Influence of Various Physio-Chemical Parameters on the Adsorption of Copper Ions using Activated Charcoal

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Submitted by

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Dedication

DEDICATED TO MY LOVING PARENTS

ESPECIALLY

MY FATHER

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List of Acronyms

SEM (Scanning Electron Microscopy)

X-RD (X-Ray Diffraction)

FTIR (Fourier Transform Infrared Spectroscopy)

TGA (Thermo Gravimetric Analysis)

UV/Visible (Ultra Violet/Visible spectroscopy)

Abstract

The work presented in this thesis was carried out in three parts. The first part deals with the characterization of a commercial activated charcoal. This includes the instrumental and chemical methods for the determination of moisture content, elemental analysis, total volatile product, bulk density, particle size analysis, surface area measurement, FTIR study, XRD, surface functional groups and point of zero charge (PZC). The results reveal that the activated charcoal is semi-crystalline having C 69.34 %, S 0.431 %, H 0.982 %, N 0.195 %, surface area 1073 m^2/g, total volatile product 27.66 %, ash content 0.183 %, moisture content 5.10 %, pH(PZC) 6.93 and average particle size 36.20 μm. The surface of the activated charcoal contains 7.5 mmoles/g and 1.5 mmoles/g of acidic and basic functional groups respectively. FTIR study also indicates the presence of acidic groups (i.e. phenol –OH and lactones).

The second part deals with the adsorption studies of copper ions on activated charcoal from solutions. The adsorption experiments were performed by batch techniques to study the effects of stirring speed, shaking time, pH, concentration of copper ions and temperature etc. The results obtained reveal that the adsorption of copper ions is dependent on shaking time, pH, copper ions concentration, and temperature. The optimum shaking time and pH are found to be 120 minutes and 7 respectively. Low copper ions concentration and low temperature favors the adsorption process. Adsorption dynamics models such as intra-particle diffusion model, pseudo-first order kinetic model and pseudo-second order kinetic model were applied to the adsorption data to elucidate the adsorption process and its mechanism. Results show that pseudo-second order model best describes the adsorption process and the overall rate of adsorption process appears to be controlled by more than one step, namely the external mass transfer (boundary layer diffusion) and intra-particle diffusion mechanism. Rate constant values for intra-particle diffusion and boundary layer thickness were calculated as 1.06×10^{-4} ($g/g.min^{1/2}$) and 7.93×10^{-3}(g/g) respectively. Equilibrium adsorption data was tested for the Freundlich, Langmuir, Dubinin-Radushkevich (D-R) and Temkin equations. The data indicates that the Freundlich isotherm equation fits better with high value of correlation of coefficient

(R^2 = 0.994) and the adsorption of copper ions on activated charcoal is Physi-sorption process as evident from the adsorption energy values as E_a= 2.425kJ.mol$^{-1.}$ The adsorption of copper ions decreased with the increase of temperature i.e., low temperature favors the adsorption process. Calculated values of thermodynamic quantities such as ΔH, ΔS and ΔG points towards the exothermic (ΔH -6.3868 kJ.mol^{-1}) and spontaneous (negative ΔG and Δ S values) adsorption process. Desorption studies reveals that ~98% of the adsorbed copper ions on activated charcoal is recovered with 0.1 M HCl solutions.

In the third parts, the developed method was applied to remove the copper ions from actual waste solution generated in a local copper electro-plating industry for copper ions recovery. About 97% of the copper ions are recovered from waste effluents. Results reveal that the locally available commercial activated charcoal could be used to clean up the waste solution for ions before discharge to water stream.

Keywords: Copper ions, Adsorption, Desorption, Activated Charcoal, copper electroplating waste solutions

Chapter 1 Introduction

1.1 Introduction

The increasing use of technology in industry has resulted in continuous increase of discharge of polluted industrial waste into the hydrosphere. Great efforts have been made for minimizing the discharge of these harmful pollutants and therefore preventing humans, animals, and plants from their hazardous affects. The heavy metal ions are reported as priority pollutants and are considered toxic to human and living creatures even at low concentration. Health problems in plants, human beings and animals are due to the accumulation of these heavy metals as these are not biodegradable. [1].

Copper is greatly used metal in industries such as mining, dyeing and painting, smelting, electroplating, brass manufacture, petroleum refining and Cu-based agrichemicals. The industries produce massive waste water and sludge containing Cu^{2+} ions with varied concentrations. Copper may also be found as a contaminant in food and nuts. Copper is essential to life and health but like all other heavy metals is also potentially toxic as well. Copper toxicity is much ignored and excessive intake of Cu^{2+} ions has detrimental effects on human health like fatigue, premenstrual syndrome, anorexia, depression, anxiety, migraine headaches, allergies, gastrointestinal bleeding, convulsions and significant DNA damages [2-3]. Therefore it is necessary to treat the industrial waste solutions to reduce the concentration of Cu^{2+} ions to the level that satisfy environmental regulation prior to its secure disposal into hydrosphere. The maximum Cu^{2+} ions concentration in drinking water is less than 3000 $\mu g/dm^3$[4-5]. The commonly used methods for the recovery of metals ions are chemical precipitation and filtration, electrochemical treatment, reverse osmosis, solvent extraction, ion exchange, and evaporation etc. These techniques have their own advantages and disadvantages. The disadvantages associated are high cost, incomplete metal recovery, low selectivity, high energy and reagent consumption and generation of toxic slurries that are difficult to eliminate [6].

In recent years, the adsorption has become a widely used technique to remove the toxic metals ions from the aqueous solutions and/or wastewater due to its simplicity, potential to regeneration, sludge-free operation and production of high quality treated effluents. The adsorption process is quite simple, selective, high enrichment factor, high recovery, rapid phase separation, low cost and very low levels of metals can be removed from aqueous solution/wastewater. Better designed adsorption processes have high efficiency and result in high quality effluents after treatment which can be recycled or disposed off safely.

The most common adsorbent used are materials containing organic carbon such as active carbon, lignite, charcoal, wood bark and other inorganic materials. The adsorbent properties of activated carbon/charcoal are well established and have been extensively used for the adsorption of organics and in-organics from wastewater/solutions due its high purity, large surface area, micro-porous structure, high adsorption capacity and high degree of surface reactivity [7-8]. Adsorption of heavy metals by activated carbon/charcoal might be attributed to the presence of metal binding acidic and basic functional groups on the surfaces of carbonaceous substances. The acidic functional groups on the surfaces include lactones, phenolic hydroxyl group, carboxyl group, quinine type carbonyl group, carboxylic acid anhydride and cyclic peroxide etc. The basic surface group has chromene (benzpyran) [8]. The perusal of literature indicates that the adsorption of Cu^{2+} ions on activated carbon/charcoal both virgin as well as modified have been investigated and is reviewed in **Chapter 2**.

The aims of the present study were to:

- Investigate the ability of commercial activated charcoal to remove the Cu^{2+} ions from waste water.
- Characterize the activated charcoal for different parameters such as moisture content, bulk density, elemental analysis, FTIR studies, surface functional groups estimation, point of zero charge (PZC) measurement etc.
- Study the influence of various physio-chemical parameters such as shaking speed, shaking time, pH, Cu^{2+} ion concentration and temperature on the uptake of Cu^{2+} ions from solutions.

- Determine the kinetic equation best describing the data to elucidate the mechanism of Cu^{2+} uptake from solutions.
- Determine the adsorption equation that best describes the equilibrium uptake for design purpose.
- Calculate the thermodynamic parameters (ΔH, ΔS and ΔG).
- Desorption of adsorbed Cu^{2+} ions from activated charcoal surface.
- Recovery of Cu^{2+} ions from waste effluent generated in local electro-plating industry (A case study).

Chapter 2 Theory and literature review

2.1 Adsorption

It is a process in which two immiscible phases (solid/liquid or solid/gas) come into contact and it is generally observed that at the interface the concentration of one phase is higher than its concentration in bulk. The tendency of accumulation of molecules at the surface of solid is termed as adsorption. Conversely, a concentration decrease is sometimes observed and is called negative adsorption. The phase, on the surface of which a substance from the other phase accumulates is termed as adsorbent and the adsorbed substance is called adsorbate. Sometimes the accumulated substance diffuses into the adsorbent body resulting in a process known as absorption. The term sorption is encompassing both adsorption and absorption.

2.1.1 Types of adsorption

The adsorption at the interface is largely as a result of binding force between ions, molecules and atoms of the adsorbate and the adsorbent surface. According to the forces involved, there are two main type of adsorption i.e., physical and chemical.

Physical adsorption is generally due to the weak intermolecular forces which include Van der Waals forces, comprised of London dispersion force and classical electrostatic force. In this process, the electron distributions of adsorbate molecules and solid surface molecule undergo some distortions in mutual proximity; however the electrons maintain their association with the original nuclei.

Chemical adsorption is also known as chemisorption. In chemisorptions sharing and transferring of electrons occurs between the adsorbate and adsorbent species and as result chemical form of adsorbate is generally changed. The chemical bond formed in chemisorption all the features of chemical bond is stronger than the physical forces (Van der Waals forces etc.)

2.1.2 Adsorption at solid-liquid interface (adsorption from solution):

The adsorption of a solute at solid-liquid interface is a consequence of free energy of the surface. When a solution is placed in contact with the solid, the solute

molecules accumulate on the surface of the solid and the free (surface) energy of the solid is decreased. Those solutes which decrease surface energy of the adsorbent will tend to accumulate greater on the adsorbent surface and there proportion is more on interface than in bulk solution. Surface active substances are those substances which tend to reduce the surface energy of the adsorbent. But, if the solute tends to increase the surface tension, its accumulation on the solid surface will be less. This behavior is termed as negative adsorption.

Electrolytes may be adsorbed basically in two different ways. In the first, only one of the two ions is preferably adsorbed on the solid surface. This mode of adsorption is known as ionic adsorption. In the second mode, either both kinds of ions are adsorbed on the surface to some extent or non-dissociated molecule is adsorbed. This mode is termed as molecular adsorption. This kind of adsorption is usually occurred in non-electrolytes.

2.1.3 Adsorption of metal ions from solutions

In the last few years a large number of environmental related issues have been reported mainly due to the development in the industrial area. Use of heavy metals, chemicals, artificial and natural materials in the synthetic industry at a huge scale and followed by incomplete treatment of effluents has led to the production of heavy metal ions into the environment. The toxic effects of heavy metals on living beings are well documented. Efforts are going worldwide for the removal of heavy metals ions from effluents and to bring their level to the permissible limit before their discharge into the environment. Different countries of the world have made very strict rules for the safe discharge of the effluents.

For the removal of heavy metal ions from the industrial waste effluents the most economical and efficient technique among all other techniques is adsorption. Uptakes of metals ions by solid from solution are influenced by many experimental conditions and are briefly described below:

2.1.3.1 Effect of shaking speed

The shaking speed i.e., revolution per minute (rpm) is an important physical parameter which may affect the uptake of metals ions from solutions. An optimum shaking speed is recommended for the adsorption process. The agitation of the solution with adsorbent at high speed may weaken the physical bond between metal ions and the adsorbent surface results in the lowering of the uptake of metals ions from solution. Similarly, the low speed also lowers the recovery of metals ions from solutions due to the agglomeration of adsorbent particles.

2.1.3.2 Effect of surface area/amount of adsorbent

The surface area and amount of the adsorbent exerts clear effect on the metal ions adsorption. As long as other factors remained constant, an increase in the surface area and/or amounts of the adsorbent, usually results in enhanced metal ions adsorption due to increase in the number of surface sites available for adsorption process.

2.1.3.3 Effect of shaking time

The effect of shaking time on metal ions adsorption on solids provides important information about the rate of the adsorption process and controls of the residual time. It also provides information about adsorption process mechanism. Temperature, pH, concentration and the age of the adsorbent affects the time dependence studies of the metal ions from solutions. The age of the solution also influence the adsorption process.

2.1.3.4 Effect of pH of solution

The pH is one of the most important parameter which influences the adsorption of metal ions from solution. It may effects:

i. the state of metal ions in solution and the adsorbability of the different form of state of metal ions generally differ,
ii. the surface electric charge of the adsorbent, which is important for electrostatic adsorption of ions or molecules etc,
iii. HO_3^+ and OH^- ions can compete with metal ions and the extent of competition depends upon the activity/concentration of hydronium or hydroxyl ions,

iv. The properties and composition of adsorbent surface are influenced by the acidity or basicity of the solution.

v. Anions of acid and cations of bases used for pH adjustment can compete with metal ion of interest,

These effects on adsorption are often combined and therefore the pH dependences of the adsorption process may be rather complex.

2.1.3.5 Effect of temperature

The temperature can influence both the kinetics and the final adsorption values. The rate of adsorption process may be influenced by the solution temperature. The rate of the adsorption process may increase or decrease or remain constant with increasing solution temperature depending upon the nature of the adsorbent. The energy of activation and the thermodynamic quantities i.e., ΔH, ΔS and ΔG can be evaluated for an adsorption process data. If the rate of the adsorption process increases with increasing temperature, the process is called endothermic. If the rate of adsorption process decreases with rise in temperature, the process is termed as exothermic. When no effect was observed on rate of adsorption process with increase in temperature, that process is known as athermic process.

2.1.3.6 Effect of metal ions concentration

The metal ions concentration in solution strongly influences the adsorption of metal ions from solutions. Usually, the adsorption of metal ions is quite high in low concentration as compared to that in high concentration. Moreover, the initial adsorption of metal ions is more since number of sites available for adsorption process are more; and as the surface of the adsorbent becomes progressively saturated, the adsorbed amount becomes lower and lower and reaches to a constant adsorption corresponding to the adsorption capacity of the adsorbent for a given adsorbate. There are several ways of presenting and analyzing the concentration dependence of adsorption process i.e., % adsorption, distribution coefficient, % recovery and adsorption isotherm; the best is the adsorption isotherm where the adsorbed amount is plotted as a function of equilibrium concentration of the metals ions in solution. From the shapes of the adsorption isotherms, the information about the adsorption process could be deduced. Several isotherm and mechanism equations

are available in the literature to conform the adsorption process and few of them most widely used are discussed in preceding section (section 2.1.4.).

2.1.4 Adsorption mechanism

In order to understand the mechanism of adsorption numerous empirical models are reported in literature. These models relate the amount adsorbed with the most important variables such as temperature and concentration. Curves representing the adsorption as a function of concentration at constant temperature are termed as adsorption isotherms, which are useful for describing the adsorption capacity to facilitate evaluation of the feasibility for selection of the most appropriate adsorbent for a specific application. Moreover, the adsorption isotherms play a crucial role in predicting the modeling procedures for analysis and design of the adsorption systems. Voice et.al [9] has noted that any particular model may fit experimental data under one set of conditions, but may fail entirely under another. No single model has been found to be generally applicable universally. According to Veith et.al. [10], the adsorption isotherms are purely empirical in nature and cannot be used to distinguish the adsorption mechanism. A detailed description of different types of isotherms and their use is given by Travis et.al. [11]. The Freundlich, Langmuir, Dubinin-Radushkevich (D-R) and Temkin isotherms are being extensively used in describing the adsorption data.

2.1.4.1 The Freundlich isotherm equation

The empirical equation was first suggested by Boedeeker in 1859 and latter supplemented by Freundlich [12] to account for simple adsorption isotherm. It is an empirical equation without chemical significance and based on assumption that adsorption occurs on heterogeneous surfaces having sites of varied affinities. It assumes that stronger binding sites are first to be occupied and that the binding strength decreases with the increasing degree of sites occupation. The linear form of the Freundlich isotherm equation is

$$\log X = \log K_f + 1/n \log C \qquad (1)$$

where X is the amount of the adsorbate adsorbed per gram of solid (g/g) and, C is the equilibrium concentration of an adsorbate in solution (g/L), K_f is a parameter of the Freundlich isotherm related to quantity of the adsorption per gram of the solid at

equilibrium (g/g), n is a dimensionless constant related to explain the extent of adsorption and the adsorption intensity between the adsorbate concentration and the adsorbent.

There are more useful ways of interpreting the value of 1/n. In most of the cases, 1/n <1, indicates less rapid increase in the amount of adsorbed species than the concentration. In case where 1/n = 1, it indicates the equivalence of distribution law and the adsorption equation. Amount adsorbed (X) equals K_f in the case where value of 1/n approaches to zero and shows the monolayer formation without any further adsorption. Although the Freundlich equation is generally regarded as empirical, there have been some attempts to derive some information about surface heterogeneity from empirical Freundlich constant, if number of adsorption sites were known [13].

2.1.4.2 The Langmuir isotherm equation

In 1918, Langmuir [14] derived an equation for the adsorption of gases on solid surface on the basis of kinetic theory. Nevertheless, it has been adapted to the adsorption from solution on solids. He believed that adsorption was a chemical process and that the adsorbed layer was unimolecular and surface contains a finite number of adsorption sites of uniform activities with no transmigration of the adsorbate in the plane of the surfaces. Langmuir theory implies within limits to both chemical and physical adsorption. The linear form of the equation is:

$$C/X = 1/K_L X_m + C/X_m \qquad (2)$$

Where C and X have already been defined, X_m is monolayer capacity and K_L is the Langmuir constant related to the free adsorption energy.

The limitations and drawbacks in this theory are:

a. This theory is not applicable in case of multilayer formation because it is based on the assumption of monolayer formation.
b. It assumes the solid surfaces to be uniform which is not always the case.
c. It does not account for the lateral interaction among adsorbed molecules adsorbed on the adsorbent surface.

In spite of the fact that the theory has some limitations, still it finds application in large number of cases.

2.1.4.3 The Dubinin-Radushkevich (D-R) isotherm equation

Dubinin-Radushkevich (D-R) [15] isotherm is more general than the Langmuir isotherm, and assumes that there is a very small sub-region of adsorption surface that is uniform in structure and energetically homogeneous. The isotherm is based on the postulate that a fixed adsorption space is available closed to adsorbent surface where adsorption takes place and this model assumes the heterogeneity of adsorption energies within this adsorption space. The Polanyi adsorption potential, ε is the work required to remove a molecule or ion to infinity from its location in adsorption space independent of temperature. The D-R equation was formulated from the Polanyi theory especially for application to micro porous materials. However, it can be applied to experimental data for low concentration of the adsorbate and good correlations can be achieved. In addition to this, the D-R equation is used to predict the nature of the adsorption processes as physical or chemical by calculating the mean adsorption energy. The linear form of D-R equation is:

$$\ln X = \ln X_m - B\varepsilon^2 \qquad (3)$$

where $\varepsilon = RT \ln(1+1/C)$, B is the constant related to the adsorption energy, R is the gas constant and T is temperature in Kelvin. The quantities X, X_m and C have their previously defined meanings. From the value of B, the adsorption energy (E_a) is calculated using the following equation:

$$E_a = 1/\sqrt{(2B)} \qquad (4)$$

In order to know the type of adsorption occurring, the E_a value is very important. The value of E_a between 8-16 kJ/mol is an indication that the process is most likely an ion-exchange. But if the E_a value is <8 kJ/mol, then the adsorption is physical in nature [16].

2.1.4.4 The Temkin isotherm equation [17]

The Temkin isotherm is an empirical relationship, which often gives a more satisfactory model of experimental data. Its linear form can be expressed as:

$$X = (RT/b_T)\ln A_T + (RT/b_T) \ln C \qquad (5)$$

where X, C and R have their usual meanings, T is the temperature in Kelvin, A_T and b_T is the Temkin constants related to adsorption capacity and intensity of adsorption respectively.

2.2 Activated charcoal (adsorbent)

Activated charcoal is porous carbonaceous materials prepared by carbonizing and activating the organic substances mainly of biological origin. Carbonaceous materials are classified on the basis of their amorphous, crystalline and microcrystalline structure and general classification is given in **Table 2.1**.

The application of the charcoal as adsorbent to remove coloring materials is one of the oldest technique. Later, it was used to purify the raw sugar solutions. The knowledge of activation of charcoal accelerates their use as an efficient adsorbent. During the process of activation, the spaces between the elementary crystallites become cleared of various non-organized carbonaceous compounds (tarry substances) resulting in voids or pores.

Table 2.1: Classification of Carbonaceous Materials [18]

Coal	Black coal, lignite, anthracite
Chars	Unactivated: Prepared by pyrolysis of the raw materials i.e., coke, wood charcoal, animal charcoal, bone charcoal etc. (slightly porous)
	Activated charcoal: Prepared by carbonizing and activating of organic substances of biological origin such as wood, coal, coconut shell, animal blood, synthetic resin or polymer (highly porous)
Carbon Black	Prepared by burning organic substances of high carbon content (gaseous hydrocarbon, oils etc). It includes lamp, channel, acetylene and other blacks. (either porous or non-porous)
Pure Carbon (high purity and no developed porosity)	Crystalline like diamond, graphite, lustrous carbon.
	Non-crystalline like glassy carbon, vitreous carbon

The porous structure of the activated charcoal, in general is tri-disperse i.e., it contains all three kinds of pores; micro-pores, meso-pores and macro-pores. Information about the size of the pores is based on X-ray scattering, optical and electron microscopy. Additional information about the shapes and sizes of relatively varieties of pores can be obtained from optical and scanning electron microscopic study. The finest pores are the micro-pores which do not exceed 20 ^{o}A according to the IUPAC classification of pores [19]. The volume of the micro-pores usually lies in the range of 0.05 - 0.60cm^3/g and their specific surface area approximately amounts at least of 90% of the total surface area. The pores having radii between 20-500°A are called meso-pores and their specific surface area does not exceed 50 m^2/g. Activated charcoal of this type is usually used for de-coloring solutions by removing impurities with large molecules or particles with colloidal dispersity. Usually these impurities are not accessible to micro porous structured activated charcoal and their adsorption occurs only on their surfaces. The meso-pores serve as a passage for the adsorbate molecule to the micro-pores. Pores with effective radii larger than 500 ^{o}A are classified as macro-pores and the specific surface area of the macro-pores lie in the range of 1 - 4 m^2/g. These macro-pores do not play an appreciable role in the adsorption process, but act as a place for catalyst deposition when activated charcoal is used as catalyst support.

The adsorptive properties of the activated charcoal are not only determined by its porous structure but also by its chemical composition. Disturbances in the elementary and microstructure, by the presence of partially burn-off graphitic layers, changes the arrangement of electronic clouds in the carbon skeleton. As a result of this, valence or un-paired electrons appears which influences the adsorptive properties of the activated charcoal. The presence of hetero-atoms and surface complexes also affects the adsorption, catalytic and electronic properties of charcoals [20]. Of the gaseous substances chemisorbed on charcoal, oxygen is of special importance and the interaction of this gas with the charcoal surfaces depends upon the temperature of process. Reaction of gaseous oxygen with charcoal surface below 100^{0}C produce oxygen complexes which on hydration form hydroxyl or other groups which act as ion-exchanger. The surface oxides formed at 300-500^{0}C have acidic or basic character. The respective quantities of acidic and basic complexes can be determined by their neutralization by alkali or acid. Surface oxygen complexes on carbonaceous

surfaces are also formed by the action of water vapors, dinitrogen monoxide, nitrogen dioxide, carbon dioxide and others. The surface functional groups formed by oxygen on charcoal surfaces are classified as acidic or basic. The acidic group on the surfaces includes lactones, phenolic hydroxyl group, carboxylic group, carboxylic acid anhydride and cyclic peroxide group. The basic surface oxide is chromene (benzopyran). The presence of oxygen containing functional group and their ratio depends on the method of carbonization and activation.

In general, the presence of chemisorbed oxygen on the surface of charcoal has no effect on the physical adsorption of non-polar adsorbate, but these complexes tremendously affect the adsorption of polar adsorbate. The adsorption of water, methanol, ammonia, carbon dioxide, and sulphur dioxide is greatly increased due to oxygen surface complexes and so they are unreliable for surface area measurement. However, these may be useful for characterizing the polar sites. In addition to the oxygen, sulphur and nitrogen, chlorine is also present in minor quantities. The influence of sulphur on the adsorptive properties of activated charcoal is similar to that of surface complexes of oxygen.

Another factor which affects the adsorptive properties of activated charcoal, in the adsorption of electrolytes and non-electrolytes, is ash content. The ash content and its composition vary with the kind of activated charcoal and depend upon the degree of carbonization and activation of the starting materials. The ash is inorganic in nature and contains traces of potassium, aluminum, silicon, sodium, iron, magnesium, calcium, boron, copper, silver etc. The ash causes defect in the elementary structure of the charcoal to which oxygen is chemisorbed at defects and leads to increased adsorption of polar adsorbate. Moreover, the ash soluble in aqueous solutions, affects the adsorption of the adsorbate by co-adsorption. Ash can be extracted with water, acetic acid, hydrochloric or hydrofluoric acid, but treatment with these changes the porosity of the activated charcoal.

2.3 Adsorption of Cu^{+2} ions (Literature review)

The importance of recovery of Cu^{2+} ions from waste solutions have been described in Chapter 1. Activated charcoals have been extensively used for its recovery from solution based on adsorption process. Numbers of articles are available in the literature studying the adsorption of Cu^{2+} ions from different point of views using virgin, as well as modified commercial and synthesized activated carbon/charcoal. The main focus on these studies is on the development of a cheap, economical, efficient adsorbent for Cu^{2+} ions recovery to clean up the waste effluent generated in industries before discharging it into natural water streams. The literature review for Cu^{2+} ions adsorption on activated charcoal/carbon carried out by researchers from the year 2001 to 2013 is presented in **Table 2.2** for reference please.

Table 2.2: Literature review table

S#	Adsorbent	Metal ion/s.	Study	Kinetic study	Isotherm models	Thermodynamics study	Desorption study	Ref.
1	Pecan shell activated carbon	Copper ions	• Synthesis (activation by phosphoric acid) • characterization (surface functional group, surface area and pore size distribution, elemental phosphorous analysis, EDXRF study) • Adsorption study (pH and adsorption mechanism).	--	--	--	--	[21]
2	HNO_3 and NaOH modified Pitch-based activated carbon fibers	Copper, and Nickel ions	• Modification of active carbon fibers. • Characterization (surface area, surface functional groups, FTIR, PZC). • Adsorption (pH)	--	--	--	--	[22]
3	Granular and activated carbon fiber	Copper ions	• Oxidation of adsorbent with nitric acid and gaseous oxygen. • Surface functionality and acidity. • Adsorption as function of pH and its mechanism	--	--	--	--	[23]
4	Pecan shell activated carbon	Binary ions. Cu- Na Cu-Co Cu-Cr Mn-Na Mn-Cu Mn-Co	• Adsorption as a function of binary ions concentration. • Binary adsorption model developed.	--	Multi-component Freundlich model	--	--	[24]

5	Citric acid modified granular activated carbon	Copper ions	• Modification with 1M Citric acid. • Surface properties with SEM and surface area, surface functional groups. • Kinetic study at pH 4.9 (buffer solution used)	Intra-particle diffusion model	Langmuir and Freundlich	--	--	[25]
6	Tannic acid immobilized active carbon.	Cu, Cd, Zn, Mn and Fe ions	• Activation with $CaCl_2$, then treatment with tannic acid solution • Characterization BET surface area, • Adsorption studies as a function of pH, contact time, adsorbent dose, metal ions concentration, competitive adsorption. • Recovery of metal ions.	-	Langmuir and Freundlich (data better fitted to Langmuir equation)	--	Desorption with 0.1 M HCl in two steps; 1st step recovery of tannic acid (5 %) and in 2nd step recovery of Cu ions (90-98 %)	[26]
7	Activated carbon from Ceiba pentandra hulls	Copper and cadmium ions	• Synthesis (Steam activation) • Characterization (XRD, FT-IR, PZC) • Adsorption studies as a function of pH, contact time, metal ions concentration, adsorbent dose.	Pseudo-first order, and Pseudo second-order	Langmuir and Freundlich	--	Desorption with 0.05-0.3M HCl with maximum desorption 0f 88% with 0.2M HCl.	[27]
8	Acetic acid modified Coconut shell activated carbons	Copper ions	• Modification of activated carbon with sodium acetate and its regeneration by NaOH • Characterization (pH, AAS, BET Surface area) • Effect of modification on adsorption capacity of activated carbon.	--	--	--	--	[28]

9	Low cost activated carbon derived fromTerminaliaCatappa Linn shell treated with sulhuric acid.	Copper ions	• Synthesis (activation by sulphuric acid) • Characterization (PZC, surface functional groups by titration) • Adsorption as a function of metal ion concentration, contact time, pH, adsorbent dosage, competitive adsorption and temperature.	Intraparticle diffusion model	Langmuir and Freundlich (data better fitted to Langmuir equation)	Thermodynamic studies performed in the temperature range of 30-60^{0}C which shows adsorption as endothermic and physical in nature.	Desorption with HCl showing a maximum desorption of 85%.	[29]
10	Hazelnut shell activated carbon	Copper ions	• Synthesis (hot air activation with sulphuric acid) • Characterization (BET surface area, SEM,FT-IR) • Adsorption studies as a function of pH, adsorbent dosage and temperature.	Pseudo first order, Pseudo second-order, Elovich and Diffusion kinetic models	Langmuir, Freundlich and Temkin (data better fitted to Langmuir equation)	Temperature range: 20-50^{0}C Nature of adsorption: Endothermic and Physisorption	Desorption with HCl in four cycles with desorption of 74-79%.	[30]
11	Activated carbon derived from polyacrylonitrile fiber	Copper and Lead ions	• Synthesis (by steam activation) • Characterization (BET surface area, TGA, elemental composition, surface functional groups by titration) • Adsorption studies as function of pH	--	--	--	Desorption with de-ionized water showing desorption of 30%.	[31]
12	Activated Charcoal	Copper ions	• Adsorption studies as function of adsorbent dosage, contact time, pH.	Pseudo-first order, Intraparticle diffusion model, Natrajan-Khalaf, Bhattacharya and Venkobachar	Langmuir and Freundlich	Temperature range: 20-40^{0}C Nature of adsorption: Endothermic and irreversible	--	[3]

13	Activated Carbon from Rice Husk	Copper ions	• Synthesis (activation by $ZnCl_2$) • Characterization (surface morphology by SEM, TGA, elemental analysis and BET surface area) • Adsorption as a function of metal ion concentration, contact time and adsorbent dosage.	Pseudo-first order, and Pseudo second-order	Langmuir and Freundlich (data better fitted to Langmuir equation)	--	--	[32]
14	Activated carbon, carbon nanotubes and carbon-encapsulated magnetic nanoparticles	Copper ions	• Carbon materials treated with 8M HNO_3 • Surface morphology by SEM • Adsorption kinetics as function of pH	Pseudo-first order, Pseudo second-order and Intraparticle diffusion model	--	--	--	[33]
15	Activated carbon from Tunisian date stones	Copper ions	• Synthesis (activation by H_3PO_4) • Characterization (BET surface area, PZC, XRD, SEM and bulk density) • Adsorption as a function of metal ion concentration, contact time and pH.	Pseudo-first order, Pseudo second-order and Intraparticle diffusion model	Langmuir, Freundlich, and Dubinin-Radushkevich (data better fitted to Langmuir and D –R equation)	Temperature range: 10-40^{0}C Nature of adsorption: Endothermic and spontaneous	--	[34]
16	Activated carbon prepared from different agricultural materials	Copper ions	• Synthesis (activation by H_3PO_4) • Characterization (surface area (Sear's method), pH, moisture content by ASTM methods) • Adsorption as a function of adsorbent dose, particle size of adsorbent, pH, metal ion concentration, contact time)	--	Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (data better fitted to Langmuir and Temkin)	--	--	[1]

17	Activated carbon	Copper ions	• Adsorption study by continuous flow method • Adsorption as a function of time	--	Langmuir, Freundlich and Temkin (data better fitted to Langmuir equation)	--	--	[35]
18	Activated carbon from bamboo	Lead, Chromium, Copper and Cadmium	• Synthesis (activation by heating in inert atmosphere) • Characterization (BET surface area, pH and SEM) • Adsorption as a function of pH, soaking time and adsorbent dosage)	--	--	--	--	[36]
19	Activated carbon	Copper ions	• Activated carbon treated by $CuCl_2$, Na_2SO_3 and HCl. • Characterization (BET surface area, X-ray photoelectron spectroscopy (XPS), and XRD). • Adsorption as a function of contact time.	Pseudo second-order	Langmuir and Freundlich (data better fitted to Langmuir equation)	--	--	[37]
20	Activated carbon from orange peel	Lead, Ferrous, Copper and Zinc	• Synthesis (activation by $ZnCl_2$) • Characterization(surface morphology by SEM) • Adsorption as a function contact time, adsorbent dosage, pH	--	--	--		[38]

Chapter 3 Experimental

3.1 Materials used

A commercial activated charcoal was used as an adsorbent without any pre-treatment. Copper nitrate (Product No. 12831) supplied by M/s Sigma-Aldrich was used to prepare stock solutions of copper ions in doubly distilled water. Phenolphthalein (Product No.FE04950100) and Methyl Orange (Product No. AN0073) supplied by M/s Scharlu were used as indicator in titration. NaOH (Product No.B0783098 219) and $NaHCO_3$ (Product No.K20953123 442) supplied by M/s Merck, Na_2CO_3 supplied my M/s Panreac (Product No.141648), and HCl (Product No. K21842472 518) supplied by M/s BDH were used in functional groups determination. Buffer tablets supplied by M/s Lovibond were used to prepare buffer solutions.

3.2 Equipment/Instrument used

FT-IR (Varian 640-IR), UV/Visible Spectrophotometer (Thermo Scientific, Evolution 300 BB), Surface area analyzer (Sorptometer KELVIN 1042, COSTECH Instruments Inc.), Mechanical shaker (LSB, 30S, LAB.Tech), pH meter (Denver Instrument, Model 250), Elemental analyzer (Vario EL II, Germany), XRD Stoepowder diffractometer, Coulter Multisizer - 2E (U.K).

3.3 Characterization of activated charcoal

3.3.1 Moisture content

Known amount of activated charcoal was taken in a crucible and kept it in an oven at 100 ^{o}C till constant weight is reached. The percentage of moisture content was calculated in usual way.

$$\% \text{ Moisture content} = W_i - W_f / 100 \qquad (6)$$

W_i and W_f are the initial and final weight of the activated charcoal respectively. The calculated value of moisture content is given in **Table 3.1**.

3.3.2 Elemental analysis

The elemental analysis was performed by using CHNS&O Elemental Analyzer (Vario EL-II) manufactured by Analysensysteme GmbH, Germany at 1150 ^{o}C and results are given in **Table 3.1**.

3.3.3 Total volatile product

Known amount of activated charcoal was taken in a crucible and kept in a furnace at 1000 ^{o}C for one hour. After that the crucible was weighed again and the % of volatile product and ash content were calculated in usual way. The results are given in **Table 3.1**.

3.3.4 Bulk density [34]

Bulk density of activated charcoal was determined by placing the activated charcoal in a graduated cylinder and tapped several times to obtain a constant volume and then weighed. The bulk density was calculated as the ratio of weight of sample to its volume. The determined value of bulk density of the activated charcoal is given in **Table 3.1**.

3.3.5 Particle size measurement

The particle size distribution of the activated charcoal was measured by Coulter Multisizer - 2E (U.K.) and is given in **Figure 3.1**. The average diameter of the particles of the activated charcoal was determined from the figure and is given in **Table 3.1.**

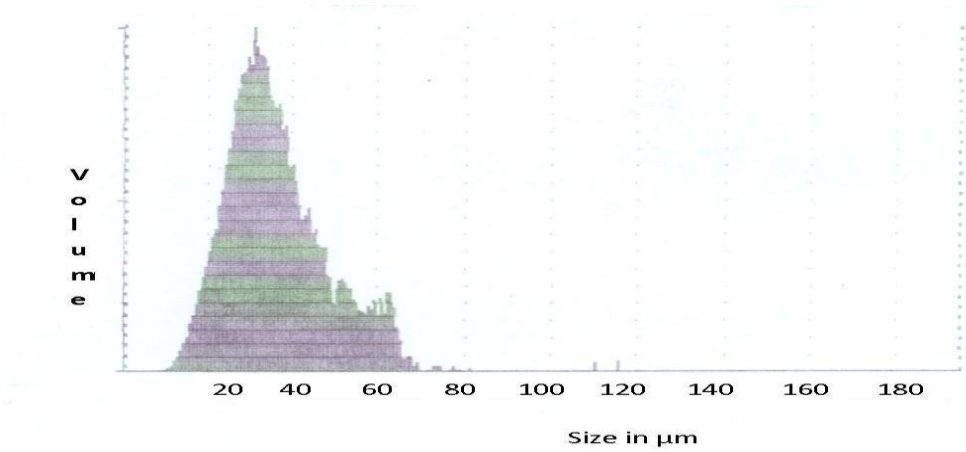

Figure 3.1: Particle size distribution of activated charcoal.

3.3.6 X-ray Diffraction study

X-ray diffraction study was carried to determine whether the charcoal used is amorphous in nature or crystalline. STOE Powder Diffractometer was used for this purpose. XRD spectrum of activated charcoal is shown in **Figure 3.2**. A result of the analysis is shown in **Table 3.1.**

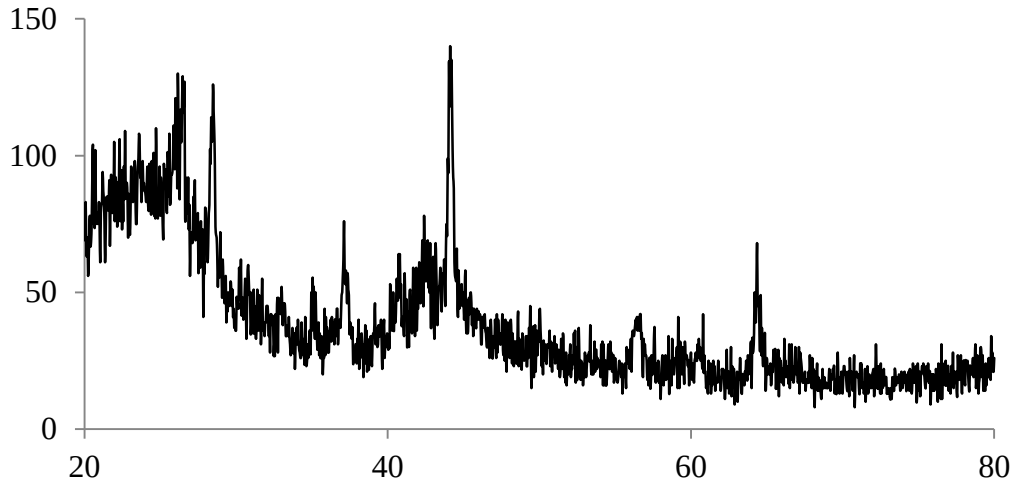

Figure 3.2: XRD spectrum of activated charcoal

3.3.7 Surface area measurement

Surface area of the activated charcoal was determined by using gas adsorption surface area analyzer; Sorptometer KELVIN 1042 manufactured by M/s COSTECH Instruments using the software Kelvin 1042 V3.12. Volumes of the nitrogen gas adsorbed on activated charcoal at 77K were measured at different relative pressures (P/P^o) using nitrogen as adsorptive gas and helium as a carrier gas and are given below:

Relative pressure (P/P^o)	Volume of N_2gas adsorbed (cm^3/g)
0.0496	47.4890
0.1000	269.932
0.1505	288.661
0.2011	302.789

B.E.T. equation was used to calculate the surface area of the activated charcoal and the determined value is given in **Table 3.1**. The sample was degassed at 150^oC under nitrogen for 185 minutes prior to the measurements. The detailed of the nitrogen adsorption method can be seen elsewhere [39].

3.3.8 FT-IR study

FT-IR spectrum of the activated charcoal was recorded on Varian 640 FT-IR system in transmission mode using Varian Resolution Pro Software. Sample was prepared in the form of KBr pellet and spectrum was recorded in the range of 400-4000 cm^{-1}. The spectrum is shown in **Figure 3.3** and the IR band observed in the spectrum as finger prints of functional groups were assigned with the help of reference literature.

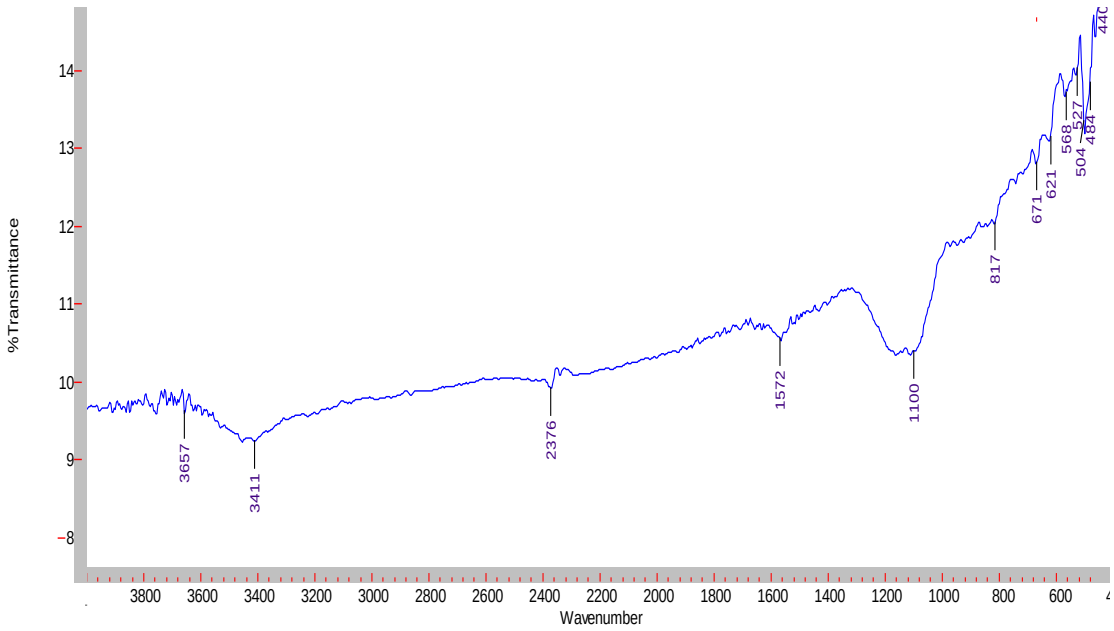

Figure 3.3: FT-IR spectrum of activated charcoal.

3.3.9 Estimation of surface functional groups

The functional groups covering the activated charcoal surface were determined by titration method described by Boehm [40]. Activated charcoal 0.15 g was added in different bottles containing 15 ml solutions of 0.1 M HCl, 0.1M $NaHCO_3$, 0.1M NaOH and 0.05M Na_2CO_3. The solutions were then shaken at 100 rpm for 48 hours at room temperature. After 48 hours, the bottles were then kept for 2 hours for settling of charcoal particles. The clear solutions were then filtered and the filtrate was back titrated against 0.1M NaOH and 0.1M HCl for the estimation basic and acidic groups respectively. Phenolphthalein and methyl orange were used as indicators to observe the neutralization points. Phenolphthalein is used for titration of strong base against strong acid and methyl orange is used for weak base against strong acid and the results are given below:

Medium	Initial Molarity	Final Molarity	Difference in Molarity
$NaHCO_3$	0.10 M	0.102 M	-
Na_2CO_3	0.05 M	0.0425 M	0.0075 M
NaOH	0.10 M	0.025 M	0.075 M
HCl	0.10 M	0.085 M	0.015 M

The amounts of functional groups were determined by translating the difference in solution concentration neutralized by the acid/base functional group per gram of activated charcoal. The calculated amount of acid functional group is 7.5mmoles/g (6.75 mmoles/g phenolic groups; 0.75 mmoles/g lactonic groups) and the basic groups are 1.5mmoles/g.

3.3.10 Determination of point of zero charge (PZC)

The point of zero charge (PZC) of activated carbon was determined by pH drift method [41]. The solution pH was adjusted by 0.1M NaOH or 0.1M HCl from 1 to 12. Activated carbon 0.15 g was placed in 50 mL of solution. The mixture was then placed in a mechanical shaker for 1 hour and then final pH was determined by pH meter. The point of zero charge was determined from the plot of initial pH of solution against final pH of solution as shown in **Figure 3.4.**

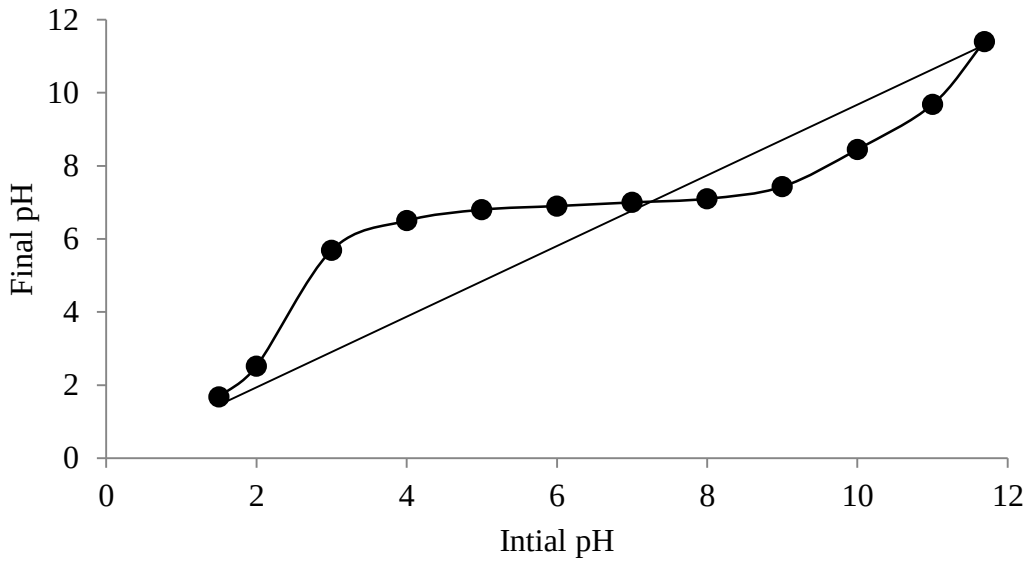

Figure 3.4: PZC plot for the activated charcoal.

Table 3.1: Determined values of various parameters of activated charcoal

Bulk Density	0.300 g/cm^3
Surface Area	1073 m^2/g (BET-nitrogen adsorption)
Average Particle Size	36.20 μm
Carbon Contents	69.34 %
Sulphur Contents	0.431 %
Hydrogen	0.982 %
Nitrogen	0.195 %
Volatile Product	27.66 %
Ash content	0.183 %
XRD	Semi crystalline
Surface functional groups	Acidic = 7.5 mmoles/g ; Basic = 1.5 mmoles/g
Moisture	5.10 %
pH $_{PZC}$	6.93

3.4 Adsorption studies

Adsorption experiments were performed by using a batch technique at room temperature 27 ± 1 ^{o}C, where otherwise specified. For this, 10 ml of copper solution of known concentration was shaken with known amount of activated charcoal at a fixed speed in 250 ml reagent glass bottle for a given time period. The solution was then filtered through Whatman filter paper No. 40 (Circular). The residue was retained for desorption studies. The concentration of copper ions in the filtrate was determined by UV-Visible spectrometer. Due to the adsorption of copper ions on the filter paper the first 2-3 ml portion of the filtrate was discarded, and was also corrected for losses due to adsorption on the walls of the glass bottles by running blank experiments (i.e., without activated charcoal added).

Percentage adsorption and amount adsorbed (g/g) were computed in usual ways:

$$\% \text{ Adsorption} = 100\ (C_o - C)/\ C_o \quad (7)$$

$$\text{Amount adsorbed (g/g)} = (C_o - C)\ V/M \quad (8)$$

where C_o and C are the initial and final copper ions concentrations in solution (μg/mL), V is the volume of the copper ion solution (ml) taken and M is the amount of the activated charcoal powder (g) used.

3.5 Desorption study

Desorption study was carried out with 0.1 M HCl solution. The activated charcoal, which was removed from filtration in section 3.4, was transferred into 250 ml stopper reagent bottle. To this 10 ml of 0.1 M HCl solution was added and shaken for 120 minutes at room temperature (27 ± 1 ^{o}C) using a mechanical shaker. The solution was then filtered and copper ions concentration in the filtrate was measured by UV-Visible spectrometer.

3.6 Recovery of Cu^{+2} ions from electro-plating industrial waste effluents- A case study

Sample of waste solution was collected from the effluent discharge point of a local electro-plating industry and filtered through Whatman No. 40 filter paper. Initial concentration of copper ions in the filtrate was determined using UV-Visible spectrometer and adsorption studies were carried out at optimized conditions for copper ions.

Chapter 4 Results and discussion

4.1 Activated charcoal's Characterization data

Various characteristic parameters of the activated charcoal such as moisture content, carbon content, ash content, surface area, particle size distribution, PZC and presence of surface functional groups etc are important in order to understand the properties that may affect the removal of the metals ions from solutions. The determined parameters of the activated charcoals, mentioned in **Table 3.1**, highlighted that the activated charcoal has bulk density (0.300 g/cm^3), moisture content (5.10 %), ash content (0.183 %), average particle size (36.20 μm). The elemental composition analysis of activated charcoal reveal contents of C (69.34 %), S (0.431, H (0.982) and N (0.195). The magnitude of these values is in line with the reported values for activated carbon derived from polyacrylonitrile fiber [42]. The activated charcoal used has semi-crystalline structure **Figure 3.2**.

The **specific surface area** of the activated charcoal was determined by applying the B.E.T. equation to the physical adsorption data of nitrogen at 77K, mentioned in section 3.3.7. Most convenient form of BET equation for application to experimental data is [43]:

$$1/V\ [(P^o/P)-1] = 1/V_mC + C-1/V_mC\ P/P^o \qquad (9)$$

where the symbols have their usual meanings. BET equation normally gives a linear relationship in the range of 0.05-0.30 relative pressure (P/P^o). Above this range of relative pressure, the experimental points deviate from linearity. Herman and Emmet [44] highlighted that BET equation gives reasonable values of surface area below $P/P^o > 0.30$, represent a condition in which the very high energy sites have been occupied and the extensive multilayer adsorption of N_2 has not yet commenced. The deviation from linearity reflects unusual surface properties of the sorbent. B.E.T. plot of nitrogen adsorption on activated charcoal is shown in **Figure 4.1.** From the slope ($C-1/V_mC$) and intercept ($1/V_mC$) of linear plot (regression coefficient $R^2 = 0.999$), the values of V_m and C were calculated and are 244.489 cm^3/g and 804.66 respectively. From the value of V_m, the surface area was calculated using known molecular cross section area of N_2 (16.2 ^{o}A at 77K) which comes out to be 1073 m^2/g.

High value of surface area is indicative of micro porous character of the activated charcoal and major contribution of the pore volume comes predominately from micro-pore.

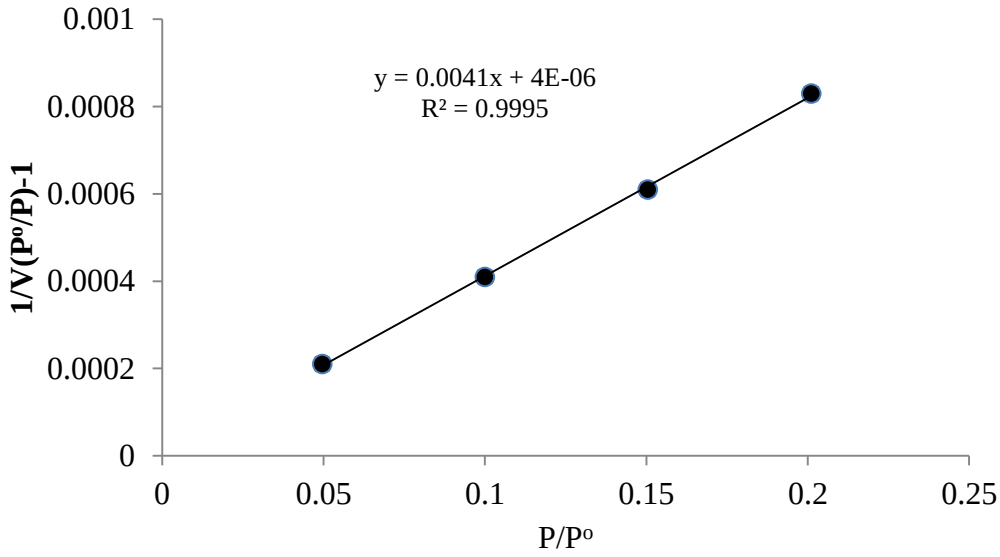

Figure 4.1: B.E.T. plot for the activated charcoal.

The **FTIR spectrum, Figure 3.2**, shows a slight absorption at 3411 cm^{-1} indicates the presence of -OH group, which is probably attributed to the adsorbed water on charcoal. 2376 cm^{-1} peak may be due to C=O stretching from ketones, carboxylic or aldehydes; peak at 1572 cm^{-1} is ascribed to the formation of oxygen functional groups like a highly conjugated C=O stretching in carboxylate moieties; peak at 1100 cm^{-1} may be due to C-O-C stretching due to ester, ether, or phenol groups; peaks at 621, 671 and 817 cm^{-1} are possibly due to out of plane bending in benzene derivatives. The results are similar to those reported in [27, 45, and 32].

Boehm titration method was used to ascertain the nature of the surface functional group of the activated charcoal, where activated charcoal was brought into contact with 0.1M $NaHCO_3$, 0.05 Na_2CO_3, 0.1M NaOH and 0.1 M HCl for specified time, as described in section 3.3.9, and the aliquots were back titrated with 0.01 M HCl and 0.1M NaOH and neutralization points were observed. The amount of each functional group was calculated by assuming that $NaHCO_3$ neutralizes only carboxylic group, Na_2CO_3 neutralizes carboxylic acid and lactones groups, and NaOH

neutralizes carboxylic, lactonic and phenol groups. HCl neutralizes basic groups [40]. The results showed the marked decrease in the concentration of NaOH (i.e., from 0.1 M to 0.025 M) indicating the presence of carboxylic, lactones and phenolic groups on the surface of the activated charcoal, whereas no change in concentration were observed in $NaHCO_3$ and Na_2CO_3 points towards the non-existence of carboxylic and lactonic groups. It means that the activated charcoal had 7.5mmoles/g of acidic groups comprising on phenolic group. This is in agreement with the FT-IR spectrum of activated charcoal which shows the peaks for phenolic group at 1100 cm^{-1}. In addition to acid groups, activated charcoal also has 1.5mmoles/g of total basic groups [42].

The point of zero charge (PZC) of activated carbon is an important parameter which affects the uptake of metal ions from aqueous solutions. PZC of the activated, determined by pH drift method [41], comes out to be 6.93. Below pH 6.93, the surface of the activated charcoal is positively charged and the adsorption of metal ions would be quite low due to electrostatic repulsion. pH beyond PZC (6.93) the negative charge on the surface increases thereby enhancing the metal ions adsorption.

4.2 Adsorption studies

The adsorption of copper ions from aqueous solutions on activated charcoal was examined by optimizing various physiochemical parameters such as shaking speed, shaking time, concentration of copper ions, pH of the solution and temperature using batch technique. Desorption studies were also carried with hydrochloric acid solutions. The criterion for the optimization was the selection of parameters where maximum adsorption occurred. All the reported results are the average of at least triplicate independent measurements. The determined relative standard deviation was within ± 3.0%.

4.2.1 Effect of shaking speed:

Initial study was performed to assess the influence of shaking speed on the adsorption of copper ions by activated charcoal. This was performed by shaking 10.0 ml of 200 µg/ml copper ions solution with 0.1g activated charcoal at different shaking speed (rpm). **Figure 4.2** shows the % adsorption with shaking speed. This indicates that adsorption is attained instantaneously and remained constant with increasing

shaking speed. This may be due to the fact that the availability of the active sites/surfaces of activated charcoal is more than the number of copper ions in solutions. In view of this observation, it was decided to select the shaking speed as 100 rpm in all the subsequent studies.

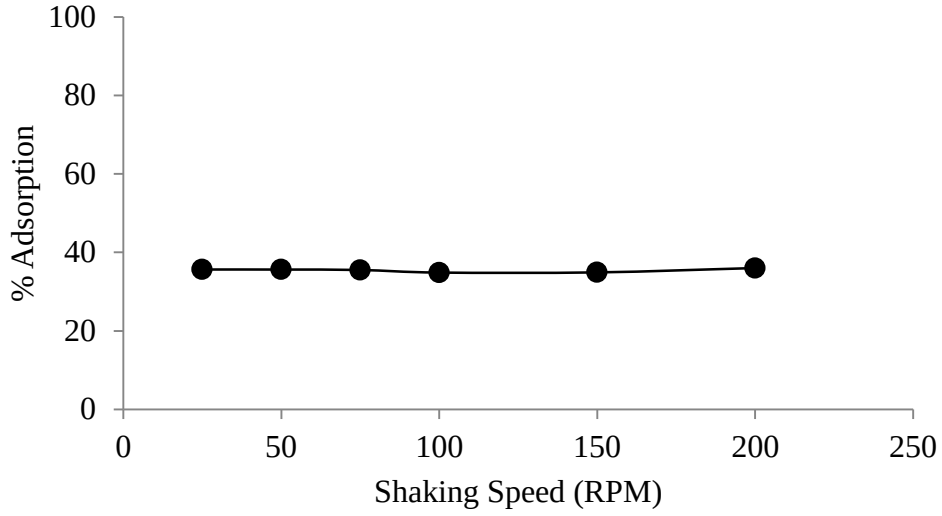

Figure 4.2: Influence of shaking speed on copper ions adsorption on activated charcoal.

4.2.2 Effect of shaking time (kinetic study)

The time dependence study of metal ions adsorption on solids provides valuable information about the rate of the adsorption process and controls of the residual time. It also provides information about adsorption process mechanism. Investigations were conducted to assess the influence of shaking time on the adsorption of copper ions onto activated charcoal. This study involved shaking of 10 ml solution containing 200 μg/ml copper ions with 0.1 g of activated charcoal for different time intervals. **Figure 4.3** represents the variation of copper ions adsorption on activated charcoal with shaking time. This figure indicates that initially the adsorption process is rapid and fast, but thereafter the process slow down. As an approximation, the two stages of adsorption process are indicative of surface adsorption and intra-particle diffusion phenomena, respectively. After the initial adsorption of copper ions on the surface of the activated charcoal, the copper ions slowly diffuses into the pores of the activated charcoal and attains constant values

after 120 minutes (i.e., when apparent adsorption equilibrium is established). The contribution of the intra-particle diffusion phenomena is low as compared to the surface phenomena, but its importance could not be ignored. The overall kinetics of the adsorption process is based on surface adsorption and intra-particle diffusion phenomena. Since the intra-particle diffusion process is slow, it is assumed to be the rate controlling step [47].

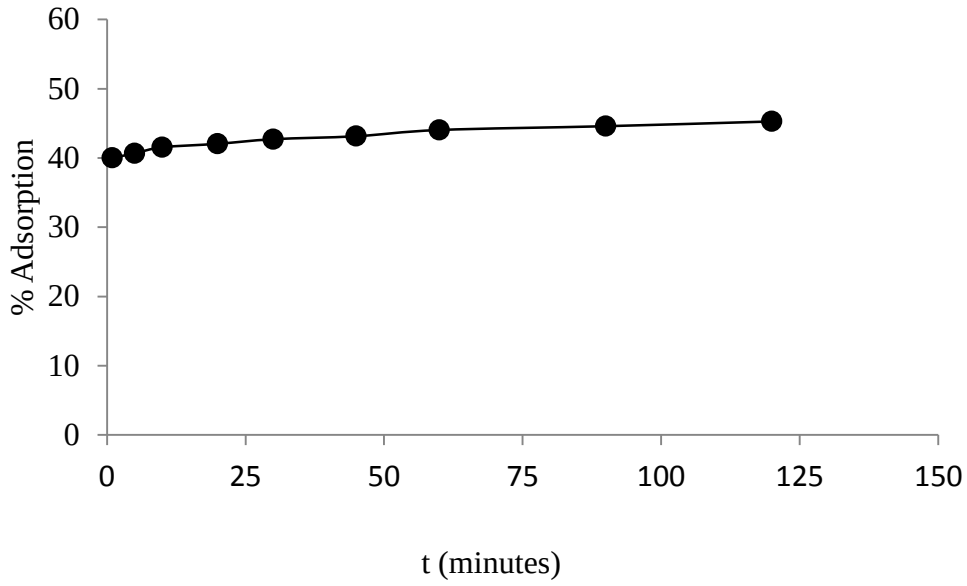

Figure 4.3: Influence of shaking time on copper ions adsorption on activated charcoal.

4.2.3 Adsorption dynamics

The adsorption dynamics was studied by applying intra-particle diffusion model (Weber and Morris equation), pseudo-first order kinetic model (Lagergren equation) and pseudo-second order kinetic model to elucidate the adsorption process and its mechanism.

Generally, the metal ions are most probably transferred from the bulk of the solution to the solid phase through intra-particle diffusion/transport process, which is often rate controlling step in many adsorption processes. The possibility of the intra-particle diffusion was explored by using the intra-particle diffusion model proposed by the Weber and Morris [47] as:

$$X_t = k_d (t)^{1/2} \quad (10)$$

Where X_t is the amount of copper ions adsorbed on charcoal surface at any time t, k_d is the intra-particle diffusion rate constant, was employed to the experimental data depicted in **Figure 4.4**. According to this equation the plot of X_t vs. $t^{1/2}$ should have zero intercept, but the plot in the present work, **Figure 4.4**, has the intercept. This confirms that intra-particle diffusion is not the only rate determining step in the adsorption process, but also the boundary layer film diffusion seems significant in rate determination, as different kinetic models may be operating simultaneously. The value of the intercept is proportional to the extent of boundary layer film thickness, and larger the intercept, greater is the boundary layer effect. This observation is in line with the observations reported by Sharma and Bhattacharyya [48-49]. It indicates that the adsorption process is controlled by film diffusion followed by intra-particle diffusion [33]. The copper ions arrive at the exterior of surface of the charcoal at a comparatively high speed, then slowly diffuse into the interior surface and eventually bind to the surface. The intra-particle diffusion rate constant and the extent of the boundary layer film thickness values for the copper ions adsorption were calculated as 1.06×10^{-4} (g/g.min$^{1/2}$) and 7.93×10^{-3}(g/g) respectively.

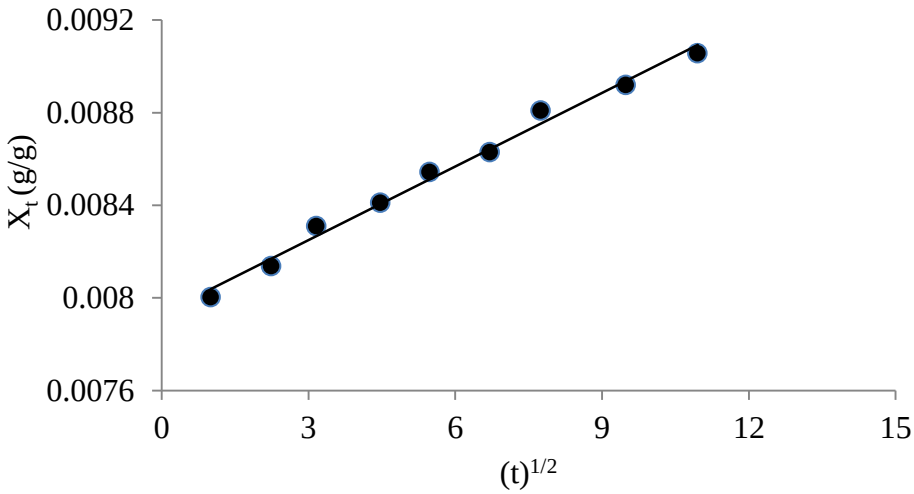

Figure 4.4: Weber and Morris's equation plot for the adsorption of copper ions.

The pseudo-first order kinetics equation is expressed in a linear form as [50]:

$$\log (X_e - X_t) = \log X_e - K_1.t /2.303 \qquad (11)$$

where X_e and X_t are the amounts of copper ions adsorbed per g of activated charcoal powder at apparent equilibration and at time t respectively, K_1 is the rate constant for copper ions adsorption (min^{-1}). The linear plot of log (X_e-X_t) versus t obtained,

Figure 4.5, apparently shows the appropriateness of the above equation and subsequently the first order nature of the process involved. The values of $K_1$and$X_e$were calculated as 0.02232 min^{-1}and0.001021g/g respectively, and correlation coefficient (R^2=0.9894). X_e value determined from the intercepts of plot does not match with the experimental X_e value (i.e., 0.009056 g/g). Non-conformity of X_e value indicates that the pseudo first order kinetics equation cannot account for the copper ions adsorption on activated charcoal [51].

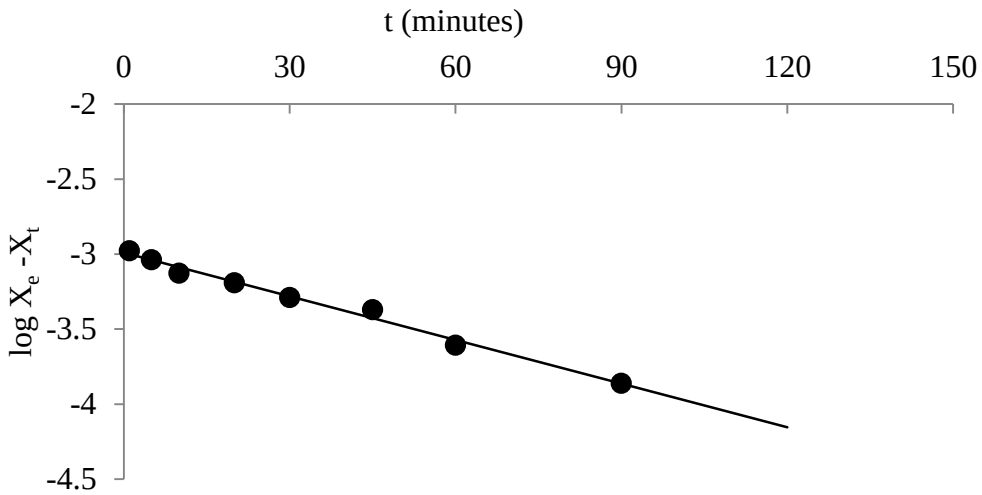

Figure 4.5: Pseudo-first order plot for copper ions adsorption.

The pseudo-second order kinetic model is based on the assumption that the rate-limiting step may be chemical sorption or chemical sorption involving forces through sharing or exchange of electron between sorbent and the sorbate. The surface site-sorbate reaction may be represented as follows [49]:

Active surface site + sorbate → surface site-sorbate surface complex.

It is assumed that the sorption capacity is proportional to the number of sites occupied on the adsorbent, the linear form of the kinetic rate law can be written as [52-53]:

$$t/X_t = 1/K_2X_e^2 + t/X_e \qquad (12)$$

where K_2 is the pseudo second order rate constant (g/g.min.), X_t, X_e and t have already been defined above. Application of this equation to adsorption data yields a straight line between t/X_t and t, confirming the suitability of pseudo second order equation to copper ions adsorption data, **Figure 4.6,** having high value of correlation coefficient (R^2= 0.999).Values of K_2 and X_e were computed from the slope and

intercept of the linear plot as 6.37E-07(g/g.min) and 0.009056 g/g respectively. There is also a good agreement between the experimental X_e values (i.e., 0.009066 g/g) and those obtained from the slope of the plot (i.e., 0.009056g/g) indicating that the adsorption of copper ions on activated charcoal follows the pseudo-second order kinetic expression well.

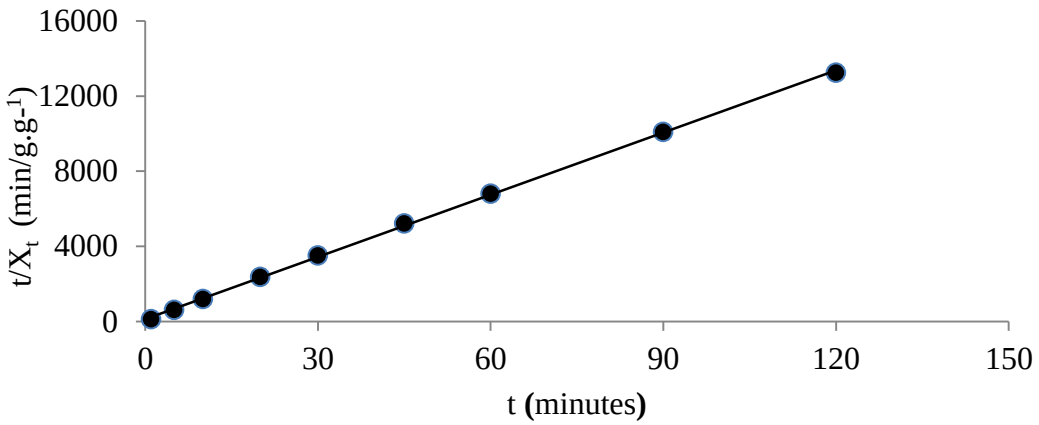

Figure 4.6: Pseudo-second order plot for copper ions adsorption.

4.2.4 Effect of pH

The pH of the adsorptive medium is one of the most important parameter controlling the adsorption process and it affect the surface charge of the adsorbent, degree of the ionization and speciation of the adsorbate. Therefore, the pH effect on the adsorption of copper ions was investigated in the pH range of 1-9. This study was performed at copper ions concentration 200 µg/mL, amount of activated charcoal 0.1 g, shaking time 120 minutes. **Figure 4.7** shows the variation of percentage adsorption with pH of the solution. This figure indicates that the percentage adsorption of copper ions increases with increasing pH of the solution and attains maximum value at pH 7. Thereafter, the adsorption process could not be followed due to the formation of precipitates of copper ions in solutions. This observation is in line with the observation reported by Nwabanne and Igbokwe [1] for copper ion adsorption on activated carbon prepared form different agricultural materials. All the subsequent studies were carried out at pH 7.

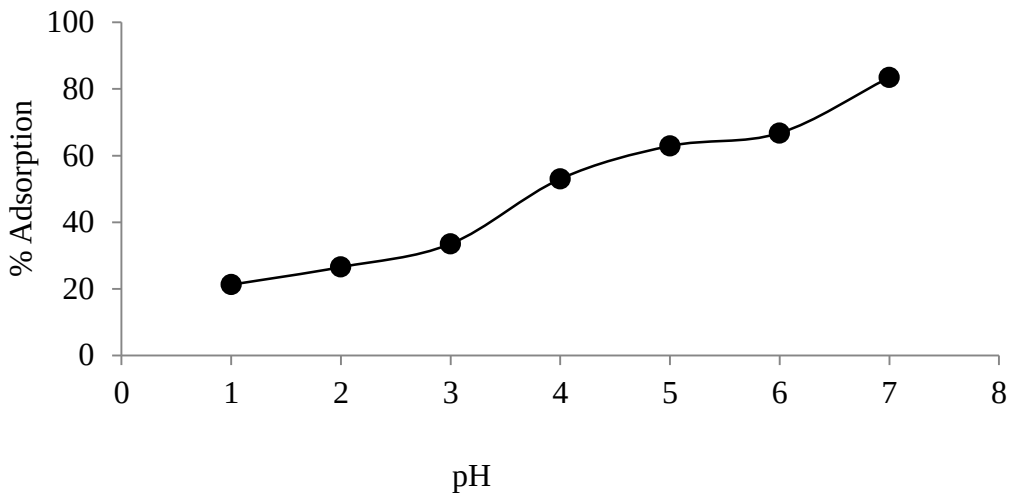

Figure 4.7: Influence of pH on the adsorption of copper ions.

The increase in the adsorption capacity of copper ions with increasing pH is attributable to surface charge density of the activated charcoal and the chemical state of copper in the adsorptive state. The copper ions in aqueous solutions undergo hydration, ionization and polymerization. Lower pH results in the protonation of the activated charcoal surface, which leads to the extensive repulsion of Cu^{2+} ions. Up to pH 3, the adsorption of copper ions was found to be low due to the competition between H_3O^+ and Cu^{2+} ions for the adsorption site. Above pH 4 the surface protonation of activated charcoal is decreasing leading to the enhancement of Cu^{2+} ions adsorption. At pH 7 and above, the Cu^{2+} ions started to precipitate as $Cu(OH)_2$.

The determined value of the point of zero charge (PZC) is 6.93, which is the point at which the net charge of the activated charcoal is zero. Below pH 6.93 the surface of the activated charcoal is positively charged and the adsorption of copper ions would be quite low due to electrostatic repulsion. With increasing pH the net positive charge decreases and leads to decrease in the repulsion between the activated charcoal surface and the copper ions, and thus enhances the copper ions adsorption [30, 54].

4.2.5 Effect of copper ions concentration

The effect of the copper ions concentration on its own adsorption on activated charcoal was investigated in the concentration range 200-3000 µg/mL **Figure 4.8**

show that adsorption decreases with the increase of copper ions concentration. The recovery of the copper ions is more in low concentration as compared to its recovery in high concentration range. This is because that the initially more unoccupied active sites are available on the activated charcoal surface and copper ions adsorbed on those active sites first yielding high values of % adsorption. As the concentration of copper ions increases, the adsorption decreases due to the prior occupation of the active sites and saturation of the activated charcoal surfaces.

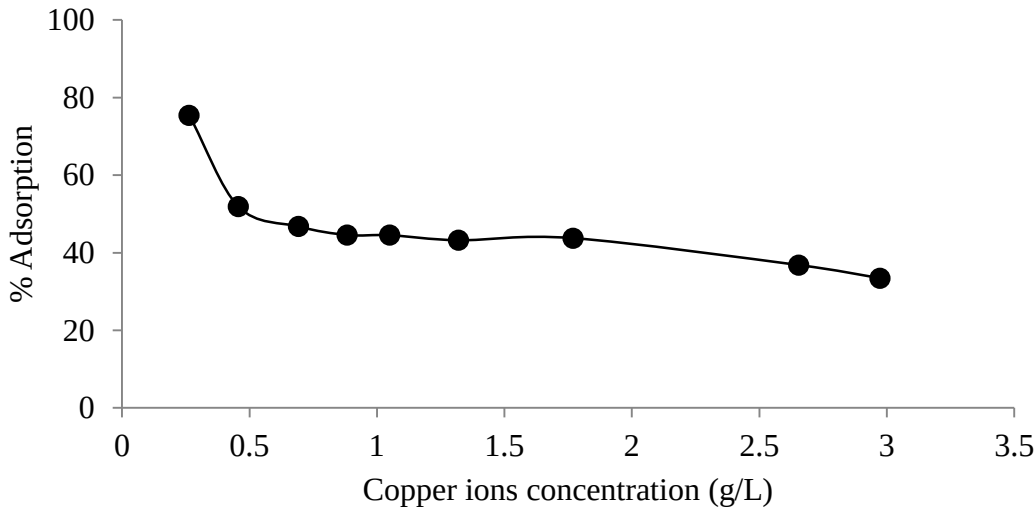

Figure 4.8: Variation of % adsorption with copper ions concentration.

4.2.6 Adsorption models

The concentration dependence of the adsorption of copper ions was analyzed using different adsorption isotherm models in order to develop an equation which accurately represented the result and could be used for design purposes. Several isothermal equations are available for analysis. In this study, the abilities of four widely used isotherms, the Freundlich [12], the Langmuir [14], the Dubinin-Radushkevich (D-R) [15] and the Temkin [17] isothermal equations were assessed by employing to the experimental data. The applicability of the isotherm models to the adsorption data was compared by judging the correlation coefficients values.

4.2.6.1 The Freundlich equation model

The Freundlich equation model is an empirical equation based on adsorption on heterogeneous surfaces having sites of varied affinities. It assumed that stronger

binding sites are first to be occupied and that the binding strength decreases with the increasing degree of sites occupation. The Freundlich equation was applied in its linear form as:

$$\log X = \log K_f + 1/n \log C \qquad (13)$$

where X and C have already defined above, K_f is a parameter of the Freundlich isotherm related to quantity of the adsorption per gram of the solid at equilibrium ($g.g^{-1}$), n is a dimensionless constant related to explain the extent of adsorption and the adsorption intensity between the adsorbate concentration and the adsorbent. The Freundlich plot of log X vs. log C, **Figure 4.9**, shows the conformity of the isotherm equation in the concentration range studied. Numerical values of the K_f (gg^{-1}) and 1/n were calculated from the intercept and slope of the straight line using least-square fit program and are given in **Table 4.1**. The correlation coefficient (R^2) of linear regression was found to be 0.994. Calculated value of 1/n is 0.68 (i.e., 1/n <1) points towards the heterogeneous surface of the activated charcoal.

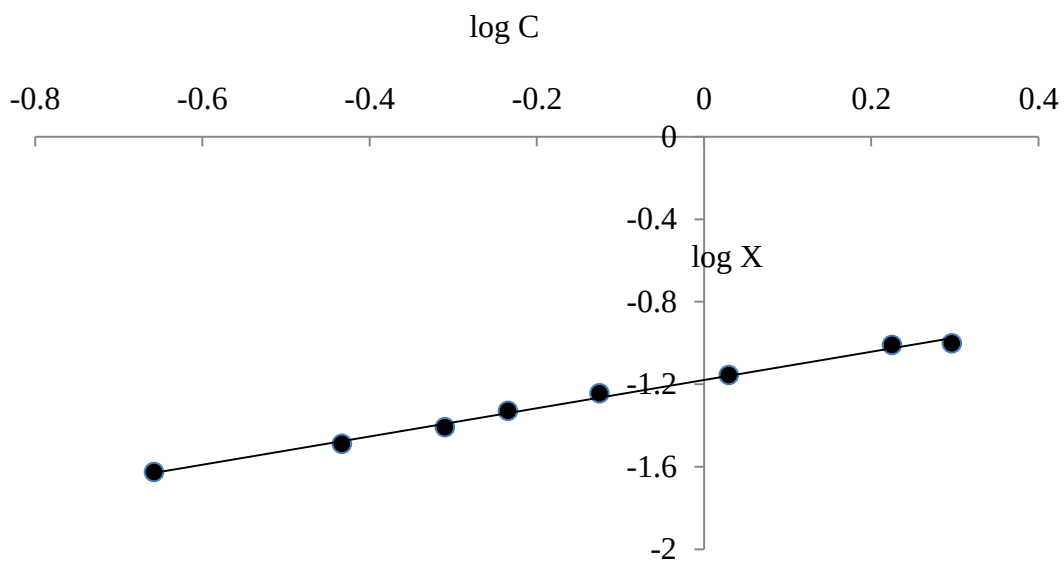

Figure 4.9: Freundlich plot for copper ions adsorption.

4.2.6.2 The Langmuir equation model

The Langmuir equation model assumes the monolayer adsorption onto a surface that contains a finite number of adsorption sites of uniform activities with no transmigration of the adsorbate in the plane of the surfaces. It is used in the in the linear form as:

$$C/X = 1/K_L X_m + C/X_m \quad (14)$$

where X and C have been already defined, X_m is the measure of monolayer capacity and K_L is the Langmuir constant related to the free adsorption energy. A straight line was obtained by plotting C/X against C **(Figure 4.10),** indicating the suitability of the data in the entire concentration range studied, Values of constant X_m and K_L calculated from the slope and intercept of the plot are given in **Table 4.1**. The correlation coefficient (R^2) of linear regression was found to be 0.963.

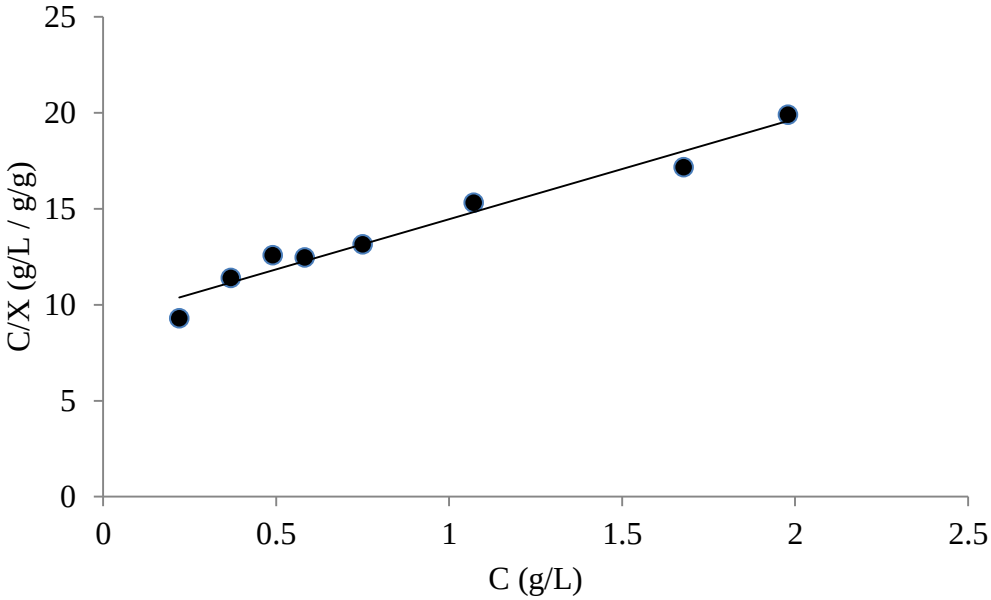

Figure 4.10: Langmuir plot for the adsorption of copper ions.

The Langmuir isotherm constant, K_L can be used to predict whether an adsorption system is favorable or unfavorable by mean of R_L, a dimensionless constant referred to as separation factor defined by [55]:

$$R_L = 1/ (1 + K_L C_o) \quad (15)$$

The parameter (R_L) suggests the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$) and linear ($R_L = 1$). The calculated values of R_L at different initial copper ion concentration as:

R_L(L/g)	0.996	0.992	0.987	0.983	0.979	0.969	0.959	0.950	0.941
C_o(g/L)	0.20	0.40	0.60	0.80	1.00	1.50	2.00	2.50	3.00

are less than 1 indicating the favorable adsorption of copper ions on activated charcoal.

4.2.6.3 The Dubinin-Radushkevich (D-R) equation model

The Dubinin-Radushkevich (D-R) equation model is based on the postulate that a fixed adsorption space is available closed to adsorbent surface where adsorption takes place and this model assumes the heterogeneity of adsorption energies within this adsorption space. The D-R equation was formulated from the Polanyi theory especially for application to micro porous materials. However, it can be applied to experimental data for low concentration of the adsorbate and good correlations can be achieved. In addition to this, the D-R equation is used to predict the nature of the adsorption processes as physical or chemical by calculating the mean adsorption energy. The linear form of D-R equation is:

$$\ln X = \ln X_m - B\varepsilon^2 \qquad (16)$$

where ε= RT ln(1+1/C), B is the constant related to the adsorption energy, R is the gas constant and T is temperature in Kelvin. The quantities X, X_m and C have their previously defined meanings. A straight line was obtained upon plotting lnX vs. $\varepsilon^2$and shown in **Figure 4.11.**Values of X_m and B, calculated from the intercept and slope of the plot are also given in **Table 4.1** The correlation coefficient (R^2) of linear regression was found to be 0.897. From the value of B, the adsorption energy (E_a) of copper ions is calculated using the following equation:

$$E_a = 1/\sqrt{(2B)} \qquad (17)$$

The calculated value of E_a was found to be 2.425 kJ.mol^{-1}which points to a physical adsorption process [55].

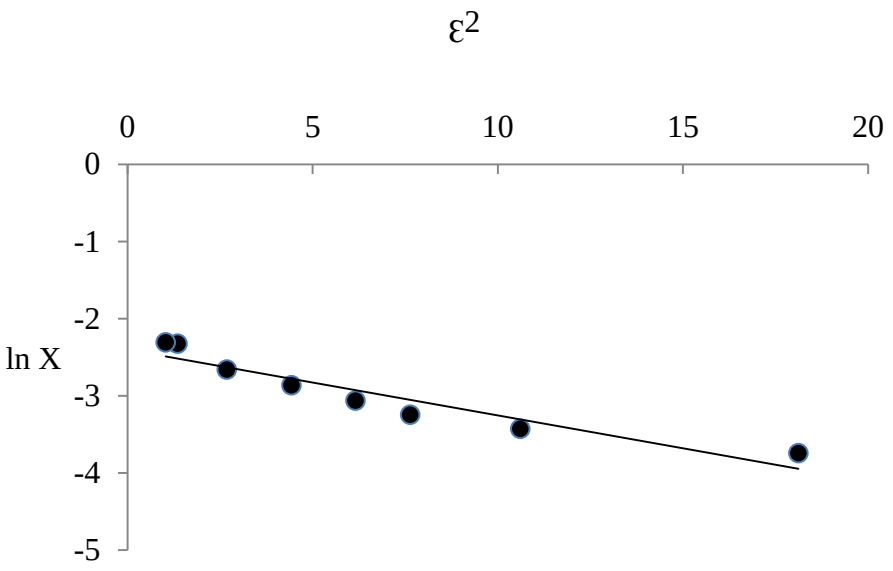

Figure 4.11: D-R plot for the adsorption of copper ions.

4.2.6.4 Temkin isotherm model

The linear form of Temkin isotherm equation is expressed as:

$$X = (RT/b_T)\ \ln A_T + (RT/b_T)\ \ln C \qquad (18)$$

Where b_T and A_T are the Temkin constants related to adsorption capacity and intensity of adsorption respectively. Straight line was obtained by plotting X against lnC **(Figure 4.12)** indicate the adsorption data fairly conform to Temkin model also. Calculated values of Temkin constants, b_T and A_T, along with the correlation coefficient are given in **Table 4.1.**

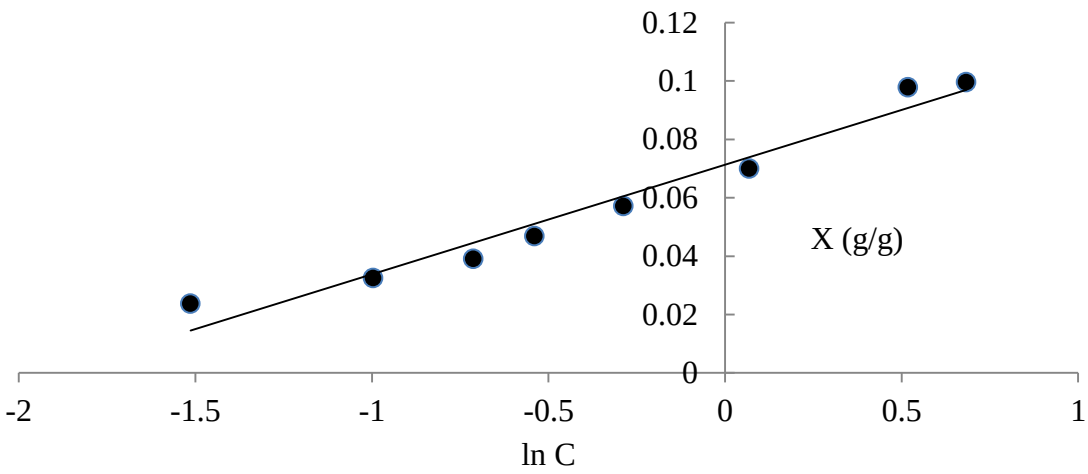

Figure 4.12: Temkin plot for the adsorption of copper ions.

Table 4.1: Calculated isotherm parameters for copper ions adsorption

Isotherm Model	Parameter	Value
Freundlich Model	n	1.464
	K_F(g/g)	0.308
	R^2	**0.994**
Langmuir Model	X_m(g/g)	0.191
	K_L(L/g)	0.021
	R^2	0.963
Dubinin-Radushkevich Model	B (mol^2/kJ^2)	0.085
	X'_m(g/g)	0.091
	R^2	0.897
Temkin Model	b_T(kJ/g)	67.162
	A_T(L/g)	6.813
	R^2	0.975

The calculated parameters of adsorption isotherms along with regression coefficients are listed in **Table 4.1**. The Freundlich isotherm model had highest value of regression coefficients (R^2) when compared to the rest of the isotherm model, which points towards the heterogeneous nature of the activated charcoal used. Applicability of the Freundlich isotherm equation to the adsorption data also shows the physio-sorption process and the type of the interaction between the copper ions and the activated charcoal is predominately Vander Waals type. The Freundlich model parameters are useful in predicting the adsorbent dose in process application by following relation [56]:

$$m = (C_o - C_e) / K_f C^{1/n} \quad (19)$$

m is the adsorbent dose, C_o and C_e is the initial and the desired final concentration of copper ions (g/L), K_f and n are the Freundlich isotherm parameters.

4.2.7 Effect of temperature (thermodynamic study)

The adsorption of metal ions onto solids is a kinetic process and the rate of adsorption process may be influenced by the solution temperature. The rate of the adsorption process may increase or decrease or remains constant with increasing solution temperature depending upon the nature of the adsorbent. To investigate the

effect of temperature on copper ions adsorption onto activated charcoal, experiments were conducted on temperatures 300 K, 313 K, 323K and 333 K at a fixed copper ions concentration of 0.2 g/mL, pH 7, amount of activated charcoal 0.1 g and shaking time 120 minutes. The results depicted in **Figure 4.13**, shows that the % adsorption decreases with increasing temperature from 300k → 323K. This indicates that low temperature is favorable for the removal of copper ions by activated charcoal from aqueous solutions. Similar finding has been reported by Chikhiet. al. [57] for the adsorption of copper ions on active carbon. Various studies of copper ions adsorption carried out by Demirbas et.al on hazelnut shell activated carbon [30], Bouhamedet. al. on active carbon prepared from Tunisian date stone [34], Bouzid et. al. on sewage sludge and pomace ashes [58] and Granados-Corea et. al by $CaCO_3$[59] reported the increasing trend of copper ions adsorption with rise in temperature; whereas no appreciable effect of temperature on copper adsorption on fly-ash was observed by Agarawal et.al. [60]. The mixed behavior of copper ions removal as a function of temperature is due to the different nature and activity of the adsorbent.

The observed decrease of copper ion adsorption may be due to a tendency for copper ions to escape from the solid phase to the bulk phase with an increase in temperature of the solutions and the adsorption mechanism associated with the removal of copper ions onto activated charcoal involves a physical process associated with weak electrostatic interaction and low adsorption heat [61]. This means that adsorption process has an exothermic character.

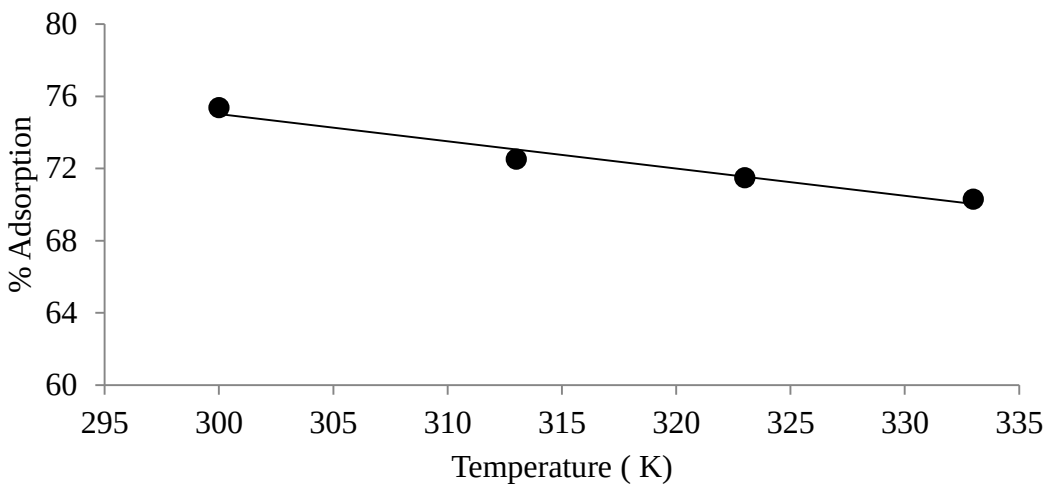

Figure 4.13: Influence of temperature on the adsorption of copper ions.

The adsorption of copper ions on activated charcoal can be expressed as:

$$S + M \underset{k_2}{\overset{k_1}{\leftrightarrow}} S\text{-}M \qquad (20)$$

where S is the activated charcoal; M is the copper ions; k_1 and k_2 are the rate constant for the adsorption and desorption processes, respectively. The equilibrium constant, $K_c$can be calculated as:

$$K_c = k_1/k_2 = C_{M,AC} / C_{M,SN} \qquad (21)$$

where $C_{M,AC}$ and $C_{M,SN}$ are the equilibrium concentrations of copper ions on activated charcoal and in solutions, respectively. Mathematically, these concentrations can be expressed as:

$$C_{M,AC} = C_{Mi}\ (F) \qquad (22)$$

and

$$C_{M,SN} = C_{Mi}\ (1\text{-}F) \qquad (23)$$

Where C_{Mi} is the initial concentration of copper ions and F is the fractional attainment of adsorption at equilibrium. On substituting the values of $C_{M,AC}$ and $C_{M\ SN}$, the equation 21 becomes:

$$K_c = F / (1\text{-}F) \qquad (24)$$

The K_c values calculated for the adsorption of copper ions on activated charcoal at different temperatures are given in **Table 4.2**. The thermodynamic quantities such as ΔH, ΔS and ΔG of copper ions adsorption on activated charcoal were calculated from the K_c values using the following equations:

$$\ln K_c = \Delta S/R - \Delta H/RT \quad (25)$$

$$\Delta G = - RT \ln K_c \quad (26)$$

where ΔH is the enthalpy change for the process, ΔS is the entropy change for the process and ΔG is the free energy change for the specific adsorption, T is the temperature in Kelvin (K) and R is the gas constant (8,314 $JK^{-1}.mol^{-1}$). Values of ΔH and ΔS were computed from the slope and the intercept of linear variation of $\ln K_c$ with the reciprocal of temperature **(Figure 4.14)** and are given in **Table 4.2** along with the values of ΔG calculated from equation 26.

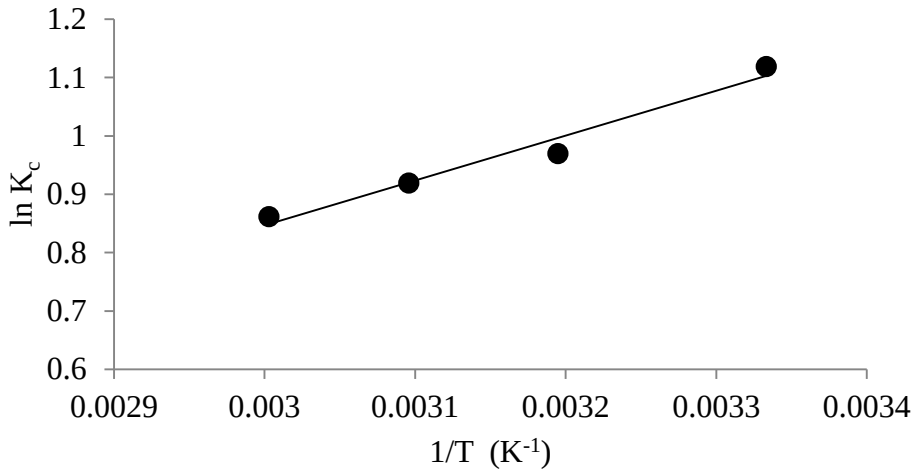

Figure 4.14: Variation of $\ln K_c$ with reciprocal of temperature for copper ions adsorption.

Table 4.2: Calculated thermodynamics parameters for copper ions adsorption.

T(K)	K_c	ΔH ($kJ.mol^{-1}$)	ΔS ($kJ.deg^{-1}mol^{-1}$)	ΔG ($kJ.mol^{-1}$)
300	3.0604	-6.3868	-0.0121	-2.7899
313	2.6369			-2.5232
323	2.5060			-2.4670
333	2.3659			-2.3841

The negative value of ΔH shows the adsorption of copper ions is exothermic and takes place via Vander Waal binding. It is also noted that the values of ΔG are negative and the values of ΔG lies in the range of Physi-sorption process (i.e., between -20 to 0 kJ/mol) [62]. The overall ΔG values during the adsorption process remained negative in the temperature range studied, corresponds to the spontaneous

physical process and that the system does not gain energy from and external source. The negative ΔG values decreases from -2.7899 to -2.3841 kJ/mol with increasing temperature from 300 to 333 K; suggests the spontaneity of the adsorption process at low temperature. The negative ΔS corresponds to a decrease of degree of freedom of the adsorbed species.

4.3 Desorption study

Desorption studies were carried out to estimate the metal releasing capacity of activated charcoal loaded with copper ions, the nature of the adsorption process, recycling of the used activated charcoal and the copper ions. Desorption studies were carried out with 0.1 M HCl solution. The results are mentioned in **Table 4.3**. Result reveals that ~98 % of the adsorbed copper ions is desorbed with 0.1 M HCl solutions, indicates that the copper ions adsorption onto activated charcoal is by Physi-sorption mechanism [29].

Table 4.3: Desorption data corresponding to copper ions.

Initial concentration	Removal Efficiency	Desorption with 0.1 M HCl
200 μg/ml	78 %	98 %

4.4 Application of the Method

The adsorption efficiency of an activated charcoal is sometimes affected by the presence of other species in aqueous solutions by their co-adsorption or by negative adsorption along with the metal ions of interest. Therefore, using the optimized conditions for the uptake of copper ions from aqueous solutions, the adsorption of spiked copper ions in tap water was also studied. The determined composition of tap water [63] is given in **Table 4.4**. Percentage recovery data for the spiked copper concentration in tap water is given in **Table 4.5;** which indicates that the presence of existing concentration of cations and anions in the medium has slightly reduced the

adsorption uptake of copper ions by activated charcoal; therefore, it could be used to combat the copper pollution in water.

Table 4.4: Determined composition of tap water [63].

Cations/Anions	Concentration (mg/L)
Ca	22.60
Mg	35.30
Na	85.60
K	5.80
Fe	0.22
Mn	0.02
Zn	0.18
Cu	0.01
Pb	52.90 (μg/L)
Cd	10.00 (μg/L)
CO_3^{-2}	0.96
HCO_3^{-2}	140.00
Cl^-	11.00
SO_4^{-2}	8.00

Table 4.5: % Recovery of spiked copper from tap water by activated charcoal.

Amount of copper ions spiked (mg/L)	% Recovery	
	Spiked copper in tap water	Spiked copper in distilled water
50	95.80	98.16
100	88.80	93.27
200	74.99	77.84

4.5 Recovery of copper ions from electro-plating industrial waste effluents- A case study

The efficacy of the developed method was checked for the removal of copper ions from waste solutions generated in copper electro-plating industry. Sample of waste solution was collected from the effluent discharge point of a local electro-plating industry and filtered through Whatman No. 40 filter paper. Initial concentration of copper ions in the filtrate was determined using UV-Visible spectrometer and its determined concentration was found as 1.5 ± 0.02 g/L. Adsorption studies were carried out at optimized conditions for copper ions and the

results are presented in **Table 4.6,** which are self-explanatory. The maximum recovery of copper ions is achieved at pH 7.

Table 4.6: Removal of copper ions from industrial waste effluent

Medium of Solution	Dilution	Amount of activated charcoal taken (g)	% Adsorption
Sample diluted with distilled water	20 times	0.1	86.94
	25 times		92.64
Sample diluted with buffer solution of pH =7	20 times	0.1	91.79
	25 times		97.40
Sample at pH 7 (adjusted)	Nil	0.5*	88.39

*Amount of activated charcoal calculated from equation No. 19 for 25 ml solution.

Based on the above data, a process flow sheet was developed for the recovery of copper ion from industrial waste effluents by commercial activated charcoal and is given information following diagram is developed to show overall process.

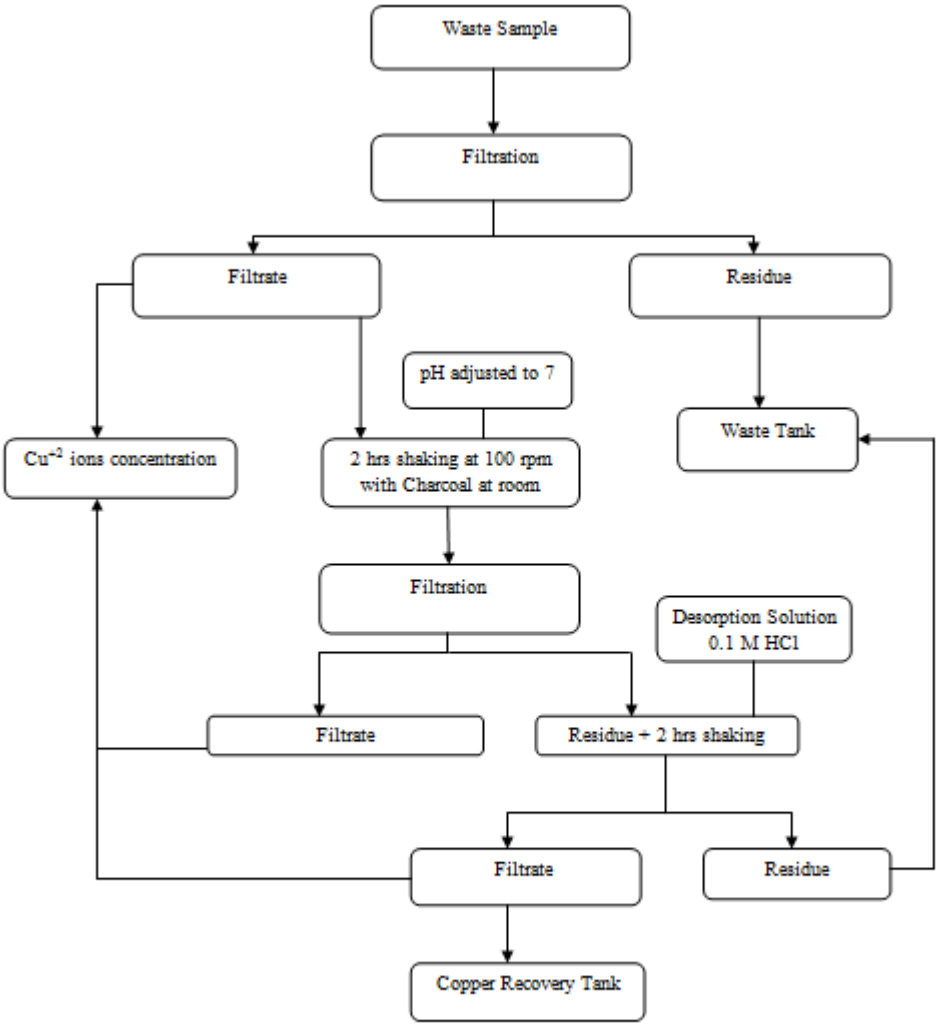

Figure 4.15 Flow diagram of copper ions adsorption process

Chapter 5 Conclusion

This study reveals the ability of a commercial activated charcoal for the adsorption of copper ions from solutions. Conditions for the uptake of copper ions were established as stirring speed 100 rpm, shaking time 120 minutes and pH 7. Recovery of copper ions from solution is favorable in low concentration. The surface adsorption and intra-particle diffusion phenomena are operative in the adsorption process. Contribution of the intra-particle diffusion is low as compared to surface phenomena towards the overall kinetics of the adsorption process and is assumed to be the rate controlling step. The adsorption process is best described by pseudo-second order kinetic equation, confirming the rate of adsorption process is controlled by more than one step as highlighted above. The Freundlich isotherm equation obeyed well in the range of copper ions concentration studied with high value of correlation coefficient (R^2 = 0.994). Low temperature favors the adsorption of copper ions on activated charcoal, and the calculated values of ΔH, ΔS and ΔG indicates the exothermic nature of the adsorption process. About 98% of the adsorbed copper ion could be recovered by 0.1 M HCl solution from the activated charcoal surface. Application of the methods to the actual industrial waste effluents generated in local copper electro-plating industry reveals that the commercial activated charcoal could be used to clean up the industrial waste for copper ions for its secure disposal into natural stream.

References

[1]. J.T. Nwabanne and P.K. Igbokwe, Mechanism of copper (II) ions removal from aqueous solution using activated carbon prepared from different agricultural materials, Intl. J. of Multidisciplinary Sciences and Engineering, 3 (7), 46-52 (2012).

[2]. Y. Yu. B. Zhang, A. Shukla, S.S. Shukla, K.L. Dorris, The removal of heavy metal from aqueous solutions by sawdust adsorption-removal of copper, Journal of Hazardous Materials, 80, 33 (2000).

[3]. P. N. Dav, N. Subrahmany and S. Sharma, Kinetics and thermodynamics of copper ions removal from aqueous solution by use of activated charcoal, Indian Journal of Chemical Technology, 16, 234-239 (2009).

[4]. S.E. Manahan, Environmental Chemistry, 5th Edition, Lewis, Chelsea MI, (1991).

[5]. L. Murley, Pollution Handbook, National Society for Clean Air and Environment Protection, Brighton, 1992.

[6]. B. Volesky, Detoxification of metal-bearing effluents: bio-sorption for the next century, Hydrometallurgy, 59, 203-216 (2001).

[7]. M. Smisck and S. Cerny, Active Carbon Manufacture, Properties and Applications, Elsevier Publishing Company, p.1,(1970).

[8]. F. Mahmood and R. Qadeer, Activated charcoal - as an adsorbent, Science Technology and Development, 12 (1), 35-39 (1993).

[9]. T.C. Voice and W.J. Weber, Water Research, 17,1433 (1983).

[10]. J.A. Veith and G. Sposito, Soil Sci. Soc. Am.J., 41, 697 (1977).

[11]. C.C. Travis and E.L. Etiner, J. Envir. Qual. 10, 8 (1981).

[12]. H. Freundlich, Adsorption is solution, Z. Phys. Chem., 57, 384-410 (1906).

[13]. S. Aksoyoglu, J. Radioanal. Nucl.Chem., 140,301 (1990).

[14]. I. Langmuir, The adsorption of gases on plane surface of glass, mica and platinum, J. Am. Chem. Soc., 40, 1361-1403 (1918).

[15]. M.M. Dubinin and L.V. Radushkevich, proc. Acad. Sci. USSR, Phys. Chem. Sec., 55,331 (1947).

[16]. W. Rieman and H. Walton, Ion-exchange in analytical chemistry, International series of monographs in analytical chemistry, 38, Pergamon press, Oxford (1970).

[17]. M.J. Temkin and V. Pyzhev, Kinetics of ammonia synthesis on promoted iron catalyst, Acta Physiochim. URSS, 12, 217-222 (1940).

[18]. M. Smisck and S. Cerny, Active Carbon Manufacture, Properties and Applications, Elsevier Publishing Company, (1970).

[19]. K.S.W. Sing, D.H. Evertt, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol and T. Siemieniewska, Pure and Applied Chemistry, 57, 603 (1985).

[20]. M.M. Dubinin, K.M. Nikolaev, G.A. Petukhove and N.S. Polyakov, Izu. Akad. Nauk. SSSR Ser Khim., 1,35 (1991).

[21]. S.A. Dastgheib and D.A. Rockstraw, Pecan shell activated carbon: synthesis, characterization and application for the removal of copper from aqueous solution, Carbon, 39, 1849-1855 (2001).

[22]. Jae-Woon Shim, Soo-Jin Park and Seung-Kon Ryu, Effect of modification with HNO_3 and NaOH on metal adsorption by pitch- based activated carbon fiber, Carbon, 39, 1635-1642 (2001).

[23]. M. Goyal, V.K. Rattan, D. Aggarwal and R.C. Bansal, Removal of copper from aqueous solutions by adsorption on activated carbons, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 190, 229-238 (2001).

[24]. S.A. Dastgheib and D.A. Rockstraw, A systematic study and proposed model of the adsorption of binary metal ion solutes in aqueous solution onto activated carbon produced from pecan shell, Carbon, 40, 1853-1861 (2002).

[25]. J.P. Chen, S. Wu and Kai-Hau Chong, Surface modification of a granular activated carbon by citric acid for enhancement of copper adsorption, Carbon, 41, 1979-1986 (2003).

[26]. A. Ucer, A. Uyanik and S.F. Aygun, Adsorption of Cu(II), Cd(II), Zn(II), Mn(II) and Fe(III) ions by tannic acid immobilized activated carbon, Separation and Purification Technology, 47, 113-118 (2006).

[27]. M.M. Rao, A. Ramesh, G.P.C. Rao and K. Seshaiah, Removal of copper and cadmium from the aqueous solutions by activated carbon derived from Ceiba pentandra hulls, Journal of Hazardous Materials, B129, 123-129 (2006).

[28]. D. Mugisidi, A. Ranaldo, J. W. Soedarsono and M. Hikam, Modification of activated carbon using sodium acetate and its regeneration using sodium hydroxide for the adsorption of copper from aqueous solution, Carbon, 45 1081-1084 (2007).

[29]. S. Arivoli, V. Nandhakumar, S. Saravanan and S. Nagarajan, Adsorption dynamics of copper ion by low cost activated carbon, The Arabian Journal for Science and Engineering, 34 (1A), 1-12 (2009).

[30]. E. Demirbas, N. Dizge, M.T. Sulak and M. Kobya, Adsorption kinetics and equilibrium of copper from aqueous solutions using hazelnut shell activated carbon, Chemical Engineering Journal, 148, 480-487 (2009).

[31]. M.A.A. Zaini, R. Okayama and M. Machida, Adsorption of aqueous metal ions on cattle-manure-compost based activated carbons, Journal of hazardous material, 170, 1119-1124 (2009).

[32]. N.K.E.M. Yahaya, M.F.P.M. Latiff, I. Abustan, O.S. Bello and M.A. Ahmed, Adsorptive removal of Cu(II) using activated carbon prepared from rice husk by $ZnCl_2$ activation and subsequent gasification with CO_2, International Journal of Engineering & Technology, 11(1), 164-168 (2011).

[33]. M. Bystrzejewski and K. Pyrzynska, Kinetics of copper ions sorption onto activated carbon, carbon nanotubes and carbon-encapsulated magnetic nanoparticles, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 377, 402-408 (2011).

[34]. F. Bouhamed, Z. Elouear and J. Bouzid, Adsorptive removal of copper (II) from solutions on activated carbon prepared from Tunisian date stone: Equilibrium, kinetics and thermodynamics, Journal of Taiwan Institute of Chemical Engineers, 43, 741-749 (2012).

[35]. M.H. Salamani, M.H. Ehrampoush, S. Sheikhalishahi and M. Dehvari, Removing copper from contaminated water using activated carbon sorbent by continuous flow, Journal of Health Researches, 1(1),11-18 (2012).

[36]. Sheng-Fong Lo, Song-Yung Wang, Ming-Jer Tsai and Lang-Dong Lin, Adsorption capacity and removal efficiency of heavy metal ions by Moso and Ma bamboo activated carbons, Chemical Engineering Research and Design, 90, 1397-1406 (2012).

[37]. N.A. Khan, Z. Hasan, K.S. Min, Seung-Min Paek and S.H. Jhung, Facile introduction of Cu+ on activated carbon at ambient conditions and adsorption of benzothiophene over Cu+ / activated carbon, Fuel processing technology, 116, 265-270 (2013).

[38]. E. Bernard and A. Jimoh, Adsorption of Pb, Fe, Cu and Zn from industrial electroplating waste water by orange peel activated carbon, International Journal of Engineering and Applied Sciences, 4(2), 95-103, (2013).

[39]. R. Qadeer, S. Akhtar, J. Hanif and A. Majeed, Nitrogen adsorption on La_2O_3 (La = Pr, Nd, Sm, Gd, Dy, Er) powder by continuous flow method, Science International (Lahore), 6(3), 2156-217 (1994).

[40]. H. P Boehm, Some aspects of the surface chemistry of carbon blacks and other carbons, Carbon, 32(5), 759-769 (1994).

[41]. Y.F. Jia and K.K. Thomas, Adsorption of Metal Ion on Nitrogen Surface Functional Groups in Activated Carbon, Langmuir, 18, 470-478 (2002),

[42]. M.A.A. Zaini, Y. Amano and M. Machida, Adsorption of heavy metals onto activated carbon derived from polyacrylonitrile fiber, Journal of Hazardous Materials, 180, 552-560 (2010).

[43]. S. Lowell, Introduction to Powder Surface Area, John Willey & Sons, N.Y., (1979), p.25.

[44]. R.G. Herman and P.H. Emmett, Catalysis Fundamental Principle (Part 1), Vol.1, Ed. P.H. Emmett, Reinhold Publication Corporation, N.Y., 1954.

[45]. M, Olivares-Marin, C. Fernandez-Gonzalez, A. Macias-Garcia, V. Gomez-Serrano, "Preparation of activated carbon from cherry stones by chemical activation with ZnCl2", Appl. Surf. Sci. 252, 5967-5971 (2006).

[46]. Y.S. Ho and G. McKay, Sorption of dyes and copper ions onto biosorbent, Process. Biochem., 38, 1047-1061 (2003).

[47]. W.J. Weber and J.C. Morris, Kinetics of adsorption on carbon from solution, J. San. Eng. Div. ASCE., 89, 31-59 (1963).

[48]. A.Sharma and K.G. Bhattacharyya, Adsorption of chromium (IV) on Azadirachta Indica (Neem) leaf powder, Adsorption, 10, 327-338 (2004).

[49]. I. Kula, M. Ugurlu, H. Karaoglu and A. Celik, Adsorption of Cd(II) prepared from olive stone by $ZnCl_2$ activation, Bioresource Technology, 99, 492-501 (2008).

[50]. S. Lagergren, ZurTheorie der Sogenannten Adsorption geloster Stoffe. Kungliga Svenska Vetens Kapsakademiens. Handlingar Band, 24 (4) 1-3 (1998).

[51]. R. Qadeer, A study of the factors affecting the adsorption of cobalt ions onto Pakistani coal powder from solutions, J. Radioanal. Nucl.Chem. 295, 2021-2028 (2013).

[52]. Y.S. Ho, Removal of copper ions from aqueous solutions by tree fern, Water Res., 37, 2323-2330 (2003).

[53]. R. Gundogan, B. Acemioglu and M.H. Amla, Copper (II) adsorption from aqueous solution by herbaceous Peat, J. Collod. Interf.Sci., 269 (92), 303-309 (2004).

[54]. D. Brady, J.R. Duncan, Bioaccumulation of metal cations by Saccharomyes cerevisiae, Appl. Microbiol. Biotechnol. 41, 149-154 (1994).

[55]. R. Qadeer, Concentration effects associated with the kinetics of ruthenium ions adsorption on activated charcoal, J. Radioanal. Nucl.Chem., 295, 1649-1653 (2013).

[56]. A.A.M. Daifullah, B.S. Girgis and H.M.H. Gad, A study of the factores affecting the removal of humeic acid by activated carbon prepared from biomass material, Colloid and Surfaces A: Physicochem. Eng. Aspects, 235, 1-010 (2004).

[57]. M. Chikhi, F. Balaska, R. Benchaabi, A. Ayat, K. Maameche and A.H. Meniai, Experimental study of coupling complexation-adsorption of Cu(II) on activated carbon, Energy Procedia, 6, 284-291 (2011).

[58]. J. Bouzid, Z. Elouear, M. Ksibi, M. Feki and A. Montiel, A study on removal characteristics of copper from aqueous solutions by sewage sludge and pomace ashes, Journal of Hazardous materials, 152, 838-845 (2008).

[59]. F. Granados-Corea, E.G. Alcantara and J. Jimenez-Becerril, Study of Co(II) and Cr(VI) adsorption from aqueous solutions by $CaCO_3$, J. Chem. Soc. Pak., 35(4), 1088-1095 (2013).

[60]. A. Agarawal, K.K. Sahu and B.D. Pandey, A comparative adsorption study of copper on various industrial solid waste, AIChE J., 50, 2430-2438 (2004).

[61]. S. Karaca, A. Gurses, M. Ejder and M. Acikyildiz, Adsorptive removal of phosphate from aqueous solutions using raw and calcinated dolomite, J. Hazardous Materials, 6, 273-279 (2006).

[62]. P.W. Atkin, Physical Chemistry, 4th Edition, Oxford University Press, London, 884-890(1990).

[63]. R. Qadeer, N. Khalid, Removal of cadmium from aqueous solutions by activated charcoal**,** Separation Science and Technology, 40,845-859 (2005).

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