REMOVAL OF HEAVY METAL IONS FROM INDUSTRIAL EFFLUENTS USING LOW COST ADSORBENTS IN PACKED BED COLUMN

A THESIS

submitted by

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of

DOCTOR OF PHILOSOPHY

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THESIS COMPLETION CERTIFICATE

This is to certify that the thesis entitled "**Removal of heavy metal ions from industrial effluents using low cost adsorbents in packed bed column**" by **Srinivas Tadepalli** in partial completion of the requirements for the award of the Degree of Doctor of Philosophy (Chemical Engineering) is an original work carried out by him under our Joint supervision and guidance.

It is certified that the work has not been submitted anywhere else for the award of any other diploma or degree of this or any other University.

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SRINIVAS TADEPALLI

DECLARATION BY THE SCHOLAR

I here by declare that this submission is my own and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which has been accepted for the award of any other Degree or Diploma of the University or other Institute of Higher learning, except where due acknowledgement has been made in the text.

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CERTIFICATE

This is to certify that the thesis titled **REMOVAL OF HEAVY METAL IONS FROM INDUSTRIAL EFFLUENTS USING LOW COST ADSORBENTS IN PACKED BED COLUMN** submitted by **SRINIVAS TADEPALLI (500024364)**, to the University of Petroleum & Energy Studies, for the award of the degree of **DOCTOR OF PHILOSOPHY** in Chemical Engineering is a bonafide record of project work carried out by him/her/them under my/our supervision and guidance. The content of the thesis, in full or parts have not been submitted to any other Institute or University for the award of any other degree or diploma.

Dr. P. Vijay
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NOMENCLATURE

AC	Activated Charcoal
BC	Bone Charcoal
AC+ BC	Mixture of Activated Charcoal and Bone Charcoal
AAS	Atomic Absorption Spectrophotometer
BET	Brauner Emmett Teller
BH	Bed height (cm)
CERCLA	Comprehensive Environmental Response Compensation and Liability Act
CBC	Cow Bone Charcoal
Cu (II)	Copper Ions
Cd (II)	Cadmium Ions
DWB	Dehydrated Wheat Bran
EBCT or EBRT	Empty Bed Contact time or Empty Bed Residence time
EPA	Environmental Protection Agency
EDTA	Ethylene Diamine Tetra Acetic Acid
FTIR	Fourier Transfrom Infra Red Spectroscopy
GAC	Granular Activated Carbon
IMC	Initial Metal Ion Concentration
KBr	Potassium Bromide
MCL	Maximum Concentration Limit or Maximum Contaminant Limit
MCLG	Maximum Contaminant Level Goals
MTZ	Mass Transfer Zone
NEQS	National Environmental Quality Standards
PFOE	Pseudo First Order Equation
PPM	Parts Per Million
PSOE	Pseudo Second Order Equation
PZC	Point of Zero Charge
RHA 300	Rice Husk Activated Charcoal Prepared From Rice Husk At 300^oC
RHA 500	Rice Husk Activated Charcoal Prepared From Rice Husk At 500^oC
RPM	Rotations Per Minute
RHA	Rice Husk Ash
SER or AER	Sorbent usage rate or Adsorbent Exhaustion rate

UNEPA	United Nation Environmental Protection Agency
USA	United States of America
WHO	World Health Organization
XRD	X-Ray Diffraction Analysis
C_o/C_t	Ratio of inlet to outlet metal ion concentration
C_t	Effluent metal ion concentration at time t (mg/l)
C_O	Initial metal Ion concentration
C_e	Equilibrium metal Ion concentration
eV	Electron Volts
k_1	First order rate constant / Pseudo first order rate constant (min^{-1})
K_{YN}	Rate velocity constant
K_{Th}	Thomas rate constant
L	Length of the column (cm)
m	Mass of the adsorbent
Q_M	Maximum uptake capacity
q_e	Adsorption capacity at equilibrium
q_t	Adsorption capacity at time t
Q_{Max}	Maximum adsorption capacity
Q	Inlet feed (metal ion solution) flow rate (ml /min)
q_o	Adsorption capacity
R^2	Correlation / Regression coefficient
t	Sampling time
τ	Time required for 50% adsorption break through
v	Volume of the solution (in l)
ΔG	Change in Gibbs free energy
ΔH	Change in enthalpy
ΔS	Change in entropy
M_{ad}	Amount of metal ion adsorbed in the column (mg/g)
m_{total}	Total amount of metal ion sent through the column
k_p	Intra particle diffusion rate constant
C_{eq}	Equilibrium concentration (mg/l)
q_{eq}	Amount of metal ion sorbed (mg/g)
b	Adsorption equilibrium constant or Langmuir Isotherm constant (l/mg)
R_L	Separation factor
B_t	Heat of adsorption
R	Universal gas constant ($\frac{J}{molK}$)
k or K_T	Temkin model constant

K_f	Freundlich isotherm constant
K_c	Equilibrium or rate constant
q_e	Uptake capcity of the adsorbent in the column
M	Adsorbent mass in the column (g)
F	Flow rate of metal ion solution (ml/min)
t_e	Exhaustion time (min)
Sh	Sherwood number
Sc	Schmidt number
Re	Reynolds number
J_D	Colburn J-factor
ρ	Density of metal ion solution (Kg/m^3)
D_{AB}	Diffusivity of water (m^2/s)
ϵ	Porosity of the bed
V	Velocity of the fluid
k	mass transfer coefficient (m/s)
Q	Volumetric flow rate (ml/min)
T	Temperature
Re_P	Reynolds number of the particle
μ	Viscosity of water
y	mass fraction of the adsorbent
q_t	Amount of heavy metal ions adsorbed (mg/g)at agitation time t (min)
t	Agitation time in minutes
χ^2	chi^2 value (Statistical Parameter)
$q_{theoritical}$	Thoretical uptake capacity from Langmuir equation (mg/g)
$q_{Experimental}$	Experimental uptake capacity (mg/g)

ABSTRACT

The present work researches the removal of Cu & Cd ions using mixed adsorbent prepared by blending activated charcoal and bone charcoal in 1:1 ratio for both batch and continuous flow operation. The adsorption mechanism follows a chemisorption process due to the synergistic effect associated by contribution of high surface area from the activated charcoal (1600 m^2/g) and negative charge from the bone charcoal. The potential capacity of the mixed adsorbent material for the removal of Cu (II) and Cd (II) from the prepared synthetic metal ion solution was studied by optimizing various parameters in the batch study and these optimized parameters are used in the continuous flow operation to find the effect of adsorbent dose and volumetric flow rate at a constant initial metal ion concentration of 100 ppm. The batch adsorption studies has been carried out for 2 hrs considering all the 6 parameters by optimizing each of them.

The effect of pH, temperature, initial metal concentration, agitation (high speed rotation) rate, adsorbent dose and contact time were studied with respect to reaction time until the achievement of equilibrium. The maximum removal for Cu (II) was 97.21% and Cd (II) was 78.76% obtained at 2 hrs for pH 6. The % removal for Cu varies from 87.16 to 99.74% at an adsorbent dosage of 5 g/L, pH 6, initial metal ion concentration of 50 mg/l, agitation rate of 180 rpm, and at a temperature of 25^{o}C. Similarly for Cd (II) it varies from 70.23 to 88.4% at 5 g/L respectively at the same operating conditions. The % removal for Cu (II) was 99.75% and for Cd (II) it was 88% at a temperature of 40^{o}C.

Confirmation experiments were carried out using the industrial effluents with mixed adsorbent, and low cost (maize cobs) in batch studies and the results were compared with synthetic solution, industrial effluents and maize cobs. The column study experiments were carried out for copper and cadmium by different bed heights (12 cm, 24 cm, 36 cm) with fixed volumetric flow rate of 10ml/min. The optimized % removal parameter for column study was found to be 36 cm and 10 ml/min, and further experiments were carried at fixed bed height of 36 cm and variation of volumetric flow rates from 10 ml/min to 30 ml/min. Simultaneous metal ion removal studies were carried out in batch mode to study the effect of pH, effect of adsorbent dosage and effect of contact time.

Maize cob was used as an adsorbent in order to evaluate its potential for the removal of copper and cadmium from industrial effluents preferably from electroplating industries. Adsorption studies were performed by batch experiments as a function of process param-

eters such as metal ion concentration of 50 ppm, adsorbent dosage of 0.5g/L to 5g/L, equilibrium time varying from 150- 180 minutes, agitation rate of 180 rpm and pH varying from 2, 4, 6, and 8.

The adsorption efficiencies for copper ions were found to be pH dependent, and increases by increasing the solution pH in the range from 4 to 6. The equilibrium time was attained after 150-180 min and the maximum removal percentage was achieved with an adsorbent dosage of 0.5g/L at different pH. The maximum % removal for maize cob was obtained as 75 % at pH 6. Similarly for the mixed adsorbent the % removal was obtained as 83.64 to 96.62 % at pH 6. The average max adsorption capacities using mixed adsorbent and maize cobs at 6 pH for copper were found to be 9.22 and 6.4 mg/g respectively. The maximum equilibrium adsorptive capacities at 180 min using maize cob for different pH 2, 4, 6 and 8 were found to be 2.82 mg/g, 4.5 mg/g, 7.53 mg/g, 1.75 mg/g respectively.

The maximum % removal for cadmium metal ion using maize cob was obtained as 53.18 % at pH 6. Similarly for cadmium using the mixed adsorbent the maximum % removal was obtained as 69.3 % at pH 6. The maximum adsorption capacities for mixed adsorbent and maize cobs for cadmium metal at pH 6 were found to be 5.98 and 4.24 mg/g respectively.The maximum equilibrium adsorptive capacities using maize cobs for cadmium at 180 min for pH 2, 4, 6 and 8 was found to be 1.95 mg/g, 3.56 mg/g, 5.32 mg/g, 1.316 mg/g respectively.

The maximum equilibrium adsorptive capacities at 180 min for different adsorbent dosages of 0.5 g/L, 1 g/L, 2 g/L, 3 g/L and 5 g/L using maize cobs for cadmium was found to be 2.09 mg/g, 1.545 mg/g, 1.06 mg/g, 0.902 mg/g and 0.691 mg/g, respectively.

Binary sorption experiments were also carried out to find the interaction of ions during simultaneous adsorption and the isotherm modeling has been done using Langmuir model and Temkin model.

Statistical analysis of copper and cadmium at different temperatures has been carried out with Langmuir model of copper and cadmium which denotes the least values of χ^2 for better suitability of the model and to find out the mechanism of adsorption at various optimized parameters.

In the continuous column flow study, the impact of volumetric flow rate and adsorbent dosage (mass of the adsorbent packed) were studies in terms of 'Break-though' curves with constant initial metal ion concentration at 100 ppm for both the divalent metals Cu (II) and Cd (II). The column studies were done at room temperature of 30^{o}C with the bed heights filled with the mixed adsorbent varying from 12cm, 24cm and 36cm and the volumetric flow rate varying from 10, 20, 30 ml/min. The potential and viable capacity

of the mixed adsorbent as a cheap and economical material for the removal of Cu (II) and Cd (II) in the continuous column flow operations from the synthetic metal ion solution has been studied. The influence of parameters like flow rate, weight of the adsorbent dosage on the breakthrough curves and adsorption performance of the mixed adsorbent were reported in terms of adsorption capacity. The adsorption data from these investigations were fitted with adsorption models such as Thomas model, Yoon-Nelson model which gave a better fit with R^2 values close to 1 under various conditions. The highest uptake capacities of 54.31 mg/g for Cu and 30.31 mg/g for Cd were obtained with an adsorbent dose of 50 g and at an constant initial metal ion concentration of 100 ppm with a volumetric flow rate of 10 ml/min.

Column studies were performed with the industrial effluents by diluting the concentration of copper and cadmium to 100 ppm, respectively. The effect of adsorbent dosage (bed height) and volumetric flow rate has been studied for both the metals in terms of breakthrough curves.

The results obtained through column operations using industrial effluent and synthetic solutions for copper were compared in terms of breakthrough time, saturation time and % removal of metal ions.

In comparison with column performance in terms of total % removal at 12 and 24 cm and a fixed vol.flow rate of 10ml/min, the more % removal was observed in case of synthetic samples having 62.13% ,67.45% than industrial effluents. The less % removal was observed for synthetic sample (78.24%) at 36 cm bed height and 10 ml/min when compared to industrial sample having 82%.

The more % removal of cadmium was observed for synthetic samples were 70.28%, 54.38%, and 44.12% when compared to industrial effluents having 52.77%, 38.18%, and 44.77% which was due to the presence of other heavy metals, waste sludges and contaminants present in the industrial effluent and reduces the % removal of cadmium.

The data obtained in the batch study for the optimized parameters were studied through fitting of kinetic models such as pseudo-first order and pseudo second order models. The experimental data obtained from column studies demonstrated that the effect of bed height, volumetric flow rate and initial metal ion concentration plays a significant role on % removal of Cu (II) and Cd (II) by the mixed adsorbent.

XRD and pore size distribution were also carried out for the adsorbent characterization. The modeling studies has been carried out with the existing data of synthetic solutions for Cu and Cd which includes intra particle diffusion study, batch isotherm study models (Langmuir model,Temkin model and Freundlich model), thermodynamic models, hydro

dynamic modeling studies in packed bed reactor, column performance calculations, various kinetic and mass transfer parameters were calculated in column studies for both copper and cadmium which includes empty bed contact time, sorbent usage rate, volume of solution treated at breakthrough point and saturation point, saturation time, breakthrough time.

Finally it was concluded that the mixed adsorbent prepared by blending activated charcoal and bone charcoal in 1:1 ratio can be taken as a better adsorbent for heavy metal ion removal. These mixed adsorbent studies can be extended to various complex industrial effluents that contains the concentration range of 100-350 ppm and can be applied to know the interaction between various parameters with respect to % removal in both batch and column studies. Comparing with the other absorbent maize cob, mixed adsorbent was superior in removing copper and cadmium both batch and column studies.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

Discharge of industrial waste water containing heavy metals (Cu, Cd, Cr, Zn, Hg, As, Pb) into the environment has become a serious threat to the human and aquatic life. The series of heavy metals that consists of many elements such as chromium, zinc, iron, lead and copper which cause the environmental pollution when they exceed their toxic limit. Heavy metals contamination in air, water and soil is a worldwide issue created by mining and refining operations, metal handling plants and waste incineration. Heavy metals are the center components of earth's outside layer which are consolidated by metals and metalloid's with atomic density more greater than 4000 kg/m^3. Some of the heavy metal ions are small scale supplements for living creatures, yet at higher concentration range they create serious health effects. The most harmful types of these metals in their ionic species exists in oxidation states like Cd^{2+}, Pb^{2+}, Hg^{2+}, Ag^{2+} and As^{3+} in which they react with the body bio-molecules to form extremely stable bio toxic compounds which are difficult to dissociate. In the very recent years expanding problem about the impact of poisonous metals in nature has brought about more strict ecological and environmental regulations for mechanical and industrial applications that release the metal bearing effluents. Removal of metal particles from waste water in an effective manner has turned into a vital issue. Although small concentration of heavy metals are needed to all living organisms but at high concentration of these metals can cause several diseases like neurological and psychological effect on human body [1, 2].

In the environment, the heavy metals are generally more persistent and toxic than organic contaminants such as chemicals released from pesticides, fertilizers and petroleum by products, etc. Heavy metal harming can come because of drinking water through tainting (ex. lead channels, mechanical and industrial waste) and passes through the evolved way of life through food chain or high ambient air conditions near emission sources. In natural environments these elements may be sorbed by soil components or sediments and are dissolved in aquatic solution and/ or accumulated by living organisms along with crops, vegetables and fish and then may enter into the food chain. In this manner the sorption of heavy metals on soil segments or residue relates nearly to their portability and bio-accessibility and assumes a basic part in diminishing their danger to individual and creatures [3]. Therefore, the vicinity of particles of substantial metals in waste water even at low concentrations is a huge problem to the biological community and raises numerous dangers for people and aquatic life [4–8].

1.1 Water Pollution

Water is the most fundamental prerequisite in day by day life that has been debased (reduced its quality and value) by the transfer of local, metropolitan, mechanical and industrial usage. Anything, which is not required finds its way to the closest water source or land which further dirties the ground water. In spite of the fact that 80% of the world's surface is secured by water, however, just little part was accessible for drinking, horticulture, household and mechanical, chemical industries. So there is a need to use the accessible assets successfully without contaminating the water.

The issue of satisfactory taking care of modern waste water causes more unpredictable with a great deal and causes more troublesome issues than sewage water in light of the fact that waste waters obtained from the industry are heavily laden with toxic heavy metals, organic or inorganic, mineral waste with corrosive and poisonous nature, inflammable or explosive substances which creates a serious problem to human and aquatic life.

The release of non biodegradable metals into the water is a remarkable concern on the grounds that they have a tendency to aggregate in living beings, creating different ailments and issues and there by interfering (mixing) with the pure use of water. It is well perceived that there is permissible limit of each metal, above which they are generally toxic and some forms are even fatal to human and animal beings. Keeping in view of these problems, strict environmental regulations on the discharge of heavy metals have been laid by Pollution Control Board through pollution prevention act in 1990. These laws make it important to create proficient advances for the removal of heavy metals. The harmful effects of these pollutants have been identified since long but only recently the public concern has led to the enforcement of strict legislative laws governing the discharge of toxic pollutants. This act has provisions for controlling the pollution caused by industries or manufacturing companies so as to meet even the minimum standards for any function and purpose. The expanding consideration has been set on the removal of harmful metals from waste waters for contamination control as well as to empower the reuse of water.

Adsorption is a valuable sanitization method and most generally utilized as a part of industry particularly in water and waste-water usage. The adsorption procedure has been discovered beneficial because of minimal effort of adsorbent, simple accessibility, low operational expenses, ease in handling when contrasted with different procedures, reuse of adsorbent, naturally availability of adsorbent and 100% metal ion removal. Adsorbents utilized are the most ideal path for removal of metals from wastewater on the grounds that it is readily available, efficient and modest technology including no complex mechanical assembly or equipments. It is recognized as the best method for the heavy metal ion removal in drinking water and furthermore to give a solution in terms of suitable and domain specific practical removal procedure. It was concluded from the above study that the adsorption is a significant method for controlling the level of fluid contamination in waste water treatment. The usage of ease adsorbents for the treatment of wastewater containing substantial metals was useful as a basic powerful tool and efficient method for water treatment.

The disposal with pollution of industrial waste water containing heavy metals was becoming a matter of increasing concern, because many heavy metals form stable complexes with bio-molecules and their presence in even small amounts can be detrimental to plants and animals [9]. Ingestion of polluted water could cause physiological damage. The extent of damage would depend upon several factors such as quantity, concentration, site of desorption, physical half life, biological half life, type of metal radiation and energy of metal radiation. The various sources of heavy metal pollutants generated are listed below [10].

1. Sewage
2. Plant materials
3. Organic chemical Exotics
4. Mineral chemical substances
5. Sediments
6. Radioactive waste
7. Heat

1.1.1 Distribution of Heavy metals

Heavy metals are metallic components that exists in both common and sullied situations (damage the purity or integrity of soil/ land/ water). In indigenous habitats, they exists at even low concentrations. However at high concentrations in the case of contaminated environments can result in public health impacts. The components that are of concern incorporate mercury, cadmium, lead, chromium, zinc nickel, arsenic, cadmium and copper. These metals may be discharged into the earth or human or aquatic life from metal plating, refining and petro-chemical industries, plastic manufacturing, pigments, commercial ventures, plastic and rubber industries, scrap metal, etc. On release to the air, the elements travel large distances and are deposited on the soil, vegetation, and water depending on their density. Once deposited, these metals are not degraded and persist in the environment for many years poisoning humans through inhalation, and skin absorption. Acute exposure leads to nausea, anorexia, vomiting, gastrointestinal abnormalities and dermatitis [11].

Metal contamination of soil can occur by a variety of processes but in general it can be stated that in areas of active aerial contamination and sewage sludge disposal, it tends to show highest concentrations and concentrates in the upper layers of the soil profile. The distribution and mobility of an individual metal within a specific soil cannot be determined based on physical or chemical properties alone and more over biological and climatic conditions are also taken into account. Application of sewage sludge to land has become the main cause for metallic contamination which is due to the addition of excess organic matter along with the metals. The presence of excess organic matter not only affects the distribution of the applied metal, but also the metals already present in the soil. Soil pH also effects the distribution and mobility of metals, applied with sewage sludge. In India most of the urban areas are employed for controlled dumping of domestic waste and such areas represent the potential reservoirs or storage for heavy metals. The areas are either used for vegetable growing purposes or reclaimed by local authorities by bull-dozing them flat, so that the heavy metal becomes intermixed with top soil or subsoil. Such operations invariably bring about increase in the trace element content of the soil. At this stage the enhanced levels of trace metals may produce photolytic effects or ground water pollution. When the sewage sludge was spread over the land the metals present are distributed upto different depths in the soil [11, 12].

Though metal compounds are not a normal constituent of air but are found in a great variety of forms particularly in urban areas. They occur mostly in the particulate phase with some exceptions. The sources of metallic contaminants in air are both natural (e.g. terrestrial, marine, volcanic, biogenic) and anthropogenic (e.g. industrial and auto-mobile combustion). Urban industrial air may contain suspended particulates of wide variety of pollutants including heavy metals such as lead, nickel, zinc, copper, cadmium, etc. depending upon the specific type of mining, milling or manufacturing units located in that area. Metal ions are being absorbed by the lungs are ten times more efficiently than the intestines. They are of great concern as a health hazard especially in densely populated areas and work places where high levels of metal-containing vapours and particles exist. The levels show an increasing trend in different areas was which follows as remote rural $<$ urban $<$ industrial areas [13]

There is evidence to show that high emission of toxic trace metals leads to an enrichment of the respective components even in remote environments such as Arctic areas. The atmospheric occurrence of heavy metals depends upon the source strength, atmospheric dispersion and the deposition processes. The source strength in turn depends upon the emission factors. Emission of trace metals in the northern hemisphere (80%) is much higher than in southern hemi-sphere (30%). As compared to remote and unpolluted regions there is a tremendous global increment in the air concentrations of these potentially hazardous heavy metals in urban areas. The World Health Organization (WHO) guidelines for air quality of some of these metals such as cadmium (10-20μg/year), lead (0.5-1μg/year), manganese (1μg/year) mercury (1μg/year) and vanadium (1μg/day). Absolutely pure water does not exist in nature.

1.1.2 Common metals and their sources from Industries

The substantial metal sources that are released from different commercial ventures which cause the water contamination are described as follows.

1. Copper: Bearing wear, motor parts, brake outflows, Pigments, Surface coatings, Iron and Steel producing units [14]
2. Cadmium: Tire wear, fuel igniting, batteries, Electroplating, Coatings and Finishing Laboratories, Pigments [15]
3. Lead: leaded fuel, tire wear, grease oil, bearing wear [15]
4. Zinc: Tire wear, motor oil, oil brake transmissions, utilization of electrical parts [16]
5. Chromium: Air forming coolants, engine parts, brake transmissions, Tannery, Pigments , Coatings [16]
6. Iron: Auto body rust, Engine parts, Aluminium Industry [17]
7. Nickel: Diesel fuel and gas, lube oil, brake surges and outflows [18]
8. Aluminium: Mechanical and Chemical Industries, Steel manufacturing units [19]

1.1.3 Selection of Heavy metals

This section depicts about the various sorts of heavy metals, their unsafe levels and the impacts of these substantial metals to human being and environment. The most contaminated substantial metals are lead, cadmium, copper, chromium, selenium and mercury. Lead in people with long haul presence can bring about intense or unending harm to the sensory system on people. Cadmium in individuals with the presence for a longer period of time causes renal brokenness. High metal concentration can cause obstructive lung ailment and harm to human respiratory system. Copper is a key substance to human life, however at high concentration it can bring about iron deficiency, liver and kidney harm, stomach ache and intestinal problems. Impact of the mercury was to harm the cerebrum and the vocal sensory system which causes mental impacts in youngsters [20].

Heavy metals are normal parts of the Earth's outside layer. They cannot be degraded or devastated. To a little extent, they enter our bodies through nourishment, drinking water and air. As a follow components some substantial metals (e.g. copper, cadmium, zinc,

Figure 1.1: Discharge of Industrial wastewater

lead, Selenium) are vital to keep up the digestion system of the human body. However at higher concentration they can prompt harming. Heavy metal pollution was because of drinking-water polluted through surrounding air concentration and the water obtaining from close discharge sources [21].

Heavy metals are dangerous because they tend to bio-accumulate and increase the concentration of a chemical in a biological organism over time, when compared to the chemical concentration in the environment. Compounds accumulate in living things at any time are taken up and stored faster than they broken down (metabolize) or excreted [22].

Heavy metals can enter in the water supply even from acidic downpour separating soils and industrial waste discharge units which further releases into streams, lakes, waterways, and groundwater.

1.2 Copper

Copper is a chemical element (from Latin: Cuprum) with symbol Cu and atomic number 29. It is a ductile metal and have very high thermal and electrical conductivity. Pure copper is soft and malleable and it have freshly exposed surface that has a reddish-orange color. It is used as a conductor of heat and electricity, a building material, and a constituent of various metal alloys [23, 24].

The metal and its compounds have been utilized for a huge number of years. In the Roman time, copper was primarily mined on Cyprus, subsequently the name's source of the metal as (metal of Cyprus), later abbreviated to Cuprum. Its compounds are ordinarily experienced as copper (II) salts, which regularly give blue or green hues (colour appearance parameter) to minerals, i.e., azurite, turquoise and have been broadly utilized as shades. Building structures constructed with copper consume to give green verdigris or patina which was a typical name for a green shade acquired through the use of acidic and corrosive to copper plates or the common patina framed when copper metal or bronze is weathered and presented to air or ocean water over a time frame. It exists typically as essential copper carbonate, however near to the ocean it will be a fundamental copper chloride [25].

Copper is essential to all living organisms as a trace dietary mineral because it is a key constituent of the respiratory enzyme complex containing cytochrome and oxidise. In molluscs and Crustacea, copper is a constituent of the blood pigment named hemocyanin, which is replaced by the iron-complexed haemoglobin in fish and other vertebrates. The primary body parts where copper is found in people are liver, muscle and bone [16]. Copper alloys are utilized as wood additives, bacteriologic substances, and fungicides [26].

1.2.1 Effects of Copper

Increased copper bound protein concentrations have been seen in the hepatic ailments both in adults and children. Wide variations in copper concentrations reported by different researches are found in normal and diseased liver samples which do not give any conclusion in this regard. The utility of hepatic copper estimations appear to be more in case of prolonged homoeostasis, chronic biliary cirrhosis and Wilson disease. Values of copper levels in these diseases may be up to thirty times more compared to the control levels [7].

1.2.2 Copper health issues and Toxicity

People who drink water containing copper in excess of the actual level may vary with short term exposure may experience gastrointestinal distress and with long- term exposure may create severe health problems that leads to liver or kidney damage. People with Wilson's disease should consult the doctor if the amount of copper in water exceeds the actual level. This health effect issues are not intended to categorize all possible health effects for copper but rather it was intended to inform consumers and public about the toxicity associated with it [7].

1.3 Cadmium

Cadmium is a chemical element with symbol Cd and atomic number 48. This soft, bluish-white metal is chemically similar to the two other stable metals in group 12, zinc and mercury. Like zinc, it prefers oxidation state +2 in most of its compounds and like mercury it shows a low melting point compared to transition metals. Cadmium and its congeners are not always considered transition metals, in that they do not have partly filled d or f electron shells in the elemental or common oxidation states. The average concentration of cadmium in Earth's crust is between 0.1 and 0.5 parts per million (ppm). It was discovered in 1817 simultaneously by Strom eyer and Hermann, both in Germany, as an impurity in zinc carbonate [7].

Cadmium occurs as a minor component in most zinc ores and therefore is a by-product of zinc production. Cadmium was used for a long time as a pigment and for corrosion-resistant plating on steel, whereas cadmium compounds were used to stabilize plastic. The use of cadmium is generally decreasing due to its toxicity. It was specifically listed in the European restriction of hazardous substances that replacement of nickel-cadmium batteries with nickel-metal hydride and lithium-ion batteries are in progress. One of its new uses is it was used in the manufacture of Cadmium - Tellurium solar panels. Although cadmium has unknown biological function in higher organisms, a cadmium-dependent carbonic anhydride has been found in marine diatoms [27, 28].

1.3.1 Effects of cadmium

This metal accumulates preferentially in the liver. It is present in negligible amounts at birth, and gradually increases with age and is responsible for extensive peri-portal, interlobular fibrosis, biliary hyperplasia and other forms of liver damage. Cadmium inhibits both the content and activity of drug-metabolising enzymes. Hepatic damage is one of the serious effects of acute cadmium toxicity. High protein diet (particularly Steiner rich) protects the liver from cadmium-mediated damage. Following oral ingestion or inhalation, cadmium accumulates in the liver. In human beings, cadmium intoxication leads to two types of syndromes-pulmonary and gastric. In both the cases it was associated with liver damage ranging from an increase in the size of the organ to cirrhosis and organ dysfunction. The metal is bound to methionine in liver and the complex so formed is transported to kidney. Its concentration is higher in the cortex region than in medulla oblongata. Tubular damage may also occur along with glomerculer damage or even independently. This proteins are electro-phoretically different from protein excreted [25].

Some of the harmful effects of Cd (II) include chronic and acute metabolic disorders such as itai-itai disease, renal damage, emphysema and testicular atrophy. Due to its toxic properties and tendency for bio-accumulation in food chain, it is imperative to take effective precautions and to reduce the concentration levels of heavy metals in waste water [25]. Cadmium is one of the heavy metals with a high potential hazard to human being and en-

Table 1.1: Permissible limits for metals in water according to USEPA

Metal	**Concentration (ppm)**
Copper (Cu)	1.3
Cadmium (Cd)	0.005
Lead (Pb)	0
Iron (Fe)	0.3
Zinc (Zn)	5

vironment. It enter to the water bodies through waste water from metal plating industries, Cd-Ni battery industries, mining, stabilizers and alloys. Poisoning of Cadmium in human can causes high blood pressure, kidney damage and sometimes destruction of testicular tissue and red blood cells. In small amounts cadmium is associated with hypertensive diseases and considered as carcinogenic to men [9].

1.3.2 Cadmium health issues and Toxicity

Individuals who beverage water containing cadmium well in over-abundance of the maximum contaminant level (MCL) for few days or weeks can cause nausea, vomiting and diarrhoea. It will suffer on muscle cramps, liver injury. Intake of drinking water containing cadmium for more years could lead to kidney damage and it will cause prostate cancer. The permissible limits of Cd (II) according to Indian Standards : 10500 in the year 1992 for drinking water, surface-water and public sewers are 0.01 ppm, 2.00 ppm, and 1.00 ppm respectively [25]. The permissible limits for heavy metals according to USEPA are reported in Table 1.1 as shown.

1.4 Available Technologies for the removal of metals from waste water and their limitations

Heavy metals are of special concern because they are non-degradable and thus persistent. Heavy metals have harmful effect on the human body, physiological and other biological systems when they exceed the tolerance levels [29]. Exposure to these metals can cause liver diseases, brain damage, kidneys failure and even to death ultimately. Besides chronic exposure to these contaminants present even at low concentrations in the environment they also proved to be harmful to the human health. Due to the above reasons the heavy metals must be removed from industrial effluents [16].

Many procedures have been adopted in order to remove heavy metals from aqueous streams, among the most commonly used techniques are coagulation, In-situ reduction process, co-precipitation, evaporation, chemical coagulation/floatation, flocculation, cementation, heavy metal removal from biosurfacants, biosorption, ion exchange,chemical precipitation, chemical oxidation and reduction, ion exchange, filtration, electrochemical treatment, reverse osmosis (membrane technologies), evaporative recovery and solvent extraction. These classical or conventional techniques give rise to several problems such as unpredictable metal ions removal and generation of toxic sludge which are often difficult to de-water (remove the contaminants) and require extreme caution in their disposal. Besides that, most of these methods also have some limitations whereby they are economically viable at high or moderate concentrations of metals but not at low concentrations, which means the dilute solutions containing from 1 to 100 mg/l of dissolved metals. Heavy metals removed by classical techniques involve expensive methodologies. These are due to high energy and frequent reagent requirements. Some of them are explained in brief with their disadvantages [30].

Several technologies exist for the remediation of heavy metals contaminated ground water and soil and they have some definite outcomes such as:

- Complete or substantial destruction/ degradation of the pollutants
- Extraction of pollutants for further treatment or disposal
- Separation of non-contaminated materials and their recycling from polluted materials which requires further treatment
- Contaminant polluted material restrict exposure to the wider environments.

There is a long series of technologies involved in the removal of heavy metals from various types of industrial waste-water and mine drainage. The conventional heavy metal ion remedial technologies have some major technical shortcomings. Some of the disadvantages of the conventional metal ion re-mediation technologies have been reported in Table 1.2.

Comparing with conventional methodologies, generally the adsorption and bio sorption of heavy metals is a very cheap, eco-friendly and efficient methodology. Bio-remediation processes include the use of biomass. These are not only cheap but also do not produce any secondary chemical sludge which is the main advantage of bio-sorption process. The biosorbents are readily available and they are quite efficient for the remediation of heavy metals below a minimum concentration of 100 mg/l. The way of bonding between the adsorbate and the adsorbent's surface recognizes the sorts of adsorption.

Table 1.2: Limitations of various conventional metal ion remediation technologies

Methodology	**Shortcomings**	**Reference**
Ion exchange	Input and maintenance cost is very high	[31]
In-Situ reduction process	Toxic gas intermediate, handling is difficult	[32]
Adsorption	Efficiency of the process depends on type of the adsorbent and chemical pretreatments are required to improve performance of adsorbent	[33]
Chemical Precipitation	Input of chemicals is required, problem of secondary sludge generation, disposal of secondary sludge	[34]
Membrane separation and ultrafiltration	Input and maintenance cost is very high, fouling of membranes, operation cost is very high, limitation of flow rates and efficient removal of other metals decrease in presence of combination with other metals	[33]
Flotation	Input, maintenance and operational cost are very high	[34]
Electro kinetic remediation	The process depends on soil pore, water current density, grain size, ionic mobility, contaminant concentration and total ionic concentration	[19]
Chemical Coagulation and flocculation	Input cost is very high, involves huge amount of chemicals and generation of secondary sludge	[34]
Photo catalysis	Input cost is very high, involves semiconductor electrolyte.	[35]
Electro Chemical treatments	Input cost is very high, filtration was required for the removal of flocks, initial pH and current density of the solution is required to be adjusted	[36]

Adsorption system for waste water treatment has become significant technique that has received a considerable attention for the development of an effluent clean and economical technology.

In general, adsorption of inorganic and organic pollutants on the surface of the adsorbents are studied under various experimental conditions to optimize maximum removal. The excessive intake of these metals by man leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, Central nervous problems followed by depression, gastrointestinal irritation and possible dangerous changes in liver and kidney [37]. Adsorption is proven technology for the removal of Cu^{2+}, Cd^{2+}, Fe^{2+} ions from synthetic and real industrial effluents.

The discharge of effluents in the industrial waste causes toxic effect on the living species and sometimes even death at higher concentrations. The stable metal ions which cannot be metabolized by the body are not passed up in the food chain and create severe health problems such as vomiting, headache, nausea, brain damage, liver and kidney failure and death. An increase in the population and industrialization leads to several waste water effluents which contain the metals lead, mercury, cadmium, nickel, copper, chromium, manganese, iron, zinc etc that causes the pollution.

Various types of microbial biomass can retain/bind relatively at high quantities of metal ions on their cell wall due to its structural characteristics. The metabolism independent mechanism is called biosorption which is regarded as an inexpensive biological treatment for high volume and low concentration complex waste waters containing heavy metals in the order of 0.01-100 mg/l [38].

1.4.1 Reverse Osmosis

It is a process in which heavy metals are separated by a semi-permeable membrane at a pressure higher than osmotic pressure caused by the dissolved solids in waste water. The disadvantage of this method is that it is expensive [39].

1.4.2 Electro Dialysis

In this strategy the ionic sections (generous metals) are disconnected using semi- permeable particular layers. Utilization of an electrical potential between the cathode and anode causes a movement of cations and anions towards separate terminals. Because of the alternate spacing of cation and anion permeable membranes, cells are concentrated and dilute salts are formed. The disadvantage is the formation of metal hydroxides which block the membrane [1].

1.4.3 Ultra filtration

They are pressure driven film operations that use penetrable layers or porous membrane for the removal of heavy metals. The main disadvantage of this method is the formation of secondary seepage/sludge [19].

1.4.4 Ion exchange

Molecule exchange is an adsorption process in which charged ions called particles, in the solution are exchanged for other ions on the surface of an adsorbent.Ion exchange only removes compounds that ionize. It is also a concentration process.The process of ion exchange occurs in special synthetic resins and in many natural solids. Ion exchange is a practice in which ions are replaced among a solution and insoluble matrices, typically synthetic organic ion exchange resins which reveal an elevated specificity for certain metals with capability to attain ppb levels of clean up while treatment of huge volumes of industrial effluent [30, 40]. However a high cost of resins (1800-3000/kg) and capital expenditures are constrains to operate such a system [19]. In this phenomena, metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the exchange resin. The disadvantages includes high cost and partial removal of certain ions.

1.4.5 Adsorption

Adsorption refers to the selective collection and concentration of a particular type of molecules contained in a fluid phase onto a solid surface. The molecules of the adsorbate come from the fluid phase into the interface, where they remain for a period of time. In a reversible process, the molecules go back to the phase from which they came or reversibly passes into another phase while other molecules replace them at the interface. On reaching the solid surface the adsorbed molecules exchange energy with structural atoms of the surface and if sufficient time is given for adsorption, the adsorbed molecules and the surface atoms reach thermal equilibrium. At equilibrium, the number of molecules arriving at the interface in a given time is equal to the number of molecules leaving the interface to go into the fluid phase [41].

Molecular or atomic interactions occur at interfaces between gas and solid, gas and liquid, liquid and solid, two liquids and sometimes between solid phases. Interaction at an interface causes the transition of a molecule from one phase to another which is called as sorption of the molecule by the given phase. Adsorption of atoms or molecules on to a solid from a fluid phase takes place when the sorbed molecules or atoms concentrated only at the interface. Thus the substances contained in a fluid phase is said to be adsorbed on a solid phase when its concentration in the boundary region is higher than that in the bulk of the fluid phase. The substance which is adsorbed is called adsorbate (metal ions) and the phase of boundary which adsorption occurs is called adsorbent. For adsorption to take place on the surface of an adsorbent it should have the larger surface area accessible to the adsorbate, preferential ability to take up the adsorbate. Large surface areas are available from substances which are both very porous and finely divided [31].

Adsorbents are usually highly porous materials and adsorption takes place primarily on the walls of the pores or specific sites inside the particle. The surface area available for some adsorbents may be as high as 2000 m^2/g. Activated carbon, activated alumina, molecular sieve and silica gel are widely used as adsorbents. When the adsorbent reaches its saturation capacity, the adsorbed material can be removed by the industrial methods such as displacement of adsorbate, desorption of the adsorbate, combustion of the adsorbate decomposition or radioactive decay of the adsorbate. If the combustion of the adsorbate is used in the operation it is called reactivation and when the displacement or desorption of adsorbate is used; the operation is called regeneration [11]

All the adsorption processes are exothermic. The heat of adsorption may be defined as the decrease in the heat content of the system. Adsorption on solid surfaces may be classified on the basis of the magnitude of the energy of adsorption [42].

van der Waals or physical adsorption refers to a process in which energy changes are very small. When the energy changes are greater the process is called chemisorption or chemical adsorption [31].

In case of physical adsorption, the adsorbate merely condenses in a thin film on the surface of the adsorbent. The forces which retain the adsorbate in this state are purely physical and are called as vanderwaals forces (weak). They are very weak molecular attractions and physically adsorbed substances are loosely bound. In chemical adsorption the adsorbate is much more strongly bound when compared to physical adsorption and the intermolecular forces of attraction are very strong. The heats of adsorption are in the same order of the magnitude as of the corresponding chemical reactions. The actual Chemical combination occurs between the adsorbed molecule and the active centre on the surface of the adsorbent [23].

Chemisorption plays an important role in Adsoprtion and Catalysis. In the physical adsorption the removal of adsorbed molecule can be very easy where as in chemical adsorption the removal of adsorbate is very difficult. Physical adsorption is usually instantaneous while chemical adsorption generally requires activation energy and in some cases it may be instantaneous [43].

The equilibrium between the concentration or partial pressure of the adsorbate in the liquid/fluid phase and the concentration of the adsorbate held by a particular adsorbent is called isotherm of the solute and adsorbent system at a given temperature. An adsorption isotherm is a plot of volume of gas adsorbed against partial pressure at various parameters of constant temperature. There are many equations which represent the equibrium adsorption data and of these two widely used are Freundlich equation and Langmuir equation. The Langmuir equation is theoretical, but does not hold for many substances. On the other hand, Freundlich equation is empirical and holds good in many cases where Langmuirs does not fit [3, 44, 45].

There are various types of equipments used for adsorption such as Fixed bed adsorbers, stirred tank adsorbers and continuous adsorbers. Fixed bed adsorbers are used for the adsorption of solvent vapours from gases, dehydration of gases and liquids, decolouring mineral and vegetable oils. Generally two beds are used. When one is in operation the other is regenerated. The bed length varies from 0.3 m to 1.3 m. The gas is fed downward through adsorbent particles in the bed. The superficial gas velocity various from 0.25 to 0.6 m/s. Inside the bed, the adsorbent particles are placed on a screen, or on a perforated plate. Up flow of feed is usually avoided because of the tendency of fluidization of the particles at higher rates [46].

When adsorption reaches the desired value, the feed goes to the other bed through an automatic valve (equipment inbuilt) and the regeneration process starts. Regeneration is usually carried out by steam, provided the solvent is immiscible with water. Sometimes it may takes place by hot inert gases. The hot gas or steam supplies the heat to the solid and the desorption process starts. The solvent is condensed to separate it from the water and dried before reuse. The bed is then cooled and dried by an inert gas though this is not done in all the cases. The adsorption cycle usually varies from 2 to 24 hrs. For a large bed, the adsorption cycle is high along with the pressure drop and capital cost. For a smaller bed the pressure drop is less but separation is incomplete and more energy is required for regeneration [47].

Stirred tank adsorbers are generally used for removing pollutants and heavy metals from industrial effluents. It consists of an cylindrical tank fitted with a stirrer or air sparger. The air sparger or stirrer keeps the particles in the tank in suspension. The adsorbent is powdered carbon which is added to the solution in the tank. Used carbon is removed by sedimentation or filtration. The mode of operation may be batch or continuous [4, 48, 49].

In the continuous absorber , the solid and fluid move through the bed counter currently and come in contact with each other through the entire apparatus without periodic separation of the phases. The solid particles are fed from the top and flow down through the adsorption and regeneration sections by gravity and then returned to the top of the column by an air lift or mechanical conveyor. The fine particles use multi-stage fluidized beds, in which the fluidized solids pass through down comers from stage to stage [48].

Adsorption may occur in two different ways according to the interactions of the adsorbent and adsorbate which are named as physical adsorption (physisorption or van der Waals) and chemical adsorption (chemisorption). The adsorption processes with nonspecific interactions are generally referred as physisorption. In chemisorption processes, electrons are shared or transferred between two phases. Since chemical bonds occur between the adsorbate and the surface of the adsorbent, new chemical compound is formed. As a result of this, interactions are very strong at the chemisorption processes with respect to the physisorption processes. Also only monolayer is observed in chemisorption and it is slower than the physisorption process [21].

Dispersion and short range repulsive forces, hydrogen-bonds and covalent bonds can be involved in adsorption processes. In addition, if the solid or the gas is polar in nature, there will be also electrostatic (coulombic) forces comprising dipole-dipole, dipole-induced dipole interactions.

Due to the specific interactions between adsorbate and adsorbent, the heat of adsorption of chemisorption is higher than physisorption and is observed in the short range. However, there are different heat of adsorption ranges for physical and chemical adsorption processes which varies from 10 to 40 kJ/mol and 40 to 800 kJ/mol, respectively [7], [50].

Adsorption of vapour on to a solid surface is a spontaneous in nature, so the overall free energy change for the process is negative. On the other hand, during the adsorption process, the adsorbing molecules lose a degree of freedom and their entropy decreases. From the thermodynamic relationship given in Equation it is obvious that for ΔG to be negative, ΔH should be negative. So, adsorption process generally becomes exothermic.

$$\Delta G = \Delta H - T\Delta S$$

However, endothermic trend can also be observed in some cases. For instance, due to the lateral protein-protein interactions and conformational changes in the adsorbed protein, adsorption becomes endothermic [51].

1.4.5.1 Physisorption

The fundamental interacting force of physisorption is caused by weak van der Waals force. Even though the interaction energy is very weak ($\sim$10 to 100 m eV) and physisorption plays an important role in adsorption system. van der Waals forces originate from the interactions/metal binding tendencies between induced and permanent or transient electric dipoles.

In contrast with chemisorption, in which the electronic structure of bonding atoms or molecules is changed and covalent or ionic bonds are formed where as physisorption can only be observed in the environment of low temperature (thermal energy at room temperature which is equal to 26 m eV) and the absence of the relatively strong chemisorptions. In practice, the type of a particular adsorption as physisorption or chemisorption depends principally on the binding energy of the adsorbent to the substrate or adsorbate [52].

The strength by which adsorbate molecules are attached/ bonded with the adsorbents determines the nature of adsorption. Normally the release of energy is in the range of 8 to 25 kJ/mole due to adsorption which is defined as physisorption and a much larger energy is required for the formation of chemical bonds which leads to chemisorption. There are always some exceptions (excluded from) these values. The prescribed value of energy differentiating physisorption and chemisorption are based on general experience.

When an adsorbed molecule receives energy equal to or higher than the energy of adsorption, it will leave the surface. This phenomenon is the reverse of adsorption and is called as desorption. When the number of molecules hitting the surface and staying there is equal to the number of molecules that are leaving or evaporating the surface of the system, it is said to be in equilibrium. All the atoms or molecules adsorbed on the surface do not have similar environment since distribution of free energy on the surface is not always smooth because of the differences in the energy of the molecular orbitals of the adsorbent and also due to other internal interactions [38, 50].

Physisorption is due to the absence of chemical bonds and the molecule retains its gas phase electronic structure, although some disturbances are still possible. The binding energy depends on the polarizability and on the number of atoms involved which varies between few milli eV for light gases and several eV for heavy metals and large organic molecules).

1.4.5.2 Chemisorption

Chemisorption is a kind of adsorption which involves a chemical reaction between the adsorbent surface and the adsorbate. New chemical bonds are generated at the adsorbent surface. The strong interaction between the adsorbent and the substrate (adsorbate) surface creates new types of electronic bonds [53, 54].

In comparison with physisorption, chemisorption leaves the chemical species of the adsorbate on surface to interact. It is conventionally accepted that the energetic threshold limit separating the binding energy of physisorption from that of chemisorption is equivalent to 0.5 eV per adsorbed species. Due to specificity, the nature of chemisorption can greatly differ, depending up on the chemical identity and the surface structure of the adsorbent [52]. In chemisorption, there is stronger perturbation of the molecular electronic structure with formation of chemical bonds along with the substrate molecules and the energies typically is of several eV.

1.5 Adsorbents

There are various types of adsorbents used for the heavy metal ion removal based on the functional groups present in the adsorbent-adsorbate system, nature of the solute-solvent system, bonding and attraction between the species. They are classified as natural adsorbents, biosorbents, agricultural adsorbents, etc [55]. The various adsorbents used in the adsorption process for the removal of metal ions such as mustard oil cake, agricultural waste like coconut husk, rice husk, neem barks, saw dust, orange peels. The combination of two or more adsorbents can also be used for the removal of metal ions.

Biosorbents that are used in the removal of heavy metal ions include micro-organisms, fungi, green plants or their enzymes. Heavy metal bio remediation involves removal of heavy metals from waste water and soil through metabolically mediated or physio-chemical pathways. Algae, bacteria and fungi and yeasts have proved to be the potential biosorbents in metal ion removal from the waste water [19, 56].

1.5.1 Selection of the adsorbent

The selection of a suitable adsorbent depends upon the characteristics and affinity of the adsorbate-adsorbent system. It was based on the facts which state that

- Chemisorption is significantly more specific than physisorption

- The higher the molecular weight, the stronger the retention of the adsorbent.
- Dynamic and steric effects may overhaul or to enhance the selectivity of the adsorbent.
- Inorganic sorbets (silica gel, alumina, molecular sieves, commercially available charcoal) are particularly suitable for dehydration and retaining the hydrophilic substances.
- Heavy metals are retained by activated and bone charcoal (blended Adsorbent)

Separation by adsorption depends on one or more components being more readily adsorbed than another based on their 'Atomic' size, 'Electro-Negativity'. The selection of a suitable process depends on the easiness with which the separated components can be regenerated or recovered. Adsorbents are readily available in the form of extruded pellets, formed spheres and irregular granules. The size signifies, the need to pack as much surface area as possible into a given volume of the bed and at the same time minimize the pressure drop for flow through the bed. Sizes of about 6 mm are commonly used as adsorbents. In this work, both the Activated Charcoal and Bone Charcoal are mixed in 1:1 ratio contributing high surface area from Activated charcoal and '-ve' charge from bone charcoal for the adsorption purpose [42]. Size of the mixed adsorbent was calculated using particle size analyser and found to be 572.2 nm.

1.5.2 Features of the adsorbent

The most important technical adsorbent's are Activated Charcoal and Bone Charcoal which are used for almost all duties. Typical requirements for commercial adsorbents are:

- High porosity and internal surface area
- High adsorption efficiency in a wide range of adsorbate concentrations
- Good balance between macro-pores (for very fast internal transport) and micro-pores (for large internal surfaces)
- Hydrophobic chemical structure (for treatment of moist and industrial gases separation) unless the adsorbent is to be used as a desiccant
- Thermal stability should be unaffected by a cyclic recovery / regeneration of the adsorbent
- Low pressure drop over the absorber bed
- Low cost for acquisition and eventually for the disposal of the adsorbent

1.5.3 Properties of the adsorbent

Some thermo-physical properties that are required for a good choice of adsorbent are high surface area, high adsorption capacity, quick response of adsorption capacity to temperature change, high thermal conductivity because of the blended nature, high mass diffusivity, thermal stability.

Adsorbent can be classified according to their pore sizes, nature of surfaces and structures and also based on large internal surface area. The surface area should be available through pores big enough to admit the molecules to be adsorbed. The adsorbent should be capable of being easily regenerated. It should not lose its adsorptive capacity through continuous recycling. The adsorbent should be mechanically strong enough to withstand and undertake the bulk handling system, vibrations that are encountered in any lab scale/ industrial units [57, 58].

1.5.4 Activated Charcoal

Carbon, Activated Charcoal and Granular Activated Carbon (GAC) are for the most part used for the removal of considerable metals, regular constituents and remaining disinfectants in water samples. This upgrades the taste and minimizes prosperity threats and also shields from other water treatment units such as reverse osmosis, membranes and ion-exchange pitches/resins from possible damage due to oxidation or organic fouling. Activated charcoal was a favoured and suitable adsorbent in water treatment method because of its multifunctional nature and the way that it adds nothing to the treated water. Most Activated carbons are made utilizing unrefined materials such as nutshells, wood, coal and petroleum and agricultural products [28, 59, 60].

Typical surface area for activated carbon is approximately 1000 m^2/g. However different raw materials produce different types of activated carbon and charcoal varying in hardness, density, pore and particle sizes, surface areas, extractable ash and pH. These differences in properties make certain carbons preferable over others in different applications [61, 62].

The two essential parts by which activated charcoal removes the contaminants from waste water through adsorption (diminishment/removal) of metal particles because of high surface area. Organics/metals are removed by adsorption and remaining disinfectants are removed by reactant removal[21, 63].

Activated Charcoal are carbonaceous solids with a specific surface structure. The surface of the activated carbon is generally non polar. However the surface oxide groups in the structure of the activated carbon makes the surface slightly polar. Therefore, although activated carbon has a hydrophobic surface, water can be adsorbed in oxygen containing sites.

Activated Charcoal has a high surface area and micro pore volume. Additionally the bimodal (infrequently trimodal) pore size appropriation empowers the adsorbate atoms to get accumulate /adsorb inside the strong effluent solution [64]. The property of large pore volume enables activated charcoal to adsorb on non-polar or weakly polar molecules more easily than other adsorbents. For example, equal weight of activated charcoal can adsorb methane twice that of zeolite 5A that can adsorb under the same conditions [65]. Since only non-specific in nature vander waals forces are available as the main force for adsorption, the heat of adsorption of activated charcoal is usually lower than the other adsorbents. Activated charcoal are available in different forms such as powders, microporous, granulated, molecular sieves and carbon fibers. The disadvantage of the carbon fibre is the low thermal conductivity which was as low as 0.0893 W/mK and is nearly acts as a insulating material [66].

1.5.5 Bone Charcoal

Bone charcoal is a black carbon material obtained by de blazing of animal bones at high temperatures of 1000^o C. Bone charcoal having the composition contains 10% carbon and 90% calcium phosphate, is fundamentally conveyed by warm/thermal treatment of bones. Essentially calcium phosphate in bone charcoal is in the hydroxyapatite structure. Bone charcoal has been extensively used in sugar refining industry to remove colour from sugar solutions. Very recent studies have used bone charcoal to adsorb radioisotopes of antimony and uranium particles from radioactive misuses /waste. Hydroxyapatite has the capacity to uproot inorganic cations while carbon can remove some organic compounds due to its significant alkaline/ basic properties. The composition of the Bone charcoal is Hydroxyapatite- 70 to 76%, Carbon - 9 to 11%, $CacO_3$ varies from 7 to 9%. The Total surface area varies from 267-283m ^{2}/g and the Carbon surface area varies from 50.6 to 58.3 m^2/g [67].

1.6 Thesis Organisation

Chapter 1 describes about the various sources and uptake of heavy metals and the available technologies that are applicable for the removal of heavy metal ions. A brief description of various type of adsorbents availability, selection and features of the adsorbent and factors that effect the performance of the mixed adsorbent were reported. A brief about the Cu (II) and Cd (II) metal ions and their effects, health issues and toxicity, physical and chemical properties, uses have been discussed.

Chapter 2 discuss about the literature review carried out in the past by various researchers using activated charcoal, bone charcoal, activated maize cobs, natural zeolites, agricultural absorbents, chemically treated absorbents, various types of biosorbents, plant absorbents, fruit peel absorbents, sawdust, biomass such as algae, fungi, nano-materials, bagasse, flyash, maizecobs, synthetic and commercially available adsorbents that were used for the removal of heavy metals such as Cu (II) and Cd (II), Ni, Pb, Cr etc.

Chapter-3 describes the materials and methodology used for this work, which gives an idea about characterization of the maize cob and mixed adsorbent, proximate and ultimate analysis of the mixed adsorbent, FTIR analysis, XRD analysis, pore size distribution of the mixed adsorbent, Bauner-Emmett-Teller (BET) Analysis.

The procedures for adsorption through batch studies has been carried out by synthetic solutions and industrial effluents using mixed adsorbent and maize cobs. Continuous column flow operations has been carried out using industrial effluents, synthetic solutions and the results were compared. Modeling studies emphasizes on batch isothermal modeling, thermodynamic modeling, intraparticle diffusion modeling and hydrodynamic modeling. The various kinetic modeling studies for batch and continuous mode in terms of pseudo first order model, pseudo second order model and Thomas model, Yoon-Nelson model has been studied.

Chapter-4 describes and explains about the significant results that were obtained from characterization procedures, batch study and column study as discussed in chapter-3. In batch studies the effect of various parameters such as pH, initial metal ion concentration, temperature, adsorbent dosage, agitation rate and contact time were presented for synthetic metal ion solutions. These results obtained were optimized and are used in the continuous flow operation to obtain the breakthrough curves for Cu (II) and Cd (II).

The results obtained in this studies were interpreted in terms of optimized parameters of the batch study, adsorption capacity (mg/g), % removal of copper and cadmium in batch (using industrial effluent, maize cobs, simultaneous removal of metal ions and synthetic solutions) and column studies (using industrial effluents, synthetic solutions). The equilibrium time for batch study experiments have been reported. Break through time, saturation time in column studies at different flow rates and bed heights have been reported for both the metals.

Comparison studies for industrial effluents and synthetic solutions have been reported for both batch and column operation. Comparison studies were reported for maize cob and mixed adsorbent in-terms of (% removal, adsorption capacity) in batch operation.

Simultaneous metal (copper and cadmium) ion removal studies have been carried out to know the interaction of the metal ions and the same data have been used for isothermal modeling using Langmuir and Temkin models.

XRD and pore size distribution for the mixed adsorbent before and after adsorption were carried out and the results were reported.

Intra particle diffusion studies have been carried out for both copper and cadmium using the data obtained from effect of agitation rate from the synthetic metal ion solution.

Similarly analysis of isothermal modeling (Langmuir,Temkin, Freundlcih models) have been done for the synthetic solution data obtained at different temperatures (effect of temperature) and the results were compared for copper and cadmium.

The analysis of thermodynamic studies have been carried out for both the metals at various temperatures (using the data obtained from effect of temperature using synthetic solution) and the results were compared in terms of regression analysis, Change in Gibb's free energy, Change in enthalpy, Change in entropy and equilibrium constant k_c).

The column study data obtained from the synthetic solutions for copper and cadmium have been used to calculate the various column parameters such as empty bed contact time, volume of solution treated at the breakthrough point, saturation point, breakthrough time, saturation time, sorbent exhaustion rate, total metal adsorbed in the fixed bed column (m_{ad}), total amount of metal ion sent through the column (m_{total}) and total % removal in column at different bed heights and volumetric flow rates.

Hydrodynamic behavior study was carried out from the synthetic solution data obtained and the various mass transfer parameters such as Sherwood number, Schmidth number, Reynolds number of the particle, Chilton-Colburn factor, mass transfer coefficient were calculated. A graph between ratio of $\frac{Sh}{Sc}$ vs Reynolds number has been plotted at different bed heights and volumetric flow rate and regression analysis was carried out which indicates that the column hydro dynamics gave a better fit with higher (R^2) values for the adsorption system.

Further the column studies have been done to find the effect of bed height / adsorbent dosage for copper and cadmium removal from the industrial effluents. The breakthrough curves were plotted for copper and cadmium at fixed volumetric flow rate of 10 ml/min and different bed heights (12cm, 24cm, 36cm); and fixed bed height of 36cm and different volumetric flow rates of (10, 20, 30 ml/min).

Comparison studies were made for industrial effluents and synthetic sample for both copper and cadmium in-terms of column performance parameters and the results were reported.

The mixed adsorbent % removal and uptake capacity were more due to high surface area and less particle size of the mixed adsorbent in comparison with maize cobs. In comparison between synthetic solutions and industrial effluents in batch and column, synthetic solution performance was more in terms of % removal for both copper and cadmium and it was due to the presence of other heavy metals, phenols, cresols, waste sludge present in industrial effluent.

Statistical analysis have been carried out at various optimized paramters (data obtained from synthetic solution) using Langmuir model equation by evaluating the the χ^2 test (χ^2 value) through the experimental and theoretical data of uptake capacity (mg/g) and there by suggesting the dominance of both copper and cadmium ion sorption mechanism as chemisorption rather than physisorption.

A detailed kinetic modeling of batch and column operation has been studied in terms of pseudo first order model, pseudo second order model, Thomas model and Yoon-Nelson model for both the metals using the data obtained from synthetic solution. The suitability of the models were reported based on higher regression or correlation coefficient R^2 values close to 1.

Chapter 5 describes about the conclusions obtained from various experimental, characterization and modeling studies which interprets the better isotherm model, thermodynamic model, intraparticle diffusion model, hydrodynamic model for copper and cadmium, % removal and uptake of copper and cadmium in batch studies for (synthetic solutions, industrial effleunts, maize cobs). In continous column studies the effect of breakthrough curves using synthetic solution and industrial effluents were reported and gives an about the various column performance parameters for both copper and cadmium.

It was finally concluded that mixed adsorbent was a suitable adsorbent material that can be used for the removal of Cu (II) and Cd (II) and these studies can be extended to various complex industrial heavy metals containing extremely high concentration range of 100-350 ppm.

The maize cob an agricultural biosorbent which is cheaply available gives competitive results with mixed adsorbent, but more % removal and adsorption capacities were reported for mixed adsorbent due to high surface area and less particle size.

CHAPTER 2

LITERATURE REVIEW

Advances in science and technology have brought progress and developments in many spheres of the society but in the process also contributed to the degradation of environment. Due to rapid industrialization and very little attention has been paid to the treatment of industrial effluents. Industrial pollution has been continued to be a major factor causing the degradation of the environment around us, affecting the water we use, the air we breathe and the soil we live on.

Man in his interest towards the development got addicted to various luxuries and comforts which have resulted in continuously increasing adverse impact on the environment adding to the already existing complexities of the nature. The efforts of removing pollutants from the natural environment have been unable to keep place with the increasing amount of waste materials and a growing population is further causing aggression to the situation. Due to this our ecological system was affected by significant discharge through several health hazards.

The trace metals present are divided into heavy metals and light metals on the basis of their densities. Light metals are those whose densities are less than 5 g/cm^3 and those metals having density greater than 5 g/cm^3 are called heavy metals [17, 61]. Trace metals are of environmental interest both as limiting nutrients and toxins. Toxic heavy metals include Cd, Hg, Ag, Pb, Sn and Cr. Although several nutrients metals, preferably, Zn, Cu, Ni, Hg, Cd [11] can also be extremely toxic at elevated concentrations. The industrial and domestic waste water, if not properly managed, was responsible for severe damage to the environment and adversely affecting the health of the people [11, 34].

The discharge of non-biodegradable heavy metals into water stream is hazardous because the consumption of polluted water causes various health problems. Waste streams containing heavy metals such as Cu, Ni, Pb, Cd,Fe and Cr are often encountered in various chemical industries. When copper, cadmium, iron enters the gastric system, epigastria pain, nausea, vomiting, severe diarrhoea, corrosion of skin, respiratory track and lungs carcinoma are noticed. These heavy metal ions when discharged into potable water sources like rivers etc. creates a large area stand exposed to the ill effects of these ions, most of which are carcinogenic. Their removal thus becomes an absolute necessity [68].

Among the various techniques available for the removal of heavy metals from industrial effluents the most commonly used are reduction followed by precipitation, use of ion exchangers and adsorption of inert adsorbents. Most of the methods suffer from the high capital and operational costs, difficulties in the treatment and disposal of the residual metal sludges. Although the treatment cost for precipitation-filtration methods is comparatively cheap, the treatment procedure is complicated due to the use of other chemicals. On the other hand, separation with ion exchangers and use of membrane technology is of a limited application especially in the developing countries due to high cost. It is worthwhile to develop an economical adsorbent for the removal of heavy metals from waste water effluents [69]. Generally the adsorbents used are usually in the form of spherical pellets, rods, mouldings or monoliths with hydrodynamic diameters between 0.5 to 10 mm. They must have high abrasion resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and hence high surface capacity for adsorption. The adsorbents must also have a distinct pore structure which enables fast transport of heavy metals, adsorbate particles, gaseous vapours In many countries water is becoming an increasingly scarce resource and planners are forced to consider any source of water which might be used economically and effectively to promote further development. The potential for irrigation to raise both agricultural productivity and the living standards of the rural poor has long been recognized and at the same time, with the population expanding at a high rate, the need for increased food production is apparent [70]. Irrigated land occupies approximately 17 per cent of the worlds total arable land but the production from this land is about 34 per cent of the worlds total production. So the effluent water coming from various industries have to be treated.

Adsorption technique for waste water treatment has received considerable attention for the development of an effluent clean and economical technology. In general, adsorption of inorganic and organic pollutants on the surface of the adsorbent are studied under various experimental conditions to optimize maximum removal. The heavy metals such as cadmium, chromium, copper, nickel, zinc, lead etc are present in the waste water from various industries such as metal cleaning and plating baths, refineries, paper and pulp, fertilizers and wood preservatives. The excessive intake of these metals by man leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, Central nervous problems followed by depression, gastrointestinal irritation and possible necrotic changes in liver and kidney [71, 72]

Effective methods for the removal of the copper are ion exchange, reverse osmosis, electrochemical treatment, evaporation and adsorption. As stated earlier the application of this process is limited due to the economic constraint. Adsorption is proven technology for the removal of Cu^{2+}, Cd^{2+}, Fe^{3+} ions from synthetic and real industrial effluents [73, 74].

There are various adsorbents used in the adsorption process for the removal of metal ions such as mustard oil cake, agricultural waste like coconut husk, rice husk, neem barks, saw dust, orange peels that are reported in literature. The combination of two or more adsorbents can also be used for the removal of metal ions. Bioremediation can be defined as any process that uses microorganisms, fungi, green plants or their enzymes to return the natural environment altered by contaminants to its original condition. Heavy metal bioremediation involves removal of heavy metals from waste water and soil through metabolically mediated or physic-chemical pathways. Algae, bacteria and fungi and yeasts have proved to be potential in metal removal from the waste waters.

2.1 Adsorption and Coagulation

At present a few coagulants has been utilized to remove the substantial metals in drinking water. As the flocculates formed by the hydrolysis of aluminium salts and ferric salts have no affinity to heavy metals, the research of special coagulants become a hot focus. Many investigators have developed some composite coagulants but up to now, only limited results were obtained [19, 75].

In the past study a sort of particles having (10-100 nm) of molecule size were shaped over the span of hydrolysis of tetra ethoxy-silane and these particles are adjusted by 3-mercaptopropyl and tetra-ethoxy-silane .The vast specific surface area of these particles gives more attractive nature propensity (tendency) of the adsorbate to adsorb on the dynamic's surface zones present on the adsorbent for the adsorption of substantial metal ions and it was initially utilized for the treatment of effluents polluted by Pb and Cr [15].

2.1.1 Various adsorbents for the removal of Cu (II) and Cd (II)

Removal of heavy metal pollutants at high concentrations from water can be readily accomplished by chemical precipitation or electrochemical methods. At low concentrations, removal of such pollutants is more effective by ion-exchange or adsorption on solid sorbents such as activated carbon [4, 76] and activated carbon prepared from rice hulls and coal fly ash [13, 77]. Some investigators have studied the removal of inorganic metal ions namely cadmium (II) and copper (II). The activated carbon from rice hulls has been used for separation of metals by adsorption [22, 30]. At present there is growing interest in using low-cost, commercially available materials for the adsorption of heavy metals [78].

A wide variety of materials are being used as low-cost adsorbents which are alternatives to expensive adsorbents such as maize cobs, corn waste powder, modified rice husk based adsorbents, sugarcane bagasse, fly ash, peanut husk, sawdust, wheat bran, palm kern shells, orange peels, natural zeolites such as clinoptilite, chemically modified chitosan beads, membrane adsorbents such as bipolymer materilas of hydro-gels, silica gels, and biosorbents such as alage, fungi etc are used in the adsorption and biosorption systems. [60, 79, 80].

2.2 Natural Adsorbents

Different characteristic adsorbents for the removal of Cu (II) has been discussed in the following sections.

Omar Abdel Salam, E. et.al [79] studied the adsorption behavior of some low-cost adsorbents such as Peanut Husk Charcoal (PHC), fly ash, and natural zeolite, with respect to Cu^{2+}, and Zn^{2+} ions, has been studied in order to consider its application to the purification of metal finishing wastewater. The batch method was employed: parameters such as pH, contact time, and initial metal concentration were studied. The influence of the pH of the metal ion solutions on the uptake levels of the metal ions by the different adsorbents used were carried out between pH 4 and pH 11. The optimum pH for copper and zinc removal was 6 in the case of peanut husk charcoal and natural zeolite, and it was 8 in case of fly ash. An equilibrium time of 2 hr was required for the adsorption of Cu(II) and Zn(II) ions onto peanut husk charcoal and fly ash and an equilibrium time 3 hr was required for the adsorption of Cu(II) and Zn(II) ions onto natural zeolite. Adsorption parameters were determined using both Langmuir and Freundlich isotherms, but the experimental data were better fitted to the Langmuir equation than to Freundlich equation. The results showed that peanut husk charcoal, fly ash and natural zeolite all hold potential to remove cationic heavy metal species from industrial wastewater in the order fly ash $<$ peanut husk charcoal $<$ natural zeolite.

Adsorption of heavy metals on conventional adsorbents such as activated carbon have been used widely in many applications as an effective adsorbent, and the activated carbon produced by carbonizing organic materials is the most widely used adsorbent. However, the high cost of the activation process limits its use in wastewater treatment applications [81]. Agricultural waste is one of the rich sources of low-cost adsorbents besides industrial by-product and natural material. Due to its abundant availability agricultural waste such as peanut husk, rice husk, wheat bran and sawdust offer little economic value and, moreover, create serious disposal problems. Activated carbons derived from peanut husk and rice husk have been successfully employed for the removal of heavy metals from aqueous solutions. The use of peanut hull carbon for the adsorption of Cu(II) from wastewater was studied by Periasamy and Namasivayam [82] and their comparative study of commercial granular activated carbon (GAC) showed that the adsorption capacity of PHC (Peanut Husk Charcoal) was 18 times larger than that of GAC.

Fly ash is a waste material that is produced from the combustion of coal in thermoelectric power plants [79]; many researchers have reused fly ash for wastewater or air pollutants control and studied the removal characteristics of heavy metal ions from aqueous solutions [79]. The adsorption characteristics of heavy metals using various particle sizes of bottom ash were reported by Shim et al. [14]. In another study, fly ash from a coal-fired power plant was used for the removal of Zn(II) and Ni(II) from aqueous solutions; it is proved to be effective as activated carbon at high dosages [79].

Natural materials locally available in certain regions can be employed as low-cost adsorbents due to their metal binding capacity. Zeolites are naturally occurring hydrated aluminosilicate minerals. Most common natural zeolites are formed by the alteration of glass-rich volcanic rocks (tuff) by fresh water in playa lakes or by sea water. The structures of zeolites consist of three-dimensional frameworks of Si^{4+} and AlO^{4+} tetrahedra. The fact that zeolite exchangeable ions are relatively innocuous (sodium, calcium and potassium ions) makes them particularly suitable for removing undesirable heavy metal ions from industrial effluent waters. The adsorption behavior of natural zeolite (clinoptilolite) with respect to Co^{2+}, Cu^{2+}, Zn^{2+} and $Mn^{2+}$was studied by Erdem et al. [83]. The results show that natural zeolite can be used effectively for the removal of metal cations from wastewater. Besides, the adsorption behavior of formulated zeolite portland cement mixture for heavy metals removal efficiency was studied as a substitute for activated carbon for wastewater treatment [84]. Other researchers have studied arsenic adsorption and phosphate ions adsorption from aqueous solutions on synthetic zeolites [85].

Low-cost adsorbents like peanut husk charcoal, fly ash and natural zeolite are effective for the removal of Cu^{2+} and Zn^{2+} ions from aqueous solutions. The batch method was employed; parameters such as pH, contact time, adsorbent dose and metal concentration were studied at an ambient temperature 27 °C. The optimum pH corresponding to the maximum adsorption of copper and zinc removal was 6 to 8. Copper and zinc ions were adsorbed onto the adsorbents very rapidly within the first 30 min, while equilibrium was attained within 2 to 3 hr for copper and zinc ions using different adsorbents. The Langmuir isotherm better fitted the experimental data since the correlation coefficient for the Langmuir isotherm was higher than that of the Freundlich isotherm for both metals [79].

Heavy metal pollution has become one of the most serious environmental problems nowadays. The removal of heavy metals from the environment is of special concern due to their persistence. Batch experiments were conducted to test the ability of activated carbon for the removal of lead, cadmium, nickel, chromium and zinc from water. The Langmuir and Freundlich adsorption isotherms were used to verify the adsorption performance. Nickel showed the highest removal percentages by activated carbon at all concentrations and the removal percentages decreased as the concentration of heavy metal increased. The obtained correlation coefficient (R^2) for different adsorbents suggested poor fitting of the experimental data to Langmuir isotherm for Cd, Pb, Ni, and Zn, while R^2 obtained using Freundlich model for different adsorbents indicated that it fitted the experimental data well. Silica/activated carbon (2:3) composite was more efficient in the removal of nickel ions than activated carbon and silica nanoparticles [86].

Mona Karniba et.al [87] described that activated carbon showed the greatest affinity towards nickel with 90 % removal percentage; the shifts in IR wave numbers reflected the bondings between AC and the adsorbed metals as presented by Freundlich isotherm. Silica/AC (2:3) composite showed the greatest removal percentage for 30 & 200 ppm nickel. SEM images revealed that AC was a micro particle with an average size of 25 μm, while silica were nanoparticles having an average size of 12 nm. Silica/AC (2:3) composite was the most effective micro-particle for nickel removal and it is highly recommended to be used in water treatment for its high adsorptive capacity followed by activated carbon and silica nanoparticles [87].

Innovative processes for treating industrial wastewater containing heavy metals often involve technologies for reduction of toxicity in order to meet technology-based treatment standards M.A. Barakat [35]. This literature gives the recent developments and technical applicability of various treatments for the removal of heavy metals from industrial wastewater. A particular focus is given to innovative physico-chemical removal processes such as; adsorption on new adsorbents, membrane filtration, electrodialysis, and photocatalysis. The main operating conditions such as pH and treatment performance are presented. However, in the near future the most promising methods to treat such complex systems will be the photocatalytic ones which consume cheap photons from the UV-near visible region. They induce both degradation of organic pollutants and recovery of metals in one-pot systems. On the other hand, from the conventional processes, lime precipitation has been found as one of the most effective means to treat inorganic effluent with a metal concentration of > 1000 mg/l. It is important to note that the overall treatment cost of metal-contaminated water varies depending on the process employed and the local conditions. In general, the technical applicability, plant simplicity and cost-effectiveness are the key factors in selecting the most suitable treatment for inorganic effluent.

Sorption actually describes a group of processes, which includes adsorption and precipitation reactions. Recently, adsorption has become one of the alternative treatment techniques for wastewater laden with heavy metals. Basically, adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/ or chemical interactions (Kurniawan and Babel et.al) [88]. Various low-cost adsorbents, derived from agricultural waste, industrial by-product, natural material, or modified biopolymers, have been recently developed and applied for the removal of heavy metals from metal-contaminated wastewater. In general, there are three main steps involved in pollutant sorption onto solid sorbent:

- The transport of the pollutant from the bulk solution to the sorbent surface.
- Adsorption on the particle surface and
- Transport within the sorbent particle

Technical applicability and cost-effectiveness are the key factors that play major roles in the selection of the most suitable adsorbent to treat inorganic effluent. Adsorption on modified natural materials Natural zeolites gained a significant interest, mainly due to their valuable properties as ion exchange capability. Among the most frequently studied natural zeolites, clinoptilolite was shown to have high selectivity for certain heavy metal ions such as Pb(II), Cd(II), Zn(II), and Cu(II) [83].

It was demonstrated that the cation-exchange capability of clinoptilolite depends on the pre-treatment method and that conditioning improves its ion exchange ability and removal efficiency [89]. The ability of different types of synthetic zeolite for heavy metals removal was recently investigated. The role of pH is very important for the selective adsorption of different heavy metal ions by using NaA zeolite for removal of Cr(III) at neutral pH [90], while Barakat et.al [91] used 4A zeolite which was synthesized by dehydroxylation of low grade kaolin. Barakat reported that Cu(II) and Zn(II) were adsorbed at neutral and alkaline pH, Cr(VI) was adsorbed at acidic pH while the adsorption of Mn(IV) was achieved at high alkaline pH values. Nah et al.[92] prepared synthetic zeolite magnetically modified with iron oxide zeolite (MMZ). MMZ showed high adsorption capacities for the Pb(II) ion and a good chemical resistance in a wide pH range 5 to 11. The natural clay minerals can be modified with a polymeric material in a manner that this significantly improves their capability to remove heavy metals from aqueous solutions. These kinds of adsorbents are called claypolymer composites [93]. Different phosphates such as calcined phosphate at 900 °C, activated phosphate (with nitric acid), and zirconium phosphate have been employed as new adsorbents for removal of heavy metals from aqueous solution [94].

Industrial by-products such as fly ash, waste iron, iron slags, hydrous titanium oxide, can be chemically modified to enhance its removal performance for metal removal from wastewater.

2.2.1 Sand

The removal of copper metal particles from liquid effluents using sand as an adsorbent was pondered. The substantial metal-sand adsorption marvels can be shown on the association's between surface practical gathering of silicates (sand) and the metal particles. It was predicted that sand can be utilized as a economical adsorbent for the expulsion of substantial metal ions from wastewater (containing low concentration of metals particles) particularly in the advanced or development nations [95].

2.2.2 Greensand

Several studies have been conducted [96] using green sands, another by-product from the iron foundry industry, for Zn(II) removal. Feng et al. [97] investigated Cu(II) and Pb(II) removal using iron slag. A pH range from 3.5 to 8.5 [for Cu(II)] and from 5.2 to 8.5 [for Pb(II)] was optimized. Fly ashes were also investigated as adsorbents for removal of toxic metals. Gupta et al. [98] explored bagasse fly ash, a solid waste from sugar industry, for Cd(II) and Ni(II) removal from synthetic solution at pH ranging from 6.0 to 6.5. Alinnor [99] used fly ash from coal-burning for removal of Cu(II) and Pb(II) ions. Sawdust treated with 1,5-disodium hydrogen phosphate was used for adsorption of Cr(VI) at pH 2. Iron based sorbents such as ferrosorp plus (Genc-Fuhrman et al.) [100] and synthetic noncrystalline akaganeite (Deliyanni et al.,) [101] were recently used for simultaneous removal of heavy metals. Ghosh et al.[102] and Barakat [35] studied hydrous titanium oxide for adsorption of Cr(VI) and Cu(II), respectively. Barakat [35] reported that the adsorbed Cu(II) aqueous species can undergo surface hydrolysis reaction as pH rises. This yields a series of surface Cu(II) complex species.

2.2.3 Natural Zeolite

The adsorption behavior of natural zeolites (clinoptilite) with respect to Cu^{2+} has been studied in order to consider its application to purity metal finishing wastewaters. The batch method has been employed, using metal concentrations in solution ranging from 100 to 400 mg/l. The results show that natural zeolites hold great potential to remove copper ions from industrial wastewater. This naturally occurring material provides a substitute for the use of activated carbon as adsorbent due to its availability and its low cost [103].

2.2.4 Cow Bone Charcoal

Jaun Carlos Moreno et.al [104] has worked on the removal of heavy metal ions such as Mn, Fe, Ni, and Cu from waste water using Cow bone charcoal. Two different adsorption models were used for analysing the data. Adsorption capacities were determined and copper ions exhibit the greatest adsorption on cow bone charcoal because of their size and pH conditions. Adsorption capacity varies as a function of pH. Adsorption isotherms from the aqueous solutions of heavy metal ions on Cow Bone Charcoal (CBC) were determined. Adsorption isotherms are consistent with Langmuir's isotherm model. Adsorbent quantity and immersion enthalpy were studied. At present, adsorption is widely accepted in environmental treatment applications throughout the world.

A number of low-cost agricultural wastes such as mud, tyre, rubber and fly ash have been used for the removal of metal ions. Other minerals and materials such as sodium calcium bentonite, peat, coal chitosan beads and bone char with potential for exchange of metal ions cadmium, copper and zinc have been tested [105]. Bone charcoal a mixed adsorbent containing around 10% carbon and 90% calcium phosphate is mainly produced by thermal treatment of bones. Structurally calcium phosphate is the main constituent of bone charcoal that is available in the hydroxyapatite form [106].

Bone charcoal has traditionally been used in the sugar refining industry to remove colour from sugar solutions. Recent studies have used bone charcoal to adsorb radioisotopes of antimony and europium ions from radioactive wastes [107]. Those authors suggested that chemisorption was the main operating mechanism for Eu^{3+} removal from the aqueous solution with a high degree of irreversible fixation on bone charcoal. They claimed that sorption is due to cation exchange of metal ions onto hydroxyapatite.

The adsorption of manganese, iron, nickel and copper ions from solutions onto bone charcoal in an agitated batch adsorber vessels was studied. This study gives an clear cut idea about the ability of bone charcoal to remove these metal ions from aqueous solution and therefore evaluate its potential to be used in waste water treatment systems.

The BET surface area of the prepared cow bone charcoal was found to be 283 m^2/g. Pore volume was found to be 0.28 cm^3/g. The mechanism of adsorption involves an ion exchange process and high copper capacity of 34.9 mg/g was achieved at relatively low surface area of 283 m^2/g. The mechanism of adsorption process was due to the involvement of calcium phosphate which not only acts as a source of adsorption but enables the ion exchange process. From the experiments it was concluded that the CBC (Cow Bone Charcoal) has the ability to retain Mn^{2+}, Fe $^{2+}$, Ni $^{2+}$, and Cu $^{2+}$ metal ions from aqueous solutions at the studied concentrations. Removal of heavy metal ions from aqueous solution was possible using Activated carbon obtained from Cow Bone Charcoal. It has observed that the adsorption took place for four metals within 25 minutes for the concentration levels studied. pH plays an important role in the adsorption process particularly in the adsorption capacity. The pH selected for an optimal rate of adsorption was 5.1 for all the metal ions investigated. The quantities adsorbed per gm of Cow Bone Charcoal (CBC) at equilibrium are 29.56 mg/g for Mn^{2+}, 31.43 mg/g for Fe^{2+}, 32.54 mg/g for Ni^{2+}, 35.44 mg/g for Cu^{2+}. The adsorption was described by an isotherm of type I and is fully matched by the Langmuir isotherm. The kinetics of the manganese, iron, nickel and copper adsorption on the CBC (Cow Bone charcoal) was found to follow Pseudo-Second order rate equation. This method has an additional advantage as it could be applied in developing countries due to low cost [104] .

2.2.5 Saffron Leaves

Shidvash Dowlatshahi et.al [108] has worked on the removal of copper, lead and cadmium from aqueous solutions by activated carbon prepared from saffron leaves.

Batch experiments were performed on real and synthetic samples at room temperature of 27 °C. The effect of pH, adsorbent dose, initial concentration and contact time were studied. The adsorption isotherms of the heavy metals were determined. The removal efficiency was evaluated on the basis of real/ industrial waste water.

The maximum removal efficiency of heavy metals (copper, cadmium and lead) by activated carbon adsorbent prepared from saffron leaves was obtained at pH 7. The amount of adsorbent used was 0.6 g, and the optimum contact time were 45 min each for copper and cadmium and 90 min for lead ion respectively. At these optimum conditions the removal efficiencies were 76.36%, 91.25% and 97.5%, respectively. The removal efficiencies of heavy metals from actual samples (copper industry and the battery industry) in the optimum conditions were 82.25%, 69.95% and 91.23% respectively. The results obtained showed the highest correlation with Langmuir isotherm model. Based on the results obtained the activated carbon produced from saffron leaves has a good capability in removal of the metal ions from the aqueous solutions.

2.2.6 Peat Hulls

Peat is a complex material with lignin and cellulose as major constituents. Lignin and humic acid bear polar functional groups such as alcohols, aldehydes, ketones, carboxylic acids, phenolic hydroxides and ethers that are involved in chemical bonding [72]. The sorbent capacity in the column was 0.028 and 0.025 m mol g^{-1} for copper respectively in mono and tri- component systems. A decrease in the adsorption capacity for copper (50%) was observed when dealing with the real effluents [109]. 90% of Cu (II) was removed at pH 4 [6].

2.3 Agricultural Adsorbents

Different agricultural adsorbents for the removal of heavy metals has been examined in this section.

2.3.1 Adsorption on modified agriculture and biological wastes, membrane materials and Hydrogels

Adsorption on modified agriculture and biological wastes (bio-sorption) Recently, a great deal of interest in the research for the removal of heavy metals from industrial effluent has been focused on the use of agricultural by-products as adsorbents.The use of agricultural by-products in bioremediation of heavy metal ions, is known as bio-sorption. This utilizes inactive (non-living) microbial biomass to bind and concentrate heavy metals from waste streams by purely physico-chemical pathways (mainly chelation and adsorption) of uptake [110]. New resources such as hazelnut shell, rice husk, pecan shells, jackfruit, maize cob or husk can be used as an adsorbent for heavy metal uptake after chemical modification or conversion by heating into activated carbon. Ajmal et al. [111] employed orange peel for Ni(II) removal from simulated wastewater. They found that the maximum metal removal occurred at pH 6.0. The applicability of coconut shell charcoal (CSC) modified with oxidizing agents and/or chitosan for Cr(VI) removal was investigated by Babel and Kurniawan [88]. Cu(II) and Zn(II) removal from real wastewater were studied using pecan shells-activated carbon (Bansode et al.) [112] and potato peels charcoal [113]. Bishnoiet al. [114] conducted a study on Cr(VI) removal by rice husk-activated carbon from an aqueous solution. They found that the maximum metal removal by rice husk took place at pH 2.0. Rice hull, containing cellulose, lignin, carbohydrate and silica, was investigated for Cr(VI) removal from simulated solution [115]. To enhance its metal removal, the adsorbent was modified with ethylenediamine. The maximum Cr(VI) adsorption of 23.4 mg/g was reported to take place at pH 2. Other type of biosorbents, such as the biomass of marine dried green alga (biological materials) [35] were investigated for up-taking of some heavy metals from aqueous solution. Some of the used alga wastes were; *Spirogyra species*, *Ecklonia maxima*,*Ulva lactuca*, *Oedogonium sp.*, *Nostoc sp* and *brown alga Fucus serratus* [35]. On the whole, an acidic pH ranging 2 to 6 is effective for metal removal by adsorbents from biological wastes. The mechanism of up-taking heavy metal ions can take place by metabolism-independent metal-binding to the cell walls and external surfaces [101]. This involves adsorption processes such as ionic, chemical and physical adsorption. A variety of ligands located on the fungal walls are known to be involved in metal chelation. These include carboxyl, amine, hydroxyl, phosphate and sulfhydryl groups. Metal ions could be adsorbed by complexing with negatively charged reaction sites on the cell surface.

Adsorption on modified biopolymers and hydrogels biopolymers are industrially attractive because they are, capable of lowering transition metal ion concentrations to sub-part per billion concentrations, widely available, and environmentally safe. Another attractive feature of biopolymers is that they posses a number of different functional groups, such as hydroxyls and amines, which increase the efficiency of metal ion uptake and the maximum chemical loading possibility. New polysaccharide-based-materials were described as modified biopolymer adsorbents (derived from chitin, chitosan,and starch) for the removal of heavy metals from the wastewater [116].

There are two main ways for preparation of sorbents containing polysaccharides: (a) crosslinking reactions, a reaction between the hydroxyl or amino groups of the chains with a coupling agent to form water-insoluble crosslinked networks (gels); (b) immobilization of polysaccharides on insoluble supports by coupling or grafting reactions in order to give hybrid or composite materials [116]. Chitin is a naturally abundant mucopolysaccharide extracted from crustacean shells, which are waste products of seafood processing industries.

Chitosan, which can be formed by deacetylation of chitin, is the most important derivative of chitin. Chitosan in partially converted crab shell waste is a powerful chelating agent and interacts very efficiently with transition metal ions [117]. Recently other modified chitosan beads were proposed for diffusion of metal ions through crosslinked chitosan membranes [118]. The excellent saturation sorption capacity for Cu(II) with the crosslinked chitosan beads was achieved at pH 5. Liu et al. [119] prepared new hybrid materials that adsorb transition metal ions by immobilizing chitosan on the surface of non-porous glass beads. Column chromatography on the resulting glass beads revealed that they have strong affinities to Cu(II), Fe(III) and Cd(II). Yi et al. [120] proposed the use of chitosan derivatives containing crown ether. The materials had high adsorption capacity for Pb(II), Cr(III), Cd(II) and Hg(II).

The materials can be regenerated and their selectivity properties were better than cross-linked chitosan without crown ether. The sorption mechanism of polysaccharide-based-materials is different from those of other conventional adsorbents. These mechanisms are complicated because they implicate the presence of different interactions. Metal complexation by chitosan may thus involve two different mechanisms (chelation versus ion exchange) depending on the pH since this parameter may affect the protonation of the macromolecule [116]. Chitosan is characterized by its high percentage of nitrogen, present in the form of amine groups that are responsible for metal ion binding through chelation mechanisms. Amine sites are the main reactive groups for metal ions though hydroxyl groups, especially in the C-3 position, and they may contribute to adsorption. However, chitosan is also a cationic polymer and its pKa ranges from 6.2 to 7. Thereby, in acidic solutions it is protonated and possesses electrostatic properties. Thus, it is also possible to sorb metal ions through anion exchange mechanisms. Sorbent materials containing immobilized thiacrown ethers were prepared by immobilizing the ligands into solgel matrix [121]. The competitive sorption characteristics of a mixture of Zn(II), Cd(II), Co(II), Mn(II), Cu(II), Ni(II), and Ag(I) were studied.

Hydrogels, which are crosslinked hydrophilic polymers, are capable of expanding their volumes due to their high swelling in water. Accordingly they are widely used in the purification of wastewater. Various hydrogels were synthesized and their adsorption behavior for heavy metals was investigated. Kesenci et al. [122] prepared poly(ethyleneglycol dimethacrylate-coacrylamide) hydrogel beads with the following metals in the order Pb(II) $>$ Cd(II) $>$ Hg(II); Essawy and Ibrahim [123] prepared poly(vinylpyrrolidone-co-methylacrylate) hydrogel with Cu(II) $>$ Ni(II) $>$ Cd(II); while Barakat and Sahiner [124] prepared poly(3-acrylamidopropyl)trimethyl ammonium chloride hydrogels for As(V) removal. The removal is basically governed by the water diffusion into the hydrogel, carrying the heavy metals inside especially in the absence of strongly binding sites. Maximum binding capacity increases with pH increase to > 6 [35].

2.3.2 Saw dust

Sawdust *Dalbargia sissoo* as the adsorbent was used for the removal of copper metal ion particles from mechanical or industrial wastewater. The effects of contact time, pH, Metal ion concentration and temperature have been inspected. The probable mechanism of copper (II) adsorption at solid-solution interface was predicted as ion-exchange and covalent binding of metal ions [125].

2.3.3 Pine Fruit

The pine fruit was used as solid adsorbent for the removal of copper ions from aqueous solutions through batch equilibrium technique. The influence of contact time, pH of the solution and initial concentration on the adsorbed amount of metal ions were investigated. Adsorption of copper ions was dependent on pH and the results indicate that the optimum pH for the removal of Cu^{+2} was 7.0. The highest adsorption capacity was found to be 14.1 mg of copper ion per gram of adsorbent at initial concentration of 57.6 mg/l of copper ions. Copper ion removal was observed to be 94.1-96% with the studied metal ion concentration [24].

2.3.4 Rice Husk

Rice husk is less costly adsorbent as compared to activated carbon or synthetic ion-exchanger and is available in abundant quantity for heavy metal ions.Various modifications on rice husk have been reported in order to enhance adsorption capacities for copper ions removal and other pollutants. Batch studies were conducted to find out the optimum dose of adsorbent, optimal pH and contact time for individual metal solution. It was found that the equilibrium was attained after 40 min for Cu and the maximum removal efficiency was attained at a pH of 7 for Cu. Copper (II) ions adsorbed on rice husk which was extracted from rice husk cellulose was heated to 300 °C (RHA 300) and rice husk heated to 500 °C (RHA 500) and these were investigated in order to understand the mechanism of adsorption.

The adsorption of copper on rice husk ash was studied by using batch technique. The quantities of copper metal before and after the treatment of their standard solutions with rice husk ash were determined by atomic absorption spectrophotometer. Percentage adsorption was calculated for Rice Husk Activated Carbon-Copper solution system. The effects of various parameters, such as pH of the solution, contact time, temperature and adsorbate concentration were studied. It was observed that adsorption of copper increased with increasing contact time, temperature, pH and decreased with increasing adsorbate concentration. The utility of rice husk ash as an adsorbent for copper metal ions from acid mine water was tested. Study from Chockalingam et al. [126] revealed that about 95% Cu^{2+} uptake was achieved from acid mine water, with increase in pH value by two units using rice husk as adsorbent.

Adsorption behaviour of Ni(II), Zn(II), Cd(II) and Cr(VI) on untreated and phosphate-treated rice husk (PRH) showed that adsorption of Ni(II) and Cd(II) was greater when PRH was used as an adsorbent. Sorption of Cd(II) was dependent on contact time, concentration, temperature, adsorbent doses and pH of the solution. The Langmuir constants and thermodynamic parameters have been calculated at different temperatures. It was found that recovery of Cd(II) from synthetic wastewater by column operation was better than a batch process [127].

2.3.4.1 Removal of Cadmium in the packed bed column with rice husk

Sunil J. Kulkarni et.al [74] has worked on the removal of Cadmium in the packed bed column with low cost adsorbent. In this literature review removal of cadmium from the effluent using rice husk adsorbent was studied in packed bed column with respect to various parameters like initial concentration, adsorbent dose, bed height and pH. Also the solute uptake data was analysed for first and second order kinetic equations by varying these parameters. The effect of these parameters on kinetics of solute uptake was reported.

It was observed that with increase in initial concentration from 10 mg/l to 50 mg/l, the exhaustion time decreased from 830 min to 570 min and break through point time decreased from 330 minutes to 120 minutes. Also with increase in flow rate the exhaust time and break through time decreased significantly. The alkaline conditions favoured the adsorption with optimum pH of 6. The exhaustion and break through delayed with increasing bed height. The kinetics of cadmium removal was affected by initial concentration and flow rate.

The optimum bed height, initial concentration, flow rate and pH values reported were 50 cm, 30 mg/l, 60 ml/min and 6 respectively. The adsorption efficiency was estimated to be 69% for optimum values of pH, initial concentration, bed height and flow rate [73].

2.3.5 Palm kernel shell prepared from activated carbon

A series of batch experiments were conducted in order to investigate the feasibility of Elais Guineensis kernel or palm kernel shell (PKS)-based activated carbon for the removal of copper from aqueous solution by the adsorption process. Investigation was carried out by studying the influence of initial solution pH, adsorbent dosage and initial copper concentration . All batch experiments were carried out at a constant temperature of 30°C using mechanical shaker which was operated at 100 rpm. It was also investigated that up to 95% copper (II) removal was obtained in concentration below 4 x 10^{-4} M (68.216 mg/l) and about 85% removal was achieved in the concentration range between 4 x 10^{-4} M to 1 x 10^{-3} M by (PKS)-based Activated Carbon [128].

2.3.6 Wheat Straw and Wheat Bran

Citrus concentrate fictionalizing wheat straw was inspected as an adsorbent for copper particles removal from liquid effluents. Most noteworthy removal was seen at pH 4-5. 96% copper were removed from metal ion solution using wheat straw [129].

The adsorption of copper (II) ions on to dehydrated wheat bran (DWB) a by-product of the flour process, was investigated as a function of initial pH, temperature, initial metal ion concentration and adsorbent dosage. The percent adsorption of copper (II) ions by dehydrated wheat bran was 96.4% due to increase in the surface area of the wheat bran resulting in acid treatment while 12% of the copper (II) ions in solution were removed by using the raw wheat bran at optimum adsorption conditions [130].

2.3.7 Orange peel

The removal of copper was studied by using orange peel as adsorbent. High percentage rate of removal was observed at lower concentration of copper for all the adsorbents but the uptake of copper by unit weight of the adsorbent was same. The equilibrium was attained at 7 minutes for the adsorbent [131].

2.4 Removal of cadmium from aqueous solutions using Bagasse

P. Akhila Swathanthra et .al, [132] has worked on the removal of cadmium from Aqueous Solutions using bagasse as a potential adsorbent. The main parameters influencing cadmium metal adsorption on bagasse are initial metal ion concentration, amount of adsorbent, temperature and pH of solution. The maximum percent metal removal was obtained after 3 hrs. Batch experiments results showed that the adsorptive capacity of bagasse was 17.73 mg/g at pH 4. The Langmuir isotherm and Freundlich isotherm model were used to describe the adsorption equilibrium of cadmium on bagasse. The both isotherm constants for Cadmium on bagasse were determined and the goodness of fit was obtained for Langmuir and Freundlich adsorption isotherms from the equilibrium adsorption data. The adsorbent can be effectively regenerated using 0.1N strong acid and reused.

This literature study indicates that bagasse has rapid adsorption rate and good adsorption capacity for cadmium. The use of these low-cost adsorbents was recommended since they are relatively cheap or of no cost, easily available, regenerative and show high affinity for heavy metal ion removal. The process of adsorption requires further investigation in the direction of modelling, regeneration of adsorbent for enhanced efficiency and recovery. The cadmium adsorption was found to be dependent on agitation time, pH and contact time, temperature. The adsorption of cadmium was found to be fitted the Langmuir isotherm model, which suggests the monolayer coverage of adsorbent surface.

This literature work proved that bagasse could be used as a good adsorbent material for cadmium removal from dilute aqueous solution. Taking into account bagasse was readily obtained as a waste product from sugar industries .This material can be used as as a low cost adsorbent and environmental friendly alternative material for the treatment of heavy metals [133, 134].

Flaviane Pereira.V et.al, [135] study aims in investigating the removal of zinc (II) from aqueous single metal solution and electroplating wastewater using sugarcane bagasse and wood sawdust chemically modified with succinic anhydride [135]. Many efforts have been made recently to find cheaper and effective methods and materials for water pollution control [136, 137]. Among these methods, adsorption is by far the most versatile and widely used for the removal of different pollutants [138] from water and wastewater. One of the most popular adsorbent are the lignocellulosic materials, because they are natural materials available in large quantities that can be a byproduct of industrial wastes [139, 140]. These materials, including wood sawdust [140, 141] sugarcane bagasse, coir pith [142], peanut shells [143], corn cobs [144], olive cake [145], and chemically modified cellulosic materials [139, 146] show great potential for water treatment. Surface modification of such low-cost materials has become a solution to improve the adsorption capacity of cellulosic materials, and for this many methods have been developed [139], [147, 148] have recently reported the use of sugarcane bagasse modified with succinic anhydride for removal of Cu (II), Cd (II) and Pb (II) from aqueous solutions, resulting in an increase of metal adsorption by new material containing carboxylic acid functional groups introduced in the fiber.

2.5 Biosorbents

This section deals about the various living and non-living biosorbents that are used for the metal ion removal.

2.5.1 Biosorption of metallic ions from solutions by live or died biomass

The bio-sorption (sorption of metallic ions from solutions by live or dried biomass) offers an alternative to the remediation of industrial effluents as well as the recovery of metals contained in other media [86]. Biosorbents are prepared from naturally abundant and/or waste biomass. Due to the high uptake capacity and very cost-effective source of raw materials, biosorption is a progression towards a perspective method [86]. These agricultural byproducts are capable of binding to heavy metals by adsorption, chelation and ion exchange. Several sorbents which can be used includes bacterial and algal [149] fungal biomass, biopolymers, sunflower stalks, maize cob and husk, chitosan and n-carboxy-methyl chitosan, chemically modified and unmodified cassava waste. The use of many other sorbents is under study in our laboratory, which include coconut fiber, sugarcane bagasse, tiger nuts waste biomass, great-millet and cocoa pod waste biomass [149].

2.5.2 Non-living biomass as adsorbent

Various types of biological materials such as non-living biomass of algae, aquatic ferns and seaweeds, waste biomass originated from plants have been investigated as efficient biosorbents. *Claymperes Delessertti* (moss) was used for the adsorption of copper from aqueous solution [150].

2.5.3 *Cercis siliquastrum L.* leaves

The ability of *Cercis siliquastrum L.* leaves for the adsorption of Cu (II) ions was studied. The effects of different parameters such as contact time of biosorbent and sorbents, pH of metal solution, and initial metal ion concentration on the adsorption were investigated. The maximum adsorption of copper ions was obtained at pH 4. Increasing the initial metal concentration at lower values caused a steep growth in adsorption, which was not observed in higher values [128].

Esteves et al.[151] used a waste biomass *Sargassum sp.* (brown macroalga) from an alginate extraction industry from Rio de Janeiro, Brazil to cleanup metals in wastewater via biosorption. Biosorption is sorption of metals onto biological materials. It could become an alternative way to remove toxic and recover precious metals from industrial discharge. In this work, the ability of *Sargassum sp.* to remove cadmium and zinc from a real effluent was investigated as well as its suitability to be reused in several consecutive metal adsorption desorption cycles were investigated. The results showed that it could biosorbed 100% of Cd^{2+} and 99.4% of Zn^{2+} from 3 and 98 mg/l industrial discharge at pH 4.5 respectively, using HCl, $CaCl_2$, and NaOH, as adsorbent-desorbent. On the other hand, when $CaCl_2$ was used as desorbent, the metal removal efficiency after the first cycle can achieve recovery at about 40%. The potential for metal recovery suggests that *Sargassum sp.* based adsorption can be used as an alternative treatment method.

2.5.4 Removal of heavy metals from waste water using membrane

Kosarek [152]found that efficiencies of removal of As, Cd, Cu, Pb, Hg, Ni, Se and Zn were 75-98%. The results also showed that for water treatment with polymer prior to chemical treatment, the percentage removal increased to 90-99%. Fane [153] informed the results from the recovery of heavy metals from wastewater using three systems, nanofiltration, ultrafiltration coupled with ion exchange resin and liquid membrane contractor. Fane found that nanofil-tration can remove all heavy metals in one step, the second system gave high efficiency of filtration but was more suitable for batch process, and the last method had the problem of phase leakage.

Adsorption for wastewater treatment has been extensively studied and practiced method. It can selectively used for removal of certain pollutant by selection of suitable adsorbent. The used adsorption has to be discarded after it becomes exhausted. Commercial adsorbents can be regenerated and reused. The disposal of adsorbent is again solid treatment and disposal problem. The maximum regeneration and reuse is advised in order to make the operation environmental friendly. The past investigations aim at explore the possibility and effectiveness of low cost adsorbent regeneration. The results indicate that cadmium desorption up to 25.1 and 26.03 is possible for Ground nut shell activated carbon and Rice husk Activated carbon adsorbents respectively. The results indicates that there is need to study desorption of cadmium and explore more economical and effective option for adsorbent regeneration [154].

De-Kui Bai et.al [155] describes an experimental study for the removal of copper ions from electroplating wastewater. Different metal ions are added to the wastewater to remove copper ions by coprecipitation and the copper-based supramolecular materials with layered structures are obtained. It is found that the best results are obtained with the addition of Mg^{2+},Al^{3+} mixture with ratio of $3:1$, pH = 10, and aging for 1 day at 60 °C. With these conditions, the residual copper in the electroplating wastewater satisfies national emission standards and wastewater handling capacity of up to 30 ml can be achieved. The properties of the copper-based supra molecular materials prepared under these optimal conditions are characterized. The results show that the materials have a layered structure and good thermal and structural stability and achieve a saturated adsorption of iodide ions of 41.23 mg/g. Conclusions from the above study reveals that Mg^{2+},Al^{3+} coprecipitation is effective at reducing the content of copper in electroplating wastewater so that the residual copper is in conformity with national emission standards. The copper is removed as Cu,Mg,Al layered double hydroxides are formed by reaction between $Mg^{2+}Al^{3+}$ and Cu^{2+}. The Cu Mg Al layered double hydroxides have typical layered structures, good thermal and structural stability, and good adsorption capacity for removal of metal ions.The results of this study are significant for environmental pollution control applications, and further investigations will consider whether the method can be applied to other inorganic metal ions and to the treatment of organic liquid wastes [155].

2.6 Maize cobs

Maize cob readily available was used as sorbent for the removal of lead ions from aqueous media. Adsorption studies were performed by batch experiments as a function of process parameters such as sorption 500 ppm, 2.5g, 400 minutes, 400 rpm and 5 pH in terms of Concentration, Dosage, time, rpm, and pH. I have found that the optimized parameters are Freundlich model fits best with the experimental equilibrium data among the three tested adsorption isotherm models. The kinetic data correlated well with the Lagergren first order kinetic model for the adsorption studies of lead using maize cob. It was concluded that adsorbent prepared from maize cob as to be a favorable adsorbent and easily available to remove the heavy metal lead (II) is 95 % and can be used for the treatment of heavy metals in wastewater [156].

This literature study shows that chemically treated maize cob is an effective adsorbent for the removal of lead ions from aqueous solutions. The adsorption process is a function of the adsorbent and adsorbent concentrations, dosage, time, rpm and temperature. The maximum percentage removal was increased from 50 to 95%. Equilibrium was achieved practically in 2 hrs. The equilibrium adsorption data are satisfactorily fitted in the order: Langmuir $>$ Temkin $>$ Freundlich, in the case of lead ions. The adsorbent proved to be very effective on industrial waste water, waste water from a leather industry in Vellore, Tamil Nadu was collected and was tested for the presence of lead. It was found to contain 0.96 mg/l of lead. And after treating the effluent with the bioadsorbant, it was found to remove 95% of lead from the waste water.

The adsorption of Nickel (II) on Maize cob has been studied using atomic absorption spectroscopy for metal estimation. Parameters like heavy metal concentration, adsorbent dose, contact time and agitation speed were studied. Langmuir and Freundlich isotherms were employed to describe adsorption equilibrium. Maximum amount of nickel adsorbed as evaluated by Freundlich isotherm. Study concluded that Maize cob, a waste material, have good potential as an adsorbent to remove toxic heavy metal like nickel from industrial waste water.

It is found that maize cob which is cheap and available in abundance locally is the most economical among all the developed low cost adsorbents and much cheaper than activated carbon interms of cost and availability of biosorbent. The result is not only important for the industries but also to the planet earth in general due to the resultant social and environmental benefits. To conclude, instead of chemicals, nonhazardous agro-waste materials like maize cobs can be used as heavy metal removers from wastewaters and industrial effluents to overcome water pollution. [156].

Maize is widely believed to have the greatest potential among food crops for attaining the technological breakthroughs that will improve food production (Smith et. al)[157]. Almost all the different uses of maize dispose of the cobs. The cobs were therefore used as potential adsorbents for Pb^{2+} removal from wastewater particularly since conventional methods are expensive. Maize cob was used as an adsorbent in order to evaluate its potential for the removal of lead from aqueous solutions and effluents from battery and paint industries with Dowex (synthetic resin) as control. Experimental data were analyzed in terms of Freundlich isotherm model. Equilibrium was attained at 2 h and adsorption rate constants for maize cob and dowex were 7.26 x 10^{-2} and 7.58 x 10^{-2} min^{-1}, respectively. Equilibrium pH value was 6; shaking at 150 rpm enhanced adsorption with maximum adsorption by both adsorbents in battery and paint effluents. Optimal weight at equilibrium for the adsorbents in Pb^{2+} solution was 16 mg/g of solution. Pb^{2+} removal by maize cob from battery effluent was 99.99% while it was 47.38% for Dowex. Corresponding values from paint effluents were 66.16 and 27.83%. The study concludes that maize cob has great potentials to remove Pb^{2+} from industrial effluents.[158]

Two adsorbents maize cob *(Z. mays)* and dowex (a synthetic adsorbent) were used to bind Pb^{2+} from standard aqueous solutions. Effects of adsorbent weight, Pb^{2+} concentration, contact time and pH were assessed to determine equilibrium conditions for adsorption. Adsorption rate constant for both adsorbents were comparable to those of previous studies and both fitted well into Freundlichs adsorption isotherm. The implication of this is that adsorption processes occurred on nonuniform surfaces; hence, adsorbents were multi-layered such that percentage adsorption will increase as long as concentration increases. Comparative assessment of shaken and unshaken experiments revealed that shaking enhanced percentage adsorption by both adsorbents except maize cob at 60 min. Since maize cob have the potential to remove Pb^{2+} from aqueous solutions and industrial effluents, it implies that it may also decontaminate wastewater containing other divalent metal ions such as Zn^{2+}, Cd^{2+}, amongst others. There is therefore the need for more extensive research on possibility of removing such metals using other crop residues since typical wastewater contain mixed metal ions. This may increase the extent of use and applicability of the residues in wastewater remediation[158].

Heavy metals rank as major environmental pollutants. Industrial wastewater effluents carry admixtures of these heavy metals. The competitive adsorption of Zn^{2+}, Cd^{2+} and Pb^{2+} metal ions from aqueous and non-aqueous solutions by unmodified and modified maize cob and husk was investigated. The results showed that maximum adsorption occurred at 495.9 mg/g for Zn^{2+} ion, 456.7 mg/g for Pb^{2+} ion and 493.7 mg/g for Cd^{2+} ion without modification. The adsorption in a mixture of the metal ions caused a leveling effect on the adsorption capacity of the maize cob and husk. The adsorption efficiency of each metal ion was influenced by the presence of other metal ions, presence of non-aqueous solvent and modification by carboxymethylation. The study significantly reveals the presence of other heavy metals and chemicals as design parameter in the treatment and management of heavy metal pollutants using cellulosic materials [159].

The economic feasibility of low cost adsorbents over activated carbon is estimated in this literature study. It is found that maize cob which is cheap and available in abundance locally is the most economical among all the developed low cost adsorbents, and much cheaper than activated carbon. The result is not only important for the industries but also to the planet earth in general due to the resultant social and environmental benefits [160].

The literature focuses on the use of corn cob as an effective and efficient adsorbent for the removal of Ni (II) from aqueous solution. The influence of Physico-chemical parameters such as adsorbent dosage, contact time, pH and initial concentration has been examined in batch studies. The initial and residual concentration of Ni (II) was analyzed using UV- Double beam absorption spectrophotometer at 394 nm by which the percentage removal can be calculated. The equilibrium data onto the adsorption of Ni (II) was measured using Langmuir and Freundlich isotherm model. The results revealed that Corn cob, a waste material have good potential as an adsorbent for the removal of toxic heavy metal like Ni (II) from Industrial waste waters [161].

The adsorption using agro-based plant waste consists of lignocellulosic materials that are found to be cost effective, eco-friendly and easy alternative in removing the heavy metals. The present study is aimed for the adsorption on agro industrial waste corn cob as a function of adsorbent Dosage, contact time, pH and Initial concentration then the equilibrium data for adsorption studies is explained by Langmuir and Freundlich isotherm model.[161].

This study shows that corn cob was an effectual biosorbent for the adsorption of Ni (II) ions from the aqueous solution. From the studies, the consumption of Ni (II) ions by the biomass was increased with increasing metal ion concentration. The maximum removal percentage was 70.08 % to 6 g of adsorbent and further addition of adsorbent did not cause any change in the removal efficiency. The higher percentage removal of Ni (II) at pH 6 was 71.01 % that shows the removal efficiency is minimized due to H^+ and OH_- ions present in the solution. The equilibrium agitation time for the percentage removal was 70.9 % at an optimum time of 90 min that reveals Ni (II) removal increases with an increase in the agitation time. On varying the concentration of the Ni (II), the maximum and minimum removal percentage of Ni (II) on to the adsorbent was 86.08 % for 25 ppm and 67% for 150 ppm which shows up the percentage removal is maximum at lower concentration. Adsorption Isotherms were studied using Langmuir and Freundlich model for the adsorption studies. This type of non- Hazardous agro-waste materials like corn cob appears to be low cost, eco- friendly and easy alternative instead of using chemicals for the removal of Heavy metals to overcome environmental pollution [161].

The literature [162] takes up the study of adsorption of heavy metal in an effluent from a paint industry using chemically activated maize cob as adsorbent was aimed at removal of Pb^{2+} contaminants from lead based paint effluent. The results of production, characterization and adsorption studies showed that activated maize cob with surface area of 1195.12 m^2/g and pore volume of 1.28 cm^3/g was achieved at 500 °C and 90 ml concentration by volume of phosphoric acid and zinc chloride as activating agents. It was observed that sample was being activated by agents and the volume was diluted from 50 to 120 ml at 500 °C gave the optimum value for characteristic performance in adsorption of Pb ions from effluent. Langmuir isotherm model, pseudo- first order kinetic equations were fitted with generated data. The Langmuir and pseudo- first order model fitted favourably with a correlation coefficient of 0.98 and a rate constant of 0.00104 $mgg^{-1}min^{-1}$ [162].

The carbon from corn cob is an effective adsorbent for removing heavy metals such as $Pb^{2+}$from paint effluent. However from the above study, it can be concluded that activated carbon with pore volume of 1.28 cm^3/g and surface area of 1195.12 m^2/g can be produced from corn cobs. For phosphoric acid / $ZnCl_2$ activation it is advantageous to soak the corn cobs at lower temperature because of the soft nature of the precursor. Also temperature of activation was varied from 450 500 °C and an acid concentration by volume of 70 ml and 90 ml is appropriate for getting high pore volume and surface area. In this case 500 °C and 90 ml acid concentration gave optimum values [162].

The adsorptive capacity of the developed carbon depends on the activation process which has impacts on pore size, pore volume and surface area. An adsorption capacity of 4.866 mg/g was achieved with an acid concentration of 50 mg/l. From the isotherm plot, it was observed that Langmuir plot fitted the generated data with R_L of 0.98. A pseudo-first order kinetic model with a correction factor R^2 of 0.942, and a rate constant of 0.00104 $mgg^{-1}min^{-1}$ and a standard deviation of 0.0065 were achieved as in contrast to second order model of 0.073. Therefore, a pseudo-first kinetic model is preferred to pseudo-second model for the kinetics of sorption for Pb^{2+} adsorption. The carbon with higher pore volume and surface area was found to be more effective in removing these heavy metal ions [162].

The removal of poisonous Pb (II) from wastewater by different low-cost abundant adsorbents was investigated. Rice husks, maize cobs and sawdust, were used at different adsorbent/metal ion ratios. The influence of pH, contact time, metal concentration, adsorbent concentration on the selectivity and sensitivity of the removal process was investigated. The adsorption efficiencies were found to be pH dependent, increasing by increasing the solution pH in the range from 2.5 to 6.5. The equilibrium time was attained after 120 min and the maximum removal percentage was achieved at an adsorbent loading weight of 1.5 gm. The equilibrium adsorption capacity of adsorbents used for lead were measured and extrapolated using linear Freundlich, Langmuir and Temkin isotherms and the experimental data were found to fit the Temkin isotherm model [163].

Removal of the poisonous lead ions from solutions was possible using rice husk, maize cobs and sawdust as adsorbents. Rice husk was the most effective, for which the removal reached 98.15% of Pb at room temperature. The sorption process nevertheless proceeded in two distinct phases. The rates of adsorption were fast initially, and then the rate of metal removal declined appreciably as contact time increased before attaining equilibrium. The fast-phase sorption may be explained as the passive uptake through physical adsorption, or the biosorbent surface ion exchange [164]. Since the adsorption phenomenon characteristically tends to attain instantaneous equilibrium and many agricultural wastes act as natural ion exchange agents. It is also relevant to point out that since active sorption sites in a system is a fixed number and each active site can adsorb only one ion in a monolayer (Langmuir) [165] the metal uptake by the sorbent surface will be rapid initially, slowing down as the competition for decreasing availability of active sites intensifies by the metal ions remaining in solution. The rate of metal removal is of greatest significance for developing a natural adsorbent-based water-treatment technology. The optimum pH for removal was found to be in the range from 4.5-6.5, at which Pb removal reaches 99% for the three investigated adsorbents. The effect of pH can be explained the availability of negatively charged groups at the biosorbent surface is necessary for the sorption of metals to proceed which at the highly acidic pH 2 is unlikely as there is a net positive charge in the system due to H^+ and H_3O^+. In such a system H^+ compete with metal ions [115] resulting in active sites to become protonated to the virtual exclusion of metal binding on the biosorbent surface. This means that at higher H^+ concentration, the adsorbent surface becomes more positively charged thus reducing the attraction between adsorbent and metal cations. In contrast, as the pH increases, more negatively charged surface becomes available thus facilitating greater metal uptake [166].The optimum pH for lead removal was found to be 4.5. The percentage uptake was found to be highly dependent on the initial concentration of the sorbate and sorbent fractional adsorption becomes dependent on initial concentration. For fixed adsorbent dose, the total available adsorption sites are limited thereby adsorbing almost the same amount of sorbate thus resulting in a decrease in percentage removal of the adsorbate corresponding to an increase initial sorbate concentration. Increases in the adsorbent loading weight, and contact time were found to increase the % removal of Pb. While the increase in the initial lead concentration resulted in a decrease in the removal efficiencies of the different adsorbents. The isothermal study of the Pb adsorption on the different adsorbents was found to be best fitted to the Temkin isotherm model, which reflects chemical adsorption mechanism. This work showed that locally available materials such as rice husk, maize cobs and sawdust can be used as efficient sorbents for lead ions removal, representing an effective and environmentally clean utilization of waste matter. More studies are needed to optimize the system from the regeneration point of view , to investigate the economic aspects and to confirm the applicability of this new sorbent under real conditions, such as in the industrial effluent treatment [163].

This literature study focuses on to the use low cost adsorbents, which consist of corn cobs as plant wastes adsorbents in treatment of Industrial waste water by fixed bed column technique and study the effect of two variables (pH value and contact time). The sample of plant waste (corn cobs) was tested to determine its activity which gives the best performance in heavy metals removal and other pollutants (TSS, TDS and COD). Adsorption tests showed the corn cobs adsorbents had significant heavy metal removal efficiency. The best removal efficiency 95.05% of Cr was occurred at pH 5.4 and 4.18 hr. Higher removal efficiency 99.90% of Ni was occurred at pH 6.5 and 2.38 hr. While, lower removal efficiency 91.35% for Zn obtained at pH 6.5 and 0.15hr. Removal efficiency for TDS, TSS and COD were 56%, 65.7% and 83.3% respectively [167].

The results of corn cobs showed the higher adsorption higher adsorption capacities occurred at pH 5.4 for Ni and Cr removal but 6.5 for Zn removal, nickel ions had a better adsorption efficiency giving ion concentrations at 0.002 ppm with removal efficiency 99.9%. At the same sequence, concentration of zinc ions after treatment was better at pH 6.5 that found to be 1.73 ppm with the removal efficiency 91.35%. On the other hand, lowest adsorption efficiency was recorded in case of chromium that was about 7.2 ppm after treatment, with removal efficiency 95.05%.

The pH of the adsorption process is an important controlling parameter in heavy metals adsorption process.This parameter is directly related to the competition of hydrogen ions with metal ions at active sites on the adsorbent surface. In a study carried out by Abdullah and Prasad [168] they found that the adsorption of nickel increased when the pH was increased from 1 to 6 by using tamarind bark. Dong et al [169] reported that the best pH for the chromium adsorption was 5.5 by amino starch preparation and its adsorption for Cr. Optimum pH for chromium and zinc adsorption was laid between 5 and 6 in case of using plant wastes. Regarding contact time, corn cobs exhibited high adsorption efficiency at a variable time 1.0, 2.38 and 4.18 hrs for nickel ions, for zinc ions were 0.15, 1.0 and 2.38 hrs but 5 hrs for chromium ions. Therefore, these adsorbents were found to be different in the adsorption of heavy metal ions that where zinc ions, nickel ions and chromium ions respectively. Highest efficiency of heavy metals removal (99.90%) was found in the case of nickel ions, but in case of chromium ions was 95.05%. and in the case of zinc was 91.35%, highest efficiency of (99.90%) was found with nickel ions.

Contact time is inevitably a fundamental parameter in all transfer phenomena such as adsorption. Therefore, it is important to study its effect on the capacity of retention of chromium by plant wastes adsorbent [170]. Results obtained from current study considering the required time for adsorption was in accordance with the results of [170, 171] present study it is possible to conclude the following points such as removal efficiency of corn cobs adsorbent have a significant ability in removal of zinc, chromium and nickel from industrial waste water and affected by various environmental factors such as pH and contact time [167].

The literature review ends up with the study of various findings given by different researchers using various adsorbents which includes activated charcoal, bone charcoal, agricultural adsorbents, fruit peel adsorbents, silica gels, nano materials, some biosorbents such as algae and fungi, but the novelty study of the adsorbents has been carried out by mixing AC and BC in 1: 1 ratio. Other ratio of AC and BC can not be mixed as there will not be a role of synergistic effect due to improper mixing ratio of the mixed adsorbent. The studies have also been carried out using maize cob as an adsorbent and the results are compared with the mixed adsorbent in batch studies. Simultaneous metal ion studies have been carried out to know the interaction of Cu and Cd metal ions in batch studies.

2.7 Scope and objectives of the Thesis

In many cases the sources of water have been rendered unsafe for the human consumption as well as for other activities such as industrial needs, irrigation which proved that degraded water quality can contribute to water scarcity as it limits its availability for both human use and ecosystem. Due to the strict environmental regulation on the discharge of heavy metals, it was necessary to develop low cost adsorbents for the removal of heavy metal ions. Therefore the present work deals with the removal of Cu (II), Cd (II) from industrial effluents using low cost adsorbents in both batch and continuous flow operation in a packed bed column. The studies were also carried out using agricultural adsorbent (maize cob) in batch studies. Simultaneous metal ion removal has been carried out in batch operation to know the interaction of metal ions during their adsorption.

The detailed objectives of this work were mentioned below.

- Adsorption studies in batch operations.
- To optimize the batch parameters that were obtained experimentally and to be used in continuous flow operation.
- To study the effect of various batch parameters such as effect of pH, adsorbent dosage, contact time for both copper and cadmium using industrial effluents with mixed adsorbent and maize cobs.
- To study the effect of simultaneous metal ion removal (copper and cadmium) for understanding the interaction of ions.
- To study and fit the kinetics of batch data obtained from synthetic solutions using (pseudo first order and pseudo second order model equations), intra particle diffusion model, detailed batch isotherm studies and thermodynamic study.
- Langmuir model and Temkin model analysis were carried out from the data obtained from simultaneous metal ion removal studies using industrial effleunts.
- To study the breakthrough curves for Cu (II) and Cd (II) in terms of effect of adsorbent dosage, effect of volumetric flow rate at a fixed initial metal ion concentration of 100 ppm.
- To study and compare the column performance calculations for industrial effluents and synthetic solution.

- To study the hydrodynamic modeling of the packed bed at various flow rates and bed heights.
- To study the kinetic models in continuous flow operations using Thomas model and Yoon-Nelson model.

CHAPTER 3

MATERIALS AND METHODOLOGY

This chapter gives the details of materials and methodologies that were used in batch and continuous column flow operation.This section also describes the characterization of adsorbents and study of various kinetic models, isotherm models, intraparticle diffusion models in batch and Thomas model, Yoon Nelson model in continuous flow operation.

3.1 Chemicals used

Analytical grade salts of $CuSO_4{\cdot}H_2O$, $CdCl_2{\cdot}H_2O$, purchased from Sigma Aldrich were used for the preparation of synthetic effluents. Activated charcoal (AC) and Bone charcoal (BC) purchased from Sigma Aldrich with a purity of 95% were used as a mixed adsorbent by blending in (1:1 ratio) for this study.

3.2 Mixed adsorbent preparation

The mixed adsorbent was prepared by mixing activated charcoal (AC) and bone charcoal (BC), in 1:1 ratio and particle size analysis (Malvern, Malvern Instruments Ltd, United Kingdom) was carried out in particle size Analyzer to determine the particle size of the mixed adsorbent. The average particle size of the mixed adsorbent and maize cob was reported as 572.2 nm and 634.4 nm respectively.

3.3 Characterization of the mixed adsorbent

Physical characterization such as proximate and ultimate analysis [33], FTIR and BET analysis were carried out to determine the physico-chemical properties and different functional groups that were available for adsorption. The surface area of the mixed adsorbent and maize cob were found to be 951 and 636.6 m^2/g respectively.

3.3.1 BET analysis

BET theory explains the physical adsorption of gas molecules on a solid surface and serves as the basis for the measurement of the specific surface area of the mixed adsorbent [172]. The specific surface area of a powder (adsorbent) is determined by physical adsorption of a gas on the surface of the solid and by calculating the amount of adsorbate gas corresponding to a monomolecular layer on the surface. Physical adsorption results from relatively weak forces (van der Waals forces) between the adsorbate gas molecules and the adsorbent surface area of the test powder. The determination is usually carried out at the temperature of liquid nitrogen of -196 °C.The amount of gas adsorbed can be measured by a volumetric or continuous flow procedure. The specific surface area of a powder is estimated from the amount of nitrogen adsorbed in relationship with its pressure, at the boiling point temperature of liquid nitrogen under normal atmospheric pressure (Make Micrometrics Gemini 2375)-Micro metrics Instrument Corporation, U.S.A.

The BET method leads to a surface area parameter which allows to compare, classify and evaluate different samples and to take into account pores (micro-, meso- and macro pores), roughness and particle shapes by measurement [173].

The BET surface area which predicts from complete adsorption and desorption isotherm can be utilized as an integral parameter for the determination of pore volume and pore size distribution. The BET surface area of the mixed adsorbent was found to be 951 m^2/g.

3.3.2 XRD Analysis

X-Ray Diffraction Analysis (XRD) investigates crystalline material structure, including atomic arrangement, and imperfections. XRD analysis was based on constructive interference of monochromatic X-rays and a crystalline sample.The X-rays were generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate and directed towards the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Braggs law. This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample.

3.3.3 Proximate and Ultimate analysis

Proximate analysis is a type of assay for the determination of different constituents present in the coal sample. Standard procedures were followed to determine the bulk density, average particle size diameter, moisture content, volatile content, ash content, fixed carbon and surface area. Ultimate analysis gives the composition of the sample in terms of wt% of carbon, nitrogen, hydrogen, oxygen and sulfur. The carbon content determination includes the carbon present in the organic coal substance and as mineral carbonates. Hydrogen determination gives the hydrogen content in the organic materials with the coal. All the nitrogen determined was assumed to be the part of the organic materials in the coal. The results of the proximate and ultimate analysis are reported in section 4.1.2. The physical properties and proximate analysis of the maize cobs are reported in section 4.1.3.

3.3.4 FTIR Analysis

An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present.

Fourier Transform Infrared (FTIR) Spectroscopy is a technique used to determine qualitative and quantitative features of IR-active molecules in organic or inorganic solid, liquid or gas samples. It is a rapid and relatively inexpensive method for the analysis of solids that are crystalline, microcrystalline, amorphous, or films. Another advantage of the IR technique is that it also can provide information about the light elements such as hydrogen and carbon in inorganic substances. FTIR analysis has been carried out for the mixed adsorbent before and after adsorption of copper and cadmium and the results are reported in section 4.

3.3.5 Pore size distribution

The pore size distribution analysis of the mixed adsorbents has been carried out before and after adsorption for both copper and cadmium using liquid nitogen gas at a temperature of -196°C using surface area analyzer and the total pore volumes of pores less than 314.768 nm was reported. Adsorption and desorption cumulative volumes of the pore between 1.7 and 300 nm, average pore width, adsorption and desorption average pore width before and after adsroption of copper and cadmium were reported in 4.1.5 and 4.1.6 section. After adsorption as the pores were blocked by the metal ions, both the pore volume and pore width has been decreased.

3.3.6 Working of particle size analyzer

The particle size analyzer works on the principle of dynamic light scattering where He-Ne laser acts as a light source. There should be brownian motion in the solution for the uniform distribution of the particle size. The Zetasizer Nano series performs size measurements using a process called dynamic light scattering (DLS). Dynamic Light Scattering (also known as PCS- Photon Correlation Spectroscopy) measures brownian motion and relates this to the size of the particles. It does this by illuminating the particles with a laser and analyzing the intensity fluctuations in the scattered light.

3.4 Batch studies

Following a systematic procedure for the removal of heavy metal ions, initially the pre-sterilizing flasks containing heavy metal ion solution of 50 mg/l of Cu (II) and Cd (II) were prepared and the mixed adsorbent of 0.5 g/L of mixed adsorbent was added after maintaining the desired pH. pH was adjusted by adding 0.1 M NaOH or 0.1 M HCl. Adsorption process was carried out in the rotary shaker/agitator until the equilibrium was attained. The analysis was done for the filtered samples by Atomic Absorption Spectrophotometer (AAS) (Thermo Scientific) to find the residual concentrations at various time intervals from the collected samples. After the analysis equilibrium time and the residual concentration were reported. The data obtained in the present studies were used to calculate the % removal of the heavy metal ions and the equilibrium metal adsorptive amount/ quantity (mg/g) by using the mass balance relationship. Experiments were done thrice and the average values were reported for the adsorption system.

The equilibrium adsorptive quantity (capacity) of the metal particles (q$_e$) and % removal were evaluated by utilizing mass balance relationship given by the mathematical equations (Eqs. 3.1 and 3.2)

$$q_e = (C_o - C_e)\frac{V}{M} \tag{3.1}$$

$$\%\ \text{removal} = \frac{(C_o - C_e)}{C_o} \times 100 \tag{3.2}$$

where q_e is the amount of heavy metal ion adsorbed per unit weight of adsorbent in mg/g, V is the volume of the solution treated in liter (s). C$_o$, C$_e$ is the initial and equilibrium concentration of metal ions in mg/l, M is the mass of the adsorbent in g.

3.4.1 Industrial effluents collected from BHEL, Haridwar

Confirmation experiments have been carried out for both copper and cadmium in batch and column studies using industrial effluents collected from BHEL, Haridwar plant. The initial metal ion concentration of copper and cadmium in the industrial effluent was found to be 350 ppm and 180 ppm respectively. Further studies were carried out in batch and column by diluting the Copper and Cadmium to 50 ppm each (batch) and 100 ppm each (column) respectively. The effect of pH, adsorbent dosage, contact time were studied for both the metals in batch studies. The effect of bed height (12,24, 36 cm) at fixed volumetric flow rate of 10 ml/min have been studied for both the metals.

After optimizing the bed height at 36cm, and 10 ml/min volumetric flow rate, further studies were carried out at fixed bed height of 36cm and different volumetric flow rates (10, 20, 30 ml/min) for both the metals.

3.5 Removal of Cu (II) and Cd (II) in batch using maize cob as an adsorbent for industrial effluents

Low cost adsorbent studies were carried out for the removal of copper and cadmium using maize cobs as an adsorbent in batch mode.

Maize cob was used as an adsorbent in order to evaluate its potential for the removal of copper and cadmium from industrial effluents preferably from electroplating industries.

Maize cobs which is a cheap and agricultural biosorbent was readily available to be used as an adsorbent for the removal of Cu and Cd ions from aqueous media. Adsorption studies were performed by batch experiments as a function of process parameters such as metal ion concentration of 50 ppm, adsorbent dosage of 0.5 to 5 g/l, equilibrium time varying from 150-180 minutes, agitation rate of 180 rpm and pH varying from 2, 4, 6, 8.

3.5.1 Maize cob as an adsorbent

Maize cob was collected from agricultural fields and washed with double distilled water. The washed samples were then drenched in 1N concentrated nitric acid solution for 12 hrs. The drenched samples were washed with distilled water until the soluble and colored components were removed and were dried in sun light for few hrs and further dried in hot air oven at 110 °C for 12 hrs. Then the maize cobs were crushed in mortar and pestle to further make into small size pieces and were heated in a gas flame for 20-30 minutes to obtain the activated carbon from the maize cobs. Further they were crushed with mortar and pestle to obtain the uniform size. The sample (activated charcoal obtained from maize cob) was put into a mechanical sieve to separate the particles based on their size. Sieve analysis has been carried out from 8 mesh to 4 mesh size sieves (micron size) and further sieved in a mesh size of 400 (micron size) to get into fine powder and kept in a plastic container to be used for batch studies. The particle size of the maize cob was analyzed through particle size analyzer and was found to be 636.6 nm and the other physical properties such as surface area,pore volume were found. The proximate analysis of the activated charcoal prepared from maize cob were reported in Table 4.4.

3.5.2 Atomic Absorption Spectrophotometer

A standard pH meter was used for the adjustment of pH the metal ion solution. After the adsorption process was carried out in a rotary shaker, the final residual concentration of the solution was measured by Atomic Absorption Spectrophotometer (AAS). Various batch studies were conducted using industrial effluents (by diluting the concentration from 350 ppm to 50 ppm) for copper. Similarly for cadmium the concentration was diluted from 180 ppm to 50 ppm. The pH of the solution was adjusted by adding 0.1N NaOH and 0.1 N HCl solutions. The 50 ppm metal ion concentration solutions were prepared and pH was varied from 2, 4, 6, 8. The rotational speed (agitation rate) was fixed at 180 rpm, and the adsorbent dosage of 0.5 g/l was added at different pH. Each conical flask was rotated for about 1 hour in orbital shaker equipment. Then all the solutions were filtered at respective time intervals from 15 min to 3 hr and the supernatant clear liquid was analyzed for final residual Cu (II) and Cd (II) concentration in atomic absorption spectrophotometer. The removal capacity and the % removal of the adsorbent was calculated by using the mass balance relationship formula given by mathematical equations Eqs. 3.3 and 3.4.

$$q_e = (C_o - C_e)\frac{V}{M} \tag{3.3}$$

$$\%\text{ removal} = \frac{(C_o - C_e)}{C_o} \times 100 \tag{3.4}$$

where q_e is the amount of heavy metal ion adsorbed per unit weight of adsorbent in mg/g, V is the volume of the solution treated in (l). C_o, C_e is the initial and equilibrium concentration of metal ions in mg/l, M is the mass of the adsorbent in g.

Similarly after optimizing pH to 6, the batch studies were carried to find the effect of adsorbent dosage from 0.5, 1, 2, 3, 5 g/L, metal ion concentration of 50 ppm, equilibrium time varying from 150-180 minutes, agitation rate of 180 rpm . Then after optimizing pH to 6, adsorbent dosage to 5 g/L, further studies were carried out to find the effect of contact time on Cu % and Cd % removal by varying time from 15 min to 3 hrs (collected sample for every half an hour) and the average equilibrium adsorptive capacities were found along with % removal was reported. The influence of pH, contact time, adsorbent dosage on the selectivity of the removal process was investigated.

3.5.3 Binary sorption experiments for the simultaneous removal of Cu (II) and Cd (II) in batch studies using industrial effluents

The initial metal ion concentrations in the feed containing Cu (II) and Cd (II) from the industrial effluents have been found to be (Cu 350 ppm) and (Cd 180 ppm) respectively. Hence, Cu (II) metal ion concentration was diluted from 350 ppm to 50 ppm . The cadmium concentration can be found by using C_oV_o = C_2V_2, by substituting C_o= 350 ppm, V_o = 14.3 ml, and V_2 = 100 ml, C_2 and the initial concentration of Cadmium were found to be 25.74 ppm.

Hence the batch studies can be carried out simultaneously to find the effect of Cu (II) having initial concentration of (50 ppm) and Cd (II) having initial concentration of (25.74 ppm) and the % removal, adsorption capacity were found.

Two parameters were studied namely the effect of adsorbent dosage, contact time and those results were reported. The results were shown in Figs 4.43 to 4.48 and the % removal, adsorption capacities were reported for both the metals. The batch studies has been carried out at room temperature of 25 °C, agitation rate of 180 rpm, contact time of 2 hr, pH 6 by varying the adsorbent dosage from 0.5, 1, 2, 3, 5 g/L. After optimizing the maximum % removal from the adsorbent dosage, the experiments were conducted to find the effect of contact time.

3.5.4 Model equation for batch studies

In order to research the system of adsorption and potential rate controlling steps; for example, transport and chemical reaction phenomena, dynamic models were utilized to test the obtained data. The kinetic models includes the pseudo-first order and pseudo-second order model.

3.5.4.1 Pseudo first order equation

Considering the reversible binding of metal ions with the adsorption on active sites present on adsorbent surface, the rate of adsorption is directly proportional to the number of vacant sites [28, 46].

The pseudo-first order equation was represented by Eq. 3.5

$$\frac{\mathrm{d}q}{\mathrm{d}t} = k_1\left(q_e - q_t\right) \tag{3.5}$$

where q_e and q_t are the adsorption capacity at equilibrium, and at time t respectively (mg/g). k_1 is the rate constant of pseudo first order equation (min^{-1}). Integrating the above equation and applying the boundary conditions from t = 0 to t = t, and $q_t = 0$ to $q_t = q_t$, the integrated form of Equation 3.5 becomes

$$\log\left(q_e - q_t\right) = \log\left(q_e\right) - \frac{k_1 t}{2.303} \tag{3.6}$$

Eq. 3.6 is applicable to the experimental results but generally differs from a true first order equation in two ways: (i) The parameter $k_1(q_e\text{-}q_t)$ does not represent the number of available sites and (ii) the parameter $\log(q_e)$ is an adjustable parameter and often it was found not equal to the intercept of a plot between log (q_e-q_t) vs t, where as in a true first order $\log(q_e)$ should be equal to the intercept of the plot drawn between log (q_e-q_t) against t.

In order to fit the equation to the experimental data, the equilibrium adsorption capacity q_e must be known. In many cases q_e is unknown and as chemisorption tends to become immeasurably slow, the amount sorbed is still significantly smaller than that of the equilibrium uptake capacity [46]. In most cases in the literature, pseudo first-order equation of Lagergren does not fit well for the whole range of contact time and is generally applicable over the initial period of 20 to 30 minutes after the start of adsorption process.

3.5.4.2 Pseudo second order equation

In this model it was assumed that adsorption/binding of metal ion/ adsorbate on the adsorbent surface is mediated by chemical forces rather than physical forces of attraction.

Non-linear form of the model is given as

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_2 \left(q_e - q_t\right)^2 \tag{3.7}$$

Upon integration with boundary conditions from q_t = 0 at t = 0, q = q_t at t = t, the above equation (Eq. 3.7) reduces to

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3.8}$$

where q_e and q_t are the adsorption capacities at equilibrium, and at time t respectively (mg/g). k_2 is the rate constant of pseudo second order equation (g/mg.min). A plot of t/q_t vs t for the pseudo second order equation holds a straight line relationship and the parameters q_e and k_2 can be determined from the slope and intercept.

3.6 Continuous column flow studies

Persistent column flow operation analyses were conducted in a cylindrical round and hollow plastic cylinder (4 cm internal diameter and 100 cm height) as shown in the Fig. **??**. A 20 mesh size stainless sieve was attached to the bottom of the column. A known quantity of the mixed adsorbent in 1:1 ratio was added in the column from top to yield the desired bed weight of 50 g, 100 g, 150 g, respectively. Cu (II) & Cd (II) effluent solutions of known concentration (100 mg/l) were pumped into the column from the bottom using a 40 W submersible pump at the desired flow rates of (10, 20, 30 ml/min) respectively.

Samples were collected from the exit of the column at different bed heights at different intervals of time until the equilibrium was attained and the residual metal ion concentration (MIC) were analysed using AAS (Atomic Absorption Spectrophotometer) (Make -Thermo Scientific).

The parameters that were studied in the continuous flow operations involves the study of breakthrough curves with respect to weight of the adsorbent, volumetric flow rates, initial metal ion concentration. The parameters that were involved in the column design are

- weight of the mixed adsorbent added 50 g, 100 g, and 150 g
- inner Diameter of the column 4 cm
- total height of the column = 100 cm
- adsorbent ratio = 1:1 (AC+ BC)

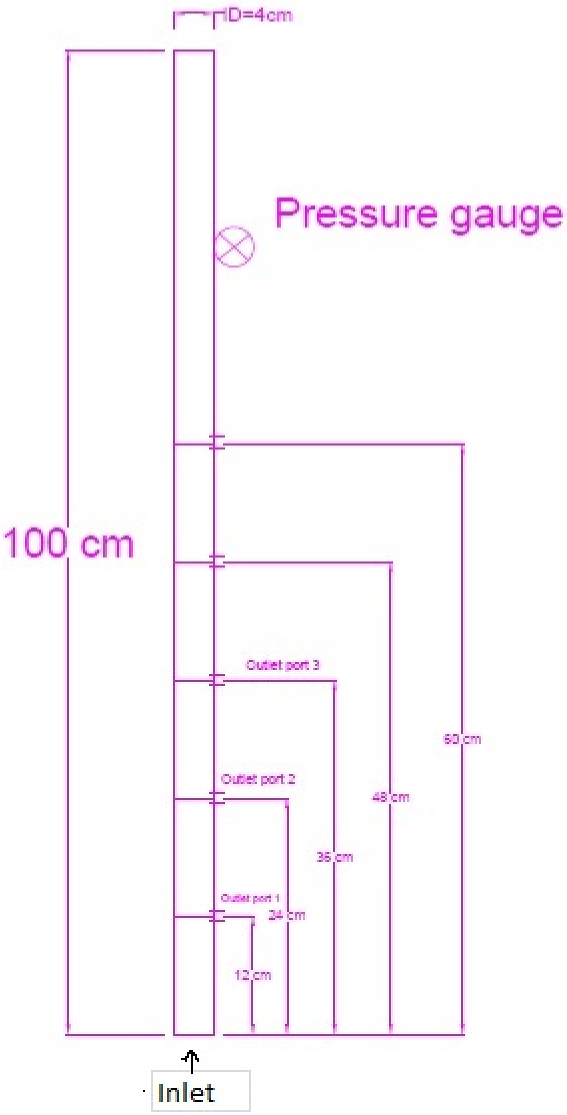

Figure 3.1: Experimental set up of the packed bed column

- submersible pump for sending effluent from bottom to top (into the column) = 40 Watt.
- Initial concentration of the metal ions Cu and Cd (C_o = 100 ppm)
- effect of volumetric flow rates (10, 20, 30 ml/min)

3.6.1 Model equation for Continuous flow Column

Different types of models are used to analyze the column performance depending on the regression coefficient (R^2) and the best fit of the straight line, the most suitable type of adsorbent model was studied. In this work, Yoon-Nelson model and Thomas model were studied for both the divalent metal ions Cu (II) and Cd (II).

3.6.1.1 Thomas model

Thomas [174] developed a model for adsorption processes in which external (outward) and internal (inward) diffusion limitations are not present. The linearized form of the Thomas model can be expressed by Eq. 3.9 [56].

$$\ln\left(\frac{C_0}{C_t}-1\right)=\frac{k_{Th}q_0m}{Q}-\frac{k_{Th}C_0t}{m} \tag{3.9}$$

where K_{Th} is the Thomas model constant (ml/min.mg), q_o is the equilibrium uptake capacity of the Cu and Cd (mg/g), C_o is the inlet concentration (100 mg/l), C_t is the effluent metal ion concentration at time t (mg/l), m is the mass of the adsorbent (g), Q is the inlet flow rate (ml/min) and t is the flow time (min). The value of (C_o/C_t) is the ratio of inlet to outlet metal ion concentration. A linear plot of ln [(C_o/C_t) -1] against time (t) was plotted to determine the values of q_o and K_{Th} from the intercept and slope respectively.

3.6.1.2 Yoon-Nelson model

Yoon and Nelson developed a model to describe the adsorption behaviour in the continuous column flow operations. The linearised form of the Yoon-Nelson model was expressed by Eq.3.10 given as

$$ln\left(\frac{C_t}{C_0-C_t}\right)=k_{YN}t-\tau k_{YN} \tag{3.10}$$

where K_{YN} is the rate velocity constant (l/min) and τ is the time (min) required for 50% adsorbate breakthrough. A linear graph of ln (C_t/(C_o- C_t)) against sampling time (t) was used to determine the values of K_{YN} and τ from the slope and intercept of the plot respectively. The calculated τ from the experiment was compared with the value obtained from the linear model.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization study results of the mixed adsorbent and maize cobs

The various characterization studies results such as FTIR analysis, BET analysis, particle size analysis, pore size distribution analysis, XRD analysis, proximate analysis of the mixed adsorbent before and after adsorption were reported. Apart from these; particle size analysis, BET surface area, proximate analysis of the maize cob have been reported.

4.1.1 FTIR analysis of the mixed adsorbent

The mixed adsorbent surface was analyzed by Fourier Transformation Infra-red spectroscopy (FTIR) before adsorption were shown in Fig. 4.1. FTIR spectrum was got after 32 combined outputs with KBr pellets of 1% (w/w). The pellet was subjected to FTIR (ThermoNecolet manufactured) spectrum between wave numbers ranging from 3425-1025 cm^{-1} before adsorption and 3424-510 cm^{-1} after adsorption.

Wave number 3500-3000 indicates the -O-H and -NH groups; wave number 2900-2800 indicates symmetrical or asymmetrical -C-H stretching of aliphatic acids.

Wave number 1700-1600 cm^{-1} indicates -C = C (ketone group), wave number 1550-1300 indicates -C-H stretching and -C = C.

Wave number 1106-1024 demonstrates C-O extending, - C-H fragrant, random oxides and -S-O symmetrical vibrations (fragile reflectance).

The FTIR Spectrum of the mixed adsorbent (activated and bone charcoal) after adsorption for Cu (II) and Cd (II) were shown in Figs. 4.2 and 4.3, with different wave numbers and frequencies which indicates the various functional groups that are represented below.

Wave number 3600-3000: -O-H and -N-H.

Wave no: 2900-2800 Symmetrical or asymmetrical -C-H stretching of aliphatic acids.

Wave no: 1700-1600: -C = C.

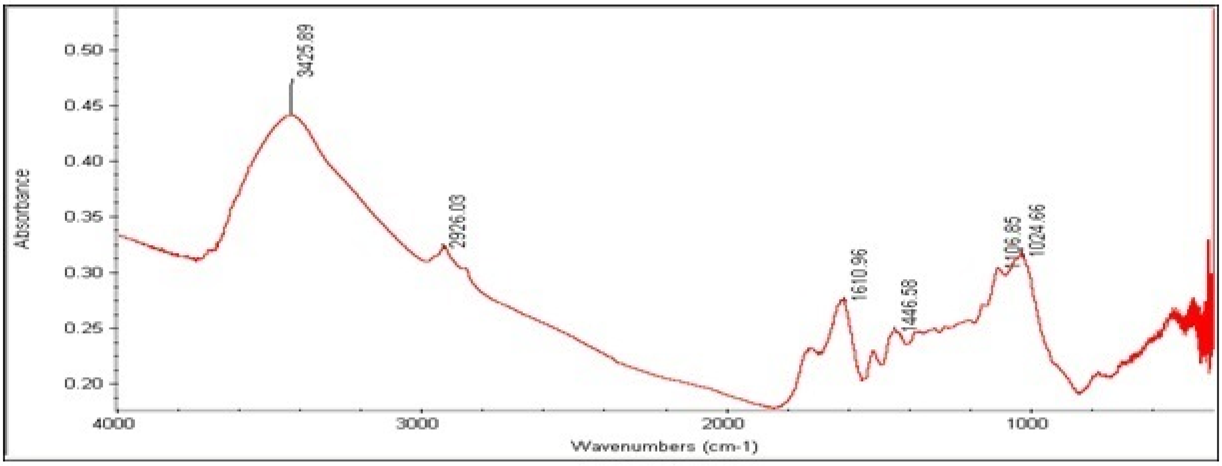

Figure 4.1: FTIR spectrum of the mixed adsorbent before adsorption

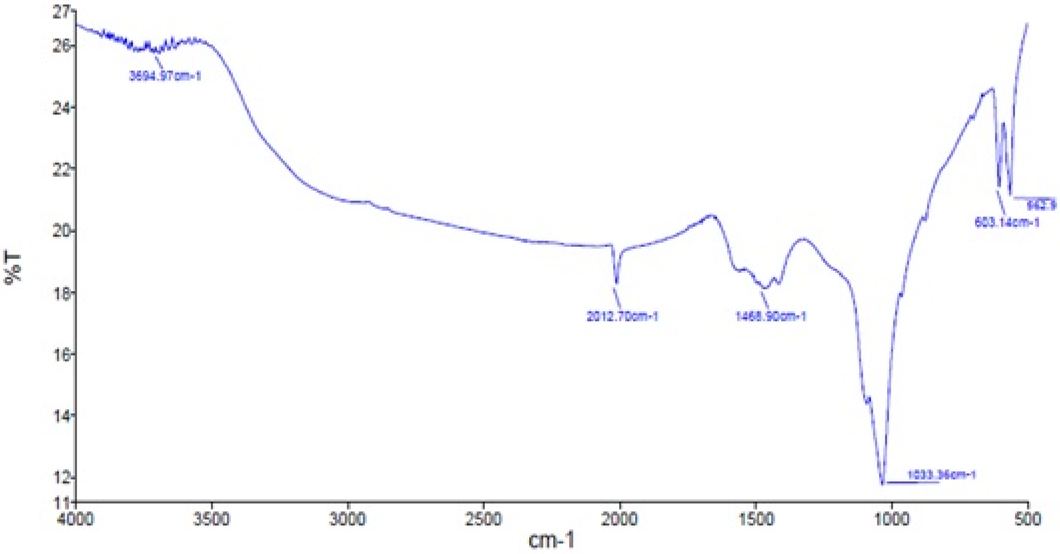

Figure 4.2: FTIR spectrum of the mixed adsorbent after adsorption for Cu

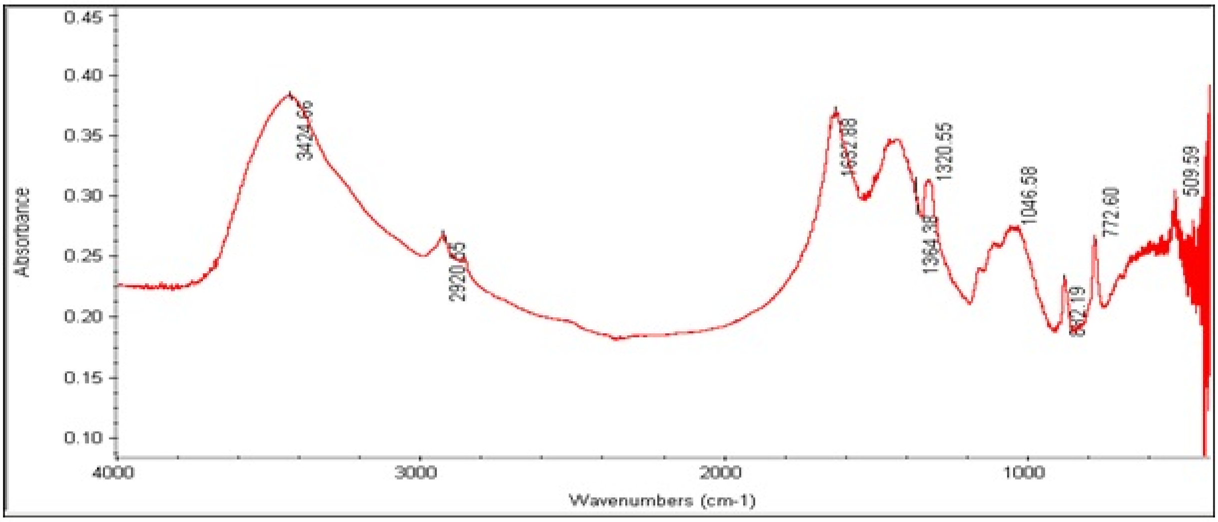

Figure 4.3: FTIR spectrum of the mixed adsorbent after adsorption for Cd

Wave no: 1550-1300:-C-H Stretching, -C=C.

4.1.2 Characterization of the mixed adsorbent

The various characterization studies such as proximate analysis,ultimate analysis, physical properties of the mixed adsorbent were shown in Tables 4.1, 4.2 and 4.3 respectively.

Table 4.1: Proximate analysis of the mixed adsorbent

Property	**Composition of the mixed Adsorbent**
Bulk Density (g/cc)	0.74
Average particle diameter	572.2 nm
Moisture content	4.24%
Volatile matter	23.61%
Ash Content	4.39%
Fixed carbon	68.57%
Surface area (m^2/g)	951

4.1.3 Proximate analysis and physical properties of the activated charcoal prepared from maize cobs

The particle size of the maize cob was analyzed through particle size analyzer and was found to be 636.6 nm. The other physical properties and the proximate analysis of the activated charcoal prepared from maize cob were reported in Table 4.4.

Table 4.2: Ultimate Analysis of the mixed adsorbent

Component	**Composition (%)**
Carbon	65.12
Nitrogen	9.41
Hydrogen	6.63
Oxygen	18.85
High heating value	33.28

Table 4.3: Physical properties of the mixed adsorbent

Adsorbent type	**Surface area** (m^2/g)	**Moisture** (%)	**Particle size** (nm)	**Charge**
Pristine AC	1600	5	980	neutral
Pristine BC	267	3.43	681	-ve
50 % each	951	4.24	572.2	-ve

Table 4.4: Proximate analysis and physical properties of the activated charcoal prepared from maize cobs

Property	**Composition of the maize cob**
Moisture content	10%
Volatile matter	66 %
Ash content	7.5 %
Fixed carbon	16.5 %
Surface area (m^2/g)	634.4
Pore volume (cm^3/g)	0.412
Avg particle size (nm)	636.6

4.1.4 XRD Studies for the mixed adsorbent before and after adsorption of Cu (II) and Cd (II)

X-ray diffraction shows the peaks at 2 theta of (5.05, 13.36. 26.66, 31.73) and the corresponding counts of (244, 544, 221, 188 sec) before adsorption of the mixed adsorbent. After adsorption of copper the angle 2 theta of (5.11, 13.78. 26.83, 31.83) and the corresponding counts of (192, 507, 472, 156 sec) were observed. Similarly after adsorption of cadmium the angle 2 theta of (5.00, 13.2. 26.7, 31.73) and the corresponding counts of (204, 505, 368, 191 sec) were observed. Several matches have been found for both Cu and Cd, mixed adsorbent samples.

The mixed adsorbent have the same crystalline structure matched with $C_{12}H_{13}N_2O_3$ with monoclinic crystal system having atomic positions (a= 10.09, b= 7.064,c =15.3) and the hexagonal angles $\beta = 96.28$ in comparison with the data base library of the instrument. The mixed adsorbent matches with the orthorhombic $C_{12}H_{13}N_3O_4$ triclinic $C_{14}H_{15}N_5O_3$ and monoclinic, tetragonal crystal systems.

Similarly after adsorption of copper and cadmium onto the mixed adsorbent the matches were found at $C_{32}H_{50}N_2O_4$ (tetragonal having a= 8.25, c= 42.59 crystal vol = 2899.12) $C_9H_7N_3O_2$ (monoclinic $\beta = 94.46$) $C_{13}H_{14}N_6O_6$ (Triclinic) $C_{10}H_{17}NO_2$(Triclinic). The Figs 4.4 and 4.6 indicates the XRD pattern for Cu before and after adsorption with the highest peak at (2 theta = 13.36 and 13.78 corresponds to peaks 548, 507) shows the crystalline nature of the mixed adsorbent before and after adsorption of copper. Fig 4.8 indicates the XRD pattern for cadmium (II) after adsorption and the broad peak were observed at (2 theta = 13.2, corresponds to peak 505) shows the crystalline nature of the mixed adsorbent after adsorption of Cd. Miller indices form a notation system in crystallography for planes in crystal (Bravais) lattices. In particular a family of lattice planes was determined by three integers h, k, and l, the Miller indices. The Miller indices values were shown in Figs 4.5 and 4.7 for the mixed adsorbent before and after adsorption at their highest peaks.

4.1.5 Pore size distribution of the mixed adsorbent before adsorption

The pore size distribution of the mixed adsorbent was performed before adsorption and the total pore volume of pores less than 314.768 nm diameter was reported to be 0.67425 cm^3/g as shown in the Fig. 4.9 respectively. Adsorption and desorption cumulative volumes of pores between 1.7000 nm and 300.0000 nm diameter were found to be 0.615 cm^3/g and 0.6388 cm^3/g respectively. The average pore width (4 V/A by BET) was found

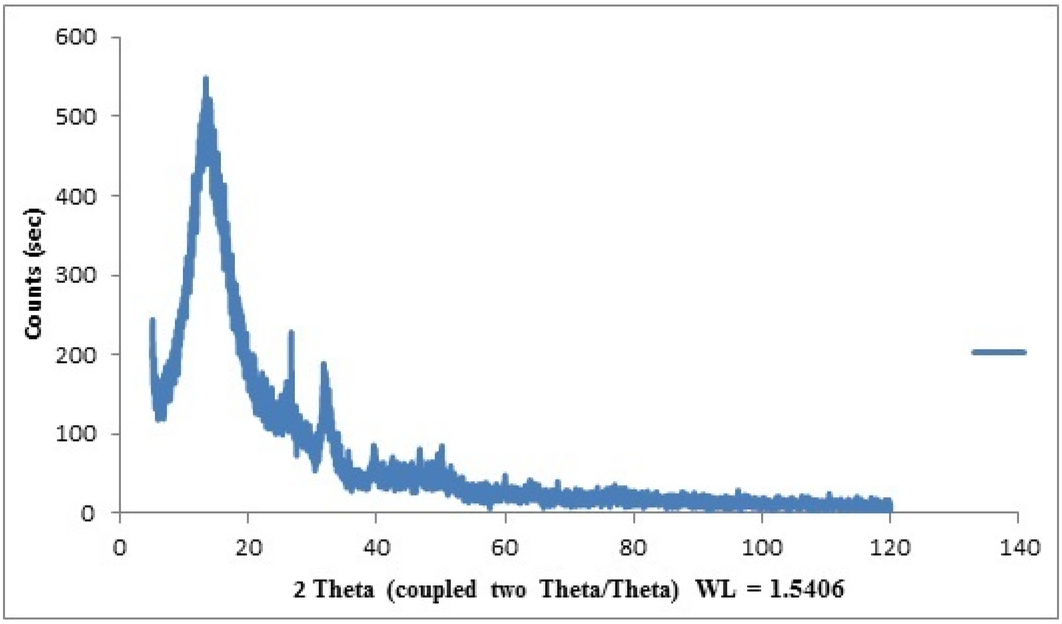

Figure 4.4: XRD pattern of the mixed adsorbent before adsorption (pure)

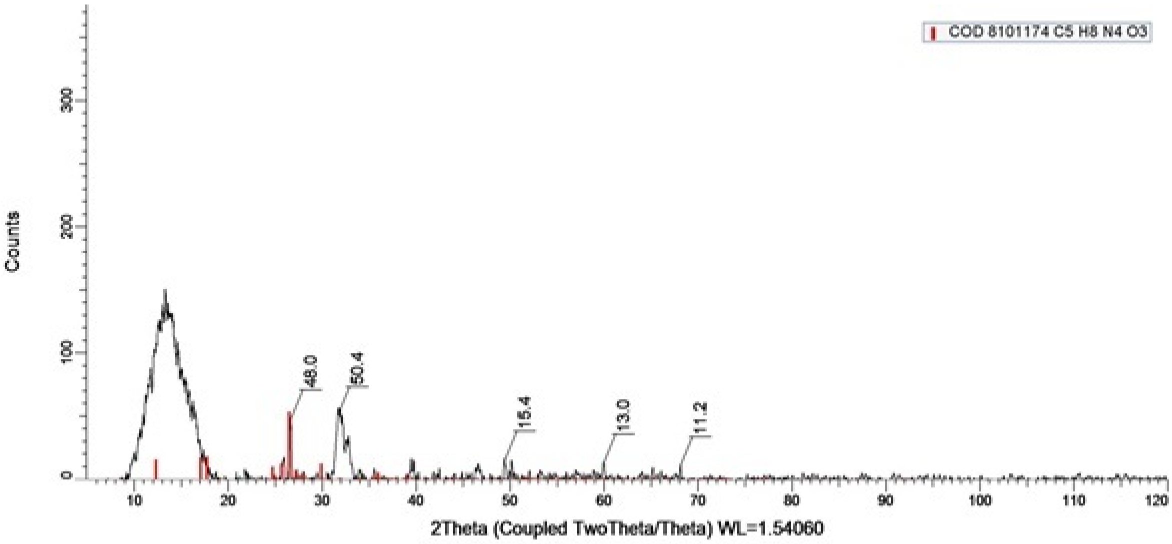

Figure 4.5: XRD of the mixed adsorbent before adsorption of copper showing the peaks and miller indices

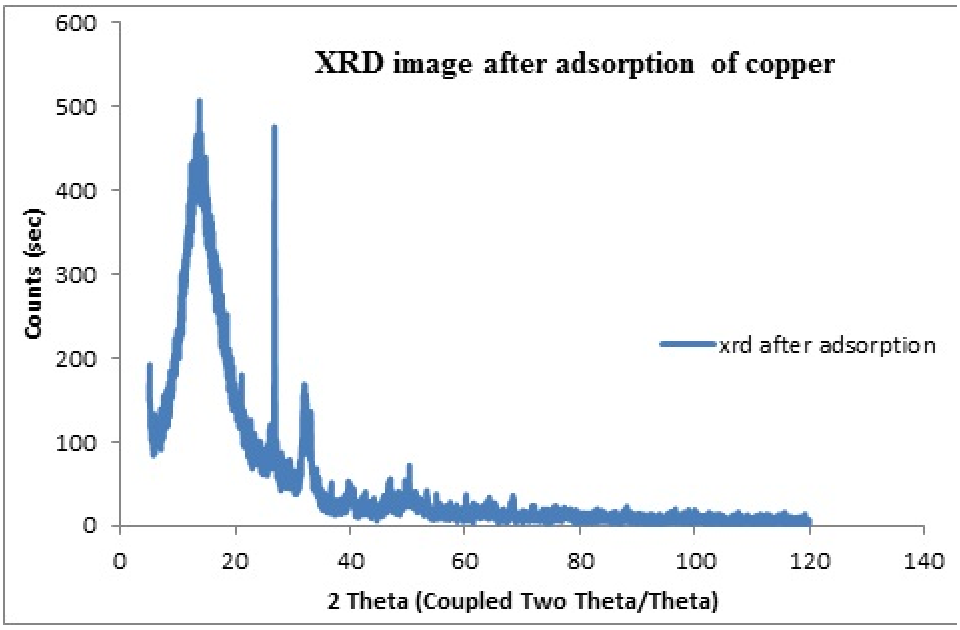

Figure 4.6: XRD of the mixed adsorbent after adsorption of copper

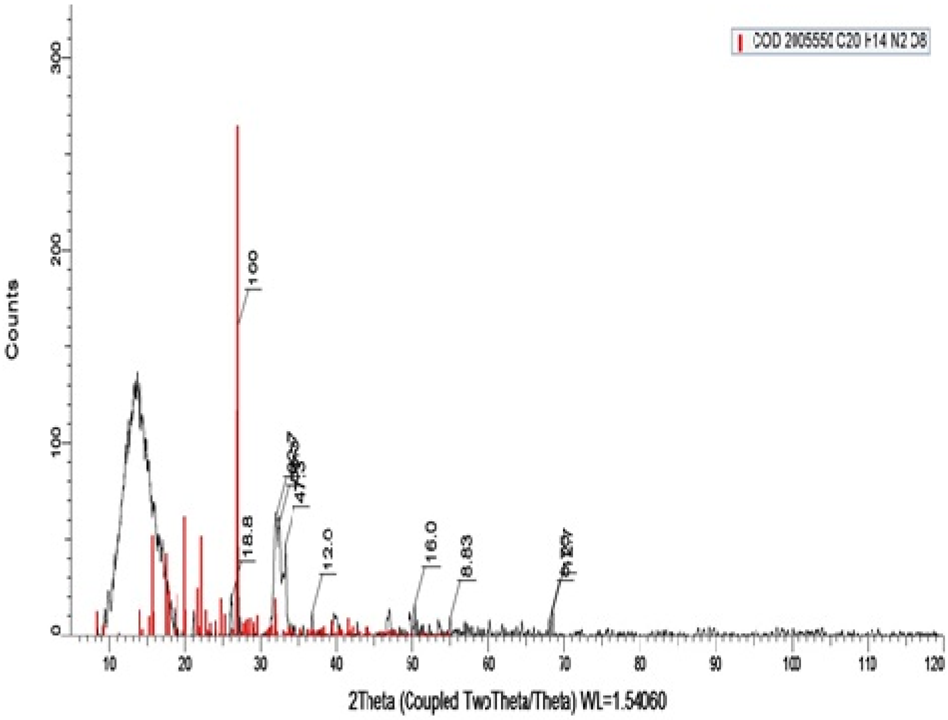

Figure 4.7: XRD of the mixed adsorbent after adsorption of copper showing the peaks and miller indices

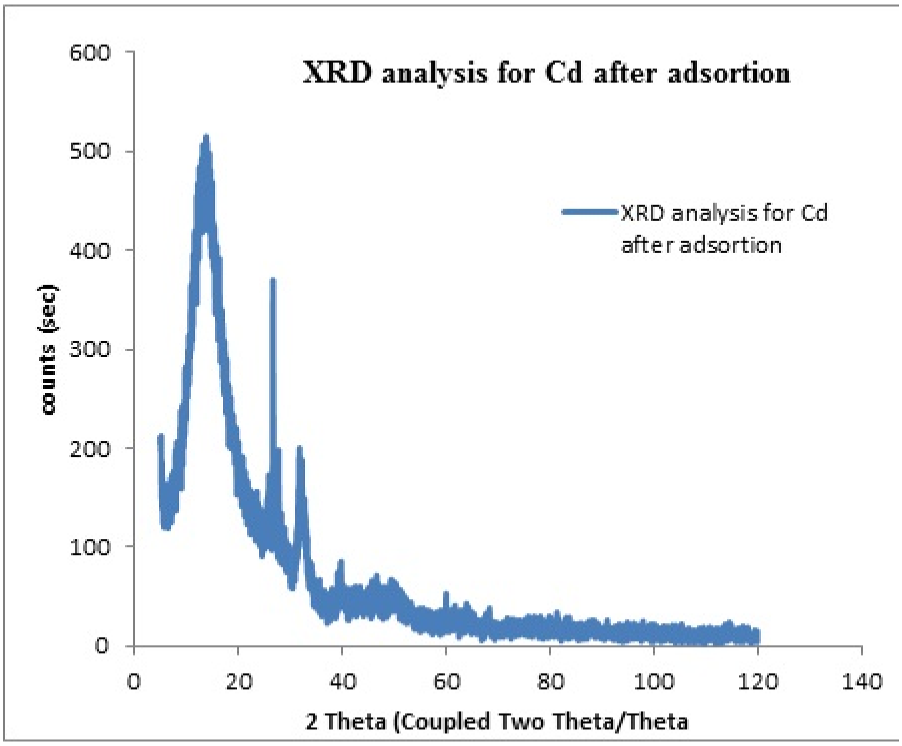

Figure 4.8: XRD of the mixed adsorbent after adsorption of cadmium showing the peaks

to be 4.25 nm. Adsorption and desorption average pore width was found to be 4.59 nm and 4.24 nm respectively.

4.1.6 Pore size distribution of the mixed adsorbent after adsorption of Cu (II) and Cd (II)

The pore size distribution of the mixed adsorption were shown after adsorption and the total pore volume of pores less than 243.28 nm diameter was reported for Cu (II) and Cd (II) as 0.3937 cm^3/g and 0.324 cm^3/g as shown in the Figs. 4.10 and 4.11 respectively. Adsorption and desorption cumulative volumes of pores between 1.7000 nm and 300.0000 nm diameter were found to be 0.2848 cm^3/g and 0.2987 cm^3/g respectively. The average pore width (4 $\frac{V}{A}$ by BET) was found to be 3.68 nm. Adsorption and desorption average pore width was found to be 5.01 nm and 4.51 nm respectively. After adsorption as the pores were blocked by the metal ions both the pore volume and the pore width has been decreased respectively.

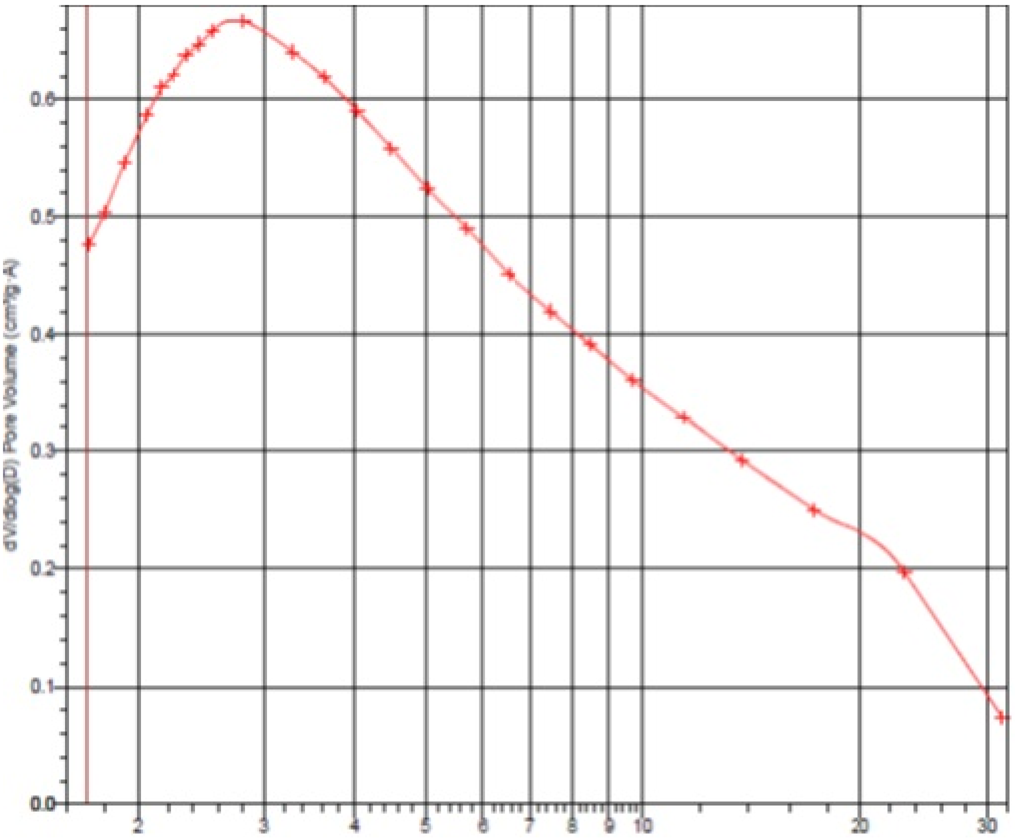

Figure 4.9: Pore size distribution of the mixed adsorbent before adsorption

4.1.7 Particle size analysis of the mixed adsorbent and maize cobs

The particle size of the mixed adsorbent and maize cobs were reported in the Figs. 4.12 and 4.13 and was found to be 572.2 nm and 634.4 nm respectively.

4.2 Batch Studies

This Section deals with the results of the batch studies which involves the effect of pH, temperature, initial metal ion concentration, adsorbent dosage, agitation rate and contact time, for both the divalent metals Cu (II) and Cd (II) and also gives the optimum parameters of the batch study. Further, it elaborates about the kinetic modeling of batch studies which includes the pseudo first order model and pseudo second order models.

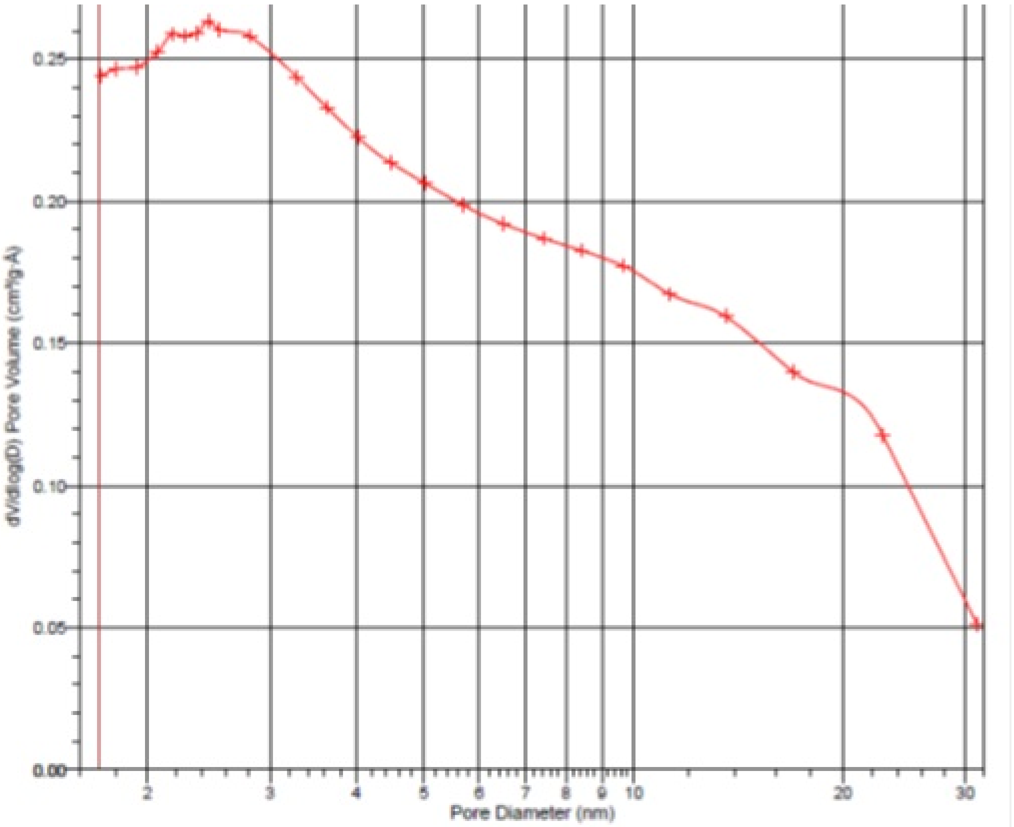

Figure 4.10: Pore size distribution of the mixed adsorbent after adsorption of Cu (II)

4.2.1 Effect of pH

pH is considered to be the most important factor influencing not only the site dissociation but also the solution chemistry of the heavy metals, hydrolysis, complexation by organic and or inorganic ligands [56]. Redox responses, precipitation were significantly effected by pH and on the other side, firmly impact the speciation and adsorption possibility of the substantial metals. Adsorption was mainly dependent on the type of the adsorbent particle which have useful ligands that were present in the mixed adsorbent [175]. Similarly at low pH values, the surface of adsorbent would be occupied by hydronium particles which diminish the metal ions distributions with the blended (mixed) adsorbent by negative interactions and by this manner lower adsorption occurs.

Interestingly as the pH increased the impact of hydrogen ions diminished and more ligands were accessible for the adsorption. In this manner at higher pH values the general surface on the blended adsorbent turned out to be more negative and the rate of adsorption increased. Similarly at pH higher than 8, insoluble copper and cadmium hydroxides were formed due to precipitation and restricted the true adsorption studies [176]. The experiments were conducted with the adsorbent conditions at a temperature of 25°C, 50 mg/l of

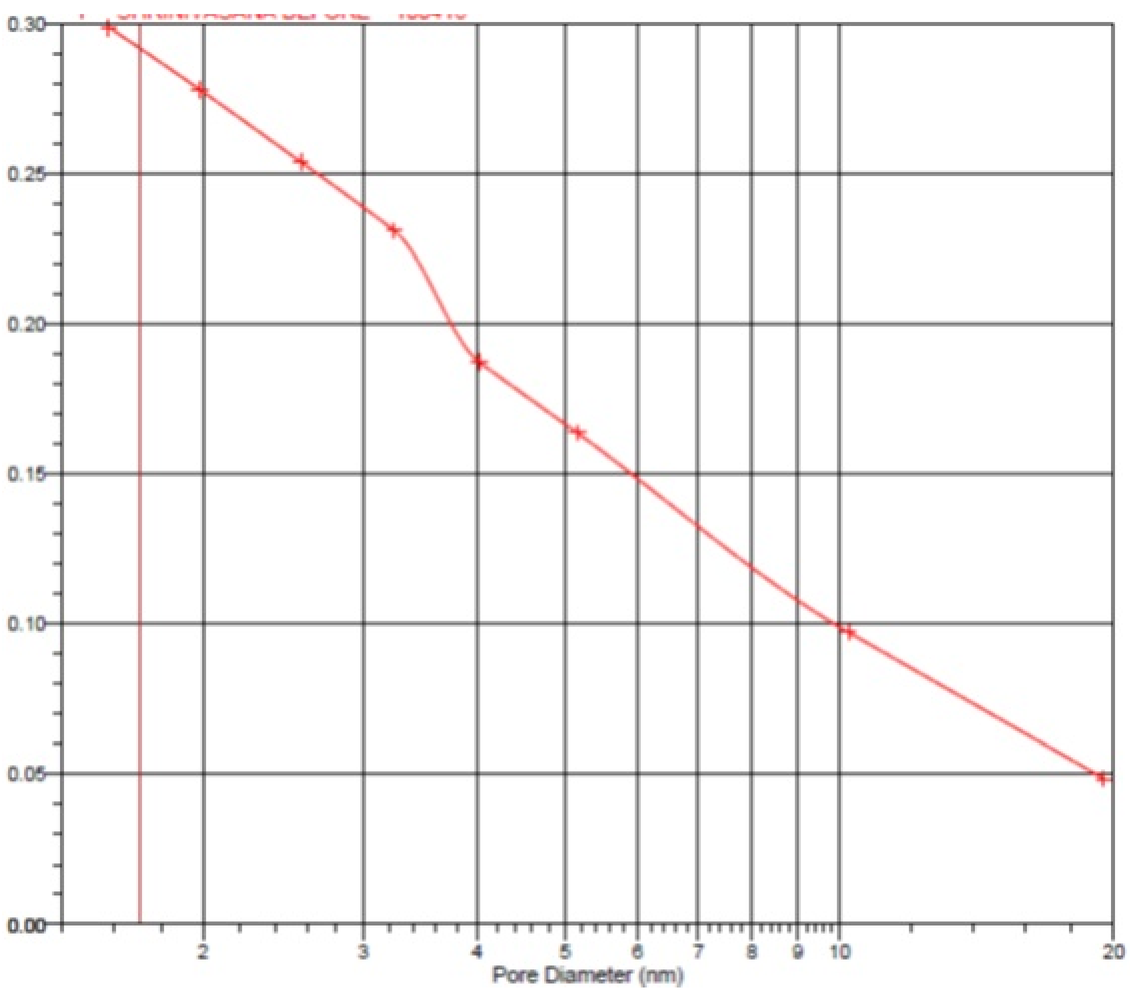

Figure 4.11: Pore size distribution of the mixed adsorbent after adsorption of Cd (II)

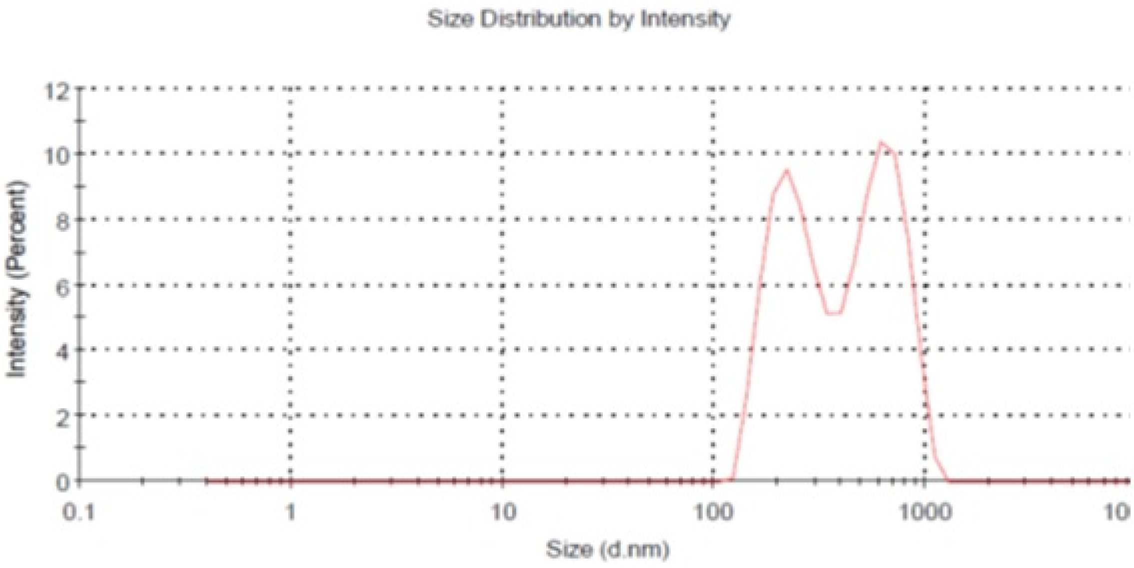

Figure 4.12: Particle size of the mixed adsorbent

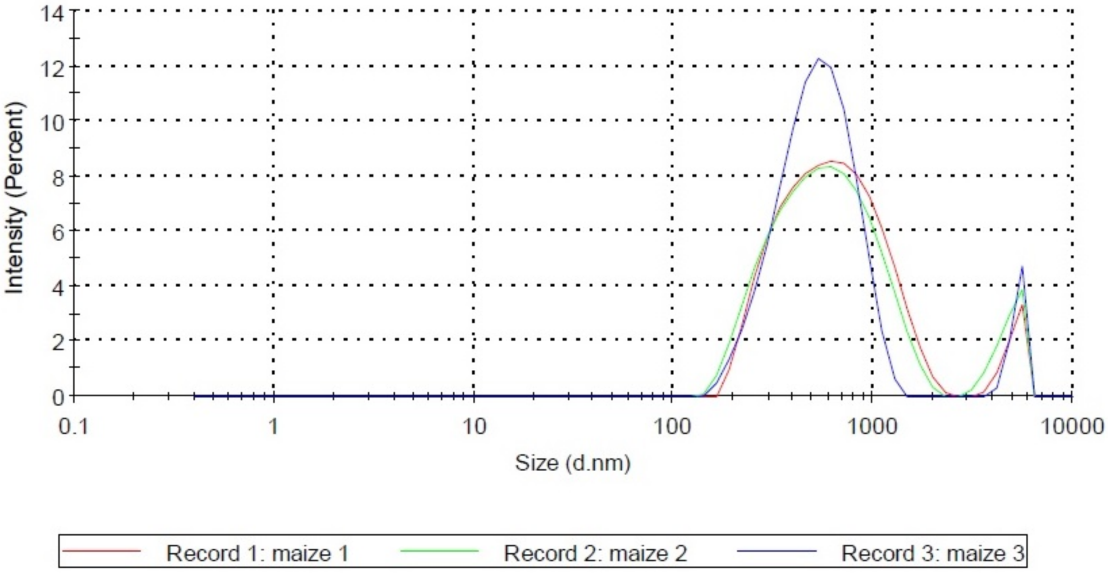

Figure 4.13: Particle size of the maize cobs

initial metal ion concentration for 120 minutes with an adsorbent dose of 0.5 g/L of the mixed adsorbent (1:1 ratio).

4.2.1.1 Effect of pH for AC, BC and mixed adsorbent

The graphs in Figs. 4.14 and 4.15 shows the % removal vs pH for different adsorbents (pristine activated carbon, pristine bone charcoal and 50% mixed AC + BC). The graph signifies that the highest % removal of 97.21 and 78.77 was obtained at optimized pH 6. This was due to the synergistic effect of the mixed adsorbent by mixing pure activated charcoal having high surface area of 1600 m^2/g and pure bone charcoal having negative charge. The combination of both activated charcoal and bone charcoal plays a significant role as a mixed adsorbent for the removal of both the metal ions due to the influence of synergistic effect. This huge difference in the % removal for Cu (II) and Cd (II) was due to the more atomic weight of Cd (112.4) when compared to Cu having 63.5.

In the acid range the % removal of heavy metal ion increases with the increasing order of pH as $6 > 4 > 2$ for both the metals and in the base range it forms as hydroxide precipitate at pH ($>= 8$). The maximum % removal was obtained at 120 min and pH 6 for both the metals. The experiments were conducted with the adsorbent conditions at a temperature of 25°C, 50 mg/l of initial metal ion concentration, contact time of 120 minutes with an adsorbent dose of 0.5 g/L each for pristine activated carbon , pristine bone charcoal and the 50% each [mixed adsorbent of 1:1 ratio] respectively.

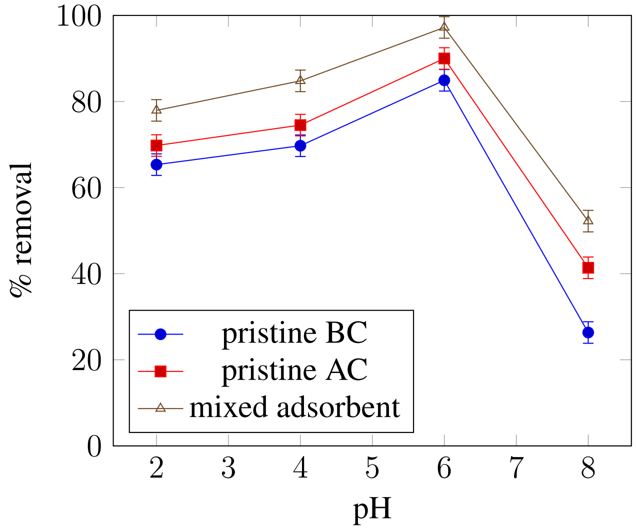

Figure 4.14: Effect of pH on Cu metal ion removal for pristine AC, pristine BC and mixed adsorbent at 25°C, 120 min, 50ppm, 0.5 g/L of ads dosage, 180 rpm

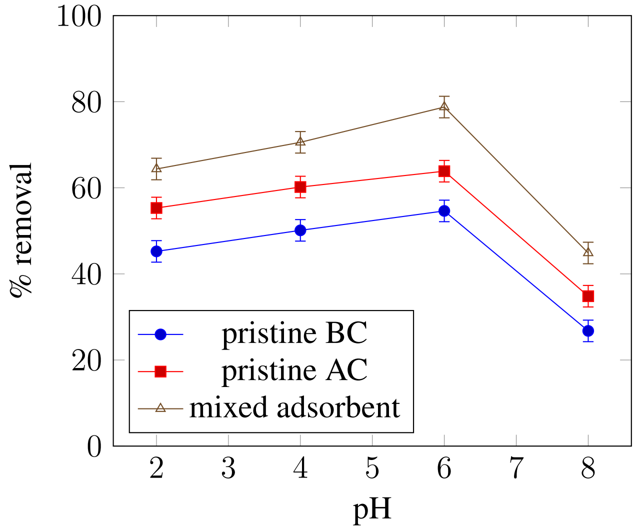

Figure 4.15: Effect of pH on Cd metal ion removal for pristine AC, pristine BC and mixed adsorbent

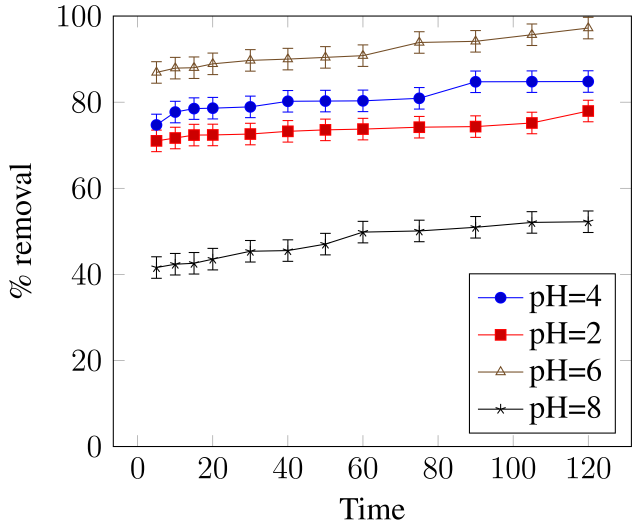

Figure 4.16: Effect of pH on Cu (II) removal at 25°C, 120 min, 50 ppm, 0.5 g/l of ads dosage, 180 rpm

It became evident from Fig. 4.16 for Cu (II) with respect to the increase of pH the % removal increased for 50% each and the maximum % removal was attained to be 97.21% at a contact time of 100-120 min, pH 6. Similarly for cadmium as shown in the Fig. 4.17 with the increase of pH from 2 to 6 the % removal increased for 50% each and the maximum percentage removal was reported as 78.76% at 120 min and pH 6. This huge difference in the % removal for Cu (II) and Cd (II) was due to the more atomic weight of Cd (112.4) when compared to Cu having 63.5. Similarly at pH values above and equivalent to 8 the cadmium and copper metal ions got precipitated by forming hydroxides. The results indicate that the adsorption was highly pH dependent. In the acid range the % removal of heavy metal ion increases with the increasing order of pH as $6 > 4 > 2$ for both the metals and in the base range it forms as hydroxide precipitate at pH ($>= 8$). The maximum % removal for Cu (II) and Cd (II) was found to be 97.21 and 78.76 % which was obtained at 120 min and pH 6. The optimum pH were found to be 6 for both the metals. The present results obtained are in accordance with the literature [63] using activated and non activated date pit adsorbents for the removal of copper and cadmium from aqueous solutions.

4.2.2 Effect of Temperature

Initially the percentage removal vs contact time follows a chemisorption process from 5- 90 min and in the later stage the % removal became almost equivalent and negligible changes have been observed from 90- 120 min which further interprets the attainment of equilibrium in between 100-120 min as shown in Fig 4.18.

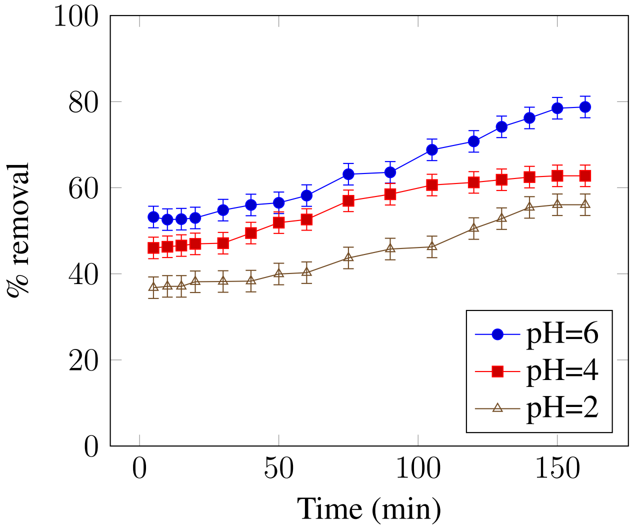

Figure 4.17: Effect of pH on Cd (II) removal at 25°C, 120 min, 50ppm, 0.5 g/l of ads dosage, 180 rpm

Conventionally, with the increase of temperature the adsorption decreases. However; for the mixed adsorbent the overall charge being -ve, the % removal of ions increases with the increase of temperature and the % removal was highly dependent upon temperature at initial adsorption process from 5- 90 min.

The % removal with respect to increase of temperature follows a chemisorption process and the maximum % removal of 99.75 were reported at T = 40 °C. The % removal was almost constant at different temperatures ranging from 25 to 40 °C and it can be interpreted that the % removal was independent of temperature with respect to contact time of 90-120 min. Similarly for the temperature range from T $(40 > 35 > 30 > 25)$ the % removal for Cu (II) was $99.41 > 98.85 > 97.92 > 96.13$ respectively and almost negligible change of % removal was observed after the attainment of equilibrium as shown in Figs. 4.18 and 4.19. Similarly for Cd (II) the % removal increased in the order as $88.12 > 85.25 > 82.18 > 78.77$ with respect to increase of temperature T $(40 > 35 > 30 > 25)$. The more % removal of Cu (II) was due to low atomic weight when compared to Cd (II) having higher atomic weight.

The optimum temperature was found to be 40 °C for both the metals. Increasing temperature likely influenced the internal structure of the adsorbent and sorted the metal ion distribution in the mixed adsorbent inter-spaces which further enhances the % removal of metal ions.

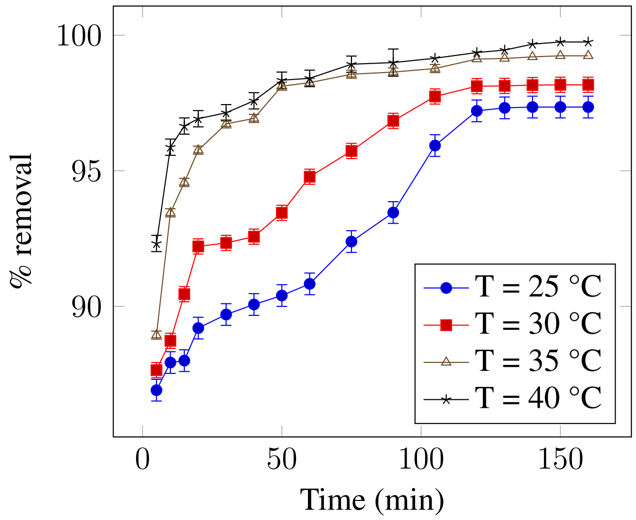

Figure 4.18: Effect of temperature on Cu (II) removal at pH 6, 120 min, 50 ppm, 0.5 g/l of ads dosage, 180 rpm

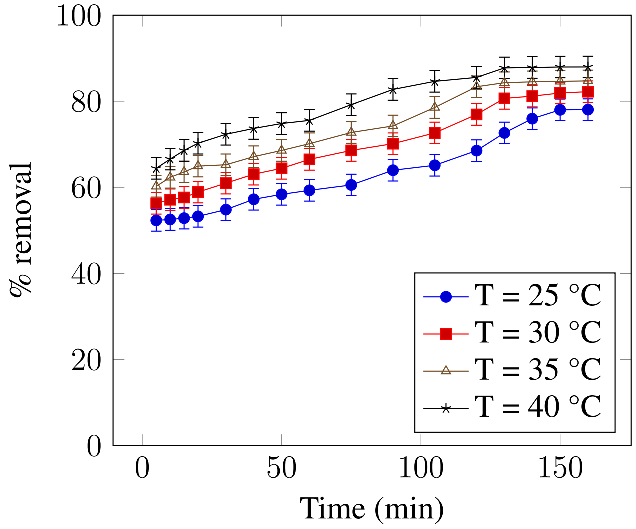

Figure 4.19: Effect of temperature on Cd (II) removal at pH 6, 120 min, 50ppm, 0.5 g/l of ads dosage, 180 rpm

4.2.3 Effect of adsorbent dosage

The parameter adsorbent dose was considered to be significant for effective metal ion removal as it determines sorbent- sorbate equilibrium of the system. It was observed that the amount of copper adsorbed varies with different mixed adsorbent concentration or adsorbent dose (g/L). The amount of copper adsorbed per unit mass of the mixed adsorbent decreases with an increase in adsorbent dosage from 0.5 to 5 g/L which determines the number of binding sites available for adsorption. The number of adsorption sites or surface area increases with the adsorbent dosage and hence results in a higher percentage removal at more dose [177]. The experiment was conducted at 25 °C, 50 mg/l concentration, contact time of 5 -120 minutes at a pH of 6 for both copper and cadmium.

Adsorption of metal ions on these types of materials was generally attributed to weak interactions due to physisorption and strong interactions due to chemisorption between the adsorbent and adsorbate. The influence of synergistic effect play a significant role and the % removal increases with increase in adsorbent dosage at the early stages of adsorption and later got saturated at 100 min and 120 min for Cu (II) and Cd (II), respectively.

Surface charges on substrates or on the mixed adsorbent as well as softness or hardness of the solutes are mostly responsible for the intensity of these interactions. Coloumbic interactions can be observed for the ion exchange of cationic species with the anionic sites present in the adsorbent materials and are determined by their surface areas. The adsorption experiment was carried out at different adsorbent dosages of 0.5 g/L, 1 g/L, 2 g/L, 3 g/L and 5 g/L of the mixed adsorbent. The % removal was highly dependent on adsorbent dosage. Hence the % removal increases in the order of increasing adsorbent dosage given as $5 > 3 > 2 > 1 > 0.5$ g/L as shown in Fig. 4.20. The experiments are carried out at pH = 6,T = 25 °C, and 50 mg/l of initial metal ion concentration.

The % removal of Cu varies from 87.16 to 99.74 at 5 g/L, 77.46 to 92.35 at 3 g/L, 58.93 to 78.88 at 2 g/L, 52.87 to 70.13 at 1 g/L, and 46.9 to 60.82 at 0.5 g/L respectively as shown in Fig. 4.20. Similarly for Cd (II) it was 70 to 88.4 % at 5 g/L, 65.66 to 80.23% at 3 g/L, 52.85 to 71.37% at 2 g/L, 45.71 to 64.77 % at 1 g/L, 39.23 to 56.83 % at 0.5 g/L respectively as shown in Fig. 4.21 at the same operating conditions. The optimized adsorbent dose was found to be 5 g/L for both the metals. The present results obtained are in correlation with the past literature results that were obtained for Cu (II) and Cd (II) removal using granular activated carbons, zeolites and many agricultural adsorbents [130], [95, 131].

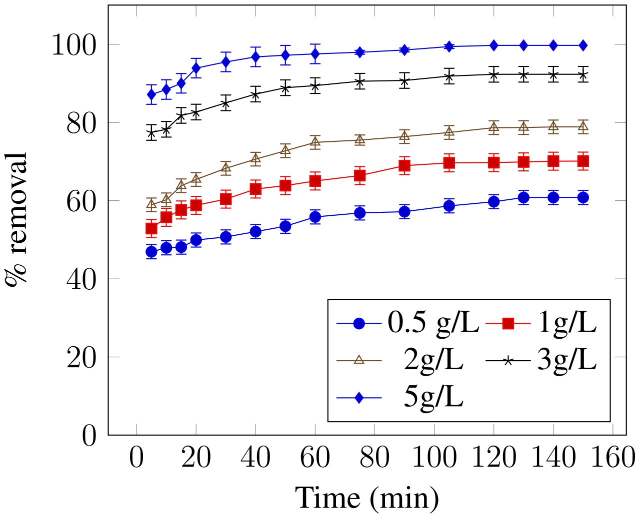

Figure 4.20: Effect of adsorbent dosage on Cu (II) removal at pH 6, 120 min, 50 ppm, 40°C, 180 rpm

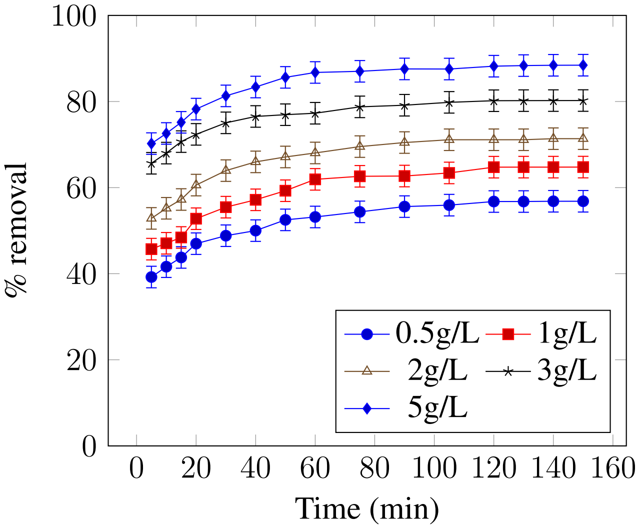

Figure 4.21: Effect of Adsorbent dosage on Cd (II) removal at pH 6, 120 min, 50ppm, 40°C, 180 rpm

4.2.4 Effect of Initial Metal ion concentration (IMC)

It was observed from the results that at lower metal ion concentrations, the ratio of surface active sites present to the total metal ions present in the solution was high and hence metal ions will interact with the adsorbent and can be removed from the solution easily. Similarly at high-concentration levels, some metal ion components were left unabsorbed in solution due to the saturation of binding sites present on the active surface. However,amount of metal adsorbed per unit weight of adsorbent q_e was higher at high concentration [178]. The experiment was conducted at a temperature of 25 °C, at different initial concentrations varying from 50 to 200 mg/L, pH 6, adsorbent dosage of 5 g/L for both copper and cadmium with an adsorbent dosage of 5g/L of the mixed adsorbent. The effect of initial metal ion concentration shows that up to 97.21% removal of Cu (II) metal ion was being adsorbed at the initial metal ion concentration of 50 mg/l within first 70 minutes and later got saturated from 80- 120 min of the reaction/contact time. Fig. 4.22 shows that the % removal decreases with an increase in the metal ion concentration from 50 to 200 ppm for Cu (II). Similarly at 100 ppm the % removal was observed to be 92.5% after attaining the equilibrium time of 120 min for the same adsorbent conditions which indicates the nearness value with a negligible difference of 4.7%. It can be predicted that with the industrial effluent whose concentration ranges between 100 to 350 ppm can be treated as an effluent and hence this 100 ppm concentration can be taken as an optimized value which can be utilized in the continuous column flow operation.

Similarly for cadmium with the increase of initial metal ion concentration from 50 to 100 mg/l the % removal decreases from 80.97 % to 78.77 % (2.2% decrement) respectively which was negligible and there were no significant removal were obtained at 200 ppm. This result signifies that gradual increase in the efficiency of the adsorbent shows the nearness to the saturation of available binding sites. The metal ion concentration of 150 ppm has the % removal of 77.37 and 64% for Cu and Cd (II) respectively, hence it can be taken as an intermediate between 100 and 200 ppm. It can be concluded that there is an negligible % removal of 2.2% was observed as shown above between 50 ppm and 100 ppm concentrations, hence the same 100 ppm IMC can be used in the continuous column flow operation for both Cu and Cd metal ions. The optimized initial metal ion concentration was found to be 100 ppm for both the divalent metals. The present results obtained are in correlation with the past results obtained from the literature [1, 18, 80].

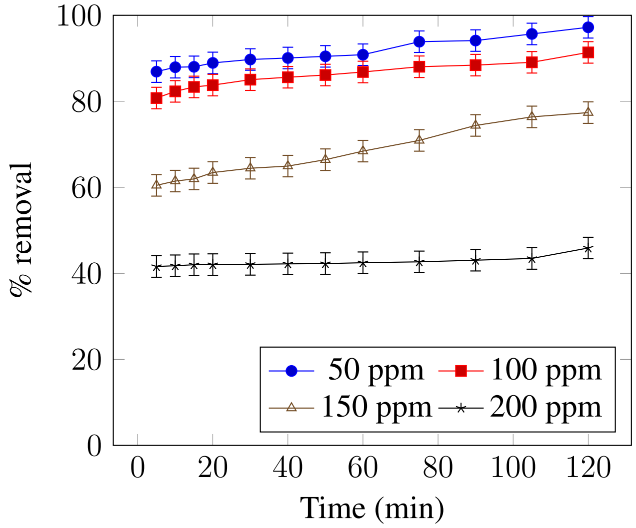

Figure 4.22: Effect of initial metal ion concentration on copper removal at pH 6, 120 min, T = 40°C, 5 g/L of ads dosage, 180 rpm

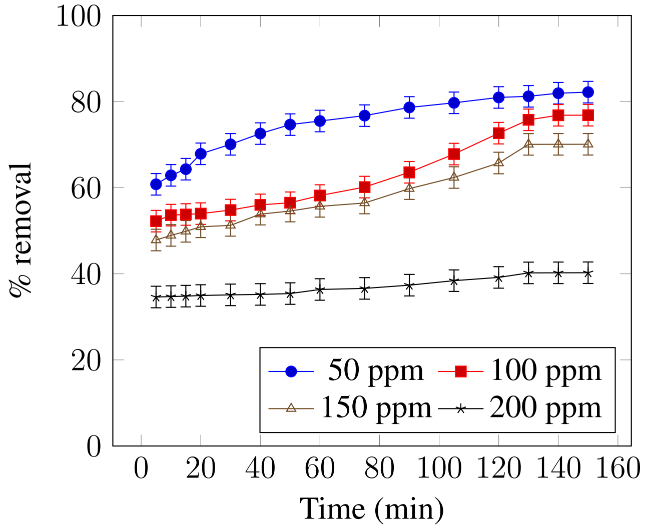

Figure 4.23: Effect of initial metal ion concentration on Cadmium removal at pH 6, 120 min, T = 40°C, 5 g/l of ads dosage, 180 rpm

4.2.5 Effect of Agitation rate

Agitation was an important parameter in adsorption because it helps in overcoming the external mass transfer resistance. At higher agitation rate the mass transfer resistance related to ion diffusion through the liquid film surrounding the mixed adsorbent was reduced as the film thickness reduces due to more shaking speed or agitation rate which results in metal ion uptake. Agitation of the solution not only results in a decrease in the film transfer resistance but also results in the abrasion of the mixed adsorbent and produces the freshly broken and highly reactive locations on the adsorbent surface. So this mechanical effect increases the number of possible adsorption locations/sites that results in an increase in the rate of adsorption. However, the production of fine particles due to abrasion has its own disadvantages and becomes difficult to separate the solute/solids from the liquid [5]. The experiment was conducted with the adsorbent conditions of 50 mg/l of metal ion concentration,5 g/L of the mixed adsorbent, contact time of 120 minutes, pH 6 for both copper and cadmium.

As agitation rate was an important factor in adsorption of batch studies for the heavy metal ions removal, it can be concluded that the more mass transfer can takes place during the reaction/agitation at higher agitation rate of 180 rpm when compared to low agitation rate of 60 rpm. The influence of turbulence effect on the % removal increases with the increase of agitation rate for the mixed adsorbent. The % removal increases with the increase of agitation rate (rpm) and the order is as follows: $180 > 150 > 120 > 90 > 60$ rpm. The maximum % removal was 92% and 86.9% at 180 rpm for Cu (II) and Cd (II), respectively as shown in the Figs. 4.24 and 4.25.

In our lab where the orbital shaker being used can withstand only upto maximum 180 rpm, and after that at higher rpm ($>$ 180), the orbital shaker produces more agitation and shaking which further leads to collision of 250 ml glass conical flasks. The rotary shaker was unable to withstand at greater than ($>$ 180 rpm). Hence the studies are carried out till 180 rpm only. Hence at 180 rpm adsorption was not declining, but due to the limitation of equipment usage upto maximum 180 rpm; further agitation studies are not carried out beyond 180 rpm.

4.2.6 Effect of Contact time

The outcomes acquired from the contact time demonstrates that the rate of adsorption increases /raises with the increment of contact time between the mixed adsorbent and metal particle/adsorbate arrangement in the metal ion solution. After certain amount of time all

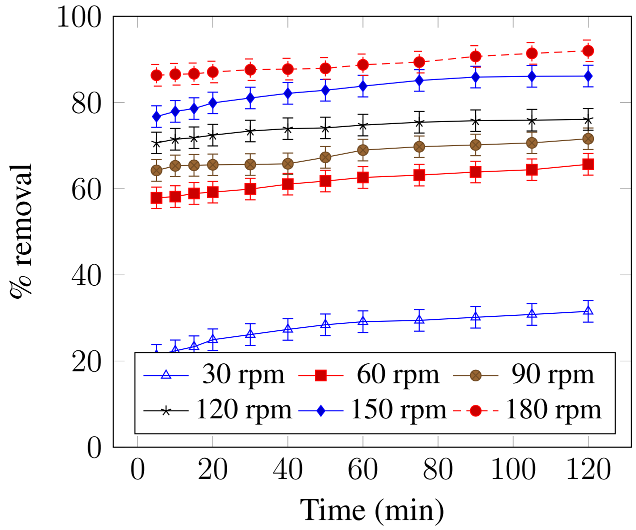

Figure 4.24: Effect of agitation rate on Cu (II) removal at pH 6, 120 min, T = 40°C, 5 g/l of ads dosage, 50 ppm IMC

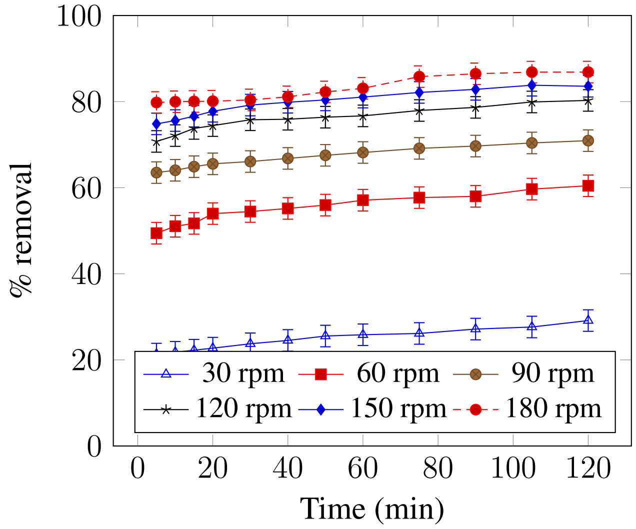

Figure 4.25: Effect of agitation rate on Cd (II) removal at pH 6, 120 min, T = 40°C, 5 g/l of ads dosage, 50 ppm IMC

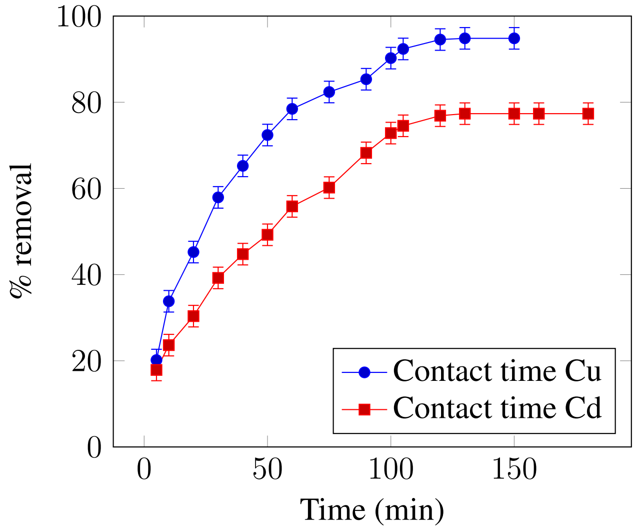

Figure 4.26: Effect of contact time for copper and cadmium at 5g/l of ads dosage, IMC of 50 ppm, pH 6,agitation rate of 180 rpm, temperature of 40°C

the active sites of the adsorbent were filled either with metal ions or the solution itself was saturated. So the increase in rate of adsorption ceases and percentage removal becomes constant and approaches a saturation point [176]. The experiment was conducted with the adsorbent conditions at 50 mg/L initial metal ion concentration (IMC), 5 g/L of the mixed adsorbent, pH 6 for both copper and cadmium with an agitation rate of 180 rotations per minute (rpm), and contact time of 5 to 120 minutes respectively.

It can be concluded that with respect to increase of contact time the % removal increases and the optimized contact time for Cu (II) with the mixed adsoebent was 105 to 120 min where (94.83% removal) was reported at pH 6. Similarly for Cd (II) the optimized contact time for mixed adsorbent was found to be 120 -130 min where the % removal was reported as (76.88-77.35%) at pH 6 as shown in Fig. 4.26.

4.3 Removal of copper and cadmium ions from batch process for industrial effluents using mixed adsorbent

The results obtained for both copper and cadmium on various parameters such as effect of pH, adsorbent dosage and contact time with industrial effluents are reported and the results are compared with the synthetic solution data obtained in batch studies.

4.3.1 Effect of pH on Cu(II) and Cd(II) removal from industrial effluent

pH is considered to be important factor influencing not only site dissociation but also the solution chemistry of the heavy metals, hydrolysis, complexation by organic and or inorganic ligands [56]. The same procedure has been carried out for industrial effluents as discussed in section 4.2 for the batch study. The % removal and metal adsorptive capacity were found using the mass balance relationship. The experiments were carried out at T = 25°C, agitation rate of 180 rpm, adsorbent dosage of 0.5 g/L and contact time of 120 min for both copper and cadmium at pH of 2, 4, 6, 8, IMC of 50 ppm. (diluted from 350 to 50 ppm for copper; 180 to 50 ppm for cadmium),

Fig 4.27 indicates that % removal of copper was highly dependent on pH and the highest % removal of 96.4% was obtained at an equilibrium time of 120 min. The % removal for synthetic sample and industrial effluent was found to be 97.21 and 96.4% respectively at 120 min for pH 6, 84.79 and 80.88% removal for pH 4, 77.94, 73.76 % removal for pH 2, 52.21 and 46.48 % removal at pH 8. The optimized pH was found to be at 6 with 96.4% removal of Cu (II).

Similarly for Cd (II), the % removal for synthetic solution and industrial effluent was 78.76 and 69.3% respectively for 120 min at pH 6, 63.42 and 57.92% removal at pH 4, 56.04, 50.94 % removal at pH 2, 44.16 and 38.4 % removal at pH 8. The Fig 4.28 shows the % removal vs time for cadmium at at 25 °C, 180 rpm, 0.5 g/L of ads dosage, 50 ppm IMC and contact time of 120 min. The optimized pH was found to be 6 having 69.3% removal of Cd (II). Overall in comparison of % removal with industrial effluent and synthetic solution a significant difference of 6-10% more removal was observed in case of synthetic solutions for cadmium.

The % removal of heavy metal ion increases with the increasing order of pH as $6 > 4 > 2 > 8$ for Cu (II) and Cd (II) metals and in the base range it forms as an hydroxide precipitate at pH ($>= 8$).

The % removal of metal ions decreased for industrial effluent sample as it contains other heavy metals, phenols, cresols, and waste contaminants,biodegradable mass and suspended solids for both the metals copper and cadmium.

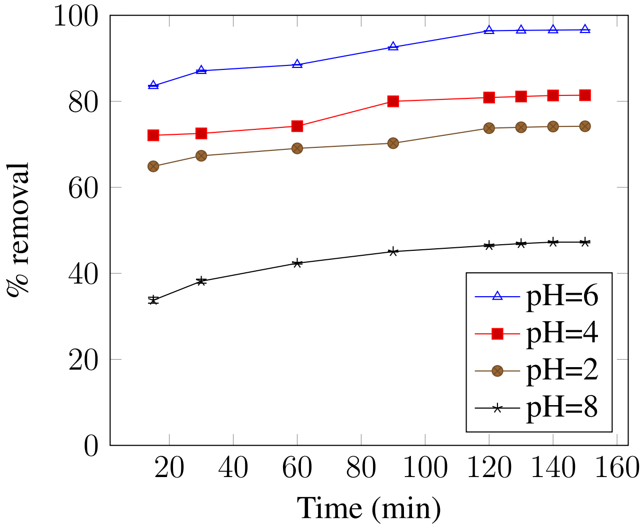

Figure 4.27: Effect of pH on Cu (II) removal using industrial effluent at 25 °C, 180 rpm, 0.5 g/L of ads dosage, 50 ppm IMC and contact time of 120 min

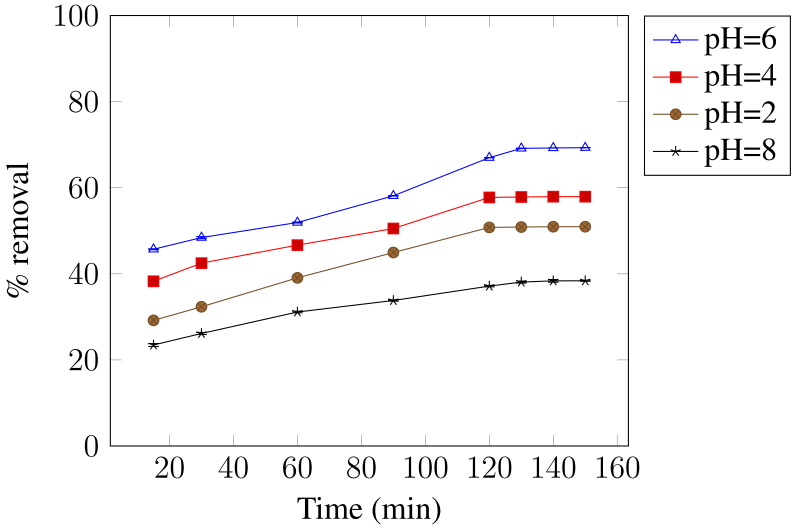

Figure 4.28: Effect of pH on Cd (II) removal using industrial effluent at 25°C, 180 rpm, 0.5 g/L of ads dosage, 50 ppm IMC and contact time of 120 min

4.3.2 Effect of point of zero charge on mixed adsorbent

Point of zero charge is the pH at which the mixed adsorbent has a net zero charge, above this pH it has a negative charge and is capable of attracting cations,below this pH it has a net positive charge capable of binding to anions. The value of pH used to describe PZC is only for the systems in which H^+ or OH^- ions are the potential determining factors and plays an important role. When the pH is lower than the PZC value, the system is said to be below PZC. Below the PZC, the acidic water donates more protons than hydroxide groups, and so the adsorbent surface was positively charged (attracting anions). Conversely, above PZC the surface was negatively charged (attracting cations/repelling anions). The pzc for the mixed adsorbent was found to be 3 as shown in Fig 4.29, which is attributed that the adsorbent surface was negatively charged which attracts cations; hence more % removal was observed in case of pH 4 and 6. The metal ions got precipitated at pH 8 by forming copper and cadmium hydroxides. The same trend was observed for cadmium and PZC was reported to be 3. Hence lower % removal was observed at pH 2 due to formation of more protons (H^+ ions) and the surface of the adsorbent is positively charged. Hence repulsion occurs between the Cu^{2+} and Cd^{2+} ions with the mixed adsorbent which leads to lower adsorption of metal ions in the solution.

The pH was controlled during the sorption process and maintained constant therefore at 2, 4, 6, 8 respectively using 0.1 M HCl and 0.1 N NaOH. Therefore a negligible change of (± 0.05 pH) was reported during the adsorption process and was adjusted using the acid and base treatments to maintain the respective pH.

The importance of this variable in the adsorption process was based on the fact that the signs of charge of adsorbate and adsorbent ideally should be opposed so that there was a greater electrostatic attraction between the two. If the charges are of same sign, then the adsoption process will be affected due to the electrostatic repulsion [179]. All the experiments were performed in acetate buffer of pH 3. An optimum effect was observed at pH 3, because at this pH the mixed adsorbents have negative potential which allows ion adsorption due to the attraction between the mixed adsorbent and the metal ions [180]. The experiments were carried from 1 to 6 pH for PZC analysis.

4.3.3 Effect of adsorbent dosage on Cu(II) and Cd (II) removal from industrial effluent

The adsorption experiments were carried out at 0.5, 1, 2, 3 and 5 g/L dosage of the mixed adsorbent. The% removal was highly dependent on adsorbent dosage. Therefore

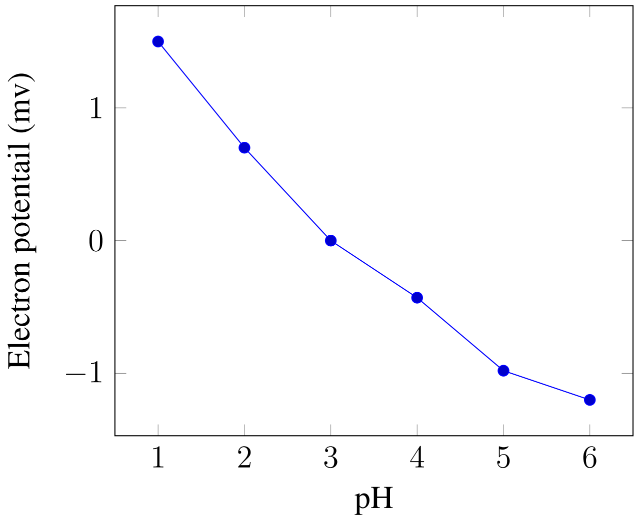

Figure 4.29: PZC analysis of the mixed adsorbent at different pH

the % removal increases in the order of increasing adsorbent dosage given as $5 > 3 > 2 > 1 > 0.5$ g/L as shown in Fig 4.30. The experiments are carried out at pH 6, T = 25°C, 50 mg/l of initial metal ion concentration, 180 rpm, contact time of 15-120 min.

The % removal of Cu varies from 83.76 to 96.2 % for industrial effluent and 87.16 to 99.74% for synthetic sample at 5 g/L respectively. The % removal varies from 68.32 to 88.48% for industrial effluent and 77.46 to 92.35% for synthetic sample at 3 g/L respectively. The % removal varies from 55.74 to 74.8 % for industrial effluent and 58.93 to 78.88 % for synthetic sample at 2 g/L respectively. The % removal at 1 g/L of dosage varies from 49.76 to 65.96 % for industrial effluent and 52.87 to 70.13% for synthetic sample respectively. The % removal at 0.5 g/L dosage varies from 43.78 to 57% for industrial effluent and 46.9 to 60.82 % for synthetic sample respectively as shown in Fig 4.30 . In comparison with synthetic sample, there was a difference of 3-4% less removal for industrial effluent of Cu (II) at 5g/L, and 4-9% less removal at 3g/L of dosage was observed. Similarly 3-4% less removal for industrial effluent at 2g/L, 1g/L, 0.5g/L of adsorbent dosage was observed in this study. The equilibrium time was found to be 120- 150 min for Cu (II) ion.

The % removal of Cd varies from 81.32 to 89.68 % for industrial effluent and 83.9 to 91.2 % for synthetic sample at 5 g/L respectively. The % removal varies from 64.72 to 83.18 % for industrial effluent and 77.66 to 89.2% for synthetic sample at 3 g/L respectively. The % removal varies from 50.92 to 70.21 % for industrial effluent and 68.84 to 85.12 % for synthetic sample at 2 g/L respectively. The % removal at 1g/L of dosage varies from 44.31 to 60.23 % for industrial effluent and 63.42 to 82.74 % for synthetic sample respectively. The % removal at 0.5 g/L varies from 40.91 to 52.81 % for industrial effluent and 53.24 to 78.76 % for synthetic sample respectively as shown in Fig. 4.31.

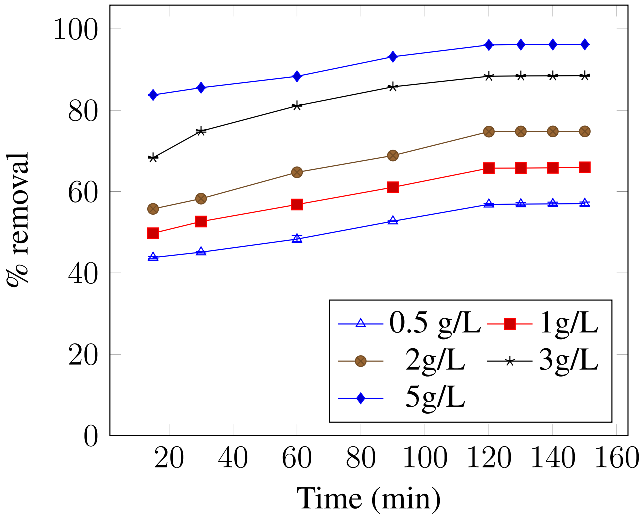

Figure 4.30: Effect of adsorbent dosage on Cu (II) removal for industrial effluent at pH 6 and T = 25 °C, 50 mg/l of initial metal ion concentration, 180 rpm, contact time of 120 min.

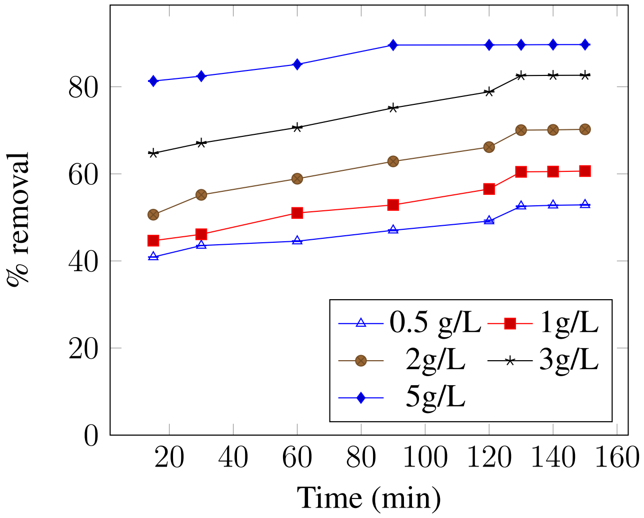

Figure 4.31: Effect of adsorbent dosage on Cd (II) removal for industrial effluent at pH 6 and T = 25 °C, 50 mg/l of initial metal ion concentration, 180 rpm, contact time of 120 min.

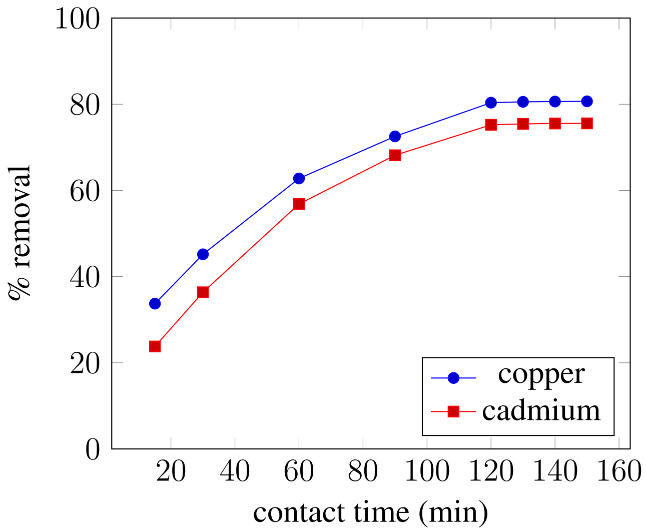

Figure 4.32: Effect of contact time on Cu (II) and Cd(II) %removal for industrial effluent at 50 mg/L of initial metal ion concentration (IMC), 5 g/L of the mixed adsorbent, agitation rate of 180 rpm, pH 6, and temperature of 25°C

4.3.4 Effect of contact time on Cu(II) and Cd (II) removal using industrial effluent

The rate of adsorption increases with the increment of contact time between the adsorbent and metal ions or (adsorbate) in the solution. After the progression of time all the active sites of the adsorbent were filled either with metal ions or the solution itself was saturated, hence the increase in rate of adsorption ceases, percentage removal becomes constant and approaches a saturation point [181].

The experiments were conducted at 50 mg/L of initial metal ion concentration (IMC), 5 g/L of the mixed adsorbent dosage, agitation rate of 180 rpm, contact time of 5-120 min, pH 6, and temperature of 25°C. It can be concluded for the industrial effluent that with respect to increase of contact time the % removal increases and the optimized contact time for Cu (II) with the mixed adsorbent was found to be 120 to 150 min where 80.68% removal was observed for copper and 75.56 % was reported for cadmium at pH 6 as shown in Fig. 4.32. Similarly for the synthetic sample the % removal for copper and cadmium are 94.83% and 77.35%. A difference of 14% was observed in case of copper and 1.8% difference in case of cadmium was observed in comparison with the industrial effluent due to the presence of other heavy metals, contaminants, suspended solids.

4.4 Comparison of mixed adsorbent and maize cob for the removal of copper and cadmium from industrial effluent in batch studies

Comparison studies have been made for the mixed adsorbent and maize cobs for the removal of copper and cadmium in terms of % removal, adsorption capacities for the parameters pH, adsorbent dosage and contact time.

4.4.1 Effect of pH

The surface of adsorbent would be surrounded by hydronium ions at lower pH values that decrease the metal ion interaction with binding sites of the maize cob by greater repulsive forces and therefore lower adsorption takes place. In contrast as the pH increased, the competing effect of hydrogen ions decreased and more ligands were available for adsorption.

Therefore for pH values, $4 \leq pH \leq 6$, the overall surface on the maize cob became more negative and adsorption increases. The study at pH higher than 8 were not conducted, because insoluble copper hydroxides got precipitated and restricted the true biosorption studies [182]. The experiment was conducted at a temperature of 25 °C, 50 mg/L metal ion concentration for 60 minutes agitation with an adsorbent dosage of 0.5g/L and the samples were collected for every 30 minutes until 3 hrs to reach the saturation and the residual concentrations were measured by using AAS.

The adsorption efficiencies were found to be pH dependent, and efficiency increases as pH is increasing from 4 to 6. The equilibrium was attained after 150-180 min for maize cob and 120-150 min for mixed adsorbent and the maximum removal percentage was achieved at an adsorbent dosage of 0.5g/L for all pH values for both the metals copper and cadmium.

Fig. 4.33 indicates the maximum % removal of Cu by maize cob was obtained as 75 % at pH 6, 45% at pH 4, 28.3 % at pH 2, and 17.54 % at pH 8, respectively. Similarly by mixed adsorbent the % removal of copper was obtained as 96.62 % at pH 6, 81.42 % at pH 4, 74.22 % at pH 2, and 47.26 % at pH 8 respectively as shown in fig 4.34. The max adsorption capacities for mixed adsorbent and maize cobs at pH 2 were found to be 7.1 and 2.33 mg/g, at pH 4 were 7.8 and 3.66 mg/g, at pH 6 were 9.22 and 6.4 mg/g, and at pH 8 were 4.43 and 1.35 mg/g respectively. The maximum equilibrium adsorptive capacities at 180 min for different pH 2, 4, 6 and 8 was 2.82 mg/g, 4.5 mg/g, 7.53 mg/g, 1.75 mg/g,

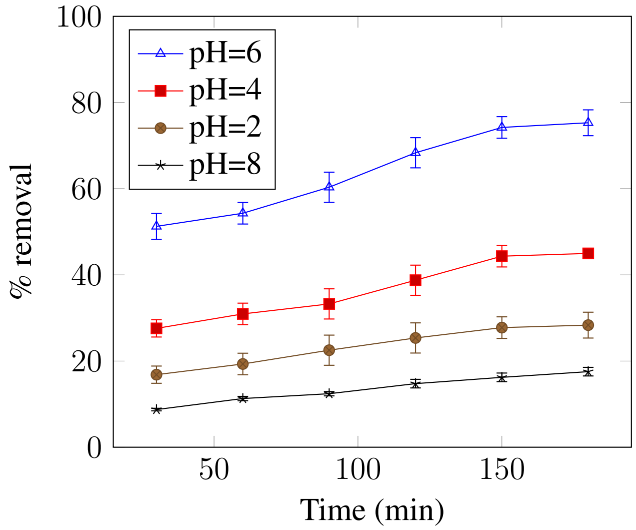

Figure 4.33: Effect of pH on industrial effluent for copper removal by maize cob at 25°C, 180 rpm, 0.5g/L of ads dosage, 50 ppm IMC and contact time of 3 hrs

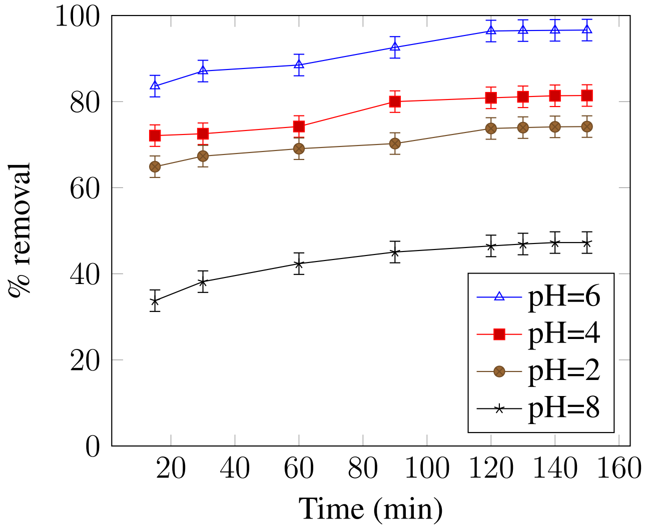

Figure 4.34: Effect of pH on industrial effluent for copper removal by mixed adsorbent at 25°C, 180rpm, 0.5g/l of ads dosage, 50ppm IMC and contact time of 2hrs

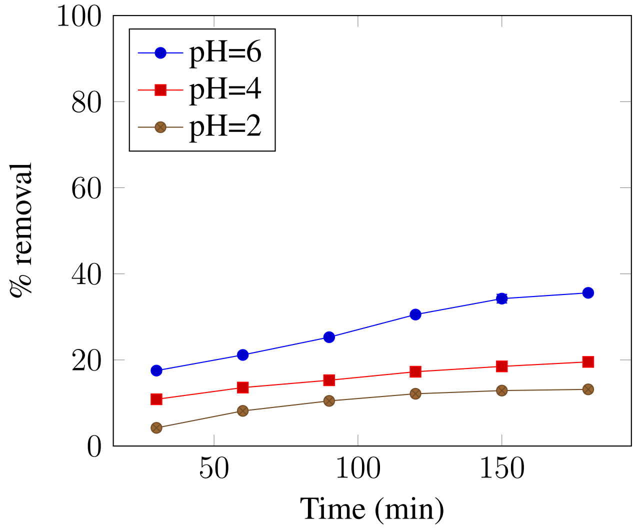

Figure 4.35: Effect of pH on industrial effluent for cadmium removal by maize cob at 25°C, 180rpm, 0.5g/L of ads dosage, 50 ppm IMC and contact time of 3hrs

respectively.

The graphs given in Figs. 4.35 and 4.36 indicates the maximum removal of cadmium by maize cob was obtained as 28.4 to 53.18 % at pH 6, 17.52 to 35.6 % at pH 4, 10.86 % to 19.54 % at pH 2, and 4.22% to 13.16 % at pH 8, respectively. Similarly for the mixed adsorbent the maximum % removal was obtained as 45.7 to 69.3 % at pH 6, 38.26 to 57.92 % at pH 4, 29.18 to 50.94 % at pH 2, and 23.46 to 38.4 % at pH 8. The max average adsorption capacities for mixed adsorbent and maize cobs for cadmium at pH 2 were found to be 4.36 and 1.58 mg/g, at pH 4 were 5.11 and 2.73 mg/g, at pH 6 were 5.98 and 4.24 mg/g, at pH 8 were 3.33 and 1.02 mg/g respectively. The graph indicates that at different pH the equilibrium time was attained between 150-180 min and got saturated and further adsorption ceases due to the blockage of pores with the metal ions which indicates the equilibrium or saturation point. The maximum equilibrium adsorptive capacities at 180 min for different pH 2, 4, 6 and 8 was 1.95 mg/g, 3.56 mg/g, 5.32 mg/g, 1.316 mg/g, respectively.

4.4.2 Effect of adsorbent dosage

The effect of adsorbent dosage was studied from 0.5, 1, 2, 3, 5 g/L for both copper and cadmium with the maize cob and mixed adsorbent. The experiment was conducted at a temperature of 25°C, 50 mg/L metal ion concentration, 60 minutes agitation with a varying adsorbent dosages of 0.5g/L, 1g/L, 2g/L, 3g/L, and 5g/l. The samples were collected for every 30 minutes until 3 hrs (for maize cobs) and 2 hrs (for mixed adsorbent) to reach the

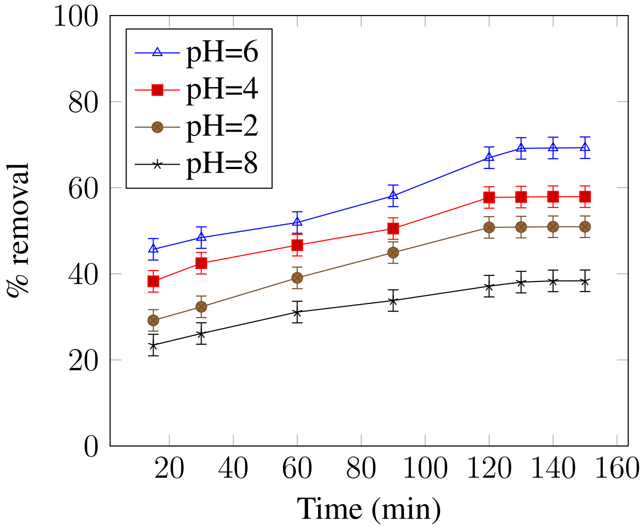

Figure 4.36: Effect of pH on industrial effluent for cadmium removal by mixed adsorbent at 25°C, 180 rpm, 0.5g/L of ads dosage, 50 ppm IMC and contact time of 2hrs

saturation and the residual concentrations were measured using AAS.

It was shown from the Figs. 4.37 and 4.38 for copper the maximum % removal by maize cobs were obtained as 14.92 to 26.56 % at 0.5 g/L, 22.52 to 41.14 % at 1 g/l, 26.98 to 58.92 % at 2 g/L, and 38.88 to 69.36 % at 3 g/L, 46.54 to 83.36 % at 5 g/L respectively. Similarly for the mixed adsorbent the % removal were obtained as 43.78 to 57 % at 0.5 g/L, 49.76 to 66 % at 1g/L, 55.74 to 74.8 % at 2 g/L, 68.32 to 88.48 % at 3 g/L, and 83.76 to 96.2 % at 5 g/L respectively. The maximum adsorption capacities for mixed adsorbent and maize cobs at 0.5g/L were found to be 5.22 and 2.17 mg/g, at 1 g/L was 3.02 and 1.7 mg/g, at 2 g/L was 1.71 and 1.13 mg/g, at 3 g/L was 1.38 and 0.94 mg/g, at 5 g/L was 0.92 and 0.644 mg/g respectively. Similarly the maximum equilibrium adsorptive capacities at 180 min for different adsorbent dosages of 0.5g/L, 1g/L, 2g/L, 3g/L and 5g/L were 2.656 mg/g, 2.06 mg/g, 1.473 mg/g, 1.156 mg/g and 0.774 mg/g respectively.

Fig 4.39 indicates the maximum % removal of cadmium for maize cobs was obtained as 8.76 to 20.92 % at 0.5 g/L, 14.16 to 30.91% at 1 g/L, 19.36 to 42.54 % at 2 g/L, and 28.54 to 54.14 % at 3 g/L, 39.38 to 69.14 % at 5 g/L respectively.

Similarly for the mixed adsorbent the % removal was obtained as 40.91 to 52.81 % at 0.5 g/L, 44.6 to 60.64 % at 1 g/L, 50.62 to 70.34 % at 2 g/L, 64.72 to 82.6% at 3 g/L, and 81.32 to 89.68 % at 5 g/L respectively. The maximum adsorption capacities for cadmium metal using mixed adsorbent and maize cobs at 0.5 g/L were found to be 4.79 and 1.577 mg/g, at 1 g/L was 2.7 and 1.177 mg/g, at 2 g/L was 1.57 and 0.803 mg/g, at 3 g/L was 1.25 and 0.72 mg/g, at 5 g/L was 0.87 and 0.571 mg/g respectively. Similarly the maximum

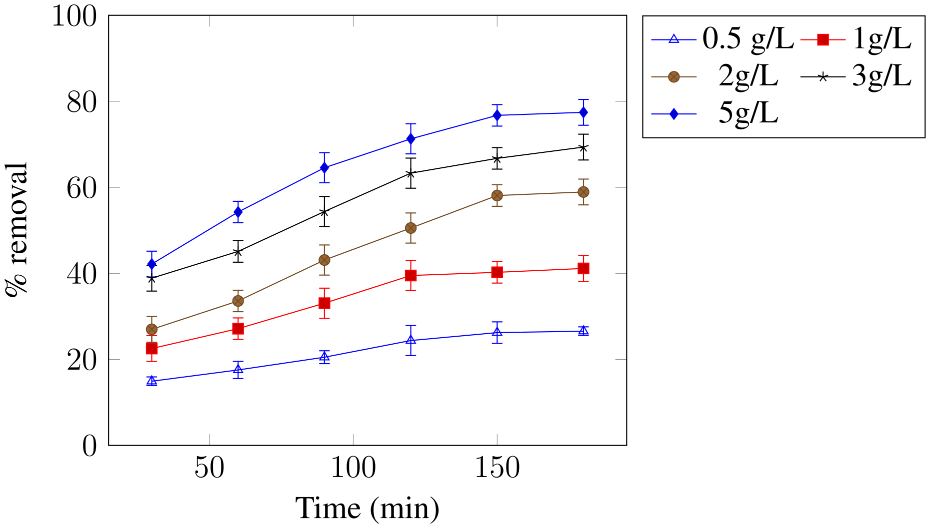

Figure 4.37: Effect of adsorbent dosage on industrial effluent for copper removal by maize cob at 25°C, 180rpm, pH 6, 50 ppm IMC and contact time of 3hrs

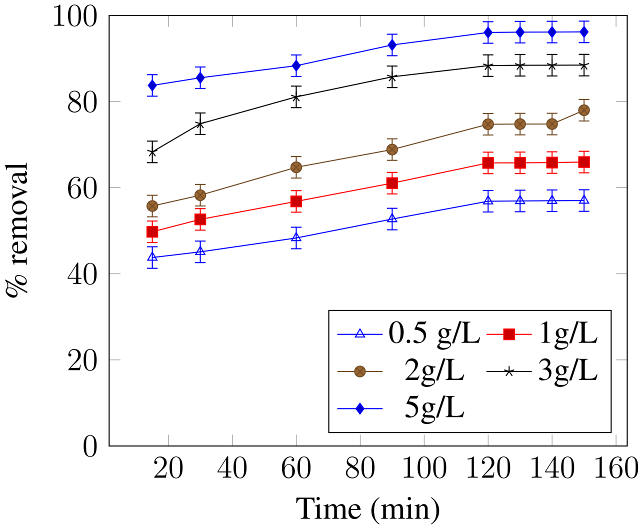

Figure 4.38: Effect of adsorbent dosage on industrial effluent for copper removal by mixed adsorbent at 25°C, 180 rpm, pH 6, 50 ppm IMC and contact time of 2hrs

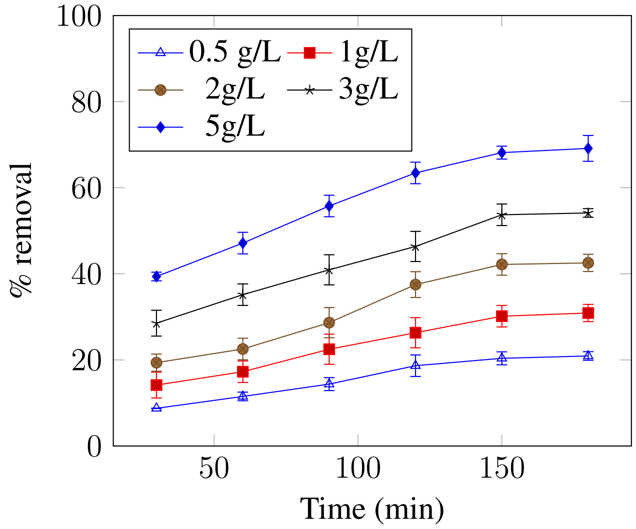

Figure 4.39: Effect of adsorbent dosage on industrial effluent for cadmium removal by maize cob at 25°C, 180 rpm, pH 6, 50 ppm IMC and contact time of 3hrs

equilibrium adsorptive capacities at 180 min for different adsorbent dosages of 0.5, 1, 2, 3 and 5 g/L were found to be 2.09 mg/g, 1.545 mg/g, 1.06 mg/g, 0.902 mg/g and 0.691 mg/g respectively.

4.4.3 Effect of contact time for the removal of copper and cadmium by maize cobs and mixed adsorbent

After optimizing the pH and adsorbent dosage, the experiments were carried out at to find the effect of contact time on % removal for maize cobs and mixed adsorbents for both the metals.The experiment were conducted at a temperature of 25 °C, 50 mg/L metal ion concentration for 60 minutes agitation with an adsorbent dosage of 5 g/L and the samples are taken at every 30 minutes time interval and analyzed through AAS to find the metal ion concentration. Fig. 4.42 indicates the maximum % removal of copper by mixed adsorbent was reported as 33.72 to 80.7 % at 5 g/L, and for maize cob it was 46.54 to 83.36 % at 5 g/ L of adsorbent dosage.

The maximum adsorption capacities for mixed adsorbent and maize cobs at 5 g/l for copper were found to be 0.92 mg/g and 0.644 mg/g, respectively. Similarly the maximum equilibrium adsorptive capacities for copper at 180 min using maize cobs were 0.7744 mg/g, and for mixed adsorbent at 150 min was 0.962 mg/g, respectively.

Fig.4.42 shows the maximum % removal of cadmium by mixed adsorbent was reported as 23.78 to 75.56 % at 5g/l, and by maize cobs it was 39.38 to 69.14 % at 5g/l of adsorbent

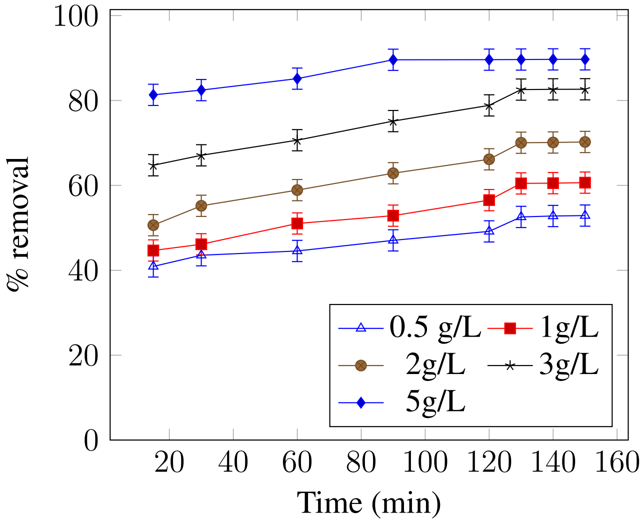

Figure 4.40: Effect of adsorbent dosage on industrial effluent for cadmium removal by mixed adsorbent at 25°C, 180rpm, pH 6, 50 ppm IMC and contact time of 2 hrs

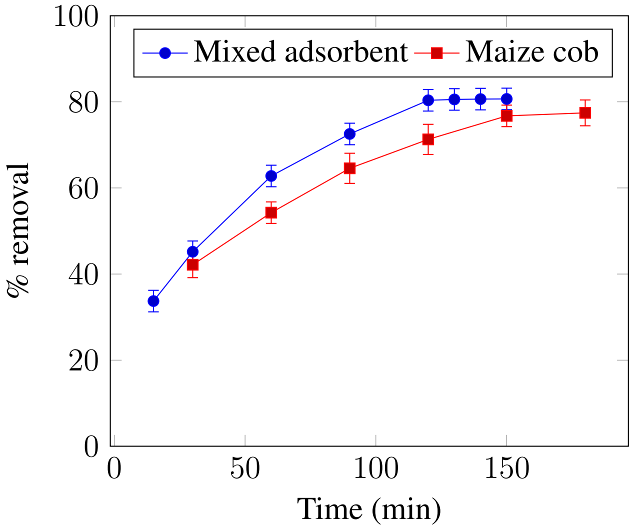

Figure 4.41: Effect of contact time on copper removal for mixed adsorbent and maize cobs using industrial effluent at 25°C, 180 rpm, pH 6, 50ppm IMC and ads dosage of 5g/L

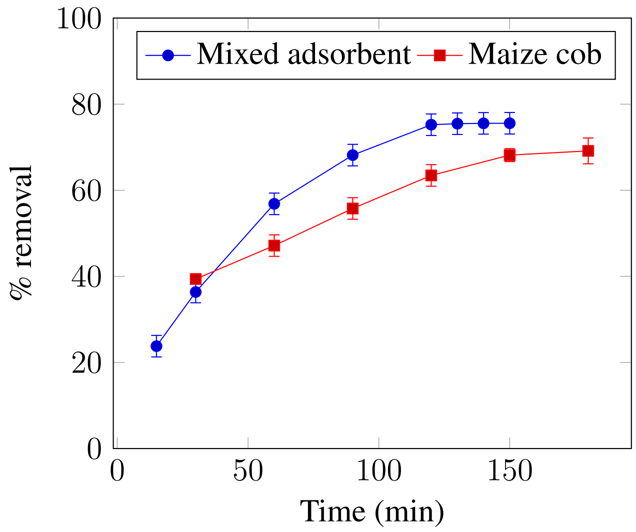

Figure 4.42: Effect of contact time on cadmium removal for mixed adsorbent and maize cob for industrial effluent at 25°C, 180 rpm, pH 6, 50 ppm IMC and ads dosage of 5g/L

dosage. The maximum adsorption capacities for mixed adsorbent and maize cobs at 5 g/l were found to be 0.61 mg/g and 0.571 mg/g respectively. Similarly the maximum equilibrium adsorptive capacities at 180 min for maize cobs were 0.691 mg/g and for mixed adsorbent at 150 min was 0.7554 mg/g.

In comparison with the maize cobs, the highest % removal was obtained for mixed adsorbent (AC+ BC) due to the high surface area of the activated charcoal as well as negative charge from the bone charcoal which induces the synergistic effect (from the mixed adsorbent) as well as less particle size and more pore volume in comparison with maize cobs for all the three parameters studied.

Initially almost competitive adsorption between maize cob and mixed adsorbent occured for the parameter contact time. The competitive % removal was observed due to high adsorbent dosage as the sites are unoccupied by the metal ions initially and at a later stage with the progress of time, the pores got blocked with the metal ions and % adsorption rate decreases for maize cobs gradually and reaches a saturation point in between an equilibrium time of 150-180 min.

It was concluded based on the results that mixed adsorbents have more potential when compared to maize cobs for the removal of copper and cadmium from the complex industrial effluents [158],[163].

4.5 Simultaneous copper and cadmium metal ion removal in batch studies using industrial effluents and their data analysis by isotherm models

Simultaneous metal ion removal for copper and cadmium has been carried out in batch operation to study the effect of adsorbent dosage and effect of contact time.

In this isothermal modeling for simultaneous removal, Langmuir isotherm models have been shown at different adsorbent dosage (0.5, 1, 2, 3, 5 g/L), pH 6, 180 rpm, 2 hrs contact time and temperature of 25°C. Similarly Temkin model was studied at an adsorbent dosage of 5g/L, pH 6, 180 rpm, 2 hrs contact time and temperature of 25°C for simultaneous (Cu (II) and Cd (II) ions removal) and the regression analysis was performed to know the suitability of the model based on the R^2 values.

The Temkin isotherm equation is as follows: $q_e = B_t(\ln K) + B_t (\ln C_e)$, where $B_t = \frac{RT}{b}$ where the constant B_t is related to the heat of adsorption or variation of adsorption energy (J/mol), R is the universal gas constant (J/ mol K), T is the temperature (K). A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants B_t and K from the slope and the intercept respectively [183] [184] [185].

4.5.1 Effect of adsorbent dosage on simultaneous Cu (II) and Cd (II) removal

The effect of adsorbent dosage on simultaneous removal of Cu (II) and Cd (II) has been studied and predicted that more % removal was obtained for Cu (II) when compared to Cd (II). The reason behind the decrease of cadmium % removal was due to more atomic weight of Cd (II) than Cu (II) (112.4 > 63.5). The maximum % removal obtained for Cu (II) and Cd (II) at 0.5 g/L are 30.46 %, 20.12 % respectively, at 1g/L are 38.96%, 28.67% respectively, at 2g/L are 44.75 %, 37.86 % respectively, at 3g/L are 54.56 %, 48.11% respectively and at 5g/L are 80.62 % and 75.95 % respectively at the saturation time of 120-150 min for both the metals as shown in Figs.4.43 to4.47. The maximum adsorption capacity for Cu (II) and Cd (II) at 0.5g/L were 2.1 mg/g and 1.13 mg/g respectively, at 1g/L were 1.45 mg/g and 0.97 mg/g respectively, at 2g/L were 0.88 mg/g and 0.65 mg/g respectively, at 3 g/L were 0.75 mg/g and 0.57 mg/g respectively, at 5g/L were found to be 0.7 mg/g and 0.497 mg/g respectively. The equilibrium time for both the metals were found to be 120-150 min. The % removal increases with the increase of adsorbent dosage from 0.5 to 5g/L which due to presence of more binding sites available for adsorption.

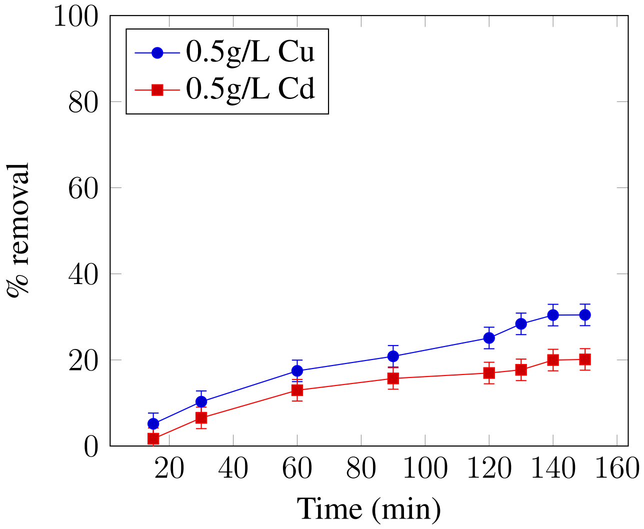

Figure 4.43: Effect of simultaneous metal ion removal by the mixed adsorbent at 0.5g/L of ads dosage

More number of active sites are available for simultaneous (copper and cadmium) ions due to the presence of synergistic effect as well as interaction of the metal ions that bind with the mixed adsorbent with the increase of adsorbent dosage. Hence % removal increases with increase in more dose.

4.5.2 Effect of contact time for simultaneous Cu (II) and Cd (II) removal

The effect of contact time on simultaneous removal of Cu (II) and Cd (II) has been studied and predicted that more % removal was obtained for Cu (II) when compared to Cd (II). The maximum % removal obtained for Cu (II) and Cd (II) were 80.62 % and 75.95 % respectively at the saturation time of 120-150 min for both the metals. The maximum adsorption capacity for Cu (II) and Cd (II) were found to be 0.7 mg/g and 0.497 mg/g respectively. The reason behind the decrease of cadmium % removal was due to more atomic weight of Cd (II) than Cu (II) ($112.4 > 63.5$). The rate of adsorption increases with the increase of contact time between the mixed adsorbent and the metal ions present in the solution. After the progression of time, all the active sites got saturated by filling with metal ions or solution itself became saturated and reaches an equilibrium state and the rate of adsorption ceases, and percentage removal becomes constant. The optimized contact time for simultaneous removal of metals ions were found to be 120-150 min as shown in Fig 4.47.

In comparison from the graphs drawn for simultaneous removal of copper and cad-

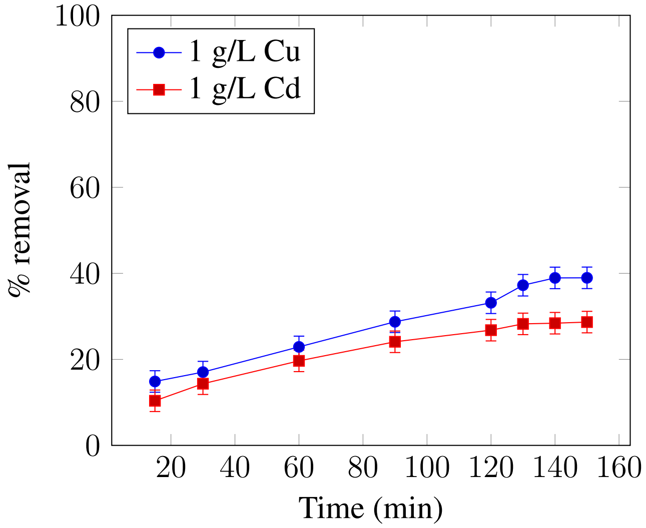

Figure 4.44: Effect of simultaneous metal ion removal by the mixed adsorbent at 1 g/L of ads dosage

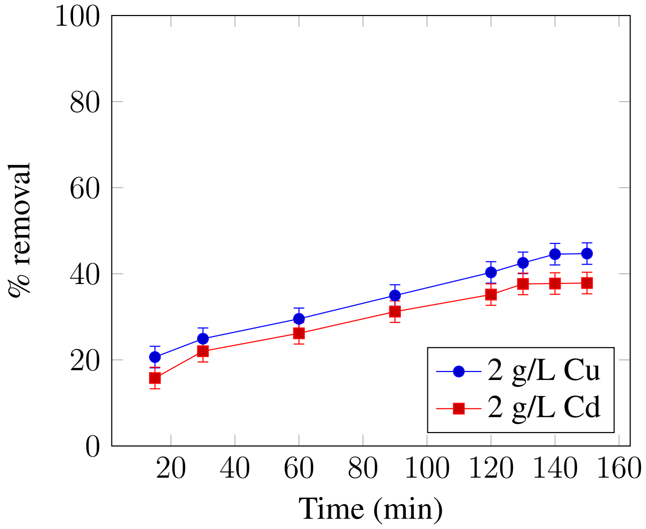

Figure 4.45: Effect of simultaneous metal ion removal by the mixed adsorbent at 2 g/L of ads dosage

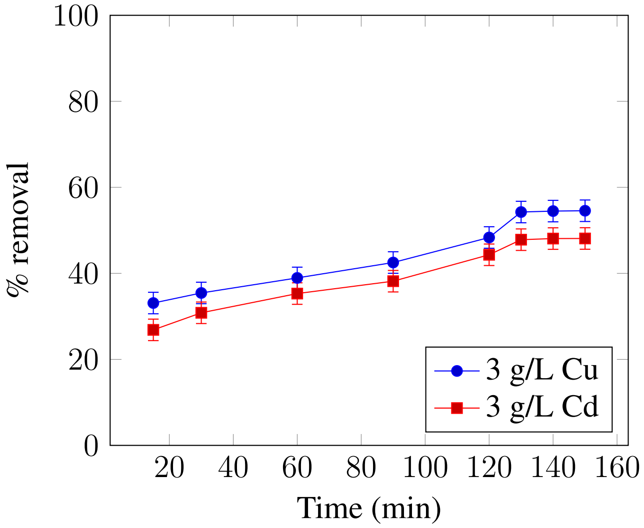

Figure 4.46: Effect of simultaneous metal ion removal by the mixed adsorbent at 3 g/L of ads dosage

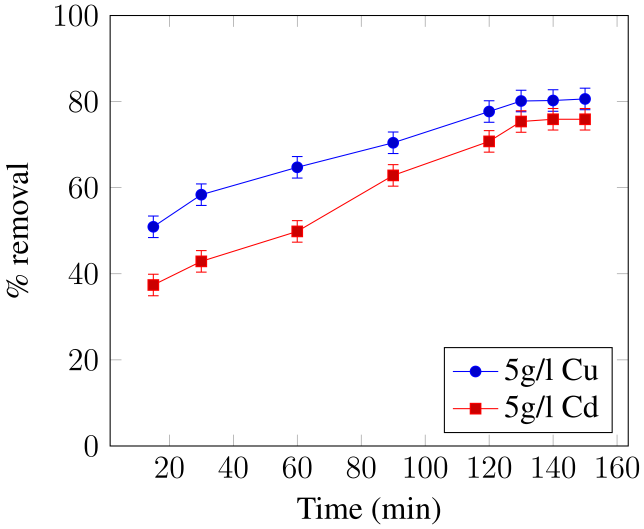

Figure 4.47: Effect of simultaneous metal ion removal by the mixed adsorbent at 5 g/L of ads dosage

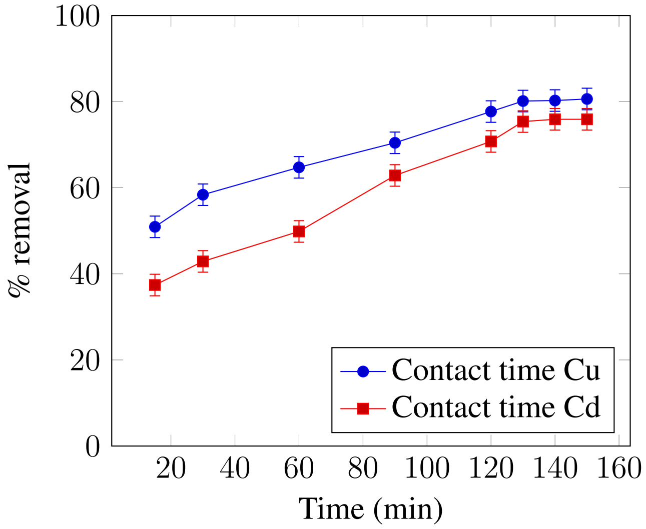

Figure 4.48: Effect of contact time on simultaneous metal ion removal by the mixed adsorbent at 5 g/L of ads dosage, pH 6

mium for the adsorbent dosage and contact time the highest % removal and adsorption capacity was obtained for Cu (II) than Cd (II) due to lower atomic weight of Cu when compared to Cd.

4.5.3 Analysis of Langmuir isotherm data for simultaneous Cu (II) & Cd (II) removal

It was concluded from the Table 4.5 that the separation factor (R_L) values (< 1) which indicates that Langmuir model is an favorable adsorption model for both Cu (II) and Cd (II) at 25°C, adsorbent dosage of (0.5 to 5 g/L), agitation rate of 180 rpm, pH 6, and contact time of 2 hrs. Moreover correlation coefficients R^2 values were in the range of 0.8 to 0.98 which predicts the suitability and linear regression fit of models for both Cu (II) and Cd (II). The higher R^2 values were seen in case of Cu (II) which indicates the better fit when compared to Cd. The graphs for Langmuir isotherm model (c_e vs c_e/q_e) were plotted at different adsorbent dosage of (5, 3, 2, 1, 0.5g/L) and pH 6, 180 rpm, 2 hrs contact time, 25°C and were shown in Figs. 4.49 to 4.53 respectively.

4.5.4 Analysis of Temkin model

Temkin model has been studied for the obtained data and the variation of heat of adsorption (B_t) values for simultaneous (Cu and Cd) has been found at 5g/l. More over higher R^2 values for both Cu (II) and Cd (II) predicts the suitability of this isotherm model at 5

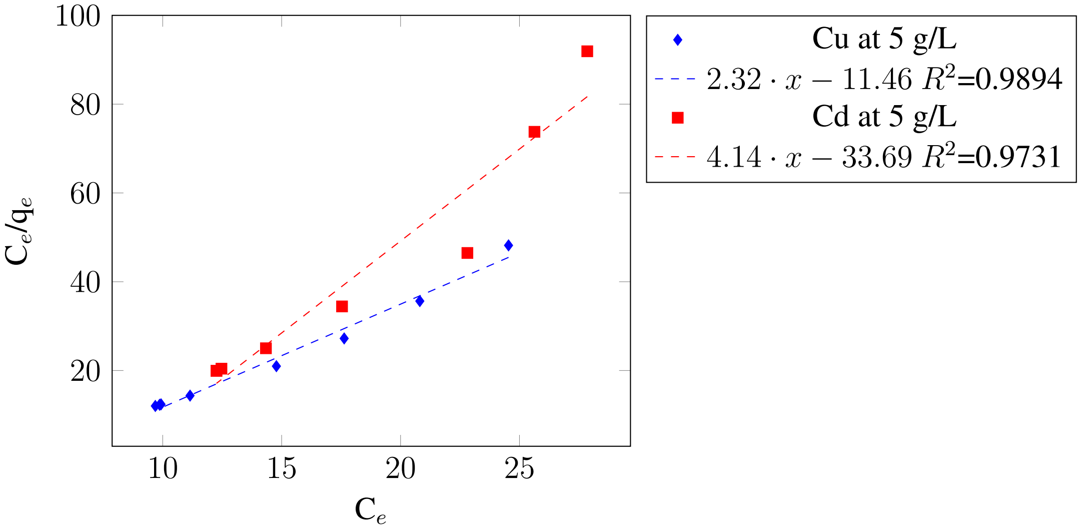

Figure 4.49: Langmuir isotherm plot for Cu and Cd at 5 g/L adsorbent dosage, pH 6, 180 rpm, 2 hrs contact time, 25°C

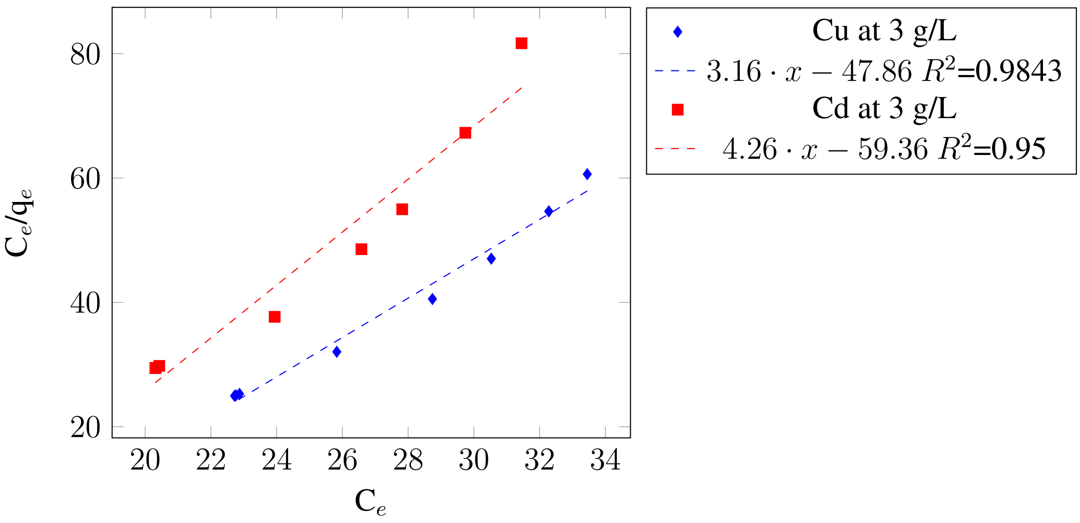

Figure 4.50: Langmuir isotherm plot for Cu and Cd at 3 g/L adsorbent dosage, pH 6, 180 rpm, 2 hrs contact time, 25°C

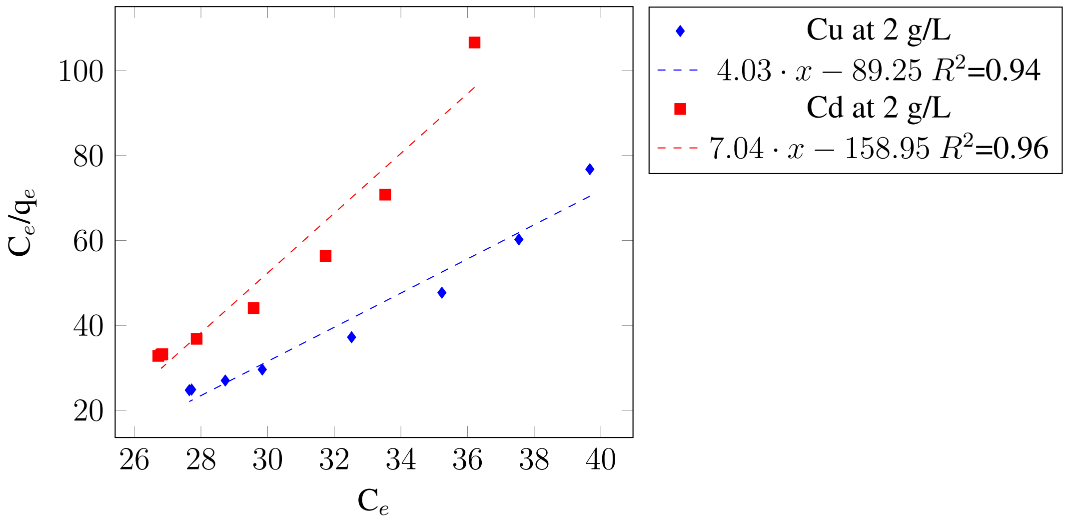

Figure 4.51: Langmuir isotherm plot for Cu and Cd at 2 g/L adsorbent dosage, pH 6, 180 rpm, 2 hrs contact time, 25°C

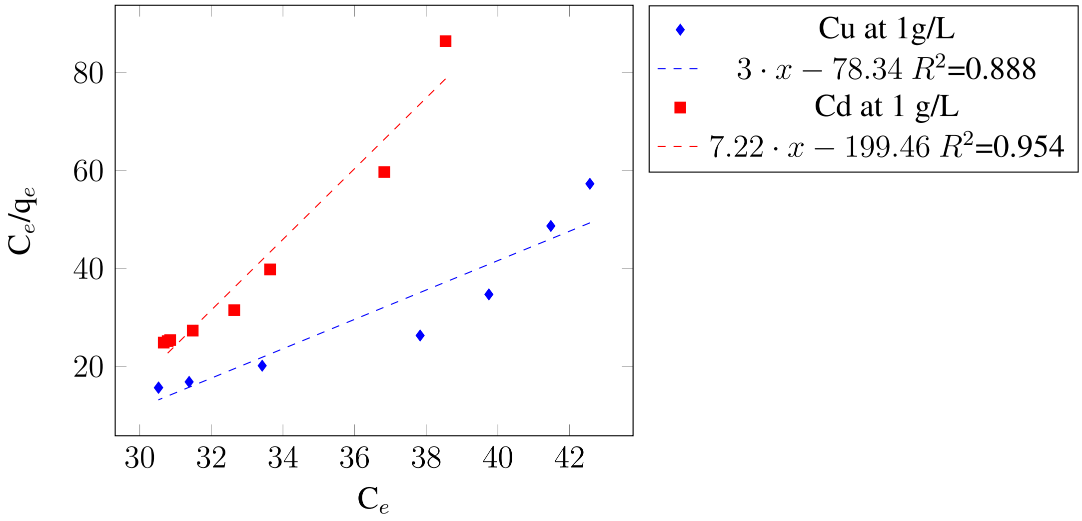

Figure 4.52: Langmuir isotherm plot for Cu and Cd at 1 g/L adsorbent dosage, pH 6, 180 rpm, 2 hrs contact time, 25°C

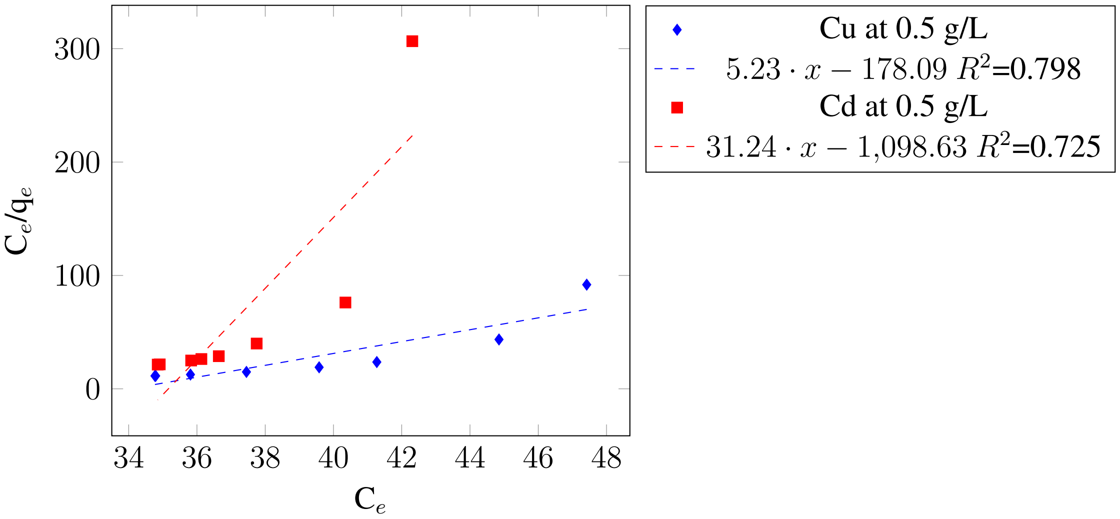

Figure 4.53: Langmuir isotherm plot for Cu and Cd at 0.5 g/L adsorbent dosage, pH 6, 180 rpm, 2 hrs contact time, 25°C

Table 4.5: Analysis of Langmuir Isotherm data for simultaneous Cu (II) and Cd (II) removal at pH 6, 180 rpm, 2hrs contact time, 25°C

metal	**ads dose** (g/l)	**slope** 1/q$_{max}$	**Intercept** 1/(bq$_{max}$)	**q$_{max}$** (mg/g)	**b** (Langmuir constant)	**IMC (ppm)**	**R$_L$**	**R^2**
Cd	5	4.3	-35.3	0.232	-0.121	25.74	-0.2	0.97
Cu	5	2.32	-11.45	0.4313	-0.202	50	-0.13	0.98
Cd	3	4.25	-59.35	0.235	-0.071	25.74	-0.39	0.95
Cu	3	3.26	-47.85	0.306	-0.068	50	-0.52	0.98
Cd	2	7.04	-159	0.142	-0.044	25.74	-0.82	0.94
Cu	2	4.02	-89.25	0.248	-0.045	50	-1.07	0.96
Cd	1	7.21	-199.45	0.138	-0.036	25.74	-1.24	0.95
Cu	1	2.99	-78.35	0.334	-0.038	50	-1.56	0.888
Cd	0.5	31.21	-1097.9	0.032	-0.028	25.74	-2.37	0.725
Cu	0.5	5.23	-178.1	0.191	-0.029	50	-3.8 1	0.798

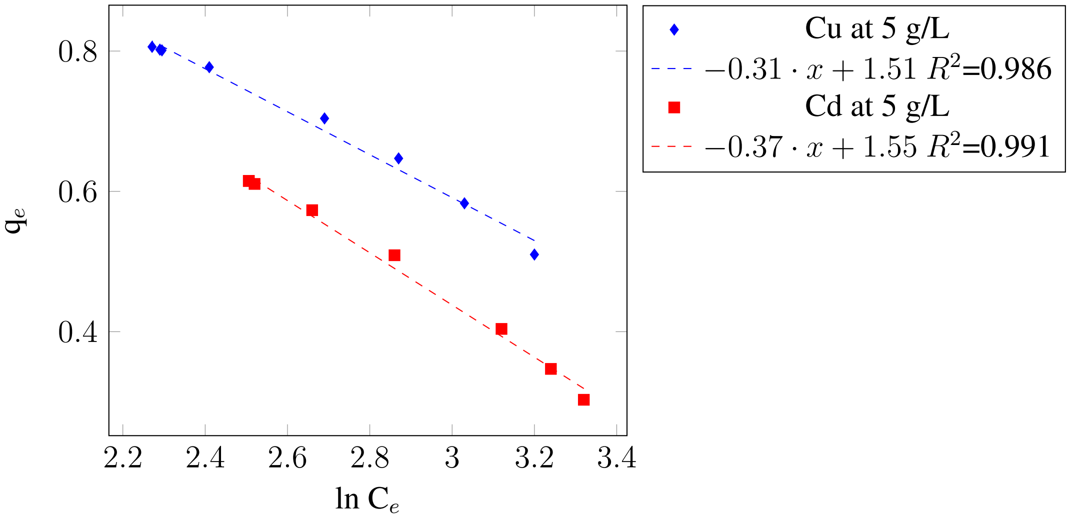

Figure 4.54: Temkin isotherm plot for Cu and Cd at 5 g/L adsorbent dosage, pH 6, 180 rpm, 2 hrs contact time, 25°C

Table 4.6: Analysis of Temkin isotherm data for simultaneous Cu (II) and Cd (II) removal

metal	**ads dosage**	**slope (B_T)** (J/mol)	**Intercept** (B_T)ln K_T	**ln K_T**	**Temkin constant** (K_T) mol/J	**R^2**
Cu	5g/l	-0.31	1.51	-4.93	0.007193	0.986
Cd	5g/l	-0.37	1.548	-4.19	0.015147	0.99

g/L, pH 6, 180 rpm, 2 hrs contact time, 25°C. The value of B_T (heat of adsorption) for Cu (II) at 5 g/ L adsorbent dosage are -0.31, -0.37 J/mol respectively. The Temkin isotherm constant values was reported as 0.0072 for Cu and 0.0151 for Cd respectively as shown in Table 4.6. Fig 4.54 shows the Temkin isotherm model for Cu and Cd at 5g/L of ads dosage and different adsorbent conditions of pH 6, 2 hrs contact time and temperature of 25°C. It was concluded that Langmuir model and Temkin models fit the simultaneous Cu and Cd removal in batch studies with higher R^2 values.

4.6 Intra particle diffusion model study for the synthetic solution data

The agitation rate significantly effects the metal ion adsorption on its surface. The results obtained in Figs. 4.24 Fig 4.25 from the effect of agitation rate for copper and cadmium (synthetic solution data) indicated that film/boundary diffusion and pore/ intra particle diffusions were involved in governing reaction rate.

The sorption rate is shown to be controlled by several factors including the following processes which involves [186, 187]

- Diffusion of the solute from the solution to the film surrounding the particle
- Diffusion from the film to the particle surface (external diffusion)
- Diffusion from the surface to the internal sites (surface or pore diffusion)
- Uptake which involves several mechanisms such as physico chemical sorption, ion exchange, precipitation or complexation

Due to rapid stirring during the batch experiments there was a possibility of transport of heavy metal ions from the bulk into pores of the adsorbent as well as adsorption at the outer surface of the adsorbent. The rate-limiting step may be either film diffusion or intra particle diffusion. As they act in series, the slower of the two will be the rate determining step [188]. The possibility of the heavy metal ions to diffuse into the interior sites of the particles of adsorbent was tested with Weber-Morris equation [187].

Hence the intra particle diffusion model was evaluated to determine the reaction rate limiting step. Eq.4.1 gives the intra particle diffusion model (Weber-Morris equation) as follows:

$$q_t = k_p t^{0.5} \tag{4.1}$$

Where, q_t is the amount of heavy metal ions adsorbed (mg/g), k_p is the intra particle diffusion rate constant and t is the agitation time in minutes. The rate constant k_p for intra particle diffusion for 180 rpm of agitation rate using the mixed adsorbent were determined from the slope of plot between the amount of heavy metals adsorbed (q_t) vs square root of time ($t^{0.5}$). The best fit of the intra particle diffusion model was calculated in terms of linear regression coefficient. The results of intra particle diffusion model have been shown in Figs 4.55 and 4.56 and Table 4.7 for Cu (II) and Cd (II) respectively.

Table 4.7: Intra particle diffusion model parameters for copper cu(II) and cd (II) at 180 rpm, pH 6, 120 min, T = 40°C, 5 g/l of ads dosage, 50 ppm IMC

Metal	**Equation**	**slope(m)**	**($K_{p)}$)** **Intra particle diffusion constant**	**R^2**
Cu (II)	y = -0.3161x + 0.2996	-0.3161	2.01	0.7506
Cd (II)	y = -0.2389x + 0.4322	-0.2389	2.7	0.7787

Various studies [189, 190] have already speculated that intra particle model (also known as Webber and Morris model) may produce multi linear curves, representing the different stages of adsorptive mass transfer. Kinetic data derived by the batch studies in the present work were applied over this model and the plot of log (q_t) versus log $t^{0.5}$ was obtained with

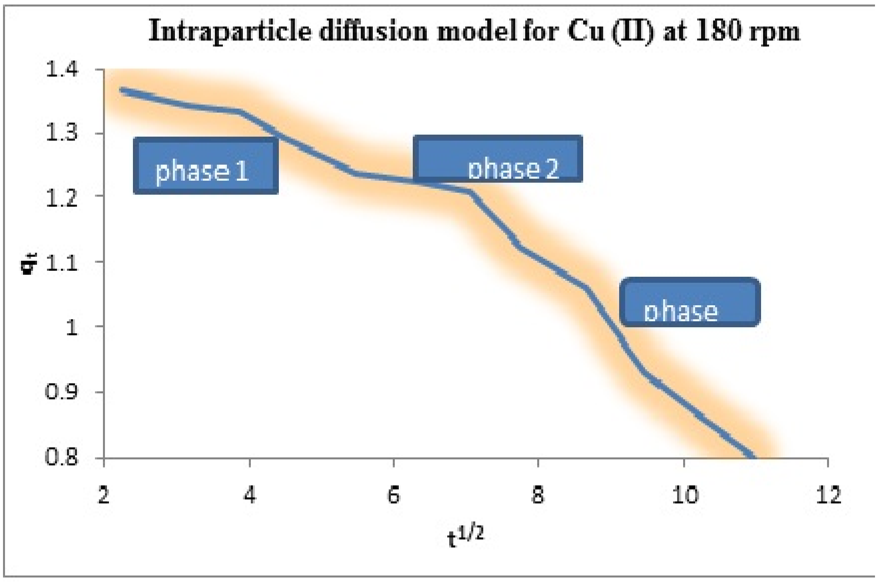

Figure 4.55: Intra particle diffusion model for copper at pH 6, 120 min, T = 40 °C, 5 g/L of ads dosage, 50 ppm IMC and 180 rpm

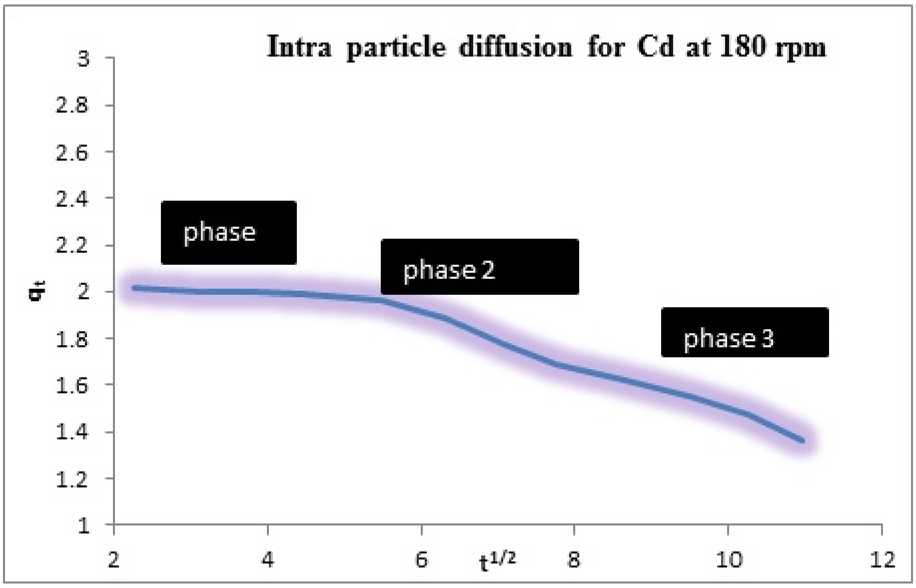

Figure 4.56: Intra particle diffusion model for cadmium at pH 6, 120 min, T = 40°C, 5 g/L of ads dosage, 50 ppm IMC and 180 rpm

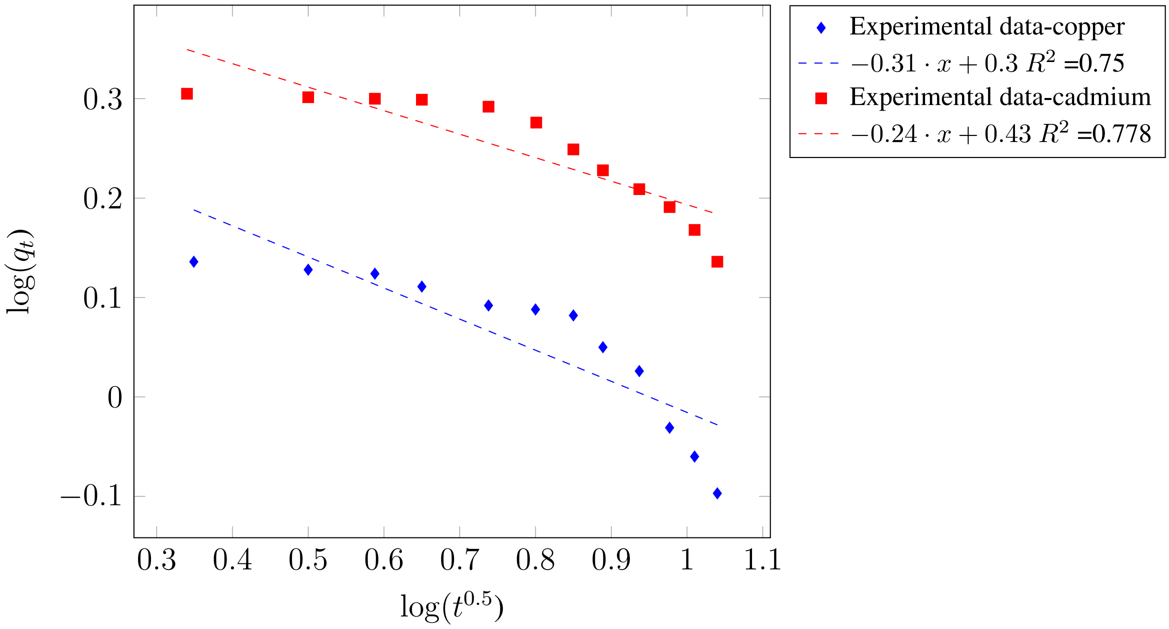

Figure 4.57: Intra particle diffusion model for copper and cadmium at 180 rpm, pH 6, 120 min, T = 40°C, 5 g/L of ads dosage, 50 ppm IMC

multi linear curve having three different phases shown in Figs. 4.55 and 4.56. It was evident from the Figs 4.55 and 4.56 that the adsorption of Cu (II) and Cd (II) onto surface of the mixed adsorbent was mediated in three different phases. Phase 1 (at onset of process) was due to the transfer of Cu (II) ion from bulk liquid phase to external surface of the mixed adsorbent, Phase 2 indicates the significantly low velocity sorption phase and Phase 3 was the indicator of equilibrium stage due to extremely low concentration gradient between liquid and solid phase. Phase 1 was due to film or external or boundary layer diffusion of metal ion, Phases 2 and 3 are due to the intra particle diffusion. Additionally the curve of intra particle model did not pass through the origin which promptly indicated that the intra particle mass transfer was not rate limiting step. The slope of curve k_p represented the rate of metal ion adsorption on to the adsorbent surface. At initial start-up of Cu (II) and Cd (II) ions during batch process, the film/external/ boundary layer diffusion was the fastest, hence yielding Phase 1 curve with maximum slope. Phases 2 and 3 have least slope values that were dedicated to mesoporous and micro porous metal ion diffusion. This shows that the film diffusion was rate limiting step at the beginning or at the onset of process and at later stage of reaction, micro porous intra particle diffusion was rate determining phase [191]. Fig 4.57 describes the linear regression equation of intra particle diffusion model along with R^2 values. Higher R^2 values of 0.7787 for Cd (II) fits better than Cu (II) having 0.75 at 180 rpm.

4.7 Isotherm modeling of batch studies for synthetic solution data

Adsorption isotherms studies were most significant for the study of metal ion binding behaviour with adsorbent surface or in other words metal ion partition between the solid and liquid phase and to evaluate the adsorption capacity at equilibrium as a function of adsorbate concentration [192], and rate of change of temperature. Data obtained through such studies are useful in designing of batch process as well as continuous reaction columns [193, 194]. In present investigation adsorption isotherms namely Langmuir, Freundlich and Temkin model have been applied on Cu(II) and Cd (II) ion adsorption to predict the suitability of the process. The performance of isotherm curves was evaluated in-terms of linear regression coefficient R^2 obtained through linear regression analysis.

4.7.1 Langmuir model

This model assumes the monolayer coverage of adsorbent surface by adsorbate species, all energy sites are equally energetic, binding of adsorbate molecule at one site is independent of adjacent site occupancy, and dynamically metal ion adsorption rate is equal to the rate of desorption. Eq. 4.2 represents the Langmuir isotherm model [195].

$$q_{eq} = \frac{q_{max} b C_{eq}}{1 + b C_{eq}} \tag{4.2}$$

The above equation 4.2 can be rearranged to the following linear form given by Eq 4.3 4.3

$$\frac{C_e}{q_{eq}} = \frac{1}{b q_{max}} + \frac{C_{eq}}{q_{max}} \tag{4.3}$$

where C$_{eq}$ is the equilibrium concentration (mg/L); q$_{eq}$ is the amount of metal ion adsorbed (mg/g); q$_{max}$ is q$_{eq}$ for a complete monolayer (mg/g); b is sorption equilibrium constant (L/mg). A plot of C$_{eq}$/q$_{eq}$ versus C$_{eq}$ should indicate a straight line of slope 1/q$_{max}$ and an intercept of $\frac{1}{bq_{max}}$.

From the obtained intercept value of b from the graphs of isotherm models, a dimensionless parameter R$_L$ (separation factor) was estimated using the relationship given in the Equation 4.4. The effect of isotherm shape can be used to predict whether a sorption system is favorable or unfavorable in batch process.

According to Hall et al [196], the essential futures of the Langmuir isotherm can be ex-

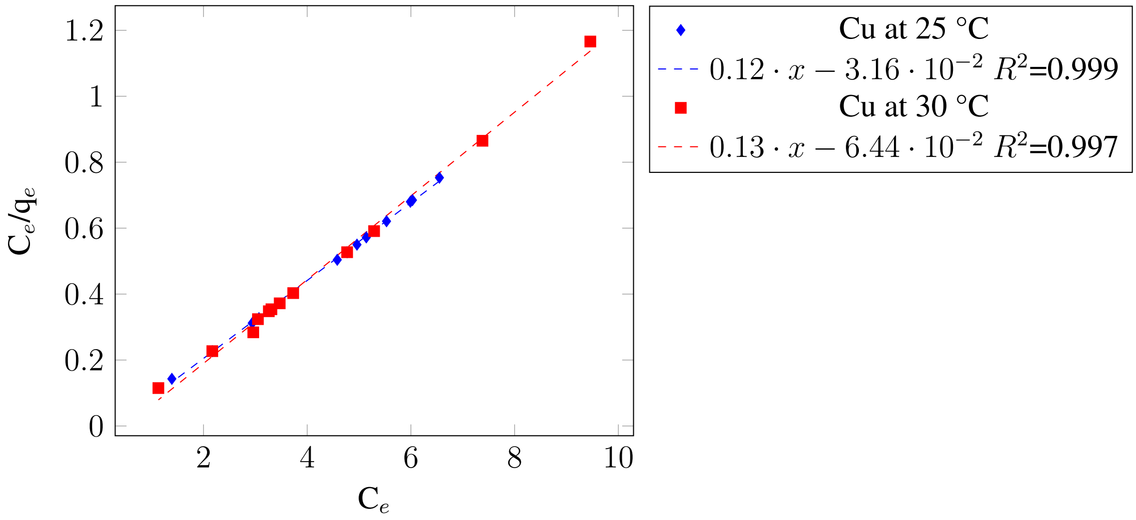

Figure 4.58: Langmuir isotherm plot for Copper at 25 and 30 °C, pH 6, 120 min, 50 ppm, 0.5 g/l of ads dosage, 180 rpm

pressed in terms of a dimensional less constant separation factor or equilibrium parameter R_L which is defined by the following equation:

$$R_L = \frac{1}{(1 + bC_o)} \tag{4.4}$$

Where R_L is a dimensional less separation factor, C_o is the initial concentration (mg/L) and b is the Langmuir constant (L/mg). The parameter R_L indicates the shape of the isotherm accordingly as shown in Table 4.8.

Table 4.8: Suitability of isotherm model based on separation factor

(R_L))	**Types of isotherm**
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$R_L < 1$	Favourable
$R_L = 0$	irreversible

Table 4.9: Analysis of Langmuir Isotherm data for Cu (II) at 50 ppm

Temperature	**slope 1/q_{max}**	**Intercept 1/bq_{max}**	**q_{max}(mg/g)**	**b(Langmuir constant)**	**R_L**	**R^2**
25	0.1184	-0.0319	8.46	-3.711	-0.0054	0.9991
30	0.1264	-0.0582	7.91	-2.172	-0.0092	0.997
35	0.1209	-0.0324	8.27	-3.731	-0.0053	0.998
40	0.1381	-0.0871	7.24	-1.585	-0.0127	0.9885

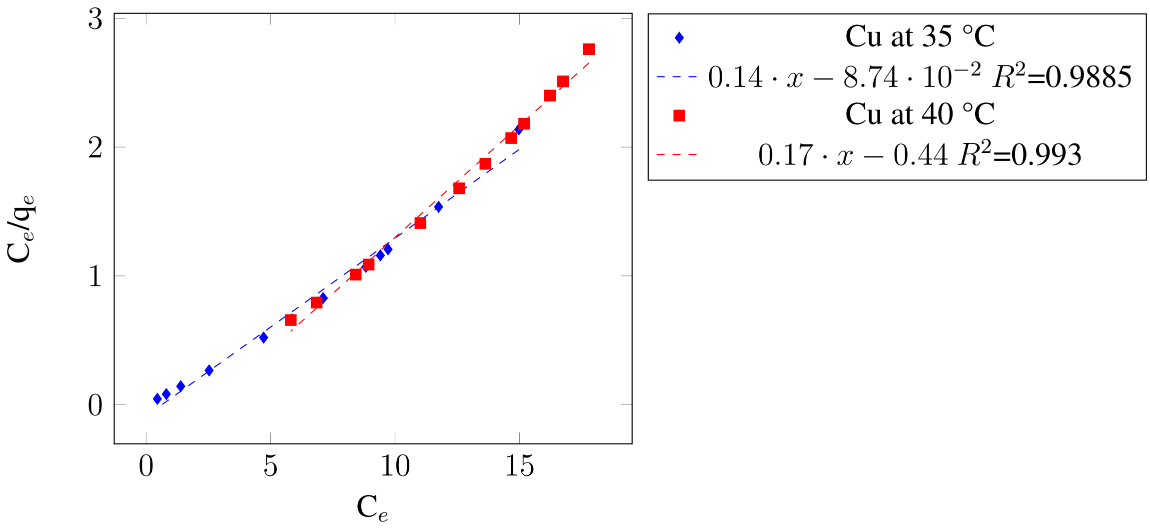

Figure 4.59: Langmuir isotherm plot for Copper at 35 and 40 °C, pH 6, 120 min, 50 ppm, 0.5 g/l of ads dosage, 180 rpm

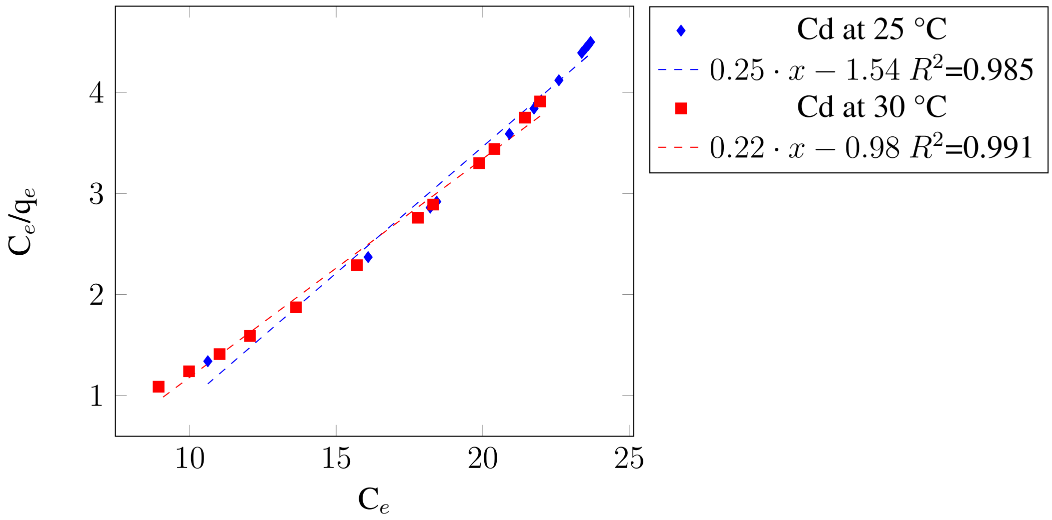

Figure 4.60: Langmuir isotherm plot for Cadmium at 25 and 30 °C, pH 6, 120 min, 50 ppm, 0.5 g/l of ads dosage, 180 rpm

Table 4.10: Analysis of Langmuir Isotherm data for Cd (II) at 50 ppm

Temperature	**slope 1/q$_{max}$**	**Intercept 1/bq$_{max}$**	**q$_{max}$(mg/g)**	**b(Langmuir constant)**	**R$_L$**	**R^2**
25	0.2499	-1.5319	4.0	-0.1631	-0.139	0.9848
30	0.2162	-0.9791	4.62	-0.2208	-0.0996	0.9911
35	0.1956	-0.7165	5.11	-0.273	-0.079	0.9899
40	0.1742	-0.442	5.74	-0.3941	-0.053	0.9932

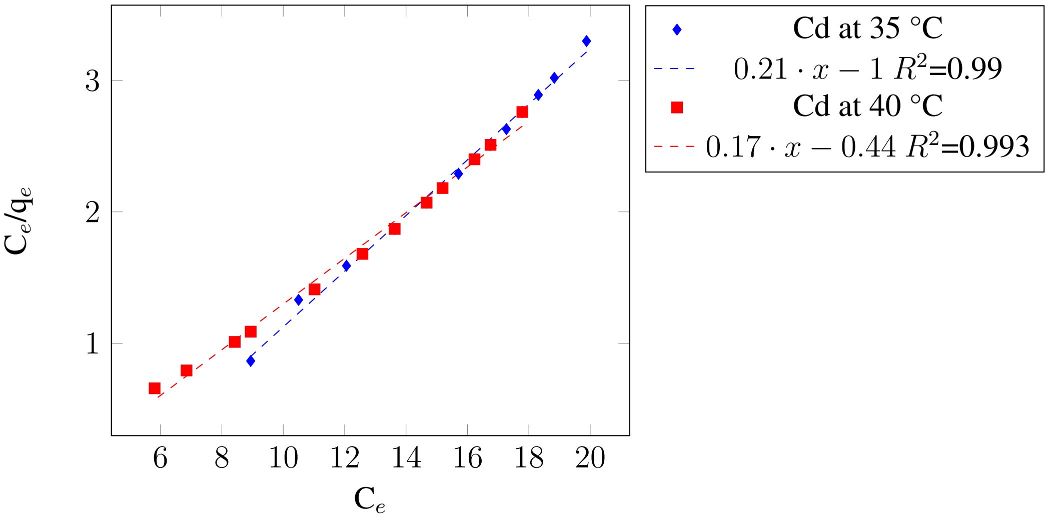

Figure 4.61: Langmuir isotherm plot for Cadmium at 35 and 40 °C, pH 6, 120 min, 50 ppm, 0.5 g/l of ads dosage, 180 rpm

4.7.2 Analysis of Langmuir Isotherm data for Cu (II) & Cd (II)

The data obtained from Table 4.9 and Table 4.10 concluded that the Langmuir model is favourable adsorption model for both Cu (II) and Cd (II) at different temperatures and an initial concentration of 50 mg/l, pH 6, 120 min contact time, 0.5 g/L of adsorbent dosage and 180 rpm. Moreover higher correlation coefficients R^2 values predict the suitability and fitting of models for both Cu (II) and Cd (II). The graphs of Langmuir model for Cu (II) and Cd (II) have been shown in Figs.4.58 to 4.61 respectively.

4.7.3 Freundlich model

Freundlich isotherm describes the non-ideal and reversible adsorption and is not restricted to the formation of monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat affinities over the heterogeneous surface. In this perspective, the amount of metal ion adsorbed is the summation of adsorption on all sites (each having bond energy) with the stronger binding sites occupied first; until the adsorption energy are exponentially decreased upon the completion of adsorption process [47]. This model assumes the multilayer coverage of adsorbent surface by adsorbate species together with consideration of adsorbent surface as heterogeneous in character. The linear form of Freundlich isotherm model [197, 198] was given as

$$log(q_e) = log(K_f) + \frac{1}{n} log(C_e) \tag{4.5}$$

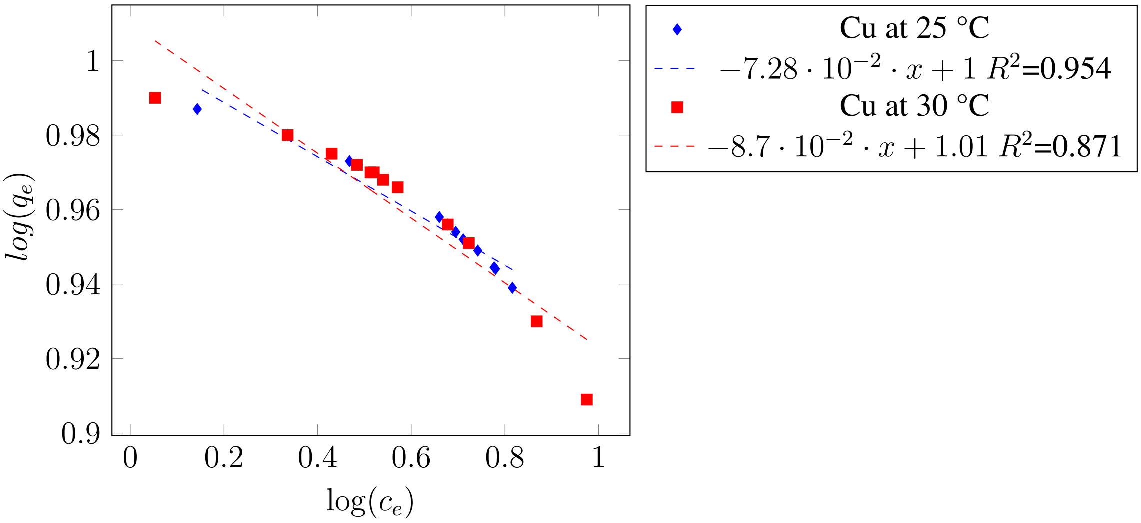

Figure 4.62: Freundlich isotherm plot for Copper at 25 and 30 °C, pH 6, 120 min, 50 ppm, 0.5 g/l of ads dosage, 180 rpm

Table 4.11: Freundlich isotherm model constants for Copper at 50 ppm, pH 6, 0.5g/L, 180 rpm, 2 hrs contact time and different temperatures

Temperature°C	**slope (1/n)**	**Intercept log K$_f$ (mg/g)**	**K$_f$(mg/g)**	**R^2**
25	-0.0738	1.0043	10.1	0.954
30	-0.0871	1.0105	10.24	0.871
35	-0.0703	0.9962	9.912	0.929
40	-0.0866	0.9921	9.82	0.81

where K_f represents the adsorption capacity or Freundlich coefficient and n represents the sorption possibilities ranging from 1 to 10. The values of K$_f$ and $\frac{1}{n}$ can be obtained from the graph between log(q$_e$) and log(C$_e$). The results of Freundlich model for copper have been shown from Figs 4.62 and 4.63 and for cadmium from Figs4.64 and 4.65 respectively.

4.7.4 Comparison of Langmuir and Freundlich isotherm model for copper

The data given in Table 4.11 and the graphs extrapolated from Figs. 4.62 and 4.63 clearly indicates the poor R^2 of Freundlich model for Cu (II) when compared to Langmuir model which predicts the superiority of Langmuir isotherm for Cu. The significant values of separation factor for Cu (II) [R$_L$ < 1] and linear regression coefficient R^2 ($>$ 0.98 and close to 1) became the indicators of Langmuir model suitability for Cu (II) ion across the liquid phase onto the mixed adsorbent surface over the Freundlich model having lower R^2 values ranges from 0.81 to 0.95 and negative value of $\frac{1}{n}$.

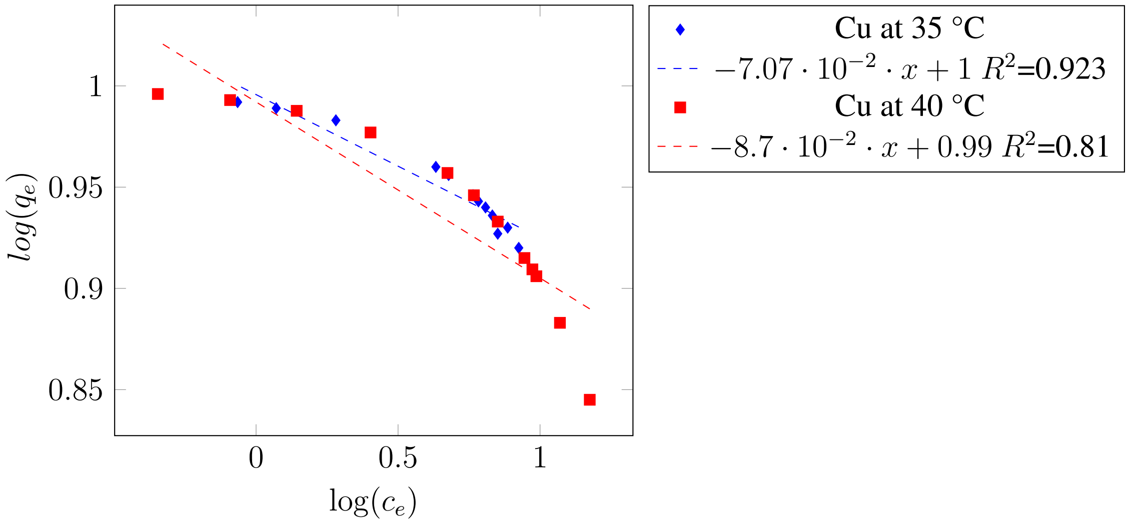

Figure 4.63: Freundlich isotherm plot for Copper at 35 and 40 °C, pH 6, 120 min, 50 ppm, 0.5 g/l of ads dosage, 180 rpm

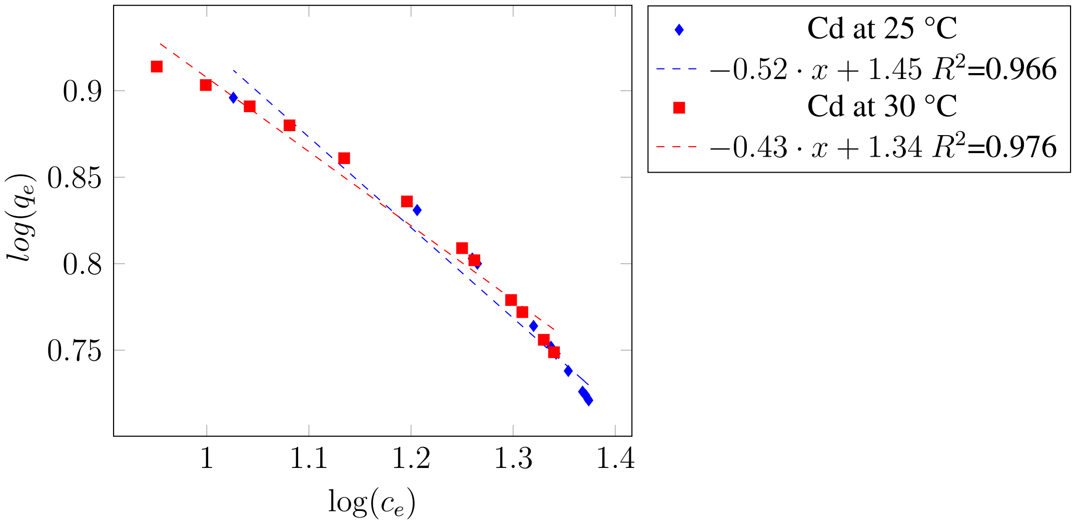

Figure 4.64: Freundlich isotherm plot for Cadmium at 25 and 30 °C, pH 6, 120 min, 50 ppm, 0.5 g/l of ads dosage, 180 rpm

Table 4.12: Freundlich isotherm model constants for Cadmium at 50 ppm, different temperatures, pH 6, 120 min, 50 ppm, 0.5 g/l of ads dosage, 180 rpm

Temperature°C	**slope (1/n)**	**Intercept log K_f (mg/g)**	**K_f(mg/g)**	**R^2**
25	-0.523	1.448	28.10	0.966
30	-0.428	1.336	21.67	0.976
35	-0.355	1.254	17.97	0.962
40	-0.283	1.176	15.01	0.967

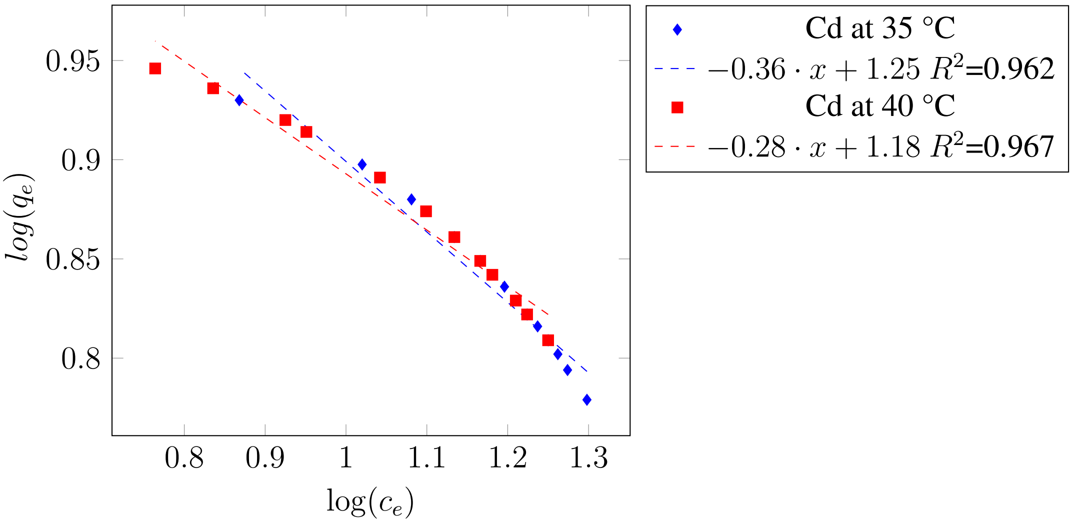

Figure 4.65: Freundlich isotherm plot for cadmium at 35 and 40 °C, pH 6, 120 min, 50 ppm, 0.5 g/l of ads dosage, 180 rpm

4.7.5 Comparison of Langmuir and Freundlich isotherm model for cadmium

The data given in Table 4.12 and the graphs extrapolated from Figs. 4.64 and 4.65 predicted that Freundlich model have negative values of n (Sorption possibilities) which indicates that this isotherm model for Cd (II) at different temperatures was not suitable when compared to Langmuir model having higher R^2 values very close to 1. So the data obtained does not fit for Freundlich model when compared to Langmuir model for both the metal ions Cu (II) and Cd (II).

4.7.6 Temkin Isotherm model

Unlike the Langmuir and Freundlich isotherm, the Temkin isotherm takes into account the interactions between adsorbents and metal ions to be adsorbed and was based on the assumption that the free energy of sorption is a function of the surface coverage [199]. The Temkin isotherm assumes that the heat of adsorption of all the molecules in a layer decreases linearly due to adsorbent-adsorbate interactions and the adsorption was characterized by a uniform distribution of binding energies [200]. The isotherm equation was given by Eq. 4.6

$$q_e = B_t[ln(k) + ln(C_e)] \tag{4.6}$$

$$\tag{4.7}$$

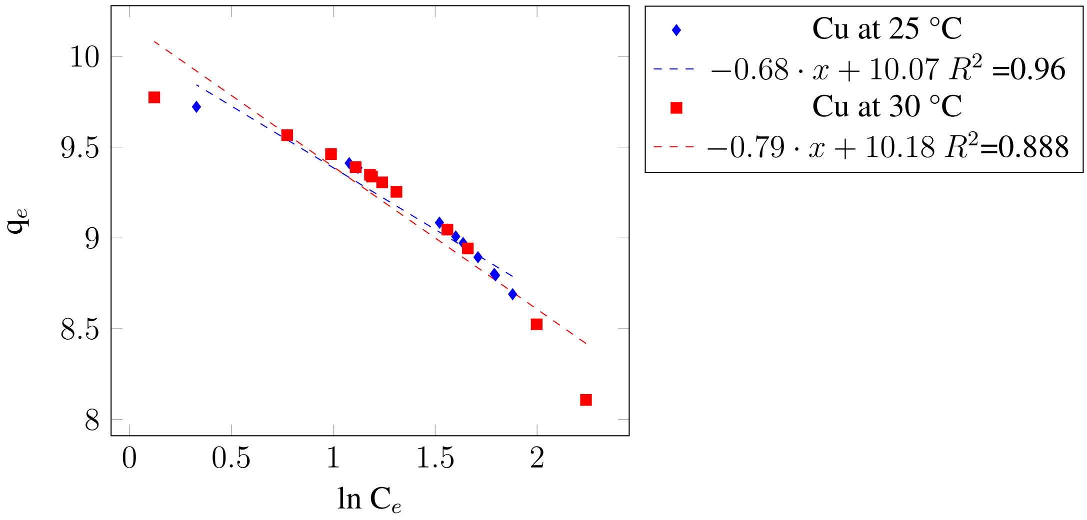

Figure 4.66: Temkin isotherm plot of Copper at 25 and 30 °C, pH 6, 120 min, 50 ppm, 0.5 g/L of ads dosage, 180 rpm

Table 4.13: Temkin isotherm model for copper at 50 ppm, pH 6, 180 rpm, 0.5g/L,contact time of 2 hrs and different temperatures

Temperature°C	**slope** (B_T) (J/mol)	**Intercept** (B_T) X ln K_T	**ln K_T**	**Temkin constant** K_T mol/J	**R^2**
25	-0.68	10.06	-14.794	375 x 10^{-9}	0.96
30	-0.783	10.18	-13	226 x 10^{-8}	0.888
35	-0.644	9.9	-15.37	21 x 10^{-7}	0.94
40	-0.754	9.8	-12.997	226 x 10^{-8}	0.845

Where

$$B_t = \frac{RT}{b} \tag{4.8}$$

$$\tag{4.9}$$

where the constant B_t was related to the heat of adsorption, R is the universal gas constant ($\frac{J}{molK}$), T is the temperature (K), k is Temkin model constant. A plot of q_e versus ln C_e determines the isotherm constants B_t and k from the slope and the intercept respectively [183–185].

4.7.7 Analysis of Temkin model for Cu (II) and Cd (II)

The Temkin model has been studied for the obtained data and the variation of heat of adsorption B_T for Cu and Cd has been found at different temperatures. More over higher R^2 values for both Cu (II) and Cd (II) indicates the suitability of Temkin isotherm model

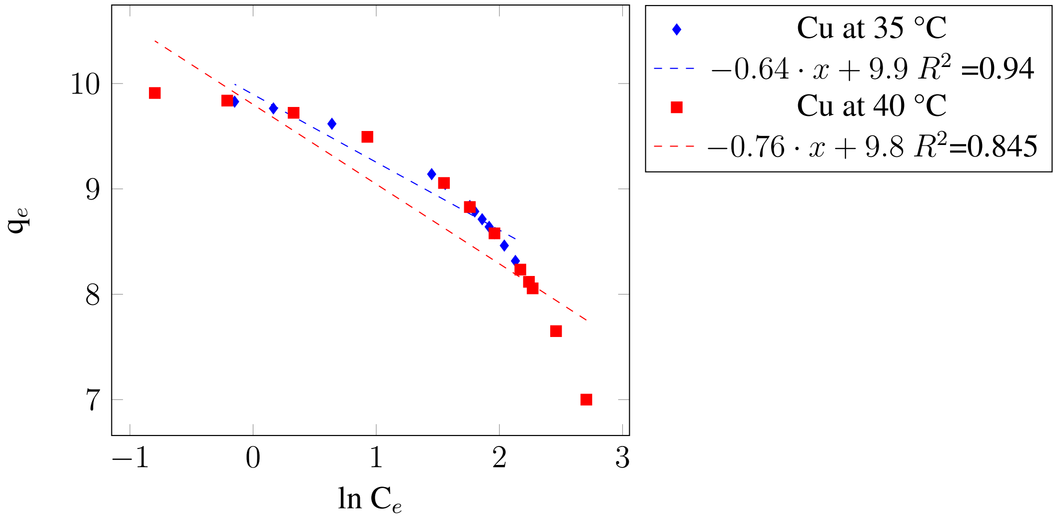

Figure 4.67: Temkin isotherm plot of copper at 35 and 40 °C, pH 6, 120 min, 50 ppm, 0.5 g/L of ads dosage, 180 rpm

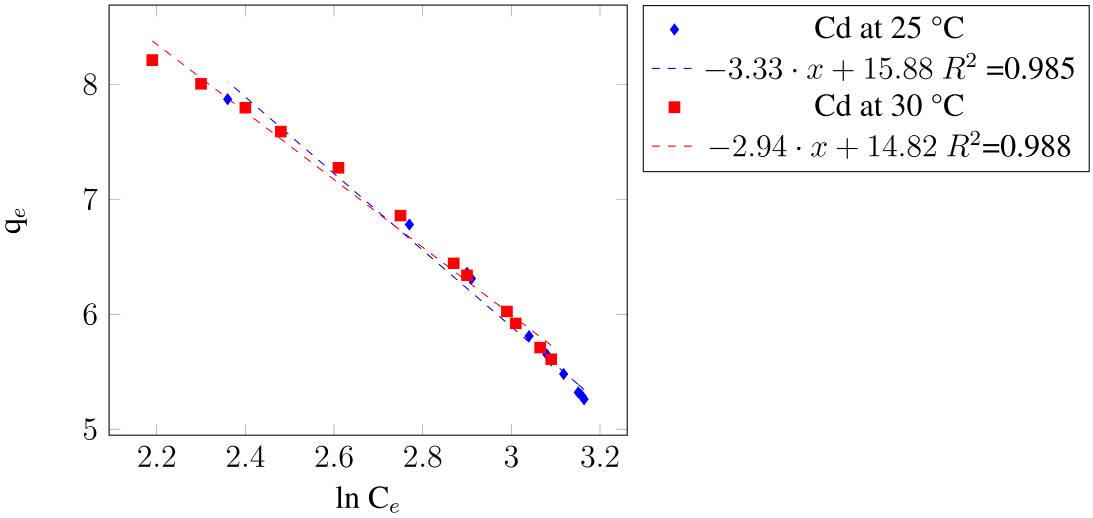

Figure 4.68: Temkin isotherm plot of cadmium at 25 and 30 °C, pH 6, 120 min, 50 ppm, 0.5 g/L of ads dosage, 180 rpm

Table 4.14: Temkin isotherm model constants for Cadmium at 50 ppm, pH 6, 180 rpm, 0.5 g/L, contact time of 2 hrs and different temperatures

Temperature°C	**slope** (B_T) (J/mol)	**Intercept** (B_T) X ln K_T	**ln K_T**	**Temkin constant** K_T mol/J	**R^2**
25	-3.352	15.954	-4.76	0.00857	0.985
30	-2.937	14.816	-5.04	0.0064	0.988
35	-2.566	13.854	-5.4	0.0045	0.979
40	-2.16	12.836	-5.94	0.0026	0.98

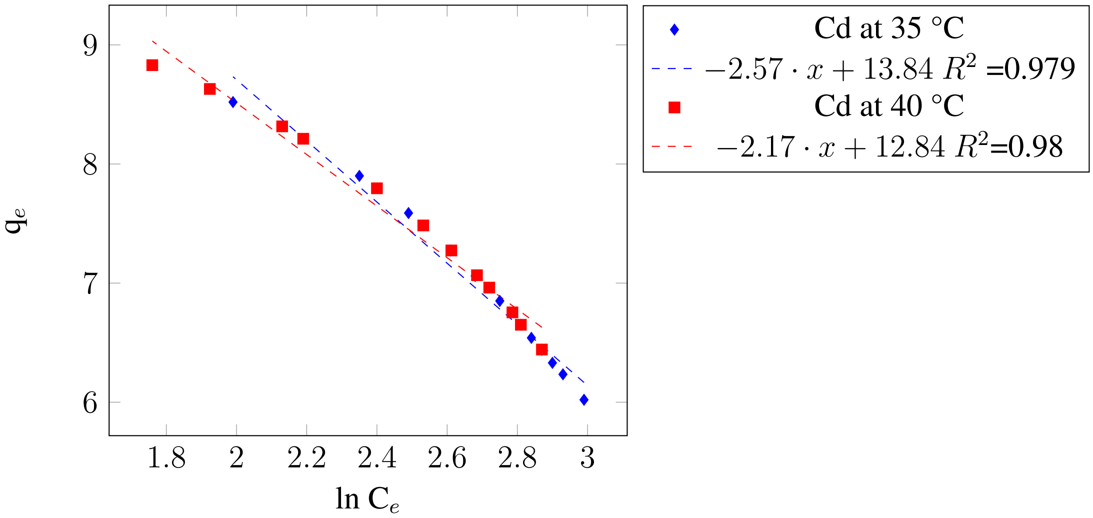

Figure 4.69: Temkin isotherm plot of cadmium at 35 and 40 °C, pH 6, 120 min, 50 ppm, 0.5 g/L of ads dosage, 180 rpm

which were shown in Figs. 4.66 and 4.67 (for copper) and 4.68 & 4.69 (for cadmium); and Tables 4.13 (for copper), 4.14 (for cadmium) at 50 ppm, pH 6, 180 rpm, 0.5 g/L, contact time of 2 hrs and different temperatures. The value of B_T (heat of adsorption) for Cu (II) at different temperatures (T = 25°C, 30°C, 35°C, 40°C) were found to be -0.68, -0.783, -0.644, -0.754 J/mol respectively. Similarly for Cd (II) the B_T values at different temperatures (T = 25°C, 30°C, 35°C, 40°C) were found to be -3.352, -2.937, -2.566, -2.16 J/mol, respectively (in increasing order trend with the increase of temperature). Very less values of isotherm constant have been reported. In comparison with Cu (II), higher R^2 values of Cd (II) better fits the Temkin model.

4.7.8 Thermo Dynamic modeling studies for copper and cadmium

The thermodynamic behavior of the adsorption for Cu (II) and Cd (II) ions onto the mixed adsorbent is well described by finding the std. Gibbs free energy which is calculated by the following equation.

$$\Delta G_o = -RTln(k_c) \tag{4.10}$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature in Kelvin and K_c is the equilibrium or rate constant calculated as the surface and solution metal distribution ratio. The negative values of ΔG_o indicates the spontaneous nature of the adsorption process. However, the negative value of ΔG_o decreases with an increase in temperature, which indicates that the spontaneous nature of adsorption was inversely proportional to the temperature. Table 4.15 and Table 4.17 describes about the various thermo dynamic

Table 4.15: Thermo dynamic constants estimation for Cu (II) at different temperatures

Temperature °C	**Temperature (K)**	$\frac{1}{T}$	**K$_c$ mol/J**	**ln K$_c$**
25	298	0.00336	0.00728	-4.922
30	303	0.0033	0.01051	-4.555
35	308	0.00325	0.00936	-4.6717
40	313	0.00319	0.01664	-4.096

Table 4.16: Thermo dynamic parameters for Cu (II) at different temperatures

Temperature (Kelvin)	**K$_c$ mol/J**	**ln K$_c$** mol/J	**Δ G = -RT ln (K$_c$)** (J/mol)	**ΔH**	ΔS = $\frac{(\Delta H - \Delta G)}{T}$ (J/mol K)
298	0.00728	-4.922	12194.61	-36429	-163.165
303	0.01051	-4.555	23669.3	-36429	-198.343
308	0.00936	-4.6717	35632.18	-36429	-233.963
313	0.01664	-4.096	46291.1	-36429	-264.28

constants estimation for Cu (II) and Cd (II) respectively. Table 4.16 and Table 4.18 represent the various thermo dynamic parameter calculations such as Gibbs free energy (ΔG), Change in entropy (ΔS) and Change in enthalpy (ΔH) for Cu (II) and Cd (II) ions respectively. Fig 4.70 represents the plot of thermodynamic model for Cu (II) and Cd(II) at 180 rpm, pH 6, ads dosage of 0.5 g/L, contact time of 2 hrs and various temperatures.

4.7.9 Analysis of thermo dynamic modeling

The positive values of change in enthalpy shows that the process was endothermic in nature for Cd (II) and the negative values of change in enthalpy shows that the process is exothermic in nature for Cu (II). The standard Gibbs free energy values are positive which means that the process was not spontaneous in nature. The negative values of (ΔS) show that there was decrease in randomness at the solid/solution interface during the adsorption of copper. Similarly for cadmium the positive values of (ΔS) shows that there was an increase in randomness of the system with the decrease in temperature from 313 K to 298 K as shown in Tables 4.16 and 4.18, respectively. The lower R^2 values show that the copper does not fit the thermo dynamic model while cadmium fits the system with high R^2

Table 4.17: Thermo dynamic constants estimation for Cd (II) at different temperatures

Temperature °C	**Temperature(Kelvin)**	**1/T**	**K$_c$ mol/J**	**ln K$_c$**
25	298	0.00336	0.0292	-3.532
30	303	0.0033	0.0274	-3.595
35	308	0.00325	0.0248	-3.695
40	313	0.00319	0.0222	-3.806

Table 4.18: Thermo dynamic parameters for Cd (II) at different temperatures

Temperature (Kelvin)	**K$_c$ mol/J**	**ln K$_c$** mol/J	**△ G = -RT ln (K$_c$)** (J/mol)	**ΔH**	ΔS = $\frac{(\Delta H - \Delta G)}{T}$ (J/mol K)
298	0.02923	-3.532	8752.51	14217.77	18.34
303	0.02745	-3.595	9056.31	14217.77	17.03
308	0.02485	-3.695	9461.57	14217.77	15.44
313	0.02224	-3.806	9904.28	14217.77	13.78

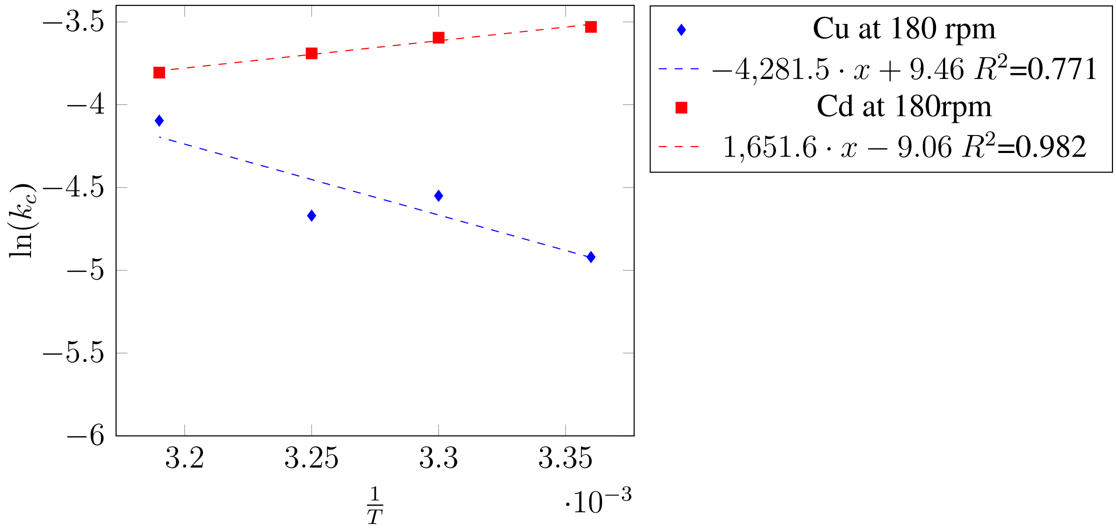

Figure 4.70: Thermodynamic model of copper and cadmium at 180 rpm, pH 6, Ads dosage of 0.5g/L, Contact time of 2 hrs and different temperatures

values of 0.9824 [201–203].

4.7.10 Kinetic modeling of batch studies

The kinetic models include the pseudo- first order equation and pseudo-second order equation. The pseudo first order and second order modeling has been carried out for both the metals at the optimized conditions of each parameter obtained in the batch study (pH 6, T = 40 °C, initial Metal ion concentration of 100 ppm and adsorbent dosage of 5 g/L).

4.7.10.1 Pseudo first order equation

In order to fit the equation to experimental data, the equilibrium adsorption capacity q_e must be known as discussed in Sec. 3.5.4.1. In many cases q_e is unknown and as chemisorption tends to become measurably slow, but the amount adsorbed was still significantly smaller than that of the equilibrium uptake capacity [46]. In most cases in the literature, the pseudo first-order equation of Lagergren does not well fit for the whole range of contact time and was generally applicable over the initial time of 20 to 30 minutes during the adsorption process.

A plot of log (q_e-q_t) against time was plotted for the obtained data at the optimized parameters for pH = 6, T = 40 °C and initial metal ion concentration of 100 ppm for both the metal ions to find the correlation coefficient or coefficient of Regression (R^2) which holds a straight line relationship and the parameters $q_e$and k_1 can be determined from the intercept and slope respectively.

The slope and intercept values are shown in Tables 4.19 and 4.20 for both the metals (Cu and Cd respectively) at the optimized conditions.

It can be concluded that the coefficient of regression (R^2) values are close to 1 in case of Cu (II) at adsorbent dosage of 5 g/L and temperature of 40 °C which indicates that the adsorption systems follows the pseudo first order equation for copper when compared to cadmium as shown in Tables 4.19 and 4.20. The tables gives the data about the first order rate constant k_1 in min $^{-1}$ and q_e in mg/g which was obtained theoretically from the slope and intercept respectively from the Figs. 4.71 to 4.78. It can be concluded that the data fits well for Cu (II) than Cd (II) with higher R^2 values in case of copper.

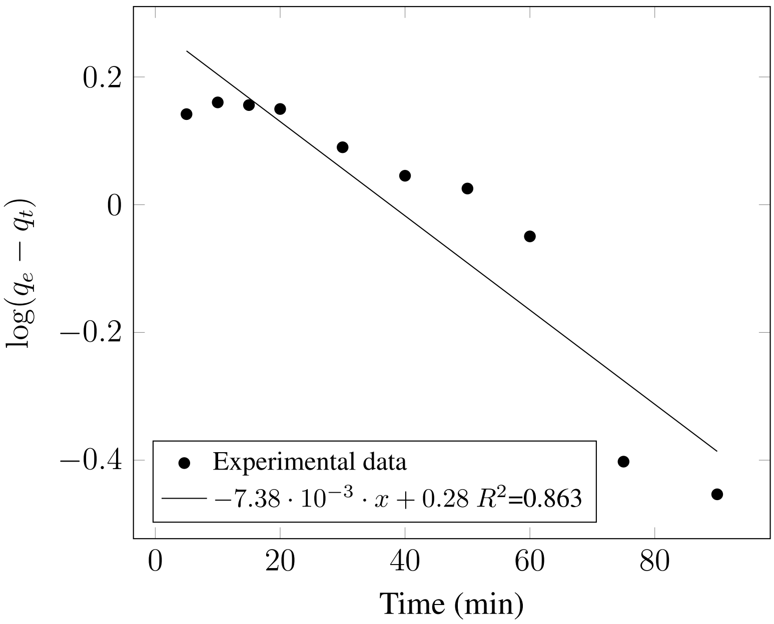

Figure 4.71: Pseudo first order equation at pH = 6 for Cd

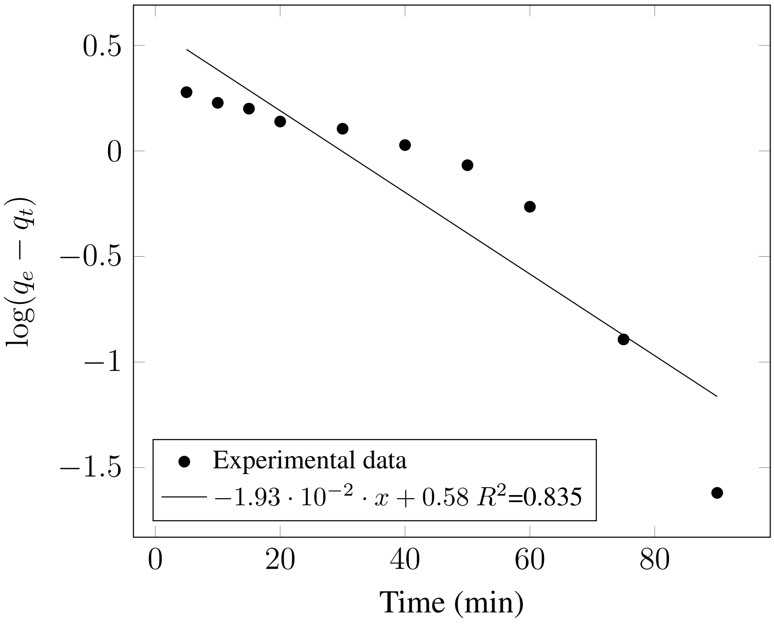

Figure 4.72: Pseudo first order equation at T= 40 °C for Cd

Table 4.19: Pseudo first order model equation for Cu (II) at optimized conditions

PFOE conditions	**model equation**	**k (min^{-1})**	**R^2**	**q_e (mg/g)**
pH 6	y= -0.0146x+0.078	0.0336	0.8192	1.2
T = 40°C	y= -0.0147x+0.51	0.0338	0.886	3.23
MIC = 100 ppm	y = 0.0113x-0.19	0.026	0.6064	0.646
Adsorbant dosage 5 g/L	y=-0.0138x-1.21	0.0318	0.97	0.06

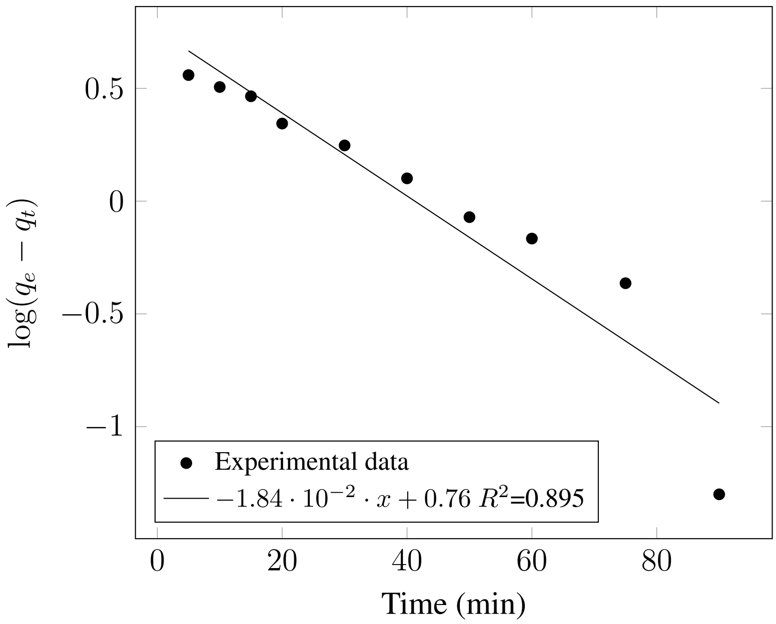

Figure 4.73: Pseudo first order equation for Cd (II) at IMC of 100 ppm

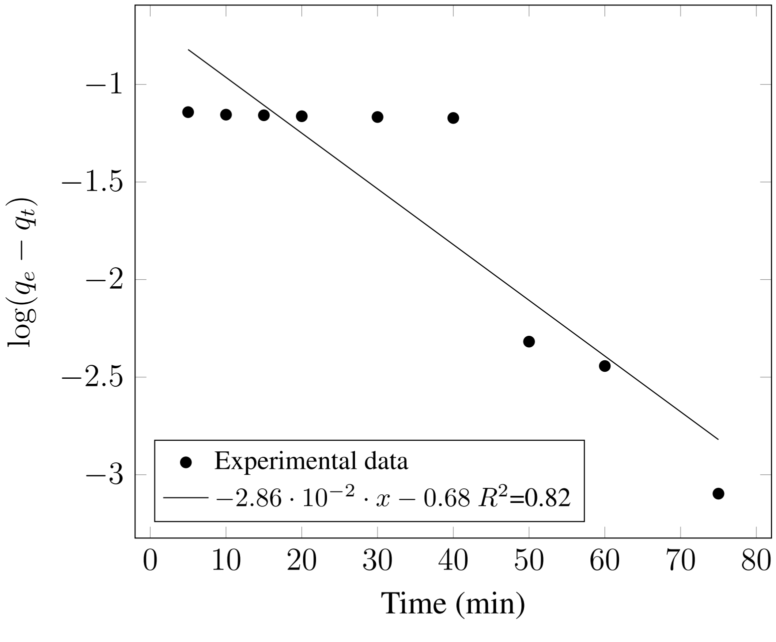

Figure 4.74: Pseudo first order equation for Cd (II) at adsorbent dosage of 5 g/L

Table 4.20: Pseudo first order equation for Cd (II) at optimized conditions

PFOE conditions	**Model equation**	**k (min^{-1})**	**R^2**	**q_e (mg/g)**
pH 6	y= -0.0074x+0.0278	0.017	0.863	1.9
T = 40 °C	y = -0.019 x+ 0.578	0.044	0.835	3.8
MIC = 100 ppm	y = -0.0184x+0.76	0.042	0.895	5.73
Adsorbent dosage 5 g/L	y= - 0.0286x-0.679	0.066	0.82	0.21

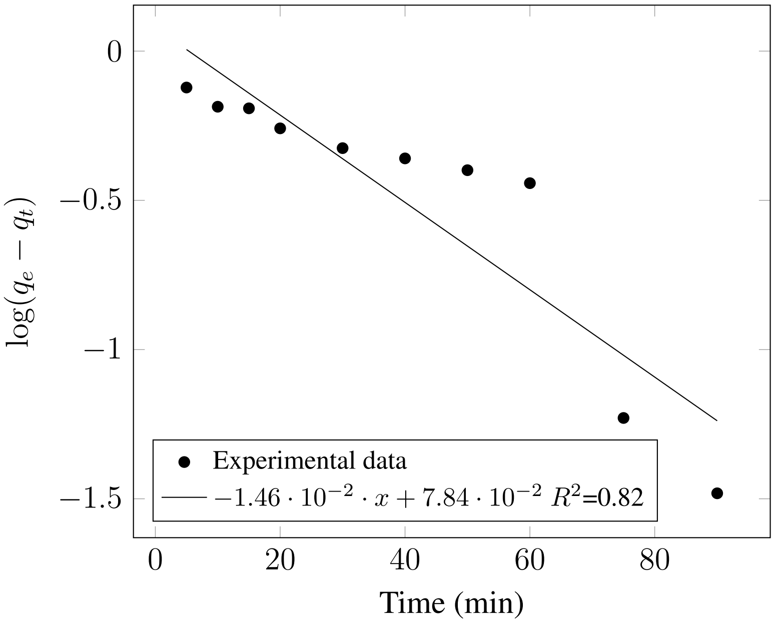

Figure 4.75: Pseudo first order equation for Cu at pH 6

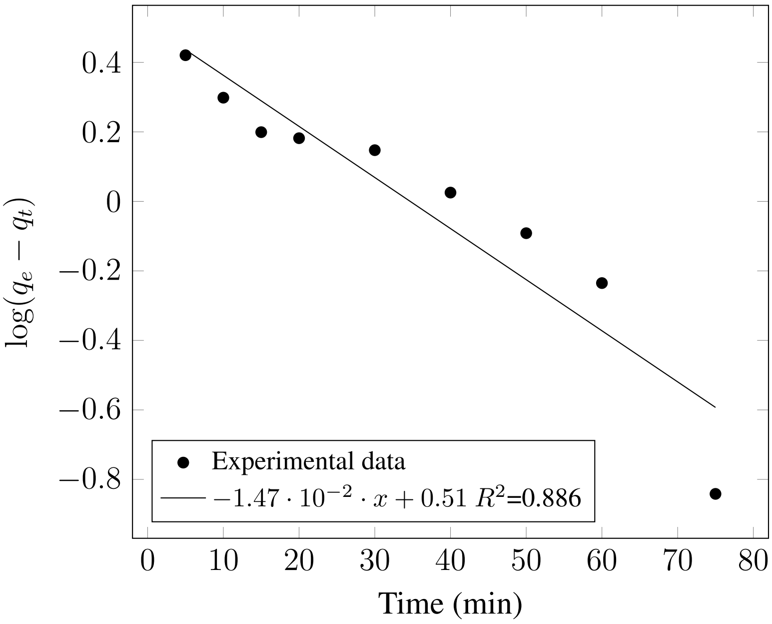

Figure 4.76: Pseudo first order equation at T= 40 °C for Cu

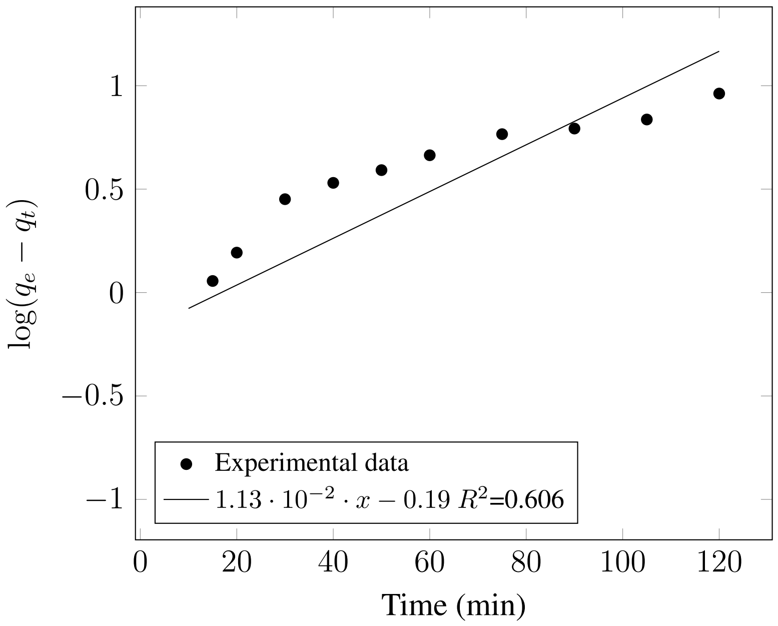

Figure 4.77: Pseudo first order equation at 100 ppm for Cu

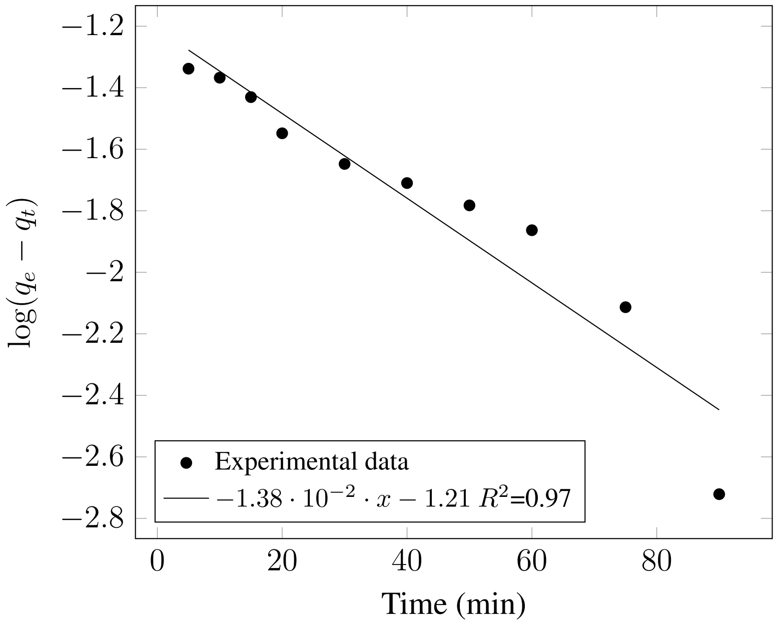

Figure 4.78: Pseudo first order equation at 5 g/L of adsorbent dosage for Cu

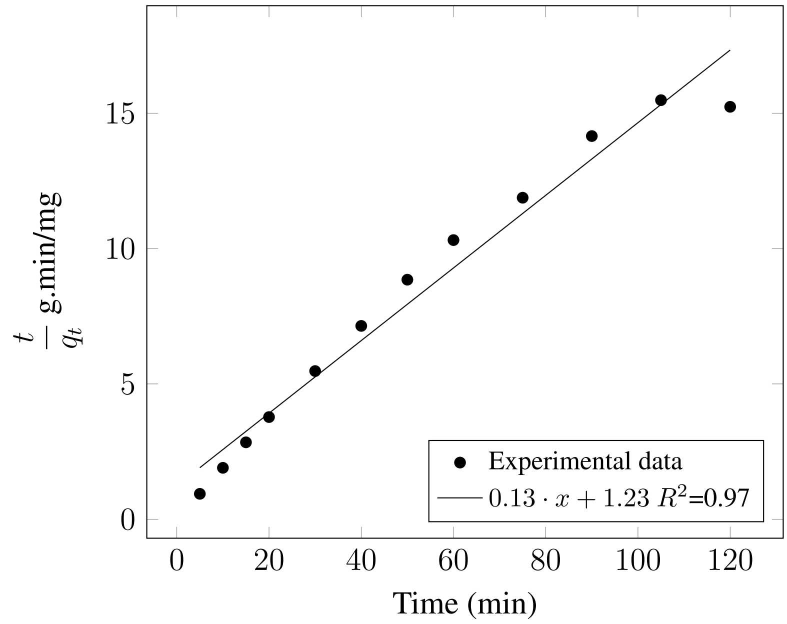

Figure 4.79: Pseudo second order equation at pH 6 for Cd (II)

Table 4.21: Pseudo second order equation at different adsorbent conditions for Cd (II)

PSOE Conditions	**Model equation**	**k$_2$ (g mg^{-1} min^{-1})**	**q$_e$ (mg/g)**	**R^2**
pH 6	y = 0.1342x + 1.2341	0.0146	7.45	0.97
T = 40 °C	y = 0.1111 x + 0.6903	0.018	9	0.995
MIC of 100 ppm	y = 0.0606x + 0.2571	0.0143	16.5	0.999
Ads dosage = 5 g/L	y = 1.0808x + 1.7903	0.652	0.925	0.999

4.7.10.2 Pseudo second order equation

In this model, it was assumed that adsorption/binding of metal particle/adsorbate on the adsorbent surface was mediated by chemical forces instead of physical forces. Non-linear type of the model was described earlier in Sec. 3.5.4.2.

A graph of t/q$_t$ vs t at different optimized conditions of pH 6, T = 40 °C and initial metal ion concentration of 100 ppm for both the metal ions was plotted to find the correlation coefficient or coefficient of regression (R^2) that determines the best fit equation and the parameters q$_e$ and k$_2$ can be determined from the slope and intercept.

The slope and intercept values were shown in Tables 4.21 and 4.22 respectively for both the metals cadmium and copper at the optimized conditions.

It can be concluded that the coefficient of regression (R^2) values are close to 1 in case of Cu (II) and Cd (II) at adsorbent dosage of 5 g/L, temperature of 40 °C, pH 6 and initial metal ion concentration of 100 ppm which indicates that the adsorption system follows the pseudo second order equation for both copper and cadmium (as shown in Tables 4.21 and

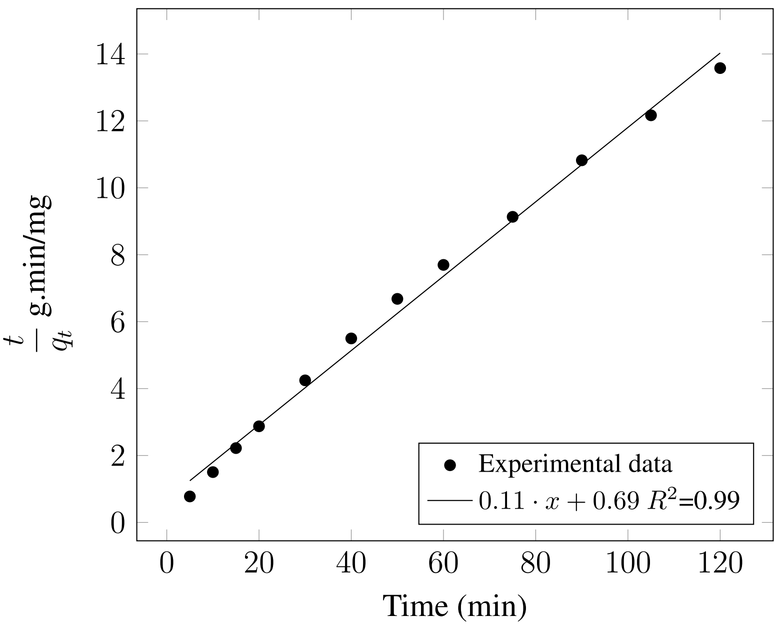

Figure 4.80: Pseudo second order equation at T= 40°C for Cd

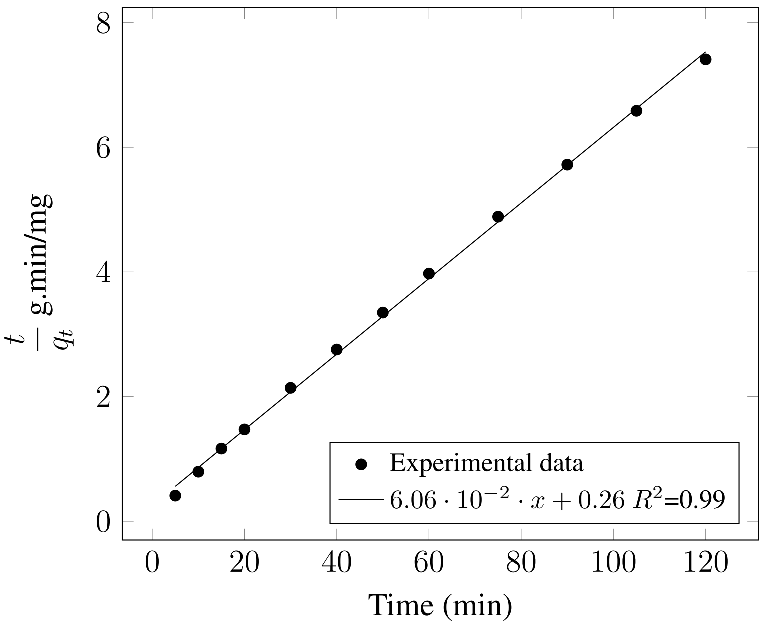

Figure 4.81: Pseudo second order equation at IMC of 100 ppm for Cd

Table 4.22: Pseudo second order equation at different adsorbent conditions for Cu

PSOE Conditions	**Model equation**	**k$_2$** (g mg^{-1} min^{-1})	**q$_e$ (mg/g)**	**R^2**
pH 6	y = 0.103x + 0.218	0.0486	9.7	0.999
T = 40°C	y = 0.098x + 0.5086	0.019	10.2	0.998
MIC = 100 ppm	y = 0.055x + 0.0989	0.03	18.18	0.9993
Ads dosage = 5 g/L	y = 1.001x + 0.9317	1.075	0.999	0.9999

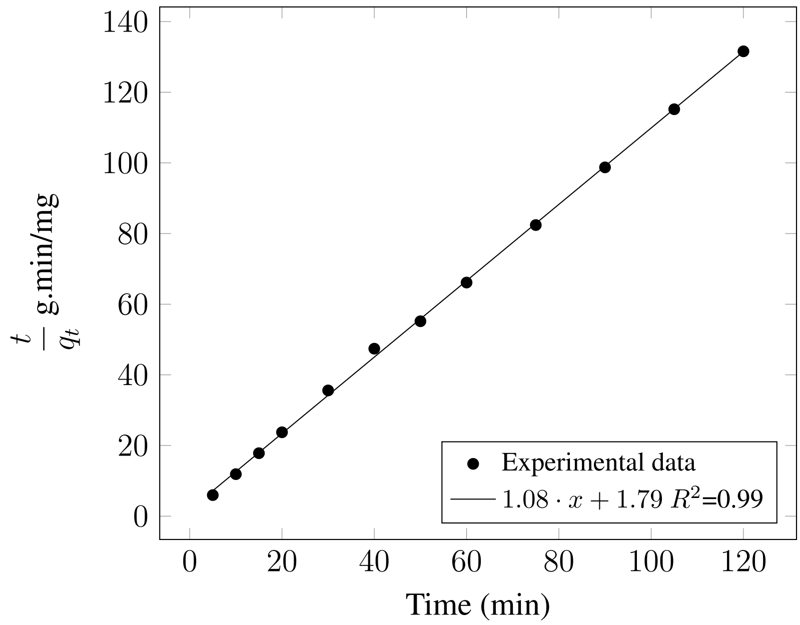

Figure 4.82: Pseudo second order equation for Cd at 5 g/L dosage

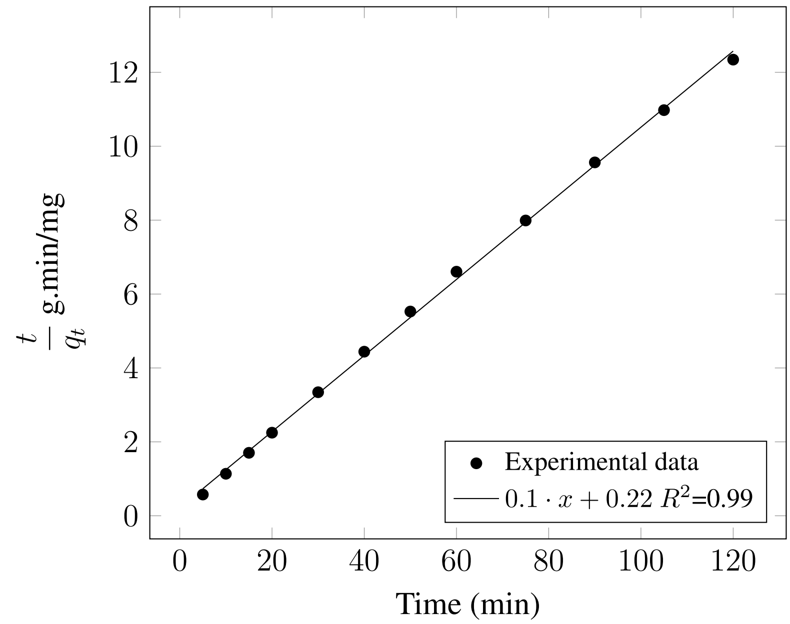

Figure 4.83: Pseudo second order equation for Cu at pH 6

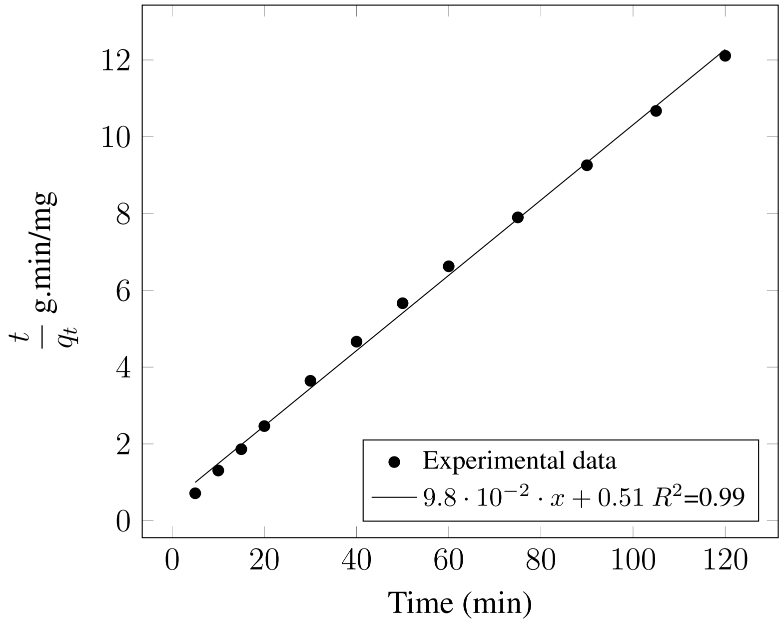

Figure 4.84: Pseudo second order equation for Cu at pH T= 40 °C

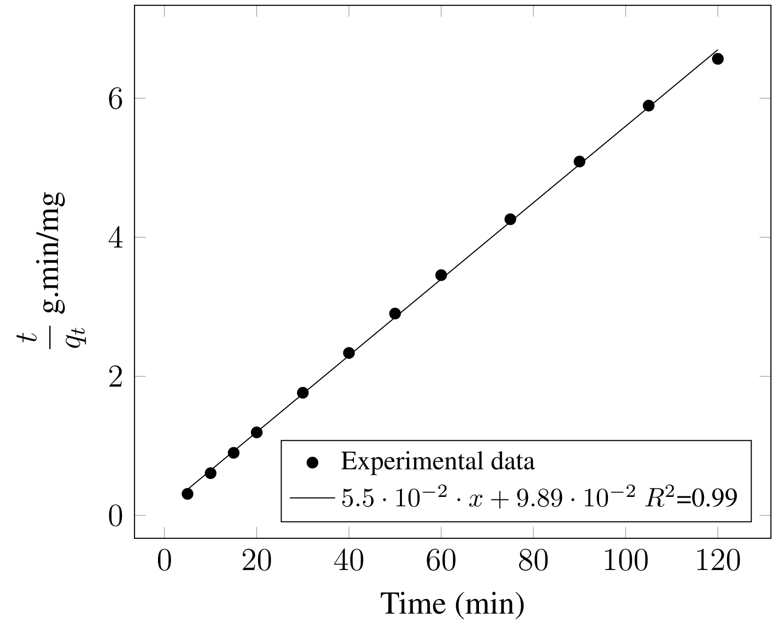

Figure 4.85: Pseudo second order equation at 100 ppm for Cu

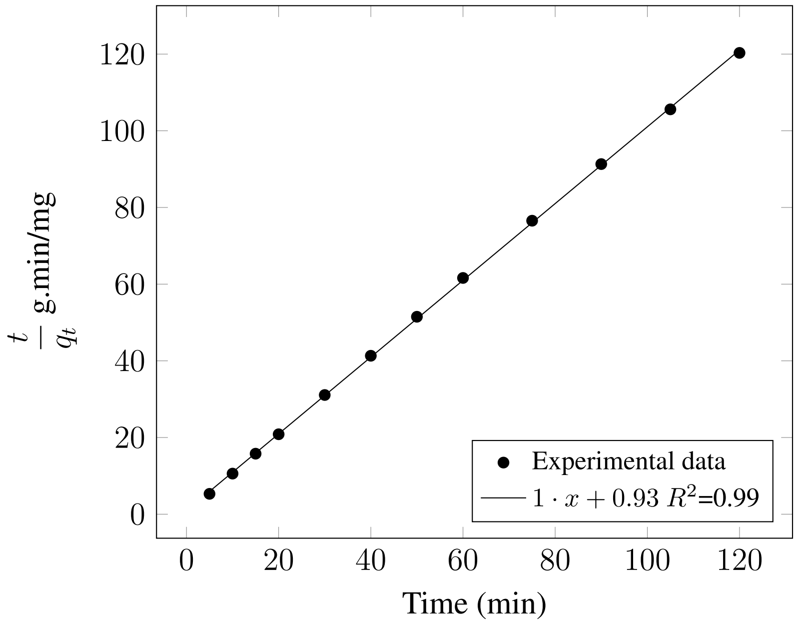

Figure 4.86: Pseudo second order equation at 5 g/L dosage for Cu

Table 4.23: Statistical analysis of copper at different temperatures for synthetic solution

Temperature °C	**q_{max} (q_{the})**	**q_e (q_{exp})**	**(q_{exp})-(q_{The})**	$(q_{exp} - q_{The})^2)$	$\chi^2 = \frac{[(q_{exp})-(q_{the})]^2)}{q_{the}}$
25	8.46	9.114	0.654	0.4277	0.0505
30	7.91	9.171	1.261	1.590	0.201
35	8.27	8.977	0.707	0.499	0.0604
40	7.24	8.707	1.467	2.152	0.2972

4.22). Second order rate constant k_2 in g mg $^{-1}$ min $^{-1}$ and adsorption capacity q_e in mg/g are obtained theoretically from the slope and intercept of the plots shown in Figs.4.79 to 4.86 and the data were shown in Tables 4.21 and 4.22 respectively.

4.8 Statistical analysis

The statistical analysis has been carried out to find out the χ^2 values using Langmuir model for copper and cadmium which indicates the least values of χ^2 values for better suitability of the model study and to find the reaction mechanism [191]. The equilibrium adsorptive capacities (q_{eq}) theoretical values was obtained from the Langmuir plot at different temperatures given by the Eq.4.11.

$$\frac{C_{eq}}{q_e q} = \frac{1}{b} q_{max} + \frac{C_{eq}}{q_{max}} \tag{4.11}$$

Table 4.24: Statistical analysis of cadmium at different temperatures for synthetic solution

Temperature °C	**q**$_{max}$ (**q**$_{the}$)	**q**$_e$ (**q**$_{exp}$)	(**q**$_{exp}$)-(**q**$_{The}$)	$[(q_{exp} - q_{The})]^2$	$\chi^2 = \frac{[(q_{exp})-(q_{the})]^2}{q_{the}}$
25	4	5.92	1.92	3.6864	0.922
30	4.62	6.81	2.19	4.7961	1.038
35	5.11	6.95	1.84	3.3856	0.663
40	5.74	7.53	1.79	3.2041	0.558

Table 4.25: Statistical analysis for Langmuir equation at optimized parameters for copper

Temperature °C	**q**$_{max}$ (**q**$_{the}$)	**q**$_e$ (**q**$_{experimental}$)	(**q**$_{exp}$)-(**q**$_{Theo}$)	$[(q_{exp} - q_{The})]^2$	$\chi^2 = \frac{[(q_{exp})-(q_{the})]}{q_{the}}$
pH 6	8.446	9.114	0.668	0.4462	0.053
T = 40	7.24	8.707	1.467	2.152	0.297
MIC 100ppm	14.75	17.178	2.428	5.895	0.4
Ads dose 5g/l	0.942	0.969	0.027	0.00073	0.001

In comparison of statistical analysis for copper and cadmium from the above Tables 4.23 and 4.24 the χ^2 values were less for copper when compared to cadmium at 25, 30, 35, 40 °C which denotes the supremacy with lower or insignificant values and further suggest the dominance of χ^2 (statistical parameter) value for copper.

In the present investigation the reaction kinetic model suitability was also accomplished by performing the statistical analysis, i.e, by evaluating the χ^2 test (χ^2 value) through the experimental and theoretical data of uptake capacity (mg/g). The below Eq 4.12 gives the evaluation of goodness of fit for reaction kinetic models.

$$\chi^2 = \frac{[(q_{exp}) - (q_{the})]^2}{q_{the}} \tag{4.12}$$

The values of χ^2 with their respective models have been shown in Tables 4.25 to 4.27 for copper and Tables 4.28 to 4.30 for cadmium. The statistical analysis of the data obtained in reaction kinetic modeling delineated the supremacy of pseudo second order

Table 4.26: Statistical analysis for pseudo first order equation at optimized parameters for copper

Temperature °C	**q**$_{max}$ (**q**$_{the}$)	**q**$_e$ (**q**$_{exp}$)	(**q**$_{exp}$)-(**q**$_{The}$)	$[(q_{exp} - q_{The})]^2$	$\chi^2 = \frac{[(q_{exp})-(q_{the})]^2}{q_{the}}$
pH 6	1.198	9.114	7.916	62.663	52.306
T = 40	3.234	8.707	5.473	29.953	9.262
MIC 100 ppm	0.646	17.178	16.532	273.31	423.076
Ads dose 5g/l	0.062	0.969	0.907	0.8226	13.269

Table 4.27: Statistical analysis for pseudo second order equation at optimized parameters for copper

Temperature °C	**q$_{max}$ (q$_{the}$)**	**q$_{e}$ (q$_{experimental}$)**	**(q$_{exp}$)-(q$_{The}$)**	$[(q_{exp} - q_{The})]^2$	$\chi^2 = \frac{[(q_{exp})-(q_{the})]^2}{q_{the}}$
pH 6	9.708	9.114	-0.594	0.352836	0.036
T = 40	10.204	8.707	-1.497	2.241009	0.22
MIC 100ppm	18.18	17.178	-1.002	1.004	0.055
Ads dose 5g/l	0.999	0.969	-0.03	0.0009	0.001

Table 4.28: Statistical analysis for Langmuir equation at optimized parameters for cadmium

Temperature °C	**q$_{max}$ (q$_{the}$)**	**q$_{e}$ (q$_{exp}$)**	**(q$_{exp}$)-(q$_{The}$)**	$[(q_{exp} - q_{The})]^2$	$\chi^2 = \frac{[(q_{exp})-(q_{the})]^2}{q_{the}}$
pH 6	4.001	5.92	1.919	3.682	0.92
T = 40	5.74	7.53	1.79	3.2041	0.558
MIC 100 ppm	9.92	14.41	4.49	20.1601	2.032
Ads dose 5g/l	0.766	0.876	0.11	0.0121	0.0158

Table 4.29: Statistical analysis for pseudo first order equation at optimized parameters for cadmium

Temperature °C	**q$_{max}$ (q$_{the}$)**	**q$_{e}$ (q$_{exp}$)**	**(q$_{exp}$)-(q$_{The}$)**	$[(q_{exp} - q_{The})]^2$	$\chi^2 = \frac{[(q_{exp})-(q_{the})]^2}{q_{the}}$
pH 6	1.895	5.92	4.025	16.2	8.549
T = 40	3.78	7.53	3.75	14.06	3.72
MIC 100ppm	4.34	14.41	10.07	101.405	23.365
Ads dose 5g/l	1.62	0.876	-0.744	0.5535	0.3417

Table 4.30: Statistical analysis for pseudo second order equation at optimized parameters for cadmium

Temperature °C	**q$_{max}$ (q$_{the}$)**	**q$_{e}$ (q$_{exp}$)**	**(q$_{exp}$)-(q$_{The}$)**	$[(q_{exp} - q_{The})]^2$	$\chi^2 = \frac{[(q_{exp})-(q_{the})]^2}{q_{the}}$
pH 6	7.451	5.92	-1.531	2.344	0.315
T = 40	9	7.53	-1.47	2.161	0.24
MIC 100ppm	16.5	14.41	-2.09	4.368	0.265
Ads dose 5g/l	0.925	0.876	-0.049	0.0024	0.0026

model for both Cu and Cd with very low or insignificant χ^2 values, when compared with the pseudo first order model and Langmuir model with higher χ^2 at different optimized conditions thereby suggesting the dominance for both Cu (II) and Cd (II) ion adsorption mechanism as chemisorption rather than physical adsorption [191].

4.9 Continuous flow studies

In the continuous flow operation, the results discussed the effect of adsorbent dosage on break through curves for different flow rates at a constant initial metal ion concentration C_o. Further based on these results it is considered to use various kinetic models in the continuous flow operation which includes Thomas Model, Yoon-Nelson Model etc.

4.9.1 Break through Curves

The performance of a fixed-bed column was assessed through the concept of the breakthrough curve. The time for breakthrough appearance and the shape of the breakthrough curve are considered to be the most important characteristics for determining the performance of the column operation and the dynamic response of an adsorption column. The loading behavior of metal ion to be adsorbed from solution in a fixed-bed is usually expressed in term of C_e/C_o as a function of time or volume of the effluent for a given bed weight approaching a breakthrough curve.

The performance of an adsorption treatment mainly depends on the thermodynamic aspects of solute-solvent-sorbent interactions and on the transport phenomena involving the diffusive-convective transport within the porous media [204, 205].

In a fixed-bed device, the contaminated water was introduced in a clean bed of mixed adsorbent from the bottom of the column and pollutant removal occurs in a narrow band at the top of the column, referred to as mass transfer or exchange zone (MTZ). As operation proceeds, the upper layers of blended adsorbent get to be saturated (soaked) with solute and the adsorption zone moves downwards until bottom of the column was reached. Under these conditions, the solute concentration in the effluent begins to increase. The MTZ extent mainly depends on liquid-solid relative velocity, and on the adsorbent properties (particle diameter, micro porous structure). The higher the MTZ extent, the lower is the efficient use of the adsorbing bed.

Experimental dynamic tests showed that an increase in initial concentration and the liquid flow rate leads to shorter breakpoint time; moreover, the breakthrough curves become steeper as a consequence of higher velocity that enhances the external mass transport.

The plot between the ratio of logarithm of equilibrium outlet concentration to the initial concentration of the metal ion, gives a relation between ln(C_e/C_o) vs reaction time in terms of various linear models (by various parameters) and predicts the nature of the adsorbent-adsorbate system are called break through curves. They depends on the effect of volumetric flow rate, weight of the adsorbent packed at different bed weights and initial metal ion concentration of the metal ion solution. The study of variation of flow rate with bed weight at a fixed initial concentration of 100 ppm gives the concentration ratio profile with respect to outlet effluent sampling time.

4.9.2 Effect of adsorbent dosage

The adsorption of metal ion in the packed bed column was directly proportionally to the quantity of adsorbent packed in the column. The mixed adsorbent of (1:1 ratio) 50 g, 100 g, and 150 g are added from the top of the column.The adsorption breakthrough curves were obtained by changing the bed height at various flow rates of 10 ml/min, 20 ml/min, 30 ml/min. Faster breakthrough curves were observed for a bed height of 12 cm, while the slowest breakthrough curve was observed at a bed height of 36 cm. Higher the absorbent weight, more the active sites that were accessible for the metal ions to attach and diffuse deep on to the pores of the adsorbents as well as to the surface [178] of the adsorbent which leads to the achievement of higher bed capacity. Furthermore an increment in the bed height brought about more contact time that was being accessible for the metal ions to interact and bind with the adsorbent [5]. This phenomena has permitted the metal ions to diffuse more deeper into the mixed adsorbent and subsequently the percentage removal of metal ions increased when the bed height was increased.

4.9.3 Effect of volumetric flow rate

The effect of flow rate on the metal ions by the mixed adsorbent was investigated by varying the flow rate of the metal ion solution from 10, 20 and 30 ml/min while maintaining the initial metal ion concentration at 100 mg/l and bed weights at 50 g, 100 g, 150 g respectively. A graph of metal ion concentration ratio on y-axis vs effluent outlet time on x-axis at different flow rates were plotted . The quicker breakthrough was observed at the lowest flow rate of 10 ml/min. When the inlet flow rate was increased from 10 ml/min to 30 ml/min, the bed capacity decreased from 30.31 to 7.02 mg/g for cadmium and 54.31 to

9 mg/g for copper, respectively as shown in the Tables 4.40 and 4.41.

Similarly, at the lower flow rates of metal ion solution, the contact time between the metal ions and adsorbent was more which results in a slower breakthrough curve [5]. Conversely at the higher flow rates the metal ion solution will leave the bed before the attainment of equilibrium. This will result in reduced amount of metal ion concentration being adsorbed from the synthetic solution. Biosorption of 2, 4-dichlorophenol in a fixed bed [206] exhibited a similar trend as observed in the present study.

The breakthrough curves for Cd (II) and Cu (II) were plotted (as shown in the Figs. 4.87 to 4.92) which indicates that the faster break through were obtained for cadmium when compared to copper. This type of trend was observed in this study due to higher covalent index of Cd (2.71) than Cu (2.61) and low ionization potential of Cd (16.91) when compared to copper (20.3). It was also reported that higher the covalent index, better is the adsorption of metal ions on to the surface of *R. Arrihuzus* and *S. Cervisiae* [207, 208].

The saturation time for Cd (II) at 50 g with different flow rates of 10 ml/min, 20ml/min, 30 ml/min were 180 min, 120 min, 80 min, respectively. The saturation time for Cd (II) at 100 g with different flow rates were 320 min, 220 min, 150 min, respectively. Similarly, the saturation time for Cd (II) at 150 g with different flow rates were 450 min, 320 min, 290 min respectively that was observed from this experimental study.

The saturation time for Cu (II) at 50 g with different flow rates of 10 ml/min, 20ml/min, 30 ml/min were 400 min, 270 min, 200 min respectively. The saturation time for Cu (II) at 100 g with different flow rates were 450 min, 370 min, 270 min respectively. Similarly, the saturation time for Cu (II) at 150 g with different flow rates were 600 min, 490 min, 350 min, respectively that was observed in this experimental study.

In the continuous column experiments, the breakthrough point shifted towards right when the adsorbent dosage was increased from 50 g to 150 g at a fixed initial metal ion concentration of 100 ppm.

4.10 Continuous column studies for the removal of copper and cadmium using industrial effluents

Continuous column study experiments were conducted for both copper and cadmium in packed bed column and the parameters such as effect of bed height (12, 24, 36cm) at fixed volumetric flow rate of 10 ml/min, and effect of volumetric flow rate (10, 20,30

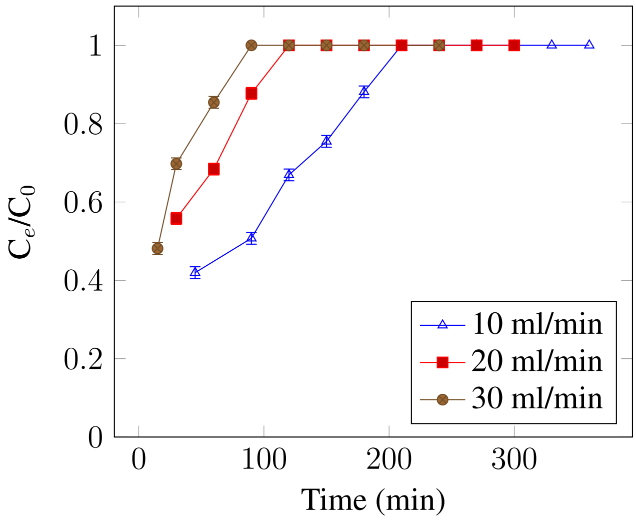

Figure 4.87: Breakthrough curves for cadmium at 12 cm bed height, IMC =100 ppm at different flow rates of 10, 20 and 30 ml/min

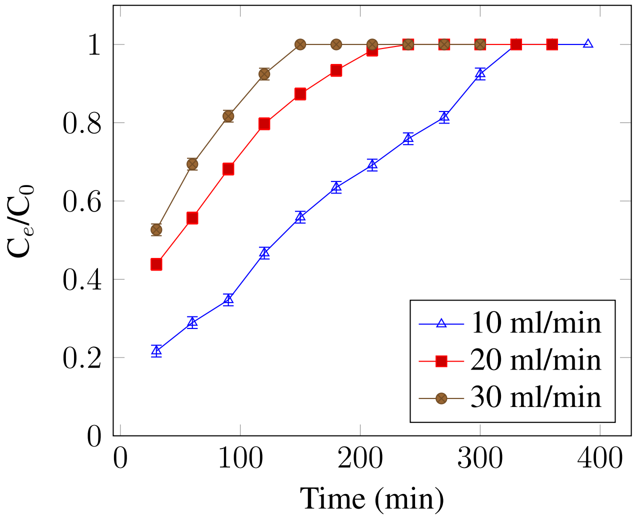

Figure 4.88: Breakthrough curves for cadmium at 24 cm bed height, IMC =100 ppm at different flow rates of 10, 20 and 30 ml/min

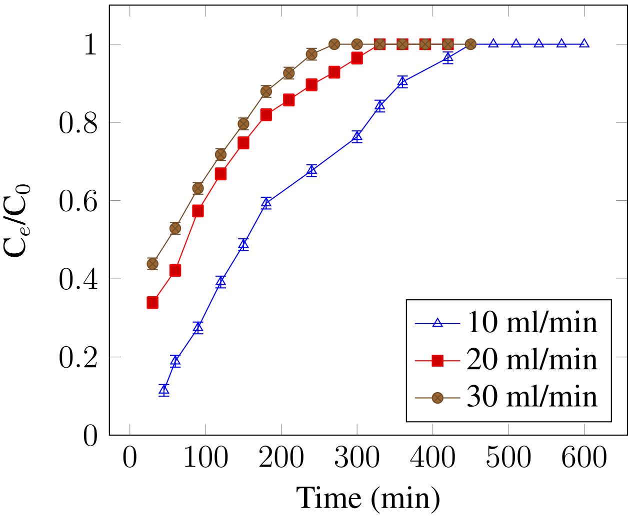

Figure 4.89: Breakthrough curves for cadmium at 36 cm bed height, IMC=100 ppm at different flow rates of 10, 20 and 30 ml/min

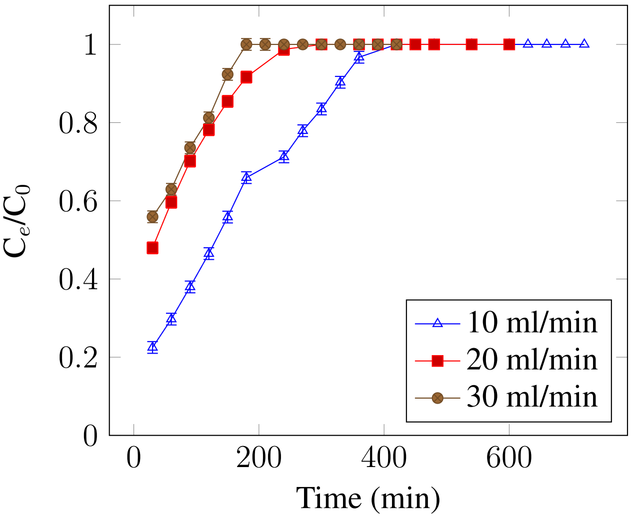

Figure 4.90: Breakthrough curves for copper at 12 cm bed height, IMC=100 ppm at different flow rates of 10,20 and 30 ml/min

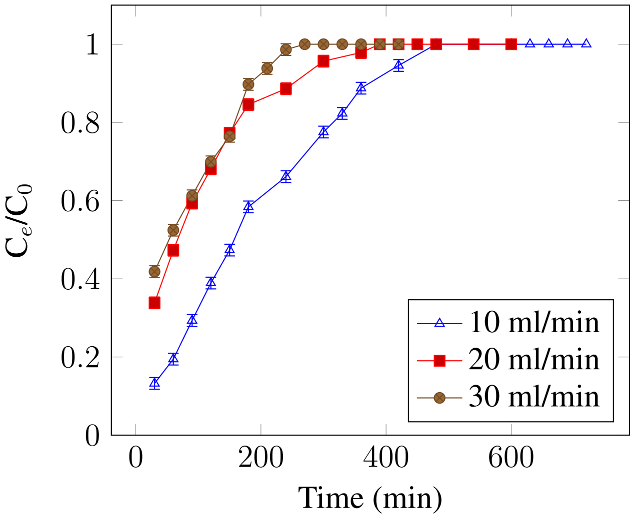

Figure 4.91: Breakthrough curves for copper at 24 cm bed height, IMC =100 ppm at different flow rates of 10, 20 and 30 ml/min

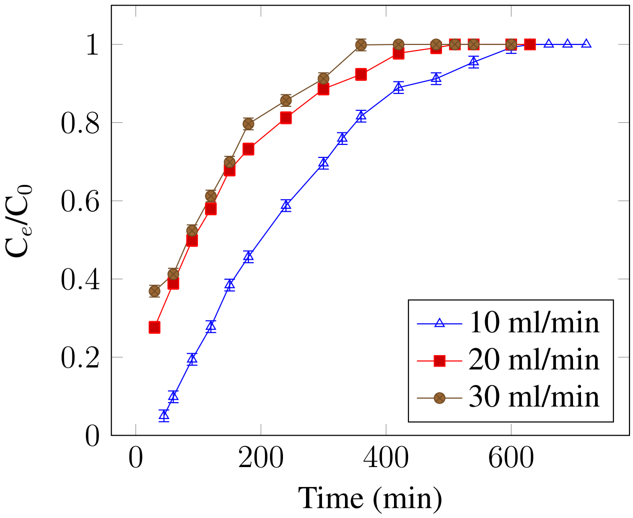

Figure 4.92: Breakthrough curves for copper at 36 cm bed height, IMC =100 ppm at different flow rate of 10, 20 and 30 ml/min

ml/min) at fixed bed height of 36cm are carried out and the results were compared with the synthetic solution data in terms of % removal, breakthrough time and saturation time.

4.10.1 Effect of bed height/adsorbent dosage for Cu (II) and Cd (II) removal from industrial effluent

It is observed that the adsorption of metal ion in the packed bed column is directly proportionally to the quantity of adsorbent in the column. The blended adsorbent (1:1 ratio) of 50 g, 100 g, and 150 g are taken in a column and experiments were carried out to investigate the parameters required to evaluate the efficiencies of column in adsorption process. The adsorption breakthrough curves are obtained by changing the bed height from 12, 24 and 36 cm at fixed volumetric flow rate of 10 ml/min. Faster breakthrough curves were obtained for a bed height of 12 cm, while the slowest breakthrough curve was observed at a bed height of 36 cm. Higher the absorbent packed in the column, more the active sites that are accessible for the metal particles to attach and diffuse deep on to the pores as well as on to the surface of the mixed adsorbent [209] which leads to the achievement of higher bed capacity. Further, when the flow rate is less,the metal ion solution has more contact time to run in the column and the increment of bed height brought more active sites that was being in contact with the metal ions to interact and bind with the adsorbent [210]. This phenomenon has permitted the metal particles to diffuse deeper into the active sites of the mixed adsorbent. Subsequently, the percentage of metal ion removal increased when the bed height was increased. Both the breakthrough time and saturation time increased for Cu (II) with the increase of bed height from 12 cm to 36 cm. The break through time at 12, 24, 36 cm and 10 ml/min for Cu (II) were 50, 90, and 150 min respectively. The saturation time for Cu (II) at 12, 24, 36cm and 10 ml/min were 420, 480, and 600 min respectively. It can be observed from Figs. 4.93 and 4.94, that optimized break through curve were obtained at 36 cm bed height and 10 ml/min and further predicts that 36 cm bed height was taken as an optimized value and further experiments were carried out at 20 ml/min, 30 ml/min with the same bed height of 36cm to study the effect of volumetric flow rate on Cu (II) and Cd (II) metal ions removal using packed bed column.

Similarly the break through time for Cd (II) at 12, 24, 36cm and 10ml/min were 50, 60, and 90 min respectively. The saturation time for Cd (II) at 12, 24, 36 cm and 10 ml/min were 210-240, 330-360, and 390-420 min, respectively.

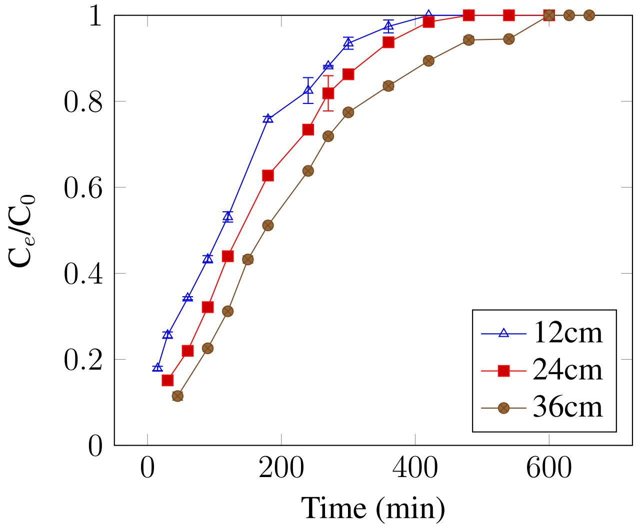

Figure 4.93: Breakthrough curves for copper at 10 ml/min flow rate, IMC of 100 ppm at different bed heights of 12, 24 and 36 cm

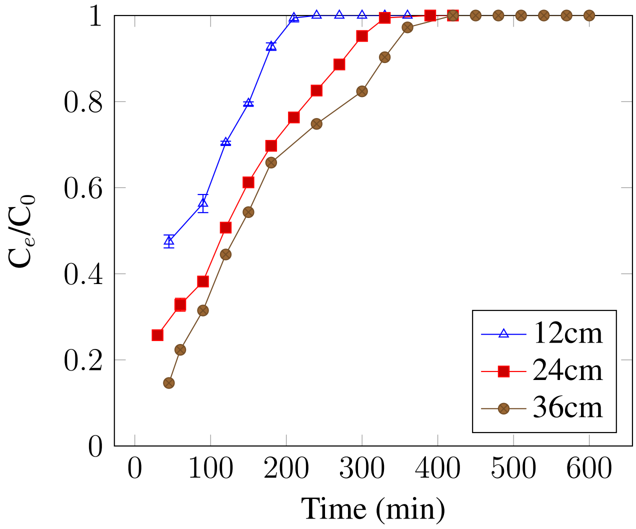

Figure 4.94: Breakthrough curves for cadmium at 10ml/min flow rate, IMC of 100 ppm at different bed heights of 12, 24 and 36 cm

4.10.2 Effect of volumetric flow rate on removal of Cu (II) and Cd (II) from industrial effluent

The effect of flow rate on Cu (II) and Cd (II) ions from industrial effluent by using the mixed adsorbent was investigated by varying the flow rate of the metal ion solution from 10, 20 and 30 ml/min while maintaining the fixed initial metal ion concentration of 100 mg/l and bed height at 36 cm (150 g) respectively. A graph of metal ion concentration ratio on y-axis vs effluent outlet time / sampling time on x-axis at different flow rates was plotted. The quicker breakthrough was observed for the highest flow rate of 30 ml/min, with a bed height of 36 cm due to less contact time between the metal ion particle and the mixed adsorbent.

When the volumetric flow rate increased, there was less contact time between the metal ion and the adsorbent which leads to the decrease of bed capacity. But at lower flow rates of metal ion solution, the contact time between the metal ions and the adsorbent were more [210] which results in a slower breakthrough curve. Conversely at the higher flow rates the metal ion solution will leave the bed before its attainment of equilibrium. This will result in reduced amount of metal ion concentration being adsorbed from the industrial effluent.

The break through time and saturation time for Cu (II) at 36 cm (150 g) with different flow rates of 10, 20, 30 were 45 and 600 min; 30 and 480 min; 15 and 360 min, respectively were observed in this experimental study. Similarly the break through time and saturation time for Cd (II) at 36 cm (150 g) with different flow rates of 10, 20, 30 ml/min were 90 and 390-420 min; 60 and 240-270 min; 30 and 210-240 min, respectively were observed. In the continuous column experiments, the breakthrough point shifted towards the right side for both Cu (II) and Cd (II) when the adsorbent dosage was increased from 50 to 150 g at a fixed initial metal ion concentration of 100 ppm. It was observed from the Figs. 4.95 and 4.96 that the optimized break through curve were obtained at 36 cm and 10 ml/min for both Cu (II) and Cd (II). A longer breakthrough time implies better adsorption capacity which means that it would take a longer time for the adsorbent material to completely get saturated with the adsorbate solution.

4.10.3 Comparative studies for industrial effluent and synthetic sample in continuous flow study

The results obtained through column studies using industrial and synthetic solutions for copper and cadmium were compared in terms of breakthrough time, saturation time and % removal of metal ions. There was no significant time difference of breakthrough

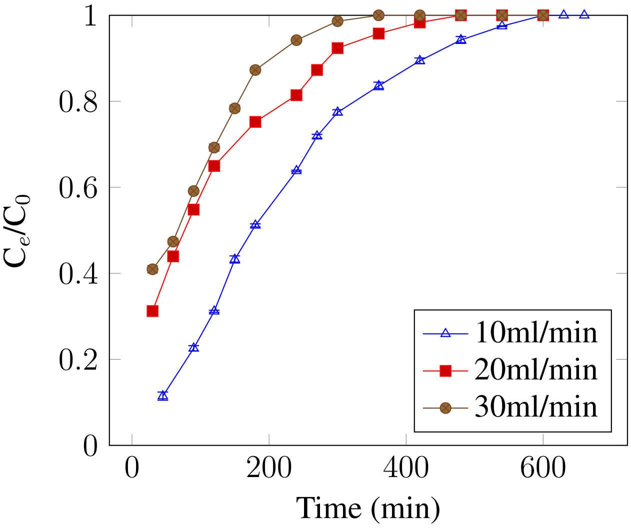

Figure 4.95: Breakthrough curves of copper at 36cm BH, IMC of 100 ppm at different flow rates of 10ml/min, 20ml/min, 30ml/min

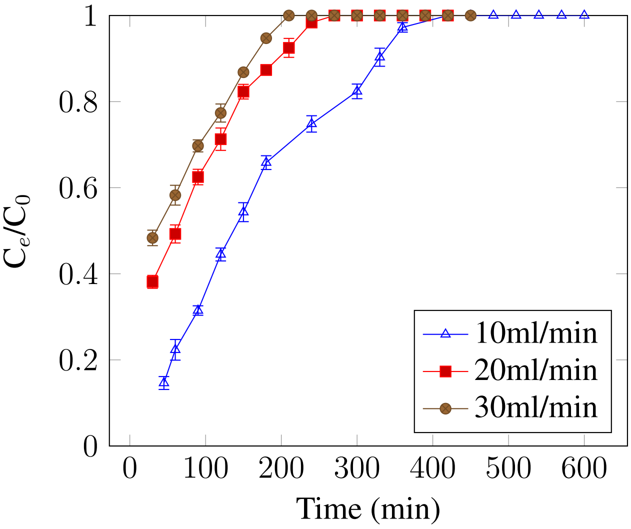

Figure 4.96: Breakthrough curves of cadmium at 36cm BH, IMC of 100 ppm at different flow rates of 10ml/min, 20ml/min, 30ml/min

time (50, 60, 65 min) for synthetic solutions at fixed volumetric flow rates and variation of bed height in comparison with industrial sample having (50, 90, 45 min) for copper. This large difference of time in industrial effluent was due to the presence of other heavy metal ions, phenol, cresols, other sludges in the effluent so that it has taken more time to reach break through points.

Similarly, the same trend for copper was observed for saturation time (more time taken in case of industrial effluent) in comparison with synthetic solution and this may be due to the presence of other heavy metals which blocks the adsorbent pores and in turn leads to more time of saturation. But in case of different volumetric flow rates and fixed bed heights of (36 cm or 150 g dosage) a negligible time gap of (5-10 min) was observed for saturation time as shown in Tables,4.31 and 4.32.

This was due to the increase in dosage from 50 g to 150 g in the column, as there were more number of active sites present in the column that are readily available for metal ions to occupy and further leads to late saturation. But in case of breakthrough time at fixed bed height of 36cm and varying volumetric flow rates there was a difference of 20 min, 25 min, 35 min were observed at 10, 20, 30 ml/min respectively. This was due to the change of volumetric flow rate from 10 ml/min to 30 ml/min. With the increase of flow rate, more metal ion solution was passed through the column and there was a competitive adsorption of metals ions for the same active sites and due to the presence of other heavy metals the pores got blocked quickly, which leads to the attainment of difference in breakthrough time.

In comparison with column performance in terms of total % removal at 12 and 24 cm and a fixed vol.flow rate of 10 ml/min, the more % removal was observed in case of synthetic samples having 62.13% ,67.45% than industrial effluents. The less % removal was observed for synthetic sample (78.24%) at 36 cm bed height and 10 ml/min when compared to industrial sample having 82% as shown in Table 4.31 and Table 4.32. This difference of 4% removal between the industrial effluent and synthetic sample for copper was due to more adsorbent dosage of 150 g at 36cm bed height. Similarly, at fixed bed height of 36 cm (150 g) and varying volumetric flow rates from 10, 20, 30 ml/min there were a difference of 4%, 9%, 4% between industrial effluent and synthetic samples for copper and this may be due to more dosage of 150 g at 36 cm bed height. Overall in the column performance comparison between synthetic samples and industrial effluents for copper, synthetic solution performance was more superior at fixed volumetric flow rates of 10 ml/min and varying bed heights from 12 cm to 36 cm.

However a reverse trend was observed for copper in case of fixed bed heights of 36 cm (150 g) and variation of volumetric flow rates from 10 ml/min to 30 ml/min which indicates that industrial effluent performance was superior when compared to synthetic solution and this may be due to more adsorbent dosage and influence of synergistic effect in the column. The data for both industrial effluent and synthetic solution for copper were shown in Table 4.31 and Table 4.32, respectively.

Similarly for cadmium there was a significant time difference of breakthrough time (50, 35, 60 min) for synthetic solutions and industrial effluent having (50 min, 60 min, 90 min) at fixed volumetric flow rates and variation of bed height for cadmium.

The breakthrough time increases for cadmium -industrial effluent due to the presence of other heavy metals, phenols, cresols, other sludge which effects the performance of the column and also gives a competitive adsorption effect for cadmium along with other metals in the column.

Similarly the same trend was observed for cadmium in-terms of saturation time in comparison with the synthetic solution and this may be due to presence of other heavy metals which blocks the adsorbent pores and in turn leads to more time of saturation at fixed volumetric flow rate of 10 ml/min and different bed heights of 12 and 24 cm. But at 36 cm and 10 ml/min, the saturation time for industrial effluent decreased (405 min) in comparison with synthetic sample having (450 min) and this may be due to the increase of bed height which leads to attainment of more adsorption capacity (due to adsorbent dose) in the column, as well as due to the presence of synergistic effect of the mixed adsorbent which leads to quick saturation.

In case of fixed bed height of 36 cm (150 g) and different volumetric flow rates from 10 to 30 ml/min, the break through time increased from 60 to 90 min at 10 ml/min, 40 to 60 min at 20 ml/min, and the same break through time of 30 min was observed at 30 ml/min as shown in Tables 4.33 and 4.34. This increase in break through time for industrial effluent was due to the presence of other heavy metals and sludge that plays a role of competitive adsorption in the column along with cadmium.

Similar to copper, a reverse trend for cadmium was observed in-terms of saturation time at fixed bed height of 36 cm and different volumetric flow rates. The saturation time was more for synthetic samples (450, 320 min) when compared to industrial effluents (405, 255 min) and this may be due to the presence of synergistic effect of the mixed adsorbent as well as high amount of dose (150 g) in the column.

The reverse trend for cadmium was observed at 30 ml/min and 150 g, where the saturation time was less in case of synthetic sample (200 min) when compared to industrial effluent having (225 min) and this may be due to more volumetric flow rate of (30 ml/min) as well as due to the presence of other heavy metals that blocks the adsorbent particles and further leads to the late arrival of saturation zone as shown in the Tables 4.33 and 4.34.

In comparison with the column performance of cadmium in terms of total % removal, at 12, 24, 36 cm and 10 ml/min (fixed volumetric flow rate), the more % removal was observed in case of synthetic samples having 32.63%, 66.47%, 70.28% in comparison with industrial sample having 28.1%, 55.35%, 52.77%, respectively.

The similar type of trend for cadmium was observed at fixed bed height of 36 cm (150 g) and different volumetric flow rates of 10, 20, and 30ml/min. The more % removal was observed for synthetic samples having 70.28%, 54.38%, and 44.12% in comparison with industrial effluents having 52.77%, 38.18%, and 44.77% which was due to the presence of other heavy metals, sludges apart from competitive adsorption of cadmium present in the industrial effluent. Overall in comparison with industrial effluents for cadmium, the synthetic solutions have proved to be more superior in terms of total % removal and better performance was observed with synthetic solutions rather than industrial effluents for cadmium as shown in Tables 4.33 and 4.34,respectively.

4.11 Column performance evaluation

The efficiency of the continuous column adsorption can be determined by using the time to reach breakthrough and the shape of the breakthrough curve. The breakthrough curves show the loading behavior of a metal ion in a continuous column [211] and are usually expressed in terms of normalized concentration defined as the ratio of the outlet concentration (C_t) to the inlet concentration (C_o) as a function of time (in minutes) [212]. The total metal adsorbed, m_{ad}(mg), in the fixed bed column can be calculated from the area under the curve multiplied by the flow rate from Eq. 4.13 which is given as follows:

$$M_{ad} = \frac{Q}{1000} \int_{t=0}^{t=total} C_{ad} dt \tag{4.13}$$

The uptake capacity (q_e) by the adsorbent for synthetic sample data was shown in Eq. 4.14 as

$$q_e = \frac{M_{ad}}{M} \tag{4.14}$$

where q_e is the adsorbent uptake capacity (mg/g), M_{ad} is the metal ion adsorbed (mg) and M is the adsorbent mass (g). The total amount of metal ion sent through the column was calculated by Eq. 4.15.

$$m_{total} = \frac{C_o F t_e}{1000} \tag{4.15}$$

where C_o is the inlet concentration of metal ion (mg/L), F is the flow rate of metal ion solution (mL/min), and t_e is the exhaustion time (minutes). The % removal of metal ions (column performance) was calculated by Total $\%$ removal $= \frac{m_{ads}}{m_{total}} \times 100$

$$\text{EBCT or EBRT} = \frac{\text{Empty bed volume}}{\text{volumetric flow rate of the fluid}}$$

$$\text{Sorbent Usage Rate or Adsorbent Exhaustion Rate} = \frac{\text{Mass of the adsorbent in the column}}{\text{volume treated at the break through point (L)}}$$

The rate of exhaustion (AER, g/L) [213] was defined as mass of sorbent deactivated per unit volume of water treated at the breakthrough point and was calculated by the following equation.

$$\text{Adsorbent Exhaustion Rate} = \frac{\text{Mass of the sorbent (g) in the column}}{\text{volume of water treated (L)}}$$

4.11.1 Effect of flow rate

Experiments were carried out by varying the flow rate of synthetic solution between 10-30 ml/min. The adsorption column data were summarized in Tables 4.35, 4.36 for copper and Tables 4.37,4.38 for cadmium, respectively. It was observed that with an increase in flow rate from 10 to 30 ml/min at 12 cm bed height both the breakthrough time and saturation time decreased from 50 to 20 min and 400 to 200 min respectively for copper, and breakthrough time and saturation time decreased from 50 to 15 min, and 180 to 80 min for cadmium, respectively.

The same pattern was followed for 100 g and 150 g at different flow rates for both the metals. With the increase of flow rate from 10 ml/min to 30 ml/min at 24 cm bed height (100 g), the breakthrough time and saturation time decreased from 60 to 40 min and 450 to 250 min respectively for copper, the breakthrough time and saturation time decreased from 35 to 25 min and 320 to 150 min respectively for cadmium. Similarly with the increase of flow rate from 10 ml/min to 30 ml/min at 36 cm bed height (150 g), the breakthrough time and saturation time decreased from 65 to 50 min and 600 to 350 min respectively for copper, the breakthrough time and saturation time decreased from 60 to 30 min, and 450 to 200 min, respectively for cadmium. The removal efficiency of the mixed adsorbent substantially decreased with an increase in flow rate at different adsorbent dosage of 50, 100, and 150 g respectively for both the metals. This can be attributed to the fact that at lowest flow rate, the residence time of Cu^{2+} and Cd^{2+}ions in the column increases and as result the Cu^{2+} and Cd^{2+} ions have more time to diffuse into the pores of the mixed adsorbent through intra-particle diffusion resulting in a longer breakthrough time and saturation time [214].

4.11.2 Effect of bed height

The removal of Cu^{2+} and Cd^{2+} ions at different bed heights were studied at 100 ppm metal ion concentration and fixed flow rate of 10ml/min. With the increase in bed height, the removal efficiency, breakthrough time and saturation time, sorbent exhaustion rate (SER) increases as shown in Table 4.36 and 4.37 for copper and cadmium respectively. The increase in removal efficiency of Cu^{2+} and Cd^{2+} ions by the mixed adsorbent was due to the availability of higher number of adsorption sites and increase in the volume of effluent. The empty bed contact time (EBCT) also increased from 15 to 45 min for both the metals. These observations suggest that the bed height of 36 cm, 10 ml/min offered optimum breakthrough curves for both the metals. [214].

4.11.3 Hydro dynamic studies

The hydrodynamic behavior of metal ion solution in packed bed column combined with forced convective mass transfer has been studied with respect to dimensionless numbers such as Sherwood number (Sh), Reynolds number (Re), and Schmidt number (Sc), Chinton-Colbourn factor (J_D), mass transfer coefficient (k). The empirical correlations for the above mentioned dimensionless numbers have been shown in Eqs. 4.16, 4.17, 4.18 respectively [215].

$$\text{Sherwood number}, Sh = J_D Re Sc^{0.33} \tag{4.16}$$

$$\frac{Sh}{Sc} = \frac{k\rho y}{Q} \times Re \tag{4.17}$$

$$\text{Schmidt number}, Sc = \frac{\mu}{\rho D_A B} \tag{4.18}$$

where the notations include

Q = volumetric flow rate (10, 20, 30 ml/min)

density of metal ion solution, ρ = 1000 kg/m^3

Viscosity of water, $\mu = 0.01 \frac{kg}{m-s}$

Diffusivity of water, D_{AB} = 1.29 *10^{-9} m^2/s

ϵ, porosity of the bed = 0.39 (Particles are in fine powder calculated after adsorption)

J_D = Chilton-Colubrn factor

k = Mass transfer coefficient (m/s)

y = mass fraction of the adsorbent varying with respect to bed heights (y for 12cm = 0.166, y for 24cm = 0.33 and y for 36 cm = 0.5)

Re$_P$ = $\frac{D_P v \rho}{\mu}$

Velocity of the fluid, V = $\frac{Q}{A}$

Mass flow rate of the fluid, m = $Q \times \rho$

Where Q is the volumetric flow rate of the fluid (ml/min) and ρ is the density of the metal ion solution.

Relationship between Sherwood number and Reynolds number for particles (dissolution method) where given by

Re = $\frac{Re_P}{(1-\epsilon)}$, which shows good agreement with the experimental data. Re$_P$ is called Reynolds number of the particle.

Correlations to find Chilton Coulbrn factor were given as [216].

J$_D$ = 5.7 Re$^{-1.22}$ for $1 < \text{Re} < 30$

J$_D$ = 1.77 Re$^{-1.56}$ for $30 < \text{Re} < 1000$

where J$_D$, k, ρ, and y are Chinton-Colbourn factor, mass transfer coefficient (m/s), density of solution, and mass fraction of the component respectively.

Finally mass transfer coefficient (k) was found from Eq.4.17 after calculating the ratio of Sh/Sc (Sherwood number to Schmidt number). The hydro dynamic modeling data has been reported in Table 4.39.

4.11.4 Hydrodynamic studies at various flow rates and bed heights

The hydrodynamic behavior of fluid flow inside the column has been shown in Table 4.39. It became evident from the Table 4.39 that the dimensionless parameters varied significantly with flow rate and bed height inside the packed bed column [217].

With the increase of flow rate there was a significant rise in the velocity of fluid inside the column which increases the Reynolds number.

The Schmidt number, Sherwood number, Colubrn factor (J$_D$) decreases in the order of bed height increase from 12 to 36 cm at a constant volumetric flow rate.

The Sherwood number decreased with the increase of flow rate from 10 ml/min to 30 ml/min. However, with the increase of bed height at fixed flow rate, there was a decrease in

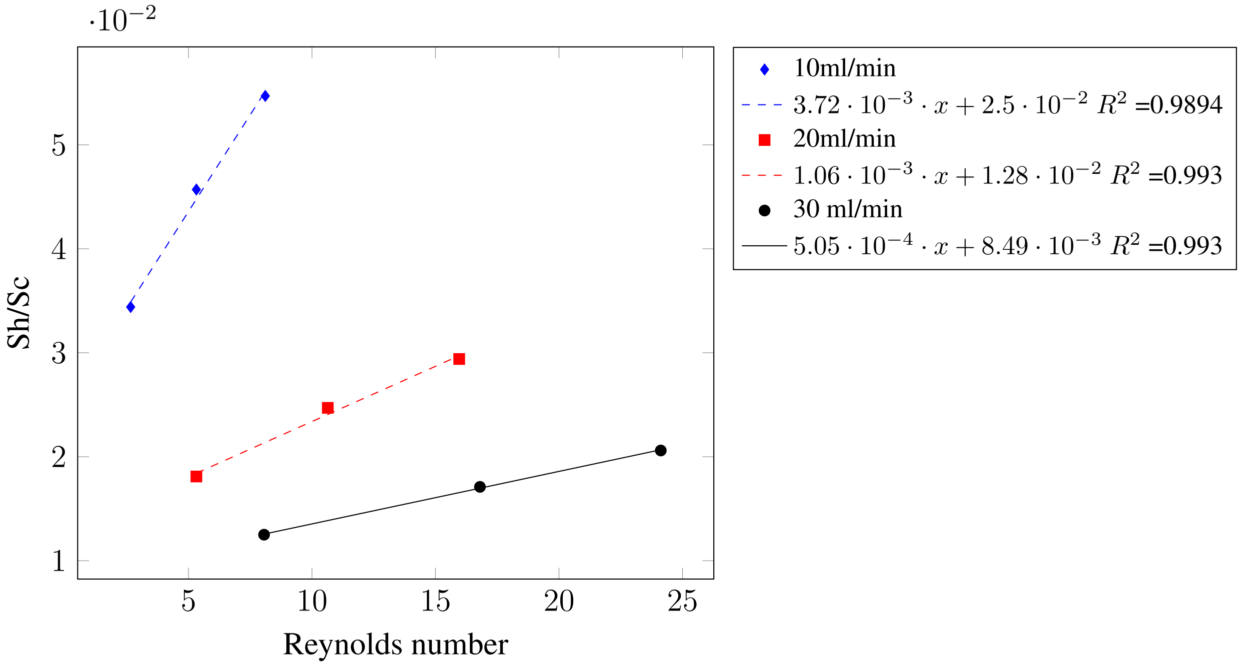

Figure 4.97: Plot between ratio of Sh/Sc vs Reynolds number at different bed heights and volumetric flow rates

velocity of the fluid, Schmidt number, Sherwood number, Colubrn factor (J_D) and increase in the Reynolds number was observed. The decrease in the values of these forced convective (inter phase) mass transfer parameters was due to the path resistance posed by the particles of bed, and this resistance increased with the increase of bed height and reduced when the flow rate was high. Therefore, in the present investigation it was summarized that large flow rates and smaller bed heights rendered the minimum possible resistance for the transfer of metal ions from liquid phase to packed bed. Figure 4.97 indicates the plot between the Reynolds number (Re) and the ratio of Sh/Sc (Sherwood number to Schmidt number) at different flow rates. The trend lines are drawn along with correlation coefficient (R^2) values to represent the column dynamics. It can be observed from the Fig 4.97 that at different flow rates the regression / correlation coefficient (R^2) values were very close to 1 which indicates that the column hydro dynamics gives best fit to the adsorption system.

4.12 Modeling of kinetic studies for continuous column operation

An adsorption model was used to predict the fixed-bed dynamics including external film diffusion and intra particle mass transport, the former resulting in the limiting step to overall mass transport in the investigated experimental conditions.

The main fluid dynamic and physical parameters such as flow rate and metal ion concentrations were investigated in order to determine their effect on the overall adsorption rate. This information was commonly considered as a fundamental for the proper device scale-up, for a cost-effective adsorption column design and for a general process optimization. Finally a thorough modeling analysis of the fixed-bed column was carried out as a support for the design of adsorption units for copper and cadmium removal from polluted/industrial waste water.

The kinetic studies in the continuous column operation were used to describe the adsorption isotherms of single-solute systems in the form of linear break through models such as Thomas model and Yoon-Nelson model which explains the mechanism of adsorption.

4.12.1 Thomas model

Thomas developed a model for adsorption processes in which external and internal diffusion limitations are not present [26]. The details of this model was discussed earlier in Sec. 3.6.1.1.

A linear graph of ln[C_o/C_t -1] against time (t) was plotted to determine the values of q_o and k_{Th} from the intercept and slope respectively.

It was concluded for cadmium metal, at a constant bed weight of 50 g and at different flow rates the Thomas rate constant values k_{Th} increased from 0.00855 to 0.0198 and the adsorption capacities decreased from 30.31 to 16.39 mg/g. Similarly at 100 g and 150 g with different flow rates the same trend has been observed and the numerical values were reported in Table 4.40 for Cadmium.

Moreover at all the flow rates and bed weights the correlation or regression coefficient R^2 values obtained are in the range of 0.95 to 0.99 which further predicts the suitability / best fit of the Thomas model for the adsorption system of cadmium.

Similarly, it was concluded for copper metal that at a constant bed weight of 50 g and at different flow rates the Thomas rate constant values k_{Th} increased from 0.006 to 0.0105 and the adsorption capacities decreased from 54.31 to 32.18 mg/g. Similarly at 100 g and 150 g with different flow rates the same trend has been observed and the numerical values were repored in the Table 4.41 for copper. Moreover at all the flow rates and bed weights the correlation or regression coefficient R^2 values obtained are in the range of 0.95 to 0.9 except for 30 ml/min and 150 g. It clearly indicates from Table 4.41 that the Thomas model gives a best fit for the adsorption system of Cu (II).

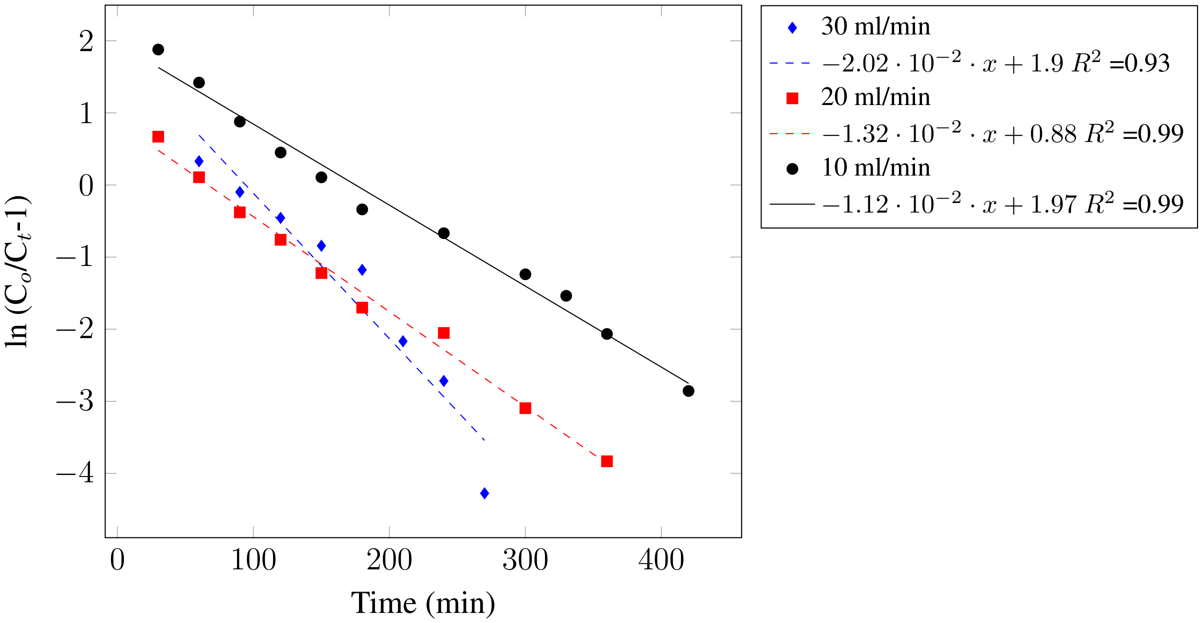

Figure 4.98: Thomas model for Cu (II) at 24 cm bed height with different flow rates

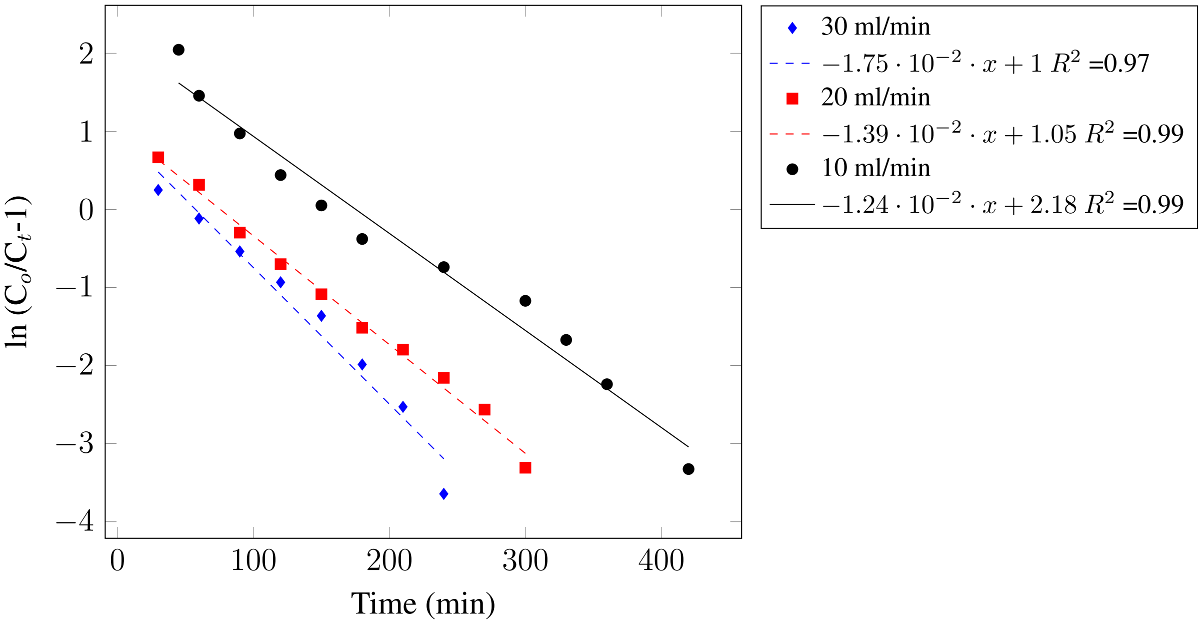

Figure 4.99: Thomas model for Cd (II) at 36 cm bed height with different flow rates

4.12.2 Yoon-Nelson model

This model is mathematically equivalent to the Thomas model, and it has been applied to a wide range of concentrations in the effluent between the breakthrough and saturation time of the column [218]. Yoon and Nelson built up a model to explain the adsorption phenomena in the continuous column flow operations as discussed in Sec. 3.6.1.2.

A linear graph of ln (C_t/[(C_o- C_t)] against effluent collection time or reaction time (t) was used to determine the values of K_{YN} and τ from the slope and intercept of the plot respectively.

The determination of mathematical equation as discussed in sec. 3.6.1.2 depend on the definition that 50 % breakthrough happens at t = τ. In this way, the sorption bed was ought to be totally soaked (saturated) at t = τ. Owing to the symmetrical nature of the breakthrough curves due to the Yoon Nelson model, the measure of metal ion being sorbed in the fixed bed is half of the aggregate (total) amount of metal ion entering the sorption bed inside 2τ period.

This model depends on the hypothesis that the rate of decrease in the probability of adsorption for every adsorbent particle is relative to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent [26, 219].

Several authors have used Yoon Nelson model in the study of column adsorption kinetics and are cited in the literature [173, 220] [221].

Yoon - Nelson model was also applied to the column data obtained from metal ion adsorption by the mixed adsorbent in the continuous flow operation. A plot of ln (C_t/(C_o-C_t) on x-axis, time (min) on y-axis gives a straight line with slope of K_{YN}, and intercept of τ K_{YN}.The values of K_{YN}, τ and adsorption capacity, q_o are calculated and are reported in Tables 4.42 and 4.43 for Cd (II) and Cu (II) respectively.

The results proved that the Yoon-Nelson rate constant, K_{YN} increased with the increment of flow rate and bed height (adsorbent dose filled) at a constant IMC of 100 ppm. The adsorption capacity, q_o decreased with the increase in bed weight and also decreased with the increase in flow rate from 10 ml/min to 30 ml/min at a constant initial metal ion concentration. The time required for 50% breakthrough τ decreased with the increase in flow rate at fixed initial metal ion concentration and τ also increased with the increase in the bed weight (adsorbent packed in g). Higher values of correlation coefficients indicate that Yoon -Nelson model fitted equally well with the Thomas model for the obtained experimental data. This is in good agreement with the experimental results obtained from previous studies [220] and [71].

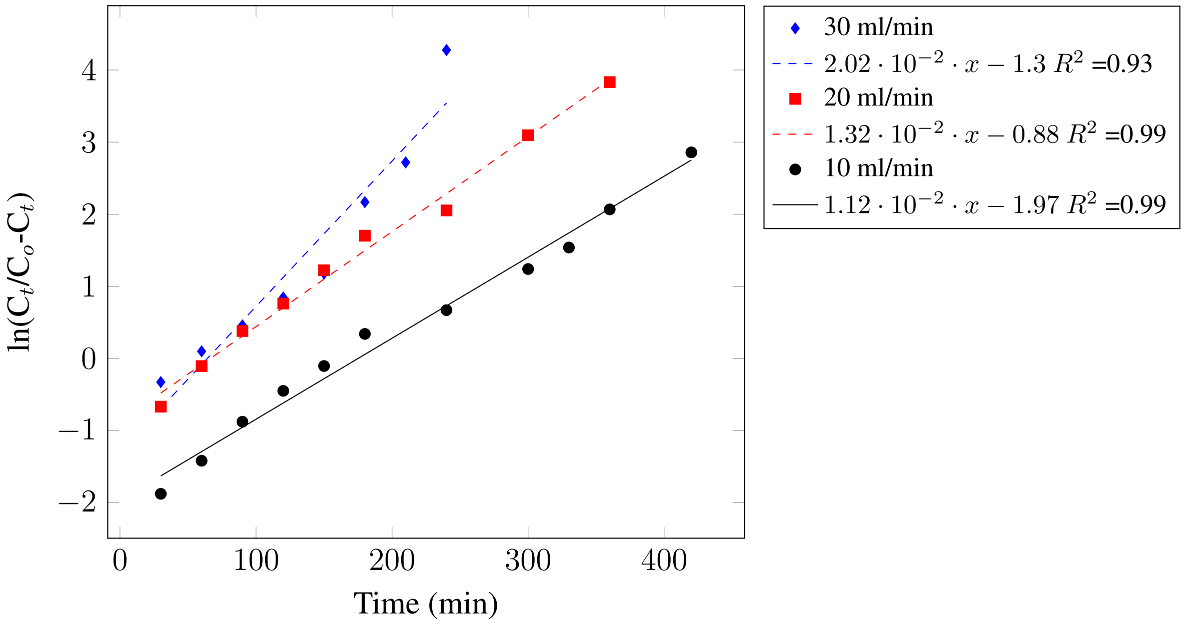

Figure 4.100: Yoon- Nelson model for Cu (II) at 24 cm of bed height with different flow rates

The results indicate that the k$_{YN}$ values increased from 0.012 to 0.020 l/min and τ values decreased from 135.78 to 26.67 min when the flow rate increased from 10 ml/min to 30 ml/min at 50 g (12 cm) of the adsorbent dosage for Cu (II) and Cd (II) as shown in Table 4.43 and 4.42 respectively.

The linear regression coefficient (R^2) was greater than 0.95 for the experimental fitted values which indicates that this model can be utilized to explain the overall kinetics in the column studies for Cu (II) and Cd (II) adsorption.

It shows that the Yoon-Nelson model was apt to describe the dynamics of the adsorption in the packed bed column. Additionally, these results indicate that the rate of decrease in the adsorption probability of metal ions onto the mixed adsorbent was directly proportional to the metal ion adsorption and breakthrough on the mixed adsorbent. This results are in good agreement with the results obtained from literature [222].

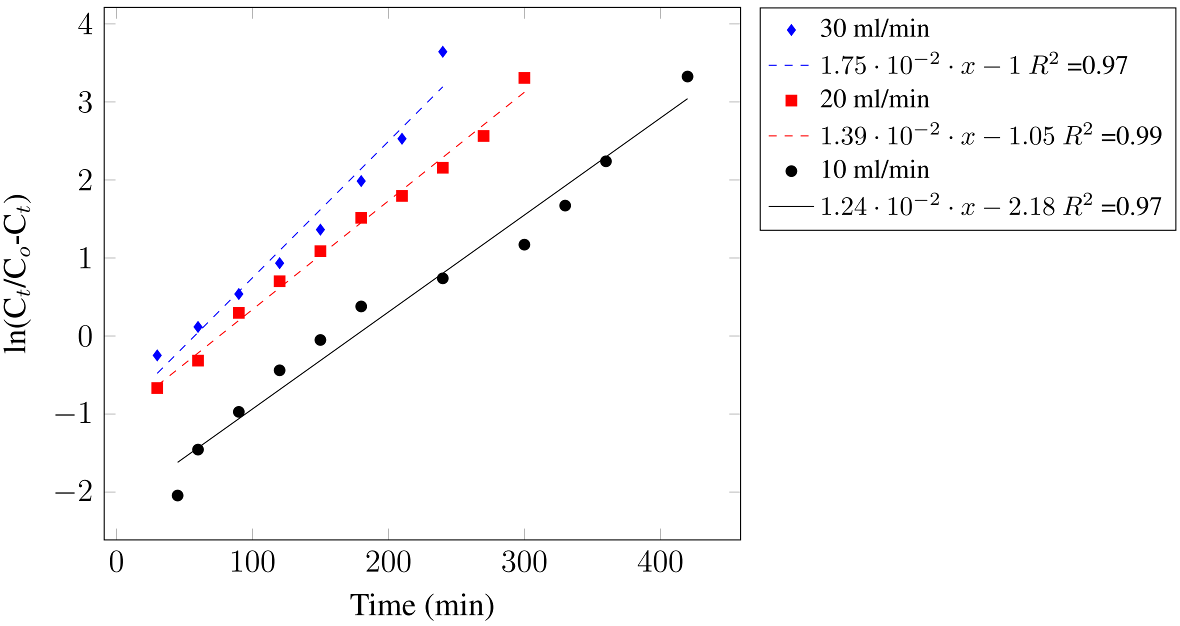

Figure 4.101: Yoon- Nelson model for Cd (II) at 36 cm of bed height with different flow rates

Table 4.31: Column performance calculations of industrial effluent for copper removal at different bed heights and volumetric flow rates

Ads dosage (g)	**Bed** height (cm)	**Vol.** flow rates (ml/min)	**IMC** (ppm)	**Break** through time (min)	**Saturation** time (min)	**Vol.** treated at break through point (ml)	**Vol.** treated at saturation point (ml)	**M**$_{ad}$**(g)**	**m**$_{total}$	**% removal**
50	12	10	100	50	420	500	4200	254	420	60.48
100	24	10	100	90	480	900	4800	264.65	480	55.14
150	36	10	100	45	600	450	6000	491.4	600	81.9
150	36	20	100	30	480	600	9600	619	960	64.48
150	36	30	100	15	360	450	10800	644.44	1080	59.67

Table 4.32: Column performance calculations of synthetic solutions for copper removal at different bed heights and volumetric flow rates

Ads dosage (g)	**Bed** height (cm)	**Vol.** flow rates (ml/min)	**IMC** (ppm)	**Break** through time (min)	**Saturation** time (min)	**Vol.** treated at break through point (ml)	**Vol.** treated at saturation point (ml)	**M_{ad}(g)**	**m_{total}**	**% removal**
50	12	10	100	50	400	500	4000	248.5	400	62.13
100	24	10	100	60	450	600	4500	303.51	450	67.45
150	36	10	100	65	600	650	6000	469.46	600	78.24
150	36	20	100	55	490	1100	9800	542.96	980	55.4
150	36	30	100	50	350	1500	10500	582.48	1050	55.47

Table 4.33: Column performance calculations of industrial effluent for cadmium removal at different bed heights and volumetric flow rates

Ads dosage (g)	**Bed** height (cm)	**Vol.** flow rates (ml/min)	**IMC** (ppm)	**Break** through time (min)	**Saturation** time (min)	**Vol.** treated at break through point (ml)	**Vol.** treated at saturation point (ml)	**M_{ad}(g)**	**m_{total}**	**% removal**
50	12	10	100	50	325	500	3250	91.3	325	28.09
100	24	10	100	60	345	600	3450	190.95	345	55.35
150	36	10	100	90	405	900	4050	213.7	405	52.77
150	36	20	100	60	255	1200	5100	194.71	510	38.18
150	36	30	100	30	225	900	6750	302.21	675	44.77

Table 4.34: Column performance calculations of synthetic solutions for cadmium removal at different bed heights and volumetric flow rates

Ads dosage (g)	**Bed** height (cm)	**Vol.** flow rates (ml/min)	**IMC** (ppm)	**Break** through time (min)	**Saturation** time (min)	**Vol.** treated at break through point (ml)	**Vol.** treated at saturation point (ml)	**M**$_{ad}$**(g)**	**m**$_{total}$	**% removal**
50	12	10	100	50	180	500	1800	58.73	180	32.63
100	24	10	100	35	320	350	3200	212.7	320	66.47
150	36	10	100	60	450	600	4500	316.25	450	70.28
150	36	20	100	40	320	800	6400	348.04	640	54.38
150	36	30	100	30	200	900	6000	264.74	600	44.12

Table 4.35: Column performance calculations for copper removal at different bed heights and adsorbent dosage for synthetic solution

Ads dosage (g)	**Bed** height (cm)	**Volumetric** flow rates (ml/min)	**IMC** (ppm)	**Break** through time (min)	**Saturation** time (min)	**Volume treated at** break through point (ml)	**Volume treated at** saturation point (ml)
50	12	10	100	50	400	500	4000
50	12	20	100	30	270	600	5400
50	12	30	100	20	200	600	6000
100	24	10	100	60	450	600	4500
100	24	20	100	50	370	1000	7400
100	24	30	100	40	270	1200	8100
150	36	10	100	65	600	650	6000
150	36	20	100	55	490	1100	9800
150	36	30	100	50	350	1500	10500

Table 4.36: Parameters of the packed bed column for the removal of Copper ions by the mixed adsorbent for synthetic solution

Ads dosage (g)	**Bed** height (cm)	**Volumetric** flow rates (ml/min)	**IMC (ppm)** (g)	**M**$_{ad}$	**m**$_{total}$	**%** removal	**EBCT** min	**SER** (g/dm^3)
50	12	10	100	248.5	400	62.13	15	497
50	12	20	100	257.77	540	47.73	7.5	429.61
50	12	30	100	269.67	600	44.95	5	449.45
100	24	10	100	303.51	450	67.45	30	505.86
100	24	20	100	356.84	740	48.22	15	356.84
100	24	30	100	376.92	810	46.53	10	314.1
150	36	10	100	469.46	600	78.24	45	722.24
150	36	20	100	544.23	980	55.53	22.5	493.61
150	36	30	100	582.48	1050	55.47	15	388.32

Table 4.37: Column performance calculations for cadmium removal at different bed heights and adsorbent dosage for synthetic solution

Ads dosage (g)	**Bed** height (cm)	**Volumetric** flow rates (ml/min)	**IMC** (ppm)	**Break** through time (min)	**Saturation** time (min)	**Volume treated at** break through point (ml)	**Volume treated at** saturation point (ml)
50	12	10	100	50	180	500	1800
50	12	20	100	25	120	500	2400
50	12	30	100	15	80	450	2400
100	24	10	100	35	320	350	3200
100	24	20	100	30	220	600	4400
100	24	30	100	25	150	750	4500
150	36	10	100	60	450	600	4500
150	36	20	100	40	320	800	6400
150	36	30	100	30	200	900	6000

Table 4.38: Parameters of the packed bed column for the removal of Cadmium ions by the mixed adsorbent for synthetic solution

Ads dosage (g)	**Bed** height (cm)	**Volumetric** flow rates (ml/min)	**IMC (ppm)** (g)	**M**$_{ad}$	**m**$_{total}$	**%** removal	**EBCT** min	**SER** (g/dm^3)
50	12	10	100	58.73	180	32.63	15	117.46
50	12	20	100	88.1	240	36.71	7.5	176.1
50	12	30	100	91.65	240	38.19	5	203.7
100	24	10	100	212.7	320	66.47	30	607.7
100	24	20	100	215.87	440	49.7	15	349.78
100	24	30	100	219.21	450	48.71	10	250.8
150	36	10	100	316.25	450	70.28	45	527.1
150	36	20	100	348.04	640	54.38	22.5	435.1
150	36	30	100	264.74	600	44.12	15	294.15

Table 4.39: Hydro dynamic modeling of column studies at different flow rates and bed heights

Flow rate (ml/min)	**Bed** height (cm)	**Reynolds** number	**Schmidt** number	**Sherwood** number	**Sh/Sc**	**Colburn** factor (J_D)	**Mass** fraction (y)	**Mass** transfer coefficient ($K*10^{-12}$)
10	12	2.66	1550	51.91	0.0334	1.728	0.166	12.9
10	24	5.32	775.2	35.15	0.0457	0.7417	0.33	4.33
10	36	8.11	516.8	28.275	0.0547	0.443	0.5	2.25
20	12	5.32	3100.78	56.02	0.0181	0.7417	0.166	6.81
20	24	10.64	1550.38	38.264	0.02468	0.318	0.33	2.34
20	36	15.96	1033.6	30.61	0.0296	0.1941	0.5	1.236
30	12	8.04	4651.16	58.48	0.01257	0.4482	0.166	4.71
30	24	16.08	2325.6	39.94	0.01717	0.1924	0.33	1.61
30	36	24.12	1550.38	31.96	0.0206	0.1173	0.5	0.854

Table 4.40: Thomas model parameters for cadmium (II)

Column Parameters	**Thomas (K_{Th}) rate constant**	**Adsorption (q_o) capacity**	**R^2**	**Model Equation**
10ml/min, 12 cm	0.00855	30.31	0.953	y = -0.017x+1.296
20ml/min, 12 cm	0.0144	20.58	0.955	y = -0.029x+0.743
30ml/min, 12 cm	0.0198	16.39	0.967	y = -0.04x+ 0.54
10ml/min, 24 cm	0.0127	13.5	0.976	y = -0.0127x+1.715
20ml/min, 24 cm	0.0231	10.54	0.953	y = -0.023x+1.217
30ml/min, 24 cm	0.0262	8.42	0.991	y = -0.0262x+0.7358
10ml/min, 36 cm	0.0186	7.81	0.973	y = -0.0124x+ 2.179
20ml/min, 36 cm	0.02	7.66	0.992	y = -0.014x+ 1.053
30ml/min, 36 cm	0.026	7.02	0.967	y = -0.0175x+1.003

Table 4.41: Thomas model parameters for copper (II)

Column Parameters	**Thomas (K_{Th}) rate constant**	**Adsorption (q_o) capacity**	**R^2**	**Model Equation**
10ml/min, 12 cm	0.006	54.31	0.954	y = -0.012x+1.63
20ml/min, 12 cm	0.009	37.22	0.96	y = -0.02x+0.9352
30ml/min, 12 cm	0.0105	32.18	0.946	y = -0.018x+ 0.4827
10ml/min, 24 cm	0.0112	17.56	0.986	y = -0.0112x+1.9676
20ml/min, 24 cm	0.0132	13.28	0.99	y = -0.0132+0.8765
30ml/min, 24 cm	0.07	10.87	0.9296	y = -0.0202x+1.91
10ml/min, 36 cm	0.01725	15.29	0.963	y = -0.0115x+ 2.64
20ml/min, 36 cm	0.0174	12.21	0.981	y = -0.0116x+ 1.177
30ml/min, 36 cm	0.02685	9	0.83	y = -0.0179x+1.64

Table 4.42: Yoon-Nelson model parameters for cadmium at different flow rates and adsorbent dosage (bed height)

Column Parameters	**Yoon-Nelson (K_{YN}) rate constant**	τ	R^2	**Model Equation**
10ml/min, 12 cm	0.0171	75.78	0.953	y = 0.0171x-1.296
20ml/min, 12 cm	0.0289	25.73	0.955	y = 0.029x-0.7437
30ml/min, 12 cm	0.0396	13.66	0.967	y = 0.0396x-0.541
10ml/min, 24 cm	0.0127	135	0.976	y = 0.0127x-1.7153
20ml/min, 24 cm	0.0231	52.7	0.953	y = 0.0231x-1.2174
30ml/min, 24 cm	0.0262	28.1	0.991	y = 0.0262x-0.7358
10ml/min, 36 cm	0.0124	175.71	0.973	y = 0.0124x-2.1789
20ml/min, 36 cm	0.0139	75.8	0.9924	y = 0.014x-1.0537
30ml/min, 36 cm	0.0175	57.34	0.967	y = 0.0175x-1.0035

Table 4.43: Yoon-Nelson model parameters for copper at different flow rates and adsorbent dosage (bed height)

Column Parameters	**Yoon-Nelson (K_{YN}) rate constant**	τ	R^2	**Model Equation**
10ml/min, 12 cm	0.012	135.78	0.9542	y = 0.012x-1.6924
20ml/min, 12 cm	0.0181	46.76	0.96	y = 0.0201x-0.9352
30ml/min, 12 cm	0.02	26.67	0.946	y = 0.0181x-0.4827
10ml/min, 24 cm	0.0112	175.67	0.986	y = 0.0112x-1.9676
20ml/min, 24 cm	0.0132	66.4	0.991	y = 0.0132x-0.8765
30ml/min, 24 cm	0.0202	64.15	0.9296	y = 0.0202x-1.296
10ml/min, 36 cm	0.0115	229.4	0.9631	y = 0.0115x-2.638
20ml/min, 36 cm	0.0116	101.5	0.9813	y = 0.0116x-1.1774
30ml/min, 36 cm	0.0179	91.6	0.8293	y = 0.018x-1.64

CHAPTER 5

CONCLUSIONS

Experiments were conducted to investigate the copper and cadmium removal from the aqueous (synthetic) solution by the mixed adsorbent prepared by blending activated charcoal and bone charcoal in 1:1 ratio. Approximately above 99% of the copper and 88-90% of the cadmium ions originally present in the synthetic solutions were adsorbed onto the mixed adsorbent within 100-120 minutes after the start of the adsorption experiments in batch studies and the equilibrium time was reached within 2 hours for both the metals.

The maximum adsorption capacity of cadmium was 6.71 mg/g at an optimized pH of 6, with the adsorbent dosage of 0.5 g/L. In case of initial metal ion concentration (IMC) and temperature, the maximum adsorption capacity Q_{max} was 19.64 mg/g at 150 ppm and 8.34 mg/g at 40 ^{o}C respectively for Cd (II).

The maximum adsorption capacity of copper was 9.44 mg/g at the optimized pH of 6, with an adsorbent dosage of 0.5 g/L. In case of the parameters metal ion concentration (MIC) and temperature the maximum adsorption capacity Q_{max} was 22 mg/g at 150 ppm and 9.64 mg/g at 40^{o}C respectively for copper. The order of affinity for Cu (II) was greater than Cd (II) due to the lower atomic weight of Cu (63.5 g/gmole) than that of Cd having (112.4 g/gmole).

The % removal of heavy metal ion increases with the increasing order of pH as $6 > 4 > 2 > 8$ for Cu (II) metal and in the base range it forms as hydroxide precipitate at pH ($>=$ 8). The optimum pH was found to be 6 for copper metals where 96.5% removal for copper (synthetic sample) and 97.21 % for industrial effluent. The same trend has been observed for cadmium having 78.76% and 69.3% synthetic and industrial effluent respectively.

The % removal was highly dependent on adsorbent dosage. The % removal increases with the adsorbent dosage as $5 > 3 > 2 > 1 > 0.5$ g/L for both the metals. The optimum adsorbent dosage was found to be 5g/L for copper having (96.2% for industrial effluent and 99.74% for synthetic sample).Similarly for cadmium 89.68% removal of industrial effluent and 91.2% for synthetic sample was reported.

In the parameter contact time for copper, the maximum % removal was 80.68 for industrial effluent, 94.83% for synthetic sample was reported. Similarly for cadmium 75.56% for industrial effluent and 77.35% for synthetic sample was reported.

The results revealed that maize corn cob, a waste material have good potential as an adsorbent for the removal of toxic heavy metals from industrial waste waters.

In comparison with the maize cobs, the highest % removal was obtained for mixed adsorbent (AC+ BC) due to the high surface area of the activated charcoal as well as 've' (negative) charge from the bone charcoal which induces the synergistic effect of the mixed adsorbent at different parameters pH, adsorbent dosage and contact time for both copper and cadmium.

Intra particle diffusion gives better fit with higher R^2 values of 0.7787 for Cd (II) when compared to Cu (II).

In isotherm modeling Langmuir model fits for copper and cadmium with higher R^2 values. The Freundlich model have low R^2 values for both Cu and Cd. Temkin model fits with higher R^2 values for both copper and cadmium. In thermodynamic modeling studies, cadmium fits with higher R^2 values when compared to copper.

In simultaneous metal ion removal studies, more % removal was obtained for Cu (II) when compared to cadmium and the reason was due to more atomic weight of Cd than Cu.

In present investigation the reaction kinetic model suitability was also accomplished by performing the statistical analysis (i.e) by evaluating the χ^2 test (χ^2 value) through the experimental and theoretical data of uptake capacity (mg/g).

The statistical analysis of the data obtained in reaction kinetic modeling delineated the supremacy of pseudo second order model for both Cu and Cd with very low or insignificant χ^2 values when compared with the pseudo first order model and Langmuir model with higher χ^2 values at the optimized conditions and thereby suggesting the dominance of both Cu (II) and Cd (II) ion sorption mechanism as chemisorption rather than physical adsorption.

Based on the analysis of data obtained in continuous flow operation from breakthrough curves and kinetic models, it was concluded that the mixed adsorbent can be treated as the better adsorbent for the removal of heavy metal ions. The experimental data obtained proved that the effect of bed weight, flow rate and initial metal ion concentration plays a significant role on the removal of Cu (II) and Cd (II).

Overall in comparison with industrial effluents for cadmium, the synthetic solutions have proved to be more superior in terms of column total % removal and better performance was observed with synthetic solutions than industrial effluents.

The basic hydrodynamic parameters of the packed bed were analyzed. The influence of different parameters such as liquid velocity, particles size and voidage on mass transfer in packed bed was studied.

The regression analysis was carried at different flow rates and the regression or correlation coefficient R^2 values are very close to 1 which indicates that the column hydro dynamics better fits the adsorption system. Therefore in the present investigation it was summarized that large flow rates and smaller bed heights rendered the minimum possible resistance for the transfer of metal ions from liquid phase to packed bed.

It was concluded that the coefficient of regression R^2 values are close to 1 indicating that the adsorption system fits equally well with the pseudo first order equation for both the metals Cu (II) and Cd (II). In case of second order system the coefficient of regression R^2 values are very close to 1 indicating that the adsorption systems follows the second order kinetics for Cu (II) and Cd (II) metal. In comparison of both the models, the pseudo second order kinetics follows a better fit for both Cu (II) and Cd (II) with higher R^2 values very close to 1. It has been shown that mixed adsorbent appears to be technically feasible sorbent material with high efficiency and removing capability of metal ions. Therefore, the mixed adsorbent can be recommended to use for the removal of other heavy metal ions from complex industrial effluents.

Major conclusions from continuous flow operation for the synthetic solutions are given in Table 5.1.

Future Scope

1. The adsorption studies can be extended to various industrial effluents containing complex heavy metals such as Zn, Hg, Pb and Cr.
2. The studies can be extended to complex heavy metals to find the various optimized parameters in batch studies and can be applicable to continuous flow operation.
3. Development of improved/modified mathematical models using linear regression analysis.
4. Factorial design methodology can be applied to know the interaction between various parameters with the % removal of metal ions.
5. Response surface methodology models can be applied to find the interaction between the heavy metal ions and the selected mixed adsorbent.

Table 5.1: Main outcomes of the column study- wrt flow rate and adsorbent dosage at fixed concentration of 100 ppm for synthetic solutions

Parameter /Models	Model Analysis	Conclusion
Effect of bed height	C_e/C_o was plotted at different bed weights and volumetric flow rates of 10, 20, 30 ml/min to find the saturation time for cadmium and copper respectively.	C_e/C_o increases with increase in the bed weight from 50 to 150 g for Cu & Cd and reached the saturation point
Effect of volumetric flow rate	C_e/C_o was plotted at different volumetric flow rates while maintaining the initial metal ion concentration at 100 mg/l and bed weights at 50 g, 100 g, 150 g respectively.	C_e/C_o increases with increase in the volumetric flow rate from 10 to 30 ml/min for both Cu (II) & Cd (II) and reached the saturation point.
Thomas model	Fitted with higher R^2 values for Cu (II) than Cd (II) at 50 g and 100 g., and for 150 g bed weight with different flow rates the Cd (II) fitted better than Cu (II).	k_{Th} increased and q_o decreased with the increase of flow rate from 10 to 30ml/min at different bed weights for both the metals
Yoon-Nelson model	Fitted the model with higher R^2 values for Cd (II) than Cu (II) at all flow rates and bed weights	τ decreased and k_{YN} increased with the increase of flow rate at various bed weights for both the metals

List of Publications

1. Biosorption of toxic heavy metals on saw dust published in Clean Soil Air Water with an impact factor of 2.046 in John WileyVCH. Volume 43, Issue 3, pages 360367, 2014. (Mr.Srinivas Tadepalli & Dr. Vishal Mishra).

2.”Removal of Copper and Cadmium from industrial effluents using the mixed adsorbent in batch study” published in International Journal of ChemTech Research with an impact factor 0.6 Vol.9(05) pages 691-704, 2016. (Mr.Srinivas Tadepalli, Dr P.Vijay & Dr. K.S.R.Murthy).

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Rebuttal against Reviewer comments

Reviewer-1 comments

C1. Title of the thesis has word ”industrial effluents”, however work has been done on synthetic solutions only.

A. Experiments were carried out both in batch and column studies using industrial effluents collected from BHEL, Haridwar and the details are discussed in Thesis Sec 4.3 and Sec 4.10.

C2. Title of the thesis has word low cost adsorbents- however work has been carried out using single adsorbent.

A. Low cost adsorbent studies has been carried out for the removal of both copper and cadmium using maize cob as an adsorbent and the details are discussed in Thesis Sec 4.4.

C3. XRD, pore size distribution, particle size, FE-SEM for adsorbent characterization studies

A. XRD, pore size distribution, particle size distribution studies has been carried out for both the adsorbents and are discussed in Sec 4.14, 4.15, 4.16 and 4.17, respectively. However, SEM anaysis has not been carried out due to time . The methodology for the above studies are discussed in Sec 3.3.2, 3.3.5, 3.3.6 respectively.

C4. Intra particle diffusion model study

A. Intra particle diffusion studies has been carried out and discussed in Sec 4.6 in detail.

C5. Detailed batch isotherm study for synthetic solution data

A. Various isotherm model studies has been carried out using Langmuir, Freundlich, Temkin models and the details has been discussed in Sec 4.7.

C6. Thermodynamic study

Thermodynamic studies have been carried out as suggested by the reviewer and the details were included in Sec 4.7.8.

C7. Column performance evaluation and Hydro dynamic modeling

Various column performance parameters such as breakthrough time, saturation time, sorbent exhaustion rate, volume treated at breakthrough point, volume treated at saturation point were discussed in Sec. 4.11.

Hydrodynamic modeling studies has been carried out and discussed in Sec. 4.11.3 and 4.11.4 .

C8. Binary sorption experiments & Modeling of data

Binary sorption experiments were carried out to know the interaction of metal ions and the results were discussed in Sec 4.5. Analysis of Langmuir and Temkin models have been discussed in Sec (4.5.3 and 4.5.4).

C 10-16 : Necessary corrections were made and incorporated in Thesis wherever required.

C17. Since pH was not controlled during the sorption process, the possible mechanism of sorption should be explained based on change in pH of the system and Point of Zero charge (PZC)

Charge was measured using Cyclic Voltammetry in terms of electron potential (voltage, mv) at different pH (pzc analysis) for the mixed adsorbent. Pzc analysis may be carried out using Zeta meter system, mass titration, Electrophoresis, XPS (X-ray Photo Spectroscopy). These equipments are very costly and moreover not available, therefore at different pH the residual adsorbate concentration was measured by UV-visible spectrometer. I have done pH monitoring experiments with carbon (mixed) adsorbent for all water samples at different pH and they were analyzed using U-V visible spectrophotometer. With these results obtained, I can correlate the pzc which was reported in the thesis at different pH.

PZC analysis of the mixed adsorbent was carried out and the detailed results are discussed in Sec 4.3.2

C18. Proper references formatting

Proper formatting of all references have been done and given in Section References at the end of the thesis.

Reviewer-II comments

C1 Overall conceptualization, thematic approach and current relevance of the topic:

To the existing knowledge, the new information that was added to the thesis was to find the % removal using the novel adsorbent by mixing activated charcoal and bone charcoal in 1:1 ratio. AC having high surface area of 1600 m^2/g, and bone charcoal having '-ve' (negative charge). In combining these adsorbents, the % removal was higher due to the influence of synergistic effect. Therefore the studies have been carried out on industrial effluent, synthetic samples & other low cost adsorbents to remove Cu and Cd ions in batch and column studies and the results were compared. The simultaneous metal ion studies were also carried out using industrial effluent in batch studies.

C2 Objectives of research

Objectives of research were framed accordingly and done in proper sequence following batch studies, column studies, kinetic modeling of batch and column studies, isotherm modeling of batch studies, thermo dynamic modeling studies, Column performance studies for both Cu and Cd, hydro dynamic modeling studies in a packed bed reactor, simultaneous Cu and Cd removal using binary sorption experiments were carried out to know the interaction of the metal ions. The same data obtained were modeling using Langmuir and Temkin model. Statistical analysis was carried out at various optimized parameters for both copper and cadmium to know the mechanism of adsorption by knowing the least χ^2 test (values) through Langmuir model (experimental and theoretical uptake).

C3 Adequacy of Literature review and Critical gaps

In the literature review part, recent developments were included using various adsorbents. In previous studies the adsorbents used were activated charcoal and bone charcoal, agricultural adsorbents, silica gels, nano materials, some biosorbents such as algae and fungi, moreover from the literature review the studies have been conducted either using AC or either BC, and an attempt was made to mix these adsorbents in 1: 1 ratio and the novelty study of the adsorbent has been carried out by mixing AC and BC in 1: 1 ratio. Other ratio of AC and BC cannot be mixed as there will not be a role of synergistic effect due to improper mixing ratio of the mixed adsorbent. Further details were discussed in Chapter-2 (LITERATURE REVIEW).

2. Scope of work

Revised Scope and objectives of the thesis were reported in Sec. 2.7

3. Materials and methodology

C4. When Activated Charcoal (AC) and Bone charcoal (BC) are purchased from Sigma, why the properties were analyzed?

The data of the particle size, surface area are not known when it was purchased, more over it was a mixed adsorbent of 1: 1 ratio (AC and BC), therefore the surface area and particle size was varied by combining these adsorbents. Hence to confirm the same, the analysis were performed to know the surface properties.

Answer for Section 3.3.1:

All the materials and methodology section has been revised and the necessary results have been shifted to Results and discussion.

Charge was measured using Cyclic Voltammetry in terms of electron potential (voltage, mv) at different pH (PZC analysis) for the mixed adsorbent. I have done pH monitoring experiments with carbon (mixed) adsorbent were done for all water samples at different pH and were analyzed by U-V visible spectrophotometer. Conclusion has been made to correlate the PZC with pH values.

C5 Statistical analysis

A. Statistical analysis has been carried out to know the mechanism of adsorption based on the χ^2 test (values) and the details have been mentioned in Sec 4.8 in thesis.

C6 You cannot say 180 rpm as optimized because as you have not shown that at 180 rpm adsorption declines?

A. Based on the working of the orbital shaker equipment, it can withstand only upto maximum 180 rpm and hence beyond 180 rpm the studies have not been carried. Further studies have been included in Thesis Sec 4.2.5 in detail.

10. Figures should have error bars

Error bars were included for the studies conducted in batch and column, and further details are given in Sec 4.3, 4.4, 4.5 for batch; and Sec 4.10 for column respectively.