

Application of adsorption model for phenol removal

M.T. Sorour, F. Abdelrasoul and W.A. Ibrahim

Sanitary Engineering Department, Alexandria University, 21544 Alexandria, Egypt

An application of a mathematical diffusion model was used to study a finite bath reactor to remove phenolic wastes. 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) solid diffusion (pore surface diffusion and pore diffusion combined) controls the reaction or particle kinetics, and 4) the isotherm followed the Langmuir's equation. The model predicts the amount of solute adsorbed per gram of sorbent and the bulk solution concentration. The model was verified using laboratory data where phenol was used as a sorbate and GAC (AquaSorb™2000) was used as a sorbent. Experiments were conducted to determine Langmuir equilibrium coefficients (α and X_m). The variable studied in this laboratory work was sorbate concentration. Pore and surface diffusion coefficients were determined using the model. The model can be used to delineate relationships which cannot be known from laboratory data, or even to look at the effect of different conditions on the efficiency of pollutant removal. The results of the model showed good agreement with the laboratory data.

في هذا البحث تم استخدام نموذج رياضي للانتشار في إزالة الفينول من المخلفات السائلة. وكانت فروض النموذج: ١) للانتشار في السوائل والمواد (Diffusion) يخضع لقانون Fick ٢) الحبيبات لها نفس الخواص، ٣) الانتشار في الجوامد (على سطح وداخل مسام الحبيبات) (Intraparticle Diffusion) هو المتحكم في التفاعل ٤) يخضع لمعادلات Langmuir النموذج يتنبأ بكمية المادة المذابة الممتزة لكل جرام من المادة المازة وكذلك تركيز المادة المذابة في المحلول. وتم التحقق من فاعلية النموذج باستخدام نتائج عملية كان فيها الفينول المادة الممتزة والفحم المنشط (AquaSorb™2000) المادة المازة. كما تم استخدام الاختبارات العملية في تحديد قيم معاملات الاتزان ل Langmuir (α, X_m) قيم معاملات الانتشار (داخل المسام وعلى الاسطح) تم تحديدها بواسطة النموذج. يمكن استخدام النموذج في وصف العلاقات التي لا يمكن معرفتها باستخدام النتائج العملية وكذلك لدراسة تأثير العوامل المختلفة على كفاءة إزالة الملوث. النموذج اعطى نتائج جيدة بالمقارنة بالنتائج العملية.

Keywords: Active carbon, Phenol, Pore surface diffusion, Pore diffusion coefficients

1. Introduction

According to Weber [1], adsorption involves the interphase accumulation or concentration of the substance at a surface or interface. The process can occur at an interface between any two phases, such as liquid, gas-liquid, gas-solid, and liquid-solid interfaces. The subject of adsorption attracts large numbers of professionals, chemist, chemical engineers, ground water engineers, soil scientists and environmental engineers. There are three types of adsorption: 1) physical adsorption, 2) chemisorption, and 3) exchange sorption (ion exchange).

Physical adsorption does not involve the sharing or transferring of electrons and is not site-specific. The interactions are fully reversible. The heat of physical adsorption is

low compared to that of chemisorption. The mechanism of physical adsorption is diffusion.

Rosen [2] studied the kinetics of a system consisting of a single solute liquid solution flowing through a fixed bed of homogeneous spherical particles of uniform radius, though which the liquid solution flowed with a constant linear velocity. In this work, the rate of adsorption was determined by the combined effect of liquid film and solid diffusion into spherical particles.

Edeskuty and Amundson [3] studied the effect of intraparticle diffusion in liquid-solid adsorption systems. They assumed that particles were cylinders with impervious ends and that the isotherm was a linear one. They used a high level of agitation, consequently they neglected mass transfer resistance. Experimental confirmation of the theoretical

equation was obtained using activated carbon as an adsorbent and phenol in water solution as adsorbate.

Weber and Morris [4] used batch system with activated carbon as an adsorbent and various adsorbates to study the effect of pH, temperature, concentration of solute, molecular size of adsorbate, molecular configuration of substrate, carbon particle size, and concentration of carbon on kinetics of adsorption or adsorption rate.

Weber and Rumer [5] estimated adsorption kinetics as a diffusion process. They developed a mathematical model based on the materials balance principle for cylindrical particles. They assumed Langmuir relation applicability for equilibrium.

Hendricks and Kuratti [6, 7] conducted experimental work on batch reactors using five sorption rate equations to test whether they would fit the experimental data. The experimental conditions included two sorbate-sorbent combination, four temperatures and thirty initial concentrations of sorbate, giving a total 240 tests. The validity of one of the equations was ascertained.

The aim of this research is to study the efficiency of the removal of phenol as sorbate by Granular Activated Carbon (AquaSorb™ 2000) as sorbent, and conducting experiments to verify a diffusion model based on intraparticle diffusion only (pore and pore-surface diffusion). The variable studied in this laboratory work was sorbate concentration. Pore and pore-surface diffusion coefficients were determined using the model. The model can be used to delineate relationships which cannot be known from laboratory data, or even to look at the effect of different conditions on the efficiency of pollutant removal

2. Combined diffusion (pore and surface-pore diffusion) model equation

The diffusion model and the Fortran program were taken from [8]. The model equation which is a combination of pore and surface-pore diffusion is shown below:

$$\varepsilon \frac{\partial C}{\partial t} + (1 - \varepsilon)\rho \frac{\partial X}{\partial t} = D_p \left[\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right] + D_s \rho \left[\frac{\partial^2 X}{\partial r^2} + \frac{2}{r} \frac{\partial X}{\partial r} \right] \quad (1)$$

Where:

- ε = interparticle void fraction,
- C = solute concentration in pore voids (g/cm³),
- ρ = particle dry density (g/cm³),
- X = solid phase uptake (g sorbate/g sorbent),
- T = time in seconds,
- R = radial coordinate (cm),
- D_p = pore diffusivity (cm²/s), and
- D_s = pore surface diffusivity (cm²/s).

The model equation was solved by finite difference and a 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 g/cm³).

3. Materials and methods

3.1. Experimental set-up

Laboratory experiments were used up to determine: 1) solid phase uptake X (gm/gm), 2) bulk solution sorbate concentration versus time C (g/m³), 3) equilibrium data, 4) the equilibrium coefficients α and X_m and 5) the kinetic parameters.

The experimental work was carried out to verify the mathematical model with batch reactor using phenol with concentrations (20, 50, 100, 150, 200, 250, 275 and 300 mg/l) as sorbate and 1 gram active carbon (Aqua Sorb™ 2000) as sorbent in each 1 liter flask.

The experimental system was designed to determine the equilibrium data. Samples were taken at time zero then after each hour until equilibrium was reached. The sample volume was 5 ml for all sampling points. All flasks were stirred. Phenol was measured by photometric method using spectrophotometer and according to the Standard Method for the Examination of Water and Wastewater [9].

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- Solid diffusion (pore surface diffusion and pore diffusion combined) controls the reaction or particle kinetics.
- 4- The isotherm follows Langmuir's equation.

3.3. Langmuir isotherm

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

$$X = \frac{X_m \alpha C_e}{1 + \alpha C_e} \quad (2)$$

The linearized form of the Langmuir isotherm is:

$$\frac{1}{X} = \frac{1}{X_m} + \left[\frac{1}{C_e} \right] \left[\frac{1}{\alpha X_m} \right] \quad (3)$$

Where:

- X = amount of solute adsorbed per unit weight of adsorbent,
 C_e = equilibrium concentration of solute (g/cm³),
 X_m = maximum amount of solute adsorbed per unit weight of adsorbent, and
 A = Langmuir constant (l/g).

4. Results and discussion

The results include 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 were 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 figs. 1 and 2. Fig. 1 shows the isotherm, while fig. 2 shows the linearized form of the isotherm from which the Langmuir constants, α and X_m , were determined using the slope and intercept. The Langmuir constants were key factors in the kinetic model. The model was verified by simulating laboratory conditions for the eight lab runs. The model results were compared with those from laboratory.

Table 1
Laboratory results at equilibrium

C _o mg/l	C* mg/l	X* mg/g
20	0.0	20.0
50	0.0	50.0
100	0.0	100.0
150	0.0	150.0
200	29	175.93
250	62	199.78
275	72	214.32
300	102	219.42

The model can be used to delineate relationships, which cannot be known from laboratory data, or even to look at the effect of conditions for the variables studied in the laboratory.

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 fit with the data which was selected as a database for model calibration.

Table 2 presents the final values of diffusion coefficients which were determined using a trial and error procedure using the model for one experiment then the same diffusion coefficients were used for a range of sorbate concentrations. These diffusion model

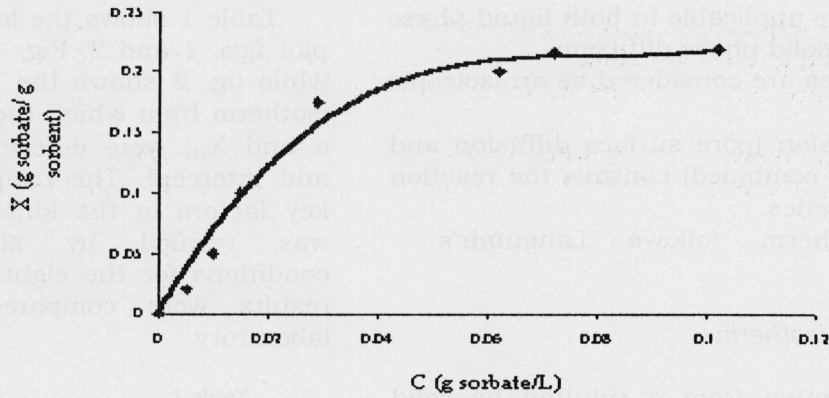


Fig. 1. Langmuir isotherm.

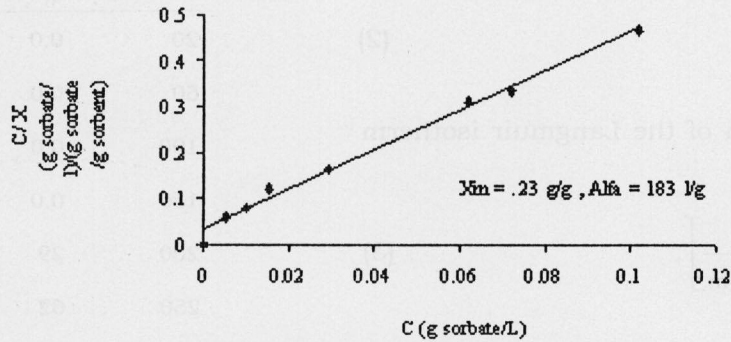


Fig. 2. Linearized isotherm.

Table 2
Final model key parameters

Phenol concentration	From 0 to 100 mg/l	From 100 to 200 mg/l	From 200 to 300 mg/l
D_p	1×10^{-6}	3×10^{-5}	2×10^{-5}
D_s	8×10^{-11}	5×10^{-11}	5×10^{-11}

coefficients or curve fitting coefficients, considering that these values are applicable for the very small pores inside the particles and not for free solution.

Figs. 3-a, 4-a, and 5-a , show the actual data points with the calibrated simulations of phenol concentration.

4.3. Model verification

The proposed model was verified against the actual data points. Figs 3-b, 3-c, 4-b, 5-b and 5-c, show the measured and simulated data. The result of the model showed good agreement with the laboratory data. More details on the laboratory measurements and parameters estimation can be found elsewhere [10].

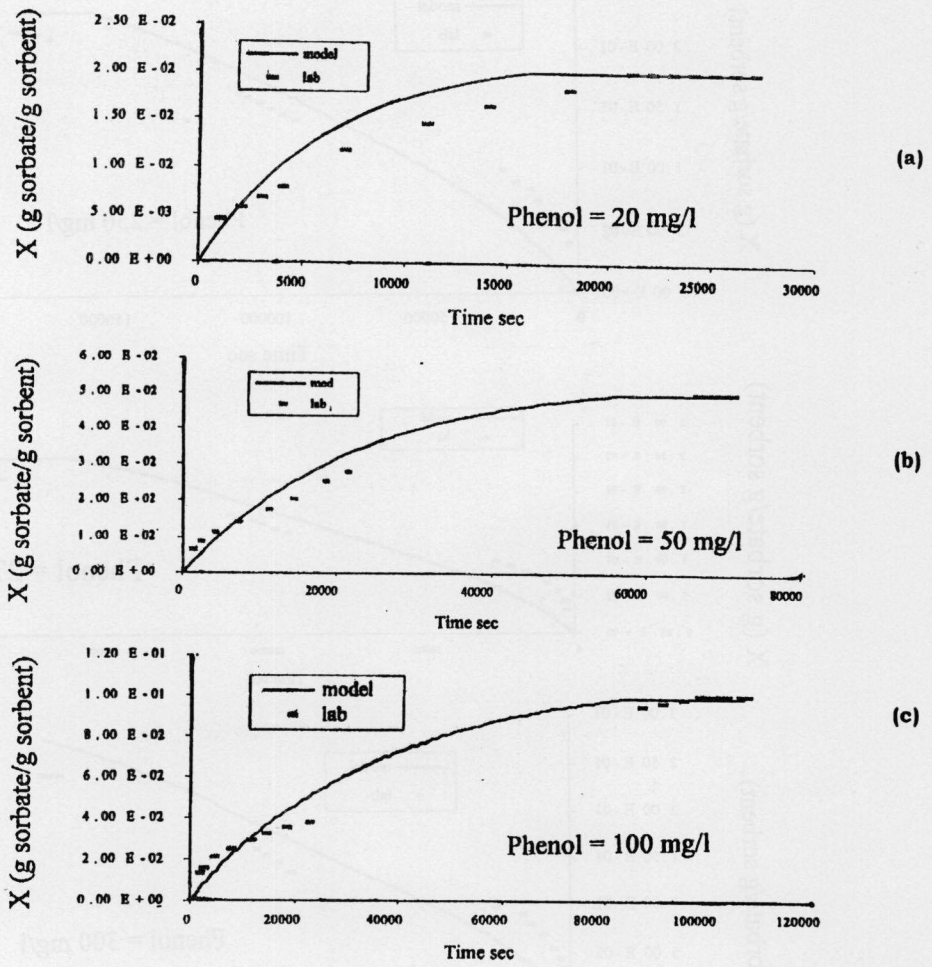


Fig. 3-a. The actual data points with the calibrated simulations for phenol =20 mg/l, b. and c. the measured and simulated data for phenol = 50, 100 mg/l.

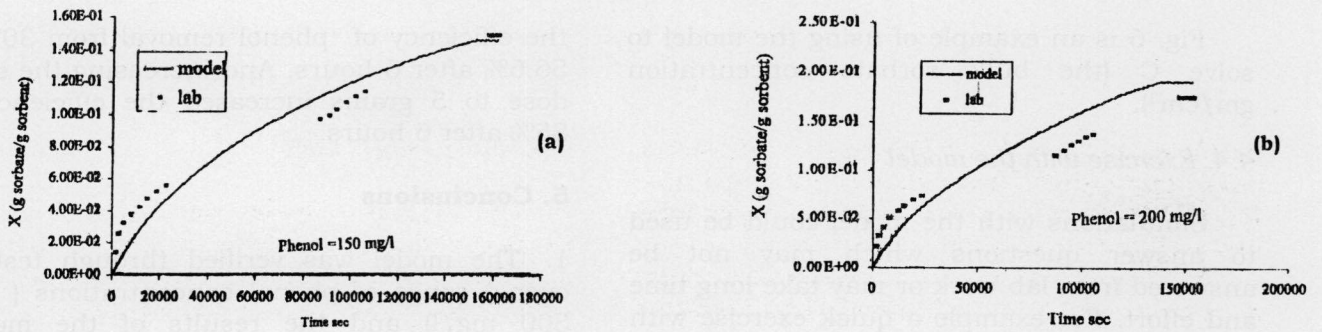


Fig. 4-a. The actual data points with the calibrated simulations for phenol =150 mg/l, b. the measured and simulated data for phenol = 200 mg/l.

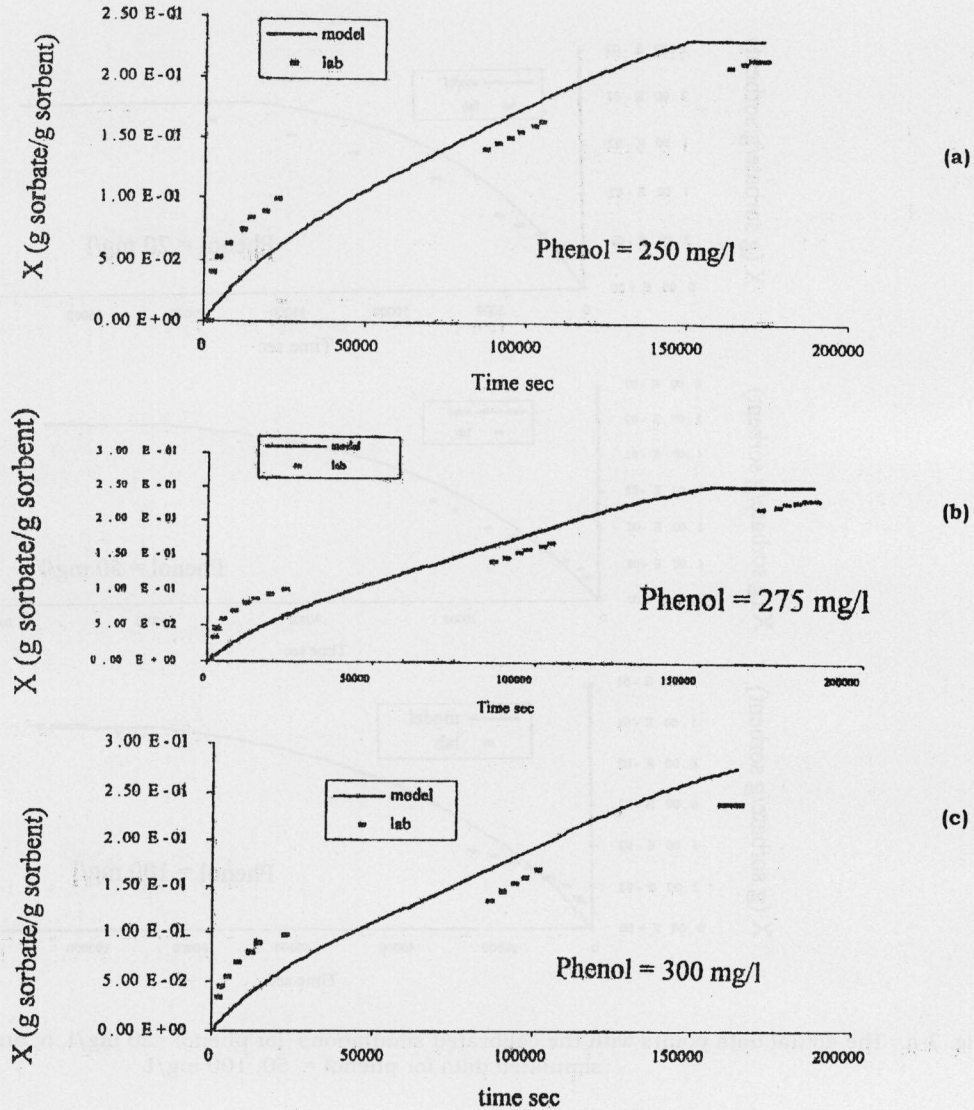


Fig. 5-a. The actual data points with the calibrated simulations for phenol =250 mg/l, b. and c. show the measured and simulated data for phenol = 275, 300 mg/l.

Fig. 6 is an example of using the model to solve C (the bulk sorbate concentration gm/cm³).

4.4. Exercise with the model

Simulations 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 activated carbon dose in the batch reactor for initial phenol concentration of 300 mg/l from 1 gram to 2 grams, showed an increasing in

the efficiency of phenol removal from 30% to 56.6% after 6 hours. And increasing the same dose to 5 grams increased the efficiency to 85% after 6 hours.

5. Conclusions

1. The model was verified through testing over a range of phenol concentrations (20-300 mg/l) and the results of the model showed good agreement with the laboratory measurements.
2. The higher the phenol concentration, the lower values of D_p and D_s .

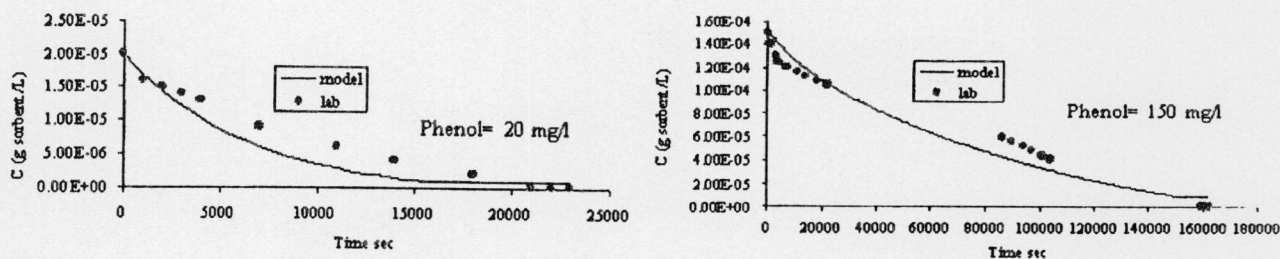


Fig. 6. The actual data points with the calibrated simulations for phenol =20 and 150 mg/l.

3. The same procedure and the model may be helpful for future work. For example the removal of the other pollutants as well as studying more variables.

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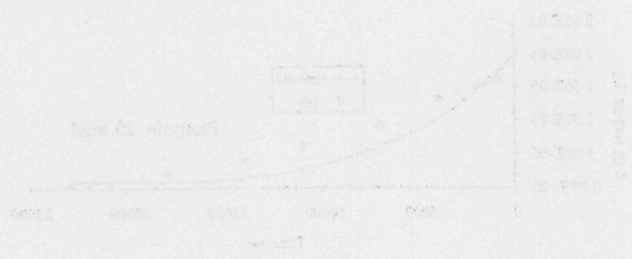


Fig. 6. The evolution of the estimated minimum for point 50 and 150 (g/L).

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The same procedure and the model may be applied for other water quality parameters, for example the removal of other pollutants as well as studying more variables.

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