

Adsorption of BTEX from aqueous solution by macroreticular resins

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Abstract

Theoretical and experimental investigations were conducted on the adsorption of benzene, toluene, ethylbenzene and xylene (BTEX) by macroreticular resins. A mass transfer model based on the squared-driving force principle is presented for describing the BTEX transfer between the aqueous and solid phases. Also proposed is a theoretical model for describing the BTEX breakthrough curves of the adsorption column. While the mass transfer model involves only an overall mass transfer coefficient, the column adsorption model has two model parameters. Those parameters are conveniently estimated using the observed mass transfer and breakthrough data. The predictions using the proposed models were found to compare well with the experimental data of batch and column BTEX adsorption tests. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Macroreticular resin; BTEX adsorption; Mass transfer model; Column adsorption model

1. Introduction

Many hazardous organic compounds are often present in the wastewater from the chemical and petrochemical industries. Because of their toxicity to human and marine life, stringent regulations have been imposed on the concentrations of these compounds in such wastewaters for safe discharge. Benzene, toluene, ethylbenzene and xylene (BTEX) are typical toxic organic compounds that appear very often in chemical and petrochemical wastewaters. They are designated by the US EPA as priority chemicals that need to be reduced to a very low level in those wastewaters for safe discharge. Treatment of BTEX-containing wastewater thus has become an integral part of wastewa-

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ter treatment of the chemical and petrochemical industries. Traditionally, activated sludge treatment has been the most widely used method. The microorganisms in an activated sludge system, even well acclimatized, still can only deal with chemical wastewater containing relatively low BTEX concentration, usually much less than 100 mg/l, due primarily to low biodegradability and/or inhibitory effects of these compounds [1,2]. Unfortunately, there are various kinds of chemical and petrochemical wastewaters that contain BTEX far exceeding this concentration level. For such cases, chemical or physical treatment methods may offer acceptable alternatives.

Incineration is such a chemical alternative. It is practical for dealing with waste solvents, but is considered too costly for other practical applications. In the past two decades, wet air oxidation (WAO) process has emerged as another potential alternative and has received considerable attention [3–9]. The WAO method is capable of oxidizing high concentrations of organic compounds in the aqueous solution under elevated temperatures and pressures. The oxidation decomposition process has been found to be rapid and efficient [3–9]. However, to maintain the reaction conditions at high temperatures and pressures is not an easy task and can be rather expensive also due to high capital investments and operating costs. Furthermore, in the WAO oxidation treatment, BTEX is chemically decomposed. In fact, those organic compounds are important raw materials for a wide variety of products in the chemical industries. Hence, a better alternative is to remove BTEX from the aqueous solution by adsorption which permits recovery of these compounds for possible recycling to the manufacturing process. The adsorption of BTEX can be realized by macroreticular resin [10–15], activated carbons [16,17] and organoclays [18,19]. Among them, adsorption by macroreticular resins is the most promising one due to their easy regeneration and is well received in industrial practices [10–15].

Previous investigations of Fox [10,11], Crook et al. [12], Cornel and Sontheimer [13], Kindzierski et al. [14] and Gallup et al. [15] placed major emphasis on the practical and limited theoretical aspects of the BTEX adsorption process. Many examples of practical industrial applications of this process were illustrated in previous studies [10–12,15]. However, there is a lack of fundamental understanding of the mass transfer and column adsorption processes. In the present study, a mass transfer model is employed to describe a batch adsorption system. Also proposed is a theoretical equation for modeling the column adsorption process. The mass transfer model and the column adsorption equation can offer convenient tools for predicting the BTEX transfer rates and the breakthrough curves of BTEX adsorption process.

2. Materials and methods

The macroreticular resin employed here was the Amborsorb 563, 572 and 600, obtained from Rohm and Haas, Philadelphia, PA, USA. They are partial pyrolyzed resins of sulfonated styrene/divinylbenzene polymer. Their BET surface areas, measured by a Micromeritics porosimeter (Model ASAP 200, Micromeritics Instrument, Norcross, GA, USA), pore volume and other properties are listed in Table 1. For

Table 1
Properties of the Ambersorb resins

Property	Ambersorb 563	Ambersorb 572	Ambersorb 600
BET surface area, m ² /g	580	1100	550
Microporosity (< 40 Å), ml/g	0.22	0.41	0.23
Mesoporosity (50–500 Å), ml/g	0.17	0.19	0.14
Macroporosity (> 500 Å), ml/g	0.21	0.24	0.23
Particle size, mesh	20–40	20–50	20–50
Bulk density, g/ml	0.54	0.49	0.53

pretreatment, the macroreticular resins were washed several times with hexane and deionized water and dried at 40°C in an electric oven for over 24 h. It was then placed in a desiccator for cooling.

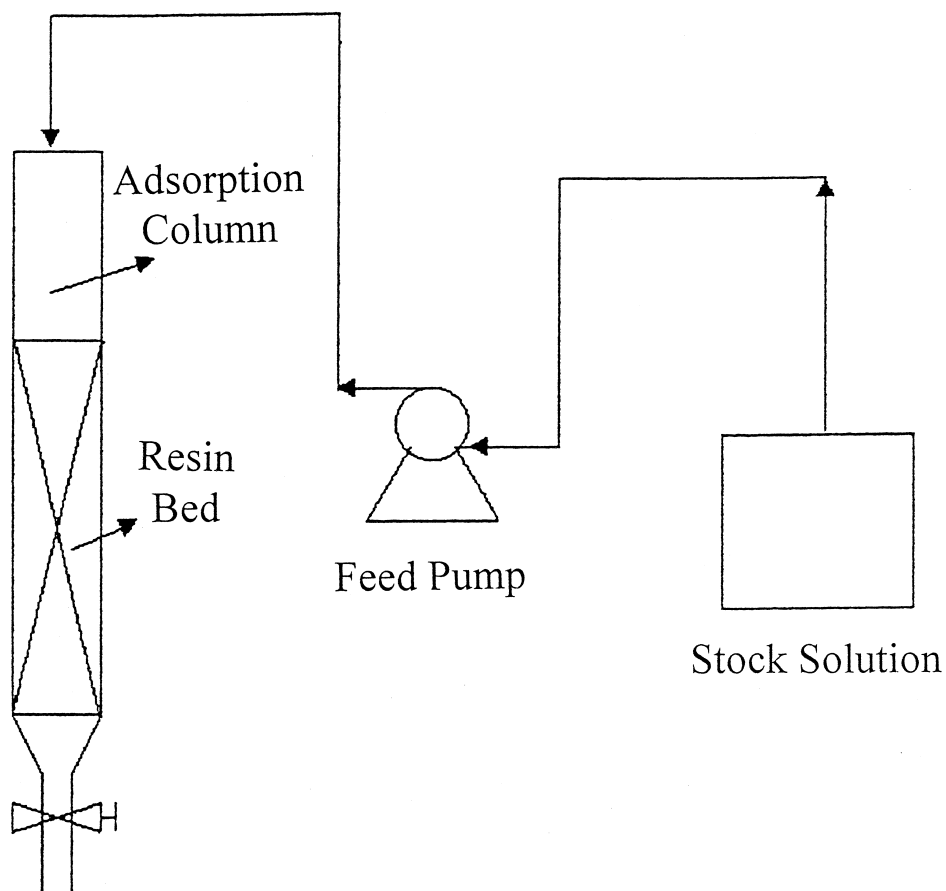


Fig. 1. Experimental apparatus for column BTEX adsorption.

The organic compounds (BTEX) were GR grade solvents, obtained from E Merck (Darmstadt, Germany). The stock BTEX solution was prepared by mixing an appropriate quantity of the solvents with deionized water. To determine the equilibrium BTEX adsorption capacity of Amborsorb, a 250-ml Erlenmeyer flask was placed in a temperature bath for temperature control. A 250 ml of the stock solution was put in the flask and 0.5 g of pretreated Amborsorb resin was added. The flask was completely sealed. The speed of the constant temperature shaker was set at 100 cycles/min and the temperature was maintained at 30°C to 60°C \pm 0.5°C. After a test run was started, the flask was opened periodically and the aqueous sample was taken for BTEX concentration measurements. A Hewlett Packard gas chromatograph (model 5890 series II, Hewlett Packard Instrument, CO, USA) equipped with FID detector and Carbopack SP-1000 packed column was used for the BTEX concentration determination. The batch equilibrium test run continued for over 15 h to ensure that an adsorption equilibrium had been reached. Each of the equilibrium batch runs was repeated at least once to insure the accuracy of the obtained data.

The experimental apparatus for the column adsorption test is shown in Fig. 1. The adsorption column was a pyrex glass tube of 1.88 cm I.D. and 10.5 cm high. It was equipped with a water jacket for temperature control. The adsorption column was packed with 10 g of Amborsorb resin to an adsorption bed volume of 20.5 cm³. In each test run, the stock BTEX solution was pumped by a feed pump to the adsorption column and its flow rate was regulated by a precision flow meter. After a test run was started, the exiting aqueous solution was sampled periodically and the BTEX concentration determined using HP 5890 GC.

3. Results and discussion

3.1. Adsorption characteristics and equilibrium isotherms

The BTEX adsorption characteristics by Amborsorb resins are shown in Fig. 2 for benzene and toluene and in Fig. 3 for ethylbenzene and xylene. Due to their low solubilities, the initial ethylbenzene and xylene concentrations (150 mg/l) in the stock solution were significantly lower than those of benzene and toluene (500 mg/l). As seen in Fig. 2, Amborsorb 572 performs better than the two other Amborsorb resins in benzene and toluene adsorption, but there is not much difference in ethylbenzene and xylene adsorption by any particular Amborsorb resin in Fig. 3.

A different way for expressing adsorption of Amborsorb resin is in terms of the BET surface area instead of the unit weight. Fig. 4 displays adsorption per m² BET surface area for benzene and toluene and Fig. 5 for ethylbenzene and xylene. In both figures, Amborsorb 563 consistently shows the best performance, closely followed by Amborsorb 600 and Amborsorb 572 was the last. This is due primarily to the increasing BET surface areas of 550, 580 and 1100 m²/g for Amborsorb 600, 563 and 572, respectively, as seen in Table 1. Certainly, the pore size and its distribution of the Amborsorb resin, shown in Table 1, may play a role also. It is noted that the differences in the BET surface area and pore size are caused by the extent of resin pyrolysis during the manufacturing stage.

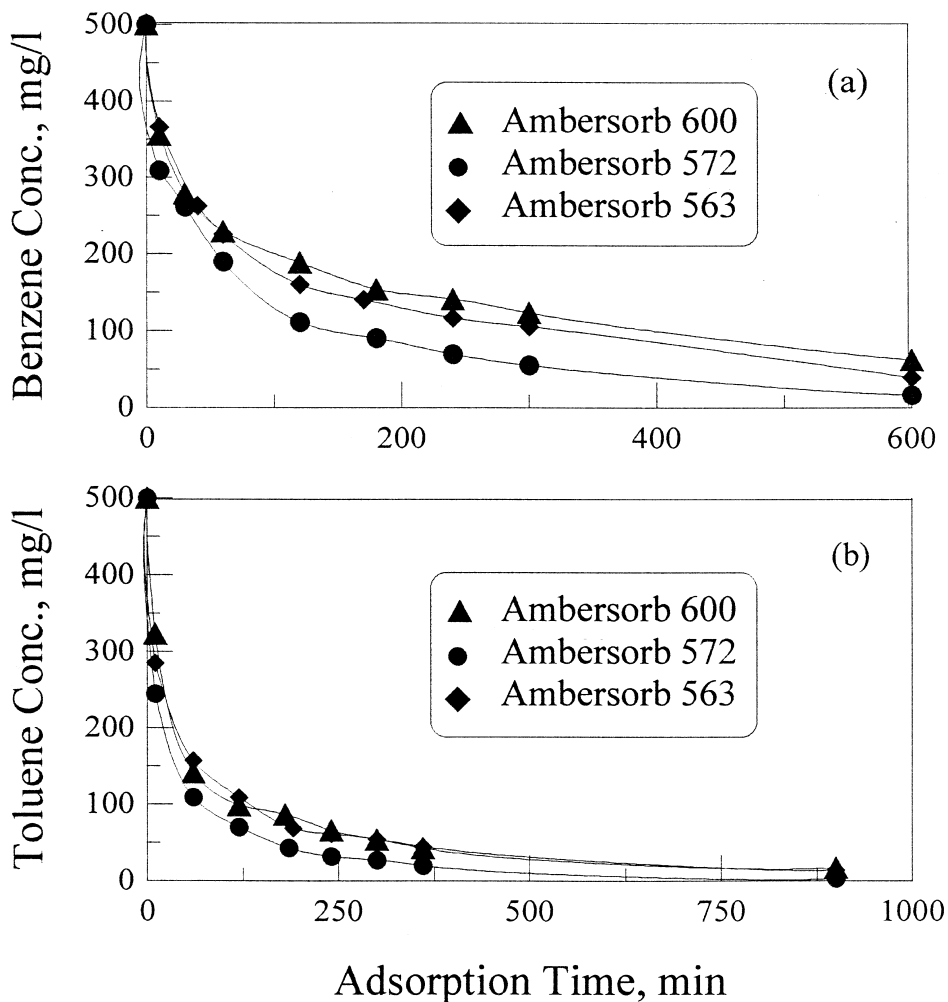


Fig. 2. Benzene (a) and toluene (b) adsorption by Ambersorb resins with 0.5 g adsorbent, 500 mg/l inlet concentration and at 30°C.

The two general adsorption isotherms can be represented by the monolayer Langmuir and the empirical Freundlich models [20,21]:

$$Q_e = \frac{abC_e}{1 + bC_e} \quad (1)$$

$$Q_e = KC_e^{1/n} \quad (2)$$

where Q_e is the equilibrium adsorption capacity of the resin (mg/g adsorbent), C_e is the equilibrium BTEX concentration (mg/l), and a , b , K and n are the isotherm parameters to be determined. C_e in the liquid phase was measured by the HP Model 5890 GC

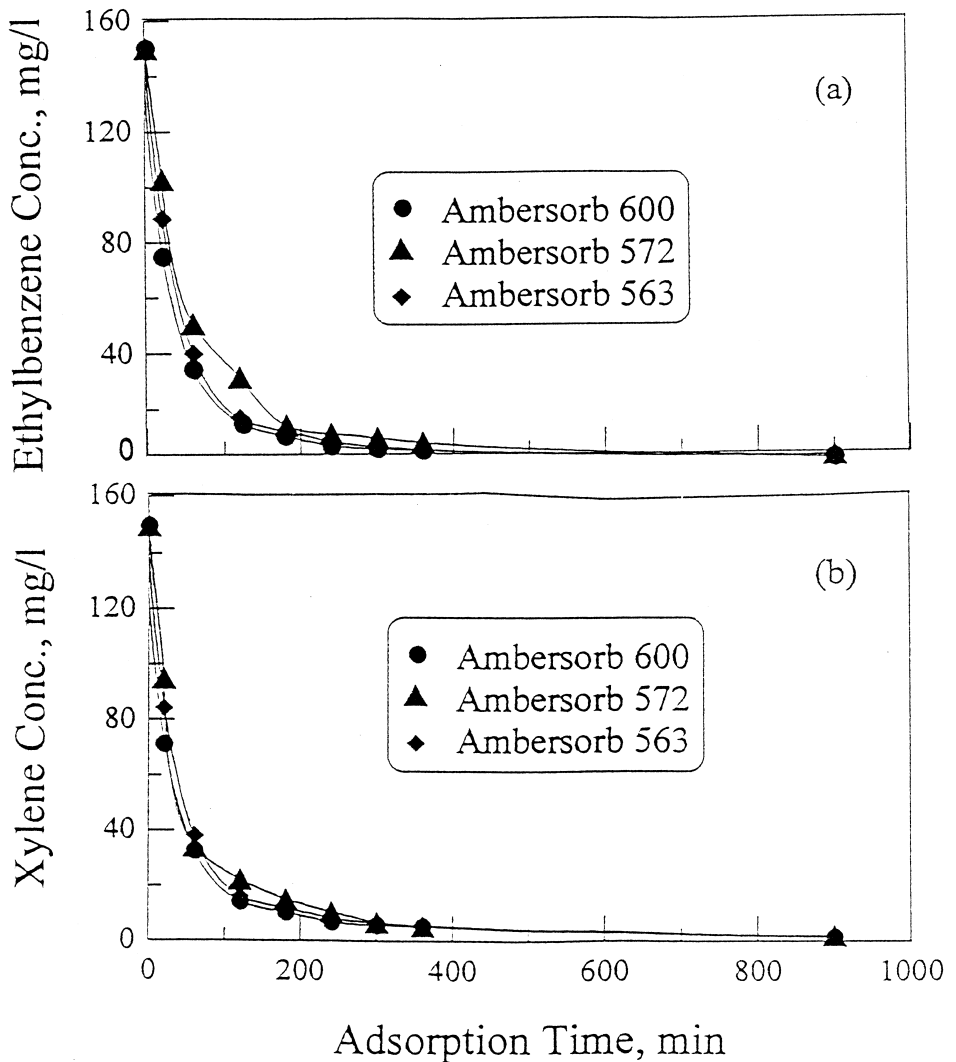


Fig. 3. Ethylbenzene (a) and xylene (b) adsorption by Ambersorb resins with 0.5 g adsorbent, 150 mg/l inlet concentration and at 30°C.

after the adsorption equilibrium was reached. With a known initial BTEX concentration (C_0) and known amount of adsorbent, Q_e was determined. Using the observed data (Q_e and C_e), the isotherm parameters in Eqs. (1) and (2) can be obtained by plotting C_e/Q_e against $1/C_e$, according to Eq. (1) and $\ln(Q_e)$ against $\ln(C_e)$ according to Eq. (2). Fig. 6(a),(b) and (c) compare the experimental equilibrium benzene adsorption capacities and the predicted ones for Ambersorb 563, 572 and 600, respectively. The three figures show that the empirical Freundlich isotherm represents the isotherm data slightly better than the monolayer Langmuir alternative. The same results were observed for toluene,

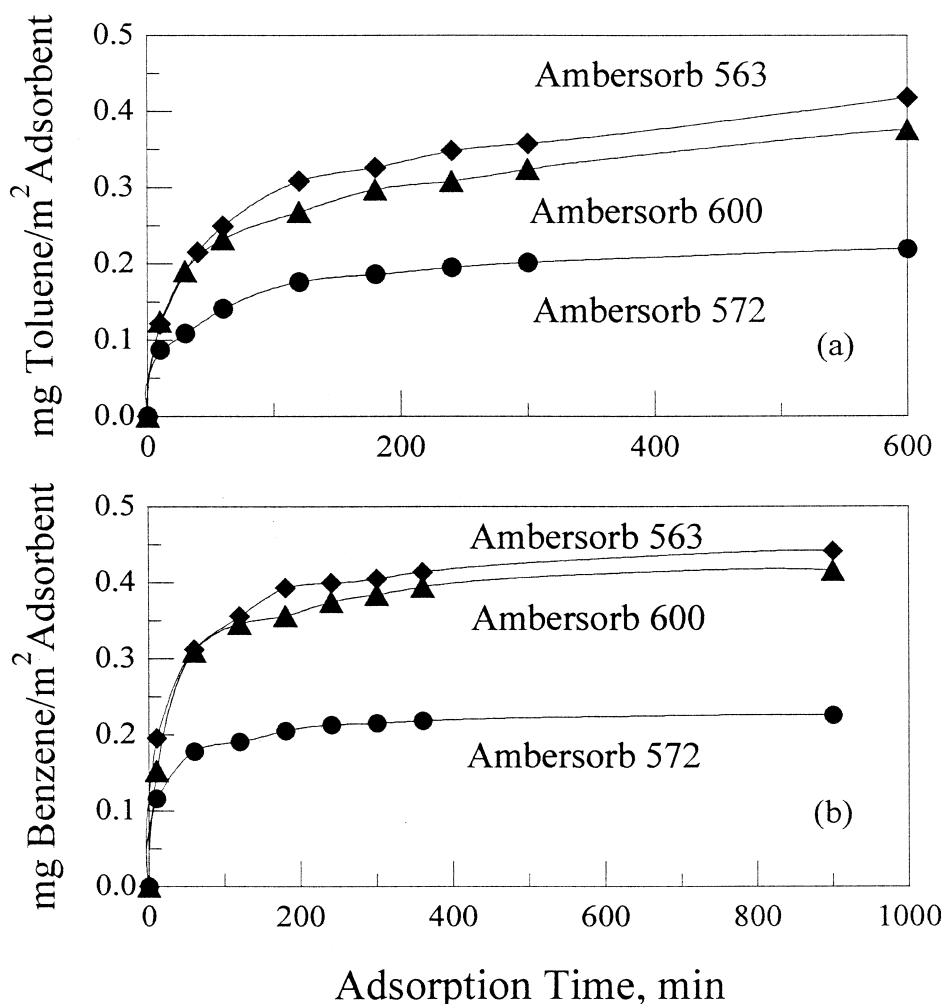


Fig. 4. Benzene (a) and toluene (b) adsorption capacities in mg/m² adsorbent by Ambersorb resins with 0.5 g adsorbent, 500 mg/l initial concentration and at 30°C.

ethylbenzene and xylene. The isotherm parameters estimated by the technique outlined above and using the experimental data are listed in Table 2. The correlation coefficients for the parameter estimations were consistently over 0.98 which was quite good.

3.2. Mass transfer characteristics

BTEX transfer from the aqueous solution to the resin solid phase in a batch adsorption process could be governed by various mass transfer resistances between the two phases. Different models of varying complexity have been proposed for describing the mass transfer processes [20,21]. All the mass transfer models involve a number of

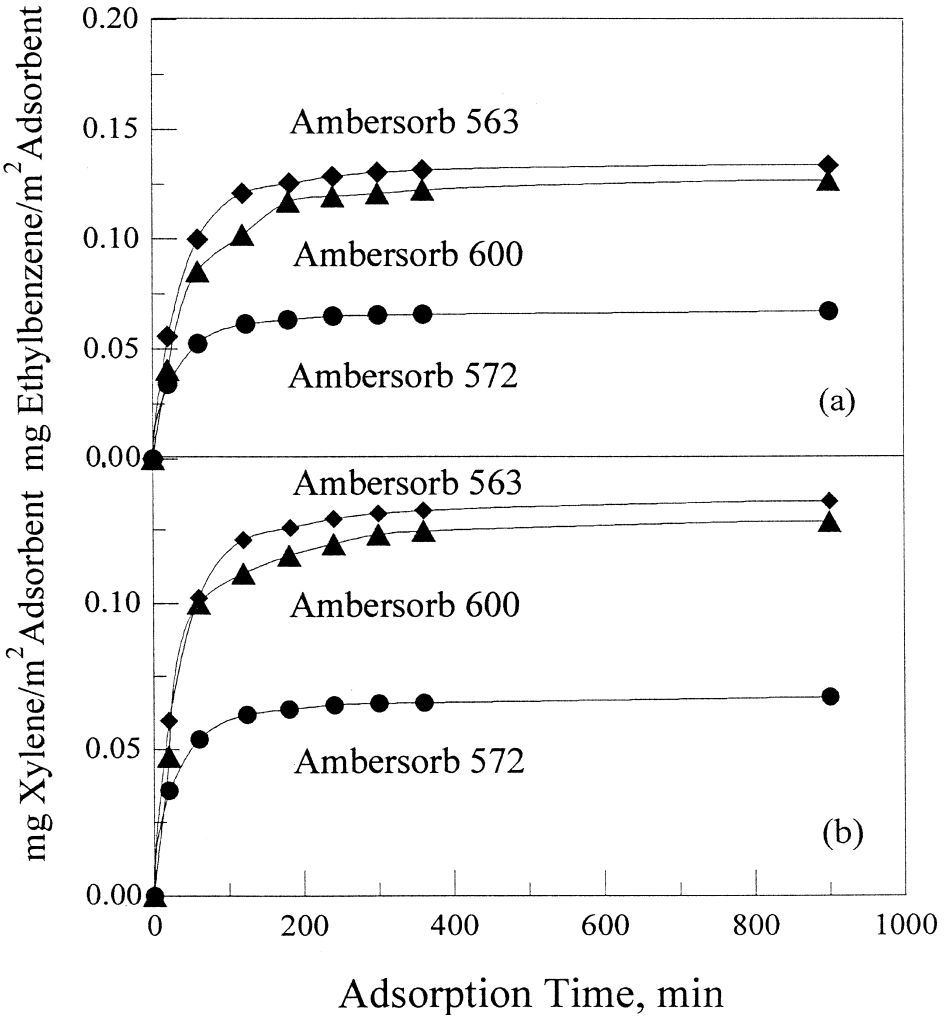


Fig. 5. Ethylbenzene (a) and xylene (b) adsorption capacities in mg/m² adsorbent by Ambersorb resins with 0.5 g adsorbent, 150 mg/l initial concentration and at 30°C.

parameters which need to be estimated with a certain degree of certainty. The squared driving force mass transfer model proposed by Jiang et al. [21] has the advantages of relative simplicity and reasonable accuracy. The model is represented by:

$$\frac{dC_s}{dt} = KC(C_s^* - C_s) \tag{3}$$

in which C is the BTEX concentration in the liquid phase, C_s is that in the solid phase (resin), C_s^* is that of the solid phase in equilibrium with C_e in the liquid phase, K is the overall mass transfer coefficient and t is the time. It should be noted that the equilibrium

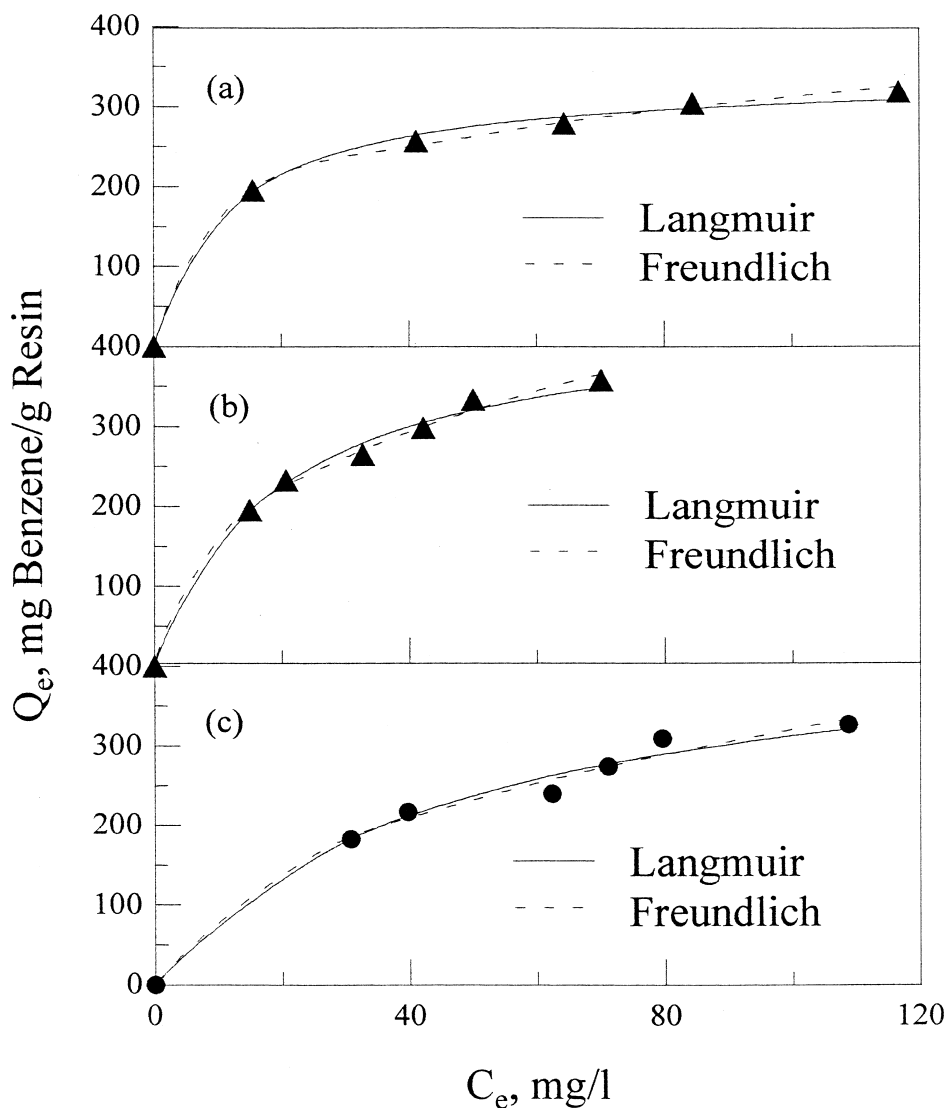


Fig. 6. Comparison of the model fit of benzene adsorption isotherms by Ambersorb 563 (a), 572 (b) and 600 (c) with 0.5 g adsorbent and at 30°C.

BTEX concentration of the resin (C_s^*) in the above-equation is in fact equal to the product of Q_e given by Eq. (1) or Eq. (2) and the density of the resin. According to Eq. (3), the BTEX concentration in the solid phase is assumed to be uniform for pseudo steady state condition. Simple material balance would give:

$$C_s V_R = (C_0 - C) V_L \quad (4)$$

Table 2
Parameters of the Freundlich isotherm at 30°C

Parameter	Ambersorb 563	Ambersorb 572	Ambersorb 600
<i>Benzene</i>			
<i>K</i>	100.6	68.7	38.2
<i>n</i>	4.05	2.51	2.12
<i>Toluene</i>			
<i>K</i>	87.2	86.6	24.2
<i>n</i>	2.33	2.31	1.58
<i>Ethylbenzene</i>			
<i>K</i>	56.9	201.8	110.5
<i>n</i>	0.94	1.34	1.47
<i>Xylene</i>			
<i>K</i>	52.1	79.3	133.1
<i>n</i>	1.20	1.23	1.87

where C_0 is the initial BTEX concentration in the liquid phase, and V_R and V_L are the volumes of the solid and liquid phases, respectively. Eliminating C from Eqs. (3) and (4) and integrating yields Eq. (5):

$$\frac{1}{C_0 - mC_s^*} \ln \left[\frac{C_s^* (C_0 - mC_s)}{C_0 (C_s^* - C_s)} \right] = Y = Kt \quad (5)$$

in which m is the volume ratio of the solid and liquid phases (V_R/V_L). Knowing C_0 , V_R and V_L and with measured liquid phase BTEX concentration (C), C_s can be calculated from Eq. (4) and the left-hand quantity of Eq. (5) is known. According to Eq. (5), a plot of the left-hand quantity (Y) against t would yield a straight line with a slope of K . Fig. 7 shows the Y vs. t plots for benzene and toluene and Fig. 8 displays those for ethylbenzene and xylene. The experimental data follow the linear $Y-t$ relation reasonably well. Hence, adoption of the pseudo steady state squared driving force mass transfer model is justified. The overall mass transfer coefficient obtained from the $Y-t$ plots were found to be temperature dependent. The temperature dependence of the overall mass transfer coefficient is represented by the Arrhenius equation:

$$K = A \exp \left(- \frac{\Delta E}{RT} \right) \quad (6)$$

in which A is the frequency factor, ΔE is the activation energy, R is the gas constant and T is the absolute temperature. The activation energies obtained using Eq. (6) for different adsorbents are listed in Table 3. It is seen in this table that the activation energies for all Ambersorb adsorbents are relatively small and are close to or less than 10 kcal/mol K which are typical of physical adsorption [22].

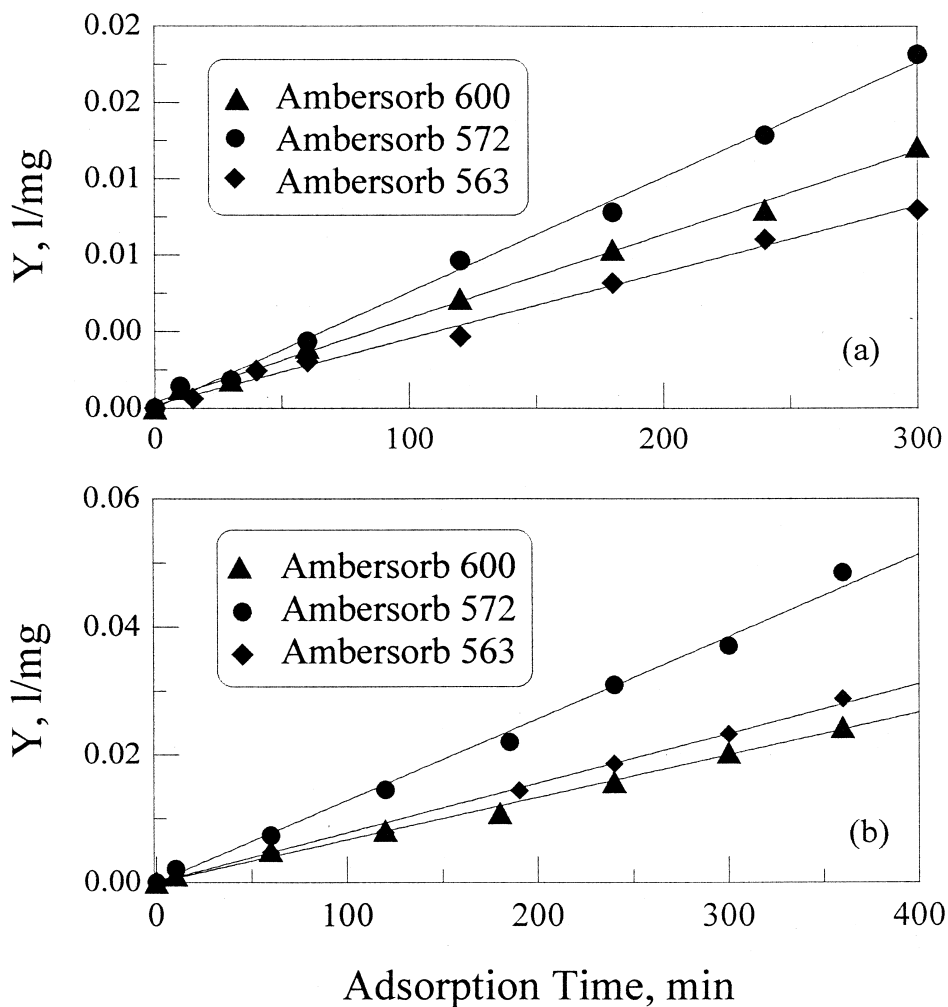


Fig. 7. Comparison of the predictions by the proposed mass transfer model and the experimental data for benzene (a) and toluene (b) adsorption by Ambersorb resins with 0.5 g adsorbent, 500 mg/l initial adsorbate concentration and at 30°C.

3.3. Column adsorption model

In this section, a theoretical model was proposed for describing the BTEX concentration change exiting the adsorption column. In the adsorption column, the entering liquid solution flows through the stationary bed of adsorption resin and some of the BTEX in the liquid solution get adsorbed on the activated sites while the others pass through the bed. Note that the fraction of BTEX being adsorbed is A and the fraction of that remaining in the liquid solution and passing through the stationary resin bed is P . It is

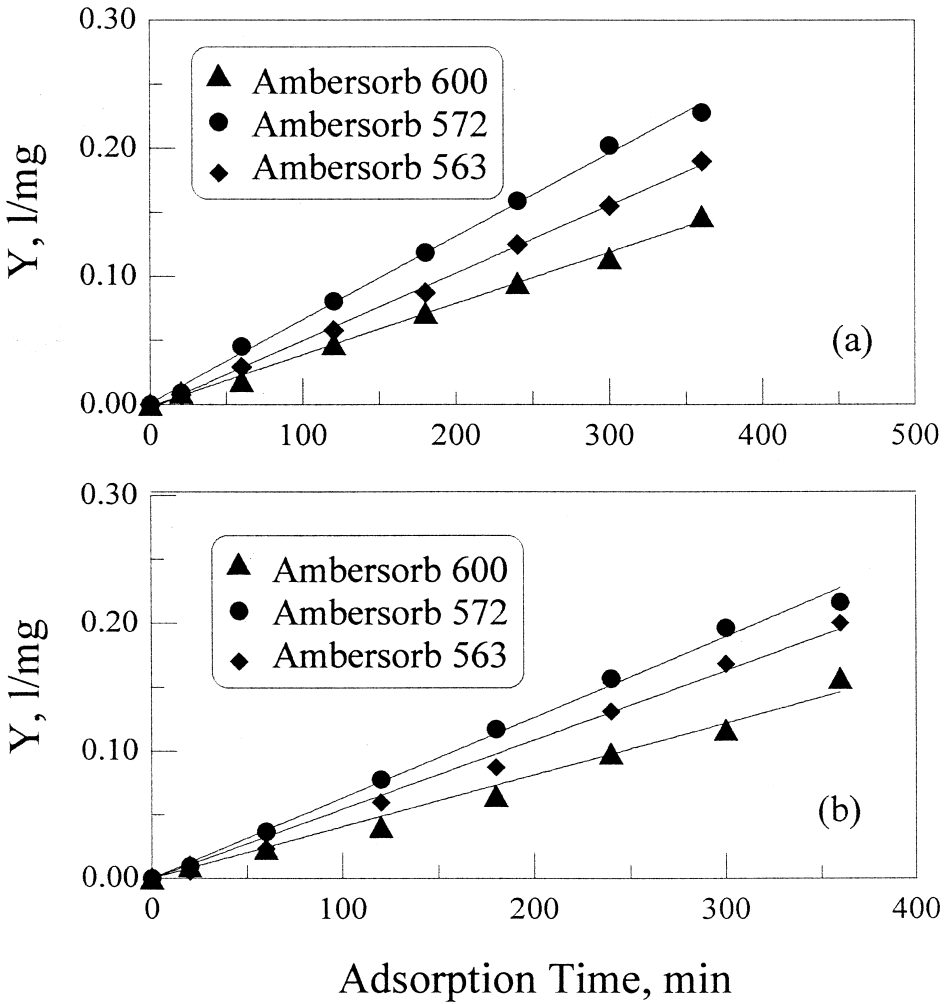


Fig. 8. Comparison of the predictions by the proposed mass transfer model and the experimental data for ethylbenzene (a) and xylene (b) adsorption by Ambersorb resins with 0.5 g adsorbent, 150 mg/l initial adsorbate concentration and at 30°C.

reasonable to assume that the rate of decrease in the adsorption fraction of BTEX is proportional to A and P as represented by:

$$-\frac{dA}{dt} \propto AP \tag{7}$$

or

$$-\frac{dA}{dt} = kAP. \tag{8}$$

Table 3

Activation energy of overall mass transfer coefficient for different adsorbents

Activation energy in cal/mol K.

Adsorbent	Amborsorb 563	Amborsorb 572	Amborsorb 600
Benzene	5304.2	7566.2	4350.3
Toluene	9931.7	9936.1	8341.4
Ethylbenzene	6900.1	8048.5	7853.8
Xylene	10,143.6	16,827.1	11,400.5

It is noted in the above-equation that $P = 1 - A$. In fact, Eq. (8) is similar to the logistic function which was originally proposed to describe the phenomena of biological growth and decay [23]. Although nonlinear, this equation can be integrated with an initial condition of $A = A_a$ at $t = t_a$:

$$\ln \left[\frac{A(1 - A_a)}{A_a(1 - A)} \right] = k(t_a - t) \quad (9)$$

which is the same as:

$$\ln \left[\frac{P_a(1 - P)}{P(1 - P_a)} \right] = k(t_a - t). \quad (10)$$

For BTEX removal at $P_a = 0.5$, the adsorption time (t_a) is denoted as τ and Eq. (10) becomes:

$$P = \frac{1}{1 + \exp[k(\tau - t)]} \quad (11)$$

or

$$t = \tau + \frac{1}{k} \ln \left(\frac{P}{1 - P} \right). \quad (12)$$

The BTEX fraction (P) that passes through the adsorption column is equal to C/C_0 with C being the BTEX concentration in the aqueous solution exiting the adsorption column at time t and C_0 the inlet concentration. According to Eq. (12), a plot of adsorption time (t) vs. $\ln[C/(C_0 - C)]$ yields a straight line with the intercept and slope of the straight line equal to τ and $1/k$, respectively. The top graph of Fig. 9 shows such a plot for typical benzene adsorption in a Amborsorb 572 column under different flow rates. Alternatively, τ can also be obtained at the adsorption time when $\ln[C/(C_0 - C)]$ is zero because of the fact that by definition, τ is the adsorption time when C is one-half of C_0 . With k and τ determined in this fashion, Eq. (12) can be used to establish the entire breakthrough curve. Since only two model parameters are involved in Eq. (12), two accurate experimental data points of C as a function of adsorption time (t) would be theoretically sufficient to establish those two parameters. However, for accurate estimation of the model parameters, a complete breakthrough curve would be recommended as necessary.

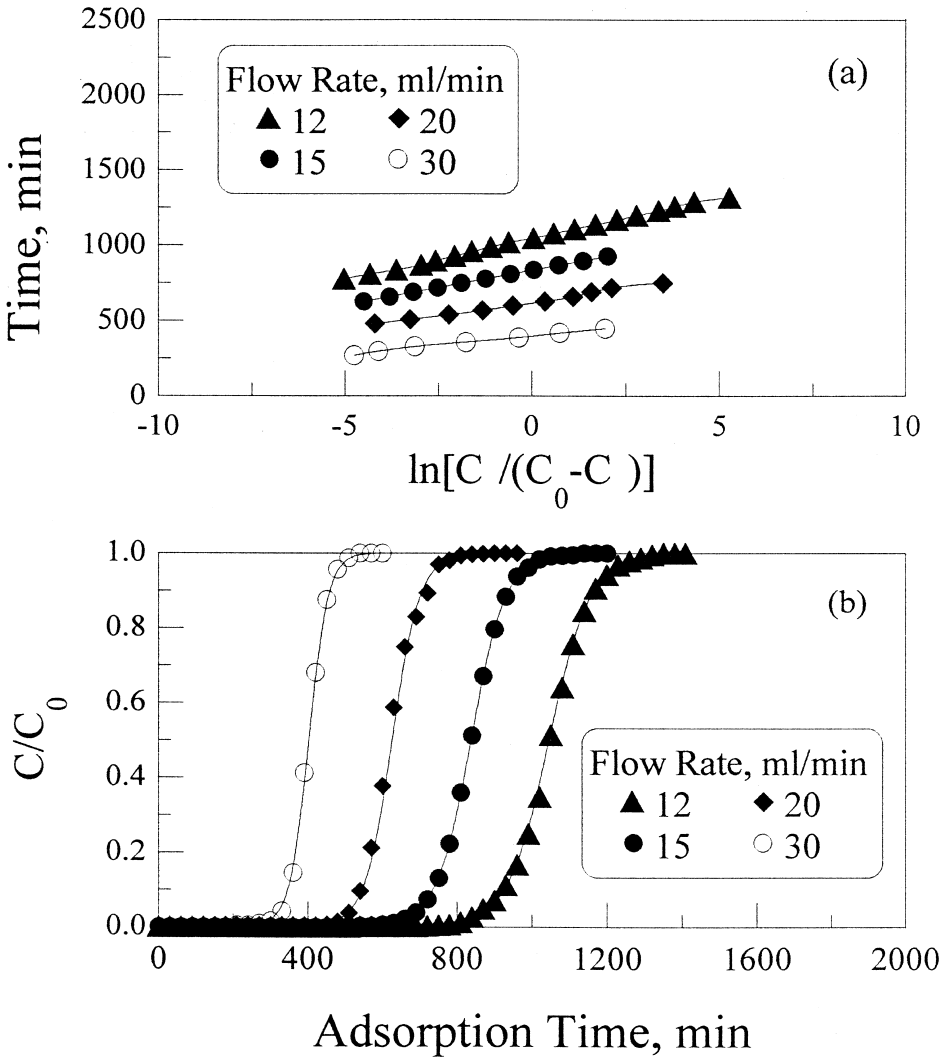


Fig. 9. Linear plots of t vs. $\ln[C/(C_0 - C)]$ (a) and comparison of the observed and predicted breakthrough curves (b) of benzene adsorption in a column Ambersorb 572 adsorber with 500 mg/l inlet benzene concentration and at 30°C.

The derivation for Eq. (12) was based on the definition that 50% breakthrough occurs at τ . Accordingly, the resin bed should be completely saturated at 2τ . Due to the symmetrical nature of the breakthrough curve, the amount of BTEX being adsorbed by the resin bed is one-half of the total BTEX entering the adsorption column within the 2τ period. Hence, the following equation can be written:

$$W_c = \frac{1}{2} C_0 F(2\tau) = C_0 F\tau. \tag{13}$$

Table 4

Parameters for benzene adsorption by Ambersorb 572 in a column adsorber
Adsorption with 500 mg/l inlet benzene concentration and at 30°C.

Flow rate, ml/min	K , l/min	τ , min
12	54.6	1064
15	46.1	837
20	36.9	626
30	25.8	402

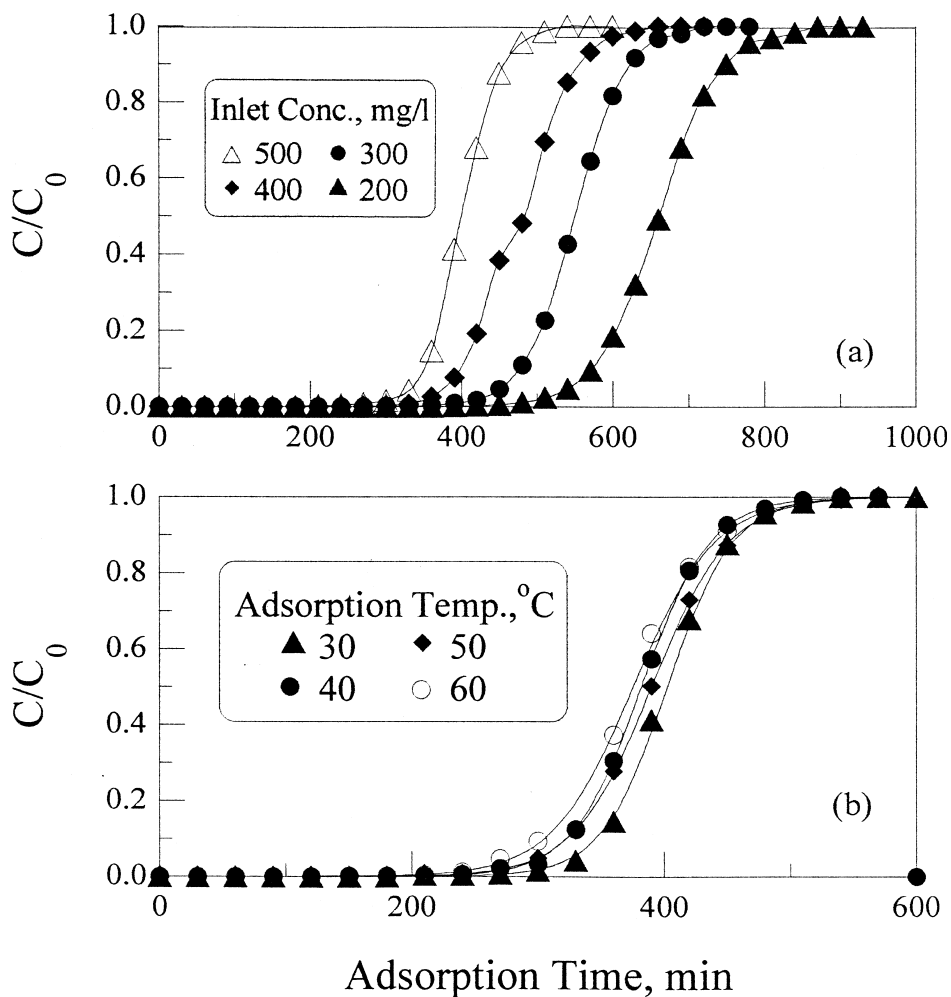


Fig. 10. Comparison of the observed and predicted breakthrough curves of benzene adsorption with different inlet benzene concentrations (a) and at different temperatures (b).

The above equation establishes the relation among the adsorption capacity of the column (W_c), inlet BTEX concentration (C_0), liquid flow rate (F) and the 50% breakthrough time (τ).

Using the plots in Fig. 9(a) for various flow rates, the model parameters can be obtained. Table 4 lists the model parameters obtained as a function of the benzene flow rate. Based on those model parameters, the predicted benzene breakthrough curves are compared with the experimental ones in Fig. 9(b). It is apparent that predicted and experimental breakthrough curves compare very well. The same procedure was repeated for benzene adsorption in a Ambersorb 572 column with different inlet benzene concentrations (C_0) and at different adsorption temperatures (T). Fig. 10(a) and (b) show the predicted and experimental breakthrough curves with different inlet benzene concentrations and at different adsorption temperatures, respectively. The figure shows quite good agreement between the predicted and the experimental breakthrough curves for both cases. Hence, the proposed model and the procedure for model parameter estimation can be recommended.

4. Conclusions

BTEX adsorption by new types of commercially available macroreticular resins (Ambersorb) in a batch or continuous process was investigated experimentally and theoretically. The experimental results demonstrate that these new type adsorbents are highly efficient for BTEX adsorption. The empirical Freundlich isotherm describes the equilibrium adsorption data better than the Langmuir alternative. A theoretical model based on the empirical squared-driving force principle was adopted for describing the mass transfer between the aqueous phase and the solid phase (resin). The model involves only one constant parameter (the overall mass transfer coefficient) which can be conveniently estimated using the experimental mass transfer data. Also proposed in the present work was a theoretical model for predicting the BTEX breakthrough curve in the adsorption column. The model required empirical estimation of two model parameters by using the breakthrough curve data. The model was employed to test the breakthrough curves obtained at various liquid flow rates, inlet BTEX concentrations and adsorption temperatures. A comparison of the experimental and the theoretical results showed that the model predicted closely the breakthrough curves for the test cases conducted in the present study. Hence, the proposed model can be conveniently used to estimate the BTEX breakthrough time and the adsorption capacity of an adsorption column.

Acknowledgements

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References

- [1] M.K. Chang, T.C. Voice, C.S. Criddle, *Biotechnol. Bioeng.* 41 (1993) 1057–1065.
- [2] A.R. Bielefeldt, H.D. Stensel, *Water Res.* 33 (1999) 707–714.
- [3] G.H. Teletzke, *Chem. Eng. Prog.* 60 (1964) 33–39.
- [4] R.F. Peoples, P. Krishnan, R.N. Simonsen, *J. Water Pollut. Cont. Fed.* 44 (1972) 2120–2128.
- [5] H.R. Devlin, I.J. Harris, *Ind. Eng. Chem. Fundam.* 23 (1984) 387–394.
- [6] H.S. Joglekar, S.D. Samant, J.B. Joshi, *Water Res.* 25 (1991) 135–142.
- [7] L. Li, P. Chen, E.F. Gloyna, *AIChE J.* 37 (1991) 1687–1695.
- [8] S.H. Lin, T.S. Chuang, *J. Environ. Sci. Health A* 29 (1994) 547–564.
- [9] S.H. Lin, Y.F. Wu, *Environ. Technol.* 17 (1996) 175–183.
- [10] C.R. Fox, *Hydrocarbon Proc.* 54 (7) (1975) 109–111.
- [11] C.R. Fox, *Hydrocarbon Proc.* 57 (11) (1978) 269–273.
- [12] E.H. Crook, R.P. McDonnell, J.I. McNulty, *Ind. Eng. Chem. Prod. Res. Dev.* 14 (1978) 113–118.
- [13] P. Cornel, H. Sontheimer, *Chem. Eng. Sci.* 41 (1986) 1791–1800.
- [14] W.B. Kindziarski, M.B. Gray, P.M. Fedorak, S.E. Hrudey, *Water Environ. Res.* 64 (1992) 766–772.
- [15] D.L. Gallup, E.G. Isacoff, D.N. Smith, *Environ. Prog.* 11 (1996) 197–204.
- [16] K.E. Noll, V. Gounaris, W.S. Hou, *Adsorption Technologies for Air and Water Pollution Control*, Lewis Publishers, Chelsea, MI, 1994.
- [17] E.G. Furuya, H.T. Chang, Y. Miura, K.E. Noll, *Sep. Purif. Technol.* 11 (1997) 68–78.
- [18] M.M. Mortland, S. Shaobai, S.A. Boyd, *Clays Clay Miner.* 34 (1986) 581–592.
- [19] S.K. Dentel, J.Y. Bottero, K. Khatib, H. Demougeot, J.P. Doguet, C. Anselme, *Water Res.* 29 (1995) 1273–1280.
- [20] D.M. Ruthven, *Principles of Adsorption and Adsorption Processes*, Wiley, New York, 1984.
- [21] C.S. Jiang, C.C. Can, C.S. Sung, *Ion Exchange Separation Engineering*, Tienjing University Press, Tienjing, China, 1992.
- [22] A.W. Adamson, *Physical Chemistry of Surfaces*, 4th edn., Wiley, New York, 1990.
- [23] E. Beltrami, *Mathematics for Dynamic Modeling*, Academic Press, New York, 1987.