APPLICATION OF ADSORPTION MODEL FOR DYE REMOVAL

F. Abdelrasoul

Sanitary Engineering Department, Alexandria University, 21544 Alexandria, Egypt

ABSTRACT

An application of a mathematical diffusion model was used to study a finite bath reactor to remove dye. 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 coconutshell based activated carbon [AquaSorb^{TM}CS] and methylene blue as sorbate through testing over a range of methylene blue concentrations (50, 100, 150 and 200 mg/l). Experiments were conducted to determine the Lamgumir equilibrium coefficients (α and Xm). 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: methylene blue, surface diffusion model, coconutshell based activated carbon, Langmuir isotherm, batch reactor.

INTRODUCTION

Synthetic dyes and pigments are extensively used for dyeing and printing in industry over $7*10^5$ tons and approximately 10000 dyes are produced annually worldwide, of which 10 % is lost in the industrial effluents [1].

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 [2]) and (Crittenden, [3]).

Seung-Mok Lee et al. [4] used trichlorethane (TCEH) and trichloroethylene as an adsorbate and granular activated carbon as an adsorbent. They determined Langmuir constants using batch experiment data.

Orna Duggan and Stephen J. Allen [5] used different carbons and different sorbates such as phenol and basic red dye. They determined Freunlinch and Langmuir constants.

Yuxin Wang and JianYu [6] studied adsorption of 3 dyes (azo, anthvaquinone and indigo) on living and dead mycelia of Trametes Versicolor. They found that the living mycelia gave better adsorption than the dead ones. They also determined Langmuir constants for the living and dead fungi.

Konduru R. Rama Krishna and T. Viraraghavan [7] studied low cost adsorbents available in Canada. They used peat, steel plant slag, bentonite clay and fly ash and compared them against activated carbon. As adsorbate they prepared from commercial grade acid, basic and disperse dyes. Batch kinetic and isotherm studies, and column studies were undertaken. The data were evaluated in accordance with the Langmuir, Ftrundlich and BET isotherm models.

Mamdouh Mahmoud Nassar [8] studied the adsorption of two dyes, basic red and basic yellow on palm fruit bunch. He showed a relationship of the equilibrium isotherm. He also determined intraparticle rate diffusion experimentally.

The aim of this research is to study the efficiency of the removal of dye as sorbate by granular coconutshell based activated carbon [AquaSorbTMCS], and conducting experiments to verify a mathematical model. The variables studied in this laboratory work were sorbate concentrations. The model can delineate relationships, which cannot be known from laboratory data, and can look at the effect of different conditions on the adsorption process.

MECHANISM OF ADSORPTION

According to Weber [9], 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**: This is usually rapid due to the mixing of flow.
2. **Film transport**: This step involves diffusion of the solute through a hypothetical film which is used to describe the resistance to mass transform of the surface particle. This step could be neglected in case of high agitation.
3. **Intrapaticle transport**: Intraparticle transport or internal diffusion involves transport of the adsorbate from the particle surface into interior sites by diffusion within pora-fillles and migration along the solid surface of the pore (surface diffusion).
4. **Adsorption of the solute on active sites**: The fourth step in adsorption on interior particle surfaces is adsorption of solute on active sites, usually every rapid process.

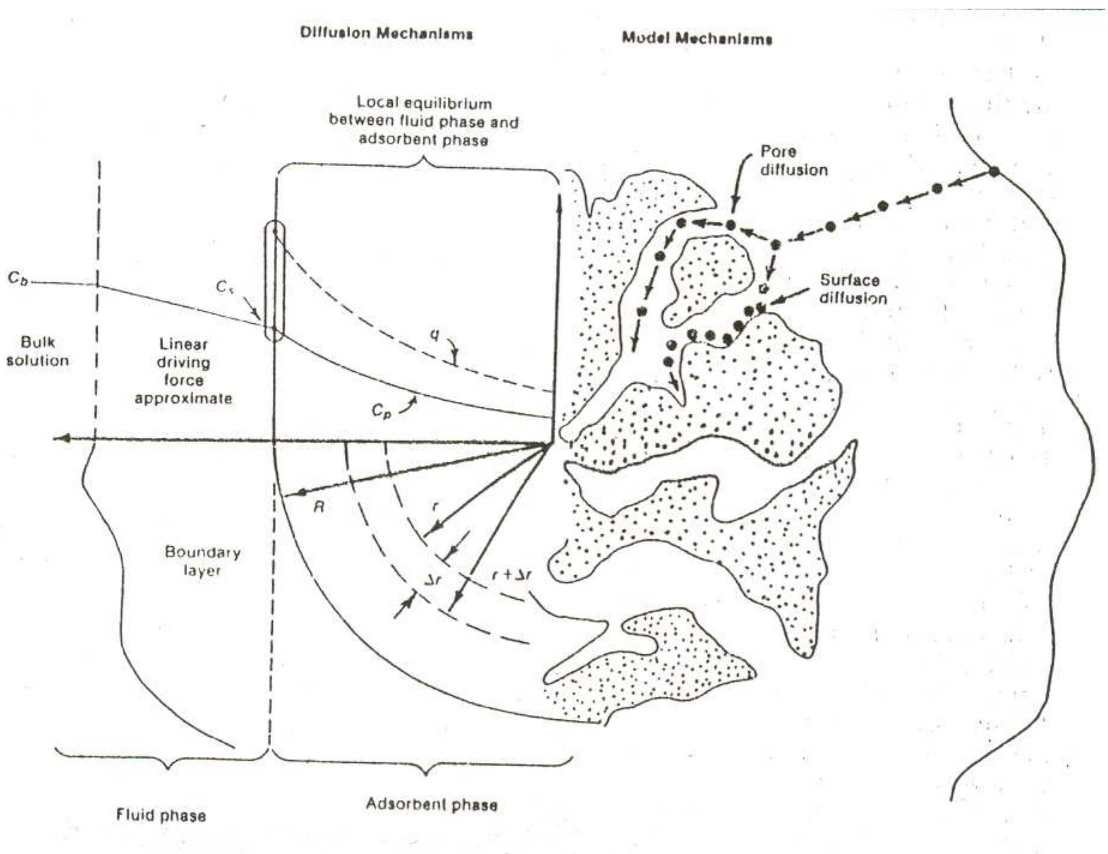

Figure 1. Diffusion mechanisms involved in the adsorption process

SURFACE DIFFUSION MODEL EQUATION

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 [10] and Mathews [11]:

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

in which,

X = solid phase uptake (gm adsorbate/gm adsorbent).
t = time in seconds.
r = radial coordinate (cm).
D_s = pore surface diffusivity (cm^2/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/gsorbent) and C (the bulk sorbate concentration g/cm^3). The algorithm for the FORTRAN program is shown in figure 2.

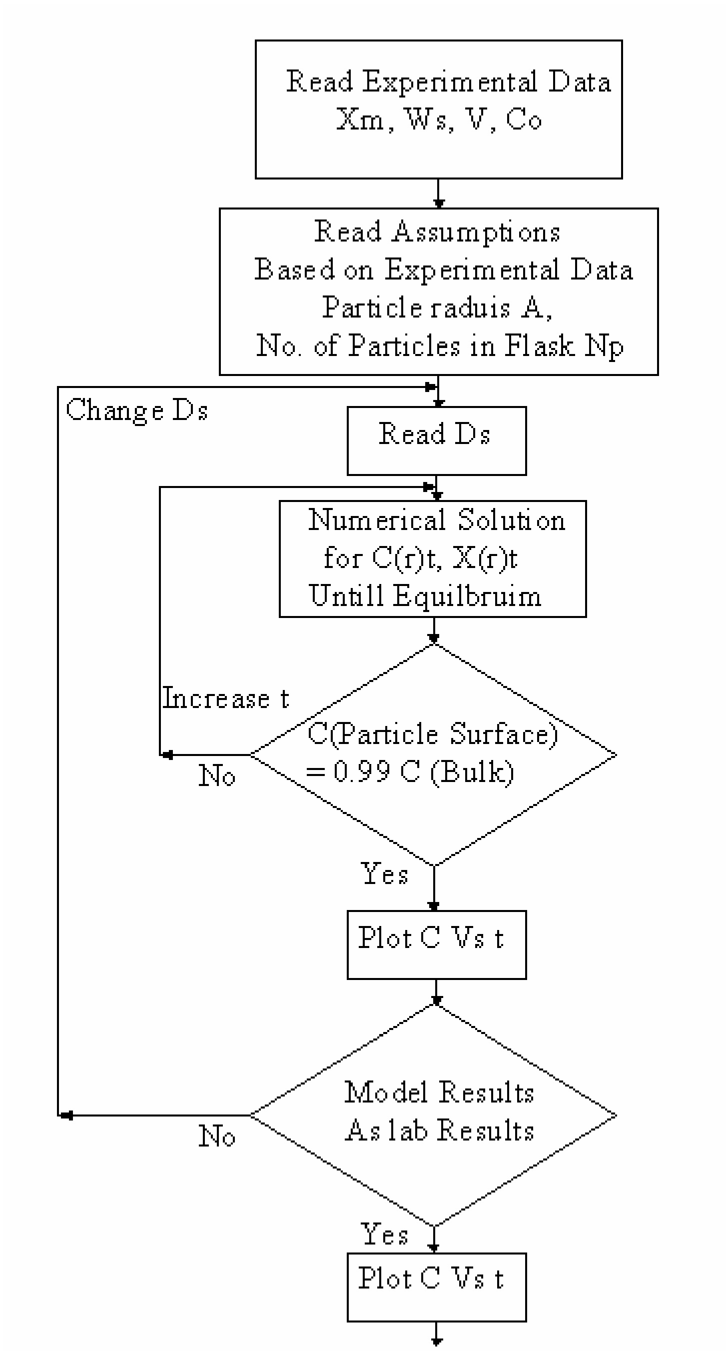

Figure 2. General logic for computer algorithm

MATERIALS AND METHODS

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^3), 3) equilibrium data.

The experimental work was carried out to determine the Langmuir coefficients (α and X_m) using methylene blue with concentrations (20, 50, 100, 150, 200, 250, 300 and 350 mg/l) as sorbate and 1 gram granular coconut shell based activated carbon [AquaSorbTMCS] as sorbent in each 1 liter flask. and to verify the mathematical model with batch reactor using methylene blue with concentrations(50, 100, 150 and 200 mg/l) as sorbate and 1 gram granular coconutshell based activated carbon [AquaSorbTMCS] as sorbent 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 samples volume was 5 ml for all sampling points. Methylene blue concentration was measured by photometric method using spectrophotometer according to the Standard Methods for Examination of Water and Wastewater [12].

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. 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.
α = Langmuir constant (l/gm).

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.

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 coconutshell based activated carbon [AquaSorbTMCS] as sorbent and methylene blue as sorbate. From linearized form the Langmuir constants, α and Xm, were determined using the slope and intercept.

Table 1. Laboratory results at equilibrium

C_o (mg/l)	C_e (mg/l)	X_e (mg/gm)
20	0.0	20.00
50	0.0	50.00
100	0.0	100.00
150	0.0	150.00
200	12	191.43
250	34	227.78
300	72	243.78
350	114	252.32

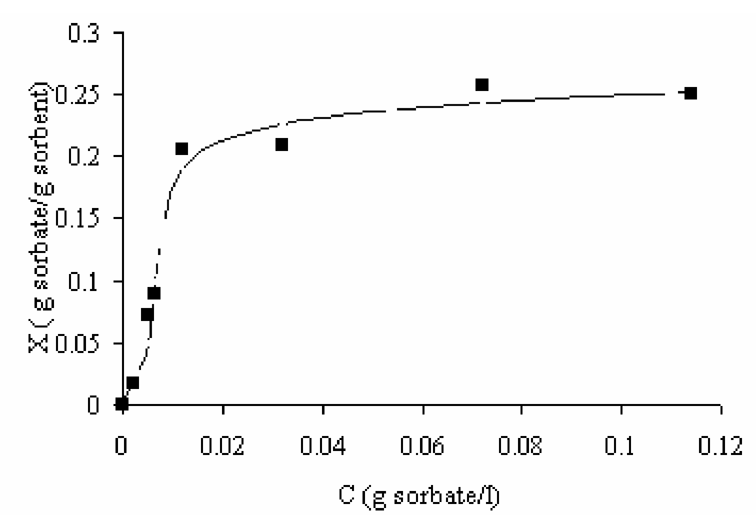

Figure 3. Langmuir isotherm

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 coconut shell based activated carbon [AquaSorbTMCS] as sorbent and methylene blue 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 (100 and 200 mg/l) then use the same surface diffusion coefficient for the other sorbate concentration. The value of the surface diffusion coefficient (D_s) is $5*10^{-11}$.

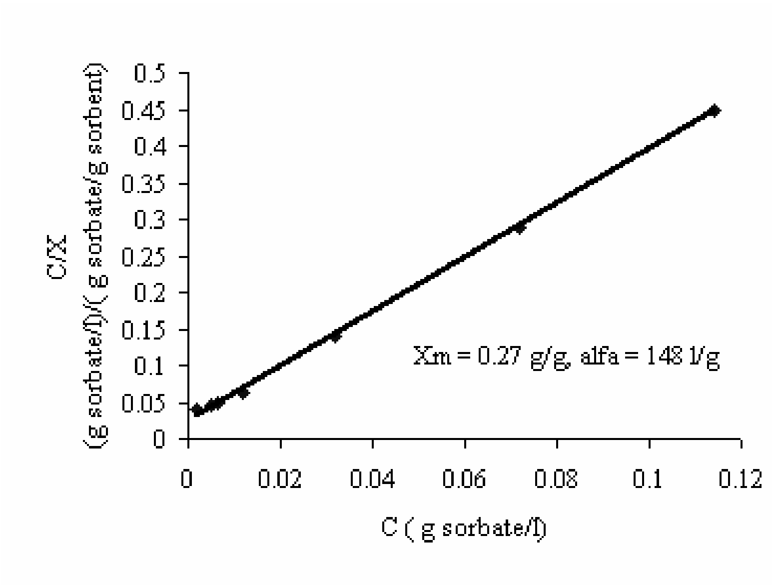

Figure 4. Linaerized isotherm

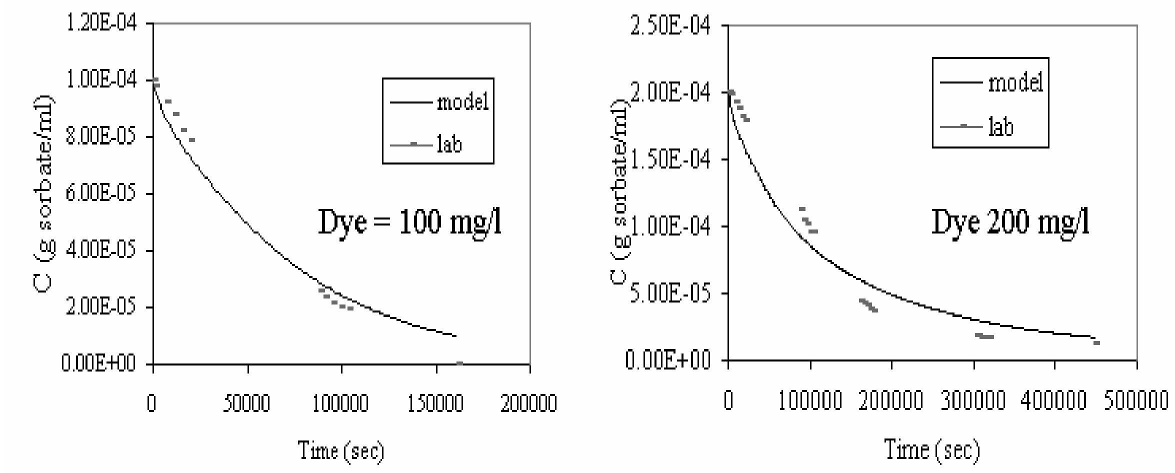

Figure 5. The lab data points with the calibrated simulations for methylene blue 100 mg/l and 200 mg/l

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. 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 coconutshell based activated carbon [AquaSorb^{TM}CS] dose in the batch reactor for initial dye concentration 350 mg/l from 1 gram to 3 grams, shoed an increasing in the efficiency of methylene blue removal from 28 % to 72 % after 6 hours. And increasing the same dose to 5 grams increased the efficiency to 93% after 6 hours.

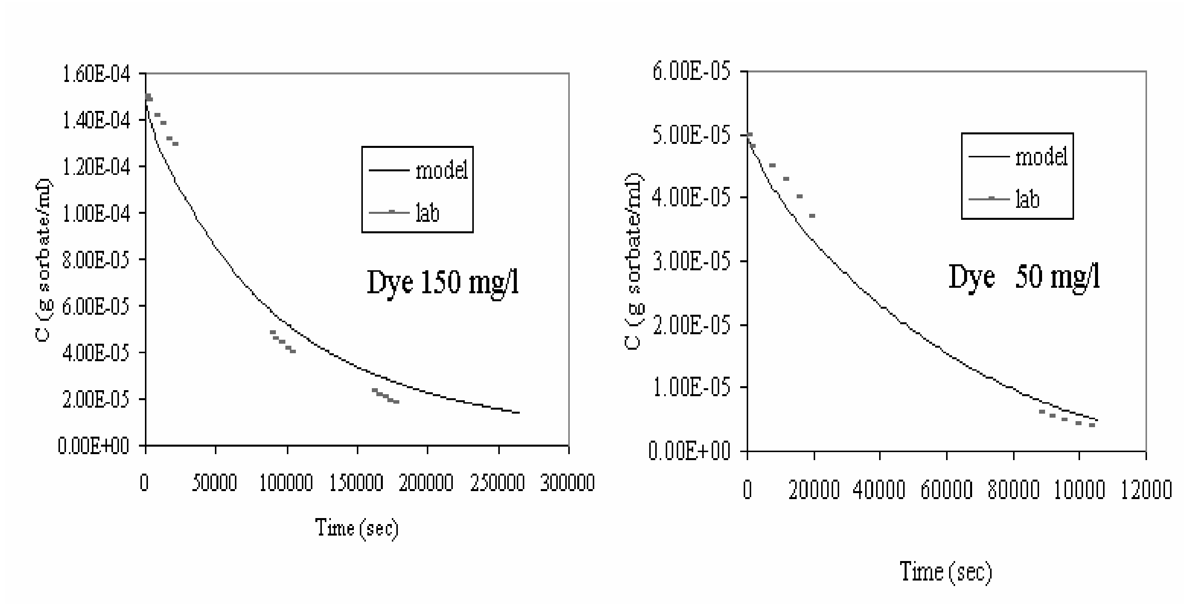

Figure 6. The lab data points with the calibrated simulations for methylene blue 50 mg/l and 150 mg/l

CONCLUSIONS

(1) The model was verified for granular coconutshell based activated carbon [AquaSorb^{TM}CS] as sorbents and phenol as sorbate through testing over a range of methylene blue concentrations (50-200 mg/l) and the results of the model showed good agreement with the laboratory measurements.

(2) Diffusion coefficients are not concentration dependent.

RECOMMENDATIONS

It is recommended to conduct further studies with granular coconutshell based activated carbon [AquaSorbTMCS] using other pollutants. Also an economic comparative study with other coals will be helpful.

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