

## Removal of Cadmium(II) Onto Granular Activated Carbon And Kaolinite Using Batch Adsorption

Dr.Jenan A. Al-Najar\*, Dr. Ramzy S. H\* & Dr. Zaydoon M. S.\*

Received on: 22/7/2009

Accepted on:16/2/2010

### Abstract

The removal of Cd(II) onto granular activated carbon (GAC) and kaolinite in single component systems has been studied using batch adsorption. Batch adsorption studied were carried out under various amount of GAC and Kaolinite, Cd(II) ion concentration, pH and contact time. The experimental data was analyzed by Langmuir, Freundlich and Redlich-Peterson isotherms. The equilibrium adsorption capacity of Cd(II) was determined from Langmuir isotherm equation and found to be 3.002 mg/g for GAC and 1.837 mg/g for kaolinite. Pore diffusion model for batch adsorption is used to predict the concentration-decay curve for adsorption of Cd(II) onto GAC and kaolinite.

**Keywords:** Adsorption, GAC, Kaolinite Isotherm, Pore diffusion model

### ازالة الكاديوم باستخدام الكربون المنشط الحبيبي والكاولينات بواسطة الامتزاز في عملية دفعية

#### الخلاصة

تم دراسة ازالة الكاديوم بواسطة الامتزاز على الكربون المنشط الحبيبي وطين الكاؤولينات كمواد ممتازة في عملية دفعية. البحث يتضمن دراسة تاثير وزن المادة، الممتزة، تركيز الكاديوم، حامضية المحلول، زمن التماس ودرجة الحرارة على عملية ازالة الكاديوم. النتائج المختبرية تم تحليلها باستخدام معادلة لانكماير، معادلة فرنديلج ومعادلة ريدلج بيترسون. تم مطابقة النتائج العملية للطرق الثلاث المستخدمة ووجد ان معادلة لانكماير اعطت اكثر تطابق من معادلات الاتزان الاخرى والتي استخدمت لحساب سعة الامتزاز ووجد انها 3.002غم/ملغ في حالة استخدام الكربون المنشط و 1.837غم/ملغ في حالة استخدام الكاؤولينات. استخدم موديل رياضي لتمثيل عملية الامتزاز في عملية دفعية.

### 1. Introduction

The main sources of toxic metals are industrial wastes from processes such as electroplating, metal finishing, chemical manufacturing and nuclear fuel processing. The increasing levels of heavy metals that are discharged to the environment represent a serious threat to

human health, living resource and ecological system [1]. Since most of heavy metals are non degradable into nontoxic metals end products, these concentration must be reduced to acceptable levels before discharged them into environment. Otherwise these could pose threat to public health and/or affect the quality of

potable water [2]. According to the World Health Organization (WHO) the most toxic metals are aluminum, chromium, magnesium, iron, cobalt, nickel, copper, zinc, cadmium, mercury and lead. Cadmium is introduced into nature water from plating, cadmium-nickel batteries, phosphate fertilizer and alloy industries. The drinking water guideline value recommended by World Health Organization (WHO) is 0.005 mg Cd(II)/ l [3].

Adsorption is one the most commonly methods used to remove heavy metal ions from various aqueous solution [4]. Adsorption by activated carbon has been widely studied as an effective technique for removing heavy metal from aqueous solution and wastewater. The clay minerals such as kaolinite play an important role in the environment by acting as a natural remover of pollutants from water through both adsorption and ion exchange mechanisms [5].

The aim of the present work is used to study the adsorption capacity of both GAC and kaolinite for adsorption of Cd(II) by determining the equilibrium isotherm. The effect of weight of adsorbent, pH, concentration of Cd(II), contact time and temperature was also studied. Pore diffusion model for batch adsorption is used to determine the concentration-decay curve for the adsorption of Cd(II) by GAC and kaolinite.

## 2. Mathematical Model

In the present work pore diffusion model (PDM) is used to describe the adsorption of single metal ion adsorbed onto porous media in batch adsorber. Film and intraparticle transport are the major factors controlling rates of adsorption of

solute by porous adsorbents. Transfer of solute across the film can only occur by molecular diffusion. Once a solute molecules reaches the opening of a pore at the particle surface it must be diffuse through the liquid which fills a typically tortuous network of interconnected pores. Two major resistance to mass transfer should be considered: the external resistance in the liquid phase and internal resistance in the solid phase [6].

The following assumptions are made to formulate the pore diffusion model :

- Assuming linear driving force describes the liquid film transport resistance at the outer surface of the particle.
- The equilibrium of the adsorption is described by Langmuir isotherm.
- The adsorbent particles are assumed to be homogeneous solid and identical spheres.
- The intraparticle mass is characterized by the pore diffusion coefficient,  $D_p$ .
- Surface diffusion is neglected contribution to mass transfer.

The adsorption mechanism is describe as follows:

1. Assuming linear driving force, the film transport from the solution bulk to the adsorbent particle surface measured by the external mass transfer coefficient  $k_f$  [7] as:

$$V \frac{dC_b}{dt} = k_f A (C_b - C_s) \quad \dots \quad (1)$$

where

$$A = \frac{3W}{r_p R_p}$$

The following initial conditions are considered:

$$\text{I.C.: } C_b = C_{b0} \quad t = 0$$

The external mass transfer coefficient  $k_f$  is estimated from the theoretical boundary layer studies in term of system parameter [8]. Williamson et.al [9] suggested two correlations as:

$$\frac{k_f}{n_s} Sc^{-0.58} = 2.4 Re^{-0.66} \quad (2)$$

for  $0.08 < Re < 125$

$$\frac{k_f}{n_s} Sc^{-0.58} = 2.4 Re^{-0.31} \quad (3)$$

for  $125 < Re < 5000$

where

$$Sc = \frac{m}{rD_l}, \quad Re = \frac{rd_p n_s}{em}$$

2. Intraparticle transport involves two mass transfer processes, pore and surface diffusion which act in parallel. The mass balance equation describing both pore and surface diffusion for a spherical particles giving below:

$$e_p \frac{\partial C}{\partial t} + r_p \frac{\partial q}{\partial t} - e_p D_p \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial C}{\partial r}) + r_p \frac{D_s}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial q}{\partial r}) = 0 \quad (4)$$

Assuming pore diffusion, then equation (4) reduces to:

$$e_p \frac{\partial C}{\partial t} + r_p \frac{\partial q}{\partial t} - e_p D_p \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial C}{\partial r}) = 0 \quad (5)$$

The initial and boundary conditions are:

$$\text{I.C.: } C = 0, q = 0 \quad t = 0 \quad 0 < r < R$$

$$\text{B.C.: } \frac{\partial C}{\partial r} = 0, \quad \frac{\partial q}{\partial r} = 0 \quad r = 0,$$

$$e_p D_p \frac{\partial C_p}{\partial r} = k_f (C_b - C_s) \quad r = R_p$$

Where  $C_b$  and  $C$  are the solute concentration in the bulk liquid and particle phase respectively.

Equilibrium exists between the solid and liquid phase solute concentration at the interface. It is described by non linear isotherm such Langmuir and Freundlich isotherm.

$$q_e = \frac{abC_s}{1 + bC_s} \quad (6)$$

$$q_e = KC_e^{1/n} \quad (7)$$

Equations 1 and 2 with the initial and boundary conditions are solved numerically using a numerical computer program in MATLAB v.7 to give the bulk concentration of the solute as a function of time and the results expressed as a concentration decay ratio  $C/C_0$  as a function of time. The principle parameters required for use the program are the external mass transfer coefficient  $k_f$  and the pore diffusion coefficient  $D_p$ . The external mass transfer coefficient  $k_f$  can be obtained by the numerical solution for equation 1:

$$k_f = \frac{R_p r_p V}{3Wt} \ln \left( \frac{C_t}{C_0} \right) \quad (8)$$

The following condition is used to obtain  $k_f$  :

$$t = 0, \quad C_s = 0, \quad C_b = C_o$$

pore diffusion coefficient is obtained by matching between the theoretical and experimental concentration decay curves by minimizing the differences between the two curves.

### 3. Experimental Work and Procedure

*Adsorbate:* Standard stock solution of Cd(II) is prepared by dissolving  $Cd(NO_3)_2 \cdot 4H_2O$  in distilled water. The chemicals used are annular grade produced by Fluka and Aldrich-Sigma.

*Adsorbent:* The adsorbents used are granular activated carbon (GAC) and kaolinite, which were supplied by Sigma-Aldrich.Com., United Kingdom. These adsorbents were used directly without any treatment. The mean diameter of the GAC particles is 0.5 mm and kaolinite 0.005 mm. Kaolinite used was powdered. The physical properties of both GAC and kaolinite were measured by Thermochemistry Laboratory, Chemical Science (FH&MS), University of Surrey, United Kingdom and are presented in Table 1 and 2 respectively.

All the experiments were adjusted at initial pH of 5 for Cd(II) which was determined experimentally. The pH values were adjusted with 0.1M NaOH and 0.1M HCl. The temperature was controlled with a water bath at a temperature of 25°C for all studies.

The following experiments were carried out:

#### 3.1 Methods

##### 3.1.1 Equilibrium isotherm studies

A volume of 10 ml of Cd(II) solution with a concentration in the range 50-500

mg/l was placed in test tubes. An accurate mass 0.5g of each GAC and kaolinite was then added to the solution. The test tubes were then shaken at a constant speed of 250 r.p.m. in a shaking water bath at 25°C  $\pm$  1 for 24 hrs. After shaking the adsorbent was separated by centrifuge and filtration through a membrane filter 0.45 $\mu$ m. The filtrate was analyzed for the remaining metal ion concentration by atomic absorption spectrometer AAS. The adsorbed capacity was calculated using the following equations:

$$q_e = \frac{V}{W} (C_o - C_e) \quad (9)$$

##### 3.1.2 Effect of weight of adsorbent

A range of from 0.05 to 2 g of each GAC and kaolinite was treated with 10 ml of 60 mg/l Cd(II) standard solution and agitation speed of 250 rpm for 24 hr was employed. The final concentration were determined using AAS.

##### 3.1.3 Effect pH of solution

0.5 g of each GAC and kaolinite samples were treated with 10 ml of 60 mg/l Cd(II) standard solution of pH 3, 5, 6, 7 and 9, and agitation speed of 250 rpm was employed for 24 hr. The final concentration were determined using AAS.

##### 3.1.4 Effect of contact time

A volume of 500 ml of Cd(II) ion solutions of concentration 50 mg/l were placed in two beaker of 1 liter and the agitation started before adding the adsorbents. At time zero 25 g of GAC and 25g kaolinite were added to the first and the second beaker respectively then shaking at 800 rpm. The samples were taken every 5 min from each beaker and the concentration were determined using AAS.

## 4. Results and Discussion

### 4.1 Equilibrium isotherm studies.

The adsorption isotherm curves were obtained by plotting the weight of the solute adsorbed per unit weight of the adsorbent ( $q_e$ ) against the equilibrium concentration of the solute ( $C_e$ ) [10].

Fig. 1 shows the adsorption isotherm curves for single metal ions Cd(II) onto activated carbon and kaolinite at 25°C respectively.

The experimental data are plotted with the theoretical data obtained from using Langmuir and Freundlich isotherm for both GAC and kaolinite. The correlation coefficient,  $R^2$ , for the Langmuir isotherm are 0.996 and 0.999 in the using GAC and kaolinite respectively and the correlation coefficient,  $R^2$ , for the Freundlich isotherm are 0.979 and 0.88 in the using GAC and kaolinite respectively. It can be seen from the values of  $R^2$  and from Fig.1 that the experimental data follow the Langmuir isotherm model better than the Freundlich isotherm model. In which the Langmuir parameter a, b are evaluated to be as follows:

For GAC:  $a = 2.760$  mg/g,  $b = 0.242$  L/mg

for kaolinite:  $a = 1.837$  mg/g,  $b = 0.055$  L/mg

The values of a indicate the adsorption capacity of the adsorbent. It is clear from the values of a that the adsorption capacity of GAC is greater than the adsorption capacity of kaolinite for the adsorption of Cd(II).

### 4.2 Effect weight of adsorbent.

The effect of the weight of the adsorbents, GAC and kaolinite on the percentage removal of Cd(II) are shown in Fig.2. Fig.2 indicates that the percentage

removal of Cd(II) increased with increasing the weight of GAC and kaolinite up to a certain value and then there was no further increase in the percentage removal of Cd(II) with increasing in the weight of the adsorbent. Also Fig.2 show that the percentage removal of Cd(II) onto GAC is more than onto kaolinite at the same weight of the adsorbent.

### 4.3 Effect pH of solution.

The effect of pH on the adsorption of Cd(II) onto GAC and kaolinite is presented in Fig.3. It is clear from this figure that the adsorption is low at low pH and increased with increasing pH of the solution up to a certain value the the removal percentage remain constant. As seen in Fig.3 the optimum value of pH is 5 which give the best removal of Cd(II) onto both GAC and kaolinite.

### 4.4 Effect of contact time

Figs.4 and 5 show the effect of contact time on the removal of Cd(II) onto GAC and kaolinite. Fig.4 gives the percent removal of Cd(II) onto GAC and kaolinite as a function of time. Fig. 5 gives the concentration decay curve for removal of Cd(II) onto GAC and kaolinite. These figures show that the removal of Cd(II) increases with increasing the contact time until reaches equilibrium. Thus the time required to reach equilibrium state is 240 and 200 min for GAC and kaolinite respectively. The percent removal of Cd(II) is 96% for GAC and 78% for kaolinite.

### 4.5 Pore diffusion model

#### 4.5.1 External mass transfer coefficient:

The external mass transfer coefficient  $k_f$  for removal of Cd(II) onto GAC and kaolinite was calculated using equation 8.

The concentration ratio  $C/C_0$  is obtained from the experimental concentration decay curve. The resulting values of  $k_f$  are 1.631E-06 and 1.102E-08 for GAC and kaolinite respectively.

#### 4.5.2 Pore diffusion coefficient:

Pore diffusion model is used to obtain the concentration decay curve and pore diffusion coefficient from the numerical solution of equations 1 and 5. A numerical computer program was used to give the theoretical concentration decay curve. Pore diffusion coefficient is obtained by matching the experimental concentration decay curve with that obtained from the model. As shown in Fig.5 there is a good matching between the experimental data and the theoretical data obtained by the model. The value of pore diffusion coefficient are:

For GAC  $D_p = 2.989E-11$

For kaolinite  $D_p = 1.911E-15$

#### Nomenclature:

A	Total interfacial surface area, $m^2$
a	Langmuir constant related to adsorption capacity, $kg/kg$
b	Langmuir constant related to energy of adsorption, $m^2/s$
C	equilibrium concentration of solute in the fluid phase, $kg/m^3$
$C_b$	Solute concentration in the bulk fluid, $kg/m^3$
$C_0$	Concentration of solute at the adsorbent particle, $kg/m^3$
$C_s$	Initial liquid-phase concentration of solute, $kg/m^3$
$D_1$	Liquid phase diffusivity, $m^2/s$
$D_p$	Pore diffusion coefficient, $m^2/s$
$D_s$	Surface diffusion coefficient, $m^2/s$
$d_p$	Particle diameter, $m$

K	Constant in Freundlich
$k_f$	External mass transfer coefficient, $m/s$
n	Constant in Freundlich equation
q	Adsorption Capacity, $kg/kg$
$q_e$	Adsorption capacity at equilibrium, $kg/kg$
$R_p$	Radius of particle, $m$
Sc	Schmidt number, $Sc = m_w / r_w D_m$
t	Time, $s$
V	Volume of the solution, $m^3$
W	Mass of granular activated carbon, $kg$
$\epsilon_p$	Porosity of adsorbent particle
v	Superficial velocity, $m/s$
$\mu$	Viscosity of water, $Pa.s$
$\rho$	Density of water, $kg/m^3$
$\rho_p$	Particle density, $kg/m^3$
subscript	
b	Bulk fluid phase
e	Equilibrium
GAC	Granular activated carbon
l	Liquid phase
o	Initial
p	Particle phase

#### Conclusions

1. Pore diffusion model has successfully used to describe the adsorption process and to predict the concentration decay curve for single system adsorption of Cd(II) onto GAC and kaolinite in batch adsorber.
2. The equilibrium isotherm curve for adsorption of Cd(II) onto GAC and kaolinite in batch adsorber is of favorable type and the Langmuir isotherm model gives the best fit to the experimental data in comparison to the other isotherm model.
3. the adsorption capacity of GAC is greater than the adsorption capacity of kaolinite for the adsorption of Cd(II).

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**Table (1a) Physical properties of granular activated carbon**

<b>Bulk density, kg/m<sup>3</sup></b>	<b>336</b>
<b>BET surface area, m<sup>2</sup>/g</b>	<b>602.97</b>
<b>pH</b>	<b>6</b>

**Table (1b) Physical properties of kaolinite**

<b>Bulk density, kg/m<sup>3</sup></b>	<b>432</b>
<b>BET surface area, m<sup>2</sup>/g</b>	<b>20.3</b>
<b>pH</b>	<b>5</b>



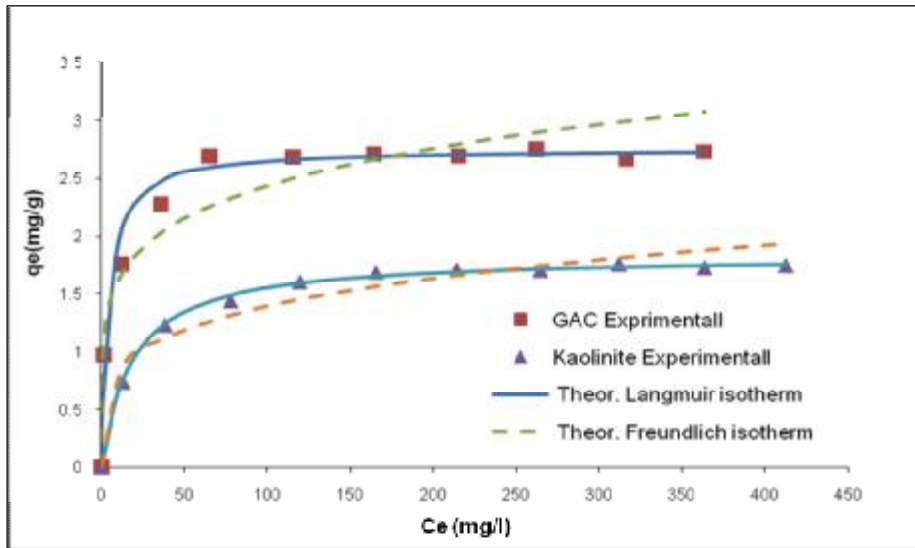


Figure (1) Isotherms for adsorption of Cd(II) using GAC and kaolinite

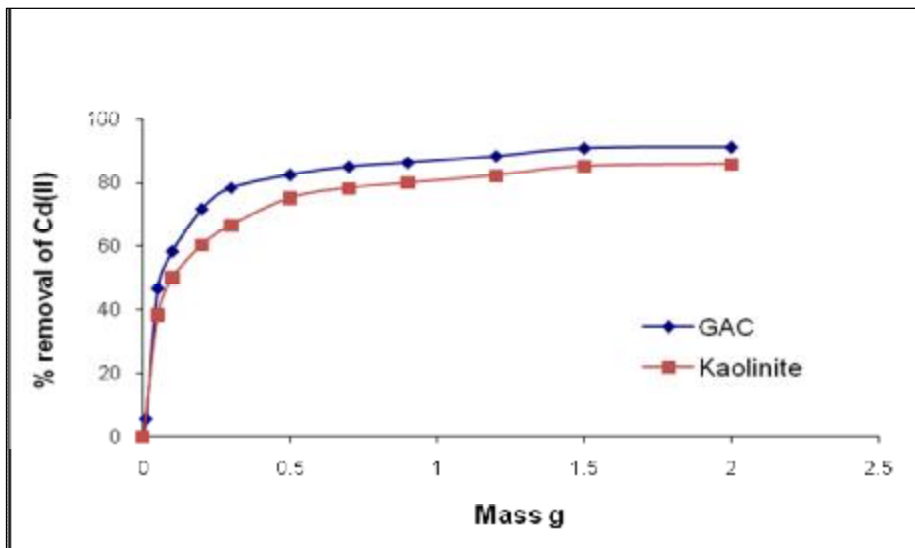


Figure (2) Effect of weight of GAC and kaolinite on the adsorption of Cd(II)

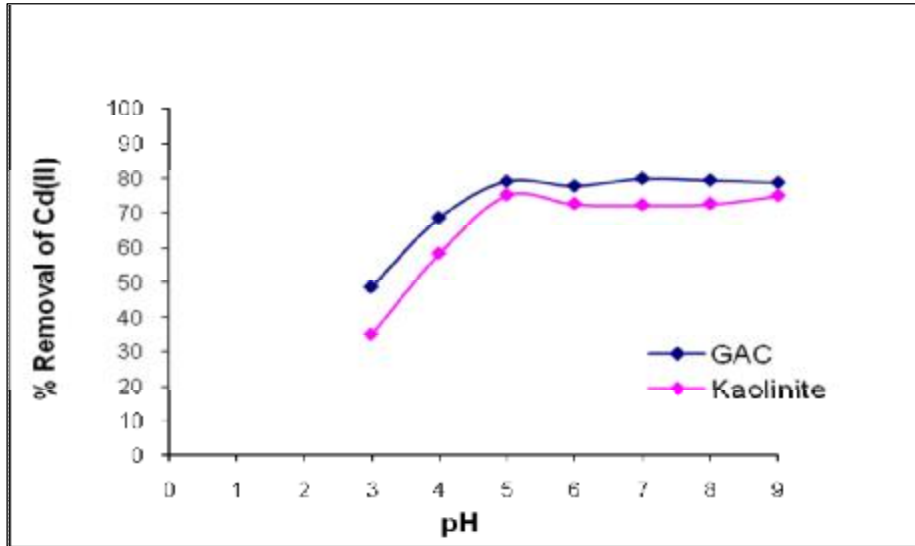


Figure (3) Effect of pH of solution on the adsorption of Cd(II)

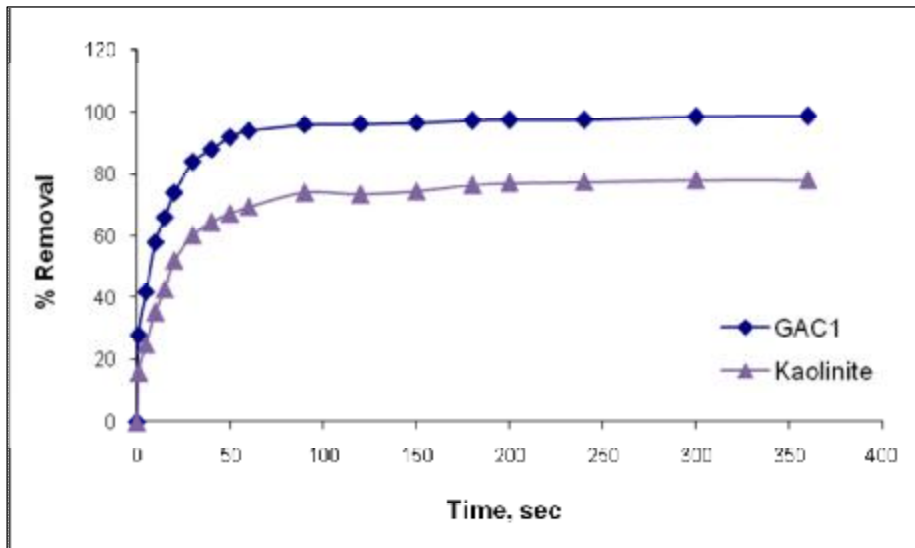


Figure (4) Effect of contact time on the adsorption of Cd(II) onto GAC and Kaolinite

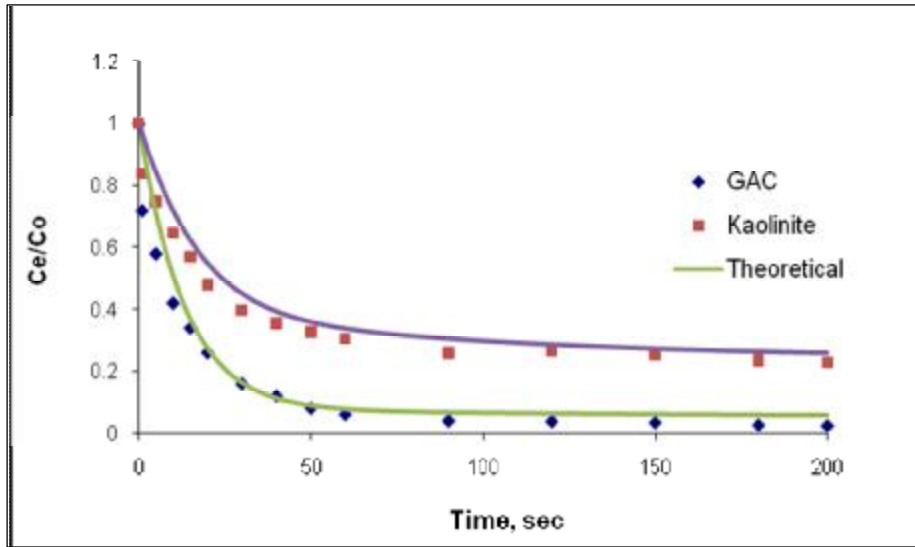


Figure (5) theoretical and experimental concentration decay curve for adsorption of Cd(II) onto GAC and Kaolinite