

Application of adsorption packed-bed reactor model for phenol removal

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An application of an adsorption packed-bed reactor model was used to study the efficiency of the removal of phenolic wastes. The model equations are a combination of Particle Kinetics and Transport Kinetics. The model predicts the relations between sorbate concentration and flow rate as variables with column depth at any time. The model was verified for Granular active carbon [AquaSorb™2000] and for Filtration anthracite [AMSI/AWWA 8100-96] as sorbents and phenol as sorbate through testing over a range of phenol concentrations (100-300 mg/l). Experiments were conducted to determine the Langmuir equilibrium coefficients (α and X_m) and to determine the bulk sorbate solution concentration versus different adsorption column depths and different time as well. The model can predict any data, which is hard or cannot be known from laboratory work. So the model can answer any questions may be asked by engineers or column designers to help them for better and economic design. The results of the model showed good agreement with the laboratory data.

Keywords: Adsorption packed-bed reactor model, Granular active carbon, Filtration anthracite, Phenol, Particle kinetics, Transport kinetics

1. Introduction

Phenol is an inhibitory and toxic compound present in wastewater from petroleum refining, petrochemical, coke conversion and pharmaceutical plants [1].

Adsorption process, and in particular those using activated carbon, are finding increased use in wastewater treatment for phenol removal. Adsorption on Granular Activated Carbon (GAC) is one of the best commercial proven methods for removing toxic organic chemicals, such as phenol, from wastewater [2].

A fixed-bed column is used commonly for contacting wastewater with GAC. Fixed-bed columns can be operated singly, in series, or in parallel. The water to be treated is applied to the top of the column and withdrawn at the bottom. The advantage of a downflow design is that adsorption of organics and filtration of suspended solids are accomplished in a single step [3].

Computer modeling of adsorption in packed bed reactors has been developing since about 1965 based on the materials balance principle, described by [4]. The modeling

results may be in terms of either the adsorbate concentration distance profile, or the concentration time curve at the end of the column, i.e, the breakthrough curve. Most computer modeling, and pilot plant studies, have focused on defining the breakthrough curve, since the output at the end of the column is a measure of performance.

This work focuses on the concentration profile, especially the portion where mass transfer occurs, i.e, the "wave front". The behavior of the wave front relates directly to design as its velocity and length determine the column length and the time of operation. Also, from a conceptual standpoint, the wave front shape and velocity integrate all of the complex phenomena that occur within the reactor bed. The wave front concept was discussed by [5, 6], but the characteristics were not established, nor was the wave front used as a basis for design. Instead, the document used the ideas of carbon use rate and contact time as parameters for sizing an adsorption reactor column. Practice has evolved largely along the latter path.

The aim of this research is to study the efficiency of the removal of phenol as sorbate by

Granular activated carbon [AquaSorb™2000] and by Filtration anthracite [AMSI/AWWA 8100-96] fixed beds, and conducting experiments to verify a mathematical model. The variables studied in this laboratory work were sorbate concentration and flow rate. The model can delineate relationships, which are hard or cannot be known from laboratory data, and can look at the effect of different conditions on the efficiency of pollutant removal.

2. Packed – bed reactor kinetics

The two reactions that govern kinetics in packed-bed columns are particle kinetics and transport kinetics.

2.1. Particle kinetics

The kinetic sub-model for the rate of mass transfer from the solution into the granular particle was delineated from a study by [7] and was used because experimental coefficients were readily available, and it was easy to apply to the modeling scheme. The relationship is stated:

$$(\delta\bar{X} / \delta t)_P = \bar{D}.C(\bar{X} - \bar{X}^*), \quad (1)$$

in which,

- $(\delta\bar{X} / \delta t)_P$ is the kinetic term when solid phase diffusion is rate controlling ($\mu\text{g adsorbate/gm adsorbent/min}$),
- \bar{D} is the kinetic coefficient in solid phase ($\text{ml solution} / \mu\text{g adsorbate/min}$),
- C is the concentration of adsorbate species in aqueous phase ($\mu\text{g adsorbate/ml solution}$),
- \bar{X} is the average concentration of adsorbate within adsorbent particle ($\mu\text{g adsorbate/gm adsorbent}$),
- \bar{X}^* is the concentration of adsorbate in solid phase at equilibrium with aqueous phase adsorbate concentration, C^* , determined in accordance with Langmuir isotherm expression ($\mu\text{g adsorbate} / \text{gm adsorbent}$), and

C^* is the equilibrium concentration of adsorbate ($\mu\text{g adsorbate/ml solution}$).

The kinetic coefficient, \bar{D} , in eq. (2) was found to be a function of C and X / \bar{X}^* :

$$\bar{D} = [I_0 - b. X / \bar{X}^*].C^n, \quad (2)$$

in which,

- I_0 is the coefficient for which $\log I_0 = \log \bar{D}$ when $C = 1$ and $X / \bar{X}^* = 0$ ($\text{ml solution}/\mu\text{g adsorbate}\cdot\text{min}$),
- b is the kinetic coefficient ($\text{ml solution}/\mu\text{g adsorbate}\cdot\text{min}$), and
- n is the slope of $\log \bar{D}$ vs $\log C$ relationship (dimensionless).

The equilibrium concentration, \bar{X}^* , can be defined by either of the classic isotherms, i.e., the Freundlich or Langmuir. The Langmuir isotherm was used in the empirical work for eq. (1) and (2), and is defined:

$$\frac{\bar{X}^*}{X_m} = \frac{\alpha C^*}{1 + \alpha C^*}, \quad (3)$$

in which,

- X_m is the maximum solid phase concentration used as a Langmuir isotherm coefficient ($\mu\text{g adsorbate/gm adsorbent}$),
- \bar{X}^* is the concentration of adsorbate in solid phase at equilibrium with aqueous phase adsorbate concentration, C^* , determined in accordance with Langmuir isotherm expression ($\mu\text{g adsorbate} / \text{gm adsorbent}$),
- C^* is the equilibrium concentration of Adsorbate ($\mu\text{g adsorbate/ml solution}$), and
- α is the equilibrium coefficient ($\text{ml solution}/\mu\text{g adsorbate}$).

2.2. Transport kinetics

Downstream from the inflection point of the wave front, Z'_0 , transport kinetics governs and assumes that the uptake of adsorbate is limited by the rate at which adsorbate molecules are delivered to the external surface of the adsorbent particles at any given infini-

tesimal column slice [8]. To model this phenomenon, an adsorbate-adsorbent collision probability function was proposed [8, 9, 10, 11] based upon observations of $C(Z)t$ curves for dilute solutions and fresh adsorbent, i.e.,

$$C(Z) = C_0 \exp[-\lambda(Z - Z_0)], \quad (4)$$

in which,

- $C(Z)$ is the concentration in column as a function of distance, Z (μg adsorbate/ml solution),
 λ collision probability coefficient (cm^{-1}),
 Z_0 is the distance from top of the column to the inflection point (cm), and
 Z_0 aqueous phase concentration at the inflection point of the $C(Z)t$ curve (μg adsorbate/ml solution).

Substituting first and second derivatives of eq. (4), for the condition that $\delta C / \delta t = 0$ (assuming approximate steady state), gives:

$$(\delta \bar{X} / \delta t)_r = (1/\rho)(P/(1-P))(V + D\lambda) \lambda C_0 \exp[-\lambda(Z - Z_0)], \quad (5)$$

in which,

- $(\delta \bar{X} / \delta t)_r$ is the kinetic term when advection-dispersion transport is rate controlling (μg adsorbate/gm adsorbent/min),
 ρ is the dry density of the granular adsorbent particles (gm/ml),
 P is the porosity of the packed bed,
 V interstitial flow velocity (cm/min), and
 D coefficient of dispersion (cm^2/min).

The coefficient, λ , is a measure of the probability that an adsorbate molecule will collide with an adsorbent particle (or the number of collisions per unit length of travel in the column). The coefficient, λ , was determined empirically [8] to have the form:

$$\lambda = (c / Q) + d, \quad (6)$$

in which,

- c is the experimental coefficient (min^{-1});
 Q is the flow rate (ml/min), and
 d is the experimental coefficient (cm^{-1}).

where c and d are experimental coefficients for the adsorbate-adsorbent system.

3. Materials and methods

3.1 Adsorption packed – bed reactor model

In 1991 Federico developed a numerical solution and mathematical model of adsorption packed-bed reactor. The model equations are a combination of Particle Kinetics (eq. 1) and Transport Kinetics (eq. 5). The model was verified for Dowex 50 as sorbents and Rhodamine-B dye as sorbate. In this work, an application of a adsorption packed-bed reactor model [12] was used to study the efficiency of the removal of phenolic wastes. The model was verified for Granular active carbon [AquaSorb™2000] and for Filtration anthracite [AMSI/AWWA 8100-96] as sorbents and phenol as sorbate through testing over a range of phenol concentrations (100-300 mg/l). The model predicts the relations between sorbate concentration and flow rate as variables with column depth at any time.

3.2. Experimental set-up

Part I

Laboratory experiments for part I were carried out to determine the Langmuir equilibrium coefficients (α and X_m). Using phenol with concentration (20, 50, 100, 150, 200, 250, 300 mg/l) as sorbate and 1 gram Granular active carbon [AquaSorb™2000] or filtration anthracite [AMSI/AWWA 8100-96] 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. Phenol was measured by photometric method using spectrophotometer and according to the Standard Methods for Examination of Water and Wastewater [13].

Part II

Laboratory experiments for part II were carried out to determine the bulk sorbate solution concentration versus different adsorption column depths and different time as well. The experimental work was carried out to

verify the mathematical model with packed bed reactor using phenol as sorbate with concentration (100, 200 and 300 mg/l) and flow rates (21.6 and 43.2 l/d). To achieve the objectives of this work two identical columns with internal diameter 5 cm and 100 cm long were used. The columns had holes every 10 cm to take samples. The first column was packed with Granular active carbon [AquaSorb™2000] and the second column was packed with Filtration anthracite [AMSI/AWWA 8100-96]. Feed tanks were made from plastic with capacity of 100 liters. The system was provided with two peristaltic pumps which were designed for research purpose. The peristaltic pumps were [Master Flex-U.S.A., Cole-Parmer Instrument Company] and the pumps were used as feeding pumps. Collecting tanks were made from plastic with capacity of 50 liters. The experimental set-up is shown in fig. 1.

The samples volume was 5 ml for all sampling points. Phenol was measured by photometric method using spectrophotometer and according to the Standard Methods for Examination of Water and Wastewater [13].

4. Results and discussion

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

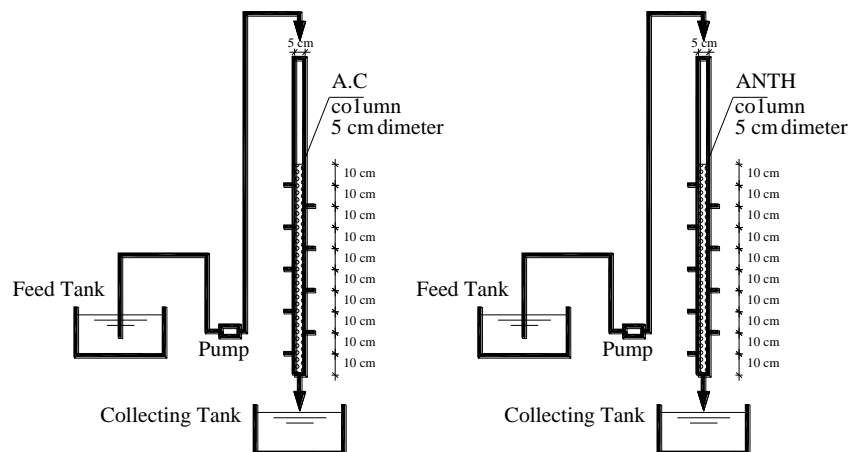


Fig. 1. Experimental set-up.

4.1. Laboratory results

Part I

The kinetics 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.

Fig. 2 shows the isotherm, while fig. 3 shows the linearized form of the isotherm for Granular active carbon [AquaSorb™2000] as sorbent and phenol as sorbate. From linearized form the Langumir constants, α and X_m , were determined using the slope and intercept.

Fig. 4 shows the isotherm, while fig. 5 shows the linearized form of the isotherm for Filtration anthracite [AMSI/AWWA 8100-96] as sorbent and phenol as sorbate. From linearized form the Langumir constants, α and X_m , were determined using the slope and intercept. The Langumir constants were key factor in the kinetic model.

Part II

The model was calibrated and verified by simulating laboratory conditions for 8 lab runs. The model results were compared with those from laboratory.

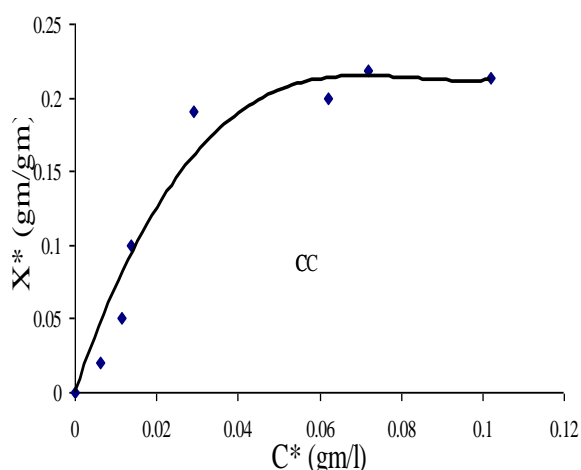


Fig. 2. Langmuir isotherm for Granular active carbon [AquaSorb™2000].

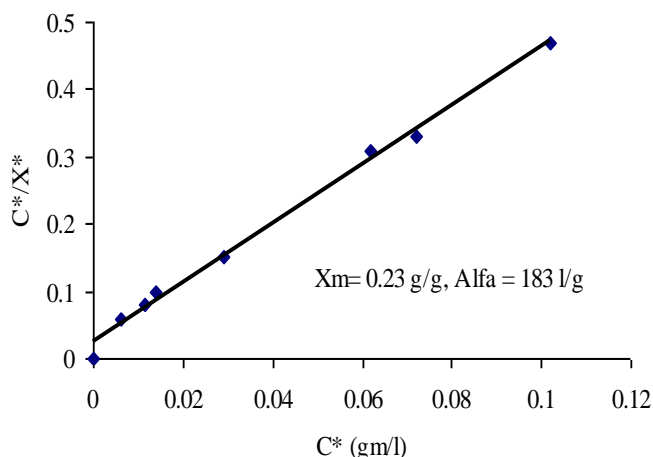


Fig. 3. Linearized isotherm for Granular active carbon [AquaSorb™2000].

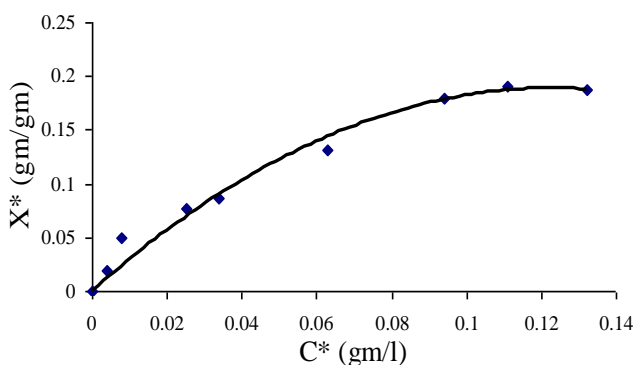


Fig. 4. Langmuir isotherm for Filtration anthracite [AMSI/AWWA 8100-96].

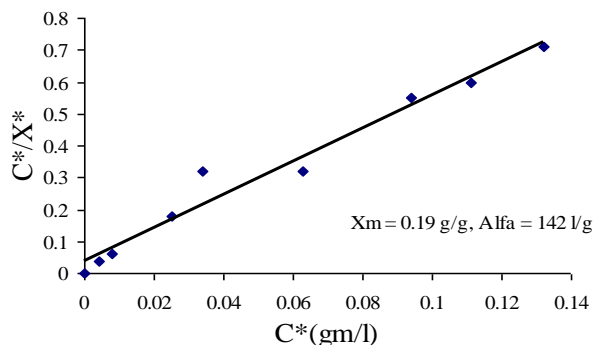


Fig. 5. Linearized isotherm for Filtration anthracite [AMSI/AWWA 8100-96].

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.

Table 1 presents the final values of c and d coefficients which were determined using a trial and error procedure using the model for one experiment then the same coefficients were used at any sorbate concentration. The c and d coefficients were used to determine collision probability coefficient λ .

Fig. 6 shows the laboratory data points with the calibrated simulations for Granular active carbon [AquaSorb™2000] as sorbent and phenol as sorbate. Fig. 7 shows the laboratory data points with the calibrated simulations for Filtration anthracite [AMSI/AWWA 8100-96] as sorbent and phenol as sorbate.

4.3. Model verification

After identifying the calibrated parameters, the model was verified against the laboratory data points. Fig. 8 shows the measured and simulated data for Granular active carbon [AquaSorb™2000] as sorbent and phenol as sorbate. Fig. 9 shows the measured and simulated data for Filtration anthracite

Table 1
Final model key parameters

Type of sorbent	GAC	ANTH
C	29	18
D	0.04	0.023

[AMSI/AWWA 8100-96] as sorbent and phenol as sorbate. The results of the model showed good agreement with the laboratory data. More details on laboratory measurements and model verification can be found in (Walid, 2005).

4.4. Exercise with the model

The mathematical model can facilitate the design of full-scale systems. Once verified, the model can be used to examine different operative conditions from those directly measured. Also the model can give predictions for a vari-

ety of circumstances that may be not easily reproduced or experimentally simulated with a pilot program. The equipment, time, and expense normally associated with pilot-scale test programs make a model an important tool for adsorption system design. For example a quick exercise with the model showed that increasing the flow rate from 21.6 l/d to 42.3 l/d under initial phenol concentration of 100 mg/l for Granular active carbon [AquaSorb™2000], showed a decreasing in the efficiency of phenol removal from 98.2% to 89.6% after nine days at 100 cm adsorption column depth. Fig. 10 shows the relation

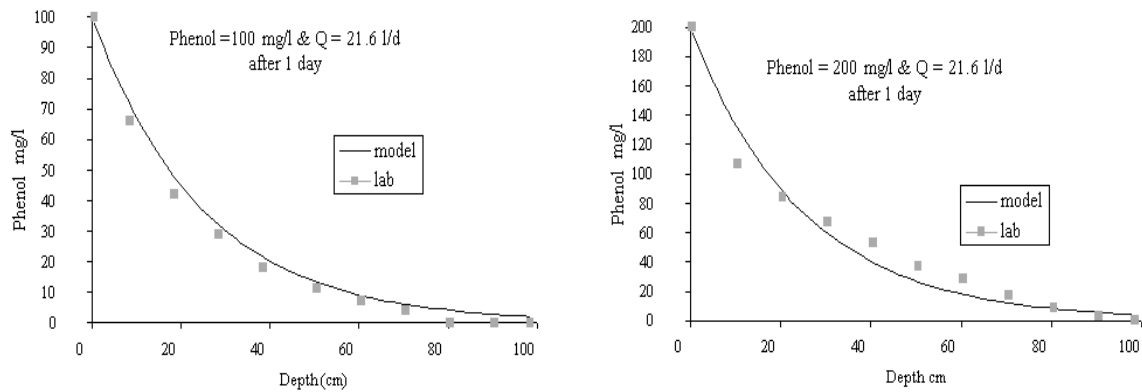


Fig. 6. The laboratory data points with final calibration simulations for granular active carbon [AquaSorb™2000].

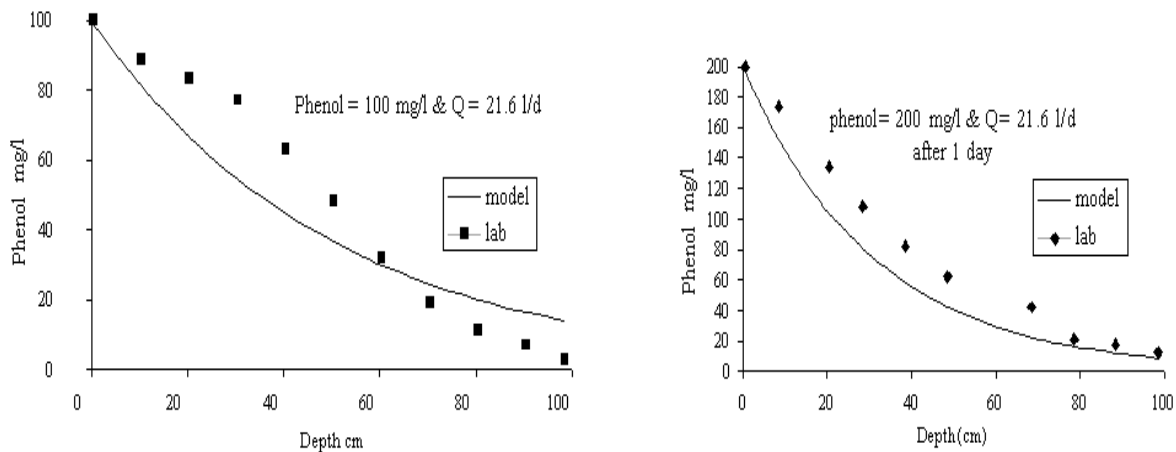


Fig. 7. The laboratory data points with final calibration simulations for filtration anthracite [AMSI/AWWA 8100-96].

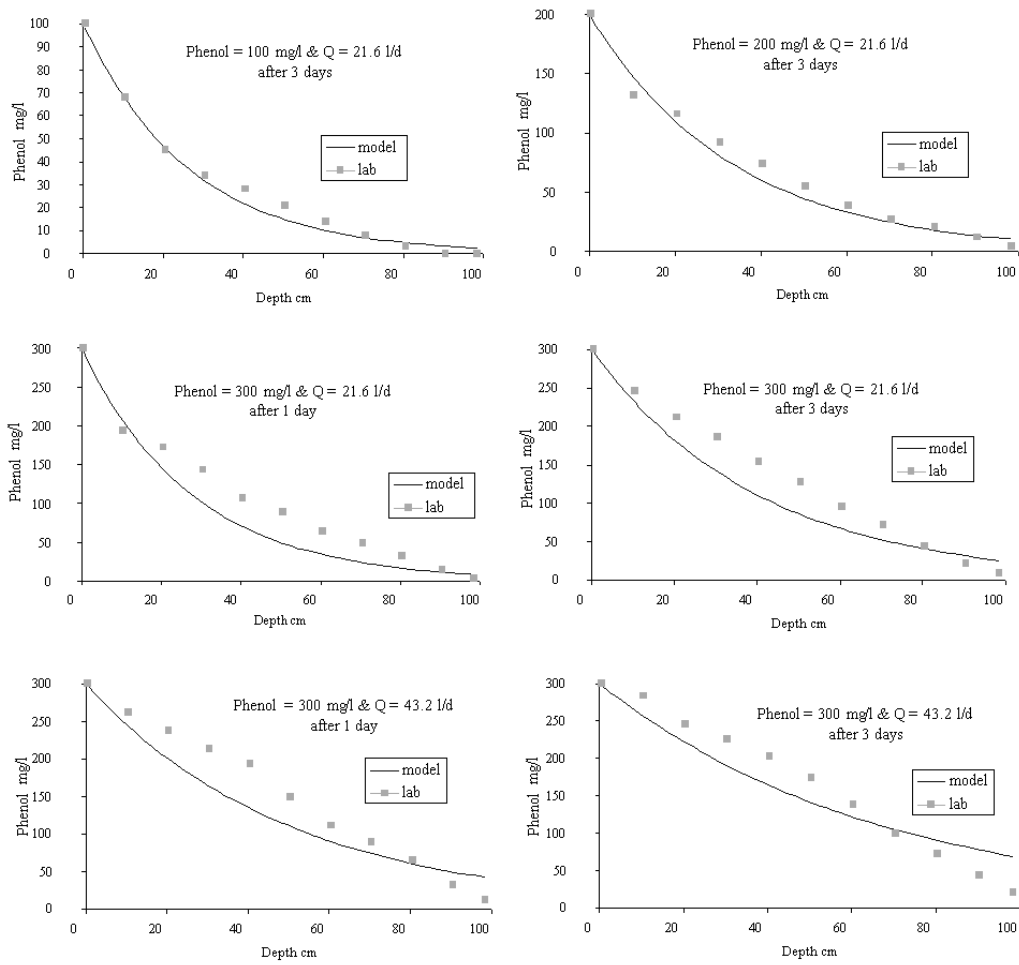


Fig. 8. The laboratory data points with calibrated simulations for Granular active carbon [AquaSorb™2000].

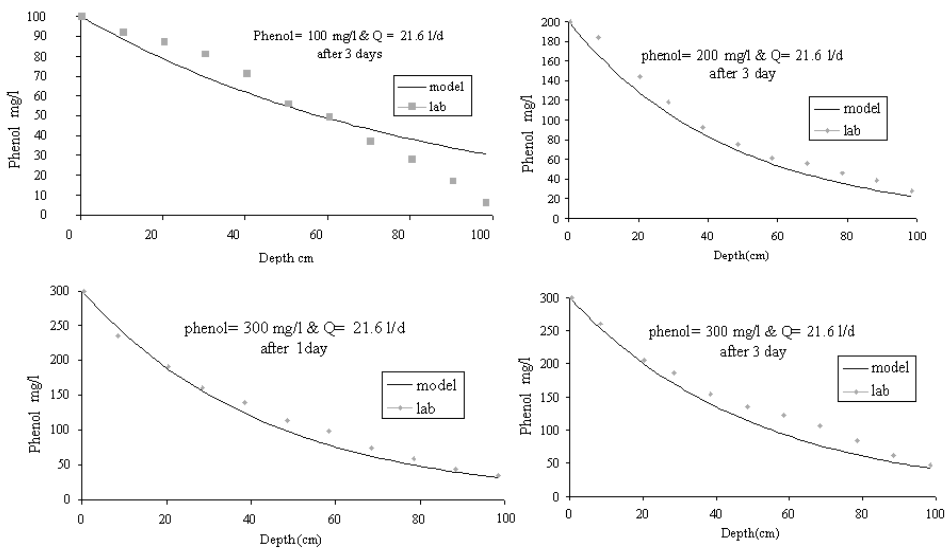


Fig. 9. The laboratory data points with calibrated simulations for filtration anthracite [AMSI/AWWA 8100-96].

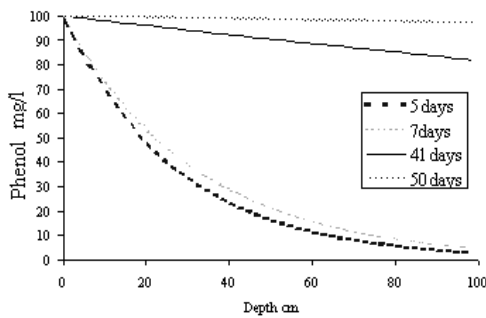


Fig. 10. The model prediction for Granular active carbon [AquaSorb™2000] as sorbents and phenol (100 mg/l) as sorbate, under flow rate = 21.6 l/d.

between sorbate concentration and the column depth after different operating days from the model. To get this relation from laboratory data, it needs a lot of time and effort.

5. Conclusions

1. The adsorption packed-bed reactor model was verified for Granular active carbon [AquaSorb™2000] and for Filtration anthracite [AMSI/AWWA 8100-96] as sorbents and phenol as sorbate through testing over a range of phenol concentrations (100-300 mg/l). The results of the model showed good agreement with the laboratory measurements.
2. The same procedure and the model may be helpful for future work. For example the removal of other pollutants as well as studying more variables.

Abbreviations

- ANTH is the filtration anthracite [AMSI/AWWA 8100-96],
b is the kinetic coefficient (ml solution/ $\mu\text{g adsorbate}\cdot\text{min}$),
c is the experimental coefficient (min^{-1}),
C is the concentration of adsorbate species in aqueous phase ($\mu\text{g adsorbate/ml solution}$),
*C** is the equilibrium concentration of adsorbate ($\mu\text{g adsorbate/ml solution}$),
C'₀ is the aqueous phase concentration at the inflection point of the $C(Z)t$ curve ($\mu\text{g adsorbate/ml solution}$),
C(Z) is the concentration in column as a

- function of distance, *Z* ($\mu\text{g adsorbate/ml solution}$),
d is the experimental coefficient (cm^{-1}),
D is the coefficient of dispersion (cm^2/min),
 \bar{D} is the kinetic coefficient in solid phase (ml solution / $\mu\text{g adsorbate}/\text{min}$),
 GAC is the Granular active carbon [AquaSorb™2000],
I₀ is the coefficient for which $\log I_0 = \log \bar{D}$ when $C = 1$ and $X / \bar{X}^* = 0$ (ml solution/ $\mu\text{g adsorbate}\cdot\text{min}$),
n is the slope of $\log \bar{D}$ vs $\log C$ relation ship (dimensionless),
P is the porosity of the packed bed,
Q is the flow rate (ml/min),
 \bar{X} is the average concentration of adsorbate within adsorbent particle ($\mu\text{g adsorbate/gm adsorbent}$),
 \bar{X}^* is the concentration of adsorbate in solid phase at equilibrium with aqueous phase adsorbate concentration, *C**, determined in accordance with Langmuir isotherm expression ($\mu\text{g adsorbate}/\text{gm adsorbent}$),
X_m is the maximum solid phase concentration used as a Langmuir isotherm coefficient ($\mu\text{g adsorbate/gm adsorbent}$),
 $(\delta \bar{X} / \delta t)_P$ is the kinetic term when solid phase diffusion is rate controlling ($\mu\text{g adsorbate/gm adsorbent}/\text{min}$),
 $((\delta \bar{X} / \delta t)_T$ is the kinetic term when advection-dispersion transport is rate controlling ($\mu\text{g adsorbate/gm adsorbent}/\text{min}$),
V is the interstitial flow velocity (cm/min),
Z'₀ is the distance from top of the column to the inflection point (cm),
 α is the equilibrium coefficient (ml solution/ $\mu\text{g adsorbate}$),
 λ is the collision probability coefficient (cm^{-1}), and
 ρ is the dry density of the granular adsorbent particles (gm/ml).

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