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 parameter 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 (Dp) were obtained from batch experiments, while the external mass transfer coefficients and axial dispersion (kD) were calculated from empirical correlations. The results shows 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; Fixed bed

Nomenclature: b: Adsorption equilibrium constant relate to affinity between adsorbent and adsorbate, m3/kg; Bi: Biot number; C: Fluid phase concentration, kg/m3; Ceq: Equilibrium liquid phase concentration, kg/m3; Ci: Initial liquid phase concentration, kg/m3; Dc: Axial dispersion coefficient, m2/s; Dm: Molecular diffusivity, m2/s; Dp: Pore diffusion coefficient, m2/s; dp: Particle diameter, mkf: MW: Molecular weight, g/mol; I: Length of the column, m; Pe: Peclet number; q: Adsorption capacity at equilibrium, kg/kg; qL: Langmuir constant related to maximum adsorption capacity, kg/kg; r: Radial coordinate, m; R: Radial coordinate, m; Re: Reynolds number, Re=ρυdp/μw; Rf: Radius of particle, m; Sc: Schmidt number, Sc= μw/ρwDm; Sh: Sherwood number, Sh=kDf/dp; t: Time, s; V: Volume of solution, m3; W: WA: Mass of granular activated carbon, kg; Z: Axial distance, m; εb: Bed porosity; εp: μw Particle porosity; Viscosity of water; w: Interstitial velocity, w=Q/πR2; εf: Density of water, kg/m3; p: Particle density, kg/m3; Subscript b: Bulk fluid phase; e: equilibrium; GAC: Granular Activated Carbon; i: Component number, 1,2,…; L: Liquid Phase; o: Initial phase; p: Particle phase; Ph: Phenol; Pb: Lead

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. Lead (II) and its organic co-pollutants often originate from industrial sources such as the iron-steel, cook, petroleum, pesticides, paints, solvent, pharmacuetics, wood preserving chemicals. Phenol containing water, when chlorinated during disinfection of water results in the formation of chlorophenol [1-3].

Adsorption is a well-established and powerful technique for treating domestic and industrial effluents. 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 group, 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-bonding, dipole dipole interactions, ion exchange, covalent bonding, cation bridging, and water bridging, can be responsible for the adsorption of organic compounds in activated carbon [4-6].

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. 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 [7-11].

Fixed bed adsorber is the most efficient arrangement for conducting 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

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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. There are several mathematical models in the literature, which have been used to represent the dynamic of the fixed bed column. Models with analytical solutions are often used to represent for fitting the breakthrough curve. These models which are available, exclude some of the important physical aspects such as axial dispersion and intra-particle resistances along the bed length and linear isotherm. However, these models applied only for mono-component system [13-17].

In the present study, as a new application onto our previous work, a general multi-component model is used to predict the breakthrough curves in fixed bed column for binary component for organic and inorganic pollutants onto 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 non-linear isotherm [18,19].

Mathematical Modeling and Simulation

In the present study, a mathematical model for the fixed-bed column is proposed by incorporation of an important parameter, external mass transfer, resistance, internal mass transfer resistance and non-linear 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 [20]:

- 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).
- 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: 

$$-D_{b} \frac{\partial^{2} C_{b}}{\partial z^{2}} + V_{b} \frac{\partial C_{b}}{\partial t} + \frac{3k_{f} (1-e_{p})}{e_{b} R_{p}} \left[ C_{b} - C_{p}(r=R_{p}) \right] = 0$$  

Continuity equation inside the particle phase:

$$\left(1-e_{p}\right) \frac{\partial C_{p}^{*}}{\partial t} + e_{p}\frac{\partial C_{p}^{*}}{\partial t} - e_{p} D_{p} \left[ \frac{\partial}{\partial r} \left( R_{p}^{2} \frac{\partial C_{p}^{*}}{\partial r} \right) \right] = 0$$  

Initial and boundary conditions:

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

Initial Condition ($t = 0$):

$$C_{bi} = C_{bi}(0, Z) = 0$$  

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

Boundary Conditions:

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

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

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

$$R = R_{p}: \frac{\partial C_{pi}}{\partial R} = k_{fi} D_{pi}(C_{bi} - C_{pi,(r=R_{p})})$$

Dimensionless Groups:

Defining the following dimensionless variables:

$$c_{bi} = \frac{C_{bi}}{C_{oi}}, c_{pi} = \frac{C_{pi}}{C_{oi}}, \epsilon_{p} = \frac{C_{pi}^{*}}{C_{oi}^{*}}, \tau = v t, r = \frac{R}{R_{p}}, z = \frac{Z}{L}$$

Also, the dimensionless parameters are defined as:

$$P_{e} = \frac{v L}{D_{oi}}, B_{i} = \frac{k_{f} R_{p}^{2} L}{e_{p} D_{pi}}, \eta_{i} = \frac{\epsilon_{p} D_{pi} L R_{p}}{v}, \zeta_{i} = \frac{3B_{i} \eta_{i}}{e_{p}} (1 - \epsilon_{p})$$

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

$$- \frac{1}{P_{e} \zeta} \frac{\partial^{2} c_{bi}}{\partial z^{2}} + \frac{\partial c_{bi}}{\partial \tau} + \frac{\partial c_{bi}}{\partial \tau} + \zeta_{i} \left( c_{bi} - c_{pi,(r=1)} \right) = 0$$  

$$\frac{\partial}{\partial \tau} \left[ \left( 1 - e_{p} \right) c_{pi}^{*} + e_{p} c_{pi}^{*} \right] - \eta_{i} \left[ \frac{1}{\tau^{2}} \left( \frac{\partial^{2} c_{pi}}{\partial \tau^{2}} \right) \right] = 0$$

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

Initial conditions become ($\tau = 0$) [21, 22]:

$$c_{bi} = c_{bi}(0, z) = 0$$  

$$c_{pi} = c_{pi}(0, r, z) = 0$$  

And boundary conditions become:

$$z = 0: \frac{\partial c_{bi}}{\partial Z} = P_{e} \left( c_{bi} - 1 \right)$$
Commercial granulated activated carbon (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-Mustansirriya University (Collage of engineering, Environmental Department) and according to the data from the supplier. The physical and chemical properties of GAC are listed in Table 2.

### Experimental Materials and Procedure

#### Adsorbate

1000 mg/l standard stock solution of Phenol and lead (II) were prepared by dissolving Ph and Pb(NO₃)₂ in distilled water. The salts was bought from local market with the following specifications in Table 1. Prepared by dissolving Ph and Pb(NO₃)₂ in distilled water. The salts was directly linked to a multi-component isotherm, which is the extended Langmuir model:

\[
\frac{c^*_p}{c^*_p} = \frac{q_{max} \rho_p b_{C_p} = \frac{\rho_p a_{C_p} C_p}{1 + \sum_{j=1}^{N} b_j c_{pj}}}{1 + \sum_{j=1}^{N} b_j c_{pj}}
\]

And in dimensionless form:

\[
\frac{c^*_p}{c^*_p} = \frac{\rho_p a_{C_p}}{1 + \sum_{j=1}^{N} b_j c_{pj} c_{pj}}
\]

Because of non-linear multi-component Langmuir isotherm is considered, finite elements 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 ordinary differential equation solver.

#### Adsorbent

| Property         | GAC                  |
|------------------|----------------------|
| Actual density, kg/cm³ | 1544                |
| Apparent density, kg/cm³ | 641                |
| BET Surface area, m²/g | 751.965            |
| Particle porosity    | 0.584               |
| Bed porosity         | 0.64                |
| Average particle diameter, mm | 0.775           |
| Pore volume, cm³/g   | 0.422               |
| Average particle diameter, mm | 1100-1130       |
| pH                | 8.15                |
| Iodine number, mg/g  | 3-5                 |

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### Adsorption

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 4 [24,25]. So, pH was adjusted with the range of (4) for all single and binary systems by adding the 0.1N HNO₃ and 0.1N NaOH for acidic and basic pH respectively.

The fixed bed adsorber studies were designed and constructed of two acrylic columns of (53 mm) I.D. and (0.5 m) height. The granular activated carbon (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.

For determination of the adsorption isotherm, a sample of (100 ml) 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 for 24 hours at 30°C to achieve equilibrium concentrations. Then the solution was filtered using filter paper type (Wattmann no. 4) 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 [26]:

\[
q_e = \frac{V_i (C_0 - C_e)}{W_A}
\]

The pore diffusion coefficient (D_p) for each solute was obtained by 2L pyrex beaker fitted with variable speed mixer. The beaker was...
filled with 1 L of 50 mg/l 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/C₀ equal to 0.05, were calculated from Langmuir isotherm model and mass balance equation as follows:

\[ W = \frac{V_L (C_0 - C_e)}{q_e} \]  

with

\[ q_e = \frac{q_m b C_e}{1 + b C_e} \]  

Results and Discussion

Adsorption isotherm

The equilibrium isotherm for the investigated solutes (Ph and Pb⁴⁺) onto GAC using multi-component Langmuir model are presented in Figure 1. The Langmuir model parameters (qₘ and b) were estimated by the non-linear regression method using STATISTICA version-6 software. The correlation coefficient (R²) 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: qₘ = 66.8234 mg/g, b = 0.0590 l/mg, R² = 0.9923
- Pb⁺²: qₘ = 37.0370 mg/g, b = 0.1258 l/mg, R² = 0.9963

Pore diffusion coefficient

Pore diffusion coefficient (Dₚ) of phenol and lead can be obtained using batch model by matching the concentration decay curve obtained from experimental data at optimum agitation speed (400 rpm) with that obtained from the batch model as shown in Figure 2. At first time the pore diffusion coefficient is assumed and the model is solved numerically. This process continue until obtain perfect matching between the theoretical and experimental concentration decay curve.

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

- Ph: Dₚ = 5.523×10⁻⁹ m²/s, R² = 0.986
- Pb⁺²: Dₚ = 3.143×10⁻⁹ m²/s, R² = 0.971

The amount of GAC used for each solute were calculated from final equilibrium related concentration of C/C₀=0.05 using the Langmuir model with mass balance in 1L of solution. The initial concentration were 50 mg/l with the doses of activated carbon of 5.530 and 5.360 g per 1L solution for phenol and lead respectively. The external mass transfer coefficient, kₑ, in fixed bed column model was calculated using the correlation of Crittenden (1987) [15].

\[ k_e = \frac{2.4 V_f}{(S_{dav} R_e^{0.66})} \]  

The liquid diffusivity coefficient was calculated using the equation:

\[ D_m = 2.74\times10^{-4} (MW)^{0.13} \]  

The axial dispersion coefficient Dₐ of the liquid flowing through fixed beds was obtained from the following correlation [27]:

\[ \frac{D_s}{D_m} = 0.67 + 1.15 \left( \frac{V_f d_p}{D_m} \right)^{1.2} \]  

Breakthrough curves of the single and binary systems

The experimental and predicated 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 Figures 3 to 12.
Figure 3: The experimental and predicted breakthrough curves for adsorption of single phenol onto GAC.

Figure 4: The experimental and predicted breakthrough curves for adsorption of single lead onto GAC.

Figure 5: The experimental and predicted breakthrough curves for adsorption of single phenol onto GAC at different flow rate.

Figure 6: The experimental and predicted breakthrough curves for adsorption of single lead onto GAC at different flow rate.

Figure 7: The experimental and predicted breakthrough curves for adsorption of single phenol onto GAC at different bed height.

Figure 8: The experimental and predicted breakthrough curves for adsorption of single lead onto GAC at different bed height.
Discussion

The adsorption capacity order for phenol and lead onto GAC was as follow:

\[ \text{Ph (66.8234 mg/g)} > \text{Pb}^{+2} (37.0370 \text{ mg/g).} \]

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:

a- Phenol has less solubility (86000 mg/l) in water in comparison with lead nitrate (520000 mg/l) and consequently with lead.

b- Molecular cross-sectional area (molecular volume) for phenol is greater than lead (30.49 \text{ Å}^2 for phenol) and consequently with lead.

c- Phenol can be adsorbed by means of electrostatic attraction between negatively charged phenols and positively charged binding sites. Physical adsorption by means of (Vander Waals, H-bonding, dipole-dipole and dipole-induced dipole) have 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.

d- The binding of Pb\(^{+2}\) to GAC is based on the formation of coordination compounds. Lead ion acts as a Lewis acid and the GAC acts as a Lewis base. However, Pb\(^{+2}\) ion haven't enough electrons to reach an inert state, and to form Lewis acid–Lewis base neutralization process.

Effect of flow rate

Figures 5, 6 and 12 shows the experimental and predicted breakthrough curves for Ph and Pb\(^{+2}\) as a single and in binary systems at different flow rates (1.39 \times 10^{-6}, 2.78 \times 10^{-6} and 4.17 \times 10^{-6} \text{ m/s}) in terms of C/C\(_0\) at these flow rates. It’s clear from this 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 no 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 effect 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 Biot
number with slight increase in Pecl number as listed in Table 3. When the Biot number is high the time of breakthrough point will appear early. The higher Biot 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. These results agree with those obtained by Sulaymoon and Ahmed [18]; Ebrahim [28]; Abdul-Hameed [29] and Nasir [30].

Effects of bed height

The bed height is one of the major parameter in the design of fixed bed adsorption column. The experimental and predicted breakthrough curves obtained for different bed height of activated carbon (0.05, 0.1 and 0.15 m) at constant flow rate and constant initial concentration are presented in Figures 7 and 8. It is clear from these figures that at smaller bed height the C/C0 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 Peclet numbers as listed in Table 4. When Peclet number is small the effect of axial dispersion is not negligible, the break point appears early and increases with the Peclet 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. Similar findings have been obtained by Sulaymoon et al. [19].

Effect of initial concentration

The change in initial concentration of Ph and Pb+2 will have a significant effect on the breakthrough curves. Figures 9 and 10 shows the experimental and predicted breakthrough curves at different initial concentration (25, 50 and 75 mg/l). These figures shows 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.

In multi-component system (binary system)

For phenol and lead, it is clear from Figures 11 and 12 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 takes the active site 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 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. These results are in agreement with that obtained by Ahmed [21] and Al-Najar [22].

Conclusions

1. The simulated breakthrough curves for adsorption of phenol and lead both in single and binary system onto granular activated carbon 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.

2. Granular activated carbon was found to be more suitable adsorbent for the removal of organic pollutants (phenol in the present work) than inorganic pollutants (heavy metals, lead).

References

1. Patterson JW (1985) Industrial wastewater treatment technology. 53-393.
2. Chirwa EN, Wang YT (2000) Simultaneous chromium (VI) reduction and phenol degradation in an anaerobic consortium of bacteria. Water Res 34: 2376-2384.
3. Akso Z, Akpinar D (2000) Modelling of simultaneous biosorption of phenol and nickel(II) onto dried aerobic activated sludge. Sep Purif Technol 21: 87-99.
4. Hassler JW (1974) Purification with Activated Carbon ; industrial, commercial, environmental. Chemical Publishing Co., New York.
5. Perrich JR (1981) Activated Carbon Adsorption for wastewater treatment. CRC Press, Boca Raton, FL.
6. Calleja G, Serna J, Rodriguez J (1993) Kinetics of adsorption of phenolic compounds from wastewater onto activated carbon. Carbon 31: 691-697.
7. Streit M, Patrick JW, Camporro MJ (1995) Sorption of phenol and para-chlorophenol from water using conventional and novel activated carbons. Water Sci Res 29: 467-472.
8. Ferro-Garcia MA, Rivera-Utrilla J, Bautista-Toledo I, Moreno-Castilla C (1996) Chemical and thermal regeneration of an activated carbon saturated with chlorophenols. J Chem Technol Biotechnology 67: 83-189.
9. Lee JH, Song DI, Jeon WY (1997) Adsorption of organic phenojs onto dual organic cation montmorillonite from water. Sep Sci Technol 32:1975-1992.
10. Edgehill RU, Lu GQ (1998) Adsorption characteristics of carbonized bark for phenol and pentachlorophenol. J Chem Technol Biotechnol 71: 27-34.
11. Akso Z, Gonen F (2005) Binary biosorption of phenol and chromium (VI) onto immobilized activated sludge in a packed bed: Prediction of kinetic parameters and breakthrough curves. Sep Purif Technol 49: 205-216.
12. ATSDR. Agency for Toxic Substances and Disease Registry, Toxicological Profile for dichlorophenol, Atlanta, Georgia :US Department of Health and Human Services, DHHS. Publication, No.TP-91/14,1992.
13. Akso Z, Gonen F (2005) Binary biosorption of phenol and chromium (VI) onto immobilized activated sludge in a packed bed: Prediction of kinetic parameters and breakthrough curves. Sep Purif Technol 49: 205-216.
14. Esposito A, Pagnanelli F, Vegliò F (2002) pH-related equilibria models for biosorption in single metal systems. Chem Eng Sci 57: 307–313.
15. Crittenden JC, Thomas FS, David WH, Paul JL, Ben L (1987) Evaluating Multi-component Competitive Adsorption in Fixed-Beds. J. Environ Eng 113: 1363–1375.
16. Bhatia SC (2005) Environmental pollution and control in Chemical process Industries. Khana publisher 250-260.
17. Volesky B, Praseky I (1994) Cadmium removal in a biosorption column. Biotechnol Bioeng 43: 1010-1015.
18. Sulaymon AH, Ahmed KW (2008) Competitive adsorption of Furfural and Phenolic Compounds onto Activated Carbon in Fixed Bed Column. J Environ Sci Technol 42: 392-397.

19. Sulaymon AH, Abid BA, Al-Najar JA (2009) Removal of lead copper chromium and cobalt ions onto granular activated carbon in batch and fixed bed adsorbers. Chem Eng Journal 155: 647-653.

20. Eggers SL, Eggers R (2000) Simulation of Frontal Adsorption, HIWI report by Hamburg-Harburg University.

21. Ahmed KW (2006) Removal of multi-pollutants from wastewater by adsorption method. Ph.D. Thesis, University of Baghdad.

22. Al-Najar JA (2009) Removal of heavy metals by adsorption using activated carbon and Kaolinite. Ph.D Thesis, University of Technology, Baghdad, Baghdad, Iraq.

23. Temkin M (1934) Die gas adsorption und der nernstscche wärmesatz. Acta Physicochim URSS 1: 36–52.

24. Weber WJ (1972) Adsorption In: Physicochemical processes for water quality control. New York, Wiley 206–211.

25. Garden AJ (2006) Application of Harkins Model in Adsorption. IAH J 7: 11-14.

26. Redlich O, Peterson DL (1959) A useful adsorption isotherm. J Phys Chem 63: 1024.

27. Hutzler NJ, Crittenden JC, Gierke JS, Johnson AS (1986) Transport of organic compounds with saturated ground water flow: experimental results. Wat Res Research 22: 285-295.

28. Ebrahim ShE (2008) Competitive Adsorption of Multi-Organic Compounds onto Organoclay from Simulated Wastewater. Ph.D. Thesis, University of Baghdad, College of Engineering.

29. Abdul-Hameed HM (2009) Competitive adsorption of heavy metals onto activated carbon in fixed bed column. Ph.D. Thesis, University of Baghdad, College of Engineering.

30. Nasir HM (2010) Competitive Adsorption of Multi-Organic Compounds onto Organoclay from Simulated Wastewater. Ph.D. Thesis, University of Baghdad, College of Engineering.