ADSORPTIVE REMOVAL OF 4-NITROPHENOL AND 2,4-DINITROPHENOL FROM AQUEOUS SOLUTION USING COMMERCIAL ACTIVATED CARBON

A DISSERTATION

Submitted in partial fulfillment of the
requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING
(With Specialization in Industrial Pollution Abatement)

By

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CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in this dissertation entitled **"ADSORPTIVE REMOVAL OF 4-NITROPHENOL AND 2,4-DINITROPHENOL FROM AQUEOUS SOLUTION USING COMMERCIAL ACTIVATED CARBON"** 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"**, submitted in the Department of Chemical Engineering, Indian Institute of Technology Roorkee is an authentic record of my own work under supervision of **Dr. (Mrs.) Shashi**, Associate Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee.

I have not submitted the matter, embodied in this dissertation for the award of any other degree.

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CERTIFICATE

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

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ABSTRACT

Batch operation studies were carried out for the removal of hazardous and toxic chemical compounds 4-Nitrophenol and 2,4-Dinitrophenol from aqueous solutions. For both adsorbates, predictive capability of three types of kinetic models and five types of adsorption equilibrium isotherms were investigated. Optimum adsorption conditions were determined with respect to contact time, pH, adsorbent dose, and adsorbate initial concentrations for both 4-Nitrophenol and 2,4-Dinitrophenol. The adsorption of both the adsorbates was found to be following pseudo-second order kinetic model with rate constants 0.0026 g mg^{-1} min^{-1} and 0.00046 g mg^{-1} min^{-1}, respectively. Among the five adsorption isotherm models examined, on the basis of calculation of various Statistical indices for 4-Nitrophenol and 2,4-Dinitrophenol it is justified that Koble-Corrigan and Sips adsorption isotherm models are best fitting model, respectively. Under optimum conditions, maximum removal efficiencies of 4-Nitrophenol and 2,4-Dinitrophenol were found to be 99 % and 99.4 % respectively. On the basis of the experimental results it was established that the AC was more compatible in the removal of both adsorbates at similar operating conditions. The study concluded that AC is an excellent and effective adsorbent for the removal of 4-Nitrophenol and 2,4-Dinitrophenol from industrial waste water because of its high efficiency and ease of availability.

Keywords:

Activated carbon, 4-Nitrophenol, 2,4-Dinitrophenol, Adsorption, Kinetic model, Adsorption isotherm model.

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NOMENCLATURE

a	Sips costant ; median association constant in Koble-Corrigan isotherm
b	affinity; Langmuir isotherm constant
A	Koble-Corrigan parameter, $(mol^{(1-n)}L^n/kg)$
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)
K	Henry's Constant (-)
k	constant in Freundlich isotherm, $(mg/g)(L/mg)^{1/n}$
k_1	Pseudo-first order adsorption rate constant, (1/min)
k_2	Pseudo-first order adsorption rate constant, (g/mg/min)
k_p	intraparticle diffusion rate constant, $(mg/g\ min^{1/2})$
m	Henry's law constant (-); mass of adsorbent dose, (g)
n	constant in Freundlich, Sips, Koble-Corrigan isotherms (-)
N	number of data points in the experimental run (-)
q_m^S	total number of binding sites in Koble-Corrigan isotherm
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 by isotherm model, (mg/g)
q_t	amount of adsorption per gram adsorbent at any time t, (mg/g)

t	time (min)
Q_0	maximum amount adsorbed on surface in
R^2	correlation coefficient, (-)
T	temperature, (K)
V	volume of solution, (L)

Abbreviations

AC	Activated carbon
NSD	Normalized standard deviation
ND	Normalized deviation
NP	Nitrophenol
DNP	Dinitrophenol
RMSE	Root mean squares of error
SEP	Standard error of prediction
SSE	Sum of the squares of the errors
TOC	Total organic carbon
TC	Total carbon
IC	Inorganic carbon

CHAPTER 1

INTRODUCTION

1.1 WASTEWATER CONTAMINANTS & TREATMENT PROCESSES

Water pollution is primarily caused by the discharge of treated or used industrial and municipal wastewater. On initial discharge, these wastewaters can contain a large amount of inorganic and organic pollutants which can be easily biodegradable, but whose impact load on the ecosystems, either in Total Suspended Solids (TSS), Bio-chemical Oxygen Demand (BOD), or Chemical Oxygen Demand (COD), may be in the tens of thousands mg/l [1].Wastewater is any water that has been adversely affected in quality by anthropogenic influence. A wide variety of inorganic and organic pollutants remain present in effluents from breweries, tanneries, dying textiles, paper and pulp mills, steel industries, mining operations etc. these include oils, greases, plastics, plasticizers, metallic wastes, suspended solids, phenols, toxins, acids, salts, dyes, cyanides, DDT etc. many of these are not readily susceptible to degradation and thus cause serious pollution that increases the hardness of water. It has disastrous effect on live organisms and corrodes concrete etc [2]. In the most common usage, it refers to the municipal wastewater that contains a broad spectrum of contaminants resulting from the mixing of wastewaters from different sources.

There are some processes that can be used to treatment of waste water depending on the type and extent of contamination or pollutants. Generally, wastewater is treated in industrial scale wastewater treatment plants which may include physical, chemical and biological treatment processes.

Primary Treatment: It includes screening, grit removal, skimming tanks, sedimentation, flotation, neutralization to remove contaminants from wastewater. In primary treatment, floating and suspended solids are settled and removed from sewage. Flow from the sewers enters a screen/bar rack to remove large floating material such as rags and sticks. It then flows through a grit chamber where heavier inorganics such as sand and small stones are removed. Grit removal is usually followed by a sedimentation tank/ clarifiers where inorganic and organic suspended solids are settled out.

Secondary Treatment: It consists activated sludge process and trickling filters for the treatment of wastewater. With secondary treatment, the bacteria in sewage are used to further purify the sewage. Secondary treatment, a biological process removes 85 % or more of the organic matter in sewage compared with primary treatment, which removes about 50 %.

Tertiary treatment: In tertiary treatment, removal of suspended solids, removal of BOD, removal of dissolved solids, removal of toxic substances has been done. Heavy metals, toxic chemicals and other pollutants can be removed from domestic and industrial wastewater to an increasing degree. Methods of advanced treatment include microfiltration, carbon adsorption, evaporation /distillation, and chemical precipitation.

Industrial Waste Treatment: Depending on the type of industry and the nature of its wastes, industries must utilize methods such as those used for advanced treatment of sewage to purify wastewater containing pollutants such as heavy metals and toxic chemicals before it can be discharged. More and more industries are approaching or attaining zero discharge by cleaning and reusing their water over and over and over.

1.2 ADSORPTION

Adsorption enables the separation of selected compounds from dilute solutions. Compared to alternative technologies, adsorption is attractive for its relative simplicity of design, operation and scale up, high capacity and favourable rate, insensitivity to toxic substances, ease of regeneration and low cost. Additionally, it avoids using toxic solvents and minimizes degradation [3]. Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting phyosisorption or chemisorption.

Physisorption or physical adsorption is a type of adsorption in which the adsorbate adheres to the surface only through Vander Waals (weak intermolecular) interactions, which are also responsible for the non-ideal behaviour of real gases.

Chemisorption is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond, as opposed to the Vander Waals forces which cause physisorption.

1.3 ADSORBENTS

1.3.1 CHARACTERISTICS AND GENERAL REQUIREMENTS

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 vapours [4].

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.

1.3.2 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 prequisite for municipal water purification is low cost. Fortunately, activated carbon offers both low cost and high effectiveness and no other adsorbents are close [4]. The choice would be easy, expect 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, regnerability, kinetics and compactibility.

Adsorption capacity (or “loading”) 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).

Selectivity is related to capacity, but there are several distinct definitions that will be discussed later in this article. The simplest 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. 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, which is mentioned later, 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. 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.

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). Despite that, kinetics has even been exploited as the basis of adsorptive separations. Perhaps the most common example is the pressure swing adsorption process that splits nitrogen from air using carbon molecular sieve, which relies on fast diffusion of oxygen compared with very slow diffusion of nitrogen. Normally, however, 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.

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 the adsorbates or contaminants. Likewise, operating conditions such as velocity, temperature, pressure, and vibration should not cause undue disintegration of the adsorbent particles.

Cost is perhaps the most subtle characteristic to understand because it may vary from week to week and from sales rep to sales rep, even for the same exact material. Prices range from $0.30 per pound to $50 per pound for materials that are not particularly exotic.

1.3.3 TYPES OF ADSORBENTS

1.3.3.1 INORGANIC MATERIALS

It seems that most minerals and many synthetic inorganic materials have been tried as adsorbents. Some have been successful, despite being poor adsorbents, simply because they were so inexpensive. Others have turned out to be immensely effective adsorbents. Many other inorganic adsorbents have been developed recently, such as pillared clays, aluminophosphates, and mesoporous adsorbents that have not yet achieved that level of prominence. The inorganic adsorbents covered below are commercial products, and are frequently encountered.

a) Alumina

Activated alumina is produced from hydrated alumina, $Al_2O_3.nH_2O$ where n=1or 3, by dehydration (calcining) under carefully controlled conditions to get n=0.5. It is a white or tan, opaque material that has a chalky appearance. Several grades of are produced by various manufacturers, including Alcan, Alcoa, Lonza, Rhône-Poulenc, and UOP. The distinctions are in the crystal structure of the alumina. Stable crystalline forms are usually not thought of as adsorbents due to their low surface areas. Conversely, transitional forms, such as gamma and eta alumina, have defect spinal forms which lead to higher concentrations of surface acid sites. Corresponding effective surface areas are from 200 - 400 m^2/g. Common forms are balls 1 to 8 mm dia., granules, extrudates (pellets) 2 to 4 mm dia., and powder.

b) Silica

Silicas are generally clear or faintly tinted, and transparent or translucent. Some silica gels, however, are manufactured with alumina blended in, and this yields an appearance of alumina, viz., opaque and white or tan. Several forms are available that encompass diverse types of silica gel, porous borosilicate glass, and aerogels. The last is a relatively new, exceedingly porous material for which few commercial applications exist. Its unique characteristics make it an interesting prospect for the future. Silica gel and porous glass are both non-dusting and resistant to attrition.

c) Zeolite

Most zeolites are aluminosilicates which could be thought of as stoichiometric blends of the two previous adsorbents, silica and alumina. Thus, they are generally white, opaque and chalk-like in appearance. One would think that given their make-up, all zeolites would be hydrophilic. Accordingly, most that have significant alumina content are hydrophilic, while those that are predominately silica are hydrophobic. Internally, zeolites are inherently crystalline and exhibit micropores within those crystals that have uniform dimensions, as depicted in the pore size distribution shown in Figure 2. The micropores are so small and uniform that they commonly can distinguish nearly identically sized molecules. As a result they have been called "molecular sieves." As mentioned earlier, Figure 3 illustrates that point, showing the Lennard-Jones (6-12) collision diameters of several simple molecules along with the micropore diameters of some common zeolites. The common empirical formula for a zeolite containing a single cation, M, of valance, n, is: $M_{2/n}.Al_2O_3.x_{sit}.yH_2O$, where x is the silica-to-alumina ratio (generally ≥ 1 to 5), and y is the molar water of hydration.

1.3.3.2 ORGANIC MATERIALS

This section discusses adsorbents that are based on organic material, whether synthetic or naturally occurring. A wide variety of organic materials have been used as for "sorption," besides activated carbon or charcoal. Some might function as solid "absorbents" rather than adsorbents. Among these are cellulose (the most abundant biopolymer in nature), chitin (the second most abundant biopolymer in nature), collagen, wool, starch-polyacrylamide gels (which absorb many times their own weight of water at ambient temperature, but release most of it by gentle heating), polysaccharides derived from corn, and miscellaneous forms of biomass (e.g., residue from crop harvests). Some of these may have niches, but none would be considered a general purpose adsorbent. Here we will focus on commercial adsorbents.

a) Activated carbon

Activated carbons are the oldest industrially-manufactured adsorbents. They are used in drinking water production and waste water treatment. Currently, activated carbons have are of significant interest and intervene in many applications, such as air treatment and adsorption of organic materials. They have also proven to be very effective for the removal of a wide range of pesticides, dissolved organic compounds from water and waste water, and elimination of heavy metals.

The adsorbent properties of activated carbons are essentially attributed to their large surface area, a well-developed porous structure, and a favorable pore size distribution which make the internal surface accessible and enhance the adsorption rate. The control of pore size distribution in activated carbon depends upon the type of the raw materials and the method of activation. The preparation of activated carbon by physical or chemical activation is very important from the industrial point of view. Since commercial activated carbon is relatively expensive, it is seldom possible to use it in the treatment process and operation of contaminated air and water in developing countries. However, previous research works have demonstrated that activated carbons can be produced from agricultural waste products (fruit stones, coconut shells, etc.). Various raw materials have been used for the production of low-cost adsorptive material, for example, olives wastes, apricot stones, ears of palm tree and peach stones.

Effective surface areas generally range from 300 to 1500 m^2/g depending on the base material, activation method, density, etc., although some made from petroleum coke exceed 3000 m^2/g. Surface areas are treated about the same as engine horsepower or displacement is for automobiles: those with the largest tend to imply that they are the best. Assuming that area correlates with capacity, and that all other factors are equal, that assertion might be valid. Otherwise, it is prudent to make an objective assessment of all the performance criteria.

Activated carbons (ACs) are made up of small hydrophobic graphite layers with disordered, irregular, and heterogeneous surfaces bearing hydrophilic functional groups. The adsorbent properties of ACs depend on their composition, physicochemical properties and mechanical strength. In order to control the ACs pore-size distribution and/or to increase porosity, surface modification and improvement of carbonization, activation by physical activation, by chemical activation or by a combination of both has been considered. ACs are usually produced from low-cost materials , a field in which the reliability and constancy of the resource supply, ease of activation, capacity, selectivity, regenerability and cost, and are decisive on applicability.

b) Minerals

Mineral adsorbents include various types of materials like siliceous materials, clay and natural zeolites, which also show ion exchange ability.

c) Resins

Synthetic polymeric adsorbents include materials with hydrophilic or hydrophobic nature, such as polystyrene–divinylbenzene copolymers, polymethacrylate, divinylbenzene-ethylvinylbenzene copolymers, and vinylpyridine. Even though the effective surface areas are smaller than in the case of ACs, polymeric adsorbents are durable, chemically inert and stable, and possess high adsorption capacity, efficiency, selectivity and ease of regeneration, with relatively low cost and limited toxicity.

Ion-exchange resins are composed of a polymer matrix, based on inorganic compounds, polysaccharides, or synthetic resins, and a functional group. Depending on the positive or negative charge of the ion-active group, the resins act as cation or anion exchangers and depending on the affinity for counter ions each type can be act as strong or weak exchangers. The strong cation exchangers contain sulfuric acid functional groups, and the weak cation exchange resins carboxylic acid functional groups. The strong anion exchange resins have quaternary ammonium group sand the weak anion exchangers have tertiary amine substitutes.

d) Industrial and agricultural wastes

Low-cost materials obtained from natural, bionenewable resources to replace commercial polymers represent a potential way to valorize residues from agriculture or industry is abundant and inexpensive. Next lines refer to mineral, lignocellulosic and polysaccharide materials, although less conventional materials, such as chicken feathers, human hair waste and collagen fibers from hide powder have been also proposed.

e) Fly ash

This by-product of coal-fired power stations has hydrophilic surface and porous structure. Its current disposal on landfill causes environmental concerns, since trace metals can be released.

f) Polymers

Polymeric adsorbents tend to be opaque spherical beads, but the colour depends strongly on the product. Most commonly they are white or tan, but some are brown, orange, or black. The first materials were originally the inert particles that would otherwise have been further treated to make macro porous ion exchange resins. As such, they were typically polystyrene/divinylbenzene copolymers having a spherical shape and high pore volume. Some are still that sort of by-product, but most are manufactured separately, with high performance in adsorption as their purpose. Internally, the polymer beads contain "microbeads" that are joined together at a few points each, creating a macropore structure. Each microbead is usually comprised of a gel, but may be made porous. In addition, some polymeric adsorbents are activated via pyrolysis, in much the same way as carbon (yielding the black materials alluded to above), yet the particles retain their strength and spherical shape.

1.4 ACTIVATED CARBON:

Activated carbons are made up of small hydrophobic graphite layers with disordered, irregular and heterogeneous surfaces bearing hydrophilic functional groups [3]. Activated carbon is highly porous, amorphous solid consisting of microcrystallites with a graphite lattice, usually prepared in small pellets or a powder. It is non polar and cheap. One of its main disadvantages is that it is combustible. Activated carbon can be manufactured from carbonaceous material, including coal (bituminous, subbituminous, and lignite), peat, wood, or nutshells (e.g., coconut).

1.4.1 MANUFACTURING PROCESS: CARBONIZATION AND ACTIVATION

The manufacturing process consists two phases, carbonization and activation. The carbonization process includes drying and the heating to separate by products, including tar and other hydrocarbons, from the raw material, as well as to drive off any gases generated. The carbonization process is completed by heating the material at 400-600 ^{0}C in an oxygen-deficient atmosphere that cannot support combustion.

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

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

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

1.4.2 ADVANTAGES AND DISADVANTAGES OF ACTIVATED CARBON:

Carbon adsorption has gained wide application because of its ease, consistent and well defined process configuration substances even at parts per million levels with high efficiency. Activated carbon has been designed by the U. S. EPA as the best available technology (BAT) for the organic component removal. 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. Activated carbon as adsorbent is used on large scale for the treatment of wastewater in domestic and industrial fields. Activated carbon is used in sewage treatment, gold purification, metal extraction, water purification, medicine, gas purification, decaffeination, air filters in gas masks and respirators, filters in compressed air and many other applications. One major industrial application involves use of activated carbon in the metal finishing field. It is very widely employed for purification of electroplating solutions. For example, it is a main purification technique for removing organic impurities from bright nickel plating solutions. Due to passage of direct current and electrolytic reactions of anodic oxidation and cathodic reduction, organic additives generate unwanted break down products in solution. Their excessive build up can adversely affect the plating quality and physical properties of deposited metal. A variety of organic chemicals are added to plating solutions for improving their deposit qualities and for enhancing properties like brightness, smoothness, ductility, etc. Activated carbon treatment process removes such impurities and restores plating performance to the desired level. The major advantages and disadvantages of activated carbon are given in table:

Table 1: Merits and demerits of activated carbon

Adsorbent	Merits	Demerits
Activated carbon	The most effective adsorbent	Expensive
	Very high surface area	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 adsorption 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

1.4.3 CLASSIFICATION OF ACTIVATED CARBON

Activated carbons are complex products which are classify on the basis of their behaviour, surface characteristics and preparation methods. However, some broad classification is made for general purpose based on their physical characteristics.

A) POWDERED ACTIVATED CARBON (PAC)

Traditionally, active carbons are made in particulate form as powders or fine granules less than 1.0 mm in size with an average diameter between 0.15 and 0.25 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.

B) 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 are faster. Granulated carbons are used for water treatment, deodorization 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. A 20×40 carbon is made of particles that will pass through a U.S. Standard Mesh Size No. 20 sieve (0.84 mm) (generally specified as 85% passing) but be retained on a U.S. Standard Mesh Size No. 40 sieve (0.42 mm) (generally specified as 95% retained). AWWA (1992) B604 uses the 50-mesh sieve (0.297 mm) as the minimum GAC size. 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.

C) 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.

D) BEAD ACTIVATED CARBON (BAC)

Bead activated carbon is made from petroleum pitch and supplied in diameters from approximately 0.35 to 0.80 mm. Similar to EAC; it is also noted for its low pressure drop, high mechanical strength and low dust content, but with a smaller grain size. Its spherical shape makes it preferred for fluidized bed applications such as water filtration.

E) 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.

F) 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.

1.5 NITROPHENOLS: HAZARDOUS INDUSTRIAL AND MUNICIPAL WASTE:

Organic compounds constitute a very large group of pollutants in the wastewater. Amongst them aromatic compounds mainly phenol and its derivatives such as nitrophenols, chlorophenols are widely found in the effluent of many industries. These pollutants are recognized as carcinogens and are known to be toxic to the environment. Nitrophenols are released to the environment from pesticide application and from the effluent of mine processing facilities, foundries, metal finishing plants, refineries and dye manufacturing plants. Therefore, nitrophenols are found as contaminants in wastewaters, rivers, groundwater, soil, and in the atmosphere. Nitrophenols are highly toxic to humans and aquatic life and create an oxygen demand in receiving waters. Most nitrophenols are resistant to biological treatment because of their toxicity [5].

Phenol and its derivatives like nitrophenols are toxics and are considered as priority pollutants (11th in the list of 126 Chemicals) by the USEPA [6,7]. the European Union (EU) [8], and the Central Pollution Control Board (CPCB), India [9].. The USEPA, CPCB, India as well as the Bureau of Indian Standards (BIS) [10] have set a discharge standard of 1.0 mg/l concentration of phenolic compounds in the industrial effluents for their safe discharge into the surface wasters. These limits have generally been on the basis of the total phenols present in the effluent. These compounds impart objectionable taste and odor to drinking water at concentrations as low as 0.005 mg/l. Individual concentration should be under 0.1 mg/l. The Agency for Toxic Substances and Disease Registry (ATSDR) also reports that nitrophenols are the most frequently reported organic contaminants in ground water.

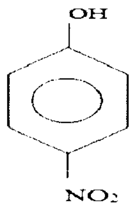
Nitrophenols are manufactured chemicals that do not occur naturally in the environment. The manufacture of one almost always produces a little of the other, so they are grouped together when discussing their properties and harmful effects. Nitrophenols are poisonous. Occasionally, nitrophenols contaminate the soil near former explosives or fabric factories and military plants, and current research is aimed at remediation.

1.5.1 4-NITROPHENOL: SOURCES, USES AND EFFECTS

4-Nitrophenol (also called p-nitrophenol or 4-hydroxynitrobenzene) is a phenolic compound that has a nitro group at the opposite position of hydroxy group on the benzene ring. 4-Nitrophenol in the environment has been detected in atmospheric emissions from the combustion of municipal solid waste, coal, wood and herbicides.

It is found in mixtures with diethyl phosphite may explode when heated. Decomposes exothermally, emits toxic fumes of oxides of nitrogen [Lewis, 3rd ed., 1993, p. 941]. Decomposes violently at 279°C and will burn even in absence of air [USCG, 1999]. Solid mixtures of the nitrophenol and potassium hydroxide (1:1.5 mols) readily deflagrate [Bretherick, 5th Ed., 1995].

Table 2: Physical and chemical properties of 4-nitrophenol

S. No.	PROPERTY	VALUE
1	Molecular formula	$C_6H_5NO_3$
2	Molecular weight	139
3	Apparent Colour	Colorless or yellow pillars
4	Solubility in water	16 g/L (25°C)
5	Boiling point	279 °C
6	Melting point	112 °C
7	Density	1.236 g/cm^3 (160 °C)
8	pKa value	7.16
9	pH	5.4 colourless 7.5 yellow
10	Heat Of Vaporization	56.2 kJ/mol
11	Vapour pressure	0.6 mm Hg at 120°C
12	Odor threshold	58.3 mg/L
13	Air & Water Reactions	Soluble in hot water and more dense than water
14	Structure	

It is used in the manufacturing of pharmaceuticals, fungicides, dyes. 4-Nitrophenol is an intermediate in the synthesis of paracetamol. It is reduced to 4-aminophenol, then acetylated with acetic anhydride. 4-Nitrophenol is used as the precursor for the preparation of phenetidine and acetophenetidine, indicators, and raw materials for fungicides. Bioaccumulation of this compound rarely occurs. In peptide synthesis, carboxylate ester derivatives of 4-nitrophenol may serve as activated components for construction of amide moieties. 4-Nitrophenol is a product of the enzymatic cleavage of several substrates. Amounts of 4-nitrophenol produced by a particular enzyme in the presence of its corresponding substrate can be measured with a spectrophotometer at or around 400 nm and used as a proxy measurement for the amount of the enzyme in the sample. It is health hazardous compound of phenol. Inhalation or ingestion causes headache, drowsiness, nausea, and blue colour in lips, ears, and fingernails (cyanosis). Contact with eyes and skin causes irritation; can be absorbed through skin to give same symptoms as for inhalation.

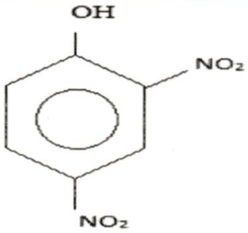
1.5.2 2, 4-DINITROPHENOL: SOURCES, USES AND EFFECTS

2,4-Dinitrophenol (DNP) is a cellular metabolic poison and uncouples oxidative phosphorylation by carrying protons across the mitochondrial membrane, leading to a rapid consumption of energy without generation of ATP. Dinitrophenols as a class of compounds, of which there are six members, do not occur naturally but are all manufactured compounds. 2,4-Dinitrophenol is a yellow, crystalline solid that has a sweet and musty odor. It sublimes when carefully heated and is volatile with steam. It is soluble in benzene ethyl acetate, carbon tetrachloride, acetone, chloroform, pyridine, toluene, alcohol, and aqueous alkaline solutions. Its crystalline sodium salts are also soluble in water. It forms explosive salts with ammonia and alkalies and emits toxic fumes of nitrogen oxides when heated to decomposition. It is incompatible with heavy metals and their compounds.

Dinitrophenol (DNP) is primarily used for scientific research purposes and in various manufacturing processes. It has been used at times to make dyes, other organic chemicals and wood preservatives. It has also been used to make photographic developer, explosives, and pesticides. DNP is often used in biochemistry research to help explore the bioenergetics of chemiosmotic and other membrane transport processes.

DNP is considered as an important environmental contaminant by the United States Environmental Protection Agency (USEPA). It has been found in 61 of 1400 priority sites that need clean-up of industrial waste. The major site of degradation is the soil, where microorganisms metabolize it. However, the effects of DNP on anaerobic micro-organisms are still largely undetermined. Some studies suggest that there is anaerobic toxicity due to a reduced methane production. It can enter in the air from automobile exhaust, burning of industrial substances and from reaction of nitrogen in air with other atmospheric chemicals.

Table 3: Physical and Chemical Properties of 2, 4-Nitrophenol

S. NO.	**PROPERTY**	**VALUE**
1	Molecular formula	$C_6H_5N_2O_5$
2	Molecular weight	184
3	Apparent Colour	Light yellow crystal powder
4	Solubility in water	0.6 g/100 mL (18 ^{0}C)
5	Boiling point	113^{0}C
6	Melting point	108^{0}C
7	Density	1.683 g/cm^3
8	pKa value	4.11
9	pH	2.8 colourless 4.7 yellow
10	Heat Of Vaporization (specific)	0.336 KJ/g
11	Vapour pressure	1.42×10^{-7} mm Hg at 25 °C
12	Structure	

1.6 OBJECTIVES OF THESIS

- Development of *Parthenium Hysterophorous* weed based activated carbon.
- Characterization of activated carbon as an adsorbent to be carried out including XRD, BET, FTIR, TGA.
- Determine the adsorption efficiency of the activated carbon for the toxic and hazardous pollutants i.e. 4-nitrophenol and 2,4-dinitrophenol.
- Examine the study of the effect of various parameters on the adsorption of 4-nitrophenol and 2,4-dinitrophenol over commercial activated carbon i.e., effect of contact time, effect of pH, effect of adsorbent doses, effect of initial concentrations.
- Fitting of the various rate equation models to search for the appropriate kinetics for the process of adsorption.
- To be fit the various Isotherm models and determine the Parameters in the equations to select the isotherm which conforms to the present adsorption process.
- Calculation of Statistical indices for various isotherm models for both compounds.
- TOC Measurements of 4-NP and 2,4-DNP.

CHAPTER 2

LITERATURE REVIEW

The most commonly used feed stocks include [1] coal, [2] Coconut shells and coconut shell fibers, [3] wood, [4] lemon peel, [5] sawdust, [6] sugarcane dust, [7] bagasse, [8] oil palm, [9] orange peel, [10] coir pith, and [11] ground nut shell, [12] fertilizers waste, etc.

2.1 ACTIVATED CARBON BASED LITERATURE:

Mohan et al. [11] developed a variety of low cost activated carbons from agricultural waste materials, characterized and utilized for the removal of hexavalent chromium from wastewater. Systematic studies on chromium (VI) adsorption equilibrium and kinetics by low cost activated carbons as well as commercially available activated carbon fabric cloth were carried out at different temperatures, particle size, pH, and adsorbent doses. Both Langmuir and Freundlich models fitted the adsorption data quite reasonably. The results indicate that the Langmuir adsorption isotherm model fits the data better than the Freundlich adsorption isotherm model. Further, the data are better correlated with the nonlinear form than the linear one. The kinetic studies were conducted to delineate the effects of temperature, initial adsorbate concentration, adsorbent particle size, and solid-to-liquid ratio. The adsorption of Cr (VI) follows pseudo-second order rate kinetics. On the basis of these studies, various parameters such as the effective diffusion coefficient, activation energy, and activation entropy were evaluated to establish the mechanisms. The adsorption capacities of the tested adsorbents were found to be comparable to those of the available adsorbents/activated carbons.

Wang Qin et al. [12] prepared Polystyrene-based activated carbon spheres (PACS) by steam activation and their adsorption performance to a sulphur-containing dibenzothiophene (DBT) was studied. The textural structure of PACS was characterized by scanning electron microscopy, N_2 adsorption, and thermal gravimetric and aqueous adsorption. Results showed that PACS with BET surface areas up to 979-1672 m^2/g were obtained. The BET surface areas and pore volumes increased with activation time and steam flow rate except for the volume of narrow micropores (< 0.7 nm). The maximum adsorption capacity of PACS to DBT was 109.36 mg/g and the adsorption capacity was related to the volume of narrow micropores, independent of surface area and total pore volume. Irreversible adsorption existed between DBT and PACS. The larger the volume of the narrow micropores, the higher the desorption temperature and the larger the amount of sulphur retained after heating.

Awarna et al. [13] produced Activated carbon from corncob using CO_2 for the activation process. This research investigated that the effect of the remaining volatile matter in corncob char combined with CO_2 activation to improve the pore properties of corncob activated carbon. The pore structure was characterized using the Brunauer–Emmett–Teller (BET) surface area test, total pore volume, mesopores volume, micropore volume and average pore diameter. This study discovered that the amount of volatile matter in corncob char is about 17–25% and results in a BET surface area range of 919–986 m^2/g by the CO_2 activation process. Therefore, the optimum temperature for the activation process should start at 450–550 °C and increase until the temperature reaches to 800 °C. Activated carbon from corncobs at 450–550 °C contained a suitable amount of volatile matter, 17–25%, for pore development.

Zaini et al. [14] examined the suitability and performance of cattle-manure-compost (CMC) based activated carbons in removing heavy metal ions from aqueous solution. The influence of $ZnCl_2$ activation ratios and solution pH on the removal of Cu (II) and Pb (II) were studied. Pore texture, available surface functional groups, pH of points zero charge (pH_{PZC}), thermo gravimetric 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 equilibrium data were characterized using Langmuir, Freundlich and Redlich–Peterson models. It was found that the uptake of aqueous metal ions by activated carbons could be well described by Langmuir equation. It is suggested that the increase of surface area and mesopores ratio as a result of increasing activation ratios favoured the removal of Cu (II), while activated carbon rich in acidic groups showed selective adsorption towards Pb (II). 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.

Hong et al. [15] examined the adsorption capacity of activated carbon for the natural gas contaminant dimethylsulfide (DMS) was improved by impregnating it with $FeCl_3$ introduced in solution to affect surface modification. A DMS adsorption mechanism and roles of impregnated $FeCl_3$ on the capacity enhancement were proposed based on experimental tests results. Samples of activated carbon and activated carbon impregnated with $FeCl_3$ were tested as DMS sorbents. Samples loaded with DMS were subsequently extracted with *n*-octane and the resulting solvents were analyzed for sulphur species using a gas chromatograph equipped with a sulphur chemiluminescence detector. No other sulphur compounds were detected in the liquid samples other than DMS. DMS, dimethyl disulfide, and carbonyl sulphide were recovered from identical DMS-adsorbed samples of activated carbon impregnated with $FeCl_3$ subjected to temperature programmed desorption (TPD) in a nitrogen gas stream. Only DMS was recovered from the activated carbon samples. The TPD patterns indicate different kinetics of DMS desorption related to the carbon phase and the new active sites created by the $FeCl_3$ impregnation. The new active sites improved DMS adsorption capacity and likely had stronger affinity with DMS molecule. As a reference, similar tests were investigated using methyl mercaptan (MM) as an adsorbate on the carbon sorbents. A different adsorption mechanism was found and discussed from these experimental results. Regeneration of the used carbon sorbents by thermal desorption was also explored.

Kumangai et al. [16] evaluated the capacity of risk husk activated carbon (RHAC) to adsorb refractory sulphur compounds of dibenzothiophenes (DBTs) from commercial kerosene in terms of their textural and chemical characteristics. Rise 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 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.

Ahmad et al. [17] used Low-cost activated carbon, derived from nut shells, and its modified sample have been used 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. The activated carbon has been derived, characterized, treated with sulphur and then utilized for the removal of Cd^{2+}. Samples were then characterized and tested as adsorbents of cadmium. Effect of some parameters such as contact time, initial concentration and pH were examined.

Didem et al. [18] used activated carbons prepared from chestnut shell and grapeseed were used as adsorbent for the removal of Cu (II) ions from aqueous solutions. Adsorption experiments were performed by varying initial metal ion concentration, temperature and pH. Freundlich and Langmuir isotherms were used to analyze the equilibrium data obtained at different adsorption conditions. It was observed that Freundlich adsorption isotherm provided better fit to the equilibrium data than Langmuir adsorption isotherm. Effects of temperature, pH and adsorbent surface area on the adsorption capacity constant of Freundlich and Langmuir adsorption isotherm models were statistically investigated by using a two-level factorial design technique and empirical regression equations were developed.

Li Wang et al. [19] prepared low cost activated carbon was prepared 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 Orientale Linn activated carbon (OLAC) 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 malachite green (MG) adsorption, whereas acidic pH was better for rhodamine B (RB) uptake. Adsorption of dyes on Orientale Linn activated carbon (OLAC) 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 adsorption isotherm model. Thermodynamic study showed that the adsorption was a spontaneous and endothermic process.

Nethaji et al. [20] used chemically prepared activated carbon derived from Borassus aethiopum flower was used 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 Malachite Green (MG) concentration and temperature with three different particle sizes such as 100 μm, 600 μm and 1000 μm. The zero point charge was 2.5 and the maximum adsorption occurred at the pH range from 6.0 to 8.0. Experimental data were analyzed by model equations such as Langmuir, Freundlich and Tempkin adsorption isotherm models and it was found that the Langmuir adsorption isotherm model best fitted the adsorption data. Thermodynamic parameters such as ΔG, ΔH and ΔS were also calculated for the adsorption processes. Adsorption rate constants were determined using pseudo first-order, pseudo second-order rate equations and also Elovich model and intraparticle diffusion models. The results showed that the adsorption of Malachite Green (MG) onto PFAC followed pseudo second-order kinetic model and the adsorption was both by film diffusion model and by intraparticle diffusion model.

2.2 ADSORBATE BASED LITERATURE

Chern et al. [21] describes the adsorption isotherm of p-nitrophenol onto granular activated carbon in 251 ^{0}C aqueous solution was experimentally determined by batch tests. Both the Freundlich and the Redlich-Peterson models were found to fit the adsorption isotherm data well. A series of column tests were performed to determine the breakthrough curves with varying bed depths (3–6 cm) and water flow rates (21.6–86.4 cm3/h). Explicit equations for the breakthrough curves of the fixed-bed adsorption processes with the Langmuir and the Freundlich adsorption isotherms were developed by the constant-pattern wave approach using a constant driving force model in the liquid phase. The results show that the half breakthrough time increases proportionally with increasing bed depth but decreases inverse proportionally with increasing water flow rate. The constant-pattern wave approach using the Freundlich isotherm model fits the experimental breakthrough curves quite satisfactorily. A correlation was proposed to predict the volumetric mass transfer coefficient in the liquid phase successfully. The effects of solution temperature and pH on the adsorption isotherm were also studied and the Tooth model was found to fit the isotherm data well at varying solution temperatures and pHs.

Rengaraj et al. [22] prepared activated carbon from rubber seed coat (RSCC), an agricultural waste by product, has been used for the adsorption of phenol from aqueous solution. In this work, adsorption of phenol on rubber seed coat activated carbon has been studied by using batch and column studies. The equilibrium adsorption level was determined to be a function of the solution pH, adsorbent dosage and contact time. The equilibrium adsorption capacity of rubber seed coat activated carbon for phenol removal was obtained by using linear Freundlich isotherm. The adsorption of phenol on rubber seed coat activated carbon follows first order reversible kinetics. The suitability of RSCC for treating phenol based resin manufacturing industry wastewater was also tested. A comparative study with a commercial activated carbon (CAC) showed that RSCC is 2.25 times more efficient compared to CAC based on column adsorption study for phenolic wastewater treatment.

Riaz et al. [23] studied commercial activated carbon as an adsorbent for the removal of phenol from aqueous solutions. The optimum conditions for maximum adsorption in terms of shaking time, amount of the adsorbent, and concentration of the adsorbate were identified. The adsorption data fitted the Langmuirisotherm equation in the whole range of concentrations studied. The adsorption of picric acid, pyrogalloland salicylic acid at selected conditions for phenol was also studied. Elution studies to recover the adsorbed phenol from active carbon were performed with distilled water, NaOH and HCl solutions.

Kumar et al. [24] carried out batch studies for studying the adsorption behaviour of phenol and 4-nitrophenol on granular activated carbon from a basal salt medium (BSM) at pH 7.1 and temperature 30 ^{0}C. The literature review was done in order to review the information for comparison purposes on equilibrium models of phenol and 4-nitrophenol adsorption on activated carbon. In all, six models of Freundlich, Langmuir, Redlich–Peterson, Radke–Prausnitz, Toth and Fritz–Schlunder as reported in the literature have been fitted to the data of phenol/activated carbon and 4-nitrophenol/activated carbon systems of the present studies using nonlinear regression technique. Based on maximum deviations and correlation coefficients, Langmuir gave the poorest fit for both compounds; Redlich–Peterson, Radke–Prausnitz, and four parameter model of Fritz–Schlunder could represent the data with similar accuracy, i.e. with R^2-value of 0.98 and maximum deviation 12%. However, for phenol, two parameter model of Freundlich may be recommended because of ease in its parameter estimation and better accuracy. 4-Nitrophenol was found to be more adsorbed than phenol, which is consistent with the result found in literature. The kinetics of the adsorption was found to be intra-particle diffusion controlled with diffusion coefficient values of the order of 10−13 m^2 /s. Three distinct phases of kinetics – rapid, medium, and slow – have been observed in this study.

Uddin et al. [25] studied about the potential of water hyacinth ash for phenol adsorption from aqueous solution. Batch kinetic and isotherm studies were carried out under varying experimental conditions of contact time, phenol concentration, adsorbent dosage and pH. The adsorption of phenol decreased with increasing pH. The Freundlich and Langmuir adsorption models were used for the mathematical description of adsorption equilibrium and it was found that the experimental data fitted very well to the Langmuir model. Batch adsorption models, based on the assumption of the pseudo-first-order and pseudo-second-order models, were applied to examine the kinetics of the adsorption. The results showed that kinetic data followed closely to the pseudo-second-order model.

Pan et al. [26] prepared a hyper-cross-linked polymeric adsorbent (NDA-701) possessing a uniquely pore size distribution for 4-nitrophenol (4-NP) adsorption from water. A macroporous polymeric adsorbent Amberlite XAD-4 and a granular activated carbon GAC-1 were chosen for comparison. NDA-701 exhibited better mechanical strength and higher capacity of 4-NP than XAD-4, which possibly resulted from its hyper-cross-linking nature and micropore structure, respectively. 4-NP adsorption isotherm onto NDA-701 is well described by the Freundlich model, and its better kinetics performance than GAC-1 resulted from its macropore structure. After adsorption NDA 701 was amenable to an entire regeneration by using NaOH solution as regenerant, whereas only 75% regeneration efficiency was observed for GAC-1. Results of continuous fixed-bed runs in pilot and industrial scale demonstrated that NDA-701 is capable of completely removing 4-NP from chemical effluent with no capacity loss, and 4-NP can be readily recovered by further treatment of the concentrated regenerant solution. It is attractive that the value of the recovered 4-NP from chemical wastewater will even engender a surplus after countervailing all the operation cost during field application.

Okasha et al. [27] found that the pollution of water with phenol from petrochemical industries is a highly important environmental problem, first of all because of the propagation of the pollution, and second because of its unfavourable consequences on the aquatic life, on the organoleptic properties and uses of water. The potential of (local waste materials) Almond Shell residues, Date stones, Coffee ground, Black Tea Leaves, Olive Leaves and Activated Carbon for phenol adsorption from aqueous solution was studied. Batch process and isotherm studies were carried out under varying experimental conditions of contact time and phenol concentration. The suitability of the Freundlich and Langmuir adsorption models to the equilibrium data were investigated for each phenol-adsorbent system. The results showed that the equilibrium data for the phenol-adsorbent systems fitted the Freundlich model best within the concentration range studied, specially the concentrations below 100 ppm. The study showed that, there are some local materials can be used as low-cost alternatives for phenol removal from water and wastewater.

Mutairi et al. [28] researched to evaluate the adsorption capability of non-conventional, low-cost adsorbents at elevated 2, 4-dinitrophenol (DNP) concentrations. Commercial activated carbon was also evaluated in an attempt to identify the sorption mechanism. Isotherms for adsorption of 2, 4-dinitrophenol from water and basal salt medium onto date seeds and activated carbon were determined. These isotherms were modeled by the Freundlich isotherm. The experimental results showed that only 0.5 g of date seeds, with a 125 ml salt medium, were a suitable adsorbent for the removal of DNP from samples. The studies showed date seeds to be an efficient sorbent material for DNP removal from solutions. Of the parameters investigated, pH was determined to be most crucial, with an optimum pH range of 4.0 to 5.0 for good DNP removal. The DNP adsorption capacity of both adsorbents exceeded the original value of the raw material when regenerated by microwave irradiation. The regeneration efficiency of date seeds was 96% compared to 85% of activated carbon. In addition, the use of basal salt medium solution does not appear to play a significant role in DNP adsorption by activated carbon compared to water medium. However, the basal salt medium was associated with a higher adsorption capacity when used with date seeds. Finally, the treatment of a high DNP concentration with date seeds and activated carbon significantly reduced the toxicity of the DNP effluent.

Kiran et al. [29] found cyanide and phenol are extensively in the effluents of refinery, coke plant, electroplating industries and are extremely dangerous to environment. Commercial granular activated carbon (GAC) was used as an adsorbent for the simultaneous removal of cyanide and phenol in the present study. The effect of process parameters such as pH, temperature, adsorbent dose and contact time on the performance of adsorption was investigated. Optimum pH was found to be 8 for simultaneous removal of cyanide and phenol. Temperature did not have any significant on cyanide removal, but phenol removal was observed to increase with the increase in temperature. Both compounds were optimally removed at 35 ^{0}C. The percentage removal of compounds increased with an increase in the concentration of GAC. However the specific uptake did not increase on GAC concentration's greater than 30 g/l, which was considered as the optimum dose of adsorbent. Removal of cyanide was slightly higher than that of phenol, but the difference is not significant, at optimum conditions.

Cannata et al. [30] reported the adsorption of phenol and nitrophenols (2,4 Dinitrophenol, 4-nitrophenol and 2-nitrophenol) on a novel carbon material: carbon nanospheres (CNS). CNS were prepared by the direct pyrolysis of benzene and characterized by N2 adsorption–desorption, X-ray diffraction analyses (XRD), scanning and transmission electron microscopy (SEM and TEM) and Raman spectroscopy. Adsorption isotherms were obtained in the range 20–200 mg/l of phenolic compound, the effect of pH on adsorption was studied at acidic, neutral and alkali media. CNS showed a specific competitive adsorption mechanism and nonlinear adsorption isotherms were obtained with the tested phenolic compounds. The adsorption capacity of CNS followed the sequence: 2, 4-dinitrophenol > 4-nitrophenol > 2-nitrophenol > phenol. The adsorption was favoured under acidic conditions (pH 3), moreover, the presence of ionic salts (e.g. NaCl) in solution increased the ability of CNS to remove phenol and nitrophenols from aqueous solutions (pH 7).

CHAPTER 3

MATERIALS AND METHODS

3.1 *Parthenium hysterophorus* WEED FOR THE PREPARATION OF ACTIVATED CARBON

It is also known as Carrot weed or gajar ghas, is a genus of flowering plants in the aster family, Asteraceae and a native of Tropical America. It has been declared noxious weed in America, Australia, India and many other countries especially those having tropical climates. It is very poisonous, allergic and aggressive weed posing a serious threat to human beings by causing diseases like allergies, dermatitis, eczema, asthama, bronchitis, high fever. Uprooting it manually is the finest option for its eradication [40]. Previous studies on parthenium based activated carbon have been on the removal of dyes, pigments, metal ions, p-cresol, trichloroethylene and tetrachloroethylene.

3.2 PREPARATION FOR *Parthenium* BASED ACTIVATED CARBON (PAC)

The stems of parthenium plants were collected from nearby places of Roorkee (India) and washed with water to remove dirt and dust. These stems were cut into small pieces in the size of 5–10 mm and dried in sunlight. The activated carbon was then prepared by chemical activation process. According to this process, the dried parthenium mass was impregnated with concentrated H2SO4 in the ratio of 1:2 by weight (weight of parthenium: weight of acid) and was kept at 130 ± 5 °C for 24 h for carbonization. The carbonization was made in an inert atmosphere in a horizontal furnace. The carbonized material was washed several times with distilled water to remove free acid. It was further soaked into 1% sodium bicarbonate solution and kept overnight for the complete removal of acid. The resulting carbon was again washed many times with distilled water in order to remove fines and leachable matter and it was dried at 110 °C in an oven. Finally, the dried activated carbon was subsequently pulverized and sieved to get the particles of size less than 0.5 mm [5].

The experiments have been carried out for the removal of 4-NP and 2,4-DNP by using parthenium based activated carbon (PAC). But the removal efficiency is about 30-40 % for both adsorbates by PAC which is very less in comparison of commercial activated carbon which gives more than 90 % removal efficiency. Although, parthenium is good for the removal of dyes, metal ions, pigments, p-cresol, trichloroethylene and tetrachloroethylene but not for the nitrophenols. Therefore, we will not further study on parthenium for adsorption of 4-NP and 2,4-DNP. Since our study will be based on commercial based activated carbon for the removal of 4-NP and 2,4-DNP because of getting better adsorption.

3.3 COMMERCIAL ACTIVATED CARBON

The commercially available activated carbon was granular LR grade in the size range of 2–5 mm and supplied by S.D. Fine Chemicals, Boisar, India. It was grounded to make it suitable for present study and sieved through 18 to 44 BS mesh. The average particle size so obtained was 0.536 mm. The sieved carbon was further washed many times with distilled water to remove any attached fines and leachable matter. After washing, it was dried in an oven at 105 ^{0}C for 72 hours and stored in an air tight bottle [5].

3.4 CHARACTERIZATION OF AC

3.4.1 THERMOGRAVIMETRIC ANALYSIS (TGA)

To determine the physical and chemical properties of the prepared AC, 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 35 ^{0}C to 950 ^{0}C at a heating rate of 10 ^{0}C/min under nitrogen atmosphere. The temperatures of the melting and decomposition were determined as the temperature of corresponding endothermic maxima.

3.4.2 X-RAY DIFFRACTION (XRD)

The crystalline structure of samples was studied by using bruker AXS D8 Advanced x-ray diffractometer (graphite monochromator on reflected beam) with CuKα radiation (40kV, 40mA), employing the powder method. Each scan was recorded in the range of $2\Theta = 5\text{-}100^0$ in the step by step mode with 0.05^0 interval.

3.4.3 FOURIER TRANSFORM INFRARED ANALYSIS (FTIR)

The AC 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 sample was scanned at resolution between 4000 and 500 cm^{-1}. The software used for this purpose was OMNIC.

3.4.4 BET SURFACE AREA ANALYZER

To determine BET (Brunauer-Emmett-Teller) surface area, monolayer volume, total pore volume by using Chemisorb- 2720 model (Micromeritics, USA) with the help of software Chemisoft TPx. The mass of the sample was 0.0730g at the time of analysis.

3.5 PREPARATION OF ADSORBATE SOLUTION

The adsorbates 4-NP and 2,4-DNP were of Analytical Reagent (AR) and Laboratory Reagent grades (purity > 99%) and supplied by Loba Chemical Pvt. Limited, Mumbai (India) and Hi Media Laboratories Pvt. Limited, Mumbai (India) respectively. They were used to prepare synthetic adsorbate solutions of 200 mg/L concentration initially. To obtain solutions of required 20 -200 mg/L the prepared solutions 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.

3.6 MATERIALS PROCUREMENT AND CALIBRATION

All the reagents were of analytical reagent grade (purity > 99%) and procured from Merck. The adsorbate solution of 4-NP and 2,4-DNP were simulated in the laboratory by preparing aqueous solution whose initial concentration were kept in the range 20-200 mg/L. The calibration of the adsorbate solutions and the concentration detected were carried out in a UV (UV-1800) Visible Spectrophotometer (Shimadzu Corporation, USA) at maximum wavelengths of 318 and 360 respectively. The concentration ranges were taken 10-50 mg/L for both adsorbates for this analysis. The software for this analysis was UV PROBE. Calibration curves were obtained between known values of concentration of adsorbates and corresponding absorbance as shown in figures 1 and 2 respectively.

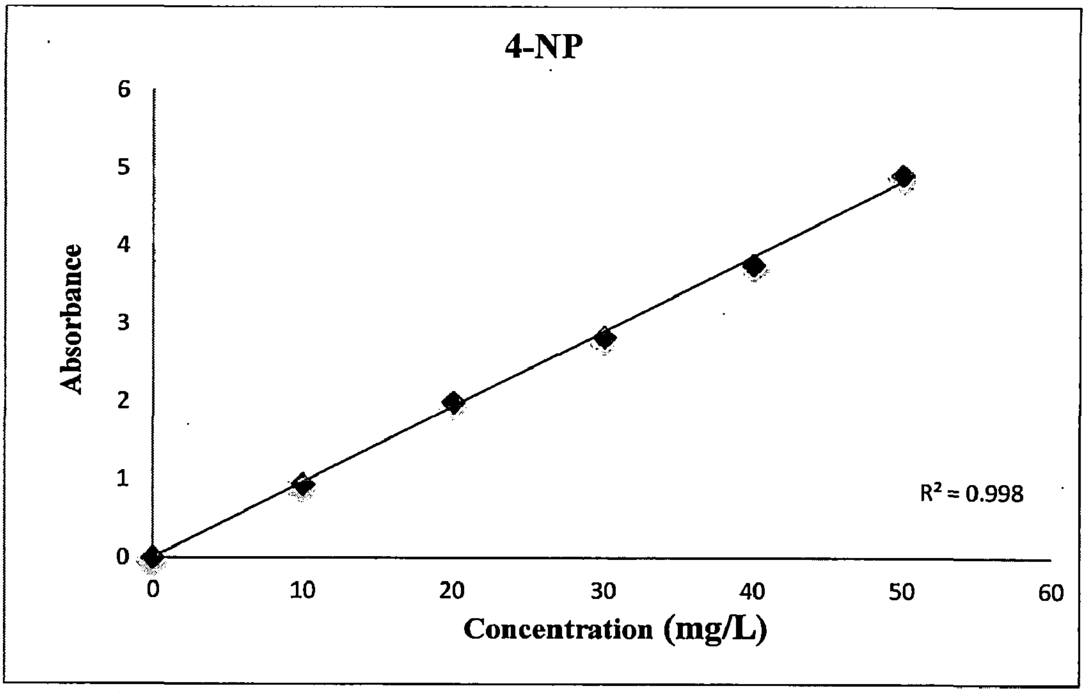


Figure 1: Calibration curve for 4-NP

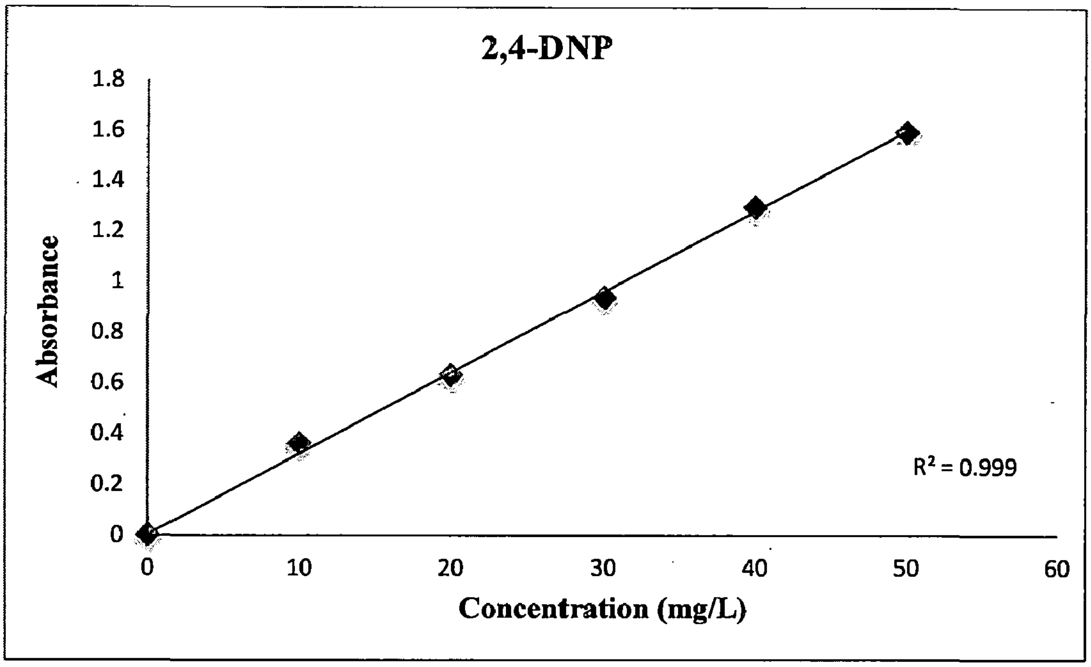


Figure 2: Calibration curve for 2,4-DNP

3.7 EXPERIMENTAL PROCEDURE

The batch isothermal studies were conducted as an experiment for analysing the potential of AC to adsorption of the two components 4-NP and 2,4-DNP separately. Equilibrium parameters and rate of adsorption were established for both the components. A stock solution of known initial concentration for 4-NP and 2,4-DNP were prepared by dissolving an appropriate amount in distilled water. Batch adsorption experiments were performed by shaking 50 ml. of aqueous 4-NP and 2,4-DNP solution samples with known initial concentration, pH, and known adsorbent dose in 250 ml. stoppered conical flasks. These mixtures were shaken on a reciprocating type horizontal shaker (Metrex Scientific Instruments (P) Ltd., New Delhi) with temperature control. The shaker was set at a temperature of 303 ± 1 K at a speed of 150 ± 1 rpm. Initial solution concentration range 20-200 mg/L were prepared by diluting the stock solution with the adequate amount of distilled water. The pHs of the solutions were adjusted using 0.1N NaOH and 0.1HCl solutions. Adsorbent were weighted accurately on aluminium foils using an analytical balance. The weighted adsorbent doses were mixed with adsorbates into the conical flasks. The sample flasks were taken out from the shaker at appropriate time of intervals and then filtered through a filter paper (Watman No. 42). Finally, 4-NP and 2,4-DNP concentrations in each flasks were determined using a UV Visible Spectrophotometer at a maximum wavelengths 318 nm and 360 nm respectively. This procedure was followed in adsorption kinetics, equilibrium, and isotherm studies at various operating conditions as discussed below.

In industrial liquid effluents, the concentration of nitrophenols varies not more than 200mg/L. Therefore, in the present experimental study, the concentration of 4-NP and 2,4-DNP in aqueous solution is chosen to be in the range of 20 – 200 mg/l. The experiments for adsorption kinetics and equilibrium studies were conducted at 30 ^{0}C by using initial 4-NP and 2,4-DNP concentrations: 20, 40, 50,60,80,100, and 200 mg/l. In each flask, a fixed adsorbent dose (AC) was added. The pH was maintained at 2 for both adsorbates by adding HCl or NaOH as required. The samples were withdrawn at prespecified time intervals (one at a time) and filtered. The filtrate samples were taken at different time intervals and the concentrations C_t were estimated. For 4-NP, equilibrium condition was established after 8h and for 2,4-DNP, the equilibrium condition was established after 9 h. At equilibrium, the samples were taken and the equilibrium concentrations C_e were calculated for each run. The amount of adsorption of 4-NP and 2,4-DNP per gram adsorbent, q_t (mg/g) at any time t was calculated by:

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

Where, C_o and C_t are the concentrations of 4-NP and 2,4-DNP at the initial and time t, respectively, V is the volume of adsorbate solution, and m is the mass of adsorbent dose used in the run. At equilibrium condition, the amount of adsorption per gm of adsorbent, q_e (mg/g), was calculated by:

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

To study the effect of pH on adsorption of 4-NP and 2,4-DNP, the experiment were carried out for initial pH values in the range of 2–8 at 30 ^{0}C upto equilibrium time. The pH of solution was changed from 2–8 by adding NaOH and HCl in appropriate amount. The initial concentrations were kept at 50 mg/l and the adsorbent dose was kept at 50 g/l for both 4-NP and 2,4-DNP.effect of adsorbent dose was estimated by using 0.2, 0.4, 0.8, 1, 1.2, 1.6, 2 g/L for both adsorbates by keeping all other parameters constant. Similarly effect of initial concentration was studied by varying the concentration from 20 – 200 mg/L.

In the isotherm studies, initial concentration of 4-NP and 2,4-DNP was fixed. Adsorbent was varied from 0.2 – 2 g/L. for both adsorbates separately. The equilibrium constant time was determined from the kinetics was used for these tests. After the attainment, the flasks were taken out of the shaker, and the solution was filtered and analyzed as per procedure to estimate the residual concentration in the solution.

3.8 KINETIC MODELLING

For the adsorption equilibrium studies of 4-NP and 2,4-DNP it is necessary to analyze the adsorption rate and finally the equilibrium condition after which the variation of the unadsorbed 4-NP and 2,4-DNP concentrations in the solution is negligible. The most widely applied kinetic models for adsorption of phenolic compounds on activated carbon are pseudo-first order and pseudo-second order kinetic models. In this study, the predictive capabilities of these two types of kinetic models regarding adsorption of 4-NP and 2,4-DNP on AC examined. The pseudo-first order kinetic model is expressed as:

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

Where, k_1 is pseudo-first order adsorption rate constant (min^{-1}). q_e and q_t are the amounts of 4-NP and 2,4-DNP adsorbed per unit mass of adsorbent at equilibrium and at time t, respectively. The integrated form of this equation at the boundary conditions at $qt(t = 0) = 0$ becomes

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

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 and intercept.

The pseudo-second order kinetics model is expressed as:

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

Where, k_2 is the pseudo-second order adsorption rate constant ($g\ mg^{-1}\ min^{-1}$). The integrated form of this equation with the boundary conditions, $q_t (t = 0) = 0$ becomes

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

Here, q_e and q_t are the amounts of 4-NP and 2,4-DNP adsorbed per unit mass of adsorbent at equilibrium and at time t, respectively.

If a linearized plot of $\frac{t}{q_t}$ vs t is obtained with slope and an intercept, 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.

3.9 EQUILIBRIUM MODELLING

Adsorption studies are carried out for both compounds 4-NP and 2,4-DNP, till equilibrium is achieved. At equilibrium, there is no further change in the concentrations of the adsorbates in the liquid and on the surface of solid adsorbent. 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) isotherm, Langmuir isotherm, Kolbe-Corrigan (three parameter) isotherm, Sips isotherm, and Henry's Law (two- parameter) models.

The Langmuir adsorption model [31] assumes a monolayer adsorption process on a homogeneous surface. The binding sites have the same adsorption affinity, while they are homogeneously distributed over the surface of the sorbent. Additionally no interactions between the adsorbed molecules are considered. The mathematical expression of the model for a single component is described by Eq. (8)

$$q_e = \frac{Q_0 b C_e}{1+bC_e} \tag{8}$$

Where Q is the metal uptake, C is the concentration of the solution at equilibrium, while b and Q_0 are related to the affinity and maximum sorption capacity, respectively.

The Freundlich model (two-parameter) [32], which is usually applied in a strictly empirical sense, can be of theoretical interest in terms of adsorption onto an energetically heterogeneous surface assuming a heterogeneous valence distribution. According to this model the adsorbed mass per mass of adsorbent can be expressed by a power law function of the solute concentration as follows:

$$q_e = kC_e^{\frac{1}{n}} \tag{9}$$

Where, k and n are constants related to the amount sorbed and sorption intensity, respectively.

Henry's Law (with constant) model equation [33] can be given as follows:

$$q_e = KC_e + m \tag{10}$$

Where, q_e is the adsorbed amount at equilibrium (mg/g), C_e is the adsorbed equilibrium concentration (mg/L) and K is the Henry's constant. (All the terms used have the same connotation as that in Mono-parametric model).

The Sips model [34] is empirical adsorption equation that is widely used for the interpretation of adsorption data. The model, which can be considered as a combination of Langmuir and Freundlich equations, for a single component is expressed as follows:

$$q_e = \frac{q_m^S \, aC_e{}^n}{1+aC_e{}^n} \tag{11}$$

Where, q_m^S can be associated with the total number of binding sites, a is the median association constant and 1/n, is the heterogeneity factor. Values for 1/n close to zero indicate heterogeneous adsorbents, while values closer to or 1.0 indicate a material with relatively homogenous binding sites. In this case, the Sips model is reduced to the Langmuir.

The Kolbe-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:

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

Where, n=1, the equation reduces to Langmuir equation. If $BC_e^n \ll 1$, the adsorption is very low and it becomes Freundlich equation. If $BC_e^n \gg 1$, it indicates that the sorption is very high and the adsorbed adsorbate quantity per unit weight of adsorbent at equilibrium remains constant [35].

3.10 MODEL VALIDATION

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

The sum of the squares of the errors (SSE): The function will result in the calculated isotherm parameters providing a better fit at the higher end of the liquid-phase concentration range. This is because the magnitude of the errors and hence the square of the errors will increase as concentration increases [36]:

$$\mathrm{SSE} = \sum(q_{e,exp} - q_{e,cal})^2 \tag{13}$$

Root mean squares of error (RMSE): It is a frequently used measure of the differences between values predicted by a model or an estimator and the values actually observed. It is a good measure of accuracy. [37].

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

Standard error of prediction (SEP): The SEP is the standard deviation of the differences b/w the predicted and the reference values for a set of samples [38]. The formula of SEP is given below:

$$\mathrm{SEP} = \frac{RMSE}{\sum(q_{e,exp}/\mathrm{N})} \times 100 \tag{15}$$

Normalized standard deviation (NSD): The formula for the calculation of NSD is given below:

$$\mathrm{NSD} = \sqrt{\frac{\sum[(q_{e,exp} - q_{e,cal})/q_{e,exp}]^2}{\mathrm{N}}} \times 100 \tag{16}$$

Normalized deviation (ND): The formula for the calculation of ND is given below:

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

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

CHAPTER 4

RESULTS AND DISCUSSION

4.1 CHARACTERIZATION OF AC

The physical and chemical characteristics of AC are given in figures below. Commercial activated carbon is again washed with distilled water and dried in hot air oven for 2-3 days for proper time intervals. BET surface area and total pore volume are determined by BET surface area analyzer. The surface area of AC was 979.01 m^2/g and pore volume was 0.4929 m^2/g. The profiles in XRD (figure 3) obtained show that the main oxidized metal compounds corresponds to CuO. The signals of Cu_2O and Cu are also present in the spectra. FTIR analysis (figure 4), Inorganic carbonate compounds are very distinctive. The strong characteristics are found around 1420 cm^{-1}, 850 cm^{-1}, and 700 cm^{-1}. In this analysis, inorganic carbonate compounds as calcium carbonate, silver carbonate and aliphatic amine groups as hexylamine, N-methylpropyleamine and alcohol functional groups as 1-pentanol, 2-butanol, 3-methyle-3-hexanol were found. Figure 5 depicts the Thermogravimetric analysis (TGA) of AC. The first weight loss around 100 ^{0}C is probably caused by thermo-desorption of physically adsorbed material such as water vapour trapped as moisture in AC. The weight decreases continuously from 100 – 600 ^{0}C indicating the evaluation of the light volatile compounds due to the degradation. Major thermal decomposition occurs around 600 – 900 ^{0}C indicating the emission of volatile matter till the residual carbon is remained. This weight constitutes the ash content in the AC which remains constant even after further increase of temperature to 950 ^{0}C. Low ash content and high carbon content imply good efficiency of the activated carbon.

Above characterization shows that commercial activated carbon is best as an adsorbent for the adsorptive removal of organic pollutants from waste water. Due to large surface area and adequate pore volume we can predict that it is best available technology (BAT) for the removal of nitrophenol like compounds which are very harmful chemical components found in waste water.

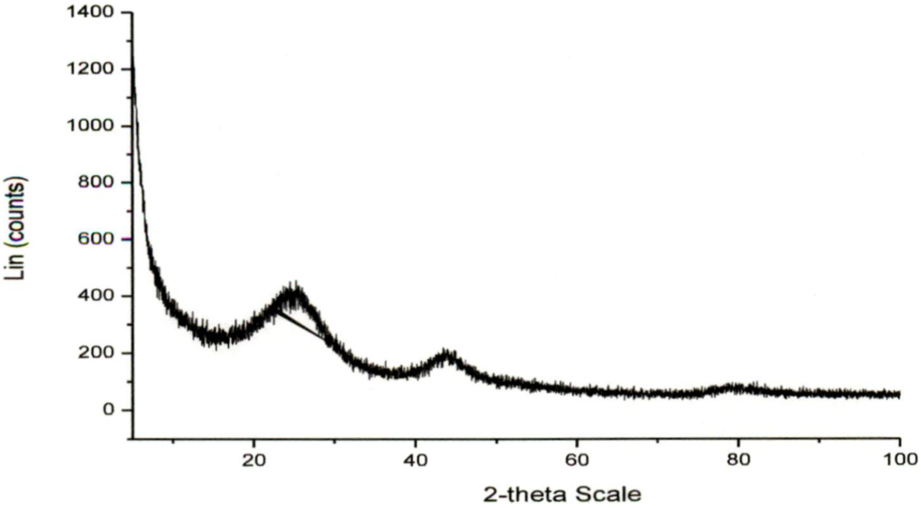


Figure 3: X-ray diffraction pattern for activated carbon

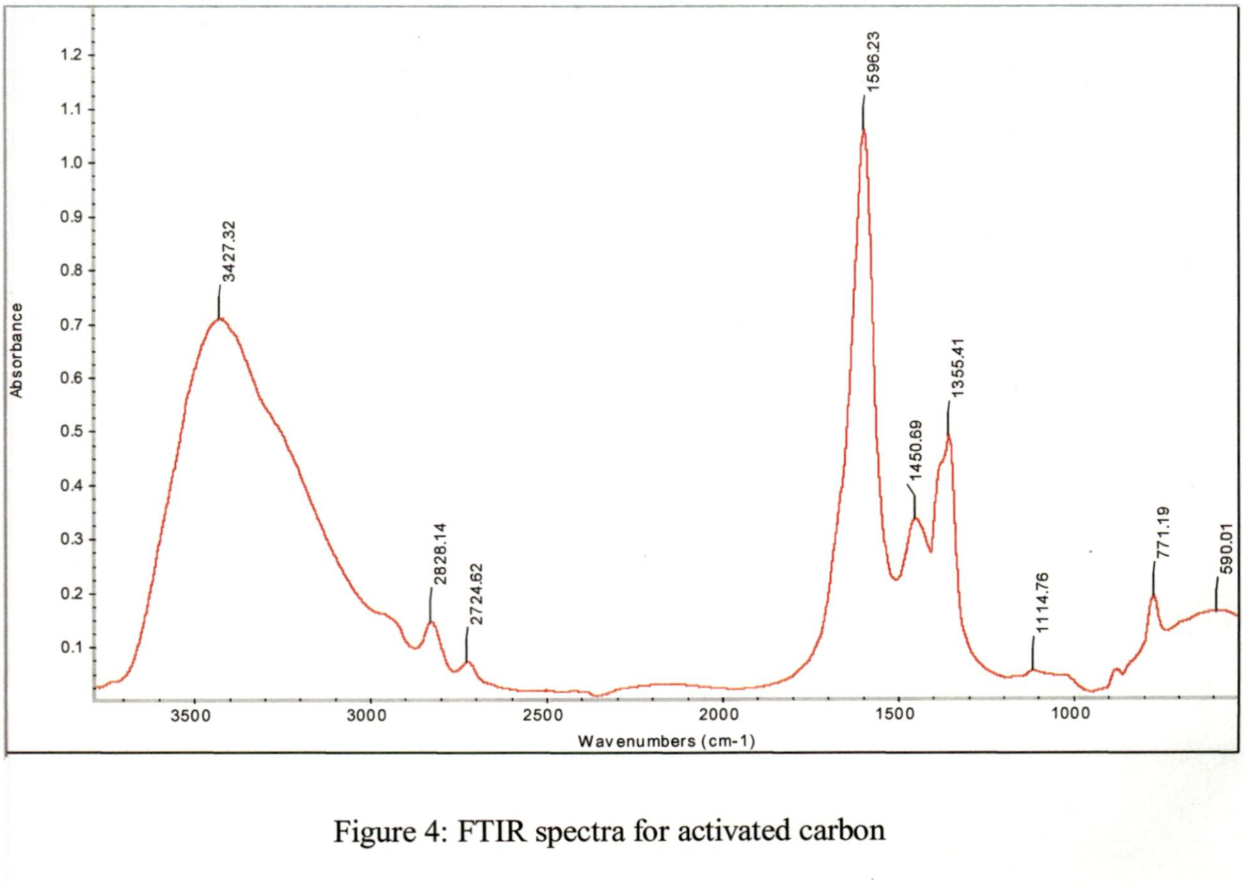


Figure 4: FTIR spectra for activated carbon

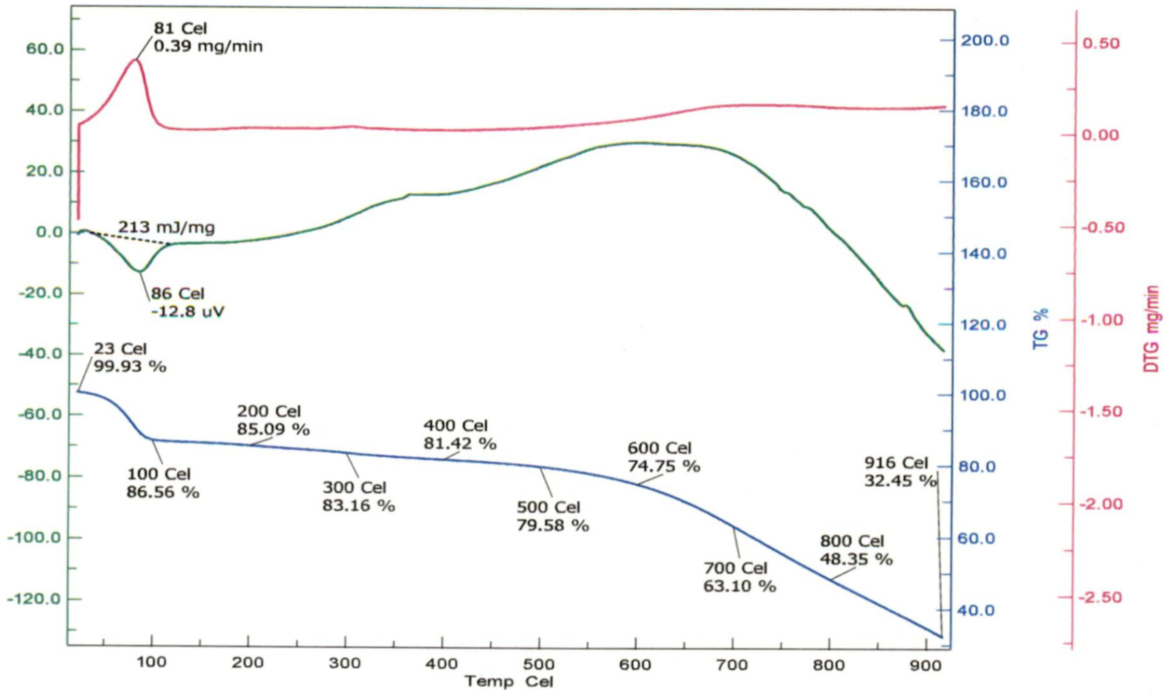


Figure 5: Thermogravimetric curve for activated carbon

4.2 UV absorbance with pH

To find change in absorbance with pH, 50 ml of 4-NP and 2,4-DNP aqueous solution with 50mg/L concentration in 250ml glass bottles and solutions were analyzed using UV (UV-1800) Visible Spectrophotometer (Shimadzu Corporation, USA) at maximum wavelengths of 318 and 360 respectively. The graphs between pH and absorbance are shown in figure 6 and 7. Absorbance increases with increase in pH but with slight change. So we can say that pH does not affect the removal of nitrophenols in broad amount.

4.3 pH variation with Time

To find change in pH with time, 50 ml of 4-NP and 2,4-DNP aqueous solution with 50mg/L concentration in 250ml glass bottles and samples were analyzed time to time by pH meter. The graphs between pH and time are shown in figure 8 and 9. pH increases with increase in pH but with very slight change or negligible change.

4.4 EFFECT OF CONTACT TIME

To obtain the optimum time, 1g/L of adsorbent were added to 50 ml of 4-NP and 2,4-DNP aqueous solution with 50mg/L concentration in 250ml glass bottles and shaken for 60min, 120min, 180min, 240min, 300min, 360min, 420min, 480min, 540min, 600min.

The results show that the equilibrium time required for the adsorption of 4-NP and 2,4-DNP on all samples is about 8 hours and 9 hours respectively as illustrated in figure 10 & 11.

4.5 EFFECT OF pH

The effect of pH on the amount of 4-NP and 2,4-DNP removal was analyzed over the pH range from 2 to 8. In this study, 50ml of 4-NP and 2,4-DNP solutions of 50 mg/L were taken in stopper plastic conical flasks and were agitated with 1.0g/L of AC using a reciprocating type horizontal shaker (Metrex Scientific Instruments (P) Ltd., New Delhi) with temperature control. The shaker was set at a temperature of 303 ± 1 K at a speed of 150 ± 1 rpm Agitation was made for 8h and 9h at constant oscillation given above respectively. The samples were then centrifuged, and the left out concentration in the supernatant solution were analyzed using UV (UV-1800) Visible Spectrophotometer (Shimadzu Corporation, USA) at maximum wavelengths of 318 and 360 respectively.

The initial pH of adsorption medium is one of the most important parameters affecting the adsorption process. The pH of the solution influences the surface charge of the adsorbent and degree of ionization of the adsorbate which in turn affects the rate of adsorption. Figure shows the effect of pH on the adsorption of 4-NP and 2,4-DNP.. From Figures 12 & 13, it was observed that the % removal of 4-NP and 2,4-DNP this state AC was decreased with increasing pH [38]. The optimum pH was found out to be 2 as there was highest adsorption observed at this pH for both adsorbates. The pKa values of 4-NP and 2,4-DNP are 7.16 and 4.11. Therefore at pH greater than these pKa values 4-NP and 2,4-DNP molecules are mainly in ionic form and much less in molecular form. At this state also high electrostatic repulsion between identical charge lowers the adsorption uptake of 4-NP and 2,4-DNP.

4.6 EFFECT OF ADSORBENT DOSE

The adsorbent dose used for the adsorption process was decided by studying the effect of variation in dosage on % removal. The study was done taking 14 flasks of 250 ml. having different dosages of adsorbent i.e. 0.2 - 2 g/L, adsorbate solution concentration 50 mg/L, pH at 2 and temperature at 30 ^{0}C. The percentage adsorbate removal increased with increase in adsorbent dosages from 0.2 - 2 g/L (figures 14 & 15). This can be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increase adsorbent dosage. But amount of 4-NP and 2,4-DNP adsorbed per unit mass of AC decreased with increase in adsorbent dosage.

4.7 EFFECT OF INITIAL CONCENTRATION

The effect of initial 4-NP and 2,4-DNP concentrations was tested by using several concentrations (10, 20, 40, 50, 60, 80, 100, and 200 mg/L). The effect of 4-NP and 2,4-DNP initial concentration variation on the percentage removal by AC is illustrated in Figures 16 & 17. The results show that the initial concentration increases as the removal of 4-NP and 2,4-DNP decreases. Maximum percentage removal of 4-NP and 2,4-DNP by AC are 98.2 and 99.8 for both adsorbates.

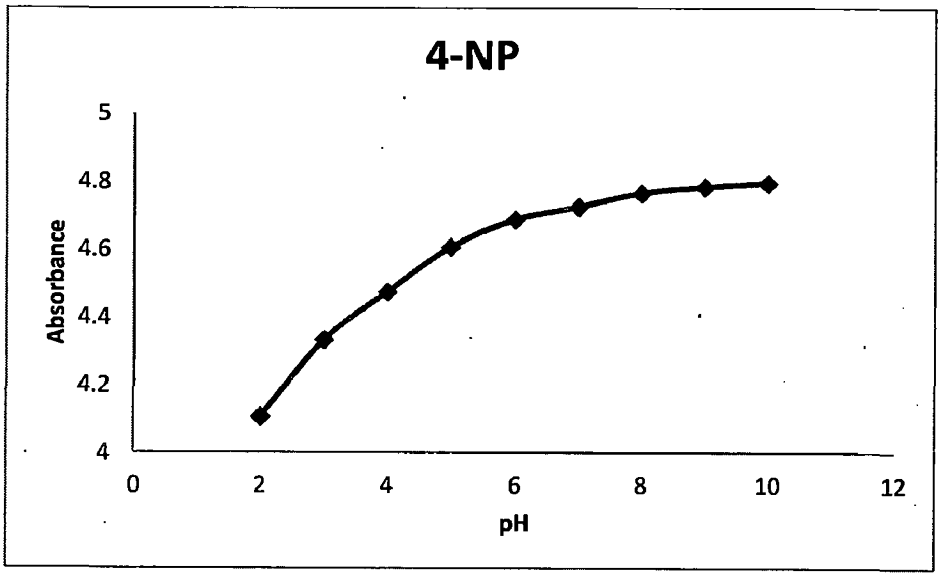


Figure 6: pH versus Absorbance of 4-NP

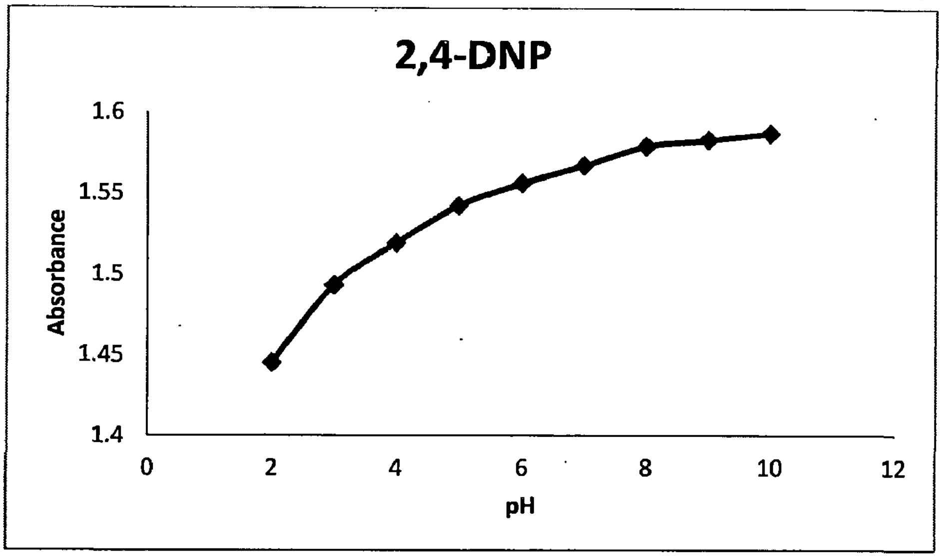


Figure 7: pH versus Absorbance of 2,4-DNP

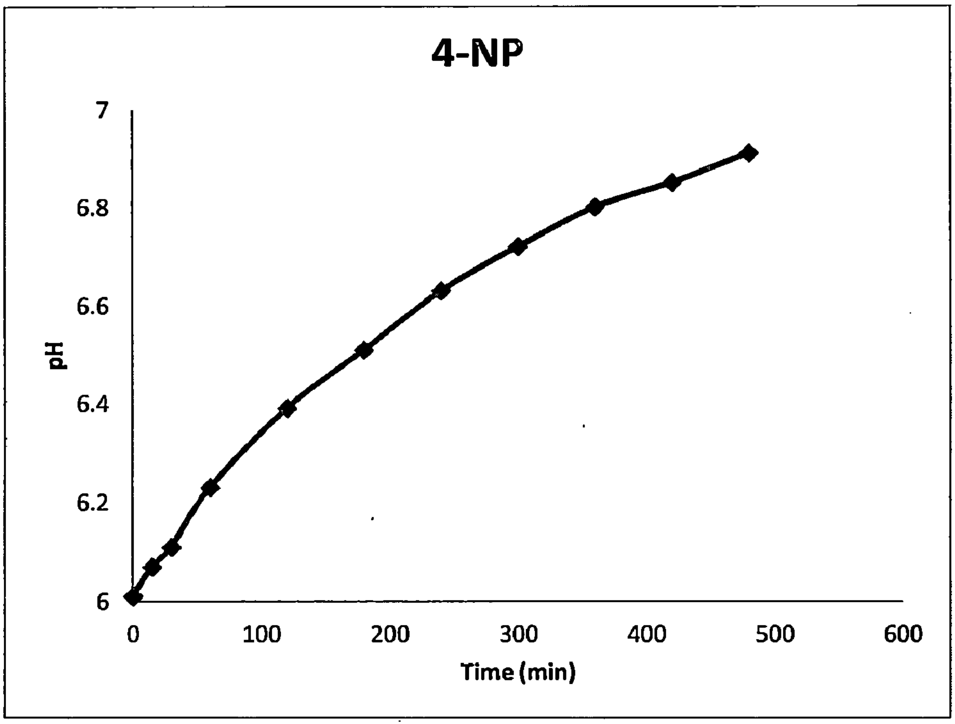


Figure 8: pH versus time of 4-NP

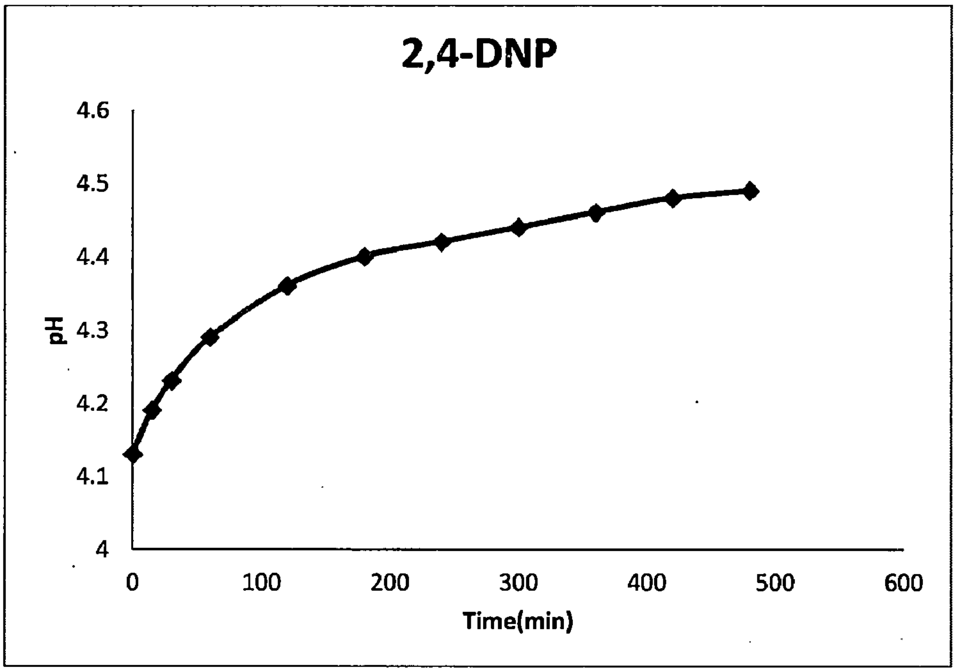


Figure 9: pH versus time of 2,4-DNP

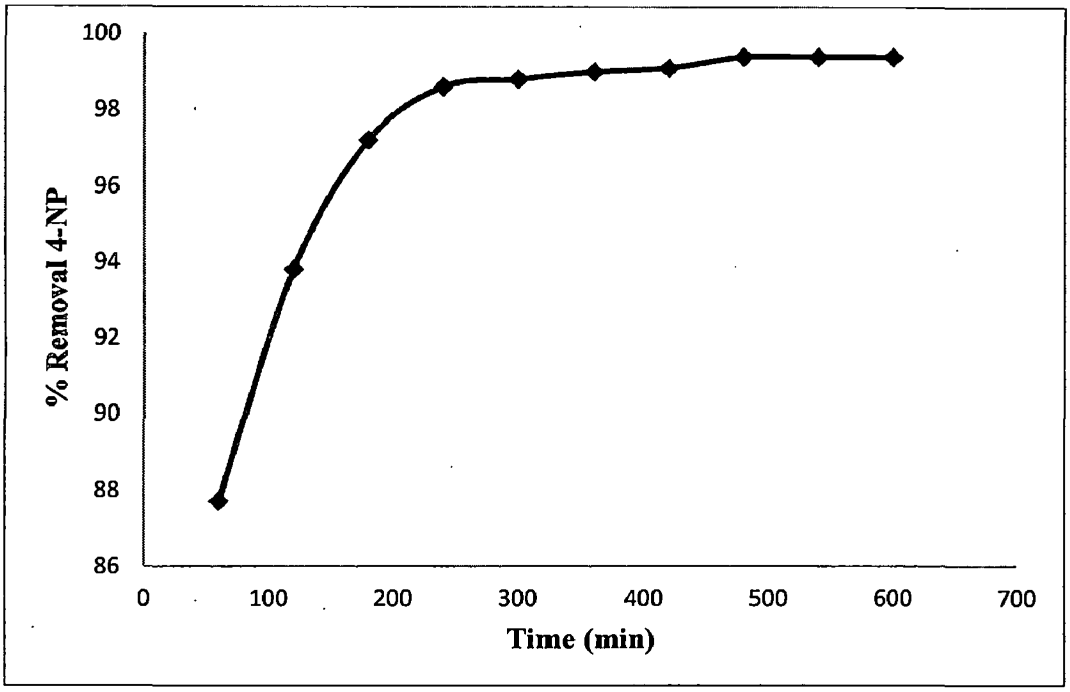


Figure 10: Percent removal of 4-NP with time

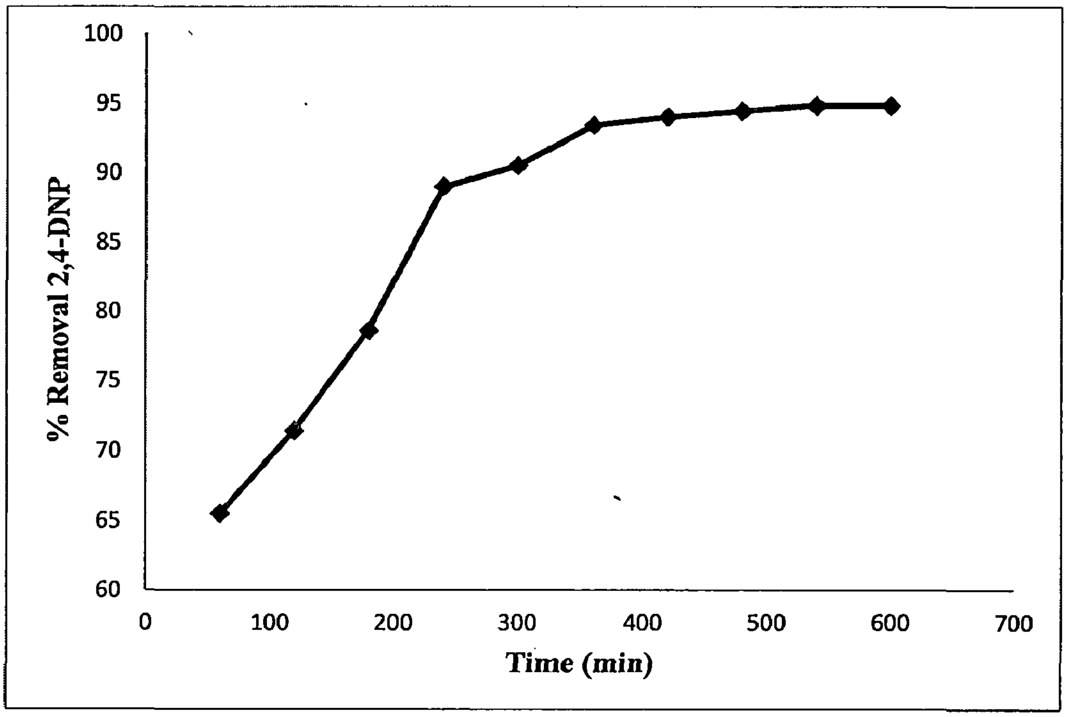


Figure 11: Percent removal of 2,4-DNP with time

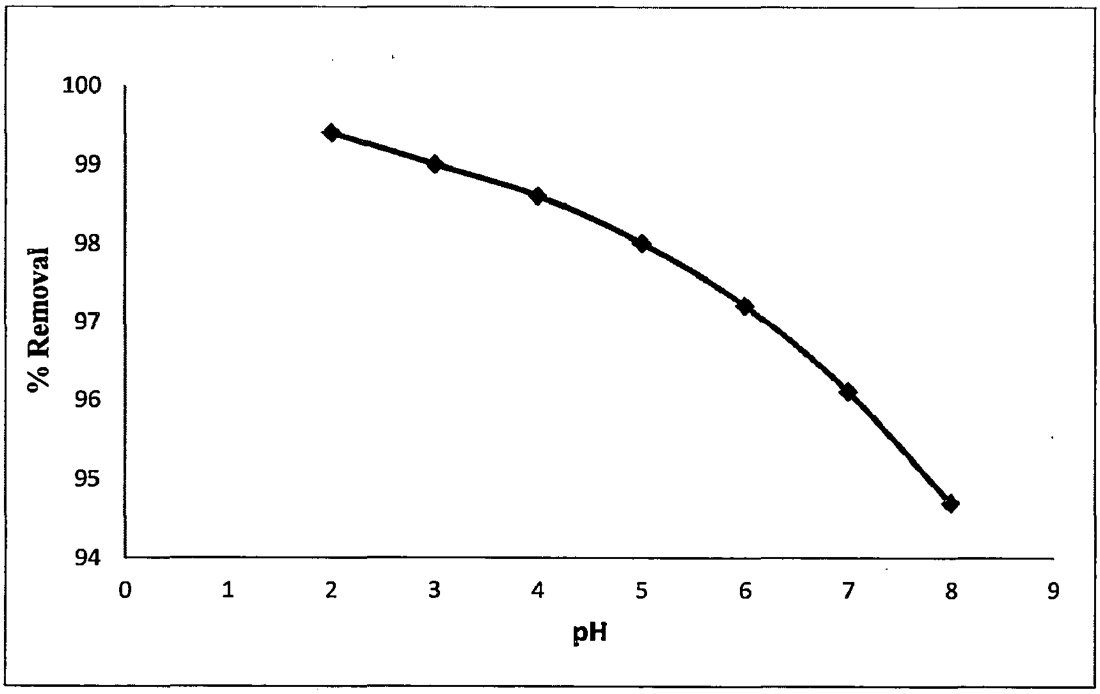


Figure 12: Effect of pH on 4-NP adsorption on AC

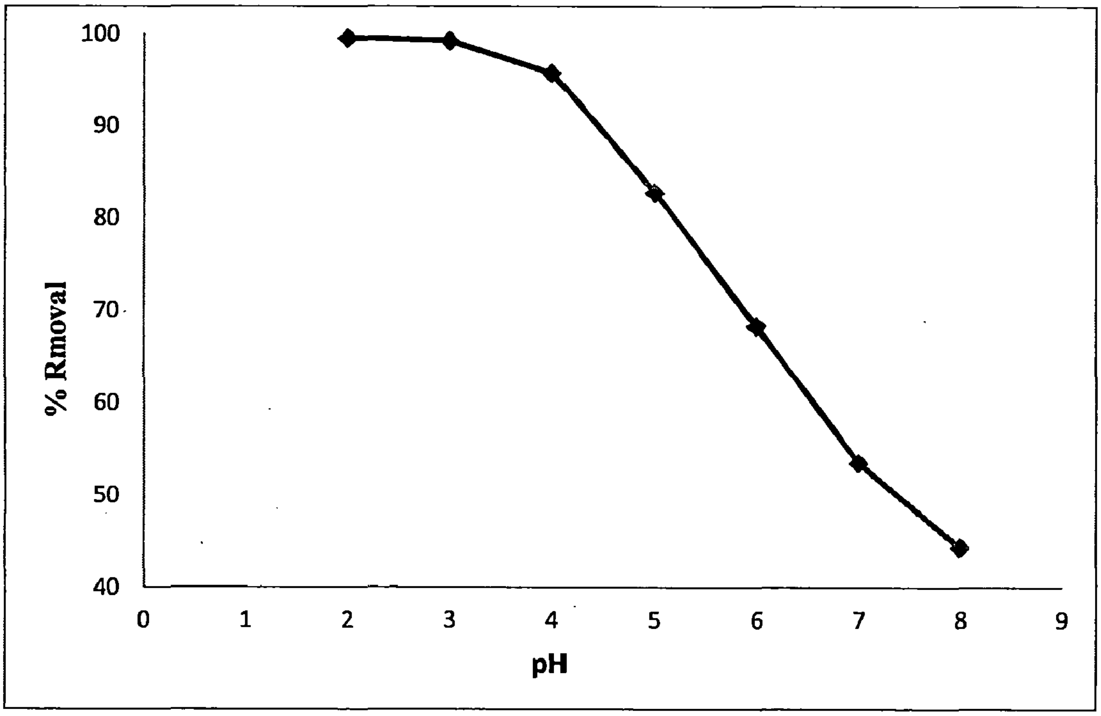


Figure13: Effect of pH on 2,4-DNP adsorption on AC

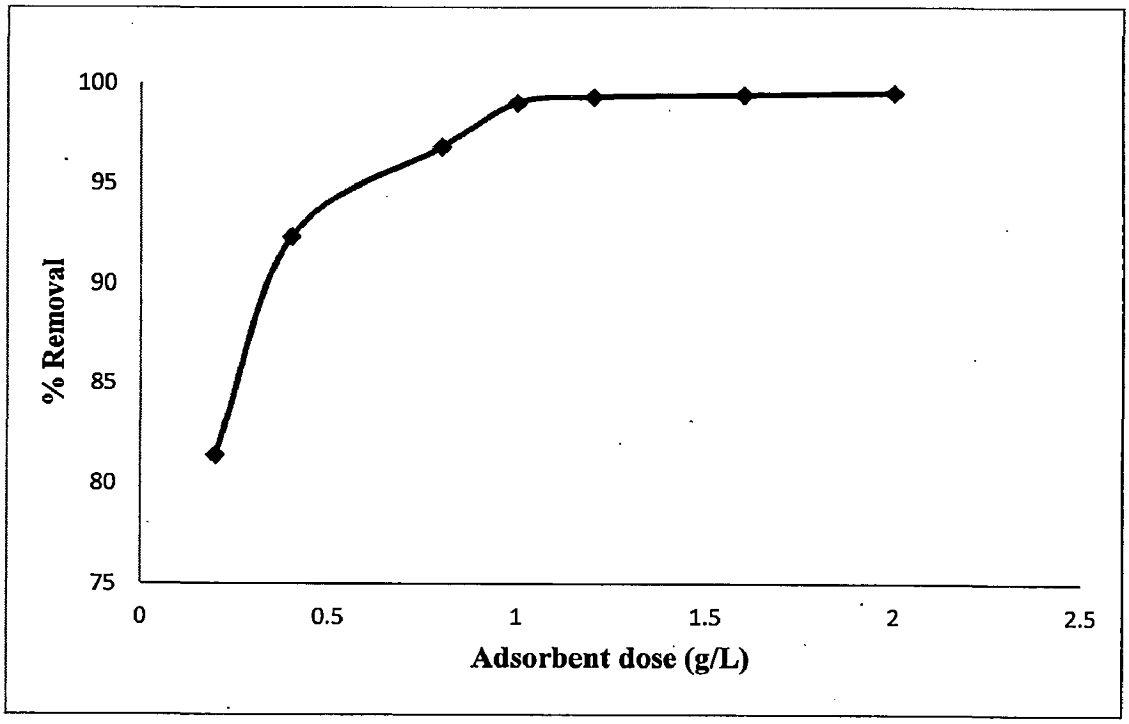


Figure 14: Effect of adsorbent dose on 4-NP adsorption on AC

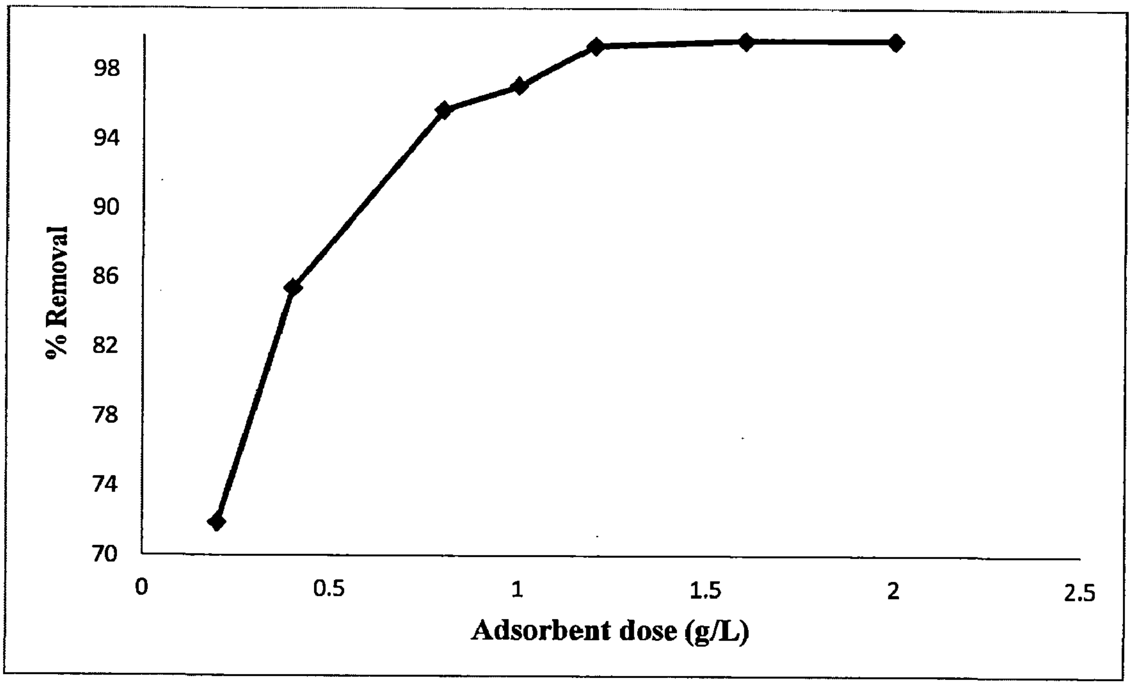


Figure 15: Effect of adsorbent dose on 2,4-DNP adsorption on AC

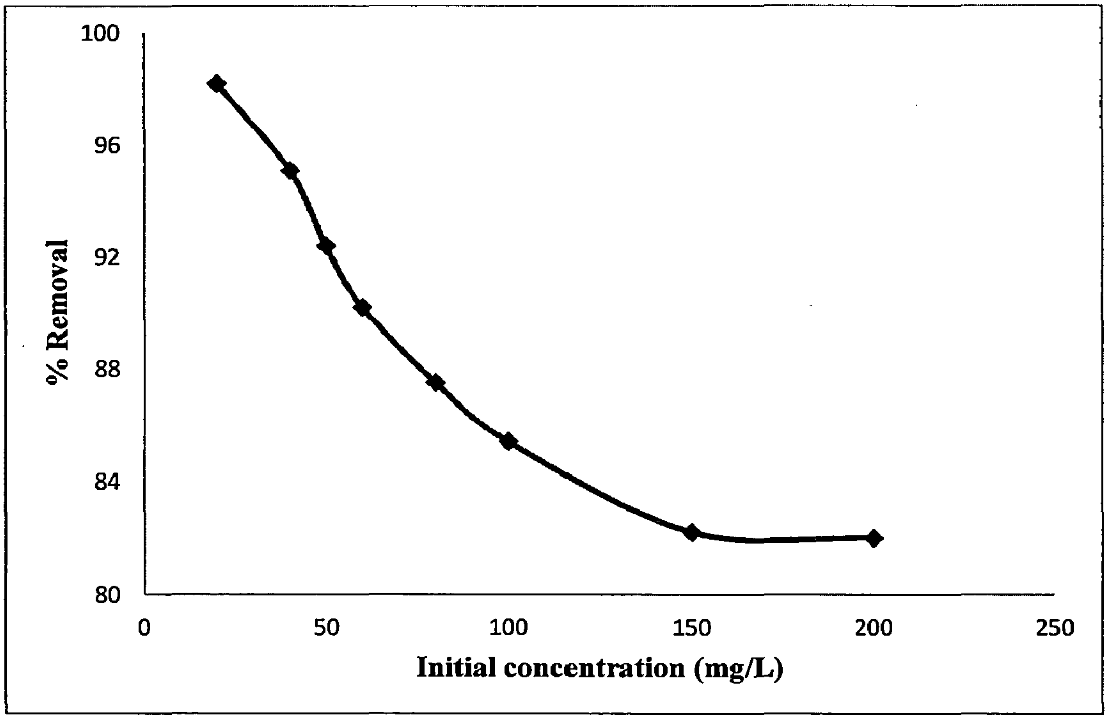


Figure 16: Effect of initial concentration on 4-NP adsorption on AC

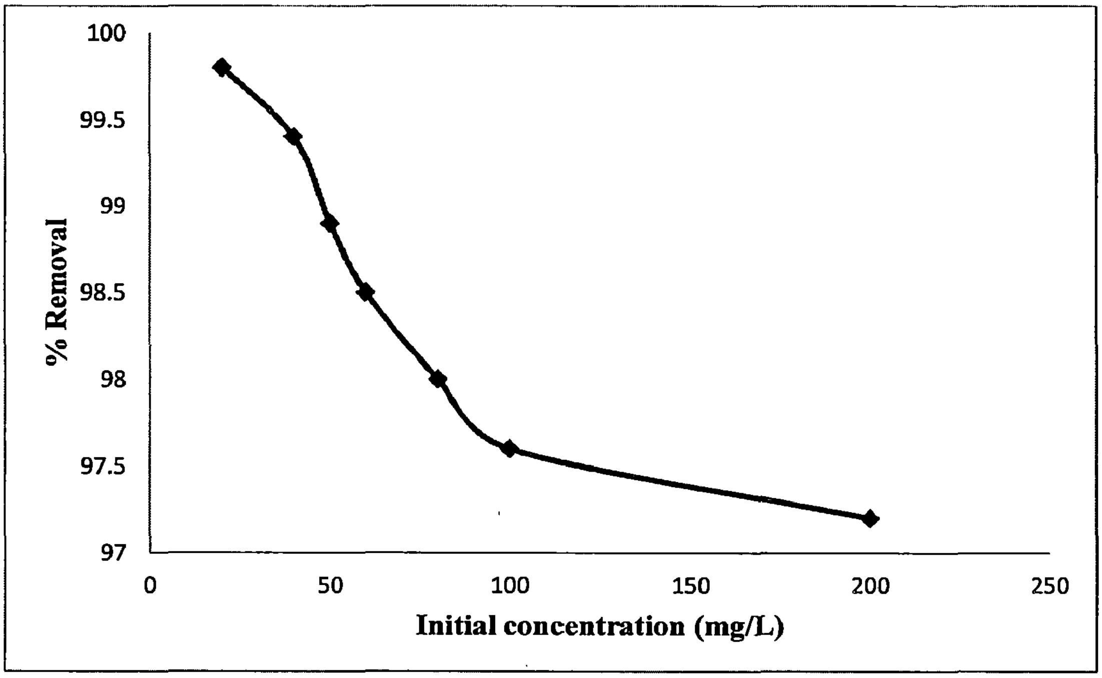


Figure 17: Effect of initial concentration on 2,4-DNP adsorption on AC

4.8 ADSORPTION KINETICS

In this study, experiments were conducted on both 4-NP and 2,4-DNP to get the variation of concentration with time. Initial concentration of 50 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 six graphs as equations (4), (6) and (7) to analyze the predictive capabilities of pseudo-first order, pseudo-second order and intraparticle diffusion models respectively. It is observed that the data do not a fit with pseudo-first order kinetics effectively giving a non-linear plot and lesser value of correlation coefficient R^2 for both 4-NP and 2,4-DNP as compared to pseudo-second order kinetics. The plots thus obtained for 4-NP and 2,4-DNP are shown in figure 18 & 19, respectively. The experimental data fits with pseudo-second order kinetics giving a linear plot with a very high correlation coefficients R^2 for 4-NP and 0.998 for 2,4-DNP. Figure 20 &21 represent the pseudo-second order kinetics for 4-NP and 2,4-DNP respectively. This results that the adsorption perfectively complies with pseudo-second order kinetics. The kinetics parameters for all three models are tabulated in table 4. It can be seen that the rate constant is very law for pseudo-second order model for both 4-NP and 2,4-DNP onto AC. And, also the amount adsorbed per unit adsorbent is high for the pseudo-second order model justifying our conclusion of selecting it is as the best fitting model. The adsorbed amounts per unit adsorbent for 4-NP and 2,4-DNP are found to be 50.50 mg/g and 51.28 mg/g, respectively. The plot of intraparticle diffusion for both 4-NP and 2,4-DNP adsorption was a non-linear curve which did not pass through the origin as represented in figures 22 & 23 respectively.

4.9 ADSORPTION EQUILIBRIUM KINETICS

Isotherm experimental studies were conducted at 30 ^{0}C and initial concentration 50mg/L of both type of adsorbates 4-NP & 2,4-DNP. Adsorbent dose was varies from 0.2 – 2 mg/L for both adsorbates. C_e values for each different adsorbent dose was determined and the experimental data is correlated with five isotherm models for both components. The shape of experimental and some models fitted isotherm curves is found to be concave upwards in nature for both compounds. The adsorption equilibrium constants derived for various models are given in table 5 for 4-NP and table 6 for 2,4-DNP. All the parameters of the isotherm models and correlation coefficients R^2 for both 4-NP & 2,4-DNP are obtained using the curve fitting tool of MATLAB 7.0.1. Figure 24 & 25 show the experimental data and the isotherm model curves obtained for 4-NP & 2,4-DNP, respectively. Four out of five isotherm models as Freundlich, Henry's Law, Sips, Koble-Corrigan gave good fitting for 4-NP and three out of five as Henry's Law, Sips, Koble-Corrigan gave good fitting and high correlation coefficient R^2. On the basis of above calculation of various Statistical indices for various isotherm models for 4-Nitrophenol and 2,4-Dinitrophenol it is justified that Koble-Corrigan and Sips adsorption isotherm models are best fitting model and pseudo-second order kinetic model is best fitting model for both types of adsorbates. The various statistical parameters determined are given in table 5 & 6 by using equations from 8 to 12.

Table 4: Kinetic parameters for the adsorption of 4-NP and 2,4-DNP on AC

Kinetic Parameters	**Adsorbate**			
	4-Nitrophenol		**2,4-Dinitrophenol**	
Pseudo I order		**Standard deviation**		**Standard deviation**
k_1 (1/min)	0.0133	23.50	0.0110	9.92
$q_{e,pred}$ (mg/g)	18.800		42.720	
$q_{e,exp}$ (mg/g)	49.7		47.4	
R^2	0.9308		0.9871	
Pseudo II order				
k_2 (g/mg/min)	0.0026	1.61	0.00046	8.02
$q_{e,pred}$ (mg/g)	50.500		51.2800	
$q_{e,exp}$ (mg/g)	49.7		47.4	
R^2	1.0000		0.99840	
Intraparticle diffusion				
k_p (mg/g/min$^{1/2}$)	0.2963		1.0275	
C	43.500		25.806	
R^2	0.7223		0.8800	

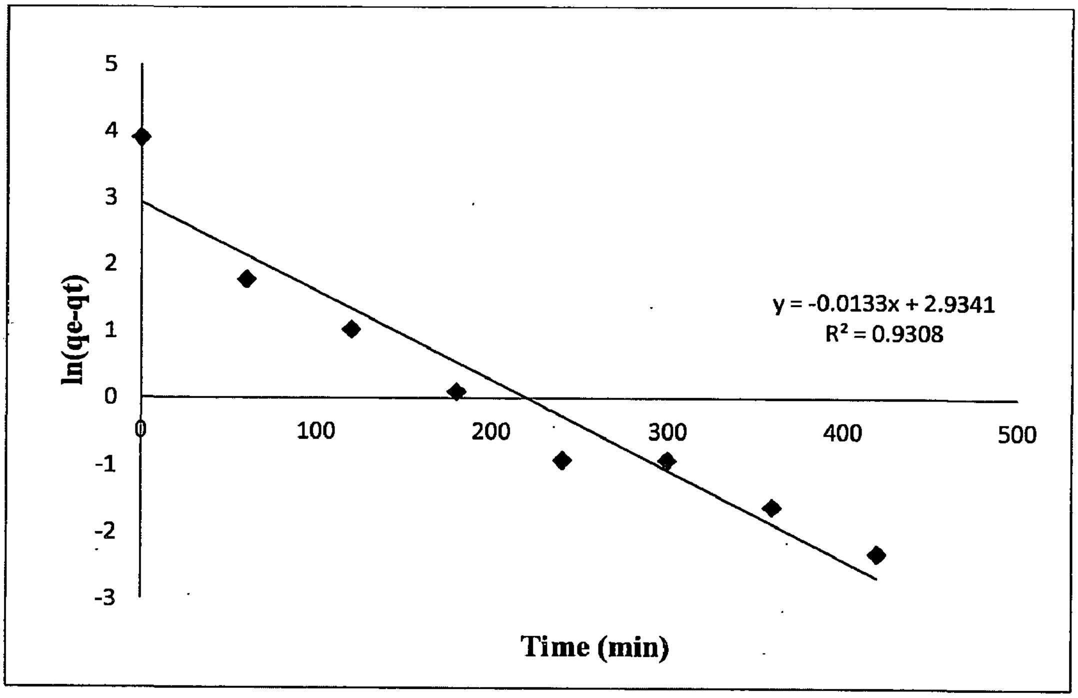


Figure 18: Pseudo-first order model plot for adsorption of 4-NP on AC

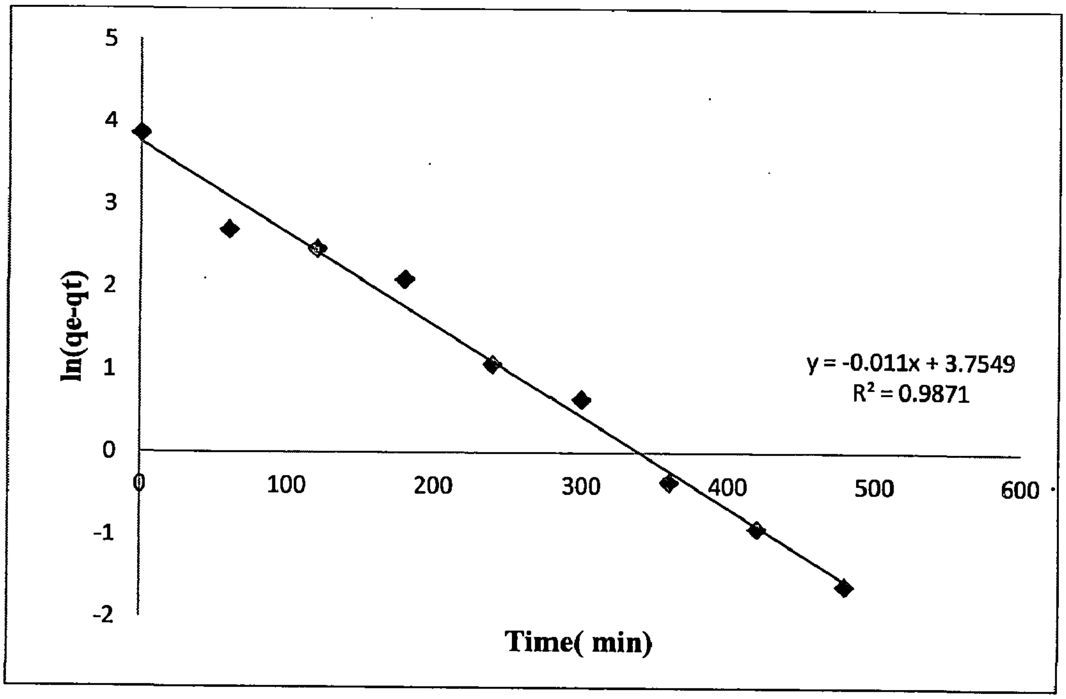


Figure 19: Pseudo-first order model plot for adsorption of 2,4-DNP on AC

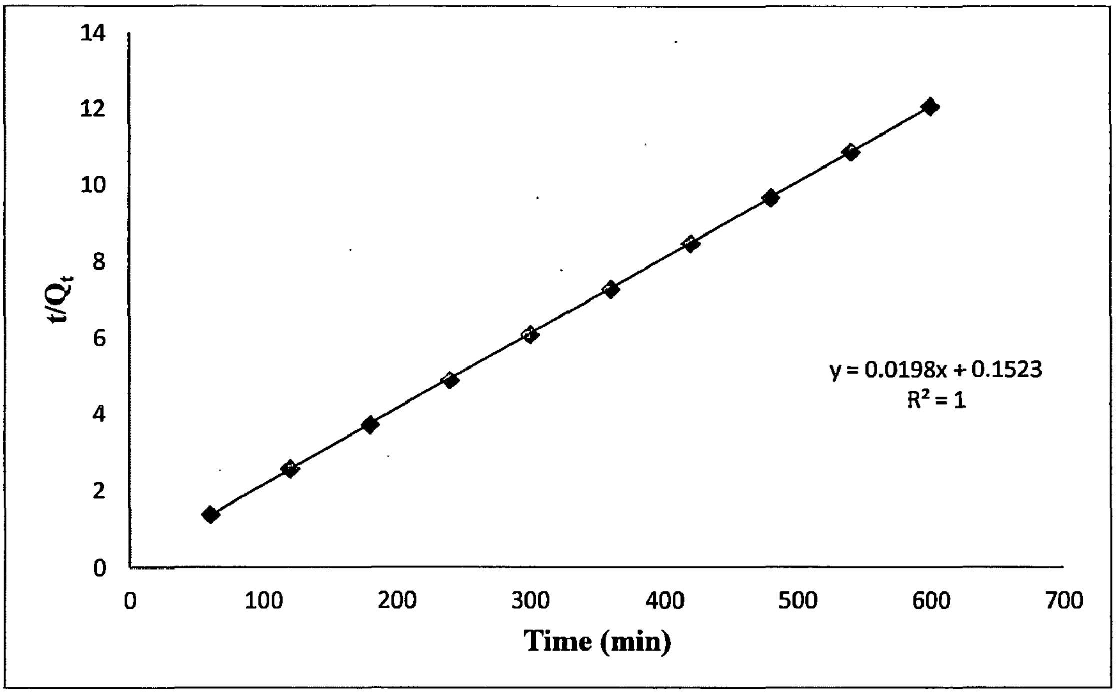


Figure 20: Pseudo-second order model plot for adsorption of 4-NP on AC

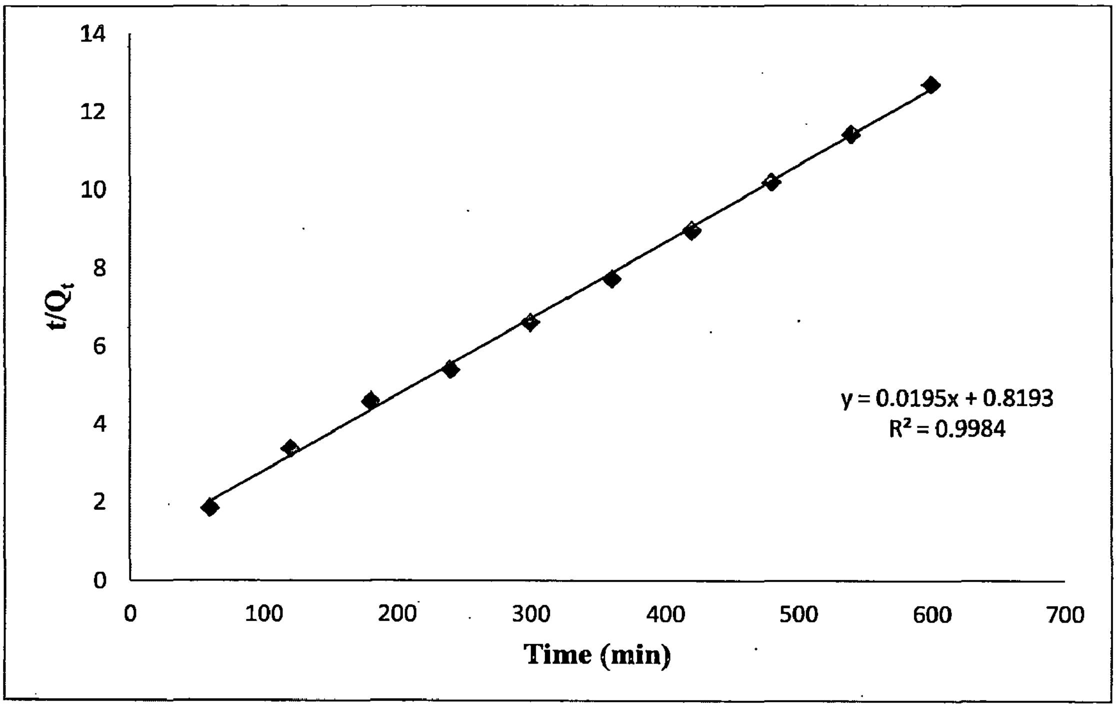


Figure 21: Pseudo-second order model plot for adsorption of 2,4-DNP on AC

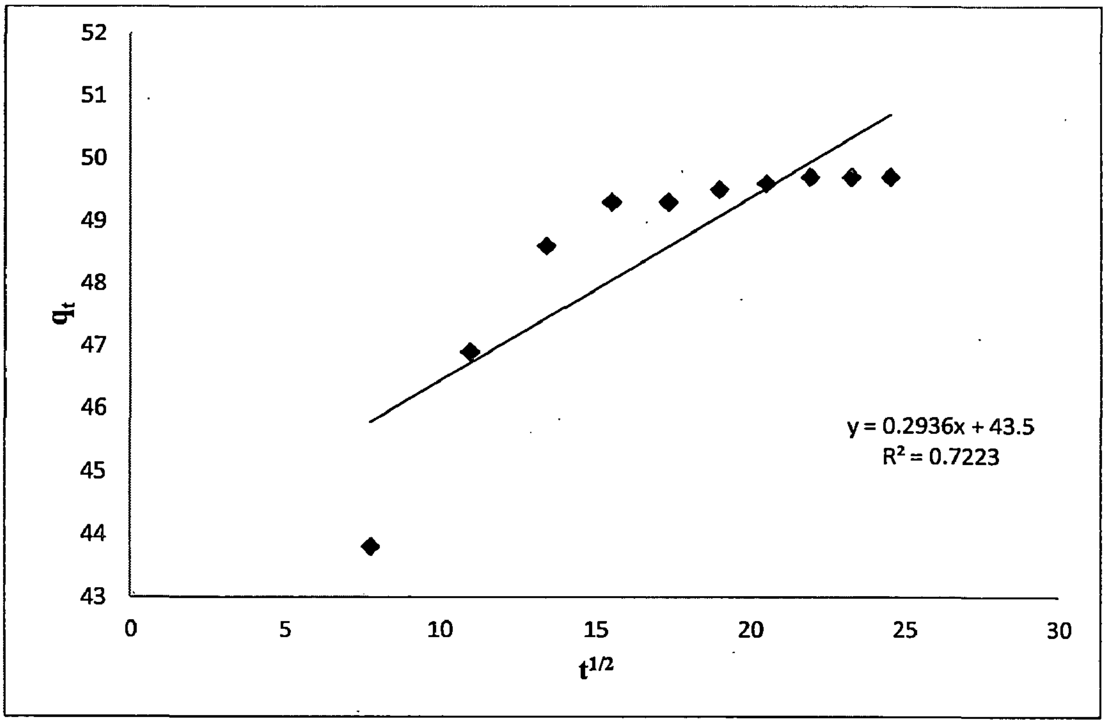


Figure 22: Intraparticle diffusion curve for adsorption of 4-NP on AC

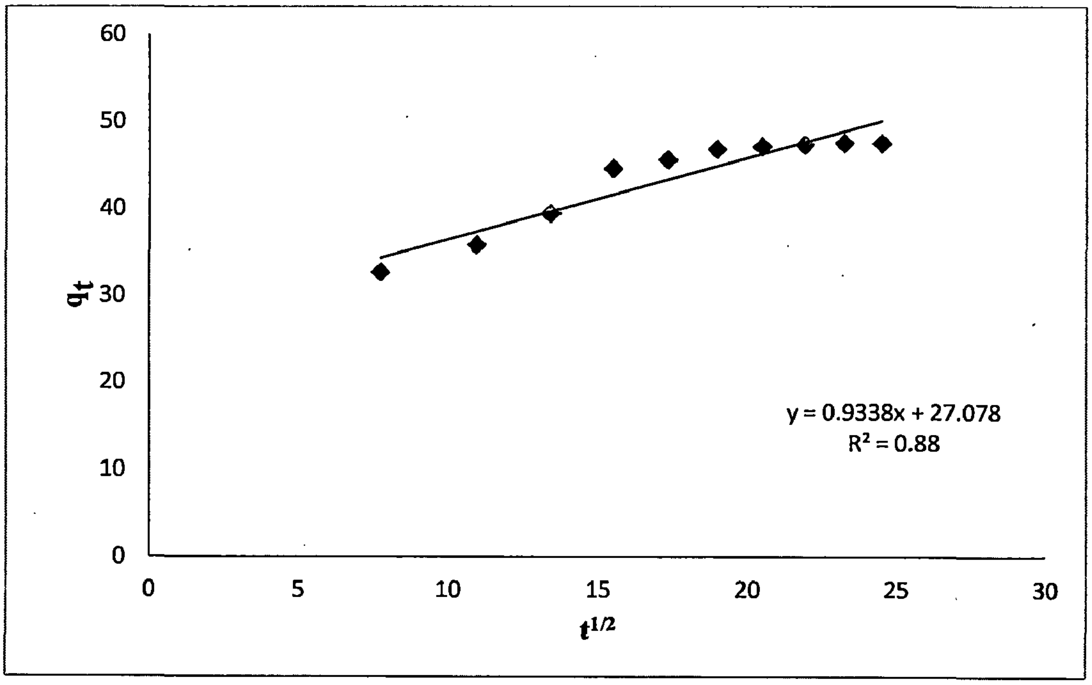


Figure 23: Intraparticle diffusion curve for adsorption of 2,4-DNP on AC

Table 5: Adsorption equilibrium isotherm constants for 4-Nitrophenol

Adsorption Isotherm Model	**Model Equations**	**Parameters**
Freundlich adsorption isotherm	$q_e = kC_e^{\frac{1}{n}}$	k = 57.36 n = 1.793 R^2 = 0.9808
Langmuir adsorption isotherm	$q_e = \frac{Q_0 bC_e}{1 + bC_e}$	Q_0 = 288.59 b = 0.269 R^2 = 0.9473
Henry's law	$q_e = KC_e + m$	K = 18.973 m = 31.662 R^2 = 0.9831
Sips adsorption isotherm	$q_e = \frac{q_m^S \, aC_e{}^n}{1 + aC_e{}^n}$	q_m^S = 8835 a = 0.006703 n = 0.5491 R^2 = 0.9799
Koble-Corrigan adsorption isotherm	$q_e = \frac{AC_e^n}{1 + BC_e^n}$	A = 39.73 B = -0.294 n = 0.321 R^2 = 0.9894

Table 6: Adsorption equilibrium isotherm constants for 2,4-Dinitrophenol

Adsorption isotherm model	**Model Equations**	**Parameters**
Freundlich adsorption isotherm	$q_e = kC_e^{\frac{1}{n}}$	$k = 47.13$ $n = 2.084$ $R^2 = 0.9761$
Langmuir adsorption isotherm	$q_e = \frac{Q_0 bC_e}{1 + bC_e}$	$Q_0 = 245.10$ $b = 0.1524$ $R^2 = 0.9544$
Henry's law	$q_e = KC_e + m$	$K = 10.53$ $m = 32.08$ $R^2 = 0.9917$
Sips adsorption isotherm	$q_e = \frac{q_m^S \, aC_e{}^n}{1 + aC_e{}^n}$	$q_m^S = 9519.66$ $a = 0.00525$ $n = 0.4384$ $R^2 = 0.9774$
Koble-Corrigan adsorption isotherm	$q_e = \frac{AC_e^n}{1 + BC_e^n}$	$A = 0.6141$ $B = -0.9869$ $n = 0.003682$ $R^2 = 0.321$

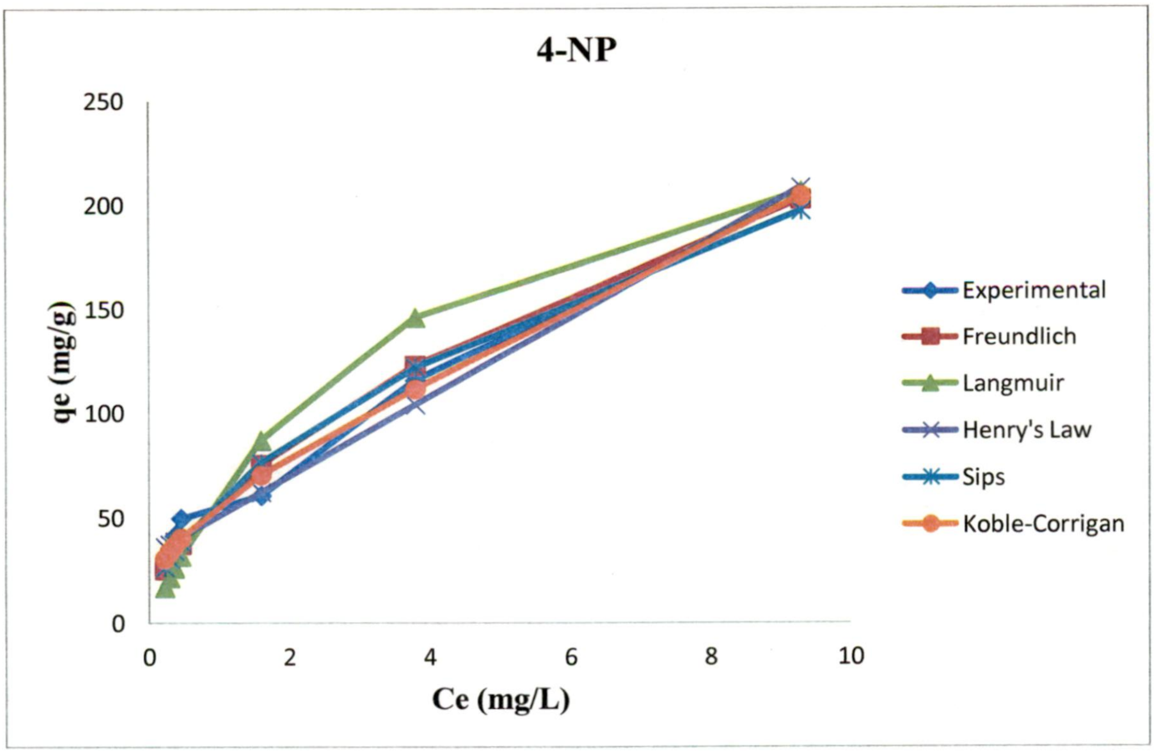


Figure 24: Comparison of various isotherm models for 4-NP

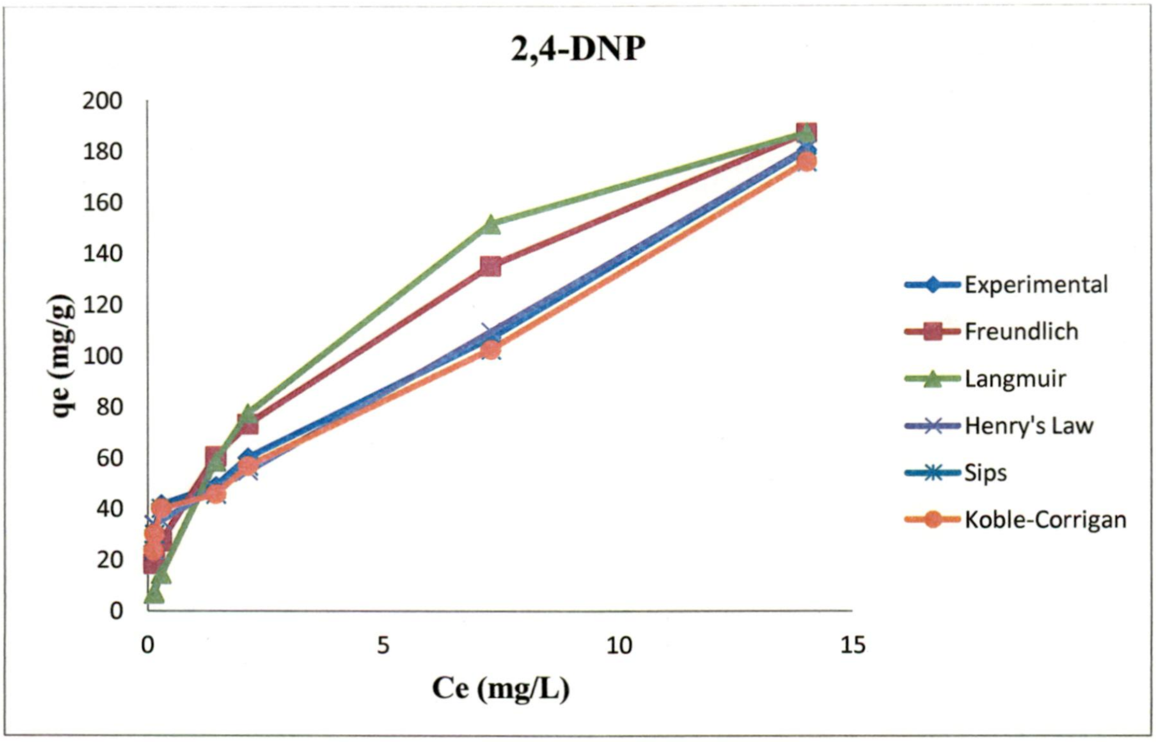


Figure 25: Comparison of various isotherm models for 2,4-DNP

Table 7: Statistical indices for various isotherm models for 4-Nitrophenol

Isotherm Models	**R^2**	**Adj. R^2**	**RMSE**	**SSE**	**SEP**	**NSD**	**ND**
Freundlich	0.9808	0.9769	9.718	472.2	12.92	15.46	2.74
Langmuir	0.9473	0.9697	18.23	1766	24.24	32.12	9.24
Henry's law	0.9831	0.9797	7.71	415.9	10.25	20.40	4.95
Sips	0.9799	0.9698	8.41	495.4	11.18	14.78	1.15
Koble-Corrigan	0.9894	0.9842	6.09	259.71	8.099	13.69	1.85

Table 8: Statistical indices for various isotherm models for 2,4-Dinitrophenol

Isotherm Models	**R^2**	**Adj. R^2**	**SSE**	**RMSE**	**SEP**	**NSD**	**ND**
Freundlich	0.9761	0.9780	971.9	13.94	19.81	27.46	3.63
Langmuir	0.9544	0.9522	2726	23.85	33.18	51.55	1.73
Henry's law	0.9917	0.9959	152.23	5.01	7.13	14.92	1.37
Sips	0.9974	0.9983	70.4	3.17	4.50	4.91	0.74
Koble-Corrigan	0.9954	0.9931	84.23	4.589	6.52	10.03	0.85

4.10 TOC ANALYSIS

To check the efficiency of activated carbon for the removal of 4-NP and 2,4-DNP by total organic carbon analysis (TOC analyser , model TOC - V CPH, Simadzu Corporation, made in Japan) has been done. The samples before and after adsorption were taken for determining total organic carbon at initial concentration and optimum condition like equilibrium time, pH, adsorbent dose as discussed above. The results regarding TOC are given below:

Table 9: TOC analysis for 4-NP and 2,4-DNP

4-NITROPHENOL		
Before adsorption		
TOC = 32.91mg/L	TC = 33.02 mg/L	IC = 0.1047 mg/L
After adsorption		
TOC = 4.033 mg/L	TC = 4.144 mg/L	IC = 0.1118 mg/L
2,4-DINITROPHENOL		
Before adsorption		
TOC = 12.82 mg/L	TC = 12.90 mg/L	IC = 0.07268 mg/L
After adsorption		
TOC = 5.039 mg/L	TC = 5.170 mg/L	IC = 0.1312 mg/L

CHAPTER 5

CONCLUSION

The following conclusions are made from the present study:

- The characterization of activated carbon was done by standard methods. The results obtained from them suggest that activated carbon 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. Based on the present study it is found that activated carbon has great potential as an economical and efficient adsorbent to remediate both adsorbate ions from aqueous solutions.
- To the removal of 4-nitrophenol and 2,4-dinitrophenol from aqueous solutions, batch adsorption studies were carried out using commercial activated carbon.
- With its BET surface area as 979.01 m^2/g, some adsorption isotherm models were appropriate for the current experimental data and some isotherm models did not fit well. The equilibrium data followed best fit of the pseudo-second order kinetics in comparison of pseudo first order kinetics and intraparticle diffusion model. The values for second order kinetic constant k_2 for 4-NP and 2,4-DNP were found to be 0.0026 g mg^{-1} min^{-1} and 0.00046 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.
- On the basis of above calculation of various Statistical indices for various isotherm models for 4-Nitrophenol and 2,4-Dinitrophenol, it is justified that Koble-Corrigan and Sips adsorption isotherm models respectively are best fitting model.
- The adsorption of 4-NP and 2,4-DNP was found to be dependent on optimum pH, adsorbent dose and initial concentration. The percent removal decreased as the pH increased from 2-8. The adsorption of both adsorbates was observed maximum at pH of 2, suggesting that acidic nature of the solution assists in the better removal of both the compounds. Thus all the further adsorption studies were carried out at pH 2.
- The optimum adsorbent dose for 4-NP and 2,4-DNP removal was estimated to be 1g/L and 1.2 g/L respectively. Through further studies 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 4-NP and 2,4-DNP were found to be 99 % and 99.4 % respectively.

- Initial adsorbate concentration for both adsorbates was varied from 20 – 200 mg/L and maximum adsorption at optimum initial concentrations were found 20 mg/L and 40 mg/L for 4-nitrophenol and 2,4-dinitrophenol, respectively.
- To better check the adsorption capacity of activated carbon, TOC analysis of 4-nitrophenol and 2,4-dinitrophenol has been carried out before and after adsorption. TOC analyser consists TOC, TC and IC details of both adsorbates.

The removal efficiencies of 4-nitrophenol and 2,4-dinitrophenol by Commercial grade activated carbon are highly satisfactory, it is concluded that commercial activated carbon is an excellent and effective adsorbent for the removal of 4-NP and 2,4-DNP from waste water.

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