by anthropogenic influence. Most wastewater is treated in industrial-scale wastewater treatment plants (WWTPs) which include physical, chemical and biological treatment processes. Soluble Organics constitute a major part of the water contaminants, most of them being chloroform, carbon tetrachloride, benzene, vinyl chloride, phenolic compounds, tri halo alkanes alkenes and alkynes, methyl-tertiary-butyl ether, trans-1,2 dichloro ethylene, toluene, xylene [1]. Among these, the tri-halo-alkanes, enes and ynes are found to be extensively found in groundwater contamination. Waste disposal practices; storage and handling of materials and wastes; agricultural activities; and saline water intrusion are the most common sources of groundwater contamination [1].

The Agency for Toxic Substances and Disease Registry (ATSDR) reports that trichloroethylene is the most frequently reported organic contaminant in groundwater, and estimates that between 9 and 34 percent of drinking water supply sources have some trichloroethylene contamination [2]. Trichloroethylene (TCE) is a man-made chlorinated solvent, used primarily to remove grease from metal parts and textiles. In addition to TCE, related chlorinated solvents, or volatile organics compounds (VOCs), include Tetrachloroethylene (PCE) which is mainly used as a dry cleaning agent with some industrial applications like degreasing. The Environmental Protection Agency (EPA) has identified 1,428 hazardous waste sites as the most serious in U.S.A and Trichloroethylene has been found in at least 861, or 60%, of the NPL sites [2]. The National Primary drinking water regulations of EPA limits the concentration of TCE and PCE at 0.005 mg/L. The MINAS standard for TCE and PCE in Industrial Effluent is 0.5 mg/L.

TCE is widely used in food processing, textiles, wood products, electroplating, paper, petroleum, rubber, leather, metals, industrial machinery, the role of TCE being a solvent, carrier, extractant, dry cleaning agent, coolant or a chemical intermediate. Also, it has been found that the residence time of TCE in ground water is much longer than in the surface waters. Exposure to low levels of TCE can cause skin, eye, and respiratory tract irritation, nausea, vomiting, headache, dizziness, unconsciousness, and memory loss whereas higher concentrations can even induce cardiac defects, liver damage, childhood leukaemia, and also liver, kidney or lung cancer. In India, TCE is listed as a hazardous chemical, at serial number 644, under the Manufacture, Storage and Import of Hazardous Chemicals Rules, 1989, notified by the Union ministry of environment and forests (MOEF).

Tetrachloroethylene is widely used in dry cleaning. Usually as a mixture with other chlorocarbons, it is also used to degrease metal parts in the automotive and other metalworking industries. It appears in a few consumer products including paint strippers and spot removers. The International Agency for Research on Cancer has classified tetrachloroethene as a Group 2A carcinogen [3]. Tetrachloroethene is a central nervous system depressant and can enter the body through respiratory or dermal exposure [4]. Tetrachloroethylene dissolves fats from the skin, potentially resulting in skin irritation. Because of its mobility in groundwater, its toxicity at low levels, and its density (which causes it to sink below the water table), cleanup activities are more difficult than for oil spills. Instead of excavation or extraction for above-ground treatment or disposal, tetrachloroethylene contamination has been successfully remediated by chemical treatment or bioremediation. Trichloroethylene is a partial degradation product of Tetrachloroethylene [5]. This is the basic reason for both TCE and PCE to occur together in most cases of groundwater pollution.

Different Practices are followed for Groundwater remediation, like Bioaugmentation [6], Chemical Precipitation [7], Ion exchange [8], Chemical oxidation [9] and Carbon adsorption [10]. Advantages and disadvantages of various treatment methods are thoroughly analyzed [11]. Even after secondary treatment and filtration, soluble organics may still be present in the wastewater. These remaining materials are called refractory organics. The most practical way to remove refractory organics is by adsorbing them on activated carbon.

1.2ADSORPTION

1.2.1 GENERAL

Adsorption is a process, similar to absorption, by which a substance in a gas or liquid becomes attached to a solid. The substance can be a pollutant, called an adsorbate, which is attracted to the surface of a special solid. Adsorption occurs naturally, but industrialists have perfected adsorption methods to clean up hazardous waste or purify drinking water. The process of adsorption is the attraction of atoms or molecules from an adjacent gas or liquid to an exposed solid surface. Such attraction forces (adhesion or cohesion) align the molecules into layers onto the existent surface.

The deposition may be driven by

- long range weak forces among atomic or molecular electric multipoles (Vanderwaals);
- short range strong ionic or metallic forces may finalize the setting of new layers onto the solid surface (without generating new chemical species) — as salt deposits (crystalline growth) from super-saturated solutions or as metal vapor deposition onto metallic surfaces.

Adsorbents are used usually in the form of spherical pellets, rods, moldings, or monoliths with hydrodynamic diameters between 0.5 and 10 mm. They must have high abrasion resistance, high thermal stability and small pore diameter, which results in higher exposed surface area and hence high surface capacity for adsorption. The adsorbents must also have a distinct pore structure which enables fast transport of the gaseous vapors.

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.

1.2.2 PRINCIPLES OF SELECTION OF ADSORBENT

All processes require a degree of effectiveness usually thought of as high adsorption capacity, coupled with high selectivity. In many cases the adsorption rate and pressure drop are also important; hence, particle size is important. Besides those, nearly every different application has a different set of additional priorities. For example, the main prerequisite for municipal water purification is low cost. Fortunately, activated carbon offers both low cost and high effectiveness and no other adsorbents are close. The choice would be easy, except that there are many activated carbon manufacturers and each of those typically offers several products. The most important attributes of an adsorbent for any application are : capacity, selectivity, regenerability, kinetics and compatibility.

Adsorption capacity is the most important characteristic of an adsorbent. Simply stated, it is the amount of adsorbate taken up by the adsorbent, per unit mass (or volume) of the adsorbent. It depends on the fluid-phase concentration, the temperature, and other conditions (especially the initial condition of the adsorbent). Typically, adsorption capacity data are gathered at a fixed temperature and various adsorbate concentrations (or partial pressures for a vapor or gas), and the data are plotted as an isotherm (loading versus concentration at constant temperature). Adsorption capacity is of paramount importance to the capital cost because it dictates the amount of adsorbent required, which also fixes the volume of the adsorber vessels, and both generally are significant if not dominant.

Isotherms have limited number of shapes, but there are dozens of empirical forms as shown in Figure 1. There are many other means to express adsorption capacity: isosteres, isobars, and various indices, such as surface area, pore size distribution, Iodine Number and Molasses Number. The latter two are used exclusively to describe activated carbons. Surface area is a relative term, usually measured by inferring the monolayer coverage within an adsorbent of a substance with known density and molecular dimensions (e.g., nitrogen near its normal boiling point). Values typically correlate with capacity, and for various adsorbents are in the range of, say, 5 to 3,000 m^2/g.

The pore size distribution is a related property that indicates the fraction of the space within a particle occupied by micropores ($dp < 20$ Å), mesopores (20 Å $\leq dp < 500$ Å) and macropores ($dp \geq 500$ Å). Pore dimensions intuitively correlate with both capacity and kinetics, but the exact dependence is subtle. Figure 2 shows the pore size distributions of some common adsorbents. The Iodine Number is a rough measure of capacity for small molecules and correlates with surface area. The Molasses Number was developed for decolorization of cane sugar, and relates to adsorption of large molecules from a liquid.

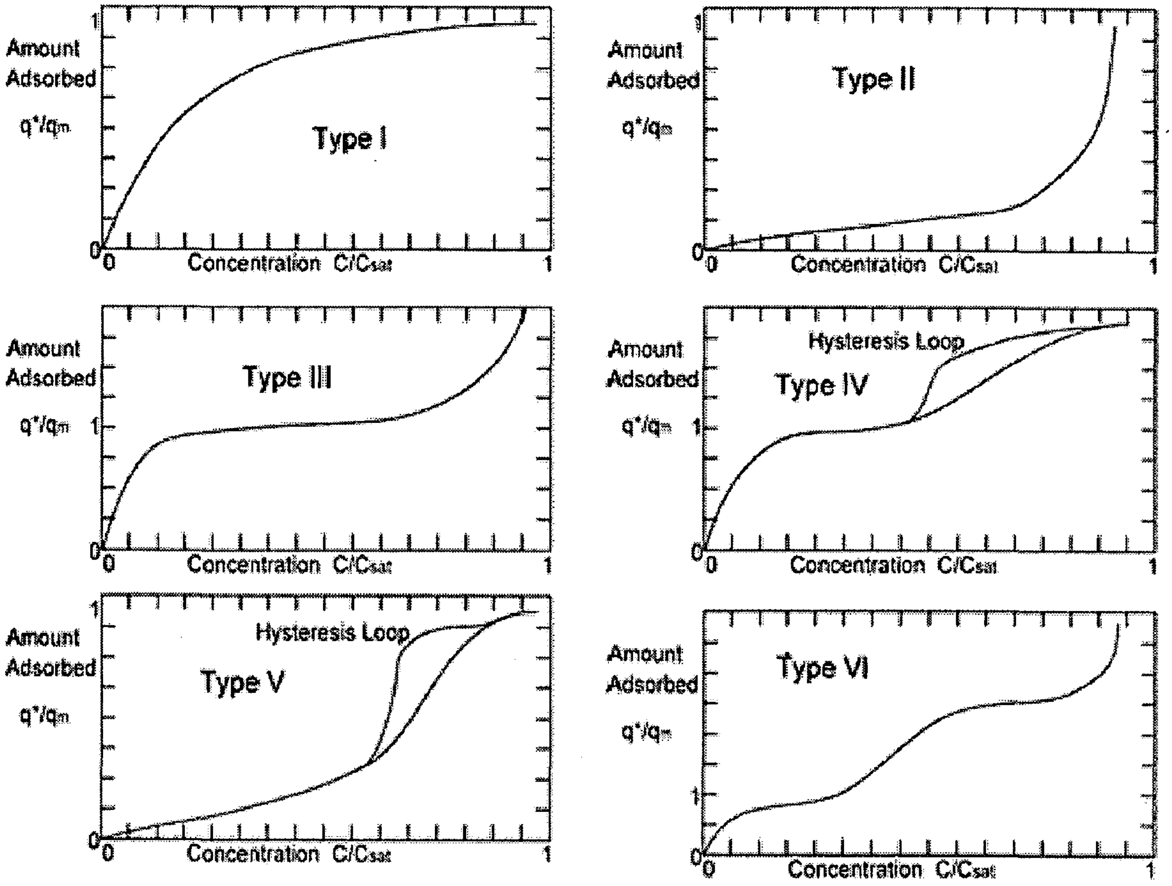

Figure 1: Classic Isotherm types

Selectivity is related to capacity. The simplest definition is the ratio of the capacity of one component to that of another at a given fluid concentration. That ratio generally approaches a constant value as concentration drops towards zero. Of course, the concentrations of interest may not be near zero, so the choice of definition becomes subtle. The closest analogy is to relative volatility (e.g., in distillation) in that the smaller the value, the larger the required equipment. An ideal situation occurs when the major component is not adsorbed much (so it can be thought of as an inert "carrier"), which leads to a very large selectivity.

All cyclic adsorption applications rely on regenerability, so that the adsorbent can operate in sequential cycles with uniform performance. This means each adsorbable component (adsorptive or adsorbate) must be relatively weakly adsorbed (or physisorbed). The heat of adsorption provides a measure of the energy required for regeneration, and in that regard low values are desirable. Regeneration might be accomplished by a thermal swing, pressure swing, chemical (e.g., by displacement, elution, or supercritical extraction), or sometimes by a combination of those. Displacement would involve introducing a species that adsorbs more strongly than the adsorbate of interest, while elution would entail dissolving the adsorbed material by a solvent that is weakly adsorbed if at all. The chemical methods all require a separate separation operation that may be costly, plus a means must be found for purging the bed of the regenerant. In some cases, regeneration takes place by contacting the adsorbent with a fluid in another phase than is used during loading. This requires draining or displacement which might be time-consuming, so it is avoided whenever possible. The regenerability of an adsorbent affects the fraction of the original capacity that is retained (sometimes called the working capacity) and the time, energy, etc. required for regeneration. Frequently, a short-term loss of working capacity occurs during the first few cycles, often followed by a gradual decay, perhaps over hundreds of cycles, e.g., due to ageing, poisoning, or other causes unrelated to regeneration, that essentially governs the life of the adsorbent.

Mass transfer kinetics is a catch-all term related to intraparticle mass transfer resistance. It is important because it controls the cycle time of a fixed bed adsorption process. Fast kinetics provides a sharp breakthrough curve, while slow kinetics yields a distended breakthrough curve. The effect of a distended breakthrough curve can be overcome by adding adsorbent at the product end, or by increasing the cycle time (which reduces the throughput per unit of adsorbent). Both of these options affect the amount of adsorbent required in that the longer the cycle time, the greater the adsorbent inventory. Despite that, kinetics has even been exploited as the basis of adsorptive separations. Generally slow diffusion of any adsorbate is a disadvantage. To compensate for slow diffusion, it is also possible to use small particles but there is a corresponding sacrifice due to increased pressure drop. The common solution to that dilemma is to use relatively large particles and to employ an extra increment of adsorbent.

Compatibility covers various possible modes of chemical and physical attack that could reduce the life expectancy of the adsorbent, such as biological fouling or attrition. For example, the adsorbent, binder, and surface groups (depending on the type of adsorbent), should be inert to the carrier or solvent, and should not irreversibly react with (or chemisorb) the adsorbates or contaminants. Likewise, operating conditions such as velocity, temperature, pressure, and vibration should not cause undue disintegration of the adsorbent particles. This could happen by crushing or abrasion, and there are standard methods for measuring those.

1.3ACTIVATED CARBON

Carbon adsorption has gained wide application because of its ease, consistent and well-defined process configuration, and most importantly the ability to remove low concentration substances even at parts per million levels with high efficiency. The major advantages and disadvantages of Activated carbon are given in Table 1.

Table 1: Merits and demerits of Activated Carbon

Adsorbent	**Merits**	**Demerits**
Activated Carbon	The most effective adsorbent	Expensive
	Very high surface areas	The higher the quality, the greater the cost
	High Capacity and high rate of adsorption	Performance is dependent on the type of carbon used
	Great Capacity to adsorb a wide range of pollutants	Requires complexing agents to improve its removal performance
	Fast kinetics	Non-selective
	A high-quality treated effluent is obtained	Problems with hydrophilic substances
		Ineffective for disperse and vat dyes
		High reactivation cost
		Reactivation results in a loss of carbon

Activated Carbon has been designated by the U.S. EPA as the best available technology (BAT) for organic chemical removal [12]. Because of its High surface area, capacity, porosity, selectivity and rate of adsorption Activated Carbon is considered as the most suitable adsorbent for organic pollutant removal.

1.3.1 CLASSIFICATION OF ACTIVATED CARBON

Some broad classification is made for general purpose based on their physical characteristics.

1.3.1.1 Powdered activated carbon (PAC)

Traditionally, active carbons are made in particular form as powders or fine granules less than 1.0 mm in size with an average diameter between .15 and .25 mm. Thus they present a large surface to volume ratio with a small diffusion distance. PAC is made up of crushed or ground carbon particles, 95–100% of which will pass through a designated mesh sieve or sieve. Granular activated carbon is defined as the activated carbon being retained on a 50-mesh sieve (0.297 mm) and PAC material as finer material, while ASTM classifies particle sizes corresponding to an 80-mesh sieve (0.177 mm) and smaller as PAC. PAC is not commonly used in a dedicated vessel, owing to the high head loss that would occur. PAC is generally added directly to other process units, such as raw water intakes, rapid mix basins, clarifiers, and gravity filters.

1.3.1.2 Granular activated carbon (GAC)

Granular activated carbon has a relatively larger particle size compared to powdered activated carbon and consequently, presents a smaller external surface. Diffusion of the adsorbate is thus an important factor. These carbons are therefore preferred for all adsorption of gases and vapours as their rate of diffusion is faster. Granulated carbons are used for water treatment, deodourisation and separation of components of flow system. GAC can be either in the granular form or extruded. GAC is designated by sizes such as 8×20, 20×40, or 8×30 for liquid phase applications and 4×6, 4×8 or 4×10 for vapour phase applications. The most popular aqueous phase carbons are the 12×40 and 8×30 sizes because they have a good balance of size, surface area, and head loss characteristics.

1.3.1.3 Extruded activated carbon (EAC)

Extruded activated carbon combines powdered activated carbon with a binder, which are fused together and extruded into a cylindrical shaped activated carbon block with diameters from 0.8 to 130 mm. These are mainly used for gas phase applications because of their low pressure drop, high mechanical strength and low dust content.

1.3.1.4 Impregnated carbon

Porous carbons containing several types of inorganic impregnant such as iodine, silver, cations such as Al, Mn, Zn, Fe, Li, Ca have also been prepared for specific application in air pollution control especially in museums and galleries. Due to antimicrobial/antiseptic properties, silver loaded activated carbon is used as an adsorbent for purification of domestic water. Drinking water can be obtained from natural water by treating the natural water with a mixture of activated carbon and $Al(OH)_3$, a flocculating agent. Impregnated carbons are also used for the adsorption of H_2S and thiols. Adsorption rates for H_2S as high as 50% by weight have been reported.

1.3.1.5 Polymer coated carbon

This is a process by which a porous carbon can be coated with a biocompatible polymer to give a smooth and permeable coat without blocking the pores. The resulting carbon is useful for hemoperfusion. Hemoperfusion is a treatment technique in which large volumes of the patient's blood are passed over an adsorbent substance in order to remove toxic substances from the blood.Activated carbon is also available in special forms such as cloths and fibres. The "carbon cloth" for instance is used in personnel protection for the military.

1.3.2 Low-cost Activated carbon

Commercial grade activated carbon is prepared from natural coal, wood and petroleum residues. For the year 1992, Wood (130,000 tonnes/year), coal (100,000 tonnes/year), lignite (50,000 tonnes/year), coconut shell (35,000 tonnes/year), and peat (35,000 tonnes/year) were used as the major suppliers of Activated Carbon [11]. But, the depleted source of commercial coal-based activated carbon results in the increase of price, which can reach as high as US$ 25/kg. The separation process thus becomes less economic because of this scenario. This has triggered a search for alternative activated carbon from abundant and inexpensive sources. Several low-cost-Activated Carbons have been investigated in the past few years, which include, vetiver roots, wood particleboard wastes, corncob, bamboo, pistachio-nut-shell, cattle manure compost, polygonum orientale Linn, oil palm empty fruit bunches, Hazelnut Shell, Borassus aethiopum flower biomass, rice husk, coconut shell, cherry stones. The list of various sources of low-cost activated carbon used in the recent studies is given in Table 2.

Table 2: Various sources of low-cost activated carbon

Bones	Cottonseed hulls	Lignite	Rubber waste
Bagasse	Corncobs	Lampblack	Rice hulls
Bark	Distillery waste	Leather waste	Refinery waste
Beatsugar Sludge	Fuller's earth	Municipal waste	Reffination earth
Borassus orthopium	Fertilizer slurry	Molasses	Scrap tires
Blue dust	Fish	Nut shells	Sunflower seeds
Coal	Fruit pits	Newspaper	Spent Fuller's earth
Coffee beans	Graphite	Oil shale	Tea leaves
Coconut shell	Human hairs	Olive stones	Wheat straw
Coconut coir	Jute stick	*Parthenium*	Wood
Cereals	Kelp and seaweed	Potassium ferrocyanide residue	
Carbohydrates	Lignin	Petroleum acid sludge	

Parthenium also called gajar ghas, is a genus of flowering plants in the aster family, Asteraceae and a native of Tropical America. Parthenium has been declared noxious in America, Australia, India and many other countries especially those having tropical climates. It is also declared as one of the 10 worst weeds in the world [12]. Scientists describe it as a "poisonous, allergic and aggressive weed posing a serious threat to human beings and livestock by causing diseases like allergies, dermatitis, eczema, asthma, bronchitis, high fever and gangrene." It squeezes grasslands and pastures, reducing the fodder supply. The presence of parthenium in cropped lands results in yield reduction up to 40 per cent. Uprooting it manually is the finest option for its eradication. Thus, Parthenium is chosen for our study for the preparation of activated carbon in the removal of Trichloroethylene and Tetrachloroethylene as it serves a dual purpose: by helping in the removal of organic pollutants by being the source of the adsorbent and; also by serving the purpose of eradication of an environmental hazard itself. Previous studies on Parthenium based activated carbon have been on the removal of dyes, pigments, metal ions and p-cresol [13-18]. But, the removal of halo-ethylenes from industrial wastewater has not yet been explored on a parthenium-based activated carbon. Thus, the present study has been taken up to prepare activate carbon from Parthenium weed and to know its compatibility in removing trichloroethylene and Tetrachloroethylene from industrial wastewater.

1.4 OBJECTIVE

The research work is carried out to determine the compatibility of Parthenium based activated carbon in removing the organic pollutants from industrial wastewater. In this process, the activated carbon is proposed to be prepared from Parthenium weed. The activated carbon thus prepared is abbreviated as PAC. The batch adsorption study is to be carried out to study the adsorption of Trichloroethylene and Tetrachloroethylene on PAC. The experimental adsorption equilibrium data is further estimated to be fitted to six isotherm models usually encountered in organic pollutant adsorption studies to determine the best isotherm. Regression analysis is to be followed to know the best fit in detail. The kinetics of adsorption of TCE and PCE on PAC is to be studied using three different kinetic models. Further, the effect of pH, adsorbent dose, temperature and initial adsorbate concentration is also to be analyzed for both the pollutants on PAC. Thermodynamic analysis is to be carried out to understand the adsorption mechanism further in detail.

CHAPTER 2

LITERATURE REVIEW

2.1 LOW-COST ACTIVATED CARBON BASED LITERATURE

Zaini et al., 2009 [19] examined the suitability and performance of cattle-manure-compost (CMC) based activated carbons in removing heavy metal ions from aqueous solution. Pore texture, available surface functional groups, pH of points zero charge (pH_{PZC}), thermogravimetric analysis and elemental compositions were obtained to characterize the activated carbons. Batch adsorption technique was used to determine the metal-binding ability of activated carbons. The preferable removal of Cu(II) over Pb(II) could be due to the rich nitrogen content as well as the higher mesoporous surface area in the CMC activated carbons. The impregnated CMC activated carbons also showed a better performance for Cu(II) removal at varying solution pH than Filtrasorb 400 (F400), while a similar performance was observed for Pb(II) removal.

Wang et al., 2010 [20] prepared low cost activated carbon from Polygonum orientale Linn by phosphoric acid activation. Its ability to remove the basic dyes, malachite green (MG) and rhodamine B (RB) was evaluated. The surface area of P. orientale Linn activated carbon (PLAC) was found to be 1398 m^2 /g. The effects of experimental parameters such as initial concentration, contact time, pH, ionic strength and temperature on the adsorption were investigated. Alkaline pH was more favourable for MG adsorption, whereas acidic pH was better for RB uptake. Adsorption of dyes on PLAC was weakly dependent on ionic strength. The adsorption kinetics was found to be best represented by the pseudo-second-order kinetic model. The mechanism of the adsorption process was determined from the intraparticle diffusion model. The equilibrium adsorption data was well described by the Langmuir model. Thermodynamic study showed that the adsorption was a spontaneous, endothermic process.

Nethaji et al., 2010 [21] used chemically prepared activated carbon derived from Borassus aethiopum flower as adsorbent. Batch adsorption studies were performed for the removal of Malachite Green (MG) from aqueous solutions by varying the parameters like initial solution pH, adsorbent dosage, initial MG concentration and temperature with three different particle sizes such as 100μm, 600μm and 1000μm. The zero point charge was 2.5 and the maximum adsorption occurred at the pH range from 6.0 to 8.0. Adsorption rate constants were determined using pseudo first-order, pseudo second-order rate equations and also Elovich model and intraparticle diffusion models. The results clearly showed that the adsorption of MG onto PFAC followed pseudo second-order model and the adsorption was both by film diffusion and by intraparticle diffusion.

Kumagai et al., 2009 [22] evaluated the capacity of rice husk activated carbon (RHAC) to adsorb refractory sulphur compounds of dibenzothiophenes (DBTs) from commercial kerosene in terms of their textural and chemical characteristics. Rice husk activated at 850 °C for 1 h showed an acceptable adsorption capacity for DBTs, despite a much lower specific surface area (473 m^2/g) and total pore volume (0.267 cm^3/g), when compared to micro-porous activated carbon fibre with a large specific surface area (2336 m^2/g) and total pore volume (1.052 cm^3 /g). The volumes of ultramicropores acting as DBTs adsorption sites and of mesopores leading DBTs into the ultramicropores were closely related to the DBTs adsorption capacity of the RHACs.

Tajar et al., 2009 [23] used low-cost activated carbon, derived from nut shells, and its modified sample as replacements for the current expensive methods of removing cadmium from aqueous solutions and waste waters. Adsorption of cadmium onto four kinds of activated carbons has been studied; prepared activated carbon (PAC), commercial activated carbon (CAC), and the sulfurized ones (SPAC & SCAC). The activated carbon has been derived, characterized, treated with sulphur and then utilized for the removal of Cd^{2+}. Sulfurizing agent (SO_2 gas) was successfully used in adsorbents' modification process at the ambient temperature. Samples were then characterized and tested as adsorbents of cadmium. Effect of some parameters such as contact time, initial concentration and pH were examined.

Amin 2009 [24] studied the use of cheap, high efficiency and ecofriendly adsorbent derived from pomegranate peel as an alternative source of activated carbon for the removal of direct blue dye from aqueous solution. A series of experiments were conducted in a batch system to assess the effect of the system variables, i.e. initial pH, temperature, initial dye concentration adsorbent dosage and contact time. The adsorption process of direct blue dye onto different activated carbons prepared from pomegranate peel was found to be spontaneous and exothermic process.

Jaramillo et al., 2009 [25] prepared some granular activated carbons (GACs) from cherry stones (CS), an agricultural waste, by thermal methods following pyrolysis in nitrogen and subsequent activation (with air, carbon dioxide and steam) or single-step activation in steam. A GAC prepared by activation with carbon dioxide was further treated with several oxidizing agents (air, air–ozone mixture, nitric acid and hydrogen peroxide). The non-oxidized GACs produced have surface areas ranged from 508 to 901m^2/g and show a predominantly micro- and macropores structure. Both, the non-oxidized and the oxidized GACs were used as adsorbent to study the adsorption of Cu(II) from aqueous solution. The results show that the Cu(II) uptake of the non-oxidized GACs is not great, but similar to that of the commercial grade Filtrasorb 400. The adsorption capacity for Cu(II) could be greatly enhanced by GAC oxidation, especially with nitric acid and ozone treatments.

Khaled et al., 2008 [26] suggested an efficient process, which does not require a huge investment for the removal of direct dye from wastewater. Activated carbon developed from agricultural waste material was characterized and utilized for the removal of Direct Navy Blue 106 (DNB-106) from wastewater. Systematic studies on DNB-106 adsorption equilibrium and kinetics by low-cost activated carbons were carried out. Adsorption studies were carried out at different initial concentrations of DNB-106 (50, 75, 100, 125 and 150mg l^{-1}), contact time (5–180 min), pH (2.0, 3.0, 4.7, 6.3, 7.2, 8.0, 10.3 and 12.7) and sorbent doses (2.0, 4.0 and 6.0 g l^{-1}). Both Langmuir and Freundlich models fitted the adsorption data quite reasonably ($R^2 > 0.97$). The maximum adsorption capacity was 107.53 mg g^{-1} for 150 mg l^{-1} of DNB-106 concentration and 2 gl^{-1} carbon concentration. Various mechanisms were established for DNB-106 adsorption on developed adsorbents. The kinetic studies were conducted to delineate the effect of initial dye concentration, contact time and solid to liquid concentration. The developed carbon might be successfully used for the removal of DNB-106 from liquid industrial wastes.

2.2 ADSORBENT BASED LITERATURE

Singh et al., 2008 [27] prepared the activated carbon from carbonaceous agriculture waste Parthenium hysterophorous 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 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 behavior 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.

Hem Lata et al., 2008 [28] investigated nickel removal efficiency of sulphuric acid-treated Parthenium carbon (SWC) from simulated wastewater. Batch mode adsorption experiments have been conducted by varying pH, nickel concentration, adsorbent dose and contact time. Ni(II) removal was pH-dependent and found to be maximum at pH 5.0. The maximum removal of Ni(II) was achieved within 4 h after the start of every experiment. The equilibrium adsorption data were fitted to Freundlich and Langmuir adsorption isotherm models to evaluate the model parameters. Both models represented the experimental data satisfactorily. The adsorbent was also characterized including infrared spectroscopy and scanning electron microscopy.

Hem Lata et al., 2008 [29] reported the removal of a basic dye (rhodamine-B) by the activated carbon prepared from Parthenium biomass by sulphuric acid treatment method (SWC). The effectiveness of the prepared adsorbent has been studied as a function of agitation time, adsorbent dosage, initial dye concentration and pH. The removal of rhodamine-B by SWC followed second order kinetic model. The second order model best describes adsorption kinetic data. Adsorption data were modelled using both Langmuir and Freundlich classical adsorption isotherms. The adsorption capacity was 18.52 mg/g at initial pH 7 for the particle size 0.3–1 mm. Maximum dye removal (99.2%) was obtained at pH 7 using an adsorbent dose of 16.0 g/L for 50 mg/L dye concentration in the aqueous solution.

Hem Lata et al., 2008 [30] studied adsorption of rhodamine-B from aqueous solution on formaldehyde treated parthenium biomass (WC) and phosphoric acid treated parthenium carbon (PWC). Aqueous solutions of various concentrations (50–500mg/l) were shaken with certain amount of adsorbent to determine the adsorption capacity of rhodamine-B on WC and PWC. The effectiveness of formaldehyde treated parthenium biomass (WC) and phosphoric acid treated parthenium carbon (PWC) in adsorbing rhodamine-B from aqueous solution has been studied as a function of agitation time, adsorbent dose, initial dye concentration and pH. The adsorption capacities of the studied adsorbents were in the order PWC >WC. Initial pH had negligible effect on the adsorption capacity. Maximum dye was sequestered from the solution within 60 min after the start of every experiment. After that, the concentration of rhodamine-B in the liquid-phase remained constant. The adsorption of rhodamine-B onto PWC and WC followed second-order kinetic model. Adsorption data were modelled using both Langmuir and Freundlich classical adsorption isotherms. The adsorption capacity was 59.17mg/g at initial pH 7.0 for the particle size 0.3–1.0mm for phosphoric acid treated parthenium carbon (PWC).

2.3 ADSORBATE RELATED LITERATURE

Erto et al., 2010 [31] adopted a new approach based on statistical treatment of modelling data for the analysis of trichloroethylene (TCE) adsorption on granular activated carbon (GAC) from synthetic groundwater. The work started from an experimental analysis aimed at the assessment of the influence of thermodynamic parameters (concentration, pH, salinity, temperature and the presence of an organic non-ionic compound, i.e. ethyl acetate) on TCE adsorption capacity. A wide range of process parameters had been considered to simulate highly polluted groundwater, as when leachate infiltrations occur at solid waste landfill. Experimental results show that adsorption capacity decreased by increasing the temperature and the ethyl acetate concentration, while neither pH nor salinity have any influence. A thorough understanding of adsorption mechanism and the individuation of the model with highest physical and mathematical significance was carried out by a thermodynamic analysis and a statistical methodology based on Analysis of Variance (ANOVA). The latter indicated that in dilute solutions the Freundlich model is the best data fitting model for TCE adsorption, among those which are commonly adopted.

Klasson et al., 2009 [32] Steam-activated carbons were made from shells from five different almond varieties and from a mix of almond types. The shells contained the same level of cellulose, but differed in their lignin and hemicellulose composition. The yield of carbon from the shells ranged from 20% to 23.5%, indicating a loss of about 80% of initial mass. Regardless of the composition, the performance of the activated carbons made from the shells was very similar in a feasibility study. The carbons were found to have a capacity of

100–105 mg/g of carbon for the two contaminants tested (dibromochloropropane and trichloroethylene). The finding that the activated carbons performed equally well, regardless of source of almond shells, suggest that that carbons could be made from almonds shells with consistent quality.

Erto et al., 2010 [33] aimed at the assessment of the factors affecting the adsorption of trichloroethylene (TCE) from water solutions onto activated carbons is presented. The influence of sorbent properties, such as B.E.T. surface area, micropore volume, chemical composition and acid /basic surface function al groups on TCE adsorption capacity is experimentally assessed by testing a set of 12 sorbents. Moreover, the effect of the presence of other species in solution, such as sodium acetate and tetrachloroethylene (PCE), is studied through parametric TCE adsorption isotherms realization. The experimental results show that the TCE adsorption capacity is promoted by a high B.E.T. surface area, micropore volume and C content and it is significantly affected by the presence of a non-ionic compound of similar structure (PCE), however it does not depend on the presence of an organic salt (sodium acetate). These results confirm that neither TCE–carbon ionic interaction nor sorbent ionization phenomena are involved in the TCE adsorption, since its mechanism is based on dispersion forces. A thorough analysis of the experimental data set suggests that, in consideration of the TCE adsorption mechanism, the maximization of basal plane extent (as the B.E.T surface area) and its effective fraction (as the C content) is a valid criterion to select or synthesize a new suitable sorbent for TCE adsorption from waters.

Wei et al., 2010 [34] injected soluble substrates (electron donors) commonly into chlorinated solvent contaminated plume to stimulate reductive dechlorination. Recently, different types of organic mulches with economic advantages and sustainable benefits have received much attention as new supporting materials that can provide long term sources of electron donors for chlorinated solvent bioremediation in engineered biowall systems. However, sorption capacities of organic mulches for chlorinated solvents have not been studied yet. In this study, the physiochemical properties of organic mulches (pine, hardwood and cypress mulches) were measured and their adsorption capacity as a potential media was elucidated. Single, binary and quaternary isotherm tests were conducted with trichloroethylene (TCE), Tetrachloroethylene (PCE), trans-dichloroethylene (trans-DCE) and cis-dichloroethylene (cis-DCE). Among the three tested mulches, pine mulch showed the highest sorption capacity for the majority of the tested chemicals in single isotherm test. In binary or quaternary isotherm tests, competition among chemicals appears to diminish the differences in Qe for tested mulches. However, pine mulch also showed higher adsorption capacity for most chemicals when compared to hardwood and cypress mulches in the two isotherm tests. Based upon physicochemical properties of the three mulches, higher sorption capacity of pine mulch over hardwood and cypress mulches appears to be attributed to a higher organic carbon content and the lower polarity.

Kilduff et al., 2001 [35] found that trichloroethylene (TCE) adsorption by activated carbon previously loaded (''preloaded'') with humic substances decreased with increasing concentrations of monovalent ions (NaCl), calcium (until solubility was exceeded), or dissolved oxygen in the preloading solution. For a given percentage of organic carbon removal during humic acid loading, greater reductions in TCE adsorption occurred with increasing monovalent ion concentration and calcium concentration at constant ionic strength. However, this effect was related primarily to the amount of humic material adsorbed the reduction in TCE adsorption was independent of the ionic composition of the preloading solution when compared at similar humic acid loading. Experiments were performed which showed that calcium ions can associate with humic material after the humic has been adsorbed, which subsequently reduces TCE uptake, but this effect does not dominate when calcium is present during humic loading. At sufficiently high calcium concentrations (approaching solubility), aggregation or co-precipitation of humic acid mitigated the effects of preloading. In contrast to the effects of ionic composition, the presence of dissolved oxygen did fundamentally change the mechanism by which organic macromolecules compete with TCE. TCE uptake was lower when preloading by polymaleic acid (PMA) occurred in the presence of dissolved oxygen, even when the amount loaded was the same. One explanation invokes a coupling mechanism promoted by the carbon surface, which results in either additional blockage of TCE sorption sites, additional site competition, or both. In all experiments, the effects of preloading were consistent with those reported previously, which have been interpreted as a loss of high-energy sites available to TCE, causing a significant reduction in the site-energy heterogeneity, and reduced uptake in the low concentration region.

Klasson et al., 2009 [36] showed that flax shive and cotton gin waste can serve as a precursor for activated carbon that can be used for adsorption of trichloroethylene (TCE) from both the liquid and gas phases. Testing was conducted on car-bon activated with phosphoric acid or steam. The results show that activated carbon made from flax shive performed better than select commercial activated carbons, especially at higher TCE concentrations. The activation method employed had little effect on TCE adsorption in gas or vapour phase studies but liquid phase studies suggested that steam activation is slightly better than phosphoric acid activation. As expected, the capacity for the activated carbons depended on the fluid phase equilibrium concentration. At a fluid concentration of 2 mg of TCE/L of fluid, the capacity of the steam activated carbon made from flax shive was similar at 64 and 80 mg TCE/g of carbon for the vapour and liquid phases, respectively. Preliminary cost estimates suggested that the production costs of such carbons are $1.50 to $8.90 per kg, depending on activation method and precursor material; steam activation was significantly less expensive than phosphoric acid activation.

Yang et al., 2009 [37] investigated the adsorption characteristics of chlorinated solvents, trichloroethylene (TC E) and perchloroethylene (PCE), in surfactant solutions with granular activated carbon (GAC) were investigated with the goal of recovering the surfactant from the effluent in surfactant enhanced remediation (SER). Triton X-100 (TX100) and X-1 65 (TX165) were selected as model surfactants, and the GAC was Darco 20–40. The adsorption amounts for the TX10 0 and TX165 onto GAC was about 0.26–0.2 7 g/g GAC. On a GAC fixed bed, the adsorbed amount s of TCE (0.19 g/g) and PCE (0.35 g/g) in the TX165 (10 g/ L) solution onto the GAC were higher than those for TCE (0.16 g/g) and PCE (0.24 g/g) in the TX 100 (10 g/L) solution. Because the ratio of surfactants/chlorinated solvents in the ordinary effluent of SER is higher than 1, activated carbon adsorption could be used as an alternative of post- treatment method in SER.

CHAPTER 3

MATERIALS AND METHODS

3.1 PREPARATION OF PARTHENIUM-BASED ACTIVATED CARBON

The parthenium weed (*Parthenium hysterophorus*) was collected from places around Roorkee, India by completely uprooting the plant and then separating the stem from leaves, dirt and dust. The stem was then cut into small pieces of 0.5-1 cm size and dried in sunlight for 10 h. Further, chemical activation process was carried out to prepare the activated carbon. In this process, the dried pieces were impregnated with conc. sulphuric acid and ammonium persulphate in the ratio of 1:1.5:0.4 (weight of parthenium: weight of H_2SO_4: weight of $NH_4S_2O_8$). Carbonization was carried out in a hot air oven at 125°C for 16 h. It was then washed several times with distilled water to remove any attached free acid. It was further soaked in 1% Sodium bicarbonate solution overnight to neutralize the remaining acid content and adjust the pH between 5 and 7. Washing was repeated many times with hot distilled water in order to remove leachable matter and fines attached to PAC. It was further dried in the hit air oven at 100°C for 6 h. It was then pulverized and further sieved to get a particle size around 0.5 mm.

3.2 CHARACTERIZATION OF PAC

3.2.1. THERMOGRAVIMETRIC ANALYSIS (TGA)

To determine the physical and chemical properties of the prepared PAC, TGA analysis has been carried out by using Thermogravimetric Analyser (Pyris Diamond, Perkin Elmer Inc., Wellesley, USA) with simultaneous recording of differential thermal analysis (DTA), thermogravimetry (TG), and derivatives thermogravimetry (DTG) curves. Each sample of 10-11 mg was heated from 20°C to 900°C at a heating rate of 10°C/min under nitrogen atmosphere. The temperatures of melting and decomposition were determined as the temperature of corresponding endothermic maxima.

3.2.2. X-RAY DIFFRACTION (XRD)

The crystalline structure of samples was studied by using Bruker AXS D8 Advance x-ray diffractometer (graphite monochromator on reflected beam) with CuKα radiation (40 kV, 40 mA), employing the powder method. Each scan was recorded in the range of $2\theta = 5 - 50°$ in the step by step mode with 0.05° interval.

3.2.3 SCANNING ELECTRON MICROSCOPY (SEM)

The surface morphology and pore size distribution of PAC was analyzed using scanning electron microscopy. Gold field emission was used to operate the instrument at an accelerating voltage of 20 KHz for 5 min. Scanning was performed unaltered on the PAC sample using scanning electron microscope model LEO 435 VP with 1000 X and 2000 X magnification.

3.2.4 FOURIER-TRANSFORM INFRARED ANALYSIS (FTIR)

The prepared PAC sample was mixed with moisture free KBr (IR grade, Qualigen) and pellets were prepared. The FTIR spectra were recorded using a Nicolet 6700 FTIR (Thermo Scientific, USA). The samples were scanned at resolution between 4000 and 500 cm^{-1}.

3.3 PREPARATION OF ADSORBATE SOLUTION

The used adsorbates, TCE and PCE were of analytical grade (purity > 99.9%) and purchased from Rankem Fine Chemical Ltd., New Delhi, India. They were used to prepare synthetic adsorbate solutions of 25 mg/L concentration initially. To obtain solutions of required concentration (3 – 20 mg/L) the prepared solution was diluted accordingly. Fresh solution for dilution was prepared every time to ensure that the organic component would not degrade with time. Successive dilution was achieved by using distilled water to prepare all the solutions.

3.4 DETERMINATION OF ADSORBATE IN THE SOLUTION

The concentrations of TCE and PCE in the solution were determined by using high performance liquid chromatograph (HPLC, Waters, USA) equipped with a symmetry C18 column and photo diode array (PDA) detector (model 2998, Waters, USA). The eluent composed of acetonitrile 80 % (v/v) in deionized water (Millipore system, USA) was prepared daily and vacuum filtered through a 0.45 μm nylon filter (Pall Corporation, Michigan, USA). The PDA detector was operated at 214 nm and the flow rate of eluent was kept at 1.0 ml/min. Standards of TCE and PCE in the range of 1-25 mg/L were used to prepare the calibration curves between the area under curve and corresponding concentration of adsorbate. The calibration curves for TCE and PCE are shown in Figures 2 and 3, respectively. The samples collected at various time intervals were also filtered through a nylon syringe filter (0.20 μm, Axiva Sichem Biotech, New Delhi, India) prior to injection.

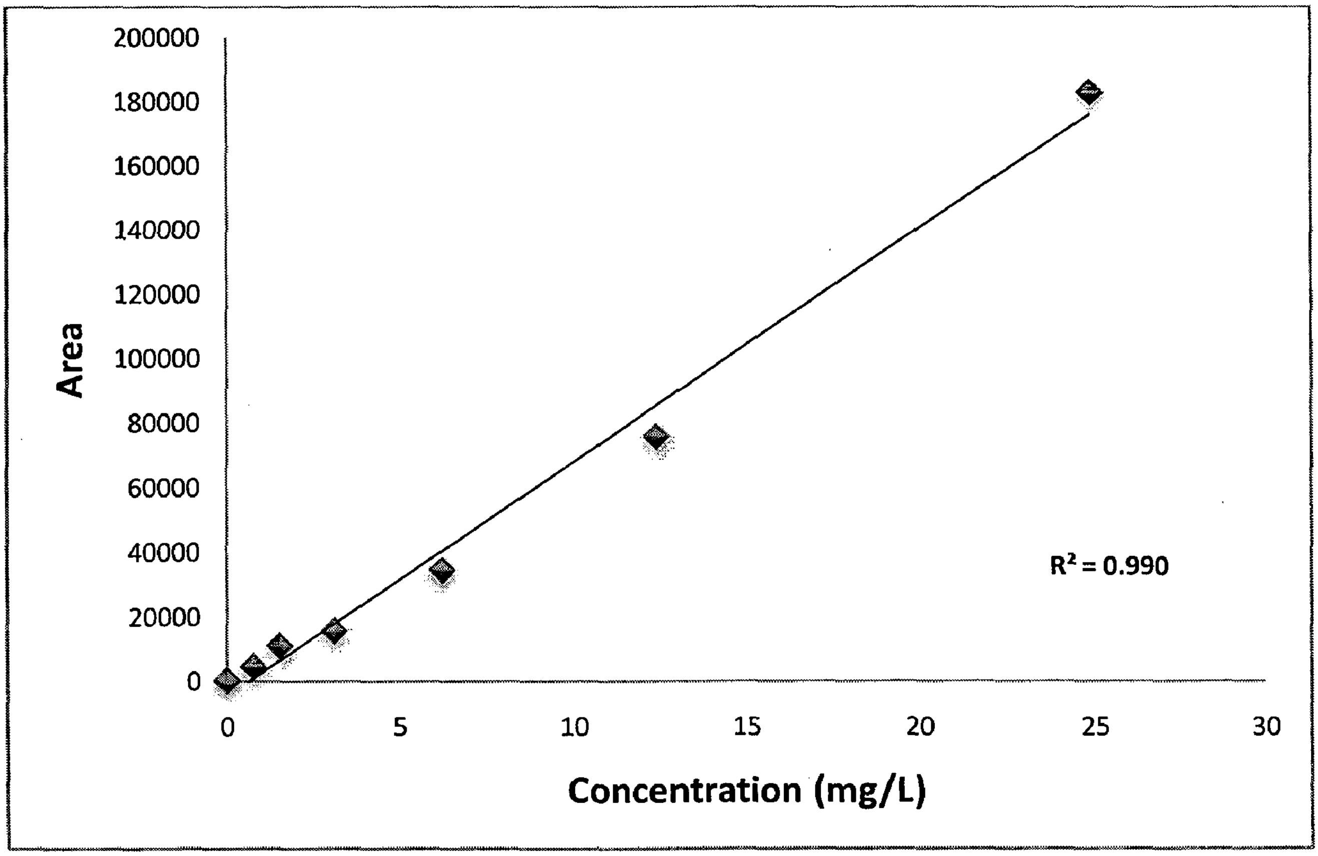

Figure 2: Calibration curve for TCE

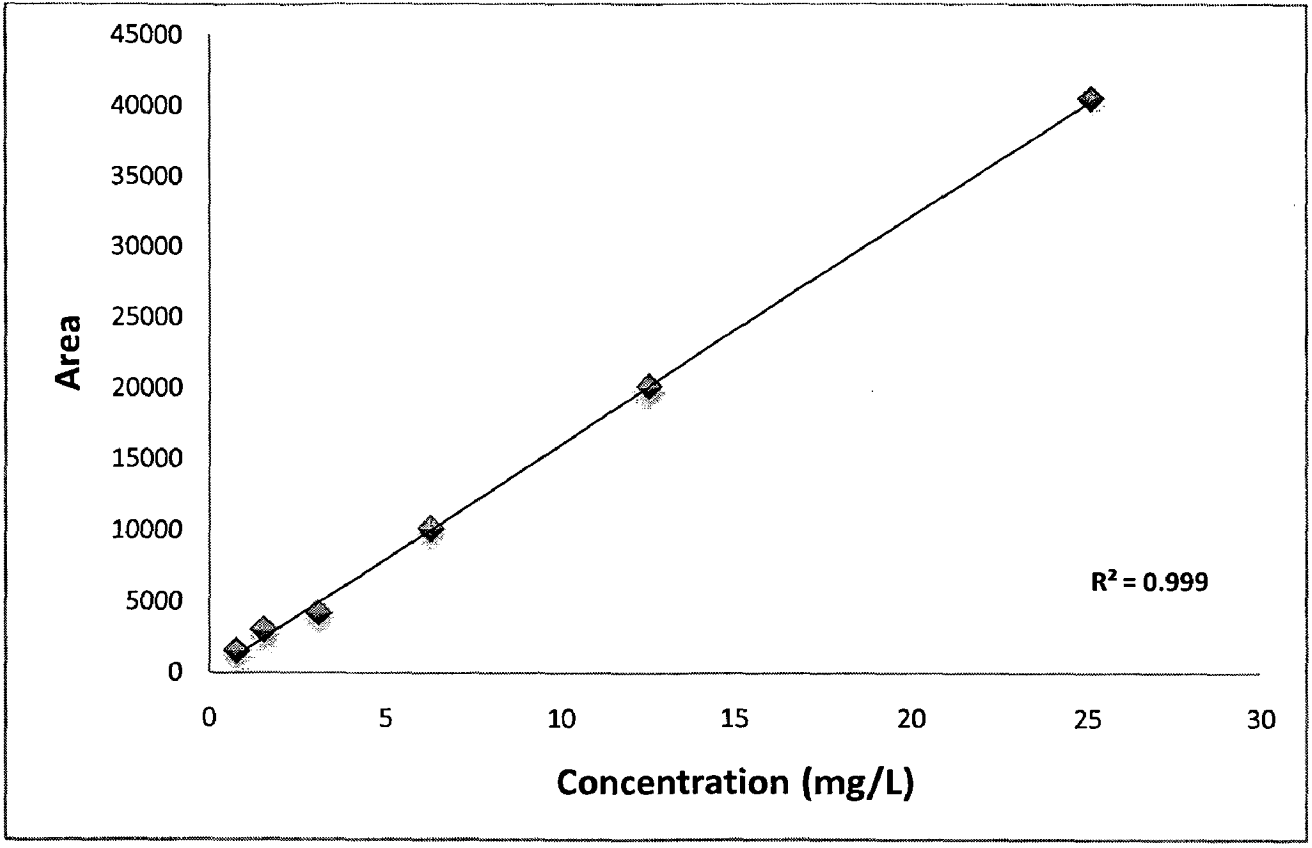

Figure 3: Calibration curve for PCE

3.5 EXPERIMENTAL PROCEDURE

The batch isothermal studies were conducted as an experiment for analyzing the potential of PAC to adsorb the two components TCE and PCE separately. Equilibrium parameters and rate of adsorption were established for both the components. The sample solutions were prepared by diluting the higher concentration TCE or PCE solutions. In each adsorption experiment, 50 ml of TCE or PCE aqueous solution sample was added to a 250 ml flask along with a certain adsorbent dosage. The initial concentration, adsorbent dose and pH of the solution were fixed or varied depending upon the experiment conducted. The flask was then, shaken on a reciprocating type horizontal shaker (S and N Electronics, Kolkata) with temperature control. The temperature was maintained at 30°C. The samples from the flask were collected at appropriate intervals of time and then filtered through a filter paper (Whatman No. 42). The amount absorbed by the solution was determined as mentioned in Section 3.4, and accordingly residual concentration of TCE or PCE and its percent removal were calculated. This course of action was followed in equilibrium, isotherm studies, effect of various process parameters, and adsorption kinetics as discussed below.

In industrial liquid effluents, the concentration of TCE and PCE varies from 3 to 20 mg/l. [31–33]. Hence, in our study, the initial concentrations of both TCE and PCE are chosen to be 5 mg/L. The experiments for equilibrium studies, isothermal studies and kinetics were conducted at 30°C; using five initial TCE and PCE concentrations: 3, 5, 10, 15, 20 mg/l. Six adsorbent doses of PAC and eleven adsorbent doses of PAC were used for TCE and PCE respectively. A broad pH range was chosen which was varied by adding HCl or NaOH as required. The samples were withdrawn at pre-specified time intervals and filtered. For the purpose of kinetics, the filtrate samples were taken at different time intervals and the concentrations C_t were determined. This study was carried out for both TCE and PCE separately. For both the adsorbates equilibrium condition was established after 12 hours. Samples were collected after the equilibrium was established and consequently the equilibrium concentration C_e was estimated. The amount of adsorption of TCE or PCE per gram adsorbent, qt (mg/g) at any time t was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

where C_0 and C_t are the concentrations of adsorbate solution 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. The amount of adsorption per gram of adsorbent at equilibrium condition, q_e (mg/g), was calculated by:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

Effect of various parameters was studied. The effect of pH of the solution on adsorption was studied over a range of 3 – 11 for both TCE and PCE at a constant temperature of 30°C. The initial concentration was kept fixed at 5 mg/l and adsorbent dose at 0.2 g/l for TCE and 0.8 g/l for PCE. Effect of temperature was analyzed by varying the temperature over a range of 10 – 40°C keeping all other process parameters constant. Effect of adsorbent dose was estimated by using six adsorbent doses, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8 g/l for TCE and eleven adsorbent doses, 0.02, 0.04, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.4 g/l for PCE by keeping all other parameters constant. Similarly, Effect of initial concentration was studied by varying the concentration from 3 – 20 mg/l.

In the isotherm studies, initial concentration of TCE and PCE was fixed at 5 mg/l. Adsorbent dose was varied from 0.05 – 8 g/l for TCE and 0.02 – 1.4 g/l for PCE. Thus, 11 sample flasks each were taken for the two adsorbates separately. The equilibrium contact time determined from the kinetics was used for these tests. After the attainment of equilibrium, the flasks were taken out of the shaker, and the solution was filtered and analyzed as per section 3.4 to estimate the residual concentration in the solution.

3.6 KINETIC MODELING

In order to determine the adsorption rate and equilibrium time after which the adsorption is negligible, various kinetic models are used to navigate the experimental data. Three kinetic models, pseudo-first order, pseudo-second order and intraparticle diffusion model are used to analyze and determine the suitable kinetic parameters. The pseudo-first order kinetic model is described by:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3}$$

where, k_1 is pseudo-first order adsorption rate constant, q_e and q_t are amounts of adsorbate adsorbed at equilibrium time and time 't' respectively which can be obtained from equations (1) and (2). The integrated form of this equation at the boundary conditions (at t=0, $q_t = 0$) is given by:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

For determining the predictive capability of pseudo-first order kinetic model, a graph between $\ln(q_e - q_t)$ and t is plotted. The model is said to be accurately fit if it gives a linear relationship with slope k_1 and intercept $\ln q_e$ and from the graph thus plotted, k_1 can be determined.

Pseudo-second order kinetic model is given by:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

here, k_2 is pseudo-second order adsorption rate constant. The integrated form of this equation at boundary conditions (at t=0, $q_t = 0$) would give:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{6}$$

If a linearized plot of $\frac{t}{q_t}$ vs t is obtained with a slope $\frac{1}{q_e}$ and an intercept $\frac{1}{k_2 q_e^2}$, it represents that the adsorption is governed by pseudo-second order kinetics.

For identifying the diffusion mechanism in the adsorption process, we consider intraparticle diffusion model. It helps in understanding the rate controlling step affecting the kinetics and to figure out the degree of boundary layer control. It is represented by the equation:

$$q_t = k_p t^{1/2} + c \tag{7}$$

For a plot of q_t vs $t^{1/2}$, if we obtain a straight line, it represents the presence of intraparticle diffusion. It becomes the rate controlling step when it passes through the origin. If it is a straight line but does not pass through the origin it represents the presence of some boundary layer control. This can also mean that both the surface adsorption and intraparticle diffusion are taking place simultaneously.

3.7. EQUILIBRIUM MODELING

Adsorption study is carried out for both the components TCE and PCE, till equilibrium is achieved. At equilibrium, there is no further change in the concentration of the adsorbate in liquid and on the solid adsorbent surface. An adsorption equilibrium curve relates the adsorbate loading on the adsorbent (q_e) and the residual concentration of the adsorbate in the solution (C_e). The various isotherm models used to correlate and fit the experimental data are; Freundlich (two-parameter), Langmuir-Freundlich, Radke-Prausnitz, Sips, Koble-Corrigan (three-parameter), and Fritz-Schlunder (four parameter) models.

The Freundlich model equation is expressed as:

$$q_e = K_F C_e^{1/n} \tag{8}$$

This is an empirical model in which K_F is the extent of adsorption capacity and n is the extent of adsorption intensity. It is based on the assumption that adsorption occurs on heterogeneous sites with non-uniform distribution of energy level with a possibility of multi-layer adsorption [38]. Even though it is accepted for a wide range of concentration, it does not follow the Henry's law at low concentration levels near zero [39].

The Langmuir-Freundlich isotherm is simple generalization of both Langmuir and Freundlich isotherms. Langmuir-Freundlich model is represented by:

$$q_e = \frac{q_{e,\max}(KC_e)^n}{1+(KC_e)^n} \tag{9}$$

where, the constant K is the equilibrium constant which represents the affinity between adsorbate and adsorbent; $q_{e,\max}$ is the maximum amount adsorbed on surface and n is the power constant. As this equation has three fitting constants it much better describes the adsorption including adsorption binding interactions among adsorbing compounds. For independent non-interacting adsorption sites similar to Langmuir model, the value of n is 1. When $n > 1$, it is concluded that there is positive co-operativity, and if $0 < n < 1$, negative adsorption co-operativity can be expected [40].

Radke-Prausnitz isotherm equation is given by the following empirical three-parameter model equation:

$$\frac{1}{q_e} = \frac{1}{KC_e} + \frac{1}{kC_e^{1/n}} \tag{10}$$

where K, k and n are Radke-Prausnitz parameters. This model is successful for fitting adsorption isotherms over wide ranges of loading and concentration. It has the tendency of reducing to Henry's law for adsorption at low concentrations and Freundlich equation at high concentrations [41].

Sips exercised the first effort to extend the Langmuir model to adsorption on an energetically heterogeneous solid in 1948. Based on the assumption of quasi-Gaussian energy distribution, Sips derived an isotherm containing the surface heterogeneity factor, m, as follows:

$$q_e = \frac{q_m a_s C_e^m}{1 + a_s C_e^m} \tag{11}$$

where, the constants q_m and a_s are the Langmuir monolayer saturation capacity and Sips isotherm constant respectively. Sips isotherm model is generally used in accounting for the heterogeneous nature of the adsorbent surface [42].

The Koble-Corrigan model is essentially a Freundlich isotherm which approaches an adsorption maximum at high concentrations of adsorbate. It is a three-parameter model represented by the model equation:

$$q_e = \frac{AC_e^n}{1 + BC_e^n} \tag{12}$$

when n=1, the equation reduces to Langmuir equation. If BC_e^n << 1, the adsorption is very low and it becomes Freundlich equation. If BC_e^n >> 1, it indicates that the sorption is very high and the adsorbed adsorbate quantity per unit weight of adsorbent at equilibrium remains constant [43].

Fritz-Schlunder model equation for isotherms is a four-parameter model given by:

$$q_e = \frac{\alpha_1 C_e^{\beta_1}}{1 + \alpha_2 C_e^{\beta_2}} \tag{13}$$

where, the parameters α_1 and α_2 are the Fritz-Schlunder model parameters, and β_1 and β_2 are Fritz-Schlunder equation exponents[44].

In order to evaluate the goodness of the fit of the experimental data and the prediction accuracy of the models used in the present study, the following statistical indices are employed [45, 46]:

$$RMSE = \sqrt{\frac{\sum (q_{e,\exp} - q_{e,cal})^2}{N}} \tag{14}$$

$$SEP = \frac{RMSE}{\sum q_{e,\exp} / N} x100 \tag{15}$$

$$NSD = \sqrt{\frac{\sum[(q_{e,\exp} - q_{e,cal}) / q_{e,\exp}]^2}{N}} x100 \qquad (16)$$

$$ND = \sum \left| \frac{q_{e,\exp} - q_{e,cal}}{q_{e,\exp}} \right| x \frac{100}{N} \qquad (17)$$

where, $q_{e,\exp}$ is experimental data point of q_e, $q_{e,cal}$ is the calculated value by the isotherm model, and N is the number of data points in the experimental run. To evaluate the goodness of the fit, the statistical indice average relative error (ARE) between the experimental and calculated values is given by:

$$ARE = \sqrt{\sum \left(1 - \frac{q_{e,cal}}{q_{e,\exp}}\right)^2 x \frac{100}{N}} \qquad (18)$$

3.8 ADSORPTION THERMODYNAMICS

Thermodynamic parameters are associated with the temperature dependence of a process. The spontaneity of a process is determined by the thermodynamics of the process taking place. Both energy and entropy factors must be taken into account while calculating the Gibbs free energy which further determines the spontaneity of the process. The amounts of TCE and PCE adsorbed at four different temperatures are considered to calculate the thermodynamic parameters of the process such as change in Gibbs free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) associated with the adsorption process. The following equations have been used in determining the parameters [47]:

$$K_D = \frac{q_e}{C_e} \qquad (19)$$

$$\Delta G^0 = -RT \ln K_D \qquad (20)$$

$$\ln K_D = \frac{-\Delta G^0}{RT} = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \qquad (21)$$

where, K_D is the distribution coefficient, q_e is the adsorption capacity and C_e is the adsorbate concentration at equilibrium. K_D helps in the determination of the capability of activated carbon to retain the solute and also the extent of movement in a solution phase and thus it helps in estimating the Gibbs free energy. A plot of $\ln K_D$ vs 1/T yields a straight line from which ΔH^0 and ΔS^0 are determined from the slope and intercept respectively.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 CHARACTERIZATION OF PAC

The physical and chemical characteristics of PAC are given in Table 3. BET surface area and total pore volume are determined by BET surface area analyzer. The physicochemical properties of PAC were found to be comparable with the properties of commercial AC [13]. Figure 4 depicts the thermogravimetric analysis of PAC. The first weight loss around 100°C is probably caused by thermo-desorption of physically adsorbed material such as water vapour trapped as moisture in the PAC. The weight almost remains constant from 100–300°C with a slight decrease indicating the evolution of light volatile compounds due to the degradation of cellulose and hemicelluloses. Major thermal decomposition occurs around 300–750°C indicating the emission of volatile matter till the residual carbon is remained which is 4.2% as noted from the Figure 4. This weight constitutes the ash content in the PAC which remains constant even after further increase of temperature to 900°C. Very low ash content and high carbon content imply good efficiency of the prepared adsorbent.

Table 3: Physicochemical properties of PAC

S No.	Properties	PAC
1	BET Surface Area (m^2/g)	234.97
2	Total Pore Volume (m^2/g)	0.1183
3	pH (1% solution)	6.4
4	Moisture content %	17.2
5	Ash Content %	4.2
6	Light Volatile Compounds %	28.45
7	Average Particle size(mm)	0.492
8	Average pore diameter(µm)	0.75

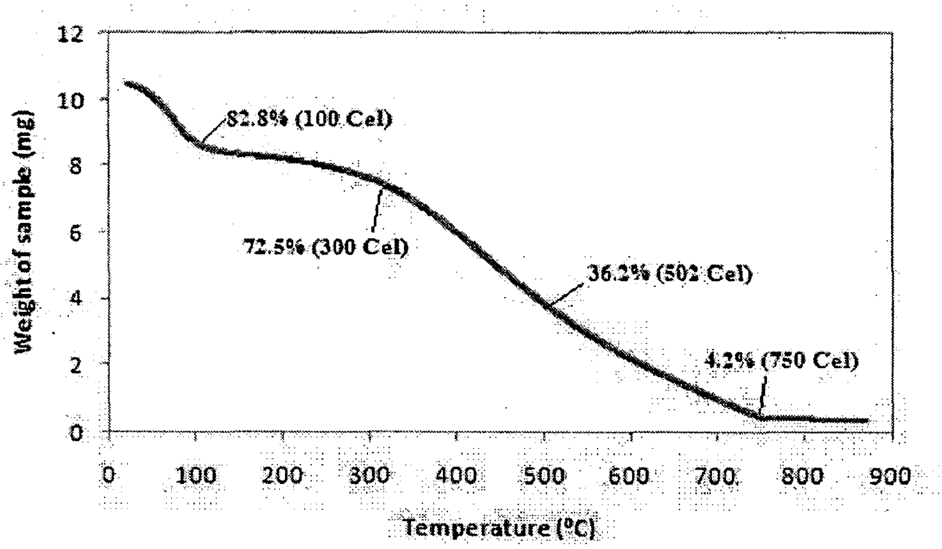

Figure 4: Thermogravimetric (TG) curve of the prepared PAC

X-ray diffraction patterns for PAC are shown in Figure 5. Most of the material shows amorphous content along with the X-ray peaks of major carbons, CaP, and CaO_2.

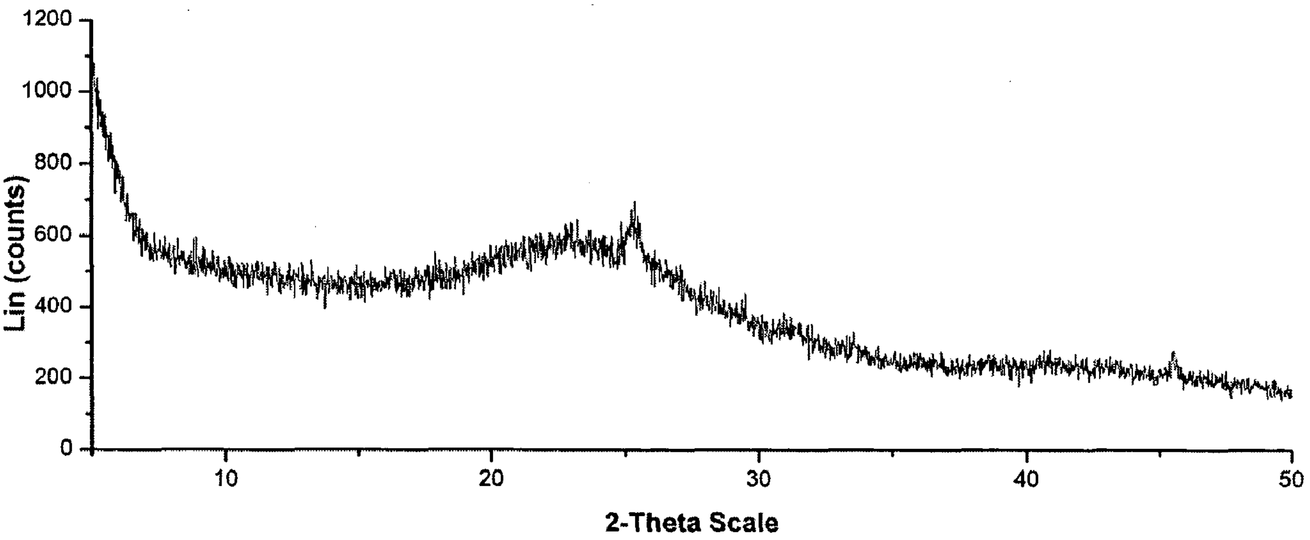

Figure 5: X-ray diffraction (XRD) curve of the prepared PAC

SEM images of PAC taken at various magnifications are shown in Figures 6, 7, 8 and 9. According to the International Union of Pure and Applied Chemistry (IUPAC), pores on activated carbon are classified by their sizes into three groups: micropores having a diameter less than 2 nm, mesopores having a diameter between 2 and 50 nm, and macropores having a diameter greater than 50 nm. Activation with concentrated sulphuric acid and ammonium persulphate mainly develops pores of large diameter of the order 0.5-1.0 µm. The activation assists in minimizing the formation of tars and other liquids, which could clog up the pores and inhibit the development of pore structures. The constructed pores of PAC are dispersed in all three categories, with the majority being macropores. This is favourable for the removal of organic compounds, as it requires large pore structures for the penetration of these large sizes of molecules.

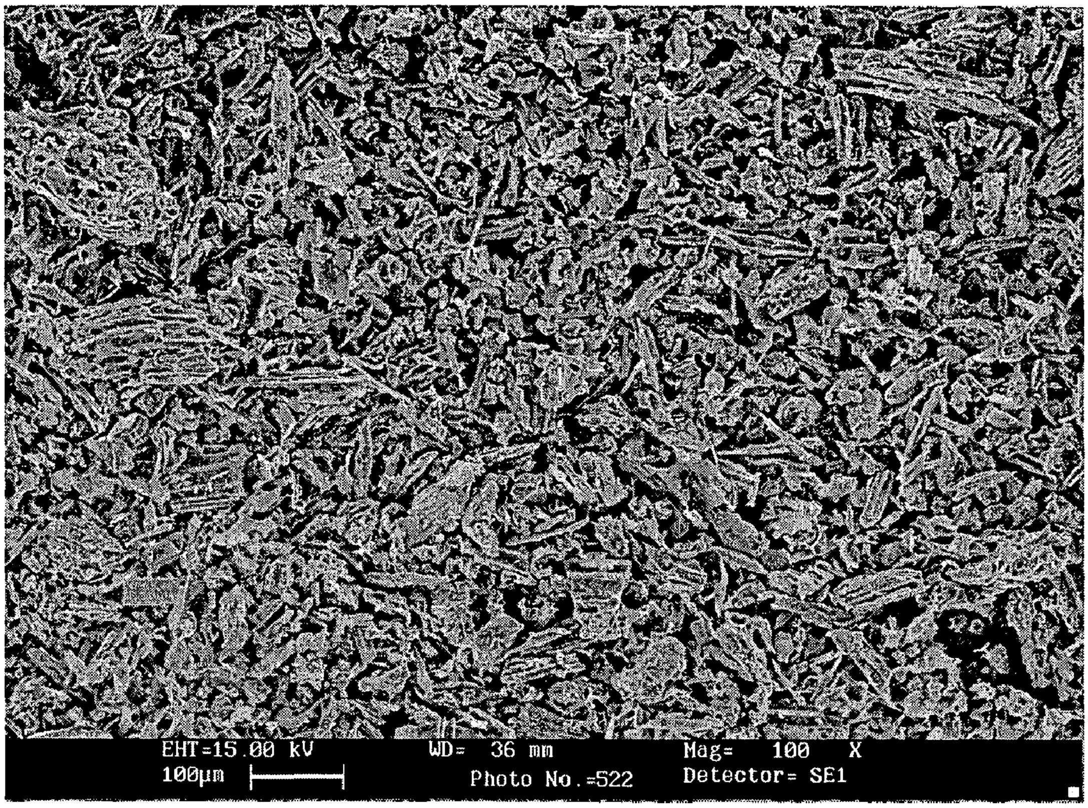

Figure 6: SEM of PAC at 100 X

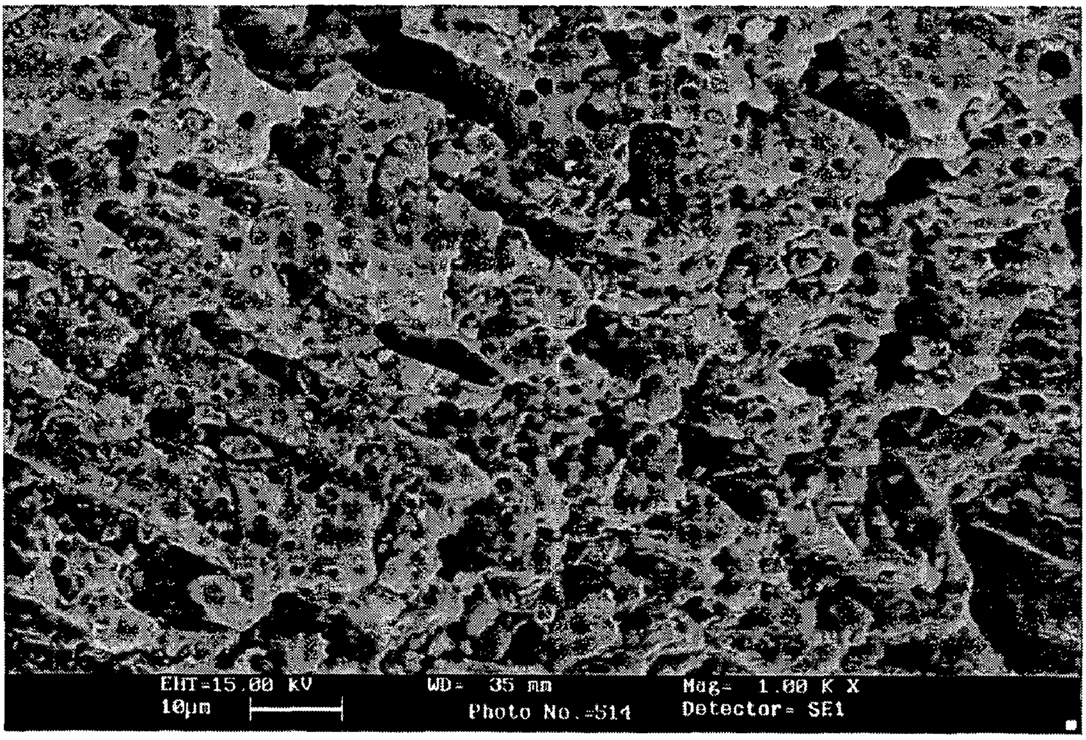

Figure 7: SEM of PAC at 1000 X

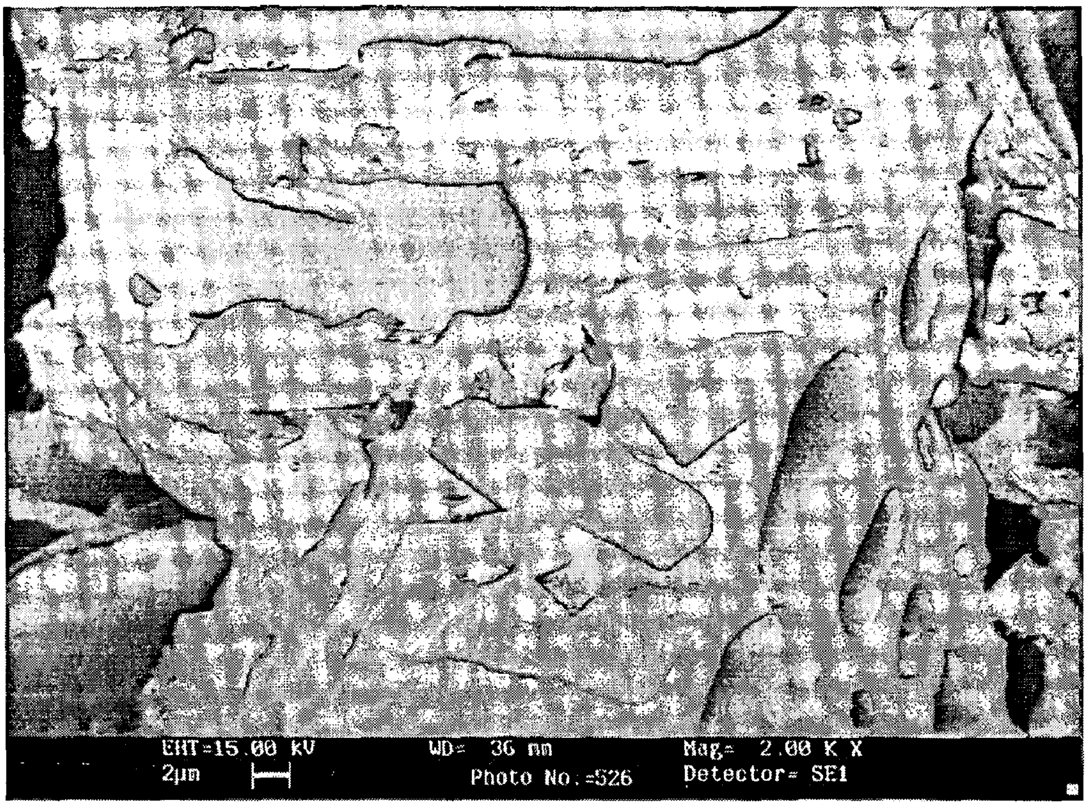

Figure 8: SEM of PAC at 2000 X

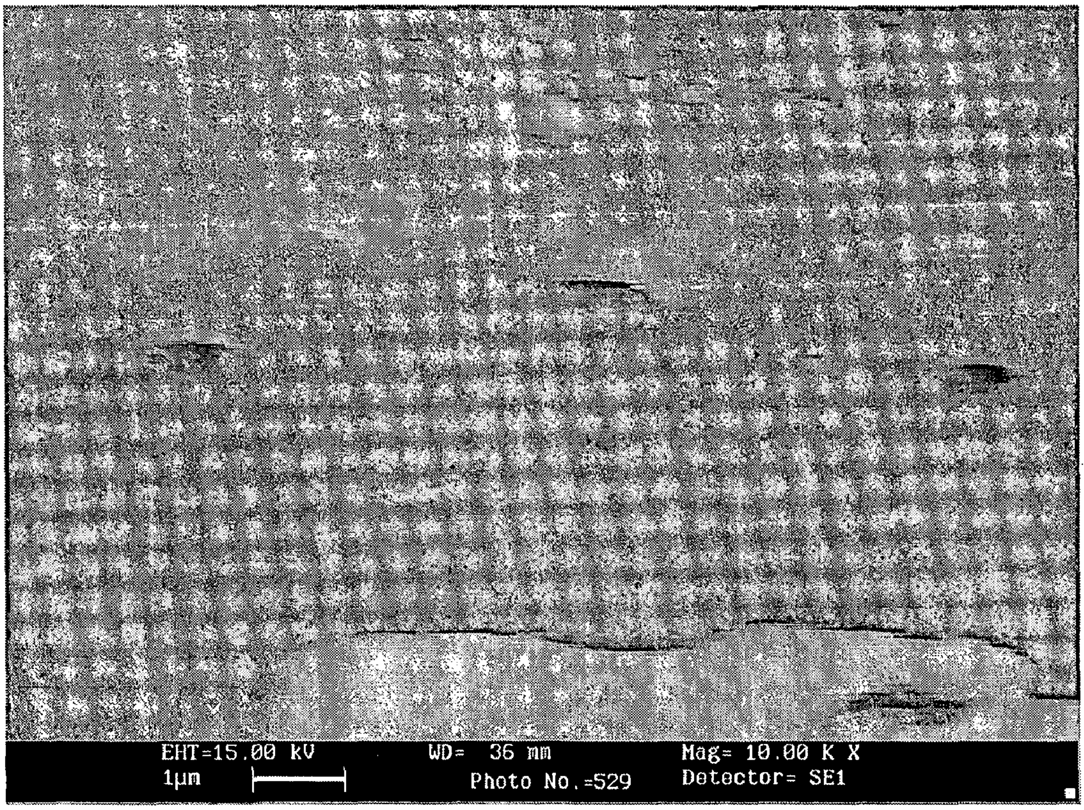

Figure 9: SEM of PAC at 10,000 X

The FTIR spectrum was recorded for the PAC prepared and is represented in Figure 10. The band found at 3436 cm^{-1} corresponds to the O-H stretching and hydrogen bonding. The band at 2818 cm^{-1} represents the presence of aldehyde groups and corresponds to the stretching of C-H in the H-C=O bond. The bands found at 1594 cm^{-1} imply the aromatic in-ring C-C stretch. The deep band formed near 1380 cm^{-1} is the equivalent for CH_3 group and the immediate 1351 cm^{-1} band represents alkanes (C-H rock). Presence of aliphatic amines is evident from the band around 1020 cm^{-1}, also suggesting a C-N stretch. The bands around 760 cm^{-1} and 580 cm^{-1} are the representation of the presence of medium level chloroalkanes.

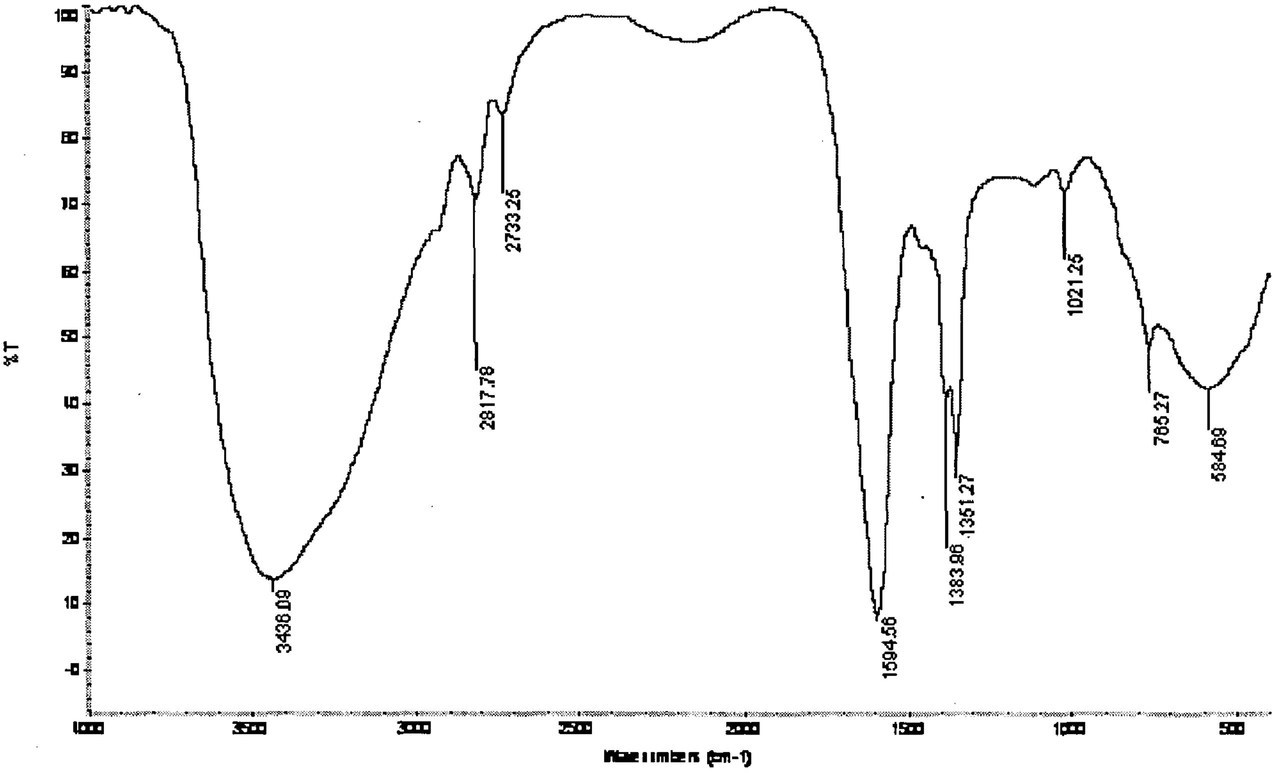

Figure 10: Fourier transform infrared (FTIR) spectra of prepared PAC

4.2 EFFECT OF pH

The surface charge of the adsorbent and degree of ionization of the adsorbate are influenced by the pH of the solution as it governs the interaction of surface with adsorbate ions. Thus, it effectively changes the amount of adsorption. Thus, initial pH of the solution plays a major part in controlling the amount of adsorption as accounted in various literature studies available [14, 19, 20]. pH_{pzc} is the limiting pH of the activated carbon at which the surface has no charge. At this point, diffusion into micropores and mesopores alone monitors the adsorption process and not the electrostatic forces. At pH higher than pH_{pzc}, the surface of activated carbon becomes negatively charged and at pH lower than pH_{pzc}, the carbon surface becomes positively charged. The experimental value of pH_{pzc} for PAC is found to be 6.4. In TCE and PCE, since hydron cation (H+) exists which being an electron-accepting group is more acidic in nature. Hence, at a pH value greater than pH_{pzc} of activated carbon, the surface of the adsorbent is negatively charged attracting acidic molecules onto its surface. Thus, we can conclude that a basic solution would be ideal for adsorption onto PAC. Effect of pH of the solution on adsorption was studied over a range of 3 – 11 for both TCE and PCE at a constant temperature of 30°C. From Figures 11 and 12, we can justify the theoretical explanation with the experimental observations for TCE and PCE, respectively. For TCE, we observe that as the pH is varied from 3 to 11, the adsorbed concentration of TCE gradually increases to a maximum and becomes constant at 10 as the basic nature of the solution is enhanced. Similarly, for PCE we can observe that as the pH is raised from 5 to 11, the adsorbed quantity increases with the basic nature of the solution with pH of 10 giving the maximum value. Therefore, a pH value of 10 which is greater than pH_{pzc} is concluded to be the optimum pH of the solution for all further experiments on TCE and PCE.

4.3 EFFECT OF TEMPERATURE

Temperature governs the adsorption of the material based on the reaction taking place. If the reaction is endothermic, the adsorption capacity increases with the increase in temperature and if the reaction is exothermic, the adsorption capacity decreases with the increase in temperature. Effect of temperature was analyzed by varying the temperature over a range of 10 – 40°C keeping all other process parameters constant. Experimental results are shown in Figure 13 and 14 for TCE and PCE, respectively. We can observe that the adsorption capacity has decreased with the increase in temperature representing an exothermic reaction taking place in both TCE and PCE adsorption. This could be due to the distortion of active sites with the increase in temperature. Thus, most effective results were obtained for the least temperature of 10°C. But, as seen from Figures 13 and 14, the difference in the adsorption capacity with the variation in temperature is not much for the chosen adsorbate-adsorbent combination, and hence, the maintenance of 10°C for the operation would become less economical than when performed at ambient conditions. Hence, the experimental condition of temperature was chose to be the ambient conditions, which in our case is 30°C.

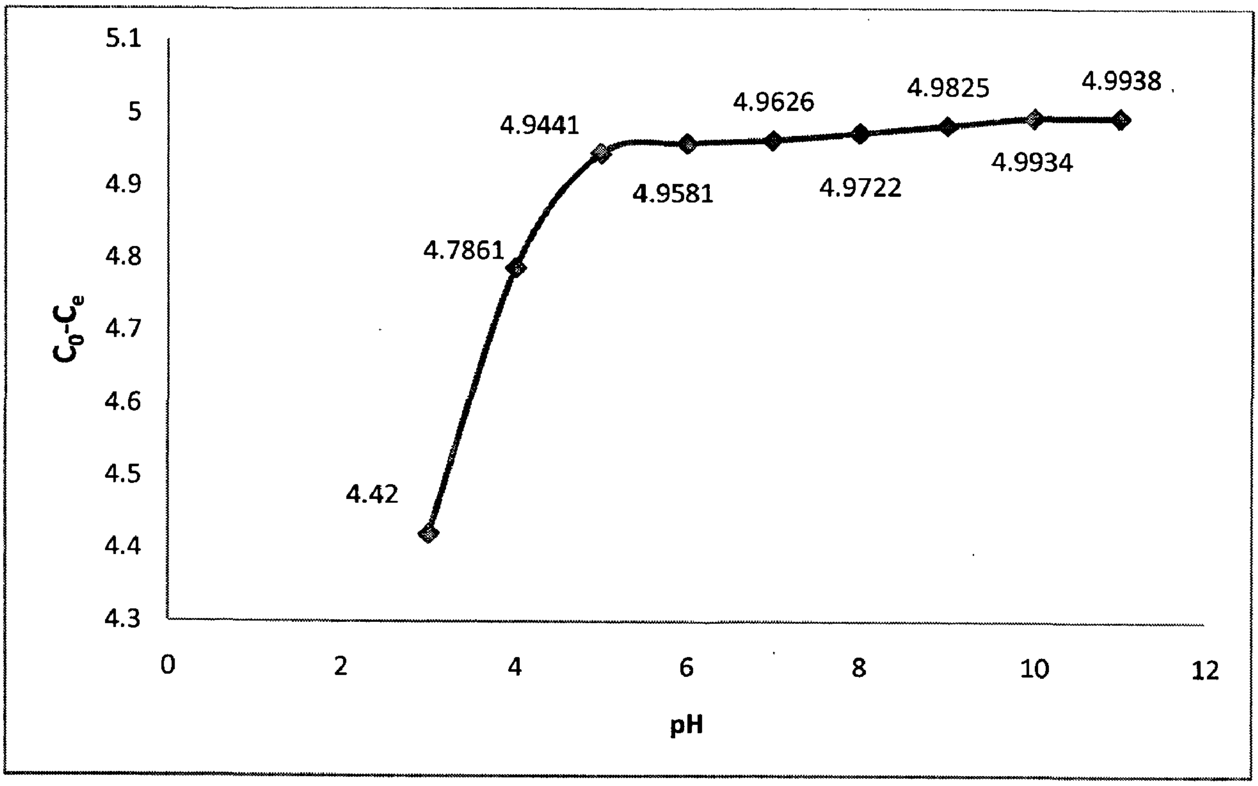

Figure 11: Effect of pH on TCE adsorption on PAC

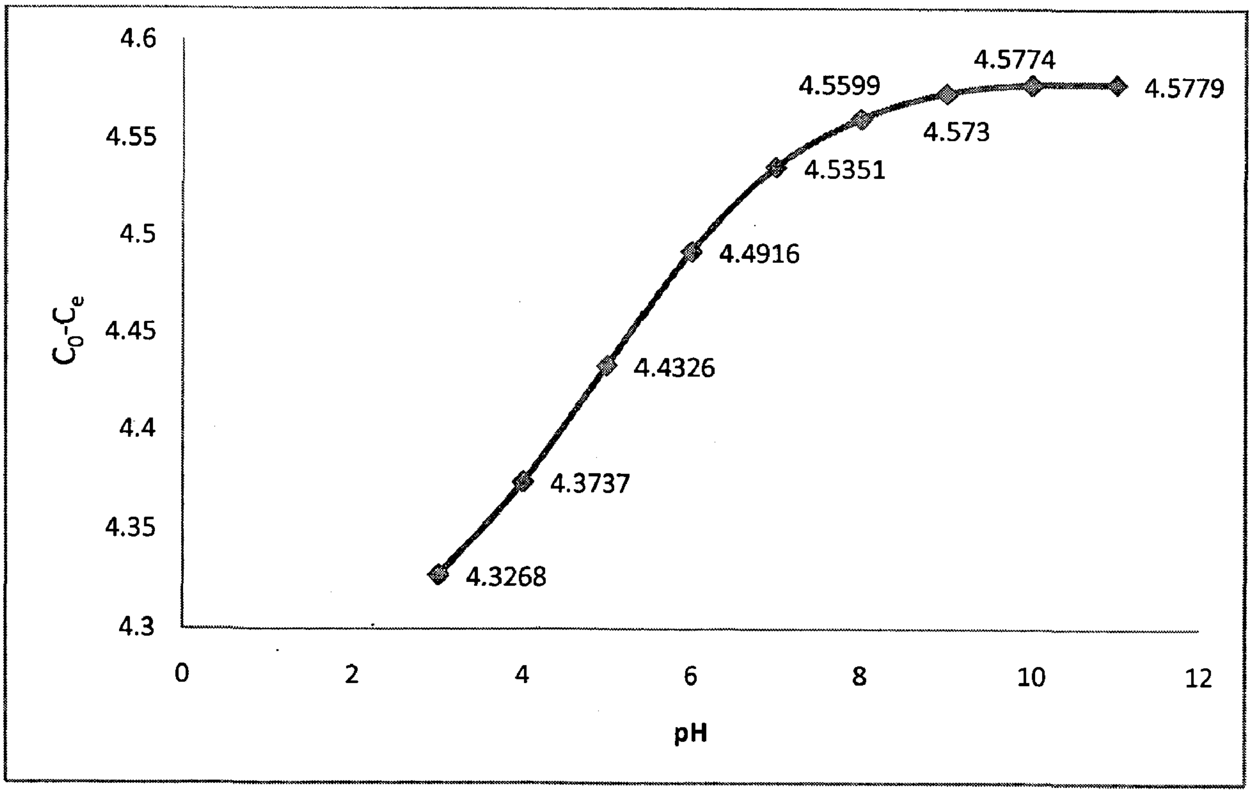

Figure 12: Effect of pH on PCE adsorption on PAC

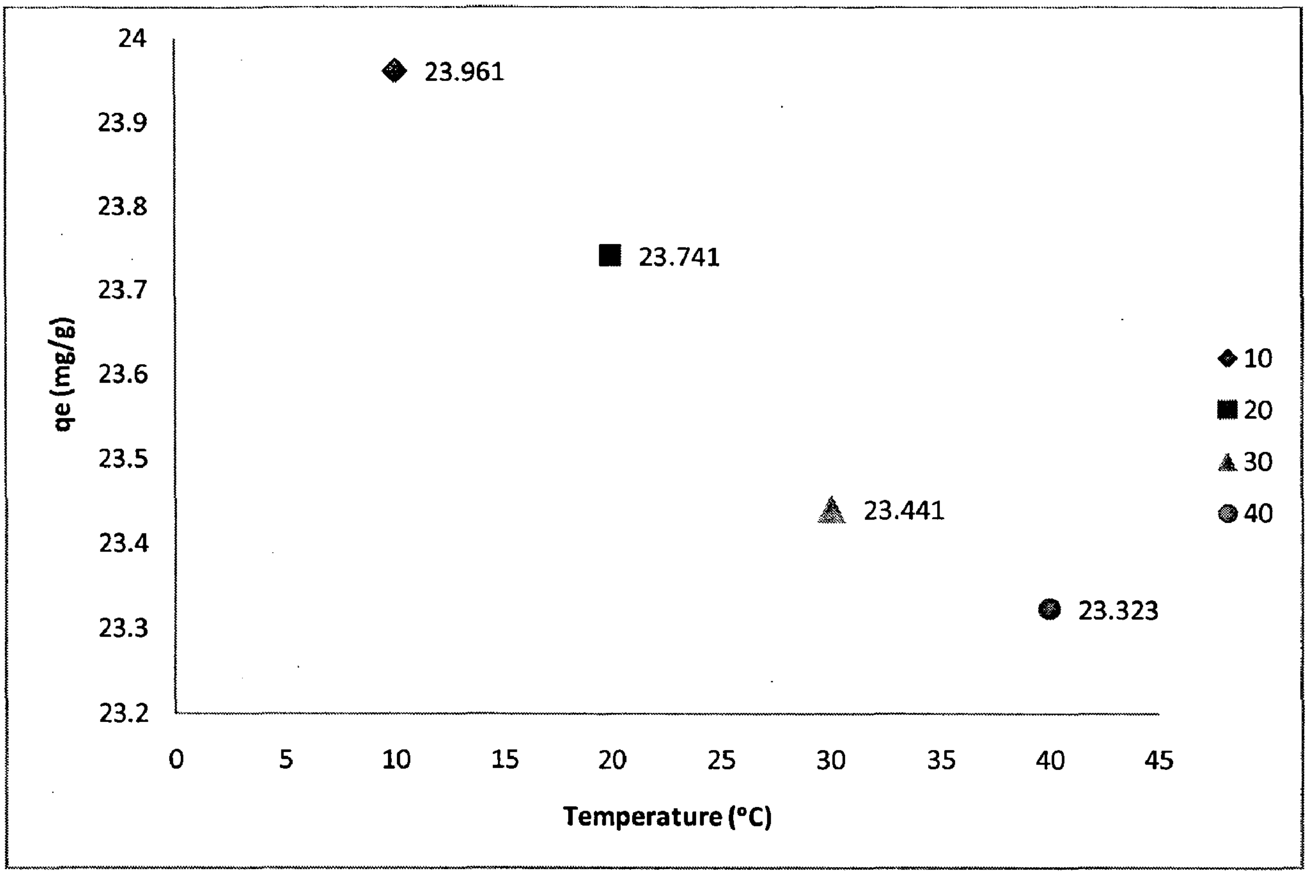

Figure 13: Effect of Temperature on TCE adsorption on PAC

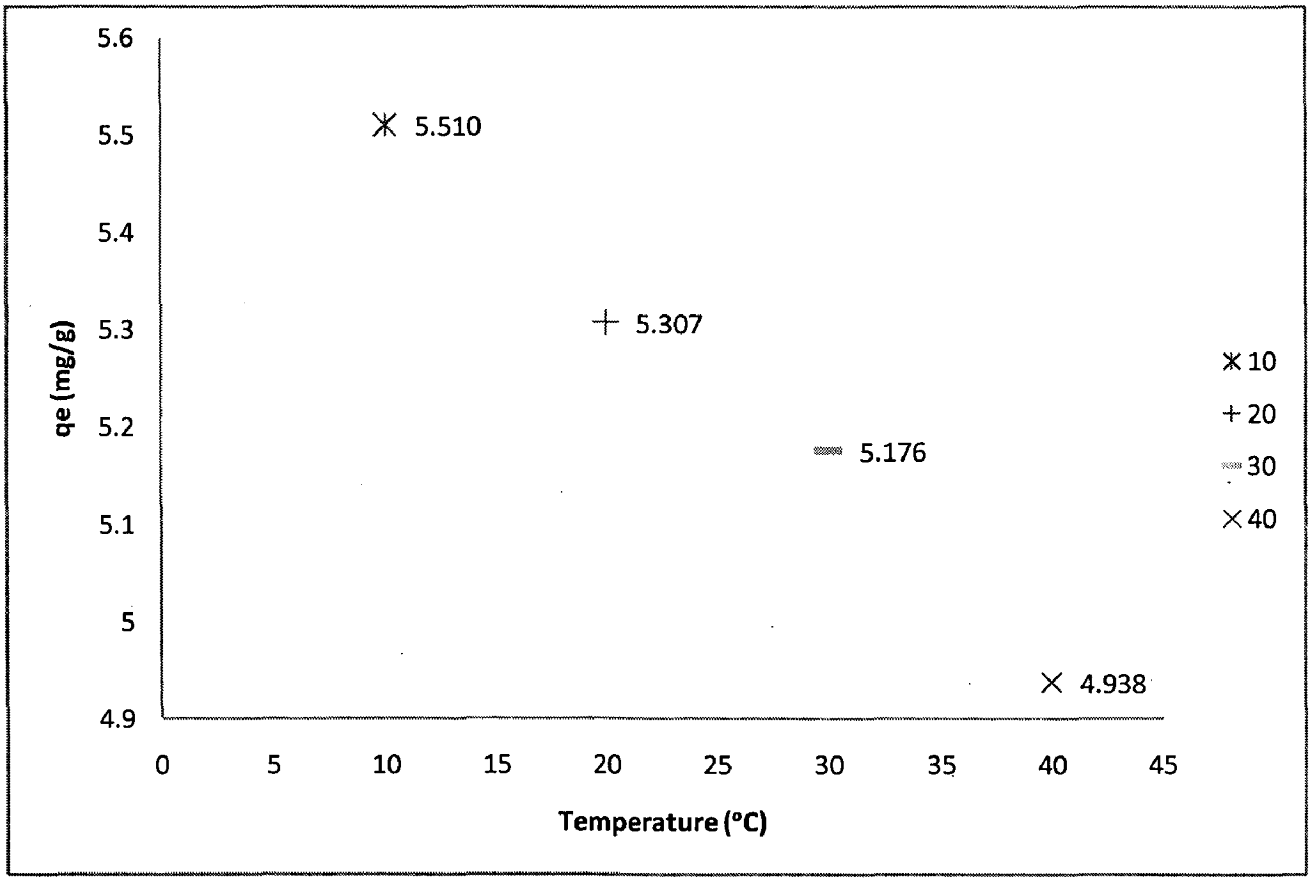

Figure 14: Effect of Temperature on PCE adsorption on PAC

4.4 EFFECT OF ADSORBENT DOSE

Determination of equilibrium time for the adsorption of TCE and PCE onto the prepared PAC is done by equilibrium studies. The time at which the adsorption reaches a saturation level for both the pollutants is determined to be 12 hours. At different time intervals, the percent removal of the pollutants was determined. The variation in the percent removal of TCE and PCE at different time intervals is represented in Figures 15 and 16, respectively.

Adsorbent dose has to be optimized in order to balance the economy of the process with the effective removal of the adsorbate. Effect of adsorbent dose for our system was estimated by using six adsorbent doses, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8 g/l for TCE and eleven adsorbent doses, 0.02, 0.04, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.4 g/l for PCE by keeping all other process parameters at their optimum values. From Figures 17 and 18, we observe that the % removal of both the adsorbates increases to certain point and then becomes constant even with a reasonable increase in the adsorbent dosage. This is because more active sites for adsorption are provided by higher adsorbent dose which results in the overall increase in the removal efficiency. But, after achieving its highest removal capacity, adsorbent dose is not much effective and most of the active sites remain unoccupied. Thus, the amount of adsorbate adsorbed per unit mass of adsorbent decreases with increase in adsorbent dose. For TCE, the optimum adsorbent dose was found to be 0.2 g/L at which we get 98.64% removal and for PCE, it was 0.8 g/L at which we get 83.75% removal. The adsorbent dose above these values would increase the cost of the process as adsorption per unit mass of adsorbent decreases. PAC gave high removal efficiency for TCE even at a low adsorbent dose whereas for PCE even at a high adsorbent dose the efficiency had a higher limit of 89.75%. This shows that the prepared PAC is more compatible in the removal of TCE than PCE.

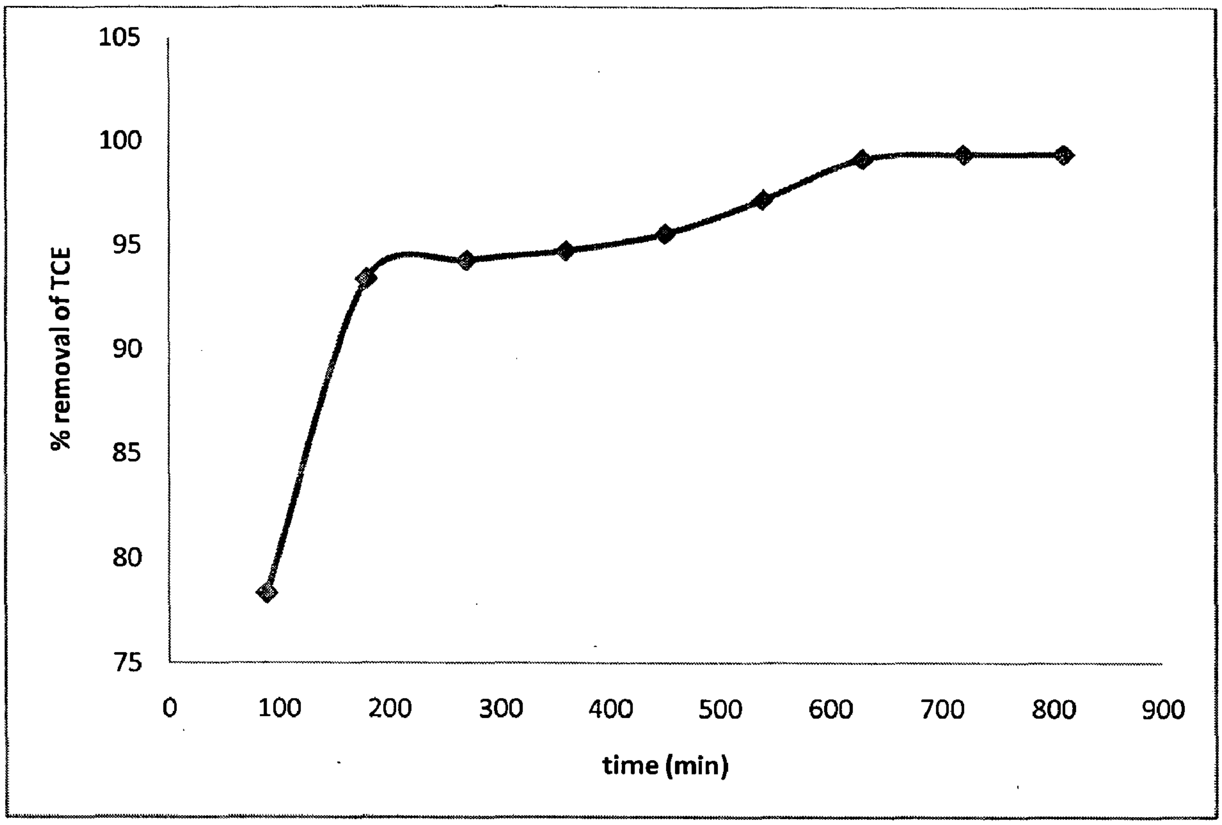

Figure 15: Percent removal of TCE with time

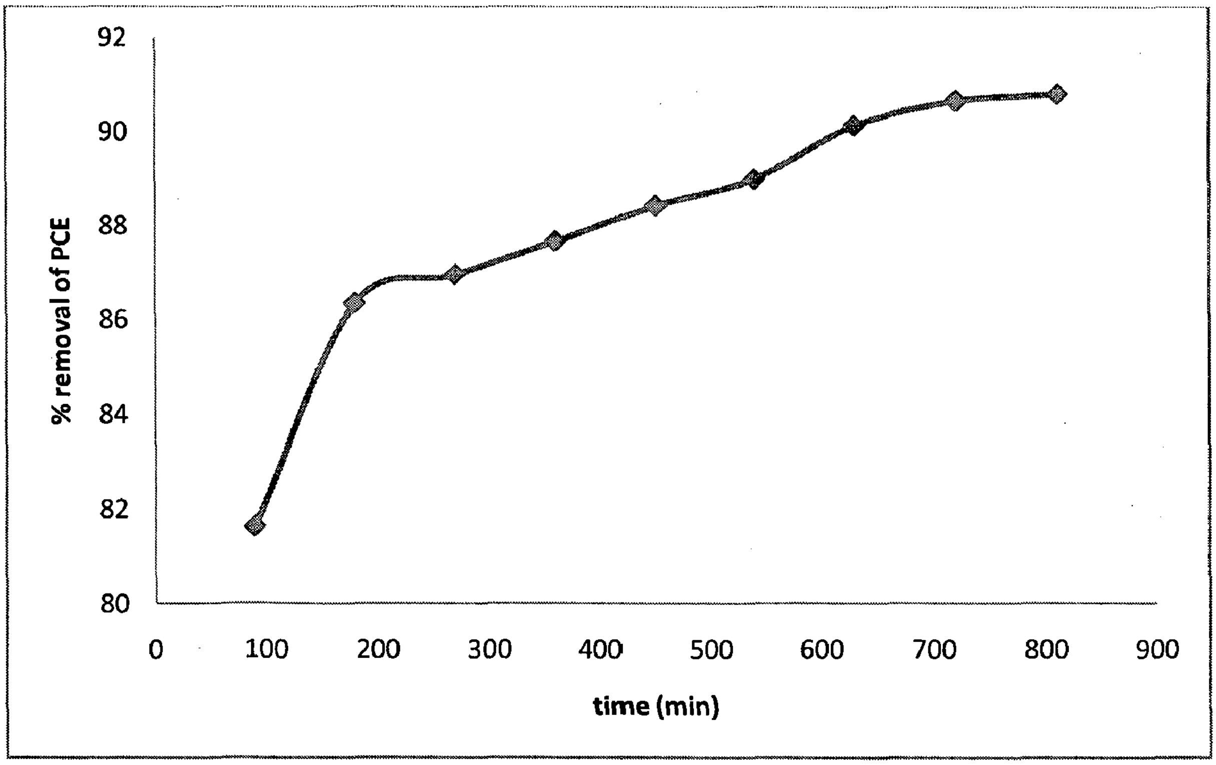

Figure 16: Percent removal of PCE with time

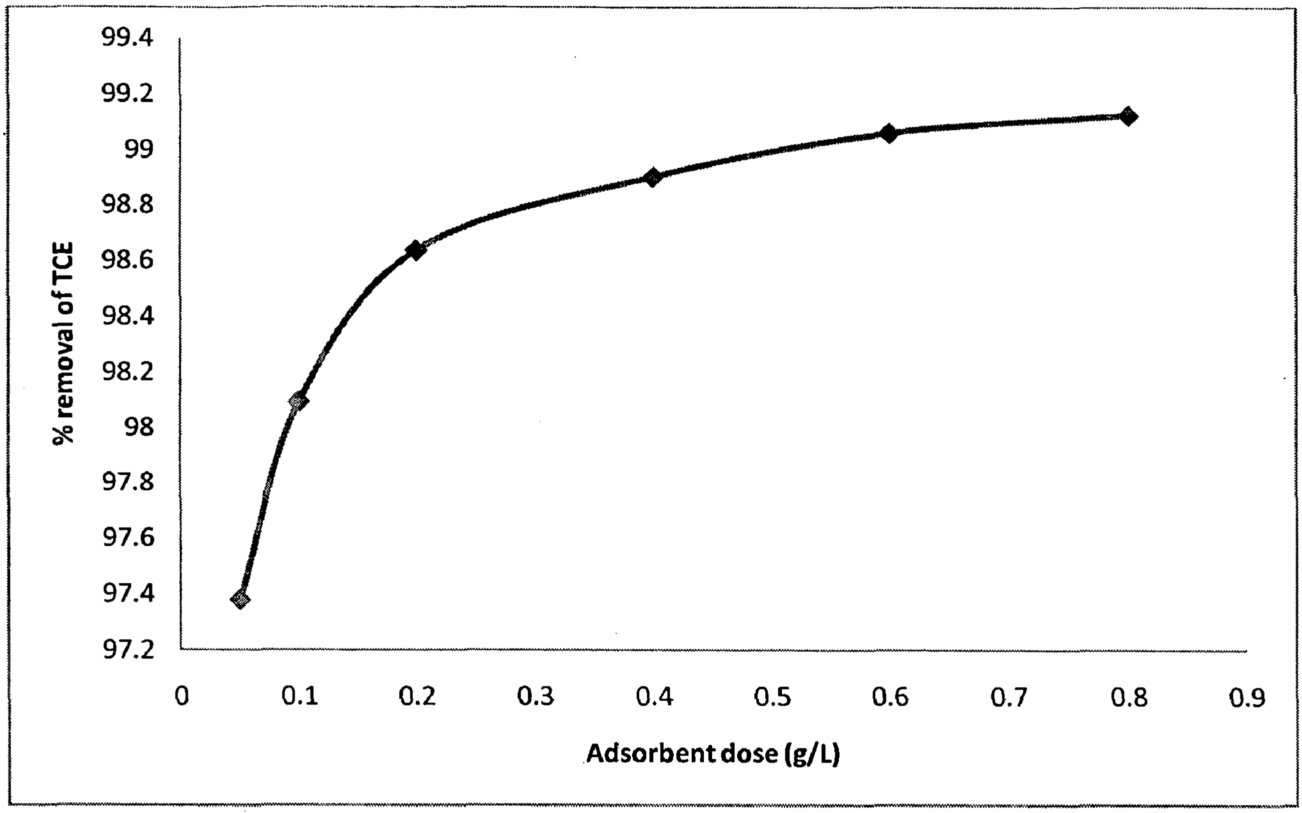

Figure 17: Effect of Adsorbent dose on adsorption of TCE on PAC

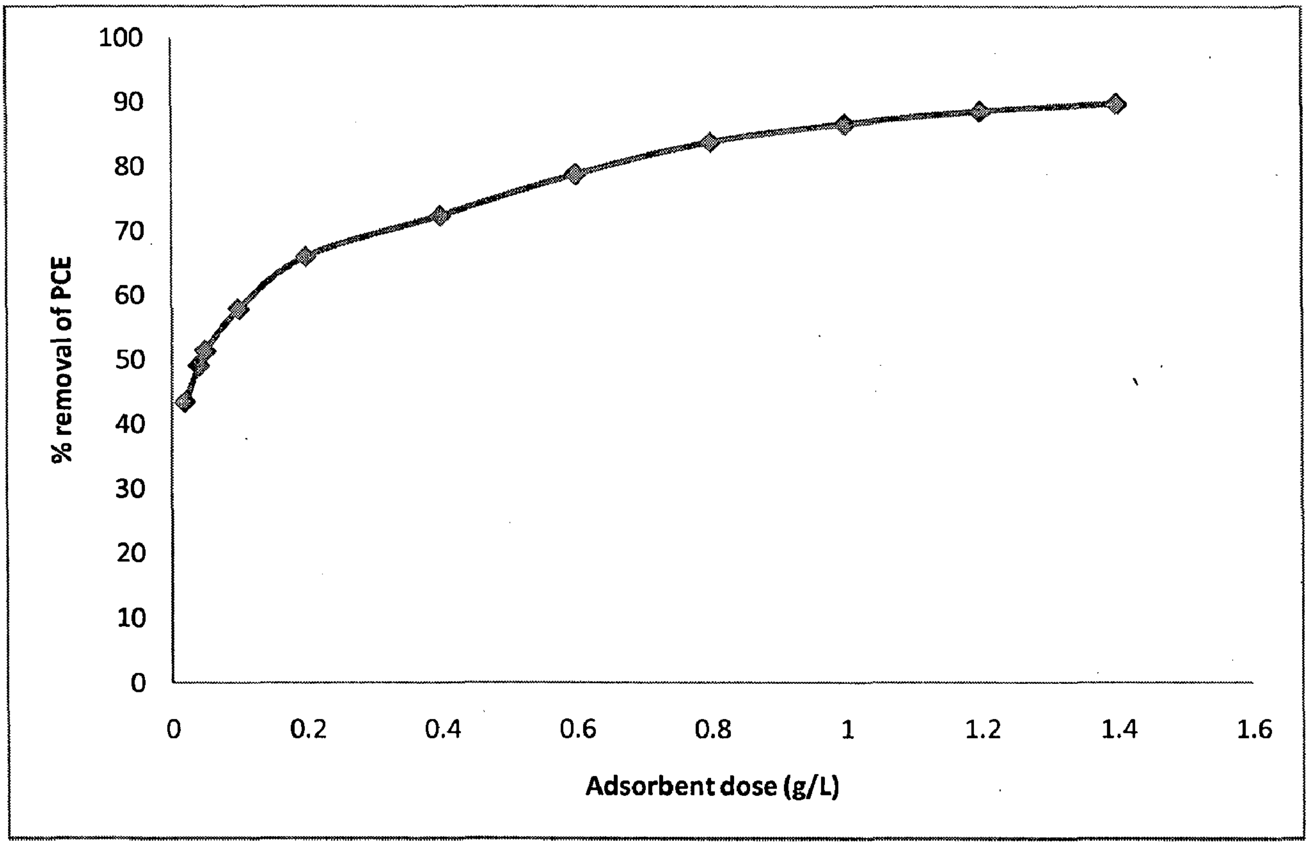

Figure 18: Effect of Adsorbent dose on adsorption of PCE on PAC

4.5 EFFECT OF INITIAL ADSORBATE CONCENTRATION

Adsorbate concentration variations are studied so that we understand the efficiency of the adsorbent for the removal of pollutants at different concentrations in the industrial wastewater. Effect of initial concentration was studied by experimenting with the concentration at five different values: 3, 5, 10, 15 and 20 mg/L by using the optimized process parameters for the study. From Figures 19 and 20, we see that the adsorption has increased gradually with time and then attained a constant value at equilibrium for all five concentrations. There is a high uptake rate initially till 60 minutes for both TCE and PCE because of adequate driving force to adsorb the molecules on vacant sites of the surface of PAC which is the difference between adsorbate concentration in the solution and the adsorbent surface. As the concentration of the adsorbate builds up on vacant sites, the driving force to adsorb molecules decreases which in turn decreases the adsorption rate. The figures also show that as the initial concentration of the adsorbate increases there is an increase in the

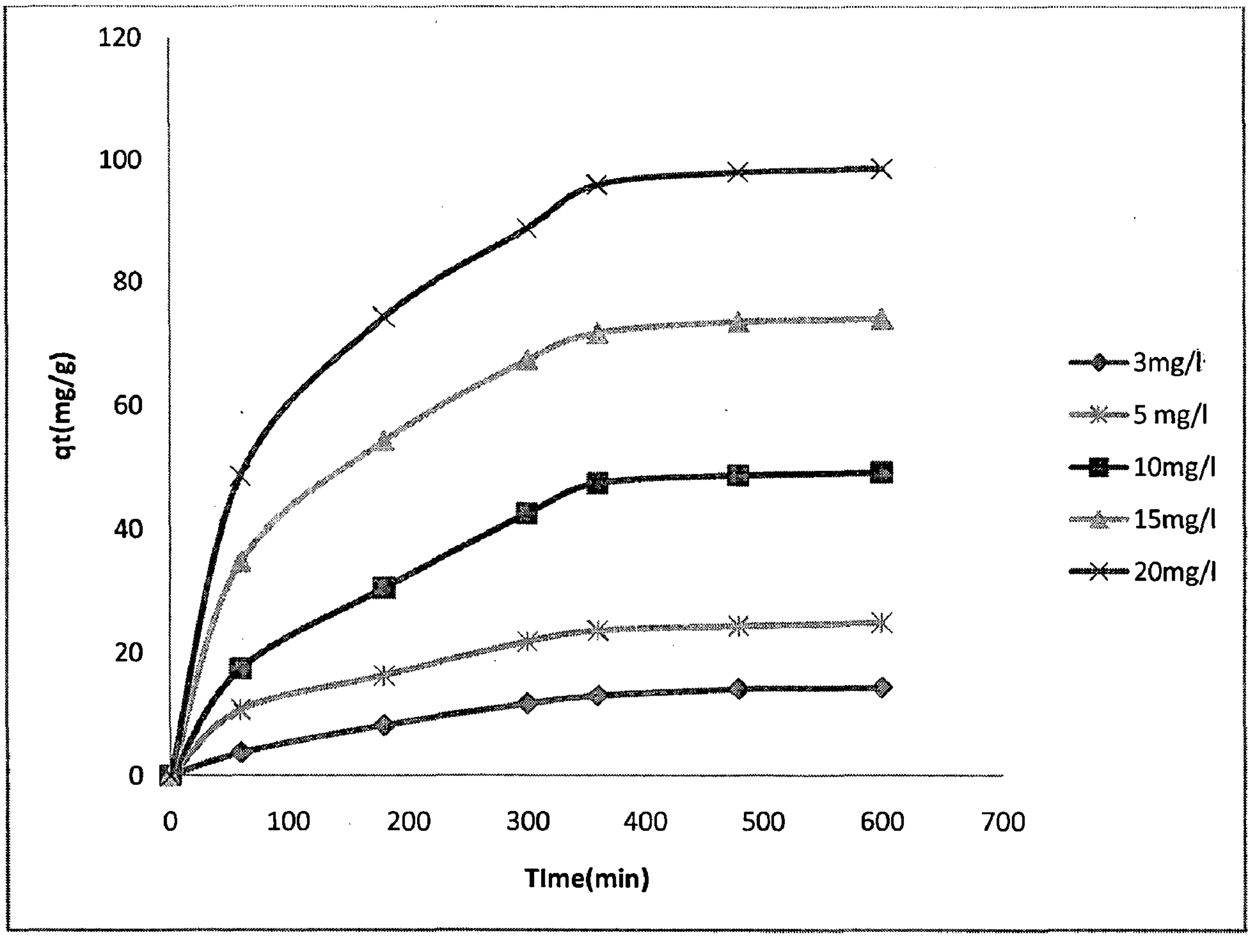

Figure 19: Effect of Initial Concentration of TCE on PAC

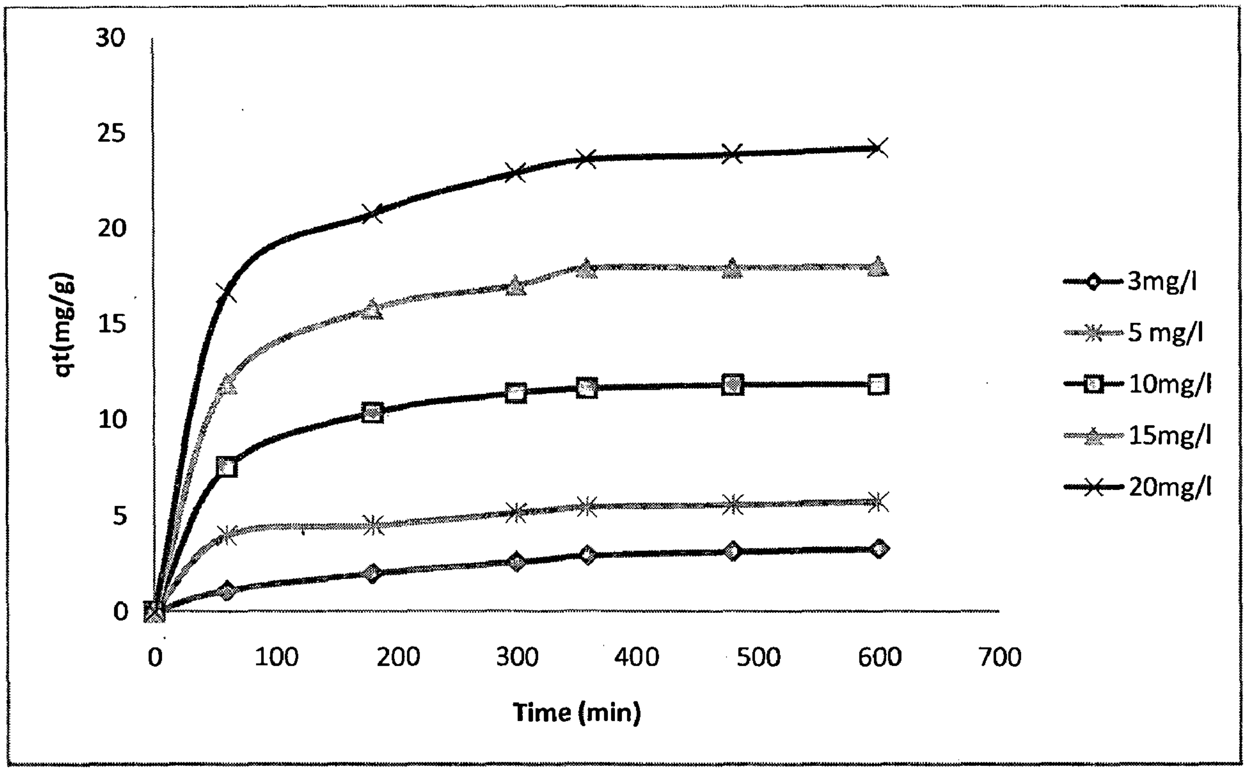

Figure 20: Effect of Initial Concentration of PCE on PAC

adsorbate uptake. The adsorption is higher for TCE than PCE for same initial concentrations depicting that the prepared PAC is more effective in removing TCE than PCE.

4.6 ADSORPTION KINETICS

In our study, experiments were conducted on both TCE and PCE to understand the variation of concentration with time. Initial concentration of 5 mg/L was used for both adsorbates, optimized values for pH, adsorbent dose and temperature were fixed and samples were collected at specified intervals of time till equilibrium was achieved. The corresponding values of q_t were calculated using equation (1). The experimental data thus obtained was used in plotting the three graphs as per equations (4), (6) and (7) to analyze the predictive capabilities of pseudo-first order, pseudo-second order and intraparticle diffusion respectively. The plot of intraparticle diffusion for both TCE and PCE adsorption was a non-linear curve which did not pass through the origin as represented in Figures 21 and 22, respectively. This implies that a combination of surface adsorption and intraparticle diffusion controlling the process. It is observed that the data do not agree with pseudo-first order kinetics effectively giving a non-linear plot and lesser value of correlation coefficient R^2 for both TCE and PCE as compared to pseudo-second order kinetics. The plots thus obtained for TCE and PCE adsorption are shown in Figures 23 and 24, respectively. The experimental data concurs with pseudo-second order kinetics giving a linear plot with a very high correlation coefficient R^2 of the order 0.993 for TCE and 0.998 for PCE. Figure 25 and 26 represent the pseudo-second order kinetics for TCE and PCE respectively. This indicates that the adsorption perfectly complies with pseudo-second order kinetics. The kinetic parameters for all three models are tabulated in Table 4. It can be seen that the rate constant is very low for pseudo-second order model for both TCE and PCE adsorption onto PAC. And, also the amount adsorbed per unit adsorbent is high for the pseudo-second order model justifying our conclusion of selecting it as the best fitting model. The adsorbed amounts per unit adsorbent for TCE and PCE are found to be 29.412 mg/g and 6.1349 mg/g, respectively.

Table 4: Kinetic parameters for the adsorption of TCE and PCE on PAC

Kinetic Parameters	**Adsorbate**	
	Trichloroethylene	**Perchloroethylene**
Pseudo-first order		
k_1 (1/min)	0.0030	0.002
q_e (mg/g)	4.095	1.465
R^2	0.961	0.88
Pseudo-second order		
k_2 (g/mg/min)	0.00032	0.0029
q_e (mg/g)	29.412	6.1349
R^2	0.993	0.998
Intraparticle diffusion		
k_p (mg/g/min$^{1/2}$)	0.648	0.098
C	9.094	3.268
R^2	0.897	0.893

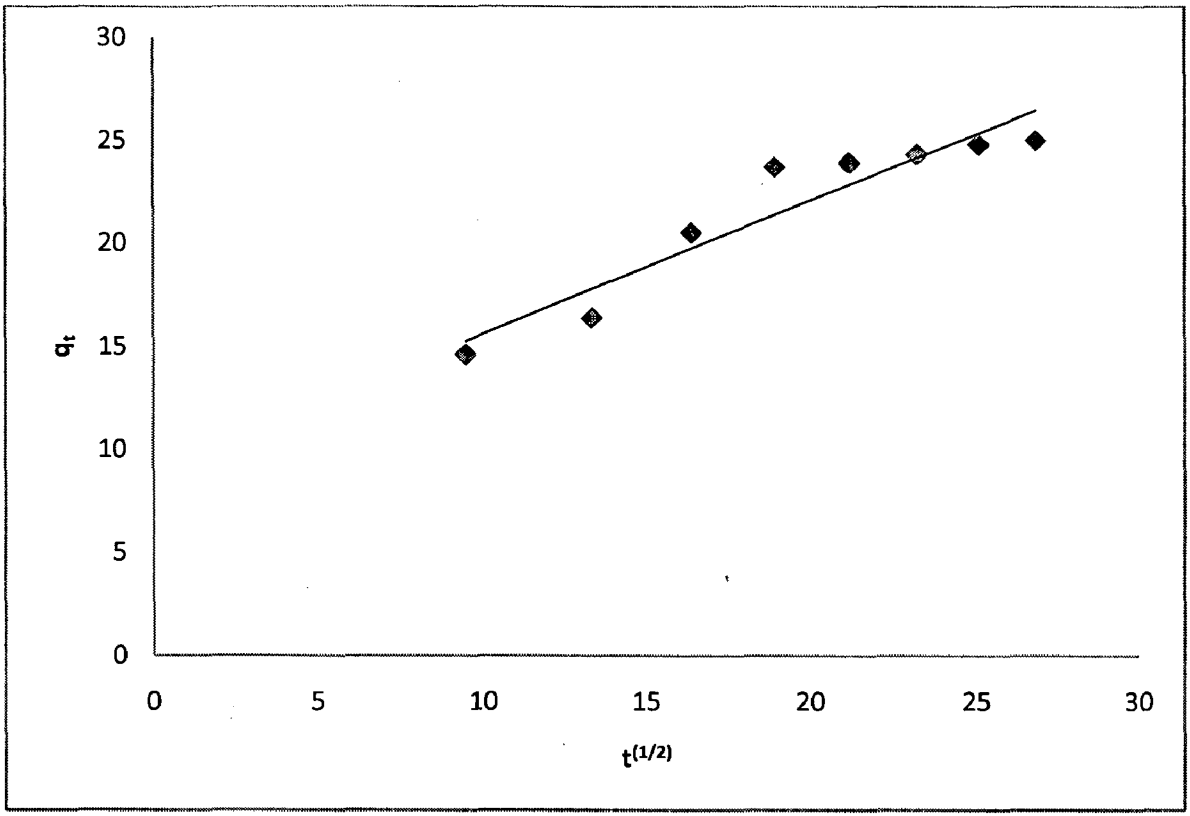

Figure 21: Intraparticle diffusion curve for TCE adsorption on PAC

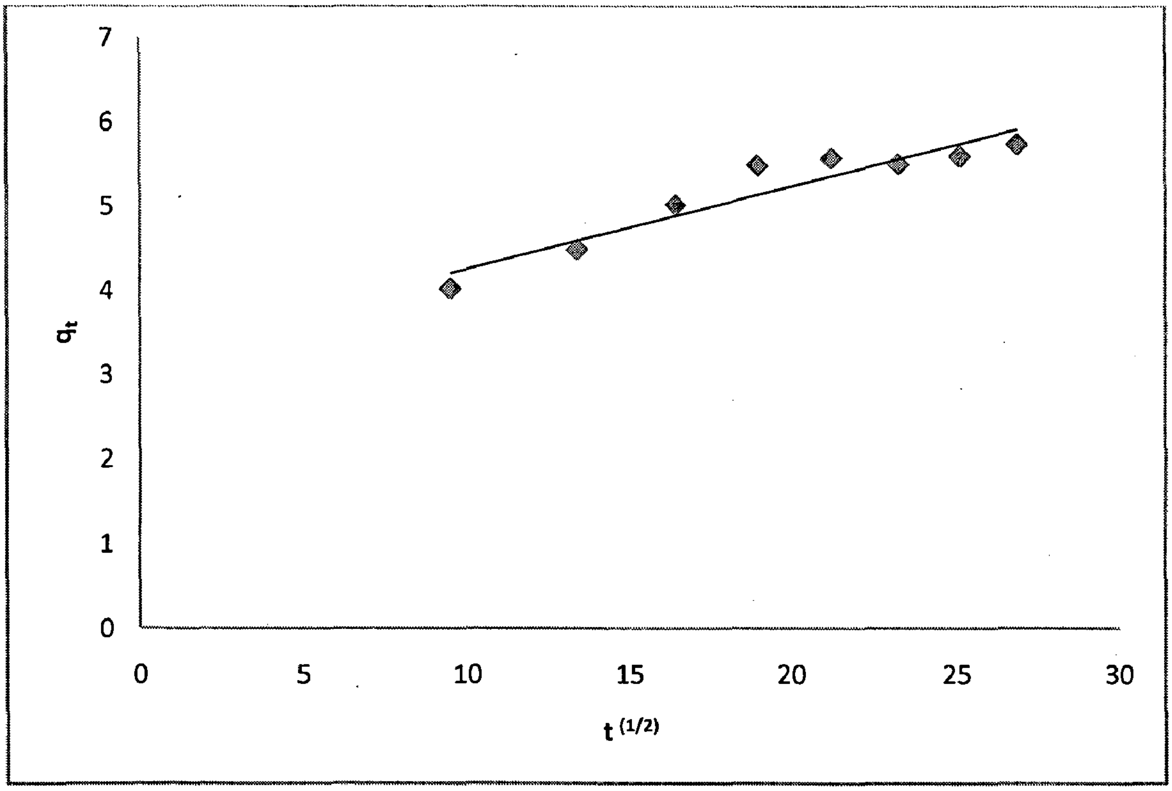

Figure 22: Intraparticle diffusion curve for PCE adsorption on PAC

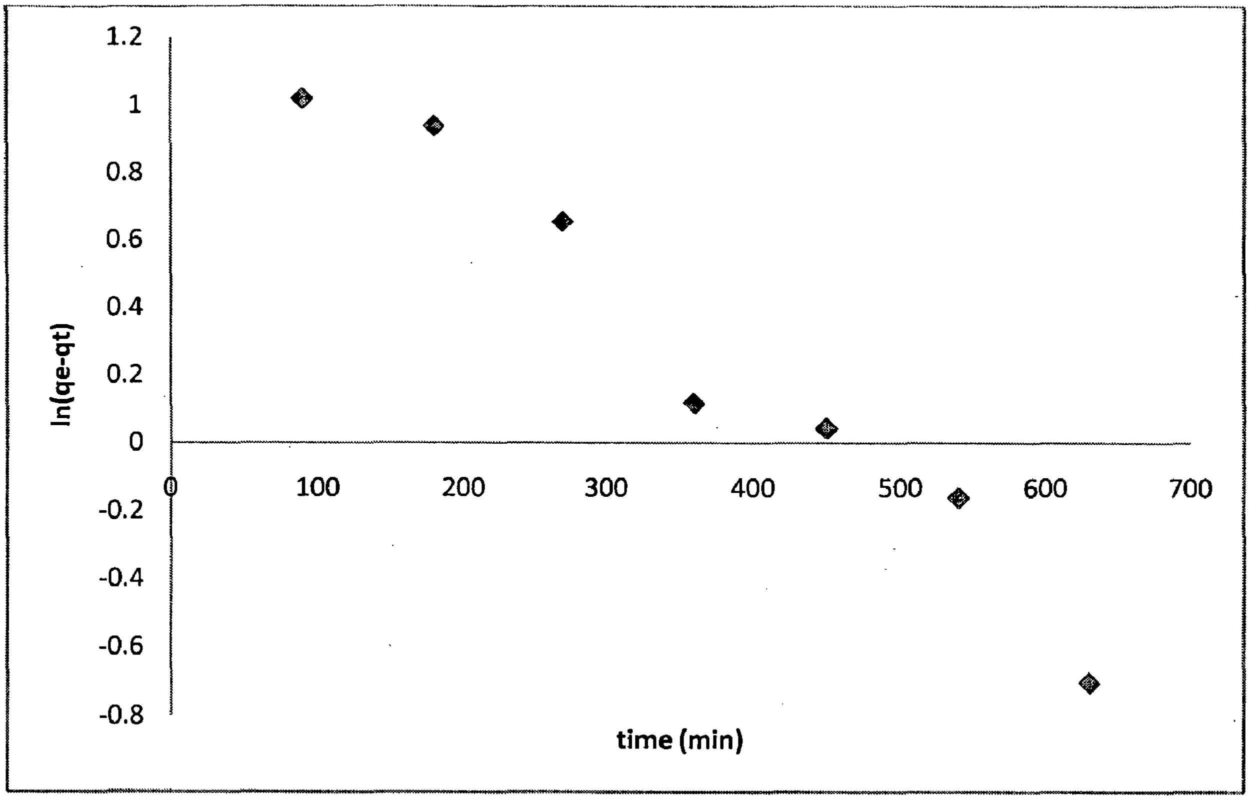

Figure 23: Pseudo-first order plot for the adsorption of TCE on PAC

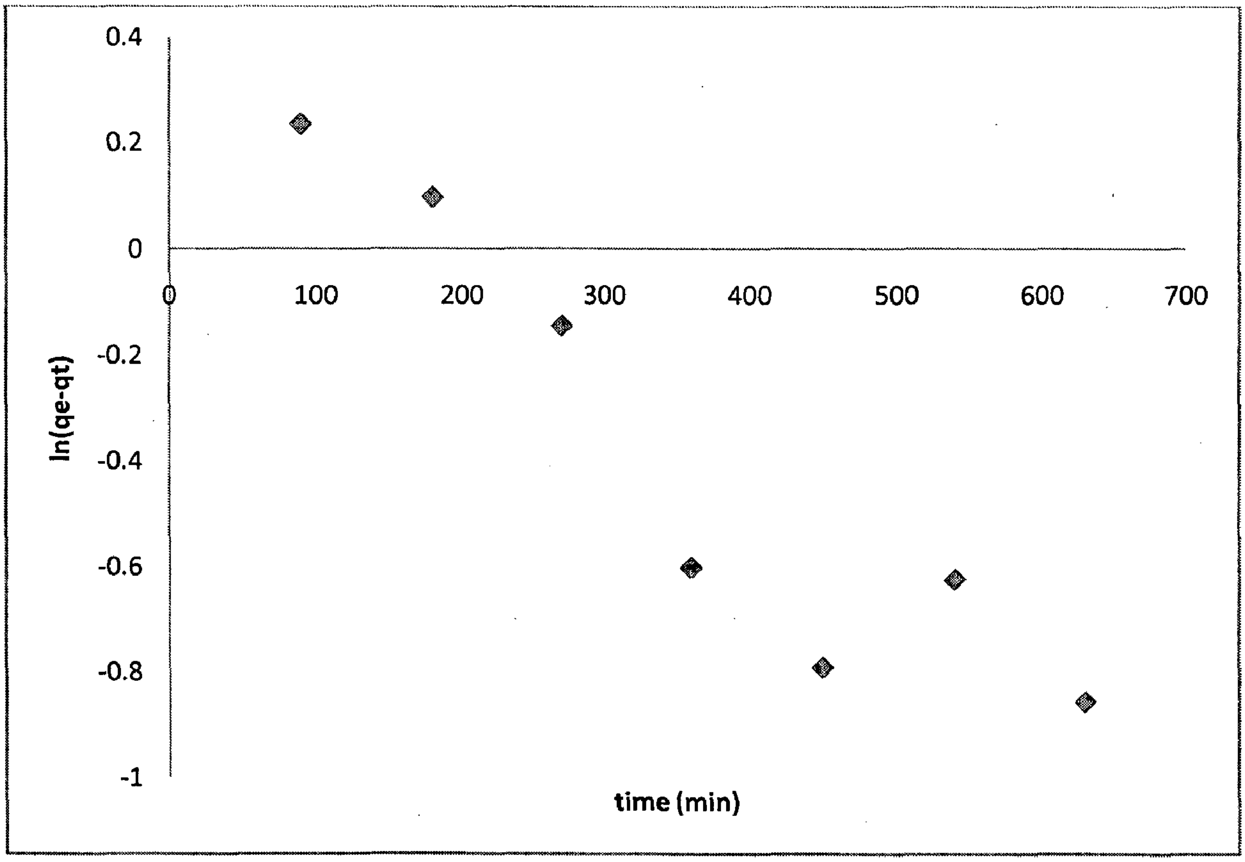

Figure 24: Pseudo-first order plot for the adsorption of PCE on PAC

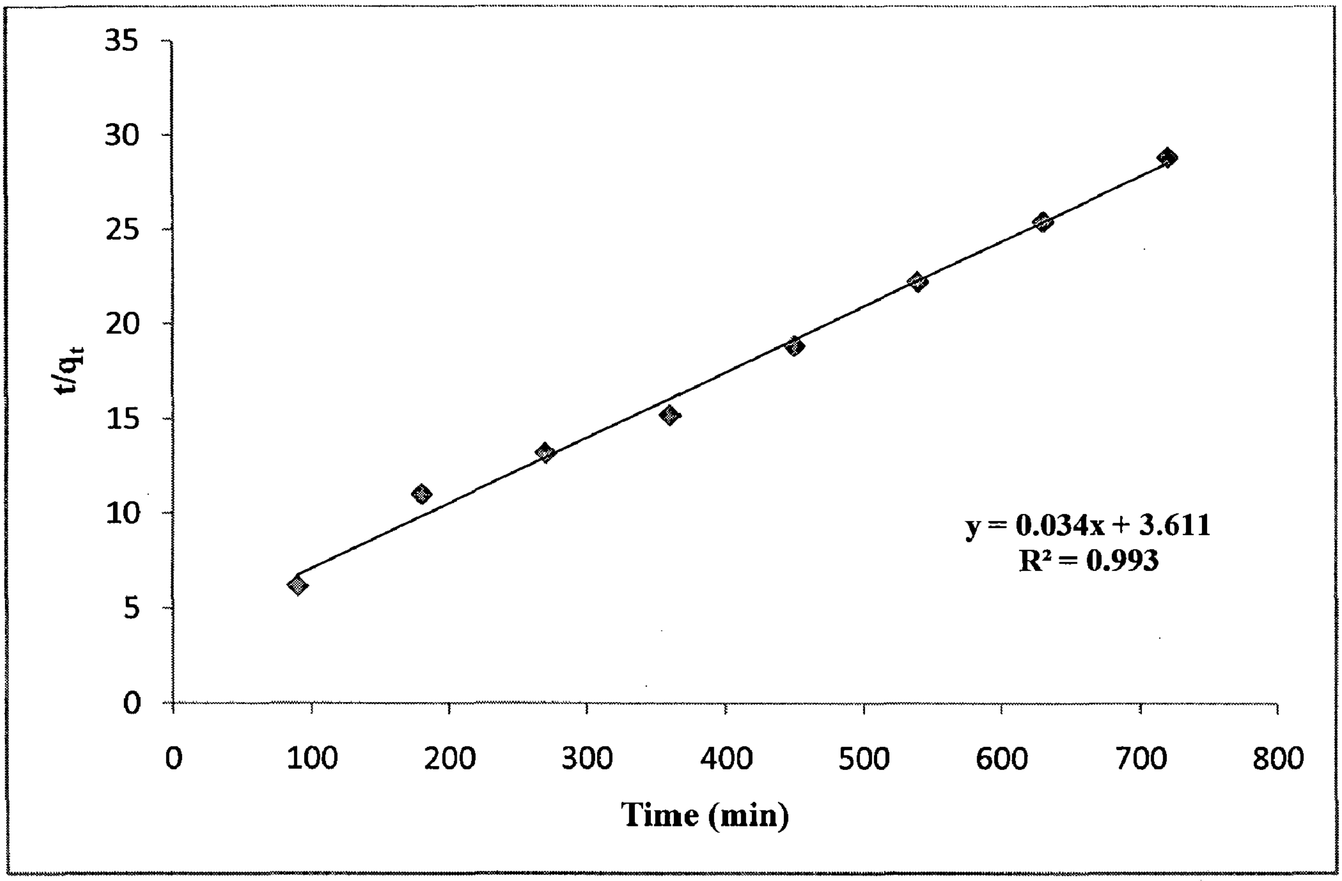

Figure 25: Pseudo-second order plot for the adsorption of TCE on PAC

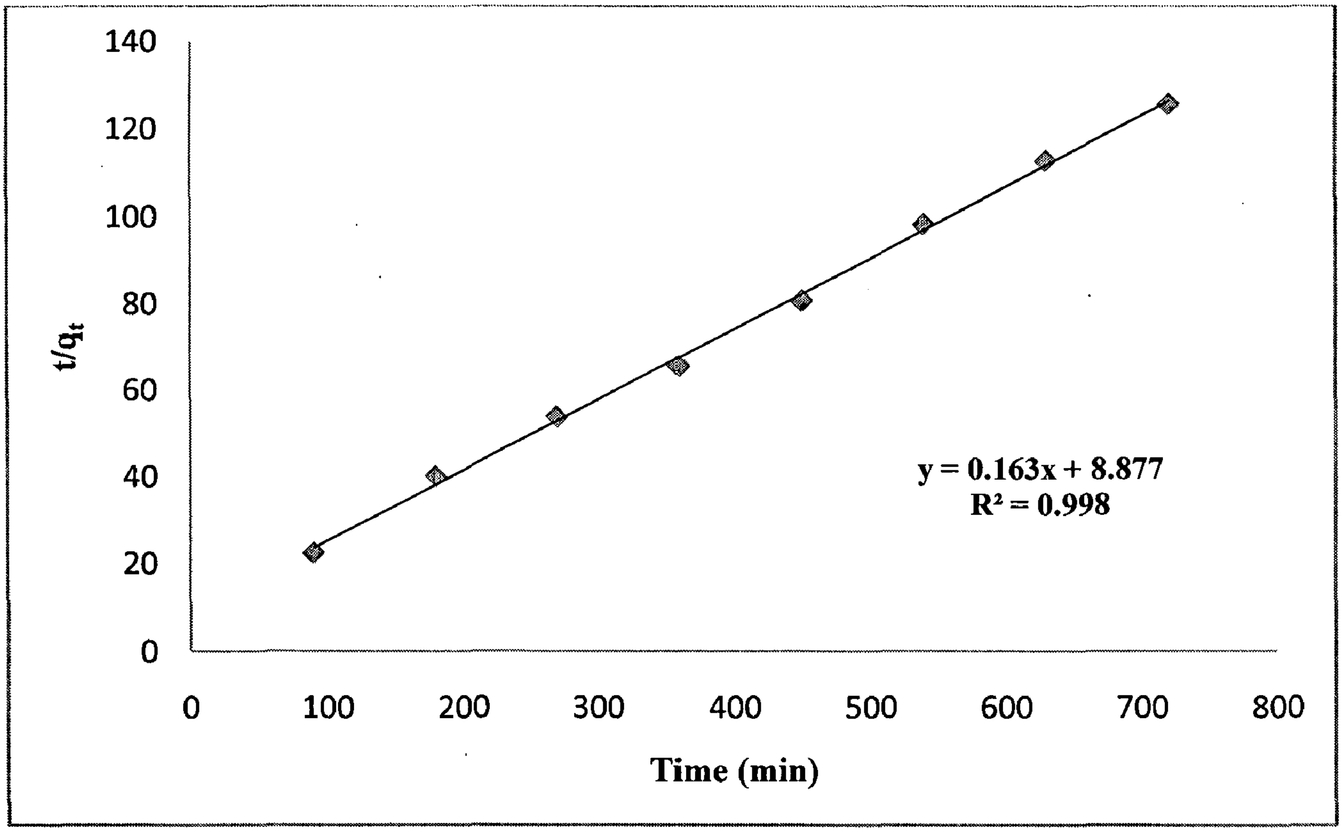

Figure 26: Pseudo-second order plot for the adsorption of PCE on PAC

4.7 ADSORPTION EQUILIBRIUM ISOTHERMS

Isotherm experiments were conducted at 30°C and initial concentration 5 mg/L of both the adsorbates. Adsorbent dose was varied from 0.05 – 8 g/L for TCE and 0.02 – 1.4 g/L for PCE. C_e value for each different adsorbent dose was determined and the experimental data is correlated with six isotherm models for TCE and five isotherm models for PCE. The shape of experimental and model fitted isotherm curves is found to be concave upwards in nature for both TCE and PCE. The adsorption equilibrium constants derived for various models are given in Table 5. All the parameters of the isotherm models and the correlation coefficient R^2 for both TCE and PCE are obtained using the curve-fitting tool of MATLAB 7.0.1. Figure 27 and 28 show the experimental data and the isotherm model curves obtained for TCE and PCE, respectively. All the six isotherm models gave a very good fit and a high correlation coefficient R^2 greater than 0.99 for TCE. Likewise, all the five isotherm models gave a very good fit with R^2 greater than 0.98 for PCE. However, the R^2 values are very close to each other in all isotherm models, hence, it is very difficult to decide the best model to represent the experimental data. Thus, we employ various statistical indices correlating the experimental data with the data calculated by the equations (14) to (18) as described in section 3.7. The various statistical parameters determined are given in Table 6.

Table 5: Adsorption equilibrium isotherm constants for TCE and PCE at 30°C

Adsorbate	Isotherm Model											
	Freundlich			Langmuir-Freundlich				Fritz-Schlunder				
	$q_e = K_F C_e^{1/n}$			$q_e = \frac{q_{e,\max}(KC_e)^n}{1+(KC_e)^n}$				$q_e = \frac{\alpha_1 C_e^{\beta_1}}{1+\alpha_2 C_e^{\beta_2}}$				
	K_F	n	R^2	$q_{e,max}$	K	n	R^2	α_1	β_1	α_2	β_2	R^2
TCE	8335	0.4569	0.9946	4877	1.314	2.213	0.9939	8335	2.189	0.3086	801.4	0.9931
PCE	1.098	0.2283	0.9835	0.0011	1.022	4.379	0.9814	0.09575	6.531	6.233	1.227	0.9985

Adsorbate	Isotherm Model											
	Sips				Koble-Corrigan				Radke-Prausnitz			
	$q_e = \frac{q_m a_s C_e^m}{1+a_s C_e^m}$				$q_e = \frac{AC_e^n}{1+BC_e^n}$				$\frac{1}{q_e} = \frac{1}{KC_e} + \frac{1}{kC_e^{1/n}}$			
	q_m	a_s	m	R^2	A	B	n	R^2	K	k	n	R^2
TCE	89.7	91.9	2.1887	0.994	4168	4168	2.189	0.994	1382	8633	0.4541	0.994
PCE	0.8969	0.5772	4.384	0.9814	0.04155	1.056	4.38	0.9814	-	-	-	-

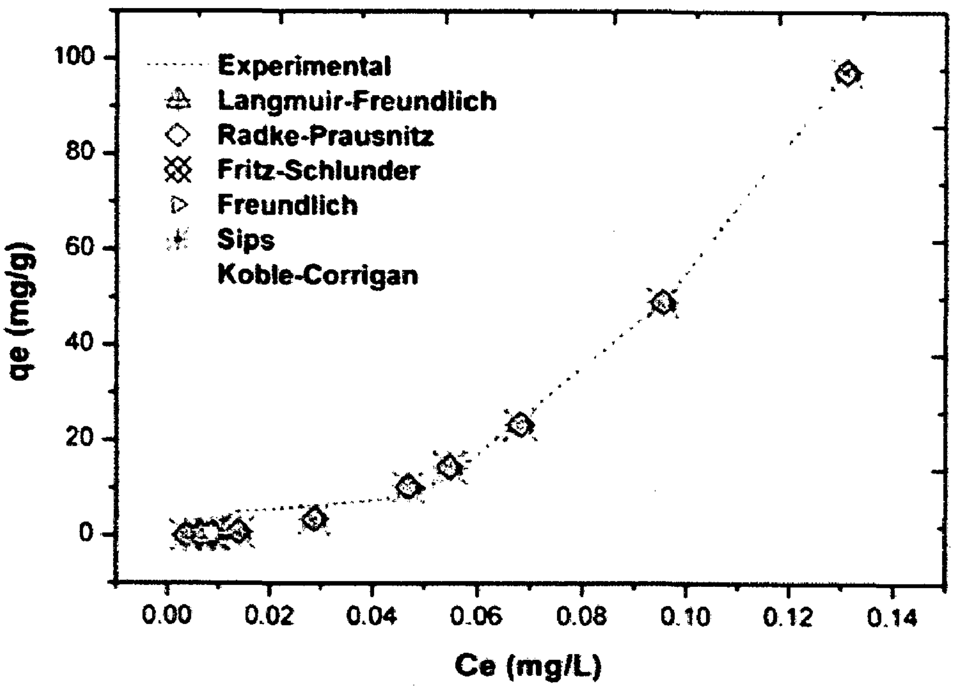

Figure 27: Comparison of various isotherm models for TCE adsorption on PAC

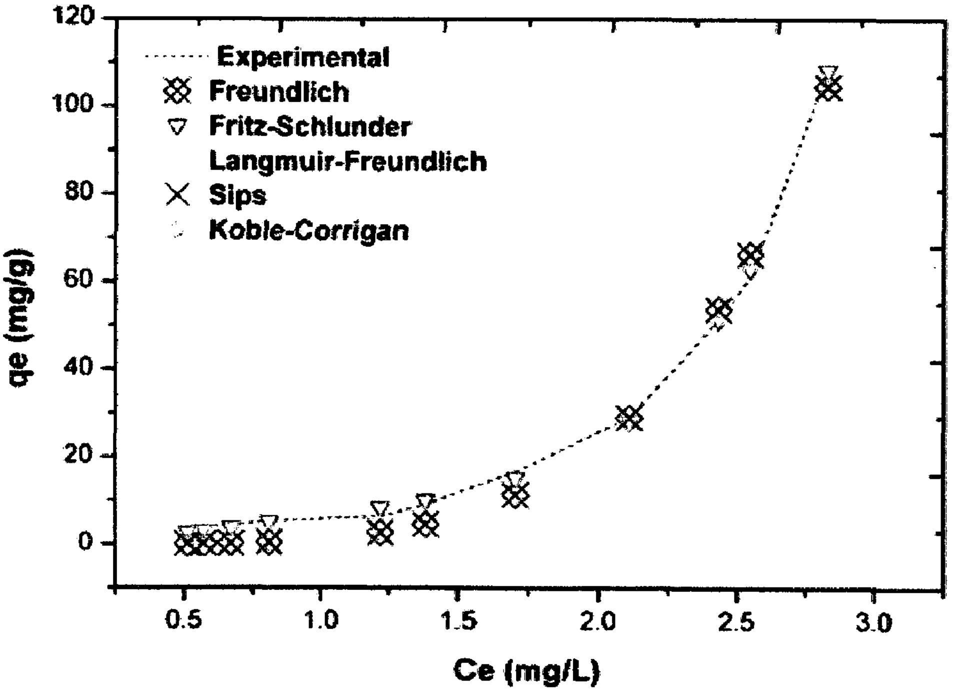

Figure 28: Comparison of various isotherm models for PCE adsorption on PAC

Based on the above findings, it is concluded that for the pollutant TCE, the best fitted isotherm models are in the order: Freundlich> Sips> Radke-Prausnitz> Koble-Corrigan> Langmuir-freundlich> Fritz-Schlunder. Likewise, for PCE, the order is: Fritz-Schlunder> Freundlich> Langmuir-freundlich> Koble-Corrigan> Sips. The differences in the calculated three parameter model values are very less possibly due to the non-linear fitting procedure. Since the adjusted R^2 values of three isotherms (Sips, Radke-Prausnitz, Koble-Corrigan) are equal in quantity for TCE, further the RMSE values are considered to sort out the best fit. For best fitted isotherms of TCE and PCE, the root mean square error (RMSE) was 1.96 and 1.02, respectively; while, the standard error of prediction (SEP) was 10.39 and 3.76, respectively (Table 6). Table 5 shows that the Freundlich isotherm model is found to fit the experimental data for TCE with highest accuracy (R^2: 0.9946). The adsorption capacity K_F and adsorption intensity n are noted as 8335 and 0.4569, respectively. This indicates that there is a high favourability of adsorption for TCE on the chosen PAC. In the Langmuir-Freundlich model data, we observe that $n>1$ indicates a positive co-operability in the adsorption process. Fritz-Schlunder is the best fit for PCE giving a R^2 value of 0.9985. It is observed that the higher R^2 values and model parameters of TCE as compared to PCE indicate the better adsorption compatibility of TCE with PAC as compared to PCE with PAC.

Table 6: Statistical indices for various isotherm Models for (a) TCE (b) PCE

Isotherm models	**R^2**	**adj. R^2**	**RMSE**	**SEP**	**NSD**	**ND**	**ARE**
For Trichloroethylene							
Freundlich	0.9952	0.9946	1.9651	10.3875	60.5142	47.5401	18.2457
Langmuir-Freundlich	0.9952	0.9939	1.9681	10.4030	60.9290	47.7911	18.3708
Fritz-Schlunder	0.9952	0.9931	1.9652	10.3875	60.5142	47.5402	18.2457
Sips	0.9952	0.9940	1.9587	10.3537	60.5134	47.5042	18.2455
Koble-Corrigan	0.9952	0.9940	1.9737	10.4327	60.4950	47.5773	18.2399
Radke-Prausnitz	0.9952	0.9940	1.9662	10.3932	60.7508	47.6792	18.3171
For Perchloroethylene							
Freundlich	0.9851	0.9835	3.9346	14.5139	63.0534	49.0661	19.0113
Langmuir-Freundlich	0.9851	0.9814	3.9345	14.5137	63.0407	49.0540	19.0075
Fritz-Schlunder	0.9989	0.9985	1.0198	3.7618	12.8689	5.19914	3.88013
Sips	0.9851	0.9814	3.9347	14.5143	63.0804	49.0915	19.0195
Koble-Corrigan	0.9851	0.9814	3.9346	14.5139	63.0531	49.0658	19.0112

Table 7: Process parameter comparison for TCE adsorption on PAC

Surface Area (m^2/g)	Operating Conditions			Adsorbate Concentration (mg/L)			Models Fitted			References
	Temp (°C)	pH	Adsorbent dose (g/L)		Freundlich	Langmuir	Langmuir-Freundlich	Radke-prausnitz	Dubinin-Astakhov	
783	20	8	2.5	5	K = 0.337, n = 0.68, R^2=0.9861					[33]
929	20	8	2.5	5	K = 0.944, n = 0.626, R^2=0.9952					
950	20	7		6	K= 0.436, n= 0.68 R^2= 0.9964	Dubinin-Radushkevich Qm=594.7, E= 10.68, R^2= 0.9959	Qm= 596.3, K= 5690, ΔG= -21.06, n= 0.771 R^2= 0.9975		Qm=1450.1, E= 7.11, n=1.42 R^2= 0.9959	[31]
0.6195	20	4.26	4	50	K = 0.292, n = 0.793, R^2=0.907	Qm= 1.261, K= 0.00012, R^2= 0.914				[34]
1.0972	20	7.43	4	50	K = 8.453, n = 0.417, R^2=0.9	Qm= 2.398, K= 0.000036, R^2= 0.914				
1.3725	20	5.15	4	50	K = 0.189, n = 0.811, R^2=0.944	Qm= 1.233, K= 0.000701, R^2= 0.959				
	20	7	1.05	8	K = 1.01, n = 0.596,				Qm=314, E= 57.8, n=1.64	[35]
273.54	30	10	0.2	5	K = 8335, n = 0.4569 R^2=0.9952	Fritz-schulnder a = 8335, b = 2.189, c=0.3086, d=801.4 R^2=0.9952	Qm= 4877, K= 1.314, n= 2.213 R^2= 0.9952	a= 1382, b=8633, c=2.202, R^2= 0.9952		Present Study

Table 8: Process parameter comparison for PCE adsorption on PAC

Surface Area (m^2/g)	Operating Conditions			Adsorbate Concentration (mg/L)	Models Fitted					References
	Temp (°C)	pH	Adsorbent dose (g/L)		Freundlich	Langmuir	Langmuir-Freundlich	Fritz-schlunder	Dubinin-Astakhov	
0.6195	20	4.26	4	50	K=14.93, n=0.518, R^2= 0.943	Qm= 1.931, K= 0.000078 R^2= 0.979				[34]
1.0972	20	7.43	4	50	K=0.000021 n=1.813, R^2= 0.934	Qm= 0.552, K= -0.00013 R^2= 0.911				
1.3725	20	5.15	4	50	K=0.000059 n=1.697, R^2= 0.924	Qm= 0.589, K= -0.000141 R^2= 0.971				
273.54	30	10	0.2	5	K=1.098, n=0.2283, R^2= 0.9851		Qm= 0.001102, K= 1.022, n= 4.379, R^2= 0.971	a = 0.09575, b = 6.531, c= 6.233, d= 1.227, R^2=0.9952		Present Study

The comparison between the studies carried out by various authors has been compared with the present work of TCE adsorption on PAC which is given in Table 7. It is concluded that the obtained parameters and values in this study are comparable to the work done previously.

Table 8 represents the process parameter comparison for PCE adsorption on the prepared PAC. It is noted that the obtained parameter values agree with the previous literature values. We can validate the selection of the process parameters values from the tables, as they show that the chosen conditions of adsorbent dose, temperature and initial adsorbate concentration are in agreement with the values chosen by different authors. The fitting of adsorption isotherm models are also similar with those chosen by the other researchers. And, the values are the indication of the high adsorption capability of the prepared PAC to adsorb both TCE and PCE.

4.8 ADSORPTION THERMODYNAMICS

The thermodynamic analysis is carried out by varying the temperature and determining the adsorption of both the pollutants onto PAC. Four different temperatures, viz. 10°C, 20°C, 30°C and 40°C were chosen for this purpose. The adsorption thermodynamic parameters are calculated by using equations (19), (20) and (21) by plotting the graph between 1/T and ln K_D. The plots thus obtained for TCE is shown in Figure 29. The thermodynamic parameters are further calculated from the plot using the above mentioned equations and the values thus obtained are tabulated in Table 9. Similarly, for PCE, the plot is represented in Figure 30. And, the thermodynamic parameters are given along with the parameters of TCE in Table 9. From the table, we can observe that the negative ΔG^0 indicates the thermodynamic feasibility, spontaneity and chemical control of the process. The ΔG^0 values for TCE and PCE are determined to be -4.8508 kJ/mol and -2280.14 kJ/mol, respectively. The negative value of ΔH^0 represents the exothermic nature of the adsorption process. The value of ΔH^0 for TCE is found to be -5.5928 kJ/mol and for PCE, it is found to be -7.054 kJ/mol. The exothermic behaviour of adsorption process is supported by the findings obtained from the effect of temperature, where the uptake capacity decreases with the increase in temperature as shown in Figures 13 and 14. The negative value of ΔS^0 indicates the decrease in the randomness at the adsorbate-adsorbent interface during the adsorption process. The value of ΔS^0 for TCE and PCE are -0.00267 kJ/mol K and -0.00203 kJ/mol K.

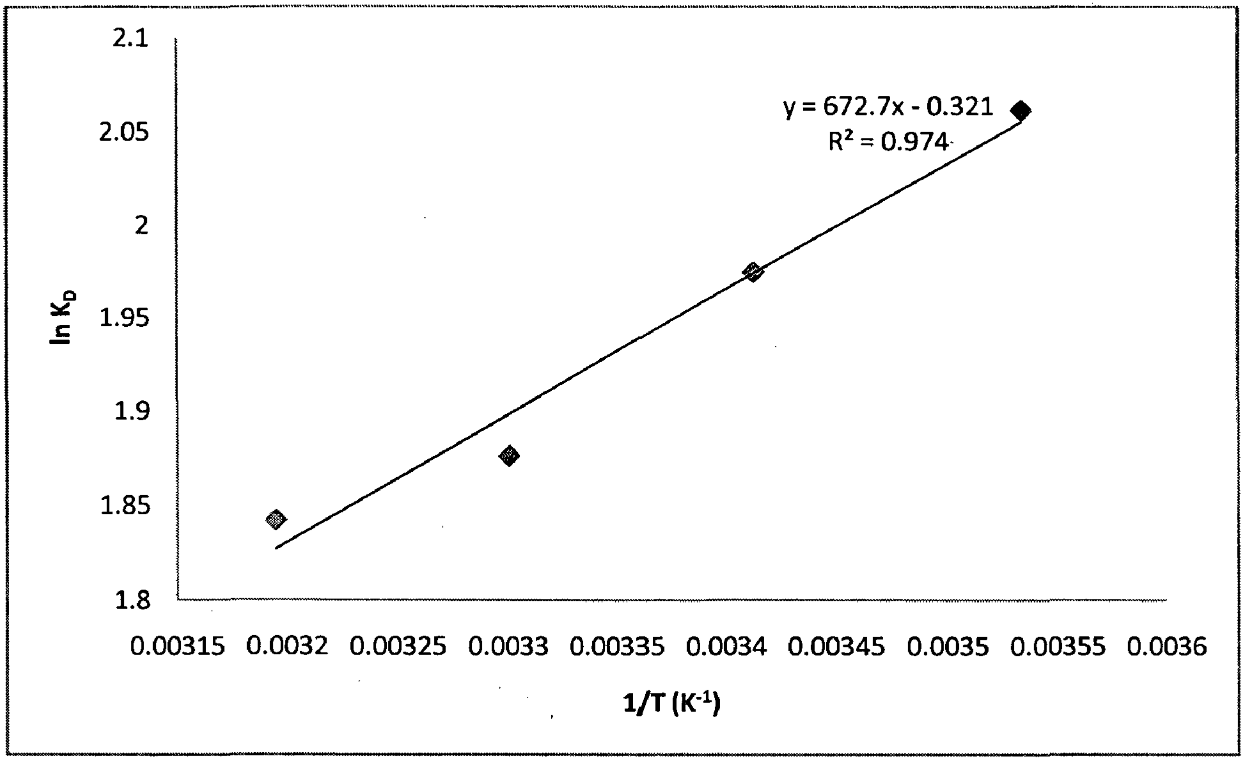

Figure 29: Thermodynamic plot for TCE

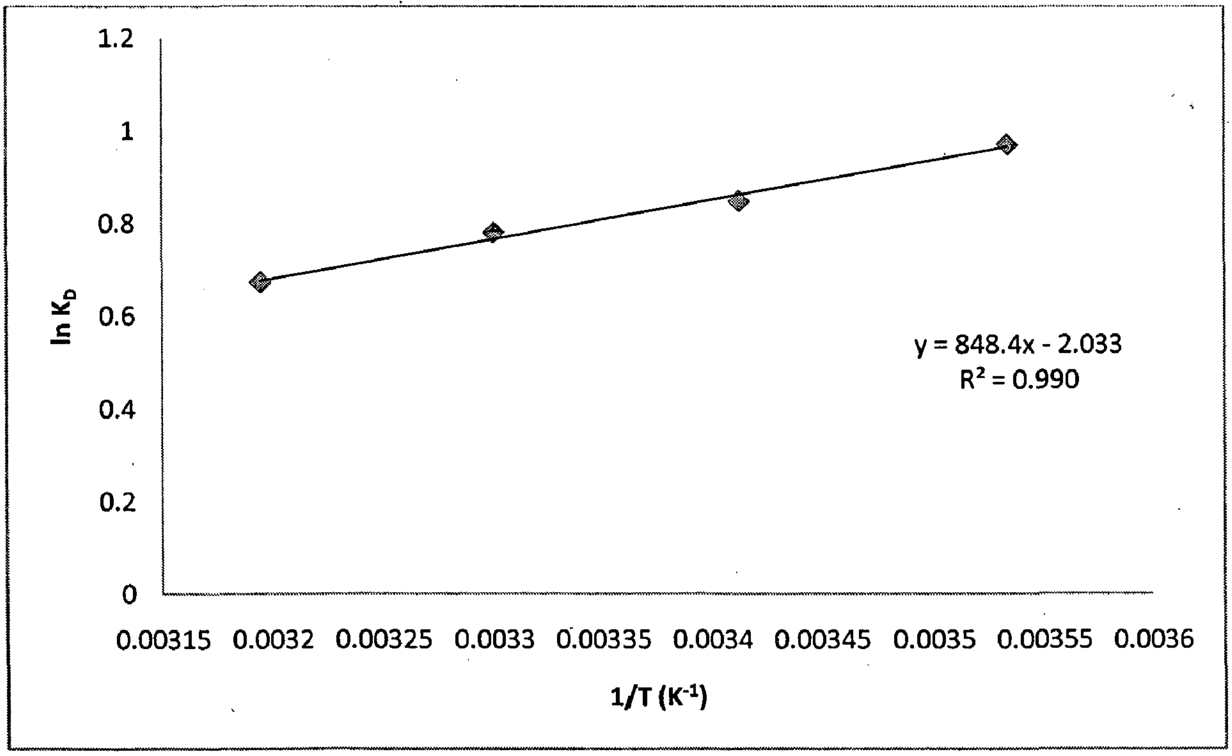

Figure 30: Thermodynamic plot for PCE

Table 9: Thermodynamic parameters for the adsorption of TCE and PCE onto PAC

Adsorbate	**Temperature (K)**	**K_D (1/g)**	**ΔG^0(kJ/mol)**	**ΔH^0(kJ/mol)**	**ΔS^0(kJ/mol K)**
Trichloroethylene					
	283	115.262	-4.8508	-5.5928	-0.00267
	293	94.3035	-4.8099		
	303	75.1939	-4.7264		
	313	69.5549	-4.7942		
Perchloroethylene					
	283	9.3131	-2280.14	-7.054	-0.00203
	293	7.0334	-2063.7		
	303	6.0212	-1964.14		
	313	4.7039	-1749.92		

The results obtained from the thermodynamic analysis indicate that the findings are favourable for the adsorption process as they support the spontaneity of the process. They show that the adsorption is exothermic in nature and thus does not require high temperatures for the feasibility of the process. The decrease in randomness at adsorbate-adsorbent interface shows that the process is approaching a stable condition as the adsorption process is carried out and it attains equilibrium in due time when all the driving forces balance each other.

CHAPTER 5

CONCLUSION

For the removal of TCE and PCE from aqueous solutions, batch adsorption studies have been carried out using activated carbon prepared from Parthenium weed. The carbonization and chemical activation of Parthenium is done with the help of conc. Sulphuric acid and Ammonium persulphate. Activation with different chemical agents in different ratios affects characteristics of activated carbon to a large extent, thus optimum impregnation ratio (PAC: H_2SO_4: $(NH_4)_2S_2O_8$ = 1:1.5:0.4) was chosen to produce activated carbon of large surface area and high pore volume. The characterization of PAC was done by standard methods. The results obtained from them suggest that the prepared PAC has a well-defined pore structure with a majority of macropores, giving an advantage for our study, since adsorbates to be adsorbed are organic compounds and they have large molecules which require large pores for penetration. The adsorption of TCE and PCE was found to be dependent on pH, temperature, adsorbent dose and initial adsorbate concentration.

The adsorption of both TCE and PCE was observed maximum at pH of 10, suggesting that alkaline nature of the solution assists in the better removal of both the compounds. Thus, all further adsorption studies were carried out at pH of 10. As temperature was increased, the adsorption capacity decreased indicating an exothermic adsorption process. Since, the difference in the decreasing values was not substantial, it was concluded that the optimum temperature for the process would be the ambient temperature (30°C) so that the process becomes more economical. The optimum adsorbent dose for TCE and PCE removal was estimated to be 0.2 g/L and 0.8 g/L respectively. Though further increase in the adsorbent dose increased the percent removal slightly, the amount of adsorbate adsorbed per unit mass of adsorbent decreased with increase in adsorbent dose. Under optimum conditions, maximum removal efficiencies of TCE and PCE were found to be 98.64% and 83.75% respectively. The lower efficiency, even at a higher adsorbent dose for PCE, suggests that the prepared PAC is more effective in the removal of TCE than PCE. Initial adsorbate concentration for both TCE and PCE was varied from 3 – 20 mg/L and it was noted that as the adsorbate concentration increased there was an increase in the adsorbate uptake.

The kinetic studies revealed that the adsorption of TCE and PCE on PAC followed pseudo-second order kinetics. The values of second order kinetic constant k_2 for TCE and PCE were found to be 0.00032 g mg^{-1} min^{-1} and 0.0029 g mg^{-1} min^{-1}, respectively. The non-linear plot of intraparticle diffusion suggested that a combination of surface adsorption and intraparticle diffusion were controlling the process. From the adsorption isotherm studies, we can deduce that Freundlich isotherm best describes TCE adsorption with a correlation coefficient R^2 of 0.9946, followed closely by Sips, Koble-Corrigan and Radke-Prausnitz isotherm models. And for PCE adsorption, Fritz-Schlunder model gave the best approximation with a R^2 value of 0.9985. It was observed that all six isotherms gave a good fit for the experimental data of TCE adsorption and all except Radke-Prausnitz model gave good approximation for PCE adsorption. The negative values of the thermodynamic parameters ΔG^0, ΔH^0 and ΔS^0 showed spontaneous, exothermic and chemically controlled nature of the adsorption process.

Commercial grade AC is expensive and thus needs regeneration, but PAC is prepared from a noxious weed which in itself is harmful to the environment, and thus does not require regeneration because of its extremely low-cost. As Parthenium is easily available in all parts of India at zero or negligible price, the potential of using it as a source of activated carbon is very high. Since the removal efficiencies of TCE and PCE are also highly satisfactory, it is concluded that PAC is an excellent and effective alternative adsorbent for the removal of TCE and PCE from Industrial wastewater.

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