



COMPETITIVE ADSORPTION OF FURFURAL AND PHENOLIC COMPOUNDS ONTO ACTIVATED CARBON IN FIXED BED COLUMN

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ABSTRACT

For a multicomponent competitive adsorption of furfural and phenolic compounds, a mathematical model was built to describe the mass transfer kinetics in a fixed bed column with activated carbon. The effects of competitive adsorption equilibrium constant, axial dispersion, external mass transfer and intraparticle diffusion resistance on the breakthrough curve were studied for weakly adsorbed compound (furfural) and strongly compounds (parachlorophenol and phenol). Experiments were carried out to remove the furfural and phenolic compound from aqueous solution. The equilibrium data and intraparticle diffusion coefficients obtained from separate experiments in a batch absorber, by fitting the experimental data with theoretical model. The results show that the mathematical model includes external mass transfer and pore diffusion using nonlinear isotherms, provides a good description of the adsorption process for furfural and phenolic compounds in fixed bed adsorber.

KEY WORDS: Competitive, Adsorption, Fixed-Bed, Activated-Carbon, Multi-component, Mathematical Model, Mass Transfer Coefficient.

INTRODUCTION

Furfural and phenolic compounds are organic compounds that enter the aquatic environment through direct discharge from oil refineries. The content of these pollutants in the industrial wastewater are usually higher than the standard limit (less than 5 ppm for furfural and less than 0.5 ppm for phenolic compounds).

Activated carbon adsorption is one of the important unit processes that is used in the treatment of drinking waters and renovation of wastewaters (Alexander, 1989).

Understanding of the dynamics of fixed bed adsorption column for modeling is a demanding task due to the strong nonlinearities in the equilibrium isotherms, interference effects of competition of solute for adsorbent sites, mass transfer resistance between fluid phase and solid phase and fluid-dynamics dispersion phenomena. The interplay of these effects produces steep concentration fronts, which moves along the column during the adsorption process, which has to be accounted for in modeling (Babu, 2004).

Several rate models have been developed that take into account an external film transfer rate step, unsteady state transport in the solid phase and nonlinear equilibrium isotherm to predict adsorption rates in batch reactor and fixed bed (Crittenden and Weber, 1978).

The key parameters for design of the adsorption system are the process parameters that are used for modeling the system for predicting the quality of effluent under a wide range of operating conditions. The key process parameters in adsorption such as isotherm constants and mass transfer coefficients are established by conducting batch studies of adsorption. Established isotherm models such as Langmuir and Freundlich are used for assessing the suitability of an adsorbent in adsorption system, where the experimental data are fitted to any one of these models.

The parameters that are responsible for mass transfer operation are the external mass transfer coefficient and intraparticle diffusivity or surface diffusion coefficient in the case of the homogeneous solid phase diffusion model.

The objective of the present research are to conduct experiments on the competitive adsorption equilibrium and adsorption kinetics in a fixed bed for removal of furfural (Fu) in the presence of phenolic compounds (Ph, PCP) from aqueous solution and to compare the experimental results with that simulated by the numerical solution of the general rate model which include axial dispersion, film mass transfer, pore diffusion resistance and nonlinear isotherms.

MODELING OF MULTICOMPONENT FIXED-BED ADSORBER

The dynamics of a fixed bed is described by a set of convection diffusion equations, coupled with source terms due to adsorption and diffusion inside the adsorbent particles.

The adsorption column is subjected to axial dispersion, external film resistance and intraparticle diffusion resistance.

A rate model which considers axial dispersion, external mass transfer, intraparticle diffusion and nonlinear isotherms is called a general multicomponent rate model. Such a model is adequate in many cases to describe the adsorption and mass transfer processes in multicomponent adsorption (Eggers, 2000; Volker, 1999).

The following equations are based on the hypothesis of an intraparticle mass transfer controlled by diffusion into macropores (pore diffusion model). This approach considers three phases:

- a. The mobile phase flowing in the space between particles.
- b. The stagnant film of mobile phase immobilized in the macropores.
- c. The stationary phase where adsorption occurs.

The following basic assumptions are made in order to formulate a general rate model (Eggers, 2000):

- Adsorption process is isothermal.
- The adsorbent particles in the column are spherical and uniform in diameter.
- The concentration gradients in the radial direction are negligible.
- An instantaneous local equilibrium exists between the macropore surface and the stagnant fluid inside macropores of the particles.
- The film mass transfer mechanism can be used to describe the interfacial mass transfer between the bulk-fluid and particle phases.
- The diffusional and mass transfer parameters are constant and independent of the mixing effects of the components involved.

Continuity equation in the bulk-fluid phase:

$$-D_{bi} \frac{\partial^2 C_{bi}}{\partial Z^2} + v \frac{\partial C_{bi}}{\partial Z} + \frac{\partial C_{bi}}{\partial t} + \frac{1 - \varepsilon_b}{\varepsilon_b} \frac{\partial q_i}{\partial t} = 0 \quad \dots 1$$

Using C_{pi} , the concentration in the stagnant fluid-phase (in the macropores), and writing the expression of interfacial flux leads to:

$$\frac{\partial q_i}{\partial t} = \frac{3k_{fi}}{R_p} (C_{bi} - C_{pi,R=R_p}) \quad \dots 2$$

Substitution of equation 2 into equation 1 gives:

$$-D_{bi} \frac{\partial^2 C_{bi}}{\partial Z^2} + v \frac{\partial C_{bi}}{\partial Z} + \frac{\partial C_{bi}}{\partial t} + \frac{3k_f(1-\epsilon_b)}{\epsilon_b R_p} [C_{bi} - C_{pi,R=R_p}] = 0 \quad \dots 3$$

The particle phase continuity equation in spherical coordinates is:

$$(1-\epsilon_p) \frac{\partial C_{pi}^*}{\partial t} + \epsilon_p \frac{\partial C_{pi}}{\partial t} + \epsilon_p D_{pi} \left[\frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial C_{pi}}{\partial R} \right) \right] = 0 \quad \dots 4$$

Initial and boundary conditions

$$C_{bi} = C_{bi}(0, Z) = 0 \quad \dots 5$$

$$C_{pi} = C_{pi}(0, R, Z) = 0 \quad \dots 6$$

$$Z = 0: \frac{\partial C_{bi}}{\partial Z} = \frac{v}{D_{bi}} (C_{bi} - C_{oi}) \quad \dots 7$$

$$Z = L: \frac{\partial C_{bi}}{\partial Z} = 0 \quad \dots 8$$

$$R = 0: \frac{\partial C_{pi}}{\partial R} = 0 \quad \dots 9$$

$$R = R_p: \frac{\partial C_{pi}}{\partial R} = \frac{k_{fi}}{\epsilon_p D_{pi}} (C_{bi} - C_{pi,R=R_p}) \quad \dots 10$$

Defining the following dimensionless variables;

$$c_{bi} = \frac{C_{bi}}{C_{oi}}, c_{pi} = \frac{C_{pi}}{C_{oi}}, c_{pi}^* = \frac{C_{pi}^*}{C_{oi}}, \tau = \frac{vt}{L}, r = \frac{R}{R_p}, z = \frac{Z}{L}$$

$$Pe_{Li} = \frac{vL}{D_{bi}}, Bi_i = \frac{k_{fi}R_p}{\epsilon_p D_{pi}}, \eta_i = \frac{\epsilon_p D_{pi} L}{R_p^2 v}, \zeta_i = \frac{3Bi_i \eta_i (1-\epsilon_b)}{\epsilon_b}$$

The model equations can be transformed into the following dimensionless equations:

$$-\frac{1}{Pe_{Li}} \frac{\partial^2 c_{bi}}{\partial z^2} + \frac{\partial c_{bi}}{\partial z} + \frac{\partial c_{bi}}{\partial \tau} + \zeta_i (c_{bi} - c_{pi,r=1}) = 0 \quad \dots 11$$

$$\frac{\partial}{\partial \tau} [(1-\epsilon_p) c_{pi}^* + \epsilon_p c_{pi}] - \eta_i \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_{pi}}{\partial r} \right) \right] = 0 \quad \dots 12$$

Initial condition becomes ($\tau = 0$):

$$c_{bi} = c_{bi}(0, z) = 0 \quad \dots 13$$

$$c_{pi} = c_{pi}(0, r, z) = 0 \quad \dots 14$$

And boundary conditions become;

$$z = 0: \quad \frac{\partial c_{bi}}{\partial z} = Pe_{Li}(c_{bi} - 1) \quad \dots 15$$

$$z = 1: \quad \frac{\partial c_{bi}}{\partial z} = 0 \quad \dots 16$$

$$r = 0: \quad \frac{\partial c_{pi}}{\partial r} = 0 \quad \dots 17$$

$$r = 1: \quad \frac{\partial c_{pi}}{\partial r} = Bi_i(c_{bi} - c_{pi,r=1}) \quad \dots 18$$

The concentration c_{pi}^* in equation 12 is the dimensionless concentration of component i in the solid phase of the particles. It is directly linked to a multicomponent Langmuir isotherm:

$$q_{e,i} = C_{pi}^* = \frac{q_i b_i C_{pi}}{1 + \sum_{j=1}^{N_s} b_j C_{pj}} = \frac{a_i C_{pi}}{1 + \sum_{j=1}^{N_s} b_j C_{pj}} \quad \dots 19$$

And in dimensionless form:

$$c_{pi}^* = \frac{a_i c_{pi}}{1 + \sum_{j=1}^{N_s} (b_j C_{oj}) c_{pj}} \quad \dots 20$$

Finite element method is used for the discretization of the bulk-fluid phase partial differential equation and the orthogonal collocation method for the particle phase equations an ordinary differential equation system is produced. The ordinary differential equation system with initial values can be readily solved using an ordinary differential equation solver such as the subroutine "ODE15S" of MATLAB which is a variable order solver based on the numerical differentiation formulas (NDFs). Optionally it uses the backward differentiation formulas (BDFs), which is also known as Gear's method.

EXPERIMENTAL WORK AND PROCEDURE

The granulated activated carbon (GAC) used in the experiments was supplied by Unicarbon, Italian. Its physical properties are listed in table 1.

The GAC was sieved into 28/32 mesh with geometric mean diameter of 0.5 mm. The GAC was boiled, washed three times in distilled water and dried at 110° C for 24 hours, before being used as adsorbent.

The aqueous solutions of furfural, phenol and parachlorophenol where prepared using reagent grades. Their properties are listed in table 2.

The experiments were adjusted at the initial pH of 5.7 for phenolic compounds (Ping and Guohua (I), 2001) and 8.1 for furfural, with 0.01 mol/l NaOH and 0.01 mol/l HCl. This is for single

component experiments, while for multicomponent systems, the pH were adjusted at 7. Solutions were not buffered to avoid adsorption competition between organic and buffer (Monneyron and Faur-Brasquet, 2002).

The experiments were carried out in Q.V.F. glass column of 50 mm (I.D.) and 50 cm in height. The GAC was confined in the column by fine stainless steel screen, at the bottom and glass packing at the top of the bed to ensure a uniform distribution of influent through the carbon bed. The influent solutions were introduced to the column through a perforated plate, fixed at the top of the column. Feed solutions were prepared in Q.V.F. vessel supplied with immersed heater with a thermocouple to adjust the temperature of the solution.

For the determination of adsorption isotherms, 250 ml flasks were filled with 100 ml of known concentration of solutes and a known weight of GAC. The flasks were then placed on a shaker and agitated continuously for 30 hours at 30° C. The concentration of furfural, phenol and parachlorophenol in the solutions were determined by a UV-160A spectrophotometer at 254, 270 and 300 nm, respectively.

The adsorbed amount is calculated by the following equations:

$$q_e = \frac{V(C_o - C_e)}{W_A} \quad \dots 21$$

The intraparticle diffusion coefficient for each solute was obtained by 2 liter Pyrex beaker fitted with a variable speed mixer. The beaker was filled with 1 liter of known concentration solution and the agitation started before adding the GAC. At time zero, the accurate weight of GAC were added. Samples were taken every 5 minutes.

The necessary dosage of GAC, to reach equilibrium related concentration of C_e/C_o equal 0.05, were calculated from isotherms model and mass balance equation as follow:

$$W_A = \frac{V(C_o - C_e)}{q_e} \quad \dots 22$$

Where:

$$q_e = f(C_e) \quad \dots 23$$

RESULTS AND DISCUSSION

Adsorption isotherm

The equilibrium isotherms for the investigated solutes onto GAC are presented in figure 1 .All the adsorption isotherm display a nonlinear dependence on the equilibrium concentration.

The adsorption data for all the system fitted by Langmuir (Lucas and Cocero, 2004), Freundlich (Weber and Walter, 1972), Radke-Prausnitz (Radke and Prausnitz, 1972), Dubinin-Radushkevich (Monneyron and Faur-Brasquet, 2002), Redlich-Peterson (Jossens et al., 1972) and combination of Langmuir-Freundlich models (Sips, 1984).

The correlation between experimental data and the theoretical models was very good for all systems. The Langmuir adsorption model was selected to be introduced in the fixed bed model, where:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad \dots 24$$

The equilibrium data for furfural, phenol and parachlorophenol (multicomponent system) aqueous solution in GAC is adapted as the competitive Langmuir isotherm model (Fahmi and Munther, 2003):

$$q_{e,i} = \frac{q_{m,i} b_i C_{e,i}}{1 + \sum_{j=1}^{N_s} b_j C_{e,j}} \quad \dots 19$$

In which the parameters $q_{m,i}$, b_i are the coefficient of the single component. The parameters are evaluated to be:

$$\begin{aligned} q_{m, Fu} &= 0.3744 \text{ kg/kg} & b_{Fu} &= 18.42 \text{ m}^3/\text{kg} \\ q_{m, Ph} &= 0.3500 \text{ kg/kg} & b_{Ph} &= 34.6 \text{ m}^3/\text{kg} \\ q_{m, PCP} &= 0.3199 \text{ kg/kg} & b_{PCP} &= 49.6 \text{ m}^3/\text{kg} \end{aligned}$$

INTRAPARTICLE DIFFUSION COEFFICIENT

There were a good matching between batch experimental results and predicted data using pore diffusion model for batch operation (Ping and Guohua (II), 2001) as shown in figure 2.

The pore diffusion coefficient for each solute are evaluated form the batch experiments to be $D_{p, Fu} = 9.870 \times 10^{-10} \text{ m}^2/\text{s}$, $D_{p, Ph} = 8.251 \times 10^{-10} \text{ m}^2/\text{s}$ and $D_{p, PCP} = 7.657 \times 10^{-10} \text{ m}^2/\text{s}$.

The external mass transfer coefficients in packed bed model for each solute were evaluated by the correlation of Wilson and Gearkoplis (Ping and Guohua (I), 2001).

$$Sh_i = \frac{1.09}{\varepsilon_b} Sc_i^{1/3} Re^{1/3} \quad \text{for } Re=0.0015-55 \quad \dots 25$$

$$\text{Where: } Sh_i = \frac{K_{f,i} d_p}{D_{m,i}}, \quad Sc_i = \frac{\mu_w}{\rho_w D_{m,i}} \quad \text{and} \quad Re = \frac{\rho_w u d_p}{\mu_w}$$

In which the molecular diffusion coefficient $D_{m,i}$ of furfural, phenol and parachlorophenol in aqueous solution are listed in table 2.

These values substitutes in equation 25 to evaluate $K_{f,i}$ at different interstitial velocity in the mathematical mode.

The axial dispersion coefficient calculated form Chung and Wen equation (Gupta et al., 2001):

$$\frac{D_b \rho_w}{\mu_w} = \frac{Re}{0.2 + 0.011 Re^{0.48}} \quad \dots 26$$

BREAKTHROUGH CURVE

Figures 3 to 10 show that the experimental and predicted breakthrough curves for multicomponent system at different flow rate, bed depth and initial concentration of solutes at constant temperature of 30° C. It is clear from these figures that:

1. The adsorption capacity order for the ternary system onto GAC as follow:

$$PCP > Ph > Fu$$



In this case, the capacity of the adsorbate seems to influence the adsorption energy greatly. The octanol-water partition coefficient K_{ow} given in table 2, shows that the parachlorophenol is more hydrophobic than phenol and furfural.

It has been clearly demonstrated that adsorption of phenolic compounds onto activated carbon induces the formation of π - π bond, where activated carbon act as an electron donor and the solute benzene ring has an electron-withdrawing character (Monneyron and Faur-Brasquet, 2002). The mesomeric and/or inductive character of the substituent of the aromatic compound influences this formation and thus the molecule's adsorption energy. This interpretation is supported by experimental results: the withdrawing inductive character of chloride substituents (Gupta, 1946) decreases the electron density of the parachlorophenol-benzene ring compared with that of phenol-benzene ring (Wheeler and Levy, 1959). The adsorption energy of parachlorophenol is higher than that of Ph. These results agree with Ping and Guohua (I) (2001).

The adverse effect of the OH group (Bartell and Miller, 1923) on adsorption of phenol may be attributed to the capability of this group to form hydrogen bonding with the water which renders the compound less liable to be adsorbed in compared with parachlorophenol.

The lower adsorption capacity of furfural may be explained by its higher solubility, low molecular weight and low octanol-water coefficient in compared with parachlorophenol or phenol.

Furfural is a polar solvent and activated carbon is generally regarded to favor the adsorption of non-polar compound rather than polar compounds. Since pure carbon surface is considered to be non-polar, but in actual practice, some carbon-oxygen complexes are present which render the surface slightly polar (Al-Bahrani and Martin, 1977).

2. In case of multicomponent systems, at the initial stage, there are a lot of active sites of GAC, the strongly and weakly adsorbed components take the active sites freely. With increasing time, the weakly adsorbed component is not easily adsorbed but moves a head with the bulk fluid and takes the active sites first in the front part of the fixed bed. Because the strongly adsorbed component tends to take the active sites instead of the weakly adsorbed component, it will displace the sites that had been taken by the weakly adsorbed components. The result is that the local concentration of the weakly adsorbed component within the fixed bed adsorber is higher (Ping and Guohua (I), 2001).

3. The frontal concentration profile of the breakthrough curves, in a fixed bed adsorber, is related to the initial solutes concentration, Biot number (Bi) and Peclet number (Pe).

4. An increase in the flow rate at constant bed depth will increase the Biot number with slight increase in Peclet number, Biot is the ratio of external mass transfer rate to the intraparticle mass transfer rate.

When Biot number is large (that is, the intraparticle mass transfer is the controlled step (Ping and Guohua (I), 2001)), the break point will appear early, this is due to the decrease in contact time between the solute and the adsorbent at higher flow rate.

5. An increase in bed depth at constant flow rate will increase the Peclet number at constant Biot number, where Peclet number is the ratio of axial convection rate to the axial dispersion rate.

When Peclet number is small (that is, the effect of axial dispersion is not negligible (Ping and Guohua (I), 2001)), the breakthrough curve become flat and the break point appear early.

6. The simulated breakthrough curves for adsorption of ternary system (furfural, phenol, and parachlorophenol) onto activated carbon are in a close agreement with the experimental results. Thus, the mathematical model which includes axial dispersion, film mass transfer, pore diffusion resistance and nonlinear isotherms provides a good description of the competitive adsorption process in fixed bed adsorber.

CONCLUSIONS

This work has studied the characteristics of the competitive adsorption of furfural in the presence of phenolic compounds in aqueous solution in a fixed bed adsorber. A mathematical model which includes external mass transfer and pore diffusion using non-linear isotherm was investigated.

The results show that the solubility and hydrophobicity has a large influence on adsorption capacity and energy respectively. These influences were confirmed by ternary adsorption.

The general rate model provides a good description of the adsorption process of furfural and phenolic compounds in fixed bed adsorber onto activated carbon.

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NOTATION

Symbols

b	Langmuir constant, m^3/kg
Bi	Biot number $\left(\frac{K_f R_p}{\varepsilon_p D_{pi}} \right)$, -
C	Concentration in fluid, kg/m^3
C_o	Initial concentration, kg/m^3
D_b	Axial dispersion coefficient, m^2/s
D_m	Molecular diffusion coefficient, m^2/s
D_p	Pore diffusion coefficient, m^2/s
d_p	Particle diameter, m
K_f	Fluid to particle mass transfer coefficient, m/s
L	Length of column, m
Pe	Peclet number $\left(\frac{uL}{D_b} \right)$, -
Q	Fluid flow rate, m^3/s
q_e	Internal concentration of solute in particle, kg/kg
q_m	Adsorption equilibrium constant defined by Langmuir equation, kg/kg
Re	Reynolds number $\left(\frac{\rho_w u d_p}{\mu_w} \right)$, -
R_p	Radius of particle, m
Sc	Schmidt number $\left(\frac{\mu_w}{\rho_w D_{m,i}} \right)$, -
Sh	Sherwood number $\left(\frac{K_{f,i} d_p}{D_{m,i}} \right)$, -
t	Time, s

Symbols

u	Interstitial velocity $\left(\frac{Q}{\pi R_p^2 \varepsilon_b}\right)$, m/s
V	Volume of solution, m ³
W_A	Mass of activated carbon, kg
Z	Axial distance, m

Greek symbols

ε_b	Bed porosity, -
ε_p	Porosity of adsorbent, -
μ_w	Viscosity of water, Pa.s
ρ_w	Density of water, kg/m ³

Subscript

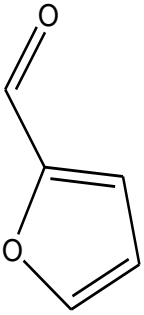
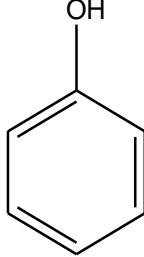
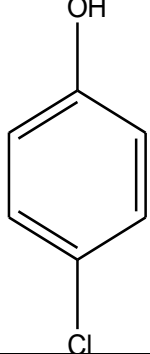
b	Bulk fluid phase
e	Equilibrium
Fu	Furfural
i	Component number (1, 2, 3 ...)
L	Liquid phase
o	Initial
p	Particle phase
PCP	Parachlorophenol
Ph	Phenol

TABLES AND FIGURES

Table 1, Physical properties of activated carbon

Raw material	Coconut shell
Apparent density, kg/m ³	480 - 490
Bulk density, kg/m ³	770
BET surface area, m ² /g	1100
Particle porosity	0.5
Bed porosity	0.41
Iodine number, mg/g	1100 - 1130
pH	10.2 - 10.6
Ash content, %	5 (max)
Particle size, %	
Mesh +12	0.2
12 - 16	20.67
16 - 20	25.05
20 - 30	34.18
30 - 40	18.83
40 -	1.08

Table 2, Main properties of adsorbates

Property	Furfural	Phenol	Parachlorophenol
Symbol	Fu	Ph	PCP
Formula	C ₅ H ₄ O ₂	C ₆ H ₅ OH	C ₆ H ₄ OCl
Structure			
Molecular weight, g/mole	96.08	94.11	129
Solubility in water (at 20° C), g/l	83	66.7	28
Log (K _{ow})	1.58	1.50	2.35
Molecular diffusion (at 20° C), m ² /s	1.04×10 ⁻⁸	9.6×10 ⁻⁹	8.82×10 ⁻⁹

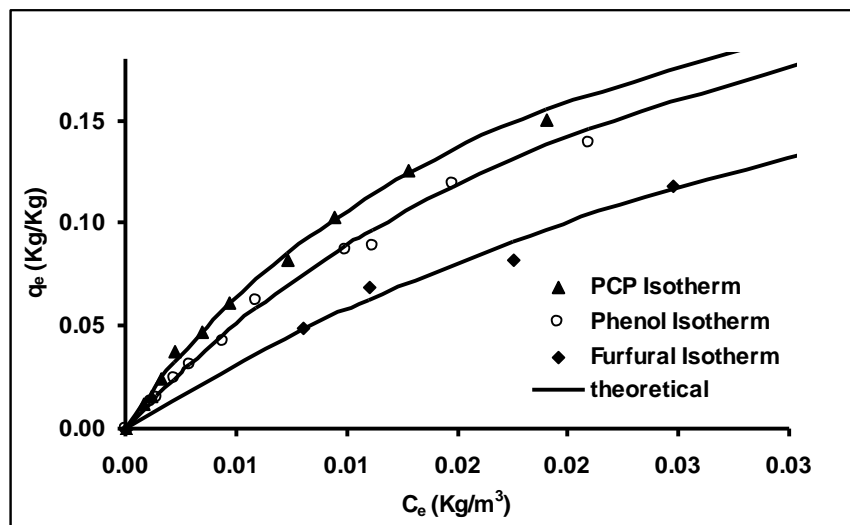


Fig (1) Adsorption isotherm for PCP, Phenol and Furfural onto activated carbon at 303 K.

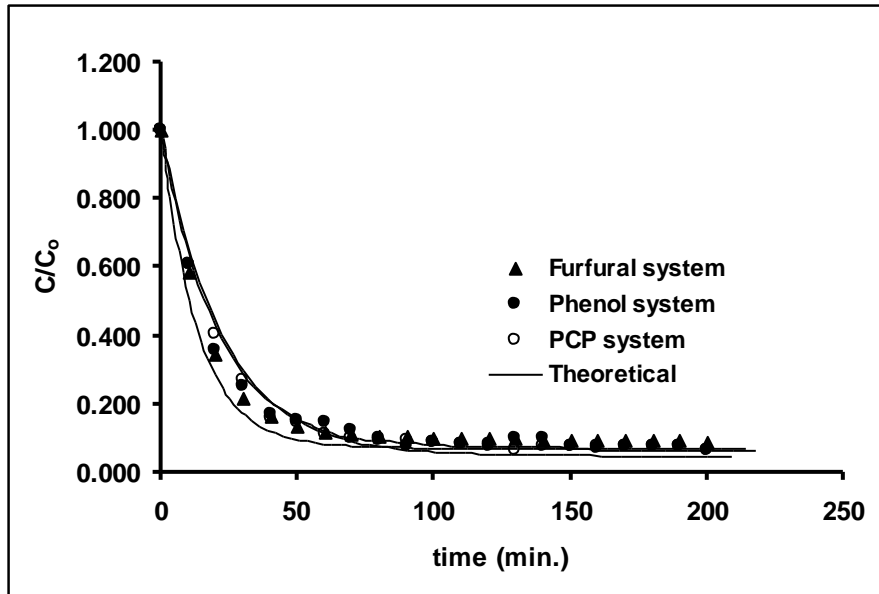


Fig (2) Comparison of the measured concentration-time data with that predicted by pore diffusion model in batch adsorber for Furfural ,Phenol and PCP systems.

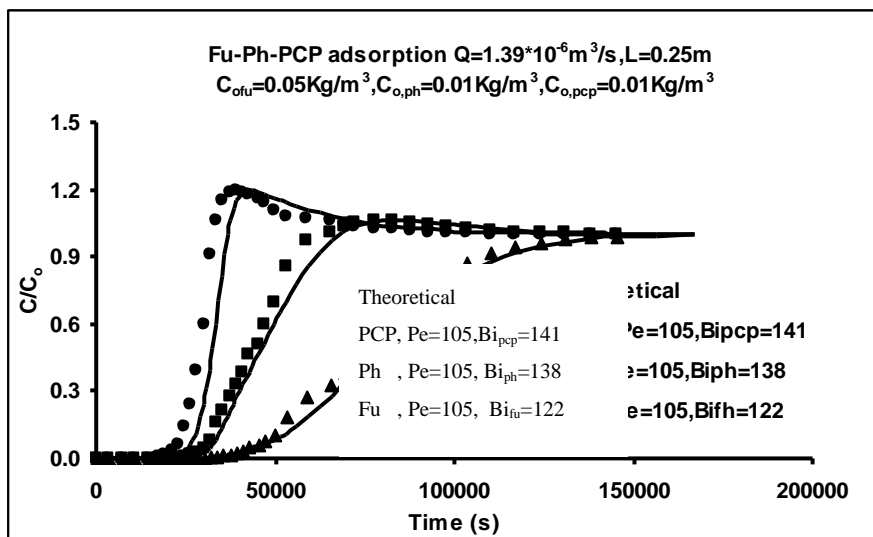


Fig (3) The experimental and predicted breakthrough curves for adsorption of Fu-Ph-PCP system onto activated carbon at $C_{o,pcp}=0.01 \text{ kg/m}^3$.

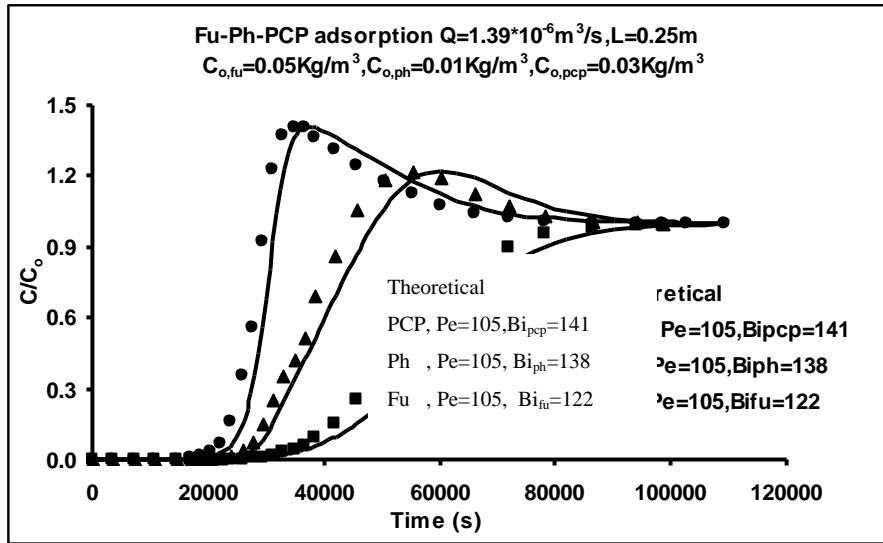


Fig (4) The experimental and predicted breakthrough curves for adsorption of Fu-Ph-PCP system onto activated carbon at $C_{o, \text{pcp}}=0.03 \text{ kg/m}^3$.

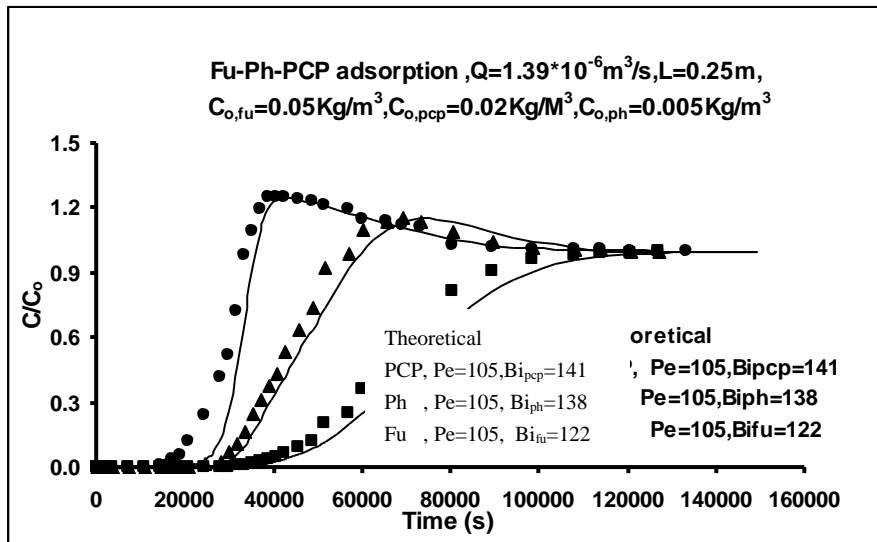


Fig (5) The experimental and predicted breakthrough curves for adsorption of Fu-Ph-PCP system onto activated carbon at $C_{o, \text{ph}}=0.005 \text{ kg/m}^3$.

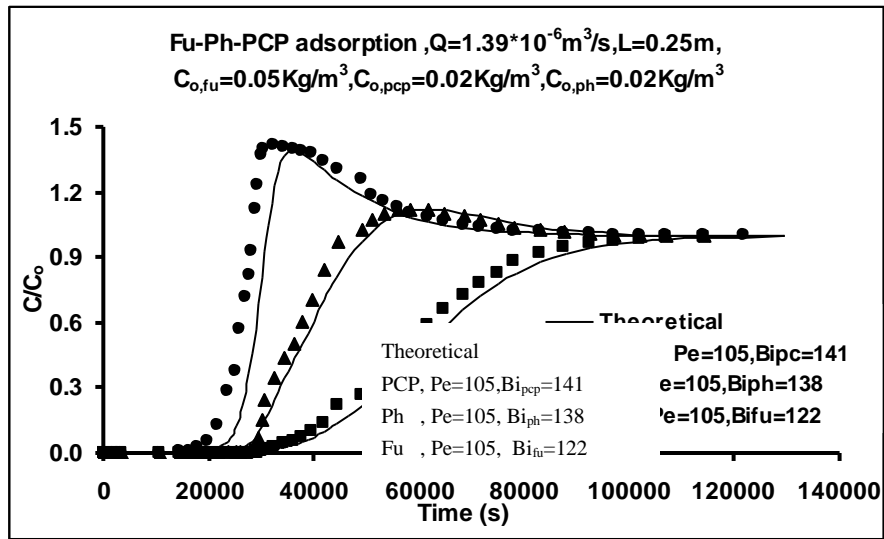


Fig (6) The experimental and predicted breakthrough curves for adsorption of Fu-Ph-PCP system onto activated carbon at $C_{0, \text{ph}}=0.02 \text{ kg/m}^3$.

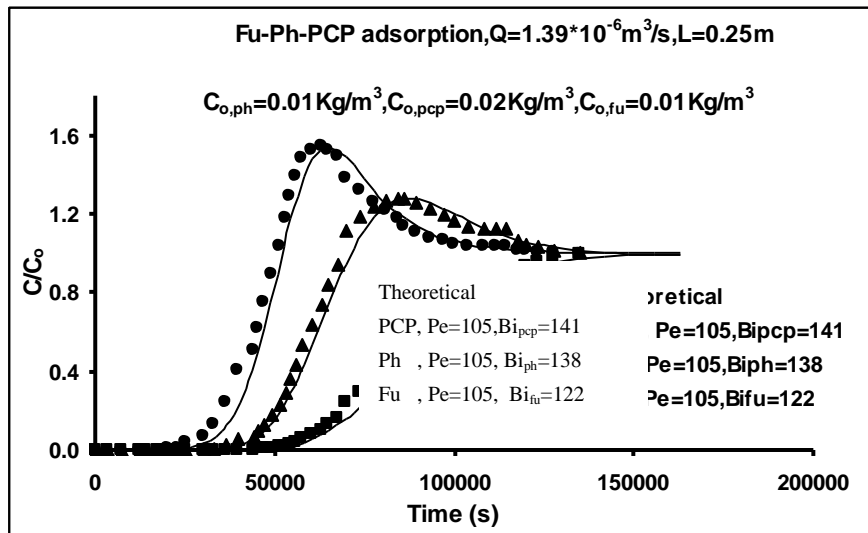


Fig (7) The experimental and predicted breakthrough curves for adsorption of Fu-Ph-PCP system onto activated carbon at $C_{0, \text{fu}}=0.01 \text{ kg/m}^3$.

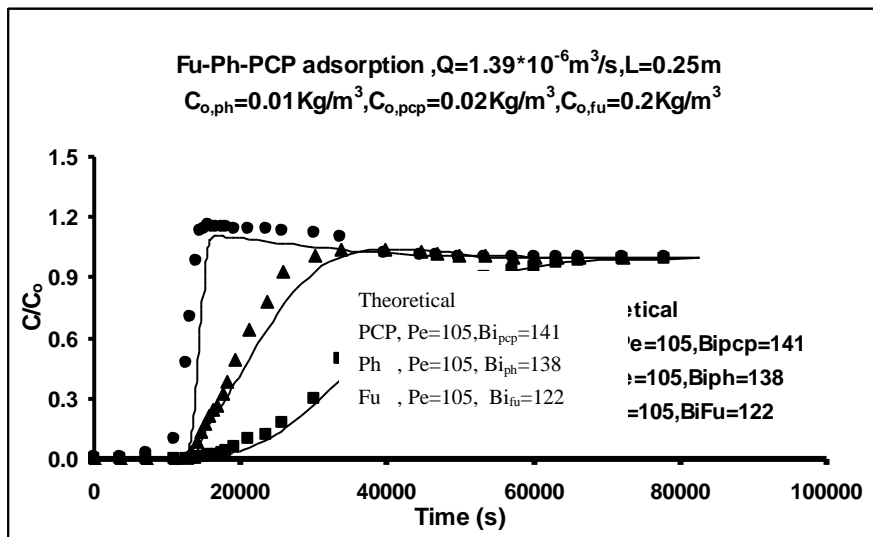


Fig (8) The experimental and predicted breakthrough curves for adsorption of Fu-Ph-PCP system onto activated carbon at $C_{o,fu}=0.2 \text{ kg/m}^3$.

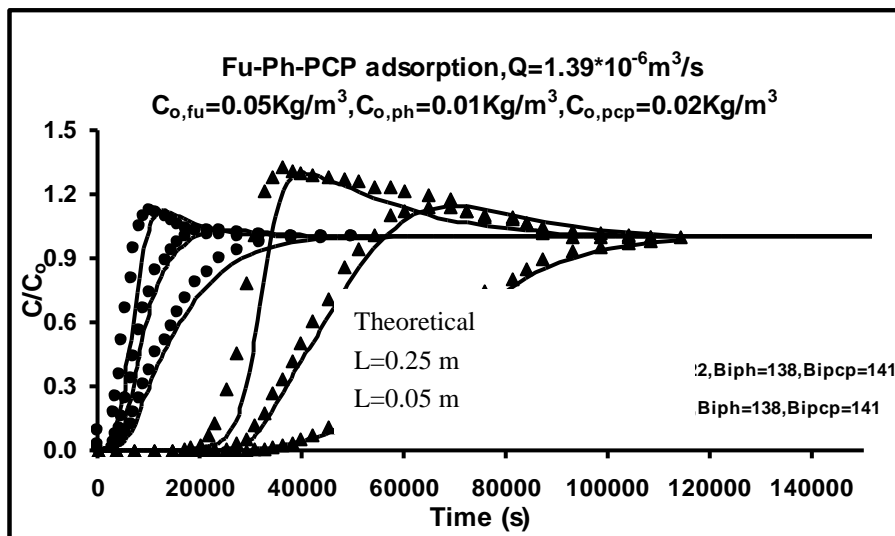


Fig (9) The experimental and predicted breakthrough curves for adsorption of Fu-Ph-PCP system onto activated carbon at different bed depth.

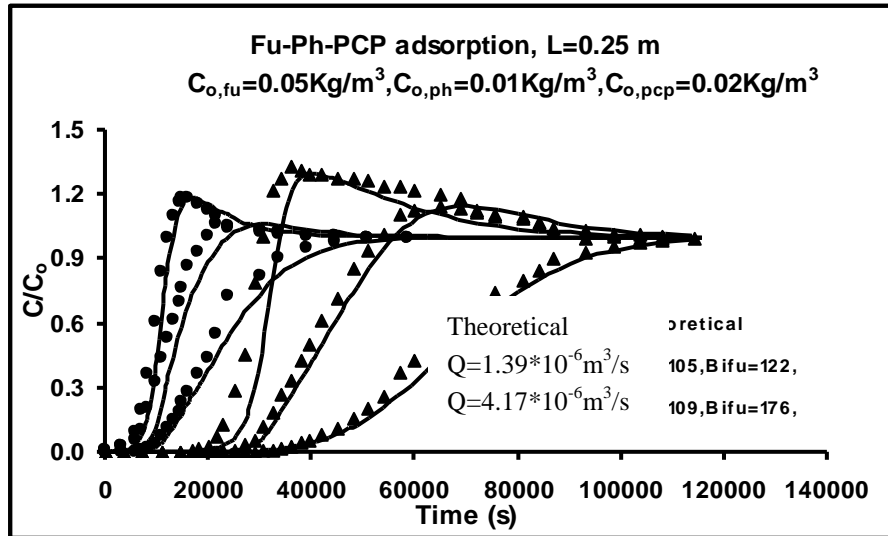


Fig (10) The experimental and predicted breakthrough curves for adsorption of Fu-Ph-PCP system onto activated carbon at different flow rate.