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Adsorption Behavior of Chlorophenols on Natural Zeolite

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Adsorption Behavior of Chlorophenols on Natural Zeolite

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Abstract: The adsorption of aqueous organic pollutants, i.e., phenol, monochlorophenols (2- and 4-), and dichlorophenols (2,4- and 3,5-) on natural Jordanian zeolitic tuff was studied. Three simplified kinetic models, viz., pseudo-first order, pseudo-second order, and intraparticle diffusion models were used to fit the kinetics data. The results revealed that at earlier stages of adsorption of phenols onto zeolite, the pseudo-second order and the bulk diffusion rate constants are dependent on the acidity and the hydrophobicity of phenols. Whereas at later stages of adsorption, the adsorption capacity and the intraparticle diffusion rate constants are affected by the molecular size and the extent of dissociation of phenols.

Keywords: Natural zeolite, phenol, chlorophenols, adsorption, pseudo-first and pseudo-second order, intraparticle diffusion

INTRODUCTION

Water is the world's most precious resource. Industry is also very prominent in today's society and its impact on water resources is increasingly significant. Benzene refining plants, oil refineries, coke plants, and plants which are processing phenols to plastic all discharge harmful

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effluents of phenols (1). They may occur in domestic and industrial waste waters, natural waters, and potable water supplies (2). The discharge of phenolic compounds into the environment represents a serious hazard, mainly due to the contamination of superficial and underground waters. Thus, at trace levels they may cause a harmful effect on the aquatic organisms; these trace concentrations can be enhanced through bioaccumulation in the food chain.

During the chlorination of water and sewage, phenol is readily transformed into chlorophenols. Chlorinated phenols may also result from the metabolism of phenoxy herbicides and could cause contamination of the surface and ground water. Chlorinated phenols are highly toxic to man and to aquatic organisms. Furthermore, it is known that chlorinated phenols might lead to the formation of the highly carcinogenic dioxines (3). Thus, chlorophenols are given the priority among the pollutants according to the USDA Records (4).

Over the last century, much researches has taken place in the area of adsorption of phenols on activated carbons which were proved to be very effective in removal of organic pollutants (5, 6). However, activated carbon has two main disadvantages:

(i) it is a limited natural resource
(ii) it is difficult to regenerate.

Okolo et al. investigated the interaction of phenol/chlorophenol(s) with activated carbon and with synthetic zeolites as well (6). Removal of phenol/chlorophenol(s) from water using zeolite has not been used as widely as activated carbon (7, 8).

Natural zeolites are classified as tectosilicates and can be best defined as crystalline hydrated aluminosilicates of the alkali and alkaline earth metals. They are cheap due to their accessibility and abundance and they can be regenerated as well. Furthermore, natural zeolites can also be modified in several ways for the purpose of increasing their adsorption capacity in pollutants removal (9, 10).

In order to get insight about the mechanism of interaction between phenols and natural zeolite, we have carried out the present preliminary study in order to investigate the kinetics of the adsorption of phenol and different substituted chlorophenols (mono- and dichloro-phenols) on natural Jordanian zeolitic tuff.

Noteworthy, in 1898, Lagergren presented the first order rate equation for the adsorption of some organic acids onto charcoal (11). Lagergren's kinetics equation may have been the first one in describing the adsorption of liquid-solid systems based on solid capacity (12, 13).

In the present work, Lagergren pseudo-first order, Eq. (1) (14) and pseudo-second order, Eq. (2) (12, 13) rate expressions were used to fit the kinetics data of the adsorption of aqueous phenols on natural zeolitic tuff.

$$\text{Lagergren pseudo-first order:} \quad dq/dt = k_1(q_e - q_t), \tag{1}$$

$$\text{which can be integrated into:} \quad q_t = q_e(1 - e^{-kt}). \tag{2}$$

$$\text{Pseudo-second order:} \quad dq/dt = k_2(q_e - q_t)^2, \tag{3}$$

$$\text{which can be integrated into:} \quad 1/(q_e - q_t) = 1/q_e + k_2 t. \tag{4}$$

The word "pseudo" is employed here because the kinetics equations are based on the adsorption capacity of solid q but not on the concentration of the adsorbate (15–18). The subscripts e and t denote equilibrium and time, respectively. Such kinetics equations have been reported in the literature for studying the adsorption of pollutants from aqueous solutions (12, 13). Although these equations cannot give definite mechanism for adsorption (19), the effect of the chloro-substituent(s) on the rate constant helps to provide a mechanistic perspective.

The adsorption mechanism of an adsorbate onto porous adsorbents follows three steps, viz. film diffusion, pore diffusion, and intraparticle transport. Weber and Morris suggested that the intraparticle diffusion controls the batch adsorption process (20, 21). Theoretical treatments of intraparticle diffusion rates yield rather complex equations differing in form for different shapes of particle (22, 23). All have the characteristic that for batch experiments the preferred function of time for plotting purposes is $t^{1/2}$. Nearly linear variation of q_t with $t^{1/2}$ is obtained for a large initial fraction of the reaction (21):

$$q_t = k_{id} t^{1/2} \tag{5}$$

To check this postulate, a plot of q_t, the amount adsorbed (μmol phenol/g zeolite) at time t, versus square root of time is drawn and then the diffusion constant k_{id} is calculated. However, such relation has been demonstrated experimentally for the adsorption of surfactants on activated carbon (20).

EXPERIMENTAL

Natural Zeolitic Tuff Preparation

Natural Jordanian zeolitic tuff (from Jebal Aritayn) was crushed using Jaw crusher, homogenized, and sieved to obtain a particle size 500–1000 μm. A 100 g of this particle size tuff was washed trice with 1 L distilled water (each for three hours) until no suspended material was observed. After filtration, using filter paper, the washed sample was dried in an oven overnight at 110°C and stored in a dessicator over anhydrous $CaCl_2$ until use.

Adsorption of Phenols

Adsorption characteristics of phenol, 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), and 3,5-dichlorophenol (3,5-DCP) on natural Jordanian zeolitic tuff were studied using the batch method. To a 0.10 g sample of zeolite adsorbent, placed in a 150 mL-stoppered Erlenmeyer flask, 50 mL of 40 ppm of one of the phenolic adsorbate solutions (phenol, 2-CP, 4-CP, 2,4-DCP, and 3,5-DCP; from G.C.C.) were added at 27°C. The flasks were placed in a shaker (GFL, model 3005) run at 150 rpm for 50 hours. Portions (100 μL) of each solution were taken at different time intervals and diluted in 10 mL distilled water. The phenols concentrations were determined spectrophotometerically using UV-Vis-spectrophotometer (Jassco, model V-530). The absorbance values of phenol, 2-CP, 4-CP, 2,4-DCP, and 3,5-DCP were measured at $\lambda = 270.0$, 280.0, 280.0, 285.0, and 284.5 nm, respectively. The adsorption procedures were performed without the addition of any buffer to control the pH so as to avoid possible complications due to the presence of an electrolyte. The pH was, however, measured for both the standard phenols solutions (in the absence of zeolite) and the phenol/zeolite systems by means of pH-meter (Metrohm 744 pH).

RESULTS AND DISCUSSION

Phenols are weak acids that dissociate to a small extent in aqueous media. The pH values for the adsorbate solutions in the absence of zeolite were 6.8, 6.3, 6.4, 6.2, and 6.3 for phenol, 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 3,5-dichlorophenol (3,5-DCP), respectively. In the presence of zeolite, the pH values for the corresponding phenols changed to 6.8, 6.6, 7.1, 7.1, and 7.3. Moreover, the pH of the distilled water (50 mL) above zeolite (0.1 g) was found to be 7.1. Accordingly, the percentages of the dissociation of phenol/chlorophenols were calculated as shown in Table 1. From the percentages values for phenol and monochlorophenols it could be concluded that the fractions of phenolates ions are nearly negligible. However, about 10–15% dissociation of the dichlorophenols may result in some repulsion between phenolates and anionic zeolite surface, which may affect their adsorption on zeolite.

Pseudo-first Order and Pseudo-second Order Models

In order to study the kinetics of the adsorption of phenols on zeolitic tuff, Lagergren pseudo-first order and pseudo-second order models were investigated. Both expressions, Eq. (1) and Eq. (3), show how the rate of adsorption dq/dt depends on the adsorption capacity q (in μmol phenol/g zeolite). The pseudo-first order and pseudo-second order rate constants k_1 and k_2 are in the units of min^{-1} and g zeolite/μmol phenol · min, respectively. The rate constants and the equilibrium sorption capacity q_e were used as adjustable parameters and were determined using nonlinear regression analysis of Eq. (2) and Eq. (4) by means of the solver of Microsoft Excel software. The results that

Table 1. Fitting kinetics parameters of adsorption of phenols on natural Jordanian zeolite (Z) according to Lagergren pseudo-first order and pseudo-second order rate expressions

	q_e (μmol phenol/g Z)		k		Sum of square residuals (SSR)				
Phenols	1st order	2nd order	1st order (min^{-1})	2nd order (g Z/μmol phenol · min)	1st order	2nd order	pKa[a]	Log total molality[a]	Dissociation (%)
Phenol	67	109	4.3×10^{-4}	2.5×10^{-6}	38	36	9.91	−0.027	0.078
2-CP	120	150	1.2×10^{-3}	8.2×10^{-6}	488	217	8.41	−0.743	1.5
4-CP	104	157	9.4×10^{-4}	4.1×10^{-6}	30	63	9.29	−0.688	0.64
2,4-DCP	57	63	3.6×10^{-3}	7.2×10^{-5}	146	109	7.85	−1.468	15
3,5-DCP	78	90	2.9×10^{-3}	3.8×10^{-5}	435	144	8.25	−1.343	10
				Total of SSR	1137	569			

[a] Ref. (24).

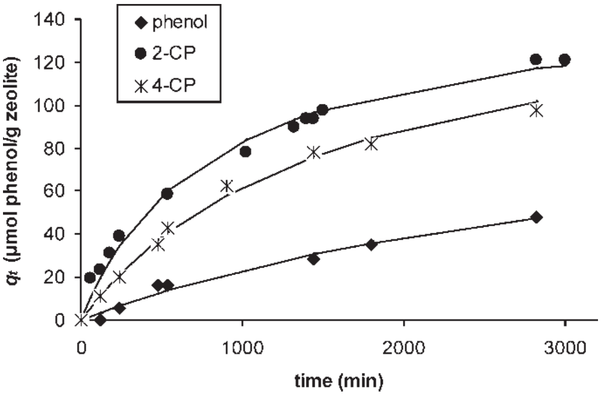

Figure 1. Plots of adsorption capacities (q_t) of phenol, 2-, and 4-chlorophenols versus time. The solid points belong to experimental data while the line is calculated from nonlinear least square regression of the data according to pseudo-second order rate expression.

give the least of residuals (difference between experimental and calculated q_t) were adapted.

The values of k_1, k_2, q_e, and the sum of square residuals (SSR) for the adsorption of different phenols are tabulated in Table 1. As revealed by the total SSR, the pseudo-second order rate equation gives a better fitting for the data than the pseudo-first order equation. Thus, the experimental data were analyzed according to the pseudo-second order equation (Table 1) and are illustrated in Figs. 1 and 2.

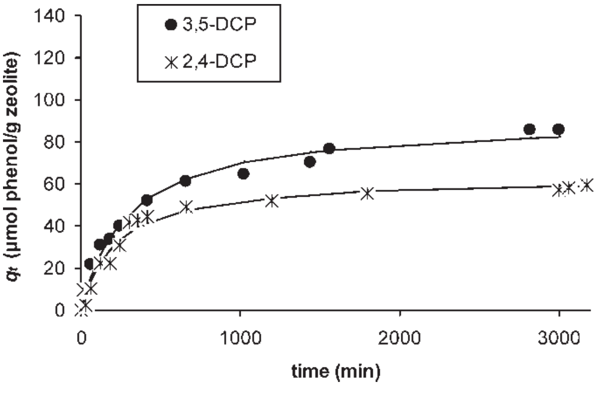

Figure 2. Plots of adsorption capacities (q_t) of 2,4-, and 3,5-dichlorophenols versus time. The solid points belong to experimental data while the line is calculated from nonlinear least square regression of the data according to pseudo-second order rate expression.

Depending on the results of the second order fitting, 2-CP and 4-CP have higher rate constants than phenol (i.e., 8.2×10^{-6} and 4.1×10^{-6} versus 2.5×10^{-6} g zeolite/μmol phenol · min). This may be due to the fact that chlorophenols have greater acidity than phenol (i.e., 8.41 and 9.29 versus 9.91 pKa values). The more acidic proton of monochlorophenols is capable of forming stronger hydrogen bonds with the oxy groups of zeolite surface (O-Si(Al)). Furthermore, the monochlorophenols were found to have higher adsorption equilibrium capacities q_e than that of phenol (i.e., 150 and 157 versus 109 μmol phenol/g zeolite), which indicates that q_e is also dependent on the acidity of phenols.

The adsorption of 2,4-DCP and 3,5-DCP were found to have much higher rate constants (i.e., 7.2×10^{-5} and 3.8×10^{-5} g zeolite/μmol phenol · min) than monochlorophenols and phenol (as shown in Table 1). Similarly, this can be ascribed to the higher acidity of the dichlorophenols. It seems that the hydrophobicity (solubility) of phenols and chlorophenols play also a role. According to the values of the log total solubility (molality) given in Table 1, the order of increase of solubility, dichlorophenol < monochlorophenol < phenol, is in a good agreement with the order of decrease of rate constants, $k_{\text{dichlorophenol}} > k_{\text{monochlorophenol}} > k_{\text{phenol}}$.

However, the adsorption of dichlorophenols was found to have significant lower q_e values (63 and 90 μmol phenol/g zeolite) than monochlorophenols and phenol (i.e., 150, 157, and 109 μmol phenol/g zeolite), which may be attributed to the larger size of dichlorophenols from one side and to the repulsion among dichlorophenolates anions and the anionic zeolite surface from the other side.

In other words, the speed of adsorption of the phenols follows the order: dichlorophenol > monochlorophenol > phenol, whereas the adsorption equilibrium capacity q_e follows the order: monochlorophenol > phenol > dichlorophenol.

Intraparticle Diffusion Model

Due to the porous nature of zeolite, the intraparticle transport is supposed to be the rate controlling step. The rate constant for the transfer of phenols species to the active adsorption sites inside the zeolite particles is slower than that of the adsorption onto the external surface sites of zeolite particles (25). Figures 3 and 4 show the correlation between q_t and $t^{1/2}$ according to Eq. (5) which gave three linear portions. The first portion is thought to be due to the external surface adsorption or instantaneous adsorption stage (bulk diffusion) while the second linear portion is due to the gradual adsorption stage where the intraparticle diffusion is rate controlled (26, 27). The proposed third portion which is due to the final equilibrium stage was not reached (see Figs. 3 and 4).

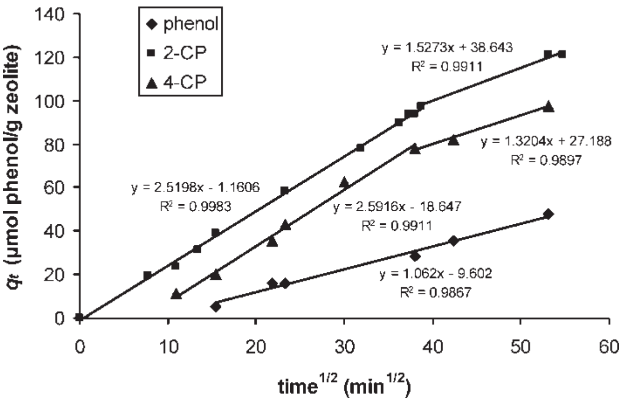

Figure 3. Intraparticle diffusion plots for the adsorption of phenol, 2-, and 4-chlorophenols on natural zeolitic tuff.

Except for phenol, two linear portions in each curve were obtained. Their k_{id} values (k_{id1} and k_{id2} for first stage and second stage, respectively), which were determined form the slopes of the lines are given in Table 2.

According to the k_{id1} values calculated from the first linear portion of plots, phenol demonstrated the lowest k_{id1} among the studied phenols. The 2,4-DCP was found to have the highest one. The other phenols were found to have intermediate values that are close to each other. In general, this trend reflects that the rate bulk diffusion is determined by the acidity of phenols. On the other hand, the k_{id2} values calculated from the second linear portion of plots were found to follow the order: k_{id2} (monochlorophenols) $>$ k_{id2} (phenol) $>$ k_{id2} (dichlorophenols). This trend

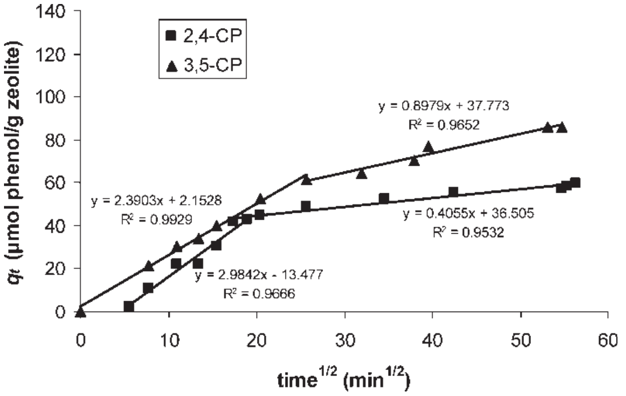

Figure 4. Intraparticle diffusion plots for the adsorption of 2,4- and 3,5-dichlorophenols on natural zeolitic tuff.

Table 2. The values of intraparticle diffusion constants (k_{id1} and k_{id2}) of adsorption of phenols on natural Jordanian zeolite. Values in brackets are for correlation factors

	k_{id} (μmol phenol/g zeolite · min$^{1/2}$)	
Phenols	k_{id1}	k_{id2}
Phenol[a]	1.06 (0.987)	1.06 (0.987)
2-CP	2.52 (0.998)	1.53 (0.991)
4-CP	2.59 (0.991)	1.32 (0.990)
2,4-DCP	2.98 (0.967)	0.406 (0.953)
3,5-DCP	2.39 (0.993)	0.898 (0.965)

[a]Only one line was obtained.

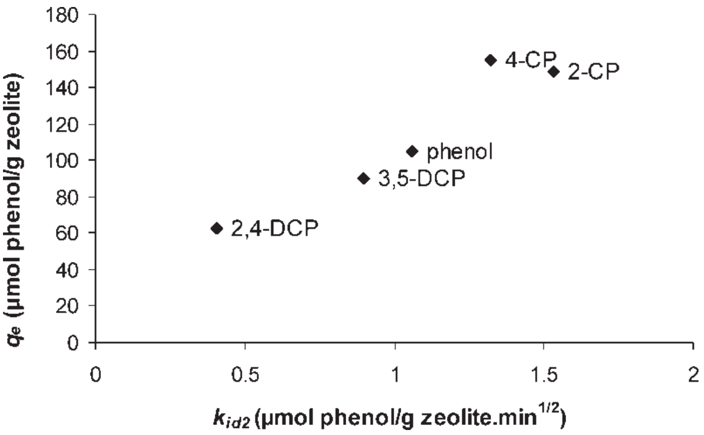

Figure 5. Plots of equilibrium adsorption capacity (q_e) versus intraparticle diffusion rate constant (k_{id2}).

indicates that the rate of intraparticle diffusion is dependent mainly on the size of phenols to a more extent than the acidity of phenols.

A plot of k_{id2} versus q_e (Fig. 5) shows that there is a good correlation between these two parameters. Thus, the k_{id2} and q_e are affected mainly by the size and the percentage of dissociation of phenols.

CONCLUSIONS

The adsorption of the phenols employed in this work on the natural Jordanian zeolitic tuff fits the second order and the intraparticle diffusion models.

It may be concluded that the acidity and the hydrophobicity of phenols and chlorophenols are the limiting factors that determine the rate constants of the adsorption of employed phenols on zeolite surface and the rate constants of bulk diffusion. On the other hand, the size and the percentage of dissociation of phenols may influence the adsorption equilibrium capacities and the rate constants of intraparticle diffusion.

NOMENCLATURE

2-CP	2-chlorophenol
4-CP	4-chlorophenol
2,4-DCP	2,4-dichlorophenol
3,5-DCP	3,5-dichlorophenol
dq/dt	rate of adsorption (μmol phenol/g zeolite $\cdot$ min)
k_1	pseudo-first order rate constant (min^{-1})
k_2	pseudo-second order rate constant (g zeolite/μmol phenol $\cdot$ min)
q_e	adsorption capacity at equilibrium e (μmol phenol/g zeolite)
q_t	adsorption capacity at time t (μmol phenol/g zeolite)
k_{id1}	rate constant for intraparticle diffusion of first stage (μmol phenol/g zeolite $\cdot$ min$^{1/2}$)
k_{id2}	rate constant for intraparticle diffusion of second stage (μmol phenol/g zeolite $\cdot$ min$^{1/2}$)
SSR	sum of square residuals

REFERENCES

1. Meyer, R.A. and Dittrick, D.K. (2000) *Environmental Pollution and Cleanup*; John Wiley and Sons: New York, pp. 439–440.
2. Mitić, S. and Živanović, V.V. (2002) A kinetic method for the determination of phenol. *J. Serb. Chem. Soc.*, 67 (10): 661.
3. Sawerysyn, J.-P., Briois, C., Visez, N., and Baillet, C. (2004) Dioxins and other products from the gas-phase oxidation of 2-chlorophenol over the range 450–900°C. *Organohalogen Compd.*, 66: 1078.
4. U.S. Environmental Protection Agency. (2004) *Health Effects Assessment for 2-Chlorophenol and 2,4-Dichlorophenol; EPA/600/8-88/052 (NTIS PB88178942)*; Washington, D.C.
5. Okolo, B., Park, C., and Keane, M.A. (2000) Interaction of phenol and chlorophenols with activated carbon and synthetic zeolites in aqueous media. *J. Colloid Interface Sci.*, 226: 308.
6. Fernandez, E.D., Hugi-Cleary, M.V., Lopez-Ramon, and Stoeckli, F. (2003) Adsorption of phenol from dilute and concentrated aqueous solutions by activated carbons. *Langmuir*, 19 (23): 9719.
7. Kawai, T. and Tsutsumi, K. (1995) Adsorption characteristics of surfactants and phenol on modified zeolites from their aqueous solutions. *Colloid Polymer Sci.*, 273 (8): 787.

8. Shu, H.T., Li, D.Y., Scala, A.A., and Ma, Y.H. (1997) Adsorption of small organic pollutants from aqueous streams by aluminosilicate-based microporous materials. *Sep. Purif. Technol.*, 11 (1): 27.
9. Musleh, S.M., Yousef, R., and Amro, A.A. (2005) Chemical and structural properties of modified Jordanian zeolite and its use in removal of heavy metals from aqueous solution. *Ultra Science*, 17 (3): 365.
10. Yousef, R.I., Tutunji, M.F., Derwish, G.A.W., and Musleh, S.M. (1999) Chemical and structural properties of Jordanian zeolitic tuffs and their admixtures with urea and thiourea: potential scavengers for phenolics in aqueous medium. *Journal of Colloid Interface Sci.*, 216: 348.
11. Lagergren, S. (1898) About the theory of so-called adsorption of soluble substances. Zur Theorie der Sogenannten Adsorption Gelöster Stoffe, Kungliga Svenska Vetenskapsakademiens. *Handlingar.*, 24 (4): 1.
12. Ho, Y.S. (2004) Citation review of Lagergren kinetic rate equation on adsorption reactions. *Scientometrics*, 59 (1): 171.
13. Ho, Y.S. (2004) Pseudo-isotherms using a second order kinetic expression constant. *Adsorption*, 10: 151.
14. Ho, Y.S. and Mckay, G. (1999) The sorption of lead(II) ions on peat. *Water Res.*, 33 (2): 578.
15. Ho, Y.S. and McKay, G. (1998) A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. *Process Saf. Environ. Prot.*, 76B: 332.
16. Ho, Y.S. and McKay, G. (1998) Kinetic models for the sorption of dye from aqueous solution by wood. *Process Saf. Environ. Prot.*, 76B: 183.
17. Ho, Y.S. and McKay, G. (1998) Sorption of dye from aqueous solution by peat. *Chem. Eng. J.*, 70: 115.
18. Ho, Y.S. and McKay, G. (1998) The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat. *Can. J. Chem. Eng.*, 76: 822.
19. Weber, W.J. and Morris, C.J. (1962) *Advances in Water Pollution Research,* Proc. 1st Int. Conf. on Water Pollution and Research, Pergamon Press: Oxford, U.K, Vol. 2, p. 261.
20. Weber, W.J. and Morris, J.C. (1963) Kinetics of adsorption on carbon from solution. *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.*, 89: 31.
21. Morris, J.C. and Weber, W.J. (1964) Removal of biologically-resistant pollutants from waste waters by adsorption. In *Advances in Water Pollution Research;* Proc. Int. Conf. on Water Pollution and Research, The Mackmillan Company, New York, September 1962, Vol. 2, p. 231.
22. Crank, J. (1975) *The Mathematics of Diffusion,* 2nd Edn.; Clarendon: Oxford, U.K., pp. 32, 82, 99.
23. Choy, K.K.H., Ko, D.C.K., Cheung, C.W., Porter, J.F., and McKay, G. (2004) Film and intraparticle mass transfer during the adsorption of metal ions onto bone char. *J. Colloid Interface Sci.*, 271: 284.
24. Wightman, P.G. and Fein, J.B. (1999) Experimental study of 2,4,6-trichlorophenol and pentachlorophenol solubilities in aqueous solutions: derivation of a speciation-based chlorophenol solubility model. *Applied Geochemistry*, 14: 319.
25. Shubha, K.P., Raji, C., and Anirudhan, T.S. (2001) Immobilization of heavy metals from aqueous solutions using polyacrylamide grafted hydrous tin(IV) oxide gel having carboxylate functional groups. *Wat. Res.*, 35 (1): 300.
26. Chabani, M. and Bensmaili, A. (2005) Kinetic modelling of the retention of nitrates by amberlite IRA 410. *Desalination*, 185: 509.
27. Vinod, V.P. and Anirudhan, T.S. (2003) Adsorption behaviour of basic dyes on the humic acid immobilized pillared clay. *Water, Air, Soil Pollut.*, 150: 193.