

## : INTRODUCTION

### 1.1 General Introduction

The tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in the aquatic environment [1]. Heavy metals are defined as the high atomic weight metals and metalloids generally considered to be of sufficient distribution and abundance as to be in some way environmentally or biologically significant as a toxic substance. These include metals such as lead (Pb), cadmium (Cd), nickel (Ni), chromium (Cr), arsenic (As), mercury (Hg) etc [2]. Unlike the organic pollutants the majority of which are susceptible to biological degradation, heavy metals do not degrade into harmless end products so easily. Therefore the elimination of heavy metals from water and waste water is important to protect the public health [3].

Cadmium (Cd), a soft bluish heavy metal is present in nature mainly in the zinc ores but seldom in the form of pure mineral [4]. Cadmium is introduced into the water bodies mainly from waste water released from the industries such as Ni-Cd battery manufacturing, metal plating industries, phosphate fertilizer, smelting, mining, pigments, stabilizers, alloys industries and sewage sludge. Besides these, cadmium is also used in low melting point alloys to make solders, in bearing alloys, electroplating, and as phosphorescent coatings in TV tubes [1, 5]. As far as Nepal is concerned there are no such industries which release the large amount of effluents containing cadmium (Cd), nevertheless there is a risk of cadmium contamination in ground water due to the lack of awareness in proper disposal of the rechargeable Ni-Cd battery which are used heavily in the urban region like Kathmandu. Shallow ground water, especially near the dumping sites, is potentially vulnerable to contamination from the Cadmium [6]. Unfortunately, no data are available for the cadmium concentration in Nepalese ground water.

Cadmium is regarded as being highly toxic and is included with mercury in the so called "Red List" of the priority pollutants published by the Department of the Environment in 1987 [7]. Cadmium mainly accumulates in liver and kidney, which will malfunction at overdoses, spilling proteins in the urine and disrupting protein metabolism [2]. The other harmful effect of cadmium includes a number of acute and chronic disorders, such as Japanese "itai-itai" disease, renal damage, high blood

pressure, destruction of testicular tissues and red blood cells [5]. The acceptable or the limiting value of cadmium in drinking water recommended by the World Health Organization (WHO) and the American association for water work is 0.005 mg/l [8].

A number of methods have been developed over the past few years to remove cadmium and other heavy metals from water by physical, chemical and biological processes. The important method includes chemical precipitation, solvent extraction, coagulation, flocculation, centrifugation, purification by membranes, ion exchange, reverse osmosis, electrodialysis, adsorption [8, 10]. The choice of the type of the process depends namely on two factors, the nature of the pollutants and economical aspect of the process [8].

However, all of the methods described above cannot be employed for the treatment of the ground water containing trace amount of cadmium for drinking purposes. Ion exchange and adsorption are the most suitable method for removal of cadmium from natural water systems as they can remove cadmium (Cd) over a wider range of pH values and lower concentration [10]. Other methods are generally used for the removal of cadmium from the industrial effluents containing very high amount of heavy metals before discharging into the water bodies.

Low concentration (less than 5mg/L) of cadmium is difficult to treat economically using chemical precipitation methodologies. Ion exchange and reverse osmosis can reduce the metal concentration to the limit required by regulatory standards but they have high operational and maintenance cost [2]. In this perspective, adsorption is most viable method for the removal of cadmium in low concentration from contaminated surface and ground water because of its efficiency and low cost. Moreover adsorption processes for water treatment have had a long history and also it is a method that necessitates careful design but little maintenance [9]. A number of adsorbents such as zeolites, clays, biosorbents, manganese dioxide, ground nut husk, red mud, bone charcoal, juniper bark, sugarcane bagasse, rice husk, perlite and activated charcoal have been used in the adsorptive removal of heavy metal ions including cadmium from water systems [2, 6, 9, 11, 12].

Among all these adsorbents, activated carbon has been widely used in water treatment to remove organic and inorganic pollutants due to its high adsorption capacity. The capacity of carbon is related to its physical and chemical properties such as porosity, specific surface area, surface functional groups and surface additives in connection with preparation conditions [8, 13].

In spite of its effectiveness in the removal of heavy metals from wastewaters, the high cost of commercial activated carbon has restricted its widespread use [3]. A lot of attentions had been directed towards the production of low cost activated carbon adsorbents derived from the cheaper and readily available carbonaceous material [17]. Various waste materials like rice hulls, coconut shell, peanut shell, rubber wood, fruit seeds, sugarcane bagasse, saw dust, bone char etc are used to make activated carbon owing to the low cost of such carbon precursors [1, 7].

In Nepal, a lot of fruit seeds containing high percentage of carbon are available as waste material. Lapsi (*Choerospondias axillaris*) is one of the very popular fruits in Nepal. Every year, tons of Lapsi are harvested in Nepal and tons of seeds generated as waste material which contain high percentage of carbon and can be used to prepare activated charcoal which may act as a potential material for adsorption of heavy metals.

## 1.2 Charcoal as an adsorbent

Activated charcoal is one of the most widely used adsorbents for adsorptive removal of heavy metals and other pollutants from water. Activated charcoal (AC) is produced by carbonizing and subsequent activation of the raw carbonaceous materials. Raw materials are mainly organic materials with high carbon content such as saw dust, coconut shell, fruit seeds, wood and agricultural wastes etc. The carbonization process involves drying and then heating to separate by products, including tars and others hydrocarbons from the raw materials as well as to drive off any gas generated at high temperature (below 800<sup>0</sup>C) in an inert gaseous atmosphere [29]. The process of activation is achieved by either thermal or chemical activation.

In thermal activation, carbonized particles are activated by exposing them to an activating agent such as steam, CO<sub>2</sub>, CO etc at high temperature which produce bigger pores [27]. Chemical activation produces mesopores and is a combined process of carbonization and activation relatively at low temperature in presence of chemicals like H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, PH<sub>3</sub> etc. Chemical activation by acids introduces oxygen containing functional groups such as carboxylic, lactones, carbonyl, phenol, quinine, pyrone and other groups on the surface of charcoal. The presence of these functionalities increases the carbon surface acidity, polarity, and its hydrophobicity and enhances the ability of charcoal to adsorb the heavy metal ions. The morphology of carbon material is very important for the physiosorption where as the carbon surface chemistry is critical for chemisorptions.

Activated Charcoal (AC) has very high surface area and high porosity. The surface area of activated charcoal can range from 500-900 m<sup>2</sup>/gm. AC is primarily composed of SP<sup>2</sup> hybridized carbon as graphite crystallites which comprise 3 to 4 parallel hexagon carbon ring layers separated by 3.44-3.65 Å interlayer spacing and are approximately 10 nm in length [26]. These micropores provide superb conditions for adsorption to occur, since an adsorbing material can interact with many surfaces simultaneously [27]. In addition to micropores, activated carbon also possesses meso and macro pores due to many defects in the crystallites including edges, dislocations, vacancies and steps. These pores are very important in facilitating the adsorption of medium and large sized adsorbate molecules to the interior of carbon particles [16].

Activated charcoal is a combination of the bulk graphite structure and the “active sites” on the carbon surface. Both the graphite structure and the active sites are affected by many factors including the elemental composition, carbonization and activation method and storage environment [28]. Since large numbers of agricultural raw materials are available as precursors, it is really a matter of interest for scientist to identify the appropriate raw material. Generally high density, woody and high carbon content raw materials are chosen as precursors because it gives activated charcoal having greater surface area, high structural strength and high porosity.

There are many kinds of fruit seeds which can be used as a precursor for the preparation of activated carbon. In fact cornelian cherry, apricot stone and almond shells have been used to prepare activated charcoal for the adsorptive removal of Cr (VI) from synthetic water solution [17]. In Nepal large quantity of seed stone of *Choerospondias axillaris* (lapsi) is available as waste and which has been used as a fuel in brick kilns. Recently activated carbon has been prepared from the seed stone of *Choerospondias axillaris* and investigated for the adsorptive removal of Cr (VI) from water by Piya [15] at Central Department of Chemistry, Kirtipur.

Considering all these factors the waste seeds of *Choerospondias axillaris* (Lapsi) may be used to prepare low cost activated carbon for the removal of toxic metal from water. The adsorptive capacity of such carbon can be further enhanced by treating the charcoal with oxidizing agent like nitric acid, phosphoric acid etc. The oxidizing agent introduces the active sites on the surface in the form of oxygen functional groups. The negative functional groups can have great potential to adsorb the positively charged metal ions from aqueous solution.

### 1.3 Characterization of Activated charcoal

#### 1.3.1 Proximate Analysis of the Adsorbent

The proximate analysis of the adsorbent is done to determine the percentage of ash, percentage of moisture and the percentage of the fixed carbon content in the charcoal. Adsorbent having low percentage of ash and moisture is regarded as a good adsorbent because such adsorbent has high percentage of fixed carbon [30]. The ash content and moisture content in percentage is determined by the formula:

$$\text{Ash content/moisture content (\%)} = \frac{W_1 - W_2 \times 100}{W_1} \dots\dots\dots (1)$$

Where,

$W_1$  = weight of sample before heating (in gm)

$W_2$  = weight of sample after heating (in gm)

Ash quantity =  $(W_1 - W_2)$  gm

Fixed Carbon (%) = 100 - (ash content % + moisture content %)

#### 1.3.2 Determination of Surface area

The adsorption of metal ions on the surface of charcoal significantly depends upon the surface area of adsorbent. Higher the surface area of the adsorbent, higher will be the extent of adsorption. The surface area of the charcoal can be determined by BET single point method or chemical/dye adsorption. The surface area is determined using the formula given by Dunicz et al (29)

$$S = (1/b) \times N \times 21 \times 10^{-20} \text{ m}^2/\text{g} \dots\dots\dots (2)$$

Where, N stands for Avogadro number

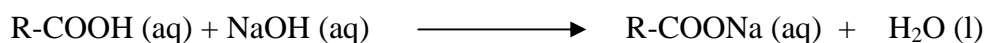
S stands for the specific surface area

b is Langmuir constant.

### 1.3.3 Functional group determination: Boehm Titration

The surface of activated charcoal is slightly acidic due to the presence of various oxygen containing functional groups namely carboxylic, lactones and phenol groups that are formed upon the oxidation of charcoal with nitric acid [29]. Besides acidic groups, the activated charcoals also possess basic property which is associated with the pi-sites of the carbon basal plane. The Lewis base property of activated carbon originates because of the Pi-electron system present in the basal plane which can be donated to any reactive electron deficient functional groups in aqueous solution [26].

The Boehm titration is the typical chemical analysis that can be used to quantify the amount of surface acidity as well as basicity of the activated charcoal. The method involves the neutralization of surface oxides with bases such as sodium hydroxide (NaOH), sodium bicarbonate (NaHCO<sub>3</sub>) and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) for acidic groups and neutralization with acids such as hydrochloric acid for basic functional groups. The acidity constants of acidic groups like carboxylic, lactones and phenols differ over several orders of magnitude and it is possible to distinguish the acidic groups on the basis of their neutralization behaviour [28]. The various free acidic groups are measured using the assumption made by Boehm that NaHCO<sub>3</sub> (pKa=6.37) neutralizes carboxylic group only, Na<sub>2</sub>CO<sub>3</sub> (pKa=10.25) neutralizes carboxylic group including lactones group and NaOH (pKa=15.74) neutralizes carboxylic, lactones as well as phenol group. The neutralization reaction in aqueous solution of Boehm titration is given as:



Where, R is a generalized representation for the surface bound carbon atom.

To sum up, the total amount of basic sites can be calculated from the amount of HCl consumed by carbon in neutralization reaction between carbon surface and HCl. The total amount of carboxylic group can be calculated by the amount of NaHCO<sub>3</sub> consumed; the amount of lactones group is calculated by neutralization difference between Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> and finally phenol group can be measured by neutralization difference between NaOH, Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub>.

### **1.3.4 Scanning Electron Microscope (SEM)**

SEM is used to characterize the surface of adsorbent. SEM images show the pore volume and nature of the surface of the adsorbent. Adsorbent possessing more pores and irregular surface is considered to have high surface area and good adsorption capacity.

## **1. 4 Determination of Cadmium (II)**

Several methods are available to determine the concentration of cadmium (II) in aqueous solution. The most commonly used methods at present, are atomic absorption spectroscopy, electrochemical methods, neutron activation analysis and spectrophotometer using the dithiozone as complexing agent. Atomic absorption spectrometry is the most widely used method which can be used to determine the cadmium concentration as low as 0.5 µg/liter in aqueous solution [20]. However careful treatment of samples and correction for interferences is needed for the analysis of samples with low cadmium concentrations.

In flame atomic absorption spectroscopy the sample containing metal ions are aspirated into the flame (Air-Acetylene) capable of atomizing the heavy metals present in solution. A light beam is directed through the flame, into a monochromator, and on to the detector that measures the amount of light absorbed by the atomized element in the flame [21]. The atomized metal ions can absorb the light of characteristic wavelength, which is in general is the wavelength of the radiation that the atoms would emit if excited from the ground state [20], therefore a lamp with a cathode made up from the pure metal or an alloy of the desired element, emitting the narrow line spectrum of this element, is used as an external light source to pass through the flame. For cadmium detection the absorption is measured at the wavelength 228.8nm which is emitted by the coded hollow cathode lamp. This makes the method relatively free from spectral or radiation interferences from other elements present in the solution and the amount of light absorbed can be directly related to the concentration of metal ions.

However the amount of energy of the characteristic wavelength absorbed in the flame is proportional only up to the certain concentration of the metal ions. Above the limited concentration range, the proportionality relationship between metal ions and the amount of light absorbed no longer remains valid [21]. The relation between the amount of light absorbed and the concentration of the metal ions up to limited concentration range is give by the Beer Lambert's law which can be expressed as [20]:

$$A = \log I_0/I_t = K L N_0 \dots \dots \dots (3)$$

Where,

A= absorbance or the optical density (OD)

$I_0$ =Intensity of the incident light

$I_t$ =Intensity of the transmitted light

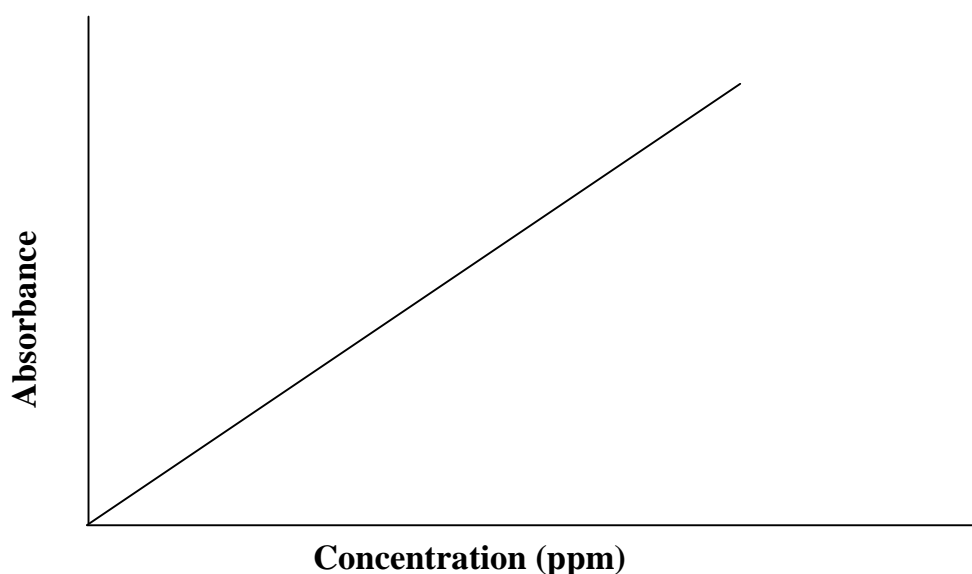
K=a constant related to the absorption coefficient

L=the path length through the flame

$N_0$ =the concentration of the atoms in the flame

The validity of Beer-Lambert's law can be checked by plotting the absorbance (A) versus the concentration of metal ions in flame ( $N_0$ ) which should give the straight line passing through the origin. However the linearity is obeyed only up to a certain concentration above which the absorbance remains almost constant. Therefore the unknown concentration of the metal ions must lie within the linear range to evaluate its value. The linear range is obtained by aspirating at least four standard solutions of desired metal which brackets the lower and the upper optimum absorbance range which is know as calibration curve (20).





**Fig1: Absorbance vs. concentration plot**

## **1.5 Adsorption of metal ions**

To determine the adsorption behavior of metal ions on adsorbent an adsorption study is generally carried out. The adsorption behavior of metal ions on adsorbent can be determined either by batch technique or by column technique.

Column adsorption test is carried out in a glass column of particular length and diameter which is packed with the required amount of adsorbent. The effluent (containing metal ions) is then passed through the column from the reservoir at the top using flow controller which provides the homogenous flow of effluents [18]. The treated effluent is collected at the bottom at definite interval of time to measure the corresponding residual metal ion concentration to evaluate the efficiency of column.

Batch adsorption experiments are conducted taking the definite amount of dried adsorbent which is agitated with the known amount of adsorbate for the definite period of time. The suspension is filtered and filtrate is analyzed by suitable techniques to determine the extent of adsorption. The amount of metal ion adsorbed,  $q_t$  at time  $t$  is calculated from the mass balance equation [10, 17]:

$$q_t = \frac{(C_o - C_t) V}{M} \dots\dots\dots (4)$$

Where,  $q_t$  represents the amount metal uptake per unit mass of adsorbent (mg/gm) at time 't'.  $C_o$  and  $C_t$  are the concentration of metal solution in mg/L initially and at time t respectively.  $V$  is the volume of the test solution in Liter and  $M$  is the mass of the dry adsorbent in gram.

The percentage removal of the metal ions (Rem %) from the aqueous solution can be calculated by using following relation (14):

$$\text{Rem (\%)} = \frac{(C_o - C_t)}{C_o} \times 100 \dots\dots\dots (5)$$

Where,  $C_o$  and  $C_t$  are concentrations of metal ions at beginning and at time t respectively.

## 1.6 Adsorption Isotherm

Adsorption isotherm is a curve which relates the amount of adsorbate adsorbed at constant temperature with the concentration of the adsorbate at equilibrium. Langmuir and Freundlich adsorption isotherm are the most important isotherms generally used to analyze the adsorptive behavior of adsorbate on adsorbent [2].

### Langmuir adsorption isotherm:

The Langmuir isotherm model is the most commonly used adsorption isotherm for the adsorption of solute from the solution. This adsorption isotherm presumes homogeneous surface adsorption with the formation of monolayer on the adsorbent surface. The basic form of the equation developed by the Langmuir (1916) can be written as:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \dots\dots\dots (6)$$

Where,

$q_e$  = the amount of adsorbate adsorbed (mg) per unit mass of the adsorbent (gm)

$q_m$  = amount of adsorbate adsorbed (mg) per unit mass of the adsorbent (gm) on complete monolayer formation, which is constant at fixed temperature. It is determined solely by the nature of adsorbent.

$b$  = the adsorption constant (L/mg) related to the energy of adsorption or net enthalpy of adsorption. The higher value of  $b$  indicates the system attains the equilibrium quickly.

$C_e$  = is the equilibrium concentration of the adsorbate (mg/L).

To analyze the validity of Langmuir adsorption isotherm the Langmuir equation is linearized as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \dots\dots\dots (7)$$

From the experimental values of  $C_e$  and  $q_e$ , a plot of  $C_e/q_e$  against  $C_e$  can be drawn from which Langmuir parameters  $q_m$  and  $b$  can be evaluated. The values so obtained provide the information of quality of adsorbent. The adsorbent with the high value of  $q_m$  is preferred since its adsorption capacity is high.

### **Freundlich adsorption Isotherm**

The variation of extent of adsorption with concentration can also be analyzed by the empirical equation given by Freundlich (1906) which can be expressed as:

$$q_e = K C_e^{1/n} \dots\dots\dots (8)$$

Where,  $q_e$  is the no of milligrams of the adsorbate adsorbed per unit gram of adsorbent,  $C_e$  is the equilibrium concentration of the adsorbent (mg/L).  $K$  and  $n$  are Freundlich constants related to the adsorption capacity and adsorption intensity of the given adsorbent.

To test the validity of Freundlich equation, the linear form of the equation is obtained by taking logarithm on both sides of the equation (8)

$$\log q_e = \log K + \frac{1}{n} \log C_e \dots \dots \dots (9)$$

Thus a plot of  $\log q_e$  against  $\log C_e$  should give a straight line with slope equal to  $1/n$  and the intercept on the y-axis equal to  $\log K$ . The value of  $1/n$  less than one indicates that the adsorbent is favorable for the adsorption of given adsorbent.

Apart from a homogenous surface adsorption, the Freundlich isotherm is also suitable for a highly non ideal sorption that involves heterogeneous surface and an adsorption isotherm lacking a plateau, indicating a multilayer adsorption.

## 1.7 Adsorption kinetics

The study of adsorption kinetics describes the solute uptake rate, which in turn governs the mechanism of adsorption of adsorbate on adsorbent [7]. It is one of the important characteristics in defining the efficiency of adsorbent. In order to understand adsorption kinetics of heavy metal ions, the adsorption process is studied monitoring percentage removal of heavy metals by the adsorbent at specified period of contact time.

The adsorption kinetics of heavy metal ions are generally described by the pseudo first order, pseudo second order and the second order rate equations. The experimental data obtain for adsorption at different interval of time is analyzed using pseudo first-order (Lagregren 1869) and pseudo second-order.

### 1.7.1 The pseudo first-order model

The adsorption of metal ion on solid may be considered as a reversible reaction with equilibrium between two phases. Such process can be described by the pseudo first order kinetics, according to Lagergren (1898) the pseudo first order equation is generally expressed as:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \dots \dots \dots (10)$$

Where,  $q_e$  and  $q_t$  are amount of metal ion adsorbed per unit mass of the adsorbent (mg/gm) at equilibrium and at time  $t$  (min) respectively.  $k_1$  is the Lagergren rate constant of pseudo first order adsorption (L/min).

After integration, the equation (10) takes the integrated form as:

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \dots \dots \dots (11)$$

The plot of  $\log (q_e - q_t)$  vs. time should give a straight line from which  $k_1$  and  $q_e$  can be calculated from the slope and the intercept respectively [17].

### 1.7.2 The pseudo second-order model

The pseudo second-order adsorption kinetic rate equation is expressed as (Ho et al., 2000):

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \dots \dots \dots (12)$$

Where,  $k_2$  is the rate constant of pseudo-second order kinetics ( $g \text{ mg}^{-1} \text{ min}^{-1}$ ).

For the boundary conditions  $t=0$  to  $t=t$  and  $q_t=0$  to  $q_t = q_t$  the integrated form of equation (12) becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{k_2 t} + \frac{q_e}{\dots\dots\dots} \quad (13)$$

This is the integrated rate law for a pseudo-second order reaction. Equation (13) can be rearranged to obtain equation (14), which has a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \dots\dots\dots (14)$$

or,

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad \dots\dots\dots(15)$$

Where,

$$h = k_2 q_e^2 \quad \dots\dots\dots (16)$$

The unit of 'h' is  $\text{g mg}^{-1} \text{min}^{-1}$

The plot of  $t/q_t$  against  $t$  should give a linear relationship from which  $q_e$  and  $k_2$  can be determined from the slope and intercept of the plot, respectively.

## 1.8 Literature Survey

Cadmium is one of the heavy metals considered to be toxic to humans and aquatic life. A lot of research had been carried out and still going on to remove cadmium from natural water and waste water systems to bring down its concentration to permissible level to ensure the public health as well as aquatic life. A number methods such as, solvent extraction, chemical precipitation, coagulation, electro dialysis, ion exchange, reverse osmosis and adsorption have been used so far [1, 10].

Among all these methods, the interest in the adsorption of metal ions by different adsorbents has increased many folds in recent years because of its simplicity, selectivity and efficiency [16]. The main advantage of adsorption is the separation of trace amount of elements from large volume of solutions.

Adsorption was first observed by Lowitz in 1785 and was soon applied as a process for removal of color from sugar during refining [25]. In the later half of the nineteenth century, American water treatment plant used non activated charcoal for water purification. Since then lots of adsorbents have been discovered to remove the contamination from water.

Khan et al [11] studied the adsorption of cadmium on sugarcane bagasse from aqueous solution. The efficiency of adsorbent was found to depend on the initial metal ion concentrations, pH, adsorbent dose and contact time. Sugarcane bagasse, an agricultural residue from sugar refining industries, had been shown to have a great potential as a low cost adsorbent for Cd (II) removal and could be applied for wastewater management strategies.

Mathialagan et al [2] investigated the adsorbent behaviour of low cost adsorbent perlite for the removal of Cd (II) from aqueous solutions. The effects of pH, initial concentrations and contact time on the adsorption were examined by batch technique method. It was found that perlite could be a potential adsorbent for cadmium removal from aqueous solution.

Karthikeyan et al (22) studied the capacity of sorbents prepared from juniper wood (JW) and bark (JB) on adsorption of cadmium from aqueous solution at different pH and their capacity was compared. The adsorption behaviour was characterized through adsorption kinetics, adsorption isotherms and edge experiments.

Soon- An Ong et al (12) studied the adsorption behaviour of Cd (II) and Cu (II) ions on to rice husk and modified rice husk treated with nitric acid. The effects of pH, contact time, adsorbent dose were conducted for both modified and non-modified rice husk to compare their capacity and potential for the adsorption of cadmium. It was observed that the adsorption capacity of rice husk improved or increased after treated with nitric acid.

Currently, adsorption on activated charcoal is recognized method for the removal of cadmium and other heavy metals in water treatment process [14, 16]. However, the cost of activated charcoal limits its wide spread use in treatment of water by adsorption. Consequently many researches have been carried out in the development of low-cost activated carbon adsorbents developed from cheaper and easily available materials [17].

Gaikward, (1) studied the removal of cadmium from aqueous solution by activated charcoal derived from coconut shell. They studied the adsorption behaviors of charcoal by varying the initial concentration of cadmium, pH of the solution, amount of adsorbent dose and contact time. It was investigated that adsorption of cadmium increased with the increased pH value and pH 6 was the optimum for the maximum removal capacity of adsorbent. The uptake of cadmium ion on activated charcoal derived from coconut shell was found to be good.

Teker et al [3] investigated the extent and variation of adsorption of cadmium ions on activated carbon derived from Rice Hulls. The parameters like pH, activated carbon dosages, contact time, initial metal ion concentration and solution temperature all were found to have effect on adsorption of cadmium

Garcia et al [23] studied the adsorption of Cadmium by commercially prepared activated carbon treated with SO<sub>2</sub> at different environmental conditions. They treated carbon by three ways: heating from an ambient temperature to 900<sup>0</sup>C, treatment at ambient temperature in presence of SO<sub>2</sub>, and successive treatment in SO<sub>2</sub> and H<sub>2</sub>S at normal temperature. The adsorption was carried out at two different temperatures 45<sup>0</sup>C and 25<sup>0</sup>C and two different pH 2 and pH 6.2 respectively. It was concluded that the treatment of activated carbon in atmosphere of SO<sub>2</sub> or SO<sub>2</sub> and H<sub>2</sub>S modified the chemical-physical properties of activated carbon and hence increased the ability to adsorb Cd (II).



Cheung et al [24] studied the adsorption of cadmium and zinc on to Bone char. The equilibrium isotherms were measured and analyzed by using Langmuir isotherm model. A new film pore diffusion model was applied to the batch contact time, result and good correlations were obtained between theoretical prediction and experimental data.

Feroz s et al [9] investigated the various parameters on the removal of cadmium using activated charcoal. They also studied the effect of the presence of another metal at various concentrations. The equilibrium time was determined as 3 hours and the metal uptake was found to increase with the increase in initial metal concentration and in the adsorbent dose but was decrease with the increase concentration of another metal present in the solution.

Chaib et al [8] studied the uptake of Cd (II) and Cr (VI) on the adsorbent made up from rough charcoal derived from Alep pine. A simple thermal treatment was done at 600<sup>0</sup> C and chemical treatment was done by sodium hydroxide. The adsorption capacities of different charcoals were determined and the modeling of isotherms was done according to Langmuir and Freundlich isotherms.

## **2. OBJECTIVES OF THE PRESENT STUDY**

A number of fruit seed stones and agricultural wastes have been identified as precursors for the preparation of low cost activated charcoal to remove cadmium from water; however no reports are available about the use of charcoal derived from the seed of *choerospondias axillaris* to remove cadmium from aqueous solution. Thus the present study is mainly concerns about investigation of charcoal from Lapsi seeds (*choerospondias axillaris* seed) as a low cost adsorbent for Cd (II).

### **2.1 General Objective**

Lapsi seeds contain high percentage of carbon and could be the potential precursor of activated charcoal. Therefore the basic purpose of the present study is to prepare activated charcoal from Lapsi seeds and to investigate adsorptive characteristic for adsorption of cadmium from water and to activate the charcoal by thermal and chemical treatment for its practical applicability.

### **2.2 The specific objectives**

The specific objectives of present work are as follows:

1. To prepare, activate and characterize the charcoal derived from *Choerospondias axillaris* seeds for the adsorption of Cd (II) from aqueous solution.
2. To compare the adsorption capacity of the adsorbent with commercially available charcoal.
3. To investigate the effect of pH, adsorbent dose, initial concentration of the cadmium and contact time on the removal of Cd (II).
4. To study the kinetics of the adsorption, equilibrium time and the adsorption isotherm using different isotherm models.

### **3. EXPERIMENTAL**

#### **3.1 Preparation of Reagents**

##### **3.1.1 Stock cadmium solution, 1000 µg/mL Cd (II)**

Stock solution of cadmium nitrate was prepared by dissolving 2.744 gm of hydrated cadmium nitrate  $[\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}]$  in 1000mL volumetric flask with 6 mL concentrated nitric acid and volume of the solution was made up to mark with distilled water.

1 mL stock solution of cadmium nitrate      1000 µg of Cd (II)

##### **3.1.2 Working cadmium (II) solution, 100 µg/mL Cd (II)**

25 mL of the stock solution of cadmium nitrate was diluted to 250 mL in a volumetric flask.

1 mL of working Cd (II) solution      100 µg/mL of Cd (II)

By following the similar dilution method, solutions of 10 µg/mL ,20 µg/mL , 30 µg/mL , 40 µg/mL , 50 µg/mL , 60µg/mL , 70 µg/mL , 80 µg/mL and 90 µg/mL were prepared in 100 mL volumetric flask with water.

##### **3.1.3 Nitric Acid solution, 0.1 M**

0.1 M nitric acid solution was prepared by pipetting 6.3 mL of conc. nitric acid in 1000 mL volumetric flask and adding water up to mark.

##### **3.1.4 Sodium Hydroxide Solution, 1.0 M**

10 gm of sodium hydroxide pellet weighed and transferred into 250 mL volumetric flask and water was added up to the mark to make 1.0 M sodium hydroxide solution.

##### **3.1.5 Hydrochloric acid solution, 0.1 M**

8.6 mL of conc. hydrochloric acid was pipette out in 1000 mL volumetric flask and water was added up to mark to prepare 0.1 N hydrochloric acid solution.

### 3.1.6 Buffer Solutions

Buffer solutions of pH 4, pH 7 and pH 9.2 were prepared by dissolving buffer tablets of pH 4; pH 7 and pH 9.2 respectively in 100 mL distilled water.

### 3.1.7 Standard Solutions

The standard solution of concentration 0.5  $\mu\text{g/mL}$ , 1.0  $\mu\text{g/mL}$ , 1.5  $\mu\text{g/mL}$  and 2.0  $\mu\text{g/mL}$  were prepared in 100 mL volumetric flask with 0.1 N  $\text{HNO}_3$  solution by diluting working Cadmium (II) solution (100  $\mu\text{g/mL}$ ).

## 3.2 Preparation of Adsorbents

### 3.2.1 Preparation of Charcoal from Lapsi (*Choerospondias axillaris*) seed (CASC)

Lapsi, *Choerospondias axillaris*, fruits were brought from Asan Bazaar, Kathmandu. The outer fleshy part of the fruit was removed and the seeds were washed with tap water. These seeds were left in sunlight for a week to dry. Then the seeds were taken in large porcelain basin and burnt by heating until blue flame covers the mouth of the porcelain basin. Then the carbonized material was covered and left with in the porcelain basin for half an hour. Then it was grounded to fine powder. Finally, the powdered material was sieved through 212 $\mu\text{m}$  sieving machine.

### 3.2.2 Activation of Charcoal

Adsorption capacity of charcoal can be enhanced by activating the raw charcoal. Activation can be done by two different process (i) Chemical activation can be done by treating charcoal with phosphoric acid, nitric acid etc., (ii) Physical activation can be done by passing steam, oxygen, nitrogen, sulphur dioxide etc to the charcoal kept at very high temperature. In comparison with the physical activation, chemical activation has several advantages.

In this study, chemical activation method was employed. The sieved raw charcoal was treated with 1:1 conc.  $\text{HNO}_3$  at temperature 60 $^{\circ}\text{C}$  to 65 $^{\circ}\text{C}$  for 3 hours. Then chemically treated charcoal was washed with distilled water until the pH was neutral.

It was then dried in oven at 120<sup>0</sup> C. The activated charcoal was used to study adsorption of cadmium.

### **3.2.3 Commercial Activated Charcoal (CAC)**

Commercial activated charcoal without any chemical activation was used to compare the adsorption capacity with laboratory prepared non activated and activated charcoal.

## **3.3 Characterization of Activated Charcoal**

### **3.3.1 Proximate analysis of the Lapsi (*Choerospondias axillaris*) Seed Charcoal**

The Lapsi seed charcoal was analyzed for its moisture content, ash content and fixed carbon (by difference) [15] .

Ash content of charcoal was determined according to the JIS (Japan Industrial Standard) 1812. It was determined by heating 1g charcoal at 500<sup>0</sup>C for an hour to an electric furnace and the temperature was raised to 815<sup>0</sup>C for half an hour.

Moisture content of the charcoal was determined by weighing 1g of charcoal in crucible and heated for 2-3 hours in an electric oven. It was heated until constant weight was obtained.

Fixed percentage of charcoal was determined by subtracting ash content percentage and moisture content percentage from the total percentage.

### **3.3.2 Determination of Surface area of Charcoal**

Surface area of charcoal was determined by chemical adsorption technique. For the determination of surface area; 0.25 g of charcoal was agitated with 25 mL of different concentration of acetic acid for 120 minutes. Then the final concentration of acetic acid was determined by titrating with 0.1N sodium hydroxide. From the acetic acid adsorbed, specific surface area of the charcoal was determined by procedure given by Dunicz [29].

### 3.3.3 Determination of Surface functional groups

The activated charcoal can have acidic as well as basic functional groups and can be conveniently determined by the titration method developed by Boehm. In a simple method, 200 mg dried charcoal (activated and nonactivated separately) was put into five 125 mL reagent bottles containing 50 mL of standard solutions of 0.02N NaOH, 0.02N NaHCO<sub>3</sub>, 0.02N Na<sub>2</sub>CO<sub>3</sub> and 0.02N HCl. The reagent bottles were then sealed and were agitated for 48 hours. After this time, the suspensions were filtered, and filtrate (5mL) of each of basic solution was titrated with 0.02N HCl while 5 mL of HCl solution was titrated with 0.02N NaOH solution using methyl orange as an indicator.

### 3.3.4 SEM Image of the charcoal

SEM image of the charcoal was taken by JEOL instrument University of Halle, Wittenberg.

## 3.4 Adsorption Study

Batch adsorption study of Cd(II) on charcoal prepared from Lapsi (*Choerospondias axillaries*) seeds was performed using Cd(II) synthetic working solutions. Required initial concentration of cadmium metal ions from 10µg/mL to 100µg/mL was prepared by diluting working cadmium solution. The pH of cadmium solutions were adjusted by using 1 M NaOH and 1 M HNO<sub>3</sub>.

For adsorption study, 25 mL of cadmium solution of known initial concentration was added to 50 mg of adsorbent in a 125 mL reagent bottle and mixture was agitated on a mechanical shaker for 5 hours at room temperature. At the end of experiment, the sample solution was allowed to settle down and filtered with the help of filter paper. The filtrates were properly diluted to bring them to measurable range of AAS and analyzed for the residual concentrations. The initial and the final concentration of Cd(II) were determined by Flame Atomic Absorption Spectroscopy (Perkin Elmer Model AAnalyst 100).

### **3.4.1 Effect of pH**

Batch pH studies were conducted by shaking 40 mL of metal solution containing approximately 10 µg/mL of cadmium ions with 100 mg of different adsorbents for 5 hours over initial pH values from 2 to 8 in increments of 1. The samples were shaken in 125 mL reagent bottles. The pH of cadmium solutions were adjusted by 1M NaOH and 1M HNO<sub>3</sub>. The pH was measured using digital pH meter (WPA CD 300). An optimum pH was selected for further study.

### **3.4.2 Effect of Adsorbent dose**

The effect of adsorbent dose was studied by varying the adsorbent dose from 10 mg to 200 mg and taking 30 mL of approximate concentration of cadmium(II) 50 µg/mL at optimum pH. The solution was shaken for 24 hours in a mechanical shaker at room temperature

### **3.4.3 Effect of Contact time**

The effect of contact time was studied at room temperature by taking a set of samples with 30 mL cadmium (II) concentration of 20µg/mL and an adsorbent dose of 50mg at optimum pH. The samples were collected at different interval of time from 15 minutes then they were filtered and analyzed.

### **3.4.4 Adsorption Isotherm**

The isotherm studies were conducted at room temperature by varying the initial concentration of cadmium from 10µg/mL to 100µg/mL. 25 mL of representative cadmium solutions were mixed with 50 mg of adsorbent and the mixtures were stirred for 24 hours in shaker. The residual metal concentrations were determined after filtering the samples. The experiments were conducted in duplicates and mean values were used in the analysis of data. This study helps in evaluating the maximum adsorption capacity of adsorbents

### **3.4.5. Adsorption Kinetics**

The measurement of adsorption kinetics was carried out by shaking 50 mg of charcoal with 30 mL cadmium solution of 20 $\mu$ g/mL 125 mL reagent bottle at room temperature. The removal kinetics of cadmium(II) was investigated by drawing the samples after desired contact time and the filtrate was analyzed for the remaining Cd(II) concentration.



## 4. RESULTS AND DISCUSSIONS

### 4.1 Characterization of the charcoal

#### 4.1.1 Proximate analysis of Lapsi (*Choerospondias axillaris*) seed Charcoal

Table 1 shows the results of proximate analysis of Lapsi seed charcoal. From the table we can see that the moisture content and ash content percentage of Lapsi seed charcoal is low. Therefore it appears to be very suitable for adsorption process.

Table 1: Proximate analysis of Lapsi seed charcoal

Adsorbent	Ash content (%)	Moisture content (%)	Fixed Carbon (%)
MCASC	3.5	0.22	96.28

#### 4.4.2 Surface Area Determination

The surface areas of Lapsi (*Choerospondias axillaris*) seed (raw) and Lapsi seed activated charcoal had been determined by Piya [15] using methylene blue and acetic acid adsorption techniques. The author found that the results obtained from both the techniques were comparable. In the present work surface areas of charcoals determined by acetic adsorption techniques and the results are listed in Table 3. Surface area of the raw Lapsi seed charcoal (CASC) is found to be very low but after chemical treatment, the surface area is greatly increased and is comparable to the surface of commercial activated charcoal

Table 2: Surface area of different charcoal

Parameter	CASC(RAW)	MCASC(Activated)	CAC
Surface area (m <sup>2</sup> /g)	45	600	799

#### 4.1.2 Surface functional group determination (Boehm's Titration):

Surface functional groups (both acidic as well as basic) were quantified by means of titrimetric techniques developed from Boehm's work. The oxygen containing functional group (acidic) can be determined by allowing the carbon to react with different bases and by applying the Boehm's assumption according to which

- (i)  $\text{NaHCO}_3$  neutralizes carboxyl group only
- (ii)  $\text{Na}_2\text{CO}_3$  neutralizes carboxyl and lactone group
- (iii)  $\text{NaOH}$  neutralizes carboxyl, lactone as well as phenol group.

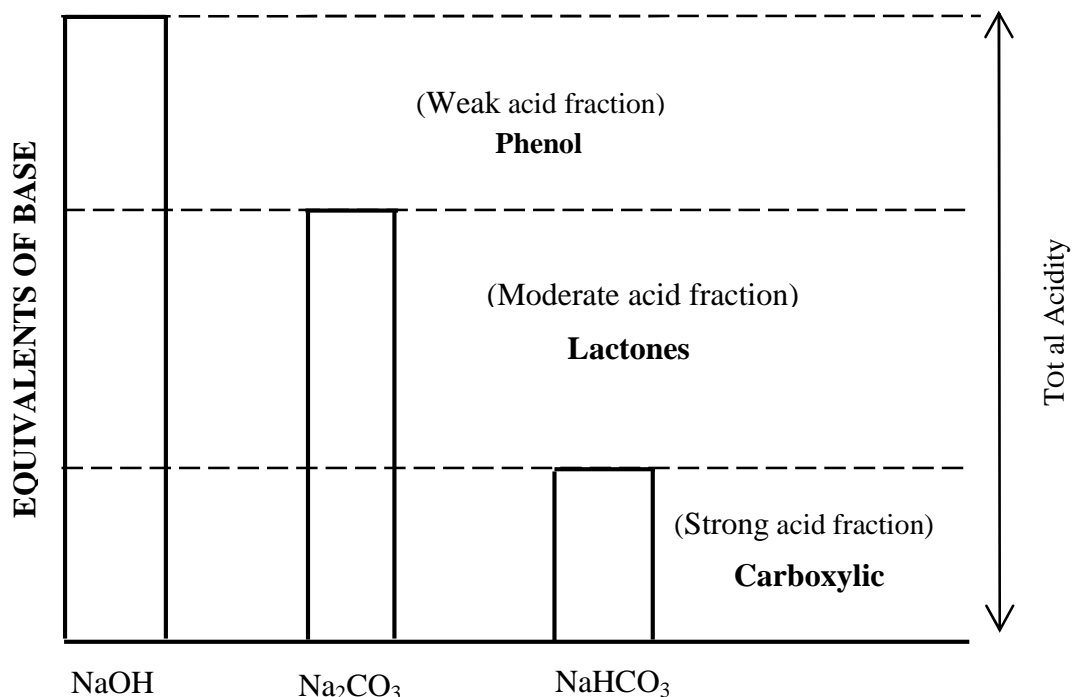
If A, B and C referred to the milliequivalents (meq) of  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$  neutralized by charcoal then,

meq of carboxyl group = A

meq of lactone group = B-A

meq of phenol group = C-B

These calculations may be illustrated by the help of figure which is given below (31):



**Figure: Illustration of the calculations used in the Boehm Titration**

The basic surface functionalities are measured as a single value from the mevt of HCl neutralizes.

In actual practice, 200 mg of dry charcoal (modified as well as non-modified) was agitated with 50 mL of 0.02 N bases namely  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{NaOH}$  and 0.02 N HCl in mechanical shaker for 48 hours. The mixture was filtered and 5 mL of filtrate was back titrated with 0.02 N HCl or 0.02 N  $\text{NaOH}$  using methyl orange as an indicator to determine the bases and acid consumed. The volumes of acid or bases consumed by modified and non-modified charcoal are given in the Table 3.

Table 3: Results of Boehm titration

Adsorbents	Volume consumed in mL			
	$\text{NaHCO}_3$	$\text{Na}_2\text{CO}_3$	$\text{NaOH}$	HCl
MCASC	11	14	20	3
CASC	3	4	8	7

On the basis of volume acid or bases consumed by the definite weight of charcoal the amount of oxygen containing functional group per gram charcoal is calculated following the Boehm procedure. As an illustration, calculation of carboxylic group from the results given in table is portrayed below.

Volume of 0.02N  $\text{NaHCO}_3$  consumed by 0.2 gm MCASC = 11 mL

Since  $\text{NaHCO}_3$  is neutralized by carboxylic group, the meq of carboxylic group present =  $0.02 \times 11 = 0.22$  meq

That is, 0.2 gm of MCASC contains 0.22 meq of carboxylic group

Therefore, 1 gm of MCASC contains  $0.22/0.2 = 1.1$  meq of carboxylic group

Hence amount of  $-\text{COOH}$  group in MCAS is 1.1 meq per gram.

The meq per gram of other functional groups present are similarly calculated following Boehm procedure.

The results obtained from the Boehm titration regarding the amount of acidic/ basic functional group is presented in Table.4

Table 4: Results of the Boehm titration (meq/gm)

Adsorbents	Functional groups milliequivalents per gram(meq/g)			
	Carboxyl	Lactones	Phenol	Basic
MCASC	1.1	0.3	0.6	0.3
CASC	0.3	0.1	0.4	0.7

From the table, it can be seen that the oxygen containing (acidic) functional group increased significantly on treating raw charcoal with conc. nitric acid at moderate temperature ( $65^{\circ}\text{C}$ ). Some other authors[28] used  $\text{H}_2\text{O}_2$  or  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  as an oxidizing agent to introduced oxygen containing surface functional group. But the present study reveals that conc. nitric acid is more effective in introducing large amount of oxygen containing surface functionalities. Nitric acid is not only oxidizing agent but also a strong acid and owing to this nitric acid has enhanced activity in introducing oxygen containing functional group in carbon surface. Moreover, it has been found that the acidic and basic surface sites coexist simultaneously but the concentration of basic sites decrease with increase in acid character of the surface

#### 4.4.4 Scanning Electron Microscope

The SEM Lapsi seed charcoal (raw) and Lapsi seed activated charcoal are shown in Figure 9 and 10 respectively. The image of activated Lapsi seed charcoal shows irregular surface and more pores indicating larger surface area.

## 4.5 Effect of pH

The effect of pH on the adsorption of cadmium on the charcoal was studied in the pH range from 2 to 8. In highly acidic medium (below pH 2), oxygen containing surface functional groups are not dissociated and consequently there is a decrease in the active sites for adsorption [10]. On the other hand, in basic medium (above pH 8), the cadmium ions get precipitated into insoluble  $\text{Cd}(\text{OH})_2$  [3]. Therefore the experiments were carried out over the pH range 2-8 where the dissociation of oxygen containing surface functional can occur and the precipitation of cadmium hydroxide does not takes place. In these conditions the metal removal can be related only to the adsorption process. The effect of pH on the adsorption of cadmium by three types of carbon (CAC, CASC, and MCASC) on synthetic water sample containing initial concentration of 10 ppm and at room temperature is presented in Figure 1. The pH of the aqueous solution is an important controlling parameter in adsorption process and since hydrogen ion concentration play a vital role in adsorption process. The adsorption capacity of CAC at pH 2 was found to be 12.12% which increased to 61.70% when pH rose to 8. Similarly the adsorption capacity of CASC and MCASC were found to increase from the initial capacities of 6.3% and 6.18% to 56.38% and 71.27% when pH rose from 2 to 8. It was observed that the adsorption capacity of all the adsorbents increases linearly between pH 2 to 6, after pH 6 there is no significant increase in adsorption and percentage removal of cadmium attains a limiting value as shown in the figure 1. It is interesting to note that on treatment of charcoal from Lapsi seed with concentrated nitric acid greatly enhanced the adsorption capacity of charcoal. This is obviously due to the formation of oxygen containing surface functional group, specifically the carboxylic group, on treatment of charcoal with concentrated nitric acid. According to literature [26,28] carboxylic group is identified as main adsorption sites for adsorption of cadmium. The pKa of carboxylic group is around 5 and attainment of limiting value for adsorption after pH 6 is in agreement with the hypothesis that surface carboxylic functional group provides the active sites for cadmium adsorption. One of the mechanisms of Cd adsorption on charcoal is by the ion exchange process. In this process Cd binds to the anion sites by displacing protons from acidic group and such process can not take place in highly acidic solution. The present result is in agreement with this fact, since the adsorption of Cd(II) in charcoal is low at low pH and attains the limiting value above pH 6.

#### 4.6 Effect of Contact time

The decrease in concentration of Cd (II) with increase in contact time for different adsorbents is presented in Figure 3. It was observed that the removal of metal ion increases with increase in contact time to some extent. Further increase in contact time does not decrease the concentration of Cd (II) significantly due to deposition of metal ions on the available adsorption sites on adsorbent material. From Figure 4, it is clear that the equilibrium time was reached after 4 hours. Therefore in each experiment the shaking time was set for 4 hours.

#### 4.7 Effect of adsorbent dose:

The variation in percent removal of Cd (II) ion with adsorbent dosages for different charcoal is shown in Figure 2. The dosages of adsorbent are varied from 0.66g/l to 5g/l. The other parameters are  $C_o=51.5\text{ppm}$ ,  $V=30\text{mL}$ ,  $\text{pH}=6$ . It is clear from the Figure 2 that as the amount of adsorbent increases, the percentage removal of cadmium also increases but only up to certain value. The percentage of adsorption increased from 33.98% to 61.16% when the adsorbent dose increased from 20 mg to 150 mg for CAC. For CASC the percentage removal increased from 27% to 55.33% and for MCASC the percentage removal increased from 35.92% to 69.90%, when adsorbent dose was increased from 20mg to 150 mg, after this there is no significant increase in the adsorption. This observation is consistent with Langmuir hypothesis of increasing competition among the adsorbent particles for metal ions with increase in number of adsorbent particles per unit volume [30]. The adsorption capacity of MCASC is much higher than CASC. Thus treatment with nitric acid had greatly increased the adsorption capacity of charcoal this is not only due to the increases in the porosity of carbon by chemical treatment but also due to the formation of carboxylic and other oxygen containing surface functionalities which acts as active sites for cadmium adsorption.

#### 4.8 Effect of initial metal ion concentration:

The effect of initial cadmium concentration on the adsorption of Cd (II) ions by different adsorbents are shown in Figure 4. The effect of Cd (II) concentration on adsorption was studied by keeping the adsorbent dose 50 mg and at pH 6. Keeping constant time 4 hours and varying the concentration of metal ions from 10 ppm to 100 ppm, it is observed that adsorption is greatly influenced by initial concentration of metal ions. The extent of adsorption increased from 4.17 mg/gm to 9.0 mg/gm for CAC, 3.98 mg/gm to 7.5 for CASC and 4.32 mg/gm to 12.1 mg/gm for MCASC when the initial concentration was increased from 10 ppm to 100 ppm. The result shows that the removal of cadmium is highly concentration dependent. From Figure 3, it is noticed that the adsorption of metal ion increases with increase in metal ion concentration and ultimately reaches to limiting value. This is because, at lower metal ion concentration, the ratio of initial number of metal ions to the available surface functional group is low, but at higher concentration, the available functional sites of the adsorbent become fewer compare to number of metal ions present and hence the uptake of metal becomes independent of the initial metal ion concentration.

#### 4.9 Adsorption Isotherms

The equilibrium data obtained was analyzed with respect to Freundlich and Langmuir isotherms.

##### Freundlich isotherm

The linear form of Freundlich isotherm is given by the following equation:

$$\log q_e = \log K + \frac{1}{n} \log C_e$$

Where  $q_e$  is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g),  $C_e$  is the equilibrium concentration;  $K$  and  $n$  are constants and are identified as adsorption capacity and adsorption intensity. The values of constants i.e. the Freundlich parameters are listed in Table (5). The plots of  $\log q_e$  against  $\log C_e$  for different charcoal are shown in Figure 5. From the slope and intercept obtained from the line of best fit the values of  $K$  and  $n$  are calculated which is given in table 5

Table.5: Values of Freundlich constants

Adsorbents	Freundlich Constants			Recommended isotherms
	K(mg/g)	n	$R^2$	
CAC	4.01	5.44	0.982	$q_e = 4.01 C_e^{0.184}$
CASC	3.89	6.71	0.914	$q_e = 3.89 C_e^{0.149}$
MCASC	4.34	4.21	0.99	$q_e = 4.34 C_e^{0.237}$

It can be observed from the table that absorption intensity,  $n$ , for different charcoals varies from 4.21 to 6.71 and the values of the quantity  $1/n$  is less than unity in all the charcoal studied which indicates adsorption isotherm is favourable for adsorptive removal of the metal ions

### Langmuir isotherm

The linear form of Langmuir adsorption isotherm equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m}$$

Where  $C_e$  is the equilibrium concentration of the adsorbate (mg/L),  $q_e$  is the mass of adsorbate adsorbed per unit mass of adsorbent (mg/g),  $q_m$  and  $b$  are the Langmuir constants related to adsorption capacity and energy of adsorption respectively. Figure 6



represents the Langmuir plots for the adsorption of Cd(II) on charcoals. The points are experimental data and straight lines are lines of best fit with correlation coefficient as given in Table 6. Langmuir and Freundlich isotherms both adequately predicted cadmium adsorption on charcoal but Langmuir equation yielded greater correlation coefficient implying that there is monolayer coverage of the adsorbate species on adsorbent surface.

The values of  $q_m$  and  $b$  were determined from the slope and intercept of plot of  $C_e/q_e$  versus  $C_e$  and are given in Table 6. The  $q_m$  is the maximum cadmium adsorption capacity of charcoal to adsorb Cd(II) from aqueous solution and helps to evaluate the quality of adsorbent. A value of 12.53 mg/g has been obtained as the maximum adsorption capacity of MCAS for Cd(II) from batch studies. This means that one gram of MCASC could absorb 12.53 gm of cadmium ions from aqueous solutions under present experimental conditions. The adsorption capacities of CAC and CASC have been found to be 9.25 mg/gm and 8.2 mg/gm respectively. A comparison of these values reveals that modified charcoal obtained from *Choerospondias axillaris* seeds (MCAS) exhibits quite a good capacity for removing cadmium from aqueous solutions and adsorption capacity of raw charcoal increases appreciably on treating with nitric acid. This may be primarily due increase in oxygen containing acidic surface functional group on treatment with conc. nitric acid.

Table 6: Langmuir adsorption Isotherm constants for adsorption of Cd (II)

Adsorbents	Langmuir constants		
	$q_m$ (mg/gm)	$b$ (L/mg)	$R^2$
CAC	9.25	0.14	0.9861
CASC	7.46	0.305	0.9941
MCASC	12.53	0.162	0.993

#### 4.10 Kinetic Study:

In order to define the adsorption kinetics of heavy metal ions, the kinetic parameter for the adsorption process were obtained for contact times between 15 minutes to 240 minutes by monitoring the removal of Cd(II) by various charcoals. The initial concentration of cadmium was taken as 20 mg/L and the pH was maintained nearly at 6. Lagergren pseudo first order reaction rate model and Ho et al's pseudo second order reaction rate model were used to describe the kinetics of cadmium adsorption on various charcoals.

Lagergren first-order model (Lagregren,1898)

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$

Pseudo second-order model (Ho,1995; Ho and Macky, 2000)

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

where  $q_t$  is the metal uptake per unit weight of adsorbent(mg/g) at time 't',  $q_e$  is metal uptake per unit weight of adsorbent (mg/g) at equilibrium and  $k_1(\text{min}^{-1})$  and  $k_2(\text{g/mg.min})$  are the rate constants of the pseudo first-order and pseudo second-order kinetic equation respectively.

Linear plots of  $\log (q_e - q_t)$  versus  $t$  and  $t/q_t$  versus  $t$  are shown in Figures 7 and 8 respectively. The slopes and the intercepts of these curves were used to determine the values of kinetics parameters  $k_1$  and  $k_2$  as well as the equilibrium adsorption capacity  $q_e$ . The first and second order kinetics constants are presented in Table 5.

Although both models adequately described the kinetic data at 95% confidence level, Ho pseudo second order model best described the kinetic data with higher  $R^2$  values

compared to the Lagergren first model which indicates that the adsorption of Cd(II) on different adsorbents follow pseudo second order kinetics.

Table 7: Pseudo first order and pseudo second order reaction rate constants for different charcoals

Adsorbents	pH	Pseudo first order		Pseudo second order		
		$K_1(\text{L}/\text{min})$	$R^2$	$K_2 (\text{g}/\text{mg}\cdot\text{min})$	$h (\text{g}/\text{mg}\cdot\text{min})$	$R^2$
CAC	6	$1.82 \times 10^{-2}$	0.9977	$1.10 \times 10^{-2}$	0.926	0.999
CASC	6	$2.3 \times 10^{-2}$	0.9809	$6.9 \times 10^{-3}$	0.415	0.998
MCASC	6	$1.36 \times 10^{-2}$	0.9186	$1.24 \times 10^{-3}$	1.30	0.99

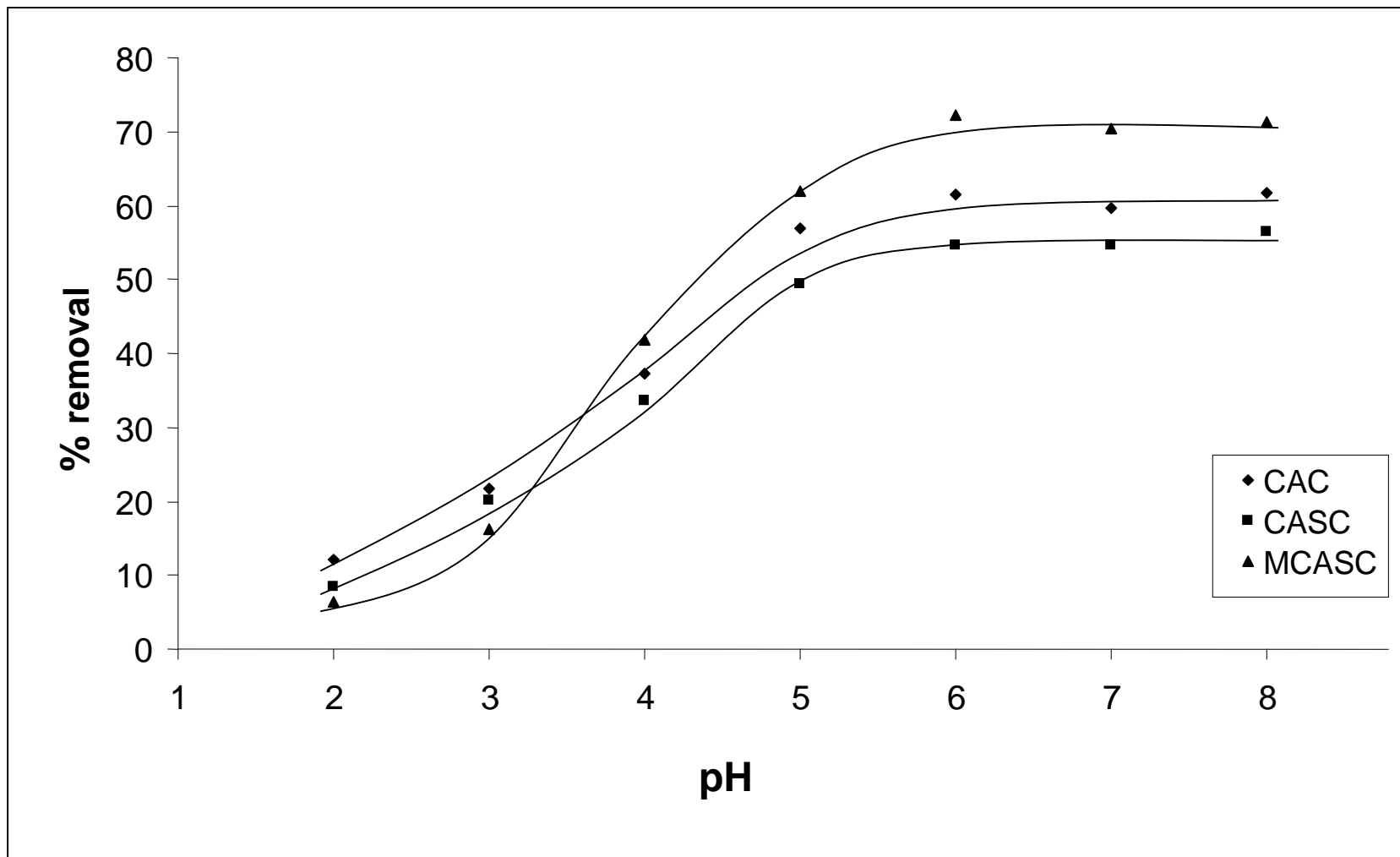
## 5. CONCLUSION

The excessive release of heavy metals into the environment is a major concern worldwide today. Adsorption process is one of the most effective techniques for heavy metals removal from waste waters and activated carbon has been widely used as an adsorbent. From the present study it can be concluded that the lapsi (*choerospondias axillaries*) seed, a common agricultural waste in our country, can be used as a precursor to obtain the charcoal by burning the seeds in its own reducing atmosphere. The effectiveness of charcoal was greatly enhanced by treating the raw charcoal with 1:1 HNO<sub>3</sub> at 60°C. The specific surface area of the charcoal, after chemical treatment, was increased from 45m<sup>2</sup>/gm to 600m<sup>2</sup>/gm. The increase in the surface area is mainly due to the increase in pore volume of charcoal. The ash content, moisture content and fixed carbon percentage of MCASC were found to be 3.5%, 0.2% and 96.3% respectively. The acidic and basic functional group present in different charcoals was determined by Boehm's titration. The oxygen containing acidic functional groups have been found to increase significantly on treating with nitric acid.

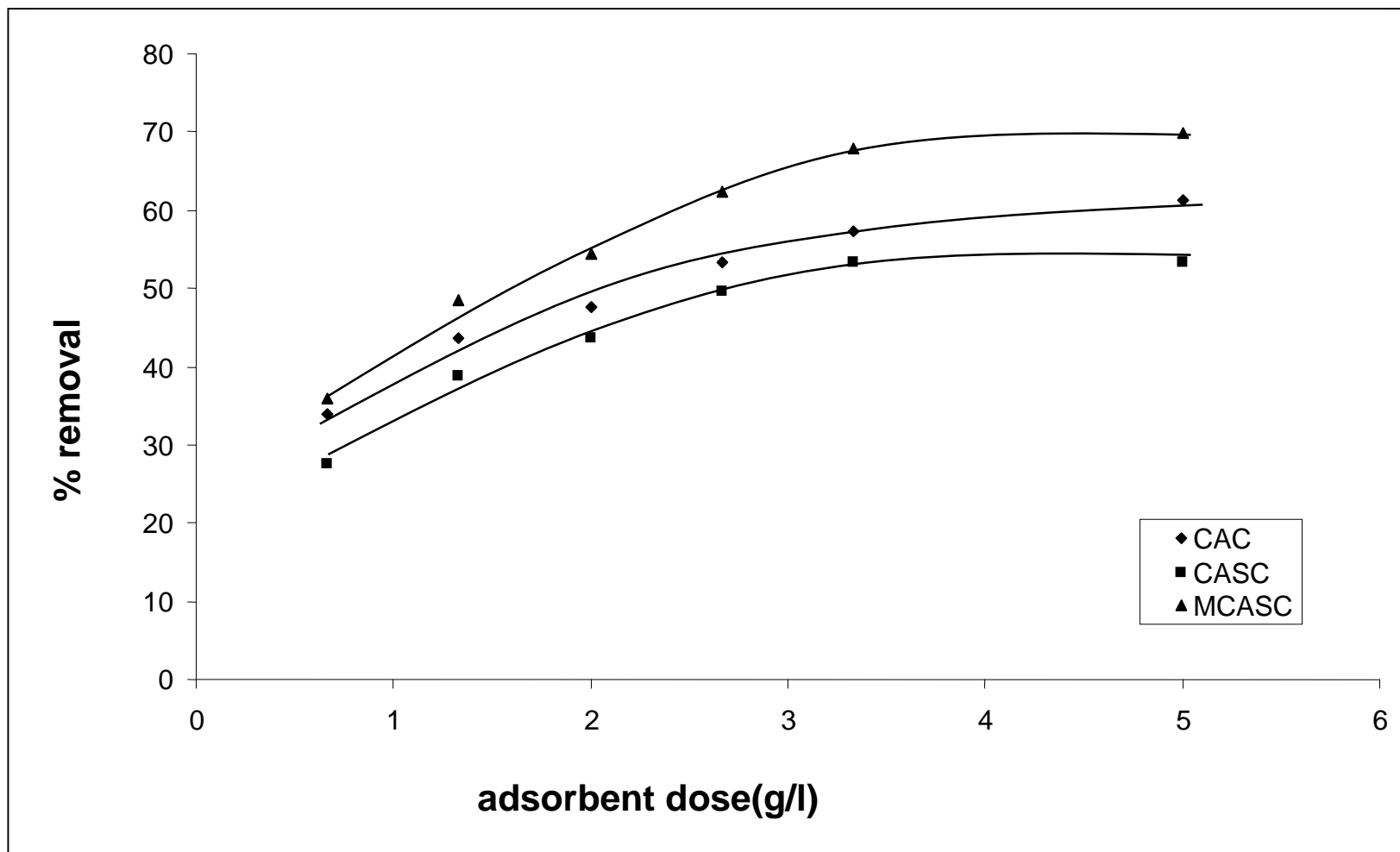
The efficiency of the adsorbent was found to be a function of initial metal ion concentration, adsorbent dose, pH and contact time. Among all, pH of the solution had great influence on the efficiency adsorptive removal of cadmium (II). The maximum adsorption of Cd(II) occurred at a pH 6 and was found to be 71.27% (mg/g). The results indicated that the adsorption process attained equilibrium within 150 minutes.

It was observed that that the removal percentage increased at the lower concentration and higher adsorbent doses. The adsorption process of Cd(II) can be described by Langmuir and Freundlich isotherm model. However, the equilibrium data was fitted very well to Langmuir isotherm model with correlation coefficient ( $R^2$ ) of 0.9913. The maximum adsorption capacity of MCASC was found to be 12.53 mg/gm from Langmuir isotherms. The kinetics analysis of data showed that the adsorption of Cd (II) ion on MCASC can be well described by pseudo second order kinetic model and the rate constant of the process was found to be  $1.73 \times 10^{-3}$  gm /mg min<sup>-1</sup>. On the basis of this study, it is concluded that the abundantly available *choerospondias axillaris* seed can be used as a precursor to make charcoal, which can be used as low cost adsorbent for Cd (II) removal and can be applied for waste water treatment.

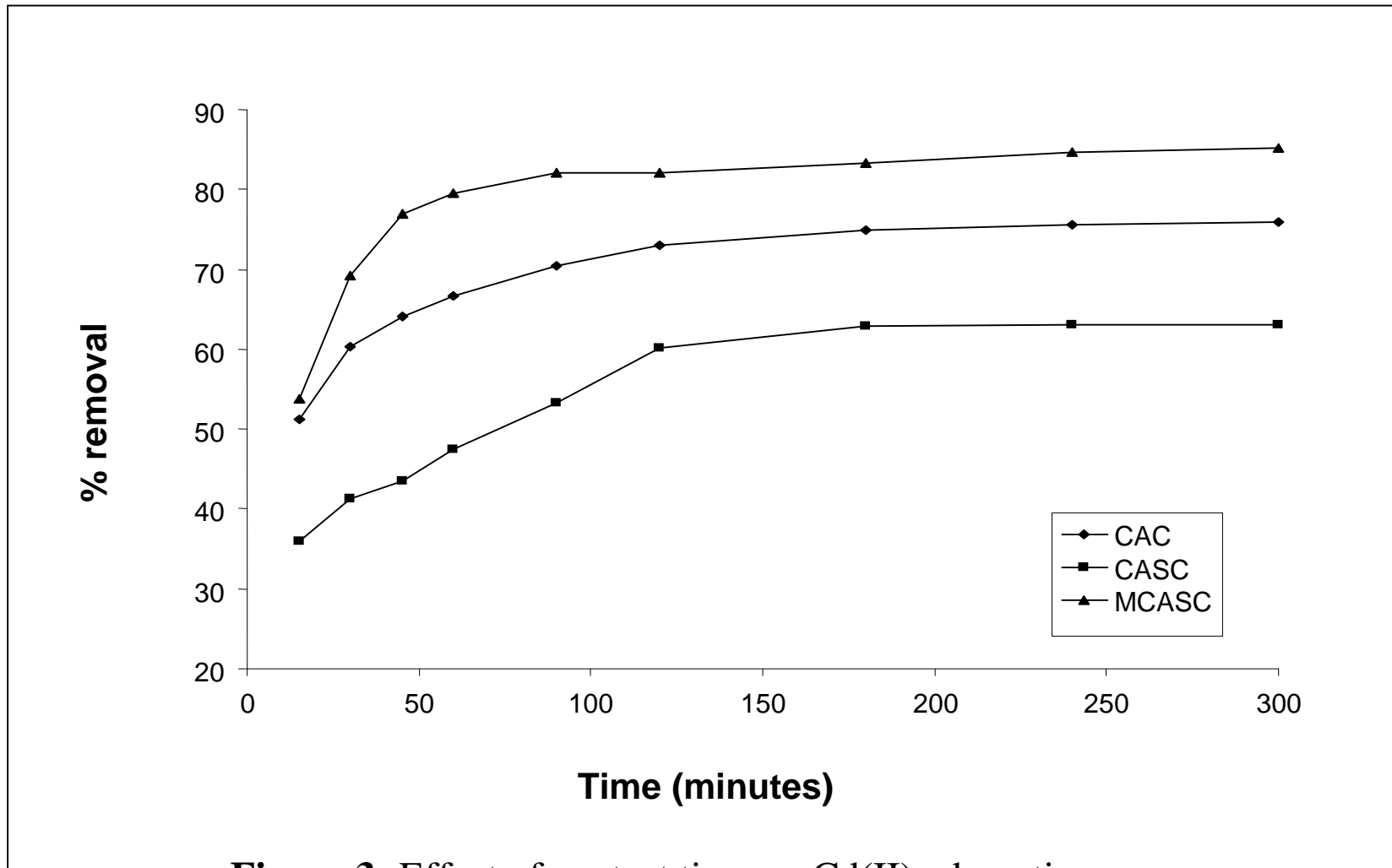
# APPENDIX



**Figure1:** Effect of pH on Cd(II) adsorption

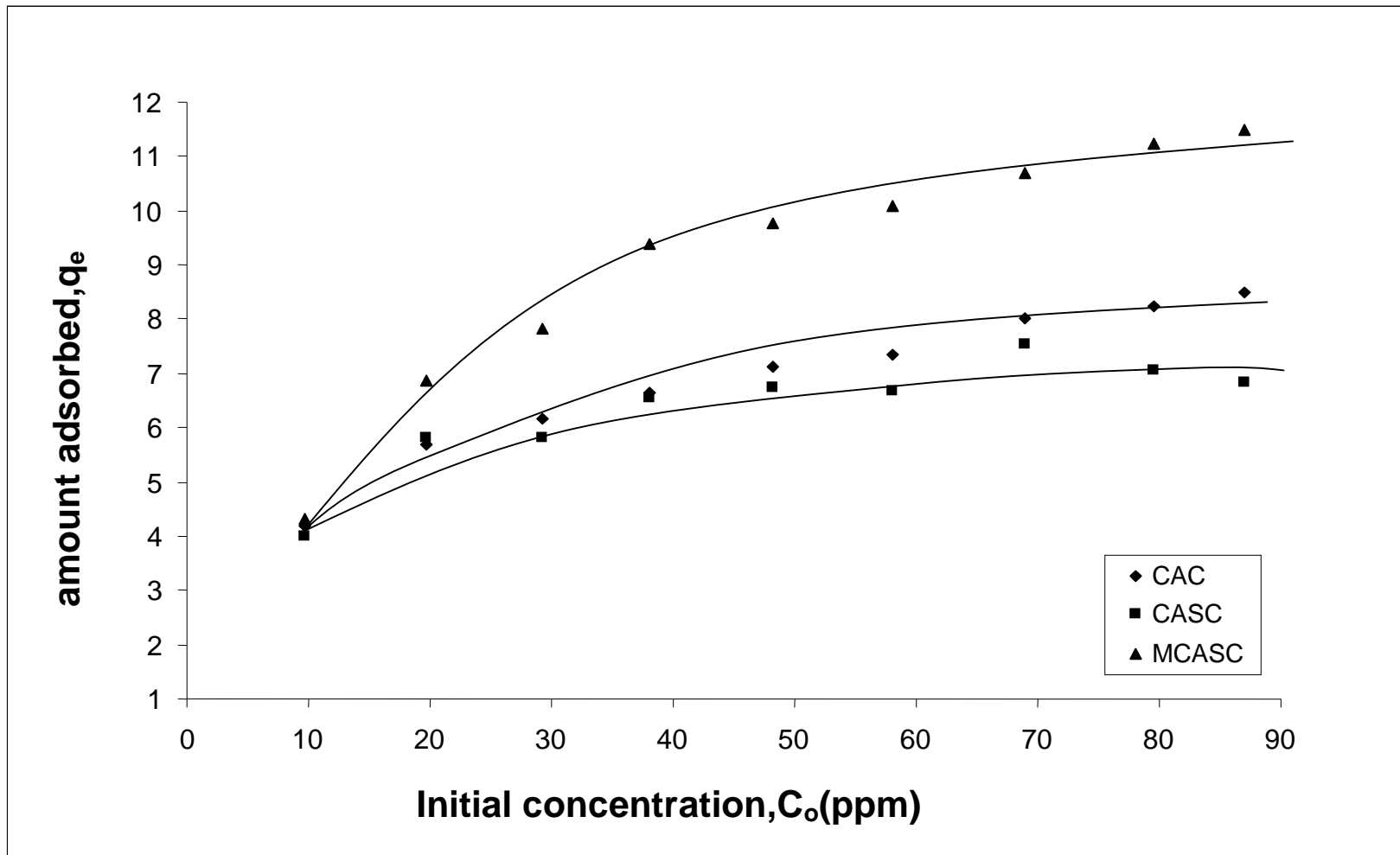


**Figure 2:** Effect of adsorbent dose on Cd(II) adsorption

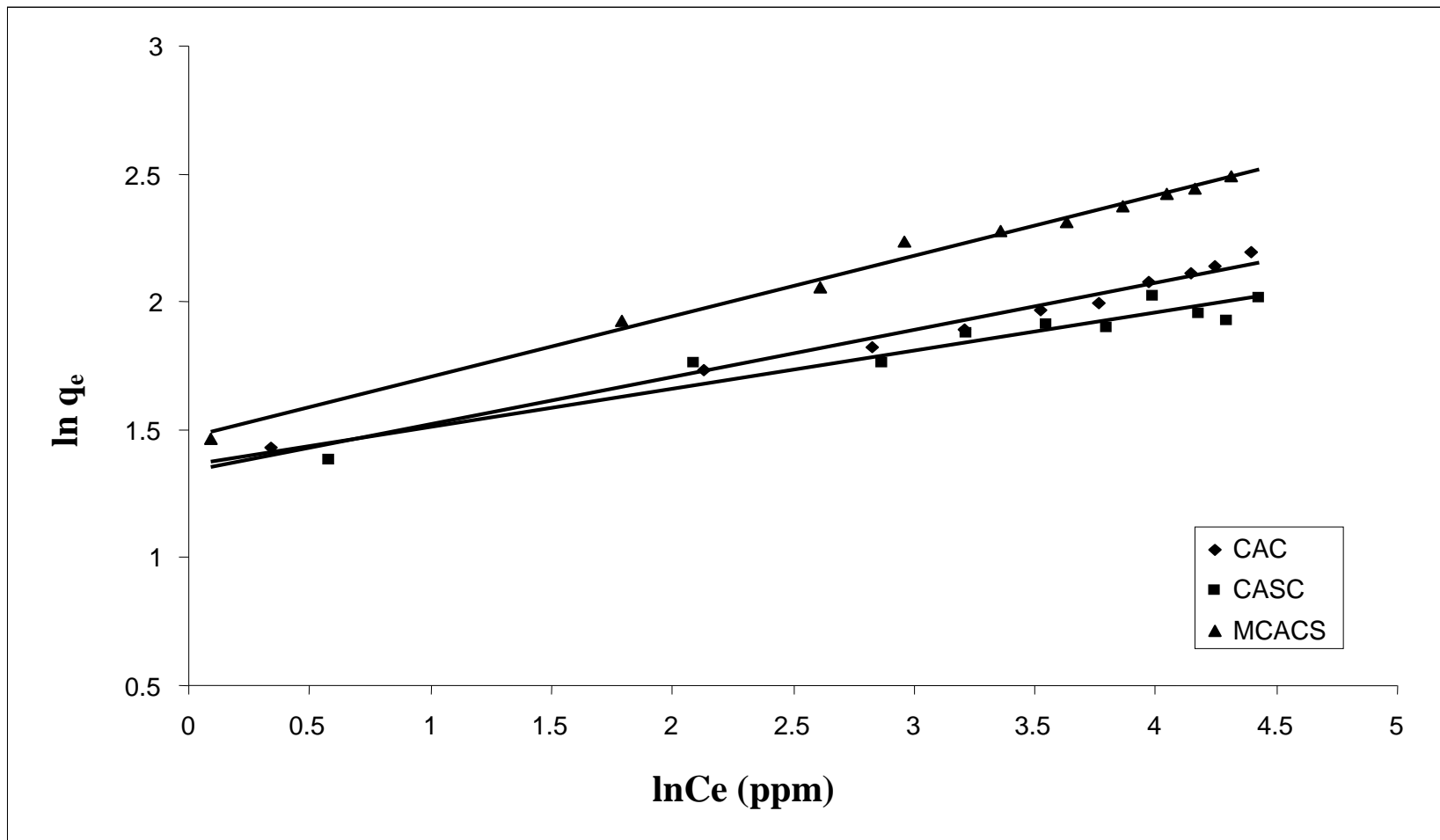


**Figure 3:** Effect of contact time on Cd(II) adsorption

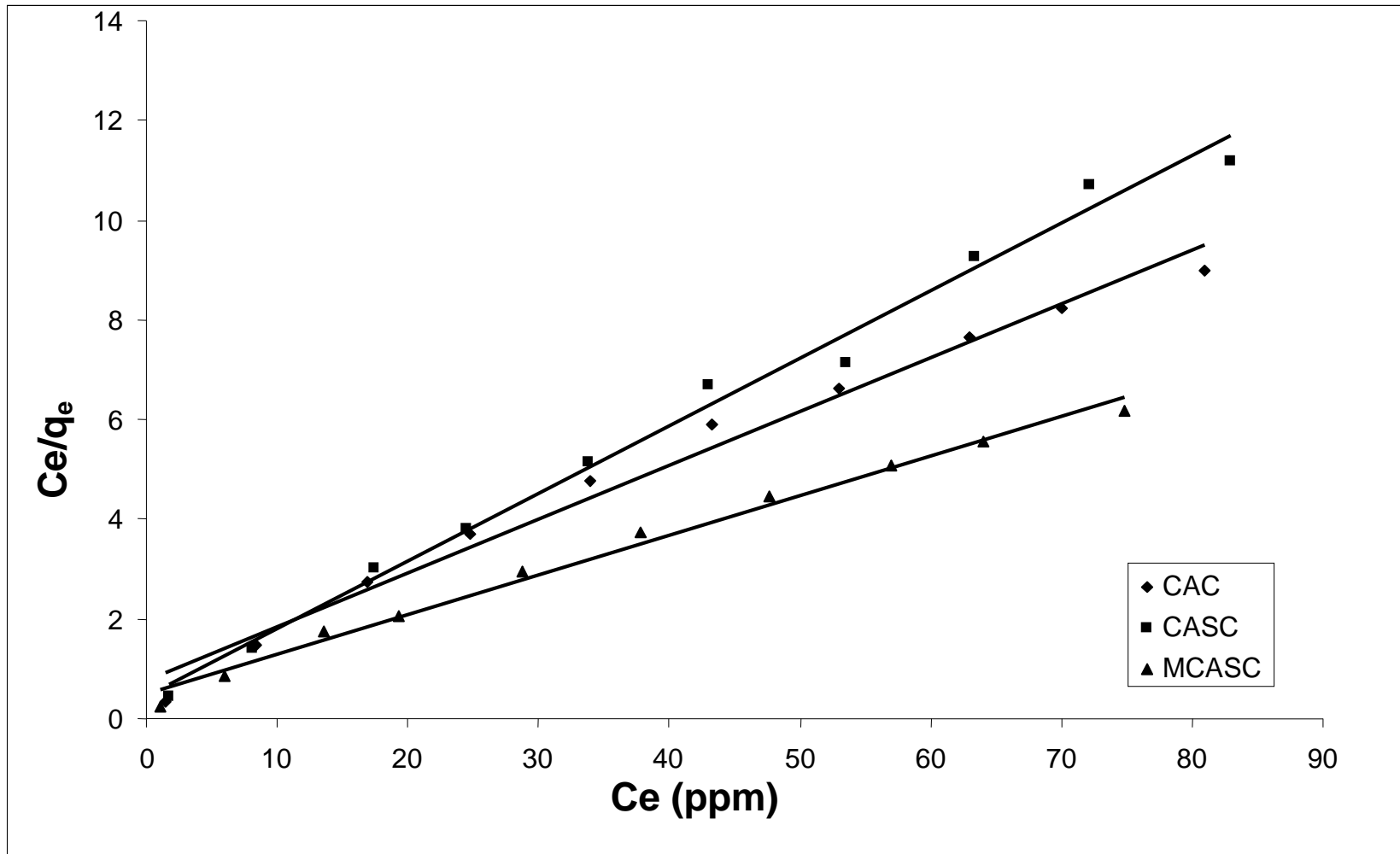




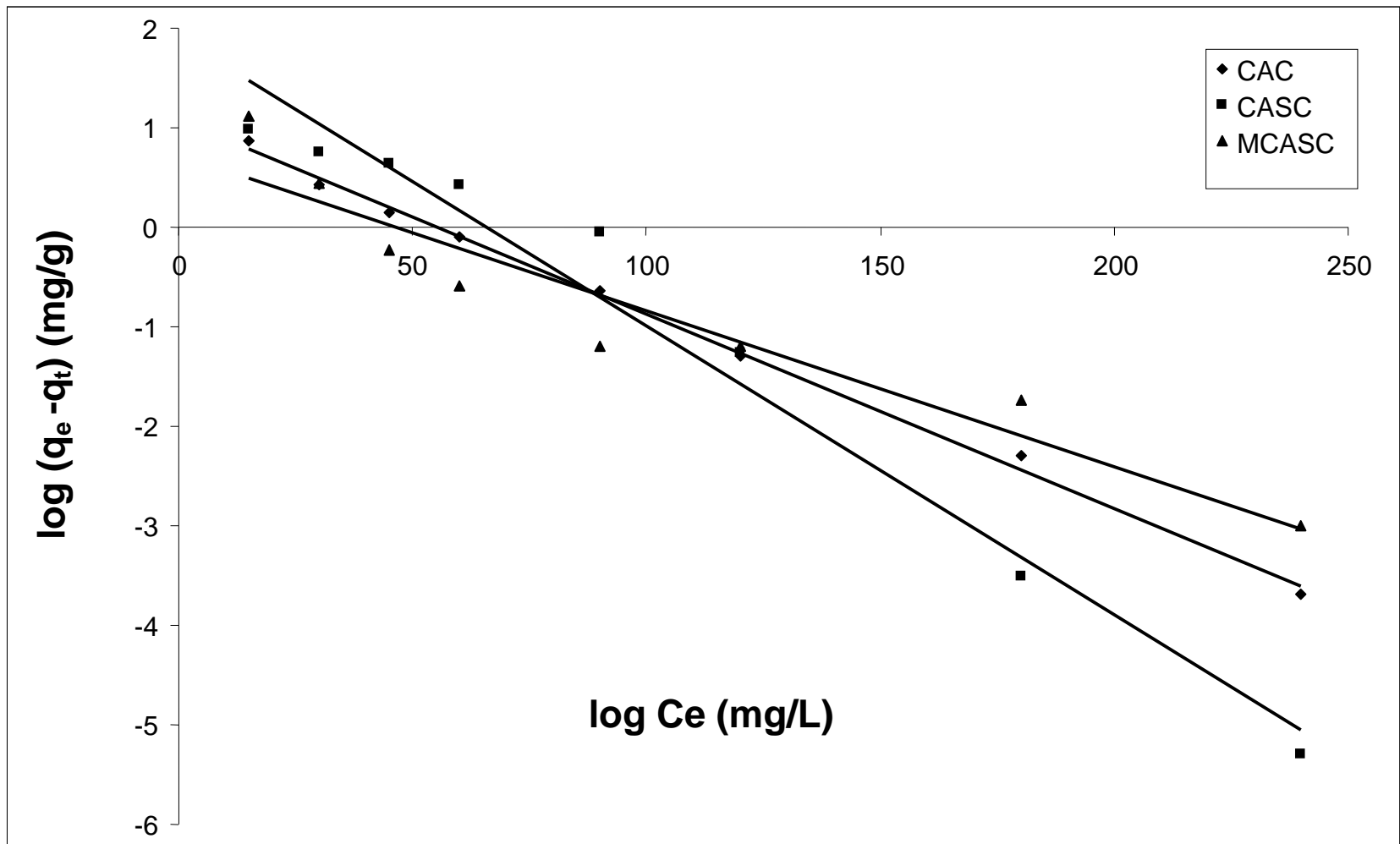
**Figure 4:** Effect of initial concentration on Cd(II) adsorption



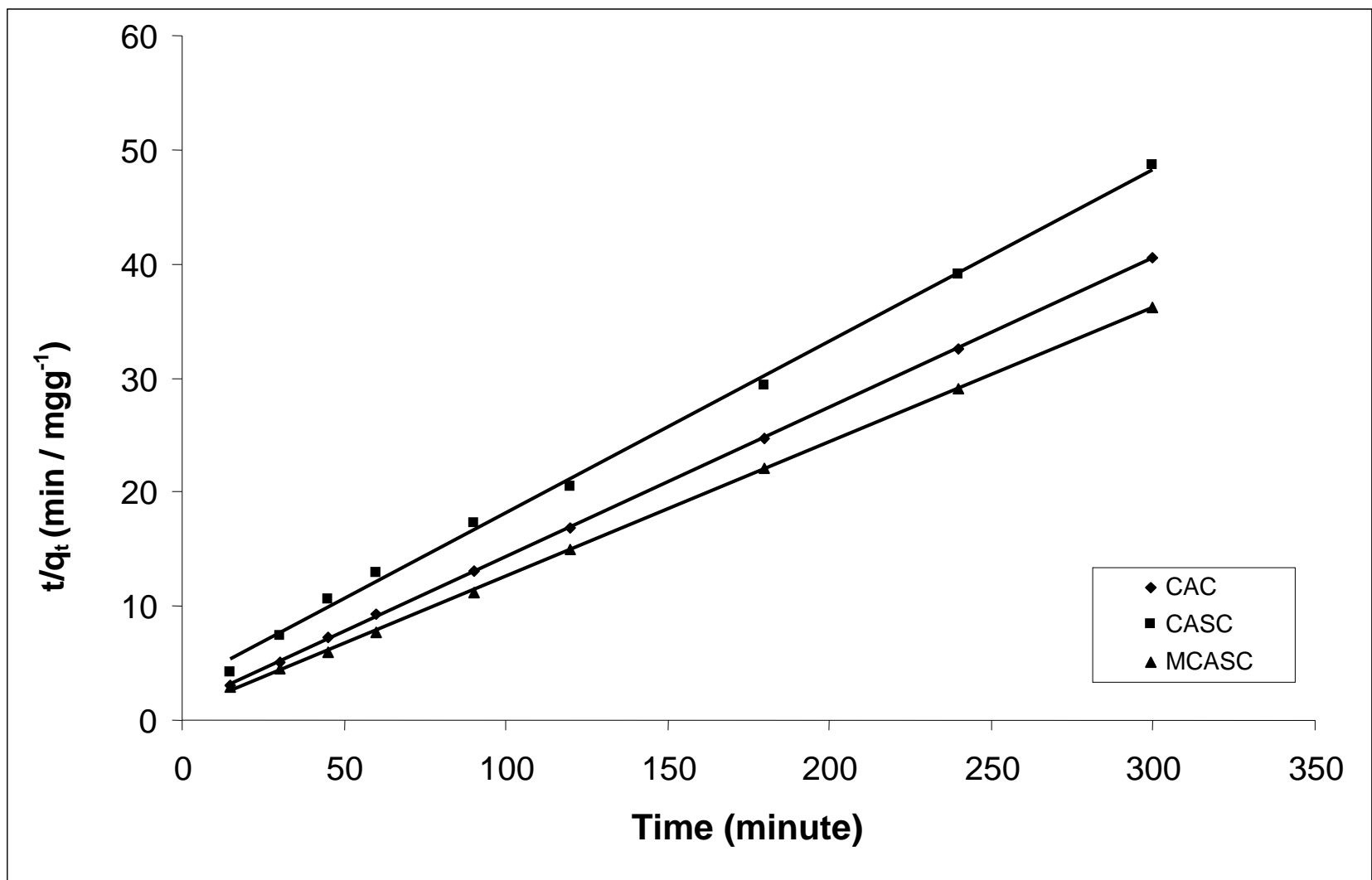
**Figure 5:** Freundlich isotherm for Cd(II) adsorption



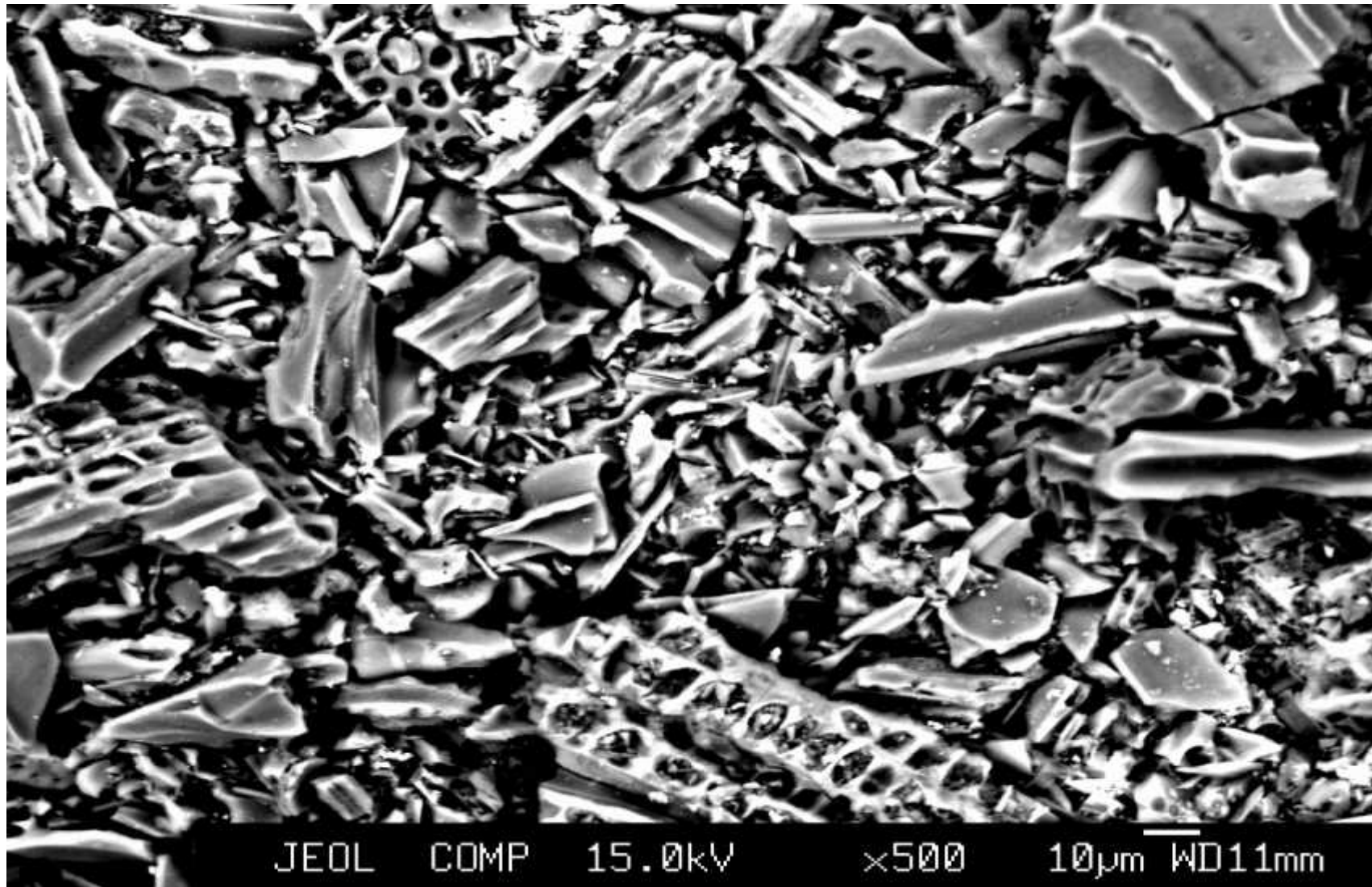
**Figure 6:** Langmuir isotherm for Cd(II) adsorption



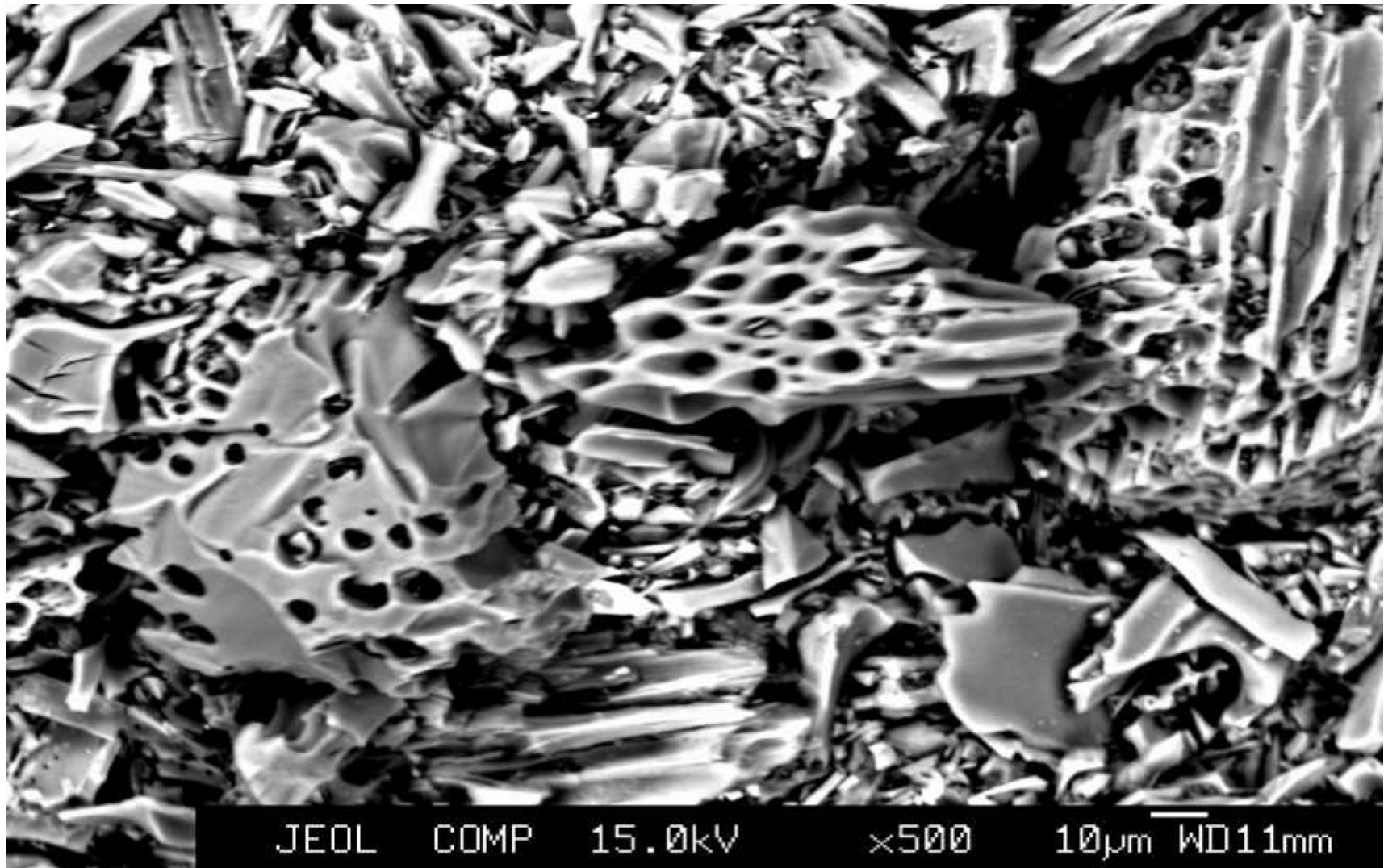
**Figure 7:** Pseudo first order kinetics for Cd(II) adsorption



**Figure 8:** Pseudo first order kinetics for Cd(II) adsorption



**Figure 9:** SEM image of Lapsi (*Choerospondias axillaris*) seed Charcoal



**Figure10:** SEM image of Modified Lapsi (*Choerospondias axillaris*) seed Charcoal

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