REMOVAL OF HEAVY METALS FROM AQUEOUS SOLUTION USING PHOSPHORIC ACID AND POTASSIUM HYDROXIDE ACTIVATED CARBON PREPARED FROM *DELONIX REGIA* PODS – A COMPARATIVE STUDY

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IN

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S. VANI

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LIST OF ABBREVIATIONS

PAAC	-	Phosphoric acid activated carbon
PHAC	-	Potassium hydroxide activated carbon
D-R	-	Dubinin-Raduskevich
EDAX	-	Energy-dispersive X-ray spectroscopy
FTIR	-	Fourier Transform Infra Red
SEM	-	Scanning electron microscope
SSE	-	Summation of Error Squares
XRD	-	X - ray diffraction
ZPC	-	Zero point charge

Chapter I

Introduction

Chapter – I

Introduction

Water contamination is becoming a great threat to the present as well as future generation. By altering the quality of water also causes serious diseases and deaths, most of these deaths due to contaminated drinking water. More than millions of people deaths per year in worldwide cause of water pollution. The biggest problematic of water pollutants are released from human activities on environment.

1.1. Classes of water pollutants

Common examples of chemical water pollutants are heavy metal ions emanating from mining activity, plating industries, agro industries and dyes from textile, paper, leather industries etc. Physical water pollutants are hot water from cooling tower in thermal power plants; garbage and floating debris cause a variety of harmful effects. The most appreciable physical pollutants are inadequate sediments, mostly arising through land use materials and refuse discarded from man-made activities. Although these substances are not harmful to human health as chemicals or pathogens they do affect the visual impact of water pollution. Radiant products are actually sub-divisions of a kind of chemical pollutants and by mass represent the smallest of the contributors to water pollution; however, their potential for harm allows recognition as a separate class.

Sources

Water pollutant sources are divided into two types: (i) point sources which can be attributed to discrete discharge from a factory or sewage outlet and (ii) non-point

sources that include urban storm stream path, agricultural runway and other area wide sources.

In general, a variety of inorganic chemical water contaminants are produced by non-point sources. However, some minerals such as Cl_2 and associated derivatives are produced from point sources, unfortunately, water treatment facilities are used. Moreover, some of the more quantity of heavy metal to ocean is fixed point industrial plants[1].

1.1.1 Dye Pollution

Textiles, leather, plastics, cosmetics, paper, pulp and food industries Dyes have been used in long periods. The colours that are pulled out of these factories have some risks and environmental problems. These colour mixture are not only delightful disgusting, but also prevents penetration of sunlight in water and affects the aquatic environment. Dyes usually contain complicated aromatic molecular structures, these are very stable and non-biodegrade. Many more dyes are poisonous to certain microbes and they prevent direct destruction or their catalytic abilities. Textile industries use dyes and pigments to produce for their different colored product. In excess of one lakh commercially available dyes approximately 1000 tons of dyes produce. Many dyes are used in textile industries such as base, acid, reactive and direct dyes. Because of their chemical composition, dyes increase the resistance to the disappearance of light and water exposure. The main causes of waste generated via the textile manufacturing are from natural fibers, dyeing and finishing methods from laundry and lighting.

Through these different types of dyes, fiber and exercise aids, these processes produce waste water for major chemical complication and variety, which are not adequately treated in the traditional sewage treatment plant. Several studies were conducted to estimate the effects of pigments in the environment. In many colorant have

been found to cause complications in water for several ways: (i) Depending on the concentration and exposure time of dyes, the dyes in living organisms can have severe and / or long-term effects (ii) The dyes are naturally very clear, the small release of waste can cause the extraordinary color of the surface water, which draws attention to the public and the authorities; (iii) The effect of dyes reflecting sunlight that enters the water, which can have serious effects on bacterial growth and violates their biotic activity; (iv) Dyes have several varied and complex molecular structures, so it is complicated to treat and interrupt municipal waste activities; (v) Dyes in waste water for sewage and chemical changes, destroying oxygen dissipated by stream and destroy aquatic organism; (vi) There is a tendency to break the metal ions that produce microscopic toxins, fish and other organisms.

1.1.2 Heavy metal pollution

Waste water from various industries such as pigments, paints, glass manufacturing, metal plating, battery production and mining operation processes are contain contaminants such as heavy metals Pb, Cd, Cr, Ni, Zn, Cu and Fe. These heavy metals in waste material are not biodegradable, which lead to life-threatening organisms in lakes and streams that lead to many health problems such as plants, animals, cancer, kidney failure, oral soreness and metabolic acidosis in stomach of the rodent[3].

Diabetes and other symptoms increase, indicating the connection between the quality of life and the rate of water from heart disease and other chronic diseases. Diseases other than cardiovascular disease have detected substantial positive interaction between the heavy metals and various types of cancers in the water and the concentration of several trace elements in water supply. The highest and lowest density of fragment toxic metals in drinking water is harmful to the human body. Aluminum and zinc in general water supply increases corrosion of vessels and fittings. The introduction of

cadmium to sewage and fertilizer from various sources leads to substantial human expression of cadmium. The health implication of cadmium exposure is absorbed by man's cousins, exposed to cadmium (which is discharged and reused by kidneys), so expressions are mainly concerned with the toxicity of the kidneys and are still subject to trial. The development of human civilization has given serious questions to the safe use of ground water for domestic applications[4].

1.2 Control measures of water pollution

The purification process to be followed is depending upon the impurities in the water. The commonly available methods are as follows.

Primary treatment: Screening, Sedimentation, Coagulation, filtration and water softening

Secondary treatment (Biological treatment): Based on the principle it is classified as attached trickling filter process, growth culture system, rotating biological contactor, suspended growth culture system, activated sludge process and oxidation ditch etc.,

Tertiary treatment: Electrolysis, Reverse osmosis, nitrification, De-nitrification, activated carbon treatment ion exchange etc.

1.2.1 Advantage of adsorption technique

The various methods are available for elimination of metal ions from industrial wastewaters such as anaerobic degradation, aerobic and membrane separation using various chemical oxidation, microorganisms, reverse osmosis, flocculation and coagulation. The adsorption technique, based on the transmission of pollutant pollution to the solid phase, is known as one of the efficient and general sewage treatment methods, extra quantity of chemical usage and lack of effective reduction. The adsorption

technique, based on the transmission of pollutant pollution to the solid phase, is known as one of the most efficient and public sewage treatment methods.

This is the best method compared to other solute reduction techniques compared with other systematic sewage treatment that initial cost, simplicity of design, ease of operation and non-toxic waste materials. Expenditure efficiency, availability and adsorptive properties are a key factor in removing organic compounds from waste products, using non-toxic and green adsorbent with huge need for large surface and reactive surface atom.

1.2.2 Adsorbent

Adsorbents are porous materials that contain many miniscule internal pores. The familiar industrial adsorbents are silica gel, alumina and activated carbon due to it contains massive surface zones per unit weight. Activated carbon is produced by heating the organic waste to granules of carbon. Animal waste and agricultural waste are the common source. Typical surface areas are 300 to 1500 m^2/g. Silica gel is a matrix of hydrated silicon dioxide. Silica is used to separate hydrocarbons. Typical surface areas are 300 to 900 m^2/g. The active alumina is usually used to eliminate mercaptans from hydrocarbons and fluorides.

Typical surface areas are 200to 400 m^2/g. The adsorbent such as zeolite, carbon molecular sieve, bone char, iron and manganese coated sand, hydrated ferric oxide and activated bauxite other synthetic media are also widely used. Activated carbon is the most useful advertising by highly developed porosity, surface chemistry characteristics, the highest level of surface efficiency and more surface area. However, due to high preparation cost, these products are more precious than other adsorbents. There are a

number of studies in the improvement of low rate adsorbent, which are given in Table 1.1 using waste materials for that purpose.

Adsorbent preparation costs can be minimized by choosing cheap raw materials or using a proper production system; nevertheless, It is a challenge for producing carbon that has more specific properties, given the size of the hole given, using low cost raw materials at low temperatures (less energy cost). Therefore, it is essential to find environmental protection, finding suitable low-cost raw materials that are economically attractive from their contribution to minimize waste costs.

Table 1.1 List of low cost adsorbents used in waste water treatment[5, 6]

Bagasse	Red mud
Bagasse fly ash	Rubber waste
Bark	Rice hulls
Coal	Refinery waste
Coconut shell	Scrap tires
Corn cobs	Slag
Clay minerals	Sludge
Fuller's earth	Sunflower seeds
Fertilizer waste	Slurry Spent Fuller's earth
Ferrocyanides	Tea leaves
Fly ash	Old tires
Lignin	Wheat straw
Lignite	Wood
Lampblack	Wool waste
Leather waste	Zeolites
Olive stones	

1.2.3 Low cost Activated carbon

Activated carbons, a widely used adsorbent in industrial practices are composed of a micro porous, homogenous structure with high surface area. The process of producing high-effective activated carbon production in the developing world is not fully studied. Also activated carbon regeneration has many problems. Nowdays, the current trade-off carbon has abundant interest in finding cheap and useful alternatives. Effective and cost effective carbon exploration can subsidize to environmental sustainability and benefits for future profitable applications.

Furthermore, there are several problems with the regeneration of used activated carbon. Nowadays, there is a great interest in finding inexpensive and effective alternatives to the existing commercial activated carbon. Exploring effective and low-cost activated carbon may contribute to environmental sustainability and offer benefits for future commercial applications. The costs of activated carbon produced from biomass materials are very less compared to the cost of commercial activated carbon. Waste materials are used to produce adsorbent in the recent past include waste trees, bagasse, coir pith, orange peel, coffee husk, rice hulls, coconut tree, pine cone, hazelnut husks, sunflower seed hull, oil palm shell, pine-fruit shell and Coconut husk[5, 6, 7] .

1.2.4 Activated Carbon

Activated carbon is a form of charcoal that has been activated by oxygen to produce millions of small holes between the carbon skeleton. Adsorbent can be produced in plant biomass with a low inorganic and more carbon content. The well-known carbon productions are from parts of trees, coconut shell and bituminous coal and charcoal etc., the carbon derived from them are easily implemented to produce high efficient adsorbent. The activation process, the individual internal pores structure is created, which enabled the carbon to provide its excellent adsorptive properties.

Activated carbons have a number of unique characteristics such as chemical properties, large internal surface area and good accessibility of internal pores. According to IUPAC definitions three groups of pores can be identified.

Macropores (above 50nm diameter), Mesopores (2-50 nm diameter), Micropores (Under 2 nm diameter), Micropores are generally contribute to a large part of the internal surface area. Macro and Mesopores are generally considered highways in carbon particles and are important for dynamical movement. An unpleasant pore structure of adsorbent production is achieved by combining the proper ingredient and appropriate activation processes.

1.2.5. Preparation of Activated Carbon:

Major carbon consisting substances can be converted to activated carbon. The final characteristics of carbon are significantly dependent on the nature of the initial substance. A number of practices have been developed for activated adsorbent in the past century. However, most processes contain pyrolysis of initial confectionery, followed by controlled oxygenation. The aim of the oxidant is to activate carbon.

Pyrolysis:

Pyrolysis process involves heating of source materials in the temperatures from 600 to 900 ºC without air condition. This method is used to removal of non-carbon element such as nitrogen, sulphur and hydrogen. The low molecular weight volatiles are first removed in the evaporation, followed by light aromatics and finally hydrogen gas, resulting in a constant carbonation charcoal. The remaining carbon atoms are divided into compressed sheets of a brief ring with a randomly cross-linked system. The combined arrangement of these aromatic enrobe is irregular and leaves free interstices between the enrobe, which may be filled with the tarry materials. To remove these tarry

materials, activation process is carried out. It also extend the diameters size of the pores, which were created during the carbonization process and producing new porosity.

Activation:

The basic properties of carbon are established during pyrolysis and are continuously designed according to oxidation.During this process, the oxidizing agent increasingly erodes the internal surfaces of the carbon, develops an extensive and fine network of pores in the carbon and changes the atoms lying on the surface to specific chemical forms which may have selective adsorption capabilities. This activation step is done by two methods physical activation or chemical activation.

Physical activation:

Physical activation or partial atmosphere typically uses oxygen, such as steam, carbon dioxide, air or mixture of gases between 750 and 1100^{o}C at maximum temperatures. Effects of chlorine, sulphur, steam, sulphur dioxide, ammonia and other substances are rarely used. Gasification of carbon substances with steam and CO_2 is caused by following endothermic reactions.

$$C + H_2O \longrightarrow H_2 + CO$$

$$C + CO_2 \longrightarrow 2CO$$

The reaction of steam with carbon is accompanied by the water gas formation reaction, which is catalyzed by the carbon surface as,

$$CO + H_2O \longrightarrow CO_2 + H_2$$

Since carbon reaction with steam and carbon dioxide is the reaction tropical, requiring external heat reactions to operate and maintain reaction temperature. The activation process is handled to produce desired properties. Operational temperature,

steam and CO_2 flow rates control the growth of hole, in turn affects the amount of whole volume dispensations and the function of activated carbon.

Chemical activation:

Chemical activation is usually carried out by stimulating raw or carbonated raw materials with activating agent between 400 and 800° C without oxygen. The most commonly used agents are H_3PO_4, HCl, H_2SO_4, alkalis KOH and NaOH, $ZnCl_2$ and alkaline metallic compounds. H_3PO_4 and KOH are used for the function of lignocellulose substances. H_3PO_4 is the most preferred processing agent due to its low environmental impact compared to KOH. The resultant activated carbon wash is then dried up to the weight and given to the desired extent. Activated carbon prepared by chemical activation generally exhibit much more open structure and bottle shape, ideal for larger molecules.

Combination of physical and chemical activation:

The chemical and physical activation can be used to prepare granulated activated adsorbent with a very great surface area and porosity adequate for certain specific applications such as gas storage gasoline and vapour control etc. Activated carbons of these types have been reported using lingo cellulosic precursors chemically activated with H_3PO_4 and KOH and later activated under a flow of CO_2. Uniform, medium-size micro porosity and surface areas above 3600 m^2/g are obtained with this mixed procedure.

Advantages of chemical activation over physical activation:

The main advantage of chemical activation is that it operates normally at lesser temperatures and in a short time than physical activation. Carbon productivity can be attained by increasing the speed of the chemistry process. Because chemicals are used with dehydrogenation properties, which prevent tar formation and reduce the production

of volatile products.Using H_3PO_4, the activation of the wood can be performed at a temperature of less than 500^oC, while Potassium hydroxide activation was carried out from 600^oC to 709^oC. According to carbonization, the formation of porosity, which is accessible when washing and removing chemicals. Consequently, the change of the chemical / precursor rate allows the repair of the meat in the final processed carbon. However, the most important drawback of chemical activation is to combine contaminants from the activation agent that can affect the chemical properties of activated carbon. Another disadvantage is the investment required for the component for improving chemical used for impregnation.

1.2.6 Applications of activated carbons[8]

- Gold purification
- Metal extraction
- Water purification
- Medicine
- Gas purification
- Sewage treatment plant
- Air filter in gas
- Filter masks
- Filter in compressed air and many other applications.

Environmental applications

Carbon as adsorbent, It has various application for removing impurities from wind (or) water both in the fields and industrial practices such as ground water remediation, portable water filtration, spill cleanup, air purification, dry cleaning, volatile organic compounds, gasoline dispensing operation and other processes.

Medical applications:

The adsorbent is used to analysis poisoning and over dosages following viva voce investigations.

Fuel Storage:

The activated carbon used to store natural gas and H_2 gas.

Gas purification:

Filters along with adsorbents are generally used in gas refinement and compressed air to remove oil vapour, odour and other C_xH_y from the air.

Distilled alcoholic beverage purification:

Carbon filters are used to filter whiskey and vodka, which are organic contaminants that affect the taste, odours and colours.

Chapter II

Objective and Scope of the Present Study

Chapter – II

Objective and Scope of the Present Study

Water pollution is an important problem in the world environment. This occurs if pollutants are either point or non-point sources discharged without sufficient treatment in water stations. Water pollution affects the life and plants of these waterways, but affects the soil.

A number of methods have been improved to remove mineral resources and organic products from the aqueous media. The methods include precipitation, electro dialysis, evaporation, electrolysis recovery, ion exchange, solvent extraction, cementation, reverse osmosis and adsorption etc.

Among these, adsorption practice is greater to any other method by virtue of its low initial cost, squat energy requirement, easiness of design and possibility of reprocessing the expended carbon via regeneration.

Activated carbon has been justified to be one of the better among various adsorbents. A recent study is the production of adsorbent from waste plant biomass and evaluating their potential as adsorbent.

With these background the present investigation is carried out with the following objectives

- To develop activated carbons from *Delonix Regia* pods using microwave radiation experimental design method.

- To optimize various experimental parameters to get an efficient carbon as an adsorbent.
- To determine the various physico-chemical properties of the activated carbon such as particle size, surface area, pore size, fixed carbon, bulk density, moisture content, zero point charge (pH_{zpc}), Infrared spectrum, XRD pattern and the SEM image.
- To study the adsorbing behaviour of the prepared carbon with the adsorbates such as heavy metals Cr(VI) ion, Ni(II) ion and Cu(II) ion.
- To study the effect of adsorption process limits such as initial pH, adsorbent dosage, contact time, initial adsorbate concentration and temperature on the adsorption of chosen adsorbates by systematic batch mode sorption studies.
- To study the dynamic aspects of the adsorption practice and intra particle diffusion using different kinetic models such as Legergren, Ho and Weber Morris.
- To fit the equilibrium data with four different adsorption isotherms to understand the nature of adsorption.
- To evaluate the thermodynamic parameters such as Free energy change, Entropy change and Heat of the adsorption practice to understand the adsorption mechanism.
- To justify the proposed mechanism using SEM, FTIR, EDAX and XRD analytical techniques.
- To find out suitable desorbing agents to recover the adsorbate sorbed and the re-use of the sorbent.

Scope

2.1 Chromium – Cr (VI) ion

Chromium is a lustrous, brittle, hard metal. Its colour is silver-gray and it can be highly polished. It does not tarnish in air, when heated it borns and forms the green chromic oxide. Chromium is unstable in oxygen, it immediately produces a thin oxide layer that is impermeable to oxygen and protects the metal below.[9]

Applications

Chromium main uses are in alloys such as stainless steel, in chrome plating and in metal ceramics. Chromium plating was once widely used to give steel a polished silvery mirror coating. Chromium is used in metallurgy to impart corrosion resistance and a shiny finish; as dyes and paints, its salts colour glass an emerald green and it is used to produce synthetic rubies; as a catalyst in dyeing and in the tanning of leather; to make molds for the firing of bricks. Chromium (IV) oxide (CrO_2) is used to manufacture magnetic tape.

Chromium in the environment

Chromium is mined as chromite ($FeCr_2O_4$) ore. Chromium ores are mined today in South Africa, Zimbabwe, Finland, India, Kazakihstan and the Philippines. A total of 14 million tonnes of chromite ore is extracted. Reserves are hestimated to be of the order of 1 billion tonnes with unexploited deposits in Greenland, Canada & USA.

Health effects of chromium

People can be exposed to chromium through breathing, eating or drinking and through skin contact with chromium or chromium compounds. The level of chromium in air and water is generally low. In drinking water, the level of chromium is usually low as well, but contaminated well water may contain the dangerous chromium(IV),

hexavalent chromium For most people eating food that contains chromium(III) is the main route of chromium uptake, as chromium(III) occurs naturally in many vegetables, fruits, meats, yeasts and grains. Various ways of food preparation and storage may alter the chromium contents of food. When food in stores in steel tanks or cans chromium concentrations may rise.

Chromium(III) is an essential nutrient for humans and shortages may cause heart conditions, disruptions of metabolisms and diabetes. But the uptake of too much chromium(III) can cause health effects as well, for instance skin rashes.

Chromium(VI) is a danger to human health, mainly for people who work in the steel and textile industry. People who smoke tobacco also have a higher chance of exposure to chromium.

Chromium(VI) is known to cause various health effects. When it is a compound in leather products, it can cause allergic reactions, such as skin rash. After breathing it in chromium(VI) can cause nose irritations and nosebleeds.

Other health problems that are caused by chromium(VI) are:

Upset stomachs and ulcers, Respiratory problems, Weakened immune systems, Kidney and liver damage, Alteration of genetic material, Lung cancer and finally death.

The health hazards associated with exposure to chromium are dependent on its oxidation state. The metal form (chromium as it exists in this product) is of low toxicity. The hexavalent form is toxic. Adverse effects of the hexavalent form on the skin may include ulcerations, dermatitis, and allergic skin reactions. Inhalation of hexavalent chromium compounds can result in ulceration and perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis,

bronchospasms and edema. Respiratory symptoms may include coughing and wheezing, shortness of breath, and nasal itch.

Carcinogenicity-

Chromium and most trivalent chromium compounds have been listed by the National Toxicology Program (NTP) as having inadequate evidence for carcinogenicity in experimental animals. According to NTP, there is sufficient evidence for carcinogenicity in experimental animals for the following hexavalent chromium compounds; calcium chromate, chromium trioxide, lead chromate, strontium chromate, and zinc chromate.

Environmental effects of chromium

There are several different kinds of chromium that differ in their effects upon organisms. Chromium enters the air, water and soil in the chromium(III) and chromium(VI) form through natural processes and human activities.

The main human activities that increase chromium(VI) concentrations are chemical, leather and textile manufacturing, electro painting and other chromium(VI) applications in the industry. These applications will mainly increase concentrations of chromium in water. Through coal combustion chromium will also end up in air and through waste disposal chromium will end up in soils.

Most of the chromium in air will eventually settle and end up in waters or soils. Chromium in soils strongly attaches to soil particles and as a result it will not move towards groundwater. In water chromium will absorb on sediment and become immobile. Only a small part of the chromium that ends up in water will eventually dissolve.

Chromium(III) is an essential element for organisms that can disrupt the sugar metabolism and cause heart conditions, when the daily dose is too low. Chromium(VI) is mainly toxic to organisms. It can alter genetic materials and cause cancer.

2.2 Nickel - Ni(II) ion

A basic Ni is insoluble in water. However, nickel compounds may be water soluble. $NiCl_2$ is highly water soluble; 553 g / L at 20ºC, 880 g / L at 99.9ºC. $NiCO_3$ is water soluble at 90 mg / L, while other nickel compounds such as NiO, NiS and $Ni(CO)_4$ are insoluble[10].

Nickel from point and non-point sources can expiration up in water. Widespread nickel emissions may be steam from power plants, waste combustion and metal industries. The nickel is directly disposed of by various industries into surface water. It is used in alloys as a catalyst and pigment in nickel-cadmium batteries to purify heavy metal contaminated surface water. Uncontaminated nickel is repeatedly used as a protecting coating in steel and copper materials. Nickel-copper alloys have been used in coins. Other alloys are cast-off in the making of kitchen products, jewellery and turbines. Nickel can be used as an anti-corrosive drug. $Ni(CH_3CO_2)_2 . X H_2O$ is used as a caustic in textile printing, and nickel carbonate is used as a catalyst for fatty hardening and ceramic paint production as nickel chloride. $Ni(CO)_4$ is a product of nickel purification, used in various manufacturing processes.

Nickel compounds are also applied in agriculture. Phosphate manures contain hints of nickel. Nickel is often existing in agricultural soils situated near fossil fuel industries. Organic substance frequently adsorbs nickel, causing coal and oil to contain traces of the element. Nickel compounds may also be found in sludge, and in slags and fly ashes from waste incinerators.

Environmental effects of nickel in water:

Nickel is a food that many organisms need, but can be toxic in large quantities. Metal nickel and some other nickel alloys are teratogenic and carcinogenic to mammals. Nickel concentrations in plants are generally 1 μg / g, and concentrations above 50 μg / g are toxic. Tea has an unusual nickel content of 7.6 mg / kg dried leaves. Nickel causes growth restrictions on algae at concentrations ranging from 0.5 to 10 ppm. Fishes are less susceptible to nickel, but this varies between species. The LD50 for Daphnia hyaline is 1.9 ppm for 48 hours. Chronic nickel toxicity for Daphnia magna is between 30-150 ppb. The LD50 for sea crabs ranges from 150 to 300 ppm. The nickel concentrations of living organisms from predominantly aquatic organisms were found to be 0.6–36 ppm (dry mass). Nickel accumulation in rats occurs mainly in the lungs, where the concentration is 4-40 times higher than that in other organs.

Most plants have relatively high nickel broad-mindedness, but many types of grains are generally more disposed. These grains may die when water with a nickel concentration of 40 ppm is added. All five naturally occurring nickel isotopes are stable. The other eight isotopes are considered unstable.

Health effects of nickel in water:

The human body contains about 10 mg of nickel. Nickel is a food that many organisms need, so it may be of importance to humans. The human food requirement is estimated at only 5 μg, which is the result of 150 μg intake. Nickel may have a function in the conversion of urea to ammonia by urease. Nickel cannot be reabsorbed in the digestive gland until it becomes complex.

Nickel breath postures a superior danger than nickel in water. It can origin lung cancer or nasal tumors. Nickel substitution of zinc and magnesium ions in DNA-

polymerase can cause nickel cancer. These observations were made mainly in the nickel-working staff. Usually smoking alone can cause this problem.

A lot of people grow dermatitis upon skin contact with nickel. The same goes for nickel solutions. Nickel allergies are more common amid women than amid men. Nickel compounds may be toxic in high concentrations, but these are often water insoluble, limiting potential harm. For example, Ni $(CO)_4$ is water insoluble, but is toxic and cancer-causing.

2.3 Copper- Cu (II) ion [11]

Copper is a reddish metal with a heavy crystal structure around the face. It imitates red and orange light and engrosses other frequencies in the visible spectrum due to its bandwidth, so it is a good red color. It is compatible, durable and an excellent conductor of both heat and electricity. It is softer than zinc and can be polished to a brighter finish. This is seen with silver and gold in the group IB of the schedule. Copper has low chemical reactivity. In wet air it gradually forms a green surface big screen called patina. This coating protects the metal from further occurrences.

Applications:

Used for most copper electrical devices (60%); Building, slating and sanitation (20%); Engineering machinery, heat exchangers (15%) and amalgams (5%). The longest-established copper alloys are bronze, brass (a copper-zinc alloy), copper-tin-zinc, which was strong sufficient to make rifles and cannons, and was called pistol metal, copper and nickel, known as capronical, for metal of low value.

Copper in the environment:

The world's copper production is still on the rise. This basically means more and more copper ends up in the environment. With the removal of copper-rich wastewater,

copper-contaminated rivers are flooding their banks. Copper enters the mid-air, mainly through the release of remnant fuels during burning. When it starts to rain, the copper in the air stays there for a good while before it settles. Then it mainly ends up in the soil. As a result, there may be excessive amounts of copper in the soil after copper migrates from the air.

Copper can be released to the environment through natural resources and human activities. Examples of natural resources include airstream blowing dust, rotting vegetation, wildfire and sea spray. Mining, metal manufacture, timber manufacture and phosphate nourishment invention are anthropological activities that underwrite to copper release. Copper is frequently found near excavating, industrial systems, landfills and waste discarding.

Most copper alloys will settle and bind to residue or earth elements. Solvable copper alloys pose an excessive danger to human health. Generally water soluble copper alloys occur in the surroundings afterward discharge in cultivation.

Health effects of copper:

Copper can be found in many types of food, water and air. Because of this we absorb the best amount of copper by eating, drinking, and breathing every day. Copper is a trace element essential for human health, but copper can cause great health problems. The concentration of copper in the air is usually very low, making it less likely to expose copper through breathing. But people living near smelters that process copper ore into metal are suffering this kind of exposure.

Prolonged exposure to copper can cause impatience to the nose, mouth and eyes and can cause headaches, stomach pain, faintness, nausea and diarrhea. Intentional

overdose of copper can cause kidney damage, liver and even death. Whether copper is carcinogenic is yet to be determined.

There are scientific articles suggesting a link between prolonged exposure to high concentrations of copper and the decline in intelligence in adolescents. Industrial exposure to copper, dust or mist can cause metallic smoke injury with atrophic changes in the nasal mucous membranes. Chronic copper poisoning causes Wilson's disease, which is characterized by brain damage, liver cirrhosis, kidney disease, demyelination and copper deposition in the cornea.

Environmental effects of copper:

When copper split ends up in the soil it binds powerfully to minerals and organic matter. As a result, it does not enter the groundwater and does not travel far after release. Copper can travel beyond in surface water, which is deferred in slag elements or free ions.

Copper does not break into the environment, which is why it can accumulate in plants and animals when found in the soil. Only a limited number of plants survive in copper-rich soils. That is why there is not much plant diversity near the copper removal industries. Copper is a serious threat to agricultural land production due to the effects of plants. Despite this, copper-containing fertilizers are still used.

Copper may interfere with soil function because it negatively affects the function of microorganisms and earthworms. As a result, the decay of organic matter can be drastically reduced. When the soil of the fields is contaminated with copper, the animals absorb concentrations that are injurious to their health. Sheep are mainly susceptible to copper toxicity for the reason that the properties of copper are manifested at very low concentrations.

2.4 Adsorbent - *Delonix Regia pod*

Delonix regia belongs to Royal Poinciana or flamboyant, a member of the bean family produces brown woody seed pods.

Plant information

Scientific name: *Delonix regia* (Bojer ex Hook.) Raf.

Common name: flamboyant

Known hazards: Roots can damage nearby building foundations, paving and drains; the branches of the tree are brittle and can fall without warning.

Taxonomy

Family: Fabaceae - Caesalpinioideae

Genus: *Delonix*

Species: *D. regia*

Class: Equisetopsida

Subclass: Magnoliidae

Delonix regia Tree

Delonix regia pods

Delonix regia is a very distinctive tree with large, bright red flowers. The species name is consequent from the Greek words *delos* (meaning conspicuous) and *onyx*,

meaning claw, denoting to the presence of the spectacular flowers. The tree is generally cultured in the *tropics* and subtropics together with Madagascar, for its ornate value but is under increasing threat in its natural habitat due to habitat obliteration.

Compared with preparation of activated carbon using conventional heating system techniques, microwave heating system has the supplementary benefits as follows: higher heating system rates, interior heating system, greater controller, selective heating system of the heating process, no unswerving contact between the heating source and heated materials and reduced equipment size and waste. Microwave action has also been start to produce corresponding changes in the textural and chemical properties of the activated carbon but over a distant shorter time of period. Henceforth in the current study, microwave radiation used for the production of activated carbon.

Delonix Regia trees are distributed elsewhere. Their pods are merely a waste material.

The present endeavour may reveal the applicability of chosen plant biomass to prepare the activated carbon and the adsorption mechanism of chosen adsorbates with kinetics and thermodynamic aspects.

The above study would definitely be helpful in the identification of much needed low cost materials in the treatment of wastewater. The mechanic aspects will serve as a tool for effective handling of such materials.

Chapter III

Review of Literature

Chapter –III

Review of Literature

3.1 Review of literature on Cr(VI) ions

Khadka Deba Bahadur and Mishra Paramatma[12] examined the potential and effectiveness of activated carbon derived from carbonization of sugarcane bagasse (Saccarhum officianrum) for adsorptive removal of Cr(VI) by adsorption technique. Activated carbon was prepared by subjecting the raw sugar cane bagasse to chemical modification using concentrated sulphuric acid in 500 g/L of ratio of adsorbent weight to volume of concentrated sulphuric acid (H_2SO_4). Boehm method was used to estimate oxygen containing functional groups. The acidic functional groups, specific surface area and adsorptive capacity all greatly increased with chemical modification. The batch removal of Cr(VI) from aqueous solution was investigated. The maximum adsorption capacity of Cr(VI) was found to be 131.68 mg/g at optimum pH of 1 at the laboratory temperature. The equilibrium time for Cr(VI) was found to be 180 minutes. The kinetics of adsorption was found to follow pseudo second order model. Both Langmuir and Freundlich adsorption isotherm could be used to describe adsorption isotherm but the Langmuir isotherm was found to be in good agreement with experimental data.

Gottipati Ramakrishna and Mishra Susmita[13] investigated the response surface methodology (RSM) involving D–optimal design to optimize the adsorption process of trivalent Chromium Cr(III) and hexavalent Chromium Cr(VI) from aqueous solutions by commercial activated carbons. From the analysis of variance (ANOVA), the significance of various factors and their influence on the response were identified. The regression coefficients (R^2) of the models developed and the results of validation experiments

conducted at optimum conditions for the removal of both Cr(III) and Cr(VI) indicated that the predicted values are in good agreement with the experimental results. Contour and response surface plots were used to determine the interaction effects of main factors and optimum conditions of process, respectively for the simultaneous removal of Cr(III) and Cr(VI).

Supriya Singh et al[14] carried out the removal of Chromium(VI) ion using biosorbent which is prepared from Mangiferaindica bark. Application of the Langmuir isotherm to the systems yielded maximum adsorption capacity of 19.64 mg/g at 303 K in 50 mg/L Cr(VI) solution of pH- 7 and biosorbent dose of 1g/L. The adsorption of Chromium (VI) was found to be maximum up to 80.2% at low values of pH – 2 having Cr(VI) concentration of 50 mg/L and adsorbent dose of 1g/L. The contact time of 60 min resulted in the 67% adsorption of metal in 5mg/L solution using adsorbent dose of 1g/L. FTIR spectra was also carried out to correlate the adsorption sites of biosorbent and hexavalent Chromium.

Kulkarni Sunil et al[15] demonstrated the use of activated carbon and sawdust for removal of Chromium from the synthetic effluent in batch operation. During the studies, both the adsorbents were found to be effective in Chromium removal. The percentage adsorption was found to be 98 to 99 percent in both the adsorbents. The optimum values of adsorbent dose, pH and initial adsorbate concentration were observed to be 0.2 gram/100 ml, 2 and 10 mg/L respectively and 0.35 gram/100ml, 4 and 10 mg/L respectively for sawdust.

Gopalakrishnanet al[16] prepared an adsorbent from *Azadirachta indica* (Neem) leaf powder for the removal of Chromium(VI) ion through adsorption. The adsorption behaviour was found to follow the Freundlich Adsorption Isotherm.

Biswajit Das et al[17] made a basic investigation on the adsorption Cr(VI) ions from aqueous solution by *Pistiastratiotes* biomass under batch mode. A biosorbent dosage of 5 g/L showed a maximum metal uptake capacity (qe) of 7.24 mg/g for an initial metal ion concentration of 10 ppm. Sorption equilibrium time was observed as 15 min. The equilibrium adsorption data were analyzed using the Freundlich, Langmuir, Dubinin-Radushkevich and Tempkin adsorption isotherm models. The kinetics of Chromium (VI) ion was discussed using pseudo first order, pseudo second order and intra particle diffusion models. It was shown that the adsorption of Chromium (VI) ions could be described by the pseudo-second order kinetic model. Thermodynamic parameters such as Gibbs free energy (ΔG^o), the enthalpy (ΔH^o) and the entropy change of sorption (ΔS^o) have also been evaluated and it has been found that the adsorption process was spontaneous, feasible and endothermic in nature. Desorption experiments with 2 M NaOH inferred the reusability of the adsorbent.

The pods of *Delonix regia* were used in preparing low cost activated carbon/ adsorbent and in the removal of hexavalent Chromium from aqueous solution by Renuga Devi et al[18]. The kinetic of the process has been calculated using Lagergren's first order equation. The results demonstrated that the carbon derived from the *Delonix regia* pods can be used as an efficient adsorbent for the removal of toxic Cr(VI) from aqueous solution. The adsorption of Cr(VI) was found to be time and concentration dependent. Maximum Cr(VI) removal (≈ 66%) was achieved with just 100 mg of the adsorbent with an optimum contact time of 180 minutes at pH~4 when the initial concentration of Cr(VI) solution was 0.06 mg/L. Confirmation of data to the Lagergren's rate equation indicated the first order kinetics.

Salah Abdel Waneesa et al[19] studied the adsorption potential of activated carbon and bentonite for the removal of Cr(VI) ions from wastewater. The adsorption process

has been fitted into pseudo-second order kinetic models. Langmuir and Freundlich adsorption isotherm models were applied to analyze adsorption data and both were found to be applicable to this adsorption process. Thermodynamic parameters, e.g., ΔG^o, ΔS^o and ΔH^o of the on-going adsorption process have also been calculated and found that the sorption process is endothermic. Finally, it can be seen that bentonite was found to be more effective in the removal of Cr(VI) than in activated carbon under the same experimental conditions.

The removal of hexavalent Chromium via adsorption on multiwalled carbon nanotubes was investigated by Mina Gholipour et al[20]. The batch experiments were conducted at 3 different temperatures (290 K, 300 K and 310 K) and showed that Cr(VI) ion removal obeyed pseudo-second order rate equation. Rate constant (K) values at three temperatures, pre-exponential factor and adsorption activation energy (E) were also evaluated. The sorption data fitted well with Freundlich isotherm adsorption model. Thermodynamic parameters such as Gibbs free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) for Cr(VI) ion adsorption were estimated and results suggest that the adsorption process is spontaneous and endothermic.

Mina Gholipour et al[21] studied the removal of hexavalent Chromium via adsorption on commercial granular activated carbon (GAC). The batch experiments were conducted at three temperatures (290 K, 300 K and 310 K) and the results showed that Cr(VI) ion removal kinetics obeys pseudo second order rate equation. Equilibrium studies showed that the experimental data fitted well with Langmuir isotherm adsorption model. Thermodynamic parameters were also determined and the results suggested that the adsorption process was spontaneous and endothermic. The reversibility of Cr(VI) ion adsorption and repeated availability performance of the adsorbent, was investigated by desorption process. In addition, Artificial Neural Network (ANN) was utilized to

simulate the experimental data. The results showed that the training step of the network was successful and therefore the simulation could be applied to predict hexavalent Chromium removal with high accuracy.

Ismaeel Ahmed et al[22] studied the adsorption of hexavalent Chromium from aqueous medium by rice husk activated carbon prepared by physical method. Optimum results were found to be 150 minutes, 20 mg/L, 2 and 5g/L for contact time, initial concentration, pH and adsorbent dose respectively. At the optimal condition the adsorption of hexavalent Chromium was found to be 95.2%.

3.2 Review of literature on Ni (II) ions

Priya .M.K et al[23] investigated the removal of heavy metals Cu(II) and Ni(II) metal ions from aqueous solution by using chemically activated phosphoric Acacia nilotica leaves (PAN) carbon. Adsorption of Ni(II) is more effective than adsorption of Cu(II) from aqueous solution by using PAN. PAN was characterized by using FTIR, SEM and XRD. Equilibrium, sorption, isotherms and kinetics are investigated. The effect of initial pH, contact, initial metal concentration and adsorption dosage of Cu(II) and Ni(II) onto PAN have been investigated. The Langmuir and Freundlich adsorption models were applied to describe the isotherms and isotherm constants. Adsorption isothermal data could be well interpreted by the Langmuir model. The rate of adsorption was found to be confirmed by pseudo-second-order kinetics with a good correlation of R^2 value [Ni(II) 0.988 and Cr(II) 0.971].Desorption studies of metals using PAN also was conducted. These results suggest that Acacia nilotica leaves heavy low-cost adsorbent potential for the heavy metal removal from waste water.

Samarghandi M.R et al[24] studied the adsorption of divalent nickel from aqueous solutions on modified holly sawdust was studied at varying contact times, pH, initial

divalent nickel concentrations and adsorbent dose. Results showed the removal efficiency by increasing of pH increased and decreased with initial nickel divalent concentration. By increasing pH from 2 to 12 (equilibrium time= 240 min, adsorbent dose= 0.6g/100 ml, divalent nickel concentrations= 60 mg/L), the removal efficiency increased from 17.47 % to 81.76 %. Also removal efficiency was decreased from 98 % to 19.3 % by increasing of initial divalent nickel concentrations from 20 mg/l to 100 mg/L. Also the results showed the removal efficiency was increased by increasing of adsorbent dose and contact time. By increasing of adsorbent dose from 0.2 g/100CC to 1 g/100CC, the removal efficiency increased from 32.78% to 99.98%. The removal efficiency increased from 34.7% to 83.67% by increasing of contact time from 5 min to 240 min. Experimental equilibrium and kinetics data were fitted by Langmuir and Freundlich isotherms and pseudo-first-order and pseudo-second-order kinetics models, respectively. The results show that the equilibrium data follow Langmuir isotherm and the kinetic data follow pseudo-second-order model. The obtained maximum adsorption capacity was 22.47 mg/g at a pH 7. The results show that the modified holly sawdust can be used for the treatment of aqueous solutions containing nickel as a low cost adsorbent.

Vijayakumaran .V et al[25]explored the removal of Ni(II) ions from aqueous solution on ODINA WODIER(OW) bark carbon. Batch mode experiments were conducted such as adsorbent dose, initial Ni(II) ions concentration, effect of solution PH, contact time and temperature. The Freundlich and Langmuir adsorption models were applied to describe the equilibrium isotherms. From these experimental data and R_L value indicate the adsorption process is favourable. The thermodynamic parameters such as ΔH°, ΔS° and ΔG°were evaluated and the adsorption process was physical adsorption. The pseudo-first-order, pseudo-second-order, Elovich kinetic models and the intra-particle diffusion model were used to fit the experimental data by using linear regression

analysis method. The high regression coefficient (R^2) values indicate the fitness of the model. The kinetic of this process having high regression correlation coefficient (R^2) were pseudo-second-order and intra-particle diffusion models. The adsorption mechanism is proved by FT-IR, XRD and SEM images. The OWbark carbon has high adsorption capacity and adsorption rate for the removal of Nickel (II)ions from aqueous solution.

Lokendrasinghthakur et al[26] investigated the activated carbon prepared from tea waste from removal of Cu, Ni and Zn heavy metal ions from aqueous solution. The experiment results showed that maximum removal of Nickel ion by tea waste is 94% and for Copper & Zinc ion are 89% & 90% respectively at optimum condition.

Prabakaran .R et al[27] studied the removal of Ni(II) ions in aqueous solution were investigated by adsorption process on low cost activated carbon prepared from Thespesia Populnea bark(TPC). Batch mode experiment were conducted, such as effect of temperature, pH and initial concentration of metal ion on the biosorption capacities, Kinetics of adsorption and adsorption isotherms have been studied. Also various thermodynamic parameters such as ΔH°, ΔS° and ΔG°were calculated. According to the results, ThespesiaPopulnea bark is recommended as cheapest and available bio adsorbent to removal of toxic metal ions from industrial waste water.

Subasri.S et al[28]exploredan adsorbent prepared from Corchorus olitorius L Leaves, by acid treatment was tested for its efficiency in removing Ni(II) metal ion. The process parameters studied include agitation time, initial concentration, adsorbent dose, pH and temperature. The adsorption followed second order reaction equation and the rate is mainly controlled by intra-particle diffusion. Freundlich and Langmuir isotherm models were applied to the equilibrium data. The adsorption capacity (Q_m) obtained from

the Langmuir isotherm plot at an initial pH of 6.5 and at 30, 40, 50, 60 ± 0.5 °C. The influence of pH on Ni(II) metal ion removal was significant and the adsorption was increased with increase in temperature. A portion of the Ni(II) ion was recovered from the spent ACONC using 0.1M HCl.

3.3 Review of literature on Cu (II) ions

Jafar and Shajudha[29] studied the use of Adathoda vasica stem as adsorbent to remove Cu(II) from industrial waste water. High grade $CuSO_4.5H_2O$ was used as heavy metal sample. Laboratory experimental investigation was carried out to identify the effect of pH (1.50–5.5), agitation time (30-240 min) varying temperature (30-50°C). Varying biomass quantities (2, 4, 6, 8, 10 g/L) and other co-existing ions were also examined. The adsorption process was tested with pseudo first order– Lagergren equation and first order reversible –Bhattacharya Venkobachar equation. Both Langmuir and Freundlich adsorption isotherm models fitted the experimental data best with regression coefficient $r^2 > 0.95$ for the Cu(II). The adsorption was endothermic and the computation of the parameters ΔG°, ΔH°and ΔS° indicated that the interactions were thermodynamically favorable. The results showed that Adathoda vasica stem carbon (AVSC) was an effective and economical bio-sorbent material for the removal and recovery of heavy metal ions from waste water.

Oyedeji and Osinfade[30]studied the use of coconut husk as a low-cost natural adsorbent for the removal of Cu(II) from simulated industrial waste effluent. The effects of varying adsorbent loadings, pH, contact time, metal ion concentration and temperature of adsorption on the adsorption process were determined. The adsorption of Cu (II) was maximum (92% ± 2.8) at pH range of 5 - 7, metal ion concentration of 50 ppm, temperature of 50°C and 30 minutes. 1 g of the adsorbent material was found to be

optimal for the metal ion; the Freundlich isotherm was found to be suitable for the adsorption of Cu(II).

Okafor etal.[31] also explored the adsorption capacity of Coconut (Cocosnucifera L.) shell for Cu(II) from aqueous solutions. The effect of various operational parameters such as concentration, pH, temperature and sorption time on the adsorption of Cu(II) was investigated using batch process experiments. The authors found that coconut shell (CNS) can be used as a low cost adsorbent for the removal of Cu(II) in aqueous solution containing low concentrations of the metal. The percentage adsorption was found to depend on the concentration of the adsorbent present, the solution pH, temperature and the sorption. The concentration of the metal ion adsorbed increased with increase in concentrations, increase in contact time, increase in temperature and increase in pH. The rate of adsorption of the metal ions by coconut shell was rapid initially but decreased gradually due to the gradual blocking of the initial available uncovered surface area of the adsorbent. Adsorption for the metal ion increased with increase in metal ion concentration because at low concentrations, the active site on the surface of the adsorbent are not completely covered. Kinetic studies showed that the sorption of the metal ions can best be described by both pseudo-second-order and intra-particle diffusion models while the adsorption characteristics of the adsorbent followed the Freundlich adsorption isotherm. The average value of the activation energy of adsorption for CNS was found to be 3.79KJ/mol which implies that the adsorption of Cu(II) on the adsorbent is physical adsorption mechanism.

The efficacy of coconut tree sawdust (CTS) as alternative low-cost biosorbent for the removal of Cu(II) ions from aqueous solutions was investigated by Wiwid et al.[32] Batch adsorption studies were carried out to evaluate the effects of solution pH and initial metal concentration on adsorption capacity. The optimum biosorption condition was

found at pH 6.0, 0.1 g biomass dosage and at 90 min equilibrium time. The adsorption data were fitted to the Freundlich and Langmuir isotherm models. The adsorption capacity and affinity of CTS was evaluated. The Freundlich constant and separation factor values suggest that the metal ion was favourably adsorbed onto biosorbents. The maximum adsorption capacities estimated from the Langmuir isotherm model was 3.89mg/g. The characterisation studies were performed using Scanning Electron Microscope (SEM), Energy Dispersive X-ray Spectrometer (EDX) and Fourier Transform Infrared Spectrometer (FTIR). It was observed that interaction with the metal ions led to the formation of discrete aggregates on the biosorbents surface. The metal ions bound to the active sites of the biosorbents through either electrostatic attraction or complexation mechanism. The presence of functional groups in the biosorbents favoured metal ion binding. The authors concluded that the use of coconut tree sawdust (which is abundantly available at low-cost) will provide a solution to their disposal.

3.4 Review of literature on Adsorbents

Joana et al.[33] reviewed the preparation of activated carbons by reutilizing various types of discarded constituents and also their usage in various aqueous-phase actions and found that conventional and non-conventional wastes can be used to produce activated carbons, that can be pragmatic in various aqueous treatment practices, namely to remove carbon-based pollutants, colorants, unstable organic compounds and dense metals.

David William O'Connell et al.[34] reviewed the contemporary state of research on the use of obviously happening material fiber, its modified forms and potential for the elimination of heavy metals from unused watercourses was studied. Adsorbents were initially evaluated on the source of straight alteration of fiber followed by subsequent transformation of monomers into parasitic backbone. The heavy metal processing capabilities for those modified cellulose products were originate to be important and, in

many cases, comparable between other naturally occurring materials and commercial ion exchange type resins.

Shrivastava V.S. et al[35] investigated activated carbon made since Leucaenaleucocephala seed pods to remove the congo red dye from the runway at room temperature. Congo red addiction depends on pH, initial concentration, adsorbent dose and contact time. Consequently, the Congo Red removal was 91% of the optimal pH at 5. Optimum contact time is 120 minutes, and Lugenena is 2 g / l of lycicapala seedlings. Freundlich and Langmuir equations are used for fibrillation imaging and various isomeram parameters are evaluated. Leucaenaleucocephala follows the ho second order kinetics.

Sachin M .Kanawade et al[36] studied The activated carbon is widely used. Water hyacinth can be a replacement for carbon. MB dye removal on activated carbon in addition to water hyacinth powder from discharge waste. Bonding mechanics and isotherm inspection are interconnected in a variety of situations, contact time, methylene blue concentration. The Freundlich and Langmuir adsorption Systems have been a calculated report of the equilibrium. Finally, the Langmuir model for two trials has found that the test data is more accurate.

Jayaraj, R. et al[37] reviewed the activated carbon (AC) prepared since marine algae was originate to be an efficient adsorbent for Congo red dye for removal since aqueous solution. The AC was prepared since Valoriabryopsis (marine algae) through treatment with conc. H_2SO_4. The surface area of the AC and its properties were studied by scanning electron microscopy (SEM). Adsorptive removal of CR dye from aqueous solution on AC has been premeditated underneath varying conditions of metal ion concentration, agitation time, pH and adsorbent dose to assess the kinetic and equilibrium

parameters.Adsorption equilibrium was establish to be touched in 180 min for 5 to 25 mg/L of CR dye concentrations. The Freundlich and Langmuir isotherms were establish to afford an excellent fitting of the adsorption records. For the Freundlich isotherm, more R^2datas were obtained (0.8460 to 0.6992) for CR dye conc. of 10 to 60mg/L, which designated favorable adsorption of CR dye on marine algae adsorbent. The adsorption capability of CR dye was originate to be 97.77%. The% removal increased with increase in pH from 1 to 5. This adsorbent was establish to be effective and economically.

Jonathan Febriantoa and co-workers[38]reviewed the biosorption of heavy metals, summarized the essential issues and reported that most studies on the biosorption of heavy metal ions by miscellaneous biosorbent types have been directed toward the uptake of single metal ion in preference to multi component systems. In particular, the Freundlich and Langmuir datas were the utmost communal isotherms for correlating biosorption test data, although other isotherms originally established for gas phase applications could also be extended to the biosorption system. In the kinetic model, pseudo-first and pseudo-second-order equations were considered.

Sarabjeet Singh et.al[39] reviewed Explored the use of microorganisms and plant-derived biomass and their potential to be exploited for heavy metal settlement and the survival of Aspergillus niger. Penicilliumchrysogenum, Rhizopus nigricans, Ascophyllum nodosum, Sargassum natans, Chlorella fusca, Oscillatoria anguistissima, Bacillus firmus and Streptomyces sp. have highest metal adsorption capacities ranging from 5 to 641 mg/ g.

Veena Devi et al[40]An adsorbent was prepared by pyrolysis from the coconut shell. It is classified as XRD and SEM. Various physical properties such as bulk density, moisture content, turbulent material content, ash content, hardness, delocalizing power,

phenolic number, iodine number and surface and porosity. The activated carbon used a bond in the removal of chromium from an electroplating industry. Readings have shown that a good bond can be used in chromium removal in energy-efficient carbon power industries.

Hema Krishna and Swamy[41] reported the removal of Cr (VI) ion since aqueous solutions using adsorbent prepared from Papaya Seeds. The optimum values of initial concentration, adsorbent dose of the adsorbate, pH, contact time and particle size were observed to be 150 mg/50 ml, 10 mg/L, 60 min, 2 and 0.6 mm respectively. The equilibrium data obtained were tested using Langmuir, Freundlich adsorption isotherm models and the kinetic data obtained were fitted to lagargren kinetic model.

Ramesh et al[42] studied the adsorption ability of MB dye since aqueous solution onto carbon prepared from *Delonix regia* pods Flame tree pods was examined under different investigational conditions. Consignment mode experiments were lead to assess the potential of the above carbon for the elimination of MB dye since aqueous solution. Equilibrium isotherm studies have been done by variable the following three limits: initial concentration of MB dye solution, adsorbent dose, volume of the dye solution and on the uptake of dye since the solution. Non-linear analysis was used to compare the best-fitting isotherms. The equilibrium statistics attained were close-fitting to Langmuir, Freundlich and Redlich-Peterson isotherm models.

Table 3.1 and 3.2 show the natural materials utilized in the preparation of activated carbon and low cost adsorbents used in wastewater treatment respectively.

Table 3.1 - Few Precursors used for the preparation of activated carbons[43, 44]

Bones	Lampblack	Corn cobs	Potassium ferro cyanide residue
Bagasse	Leather waste	Distillery waste	Rubber waste
Barks	Municipal waste	Fuller's earth	Rice hulls
Beat-sugar sludges	Molasses	Fertilizer waste slurry	Refinery waste
Blood	Nut shells	Fish	Reffination earth
Blue dust	News paper	Fruit pits	Scrap tires
Coal	Oil shale	Graphite	Sunflower seeds
Coffee beans	Olive stones	Human hairs	Spent Fuller's earth
Coconut shell	Petroleum acid sludge	Jute stick	Tea leaves
Coconut coir	Pulp-mill waste	Kelp and seaweed	Wheat straw
Cereals	Palm tree cobs	Lignin Wood	
Carbohydrates	Petroleum coke	Cottonseed hulls	Petroleum acid sludge

Table 3.2 - List of few low cost adsorbents used in wastewater treatment[43, 44]

Low cost adsorbents used in wastewater treatment		
Bagasse	Red mud	Fly ash
Bagasse fly ash	Rubber waste	Lignin
Barks	Rice hulls	Lignite
Coal	Refinery waste	Lampblack
Coconut shell	Scrap tires	Leather waste
Corn cobs	Slag	Olive stones
Clay minerals	Sludge	Old tires
Fuller's earth	Sunflower seeds	Wood
Fertilizer waste	Slurry Spent Fuller's earth	Wool waste
Ferrocynides	Tea leaves	Zeolites

Chapter IV

Experimental Methods

CHAPTER – IV

Experimental Methods

4.1 PREPARATION OF ADSORBENT

PHOSPHORIC ACID ACTIVATED CARBON [PAAC]

The air dried *Delonix Regia* pods were cut into minor portions and crushed in a pulveriser. Taguchi experimental design method was used to make and to determine optimal parameters to prepare competent carbon[45, 46].

About 20 g of the crushed pods was mixed with 75 mL of H_3PO_4 solution of desired concentration (10, 20 and 30 %). The slurry was retained at room temperature for 24 hours, to ensure the access of the H_3PO_4 to the *Delonix Regia* pods. Then the slurry was exposed to microwave heating of pre- determined power (450, 600 and 850 watts) for predetermined duration (10, 12 and 14 minutes). Carbon obtained from the above process was washed with 0.5 M HCl followed with warm distilled water and icy distilled water until the pH of the washings reaches 7. Then the carbon was sieved and desiccated at 423 K and kept in desiccator for further studies. The prepared activated designated as Phosphoric Acid Activated Carbon (PAAC)[46, 47].

POTASSIUM HYDROXIDE ACTIVATED CARBON [PHAC]

About 20 g of the crushed pods was mixed with 75 mL of KOH solution of desired concentration (10, 20 and 30 %). The slurry was retained at room temperature for 24 hours, to ensure the access of the KOH to the *Delonix Regia* pods. Then the slurry was exposed to microwave heating of pre- determined power (450, 600 and 850 watts) for predetermined duration (10, 12 and 14 minutes). Carbon obtained from the above process was washed with 0.5 M HCl followed with warm distilled water and cold distilled

water until the pH of the washings reaches 7. Then the carbon was sieved and desiccated at 423 K and kept in desiccator for further studies. The prepared activated designated as Potassium Hydroxide Activated Carbon (PHAC)[46, 47].

Thus totally 27 number of carbons were prepared by varying the concentration of H_3PO_4 solution / KOH solution, microwave watts power and irradiation time. The carbon showing maximum % removal of Methylene blue dye and having maximum surface area was chosen for further adsorption study. Hence the adsorbent prepared using 30% concentration of activating agent (H_3PO_4 /KOH) solution, 850 watts power, 12 minutes of irradiation time was chosen. The product was kept in a desiccator for further use.

4.2 Characterization of Adsorbents

The various characteristics of the PAAC and PHAC determined were collected in the table 4.1

Table – 4.1 Physico-chemical characteristics of PAAC and PHAC

S.No.	Properties	PAAC Values	PHAC Values
1.	PHzpc	6.9	6.65
2.	Particle size, µm	150-300	
3.	Surface area (BET), m^2/g	474.3462	452.062
4.	Pore volume, cm^3/g	0.330	0.321
5.	Pore size (Pore width), nm	2.257	1.947
6.	Bulk density, g/mL	0.49	0.52
7.	Fixed Carbon, %	74.65	7.32
8.	Moisture content, %	4.13	4.51

4.3 Preparation of adsorbates solution

The metal ions chosen for the adsorption studies in the present work are Cr (VI), Ni (II), Cu (II) ions. Standard solutions of 1000 mg/L were primed by dissolving required

amount of metal salt in one liter of distilled water. The weights of the respective salts taken are listed in table 4.2.

Table 4.2 Weight of the salts taken for the preparation of stock solutions

Metal ion	Metal salt	Weight (g)dissolved in one liter
Cr(VI)	$K_2Cr_2O_7$	2.828 g
Ni (II)	$Ni(NH_4)_2(SO_4)_2.6H_2O$	6.720 g
Cu(II)	$CuSO_4.5H_2O$	3.9294 g

4.4 Methodology

4.4.1 Determination of Characteristics of activated carbons

Bulk density

A 100 ml of cylinder weighs precisely. For the determination of the bulk density, a trip balance was used to fill the adsorbent in the graduated cylinder. Adsorbent size was adjusted by tapping up to 50 mL mark. The shaker attached to the balance filled the graduated cylinders to about 1 ml/sec. After completing the cylinder rolls, it was weighed precisely. Bulk density is calculated by dividing the weight of the adsorbent through 50.

Moisture content

Petri dish weighs around 10 grams of adsorbent. The dish was located in an air oven maintained at 328 ± 5 K for approximately 4 hours. Cover the dish, air-conditioned and weighed in a desiccators. The warming, refrigerating and balancing were repetitive in 30 minutes. The variance between the two successive weights of intervals is < 5 mm.

$$\text{Moisture content (percent by mass)} = \frac{100 \times (M-X)}{M}$$

Where,

M = Mass in grams of the adsorbent taken for test

X = Mass in grams of the adsorbent after drying

Loss on ignition:

Each adsorbent was placed on a silica crucible weighing about one gram, which was ignited for 4 hours at 1000ºC. Then it was ventilated for 1 hour in desiccators. The final weight was measured. Weight loss is calculated as loss on ignition.

Acid soluble matter

Under the study, the 10 grams of adsorbents were accurately weighged and turned into a beaker (one liter capacity). 300 ml of 0.25N HCl is added and stirring constantly. Afterwards the flame was detached, the stirring sustained for about 5 min. Adsorbent was later permitted to settle, the more liquid was filtered through a grouch crucible and asbestos mat was fitted. This procedure was repeated three times with a residue in a beaker using 300 ml of acid every time. After the fourth treatment, the integrated filtration is < 100 mL and 100 mm in size, exactly 50 mL. Concentration was shifted to a China dish and evaporated into water bathing. The remainder of an electric oven is finally 328 ± 5 K. Dried in hand. Then the dish closed. Drying, cooler and weighing process in the 30-minute interval, the gaps between the two gaps were again spaced less than 5 mg. The acid soluble material is calculated using the same expression as the water-soluble matter.

$$\text{Acid soluble matter (\%)} = \frac{M \times 100 \times 2}{M_1 (100\ X) / 100}$$

Where,

M = Mass of the residue in grams

M_1 = Mass of the adsorbent in grams taken for test

X = Percentage of moisture content

Water soluble matter

The 10 gram of an adsorbent of known moisture is accurately replaced by a beaker (1 liter capacity). 300 ml of distilled water was added for heating to boiling with continuous excitement. The stirring continued for about 5 min. After the flame is detached. Adsorbent was later permitted to settle, the more liquid was filtered through a cusp rock and asbestos mat was fitted. This procedure was repetitive thrice times repeatedly with a residue in the beaker using 300 ml of drained water every time. After the fourth treatment, the integrated filtration is < 100 mL and 100 mL in volumetric flask, exactly 50 mL. Concentration was shifted to a china dish and evaporated into water bathing. Finally the residue was placed in an hot air oven with 105 ± 5 dc. The residue was then sealed, cooled in the freezer and weighged. The divergence between two consecutive weights is less than 5 mg, drying up to 30 minutes interval, reacting to cool and weighing.

$$\text{Water soluble matter (\%)} = \frac{M \times 100 \times 2}{M_1 (100\ X) / 100}$$

Where,

M = Mass of the residue in grams

M_1 = Mass of the adsorbent in grams taken for test

X = Percentage of moisture content

4.4.2 pH of the solution

10 g of dried adsorbent was balanced and shifted to a beaker (1 liter capacity). 300 ml of freshly boiled and cooled water (adjusted with pH 7.0) was added and boiled. After digesting for 10 min, the solution was filtered while heated, discarding the first 20 mL of filter. The enduring filtrate was air-conditioned to room temperature and the pH was determined via pH meter.

4.4.3 Surface area

The surface area of the carbon was determined by direct reading Sarlo Erba Sorptomatic - 1800 by assuming that the adsorbed material forms a mono layer and holds a molecular cross sectional area of 16 A^2.

4.4.4 Zero point charge (pH_{zpc})

The pH for zero point charge of the adsorbent (pH_{zpc}) was measured by pH drift method[57]. The pH of the solution was accustomed between 2 and 10 by using 0.01 M NaOH or HCl. Nitrogen gas was bubbled through the solution at 298 K to remove the dissolved Carbon di oxide until the initial pH was stabilized. 50 mg of the adsorbent was added to 50 ml of the solution. After the pH had stabilized (typically for 24 hr), the final pH was recorded. The graph of final pH versus initial pH was used to conclude the points at which initial and final pH values were equal. This was taken at zero point charge of the adsorbent (pH_{zpc}).

4.4.5 Batch equilibration method

The effect of functions such as adsorbent dose, solution pH, initial concentration of adsorbate and contact time was investigated by batch technique. A 250 ml iodine flask, 50 ml and a pre-determined concentration of the adsorbate solution were transferred into the container. Then the content was rotated in a cycle using a cycle for a prearranged

duration of 180 min. The concentration of the centrifuge was measured after proper dilution using the Systronics Dual Beam UV - Visible Spectrometer: 2202.

The effect of pH was calculated via bringing the preferred pH of the solutions by adding con. 0.1 N HCl / 0.1N NaOH solution.

The kinetics investigates were performed with the working pH 7 and for contact times 5, 10, 20, 40, 60, 80, 100, 120, 140, 160 and 180 minutes[48].

All investigates were conducted in the batch system. The batch system was chosen due to its simplicity and reliability. In many applications, the initial assessment plan can take a simple probability analysis form, where adsorbent capabilities for removal of selected adsorbents are determined by simple batch tests in the laboratory. This study together with the knowledge of similar operating systems may provide sufficient capacity and design information to proceed with full scale design. In other cases considerable effort may be required for full scale implementation.

Considering this, the batch experiments were conducted in different iodine flasks with 100 ml capacity. Prior to each test, the pre-determined absorption of each jar was added. To ensure the equivalent mixture, throughout the test, there was no strain (180 RPM) for each run. Each flask was filled with 50 ml model before the classic start. The jar with a sample of time was retrieved from the shaker in the pre-determined time interval, centrifugal and the sample remaining concentration was measured.

Concentration of metal ions before and after adsorption was measured using a double beam UV Visible spectrophotometer. Standards for the establishing of calibration curves were prepared by weakening the stock solutions so as to have 10, 15, 20, 25 and 30 mg/L of the metal ions and the absorbance of the solution at the respective wave

lengths were recorded. The wave length of extreme absorbance for the Cr(VI) ion, Ni(II) ion and Cu(II) ion are 560, 590 and 580 respectively.

4.4.6 Process parameters

Dosage of adsorbents

The various doses containing of 10 to 100 mg of the carbon were diversified with adsorbate solution and the combinations were mixed in a mechanical shaker. The % of adsorption for different doses were resolute via possession all other aspects constant.

Initial concentrations of adsorbates

To determine the absorption rate with respect to different adsorbate concentrations, experiments were conducted with metal ion concentrations ranging from 5 to 40 mg/ L in a cycle depending on the particle size, Initial concentration, pH and temperature constant.

Contact time

The effect of the period of contact amongst the adsorbent and adsorbate on the elimination of the adsorbate was evaluated by measuring the concentration of the adsorbate solution at regular time intermissions till equilibrium was attained between adsorption and desorption processes, keeping particle size, readsorption processes, dosage, initial concentration and pH.

Initial pH

Adsorption experiments were carried out in 2 - 10 pH range of the solution. The acidic and basic pH of the medium was preserved by adding the required amounts of HCl and NaOH solutions. The parameters like particle size of the carbon and temperature were kept persistent while carrying out this experimentation.

Temperature

The adsorption experiments were achieved at four different temperatures viz., 305, 315, 325 and 335 K in a thermostated shaker machine (Remi, India). The dependability of the temperature was maintained with an accuracy of ± 0.5º C.

4.4.7 Desorption studies

Desorption studies help to elucidate the mechanism of adsorption and recovery of the adsorbates and adsorbents. Desorption of the adsorbent may make the dealing more inexpensive and achievable. Desorption process must be suitable for recovery process without damaging of the capability of the adsorbent. Hence desorption study was carried out with aqueous solution of various pH ranging from 2.0 to 12.0[49, 50, 51].

4.4.8 Effect of other ions

Effluent from electroplating industries or textile & chemical industries has metal ions along with some other salts those salts may influence the adsorption of metal ions. In order to know the effect of other electrolytes such as $CaCl_2$ and NaCl on adsorption experimentations were carried out with 100 mg/L metal ions solution at different concentration (20, 40, 60, 80, 100 mg/L) of chosen electrolytes at 30ºC[60].

4.4.9 Analytical measurements

The FT-IR spectra of the activated carbons before and after adsorption of adsorbates were recorded using FT- spectrometer, Make-Perkin Elmer, Model- Spectrem one, Version-5.0.1. The XRD patterns of adsorbents before and after adsorption of adsorbates were recorded using D8 Focus powder XRD, company Bruker, make Germany. The Scanning Electron Microscope (SEM) images of raw activated carbons and that loaded with adsorbates were recorded in the IIT - MADRAS, S.India.

Materials

All the chemicals employed in the contemporary study were commercially available in high purity with Analar grade (Merck, India or SRL, India) and were used exactly as received. Twice distilled water was used throughout the work and the second distillation was made over alkaline permanganate. The glasswares used in the contemporary study were of Borosil grade.

Chapter V

Results and Discussion

Chapter–V

Results and Discussion

Results obtained for the adsorption of Hexavalent Chromium [Cr (VI)] ion, Divalent Nickel [Ni (II)] ion and Divalent Copper [Cu (II)] ion onto Phosphoric Acid Activated Carbon (PAAC) and Potassium Hydroxide Activated Carbon (PHAC) were discussed in detail. Equilibrium data were processed with various isotherm equations such asFreundlich, Langmuir, Temkin and Dubinin-Radushkevich. Inferences obtained from the isotherm constants were discussed. The adsorption behaviour of the chosen adsorbate towards PAAC and PHAC were compared.

Kinetic data were processed with Legergren, Ho and Webber Morris equations. Significance of the constants obtained from those equations were discussed. Best fitting model was identified using the statistical tool Mean Summation of Error Squares (MSSE) test.

Thermodynamic factors such as ΔH°, ΔS° and ΔG° were determined using equilibrium data obtained in different temperatures. Inferences obtained from these values were discussed. Efficiency of different regenerating reagents were discussed in detail.

FTIR, XRD, EDAX and SEM studies carried out to understand the adsorbate – adsorbent interactions were discussed in detail.

5.1 Effect of adsorbent dosage

The adsorption of Cr (IV) ion, Ni (II) ion and Cu (II) ion onto PAAC and PHAC were studied by varying the dose of the adsorbent from 10 mg/50 ml to 100 mg/50 ml by taking 30 mg/L of all the adsorbates.

The percentage of removal of adsorbate from aqueous solution increased with an increase of carbon dose in all the cases which were given in Table 5.1 to 5.3 and shown in Figures 5.1 to 5.6. This is due to the increased carbon surface area and the convenience of more adsorption sites. Based on these results, the remaining experiments were carried out with the adsorbent dose of 30 mg/ 50 mL of adsorbate solution for Cr (VI) ion, Ni (II) ion and Cu (II) ion for the adsorption onto PAAC and PHAC.

Table: 5.1 Effect of dose for Cr(VI) ions onto PAAC and PHAC

(Dose= 30 mg/L; pH =2)

Dose in mg	%R of Cr(VI)	
	PAAC	PHAC
10	39	35.8
20	52	48.2
30	63.9	61.8
40	76.7	76
50	89	86.2
60	94.6	94
70	99	99
80	99	99
90	99	99
100	99	99

Table 5.2Effect of dose for Ni(II) ions onto PAAC and PHAC

(Dose= 30 mg/L; pH =5)

Dose in mg	%R of Ni(II) ions	
	PAAC	PHAC
10	48	46
20	56	54
30	65	62.3
40	74	72.1
50	81	78.9
60	91	89.3
70	99	97.4
80	99	99
90	99	99
100	99	99

Table 5.3Effect of dose for Cu(II) ions onto PAAC and PHAC

(C_i= 30 mg/L; pH = 4)

Dose in mg	%R of Cu(II) ions	
	PAAC	PHAC
10	50	48.1
20	59	57.3
30	67	65
40	77	74.9
50	89	87.2
60	98	95.4
70	99	99
80	99	99
90	100	100
100	100	100

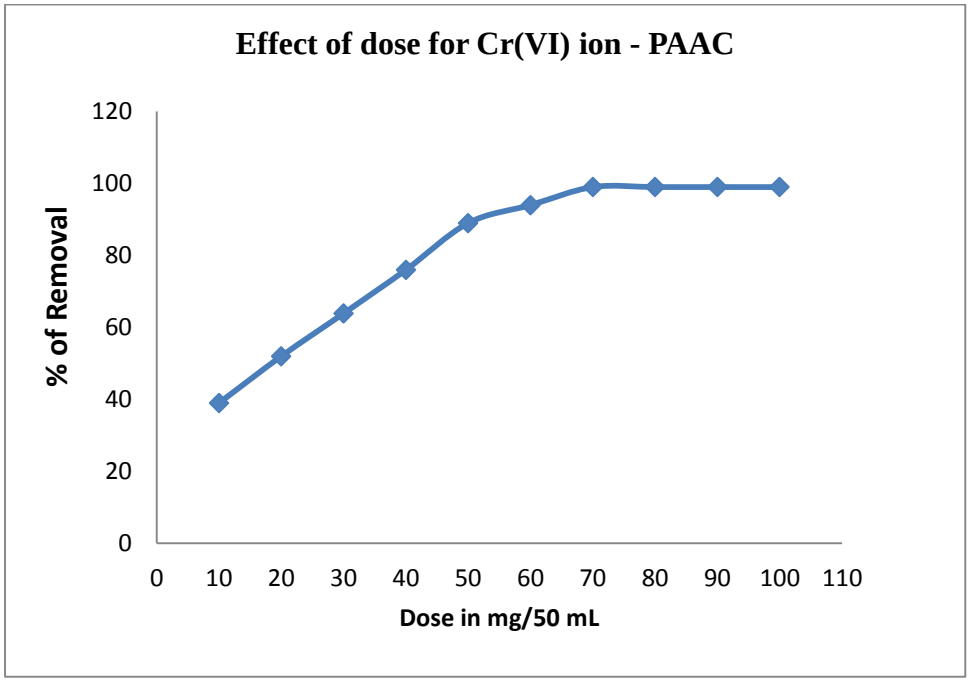


Figure 5.1

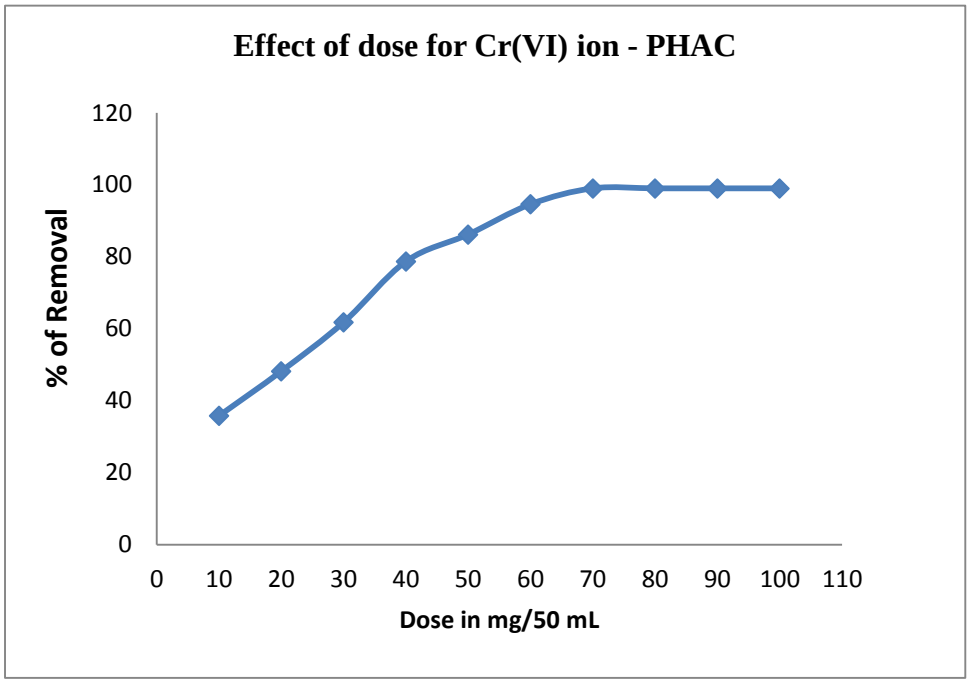


Figure 5.2

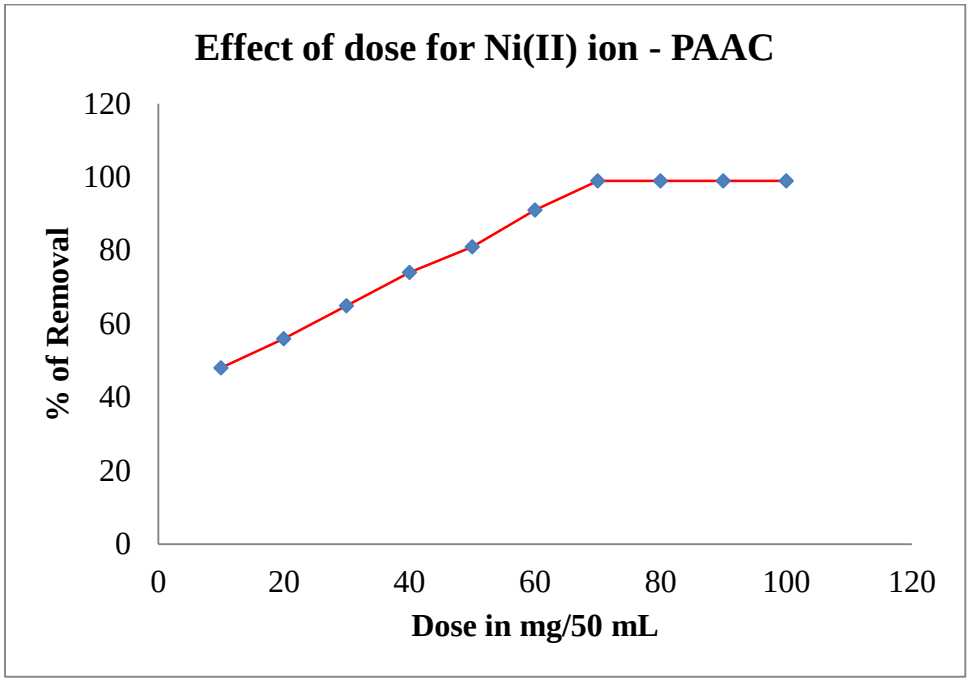


Figure 5.3

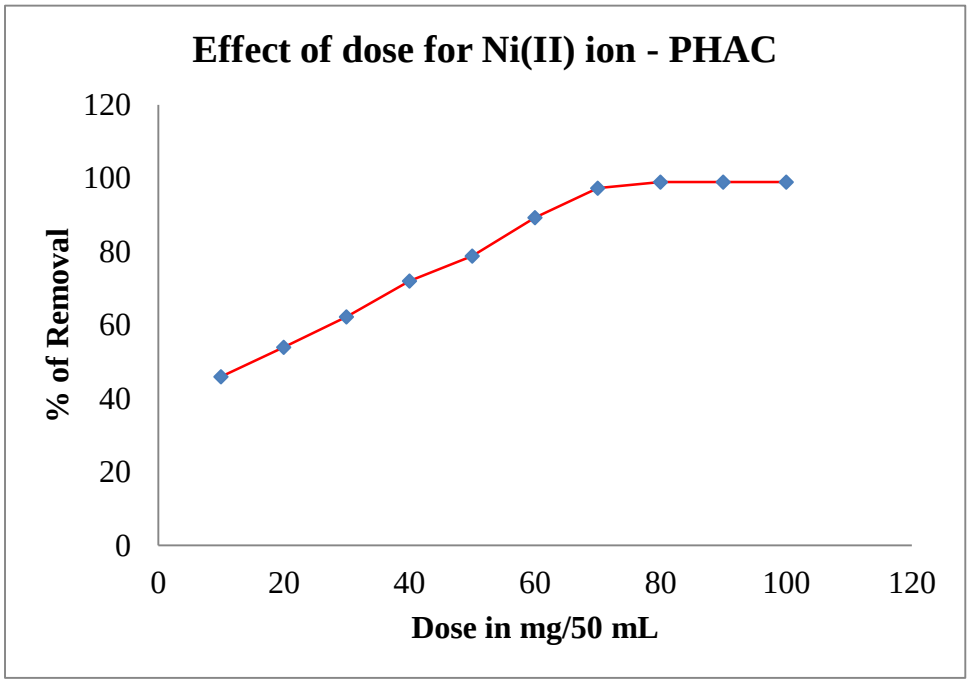
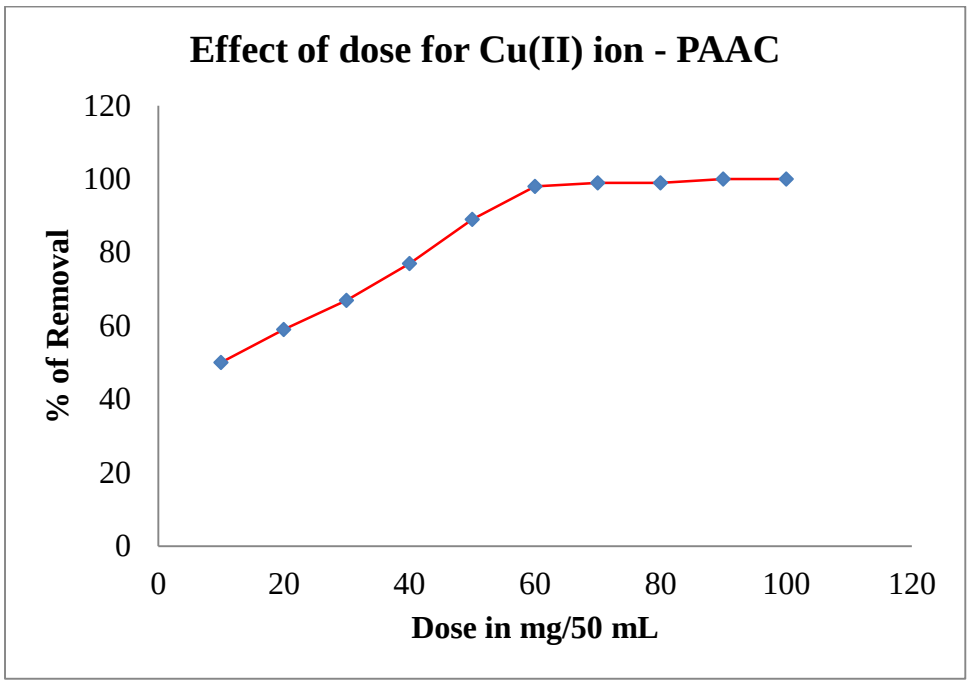


Figure 5.4



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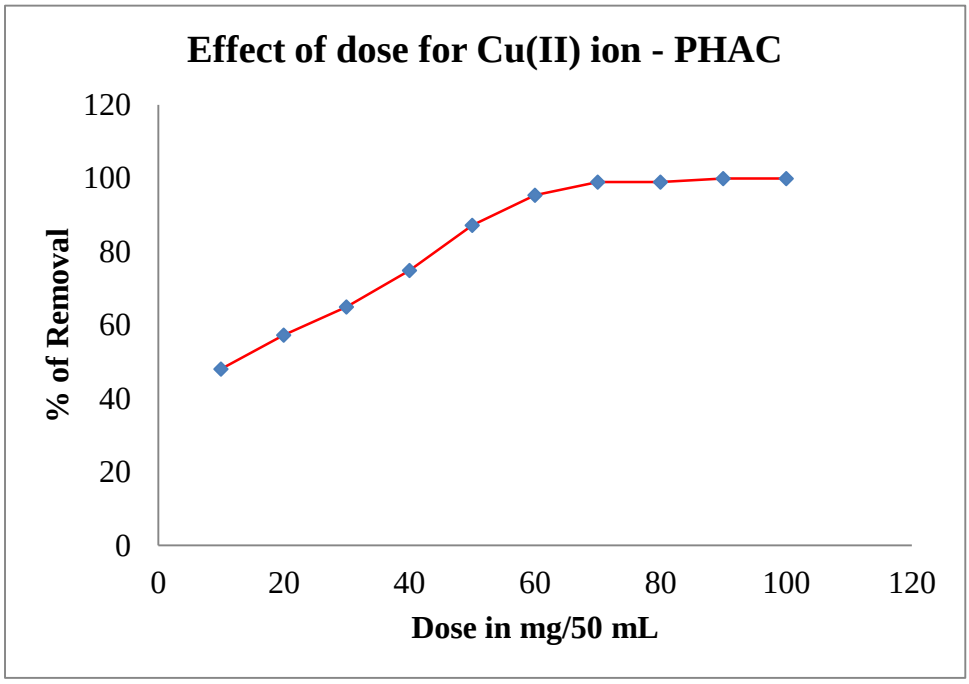


Figure 5.6

5.2 Effect of Contact time

The effect of adsorbate - adsorbent interaction time for the % of elimination of Chromium (VI) ion from aqueous solution was studied by taking 5 mg/L, 10 mg/L 15 mg/L and 20 mg/L solutions as initial concentrations for both the adsorbents PAAC and PHAC.

The effect of adsorbate - adsorbent interaction time for the % of elimination of Nickel (II) ion from aqueous solution was studied by taking 10 mg/L, 15 mg/L, 20 mg/L and 25 mg/L solutions as initial concentrations for both the adsorbents PAAC and PHAC.

The effect of adsorbate - adsorbent interaction time for the % of removal of Copper (II) ion from aqueous solution was studied by taking 10 mg/L, 20 mg/L, 30 mg/L and 40 mg/L solutions as initial concentrations for both the adsorbents PAAC and PHAC.

The results of the above study at different contact times were shown in figures from 5.7 to 5.12. The adsorption process was characterized by the quick push of adsorbate in the beginning stages. Once the equilibrium form is achieved at all times, the contact time increases and the rate of adsorption percentage was decreased when constantly changed.

At the beginning stage, the ratio of shallow area of the adsorbent to the amount of solute in liquid phase is great and hence the concentration driving force makes solute to rush towards the carbon surface. As the time increases the above ratio begins to decrease due to adsorption and hence the rate of adsorption becomes slow[60].

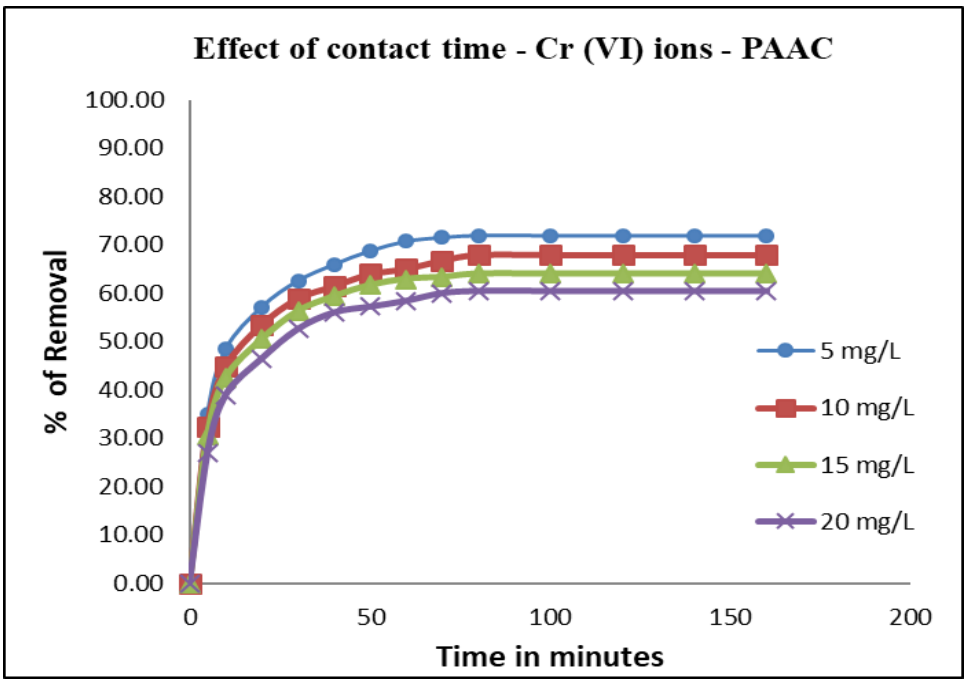


Figure 5.7

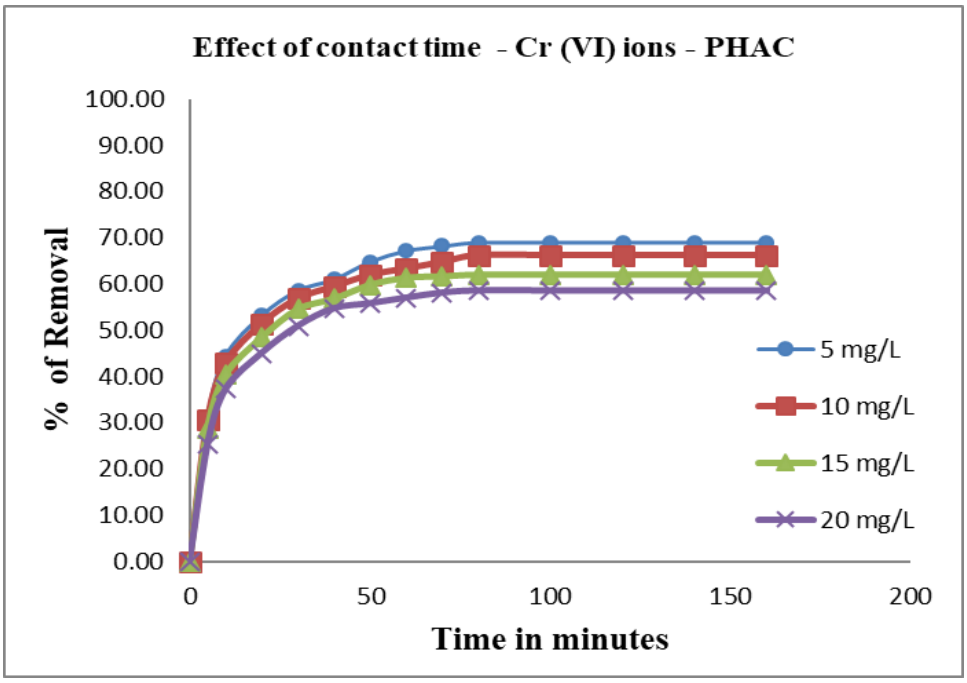


Figure 5.8

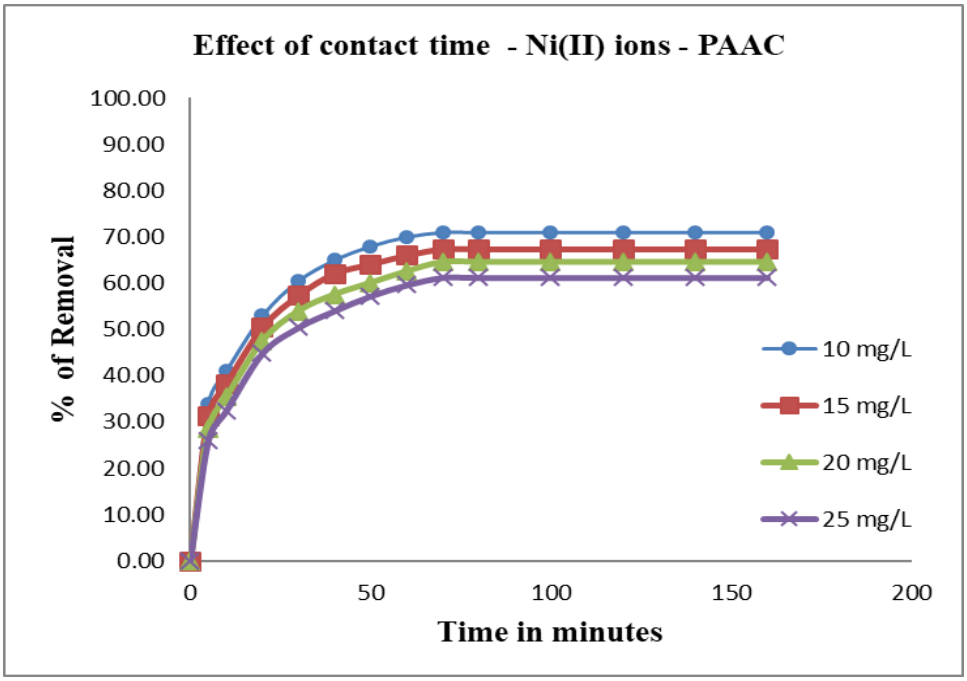


Figure 5.9

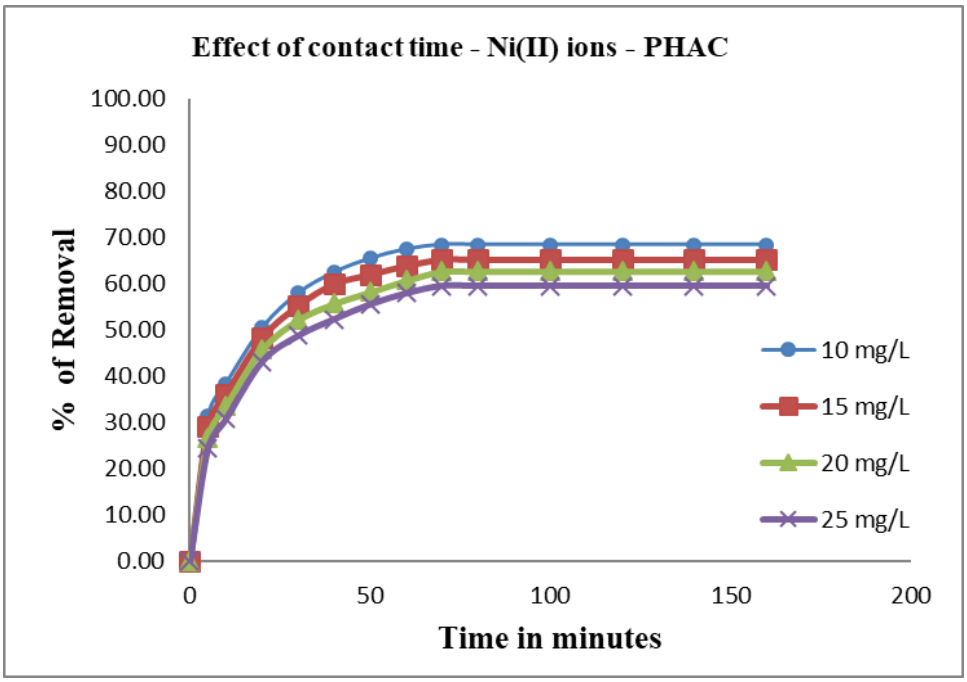


Figure 5.10

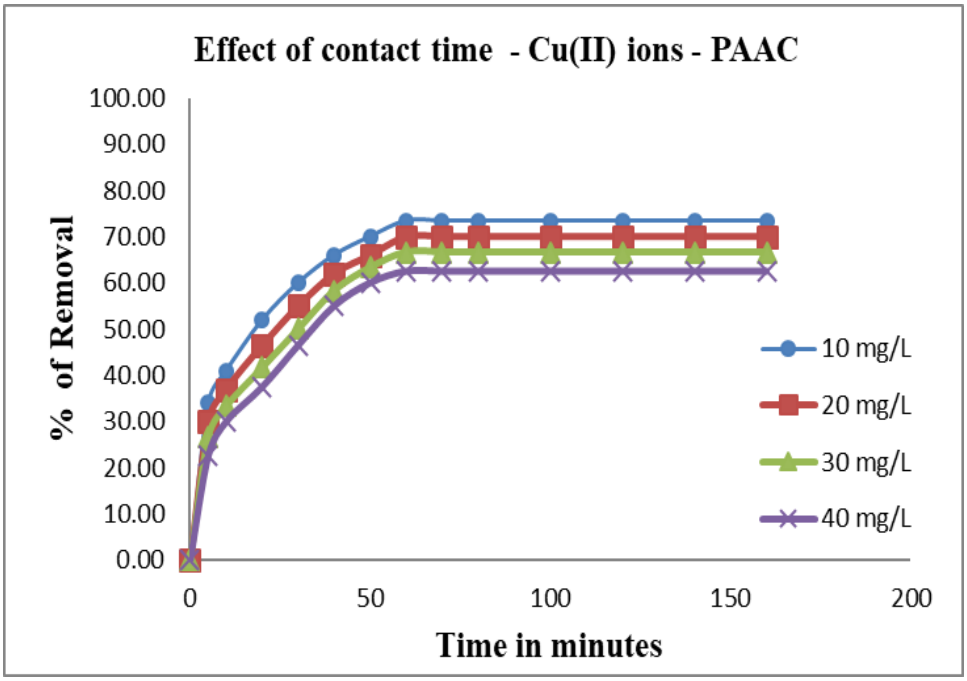


Figure 5.11

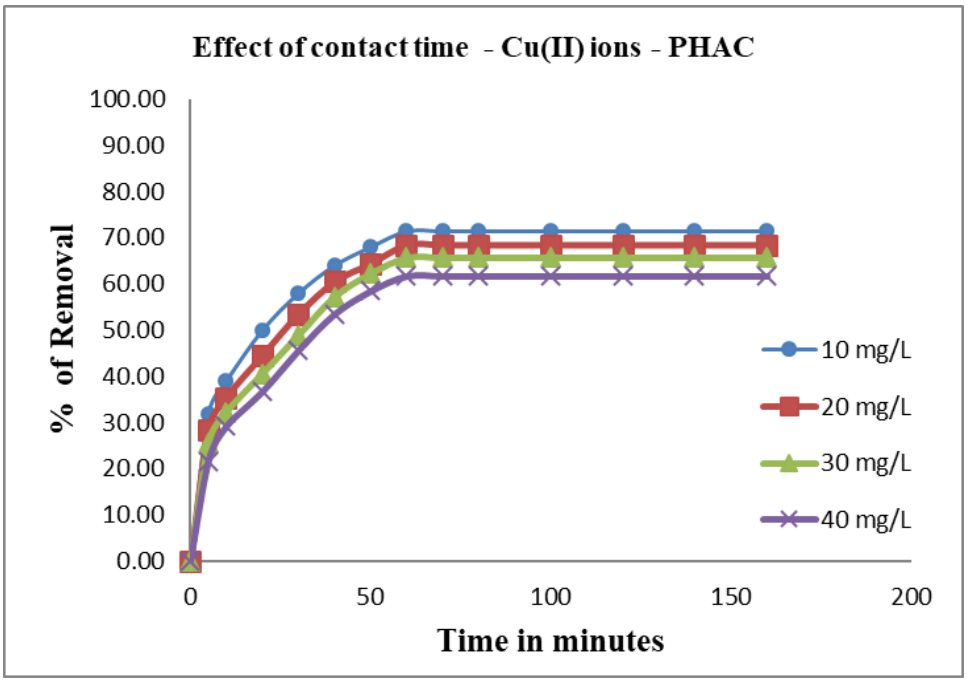


Figure 5.12

5.3 Effect of initial concentrations

The study on the consequence of initial concentration showed that the percentage of the elimination of metal ion decreased with the increase of initial concentrations of adsorbate solution.

When PAAC was used as adsorbent, the percentage elimination of Cr (VI) ion was found to decrease from 72.00 to 60.50, 73.80 to 62.05, 76.00 to 64.80 and 79.60 to 68.60 at the temperatures 305 K, 315 K, 325 K and 335 K respectively as the initial concentration of Cr (IV) ion increased from 5mg/L to 20mg/L.

The % removal of Ni(II) ion was found to decrease from 71.00 to 61.20, 74.00 to 64.00, 78.00 to 67.20 and 83.00 to 70.80 at the temperature 305 K, 315 K 325 K and 335 K respectively as the initial concentration of Ni (II) ion increased from 10 mg/L to 25 mg/L.

The % adsorption adsorbate - Cu (II) ion was ranges from 73.40 to 62.50, 76.00 to 65.20, 78.20 to 67.75 and 81.70 to 71.25 at the temperature 305 K, 315 K 325 K and 335 Krespectively as the initial concentration of Cu (II) ion increased from 10 mg/L to 40 mg/L.

When PHAC used as adsorbent, the percentage removal adsorbate - Cr (VI) ion was found to decrease from 69.00 to 58.50, 70.80 to 60.05, 73.00 to 62.80 and 76.60 to 66.60 at the temperature 305 K, 315 K, 325 K and 335 K respectively as the initial concentration of Cr (VI) ion increased from 5 mg/L to 20 mg/L.

The percentage elimination of Ni (II) ion was found to decrease from 68.50 to 59.60, 71.70 to 62.60, 75.80 to 65.68 and 80.80 to 69.32 at the temperature 305 K, 315

K 325 K and 335 K respectively as the initial conc. of Ni (II) ion increased from 10 mg/L to 25 mg/L.

The %of adsorption of Cu (II) ion was found to reduction from 71.40 to 61.75, 74.10 to 63.25, 76.40 to 66.25 and 80.00 to 70.65 at the temperature 305 K, 315 K 325 K and 335 K respectively as the initial concentration of Cu (II) ion increased from 10 mg/L to 40 mg/L. This fact is explained as follows.

The amount of solubility in the liquid is more than the initial concentration. The rate of adsorbent surface is available for solvent concentration with an initial conc. increase, so the reduction rate reduces by the initial concentration increases.

However the amount of metal adsorbed on the activated carbon increased with an increase in the initial concentration of the adsorbate solutions. The quantity of Cr (VI) ion adsorbed on PAAC was found to increase from 9.00 to 30.25, 9.23 to 31.03, 9.63 to 32.40 and 9.95 to 34.30at the temperature 305 K, 315 K, 325 K and 335 K respectively as the initial conc. of Cr (VI) ion increased from 5 to 20 mg/L.

The quantity of Ni (II) ion adsorbed on PAAC was found to increase from 17.75 to 38.25, 18.50 to 40.00, 19.50to 42.00 and 20.75 to 44.25 at the temperature 305 K, 315 K, 325 K and 325 K respectively as the initial conc. of Ni (II) ion increased from 10 to 25mg/L.

The quantity of Cu (II) ion adsorbed on PAAC was found to increase from 18.35 to 62.50, 19.00 to 65.20, 19.55 to 67.75 and 20.43 to 71.25 at the temperature 305 K, 315 K, 325 K and 335 K respectively as the initial concentration of Cu (II) ion increased from 10 to 40mg/L.

The quantity of Cr (VI) ion adsorbed on PHAC was found to increase from 08.63 to 29.25, 8.85 to 30.03, 9.13 to 31.40 and 9.58 to 33.30 at the temperature 305 K, 315 K, 325 K and 335 K respectively as the initial concentration of Cr (VI) ion increased from 5 to 20mg/L.

The quantity of Ni (II) ion adsorbed on PHAC was found to increase from 17.13 to 37.25, 17.93 to 39.13, 18.95 to 41.05 and 20.20 to 43.33 at the temperature 305 K, 315 K, 325 K and 335 K respectively as the initial concentration of Ni (II) ion increased from 10 to 25mg/L.

The quantity of Cu (II) ion adsorbed on PHAC was found to increase from 17.85 to 61.75, 18.53 to 63.25, 19.10 to 66.25 and 20.00 to 70.6 at the temperature 305 K, 315 K, 325 K and 335 K respectively as the initial concentration of Cu (II) ion increased from 10 to 40 mg/L.

The percentage of removal and quantity adsorbed with respect to initial concentration is shown in Figures5.13 to 5.24. This is because the quantity of solute adsorbed is proportional to the fraction of adsorbate transferred from liquid phase to solid phase. This fraction increases with an increase in the concentration of solution. For example $1/4^{th}$ of the fraction is assumed to be transferred; 25 mg of solute will be transferred if 100 mg/L solution is used as initial concentration. If 200 mg/L solution is used, the amount transferred will be 50 mg.

The time to reach equilibrium was detected to increase when the initial concentration of the metal ion increased. An additional sloution to be adsorbed, take extra time to penetrate into the aperture and find the place to get adsorbed, that is more time is required. Hence the time to attain equilibrium through an increase in initial concentration. A similar trend has been recorded in previous literatures[57, 60 & 61].

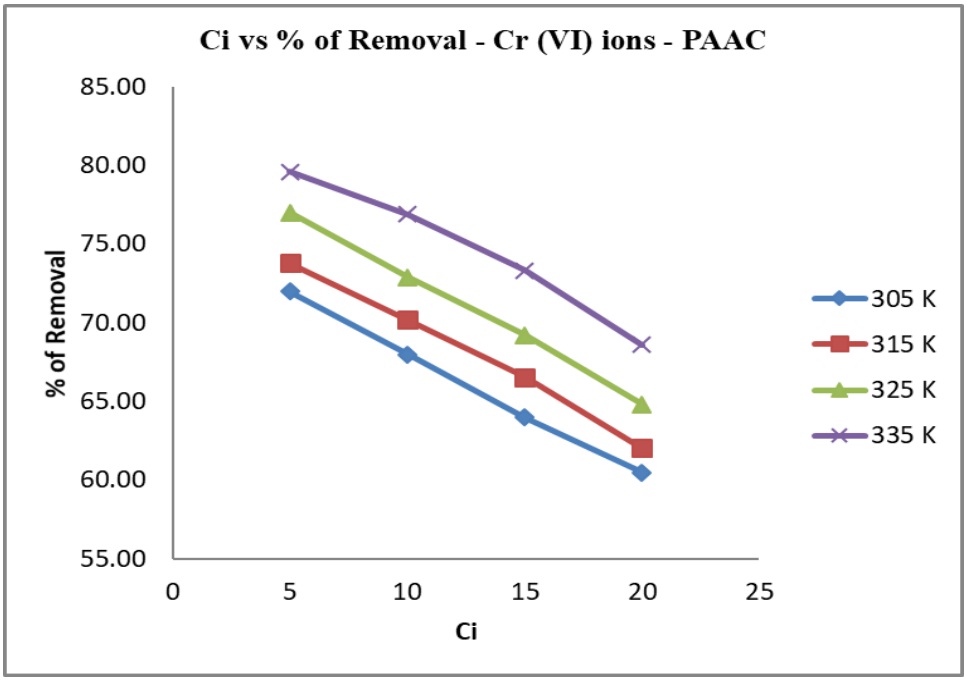
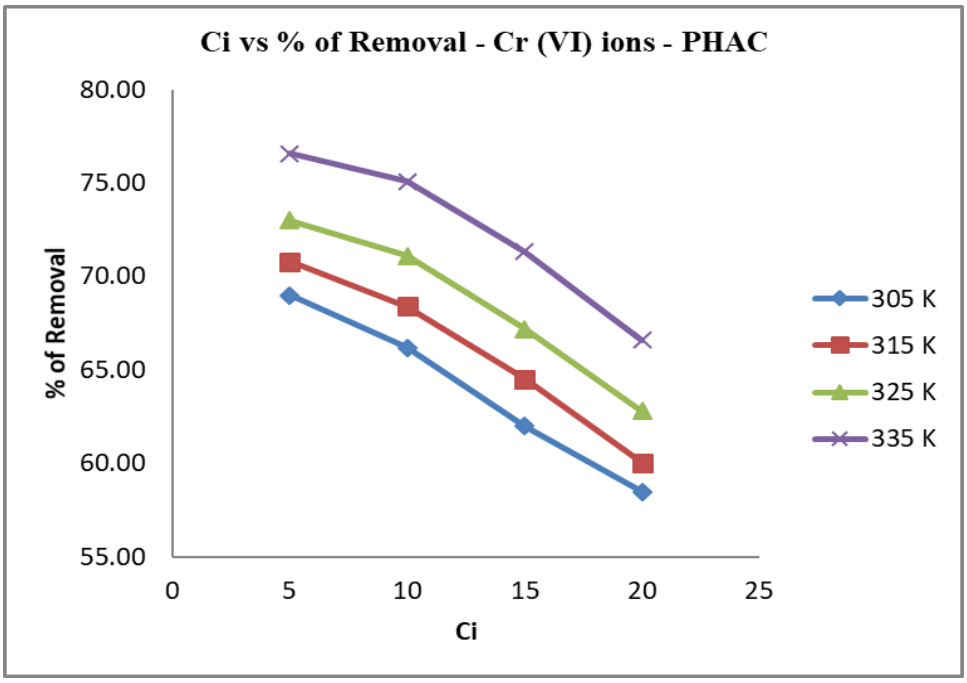


Figure 5.13



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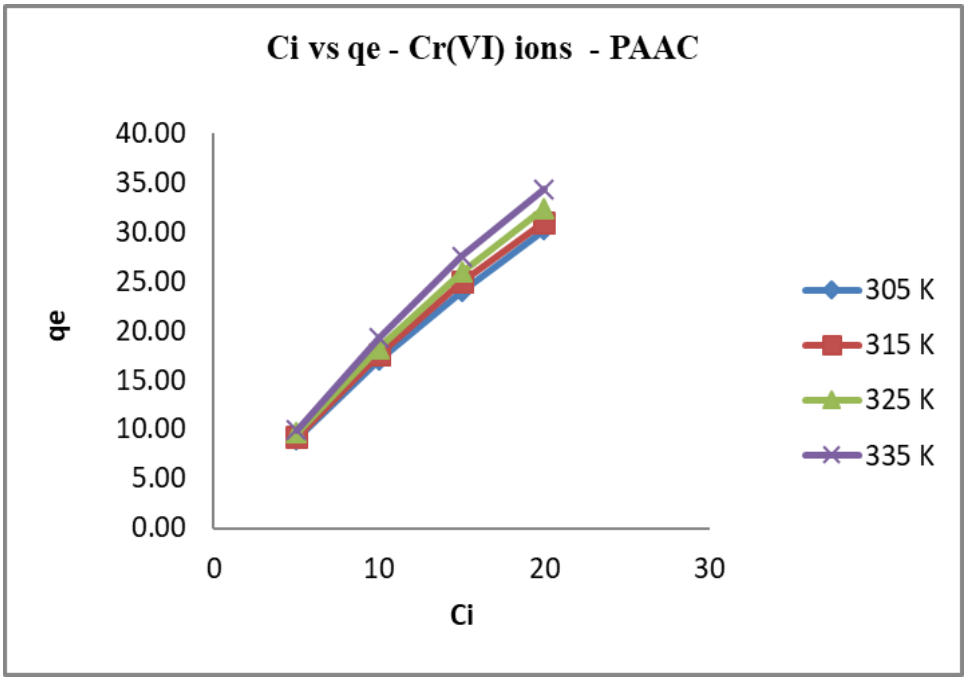

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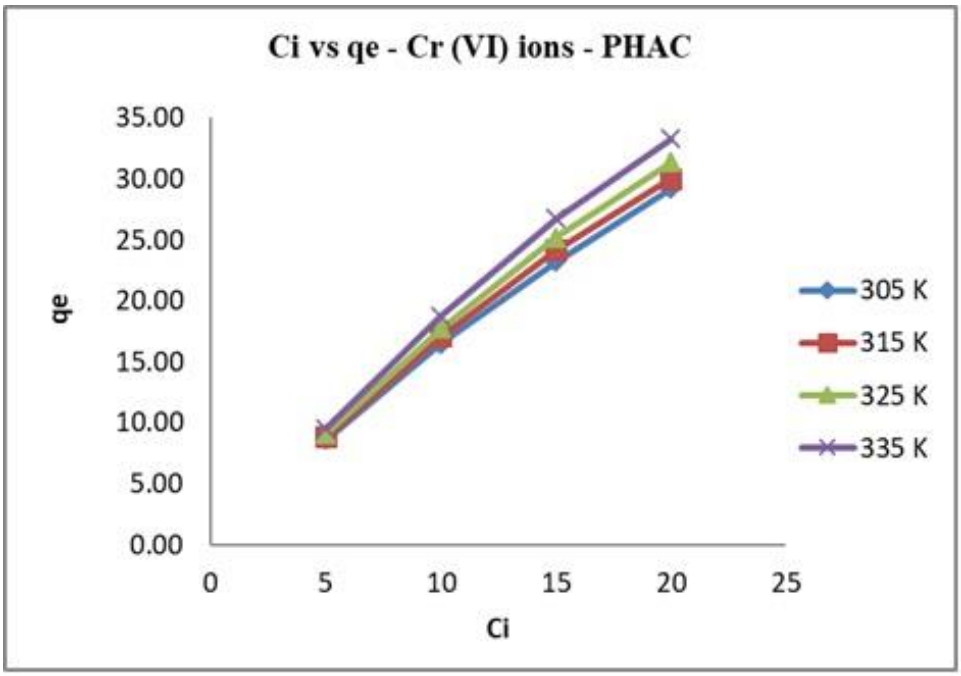

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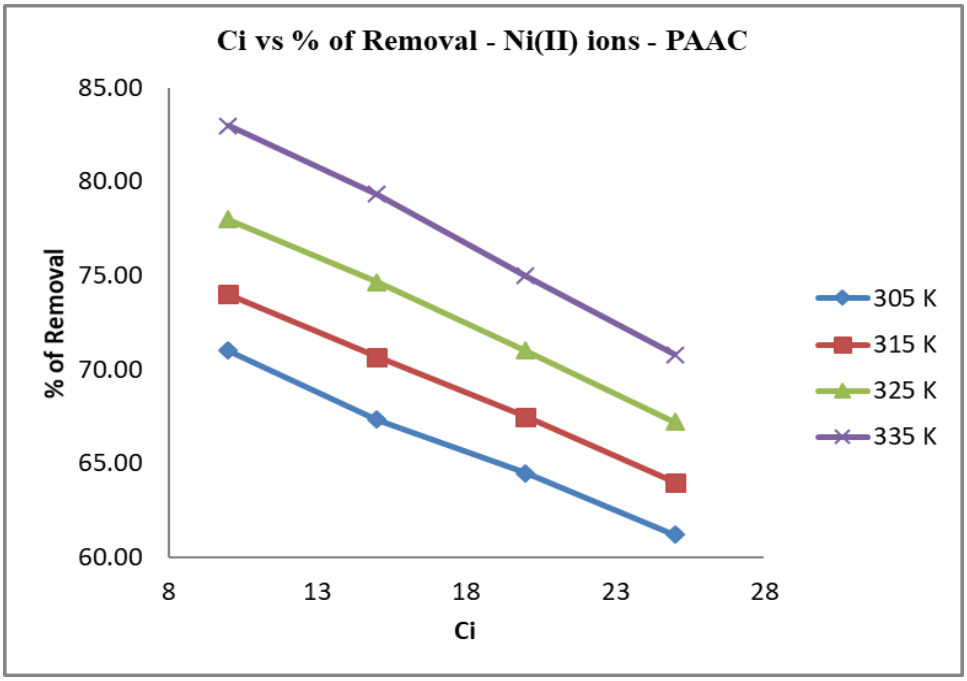


Figure 5.17

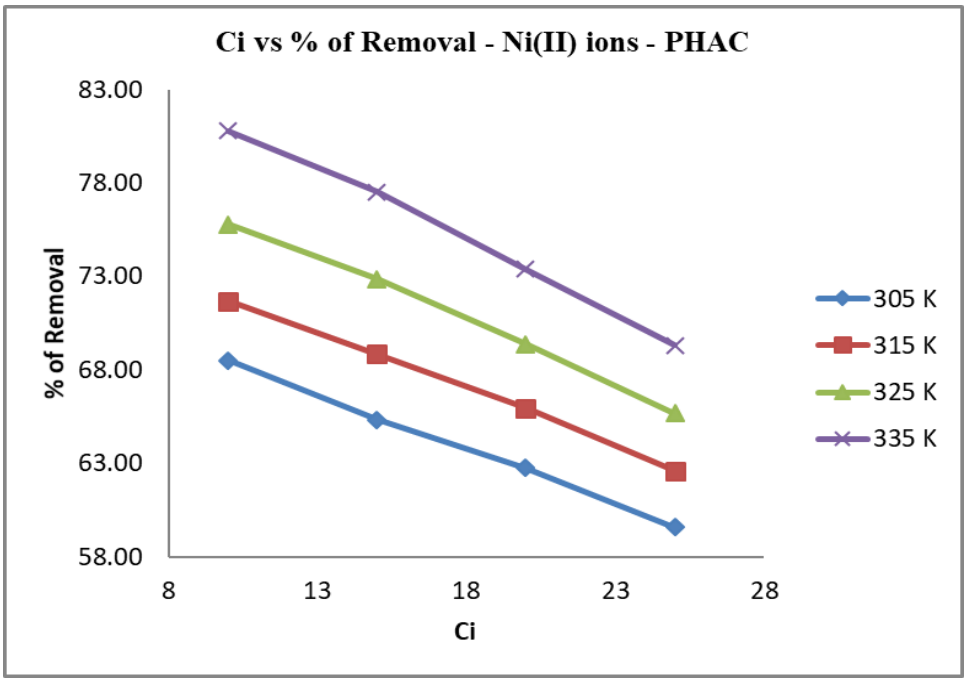


Figure 5.18

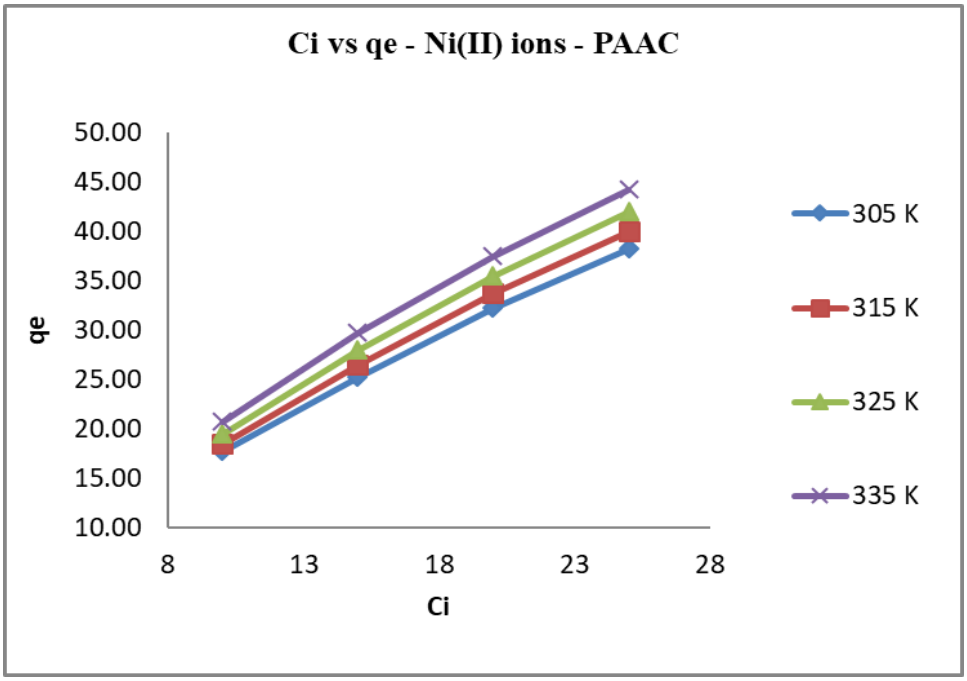
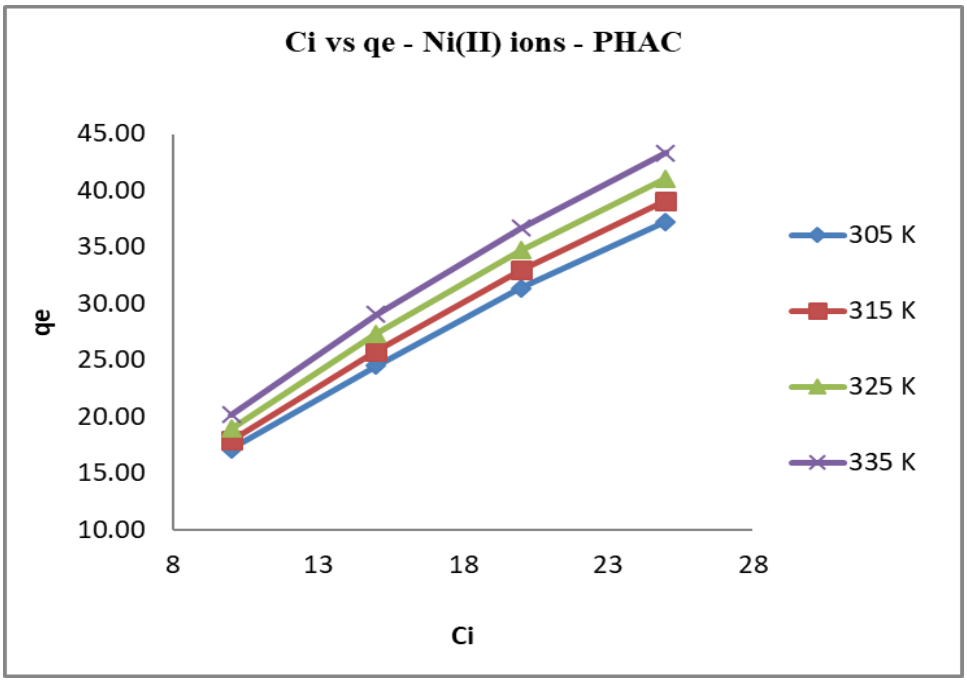


Figure 5.19



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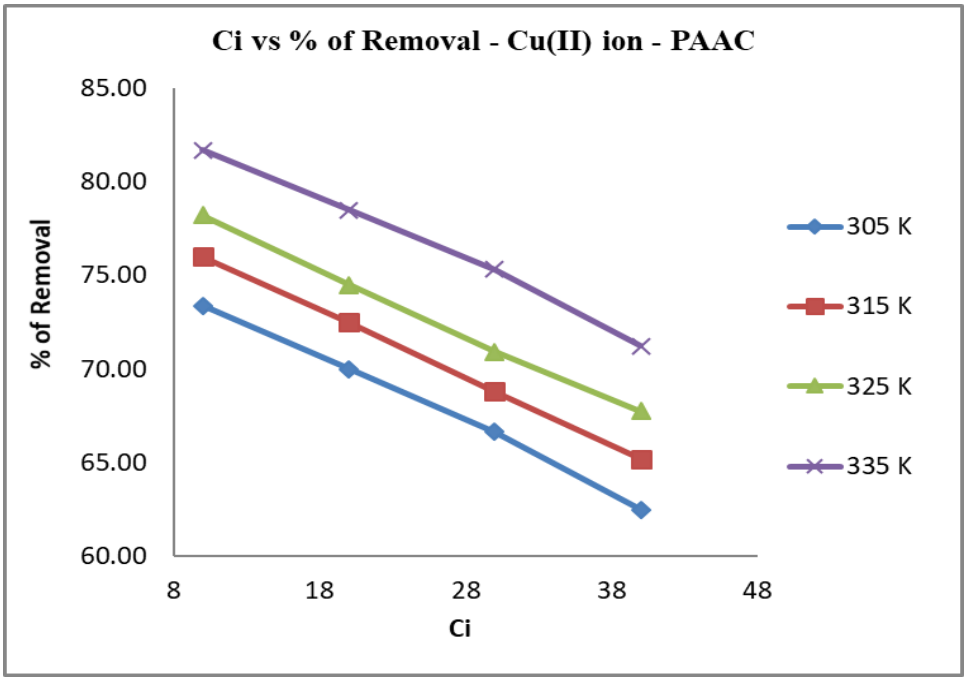

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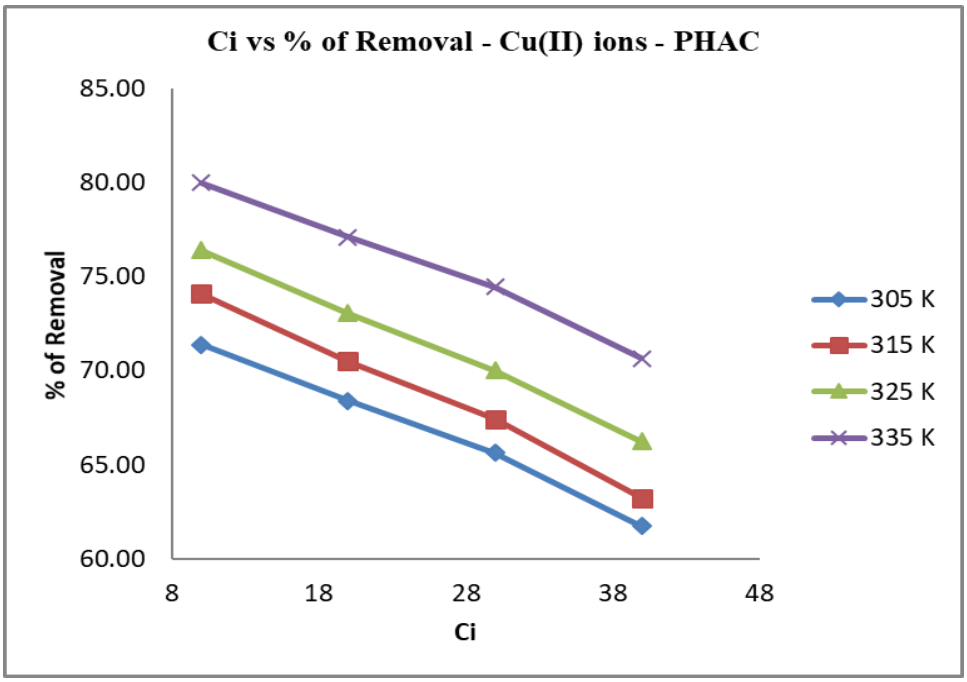

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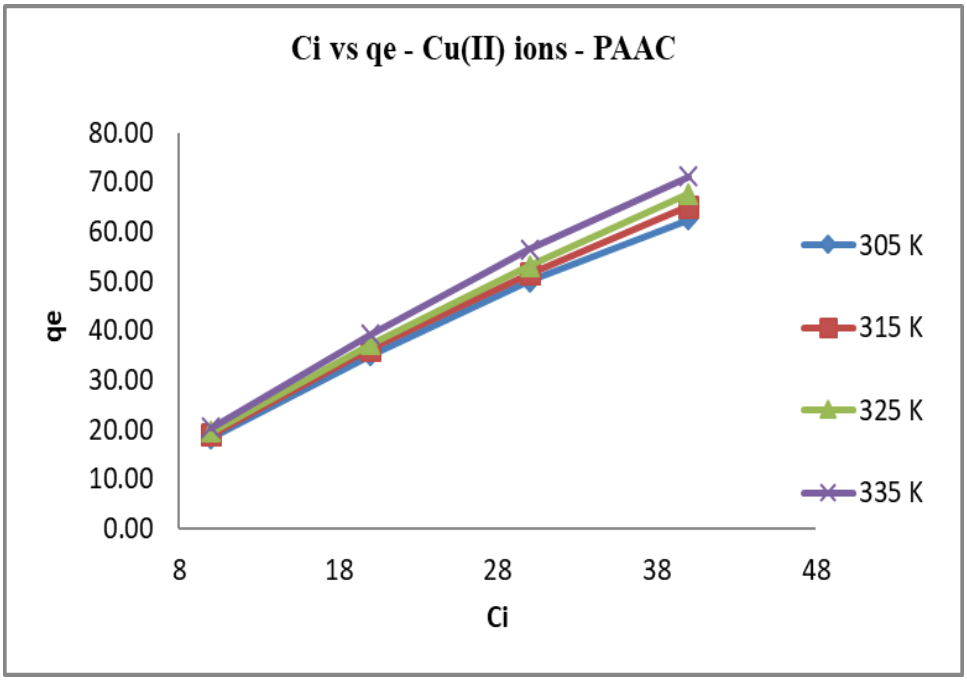


Figure 5.23

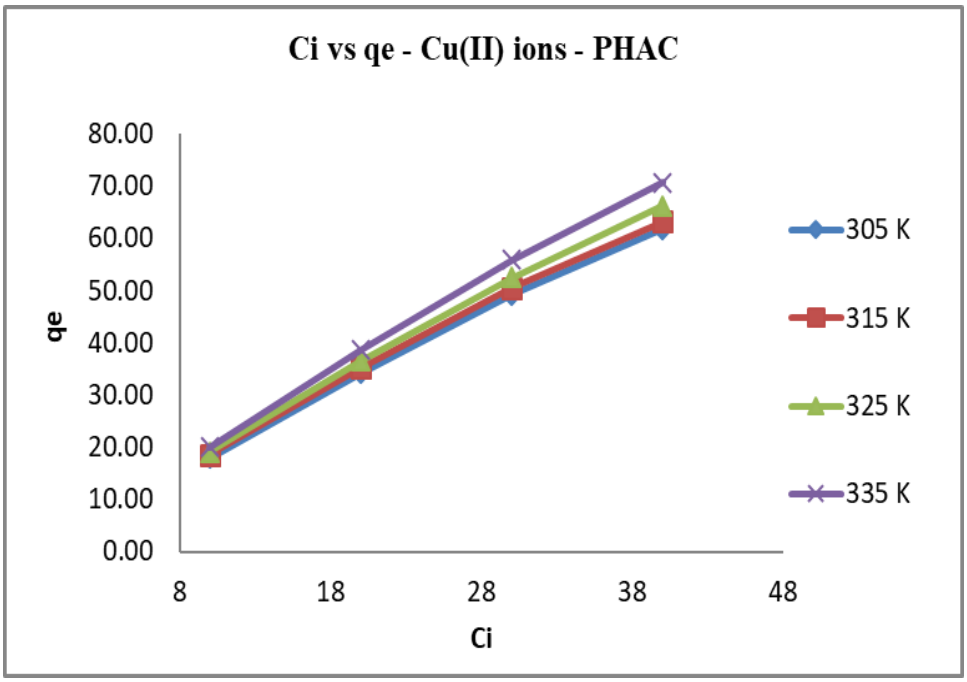


Figure 5.24

5.4 Effect of temperature

The percentage of removal improved by an increase of temperature of the solution for all studied initial concentrations of the metal ion. The results are given in Table 5.4 to 5.6. Plots of percentage removal versus temperature were given in Figures5.25 to5.36. The reason may be as follows,

At higher temperature, pores may widen up due to increased shaking. So that more number of solute may enter into the aperture and get adsorbed in the inner part of the aperture surfaces.

Table – 5.4 Effect of Temperature vs %R &Temperature vs q_e results for Cr(VI) ions onto PAAC and PHAC

Initial Concentration C_i(mg/L)	Temperature (K)	PAAC		PHAC	
		%R	Qe	%R	Qe
5	305	72.00	9.00	69.00	8.63
	315	73.80	9.23	70.80	8.85
	325	76.00	9.50	73.00	9.13
	335	79.60	9.95	76.60	9.58
10	305	68.00	17.00	66.20	16.55
	315	70.20	17.55	68.40	17.10
	325	72.90	18.23	71.10	17.78
	335	76.90	19.23	75.10	18.78
15	305	64.00	24.00	62.00	23.25
	315	66.53	24.95	64.53	24.20
	325	69.20	25.95	67.20	25.20
	335	73.33	27.50	71.33	27.75
20	305	60.50	30.25	58.50	29.25
	315	62.05	31.03	60.05	30.03
	325	64.80	32.40	62.80	31.40
	335	68.60	34.30	66.60	33.30

Table – 5.5 Effect of Temperature vs %R & Temperature vs q_e results for Ni(II) ions onto PAAC and PHAC

Initial Concentration C_i(mg/L)	Temperature (K)	PAAC		PHAC	
		%R	Qe	%R	Qe
10	305	71.00	17.75	68.50	17.13
	315	74.00	18.50	71.70	17.93
	325	78.00	19.50	75.80	18.95
	335	83.00	20.75	80.80	20.20
15	305	67.33	25.25	65.33	24.50
	315	70.67	26.50	68.87	25.83
	325	74.67	28.00	72.87	27.33
	335	79.33	29.75	77.53	29.08
20	305	64.50	32.55	62.75	31.38
	315	67.50	33.75	65.95	32.98
	325	71.00	35.50	69.40	34.70
	335	75.00	37.50	73.40	36.70
25	305	61.20	38.25	59.60	37.25
	315	64.00	40.00	62.60	39.13
	325	67.20	42.00	65.68	41.05
	335	70.80	44.25	69.32	43.33

Table – 5.6 Effect of Temperature vs %R &Temperature vs q_e results for Cu(II) ions onto PAAC and PHAC

Initial Concentration C_i(mg/L)	Temperature (K)	PAAC		PHAC	
		%R	Qe	%R	Qe
10	305	73.40	18.35	71.40	17.85
	315	76.00	19.00	74.10	18.53
	325	78.20	19.55	76.40	19.10
	335	81.70	20.43	80.00	20.00
20	305	70.00	35.00	68.40	34.20
	315	72.50	36.25	70.50	35.25
	325	74.50	37.25	73.05	36.53
	335	78.50	39.25	77.10	38.55
30	305	66.67	50.00	65.63	49.23
	315	68.80	51.60	67.43	50.58
	325	70.93	53.20	70.03	52.53
	335	75.33	56.50	74.43	55.85
40	305	62.50	62.50	61.75	61.75
	315	65.20	65.20	63.25	63.25
	325	67.75	67.75	66.25	66.25
	335	71.25	71.25	70.65	70.65

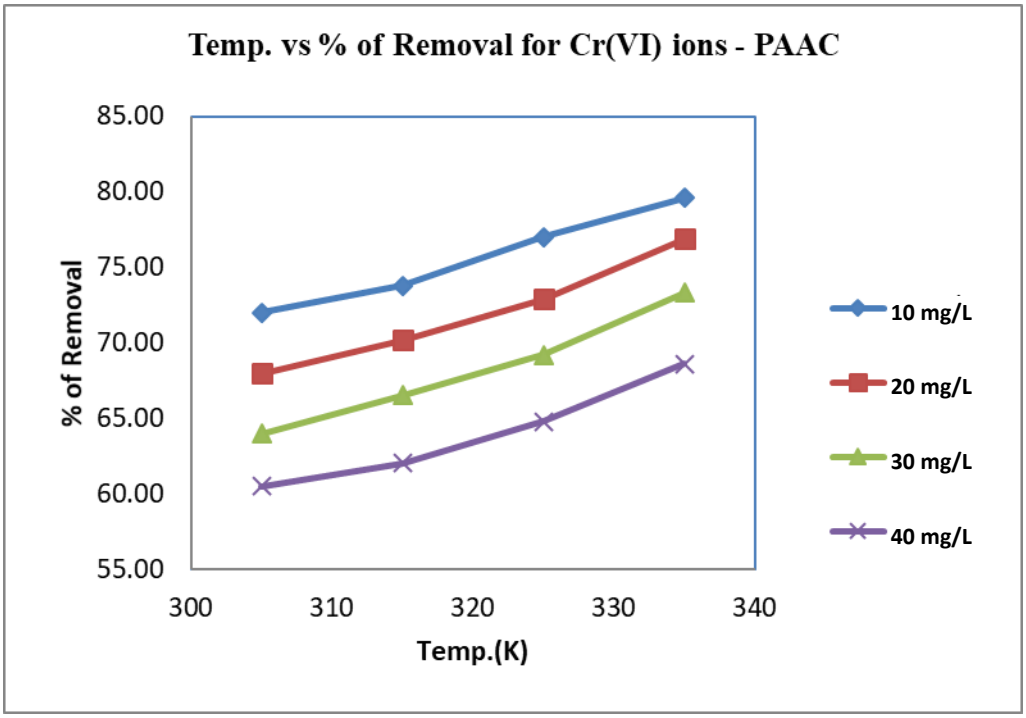
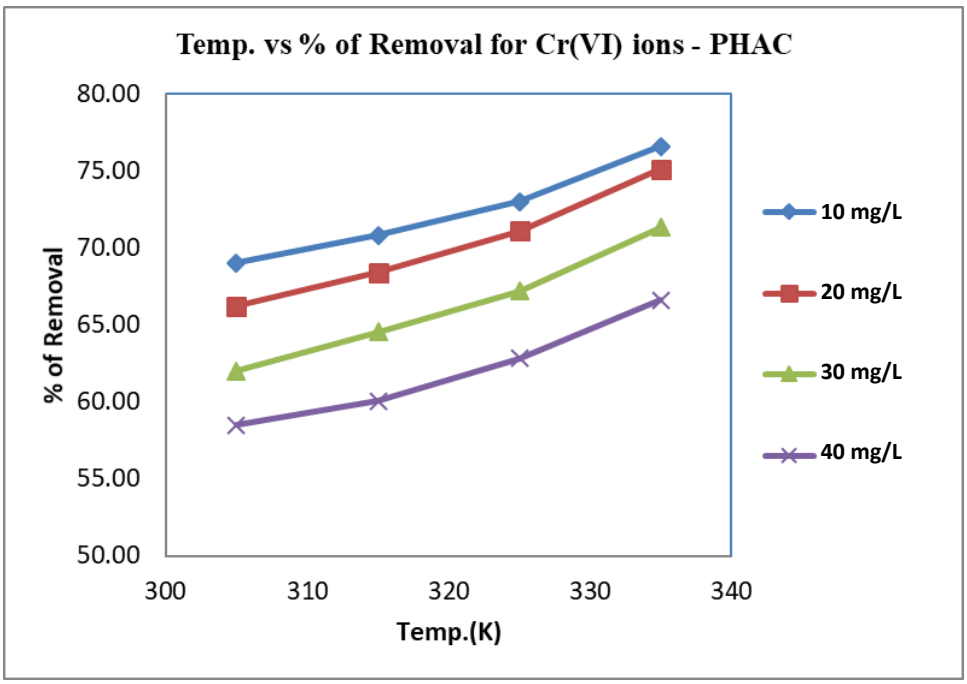


Figure 5.25



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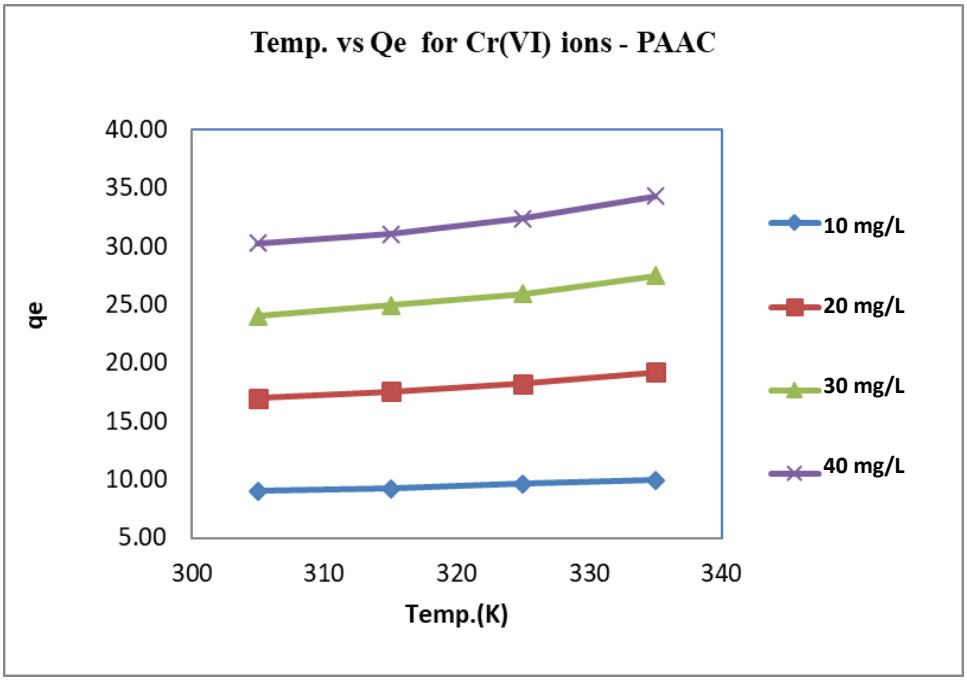

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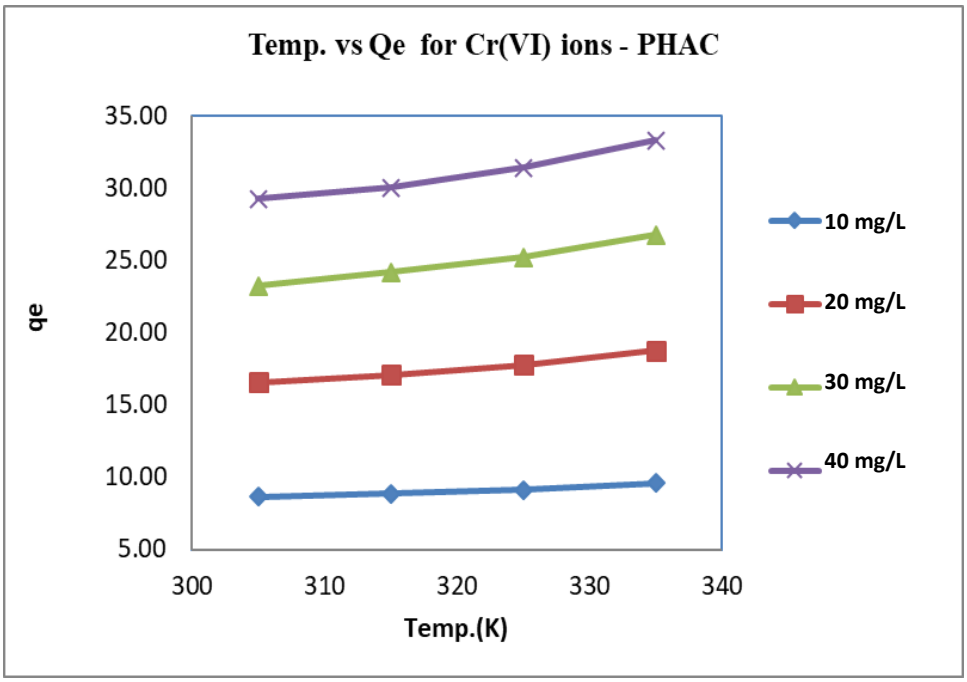

Figure 5.28

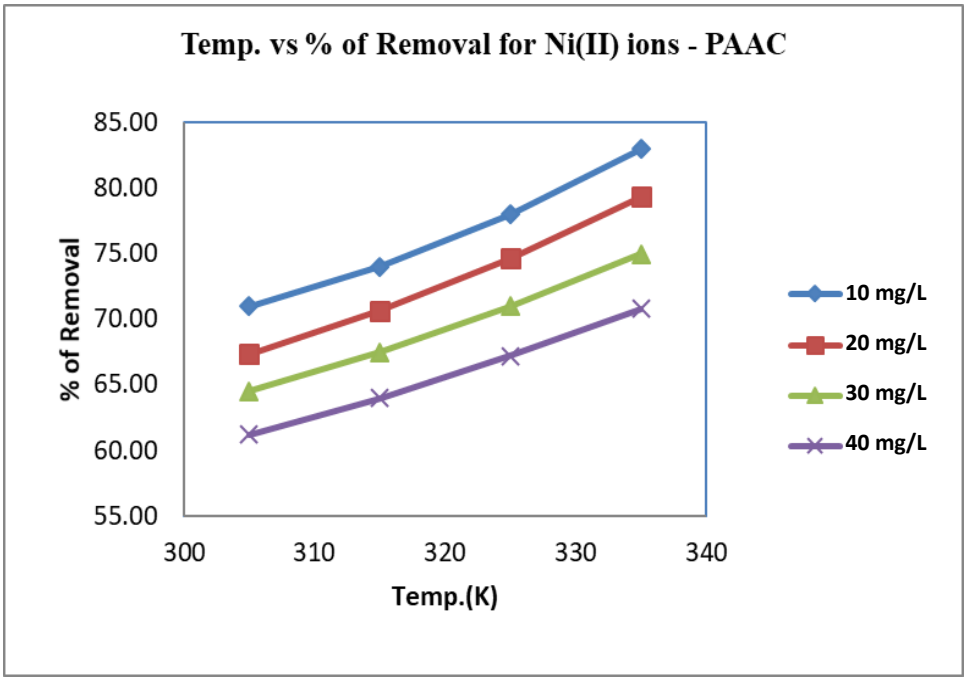

Figure 5.29

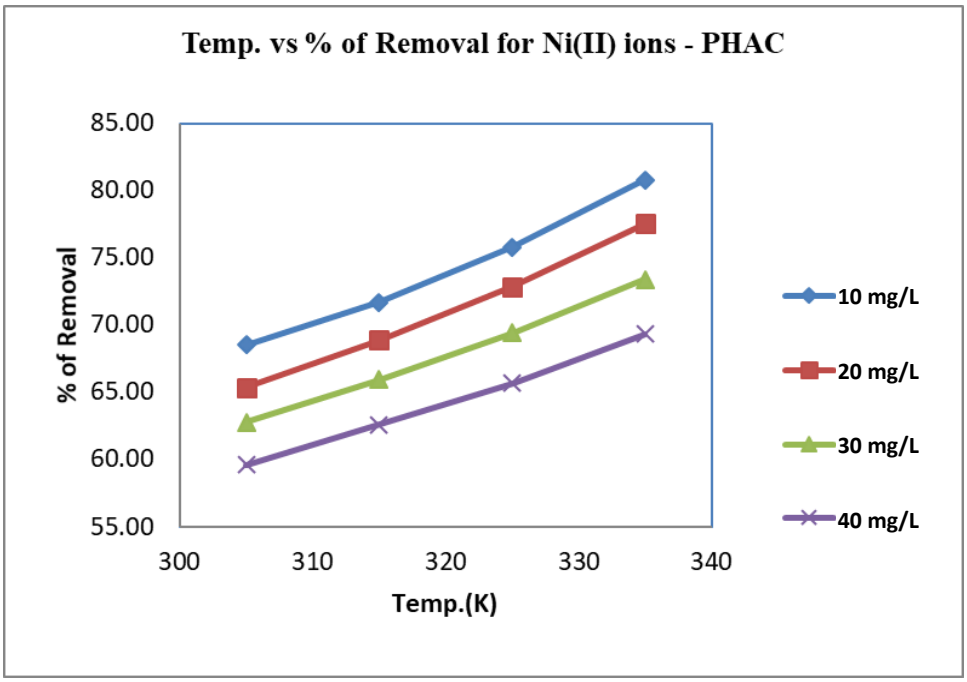

Figure 5.30

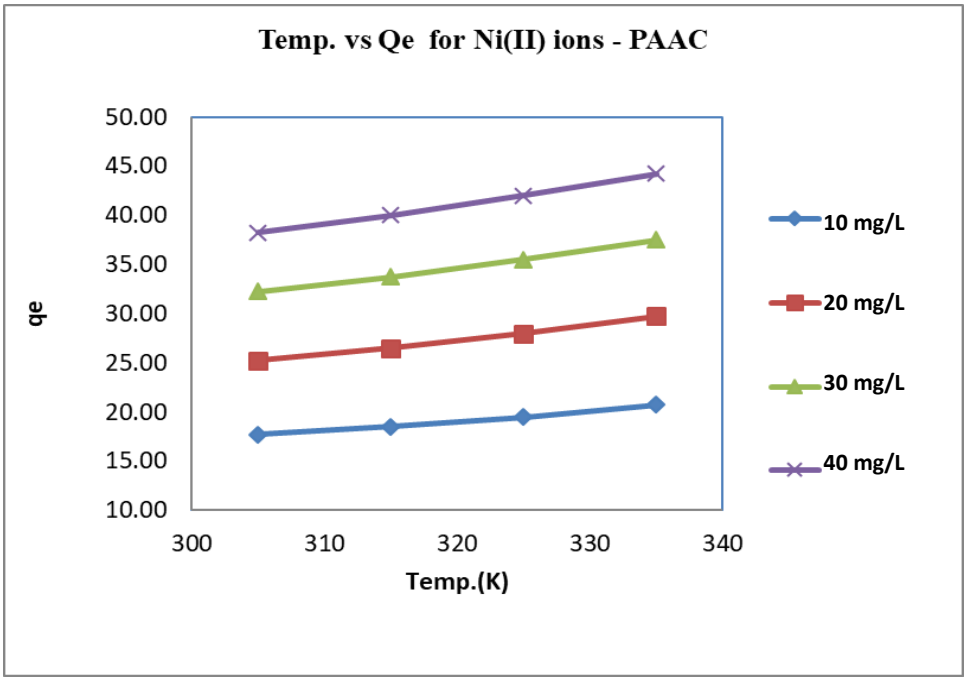

Figure 5.31

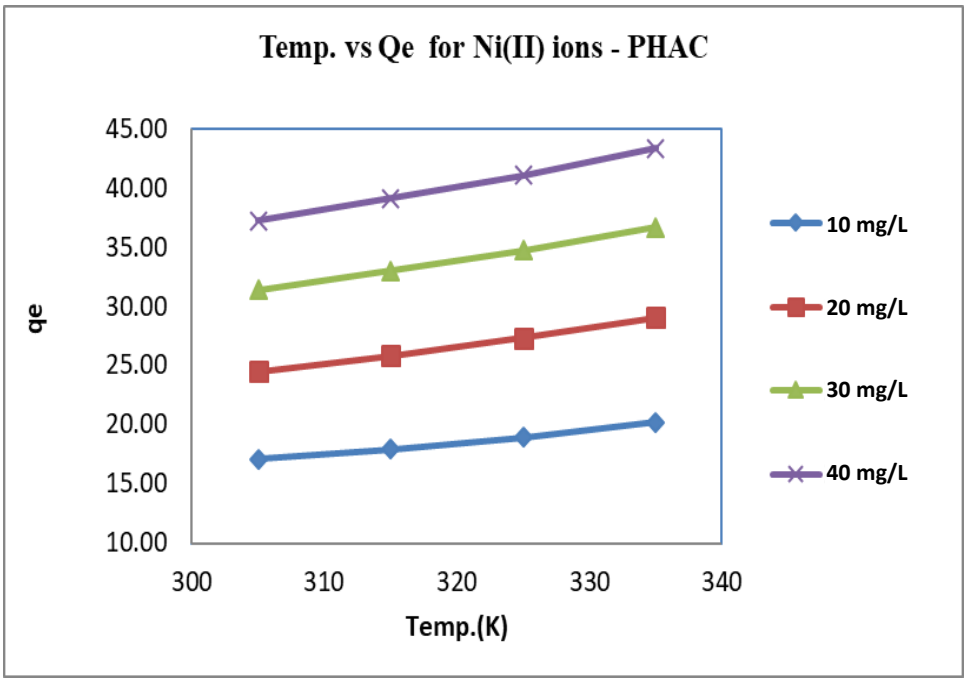

Figure 5.32

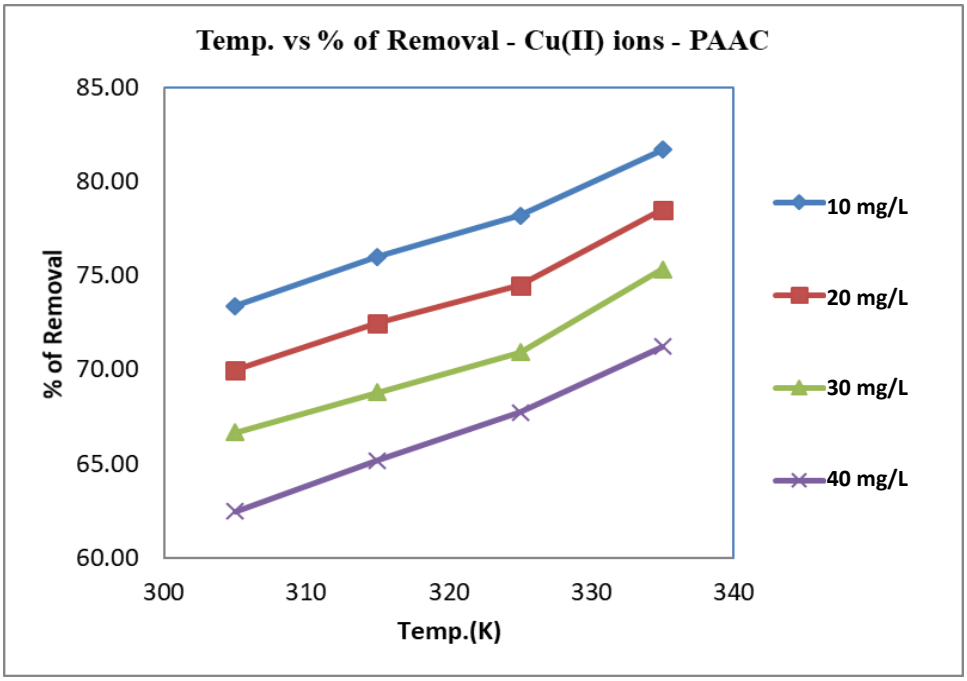

Figure 5.33

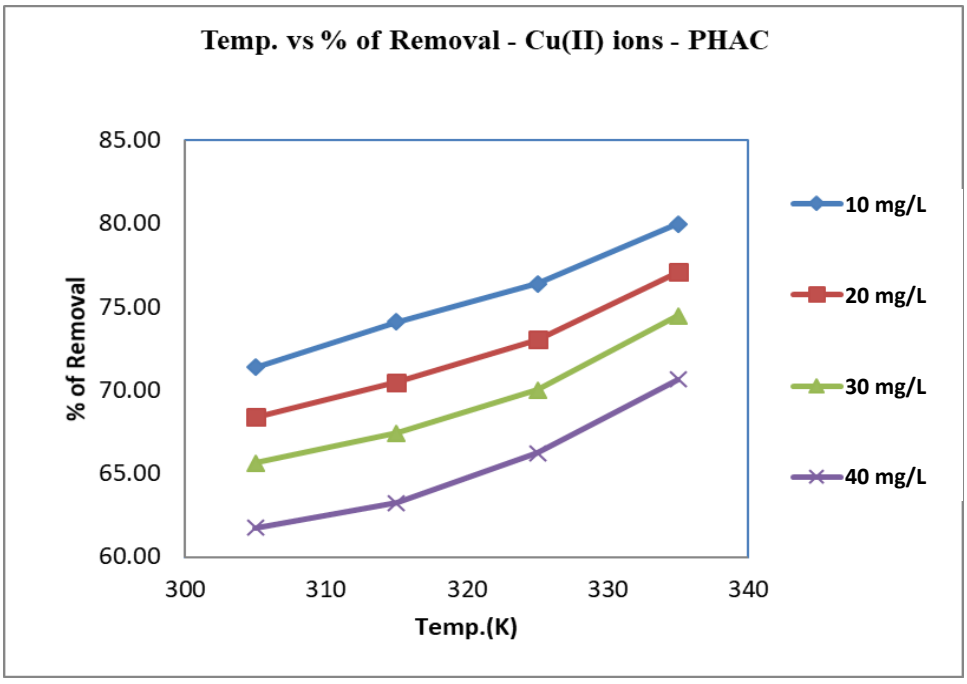

Figure 5.34

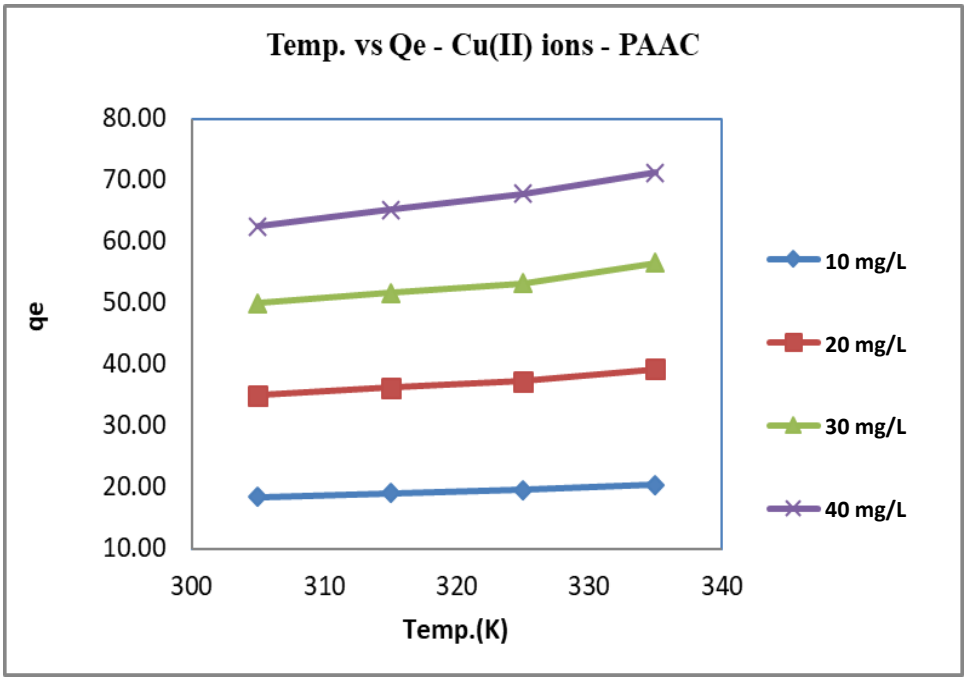

Figure 5.35

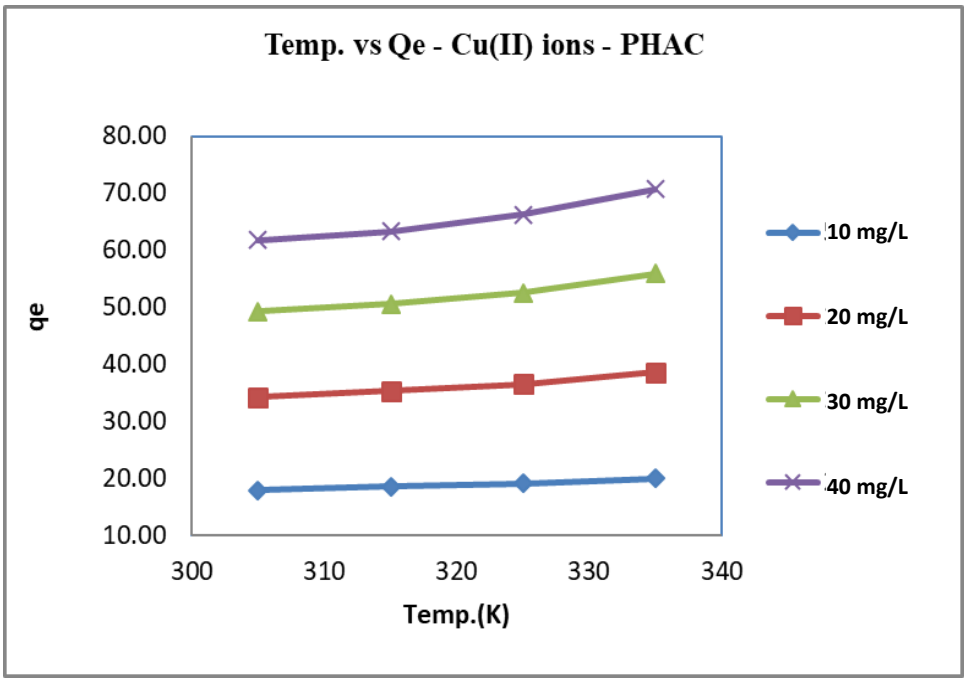

Figure 5.36

5.5 Effect of pH

The pH of the solution plays an important role for determining the quantity of solute adsorbed because the pH of the solution affects the functional groups of the activated carbon and also alters the surface charge of the carbon and governs the speciation of the solute. Here adsorption was studied ranges in between pH 2−10.

The effect of pH on the % removal of solute from the aqueous phase was detected to be varied for different solutes for the same adsorbent depending upon the nature of the solute.

Figure 5.37 and 5.38 shows the effect of initial pH of the metal ion solution on the elimination of Cr (VI) ion.

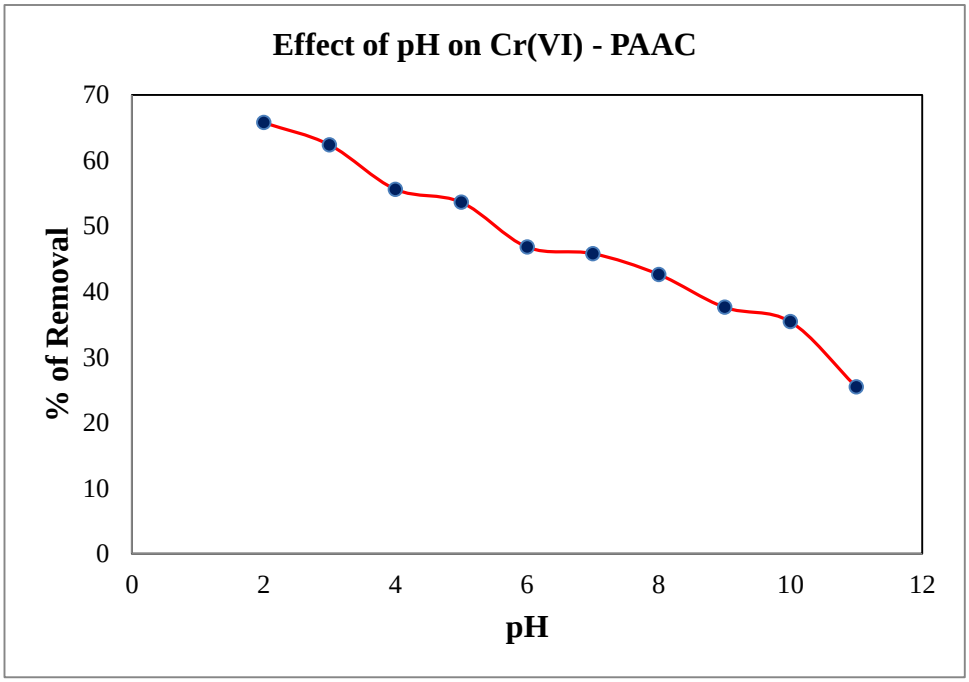

Figure 5.37

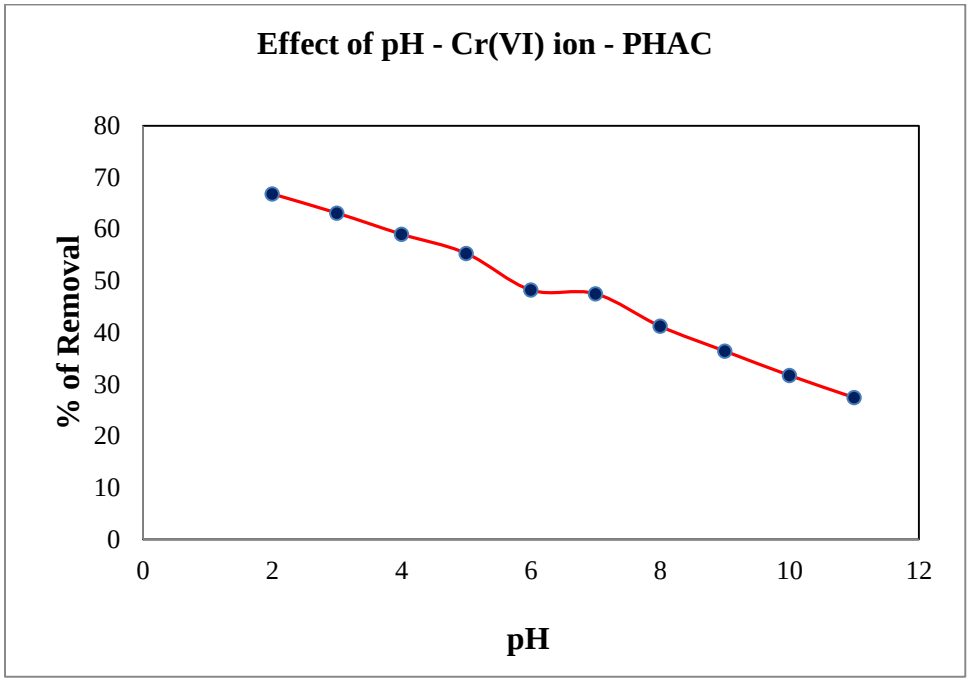

Figure 5.38

The adsorption capacities of Chromium (VI) ions onto PAAC increased significantly with a decrease of pH value and the maximum removal was attained at pH (2.0).

The reason for the high percent of removal of Cr (VI) at lower pH range was explained as below. The Cr (VI) ion be existent in different forms such as $HCrO_4^-$, $Cr_2O_7^{2-}$ and CrO_4^- ions in aqueous solution and the stability of these forms is dependent on pH of the system. The active form of Cr (VI) ion adsorbed is $HCrO_4^-$ ions. This form is stable at only lower pH range which leads to great elimination of chromium. The concentration of this form decreases with the increase of pH[53, 54 &55].

In the case of Ni(II) metal ion the highest metal ion removal efficiency was attained at pH 5, as shown in Figure 5.39 & 5.40. Ni (II) ion generates negative charged metal ions when dissolved in water.

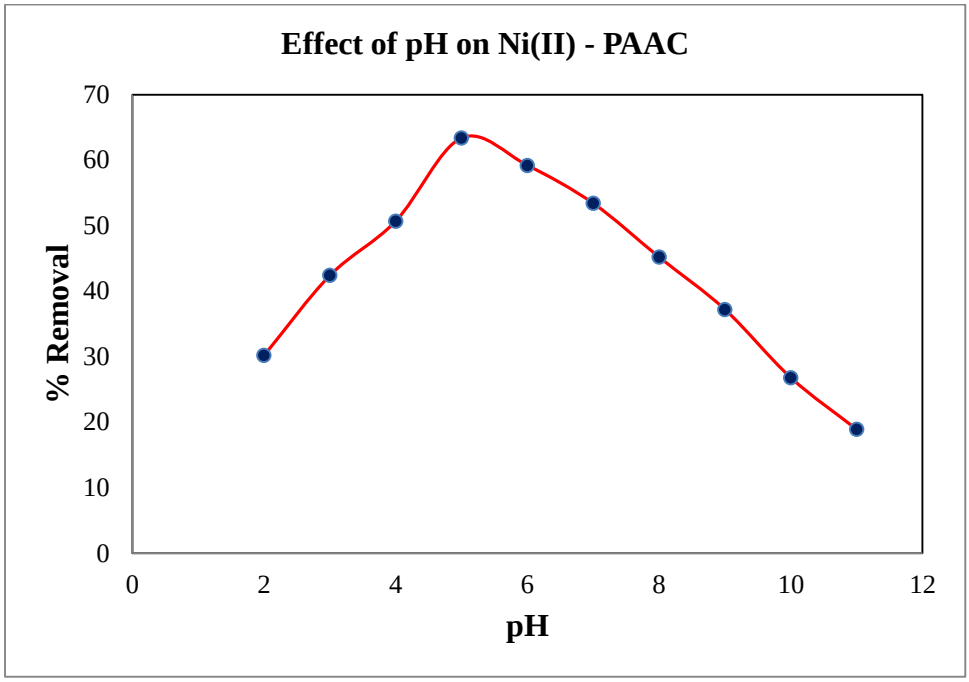

Figure 5.39

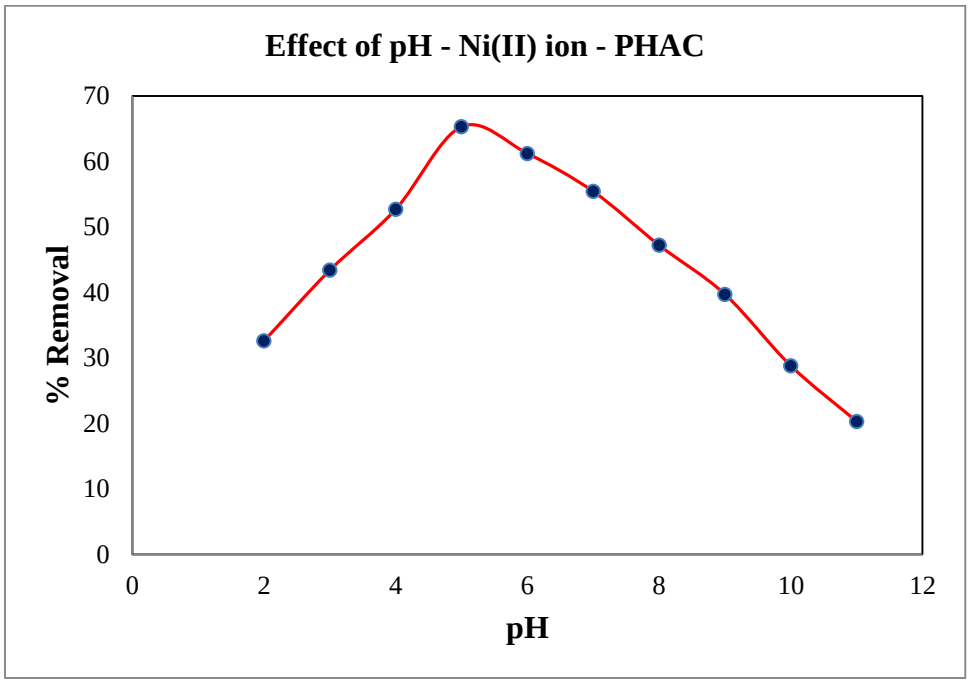

Figure 5.40

Hence the competition for the positively charged cite by OH^- ions will be low. When the pH of the solution is raised the positive charge on the surface decreases with the increase in OH^- ions concentration. The OH^- ions being smaller in size preferentially adsorb and render repulsive force towards the approaching metal ions. Hence the adsorption of Ni (II) ion was low at higher pH of the solution[52].

In the case of Cu (II) metal ion the highest metal ion removal efficiency was attained at pH 4, as shown in Figure 5.41 & 5.42. Cu (II) ion generates negative charged metal ions when dissolved in water.

When the pH is lower than pH_{zpc}, the charge on the surface of the carbon is positive. At very low pH, the positive charge accumulates on the surface of the carbon and facilitates more adsorption of metal ions. Moreover at low pH, the concentration of OH^- ions was very meager.

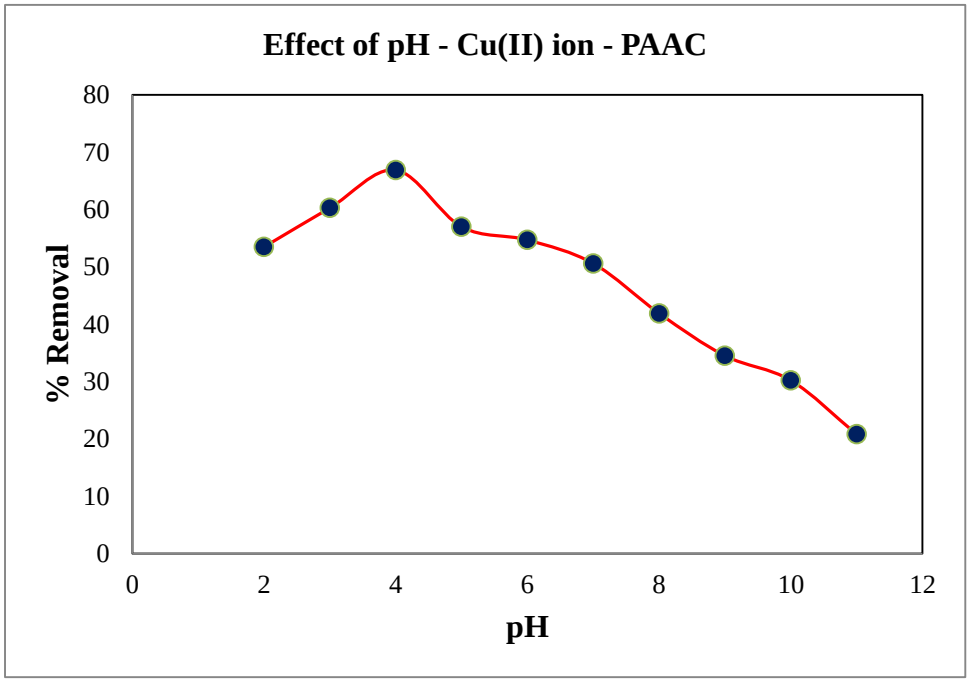

Figure 5.41

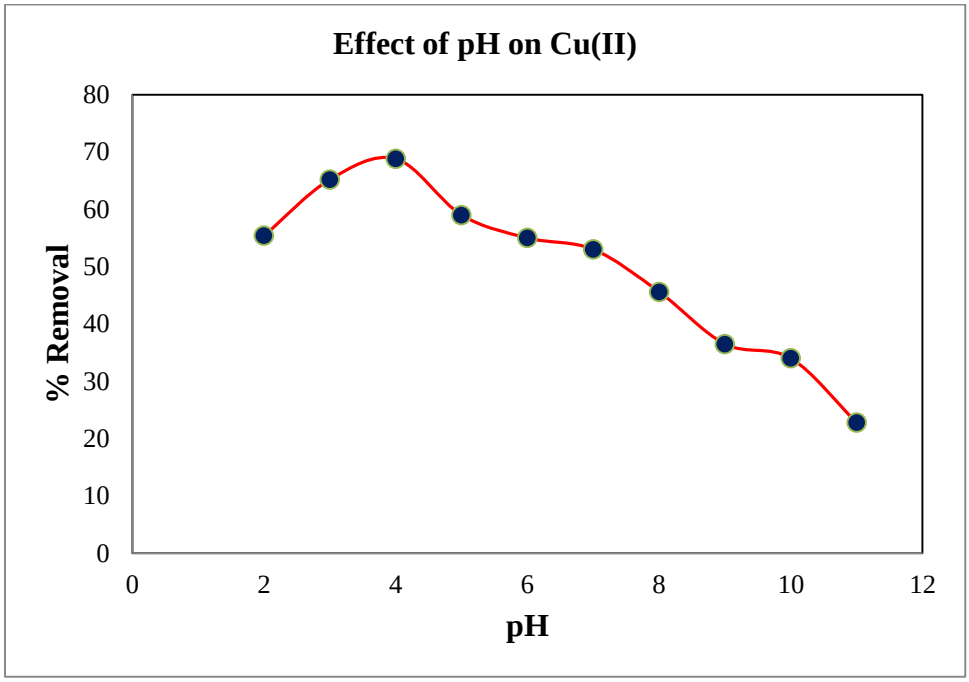

Figure 5.42

5.6 Equilibrium studies

Heavy metal ion is considered as a fast physics / chemistry process, a period of intensive concentration processes that include ion exchange, coordination, complexity, chelation, VanderWaal's gravity and microscopic precipitation. The design of systematic analysis and extraction separation processes requires a compatible balance between one of the important information.

In equilibrium, there is some relationship between the solvent concentration in the solvent and the adsorbent state (i.e., the amount of adsorbent absorbed by the solvent per unit mass). Equilibrium attentions are a role of temperature. Therefore, the absorption steadiness association at a prearranged temperature is denoted to as adsorption isotherm.

5.7 Isotherm studies

The equilibrium between the two phases (liquid and solid state) is rationalized by absorption isotherm. The equilibrium data obtained from the experiments were processed with the following isotherm equations such as Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich adsorption isotherm models. Inference obtained from each isotherm was discussed in detail one by one.

5.7.1. Langmuir isotherm

This is the greatest broadly used model to describe heavy metal ion sorption in adsorbent. The Langmuir reckoning narrates to the coverage of the molecules on a solid surface and the adsorption of the contact solution at a relentless temperature.

This isotherm is found on the following expectations, such as limited adsorption for monolayer coverage, that all surface bases are the same site with one type of adsorbate and that a molecule is capable of adsorbing on a assumed site independently of its neighbouring sites. The Langmuir - isotherm is written in the subsequent form

$$Q_e = Q_m b\, C_e / 1 + b\, C_e \qquad \ldots\ldots\ldots 5.1$$

This equation is often written in linear form as

$$C_e/Q_e = 1/Q_m b + C_e/Q_m \qquad \ldots\ldots\ldots 5.2$$

Qe is the solvent adsorbate in a unit weight of the adsorbent (mg/g), the equipoise attention of the solute in total solute (mg/L), Qm is the maximum monolayer adsorption capacity or concentration (mg/g) and b is the adsorption energy is the mutual of the concentration reaching half the concentration of the adsorbent. The linear equation is often preferred because of its ease and suitability.[60, 62.]

The important characteristics of Langmuir isotherm can be described by a separation factor, R_L, which is defined by the following equation

$$R_L = 1 / (1+ bC_0) \quad \ldots\ldots\ldots 5.3$$

where C_0 is the initial concentration of the adsorbate solution. The separation factor R_L indicates the character of the isotherm and the nature of the adsorption process as given below:

R_L value	**Nature of the process**
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

The results obtained from Langmuir model for the exclusion of Cr (VI) ion, Ni (II) ion and Cu (II) ion onto PAAC and PHAC were represented in Table 5.7 to 5.12. Concerned isotherm plots were shown in Figures5.43 to 5.48.

The square of correlation coefficient (R^2) values are ranged from 0.9808 to 0.9998 for the four studied temperatures viz. 305, 315, 325 K and 335 K for the adsorbents PAAC and PHAC with the adsorbates Cr (VI) ion, Ni (II) ion and Cu (II) ion. These results show the greatest appropriate of the equilibrium data with Langmuir isotherm.

The mono layer adsorption capacity $Q_m$values (mg/g) for adsorption of Cr (VI) ion onto PAAC system ranged from 60.728 to 61.350 and 60.976 to 64.935 for PHAC. PHAC seems to have a higher adsorption capacity than PAAC with respect to the adsorption of Cr (VI) ion for all the studied temperatures.

Table 5.7 Langmuir isotherm results for the adsorption of Cr(VI) onto PAAC.

[pH = 2; Dose =30 mg/ 50 mL; Contact time = 180 min]

Temperature (K)	Q_m (mg/g)	b (L/mg)	R_L				R^2
			5 mg/L	10 mg/L	15 mg/L	20 mg/L	
305	60.728	0.120	0.6246	0.4541	0.3568	0.2938	0.9974
315	61.350	0.135	0.5969	0.4541	0.3305	0.2702	0.9997
325	60.976	0.161	0.5545	0.3836	0.2933	0.2373	0.9987
335	60.085	0.180	0.5261	0.3569	0.2701	0.2701	0.9984

Table 5.8 Langmuir isotherm results for the adsorption of Cr(VI) onto PHAC.

[pH = 2; Dose =30 mg/ 50 mL; Contact time = 180 min]

Temperature (K)	Q_m (mg/g)	b (L/mg)	R_L				R^2
			5 mg/L	10 mg/L	15 mg/L	20 mg/L	
305	61.728	0.120	0.6246	0.4541	0.3568	0.2938	0.9974
315	61.350	0.135	0.5969	0.4254	0.3305	0.2702	0.9997
325	60.976	0.161	0.5545	0.3836	0.2933	0.2373	0.9987
335	64.935	0.180	0.5261	0.3569	0.2701	0.1272	0.9984

Table 5.9 Langmuir isotherm results for the adsorption of Ni(II) onto PAAC.

[pH = 5 ; Dose =30 mg/ 50 mL; Contact time = 180 min]

Temperature (K)	Q_m (mg/g)	b (L/mg)	R_L				R^2
			10 mg/L	15 mg/L	20 mg/L	25 mg/L	
305	76.336	0.103	0.4926	0.3929	0.3268	0.2792	0.9975
315	76.330	0.122	0.4500	0.3529	0.2903	0.2466	0.9995
325	72.993	0.165	0.3778	0.2881	0.2329	0.1954	0.9997
335	67.568	0.256	0.2805	0.2062	0.1631	0.1349	0.9985

Table 5.10 Langmuir isotherm results for the adsorption of Ni(II) onto PHAC

[pH = 5 ; Dose =30 mg/ 50 mL; Contact time = 180 min]

Temperature (K)	Q_m (mg/g)	b (L/mg)	R_L				R^2
			10 mg/L	15 mg/L	20 mg/L	25 mg/L	
305	74.64	0.085	0.4405	0.3395	0.2704	0.2003	0.9987
315	75.5	0.101	0.3973	0.2974	0.231	0.1835	0.9998
325	71.81	0.138	0.3197	0.2253	0.1656	0.1244	0.9955
335	68.93	0.211	0.2219	0.1404	0.918	0.0596	0.9996

Table 5.11 Langmuir isotherm results for the adsorption of Cu(II) onto PAAC.

[pH = 4 ; Dose =30 mg/ 50 mL; Contact time = 180 min]

Temperature (K)	Q_m (mg/g)	b (L/mg)	R_L				R^2
			10 mg/L	20 mg/L	30 mg/L	40 mg/L	
305	142.85	0.050	0.6665	0.4998	0.3998	0.3331	0.9982
315	131.95	0.066	0.6032	0.4319	33639	0.2754	0.9808
325	140.84	0.066	0.6024	0.4310	0.3356	0.2747	0.9990
335	149.25	0.077	0.5646	0.3933	0.3018	0.2448	0.9987

Table 5.10Langmuir isotherm results for the adsorption of Cu(II) onto PHAC.

[pH = 4; Dose =30 mg/ 50 mL; Contact time = 180 min]

Temperature (K)	Q_m (mg/g)	b (L/mg)	R_L				R^2
			10 mg/L	20 mg/L	30 mg/L	40 mg/L	
305	129.87	0.062	0.6182	0.4474	0.3505	0.2881	0.9995
315	131.57	0.070	0.5898	0.4182	0.3240	0.2644	0.9989
325	136.98	0.075	0.5723	0.4009	0.3084	0.2507	0.9989
335	140.13	0.096	0.5092	0.3416	0.2570	0.2060	0.9994

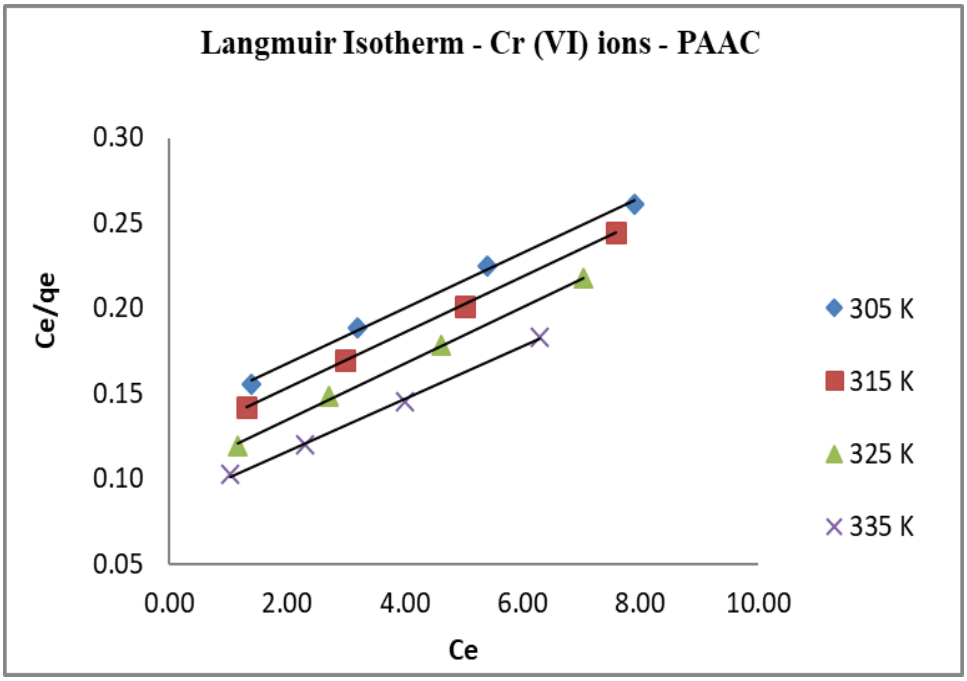

Figure 5.43

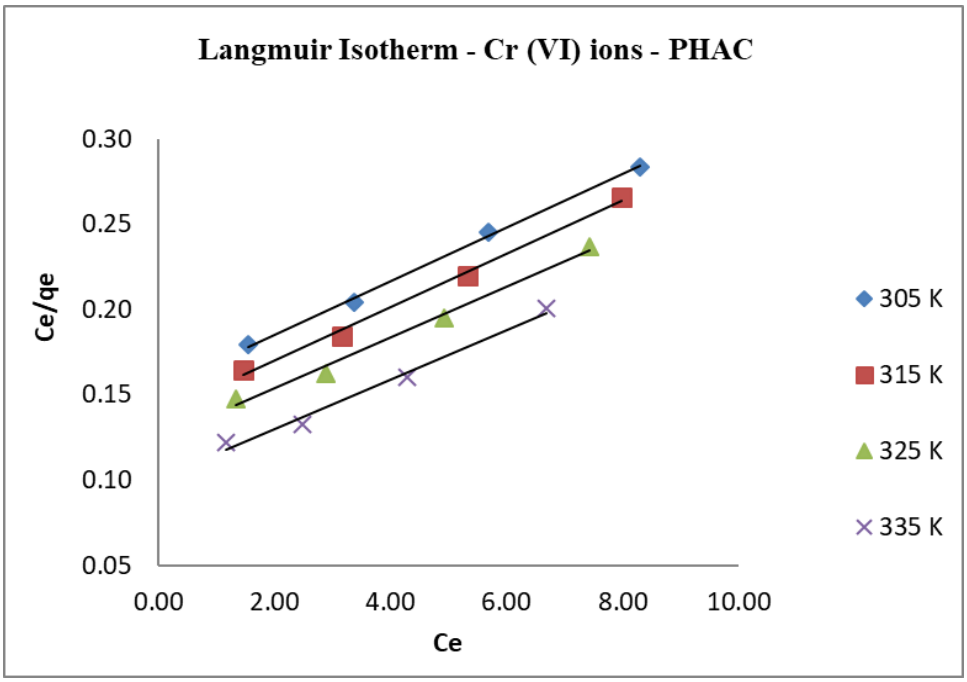

Figure 5.44

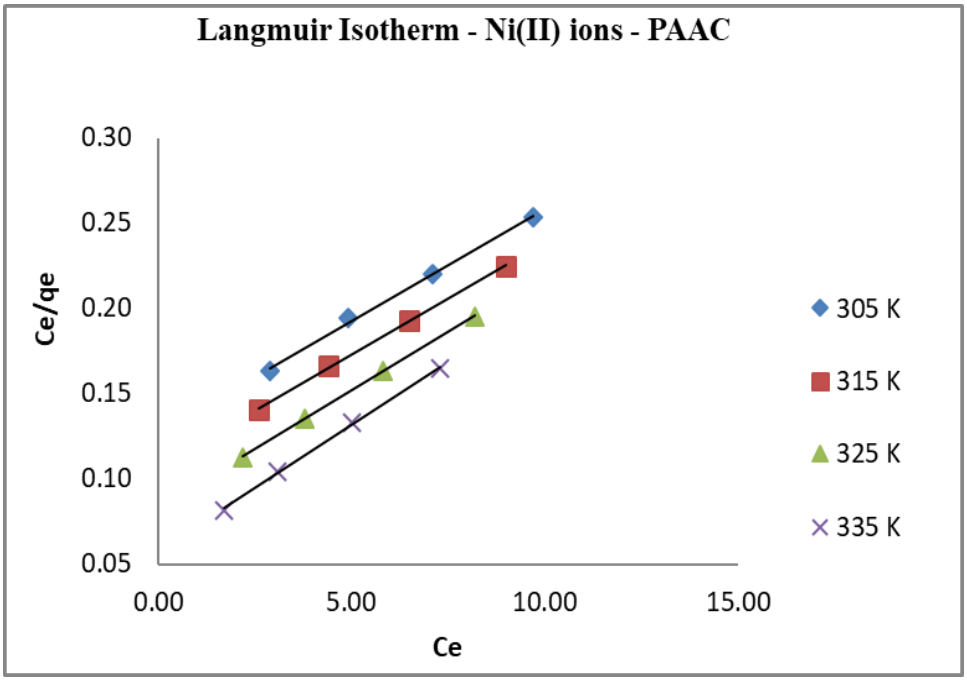

Figure 5.45

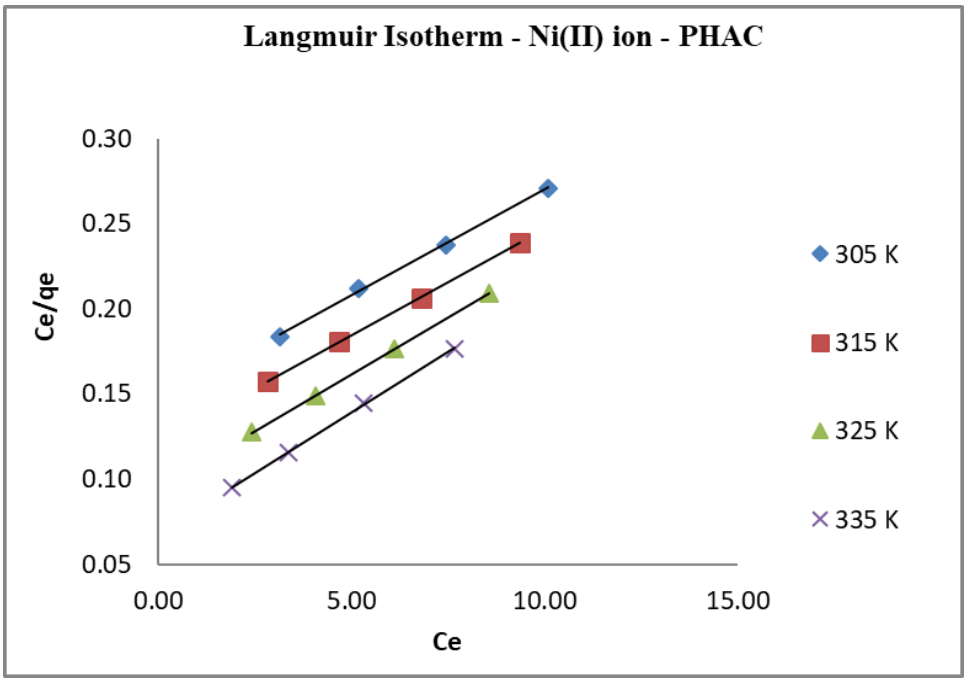

Figure 5.46

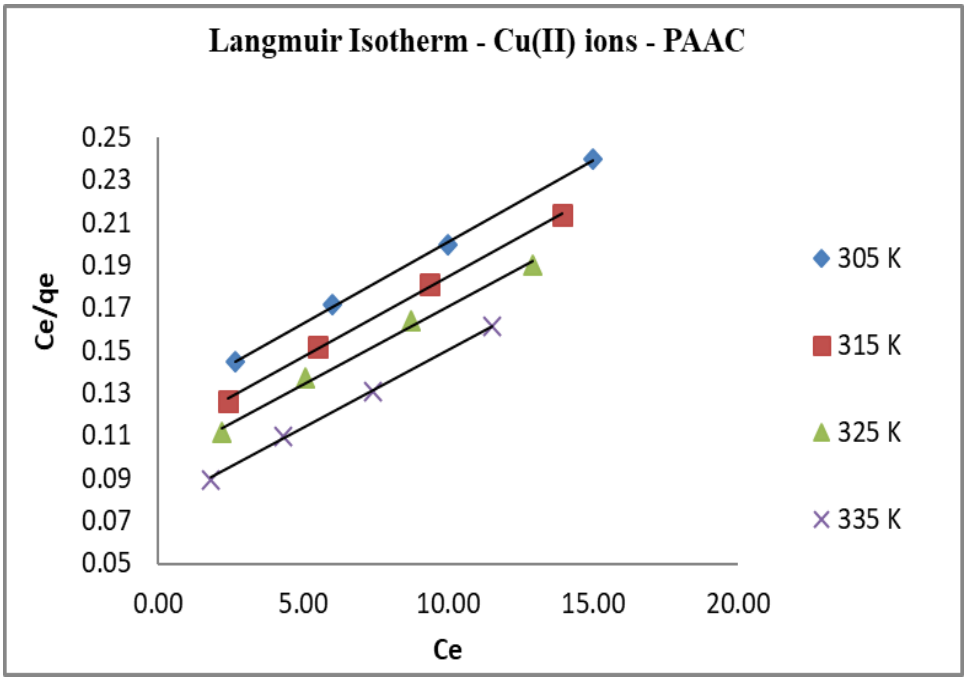

Figure 5.47

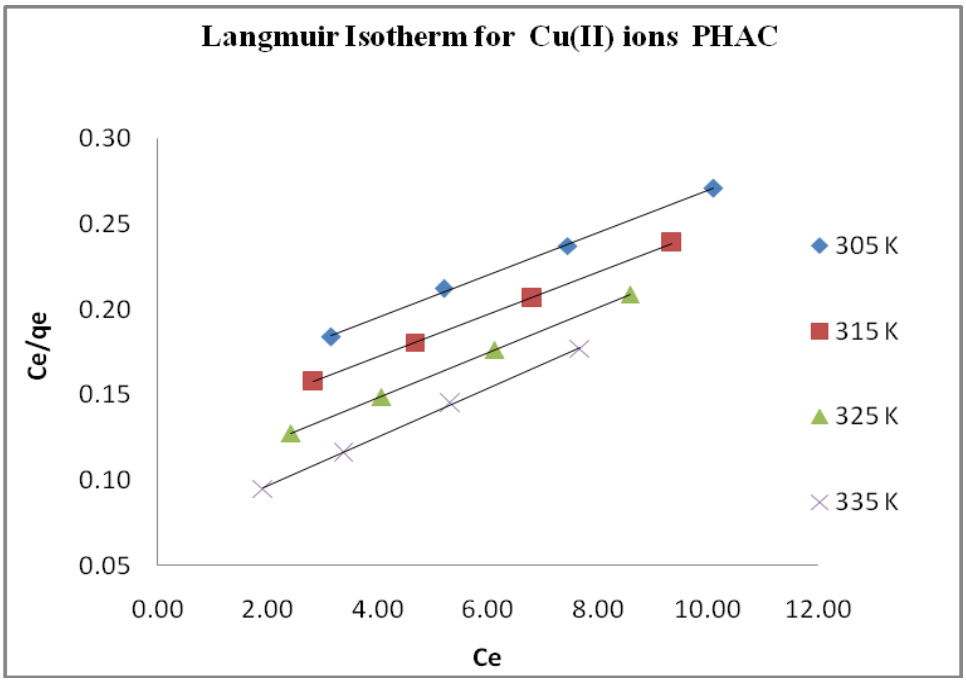

Figure 5.48

Further it is observed that adsorption capacity is slightly amplified with an increase of temperature. Table 5.15 reveals that adsorption capacities of PAAC and PHAC were almost same and quite reasonable for the adsorption of Cr (VI) ion.

The mono layer adsorption capacity Q_m values (mg/g) for adsorption of Ni (II) ion onto PAAC system the values ranged from 67.56 to 76.33 and 68.93 to 74.64 for PHAC.PAAC seems to have a higher adsorption capacity than PHAC with respect to adsorption of Cu (II) ion for all the studied temperatures.

The mono layer adsorption capacity Q_m values (mg/g) for adsorption of Cu (II) ion onto PAAC system are ranged from 131.95 to 149.25 and 129.87 to 140.13 for PHAC. PAAC seems to have a greater adsorption capacity than PHAC for all the studied temperatures. But the difference was very little. The adsorption capacity amplified with the increase of temperature[63].

The values of Langmuir constant 'b', the adsorption energy ranges from 0.050 to 0.256 for all the four systems. These values indicate that the apparent energy of sorption is less and guidelines out the probability of strong interaction between the solute and adsorption site.

The dimensionless separation factor R_L values designed for various initial concentrations at different temperatures lie between 0 and 1 which indicates the favourable adsorption of Cr (VI) ion, Ni (II) ion and Cr (VI) onto PAAC and also PHAC[61].

Comparison of the chosen adsorbates

On comparing the three adsorbates namely Cr (VI) ion, Ni (II) ion and Cu (II) metal ion, preferential adsorption is in the following order for both the adsorbents PAAC and PHAC at all studied temperatures.

Cu (II) ion	>	Ni (II) ion	>	Cr (VI) metal ion

The Q_m values (mg/g) at a particular temperature, are given in Table 5.13 and 5.14.

Table –5.13 Q_m (mg/g) values for PAAC

Temperature(K)	Cr (VI) ion	Ni (II) ion	Cu (II) ion
305	60.728	76.336	142.85
315	61.350	76.330	131.85
325	60.976	72.993	140.84
335	60.085	67.568	149.25

Table - 5.14 Q_m (mg/g) values for PHAC

Temperature (K)	Cr (VI) ion	Ni (II) ion	Cu (II) ion
305	61.728	74.64	129.87
315	61.350	73.5	131.57
325	60.976	71.81	136.98
335	64.935	68.93	135.13

The difference may be due to the following factors such as ionic charge, size, shape of adsorbates and pore volume, pore shape and surface characteristics of the adsorbents. In general Langmuir constant values infer a better performance of PAAC than PHAC.

Table - 5.15 Adsorption capacities of few adsorbents for Cr (VI) ion

Adsorbent	Adsorption capacity Q_m (mg/g)	References
Activated Carbon Rice husk – H_3PO_4 Impregnated	333.33	64
Coal	323.68	65
Rice husk	312.26	65
Cotton Waste	277.78	65
NaOH treated Raw Clay	204.00	66
Activated Carbon Sewage sludge – H_2SO_4 impregnated	194.3	56
Hair	158.23	65
Tree Leaves	133.33	67
NaOH - treated pure clay	122.01	66
Pure clay	91.87	66
Calcined pure clay	56.31	66
Calcined raw clay	13.44	66
Saw dust	32.26	68
Raw Clay	27.49	66
PHAC	**64.395**	**Present Study**
PAAC	**61.350**	**Present Study**

Table - 5.16 Adsorption capacities of few adsorbents for Cu (II) ion

Adsorbent	Adsorption capacity Q_m (mg/g)	References
Wood apple shell	13.74	69
Ricinuscommunis seed shell active carbon	7.761	70
Palm shell activated carbon	12.6	71
PEI/palm shell activated carbon	20.5	72
Acid-modified waste activated carbon	10.93	73
Fe-modified bamboo carbon	35.7	74
PHAC	**135.13**	**Present Study**
PAAC	**149.25**	**Present Study**

5.7.2 Freundlich Isotherm

The Freundlich equation is an experimental equation. This is the greatest popular model for a single solvent system based on the solvent distribution between the solid state and the aqueous phase in equilibrium. It also suggests that if the sorption middles of an adsorbent are completed, the adsorption energy decreases exponentially. The Freundlich model designates sorption only within the restricted range. It is accomplished of recitation the sorption of organic and inorganic complexes in a variability of sorbents[75.]

This equation has the following form:

$$\log q_e = \log K_f + 1/n \log C_e \quad \text{..... 5.4}$$

where qe is the quantity of adsorbate adsorbed (mg/g) in equilibrium, Ce is the symmetry attention of adsorbate in solution (mg/L), and K_f and n are constants covering all the influences that distress the adsorption capacity and intensity of adsorption, respectively.[60]

As a robust equation, the Freundlich isotherm has the capability to apply to almost all test absorption-scattering data and is best suited for data from highly heterogeneous sorbent systems. 1/n is the diversity factor and is a degree of the deviation from the linearity of the adsorption. The value of 1/n higher than unity (less than one) denotes the existence of a concave / curved upward isotherm in the non-linear form of the graph drawn between the time 't' (Qt) and the amount absorbed in time. 'D'. This concave type isotherm is also called solvent-coupling type isotherm [62]. In this case, sturdy sorption of the solvent arises as a result of hearty intermolecular magnetism within the adsorbent layers. But in many cases, the absorption assessment data is arched rather than concave.

A favourable sorption has a value of n amongst 1 and 10. The larger value indicates a stronger correlation between the adsorbent and the adsorbate, 1/n equal to 1

designates the linear adsorption, which leads to identical adsorption energies for all sites.[67, 76 & 77].

The sorbtion of the solute in any of the surfactants can be caused by physical bonding, ion exchange, complexation or a combination of these interactions. In the first case of physical bonding, the solvent is loosely bonded so it can be easily distilled using distilled water. Depending on the functional groups such as hydroxyl, carbonyl and carboxyl, the interaction between the surfactant and solvent molecules may be within the structure of the adsorbent, as mentioned above. The parameter of the 'n' freundlich isotherm expresses these occurrences.

The adsorption capacity is the greatest significant characteristic of sorbent. It is defined as the amount of sorbate occupied up by sorbent per unit mass of sorbent. This adjustable is ruled by a series of properties such as aperture size and its size spreading, specific surface area, cation exchange capacity, pH, surface functional groups and also temperature.

The results obtained from Freundlich model for the removal of Cr (VI) ion, Ni (II) ion and Cu (II) ion onto PAAC and PHAC are given in Table 5.49 to 5.54. The concerned isotherm plots are shown in Figures 5.17 to 5.22.

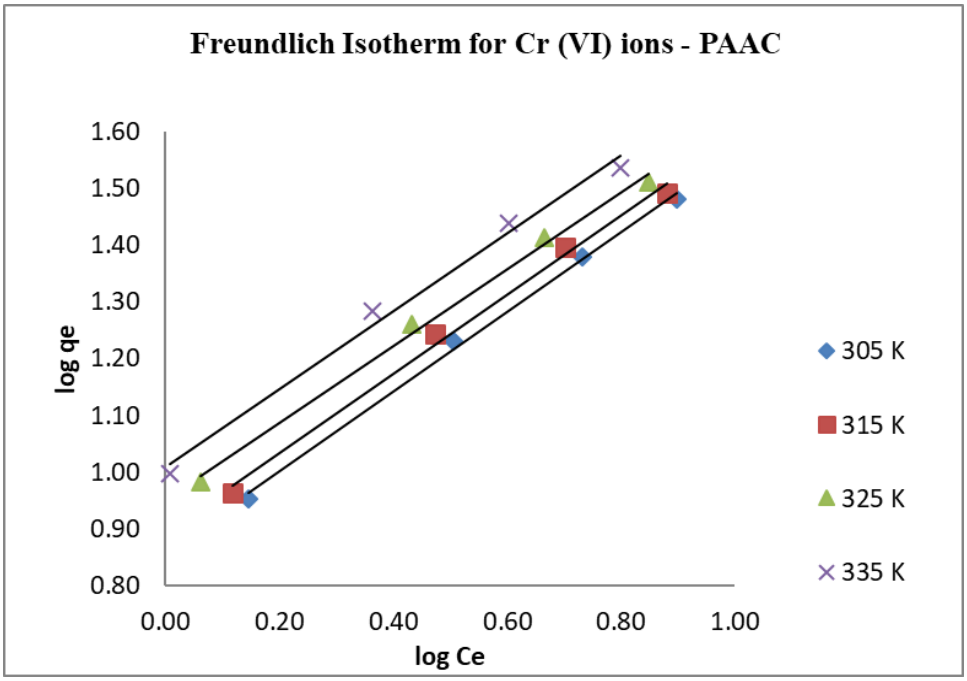

Figure 5.49

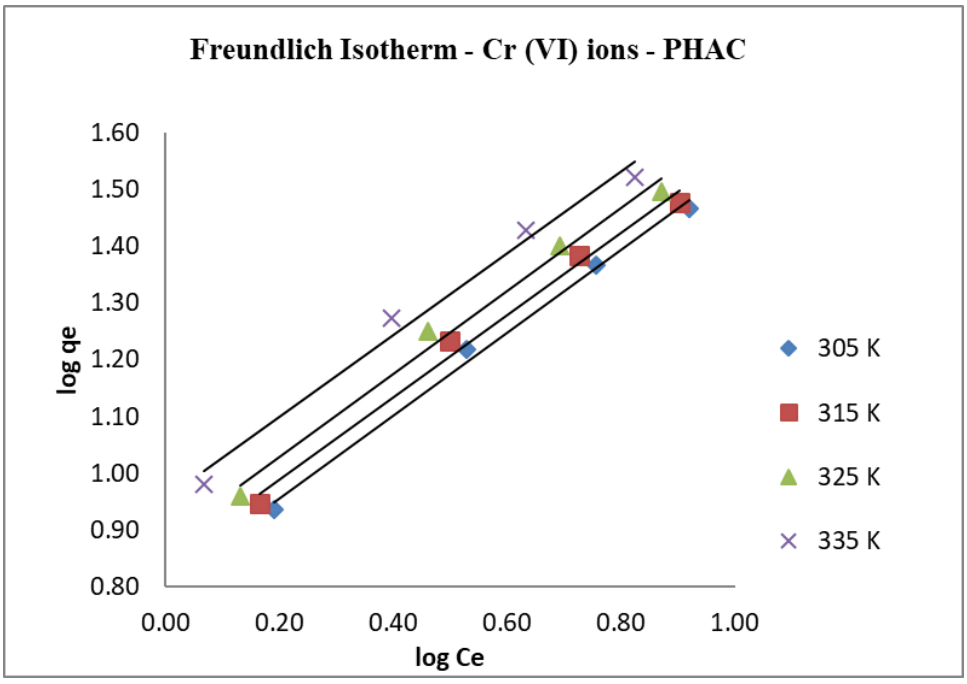

Figure 5.50

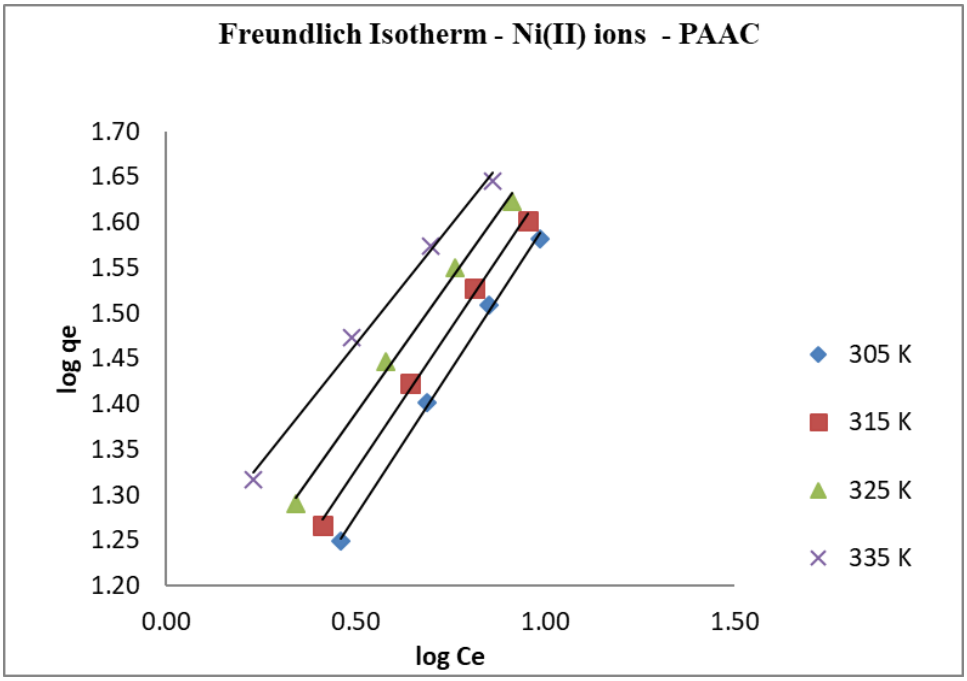

Figure 5.51

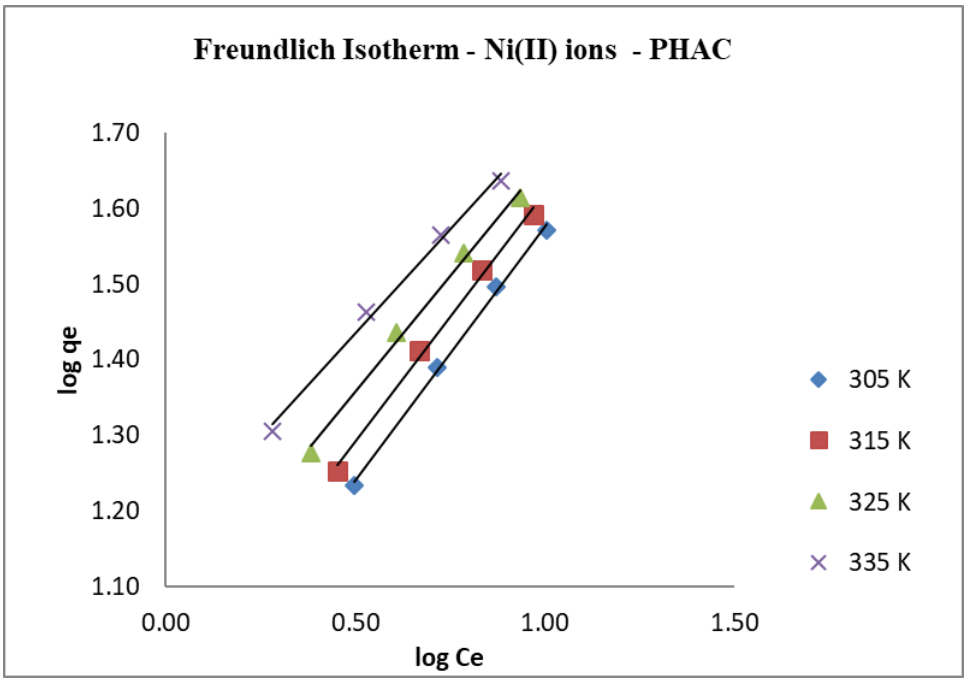

Figure 5.52

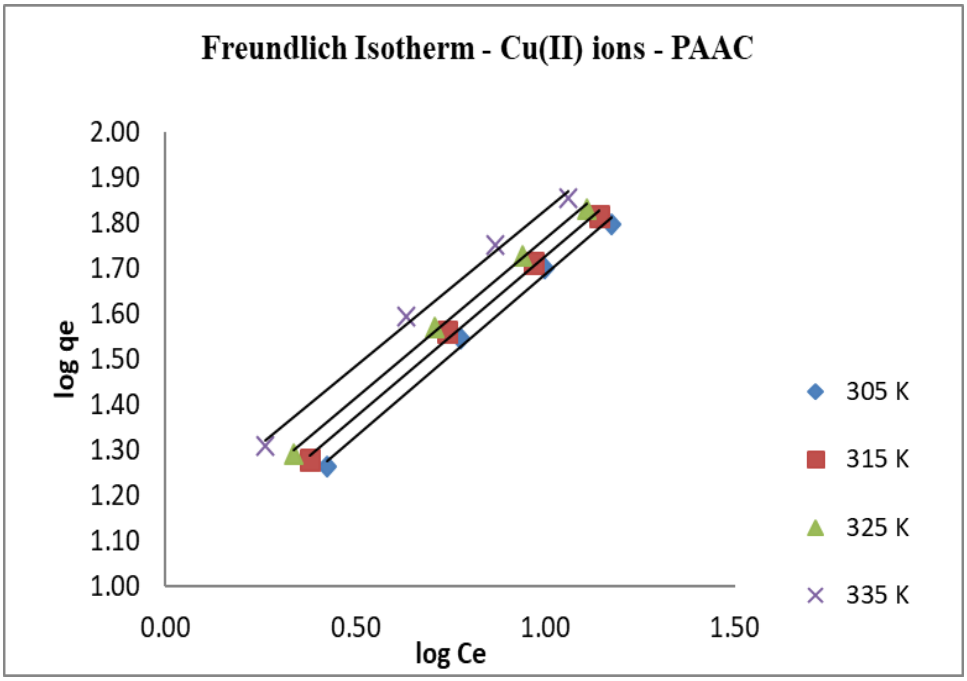

Figure 5.53

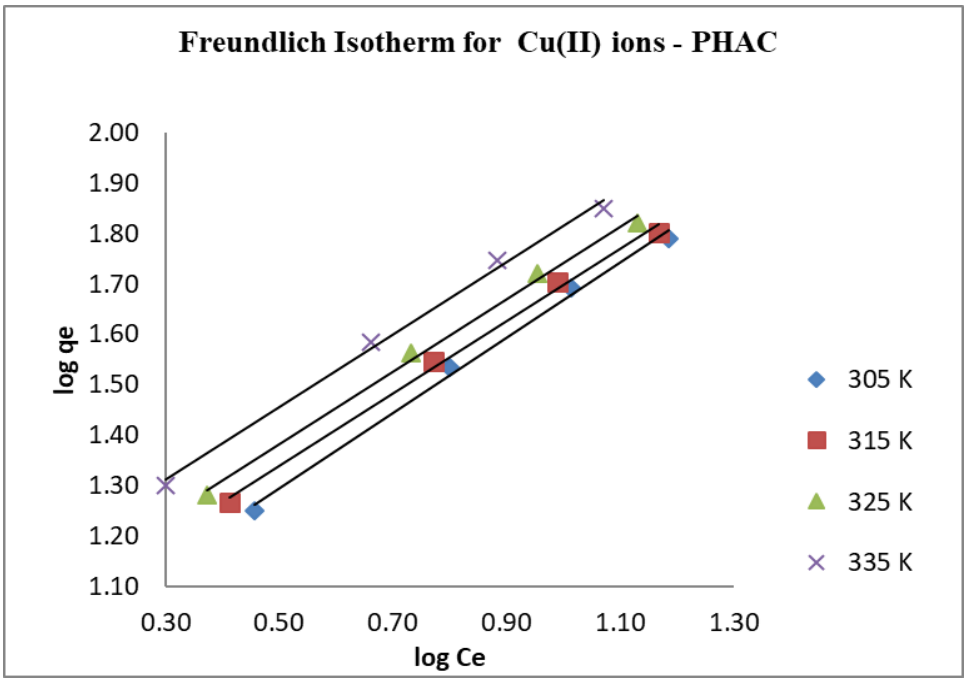

Figure 5.54

Table 5.17 Freundlich Isotherm for Cr(VI) ions onto PAAC

[pH = 2; Dose = 30 mg/ 50 mL; Contact time = 180 min]

Temperature (K)	n	k_f (mg/g)	R^2
305	1.4219	8.2196	0.9972
315	1.4335	8.8632	0.9940
325	1.4778	9.9123	0.9955
335	1.4537	12..6421	0.9899

Table 5.18 Freundlich Isotherm for Cr(VI) ions onto PHAC

[pH = 2; Dose = 30 mg/ 50 mL; Contact time = 180 min]

Temperature (K)	n	k_f (mg/g)	R^2
305	1.4219	7.2494	0.9972
315	1.4335	7.8632	0.9940
325	1.4778	8.9702	0.9955
335	1.4537	10.2164	0.9899

Table 5.19 Freundlich Isotherm for Ni(II) ions onto PAAC

[pH = 5; Dose = 30 mg/ 50 mL; Contact time = 180 min]

Temperature (K)	n	k_f (mg/g)	R^2
305	1.6006	9.0448	0.9983
315	1.6008	10.3252	0.9969
325	1.7091	12.5141	0.9954
335	1.9231	16.0583	0.9947

Table 5.20 Freundlich Isotherm for Ni(II) ions onto PHAC

[pH = 5; Dose = 30 mg/ 50 mL; Contact time = 180 min]

Temperature (K)	n	k_f (mg/g)	R^2
305	1.4872	8.0002	0.9978
315	1.5221	9.1960	0.9960
325	1.6319	11.2512	0.9943
335	1.8146	14.4178	0.9983

Table 5.21 Freundlich Isotherm for Cu(II) ions onto PAAC

[pH = 4; Dose = 30 mg/ 50 mL; Contact time = 180 min]

Temperature (K)	n	k_f (mg/g)	R^2
305	1.3968	9.5697	0.9949
315	1.4178	10.4906	0.9964
325	1.4560	13.8676	0.9946
335	1.4253	14.5239	0.9975

Table 5.22 Freundlich Isotherm for Cu(II) ions onto PHAC

[pH = 4; Dose = 30 mg/ 50 mL; Contact time = 180 min]

Temperature (K)	n	k_f (mg/g)	R^2
305	1.3358	8.3272	0.9978
315	1.3885	10.5245	0.9960
325	1.3862	12.4423	0.9943
335	1.4529	13.6583	0.9983

The square of correlation coefficient (R^2) for Freundlich isotherms are above 0.9899 for all the studied adsorbates Cr (VI) ion, Ni (II) ion and Cu (II) ion and for all the studied temperatures viz. 305, 315, 325 and 335 K. It indicates that the experimental data fit well into Freundlich model.

Freundlich constant K_f (mg/g) for adsorption of Cr (VI) ion onto PAAC system, the values ranged from 8.2196 to 12.6421and 7.2494 to 10.2164 for PHAC whereas, K_f for the adsorption of Ni (II) ion onto PAAC system the K_f values ranged from 9.0448 to 16.0583 and 8.0002 to 14.4178 for PHAC[27]. The K_f values for adsorption of Cu (II) ion onto PAAC system ranged from 9.5697to 14.5239 and 8.3272 to 13.6583 for PHAC.

PAAC seems to have s higher adsorption capacity than PHAC with respect to adsorption of Cr (VI) ion for all the studied temperatures. Further it is noticed that the adsorption capacity increased with the increase of temperature as shown in Table 5.23 and 5.24. The same trend was reported in earlier literature[180, 181]. Table 5.25 reveals that adsorption capacity of PAAC was quite reasonable when compared to other adsorbents for the adsorption of Cr (VI) ion.

On comparing the three adsorbates namely Cr (VI) ion, Ni (II) ion and Cu (II) metal ions; preferential adsorption is in the following order for all the studied temperatures.

Ni (II) ion > Cu (II) ion > Cr (VI) ion

It can be understood from the K_f (mg/g) at a particular temperature. These values are given in Table 5.23 and 5.24.

Table – 5.23 K_f (mg/g) values for PAAC

Temperature (K)	Cr (VI) ion	Ni (II) ion	Cu (II) ion
305	8.2196	9.0448	9.5697
315	8.8632	10.3252	10.4906
325	9.9123	12.5141	13.8676
335	12..6421	16.0583	14.5239

Table – 5.24 K_f (mg/g) values for PHAC

Temperature (K)	Cr (VI) ion	Ni (II) ion	Cu (II) ion
305	7.2494	8.0002	8.3272
315	7.8632	9.1960	10.5245
325	8.9702	11.2512	12.4423
335	10.2164	14.4178	13.6583

The difference may be due to the following factors such as adsorbate ionic charge, adsorbate size, adsorbate shape, pore volume, pore shape and surface characteristics of the adsorbents.

The adsorption intensity constant ‘n’ values are ranged from 1.3358 to 1.9231 for all the studied systems, i.e., between 1 and 10, which indicates the favourable physical adsorption. ‘n’ value increases with an increase of temperature for all the studied systems.In general Freundlich constant values infer a better performance of PAAC than PHAC.

Table –5.25 Adsorption capacities of few adsorbents for Ni (II) ion

Adsorbent	k_f (mg/g)	References
Activated Carbon Rice husk – H_3PO_4 Impregnated	57.54	64
NaOH treated Raw Clay	17.04	65
Activated Carbon Sewage sludge – H_2SO_4 impregnated	6.083	65
Tree Leaves	52.48	65
NaOH – treated pure clay	23.05	66
Pure clay	16.39	56
Calcined pure clay	9.01	65
Calcined raw clay	6.57	67
Saw dust	14.58	66
Raw Clay	14.85	66
PHAC	**10.21**	**Present Study**
PAAC	**12.64**	**Present Study**

5.7.3 Tempkin isotherm

Tempkin isotherm adopts that the temperature of sorption in the film reductions linearly with the attention due to the sorbate / sorbent interactions. Moreover, the drop in heat of absorption is not logarithmic, as stated in the Freundlich expression.

The linear form of Tempkin equation is[79].

$$q_e = RT/b_T \ln a_T + RT/b_T \ln C_e \quad \ldots\ldots\ldots 5.5$$

Where, b_T is the constant associated to the temperature of sorption (J/mg) and a_T the equilibrium binding constant equivalent to the maximum binding energy (L/g) The constants a_T and b_T were calculated from the slopes and intercepts of q_e versus ln C_e [60, 80].

The results obtained from Tempkin model for the removal of Cr (VI) ion, Ni (II) ion and Cu (II) ion onto PAAC and PHAC were represented in Table 5.26 to 5.31. Concerned isotherm plots were shown in Figures 5.55 to 5.60.

The square of correlation coefficient (R^2) values ranged from 0.9828 to 0.9991 for the four studied temperatures viz. 305, 315 325 K and 335 K for the adsorbents PAAC and PHAC with the adsorbates Cr (VI) ion, Ni (II) ion and Cu (II) ion. These results show the best fitting of the equilibrium data with Tempkin isotherm.

Equilibrium binding constant 'a_T' values (L/g) for adsorption of Cr (VI) ion onto PAAC system are ranged from 1.5074 to 2.8649 and 1.4074 to 1.9649 for PHAC. The Tempkin constant related to heat of sorption, $b_T$values are ranged from 215.22 J/mg to 228.67 J/mg for the four studied temperatures viz. 305, 315, 325 K and 335 K for PAAC and for PHAC these values are ranged from 207. 6795 J/mg to 215.8532 J/mg.

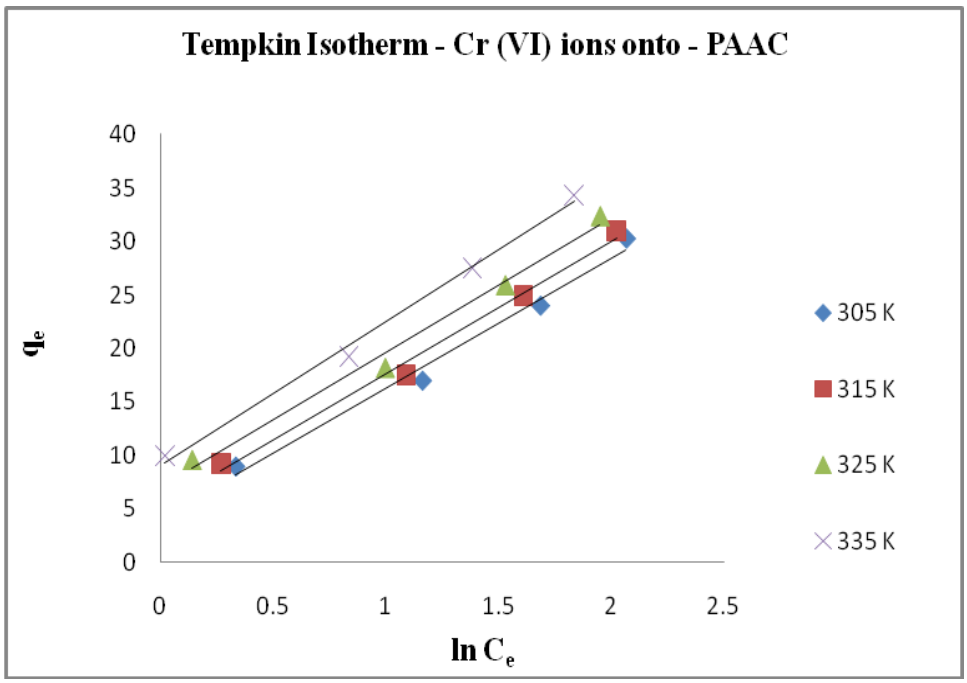

Figure 5.55

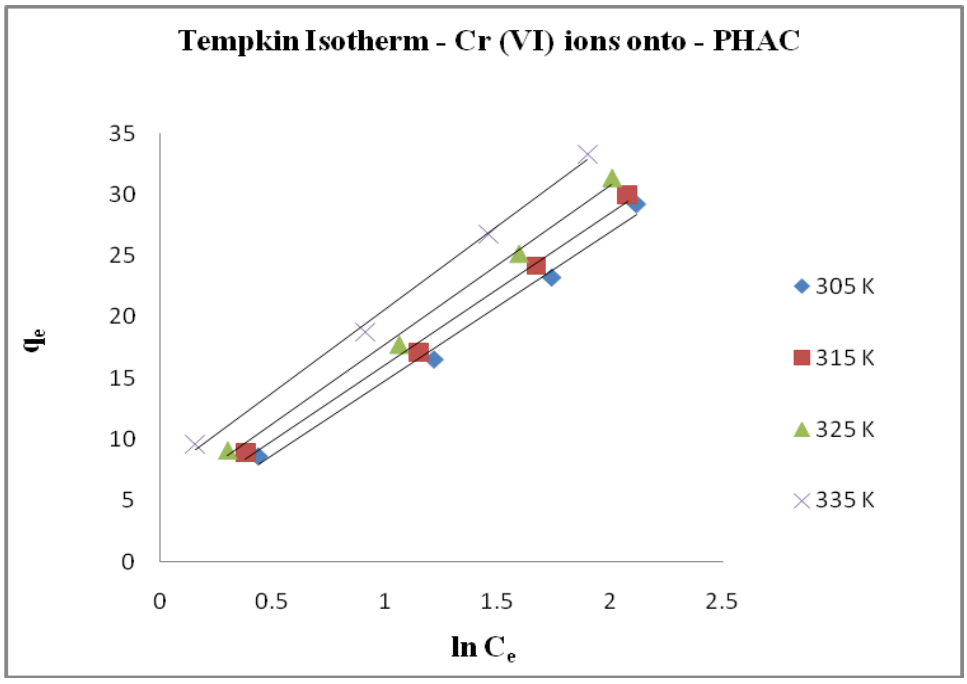

Figure 5.56

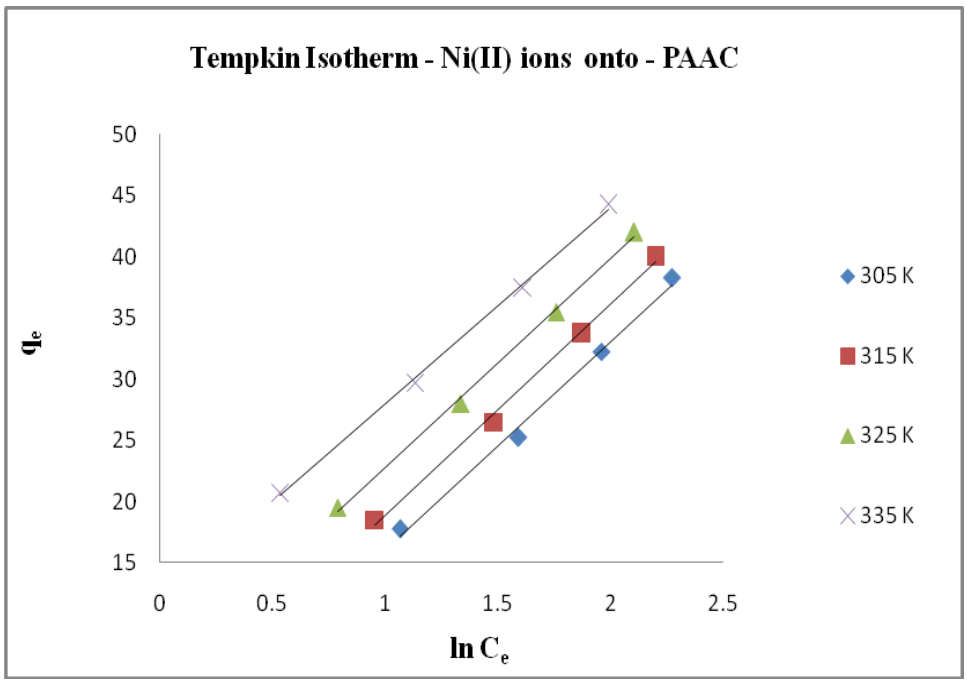

Figure 5.57

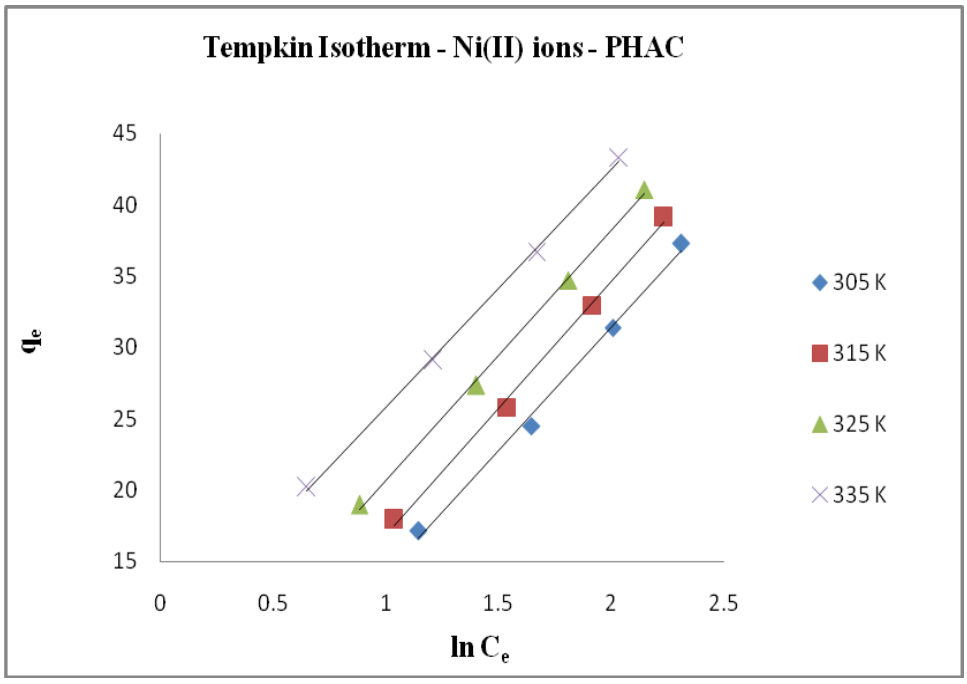

Figure 5.58

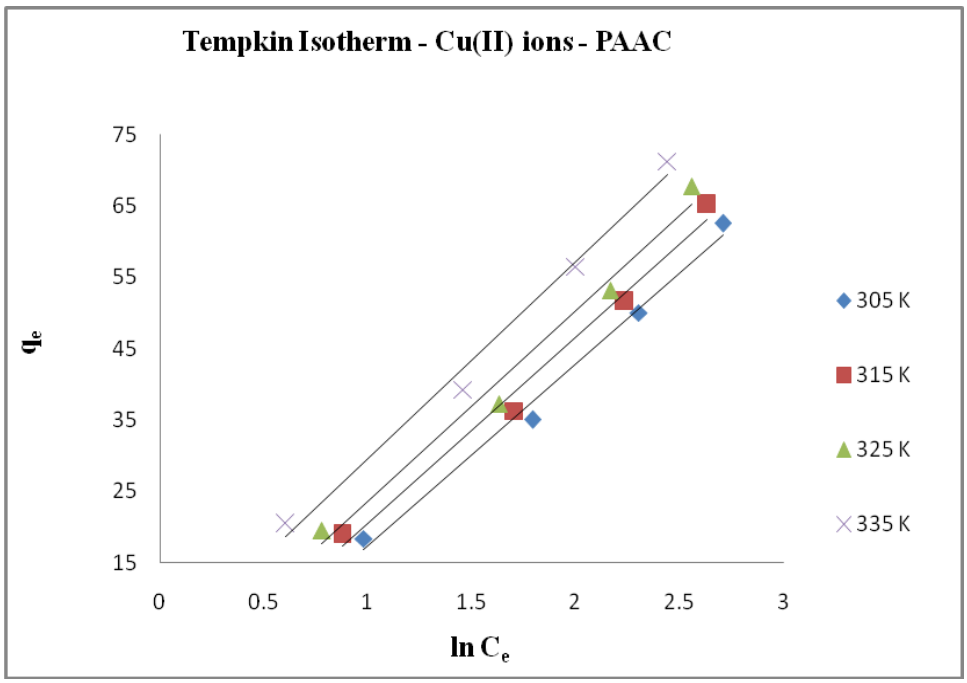

Figure 5.59

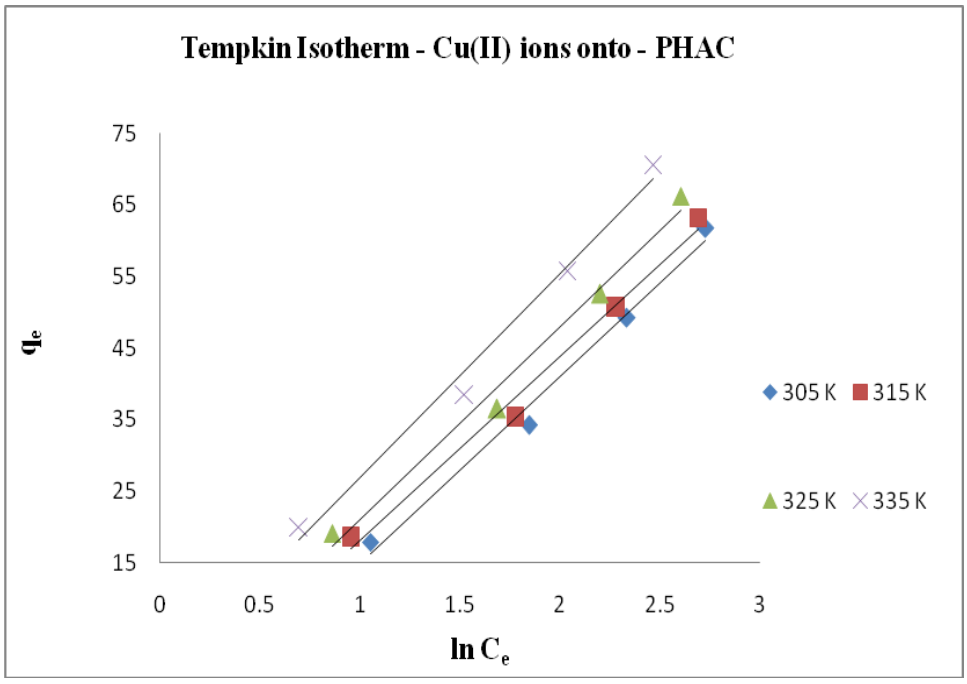

Figure 5.60

Table 5.26 Tempkin constants for the adsorption of Cr(VI) ions onto PAAC

[pH = 2; Dose = 30 mg/ 50 mL; Contact time = 180 min]

Temperature (K)	b_T (J/mg)	a_T (L/g)	R^2
305	215.2219	1.5074	0.9857
315	221.5436	1.6222	0.9909
325	226.8532	1.8621	0.9921
335	228.6795	2.8649	0.9943

Table 5.27 Tempkin constants for the adsorption of Cr(VI) ions onto PHAC

[pH = 2; Dose = 30 mg/ 50 mL; Contact time = 180 min]

Temperature (K)	b_T (J/mg)	a_T (L/g)	R^2
305	209.2219	1.4074	0.9902
315	211.5436	1.5222	0.9947
325	215.8532	1.7621	0.9957
335	207.6795	1.9649	0.9974

Table 5.28 Tempkin constants for the adsorption of Ni(II) ions onto PAAC.

[pH =5; Dose = 30 mg/ 50 mL; Contact time = 180 min]

Temperature (K)	b_T (J/mg)	a_T (L/g)	R^2
305	234.1647	2.7554	0.9942
315	231.2912	3.0202	0.9966
325	236.5447	3.8504	0.9981
335	253.9147	6.1274	0.9986

Table 5.29 Tempkin constants for the adsorption of Ni(II) ions onto PHAC.

[pH =5; Dose = 30 mg/ 50 mL; Contact time = 180 min]

Temperature (K)	b_T (J/mg)	a_T (L/g)	R^2
305	146.5424	0.8297	0.995
315	147.4861	0.9483	0.9973
325	154.7838	1.2033	0.9987
335	167.3088	1.7288	0.9991

Table 5.30 Tempkin constants for the adsorption of Cu(II) ions onto PAAC.

[pH =4; Dose = 30 mg/ 50 mL; Contact time = 180 min]

Temperature (K)	b_T (J/mg)	a_T (L/g)	R^2
305	99.6882	0.7294	0.9893
315	100.7002	0.8114	0.9868
325	101.1246	0.8868	0.9828
335	101.0371	1.0755	0.9889

Table 5.31 Tempkin constants for the adsorption of Cu(II) ions onto PHAC.

[pH =4; Dose = 30 mg/ 50 mL; Contact time = 180 min]

Temperature (K)	b_T (J/mg)	a_T (L/g)	R^2
305	97.1597	0.6520	0.9877
315	108.0364	0.7614	0.9878
325	100.5040	0.8972	0.9864
335	97.5617	0.9434	0.9872

PAAC and PHAC seems to have a lower value of a_T and b_T with respect to adsorption of Cr (VI) ion for all the studied temperatures. It is an indication of physisorption rather than chemisorption.

Equilibrium binding constant a_T values (L/g) for adsorption of Ni (II) ion onto PAAC system are ranged from 2.7554 to 6.1274 for PAAC and 0.8297 to 1.7288 for PHAC. The heat of sorption constant b_T values are ranged from 231.2912 J/mg to 253.9147 J/mg for the four studied temperatures viz. 305, 315, 325 and 335 K for PAAC and for PHAC these values ranged from 146.5424 J/mg to 167.3088 J/mg. The lower value of a_T and b_T with respect to adsorption of Ni (II) ion adsorption indicates physisorption rather than chemisorption.

Equilibrium binding constant $a_T$values (L/g) for adsorption of Cu (II) ion onto PAAC system are ranged from 0.7294 to 1.0755 for PAAC and 0.6520 to 0.9434 for PHAC. The Heat of sorption constant b_T values are ranged from 99.6882 J/mg to 101.1246 J/mg for PAAC and for PHAC these values are ranged from 97.1597 J/mg to 108.0364 J/mg. Lower value of a_T and b_T with respect to adsorption of Cu (II) ion.It is an indication of physisorption rather than chemisorption.

On comparing the three adsorbates namely Cr (VI) ion, Ni (II) ion and Cu (II) metal ion preferential adsorption is in the following order for all the studied temperature.

Ni (II) ion	>	Cr (VI) ion	>	Cu (II) ion

The difference may be due to the following factors such as adsorbate ionic charge, adsorbate size, adsorbate shape, pore volume, pore shape and surface characteristics of the adsorbents.

5.7.4 Dubinin – Radushkevich isotherm

The Linear form of Dubinin-Radushkevich isotherm[81] is

$$\ln q_e = \ln q_D - B\varepsilon^2 \quad \text{……. 5.8}$$

Where q_D is the theoretical enrichment potential (mg/g)B is a constant relative to the average free energy of sorption per mole of sorbate (mol^2/J^2) and ε is polanyi energy, which is related to equilibrium as given below

$$\varepsilon = RT \ln (1+1/C_e) \quad \text{……. 5.9}$$

The QD and B constants were calculated from the straight line slope and intercept obtained from the plot of ln q_e versus ε^2. The average free energy of sorption E calculated from B using the following equation[60].

$$E = 1/ (2B)^{½} \quad \text{…… 5.10}$$

E is a parameter used in forecasting the type of sorption. An E value less than 8 kJ/mol is an suggestion of physisorption. The results obtained from Dubinin-Radushkevich (D - R) model for the removal of Cr (VI) ion, Ni (II) ion and Cu (II) ion onto PAAC and PHAC were represented in Table 5.32 to 5.37. Concerned isotherm plots were shown in Figures 5.61to 5.66.

The square of correlation coefficient (R^2) values are ranged from 0.8803 to 0.9568 for the four studied temperatures viz. 305, 315 325 K and 335 K for the adsorbents PAAC and PHAC with the adsorbates Cr (VI) ion, Ni (II) ion and Cu (II) ion. These results show the good fitting of the equilibrium data with D-R isotherm.

The mono layer adsorption capacity q_D values (mg/g) for adsorption of Cr (VI) ion onto PAAC system are ranged from 686.7318 to 556.6292 and 644.7318 to 522.6292 for PHAC. PAAC seems to have a higher saturation adsorption capacity than PHAC with respect to adsorption of Cr (VI) ion for all the studied temperatures.

Further it is noticed that adsorption capacity increased with an increase in temperature. Values of the mean free energy of adsorption were ranged from 0.5859 kJ/mol to 0.5289kJ/molfor PAACand 0.5239kJ/mol to 516.9kJ/mol for PHAC. The very low value of E infers the physisorption interaction.

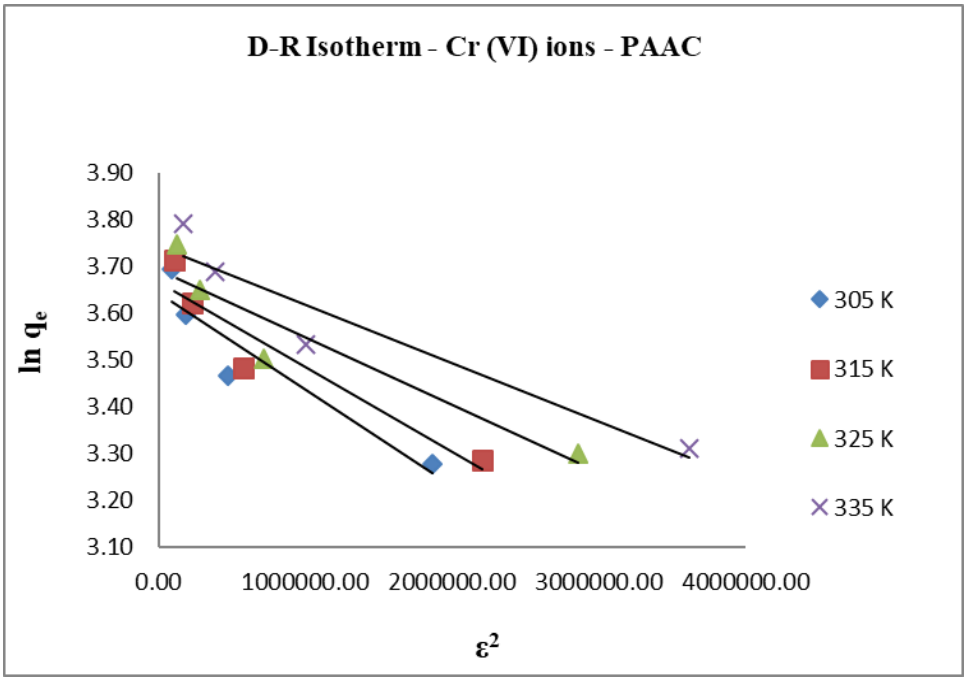

Figure 5.61

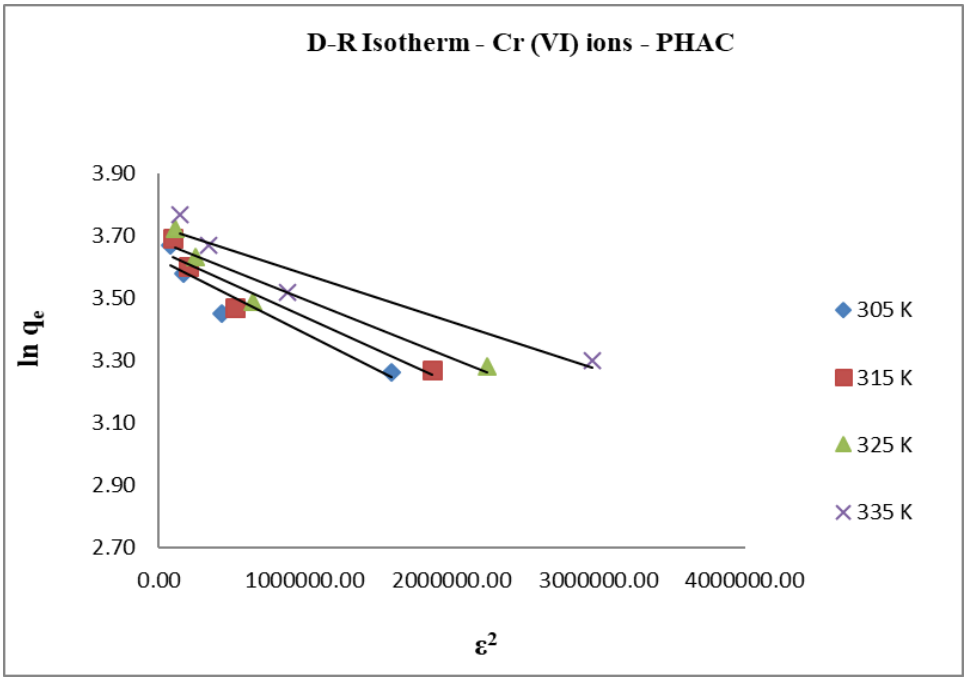

Figure 5.62

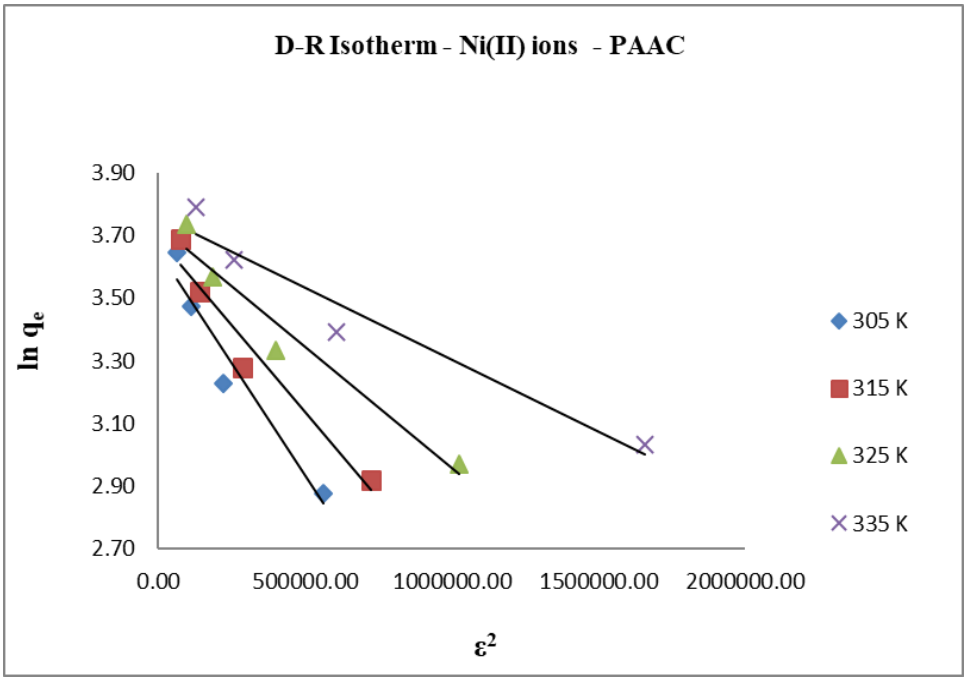

Figure 5.63

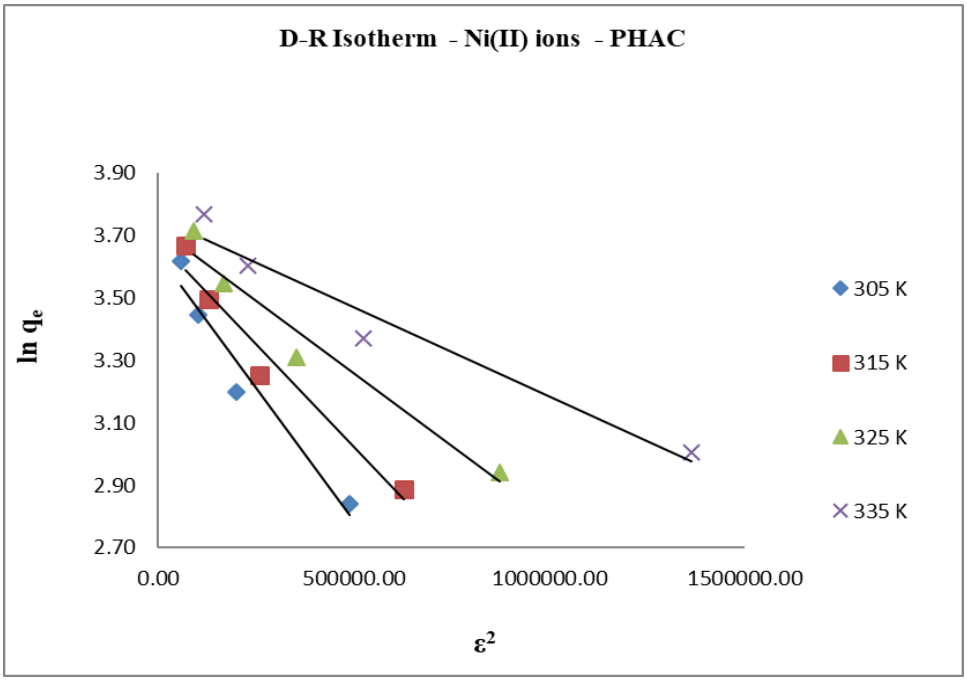

Figure 5.64

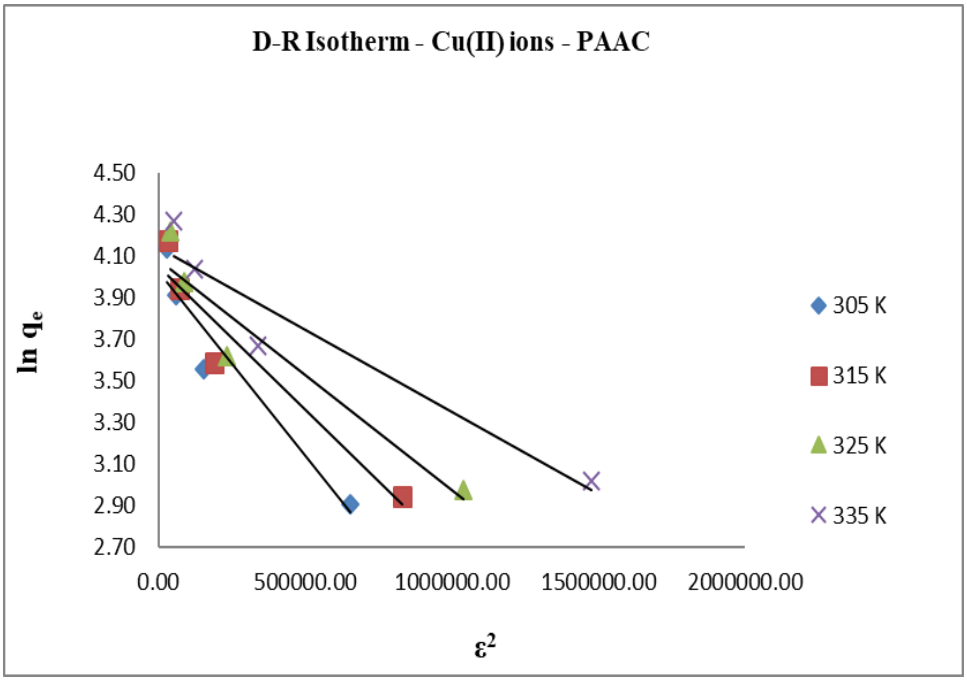

Figure 5.65

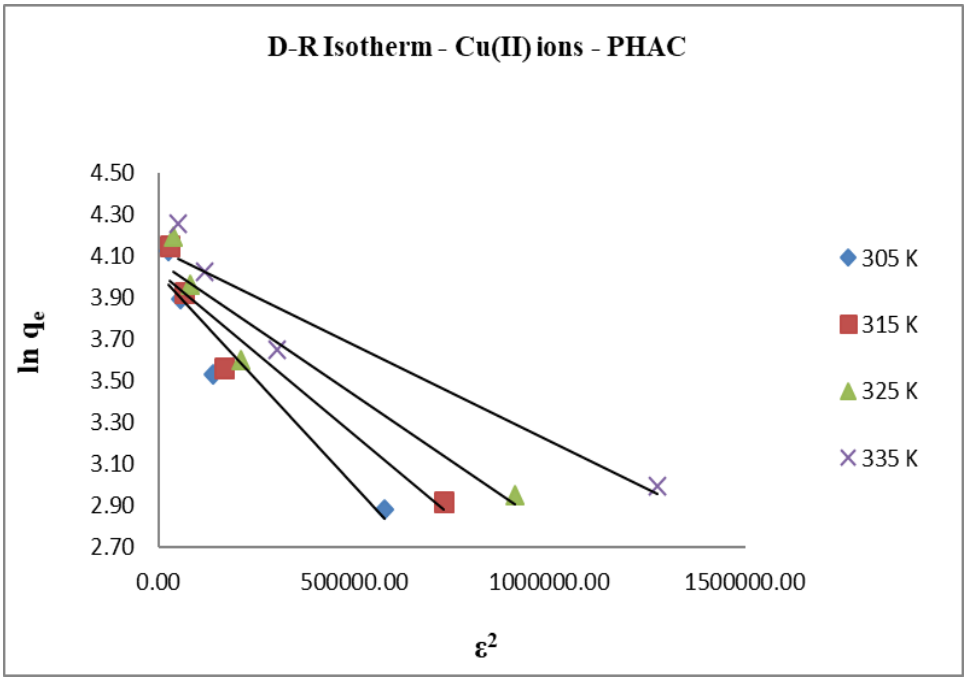

Figure 5.66

Table 5.32 D-R isotherm results for the adsorption of Cr(VI) ion onto PAAC

[pH = 2; Dose = 30 mg/ 50 mL; Contact time = 180 min]

Temperature (K)	q_D (mg/g)	E (kJ/mol)	R^2
305	686.7318	0.5859	0.9568
315	635.1921	0.5452	0.9234
325	580.5170	0.5353	0.9123
335	556.6292	0.5289	0.9243

Table 5.33 D-R isotherm results for the adsorption of Cr(VI) ion onto PHAC

[pH = 2; Dose = 30 mg/ 50 mL; Contact time = 180 min]

Temperature (K)	q_D (mg/g)	E (kJ/mol)	R^2
305	644.7318	0.5239	0.8803
315	607.1921	0.5222	0.8932
325	560.5170	0.5203	0.8847
335	522.6292	0.5169	0.9043

Table 5.34 D-R isotherm results for the adsorption of Ni(II) ion onto PAAC.

[pH = 5; Dose = 30 mg/ 50 mL; Contact time = 180 min]

Temperature (K)	q_D (mg/g)	E (kJ/mol)	R^2
305	644.7318	0.4987	0.9127
315	607.1921	0.4967	0.9293
325	560.5170	0.4949	0.9331
335	522.6292	0.4915	0.9302

Table 5.35 D-R isotherm results for the adsorption of Ni(II) ion onto PHAC

[pH = 5; Dose = 30 mg/ 50 mL; Contact time = 180 min]

Temperature (K)	q_D (mg/g)	E (kJ/mol)	R^2
305	614.7256	0.4388	0.9227
315	597.1235	0.4269	0.9191
325	530.5785	0.4146	0.9131
335	502.6985	0.4013	0.9202

Table 5.36 D-R isotherm results for the adsorption of Cu(II) ion onto PAAC

[pH = 4; Dose = 30 mg/ 50 mL; Contact time = 180 min]

Temperature (K)	q_D (mg/g)	E (kJ/mol)	R^2
305	523.7563	0.4209	0.9227
315	503.1864	0.4967	0.9191
325	486.3214	0.4946	0.9131
335	468.9875	0.4912	0.9202

Table 5.37 D-R isotherm results for the adsorption of Cu(II) ion onto PHAC

[pH = 4; Dose = 30 mg/ 50 mL; Contact time = 180 min

Temperature (K)	q_D (mg/g)	E (kJ/mol)	R^2
305	503.7318	0.4127	0.9227
315	486.1921	0.3857	0.9191
325	465.5170	0.3629	0.9131
335	425.6292	0.3355	0.9202

The mono layer adsorption capacity q_D values (mg/g) for adsorption of Ni (II) ion onto PAAC system are ranged from 644.7318 to 522.6292 and 614.7256 to 502.6985 for PHAC. PAAC seems to have higher adsorption than PHAC with respect to adsorption of Ni (II) ion for all the studied temperatures. Further it is noticed that adsorption capacity increased with the increase of temperature. Values of the mean free energy of adsorption were ranged from 0.4987 kJ/mol to 0.4915kJ/mol for PAAC and 0.4388 kJ/mol to 0.4013kJ/mol for PHAC. The very low value of E infers the physisorption interaction. The very low value of E infers the physisorption interaction.

The mono layer adsorption capacity q_D values (mg/g) for adsorption of Cu (II) ion onto PAAC system are ranged from 523.7563 to 468.9875 and 503.7318 to 425.6292 for PHAC. PAAC seems to have higher adsorption than PHAC with respect to adsorption of Cu (II) ion for all the studied temperatures. Further it is noticed that adsorption capacity increased with the increase of temperature. Values of the mean free energy of adsorption were ranged from 0.4209 kJ/mol to 0.4912 kJ/mol for PAAC and 0.4127kJ/mol to 0.3355kJ/mol for PHAC. The very low value of E infers the physisorption interaction. The very low value of E infers the physisorption interaction.

Comparison of the chosen adsorbates

On comparing the three adsorbates namely Cr (VI) ion, Ni (II) ion and Cr (VI) metal ion, preferential adsorption is in the following order for both the adsorbents PAAC and PHAC at all studied temperatures.

Cr (VI) ion	>	Ni (II) ion	>	Cu (II) metal ion

It can be understood from the q_D values (mg/g) at a particular temperature.

5.8 Kinetic study

Adsorption equilibrium studies are important in determining the effectiveness of adsorption. In addition, it is necessary to identify the adsorption mechanism in the selected system. Kinetic models have been used to test experimental data, with the aim of investigating the mechanism of adsorption and its potential rate-limiting steps, including mass transport and chemical reaction processes. Adsorption kinetics shows the evolution of absorption efficiency over time and it is important to identify the types of adsorption mechanism in a given system. In addition, information on metal ion uptake kinetics is required to select the optimum position for the full volume metal ion removal processes. Adsorption kinetics is stated as the solvent elimination rate that controls the dwelling period of the sorbate at the solution - solid interface.

In general, several steps are involved in the sorption process by porous sorbent particles: (i) total diffusion; (ii) the external mass transfer (boundary layer or image diffusion) between the outer surface of the sorbent particle and the surrounding liquid phase; (iii) particle internal transport and (iv) reaction dynamics at the stage borders.

In practice, kinetic studies have been carried out on volume reactions using various initial sorbate concentrations. Sorption kinetic models have been proposed to elucidate the sorption mechanism on an adsorbent from aqueous solution. Several adsorption kinetic models have been conventional to recognize the adsorption kinetics and the rate-limiting step. These include the pseudo-first and second-order rate model, the Weber and Morris [82] sorption kinetic models.

5.8.1 Pseudo first order kinetics

The linearised form of the pseudo-first order equation of Lagergren is generally expressed as follows:

$$\log (q_e - q_t) = \log q_e - k_1 / 2.303 \times t \quad \ldots\ldots\ldots 5.11$$

where, q_e and q_t are the adsorption capacity at equilibrium and at timet respectively (mg/g). k_1 is the rate constant of pseudo first-order adsorption. The plot of log (q_e -q_t) versus t should give a linear relationship; k_1 and q_e can be calculated from the slope and intercept of the plot, respectively[61].

5.8.2 Pseudo second order kinetics

The pseudo second order kinetic model (Ho equation) is represented by the following linear equation[65]:

$$t/q_t = 1/ k_2.q_e^2 + 1/q_e\, t \quad \ldots\ldots\ldots 5.12$$

where, q_e and q_t are the adsorption capacity at equilibrium and at time t respectively (mg/g).

The initial adsorption rate, h (mg/(g min)), as $t \rightarrow 0$ can be defined as

$$h = k_2 q_e^2 \quad \ldots\ldots\ldots 5.13$$

The Plot is drawn between of t/q_t and t. Theoretical adsorption capacity (q_e), and the second-order rate constants k_2 (g/(mg min)) can be determined experimentally from the slope and intercept of plots[61].

5.8.3 Intra particle diffusion

The process of adsorption of a sorbent in a sorbent follows a series of steps. The slowing of these steps controls the overall rate of the process. In general, aperture and inner particle dispersion often control the rate in a batch furnace, while for continuous flow mode, the image propagation is to control the rate [83]. Previous studies by various researchers have shown that the plot of qt and $t^{0.5}$ represents multiple linearity, with two or more steps in the sorption of a sorbent by adsorbate. These include the transport of solvent molecules from the aqueous phase to the surface of the solid particles and the diffusion of the solvent molecules into the interior of the pores, which is usually a slow process.

However, when controlling the pore diffusion adsorption process, the relationship between initial adsorbate concentration and reaction rate is not linear. As Weber and Morris have shown, the effect of contact time test results can be used to study the rate-limiting step in the absorption process. Since the particles were vigorously agitated during the adsorption, it is reasonable to assume that the rate is not limited by mass transfer from the total solution to the outer surface of the particle; One might say image diffusion or inner particle diffusion to control the rate. When they operate in series, the slowest of the two is the rate determinant. According to Weber and Morris [82], an inner particle distribution is defined by the co-efficient k_p equation:

$$q_t = k_p t^{0.5} + C \qquad \ldots\ldots\ldots 5.14$$

Weber and Morris plot is drawn between q_t and $t^{0.5}$ to understand the intra particle diffusion. Where K_p ($mg/g/min^{0.5}$) is the intra particle diffusion rate constant and C is the thickness of the boundary film[76]. The K_p and C values were obtained from the slope and

intercept of the linear portions of the curves drawn between quantity adsorbed in mg/g (q_t) and the square root of time ($t^{0.5}$).

5.8.4 Test for kinetics models

Best fitting kinetic model for a system can be determined by using the statistical tool Mean sum of error squares (MSSE)[84]. This can be evaluated by the following formula, The Mean sum of error squares is given as follows;

$$MSSE = \sqrt{\sum[(q_e)_{exp}-(q_e)_{cal}]^2/ N} \quad \ldots\ldots\ldots 5.15$$

where N is the number of data points, $(q_e)exp$ is the experimental q_e and $(q_e)cal$ is the calculated q_e.

Kinetic study on Cr (VI) ion adsorption

The results obtained from pseudo-first order kinetic model for the removal of Cr (VI) ion onto PAAC and PHAC were represented in Table 5.38 and 5.39 and concerned isotherm plots were shown in Figures 5.67 to 5.68. The linearity of the plots were not so high for PAAC (R^2 = 0.9627 - 0.9830) and for PHAC (R^2 = 0.9987 - 0.9993). The first order rate constant, k_1 (min^{-1}) ranged from 0.0520 to 0.0610 for PAAC and from 0.0175 to 0.0532 for PHAC. The pseudo first order theoretical adsorption capacity (q_e) values, obtained from the intercept of the linear plots, were compared with the experimental adsorption capacity q_e values (Table 5.38 and 5.39).

The pseudo first order kinetic model suffered from inadequacies when applied to Cr(VI) ion sorption on PAAC and on PHAC at varying Cr(VI) ion concentrations. The experimental q_e values differ from the corresponding theoretical values. Discrepancies of this nature have been reported by Ho and McKay[85].

The pseudo second order parameters, q_e, h, and k_2, obtained from the pseudo second order plot are presented in Table 5.38 and 5.39 and concerned plots were shown in Figures 5.69 - 5.70. The initial sorption rate, 'h', increases directly with an increase of initial Cr (IV) ion concentration at each temperature for PAAC (0.75–2.75 mg/g.min^{-1}) and for PHAC (0.25 – 2.09 mg/g.min^{-1}).

The analysis of the results obtained in the present study with two kinetic models is presented in Table 5.38 and 5.39. Between the first order and second order, second order kinetic model seems to best describe the above adsorption system as it has R^2 value which was very close to unity.

Moreover, the difference between calculated adsorption capacity ($q_e$cal) and experimental adsorption capacity ($q_e$exp) values of second order is little when compared to first order kinetic model for the both Cr(VI) ion – PAAC and Cr(VI) ion – PHAC systems for each initial concentrations at different temperatures.

Statistically it is tested with the tool Mean sum of error squares (MSSE) [86]. The Δq_e and MSSE values were given in Table 5.38 and 5.39 for both the adsorbents from which it was concluded that the second order kinetic model was more appropriate rather than the first order kinetic model.

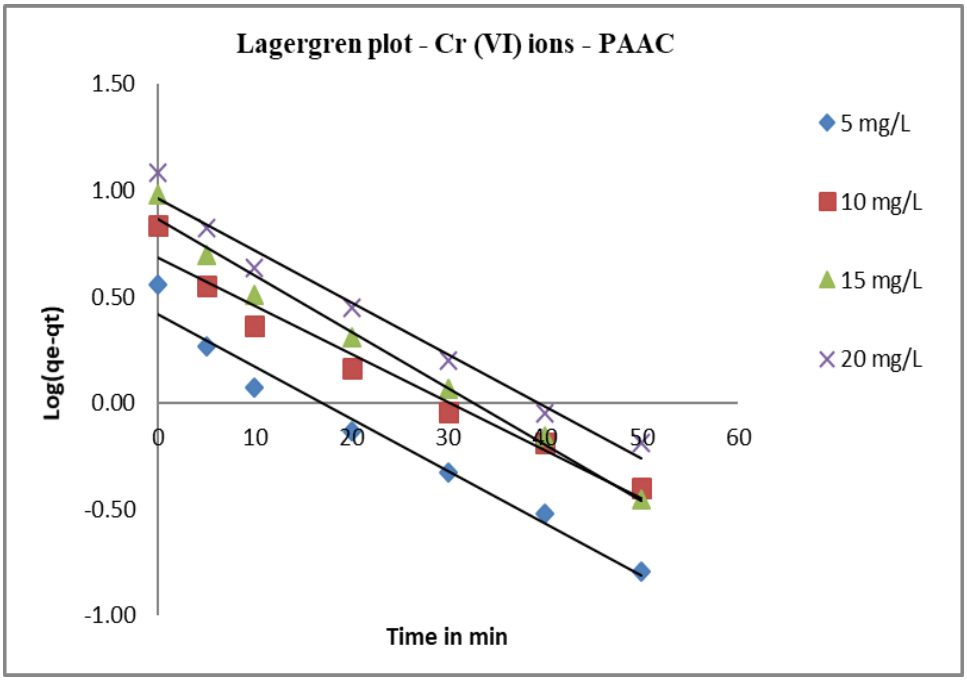

Figure 5.67

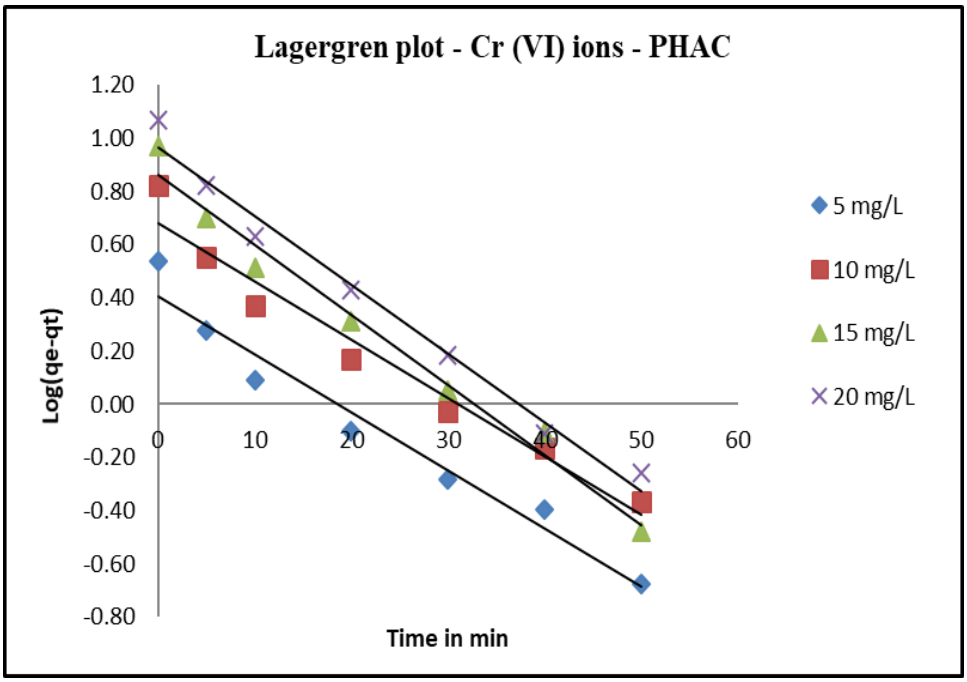

Figure 5.68

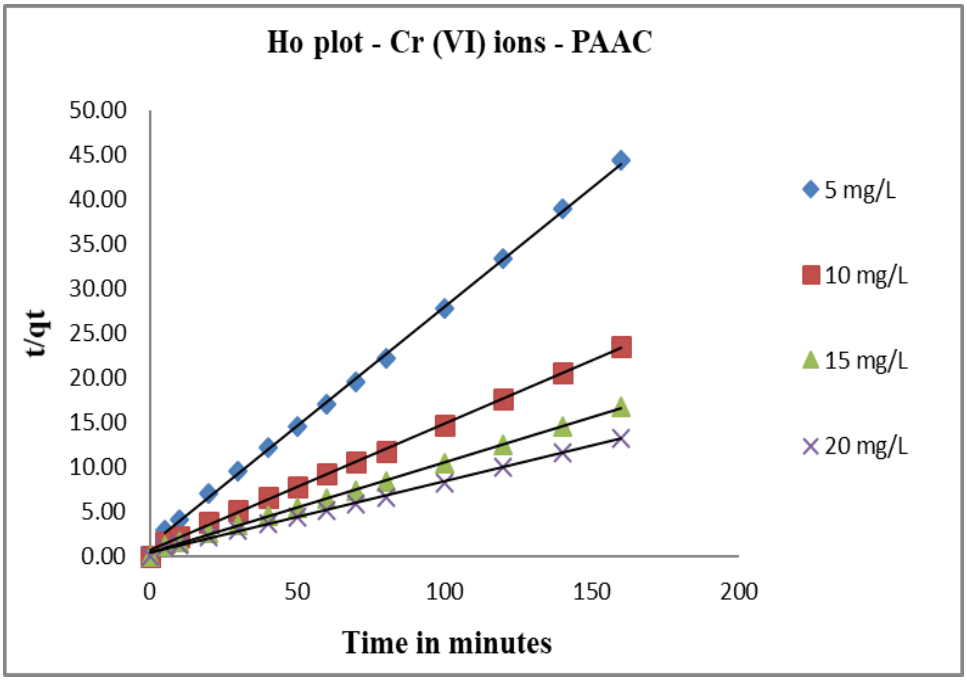

Figure 5.69

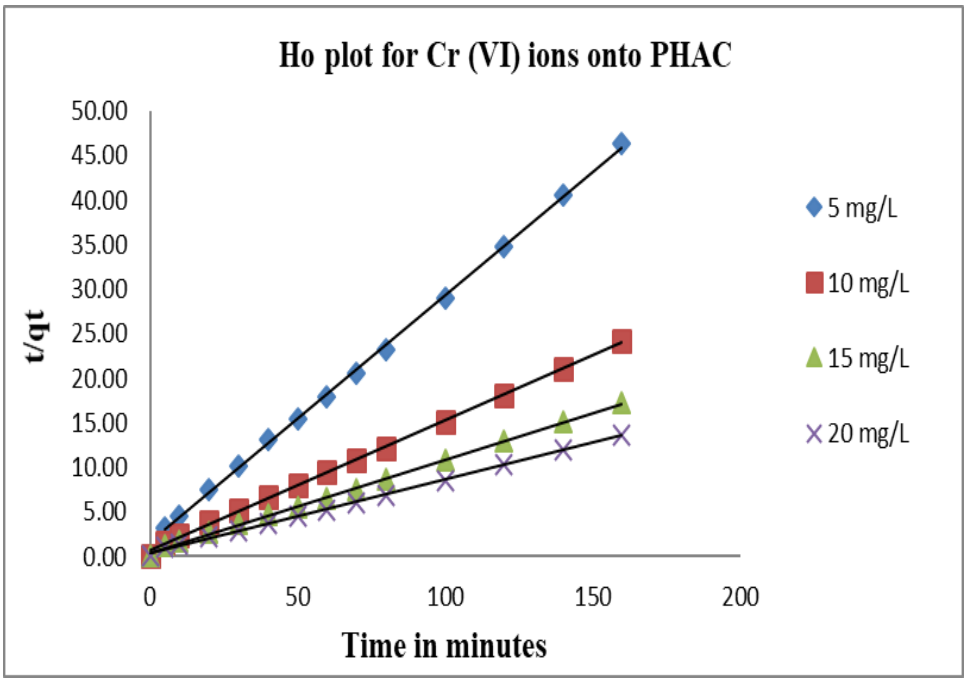

Figure 5.70

Intra particle diffusion

Concerned graphs are shown in Figures5.71 and 5.72 and the values calculated for the adsorbents PAAC and PHAC are given in Table 5.38 and 5.39. Plot of mass of metal ions adsorbed per unit mass of adsorbent (q_t) versus $t^{0.5}$is presented for Cr (VI) ion. The linear plots are attributed to the macro pore diffusion which is the accessible sites of adsorption. This is attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface.

The $K_p$values were found to increase with an increase of Cr (VI) ion concentration that reveals the rate of adsorption governed by the diffusion of adsorbed Cr (VI) ion within the pores of the adsorbent. Present results show that pore diffusion limits the overall rate of Cr (VI) ion adsorption[89, 90 &88].

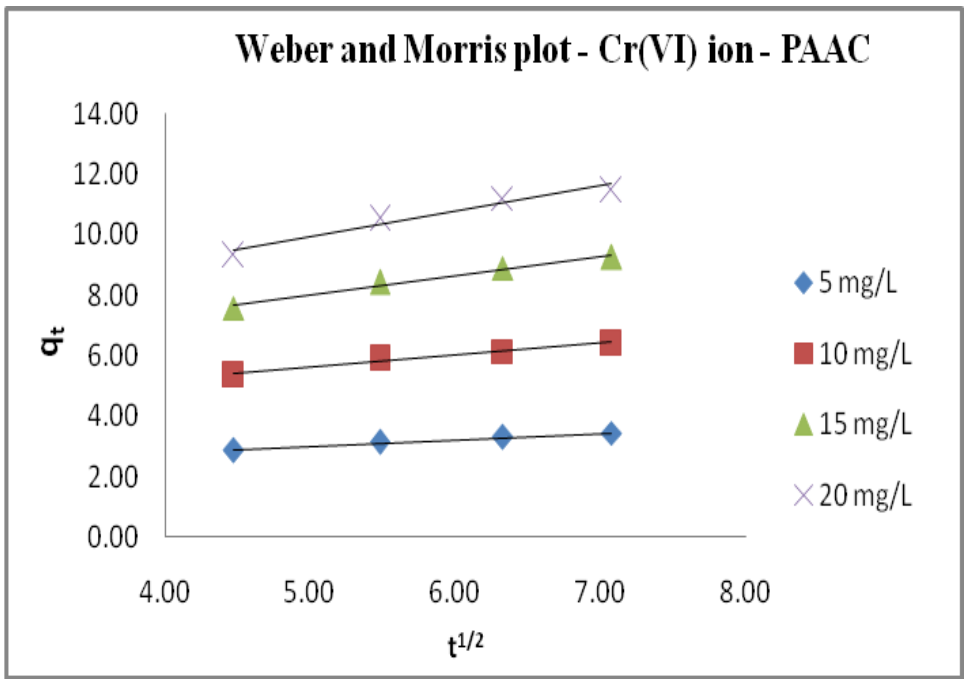

Figure 5.71

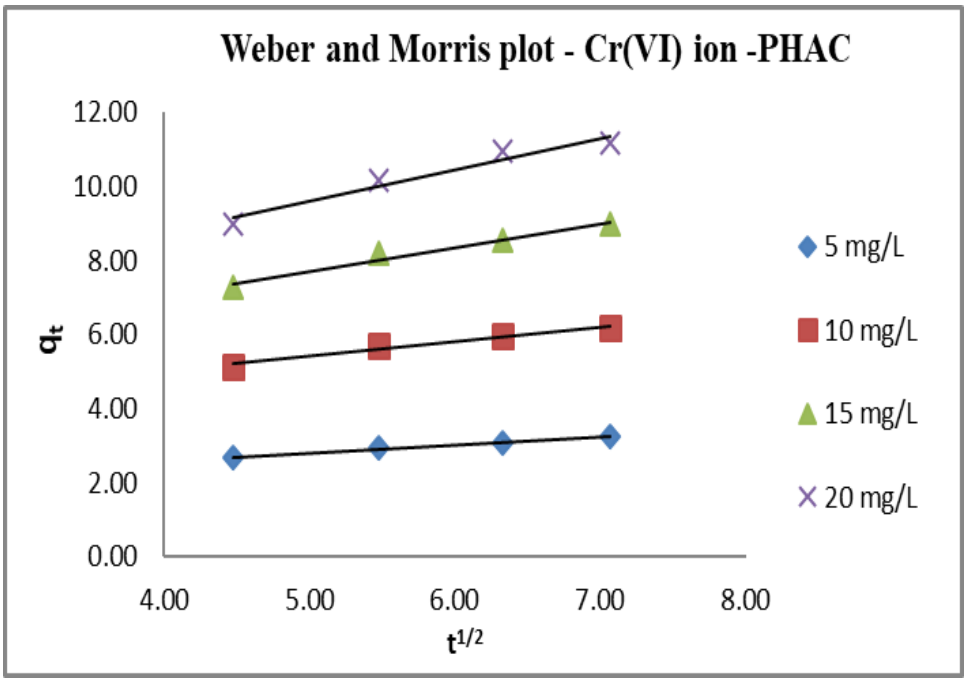

Figure 5.72

Table 5.38 Kinetics and Intra particle diffusion results for the adsorption of Cr(VI) ion onto PAAC

First Order Kinetics – PAAC					
Concentration (mg/L)	**k_1 (min^{-1})**	**$q_{e(cal)}$ (mg/g)**	**$q_{e(exp)}$ (mg/g)**	**R^2**	**MSSE**
5	0.0567	2.6285	3.60	0.9730	**1.06**
10	0.0520	4.8406	6.80	0.9627	
15	0.0610	7.3519	9.60	0.9830	
20	0.0564	9.2257	12.10	0.9769	
Second Order Kinetics					
Concentration (mg/L)	**k_2 (g/mg.min)**	**$q_{e(cal)}$ (mg/g)**	**h**	**R^2**	**MSSE**
5	0.0532	3.75	0.75	0.9995	**0.15**
10	0.0315	7.03	1.56	0.9989	
15	0.0254	9.90	2.49	0.9998	
20	0.0839	12.53	2.75	0.9988	
Intra Particle Diffusion					
Concentration (mg/L)	**k_p (mg/g/$min^{0.5}$)**			**R^2**	
5	0.0653			0.992	
10	0.8645			0.9804	
15	0.9860			0.978	
20	0.9945			0.9476	

Table 5.39 Kinetics and Intra particle diffusion results for the adsorption of Cr(VI) ion onto PHAC

First Order Kinetics – PHAC					
Concentration (mg/L)	**k_1 (min^{-1})**	**$q_{e(cal)}$ (mg/g)**	**$q_{e(exp)}$ (mg/g)**	**R^2**	**MSSE**
5	0.0532	3.75	0.75	0.9993	**0.79**
10	0.0315	7.03	1.56	0.9988	
15	0.0254	9.90	2.49	0.9988	
20	0.0175	12.53	2.75	0.9987	
Second Order Kinetics					
Concentration (mg/L)	**k_2 (g/mg.min)**	**$q_{e(cal)}$ (mg/g)**	**h**	**R^2**	**MSSE**
5	0.0232	2.75	0.25	0.9999	**0.29**
10	0.0315	3.03	1.16	0.9998	
15	0.0354	4.90	2.09	0.9998	
20	0.0475	3.53	2.05	0.9997	
Intra Particle Diffusion					
Concentration (mg/L)	**k_p (mg/g/$min^{0.5}$)**			**R^2**	
5	0.0553			0.9870	
10	0.7545			0.9804	
15	0.8560			0.9716	
20	0.8845			0.9510	

Kinetic study on Ni (II) ion adsorption

The results obtained from pseudo-first order kinetic modelfor the removal of Ni (II) ion onto PAAC and onto PHAC were represented in Table 5.40 and 5.41 and concerned isotherm plots were shown in Figures5.73 - 5.74. The linearity of the plots were not so high for PAAC (R^2 = 0.9835 - 0.9902) and for PHAC (R^2 = 0.9856 - 0.9917). The first order rate constant, k_1 (min^{-1}) ranged from 0.0504 to 0.0587 for PAAC and from 0.0502 to 0.0583 for PHAC. The pseudo first order theoretical adsorption capacity (q_e) values, obtained from the intercept of the linear plots, were compared with the experimental adsorption capacity q_e values (Table 5.40 and 5.41).

The pseudo first order kinetic model suffered from inadequacies when applied to Ni (II) ion sorption on PAAC and PHAC at varying Ni (II) ion concentrations. The experimental q_e values differ from the corresponding theoretical values[85].

The pseudo second order parameters, q_e, h, and k_2, obtained from the pseudo second order plot are presented in Table 5.40 and 5.41 and concerned plots were shown in Figures5.75 to 5.76. The initial sorption rate, h, increases directly with the increase of initial Ni (II) ion concentration at each temperature for PAAC, (1.24–2.66 mg/g.min^{-1}) and for PHAC (1.13 – 2.47 mg/g.min^{-1}).

The analysis of the results obtained in the present study with two kinetic models is presented in Table 5.40 and 5.41. Between the first order and second order, second order kinetic model seems to best describe the above adsorption system as it has R^2 value which was very close to unity.

Moreover, the difference between calculated adsorption capacity ($q_e$cal) and experimental adsorption capacity ($q_e$exp) values of second order is little when compared to the first order kinetic model for both Ni (II) ion – PAAC and Ni (II) ion – PHAC systems for each initial concentrations at different temperatures.

Statistically it is tested with the tool Mean sum of error squares(MSSE)[86]. The Δq_e and MSSE values were given in Table 5.40 and 5.41for both the adsorbents from which it was concluded second order kinetic model was more appropriate than first order kinetic model.

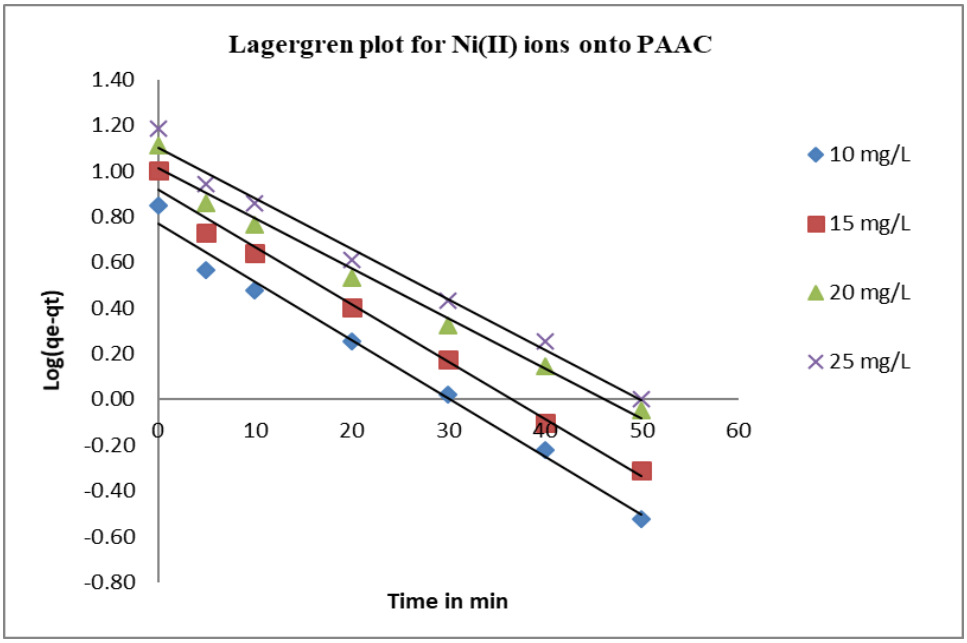

Figure 5.73

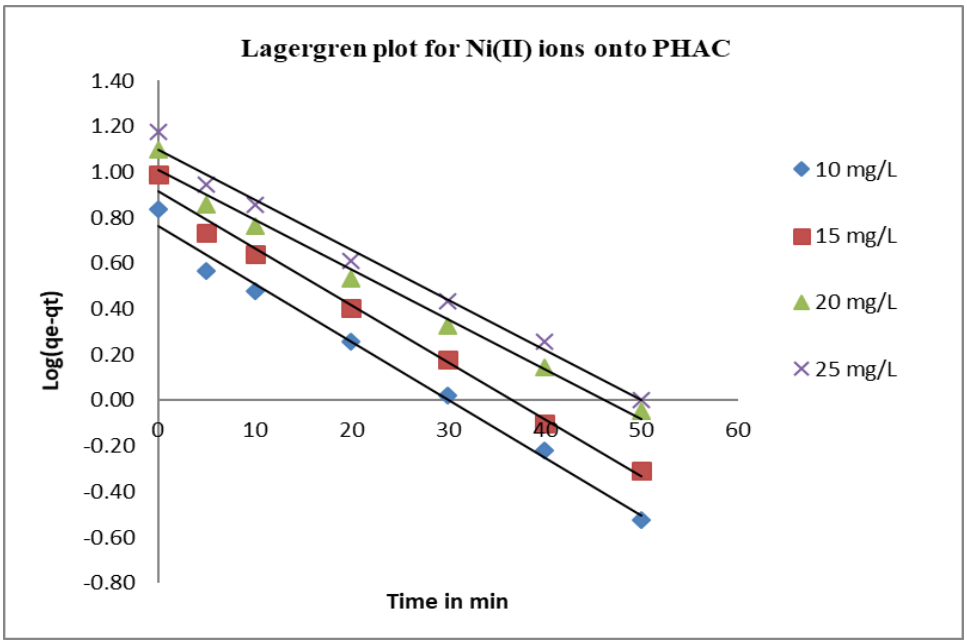

Figure 5.74

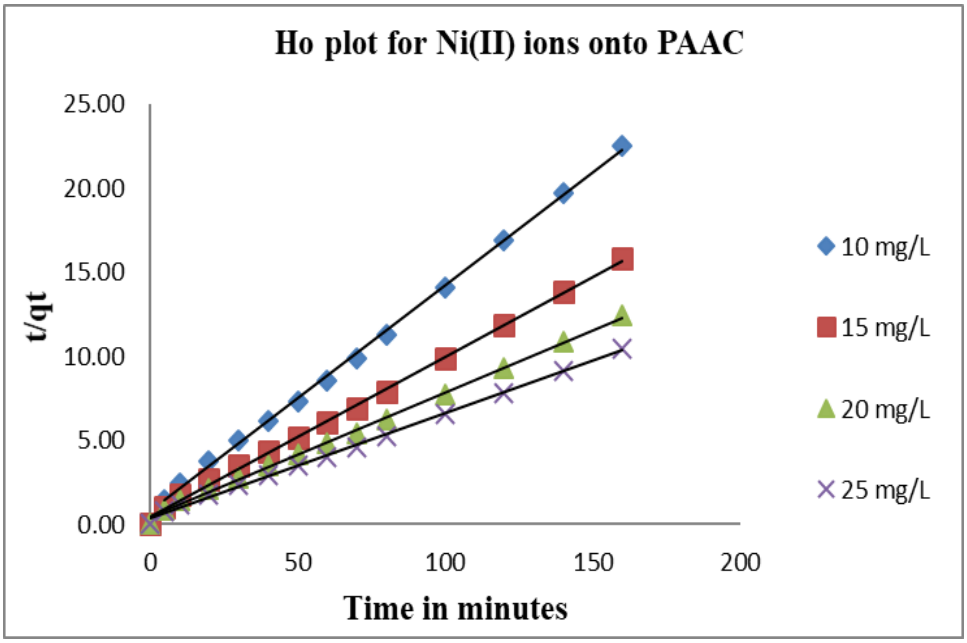

Figure 5.75

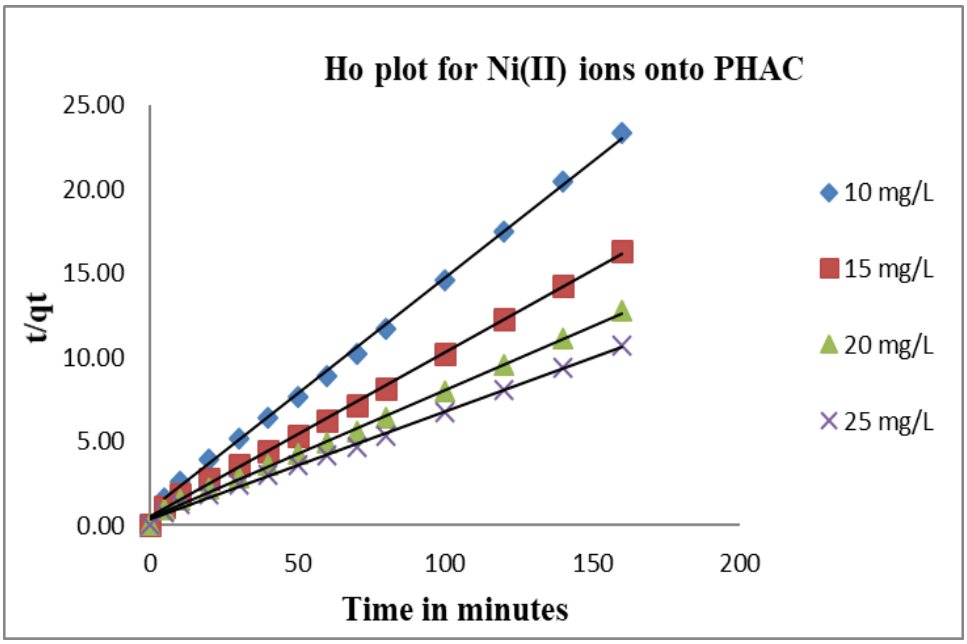

Figure 5.76

Intra particle diffusion

Concerned graphs are shown in Figures5.77 to5.78 and values calculated for the adsorbents PAAC and PHAC are given in Tables 5.40 and 5.41. Plot of mass of metal ions adsorbed per unit mass of adsorbent (q_t) versus $t^{0.5}$is presented for Ni (II) ion. The linear plots are attributed to the macro pore diffusion which is the accessible sites of adsorption. This is attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface.

The K_p values were found to increase with an increase of Ni (II) ion concentration that reveals the rate of adsorption governed by the diffusion of adsorbed Ni (II) ion within the pores of the adsorbent. Present results show that pore diffusion limits the overall rate of Ni (II) ion adsorption[58, 87 &88].

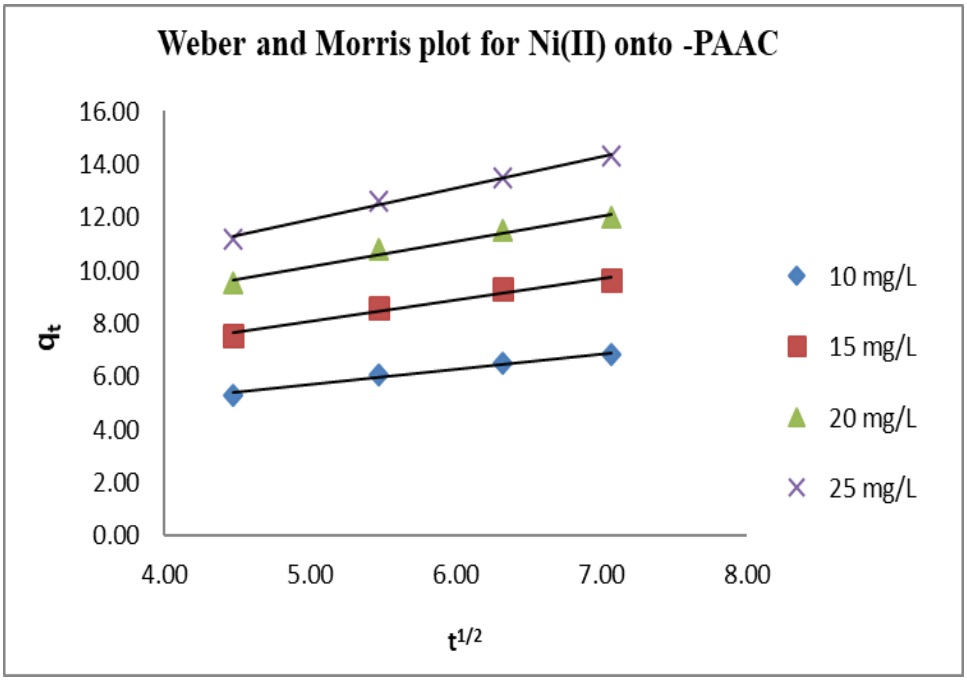

Figure 5.77

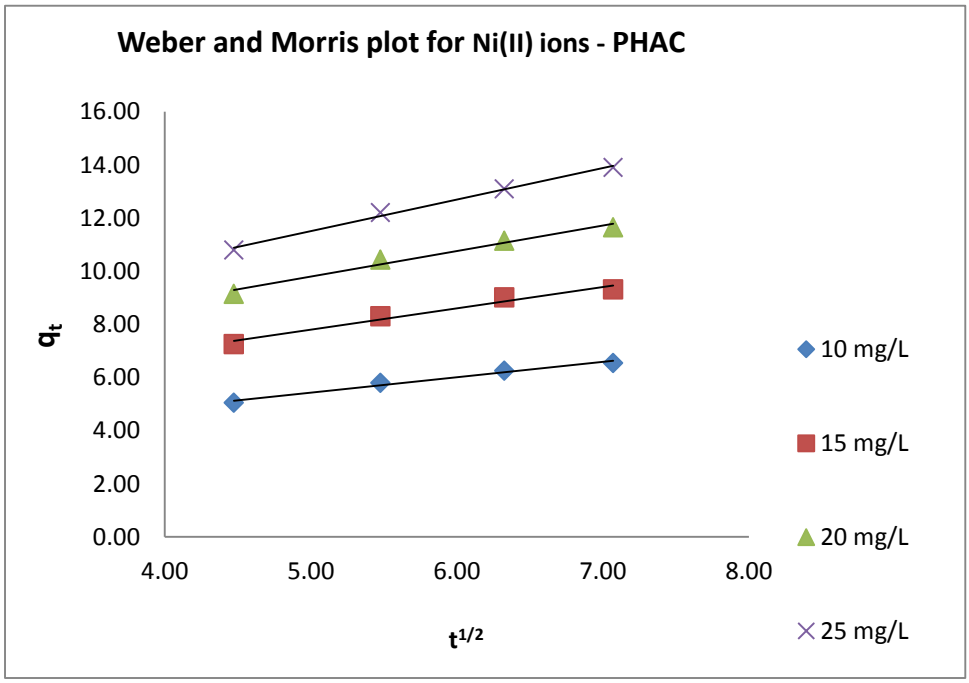

Figure 5.78

Table 5.40Kinetics and Intra particle diffusion results for the adsorption of Ni(II) ion onto PAAC

First Order Kinetics – PAAC					
Concentration (mg/L)	**k_1 (min^{-1})**	**$q_{e(cal)}$ (mg/g)**	**$q_{e(exp)}$ (mg/g)**	**R^2**	**MSSE**
10	0.0587	5.8600	7.10	0.9891	**1.08**
15	0.0578	8.3042	10.10	0.9902	
20	0.0504	10.2778	12.90	0.9835	
25	0.0509	12.6212	15.30	0.9871	
Second Order Kinetics					
Concentration (mg/L)	**k_2 (g/mg.min)**	**$q_{e(cal)}$ (mg/g)**	**h**	**R^2**	**MSSE**
10	0.0223	7.46	1.24	0.9989	**0.27**
15	0.0192	10.50	2.12	0.9982	
20	0.0130	13.48	2.36	0, 9979	
25	0.0103	16.05	2.66	0.9975	
Intra Particle Diffusion					
Concentration (mg/L)	**k_p (mg/g/min $^{0.5}$)**			**R^2**	
10	0.0125			0.9871	
15	0.0256			0.9711	
20	0.0324			0.9866	
25	0.0435			0.9879	

Table 5.41Kinetics and Intra particle diffusion results for the adsorption of Ni(II) ion onto PHAC

First Order Kinetics – PHAC					
Concentration (mg/L)	**k_1 (min^{-1})**	**$q_{e(cal)}$ (mg/g)**	**$q_{e(exp)}$ (mg/g)**	**R^2**	**MSSE**
10	0.0583	05.7810	6.85	0.9908	**0.97**
15	0.0576	08.2111	9.80	0.9917	
20	0.0502	10.1719	12.55	0.9856	
25	0.0511	12.4940	14.90	0.9888	
Second Order Kinetics					
Concentration (mg/L)	**k_2 (g/mg.min)**	**$q_{e(cal)}$ (mg/g)**	**H**	**R^2**	**MSSE**
10	0.0217	7.22	1.13	0.9988	**0.28**
15	0.0188	10.27	1.96	0.988	
20	0.0127	13.14	2.20	0.9977	
25	0.0101	15.65	2.47	0.9973	
Intra Particle Diffusion					
Concentration (mg/L)	**k_p (mg/g/min $^{0.5}$)**			**R^2**	
10	0.0156			0.9817	
15	0.0244			0.9711	
20	0.0321			0.9865	
25	0.0426			0.9912	

Kinetic study on Cu (II) ion adsorption

The results obtained from pseudo-first order kinetic model for the removal of Cu (II) ion onto PAAC and PHAC were represented in Tables 5.42 and 5.43 and concerned isotherm plots were shown in Figures 5.79 to 5.80. The linearity of the plots were not so high for PAAC (R^2 = 0.9634- 0.9829) and for PHAC (R^2 = 0.9643 - 0.9840). The first order rate constant, k_1 (min^{-1}) ranged from 0.0523 to 0.0576 for PAAC and from 0.0520 to 0.0555 for PHAC. The pseudo first order theoretical adsorption capacity (q_e) values, obtained from the intercept of the linear plots were compared with the experimental adsorption capacity q_e values (Table 5.42 and 5.43).

The pseudo first order kinetic model suffered from inadequacies when applied to Cu (II) ion sorption on PAAC and PHAC at varying Cu (II) ion concentrations. The experimental q_e values differ from the corresponding theoretical values.

The pseudo second order parameters, q_e, h, and k_2, obtained from the pseudo second order plot are presented in Table 5.42 and 5.43 and concerned plots were shown in Figures5.81 to 5.82. The initial sorption rate, 'h', increases directly with the increase of initial Cu (II) ion concentration at each temperature for PAAC, (1.13 – 3.26 mg/g.min^{-1}) and for PHAC(1.05 – 3.08 mg/g.min^{-1}).

The analysis of the results obtained in the present study with two kinetic models is presented in Table 5.42 and 5.43. Between the first order and second order, second order kinetic model seems to best describe the above adsorption system as it has R^2 value which was very close to unity.

Moreover, difference between calculated adsorption capacity (q_e cal) and experimental adsorption capacity (q_e exp) values of second order is little when compared to first order kinetic model for both Cu (II) ion – PAAC and Cu (II) ion – PHAC systems for each initial concentrations at different temperatures.

Statistically it is tested with the tool sum of error squares(MSSE %)[192]. T he Δq_e and MSSE values were given in Table 5.42 and 5.43 for both the adsorbents from which it was concluded second order kinetic model was more appropriate than first order kinetic model.

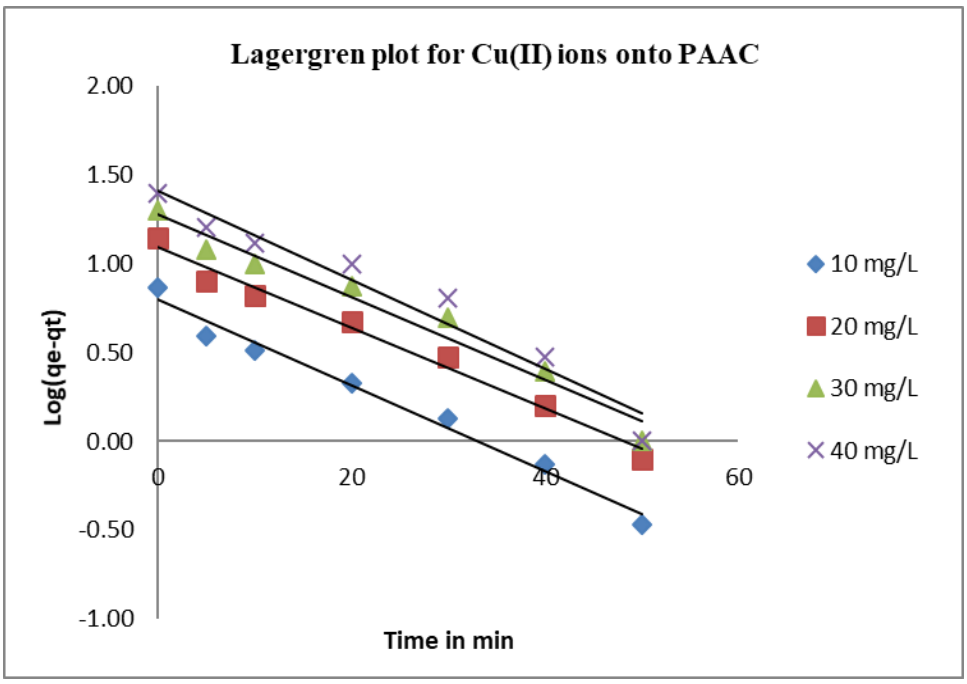

Figure 5.79

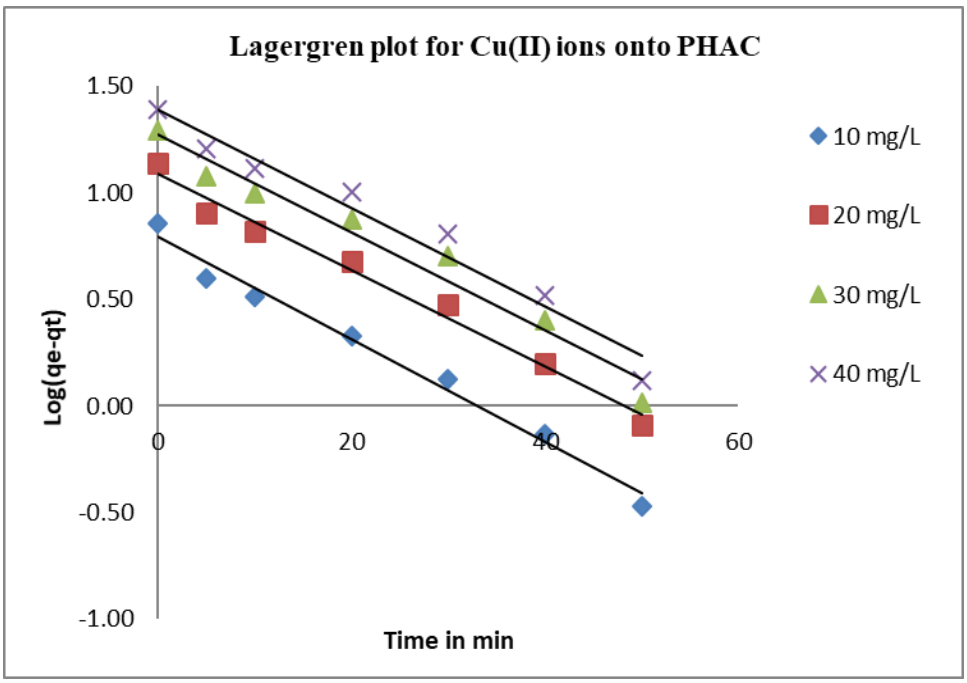

Figure 5.80

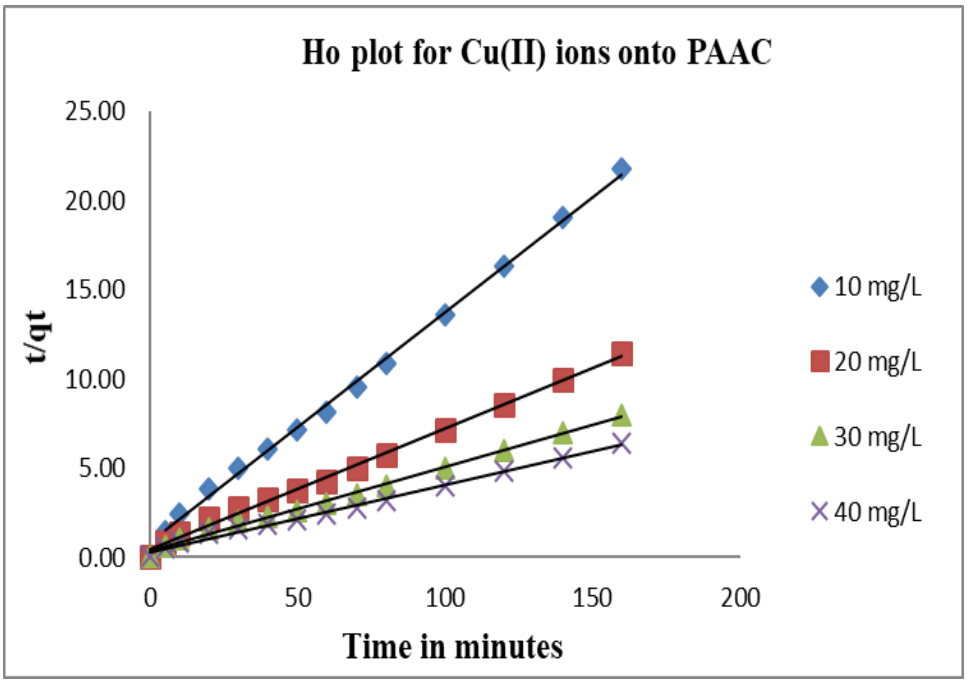

Figure 5.81

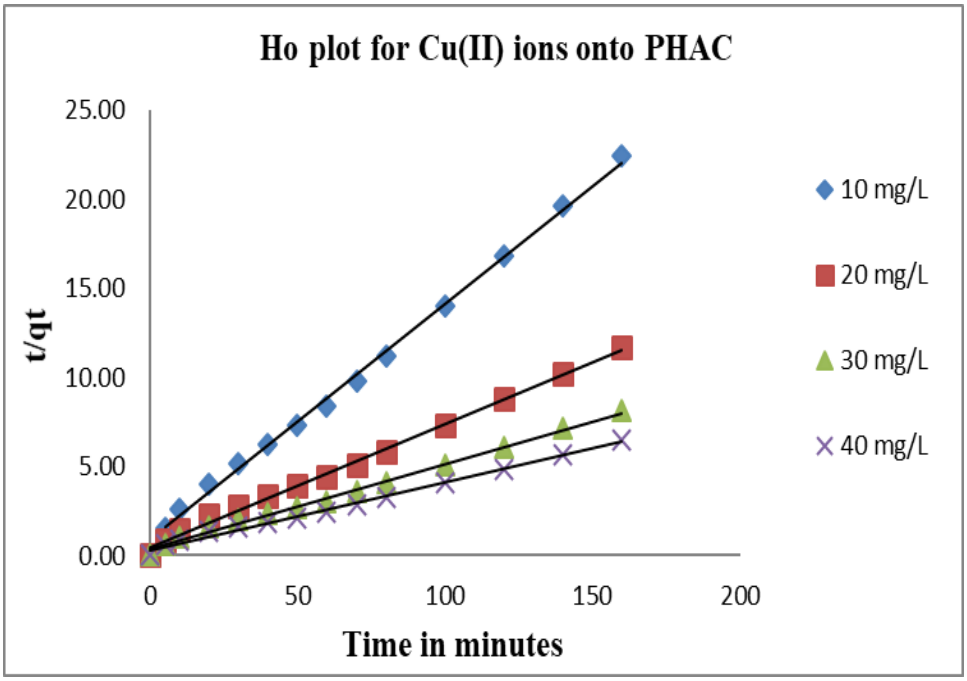

Figure 5.82

Intra particle diffusion

Concerned graphs are shown in Figures 5.83 to 5.84 and the values calculated for the adsorbents PAAC and PHAC are given in Table 5.42 and 5.43.Plot of mass of meta ions adsorbed per unit mass of adsorbent (q_t) versus $t^{0.5}$ is obtainable for Cu (II) ion. The linear plots are accredited to the macro pore diffusion which is the accessible sites of adsorption. This is attributed to the rapid utilization of the most readily available adsorbing spots on the adsorbent surface.

The K_p values were found to rise with an rise of Cu (II) ion concentration that reveals the rate of adsorption governed by the diffusion of adsorbed Cu (II) ion within the pores of the adsorbent. Present results show that pore diffusion limits the overall rate of Cu (II) ion adsorption[58, 59 &88].

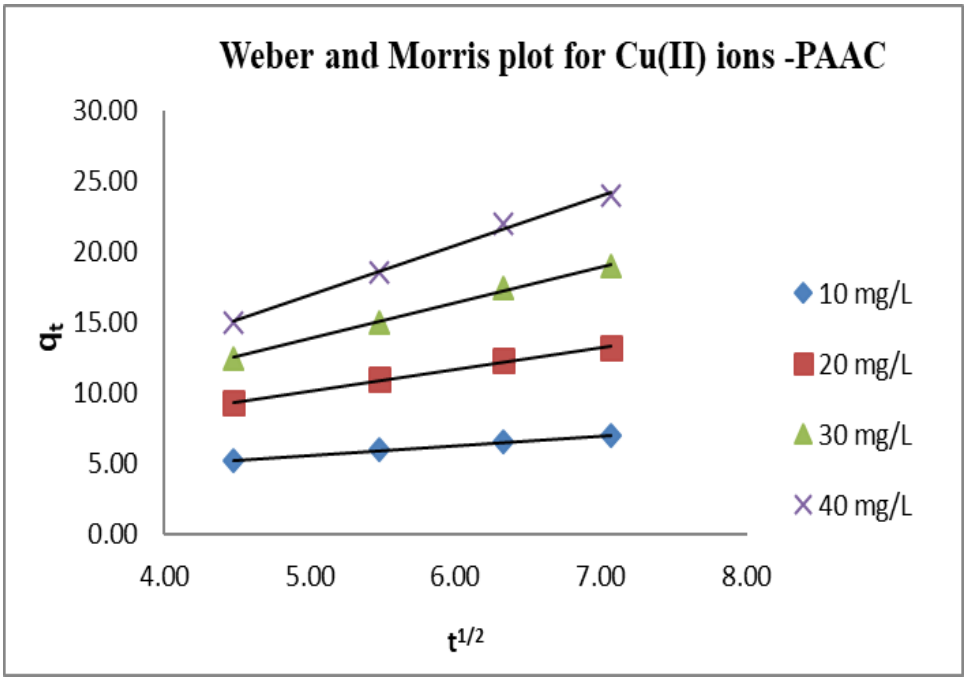

Figure 5.83

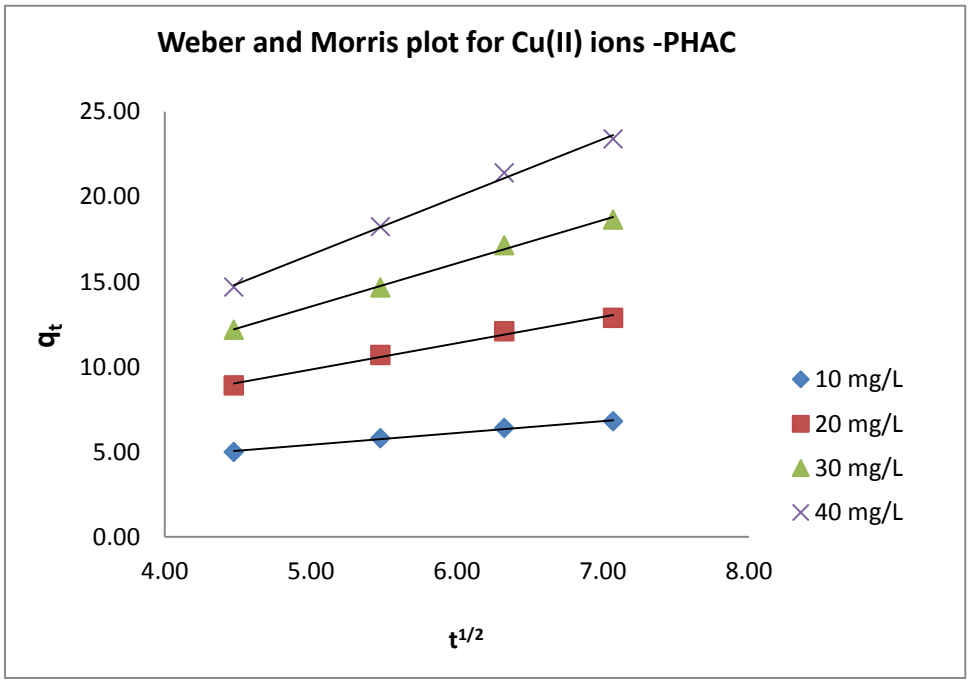

Figure 5.84

Table 5.42 Kinetics and Intra particle diffusion results for the adsorption of Cu(II) ion onto PAAC

First Order Kinetics – PAAC					
Concentration (mg/L)	**k_1 (min^{-1})**	**$q_{e(cal)}$ (mg/g)**	**$q_{e(exp)}$ (mg/g)**	**R^2**	**MSSE**
10	0.0557	6.2748	7.343	0.9829	**2.31**
20	0.0537	19.0634	14.00	0.9634	
30	0.0523	12.3737	20.00	0.9823	
40	0.0576	25.7988	25.00	0.9823	
Second Order Kinetics					
Concentration (mg/L)	**k_2 (g/mg.min)**	**$q_{e(cal)}$ (mg/g)**	**h**	**R^2**	**MSSE**
10	0.0187	7.77	1.13	0.9982	**0.56**
20	0.0104	14.75	2.25	0.9963	
30	0.0064	21.23	2.82	0.9947	
40	0.0046	26.67	3.26	0.9936	
Intra Particle Diffusion					
Concentration (mg/L)	**k_p (mg/g.min)**			**R^2**	
10	0.0265			0.9934	
20	0.0324			0.9918	
30	0.0489			0.9961	
40	0.0512			0.9954	

Table 5.43 Kinetics and Intra particle diffusion results for the adsorption ofCu(II) ion onto PHAC

First Order Kinetics – PHAC					
Concentration (mg/L)	**k_1 (min^{-1})**	**$q_{e(cal)}$ (mg/g)**	**$q_{e(exp)}$ (mg/g)**	**R^2**	**MSSE**
10	0.0555	6.2087	7.14	0.9840	**2.28**
20	0.0530	18.8712	13.68	0.9645	
30	0.0520	12.2687	19.69	0.9831	
40	0.0532	24.6037	24.70	0.9643	
Second Order Kinetics					
Concentration (mg/L)	**k_2 (g/mg.min)**	**$q_{e(cal)}$ (mg/g)**	**h**	**R^2**	**MSSE**
10	0.0183	7.58	1.05	0.9981	**0.59**
20	1.0101	14.45	2.11	0.9959	
30	0.0061	20.96	2.68	0.9944	
40	0.0044	26.46	3.08	0.9933	
Intra Particle Diffusion					
Concentration (mg/L)	**k_p (mg/g/$min^{0.5}$)**			**R^2**	
10	0.0123			0.9934	
20	0.0231			0.9892	
30	0.0354			0.9962	
40	0.0452			0.9962	

5.9 Thermodynamic study

To review the feasibility of the adsorption process, thermodynamic factors such as change in free energy ΔG° (kJ/mol), enthalpy ΔH° (kJ/mol) and entropy ΔS° (J/K/mol) can be determined.[58, 91] using the following equations.

$$k_d = C_{solid} / C_{liquid} \quad \text{…….. 5.16}$$

$$\Delta G° = -RT \ln k_d \quad \text{…….. 5.17}$$

$$\log k_d = \Delta S°/ (2.303RT) - \Delta H°/(2.303R)T \quad \text{…….. 5.18}$$

where k_d is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg/L), C_{liquid} is the liquid phase concentration at equilibrium (mg/L), T is the temperature in Kelvin and R is the gas constant. The Vant Hoff plots are drawn between $\ln k_d$ versus 1/T. ΔH° and ΔS° values were evaluated from the slope and intercept of the plot respectively. The (+) value of ΔH° indicates endothermicity and (-) value indicates the exothermicity of the adsorption process. The (+) value of ΔS° indicates that the adsorption convoys increased randomness while the (-) value concludes that the adsorption convoys decrease in the randomness. Spontaneity of the adsorption can be understood from the sign of ΔG° value. The (-) sign indicates the spontaneous process while the (+) sign designates the non – spontaneity of the process.

The thermo dynamical parameters calculated are presented in Table 5.44 to 5.49and concerned plots were shown in Figures5.85 to 5.90[82].

Table 5.44 Thermodynamic Parameters results for Cr(VI) onto PAAC

Concentration (mg/L)	Temperature (K)	k_d	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/K/mol)
5	305	5.1429	-4.1533	12.055	52.9444
	315	5.6336	-4.5282		
	325	6.3333	-4.9884		
	335	7.8039	-5.7236		
10	305	4.2500	-3.6697	12.504	52.7931
	315	4.7114	-4.0600		
	325	5.3801	-4.5476		
	335	6.6580	-5.2812		
15	305	3.5556	-3.2172	12.097	50.0453
	315	3.9761	-3.6155		
	325	4.4835	-4.0609		
	335	5.5000	-4.7489		
20	305	3.0633	-2.8393	9.9934	41.8469
	315	3.2701	-3.1035		
	325	3.6818	-3.5225		
	335	4.3694	-4.1079		

Table 5.45 Thermodynamic Parameters results for Cr(VI) ion onto PHAC

Concentration (mg/L)	Temperature (K)	k_d	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/K/mol)
5	305	4.4516	-3.7873	10.055	50.9444
	315	4.8493	-4.1356		
	325	5.4074	-4.5613		
	335	6.5470	-5.2343		
10	305	3.9172	-3.4629	8.504	48.7931
	315	4.3291	-3.8383		
	325	4.9204	-4.3062		
	335	6.0321	-5.0062		
15	305	3.2632	-2.9996	9.097	47.0453
	315	3.6391	-3.3835		
	325	4.0976	-3.8116		
	335	4.9767	-4.4704		
20	305	2.8193	-2.6287	8.9934	38.8469
	315	3.0063	-2.8831		
	325	3.3763	-3.2884		
	335	3.9880	-3.8534		

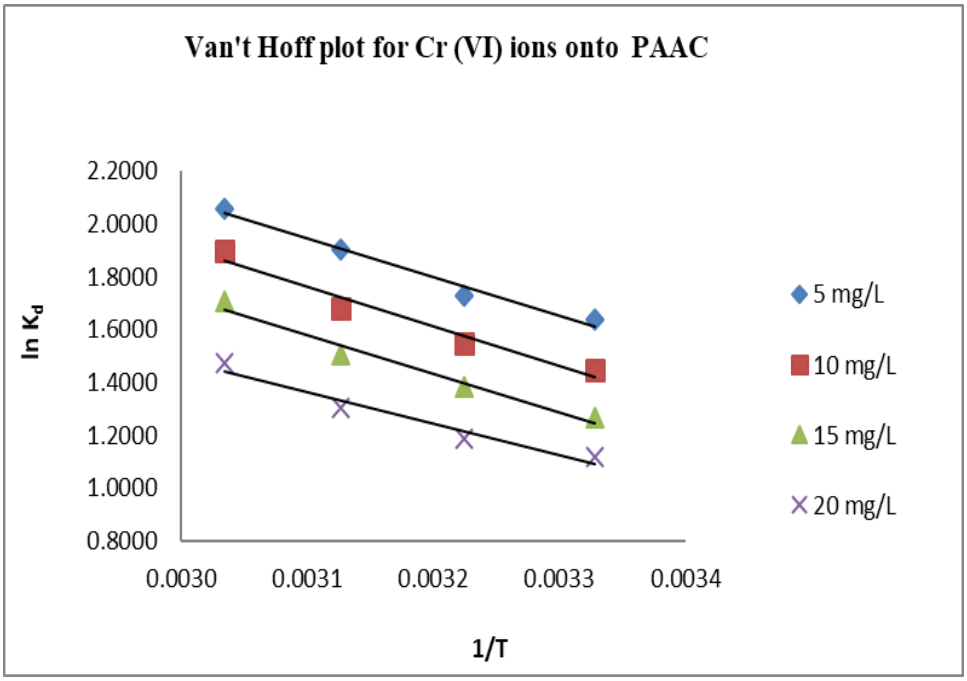

Figure 5.85

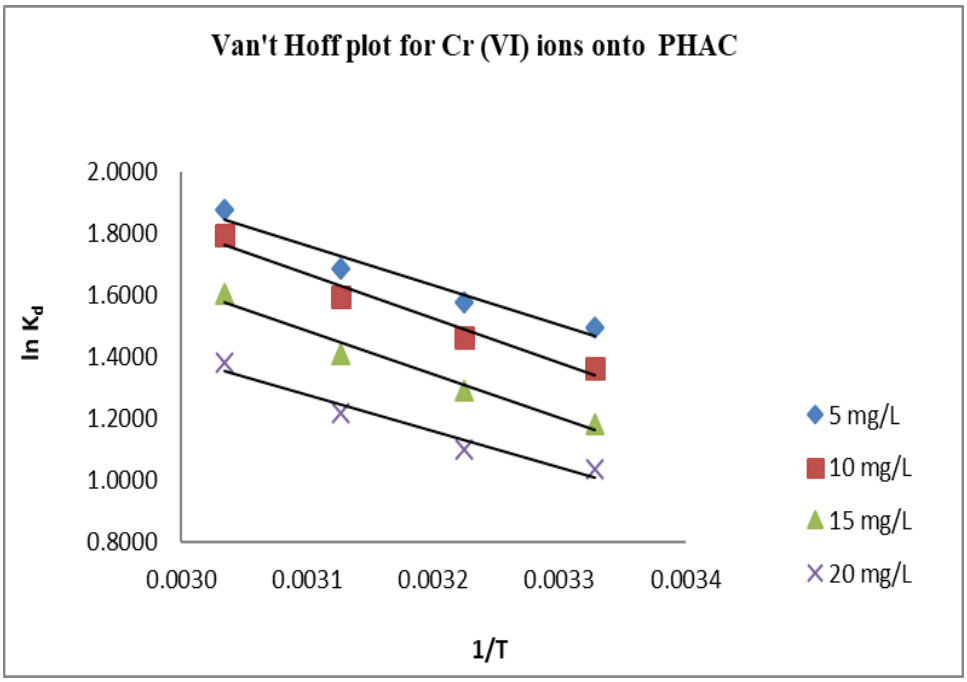

Figure 5.86

Table 5.46 Thermodynamic Parameters results for Ni(II) onto PAAC

Concentration (mg/L)	Temperature (K)	k_d	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/K/mol)
10	305	4.8966	-4.0289	19.359	76.2982
	315	5.6923	-4.5554		
	325	7.0909	-5.2938		
	335	9.7647	-6.3480		
15	305	4.1224	-3.5924	17.496	68.8798
	315	4.8182	-4.1187		
	325	5.8947	-4.7945		
	335	7.6774	-5.6780		
20	305	3.6338	-3.2724	14.135	56.8952
	315	4.1538	-3.7301		
	325	4.8966	-4.2931		
	335	6.0000	-4.9913		
25	305	3.1546	-2.9138	12.132	49.1848
	315	3.5556	-3.3227		
	325	4.0976	-3.8116		
	335	4.8493	-4.3982		

Table 5.47 Thermodynamic Parameters results for Ni(II) onto PHAC

Concentration (mg/L)	Temperature (K)	k_d	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/K/mol)
10	305	4.3492	-3.7282	18.544	72.6935
	315	5.0671	-4.2507		
	325	6.2645	-4.9589		
	335	8.4167	-5.9341		
15	305	3.7692	-3.3652	17.01	66.581
	315	4.4240	-3.8951		
	325	5.3710	-4.5430		
	335	6.9021	-5.3815		
20	305	3.3691	-3.0806	13.822	55.4685
	315	3.8737	-3.5472		
	325	4.5359	-4.0863		
	335	5.5188	-4.7584		
25	305	2.9505	-2.7441	11.976	48.158
	315	3.3476	-3.1648		
	325	3.8275	-3.6274		
	335	4.5189	-4.2016		

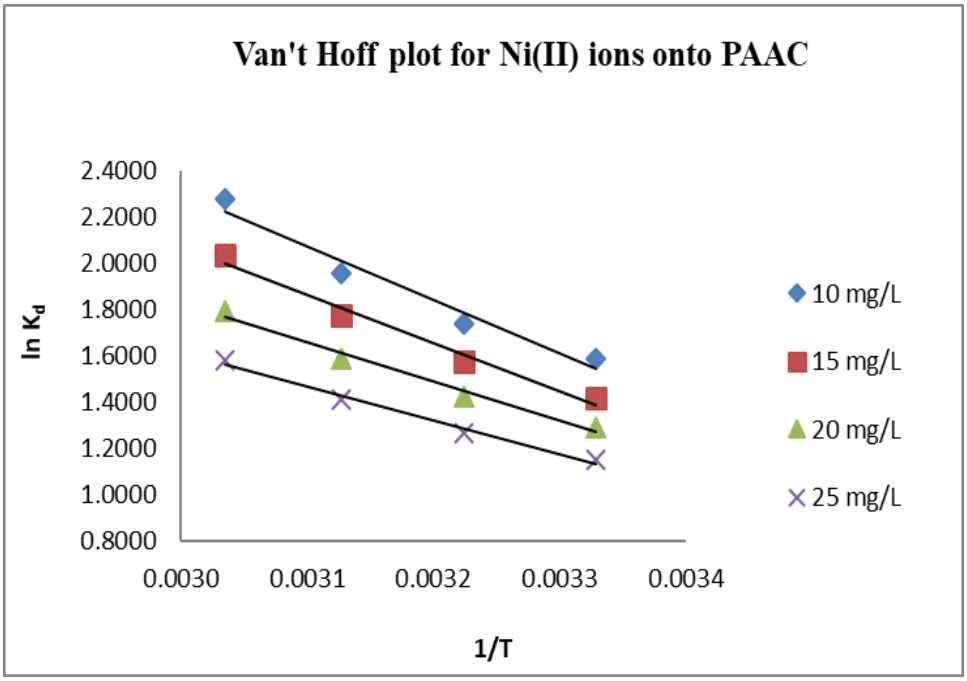

Figure 5.87

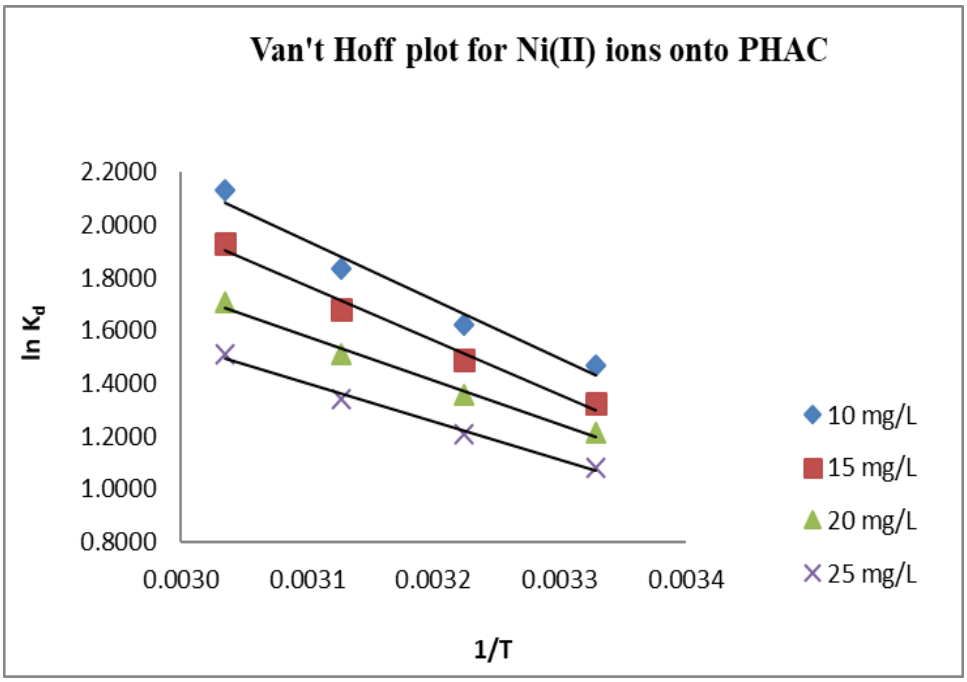

Figure 5.88

Table 5.48 Thermodynamic Parameters results for Cu(II) onto PAAC

Concentration (mg/L)	Temperature (K)	k_d	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/K/mol)
10	305	5.5188	-4.3323	13.272	57.5645
	315	6.3333	-4.8349		
	325	7.1743	-5.3254		
	335	8.9290	-6.0987		
20	305	4.6667	-3.9069	12.226	52.7124
	315	5.2727	-4.3548		
	325	5.8431	-4.7707		
	335	7.3023	-5.5385		
30	305	4.0000	-3.5160	11.578	49.2496
	315	4.4103	-3.8870		
	325	4.8807	-4.2843		
	335	6.1081	-5.0410		
40	305	3.3333	-3.0535	11.078	46.1435
	315	3.7471	-3.4602		
	325	4.2016	-3.8794		
	335	4.9565	-4.4591		

Table 5.49 Thermodynamic Parameters results for Cu(II) onto PHAC

Concentration (mg/L)	Temperature (K)	k_d	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/K/mol)
10	305	4.9930	-4.0784	13.018	55.9078
	315	5.7220	-4.5690		
	325	6.4746	-5.0480		
	335	8.0000	-5.7927		
20	305	4.3291	-3.7165	13.047	54.3927
	315	4.7797	-4.0977		
	325	5.4212	-4.5681		
	335	6.7336	-5.3126		
30	305	3.8196	-3.3989	12.334	59.0463
	315	4.1412	-3.7221		
	325	4.6741	-4.1674		
	335	5.8329	-4.9126		
40	305	3.2288	-2.9727	11.694	47.581
	315	3.4422	-3.2378		
	325	3.9259	-3.6960		
	335	4.8143	-4.3780		

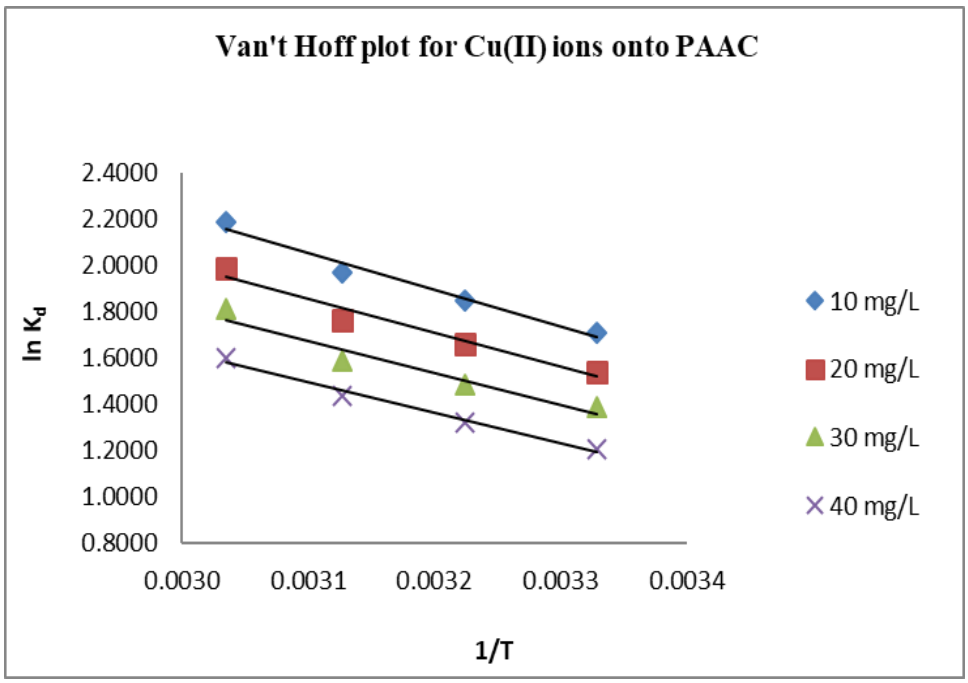

Figure 5.89

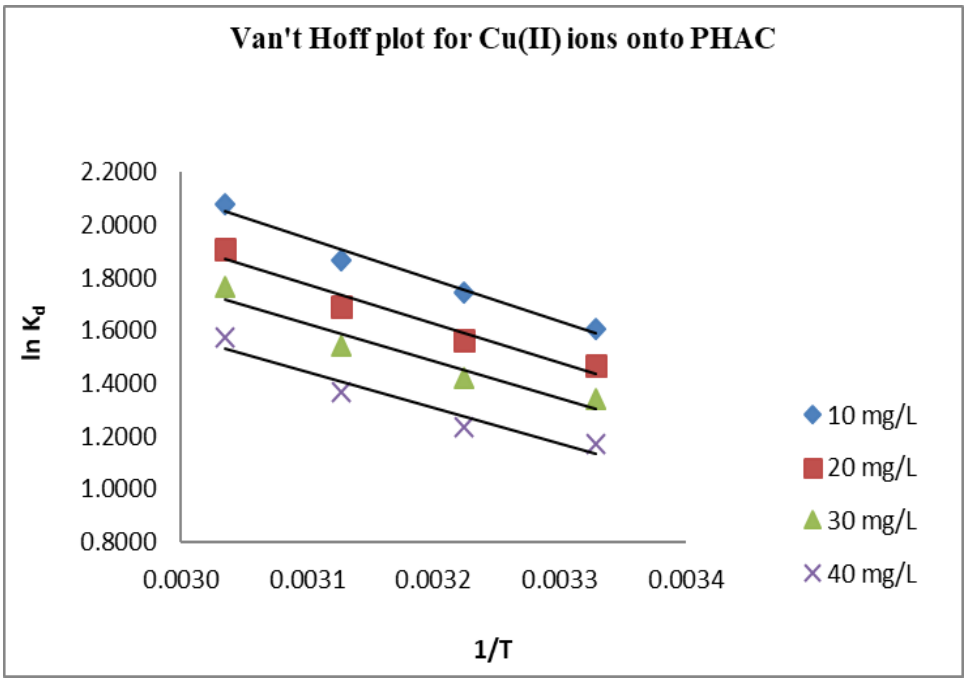

Figure 5.90

Equilibrium studies showed that the adsorption capacity of both the carbons increased with an increase in temperature from 305 to 335 K. Thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined using Equations 5.16 to 5.18. The ΔH° and ΔS° values were obtained from the slope and intercept of Vant Hoff plots drawn between ln K_d and 1/T.

The negative values of ΔG° (Table 5.44 to 5.49) show that the adsorption is highly favourable and spontaneous for all the studied systems.

The ΔH° values were within the range of 1 to 93 kJ/mol which indicates the favorability of physisorption. The positive values of ΔH° show the endothermic nature of adsorption and it governs the possibility of physical adsorption. This fact supports the physical adsorption and rules out the possibility of chemisorptions[58, 91 &92].

While comparing the ΔH° values for the adsorption onto PAAC and PHAC, the ΔH° values lesser for PHAC than that of PAAC in the case of both Cr (VI) ions and Ni (II) ions adsorption. The ΔH° values are more or less the same for both the adsorbents in the case of Cu (II) ion adsorption.

On comparing the three adsorbates the ΔH° value of Ni (II) ion adsorption is higher than the other two adsorbates of the present system which means the interaction of Ni (II) ion on the adsorbent surface was somewhat stronger than the other two adsorbates.

The positive value of the present studied system ranges from Tables 5.44 to5.49. This value is found to decrease with an increase in initial concentration of the adsorbate solution. While comparing the ΔS° values with respect to the two adsorbents, the values

are approximately the same for both the adsorbents except the Ni (II) ion ΔS° value for the adsorption on Ni (II) ion onto PAAC was found to be high when compared to PHAC.

The (+) values of ΔS° expression the increased disorder and randomness at the solid solution interface. During adsorption some structural changes occur at the superficial of the adsorbent. The adsorbed water molecules which are displaced by the adsorbate species, might have expanded more translational entropy than is lost by the adsorbate molecules, thus allowing the occurrence of randomness in the system[58, 88 & 93]. The improvement of adsorption capacity of the activated carbon at greater temperatures was attributed to the expansion of the size of the pore and the activation of the adsorbent surface.

5.10 Instrumental Study

5.10.1 SEM Analysis:

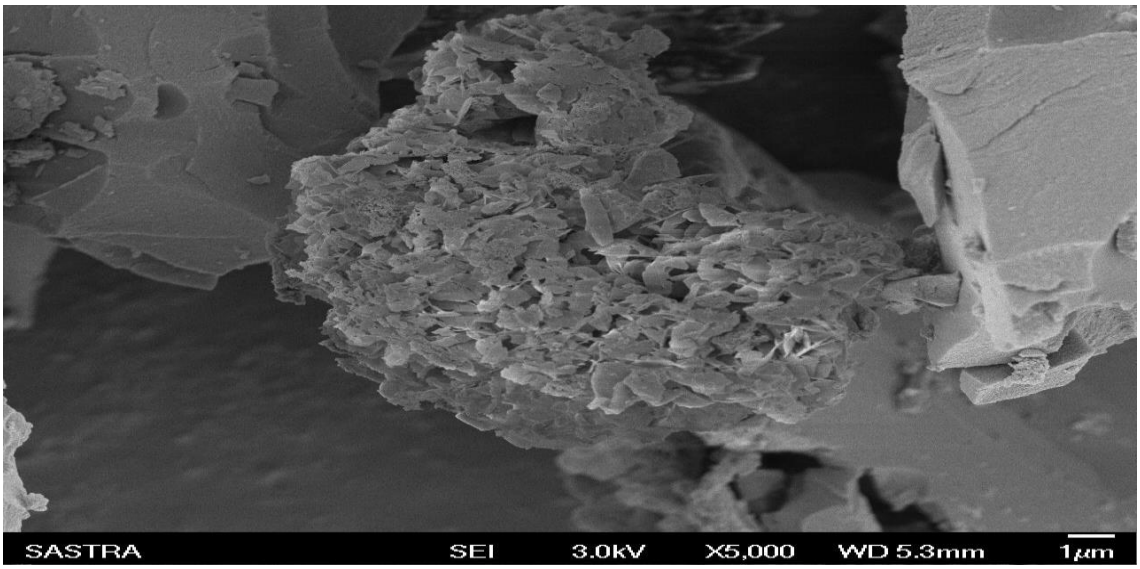

Figure 5.91 SEM image for unloaded PAAC carbon

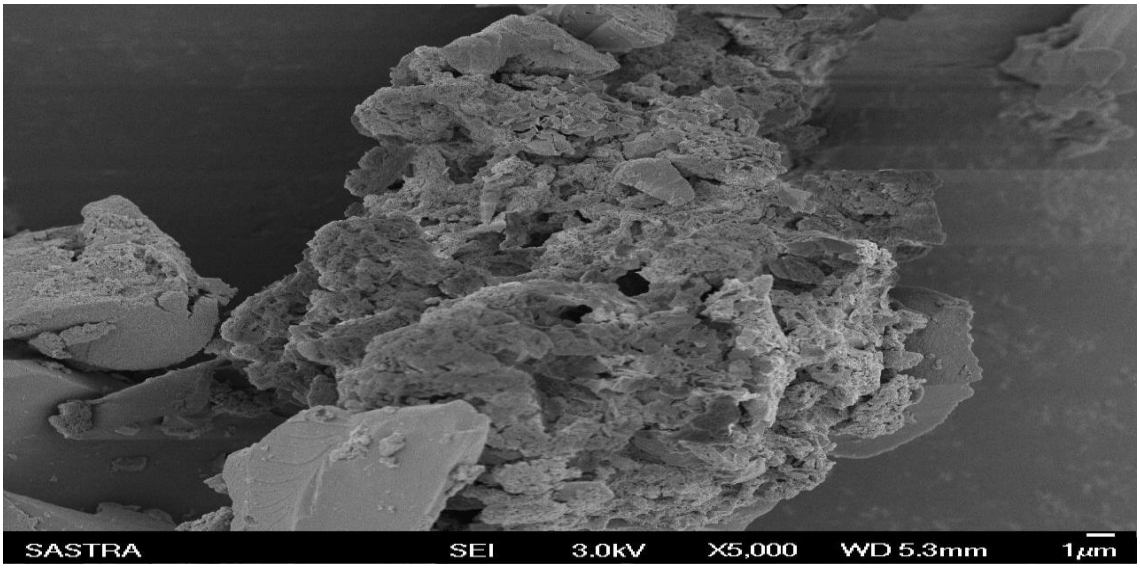

Figure 5.92 SEM image for unloaded PHAC carbon

The morphology of prepared PAAC and PHAC were examined before adsorption is shown in Figures 5.91-5.92 respectively. SEM micrographs of PAAC showed cavities, pores and rough surfaces more than that of PHAC. This shows that Phosphoric acid was

effective to create well developed pores with uniform distribution leading to large surface area and porous structure than Potassium Hydroxide.

5.10.2 FT - IR study

The FT – IR spectrum of PAAC and the PAAC loaded with Cr (VI) ion was shown in Figure 5.93-5.94. It could be seen from the spectrum that almost there is no change in the spectral pattern before and after adsorption however there is a slight reduction of absorption bands. The peak at 795 and 1080 cm^{-1} of the carbon also disappeared and a new peak appeared around 2400 cm^{-1} showed that there is a formation of bond between carbon and metal ion. The peak in the region 795 to 1080cm^{-1} disappeared in the Cr (VI) ion loaded carbon. This clearly indicates that the unsaturated group present in the PAAC might have involved in the bond formation with the Cr (VI) ion. This infers that the possibility of partial chemisorption though maximum of adsorption of Cr (VI) ion onto PAAC adsorbent is by physical forces. Same pattern was followed in PHAC and PHAC loaded with Cr(VI) ions.

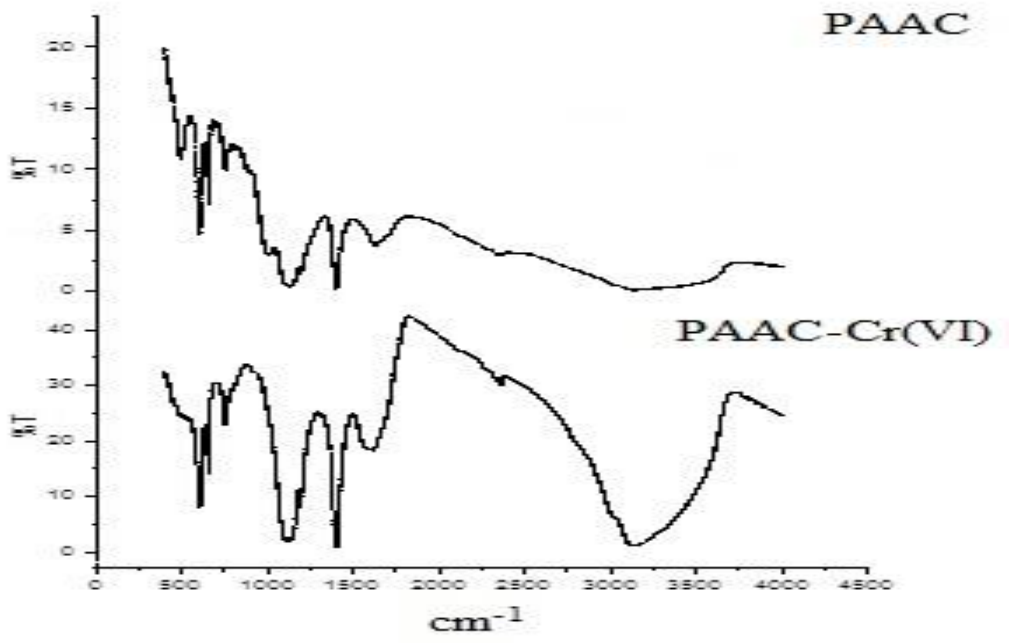

Figure: 5.93 FT – IR spectrum of PAAC and PAAC loaded with Cr (VI) ion

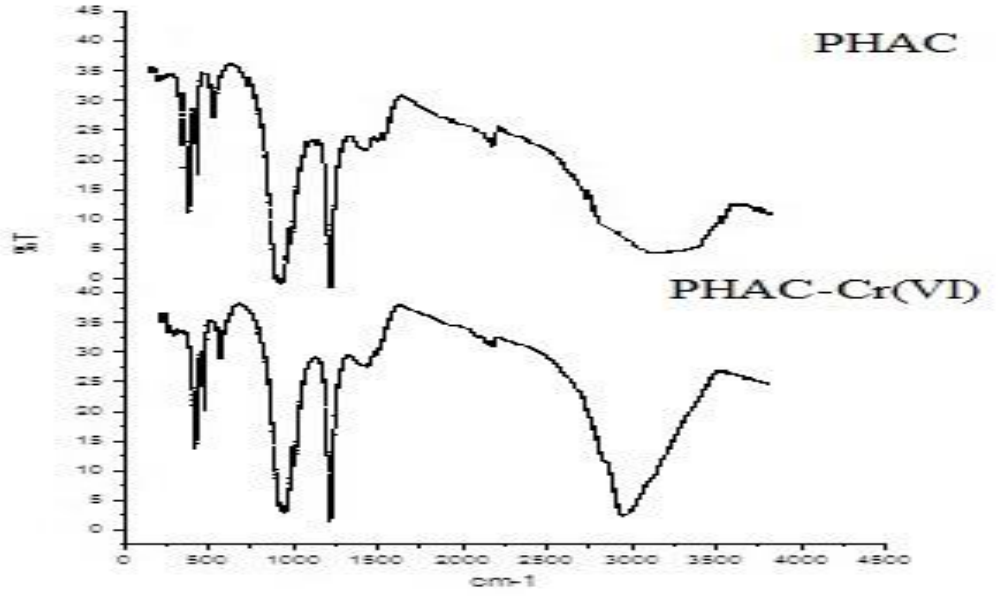

Figure: 5.94 FT – IR spectrum of PHAC and PHAC loaded with Cr (VI) ion

The FT – IR spectrum of PAAC and the PAAC loaded with Ni (II) ion was shown in Figure: 5.95 - 5.96. It could be seen from the spectra that almost there is no change in the spectral pattern before and after adsorption. The two peaks between the region of 800.91 and1000 cm^{-1}were found to disappear in the Ni (II) ion loaded carbons and a peak was slightly shifted towards right from 980-990 cm^{-1}. This indicates that the unsaturated group present in the PAAC might have involved in the bond formation with the Ni (II) ion. This infers that the possibility of partial chemisorption though maximum of adsorption of Ni (II) ion onto PAAC adsorbent is by physical forces. Same pattern was followed in PHAC and PHAC loaded with Ni (II) ions.

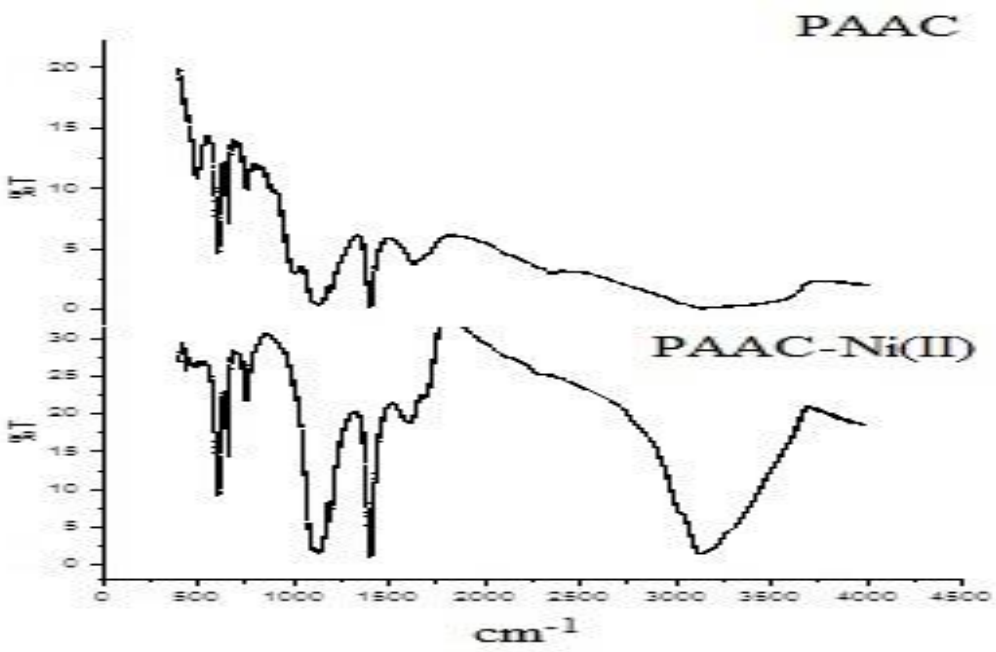

Figure: 5.95 FT – IR spectrum of PAAC and PAAC loaded with Ni(II) ion

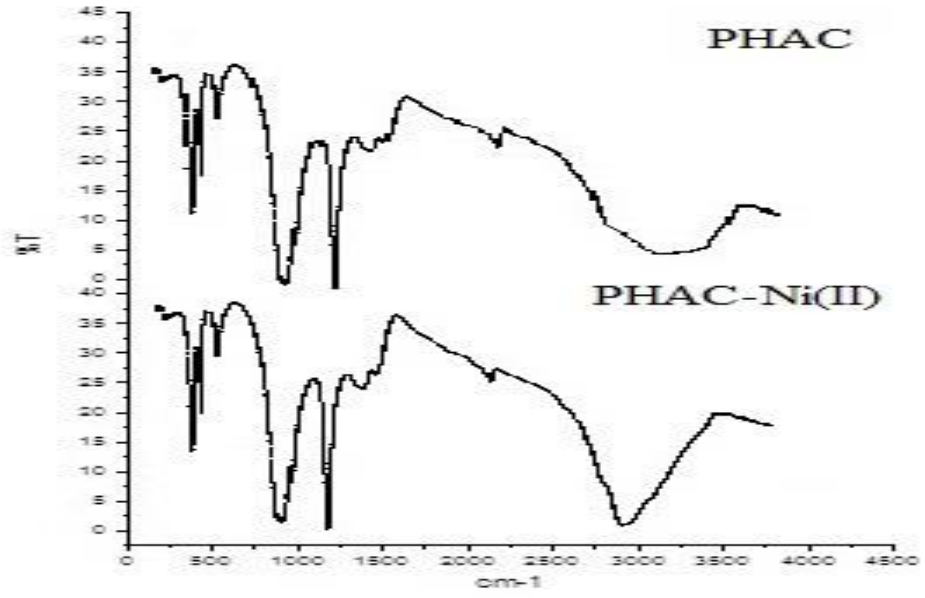

Figure: 5.96 FT – IR spectrum of PHAC and PHAC loaded with Ni(II) ion

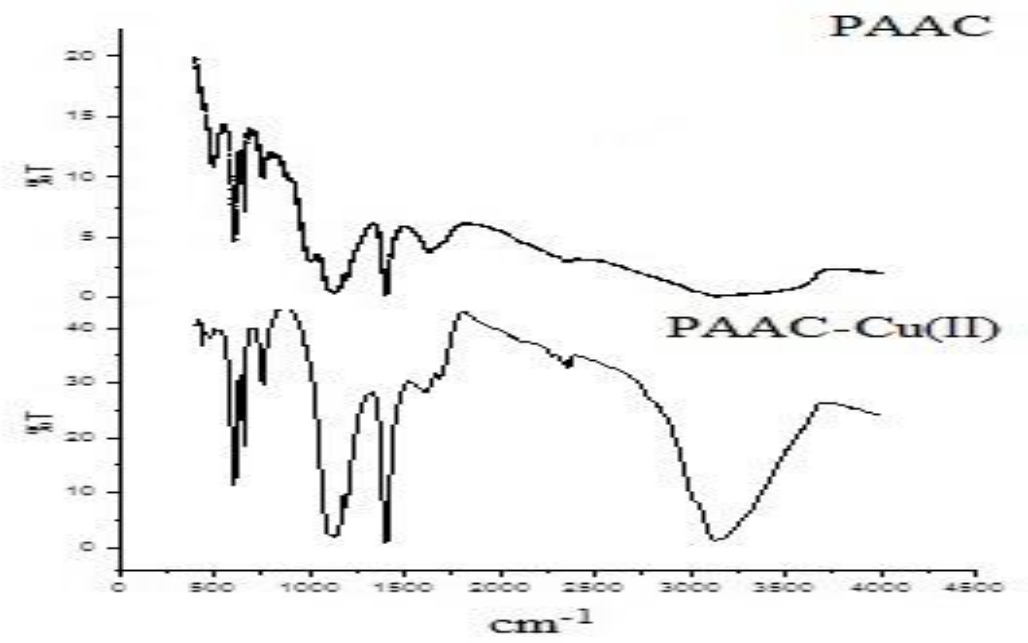

Figure: 5.97 FT – IR spectrum of PAAC and PAAC loaded with Cu(II) ion

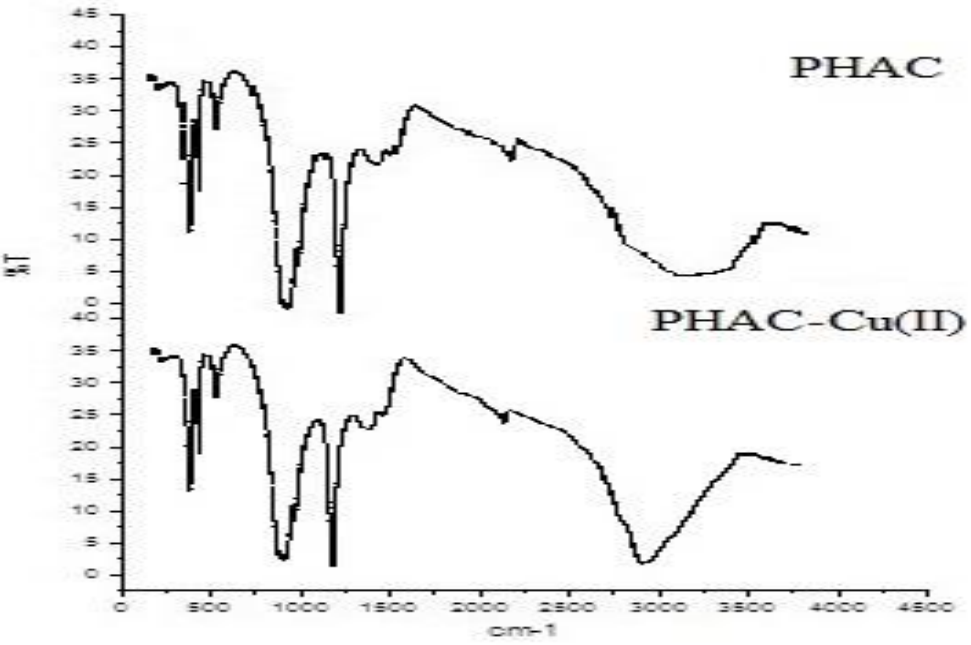

Figure: 5.98 FT – IR spectrum of PHAC and PHAC loaded with Cu(II) ion

The FT – IR spectrums of PAAC and PAAC loaded with Cu(II) ionwas shown in Figure: 5.97-5.98.it is inferred that there is no change in peak formation in before and after adsorption of Cu(II) ions. The overhead investigation infers that the major portion of adsorption takes place with physical adsorption.Same pattern was followed in PHAC and PHAC loaded with Cu(II) ions

5.10.3 Edax Pattern

Edax pattern of Cr(VI), Ni(II) and Cu(II) ions loaded with PAAC & PHAC were shown in the above Figures 5.99 to 5.101. The well defined peak of Cr(VI), Ni(II) and Cu(II) ions shows that all the ion were fitted into the crystalline arrangement of the carbon. Peaks of certain Cr(VI), Ni(II) and Cu(II) ions were very big to small which infers the surface adsorption through Vander Walls force.

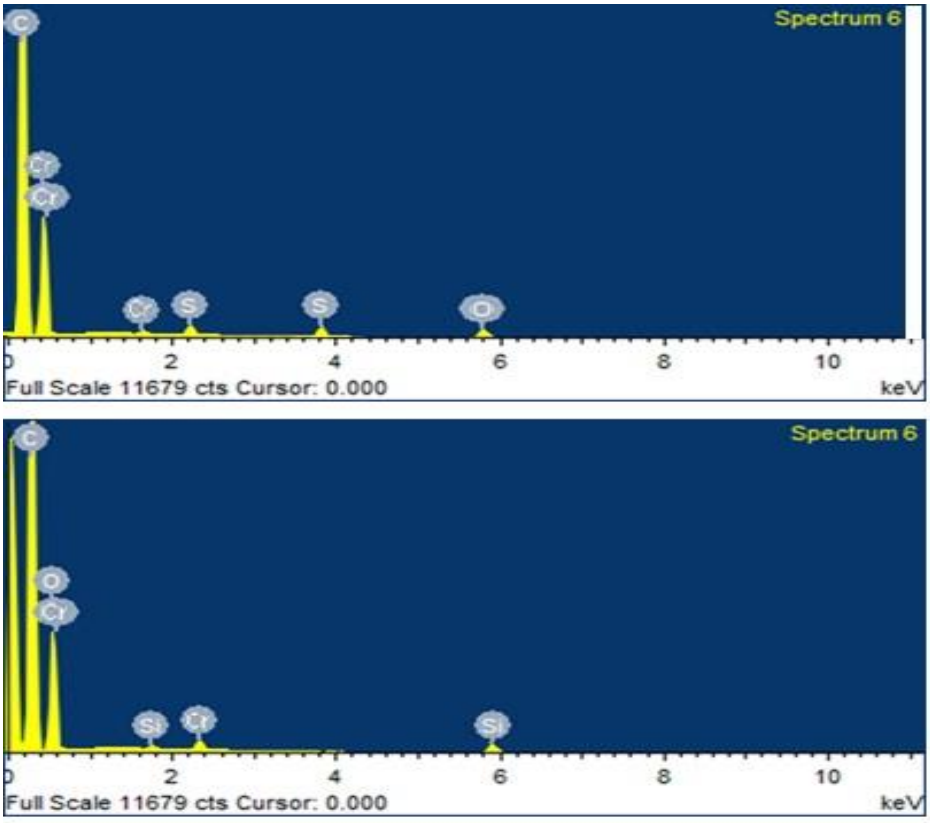

Figure: 5.99 EDAX studies for Cr(VI) ions loaded PAAC & PHAC

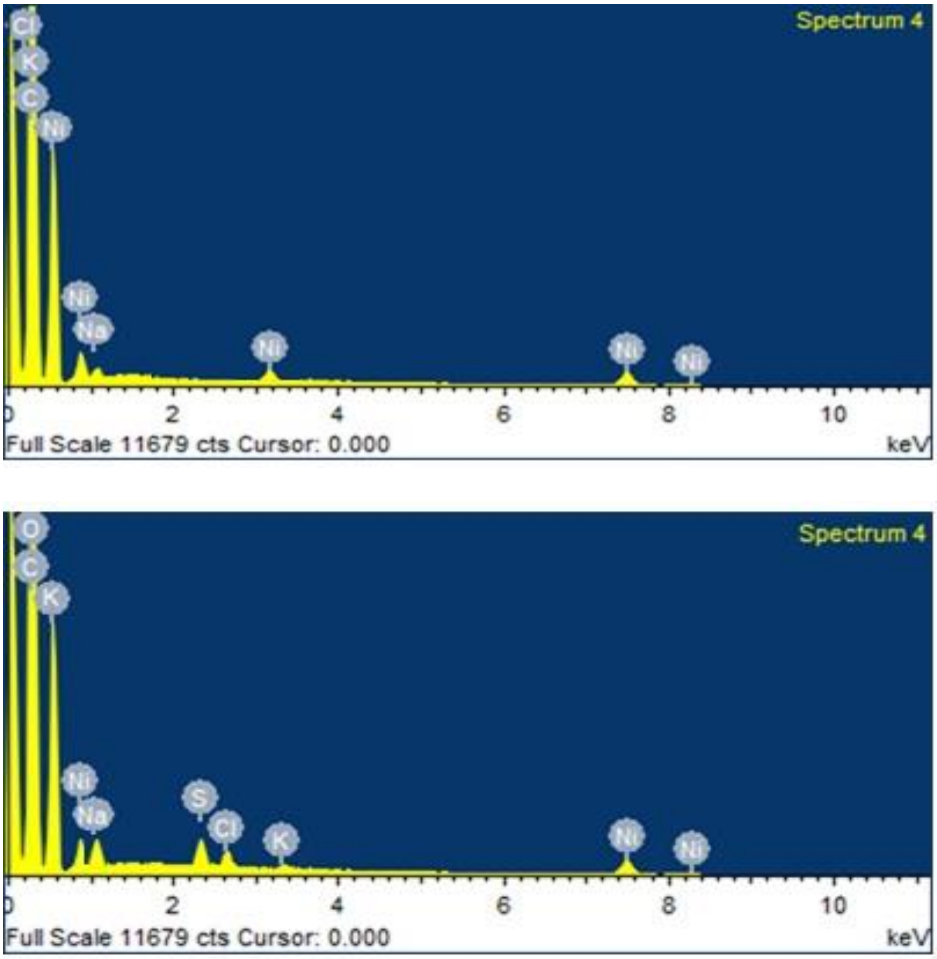

Figure: 5.100 EDAX studies for Ni(II) ions loaded PAAC & PHAC

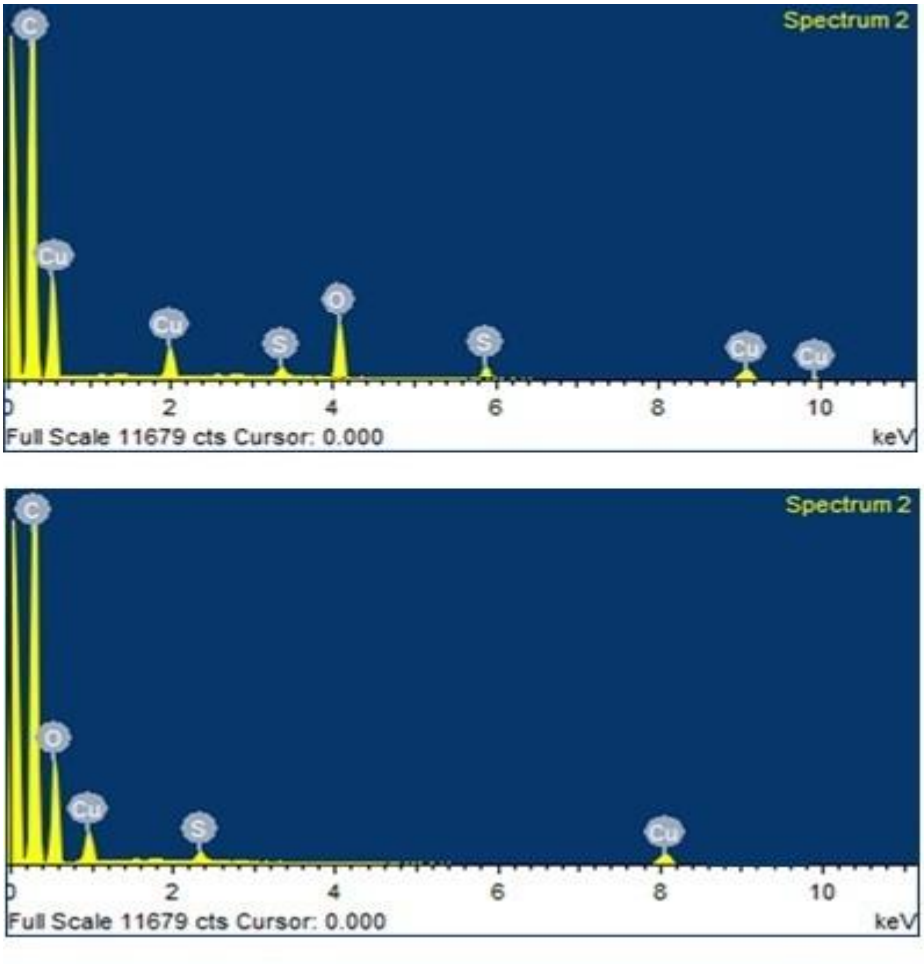

Figure:5.101 EDAX studies for Cu(II) ion loaded PAAC & PHAC

5.10.4 X ray diffraction studies

XRD results show changes in the crystallinity of the carbon well defined peaks show the crystalline nature and the hallow peak shows the non crystalline amorphous nature of the carbon[94].

XRD pattern of PAAC and PHAC loaded with Cr(VI), Ni(II) and Cu(II) ions

XRD pattern of PAAC and PHAC loaded with Cr(VI), Ni(II) and Cu(II)ions shown in Figure 5.102 to 5.107. It is observed that the XRD pattern of PAAC and PHAC loaded with Cr(VI), Ni(II) and Cu(II)ions have slightly changed when compared to unloaded carbons. The peaks between the 20 and 30 2Ɵ values became shallow. This

suggests that the metal ion molecules diffuse into micropores and macropores and adsorb mostly by physisorption and partially by chemisorption by altering the structure of the carbon. This has been attributed to the adsorption of metal ions on the upper layer of the crystalline structure of the activated carbon surface.

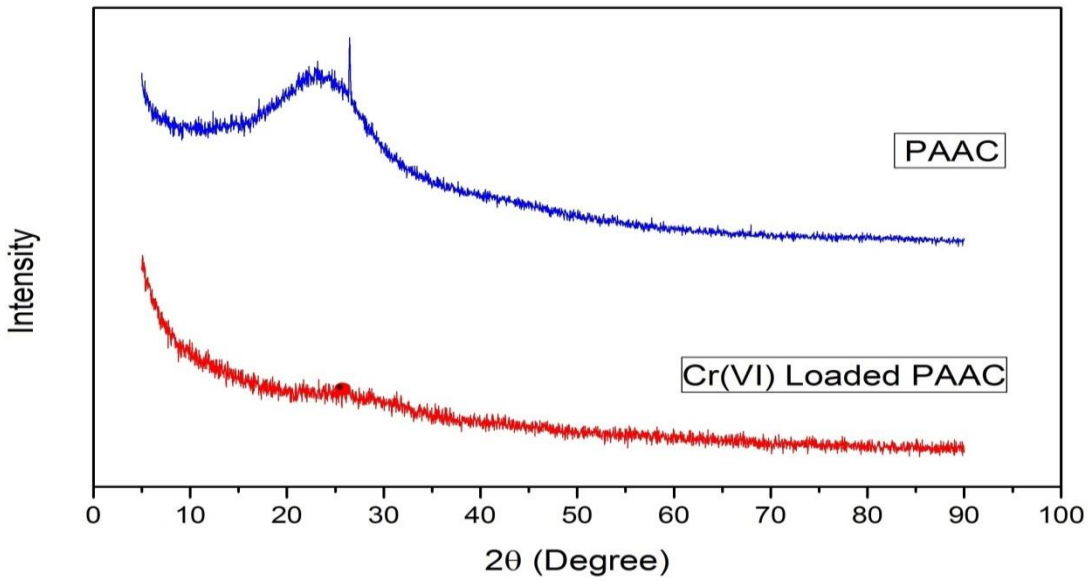

Figure: 5.102 Before and after Adsorption of Cr(VI) ions onto PAAC

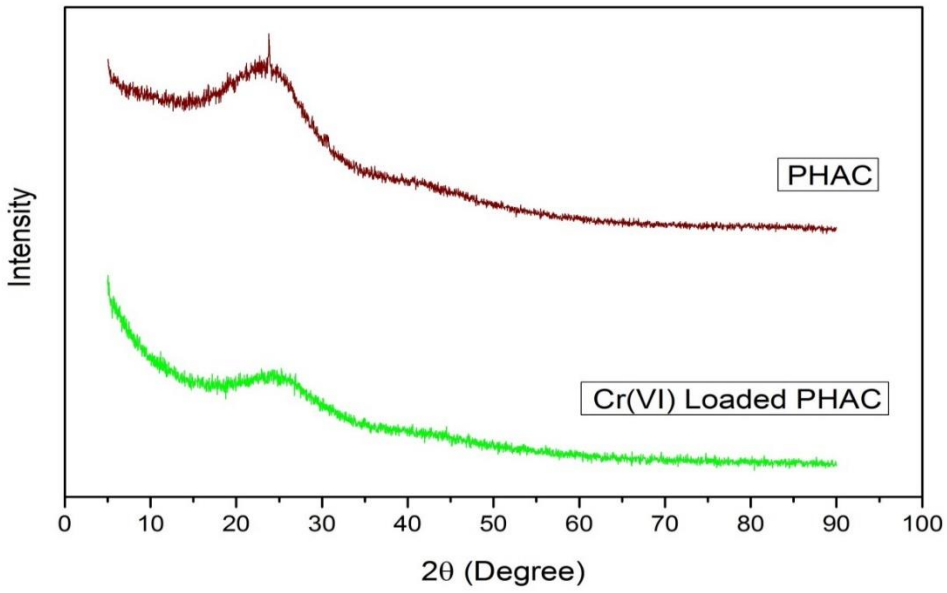

Figure: 5.103 Before and after Adsorption of Cr(VI) ions onto PHAC

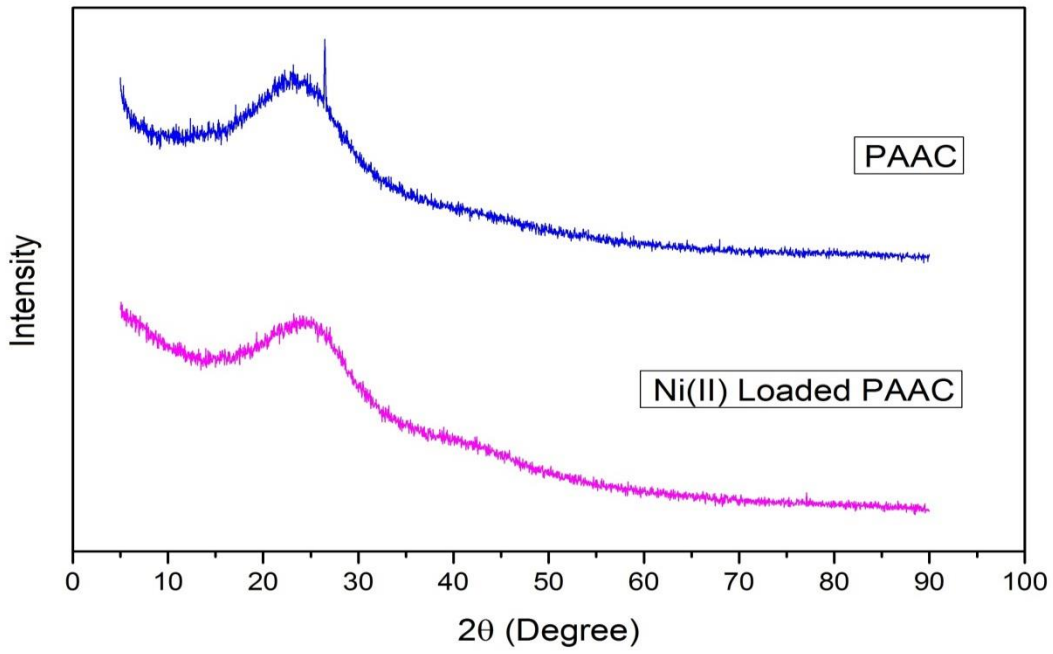

Figure: 5.104 Before and after Adsorption of Ni(II) ions onto PAAC

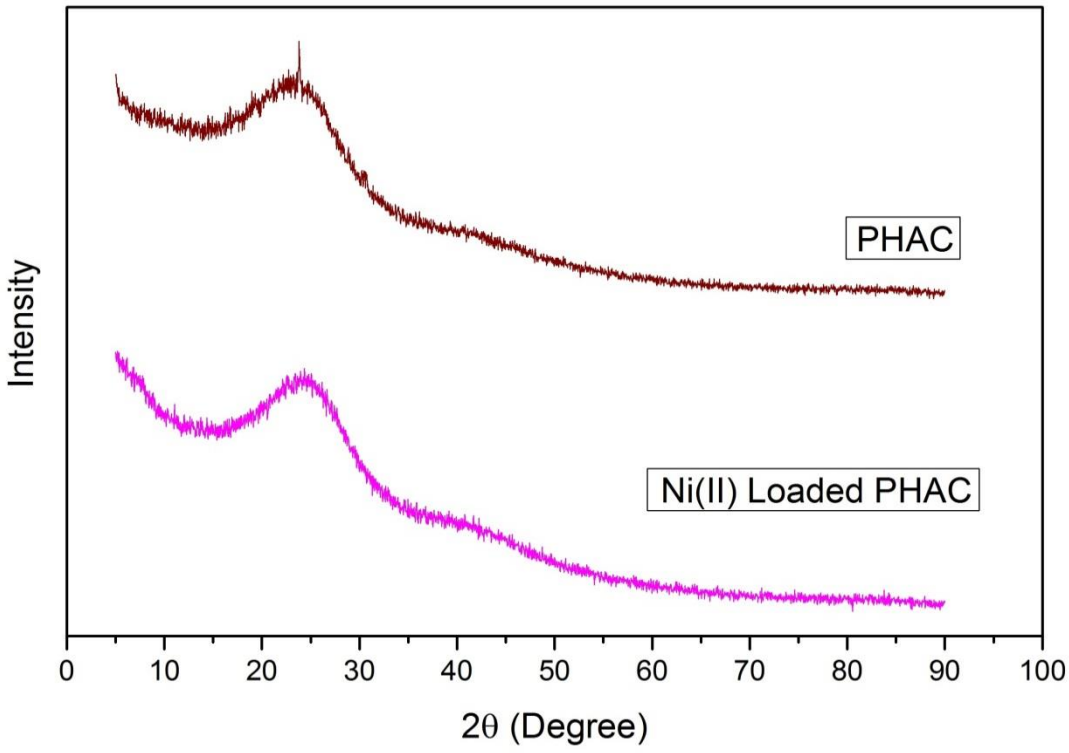

Figure: 5.105 Before and after Adsorption of Ni(II) ions onto PHAC

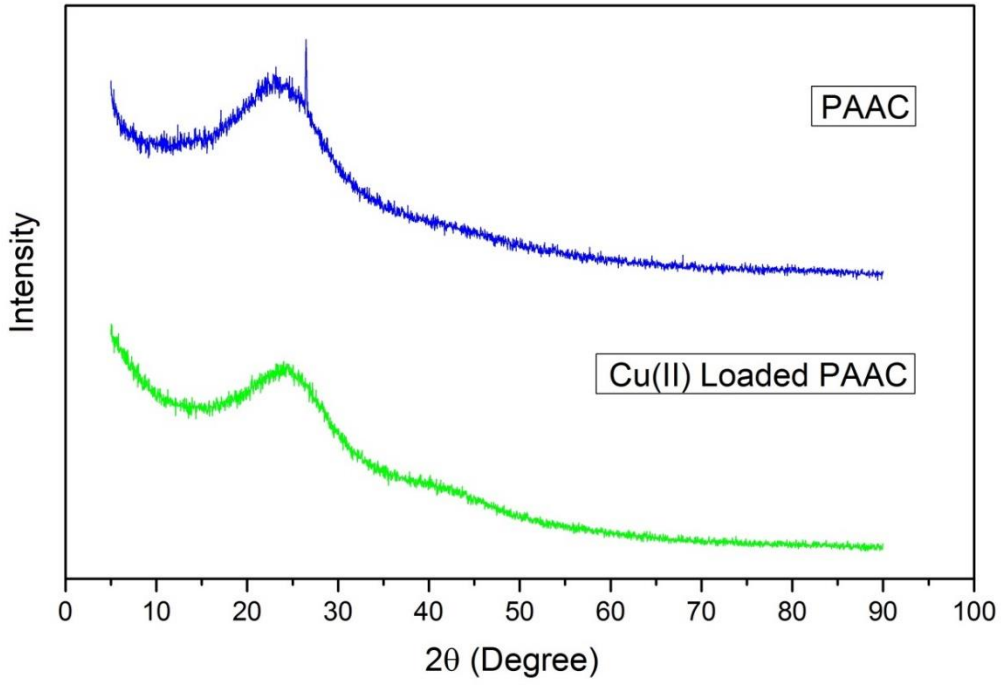

Figure 5.106 Before and after Adsorption of Cu(II) ions onto PAAC

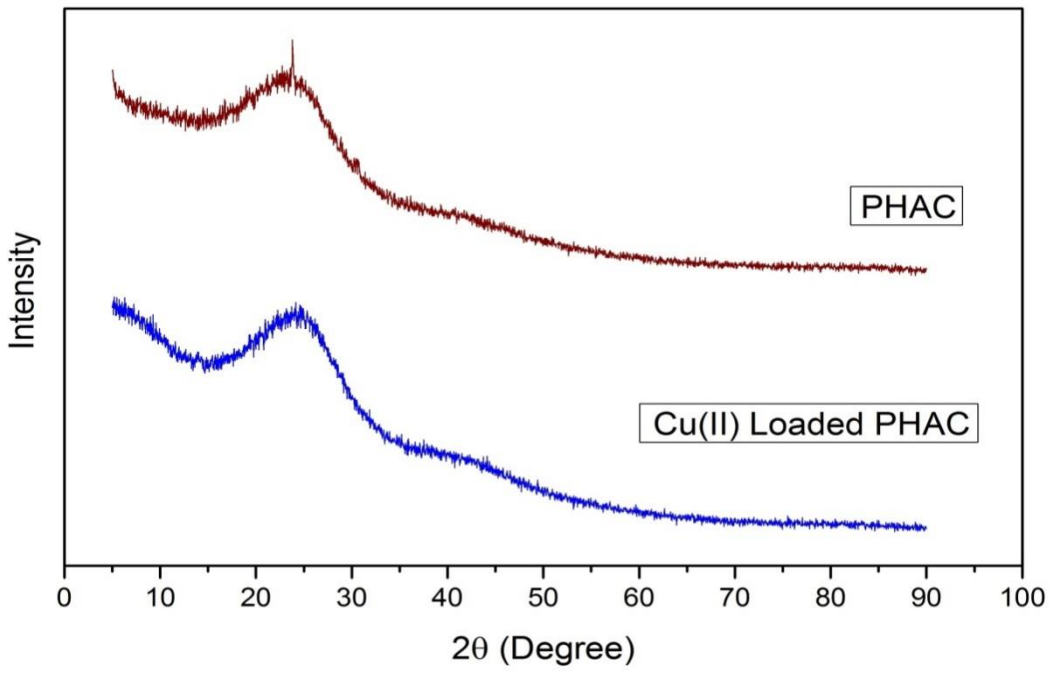

Figure: 5.107 Before and after Adsorption of Cu(II) ions onto PHAC

5.11 Regeneration study

Disposal of adsorbent as waste is not an economic option. Therefore regeneration of spent carbon and its reuse is necessary. Hence regeneration study was carried out with acidic, alkaline and neutral medium using 0.2 M hydrochloric acid, distilled water and 0.2 M sodium hydroxide[95, 96].

5.11.1 Regeneration of Cr (VI) ion adsorbed adsorbents

Regeneration study results relating to Cr (VI) ion adsorbed adsorbents are presented as bar diagram in Figure 5.108. The effects of various chemicals used for regeneration studies indicate that HCl is a superior reagent for regeneration, because beyond 71% of adsorbed Cr (VI) ion were removed from PAAC and 77 % Cr (VI) ion from PHAC. This indicates that the metal ions were adsorbed on both the carbons, PAAC and PHAC through physisorption mechanisms[97].

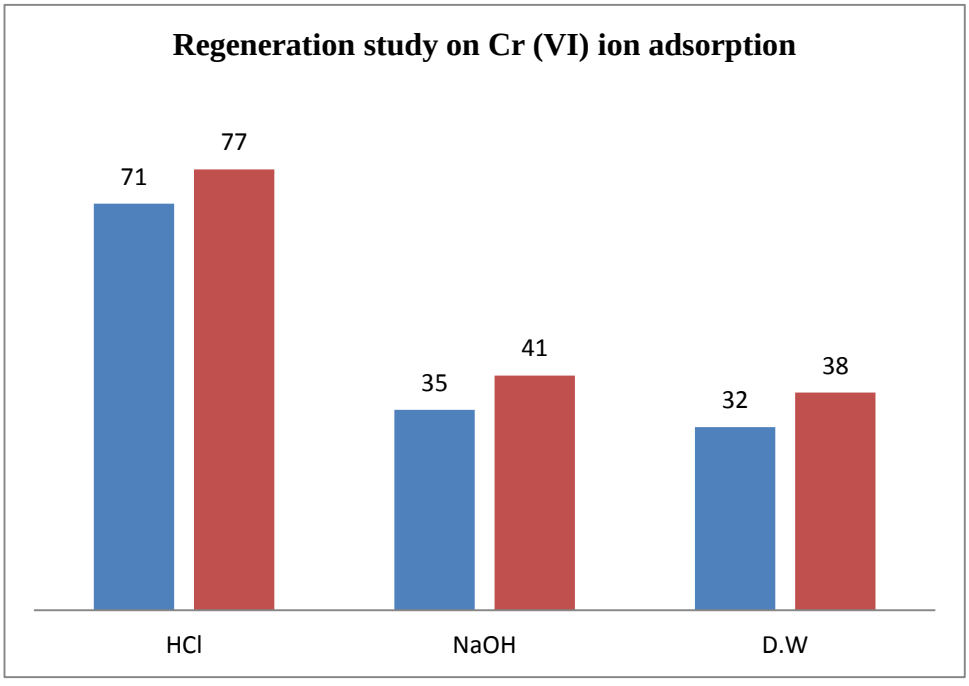

Figure 5.108

5.11.2 Regeneration study on Ni (II) ion adsorption

Regeneration study results belong to Ni (II) ion adsorbed adsorbents are obtainable as bar diagram in Figure 5.107. The effects of various chemicals used for regeneration studies indicate that NaOH is a superior reagent for regeneration, because beyond 61% of adsorbed Ni (II) ion was removed from PAAC and 64 % Ni (II) ion from PHAC. This indicates that the metal ions were adsorbed on both the carbons, PAAC and PHAC through physisorption mechanisms[98, 99].

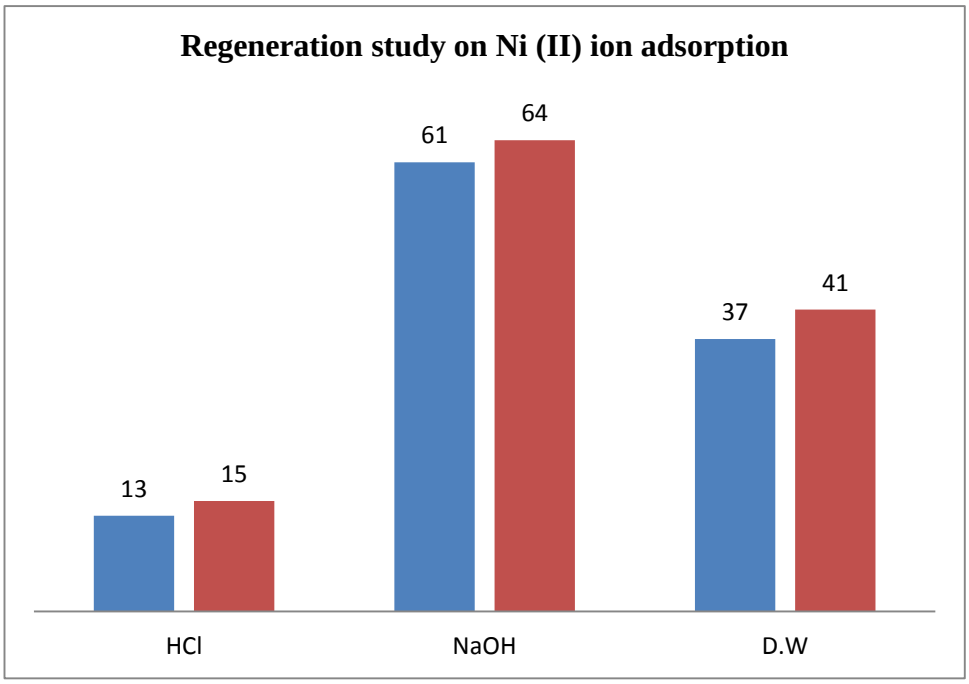

Figure 5.109

5.11.3 Regeneration study on Cu (II) ion adsorption

Regeneration study results pertaining to Cu (II) ion adsorbed adsorbents are obtainable as bar diagram in Figure 5.110. The effects of various chemicals used for regeneration studies indicate that Sodium hydroxide is a superior reagent for desorption, because beyond 66% of adsorbed Cu (II) ion was removed from PAAC and 69 % Cu (II) ion from PHAC. This indicates that metal ions were adsorbed on both the carbons, PAAC and PHAC through physisorption mechanisms[100].

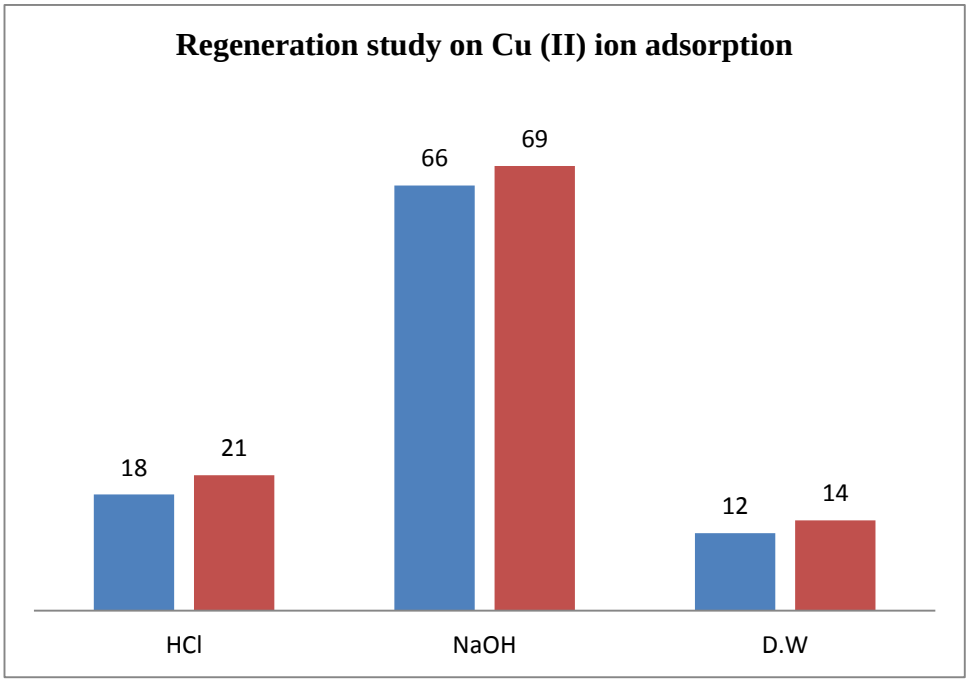

Figure 5.110

Chapter VI

Summary and Conclusion

Chapter –VI

Summary and Conclusion

Water pollution especially heavy metal ion pollution, the impact of water pollution, necessity for the deduction of those pollutants from the aqueous medium, various treatment technologies available, the uniqueness of adsorption method and the recent research belong to the search of cost in effect potential adsorbents as a replacement for commercial activated carbon and literature review for the adsorbent and each adsorbate was given in Chapter I.

Chapter II, III, IV and V deals with the objective and scope of the present study, review of the literature, experimental methods and result and discussion respectively.

In the present study microwave assisted Phosphoric Acid Activated Carbon (PAAC) as an adsorbent was prepared from the pods of *Delonix regia* and investigated its potential to abate chosen adsorbates such as Cr (VI) ion, Ni (II) ion and Cu (II) ion from aqueous solution were investigated. In order to compare the efficiency of PAAC, the same investigation was carried out with PHAC under similar experimental condition.

The work reported in this thesis deals with a detailed investigation on the equilibrium, kinetic and thermodynamic aspects of the adsorption of chosen adsorbates. The different parameters belong to the adsorption at equilibrium are determined in order to establish the adsorption behaviour.

Batch experiments were carried out. The extent of adsorption was found to be proportional to the time of contact and adsorbent dosage. The equilibrium time for the adsorption of Cr (VI) ion, Ni (II) ion and Cu (II) ion onto both adsorbent PAAC and

PHAC were 70 and 80 minutes respectively. The percentage of removal, for a given adsorbent dose, decreased with an increase in Ci metal ion and increased with increase in temperature. The quantity adsorbed for a given adsorbent dose, increased with an increase in Ci of metal ion.

The adsorption of metal ions onto PAAC and PHAC is highly influenced by the pH of the medium. In the case of Ni (II) ion, the % of removal was found to be high at pH of 5. But for Cu (II) ion, the percentage of removal was found to be high at pH of 4 and Hexavalent Chromium ion Cr (VI) ion, the maximum percentage removal was at pH 2. Reasons were explained in detail.

Equilibrium data were fitted in the linear forms of Langmuir, Freundlich, Tempkin and Dubinin−Radushkevich equation for the temperatures 305 K, 315 K, 325 K and 335 K. The equilibrium parameter R_L values obtained in Langmuir isotherm study were in between 0 and 1 showing the favorable adsorption process.

The Freundlich isotherm constants: adsorption capacity, K_f and intensity of adsorption, n were calculated. The applicability of Freundlich isotherm suggests that the adsorption of metal ions onto PAAC and PHAC may be complex in nature. The values of n were originate to be superior to one showing a favorable adsorption.

For the purpose of comparison, the values of Freundlich constants for the adsorption of the selected adsorbates on different adsorbents found in literature were presented in the respective chapters. The adsorption capabilities of the present studied adsorbent PAAC and PHAC were found to have high values.

Ni (II) ion	>	Cu (II) ion	>	Cr (VI) ion

For the purpose of comparison, the values of Tempkin constants for the adsorption of the selected adsorbates on different adsorbents found in literature were presented in the respective chapters. The adsorption capabilities of the present studied adsorbent PAAC and PHAC were found to have high values.

Ni (II) ion	>	Cr (VI) ion	>	Cu (VI) ion

The significances of different parameters obtained from the Langmuir, Dubinin−Radushkevich isotherms were discussed precisely. Values of those parameters revealed the possibility of monolayer, physisorption and heterogeneous pore distribution. On comparing the three adsorbates namely Cr (VI) ion, Ni (II) ion and Cu (II) ion, preferential adsorption is in the following order for all the studied temperature.

Cu (II) ion	>	Ni (II) ion	>	Cr (VI) ion

The difference may be due to the factors such as adsorbate ionic charge, adsorbate size, adsorbate shape, pore volume, pore shape and surface characteristics of the adsorbents.

Kinetics of sorption process onto PAAC and PHAC were evaluated with the linearised forms of the pseudo first order equation (Lagergren), pseudo second order kinetic model (Ho equation) and intra particle diffusion model (Weber Morris).

First order rate constant k_1 and second order rate constant k_2 were determined for different initial concentration at different temperatures. Theoretically evaluated quantity adsorbed at equilibrium from first order and second order rate equations were compared with the quantity adsorbed at equilibrium in the actual experiments. The statistical tool

‘Summation of error square test’ revealed that present studied all adsorbent – adsorbate system followed second order kinetics.

The intra particle diffusion rate constant Kp (mg / g / $min^{0.5}$) and the thickness of the boundary image C were obtained from the Weber Morris plot. The Kp values increased with the increase in temperature, suggesting that the absorption process is endothermic in nature. Moreover, the variation of the Kp values was proportional to the initial adsorbate concentrations, indicating that the rate of the intra-particle diffusion process is controlled.

Thermodynamic parameters were appraised consuming the values of equilibrium constants at different temperatures viz. 305 K, 315 K, 325 K and 335 K with the help of Vant Hoff’s plots. The values of free energy change (ΔG°) for the adsorption of Cr (VI) ion, Ni (II) ion and Cu (II) metal ion, onto PAAC and PHAC were found to be negative while the values of enthalpy change (ΔH°) and entropy change (ΔS°) were positive. The negative values of ΔG° indicate that the process was spontaneous with great attraction for the chosen metal ions. Further, the values of ΔG° increased with a increase in temperature, which proposes that the spontaneity of adsorption is related to temperature.

The positive values of ΔS° shows the increased disorderness at the solid -solution interface during the adsorption process and show the affinity of the adsorbent materials for the adsorbates. The positive values of ΔH° indicate that the adsorption practice is endothermic in nature. The magnitude of the ΔH° values was below 93 KJ, which suggests that most of the adsorption takes place via physisorption mechanism. This observation was well supported by FT-IR, SEM EDAX and XRD studies.

Desorption studies inferred that Sodium hydroxide solution (0.2 M) was the effective reagent for Ni (II) ion and Cu (II) metal ion, whereas Hydrochloric acid (0.2

M) was an effective reagent for the adsorbates Cr (VI) ion to desorb the adsorbed solutes. This result also favored the physisorption mechanism.

The above-mentioned study demonstrated the evaluation of the low cost adsorbents prepared from the pods of *Delonix regia* for the elimination of Cr(VI) ion, Ni (II) ion and Cu (II) metal ion from aqueous solution. The values of equilibrium parameter constants, thermodynamic parameters show the feasibility of the adsorption of these selected metal ions onto the prepared adsorbent. Regeneration studies exposed the recycle of the adsorbates and the consumed adsorbent. The investigational outcomes obtained by batch trials can be helpful for the water engineers and environmental technologists in designing experimental set up while employing the adsorbate/adsorbent arrangement studied. Further research is needed to determine the effective efficiencies and specific uses of these adsorbents with respect to other heavy metals, dyes and various real industrial waste water.

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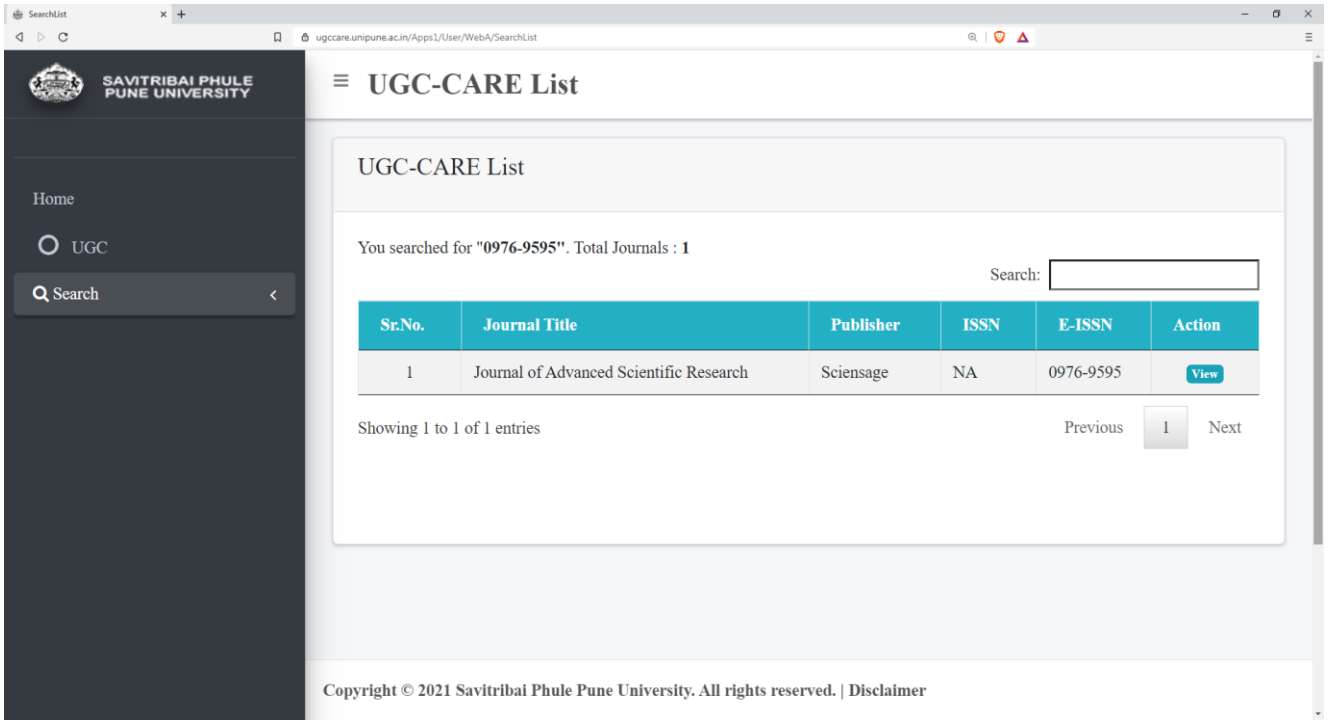
Publications

LIST OF PUBLICATIONS

1. S.Vani, S.Siavji Ganesan.Adsorption of Cr(VI) Ions onto H_3PO_4 and KOH Activated Carbon Prepared from *Delonix Regia* Pods-A Comparative Study.*Journal Of Advanced Scientific Research* . Vol. 11(4), 150-158, December **(2020).**

2. S.Vani, S.Sivaji Ganesan.Removal of Nickel (II) ions Using Microwave Assisted H_3PO_4 Activated Carbon Prepared from *Delonix Regia* Pod *Journal Of Advanced Scientific Research.*Vol. 11(4), 310-315, December **(2020).**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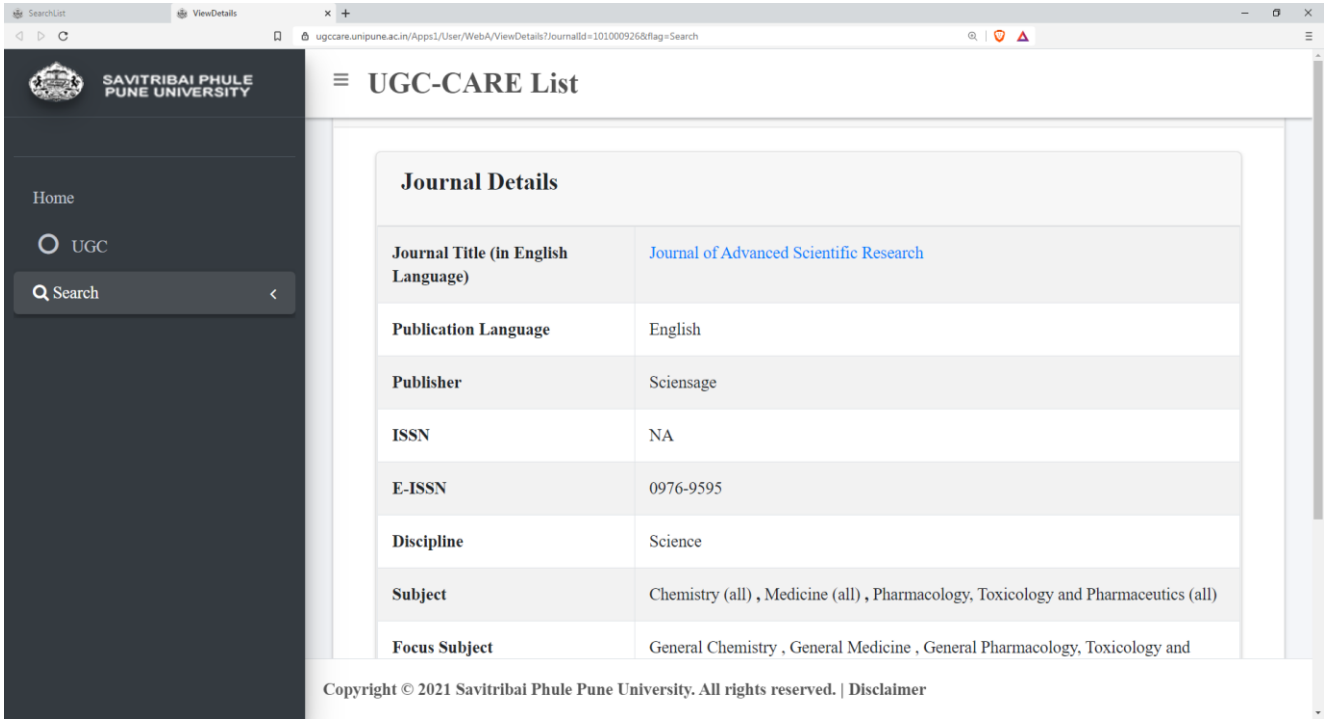
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ADSORPTION OF CR(VI) IONS ONTO H_3PO_4 AND KOH ACTIVATED CARBON PREPARED FROM *DELONIX REGIA* PODS -A COMPARATIVE STUDY

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ABSTRACT

The present work reported, the activated carbons prepared from *Delonix regia* pods using H_3PO_4 and KOH were designated as Phosphoric Acid Activated Carbon (PAAC) and Potassium Hydroxide Activated Carbon (PHAC). Adsorption experiments were carried out in a batch process and various experimental parameters such as effect of adsorbent dosage, contact time, initial metal ion concentration, temperature and pH on percentage removal have been studied. The adsorption process of Cr (VI) ions onto PAAC and PHAC is in good agreement with the Frendlich and Langmuir adsorption isotherm and follows the pseudo-second-order kinetic model. Furthermore, thermodynamics parameters were investigated.

Keywords: Activated carbon, Cr(VI) ions removal, kinetics, adsorption isotherms, thermodynamics.

1. INTRODUCTION

Heavy metal contaminants such as lead, cadmium, mercury, chromium, nickel, copper, arsenic and zinc are non-biodegradable and harmful to human and the environment [1]. Chromium is used in textile dyeing, electroplating, leather tanning, steel fabrication and metal finishing industries [2, 3]. Exposure to Cr (VI) ions causes skin allergy, ulceration of intestine, cancer in the digestive tract and lungs and causes damage to human kidney and the liver [4-8]. For the removal of Cr (VI) ions from wastewater, adsorption is most effective when compared to other conventional techniques. In adsorption, solid surface is bounded with liquid molecules. Adsorbents possess large internal surface area that permits adsorption [9]. Activated carbon, biological materials, chitosan, fly ash etc are some of the commonly used adsorbents for Cr(VI) ions removal [10,11]. *Delonix regia* (Flamboyant) tree plantation is grown around the world for ornamental reasons, preserving the soil and also protecting the environment [12]. Apart from these benefits, the tree produces pods in large quantities, which would be of benefit to the scientific community in the search for cheaper adsorbent materials. The aim of this research was evaluating the adsorption studies on the activated carbon prepared from *Delonix regia* pods for the removal of Cr(VI) ions from aqueous solutions. The effect of various parameters such as adsorbent dosage, initial metal concentration and pH has been studied.

2. MATERIAL AND METHODS

2.1. Preparation of activated carbon

The air dried *Delonix regia* pods were cut into small portions and crushed in a pulveriser. About 20 g of the crushed pods was mixed with 75 mL of KOH/H_3PO_4 solution of desired concentration (10, 20 and 30 %). The slurry was retained at room temperature for 24 hours, to ensure the access of the KOH / H_3PO_4 to the *Delonix regia* pods. Then the slurry was exposed to microwave heating of pre- determined power (850 watts) for predetermined duration (12 minutes). Carbon obtained from the above process was washed with 0.5 M HCl followed with warm distilled water and ice cold distilled water until the pH reaches 7. Then the carbon was sieved and desiccated at 423 K and kept in desiccators for further studies. The activated carbon prepared from *Delonix regia* pods using H_3PO_4 and KOH were designated as Phosphoric Acid Activated Carbon (PAAC) and Potassium Hydroxide Activated Carbon (PHAC).

2.2. Preparation of adsorbate

A standard solution of Cr (VI) was prepared (1000 mg/L) by dissolving 2.828 g Potassium dichromate salt, $K_2Cr_2O_7$ in one litre of distilled water.

2.3. Batch equilibration method

A 250 ml iodine flask, 50 ml and a pre-determined concentration of the metal ion solution was transferred into the container. Then the content was rotated in a cycle using a cycle for a prearranged duration of 180 min. The concentration of the centrifuge was measured after proper dilution using the Systronics Dual Beam UV-Visible Spectrometer: 2202. The effect of pH was calculated via bringing the preferred pH of the solutions by adding con. 0.1 N HCl/0.1N NaOH solution. The kinetics investigates were performed with the working pH 7 and for contact times 5, 10, 20, 40, 60, 80, 100, 120, 140, 160 and 180 minutes. Concentration of metal ion before and after adsorption was measured using a double beam UV Visible spectrophotometer. Standards for the establishing of calibration curves were prepared by weakening the stock solutions so as to have 10, 15, 20, 25 and 30 mg/L of the metal ions and the absorbance of the solution at the respective wave lengths were recorded.

2.4. Isotherm studies

2.4.1. Langmuir isotherm

This is the greatest broadly used model to describe heavy metal ion / dye sorption in adsorbent. The Langmuir-isotherm is write down in the subsequent form [13]

$$Q_e = Q_m b C_e / 1 + b C_e \ldots\ldots\ldots\ldots (1)$$

This equation is often written in linear form as [14]

$$C_e/Q_e = 1/ Q_m b + C_e / Q_m \ldots\ldots\ldots (2)$$

Qe is the solvent adsorbate in a unit weight of the adsorbent (mg / g), the equipoise attention of the solute in total solute (mg / L), Qm is the maximum monolayer absorption capacity or concentration (mg / g) and b is the absorption energy is the mutual of the concentration reaching half the concentration of the adsorbent. The linear equation is often preferred because of its ease and suitability. The important characteristics of Langmuir isotherm can be described by a separation factor, R_L, which is defined by the following equation

$$R_L = 1 / (1+ bC_0) \ldots\ldots\ldots\ldots\ldots (3)$$

where C_0 is the initial concentration of the adsorbate solution. The separation factor R_L indicates the character of the isotherm and the nature of the adsorption process as given below [15];

R_L value	Nature of adsorption process
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

The results were attained from Langmuir model for the exclusion of Cu (II) ion onto PHAC was represented in Table.

2.4.2. Freundlich Isotherm

The Freundlich equation is an experimental equation. This is the greatest popular model for a single solvent system based on the solvent distribution between the solid state and the aqueous phase in equilibrium.

This equation has the following form

$$\log q_e = \log K_f + 1/n \log C_e \ldots\ldots (4)$$

where qe is the quantity of adsorbate adsorbed (mg / g) in equilibrium, Ce is the symmetry attention of adsorbate in solution (mg / L), and Kf and n are constants covering all the influences that distress the absorption capacity and intensity of absorption, respectively.

2.4.3. Tempkin isotherm

Tempkin isotherm adopts that the temperature of sorption in the film reductions linearly with the attention due to the sorbate / sorbent interactions. Moreover, the drop in heat of absorption is not logarithmic, as stated in the Freundlich expression.

The linear form of Tempkin equation is

$$q_e = RT/b_T \ln a_T + RT/b_T \ln C_e \ldots\ldots\ldots (5)$$

Where, b_T is theconstant associated to the temperature of sorption (J/mg) and a_T the equilibrium binding constant equivalent to the maximum binding energy (L/g) The constants a_T and b_T were calculated from the slopes and intercepts of q_e versus ln C_e.

2.4.4. Kinetic study

Several adsorption kinetic models have been conventional to recognize the adsorption kinetics and the rate-limiting step. These include the pseudo-first and second-order rate model, the Weber and Morris sorption kinetic models.

2.4.5. Pseudo first order kinetics

The linearised form of the pseudo-first order equation of Lagergren is generally expressed as follows:

$$\log (q_e - q_t) = \log q_e - k_1 / 2.303 \times t \ldots\ldots\ldots\ldots (6)$$

where, q_e and q_t are the adsorption capacity at equilibrium and at timet respectively (mg/g). k_1 is the rate constant of pseudo first-order adsorption. The plot of log (q_e -q_t) versus t should give a linear relationship; k_1 and q_e can be calculated from the slope and intercept of the plot, respectively.

2.4.6. *Pseudo second order kinetics*

The pseudo second order kinetic model is represented by the following linear equation:

$$t/q_t = 1/ k_2.q_e^2 + 1/q_e\, t \quad \ldots\ldots\ldots\ldots\ldots(7)$$

where, q_e and q_t are the adsorption capacity at equilibrium and at timet respectively (mg/g).

The initial adsorption rate, h (mg/(g min)), as t⟶0 can be defined as

$$h = k_2 q_e^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots(8)$$

The Plot is drawn between of t/q_t and t. Theoretical adsorption capacity (q_e), and the second-order rate constants k_2 (g/ (mg min)) can be determined experimentally from the slope and intercept of plots.

2.4.7. *Intra particle diffusion*

According to Weber and Morris , an inner particle distribution is defined by the co-efficient k_p equation:

$$q_t = k_p t^{1/2} + C \ldots\ldots\ldots \quad (9)$$

Weber and Morris plot is drawn between q_t and $t^{1/2}$ to understand the intra particle diffusion. Where K_p ($mg/g/min^{1/2}$) is the intra particle diffusion rate constant and C is the thickness of the boundary film. The K_p and C values were obtained from the slope and intercept of the linear portions of the curves drawn between quantity adsorbed in mg/g (q_t) and the square root of time ($t^{1/2}$).

2.4.8. *Test for kinetics models*

Best fitting kinetic model for a system can be determined by using the statistical tool percentage of sum of error squares (SSE). This can be evaluated by the following formula,The sum of error squares is given as follows;

$$SSE\ (\%) = \sqrt{\sum[(q_e)_{exp} - (q_e)_{cal}]^2 / N} \ldots\ldots\ldots\ldots\ldots \quad (10)$$

where N is the number of data points, (q_e)expis the experimental q_e and (q_e)calis the calculated q_e.

2.4.9. *Thermodynamic study*

To review the feasibility of the adsorption process, thermodynamic factors such as change in free energy ΔG° (kJ/mol), enthalpy ΔH° (kJ/mol) and entropy ΔS° (J/K/ mol) can be determined using the following equations [16]

$$k_d = C_{solid} / C_{liquid} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

$$\Delta G° = -RT \ln k_d \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (12)$$

$$\log k_d = \Delta S°/ (2.303RT) - \Delta H°/(2.303R)T \ldots \quad (13)$$

where k_d is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg/L), C_{liquid} is the liquid phase concentration at equilibrium (mg/L), T is the temperature in Kelvin and R is the gas constant. The Vant Hoff plots are drawn between $\ln k_d$ versus 1/T. ΔH° and ΔS° values were evaluated from the slope and intercept of the plot respectively.

3. RESULTS AND DISCUSSION

3.1. Effect of adsorbent dosage

The adsorption of Cr (IV) ion onto PAAC and PHAC was studied by varying the dose of the adsorbent from 10 mg/50 mL to 50 mg/50 mL by taking 30 mg/L of adsorbate. The percentage of removal of adsorbate from aqueous solution increased with an increase of carbon dose up to 70 mg after that removal percentage remains unchanged (**Fig.1**). This is due to the increased carbon surface area and the convenience of more adsorption sites.

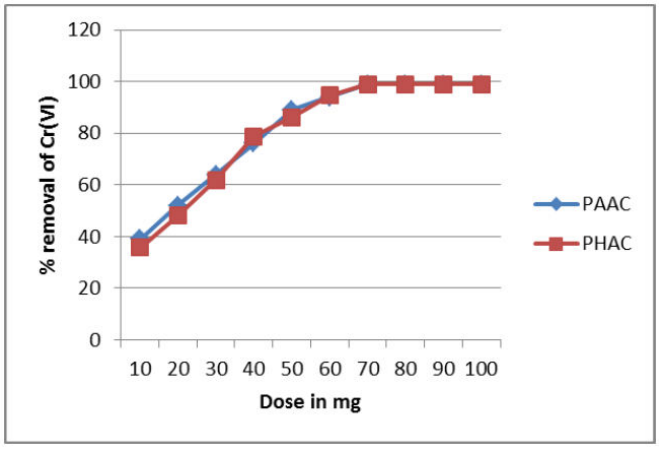

Fig. 1: Effect of dose for Cr (VI) ion onto PAAC and PHAC

3.2. Effect of interaction time

The effect of adsorbate - adsorbent interaction time for the % of elimination of chromium (VI) ion from aqueous solution was studied by taking 5 mg/L, 10 mg/L 15 mg/L and 20 mg/L solutions as initial concentrations for both the adsorbents PAAC and PHAC. The results of the above study at different contact times was shown in Fig.2 (a) & (b). According to results, an increase at contact time led to increase at surface adsorption rate to 70 min and then remains unchanged. Maximum adsorption occurred in the first 70 min. The rapid adsorption at the initial contact time is due to the availability of the positively charged surface of adsorbent.

3.3. Effect of initial concentrations

By increasing of the initial metal ion concentration, the removal efficiency decreases. With the increase in initial

metal ion concentration the active sites required for adsorption of the molecules will be lack [17]. When PAAC was used as adsorbent, the percentage elimination of Cr (VI) ion was found to decrease from 72.00 to 60.50, 73.80 to 62.05, 77.00 to 64.80 and 79.60 to 68.60 at the temperatures 305 K, 315 K, 325 K and 335 K respectively as the initial concentration of Cr (IV) ion increased from 5mg/L to 20mg/L. When PHAC used as adsorbent, the percentage removal adsorbate-Cr (VI) ion was found to decrease from 69.00 to 58.50, 70.80 to 60.05, 73.00 to 62.80 and 76.60 to 66.60 at the temperature 305 K, 315 K, 325 K and 335 K respectively as the initial conc. of Cr (VI) ion increased from 5 mg/L to 20 mg/L, shown in Fig.3 (a) & (b).

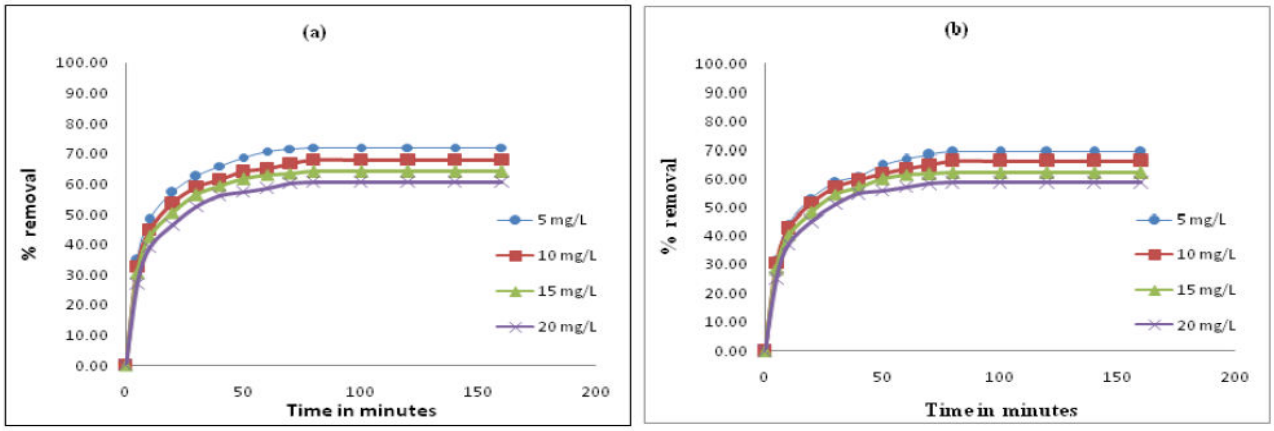

Fig. 2: Effect of contact time for Cr (VI) ion onto (a) PAAC and (b) PHAC

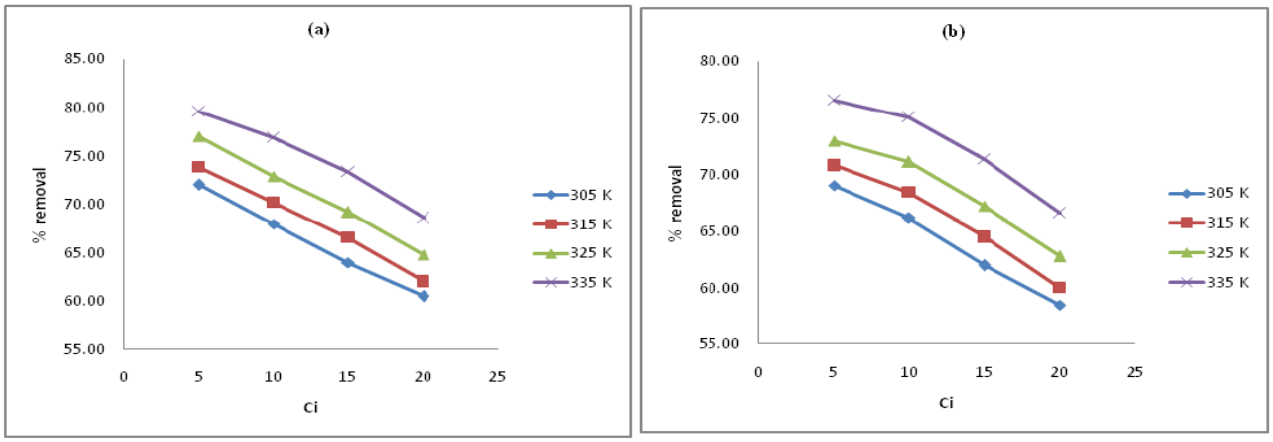

Fig. 3: Ci vs % of Removal – Cr(VI) ions onto (a) PAAC and (b) PHAC

3.4. Effect of temperature

The percentage of removal increased by an increase of temperature of the solution for all studied initial concentrations of the metal ion. The results are given in Table 1. At higher temperature, pores may widen up due to increased shaking. So that more number of solute may enter into the aperture and get adsorbed in the inner part of the aperture surfaces.

3.5. Effect of pH

The pH of the solution plays a important role for determining the quantity of solute adsorbed because the pH of the solution affects the functional groups of the activated carbon and also alters the surface charge of the carbon and governs the speciation of the solute. Here adsorption was studied ranges in between pH 2-11. Fig. 4 shows the effect of initial pH of the metal ion solution on the elimination of Cr (VI) ion, from the results, the optimum pH for removal efficiency of both adsorbent were observed as 2. High removal of Cr (VI) at low pH is probably due to reduction of hexavalent chromium to trivalent chromium ions, which is easier in removal [17] . The favorable of low pH can be attributed to the neutralization of negative charges on the surface of the

adsorption by excess hydrogen ions, thereby facilitating the diffusion of hydrogen chromate ions $(HCrO_4)^-$ and their subsequent adsorption. By increasing pH $(HCrO_4)^-$ species shifts to forms $(CrO_4)^-$ and $(Cr_2O_7)^-$. The decrease in adsorption of Cr (VI) by increasing pH is due to completion between the anions $(CrO_4)^-$ and OH^- [18,19].

Table1: Effect of Temperature vs % removal &Temperature vs q_e results for Cr(VI) ions onto PAAC and PHAC

Initial Concentration C_i (mg/L)	Temperature (K)	PAAC		PHAC	
		%R	Qe	%R	Qe
5	305	72.00	9.00	69.00	8.63
	315	73.80	9.23	70.80	8.85
	325	76.00	9.50	73.00	9.13
	335	79.60	9.95	76.60	9.58
10	305	68.00	17.00	66.20	16.55
	315	70.20	17.55	68.40	17.10
	325	72.90	18.23	71.10	17.78
	335	76.90	19.23	75.10	18.78
15	305	64.00	24.00	62.00	23.25
	315	66.53	24.95	64.53	24.20
	325	69.20	25.95	67.20	25.20
	335	73.33	27.50	71.33	27.75
20	305	60.50	30.25	58.50	29.25
	315	62.05	31.03	60.05	30.03
	325	64.80	32.40	62.80	31.40
	335	68.60	34.30	66.60	33.30

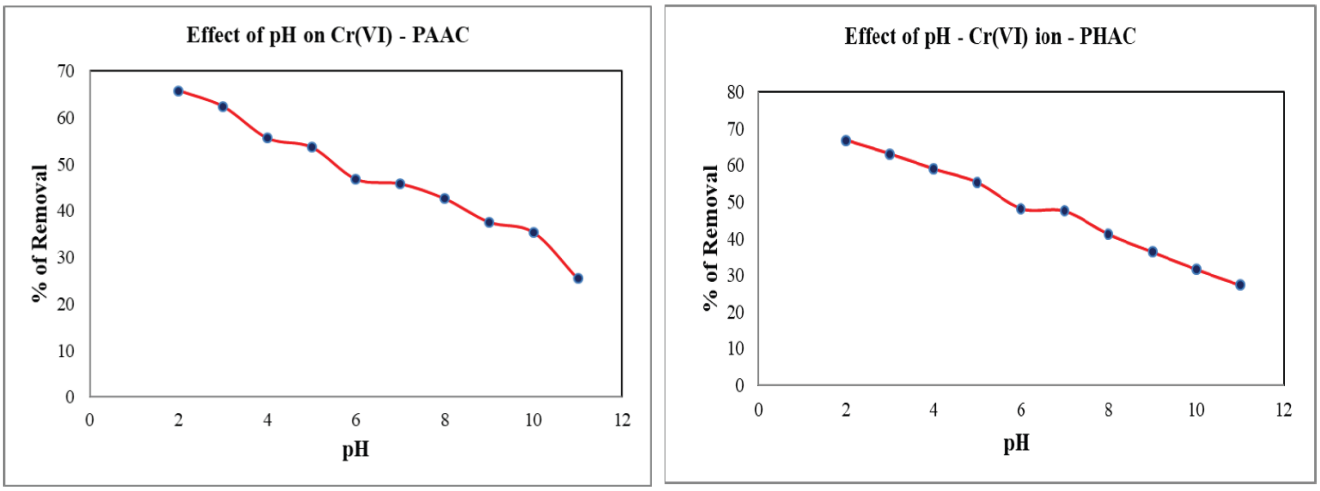

Fig. 4: Effect of pH - Cr(VI) ion on PAAC

3.6. Adsorption isotherms

3.6.1. Langmuir isotherm

The results were attained from Langmuir model for the exclusion of Cr (VI) ion, onto PAAC and PHAC were represented in Table 2. The square of correlation coefficient (R^2) values are ranged from 0.9997 to 0.9974 for the four studied temperatures viz. 305, 315, 325 K and 335 K for the adsorbents PAAC and PHAC. These results show the greatest appropriate of the equilibrium data with Langmuir isotherm. The mono layer adsorption capacity $Q_m$values (mg/g) for adsorption of Cr (VI) ion onto PAAC system ranged from 60.728 to 61.350 and 60.976 to 64.935 for PHAC. PHAC seems to have a higher adsorption capacity than PAAC with respect to the adsorption of Cr (VI) ion for all the studied temperatures. The square

of correlation coefficient (R^2) for Freundlich isotherms are above 0.99 for all the temperatures. It indicates that the experimental data fit well into Langmuir model.

3.6.2. Freundlich Isotherm

The results obtained from Freundlich model for the removal of Cr (VI) ion onto PAAC and PHAC are given in Table 3.

Table 2: Langmuir isotherm results for the adsorption of Cr (VI) onto PAAC and PHAC [pH = 2; Dose =30 mg/ 50 mL; Contact time = 180 min]

Temp. (K)	N	PAAC		PHAC	
		k_f(mg/g)	R^2	k_f(mg/g)	R^2
305	1.4219	8.2196	0.9972	7.2494	0.9972
315	1.4335	8.8632	0.9940	7.8632	0.9940
325	1.4778	9.9123	0.9955	8.9702	0.9955
335	1.4537	12..6421	0.9899	10.2164	0.9899

Table 3: Freundlich Isotherm for Cr(VI) ions onto PAAC and PHAC [pH = 2; Dose = 30 mg/ 50 mL; Contact time = 180 min]

Carbon	Temp (K)	Q_m (mg/g)	b (L/mg)	R_L				R^2
				5 mg/L	10 mg/L	15 mg/L	20 mg/L	
PAAC	305	60.728	0.120	0.6246	0.4541	0.3568	0.2938	0.9974
	315	61.350	0.135	0.5969	0.4541	0.3305	0.2702	0.9997
	325	60.976	0.161	0.5545	0.3836	0.2933	0.2373	0.9987
	335	60.085	0.180	0.5261	0.3569	0.2701	0.2701	0.9984
PHAC	305	61.728	0.120	0.6246	0.4541	0.3568	0.2938	0.9974
	315	61.350	0.135	0.5969	0.4254	0.3305	0.2702	0.9997
	325	60.976	0.161	0.5545	0.3836	0.2933	0.2373	0.9987
	335	64.935	0.180	0.5261	0,3569	0.2701	0.1272	0.9984

3.6.3. Tempkin isotherm

The results obtained from Tempkin model for the removal of Cr (VI) ion, onto PAAC and PHAC were represented in Table 4. The square of correlation coefficient (R^2) values ranged from 0.9974 to 0.9857 for the four studied temperatures viz. 305, 315 325 K and 335 K for the adsorbents PAAC and PHAC with the adsorbate Cr (VI) ion. These results show the best fitting of the equilibrium data with Tempkin isotherm. PAAC and PHAC seems to have a lower value of a_T and b_T with respect to adsorption of Cr (VI) ion for all the studied temperatures. It is an indication of physisorption rather than chemisorption.

3.7. Kinetic study on Cr (VI) ion adsorption

The results obtained from pseudo-first order kinetic model for the removal of Cr (VI) ion onto PAAC and PHAC were represented in Table 5. The linearity of the plots were not so high for PAAC (R^2 = 0.9627 - 0.9830) and for PHAC (R^2 = 0.9987 - 0.9993). The first order rate constant, k_1 (min^{-1}) ranged from 0.0520 to 0.0610 for PAAC and from 0.0175 to 0.0532 for PHAC. The pseudo first order theoretical adsorption capacity (q_e) values, obtained from the intercept of the linear plots, were compared with the experimental adsorption capacity q_e values. The pseudo first order kinetic model suffered from inadequacies when applied to Cr(VI) ion sorption on PAAC and PHAC at varying Cr(VI) ion concentrations. The experimental q_e values differ from the corresponding theoretical values.

The pseudo second order parameters, q_e, h, and k_2, obtained from the pseudo second order plot are presented in Table 5. The initial sorption rate, 'h', increases directly with anincrease of initial Cr (IV) ion concentration at each temperature for PAAC (0.75–2.75 mg/g.min^{-1}) and for PHAC (0.25 – 2.05 mg/g.min^{-1}) while an inverse relationship exists between the overall sorption rate and initial Cr(VI) ion concentration for PAAC (0.0018-0.0200) and for PHAC (0.0018-0.0094). Between the first order and second order, second order kinetic model seems to best describe the above adsorption system as it has R^2 value which was very close to unity. Moreover, the difference between calculated adsorption capacity ($q_e$cal) and experimental adsorption capacity ($q_e$exp) values of second order is little when compared to first order kinetic model for

the both Cr (VI) ion - PAAC and Cr (VI) ion - PHAC systems for each initial concentrations at different temperatures. The Δq_e and SSE % values for both the adsorbents from which it was concluded that the second order kinetic model was more appropriate rather than the first order kinetic model.

In intra particle diffusion model, the r^2-values are found to be close to unity (Table 5), indicating the application of this model. This reveals the presence of intra-particle diffusion process.

Table 4: Tempkin constants for the adsorption of Cr (VI) onto PAAC
[pH = 2; Dose = 30 mg/ 50 mL; Contact time = 180 min]

Temperature (K)	PAAC			PHAC		
	b_T (J/mg)	a_T (L/g)	R^2	b_T (J/mg)	a_T (L/g)	R^2
305	215.2219	1.5074	0.9857	209.2219	1.4074	0.9902
315	221.5436	1.6222	0.9909	211.5436	1.5222	0.9947
325	226.8532	1.8621	0.9921	215.8532	1.7621	0.9957
335	228.6795	2.8649	0.9943	207.6795	1.9649	0.9974

Table 5: Kinetics and Intra particle diffusion results for the adsorption of Cr(VI) ion onto PAAC and PHAC

Carbon	First Order Kinetics-PAAC					
	Concentration (mg/L)	k_1 (min^{-1})	$q_{e(cal)}$ (mg/g)	$q_{e(exp)}$ (mg/g)	R^2	SSE %
	5	0.0567	2.6285	3.60	0.9730	1.06
	10	0.0520	4.8406	6.80	0.9627	
	15	0.0610	7.3519	9.60	0.9830	
	20	0.0564	9.2257	12.10	0.9769	
	Second Order Kinetics					
	Concentration (mg/L)	k_2 (g/mg.min)	$q_{e(cal)}$ (mg/g)	H	R^2	SSE %
PAAC	5	0.0532	3.75	0.75	0.9995	0.15
	10	0.0315	7.03	1.56	0.9989	
	15	0.0254	9.90	2.49	0.9998	
	20	0.0839	12.53	2.75	0.9988	
	Intra Particle Diffusion					
	Concentration (mg/L)	k_p (mg/g.min)			R^2	
	5	0.0653			0.992	
	10	0.8645			0.9804	
	15	0.9860			0.978	
	20	0.9945			0.9476	
	First Order Kinetics – PHAC					
	Concentration (mg/L)	k_1 (min^{-1})	$q_{e(cal)}$ (mg/g)	$q_{e(exp)}$ (mg/g)	R^2	SSE %
	5	0.0532	3.75	0.75	0.9993	0.79
	10	0.0315	7.03	1.56	0.9988	
	15	0.0254	9.90	2.49	0.9988	
	20	0.0175	12.53	2.75	0.9987	
	Second Order Kinetics – PHAC					
	Concentration (mg/L)	k_2 (g/mg.min)	$q_{e(cal)}$ (mg/g)	H	R^2	SSE %
PHAC	5	0.0232	2.75	0.25	0.9999	0.29
	10	0.0315	3.03	1.16	0.9998	
	15	0.0354	4.90	2.09	0.9998	
	20	0.0475	3.53	2.05	0.9997	
	Intra Particle Diffusion –PHAC					
	Concentration (mg/L)	k_p (mg/g.min)			R^2	
	5	0.0553			0.9870	
	10	0.7545			0.9804	
	15	0.8560			0.9716	
	20	0.8845			0.0951	

The thermo dynamical parameters calculated are presented in Table 6 and concerned plots were shown in Fig. 5.

Equilibrium studies showed that the adsorption capacity of both the carbons increased with an increase in temperature from 305 to 335 K. Thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined using Equations 11 to 13. The ΔH° and ΔS° values were obtained from the slope and intercept of Vant Hoff plots drawn between ln K_d and 1/T. The negative values of ΔG° (Table 6) show that the adsorption is highly favourable and spontaneous for all the studied systems. The ΔH° values were within the range of 1 to 93 kJ/mol which indicates the favourability of physisorption. The positive values of ΔH° show the endothermic nature of adsorption and it governs the possibility of physical adsorption [20]. In a word, the results obtained in this study suggest that PAAC and PHAC have the potential to be an economic and efficient adsorbent for Cr (VI) ions removal from water and wastewater resources.

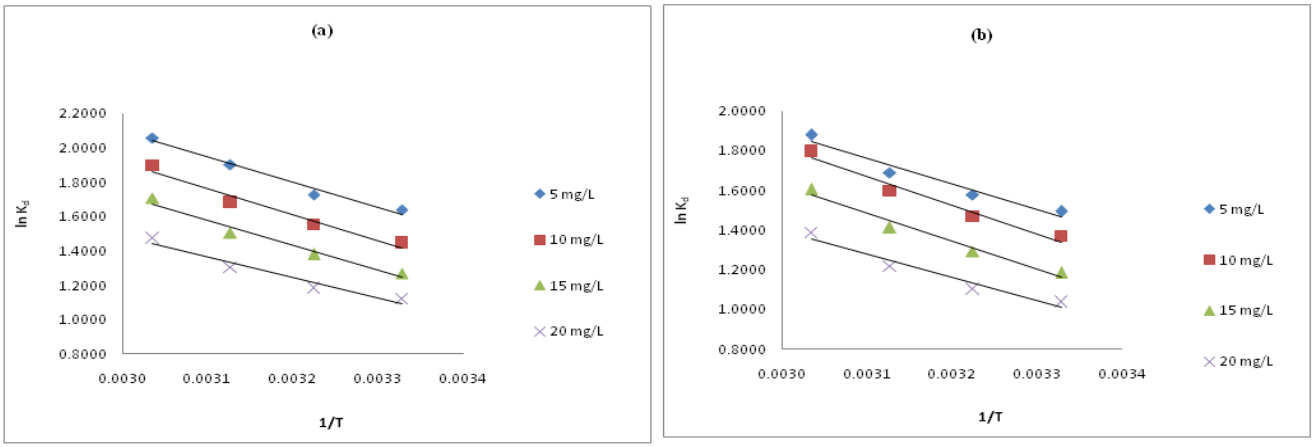

Fig. 5: Van't Hoff plot for Cr (VI) ions onto (a) PAAC and (b) PHAC

Table 6: Thermodynamic Parameters results for Cr(VI) onto PAAC and PHAC

Concentration (mg/L)	Temp (K)	PAAC				PHAC			
		k_d	ΔG° kJ/mol	ΔH° kJ/mol	ΔS° (J/K×mol)	k_d	ΔG° kJ/mol	ΔH° kJ/mol	ΔS° (J/K×mol)
5	305	5.1429	-4.1533	12.055	52.9444	4.4516	-3.7873	10.055	50.9444
	315	5.6336	-4.5282			4.8493	-4.1356		
	325	6.3333	-4.9884			5.4074	-4.5613		
	335	7.8039	-5.7236			6.5470	-5.2343		
10	305	4.2500	-3.6697	12.504	52.7931	3.9172	-3.4629	8.504	48.7931
	315	4.7114	-4.0600			4.3291	-3.8383		
	325	5.3801	-4.5476			4.9204	-4.3062		
	335	6.6580	-5.2812			6.0321	-5.0062		
15	305	3.5556	-3.2172	12.097	50.0453	3.2632	-2.9996	9.097	47.0453
	315	3.9761	-3.6155			3.6391	-3.3835		
	325	4.4835	-4.0609			4.0976	-3.8116		
	335	5.5000	-4.7489			4.9767	-4.4704		
20	305	3.0633	-2.8393	9.9934	41.8469	2.8193	-2.6287	8.9934	38.8469
	315	3.2701	-3.1035			3.0063	-2.8831		
	325	3.6818	-3.5225			3.3763	-3.2884		
	335	4.3694	-4.1079			3.9880	-3.8534		

4. CONCLUSION

The present study indicated that *Delonix regia* pods powder can be used as an effective adsorbent for the removal of Cr (VI). The results showed that increasing the adsorption dose, contact time and temperature increased the removal efficiency and increasing the pH and the initial concentration led to a decrease of removal efficiency. The sorption data is fitted with the Freundlich and Langmuir isotherm models and follows the pseudo-second-order kinetics better than Pseudo-first order kinetics. The values of ΔG° suggests that the spontaneity of adsorption is proportional to temperature. The positive value of ΔS° and ΔH° shows that increased disorderness and the adsorption process is endothermic in nature, respectively. The magnitude of the ΔH° values was below 93 kJ, which suggests that most of the adsorption takes place via physisorption mechanism. This observation was well supported by FT-IR and XRD studies. Utilization of the *Delonix regia* pods activated carbon for the treatment of aqueous solution containing Cr (VI) ions is gaining attention as a simple, effective and economical means of wastewater treatment.

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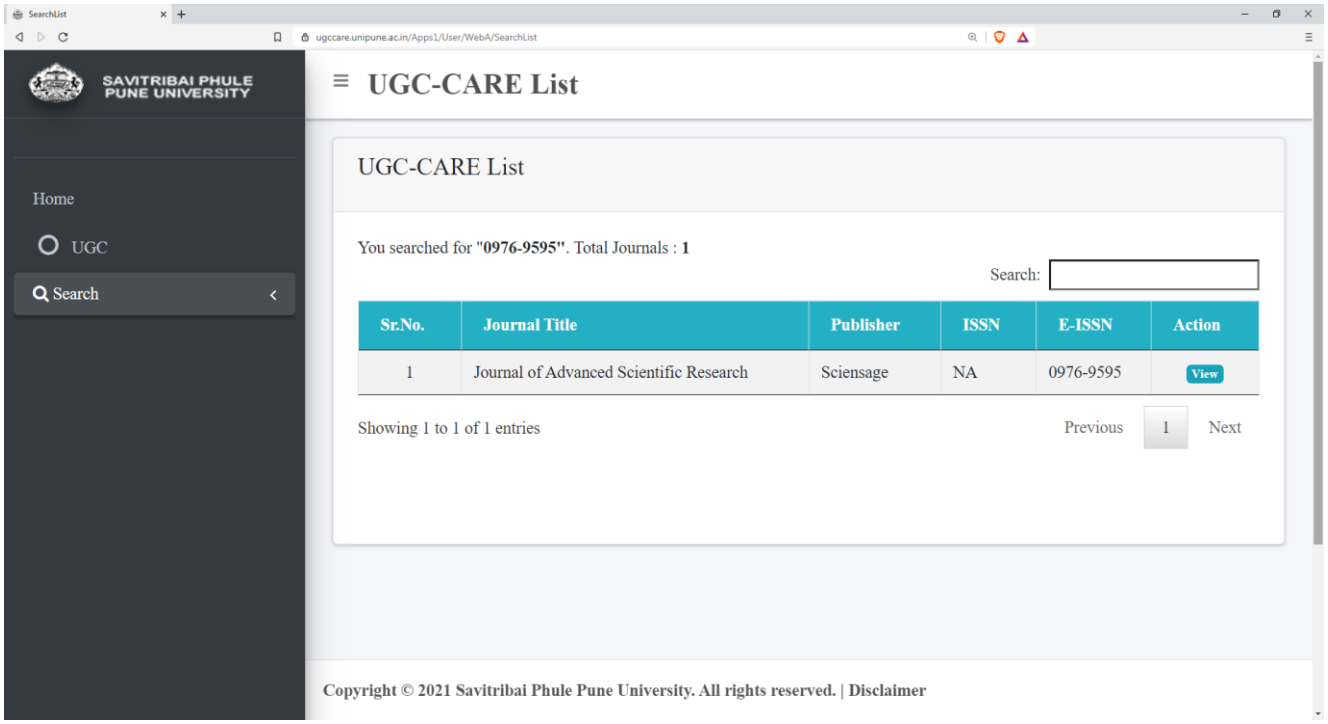
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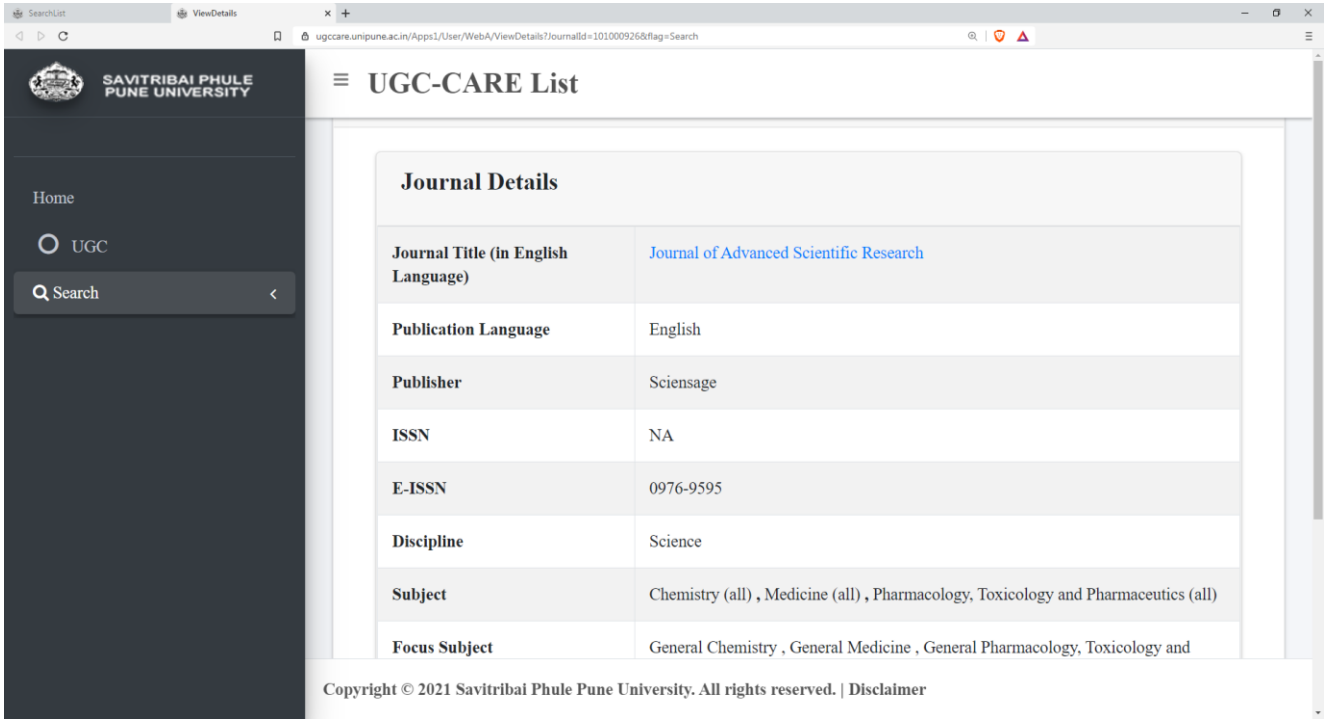
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Research Article

REMOVAL OF NICKEL (II) IONS USING MICROWAVE ASSISTED H_3PO_4 ACTIVATED CARBON PREPARED FROM *DELONIX REGIA* POD

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ABSTRACT

In the present work, Phosphoric acid activated *Delonix Regia* pod carbon was used as an adsorbent for the adsorption of Nickel (II) ions from aqueous solutions. Batch method was used to carry out all the adsorption experiments. 10-25 mg/L adsorbate solution (10 mg/L, 15 mg/L, 20 mg/L & 25 mg/L) and 30 mg of adsorbent were preferred and were predetermined. The adsorption was favoured with maximum adsorption at pH 5 and the pH of the solution was adjusted using dil. HCl and dil. NaOH. The percentage of removal was increased and decreased with increase of adsorbent dose and increase in initial concentration, respectively. Experimental data were fitted with linear forms of selected Kinetic and Isotherm results were discussed in detail.

Keywords: Adsorption, Nickel (II) ions, Kinetics, Isotherm.

1. INTRODUCTION

Water contamination is becoming a great environmental threat to the present as well as future generation. Alteration of the quality of water also causes serious problems like diseases and deaths, most of deaths are due to contaminated drinking water [1]. Waste water from various industries such as pigments, paints, glass manufacturing, metal plating, battery production and mining operation processes contain contaminants such as heavy metals Pb, Cd, Cr, Ni, Zn, Cu and Fe [2]. These heavy metals in waste material are not biodegradable, which lead to life-threatening organisms in lakes and streams that lead to many health problems such as abnormal growth of plants & animals, cancer, kidney failure, oral soreness and metabolic acidosis in stomach of the rodent [3]. The purification process to be followed depends upon the impurities in the water. The adsorption technique, based on the transmission of pollutant pollution to the solid phase, is known as one of the efficient and public sewage treatment methods. Expenditure efficiency, availability and adsorptive properties are key factors in removing organic compounds from waste products, using non-toxic and green adsorbent with huge need for large surface and reactive surface atom [4]. Activated carbon is produced by heating the organic waste to granules of carbon. Animal waste and agricultural waste are the common sources. The most commonly used agents are phosphoric acid, hydrochloric acid, sulfuric acid, alkalis like KOH and NaOH, zinc chloride and alkaline metallic compounds [5]. Recently, microwave energy has been widely used in research and industrial processes. The microwave irradiation technique has the following advantages rather than conventional heating techniques [7], i) Interior heating, ii) selection of heating, iii) Extensive heating rates, iv) Good control of heating process, v) Small equipment size, vi) Reduced wastage production, vii) No direct contact between heating source and heating materials. In the present study, an attempt has been made to prepare (flame tree) pods by microwave irradiation [8]. The above mentioned plant belongs to royal Poinciana or flame boyant which is a member of bean woody seed pods purely a waste material.

2. MATERIAL AND METHODS

2.1. Preparation of Adsorbents

About 20 g of the powdered pods was mixed with 75 mL of H_3PO_4 solution of desired concentration (10, 15 and 20 %). The slurry was kept at room temperature for 24 hours, to ensure the access of the H_3PO_4 to the *Delonix Regia* pods. Then the slurry was subjected to microwave

heating of pre-determined power (850 watts) for predetermined duration (12 minutes). Carbon obtained from the above process was washed with 0.5 M HCl followed with hot distilled water and cold distilled water until the pH of the washings reaches to 7. Then the carbon was filtered and dried at 423 K and kept in desiccator for further studies. The prepared carbon was designated as Phosphoric Acid Activated Carbon (PAAC) [9, 10].

2.2. Preparation of adsorbates solution

The metal ion chosen for the adsorption studies in the present work is Ni (II) ions. Stock solutions of 1000 mg/L were prepared by dissolving required amount of metal salt in one litre of distilled water. The weights of the respective salts taken are listed in table 1.

Table 1: Weight of the salts taken for the preparation of stock solutions

Metal ion	Metal salt	Weight (g) dissolved in one litre
Ni (II)	$Ni(NH_4)_2(SO_4)_2.6H_2O$	6.720 g

2.3. Batch equilibration method

The effect of functions such as adsorbent dose, solution pH and initial concentration of adsorbate and contact time was investigated by batch technique. A 250 ml iodine flask, 50 ml and a pre-determined concentration of the dye solution were transferred into the container. Then the content was rotated in a mechanical shaker for a prearranged duration of 180 min. The concentration of the centrifuge was measured after proper dilution using the Systronics Dual Beam UV-Visible Spectrometer: 2202. The effect of pH was calculated via bringing the preferred pH of the solutions by adding 0.1 N HCl / 0.1N NaOH solution. The kinetics investigations were performed with the working pH 7 and for contact times 5, 10, 20, 40, 60, 80, 100, 120, 140, 160 and 180 minutes [11].

3. RESULTS AND DISCUSSION

3.1. Effect of adsorbent dosage

The adsorption of Ni (II) ions onto PAAC was studied by varying the dose of the adsorbent from 10 mg/50 mL to 100 mg/50 mL by taking 50 mg/L of all the adsorbates.The percentage of removal of adsorbate from aqueous solution increased with an increase of carbon dose in all the cases, shown in Fig. 1. This is due to the increased carbon surface area and the availability of more adsorption sites [12]. Based on these results, the remaining parts of the experiments were carried out with the adsorbent dose of 40 mg/50 mL of adsorbate solution.

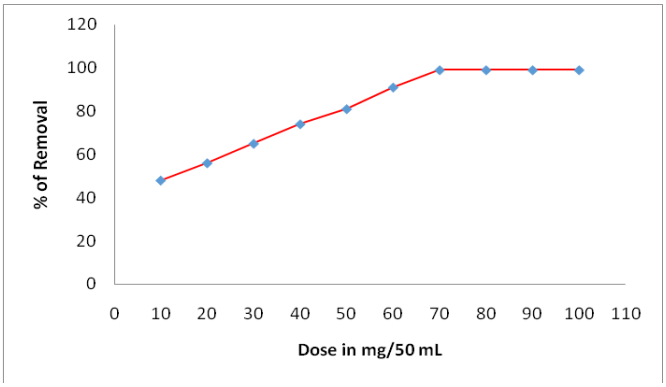

Fig: 1: Effect of dose for Ni(II) ion – PAAC

3.2. Effect of contact time

Fig. 2 inferred that the effect of adsorbate-adsorbent contact time for the % of removal of Nickel (II) ion from aqueous solution was studied by taking 10 mg/L 15 mg/L, 20 mg/L and 25 mg/L solutions as initial concentrations for PAAC. The adsorption process was characterized by the rapid push of adsorbate in the beginning stages. Once the equilibrium form was achieved at all times, the contact time increases and the rate of adsorption percentage was decreased when constantly changed [13].

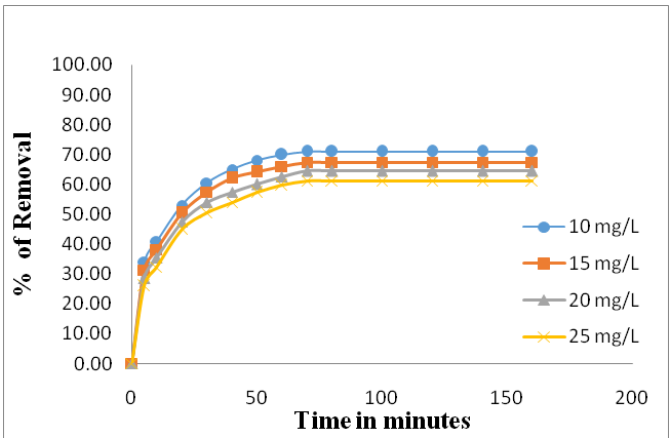

Fig.2: Effect of contact time- Ni(II) ions – PAAC

3.3. Effect of pH

The pH of the solution plays an important role for determining the quantity of solute adsorbed because it

affects the functional groups of the activated carbon and also alters the surface charge of the carbon and governs the speciation of the solute. Here adsorption was studied ranges in between pH 2-10.

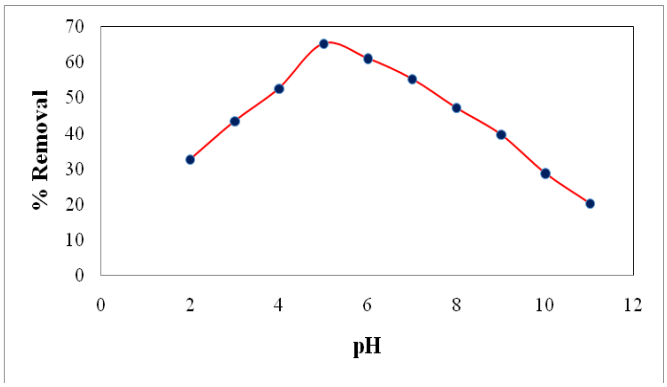

Fig. 3: Effect of pH-Ni (II) ion-PAAC

In Ni (II) metal ion, the highest metal ion removal efficiency was attained at pH 5 and is shown in fig. 3. Ni (II) ion generated negative charged metal ions when dissolved in water.

When the pH is lower than pH_{zpc}, the charge on the surface of the adsorbent is positive. At very low pH, the positive charge accumulates on the surface of the adsorbent and facilitates more adsorption of metal ions. Moreover at low pH, the concentration of OH^- ions was very meagre [14].

3.4. Effect of temperature

Fig. 4 showed that the percentage of removal increased with an increase of temperature of the solution for all studied initial concentrations of the metal ion. At higher temperature, pores may widen up due to increased vibration so that more number of solute may enter into the pore and get adsorbed in the inner part of the pore surfaces [15].

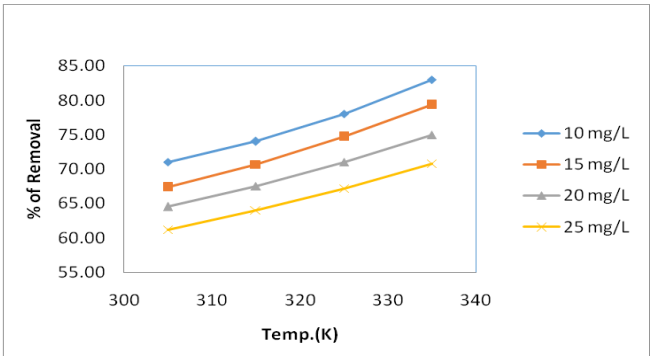

Fig. 4: Temp. vs % of Removal for Ni(II) ions – PAAC

3.5. Adsorption Kinetics

The adsorption kinetics shows the evolution of the adsorption capacity through time and it is necessary to identify the types of adsorption mechanism in a given system. Plots of different kinetic models applied are given in the Fig. 5 and the kinetic parameters calculated are given in the Table 3. Among the first order and second order, second order kinetic model seems to best describe the above adsorption system as its R^2 values were very close to unity. Moreover, difference between qe (cal) and qe (exp) values of second order is small when compared to first order kinetic model. Statistically it is tested with the tool Sum of error squares (SSE%) [16]. The Δqe and SSE % values are given in the Table 3, from which it was concluded that second order kinetic model was more appropriate rather than first order kinetic model.

Table 2: Data processing Tools

S. No.	Parameters		Formulae
1.	**Kinetic Models & SSE %**	Pseudo First order kinetics (Legergren equation)	$\log (q_e-q_t) = \log q_e - k_1/2.303 \times t$
		Pseudo Second order kinetics (Ho equation)	$t/q_t=1/k_2.q_e^2 +1/q_e\, t$
		The initial adsorption rate	$h = k_2 q_e^2$
		Sumoferror squares	$SSE\ (\%)= \sqrt{\sum[(q_e)_{exp}-(q_e)_{cal}]^2/ N}$
2.	**Isotherms**	Langmuir	$C_e/Q_e = 1/Q_0 b + C_e/Q_0$
		Separation factor	$R_L = 1 / (1+ b\, C_0)$
		Freundlich	$\log Q_e = \log K_f + 1/n \log C_e$
		Tempkin	$q_e = B_1 \ln K_T + B_1 \ln C_e$
		Dubinin – Raduskevich,	$\ln q_e = \ln q_D - B\varepsilon^2$
		Polanyi potential	$\varepsilon = RT \ln (1+1/C_e)$
		Mean free energy of adsorption	$E = 1/ (2B)^{1/2}$

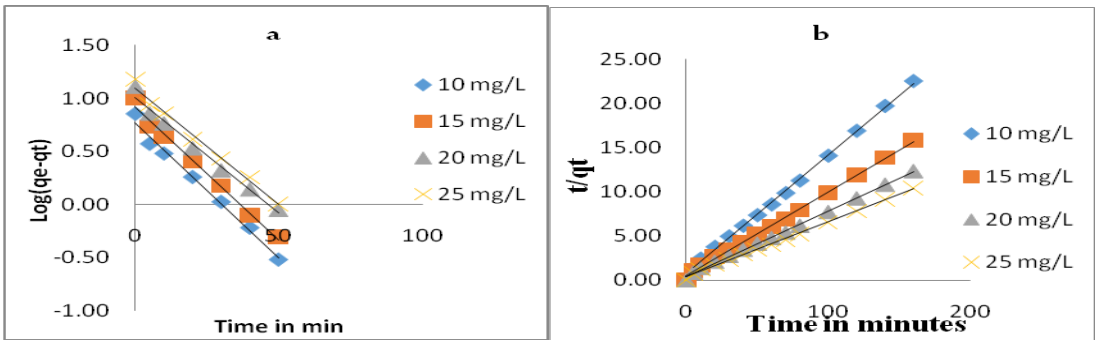

Fig. 5: (a) Lagergren plot for Ni (II) ions onto PAAC, (b) Ho plot for Ni(II) ions onto PAAC

Table: 3 Kinetic parameters for Ni (II) ions onto PAAC

Ci mg/L	Rate constants k_1 (10^{-2}) (min^{-1})	Rate constants k_2 (10^{-3}) (gmg^{-1} min^{-1})	$q_{e(cal)}$ mg/g First Order	$q_{e(cal)}$ mg/g Second order	$q_{e(exp)}$ mg/g First order	$q_{e(exp)}$ mg/g Second Order	Δq_e First order	Δq_e Second Order	R^2 First order	R^2 Second order	(SSE %) First order	(SSE %) Second Order
10	0.0587	0.0223	5.86	7.46	7.10	7.10	1.24	0.36	0.9891	0.9989		
15	0.0578	0.0192	8.30	10.50	10.10	10.10	1.80	0.40	0.9902	0.9982	**1.08**	**0.27**
20	0.0504	0.0130	10.27	13.48	12.90	12.90	2.63	0.58	0.9835	0.9979		
25	0.0509	0.0103	12.62	16.05	15.30	15.30	2.68	0.75	0.9871	0.9975		

3.6. Adsorption Isotherm Studies:

The existence of equilibrium between the liquid and solid phase is well described by adsorption isotherms. Equilibrium data collected at different temperatures were fitted in Langmuir, Freundlich, Tempkin and Dubinin-Raduskevich adsorption isotherm models [17]. These isotherms are depicted in Fig. 6. The R^2 values of these isotherm plots reveal that Langmuir isotherm well describes the present system that is the possibility of monolayer adsorption. R^2 value of Dubinin-Raduskevich isotherm is very low. In Dubinin-Raduskevich isotherm, the very low value of the constant 'B' related to the mean free energy of adsorption per mole of the adsorbate and the adsorption is physical in nature. Results of various isotherms are presented in Table 4.

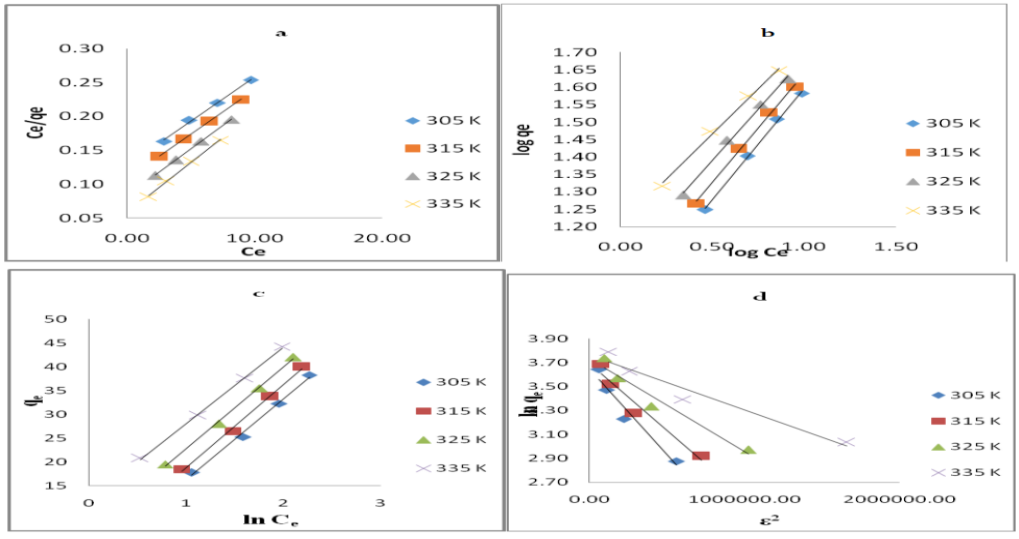

Fig. 6: (a) Langmuir Isotherm - Ni(II) ions – PAAC, (b) Freundlich Isotherm - Ni(II) ions - PAAC, (c) Temkin Isotherm - Ni(II) ions onto - PAAC , (d) D-R Isotherm - Ni(II) ions - PAAC

Table: 4 Results of various isotherms plots for the adsorption of Ni (II) ions onto PAAC

Isotherms	Temp	Parameters and their results			
	(K)	Q_0(mg/g)	B	R_L	R^2
Langmuir	305	74.336	0.103	0.4926	0.9975
	315	75.330	0.122	0.4500	0.9995
	325	76.993	0.165	0.3778	0.9997
	335	77.516	0.103	0.3886	0.9998
		n	k_f(mg/g^{-1})		R^2
Freundlich	305	1.6006	9.0448		0.9983
	315	1.6008	10.3252		0.9969
	325	1.7091	12.5141		0.9954
	335	1.9231	16.0583		0.9947
		B_1(J/mg)	K_T(L/g)		R^2
Tempkin	305	234.1647	0.9942		305
	315	231.2912	0.9936		315
	325	236.5447	0.9951		325
	335	253.9147	0.9936		335
		q_D(mg/g)	E (kJ/mol)		R^2
DubininRaduskevich	305	468.9875	420.90		0.9227
	315	486.3214	496.70		0.9191
	325	503.1864	494.60		0.9131
	335	523.7563	491.20		0.9202

3.7. Analysis of Isotherm

3.7.1. Langmuir isotherm

In the present study Q_0value ranges from 74.336 to 77.516 as the temperature increases the monolayer adsorption capacity also found to increase. These kinds of results were obtained in various similar studies [18]. The separation factor R_L values in between 0 to 1 indicate the favourable adsorption. R^2values of isotherm ranged between "0.9975to 0.9998".

3.7.2. Frendlich isotherm

The values of n were between 1 and 10 which indicates cooperative adsorption**.** The R^2 values were close to unity which reached to good fitting into frendlich isotherm [19].

3.7.3. Temkin Isotherm

$\mathbf{B}_1$-Temkin constant is related to the heat of adsorption. This $\mathbf{b}_1$ value increased from 234.1647 to 253.9147 as the temperature of adsorption increased. The temkin parameter $\mathbf{a}_T$ value gives an idea about nature of adsorption. In our present study, the $\mathbf{K}_T$ values ranged from 2.7554 to 6.1274 which indicate the adsorption is physical in nature. The R^2 value was low compared to langmuir and frendlich isotherm [20].

3.7.4. Dubinin-Raduskevich

The activation energy E value ranges from 420.90 to 491.20 and adsorption capacity $\mathbf{q}_D$ value from 468.9875 to 523.7563 indicates the physisorption. The R^2 value was very low when compared to other three isotherms. In general the fitting data in isotherm equation were in the following order Langmuir >Frendlich>Temkin> Dubinin-Raduskevich [21].

4. SUMMARY AND CONCLUSION

Adsorption of Ni(II) ions using the *Delonix Regia* Pods were optimized at pH of 5. Temperature of 325K initial metal concentration of 25 mg/L and the equilibrium time for the adsorption of Ni (II) ion on PAAC in 70 minutes. From the results of kinetic studies, it was concluded that the adsorption process followed pseudo second order kinetics. Equilibrium data is fitted in the linear form of Langmuir equation for the temperatures respectively.

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