# ADSORPTION OF HEAVY METALS FROM AQUEOUS SOLUTIONS ONTO ACTIVATED CARBON PREPARED FROM SLUDGE OF FOOD PROCESSING INDUSTRY

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## ABSTRACT

*The presentwork deals with theapplication of activated carbon for removal of some toxic heavy metals from aqueous solutions. The activated carbon was first prepared from sludge of food processing industryby activating with $ZnCl_2$ for animpregnation time of 20 hours and activation temperature of $300^{\circ}C$ for 75 min. The adsorption of Cu (II), Pb (II), and Cd(II) metal ions onto prepared product was studied and its capabilityto remove heavy metals from aqueous solutionswas assessed.Theadsorption capacity was determined as a function of pH, contact time, initial metal concentrations and adsorbent dosage by batch experiments. The optimum pH values for Cu (II), Cd (II), and Pb (II) ions were 7.0, 6.0 and 7.0 respectively, while the optimum adsorption time determined for all metals was 60 minutes.The adsorption isotherms were determined and compared with the Langmuir and Fruendlich models. The isotherm followed both the models with better correlation to Freundlich. The metal adsorption capacity for Cu (II), Pb (II) and Cd (II) was 5.030 mg $g^{-1}$, 4.498 mg $g^{-1}$ and 6.320 mg $g^{-1}$respectivelyobserved by Langmuir and 0.993 mg $g^{-1}$, 1.275 mg $g^{-1}$ and 0.132 mg $g^{-1}$ respectively by Freundlichmodel. Theadsorption capacity of productwas also compared with commercial activated carbon. Two kinetic models were selected to follow the adsorption processesviz. pseudo-first-order and pseudo-second-order equation. The adsorption of metal ions by the laterequation gave better correlation thanprevious one. The kinetic parameters of bothmodels were calculated and discussed.*
*Keywords: Activated Carbon; Adsorption; Environment; Food Processing; Heavy Metals; Kinetics*

## 1. INTRODUCTION

Heavy metals naturally occur in our environment.Although necessary for human physiology; some heavy metals may be harmful if intake is in large quantities. Other heavy metals are dangerous to humanbody without any benefit.Over the past few decades, rapid growth in the usage of heavy metals in industries has inevitably resulted in an increased flux of metallic substances in the aquatic environment. The persistent and nondegradable nature of these heavy metals caused severe environmental degradation andvarious types of health problems to human beings. Keeping in view the industrial applications and potential pollution impact on the environment, the metals of environmental concern are Pb, Zn, Cu, and Cd.  Lead heads the list of metals of great environmental threats because even at extremely low concentrations it causes brain damage in children [1].Cd is a non-essential, non-beneficial, and highly toxic element to plants and animals [2]. The toxic effects of Cu are well documented by Sobecka[3].

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The destructive impact of metals directs that there is a considerable need to treat industrial effluents containing such heavy metals prior to discharge to protect public health. There are severalways for removalof heavy metals from wastewater such aschemical method, filtration, membrane separation, electrochemical treatment, ion exchange, and adsorption [4 - 8].Except adsorption,all the abovesaid methods are costly,having low output and incapable of removing trace level ofheavy metals from wastewater. Adsorption has been shown tobe a feasible alternative method for removing heavy metalsfrom wastewater. Several adsorbents such as natural and synthetic hydrous solids have been investigated for heavy metal removal. Amongthese, metal oxides [9- 11] and activated carbon [12, 13] are the most extensively used. Theefficacyof activated carbon for metal removalis mainly due to its large micropore and mesopore volumes resulting high surface area. A number of researchers hadworked on the use of activated carbonfor heavy metal removal [14,15] but the high cost of these materials limits their large-scale application for metal adsorption [16].To debarthe limitation, an alternate and economical source for preparation of activated carbon needs to be looked for.Conversion of carbonaceous materials into activated carbon for heavy metals remediation has been reported by many researchers. For example, the use of various waste materials for preparation of activated carbon was reviewed by Dias [17]. Kongsuwan explored the use of activated carbon prepared from eucalyptus bark for sorption of $Cu^{2+}$ and $Pb^{2+}$[18]. Guo revealed that poultry litter-based activated carbon possessed significantly higher adsorption capacity and affinity for heavy metals than commercial activated carbon derived from bituminous coal and coconut shell [19].

The present paper intended to work in the above context using carbonaceous wastefor production of activated carbon. Sludge, generated after wastewater treatment in food processing industry,is rich in carbonaceous organic material and hence has great potential to be converted into activated carbons if pyrolyzed under controlled conditions or with some chemicaltreatment. This conversion will offer the combined benefits of reducing the disposable volume of sludge and producing a valuable adsorbent of lower cost than that of commercial activatedcarbon. Several investigations have been made to prove the feasibility of theconversion of sludge to activated carbon [20-34].

The aim of the present work was to investigate whether activated carbon prepared from sludge of food processingindustry could be used as a suitable alternative of commercial activated carbon for the removal of heavy metals from water and wastewater. The influences of various factors such as pH, contact time, initial metal concentration and adsorbent dose on the removal process werestudied. The experimental equilibrium adsorption data was analyzed by Freundlich and Langmuir isotherm models. The kinetics was evaluated by Lagergrenpseudo first-order and pseudo second-order kinetic models and the rate constants were determined.

## 2. MATERIALS AND METHODS

### 2.1. Materials

The dried sludge was collected from the sludge bed of wastewater treatment plant of Haldiram food processing industry, Nagpur, India.Synthetic stock solutions of heavy metal ions Cu (II), Pb (II), and Cd (II) of 1000 ppm were purchased from Merck. Standard stock solutions were further diluted with deionized water to desired concentrations to obtain test solutions. Allthe other chemicals used were of

analytical grades. Before use, all the glassware were washed with soap, rinsed with nitric acid andthen washed with deionized water. Deionized water was usedto prepare all required solutions.

## 2.2.     Productionof Sludge Based Activated Carbon

The dried sludge from food processing industrywas used as a raw material for preparation of activated carbon (sludge based activated carbon).The method followed for the preparation of activated carbonas developed by Walhof [35].According to this procedure,the raw sludge was first dried in an oven at $110°C$ for 24 h, and then crushed manually. Samples were sieved after crushing to obtain particle sizes smaller than 600 μm. Chemical activation of the sludge was then done using 2N $ZnCl_2$.Slurries of the sludge and activating agent was mixed at $85°C$ for 7 hours with amagnetic stirrer.After chemical activation, samples were dried at $110°C$ for 20 hours and were crushed again into a fine powder. The activated sampleswere exposed to light and humidity (L&H) for 22 hoursand placed into aheating device. The pyrolysis was carried out under flow of nitrogen gas (70 $mlmin^{-1}$) at300°C for 75 min.After completion of the pyrolysis, sample wasremoved and crushed using mortar and pestle.Pyrolysis was followed by rinsing using 500 ml of 1.2 M HCl and 500 ml of distilledwater to remove excess of activating agent and residual inorganic matter. Then the chemically activated product was dried and stored for further batch mode experimentation of heavy metal removal. The characterization of prepared activated carbon was performed in our previous paper.

## 2.3     Batch Mode Adsorption Studies

Effect of several factors such as pH, contact time, initial metalconcentration and adsorbent dose on adsorption of heavy metals on sludge based activated carbon was studied by batch experiments. Adsorption of metals on walls of glass flasks was determined by running blank experiments andfound negligible.Analysis of heavy metal was carried out with the Perkin–Elmer 2280 Atomic Absorption Spectrophotometer (AAS).

## 2.3.1 Batch Studies for Determination of Optimum pH

Solution containing 5 mg $l^{-1}$ copper, cadmium and lead ions each were adjusted to various pH values ranging          from          3.0-10.0          with          0.1N          HNO3          and 0.1 N NaOH. Exactly 100 ml of solution of the above desired concentration was taken in 300 ml BOD bottle          already          containing          5gm          $l^{-1}$activated          carbon by weight.The solution was first agitated for 60 min, then removed and filtered with Whatman No.42 filter paper. Estimations were carried out with Atomic Absorption spectrophotometer. The optimum pH for maximum metal adsorption was selected and utilized for further studies.

## 2.3.2Batch Studies for Determination of Optimum Contact Time

The effect of contact time on solution containingcopper, cadmium and lead was determined at their optimum pH with constant dose of previously selected activated carbon (5gm $l^{-1}$).Six sets of flasks were prepared for each metal having constant metal concentration(5 mg $l^{-1}$) and adjusted to their optimum pH value. Then,5gm $l^{-1}$ of prepared activated carbon was introduced in to each flask and allowed to shake for different period of contact time ranging from 15-90 min.At desired interval of time, one set of each metal's solution was removed and filtered on Whatman No.42 filter paper. Thefiltrate was estimated for their residual metal concentration by Absorption spectrophotometer. The minimum contact time to attain the equilibrium for each metal was determined and applied for further experiments.

### 2.4 Effect of Initial Concentration of Heavy Metal Ions

To outline the effect of initial concentration of the heavy metal ions on the removal percentage, a series of standard solutions with initial concentrations of 5, 10, 15 and 20 mg l$^{-1}$ with optimized pH (around 7.0, 6.0 and 7.0 for copper, cadmium and lead respectively) and adsorbent dose of 5gm l$^{-1}$ were prepared. The solutions were allowed to shake for 60 minutes and treated as earlier and analyzedusing atomic absorption spectrophotometer. The initial metal concentration for maximum adsorption was selected and used in further experiments.

### 2.5 Batch Mode Adsorption Isotherm Studies

To define adsorption isotherms,the batch experiments were conducted at room temperature (30°C) in 300 ml BOD bottles by agitating it on a regular shaking machine. A volume of 100 ml of metal solution of definite concentration (5 mg l$^{-1}$) was adjusted for each metal to the required optimum pH. Then different amounts of prepared activated carbon ranging from 2-10gm l$^{-1}$for copper ion, 1-7gm l$^{-1}$for lead and cadmium ions each were placed on agitator for 60 min ofcontact time. After that, metal solutions were filtered.Filtrates were analyzed to determine residual metal concentration, amount of adsorbate (metal) at equilibrium i.e. $C_e$ (mg l$^{-1}$) and metal removal percentage for each metal. Similar procedure was followed for the commercial activated carbon to compare its metal removal efficacy with that ofprepared activated carbon. Each experiment was duplicated under identical conditions.The amount of adsorption at equilibrium, $q_e$ (mg g$^{-1}$), was calculated by:

$$q_e = (C_0 - C_e) V/W \qquad (1)$$

Where $C_0$ and $C_e$(mg l$^{-1}$) are the liquid-phase concentrations of metal at initial and equilibrium, respectively. Vis the volume of the solution (l), and Wis the mass of dry adsorbent used (g).

### 2.6 Batch Kinetic Studies

The procedures of kinetic experiments were basically similarto those of equilibrium tests. The aqueous samples were takenat preset time intervals and the concentrations of metals were similarlymeasured. The amount of adsorption at time t, $q_t$(mg g$^{-1}$),was calculated by:

$$q_t = (C_0 - C_t) V/W (2)$$

Where $C_0$ and $C_t$(mg l$^{-1}$) are the liquid-phase concentrations of metals at initial and any time t, respectively. Vis the volume of thesolution (l), and Wis the mass of dry adsorbent used (g).

## 3. RESULTS AND DISCUSSION

### 3.1 Results of Batch Mode Adsorption Studies

### 3.1.1 Effect of pH on Metal Adsorption

The pH of the aqueous solution is an important controlling parameter in the adsorption process [36].Each metal has its specific pH for maximum adsorption and this depends on the ion state and nature of adsorbent. In low pH value, binding sites are generally protonated orpositively charged (by the hydronium ions). Thus, repulsion occurs between the metal cation and the adsorbent. At a higher pH value; binding sites startdeprotonating, and makes different functional groupsavailable for metal binding. In general, cation binding increases as pH increases [37, 38].

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The effect of pH on the adsorption of metal is presented in figure 1.It was observed that with the increase in the pH of the solution, the extent of removal increased between pH 3 to 7for copper & lead, pH 3 to 6 for cadmium and attained a maximum removal value of 89.5% for Cu(II), 91.18% for Pb (II) and 38.40% forCd (II). After attaining the optimum pH around 7.0, 6.0 and 7.0 for copper, cadmium and lead respectively, percentage adsorption of metal was decreased. This decrease may be due to the formation of soluble hydroxides resulted in a decrease in the removal of metals by the active sites of the adsorbent[39-42]. Further increase in pH results in increase ofadsorption because of the metal hydrolysis and precipitation. Thus, as the solution pH increased, the onset of the metal hydrolysis and the precipitation began at pH > 6 and the onset of adsorption therefore occurs before the beginning of hydrolysis[36].
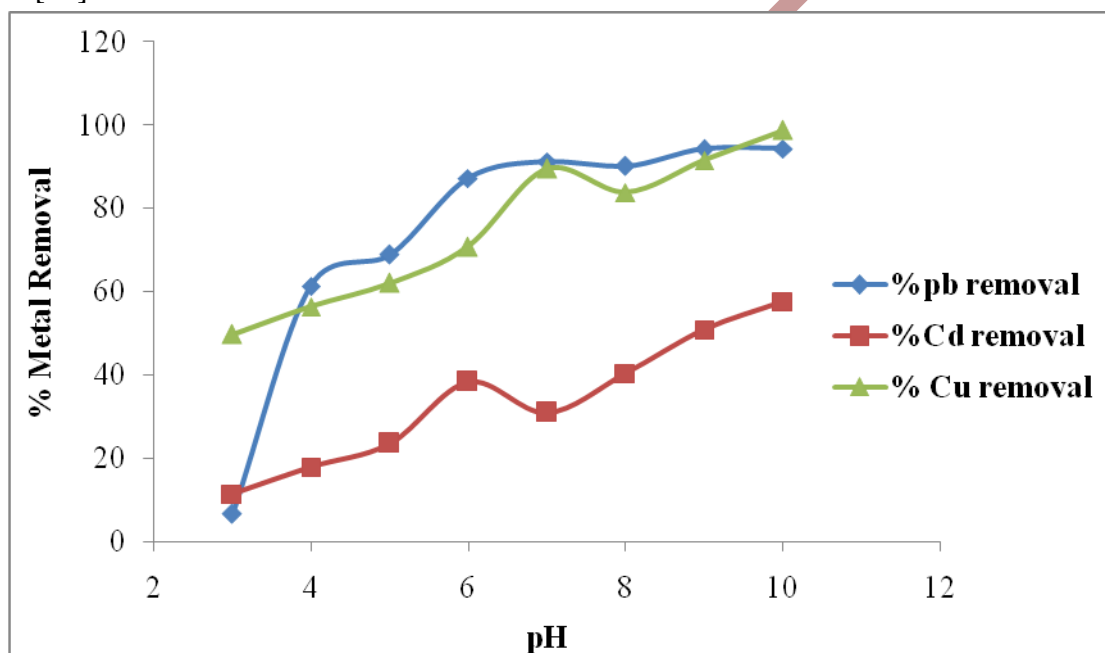


**Figure 1**

### 3.1.2   Effect of Contact Time on Metal Adsorption

Contact time is one of the important parameters for an economical wastewater treatment system [43]. The experimental results relating to the effect of contact time on removal of Pb(II), Cu(II), and Cd(II) are shown in Fig. 2. The results clearly revealed that rate of adsorption are higher in the beginning due to the availability of a large number of active sites on the adsorbent. As these sites are exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles [44].It is clear from the figure that the removal of metal ions increased with increase in agitation time and attained equilibrium in 60 min.The removal efficiency of86.2%, 88.8% and 37.6% onto the prepared activated carbon was observed for Cu (II), Pb (II) and Cd (II) respectively.For further experiment,the contact time of 60 minwas selected for all the considered metals.
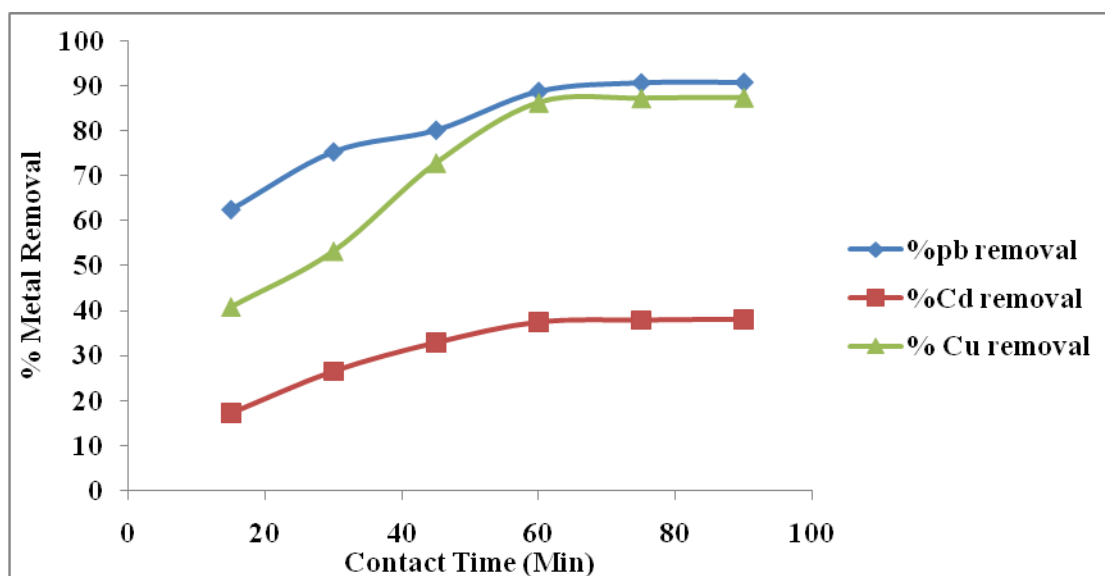
**Figure 2**

### 3.1.3   Effect of Initial Metal Concentration on Adsorption

At constant adsorbent dose (5 gm l⁻), optimized pH(7.0, 6.0 and 7.0 for copper, cadmium and lead ions respectively) and contact time (60 min),the percentage of removal efficiency for each metal decreased with increasing adsorbate concentration from 5 mg $l^{-1}$ to 20 mg $l^{-1}$.This is because at higher metal concentrations, numbers of heavy metal ions were relatively higher compared to availability of adsorption sites.The effect of initial metal concentration on adsorption process is depicted in Fig 3.At lower metal concentration of 5 mg $l^{-1}$, the removal efficiency was 87.4 %, 90.9% and 39.1% for Cu (II), Pb (II) and Cd(II) respectively; however it decreased to 55.0 %,61.2 % and 14.6% as the metal concentration increased from 5 mg $l^{-1}$ to 20 mg l⁻ for the same metalions. It was observed that at higher initial concentration Pb (II) showed greater removal than Cu (II) andCd (II) metal ions. Thus the metal concentration selected for the further experiment was 5mgl⁻¹.
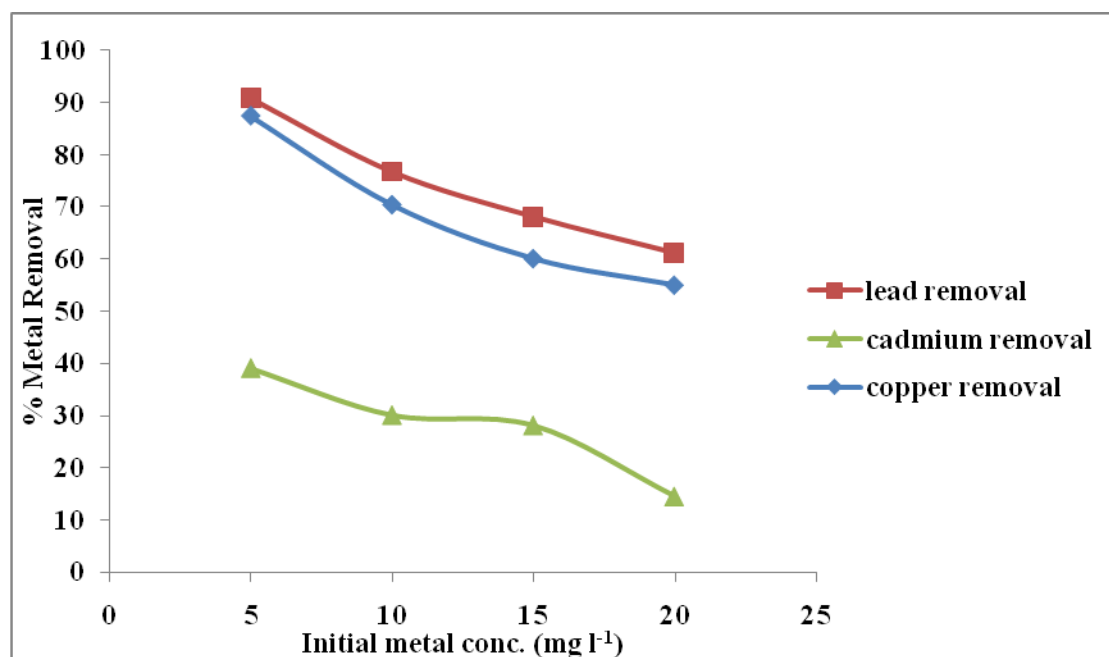
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**Figure 3**

### 3.1.4    Effect of Adsorbent Dose on Metal Adsorption

The key parameter to control both availability and accessibility of adsorption sites for metal adsorption is the adsorbent dose[45]. The effect of adsorbent dosage on the removal of Cu(II), Pb(II) and Cd(II) were presented in Fig. 4, 5 and 6respectively.Results were also compared with the metal removal efficiency of commercial activated carbon. Itcan be clearly seen from the results that the removal efficiency increases as the adsorbent dose increases.This is because with increase in adsorbent mass, the number of binding sites for ions increases. After some point, sorption capacity becamealmost stablein spite ofincrease in adsorbent concentration. This is becauseof adsorbent interactions, such as aggregation, which would lead to decrease in total active surface area of the sorbent.Metal removal efficiency increases for Cadmium from 10.7 to 46.3%, for Copper 64.0 to 92.2%, and for lead 48.2 % to92.3% as the adsorbent mass increases from 1-7gm $l^{-1}$,2-10 gm $l^{-1}$ and 1-7gm $l^{-1}$for Cd, Cu and Pb respectively. Although there is a great increase in metal removal efficiency for all the considered metals with increasing adsorbent dose but adsorption density decreased e.g. from 0.533 to 0.330mg $g^{-1}$ for Cadmium,1.601 to0.461mg $g^{-1}$ for Copperand 2.409 to 0.659 mg $g^{-1}$ for Lead.The dataalso reveals that the rate of adsorption gradually decreases with increasing adsorbent mass.The metal removal efficiencyof adsorbent indicates that the prepared activated carbon has much affinity towards lead than copper and cadmium.
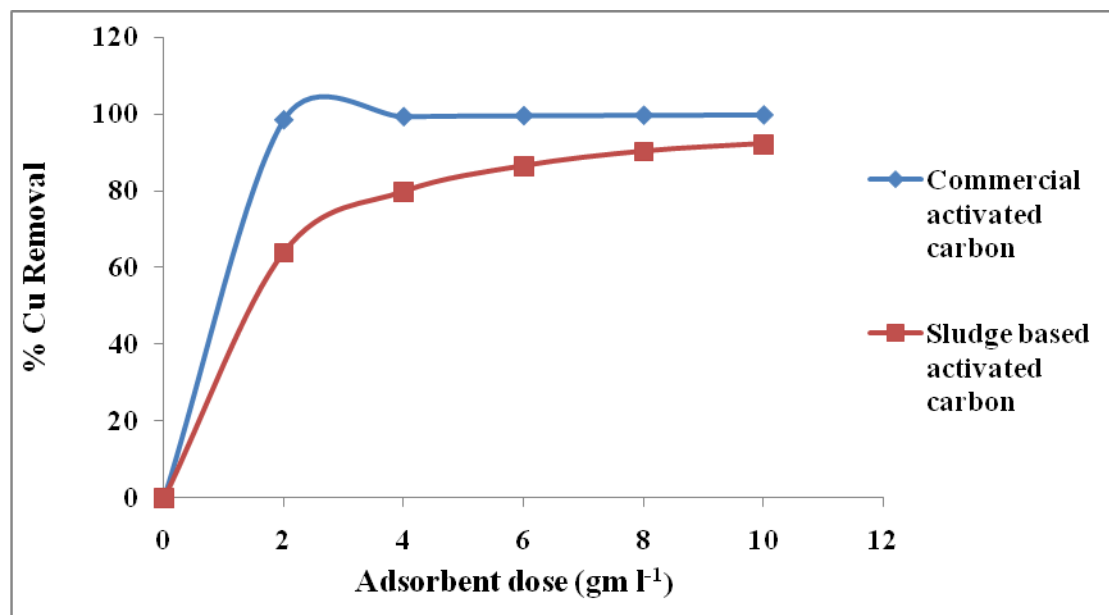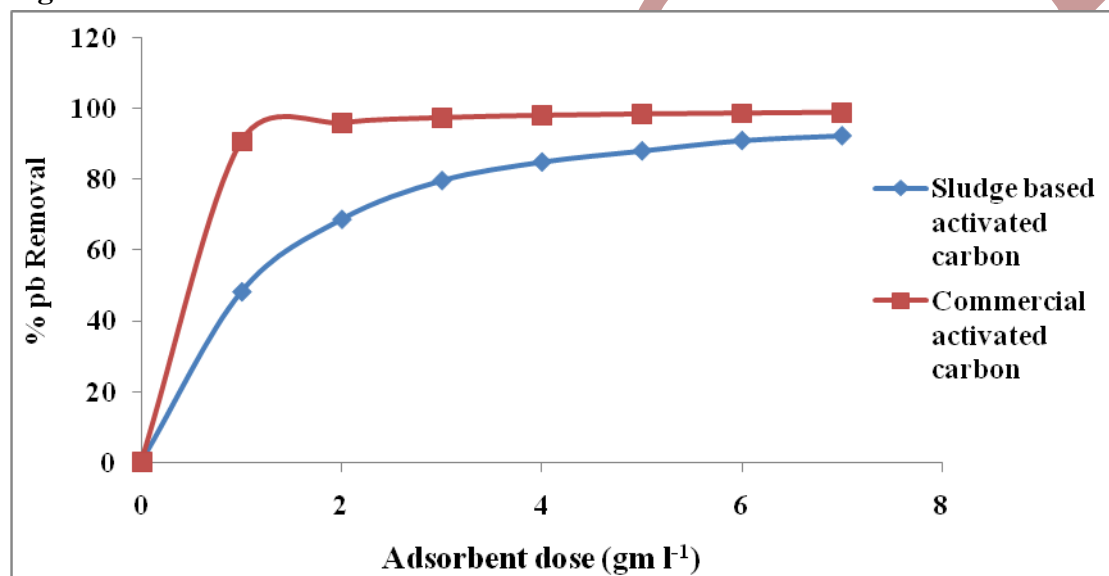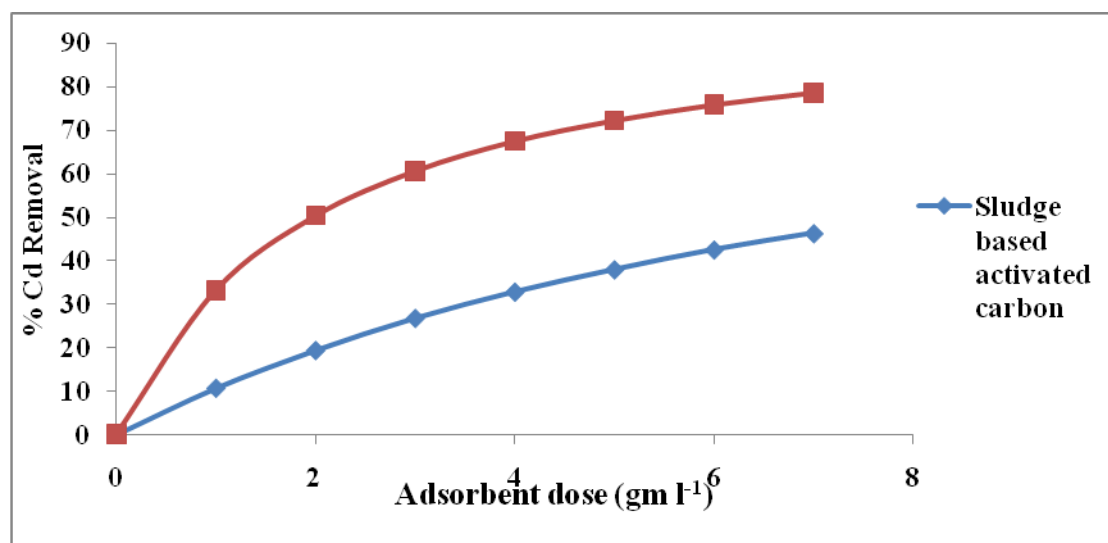
**Figure 4**



**Figure 5**

**Figure 6**

## 3.2    Results of Adsorption Isotherm Studies

An adsorption isotherm is a graphical representation showing the relationship between the amount adsorbed by a unit weight of adsorbent and the amount of adsorbate remaining in a test medium at equilibrium. It maps the distribution of absorbable solute between the liquid and solid phases at various equilibrium concentrations[46].The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose [47]. Adsorption isotherm is basically important to describe how solutes interact with adsorbents, and is critical in optimizing the use of adsorbents.

The distribution of metal ions between the liquid phase and the solid phase can be described by several mathematical model equations as the standard models are Langmuir and Freundlich isotherm model [48]. The Langmuir model assumes that the uptake of metal ions occur on a homogenous surface by monolayer adsorption without any interaction between adsorbed ionswhile Freundlich model concedes that the uptake of metal ions occur on a heterogeneous surface by monolayer adsorption.The Freundlich model is perhaps the most popular adsorptionisotherm model for a single solute system and is an empirical relation equation based on the distribution of solute between the solid phase and aqueous phase at equilibrium [49].

In the present work both the Langmuir and Freundlich adsorption isotherm models were applied to determine the metal adsorption onto activated carbon prepared from sludge of food processing industry.The applicability of the isotherm equations are compared by judging the correlation coefficients, $R^2$.

### 3.2.1. Langmuir Isotherm

The linear form of Langmuir's isotherm model is given bythe following equation:

$$C_e/q_e = 1/(Q_0 b) + (1/Q_0)C_e \qquad (3)$$

Where $C_e$ is the equilibrium concentration of the adsorbate (Metals)($mgl^{-1}$), $q_e$ the amount of adsorbate adsorbed per unit mass of adsorbent($mg\ g^{-1}$), and $Q_o$ and bare Langmuir constants relatedto adsorption capacity and rate of adsorption, respectively. When $C_e/q_e$ was plotted

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against $C_e$, straight line with slope $1/Q_o$ was obtained, indicating that the adsorption of metals on activatedcarbon follows the Langmuir isotherm. The Langmuir isotherm plots of Cu (II), Pb (II) and Cd (II) was depicted in figure 7.The Langmuir constants 'b' and '$Q_o$' were calculated from this isotherm andtheir values are given in Table 1.
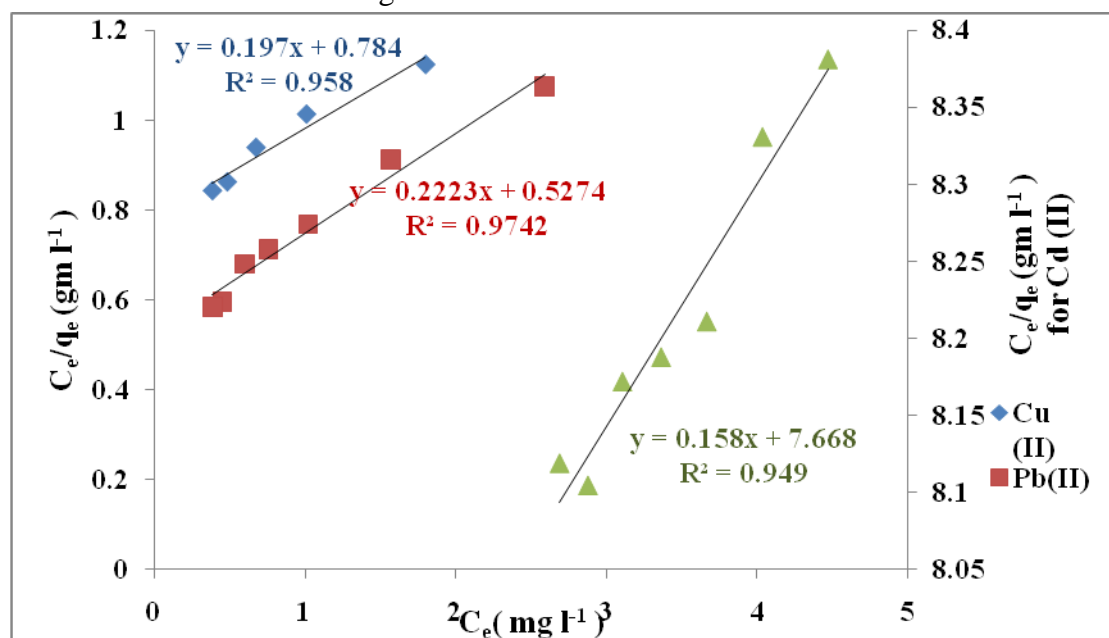


**Figure 7**

**Table 1**

| Isotherm parameters | Langmuir isotherm for sludge based activated carbon | | | Langmuir isotherm for commercial activated carbon | | |
|---|---|---|---|---|---|---|
| | Cu(II) | Pb(II) | Cd(II) | Cu(II) | Pb(II) | Cd(II) |
| $Q_o$(mg g$^{-1}$) | 5.0 | 4.5 | 6.3 | 11.4 | 14.1 | 21.7 |
| b (mg$^{-1}$) | 0.252 | 0.422 | 0.021 | 3.609 | 1.035 | 0.025 |
| $R^2$ | 0.9586 | 0.9742 | 0.9493 | 0.9914 | 0.9922 | 0.9960 |
| $R_L$ | 0.442 | 0.322 | 0.907 | 0.053 | 0.162 | 0.890 |

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter ($R_L$) [50], which is defined by:

$$R_L = 1/ (1+bC_0) \qquad (4)$$

where bis the Langmuir constant and $C_0$is the highest metal concentration (mg l$^{-1}$). The value of $R_L$ indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). Value of $R_L$ was found to be 0.442, 0.322 and 0.907 for Cu (II), Pb (II) and

Cd (II) respectively, confirmed that the activated carbon is favorable for adsorption of metals under the conditions used in thisstudy.

### 3.2.2. Freundlich Isotherm

The well-known logarithmic form of Freundlich model is given by the following equation:

$$\log q_e = \log K_F + (1/n) \log C_e \qquad (5)$$

Where $q_e$ is the amount adsorbed at equilibrium (mg g$^{-1}$), $C_e$ the equilibrium concentration of the adsorbate (metals) and $K_F$ and nare Freundlich constants, ngives an indication of how favorable the adsorption process and $K_F$ (mg g$^{-1}$) is the adsorption capacity of the adsorbent. $K_F$ can be defined as the adsorption or distribution coefficient and represents the quantity of metal adsorbed onto activated carbon adsorbent for a unit equilibrium concentration. The slope 1/nranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [51]. A value for 1/nbelow one indicates a normal Freundlich isotherm while 1/nabove one is indicative of cooperative adsorption[52]. The plot of log $q_e$ versus log $C_e$ gives straight lines with slope '1/n',which shows that the adsorption of all studied metals follows the Freundlich isotherm. The isothermplot for heavy metal adsorption onto sludge based activated carbon was given in figure 8.From the adsorption isotherms of all the studied metals, Freundlich constants ($K_F$ and n) were calculated and recorded in Table 2.
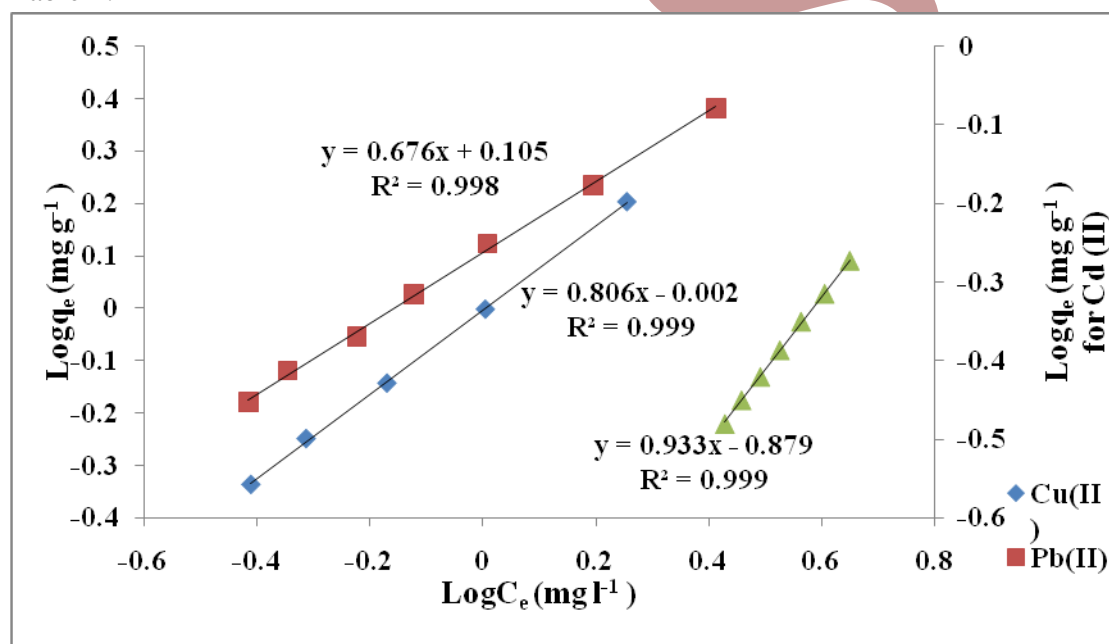


**Figure 8**

**Table 2**

| Isotherm parameters | Freundlich isotherm for sludge based activated carbon | | | Freundlich isotherm for commercial activated carbon | | |
|---|---|---|---|---|---|---|
|  | Cu(II) | Pb(II) | Cd(II) | Cu(II) | Pb(II) | Cd(II) |

| | | | | | | |
|---|---|---|---|---|---|---|
| **1/n** | 0.8064 | 0.6765 | 0.9336 | 0.8987 | 0.8505 | 0.9538 |
| **$K_F$ (mg g$^{-1}$)** | 0.993 | 1.275 | 0.132 | 25.362 | 9.139 | 0.527 |
| **$R^2$** | 0.9997 | 0.9985 | 0.9996 | 0.9990 | 0.9974 | 0.9999 |

TheLangmuir monolayer adsorption capacities, $Q_0$were foundto be5.03mg g$^{-1}$ for Cu (II), 4.50 mg g$^{-1}$for Pb(II), and 6.32 mg g$^{-1}$forCd (II)while the Freundlichadsorption capacities,$K_F$was found to be 0.993 mg g$^{-1}$for Cu (II),1.275 mg g$^{-1}$for Pb(II), and 0.132 mg g$^{-1}$for Cd (II).The value of correlation coefficient indicates that Freundlich model yields a somewhat better fit ($R^2$=0.9997, 0.9996 and0.9985 for Cu (II), Cd (II), and Pb (II)respectively) than the Langmuir model ($R^2$= 0.9586, 0.9742 and 0.9493 for Cu (II),Pb(II), and Cd (II)respectively).Analogous results were obtained byTan and Deo[53] stated that Freundlich equation generally gives better correlation than the Langmuir equation for heavy metals.

The value of Freundlich adsorption capacity of adsorbent ($K_F$)also indicates that the prepared adsorbent was suited better for Pb (II) than Cu (II) and Cd (II).As also illustrated in Table 2, the value of 1/$n$ is 0.8064, 0.6765 and 0.9336for Cu (II), Pb (II) and Cd (II) respectively which is less than one,indicates normal Freundlich adsorption isotherm [54].

The nature of isotherm for sludge based activated carbon was also compared with the commercial activated carbon. For Cu (II), Pb (II) and Cd (II),the Langmuir isotherm ispresented in figure9andthe Freundlich isotherm is in figure10.Langmuir constants (b and $Q_0$)and Freundlich constants ($K_F$ and n) were calculated and given in table 1 and 2.The nature of the isotherm and slope, which is less than one, indicates the same adsorption pattern for both sludge based activated carbon and commercial activated carbon.The value of correlation coefficients shows that the Freundlich model yields a somewhat better fit for commercial activated carbon than the Langmuir model, which is similar to the results obtained for sludge based activated carbon.
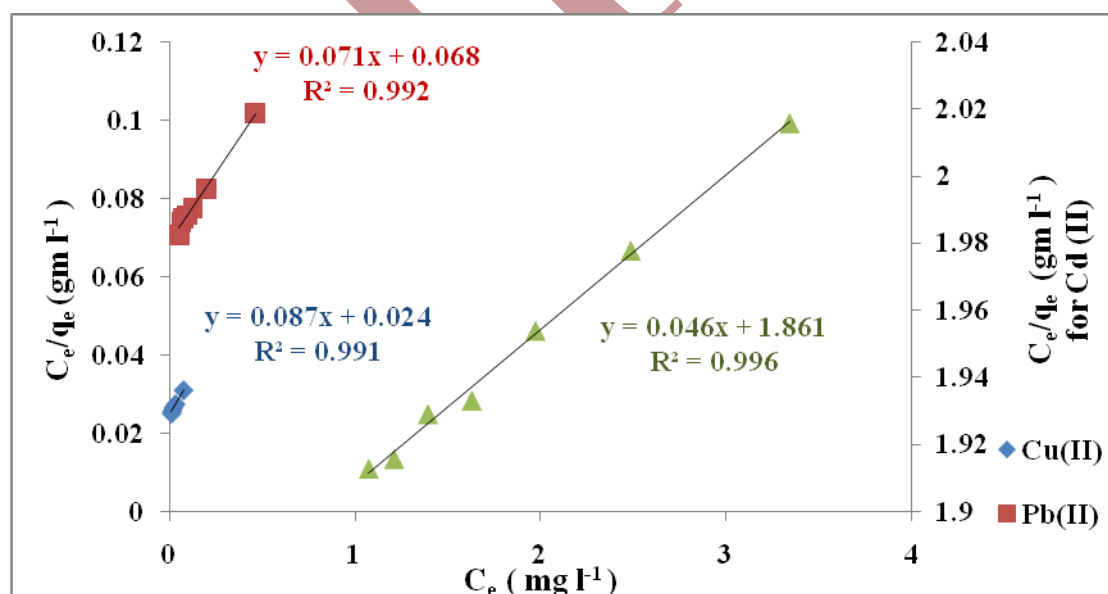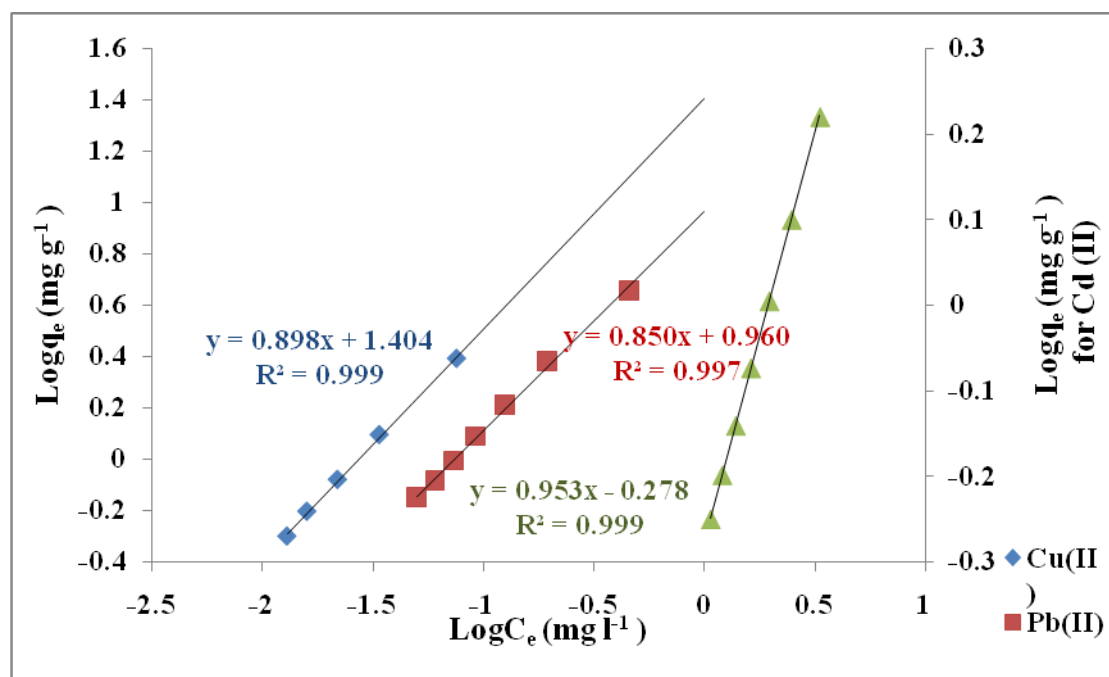


**Figure 9**

**Figure 10**

## 3.3 Kinetic Modeling of Heavy Metal Adsorption

The study of sorption kinetics describes the adsorbate uptake rate and evidently this ratecontrols the residence time of adsorbate at the solid liquid interface.Determination of adsorption kinetics is a good technique to predict the behavior of adsorption over the whole range of removal process. The kinetics of metal ion sorption on prepared activated carbon was analyzed using two kinetic models viz. the Lagergren pseudo-first order[55] and pseudo-second order [56] equations.

## 3.3.1 The Pseudo-First Order Equation

The Lagergrenpseudo-first order equation [55] is generally expressed as:

$\log(q_{e} - q_{t}) = \log q_{e} - k_{ad}t$ (6)

Where $q_{e}$ and $q_{t}$ are the sorption capacities (mg g$^{-1}$) at equilibrium and at time t,respectively. $k_{ad}$ is the rate constant of pseudo-first order sorption (min$^{-1}$). When the values of log ($q_{e} - q_{t}$) were linearly correlated with t, the plot of log ($q_{e} - q_{t}$) versust will give a linear relationship out of which $k_{ad}$ and $q_{e}$ can be determined from the slope andintercept of the graph, respectively. The plot of Lagergren first order kinetics for all the metal ions is presented in figure 11. The values of $k_{ad}$,$q_{e}$ and correlation coefficient $R^{2}$derived from pseudo-first order equation are given in Table 3.
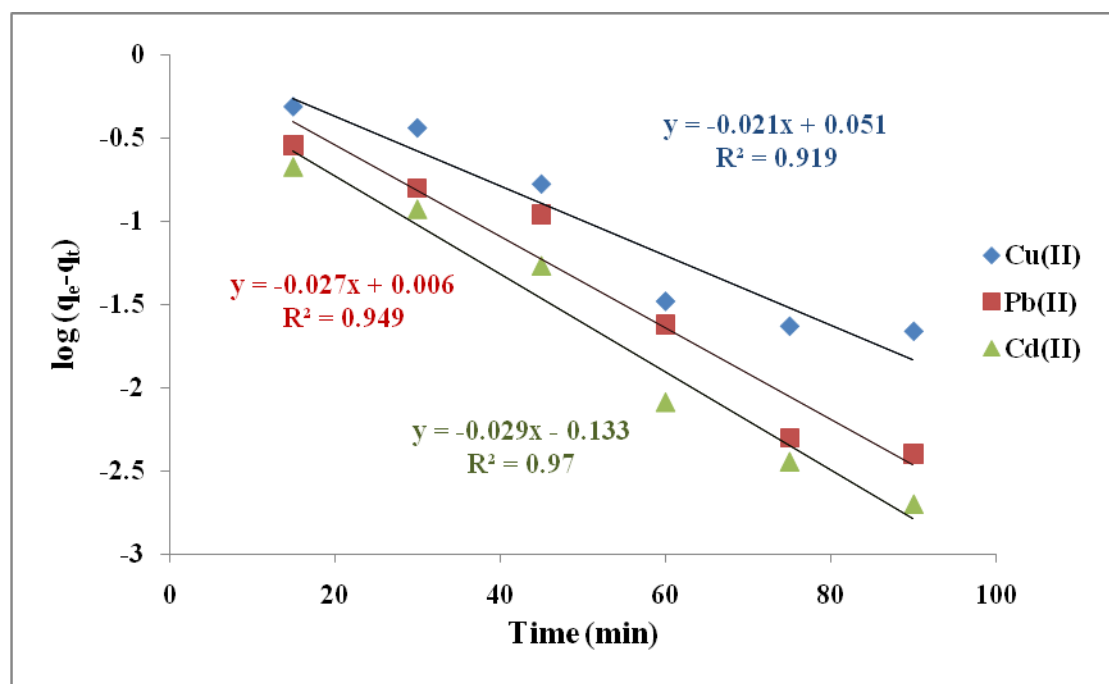
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**Figure 11**

**Table 3**

| Metals | $qe_{exp}$ (mg g$^{-1}$) | Langergren first-order | | | pseudo second-order | | |
|---|---|---|---|---|---|---|---|
| | | Kad (x 10$^{-2}$ min$^{-1}$) | $qe_{cal}$ (mg g$^{-1}$) | $R^2$ | $K_1$ (x 10$^{-2}$ g.mg$^{-1}$.min$^{-1}$) | $qe_{cal}$ (mg g$^{-1}$) | $R^2$ |
| Copper | 0.895 | 2.10 | 1.125 | 0.9192 | 2.60 | 1.225 | 0.9701 |
| Lead | 0.912 | 2.75 | 1.014 | 0.9493 | 9.71 | 1.018 | 0.9980 |
| Cadmium | 0.384 | 2.95 | 0.735 | 0.9700 | 1.89 | 1.000 | 0.9864 |

### 3.3.2 The Pseudo- Second Order Equation

The pseudo-second order chemisorption kinetic equation [56] is expressed as,

$1/q_t = 1/ (k_1 q_e^2) + t/q_e$ (7)

Where $q_e$ and $q_t$ are the sorption capacity at equilibrium and at time t, (mg g$^{-1}$) respectively and $K_1$ is the rate constant of the pseudo-second order sorption (g mg$^{-1}$ min$^{-1}$). Equation 7 can be rewritten as,

$1/q_t= 1/h + t/q_e$ (8)

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Where $h = k_1 q_e^2 (mgg^{-1}min^{-1})$ can be regarded as the initial sorption rate

If the pseudo-second order kinetics is applied to the experimental data, the plot of $t/q_t$ versus $t$ of equation (8) should give a linear relationship out of which $q_e$, $k_1$ and $h$ can be determined from the slope and intercept of the plot respectively. The plot of second order kineticsfor all the metals is presented in figure 12. The linear plots show a good agreement between experimental and calculated $q_e$ values (Table 3). The values of $k_1$, $q_e$ and correlation coefficient $R^2$ derived from pseudo-second order equation are given in Table 3.
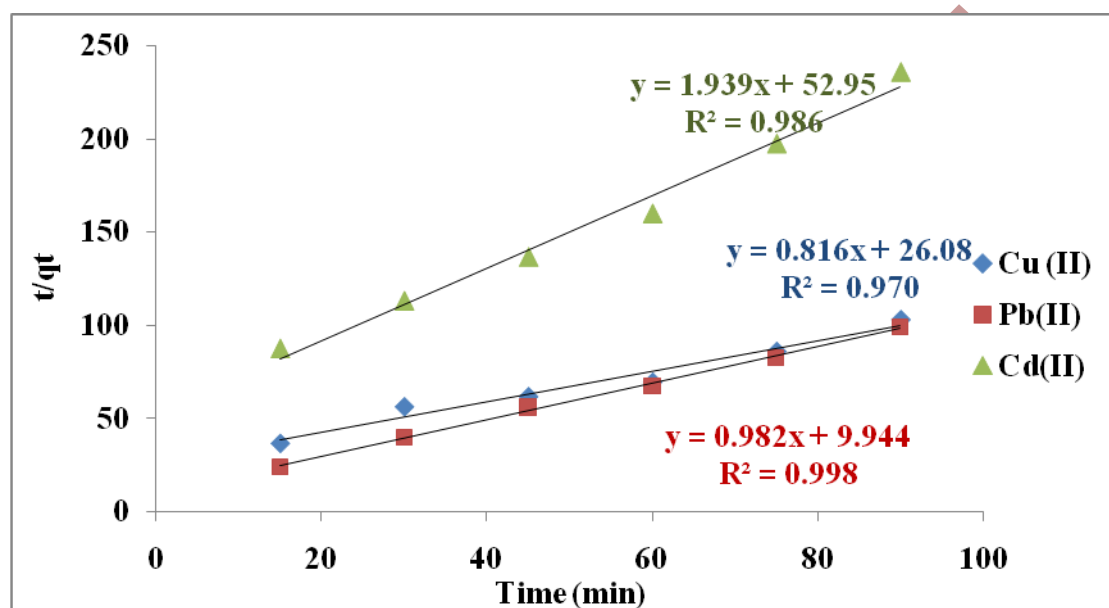


**Figure 12**

In the present study, it was found that the pseudo second-order kinetic model provided the better description of the data obtained as shown in the higher values of correlation coefficients ($R^2 = 0.9701$, 0.9980 and 0.9864 for Cu (II),Pb(II), and Cd (II)respectively) than the Lagergren first order kinetic models ($R^2 = 0.9192$, 0.9493 and 0.9700 for Cu (II),Pb(II), and Cd (II)respectively). The higher correlation coefficient for the second-order kinetic model indicatesthe applicability of this kinetic equation and the second-order nature of the adsorption process of metals on sludge based activated carbon.

## 4.    CONCLUSION

The present study reveals the feasibility of activated carbon, preparedfrom sludge of food processing industry by direct chemical activation with $ZnCl_2$, asan adsorbent for the removal of heavy metals (Cu (II), Pb (II) and Cd (II))from aqueous solution. It was observed that the adsorption performance of prepared adsorbent excelled for Pb (II) than Cu (II) and Cd (II) butcould be appliedfor heavy metal removal from wastewater streamfor purification process. The results show that the metal removal efficiency was controlled by solution pH,initial metal concentration, adsorbent dosage, and agitation times. The optimum adsorption conditions were as follow: the pH range 6.0–7.0, the equilibrium time was 60 min, initial metal concentration was 5 mg $l^{-1}$and adsorbent dosage was not less than 8 g$l^{-1}$ for

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Cu(II),7                    gl$^{-1}$                    for                    Pb(II)                    and 7 gl$^{-1}$ for Cd (II) in order to achievepercent removalefficiency of 90.26 %, 92.30 % and 46.30%respectively. Metal adsorption behavior was explained by both Freundlich and Langmuir adsorption isotherms. Freundlich model gives a better correlation than Langmuir model with an adsorption capacity of 0.993 mg g$^{-1}$, 1.275 mg g$^{-1}$ and 0.132 mg g$^{-1}$for Cu (II), Pb (II) and Cd (II) respectively,The isotherm data were also compared with commercial activated carbon and found suitable in the adsorption process but the extent of adsorption is applicable at lower concentrationsonly. The kinetics of adsorption was determined by pseudo-first order and pseudo-second order equations. The pseudo second-order model provided better description for the obtained experimental data than first order kinetic models as shown by correlation coefficients. Finally,the activated carbon prepared from sludge of food processing industry appears to be economical and effective for heavy metal adsorption and is applicable in water and wastewater treatment processes.

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