

## DETERMINATION OF SURFACE DIFFUSION COEFFICIENT FOR LEAD REMOVAL USING ADSORPTION MODEL

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### ABSTRACT

An application of a mathematical diffusion model was used to study a finite bath reactor to remove lead. The model assumptions were: 1) Fick's law is applicable for both liquid phase diffusion and solid phase diffusion, 2) the particles are considered as an isotropic medium, 3) surface diffusion controls the reactions or particle kinetics, and 4) the isotherm followed Langmuir's equation. The model predicts the amount of solute adsorbed per gram of sorbent and the bulk solution concentration. The model was verified for granular coal based activated carbon [AquaSorb<sup>TM</sup>1000] over a range of doses (0.1, 0.3, 0.5, 0.7, 0.8, 1.0) and lead as sorbate (standard lead nitrate solution of concentration 10 mg/l Pb<sup>+2</sup>/l). Experiments were conducted to determine the Langmuir equilibrium coefficients ( $\alpha$  and  $X_m$ ). The model was used to determine the surface diffusion coefficient and the model can predict any data, which is hard or cannot be known from laboratory work. The results of the model showed good agreement with the laboratory data.

**Keywords:** Lead, surface diffusion model, coal based activated carbon, Langmuir isotherm, batch reactor.

### 1. INTRODUCTION

The presence of heavy metals in the environment is a major concern because of their toxicity and threat to human life and to the environment. Lead, cadmium, mercury, arsenic and copper are examples of heavy metals that have been classified as priority pollutants. These pollutants tend to accumulate in bottom sediments from which they may be released by various processes of remobilization, thereby reaching human beings where they produce chronic and acute ailments. Lead as an example of heavy metals; it substitutes for calcium in bony tissue, and accumulates there. There are subtle effects of lead poisoning such as impaired neurological and damage of kidneys [1].

Surveys of heavy metal levels in some industrial wastes have been reported. A recent survey of storage battery producers showed that pH of wastewater at the source ranged between 1.6 and 2.9, whereas the concentration of soluble lead was in range of 5-20 ppm [2].

Adsorption modeling has attracted a large number of researchers around the 1960's. Film diffusion, intraparticle pore diffusion, and pore surface diffusion were considered each of these mechanisms separately or a combination of the three. The models were developed for batch reactors and fixed beds (Breuher [3]) and (Crittenden, [4])

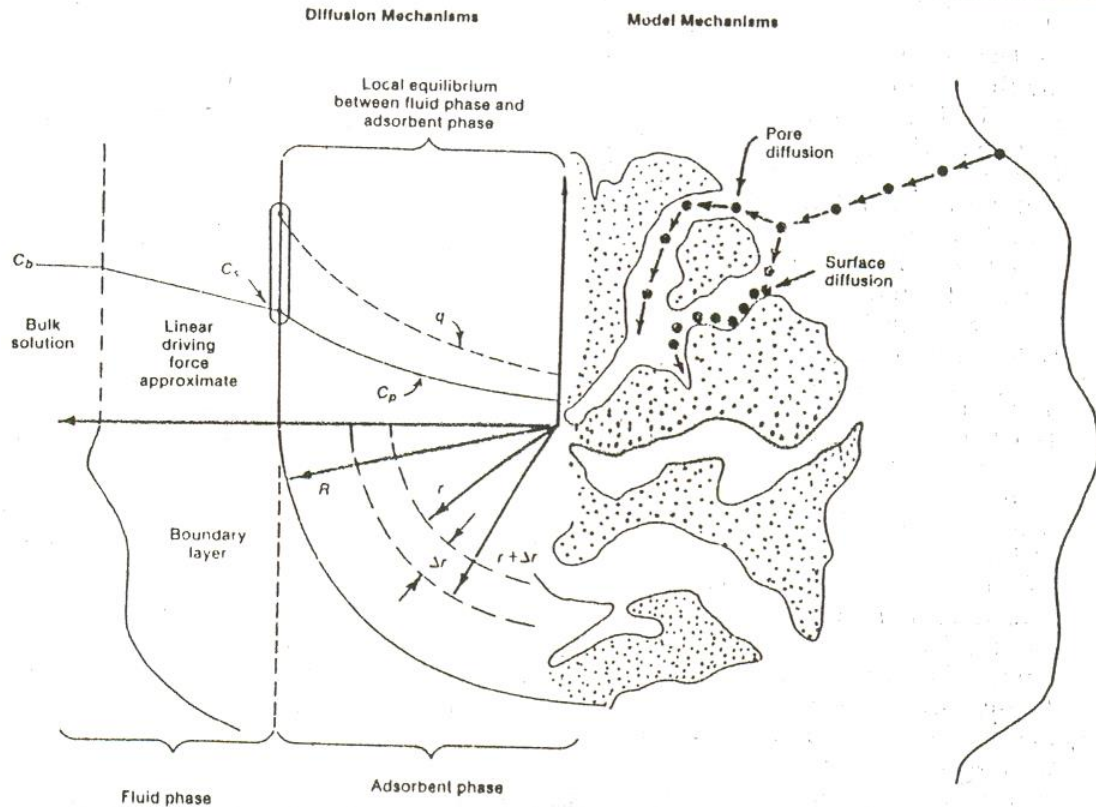
The aim of this research is to study the efficiency of the removal of lead as sorbate by granular coal based activated carbon [AquaSorb<sup>TM</sup>1000], and conducting experiments to verify a mathematical model. The variables studied in this laboratory work were sorbate concentrations. The model can determine the surface diffusion coefficient, delineate relationships, which cannot be known from laboratory data, and can look at the effect of different conditions on the adsorption process.

## 2. MECHANISM OF ADSORPTION

According to Weber [5], adsorption of solute to the interior surfaces of and adsorbent in a reactor may take four steps (as shown in Figure 1):

- 1. Bulk transport:** The adsorbates are transported to the boundary layer of water surrounding the adsorbent particle from the bulk solution. The transport occurs by diffusion if the adsorbent is suspended in quiescent water, such as in a sedimentation basin, or by turbulent mixing, such as during turbulent flow through a packed bed of GAC, or when PAC is being mixed in a rapid mix or flocculator.
- 2. Film transport:** Adsorbates are transported by molecular diffusion through the stationary layer of water (hydrodynamic boundary layer) that surrounds adsorbent particles when water is flowing past them. The distance of transport and thus the time of this step is determined by the rate of flow past the particle: the higher the rate of flow, the shorter the distance.
- 3. Intraparticle transport:** After the adsorbates pass through the hydrodynamic boundary layer, they are transported through the adsorbent's pores to the available adsorption sites. Intraparticle transport may occur by molecular diffusion through the solution in the pores (pore diffusion), or by diffusion along the adsorbent surface (surface diffusion), then adsorption takes place.
- 4. Adsorption of the solute on active sites:** After the adsorbates reach an available site, the adsorption bond is formed between the adsorbate and adsorbent. This step is very rapid for physical adsorption and so one of the preceding diffusion steps will control the rate at which molecules are removed from the solution. If a chemical reaction that changes the nature of the molecules takes place

during the adsorption step, this chemical reaction may be slower than the diffusion steps and thereby control the rate of compound removal.



**Figure 1. Diffusion mechanisms involved in the adsorption process**

Diffusion of solute molecules along the surface of the pores in porous adsorbent is described by the equation below, which is similar to the equations mentioned in Keinath [6] and Mathews [7]:

$$(\delta X/\delta t) = D_s [(\delta^2 X/\delta r^2) + (2/r)(\delta X/\delta r)] = [D_s/r^2] (\delta/r)[r^2(\delta X/\delta r)] \quad (1)$$

in which,

- X = solid phase uptake (gm adsorbate/gm adsorbent).
- t = time in seconds.
- r = radial coordinate (cm).
- $D_s$  = pore surface diffusivity ( $\text{cm}^2/\text{s}$ ).

The model equation was solved by finite difference FORTRAN program was constructed to solve for the different variables. The program was used in this research to solve for X (the sorbate solid phase uptake g/g sorbent) and C (the bulk sorbate concentration  $\text{g}/\text{cm}^3$ ). The algorithm for the FORTRAN program is shown in Figure 2.

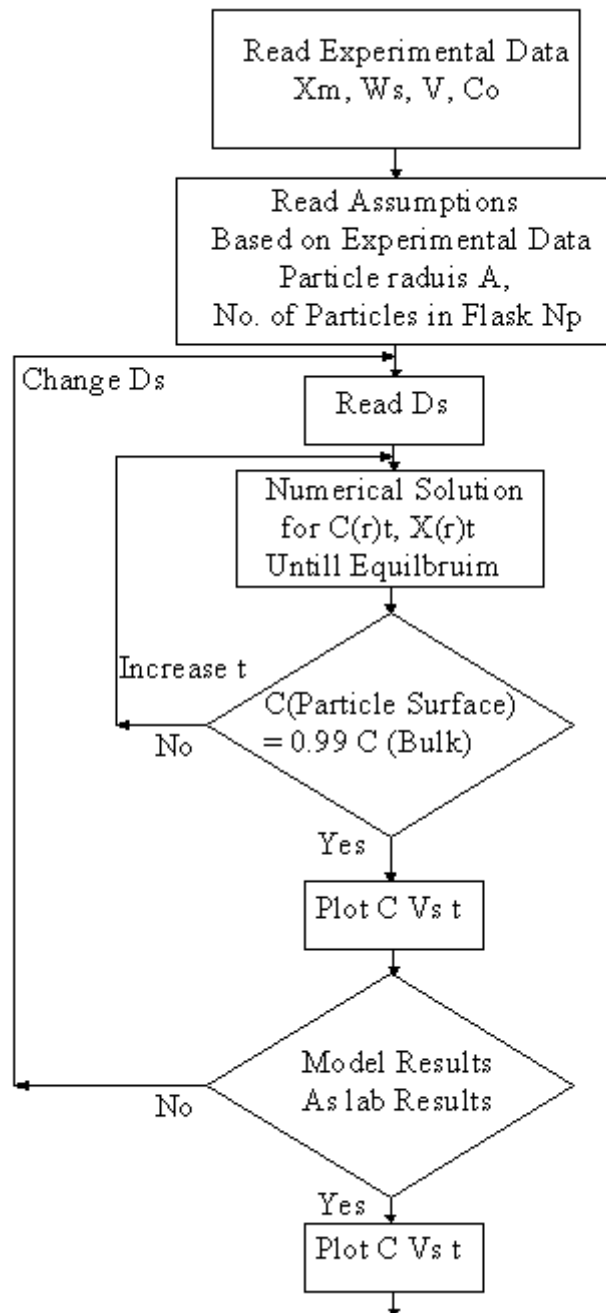


Figure 2. General logic for computer algorithm

### 3. MATERIALS AND METHODS

#### 3.1. Experimental Setup

Laboratory experiments were used to determine: 1) solid phase uptake  $X$  (gm/gm), 2) bulk solution sorbate concentration versus time  $C$  (gm/m<sup>3</sup>), 3) equilibrium data.

The experimental work was carried out to determine the Langmuir coefficients ( $\alpha$  and  $X_m$ ) using lead with standard lead nitrate solution of concentrations 10 mg  $Pb^{+2}$ /l as sorbate and granular coal based activated carbon [AquaSorb<sup>TM</sup>1000] as sorbent in the dosage of (0.1, 0.3, 0.5, 0.7, 0.8 and 1 gm/l) in each 1 liter flask.

Samples were taken at time zero then after each hour until equilibrium was reached and all flasks were stirred. The most common and accurate test of heavy metals concentration is the atomic adsorption Technique. Samples were collected, acidified to 1% (v/v) nitric acid and stored in borosilicate tubes previously decontaminated according to the method described by Henriksen and Balmer [8].

### 3.2. Model Assumptions

- 1- Fick's law is applicable in both liquid phase diffusion and solid phase diffusion.
- 2- The particles are considered as an isotropic medium.
- 3- Pore surface diffusion controls the reaction or particle kinetics.
- 4- The isotherm follows Langmuir's equation.
- 5- Diffusion coefficients are not concentration dependent.

### 3.3. Langmuir's Isotherm

For adsorption from a solution by solid adsorbent, the Langmuir adsorption isotherm is expressed as:

$$X = (X_m \alpha C_e) / (1 + \alpha C_e) \quad (2)$$

The linearized form of the Langmuir isotherm is:

$$(1/X) = (1/X_m) + (1/C_e)(1/\alpha X_m) \quad (3)$$

in which,

$X$  = amount of solute adsorbed per unit weight of adsorbent.

$C_e$  = equilibrium concentration of solute ( $gm/cm^3$ ).

$X_m$  = maximum amount of solute adsorbed per unit weight of adsorbent.

$\alpha$  = Langmuir constant ( $l/gm$ ).

## 4. RESULTS AND DISCUSSION

The results conclude the laboratory data and the mathematical model predictions. The model results were compared with those from the laboratory. This comparison was the basis for model verification.

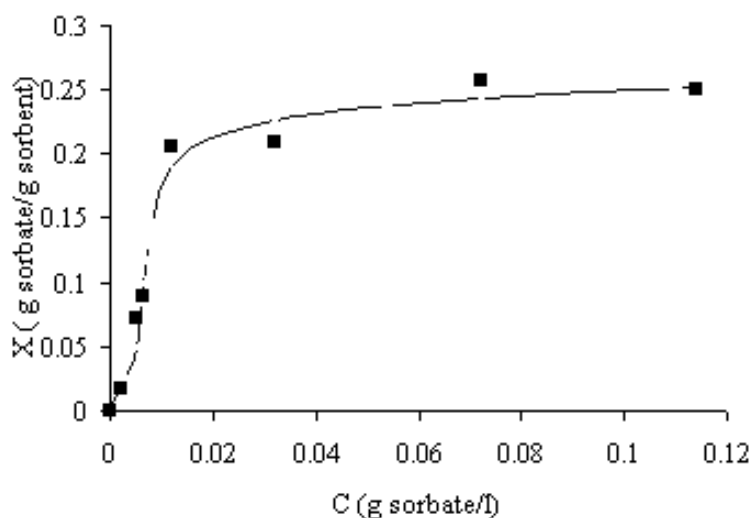
#### 4.1. Laboratory Results

The kinetic and equilibrium data were generated for different initial sorbate concentration. The system data was used to determine the sorbate-sorbent isotherm. Coincident with the isotherm generation, the corresponding uptake curves were determined for different initial adsorbate concentration.

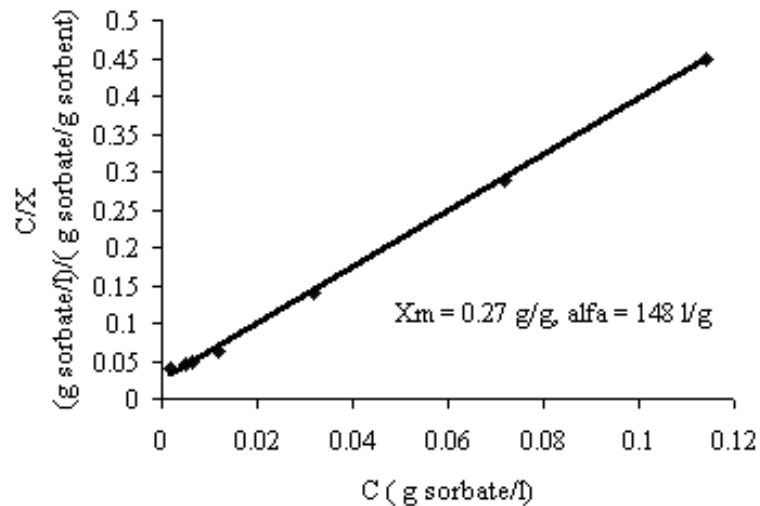
Table (1) shows the laboratory data used to plot Figure (3) and Figure (4). Figure (3) shows the isotherm, while Figure (4) shows the linearized form of the isotherm for granular coal based activated carbon [AquaSorb<sup>TM</sup>1000] as sorbent and lead as sorbate. From linearized form the Langmuir constants,  $\alpha$  and  $X_m$ , were determined using the slope and intercept.

**Table 1. Laboratory results at equilibrium**

$C_o$ (mg/l)	$1/C_e$ (mg/l)	$1/X_e$ (mg/gm)
10	0.3861	0.00518
10	0.4566	0.01314
10	0.4706	0.0215
10	0.5181	0.02702
10	0.5525	0.02944
10	0.6211	0.02896



**Figure 3. Langmuir isotherm**



**Figure 4. Linearized isotherm**

## 4.2. Model Calibration

Calibration of the model requires that parameters are quantified. The model was calibrated by varying some of the parameters to give the best fit with data which was selected as a database for model calibration.

Figure (5) shows the laboratory data points with the calibrated simulations for granular coal based activated carbon [AquaSorb<sup>TM</sup>1000] as sorbent and lead as sorbate. These data was used to determine the final value of surface diffusion coefficient  $D_s$  using a trial and error procedure using the model for two experiments (granular coal based activated carbon dosage of 0.30 and 0.7 g/l) then use the same surface diffusion coefficient for the other sorbate concentration. The value of the surface diffusion coefficient ( $D_s$ ) is  $5 \times 10^{-11}$ .

$$A.C = 0.3 \text{ g/l}$$

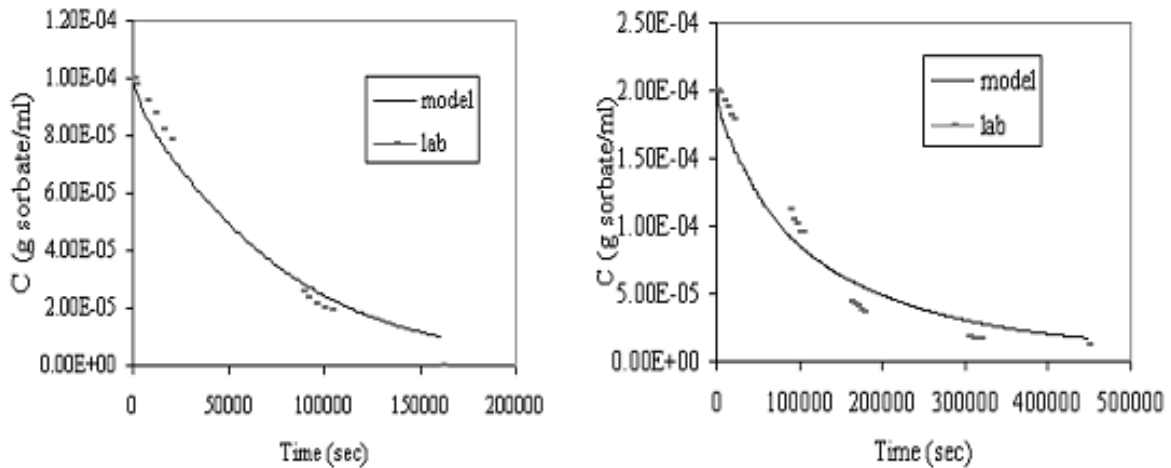
## 4.3. Model Verification

The proposed model was verified against the laboratory data points. Figure (6) shows the measured and simulated data. The results of the model showed good agreement with the laboratory data.

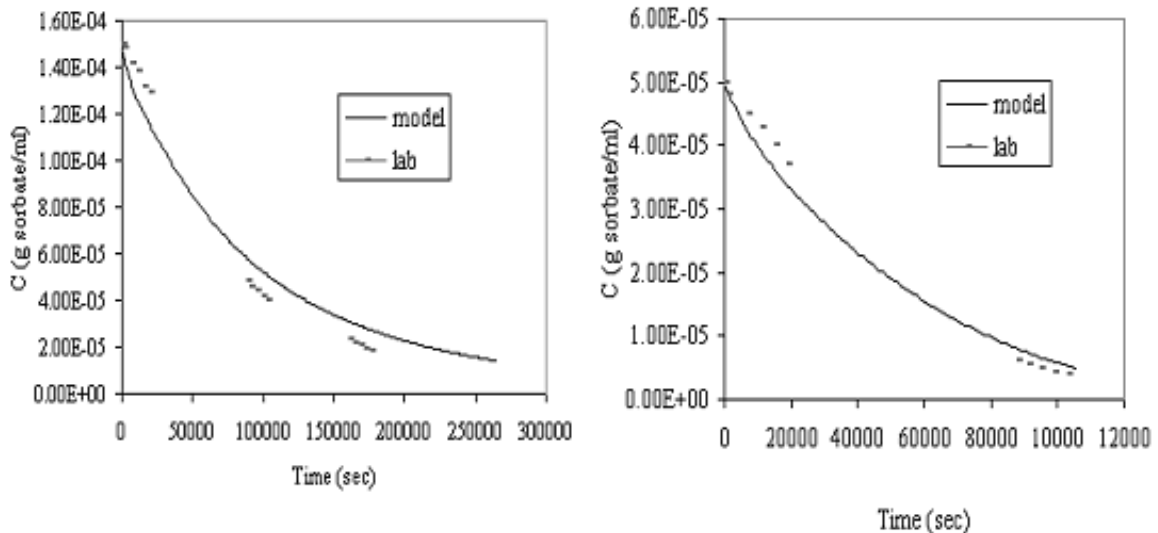
## 4.4. Exercise with the Model

Simulation with the model could be used to answer questions which may not be answered from lab work or may take long time and effort. For example, a quick

exercise with the model showed that increasing the granular coal based activated carbon [AquaSorb™1000] dose in the batch reactor for initial lead concentration 20 mg/l from 1 gram to 3 grams, shoed an increasing in the efficiency of lead removal from 28% to 72% after 6 hours. And increasing the same dose to 5 grams increased the efficiency to 93% after 6 hours.



**Figure 5. The lab data points with the calibrated simulations for granular coal based activated carbon dosage 0.30 g/l and 0.7 g/l**



**Figure 6. The lab data points with the calibrated simulations for granular coal based activated carbon dosage 0.50 g/l and 1.00 g/l**



## 5. CONCLUSIONS

- (1) The model was verified for granular coal based activated carbon [AquaSorb<sup>TM</sup>1000] as sorbents and lead as sorbate through testing over a range of granular coal based activated carbon dosage (0.10-1.00 g/l) and the results of the model showed good agreement with the laboratory measurements.
- (2) Diffusion coefficients are not concentration dependent.

## 6. RECOMMENDATIONS

- (1) It is recommended to conduct further studies with granular coal based activated carbon [AquaSorb<sup>TM</sup>1000] using other pollutants. Also an economic comparative study with other coals will be helpful.

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