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Removal of phenol and lead from synthetic wastewater by adsorption onto granular activated carbon in fixed bed adsorbers: prediction of breakthrough curves

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ABSTRACT

The adsorption of phenol and lead (II) onto granular activated carbon (GAC) in single and binary system has been studied using fixed bed adsorber. A general rate multi-component model has been utilized to predict the fixed bed breakthrough curves for dual-component system. This model considers both external and internal mass transfer resistances as well as axial dispersion with non-liner multi-component isotherm. The effect of important parameters, such as flow rate, bed height and initial concentration on the behavior of breakthrough curves have been studied. The equilibrium isotherm model parameters such as isotherm model constants, pore diffusion coefficients (D_p) were obtained from batch experiments, while the external mass transfer coefficients and axial dispersion (k_f, D_z) were calculated from empirical correlations. The results show that the general rate model was found suitable for describing the adsorption process of the dynamic behavior of the GAC adsorber column.

Keywords: Adsorption; GAC; Phenol; Lead; Langmuir isotherm model; Fixed bed

1. Introduction

The removal of toxic contaminants such as heavy metal ions and organic pollutants from industrial wastewaters is one of the most important environmental issues to be solved today. Lead (II) has been found together with a variety of aromatic compounds including phenol, naphthalene, and trichloroethylene (TCE) at high concentrations in a number of contaminated sites [1]. Lead (II) and its organic co-pollutants often originate from industrial sources such as the iron-steel, petroleum, pesticides, paints, solvent, pharmaceuticals, wood preserving chemicals. Phenol containing water, when chlorinated during disinfection of water results in the formation of chlorophenol [2,3].

Adsorption is a well-established and powerful technique for treating domestic and industrial effluents [4]. Activated carbon is the most widely and effectively used adsorbent. A typical activated carbon particle, whether in a powdered or granular form, has a porous structure consisting of a network of interconnected macropores, mesopores, and micropores that provide a good capacity for the adsorption of organic molecules due to high surface area. The surface chemistry of activated carbon and the chemical characteristics of adsorbate, such as polarity, ionic nature, functional groups, and solubility, determine the nature of bonding mechanisms as well as the extent and strength of adsorption. A variety of physicochemical mechanisms/forces, such as van der Waals, H-binding, dipole dipole interactions, covalent bonding, cation bridging, and water bridging, can be responsible

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for the adsorption of organic compounds in activated carbon [5,6].

While much research has been carried out on the uptake of single species of metal ions and organic species by activated carbon, little attention seems to have been given to the study of organic–metal ion mixtures [7]. Despite the fact that not only single toxic metallic species but organic components also exist in wastewaters and the presence of a multiplicity of metals and organics often gives rise to interactive effects, insufficient attention seems to have been paid to this problem. The examining the effects of metal ions and organics in various combinations is more representative, of the actual environmental problems faced by treatment technologies, than are single metal or organic studies [8–11].

Fixed bed adsorber is a continuous flow operation adsorption process for industrial applications in wastewater treatment [12]. The design of an adsorption column depends on various important parameters such as flow rate, initial concentration and bed height (mass of adsorbent). Understanding of adsorption characteristics, determination of break point time for adsorption operation and effective utilization of the column is possible by carrying out the mathematical modeling of fixed-bed adsorption column. Continuous adsorption studies are required to collect the experimental data for the design of adsorption column and for subsequent scale-up from pilot plant to industrial scale operation. Past studies mainly focused on analytical approach of solving the dynamics of fixed-bed adsorption column. These models, exclude some of the important physical aspects such as axial dispersion and intra-particle resistances along the bed length and linear isotherm such as: homogenous surface diffusion model (HSDM) described by Hand and Crittenden [14]; second-order reversible reaction model (SRRM) and quasichemical kinetic model (QKM) by Kim and Yung [16]. In the present study, a general multi-component model is used to predict the breakthrough curves of organic-metal ion mixtures in fixed bed column for binary component onto granular activated carbon (GAC) and compare the experimental results with that simulated by numerical solution of model which includes film mass transfer, pore diffusion resistance, axial dispersion and nonlinear isotherm [13–16].

2. Mathematical modeling and simulation

In the present study, a mathematical model for the fixed bed column is proposed by incorporation of important parameter such as external mass transfer resistance, internal mass transfer resistance and nonlinear multi-component isotherm. The proposed model can be extensively used for understanding the dynamics of fixed bed adsorption column for the adsorption of organic and inorganic (metal ions) compounds. To formulate a generalized model for the fixed bed adsorption column, following assumptions are made [17,18]:

- Equilibrium of adsorption is described by the nonlinear multi-component Langmuir isotherm.
- Mass transfer across the boundary layer surrounding the solid particles is characterized by external-film mass transfer coefficient (k_f).
- Intra-particle mass transfer is characterized by pore diffusion coefficient (D_p).
- Macro-porous adsorbent particles are spherical and homogeneous in size and density.
- Compressibility of the mobile phase is negligible.
- Fluid inside particles (macropores) is stagnant, i.e., there is no convective flow inside macropores.
- The adsorption process is isothermal. There is no temperature change during a run.
- The concentration gradients in the radial direction are negligible.
- All mechanisms which contribute to axial mixing are lumped together into a single axial dispersion coefficient.

Based on the assumption of the model, the governing equations for multi-component system can be obtained from differential mass balance of the bulk-fluid phase and the particles phase respectively:

Continuity equation in the bulk-fluid phase:

$$-D_{zi}\frac{\partial^2 C_{bi}}{\partial Z^2} + V_i\frac{\partial C_{bi}}{\partial Z} + \frac{\partial C_{bi}}{\partial t} + \frac{3k_{fi}\left(1-\varepsilon_b\right)}{\varepsilon_b R_p}\left[C_{bi} - C_{pi,R=R_p}\right] = 0 \tag{1}$$

Continuity equation inside the particle phase:

$$\left(1-\varepsilon_p\right)\frac{\partial C^*_{pi}}{\partial t} + \varepsilon_p\frac{\partial C_{pi}}{\partial t} - \varepsilon_p D_{pi}\left[\frac{1}{R_p^2}\frac{\partial}{\partial R_p}\left(R_p^2\frac{\partial C_{pi}}{\partial R_p}\right)\right] = 0 \tag{2}$$

Initial and boundary conditions:

The initial and boundary conditions may be represented by the following equations:

Initial condition (t = 0):

$$C_{bi} = C_{bi}(0, Z) = 0 \tag{3}$$

$$C_{pi} = C_{pi}(0, R, Z) = 0 \tag{4}$$

Boundary conditions:

$$Z = 0:\ \frac{\partial C_{\mathrm{bi}}}{\partial Z} = \frac{\nu}{D_{\mathrm{bi}}}\left(C_{\mathrm{bi}} - C_{\mathrm{oi}}\right) \tag{5}$$

$$Z = L:\ \frac{\partial C_{\mathrm{bi}}}{\partial Z} = 0 \tag{6}$$

$$R = 0:\ \frac{\partial C_{\mathrm{pi}}}{\partial R} = 0 \tag{7}$$

$$R = R_{\mathrm{p}}:\ \frac{\partial C_{\mathrm{pi}}}{\partial R} = \frac{k_{\mathrm{fi}}}{\varepsilon_{\mathrm{p}} D_{\mathrm{pi}}}\left(C_{\mathrm{bi}} - C_{\mathrm{pi},R=R_p}\right) \tag{8}$$

Dimensionless groups:

Defining the following dimensionless variables:

$$c_{\mathrm{bi}} = \frac{C_{\mathrm{bi}}}{C_{\mathrm{oi}}},\ c_{\mathrm{pi}} = \frac{C_{\mathrm{pi}}}{C_{\mathrm{oi}}},\ c^{*}_{\mathrm{pi}} = \frac{C^{*}_{\mathrm{pi}}}{C_{\mathrm{oi}}},\ \tau = \frac{vt}{L},\ r = \frac{R}{R_{\mathrm{p}}},\ z = \frac{Z}{L}$$

Also, the dimensionless parameters are defining as:

$$\mathrm{Pe}_i = \frac{\nu L}{D_{zi}},\ \mathrm{Bi}_i = \frac{k_{\mathrm{fi}} R_{\mathrm{p}}}{\varepsilon_{\mathrm{p}} D_{\mathrm{pi}}},\ \eta_i = \frac{\varepsilon_{\mathrm{p}} D_{\mathrm{p}i} L}{R_{\mathrm{p}}^2 \nu},\ \zeta_i = \frac{3Bi_i \eta_i\left(1 - \varepsilon_{\mathrm{b}}\right)}{\varepsilon_{\mathrm{b}}}$$

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

$$-\frac{1}{Pe_{\mathrm{i}}}\frac{\partial^2 c_{\mathrm{bi}}}{\partial z^2} + \frac{\partial c_{\mathrm{bi}}}{\partial z} + \frac{\partial c_{\mathrm{bi}}}{\partial \tau} + \zeta_{\mathrm{i}}\left(c_{\mathrm{bi}} - c_{\mathrm{pi},r=1}\right) = 0 \tag{9}$$

$$\frac{\partial}{\partial \tau}\left[\left(1 - \varepsilon_{\mathrm{p}}\right)c^{*}_{\mathrm{pi}} + \varepsilon_{\mathrm{p}} c_{\mathrm{pi}}\right] - \eta_{\mathrm{i}}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial c_{\mathrm{pi}}}{\partial r}\right)\right] = 0 \tag{10}$$

In these equations, the Peclet number (Pe_{i}) reflects the ratio of the convection rate to the dispersion rate, while the Biot number (Bi_{i}) reflects the ratio of the external film mass transfer rate to the intra-particle diffusion rate.

Initial conditions become ($\tau = 0$) [19,20]:

$$c_{\mathrm{bi}} = c_{\mathrm{bi}}(0, z) = 0 \tag{11}$$

$$c_{\mathrm{pi}} = c_{\mathrm{pi}}(0, r, z) = 0 \tag{12}$$

And boundary conditions become:

$$z = 0:\ \frac{\partial c_{\mathrm{bi}}}{\partial z} = Pe_{\mathrm{i}}\left(c_{\mathrm{bi}} - 1\right) \tag{13}$$

$$z = 1:\ \frac{\partial c_{\mathrm{bi}}}{\partial z} = 0 \tag{14}$$

$$r = 0:\ \frac{\partial c_{\mathrm{pi}}}{\partial r} = 0 \tag{15}$$

$$r = 1:\ \frac{\partial c_{\mathrm{pi}}}{\partial r} = Bi_{\mathrm{i}}\left(c_{\mathrm{bi}} - c_{\mathrm{pi},r=1}\right) \tag{16}$$

The concentration $c_{\mathrm{pi}}{}^{*}$ in Eq. (10) is the dimensionless concentration of component i in the solid phase of the particles. It is directly linked to a multi-component isotherm, which is the extended

Langmuir model:

$$C^{*}_{\mathrm{pi}} = \frac{q_{\mathrm{mi}}\rho_{\mathrm{p}} b_{\mathrm{i}} C_{\mathrm{pi}}}{1 + \sum_{j=1}^{N_s} b_j C_{\mathrm{p}j}} = \frac{\rho_{\mathrm{p}} a_{\mathrm{i}} C_{\mathrm{pi}}}{1 + \sum_{j=1}^{N_s} b_j C_{\mathrm{pj}}} \tag{17}$$

And in dimensionless form:

$$c^{*}_{\mathrm{pi}} = \frac{\rho_{\mathrm{p}} a_{\mathrm{i}} c_{\mathrm{pi}}}{1 + \sum_{j=1}^{N_s}\left(b_j C_{\mathrm{o}j}\right) c_{\mathrm{p}j}} \tag{18}$$

Because of nonlinear multi-component Langmuir isotherm is considered, finite elements method (Galerkin weighted residual method) is used for the discretization of the bulk-fluid phase partial differential equation and the orthogonal collocation method for the particle phase equation 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 V-7.3 which is a variable order solver based on the numerical differentiation formulas (NDFs).

3. Experimental materials and procedure

3.1. Adsorbate

A standard solution of phenol and lead (II) with concentration of (1000 mgl^{-1}) was prepared as follows: A (1 g) of phenol crystals was dissolved in (1 l) of distilled water and the specific concentration was measured by using gas chromatograph (GC). For lead, A (1.5985 g) of $\mathrm{Pb(NO_3)_2}$ salt was dissolved in (1 l) of distilled water and the specific concentration was measured by using atomic absorption spectrophotometer (AAS).

3.2. Adsorbent

Commercial GAC was used as an adsorbent in the present work. It was supplied by (Unicarbo, Italians) and was bought from the Iraqi markets. The physical and chemical properties were measured at the laboratories of the Ministry of Industry and Minerals (Ibn Sina State Company) , Ministry of Oil (Petroleum Development and Research Center), Al-Mustansirria University (College of engineering, Environmental Department) and according to the data from the supplier. The physical and chemical properties of GAC are listed in Table 1.

3.3. Procedure

The initial pH of Phenol and lead solutions were measured by pH meter (ORION 3 STAR, Thermo, US) and its found to be 5.45 and 4.40 respectively. The adsorption of metals and organics decrease at low pH values because of competition for binding sites between cations and protons, while at pH higher than 5.5, solubility of metal complexes decreases sufficiently allowing precipitation, which may complicate the sorption process and do not bind to the adsorption sites on the surface of the GAC. Therefore the optimum pH was found around four [21,22]. So, pH was adjusted with the range of (four) for all single and binary systems by adding the 0.1N HNO_3 and 0.1N NaOH for acidic and basic pH respectively.

The fixed bed adsorber was made of two acrylic columns of 5.3 cm inner diameter and 50 cm height. The GAC bed is confined in the column by fine stainless steel screen at the bottom and a glass cylindrical packing at the top of the bed to ensure a uniform distribution of influent through the carbon bed. The influent solution is introduced to the column through a perforated plate, fixed at the top of the column.

Table 1
Physical and chemical properties of GAC

GAC	Property
1544	Actual density, kg cm^{-3}
641	Apparent density, kg cm^{-3}
751.965	BET Surface area, m^2 g^{-1}
0.584	Particle porosity
0.64	Bed porosity
0.775	Average particle diameter, mm
0.422	Pore volume, cm^3 g^{-1}
1100–1130	Average particle diameter, mm
8.15	pH
3–5	Iodine number, mg g^{-1}

For determination of the adsorption isotherm, a sample of (100 ml) and (50 mg l^{-1}) of each solution was placed in bottles of 250 ml in volume, containing 0.05, 0.1, 0.15, …, to 0.6 g of GAC. The bottles were then placed on a shaker and agitated continuously at 250 rpm and 30°C for 24 h which was more than ample time for adsorption equilibrium according to pervious studies [18,20]. Then the solution was filtrated using filter paper type Wattmann 0.45 µm and a sample of 20 ml from each bottles were taken for analysis to measure phenol and lead concentration respectively using GC 1000, Italia and AAS, Buck, Accusys 211, USA. The adsorbed amount was calculated using the following equation [23]:

$$q_e = \frac{V_L\left(C_o - C_e\right)}{W_A} \tag{19}$$

All the experiments were carried out in duplicates and the average values were used for further calculations.

The pore diffusion coefficient (D_p) for each solute was obtained by 2 l pyrex beaker fitted with variable speed mixer. The beaker was filled with 1 l of 50 mg l^{-1} concentration and the agitation started before the adding of GAC. At time zero, the accurate weight of GAC where added and samples were taken at specified time intervals. The necessary dosage of GAC, to reach equilibrium related concentration of C_e/C_o equal to 0.05, were calculated from Langmuir isotherm model and mass balance equation as follows:

$$W_A = \frac{V_L\left(C_o - C_e\right)}{q_e} \tag{20}$$

With

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{21}$$

The Langmuir model parameters (q_m and b) were estimated by the nonlinear regression method using STATISTICA version-6 soft ware.

At first time, the pore diffusion coefficient is assumed and the model is solved numerically. This process is continued until a perfect match is obtained between the theoretical and experimental concentration decay curves. The principle parameter required for solving the batch model is the external mass transfer coefficient (k_f) and the assumed pore diffusion coefficient (D_p). The following steps must be taken to introduce the required parameter conditions:

- Estimate the optimum concentration decay curve at optimum agitation speed.

- Numerical solution of the batch model can be used to obtain the theoretical concentration decay curve.
- A good match between the experimental and theoretical concentration decay curves should be obtained.

The amount of GAC used for each solute were calculated from final equilibrium related concentration of $C_e/C_o = 0.05$ using the Langmuir model with mass balance in 1 l of solution. The initial concentration were 50 mg l^{-1} with the doses of activated carbon of 5.530 and 5.360 gl^{-1} solution for phenol and lead respectively. The external mass transfer coefficient k_f and Molecular diffusivity D_m in fixed bed column model were calculated using the correlations of Crittenden (1987) [15].

$$k_f = 2.4\, V_s / (\mathrm{Sc}^{0.58}\, \mathrm{R_e}^{0.66}) \tag{22}$$

The liquid diffusivity coefficient was calculated using the equation:

$$D_m = 2.74 \times 10^{-9}\, (\mathrm{MW})^{-1/3} \tag{23}$$

The axial dispersion coefficient, D_z, calculated at different flow rates (1.39×10^{-6}, 2.78×10^{-6} and 4.17×10^{-6} m^3 s^{-1}) of the liquid flowing through fixed bed was obtained from Chung and Wen equation [24]:

$$\frac{\nu L}{D_z} = \frac{L}{2R_p \varepsilon_b}(0.2 + 0.011\,\mathrm{Re}^{0.48}) \tag{24}$$

4. Results and discussion

4.1. Adsorption isotherm

The equilibrium isotherm for the investigated solutes (Ph and Pb^{2+}) onto GAC using multi-component Langmuir model are presented in Fig. 1. The correlation coefficient (R^2) between the experimental data and the theoretical model is 0.9923 and 0.9963 for phenol and lead respectively. The Langmuir parameters are as follows:

- Ph: $q_m = 66.8234$ mg g^{-1}, $b = 0.0590$ l mg^{-1}, $R^2 = 0.9923$
- Pb^{+2}: $q_m = 37.0370$ mg g^{-1}, $b = 0.1258$ l mg^{-1}, $R^2 = 0.9963$

4.2. Pore diffusion coefficient

Pore diffusion coefficients (D_p) of phenol and lead are obtained using batch pore diffusion model by matching the concentration decay curve obtained from experimental data at optimum agitation speed 400 rpm with that obtained from the batch theoretical model as shown in Fig. 2.

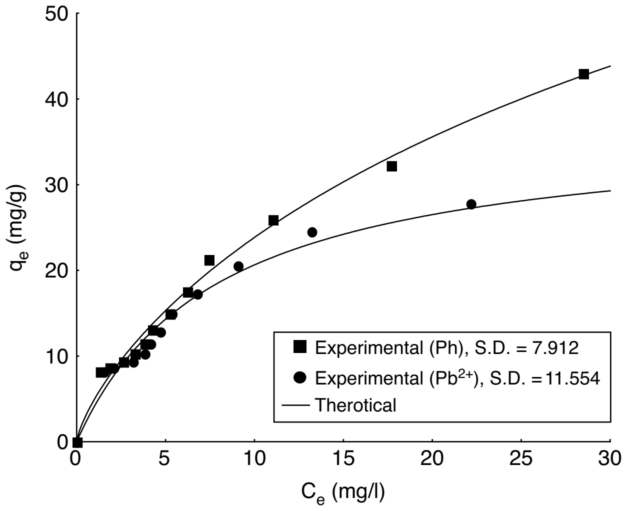

Fig. 1. Adsorption isotherm for (Ph-Pb^{2+}) onto GAC.

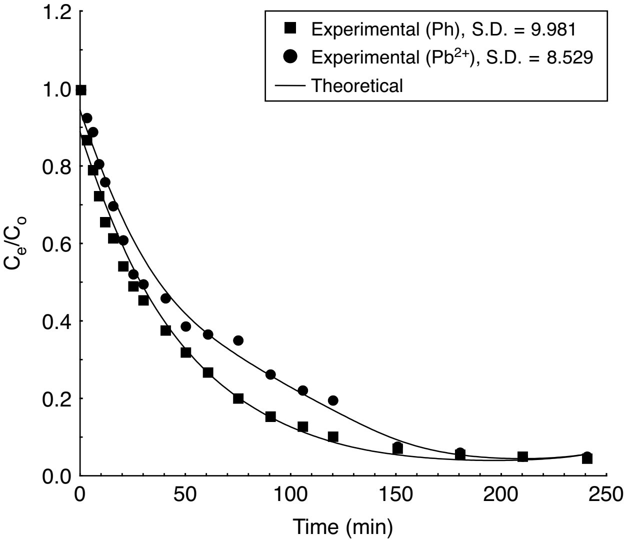

Fig. 2. Comparison of the measured concentration-time decay data with that predicted by pore diffusion model for Ph and Pb^{2+}.

The pore diffusion coefficient for each solute are evaluated from batch experiments to be:

- Ph: $D_p = 6.235 \times 10^{-11}$ m^2 s^{-1}, $R^2 = 0.9942$
- Pb^{2+}: $D_p = 4.265 \times 10^{-11}$ m^2 s^{-1}, $R^2 = 0.9891$

4.3. Breakthrough curves of the single and binary systems

The experimental and predicted breakthrough curves for single and binary system for adsorption of phenol and lead onto GAC at different flow rate, bed height and initial concentration are shown in Figs. 3–10.

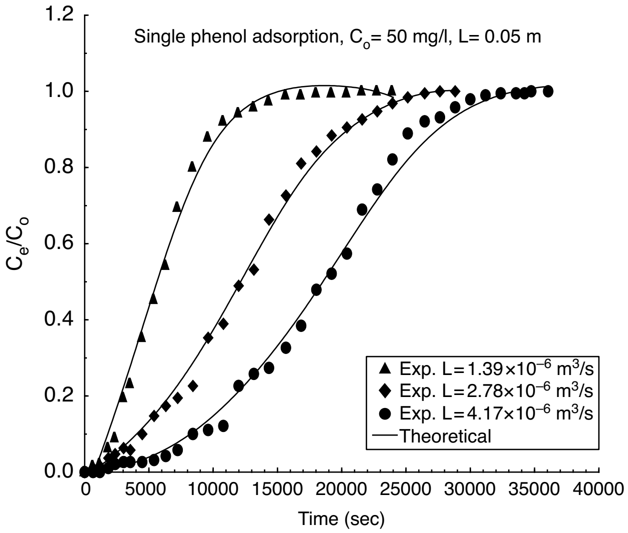

Fig. 3. The experimental and predicted breakthrough curves for adsorption of single phenol onto GAC at different flow rates.

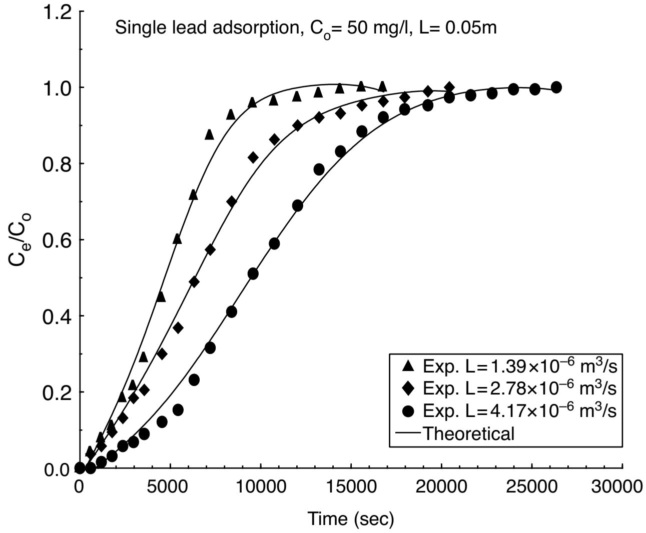

Fig. 4. The experimental and predicted breakthrough curves for adsorption of single lead onto GAC at different flow rates.

From Figs. 1–10, the following results can be drawn:

1. The adsorption capacity order for phenol and lead onto GAC was as follows:

   Ph (66.8234 mg l^{-1}) > Pb^{2+} (37.0370 mg g^{-1}) (Fig. 1). This behavior of the capacity of the adsorbate in batch system seems to influence the adsorption capacity of GAC in fixed bed adsorber. This can be explained by:

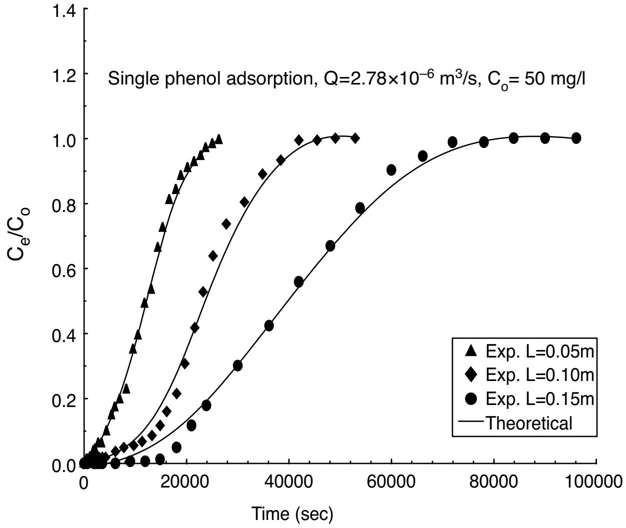

Fig. 5. The experimental and predicted breakthrough curves for adsorption of single phenol onto GAC at different bed heights.

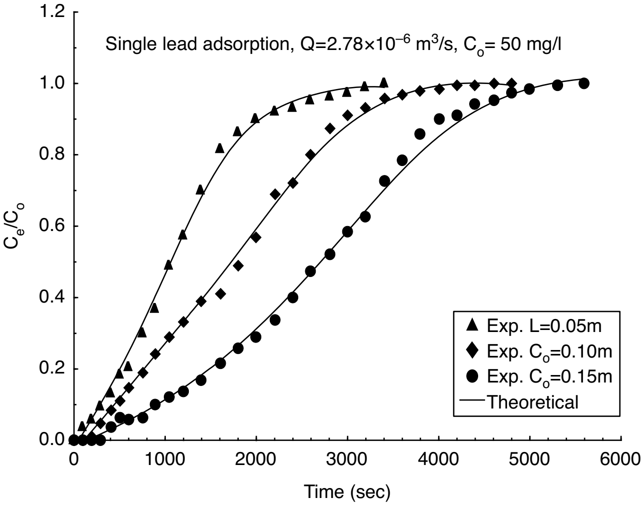

Fig. 6. The experimental and predicted breakthrough curves for adsorption of single lead onto GAC at different bed heights.

   a. Phenol has less solubility (86,000 mg l^{-1}) in water in comparison with lead nitrate (520,000 mg l^{-1}) and consequently with lead [3,12].
   b. Molecular cross-sectional area for phenol is greater than lead (21.40 Å^2 for lead and 30.49 Å^2 for phenol) [3,12].
   c. Phenol can be adsorbed by means of electrostatic attraction between negatively charged phenols and positively charged binding sites. Physical

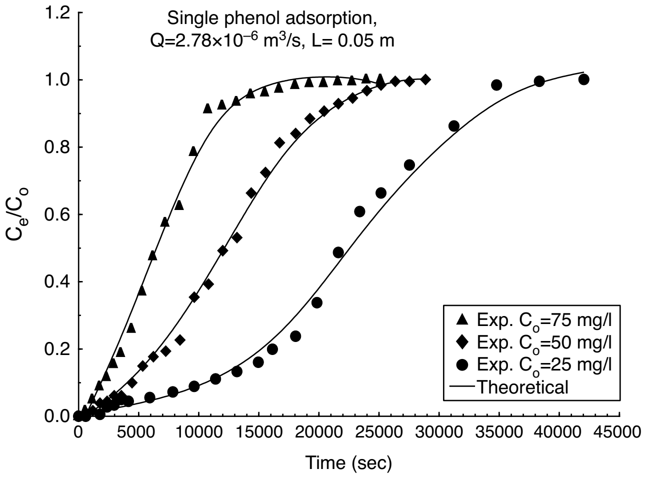

Fig. 7. The experimental and predicted breakthrough curves for adsorption of single phenol onto GAC at different initial concentration.

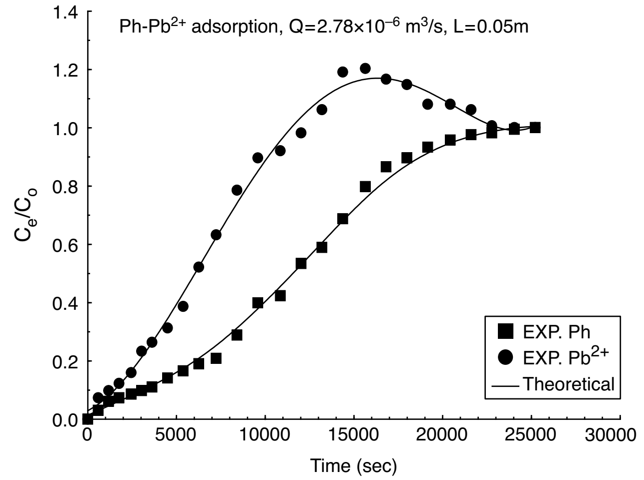

Fig. 9. The experimental and predicted breakthrough curves for adsorption of binary Ph Pb^{2+} system onto GAC.

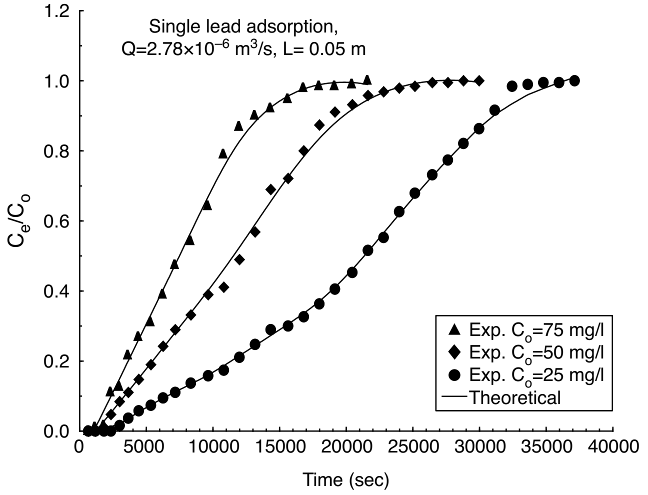

Fig. 8. The experimental and predicted breakthrough curves for adsorption of single lead onto GAC at different initial concentration.

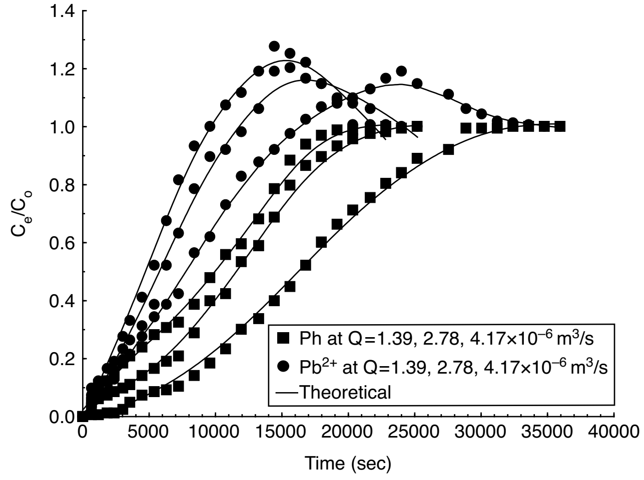

Fig. 10. The experimental and predicted breakthrough curves for adsorption of Ph Pb^{2+} onto GAC at different flow rates.

adsorption by means of Vander Waals, H-bonding, dipole-dipole and dipole-induced dipole has been the main way to adsorb organics such as phenol. However, lead adsorption depended mainly only on the activity and availability of functional groups onto GAC (electrostatic attraction) [25].

2. Effect of flow rate: Figs. 3, 4 and 10 show the experimental and predicted breakthrough curves for Ph and Pb^{+2} in single and binary systems at different flow rates (1.39×10^{-6}, 2.78×10^{-6} and 4.17×10^{-6} m^3 s^{-1}) in terms of C_e/C_o. Its clear from these figures that as the flow rate increases, the time of breakthrough point decreases. This is because the residence time of solute in the bed decreases. Therefore there is not enough time for adsorption equilibrium to be reached which results in lower bed utilization and the adsorbate solution leaves the column before equilibrium. It is expected that the change in flow rate will affect the film diffusion but not the intra-particle diffusion. The higher the flow rates, the smaller film resistance to mass transfer and hence larger k_f results. Increasing flow rate at constant bed height will increase the Bi number with slight increase in Pe number as listed in Table 2. When the Bi number is high the time of

Table 2
The values of Biot number and Peclet number at different flow rates and bed heights

Pollutants	Flow rate, $m^3\ s^{-1}$	Biot number (Bi)	Peclet number (Pe)	SD	Bed height, m	Biot number (Bi)	Peclet number (Pe)	SD
Ph	1.39×10^{-6}	200.282	32.755	11.096	0.05	258.6	31.206	5.475
	2.78×10^{-6}	258.6	33.521	6.607	0.10	258.6	62.412	15.920
	4.17×10^{-6}	303.190	33.955	10.234	0.15	258.6	93.618	8.081
Pb^{2+}	1.39×10^{-6}	229.629	32.755	7.733	0.05	296.370	31.206	10.881
	2.78×10^{-6}	296.370	33.521	7.872	0.10	296.370	62.412	12.514
	4.17×10^{-6}	347.555	33.955	11.562	0.15	296.370	93.618	5.076

breakthrough point will appear early. The higher Bi number values indicates that the film diffusion is not dominating compared to the intra-particle mass transfer and the intra-particle mass transfer is the controlling step (Fig. 10). These results agree with those obtained by Abdul-Hameed [26].

3. Effects of bed height: the bed height is one of the major parameters in the design of fixed bed adsorption column [27]. The experimental and predicted breakthrough curves obtained for different heights of activated carbon 0.05, 0.1 and 0.15 m at constant flow rate and constant initial concentration are presented in Figs. 5 and 6. It is clear from these figures that, at smaller bed height the C_e/C_o increase more rapidly than at higher bed height. Furthermore, at smaller bed height the bed is saturated in less time compared with the higher bed height. Increasing the bed height at constant flow rate increases Pe numbers as listed in Table 2. When Pe number is small, the break point appears early and increases with the Pe number. Hence, the internal and external resistance are confirmed to be the main parameters that control the adsorption kinetics with the increase in bed height. It is clear that increasing bed height increases the breakthrough time and the residence time of the phenol and lead solution in the bed, since the bed volume of GAC increased. Similar findings have been obtained by Sulaymon et al. [28].
4. Effect of initial concentration: The change in initial concentration of Ph and Pb^{2+} will have a significant effect on the breakthrough curves. Figs. 7 and 8 shows the experimental and predicted breakthrough curves at different initial concentration (25, 50, and 75 mg l^{-1}). These figures show that, as the initial concentration increases the time of breakthrough point decreases. The higher the initial concentration, the faster the breakthrough curves; however, the activated carbon loadings are higher at higher initial concentration. For high initial concentration, steeper breakthrough curves are found because the equilibrium is attained faster. Theses results are in agreement with that obtained by Ahmed [19].
5. In multi-component system (binary system) for phenol and lead, it is clear from Figs. 9 and 10 that, at the initial stage, there are a lot of active sites of GAC, and the strongly (Ph) and weakly (Pb^{2+}) adsorbed component take the active site freely. With increasing time, the weakly adsorbed component is not easily adsorbed but moves ahead with the bulk-fluid and the strongly adsorbed component tends to displace the sites that had been taken by the weakly adsorbed component. The result is that the local concentration of the weakly adsorbed component within the fixed bed adsorber is higher.

5. Conclusions

GAC was found to be more suitable adsorbent for the removal of organic pollutants (phenol in the present work) than inorganic pollutants (heavy metals, lead). The equilibrium isotherm curve of Ph and Pb^{2+} is of favorable type.

Pore diffusion model for batch adsorber is used to estimate the pore diffusion coefficient by matching the experimental concentration decay curve with the theoretical concentration decay curve obtained from the model.

The simulated breakthrough curves for adsorption of phenol and lead both in single and binary systems onto GAC are in close agreement with the experimental results. Thus, the mathematical model, which includes axial dispersion, film mass transfer, pore diffusion resistance and nonlinear isotherm, provides a good description of the single and competitive adsorption process in fixed bed adsorbed.

Fixed bed studies indicates that, as the flow rate and the initial solutes concentration increase, and the bed height decreases, the time of the breakthrough point decreases.

Symbols

Å — Angstrom
b — adsorption equilibrium constant relate to affinity between adsorbent and adsorbate, $\mathrm{l\ mg^{-1}}$
Bi — biot number
C — fluid phase concentration, $\mathrm{mg\ l^{-1}}$
C_e — equilibrium liquid phase concentration, $\mathrm{mg\ l^{-1}}$
C_o — initial liquid phase concentration, $\mathrm{mg\ l^{-1}}$
D_z — axial dispersion coefficient $\mathrm{m^2\ s^{-1}}$
D_m — molecular diffusivity, $\mathrm{m^2\ s^{-1}}$
D_p — pore diffusion coefficient, $\mathrm{m^2\ s^{-1}}$
d_p — particle diameter, m
k_f — external mass transfer coefficient, $\mathrm{m\ s^{-1}}$
L — length of the column, m
MW — molecular weight, $\mathrm{g\ mol^{-1}}$
P_e — Peclet number
Q — flow rate, $\mathrm{m^3\ s^{-1}}$
q_e — adorption capacity at equilibrium, $\mathrm{mg\ g^{-1}}$
q_m — Langmuir constant related to maximum adsorption capacity, $\mathrm{mg\ g^{-1}}$
r — radial coordinate, m
R — radial coordinate, m
Re — Renold number, $\mathrm{Re} = \rho_w \upsilon d_p/\mu_w$
R_p — radius of particle, m
Sc — Schmidt number, $\mathrm{Sc} = \mu_w/\rho_w D_m$
Sh — Sherwood number, $\mathrm{Sh} = k_f d_p/D_m$
t — time, s
V_L — volume of solution, L
W_A — mass of granular activated carbon, g
Z — axial distance, m

Greeks

ε_b — bed porosity
ε_p — particle porosity
μ_w — viscosity of water
Y — interstitial velocity, $\upsilon = Q/\pi R^2_p \varepsilon_b$
ρ_w — density of water, $\mathrm{kg\ m^{-3}}$
ρ_p — particle densty, $\mathrm{kg\ m^{-3}}$

Subscripts

B — bulk fluid phase
e — equlibrium
GAC — granular activated carbon
i — component number, 1, 2, …
L — liquid phase
o — initial phase
p — particle phase
Ph — phenol
$\mathrm{Pb^{2+}}$ — lead
SD — standard deviation

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