Modeling of Supercritical Desorbers with an Equation-of-State-Based Isotherm

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An equation-of-state-based sorption isotherm is developed and used in modeling isothermal supercritical fluid desorption in fixed beds. The conventional fixed-bed desorber model when coupled with density-dependent sorption isotherm predicts the temperature, pressure, and density effects on desorber dynamics and regeneration efficiencies that are experimentally observed in supercritical fluid regeneration of fixed beds.

Experimentally observed phenomena such as the presence of pressure-dependent optimal regeneration temperature, high-pressure-favored regeneration, and the reversal of temperature dependence of sorption isotherm—which formerly were attributed to supercritical fluid density and viscosity, and to the endothermicity of sorption isotherm—were fully predicted and explained in terms of a density-dependent sorption isotherm.

The proposed method also promises prediction of regeneration efficiencies in cosolvent-aided supercritical fluid desorption.

Introduction

Application of supercritical fluid (SCF) technology to regeneration of activated carbon beds has received widespread attention over the past years. Currently used thermal regeneration methods suffer from significant loss of carbon due to oxidation, and inventory for make-up carbon introduces a significant cost in such treatments, which are also energy intensive. Desorption of organic solutes using liquid solvents has also received considerable attention, however, the rate of desorption was found to be slow. Snoeyink et al. (1969) observed that desorption of phenol and nitrophenol with water exhibits significant hysteresis even after long desorption periods. In SCF regeneration of fixed beds, carbon dioxide is a preferred solvent due to its low critical temperature and pressure. Environmental considerations also put the supercritical carbon dioxide regeneration method into a favorable position compared to regeneration with liquid solvents, especially when desorbing hazardous organics. The regeneration of the SCF leaving the desorber can then be done with ease by changing the temperature and/or pressure in an upstream regenerator.

Regeneration of saturated activated carbon with supercritical carbon dioxide was first proposed by Modell et al. (1979), who presented experimental data and information on process development. They observed that, except after the first adsorption–desorption cycle, virtually all the phenol absorbed could be desorbed in the subsequent cycles. Recently, Grant and King (1990) have shown that the loss in capacity of the activated carbon after the first adsorption cycle could be explained with surface reactions taking place between phenolic compounds on carbon surfaces. Modell et al. also observed a relatively rapid mass transfer in both adsorption and desorption cycles. They found that, unlike desorption with liquid solvents, when desorbing phenol with supercritical carbon dioxide the concentration of solute in the regenerant peaked soon after the onset of regeneration, and that the bulk of the desorption occurred in the early stages of the desorption. They also observed that the desorption was more favorable at higher pressures, which is the opposite of what is observed at pressures far below the critical pressure of commonly used regenerants such as steam or hot gases.

Since the pioneering work of Modell et al., supercritical fluid desorption of a variety of absorbates, but mostly activated carbon as the adsorbent, has been studied. Kander and Paulaitis (1983) studied the desorption of activated carbon loaded with phenol by supercritical carbon dioxide. These au-

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thors also obtained the adsorption equilibrium data of phenol onto activated carbon, both from aqueous solution and from supercritical carbon dioxide, with which they introduced a method of developing an equation-of-state-based sorption isotherm to interpolate their fluid phase data. However, they found that the resulting equation-of-state-based isotherm predicted carbon loadings independent of the density of the supercritical carbon dioxide. They concluded that supercritical carbon dioxide offered no significant thermodynamic advantages for regeneration of activated carbon loaded with strongly adsorbed organics such as phenol. An equilibrium between alachlor (a pesticide) in the supercritical carbon dioxide phase and in the solid phase (activated carbon) has also been measured by Krukonis (1977), and very high equilibrium carbon loadings have been reported corresponding to even very low fluid phase alachlor concentrations.

Tan and Liou (1988, 1989a) studied the supercritical carbon dioxide regeneration of activated carbon loaded with ethyl acetate or toluene. These authors later (Tan and Liou, 1989b) studied the binary desorption by supercritical carbon dioxide of activated carbon loaded with benzene and toluene. In their studies, they found that the SCF regeneration method was superior to the saturated or superheated steam regeneration method. When compared with steam regeneration, the SCF regeneration method provided a significant increase in the breakthrough time in the adsorption step following desorption. Similar to the findings of Modell et al. (1978), they observed that more than 50% of the regeneration could be achieved within the first hour of desorption with supercritical carbon dioxide. The authors observed that the regeneration efficiencies (fraction desorbed) decreased with temperature when the system was below a certain pressure. However, the situation was reversed at higher pressures, suggesting a pressure-dependent optimal regeneration temperature. This reversal was explained in terms of the density and viscosity of the supercritical fluid. Also, the regeneration efficiency was found to increase with pressure at a fixed temperature. A single-parameter (desorption rate constant) model assuming linear desorption kinetics was found to match the experimental data well after regression. Tan and Liou (1989c), in another study, due to the existence of an optimal temperature, questioned the validity of obtaining the apparent desorption activation energies at fixed pressures by plotting the desorption rate constant vs. the reciprocal of temperature, that is, the Arrhenius expression. In an attempt to investigate the effect of fluid density, they studied the desorption of toluene from activated carbon by supercritical carbon dioxide at constant fluid densities. As a result of this study they found that the regeneration efficiency increased with increasing fluid density at all temperatures without the existence of an optimal regeneration temperature. At constant densities, they plotted the desorption rate constant obtained by regression of their single-parameter model against the reciprocal of temperature, and obtained a good fit. They calculated that less desorption activation energy was required at higher densities, confirming the experimentally observed fact that desorption is easier at higher pressures at a fixed temperature. In a recent work, Srinivasan et al. (1990) studied the desorption of ethyl acetate from activated carbon by supercritical carbon dioxide. In this work, the authors tried to model the process with a linear driving force, external fluid film resistance model by assuming a linear adsorption equilibrium constant. They, as well, experimentally observed the afore-mentioned characteristics of the supercritical fluid desorption process. The authors calculated the activation energies and heats of adsorption from regressed data, which indicated an endothermic adsorption. The extent of the endothermicity as well as the activation energy for adsorption were found to decrease with increasing pressure.

Quite recently, Tan and Liou reported the density-dependent equilibrium loadings of toluene (Tan and Liou, 1990a) and benzene (Tan and Liou, 1990b) from supercritical carbon dioxide onto activated carbon. When the supercritical fluid phase densities were fixed, the Langmuir isotherm was found to correlate the experimental data satisfactorily. When the supercritical phase concentrations were kept constant, at relatively high pressures, they observed the crossover of the equilibrium loadings at different temperatures. The pressure at which the crossover occurred increased with increasing supercritical phase concentrations for both toluene and benzene.

As a result of the experimental works mentioned above, all the characteristics of the isothermal supercritical fluid regeneration method have been well understood and the method has shown to be feasible. Overall, the observed retrograde effects of temperature and pressure on regeneration are very similar to those observed for solubilities encountered in supercritical fluids. However, so far there appears to be no work on modeling of the process, which will predict the retrograde behavior, at least qualitatively, and allow extrapolation of the effects of process variables on regeneration efficiency. Any further advance and widespread industrial application of this technology depend on predictive modeling, which can be used in evaluating design alternatives. The models included in the previous works can only reproduce the experimental data and can be used only for interpolation purposes since their parameters are fitted at each temperature and pressure level studied.

The objective of this work is to show the retrograde behavior encountered in isothermal supercritical fluid regeneration of fixed beds can be predicted, at least qualitatively as in the case of conventional adsorber and desorbers, without resorting to direct regression of the experimental effluent concentrations. As will be shown, this can be achieved through coupling of a density-dependent sorption isotherm with a conventional fixed-bed desorber model. In this paper, only the regeneration of activated carbon, loaded with phenol, by supercritical carbon dioxide will be considered since the required sorption data in developing the density-dependent isotherm are available only for this system. It will also be shown how the proposed method is suitable in making at least qualitative predictions regarding cosolvent aided supercritical fluid regeneration when related supercritical vapor–liquid equilibrium data are available.

Modeling of Density-Dependent Sorption Isotherm

It is a well-known fact that the propagation dynamics of concentration waves in adsorbers and desorbers depend mainly on the sorption isotherm, which characterizes the adsorbate–adsorbent interactions. Due to the bidisperse structure of the activated carbon, sorption equilibria of most of the solutes cannot be described by linear or Langmuir isotherms. The Toth isotherm can accurately represent all the phenol-activated carbon data available in the literature (Jossens et al., 1978). Thus, in this work, the density-dependent sorption isotherm is based on the Toth isotherm. When supercritical carbon dioxide regeneration of activated carbon loaded with phenol is considered, accurate equilibrium data of adsorption of phenol onto activated carbon from supercritical carbon dioxide are necessary, showing all the effects of temperature, pressure, and fluid density. Kander and Paulaitis (1983) have presented the equilibrium adsorption data of phenol onto activated carbon from aqueous solution and from supercritical carbon dioxide. Their fluid phase data are at 36°C/139 atm and 60°C/173 atm, which correspond to supercritical fluid densities of 0.787 and 0.658 g/cm^3, respectively. These data can be well represented with the Toth isotherm; nevertheless, the accuracy of such a representation will be restricted to the specific temperatures and fluid densities at which the data are taken. A method of obtaining an equation-of-state-based isotherm that will permit reasonable interpolation and extrapolation of the experimental data has been suggested by Kander and Paulaitis (1983). However, their results, after extrapolation to different temperatures and densities, show negligible dependence of carbon loadings on the supercritical carbon dioxide density. We have found that if the sorption equilibrium is independent of fluid density, most of the experimentally observed behavior in supercritical desorbers cannot be predicted. Our method, with which a density-dependent sorption isotherm is obtained, follows the procedure as outlined by Kander and Paulaitis (1983), with some modifications that emphasize the temperature dependence of some of the parameters involved.

In the first step, the Toth isotherm parameters are obtained at 36 and 60°C from the experimental data (Kander and Paulaitis, 1983) for aqueous-phase phenol concentrations vs. the corresponding carbon loadings.

The Toth isotherm is given by:

$$q_x = \frac{\theta_1 c}{(\theta_2 + c^{\theta_3})^{1/\theta_3}} \tag{1}$$

In order to be able to interpolate to temperatures between 36 and 60°C, the temperature dependence of the isotherm parameters must be established. Due to the heterogeneous surface structure of activated carbon, the heat of adsorption is not constant but depends strongly on the surface coverage (Jossens et al., 1978). However, for dilute solutions, based on the approximation that the isosteric heat of adsorption is independent of temperature, interpolation can be done using the following theoretical expression (Valenzuela and Myers, 1989):

$$\Delta H_{st} = RT^2 \left(\frac{\partial \ln c}{\partial T}\right)\Bigg|_{q_x} \tag{2}$$

First, the isosteric heat of adsorption, ΔH_{st} corresponding to a sufficiently large number of carbon loadings, q_x, is obtained from Eqs. 1 and 2 using the experimental data available at two different temperatures. Then, using the integrated form of Eq. 2:

$$\ln\left(\frac{c}{c^*}\right) = \frac{\Delta H_{st}}{R}\left[\frac{1}{T^*} - \frac{1}{T}\right]\Bigg|_{q_x} \tag{3}$$

the aqueous-phase phenol concentrations corresponding to carbon loadings at the desired temperatures between 36 and 60°C are obtained. The temperature dependence of the Toth isotherm parameters, obtained by regression based on the theoretical data generated in this way, can be represented by:

$$\theta_1(T) = 1.9694 \times 10^{-6} \exp\left(\frac{1.7801 \times 10^{+2}}{T - 2.7758 \times 10^{+2}} + 1.5988 \times 10^{-2} T\right)$$

$$\theta_2(T) = 6.2086 \times 10^{-10} \exp\left(\frac{6.9574 \times 10^{+2}}{T - 1.8365 \times 10^{+2}} + 4.7479 \times 10^{-2} T\right)$$

$$\theta_3(T) = 1.6277 \times 10^{-6} \exp\left(\frac{-1.2506 \times 10^{+1}}{T - 2.8097 \times 10^{+2}} + 3.7046 \times 10^{-2} T\right) \tag{4}$$

The Toth isotherm with these parameters fits the data well and satisfies the isosteric heat of adsorption values, Eq. 2, between 36 and 60°C. For the next step of the method, it is useful to use mole fractions instead of concentrations; this can be done using:

$$c = \beta x \tag{5}$$

where

$$\beta = \frac{10^{-6}}{[\rho_w(T)/M_w]} \tag{6}$$

$$\rho_w(T) = 1.242345 - 1.884384 \times 10^{-3} T + 3.631268 \times 10^{-6} T^2 \tag{7}$$

Figure 1 shows the experimental carbon loadings, q_x, vs. aqueous phase phenol mole fraction, x, data and the isotherm fit; the dashed lines show the interpolation of temperatures between 36 and 60°C, which satisfy Eq. 2.

In the next step, the aqueous phase fugacity–carbon loading relationship for phenol is obtained using the Toth isotherm, Eq. 1, along with the temperature-dependent parameters θ_i (T). The fugacity of phenol in aqueous solution at atmospheric pressure and a fixed temperature is represented by:

$$f_x(x,T) = x\gamma(x,T)P^s(T) \tag{8}$$

For the phenol–water system, between 36 and 60°C, and for phenol mole fractions less than about 5×10^{-5}, the activity coefficient of phenol depends only on temperature, and hence can be replaced by its value at infinite dilution. The vapor pressure for phenol, P^s, as a function of temperature can be calculated from the Antoine equation. The infinite dilution activity coefficient of phenol can be evaluated using the UNIFAC group contribution method. Its temperature dependence is correlated by the following equation:

$$\gamma^\infty(T) = 2.1227 \times 10^{+2} - \frac{9.6618 \times 10^{+4}}{T} + \frac{1.0914 \times 10^{+7}}{T^2} \tag{9}$$

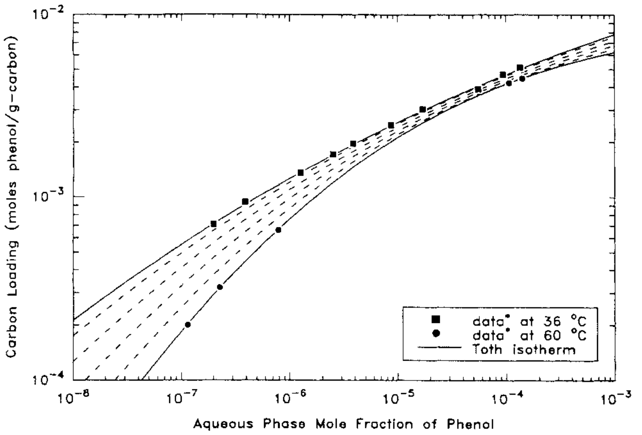

Figure 1. Adsorption isotherms for phenol on activated carbon from aqueous solution.

*Kander and Paulaitis (1983)

The temperature-dependent phenol fugacity-carbon loading relationship desired for the next step can now be obtained by combining Eq. 1 and Eq. 8. If it is assumed that the fugacity of phenol is independent of whether it is adsorbed from the aqueous phase or from the supercritical solvent, the relationship of carbon loading vs. the fugacity of phenol in supercritical carbon dioxide is established (Kander and Paulaitis, 1983). This is the most critical assumption of the method, that is:

$$f_x(x,T)\,|_{q_x} \cong f_y(y,T,P)\,|_{q_y} \qquad (10)$$

It is now necessary to obtain a fugacity-composition relationship for the phenol-supercritical carbon dioxide system. This can be obtained using an equation of state. In this work, we used the Peng-Robinson equation of state with the van der Waals one-fluid mixing rules and the nonquadratic combining rules of Panagiotopoulos and Reid (1986), which are suitable for highly polar systems:

$$P = \frac{RT}{(V-b_m)} - \frac{a_m}{(V^2+2Vb_m-b_m^2)} \qquad (11)$$

$$a_m = \sum_i\sum_j y_i y_j a_{ij} \qquad (12)$$

$$b_m = \sum_i y_i b_i \qquad (13)$$

$$a_{ij} = \sqrt{a_i a_j}\,[1-k_{ij}+(k_{ij}-k_{ji})y_i] \qquad (14)$$

$$\ln\left(\frac{f_k}{y_kP}\right) = \frac{b_k}{b_m}\left(\frac{PV}{RT}-1\right) - \ln\left(\frac{P(V-b_m)}{RT}\right) + \left(\frac{a_m}{2b_mRT\sqrt{2}}\ln\frac{V+b_m(1-\sqrt{2})}{V+b_m(1+\sqrt{2})}\right)$$
$$\left(\frac{\sum_i y_i(a_{ik}+a_{ki}) - \sum_i\sum_j y_i^2 y_j(k_{ij}-k_{ji})\sqrt{a_i a_j} + y_k\sum_i y_i(k_{ki}-k_{ik})\sqrt{a_k a_i}}{a_m} - \frac{b_k}{b_m}\right) \qquad (15)$$

The pure-component parameters of subcritical component phenol (a,b), were estimated from the technique of Panagiotopoulos and Kumar (1985). For the supercritical component carbon dioxide, the usual acentric factor correlation was utilized. Equations 11 to 15 contain two adjustable binary interaction parameters, k_{ij} and k_{ji}, which are used in the mixing rules. Equating the phenol fugacities (by assumption: Eq. 10) obtained from Eq. 8 and Eq. 15 gives:

$$x = \frac{f_y(y,T,P)}{\gamma^\infty(T)P^s(T)} \qquad (16)$$

Substituting Eq. 16 into Eq. 5 and using the resulting expression in the Toth isotherm, Eq. 1, gives the desired equation-of-state-based sorption isotherm, which describes the adsorption of phenol from supercritical carbon dioxide:

$$q_y(y,T,P) = \frac{\left[\dfrac{\theta_1(T)\beta f_y(y,T,P)}{\gamma^\infty(T)P^s(T)}\right]}{\left\{\theta_2(T) + \left[\dfrac{\beta f_y(y,T,P)}{\gamma^\infty(T)P^s(T)}\right]^{\theta_3(T)}\right\}^{1/\theta_3(T)}} \qquad (17)$$

The binary interaction parameters can now be fitted to the limited experimental data (Kander and Paulaitis, 1983) to obtain reasonably good interpolations and extrapolations to different temperatures and pressures of interest. The following expression for the temperature dependence of these adjustable parameters was found to be sufficient to obtain a good fit to the fluid phase data at 36°C/139 atm and at 60°C/173 atm:

$$k_{ij} = k_{ji} = -2.0634 + \frac{611.48}{T} \qquad (18)$$

The experimental data and the fit obtained from the fluid phase isotherm, Eq. 17, are shown in Figure 2. The discrepancy between the data and the isotherm increases for mole fractions of phenol greater than about 5×10^{-5} as the activity coefficient of phenol becomes composition dependent. The method also assumed that adsorption of carbon dioxide is negligible compared with that of phenol, which has much more affinity for activated carbon. This was shown to be true experimentally (Kander and Paulaitis, 1983).

The binary interaction parameters can also be obtained from existing experimental data for solid solubilities of phenol in supercritical carbon dioxide (Van Leer and Paulaitis, 1980), which is available at 36 and 60°C as well. If the binary interaction parameters obtained from the solubility data are used in Eqs. 11 to 15, the resulting isotherm will give carbon loadings somewhat greater than the experimentally observed values at 36°C. At 60°C, however, the predicted values would be slightly less than the experimentally observed values. Hence, if the experimental data of adsorption of a solute from a supercritical fluid are absent, the use of solute solubility or vapor-liquid

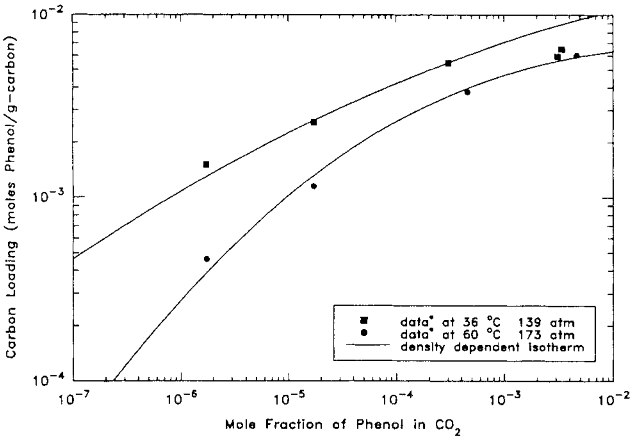

Figure 2. Adsorption isotherms for phenol on activated carbon from supercritical carbon dioxide.

*Kander and Paulaitis (1983)

equilibrium data to estimate the binary interaction coefficients should give reasonably good predictions in most cases. At this point it should be clear that the method is very suitable in predicting the sorption isotherm associated with cosolvent-aided supercritical fluid regeneration in fixed beds when the necessary vapor-liquid equilibrium data exist.

The thermodynamic correlation, Eq. 17, can now be used to generate adsorption isotherms for phenol on activated carbon from supercritical carbon dioxide at selected fluid densities. Figure 3 shows plots of equilibrium carbon loadings as a function of phenol mole fraction in the supercritical fluid at four different carbon dioxide densities. For each density, three isotherms are given at 36, 48, and 60°C. These plots show that the equilibrium carbon loadings are strong functions of the supercritical fluid phase density. The carbon loadings decrease significantly with increasing temperature at constant fluid density. At constant temperature the carbon loadings decrease with increasing pressure, which is the opposite of what is observed for pressures far below the critical pressure. Kander and Paulaitis (1983) found the isotherm they obtained through such procedure to be independent of fluid density, probably because they accounted neither for the temperature dependence of the activity coefficient of phenol in the aqueous phase nor for the temperature dependence of the Toth isotherm parameters.

Figure 4 shows the carbon loadings obtained from the derived density-dependent isotherm at 36 and 60°C, at a constant pressure of 100 atm. This is an interesting and powerful prediction in showing that at fixed pressures the equilibrium carbon loadings decrease with decreasing temperature for a certain range of fluid phase solute mole fractions. This figure, alone, explains the experimentally observed existence of optimal regeneration temperature at a fixed pressure (Tan and Liou, 1989b) in supercritical desorbers, and confirms the crossover behavior encountered in supercritical sorption equilibria (Tan and Liou, 1990a,b). It is also interesting to note that when the isosteric heat of adsorption is calculated in the range of mole fractions where carbon loadings decrease with decreasing temperatures, it may be concluded that the adsorption of phenol from supercritical carbon dioxide is endothermic, although the adsorption of phenol from aqueous solution is strongly exothermic. Srinivasan et al. (1990), as a result of their desorption experiments with ethyl acetate and carbon dioxide, attributed

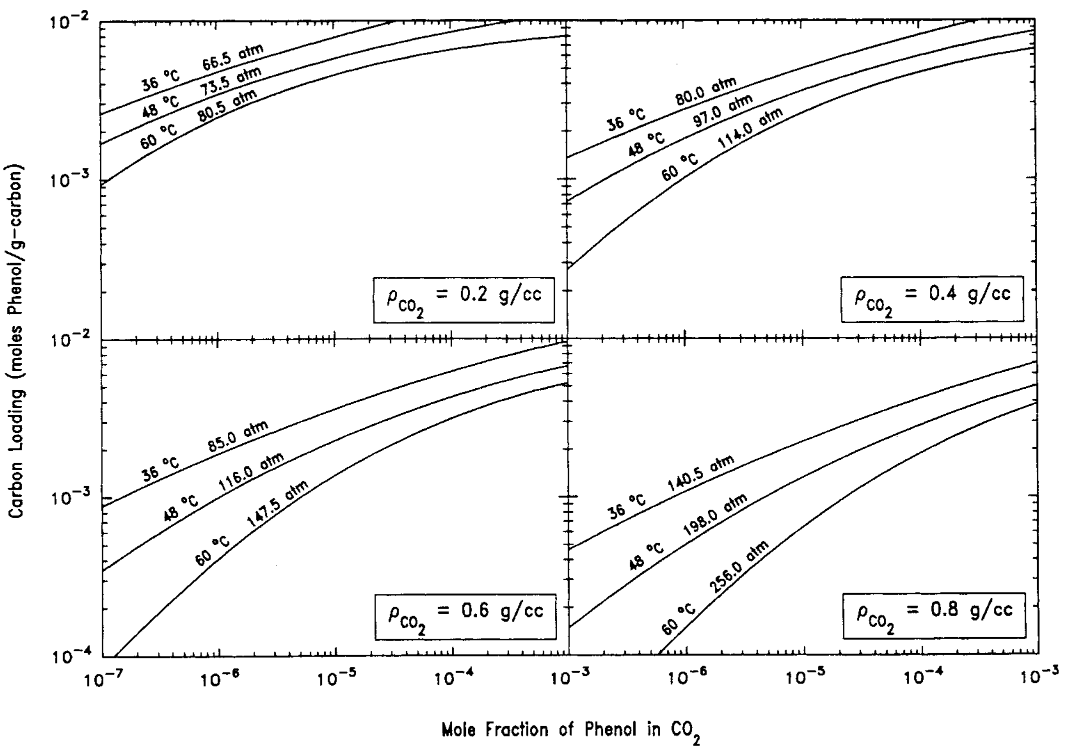

Figure 3. Calculated adsorption isotherms for phenol on activated carbon from supercritical carbon dioxide at constant densities.

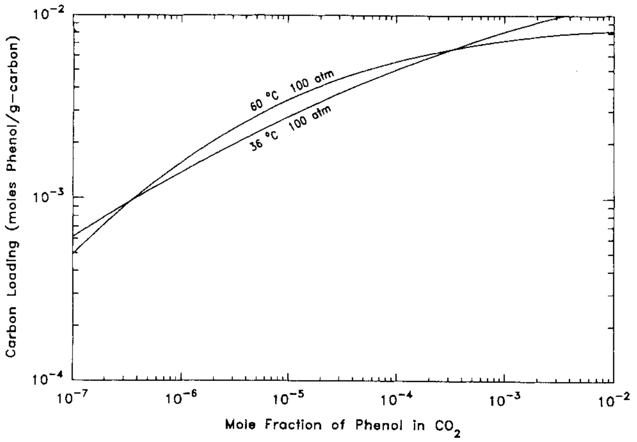

Figure 4. Calculated adsorption isotherms for phenol on activated carbon from supercritical carbon dioxide at 100 atm.

the retrograde effect of temperature at constant pressure to the endothermicity of adsorption. They reached this conclusion, however, after fitting the mass transfer coefficient and the slope of the isotherm, which was assumed to be linear, to the ethyl acetate concentration histories in the effluent stream. Although it is questionable to assume linear adsorption on activated carbon and to fit the highly correlated model parameters simultaneously, their findings qualitatively confirm the inverse temperature effect shown in Figure 4.

Modeling of Fixed-Bed Supercritical Desorber

The overall dynamics of adsorbers and desorbers strongly depend on the shape of the sorption isotherm. The shape of the isotherm solely depends on the temperature and/or pressure for a given adsorbent-adsorbate system. The aqueous phase and the supercritical fluid phase isotherms given in the previous section for phenol-activated carbon system are very favorable for adsorption, and hence, unfavorable for desorption. For certain temperatures and densities, the fluid phase isotherm becomes significantly less unfavorable for desorption compared to the aqueous phase isotherm. Hence, for a given temperature, by increasing the system pressure the fluid phase isotherm can be made much more favorable for desorption than the aqueous phase isotherm. This confirms the fact that the solutes strongly adsorbed onto activated carbon, such as phenol, the supercritical carbon dioxide regeneration is superior to regeneration with water. From Figures 3 and 4, it is clear that the enhancements in desorptive capacity of the supercritical carbon dioxide for phenol are closely related to those observed in the solubility of solid phenol in supercritical carbon dioxide (Van Leer and Paulaitis, 1980). These findings suggest that the retrograde behavior observed in supercritical desorbers can be predicted by coupling a density-dependent sorption isotherm with a conventional model for desorbers. In this section, it will be shown that all the experimentally observed effects of temperature, pressure, and density on the regeneration efficiencies in supercritical desorbers can be predicted, at least qualitatively.

The solid film, linear driving force model, with the axial dispersion term neglected, is sufficient for this purpose. The governing equations are as follows:

Mass balance for phenol in the bulk fluid:

$$\frac{\partial y(z,t)}{\partial t} = -\left(\frac{u}{\epsilon}\right)\frac{\partial y(z,t)}{\partial z} - \frac{\rho_s}{\rho}\left(\frac{1-\epsilon}{\epsilon}\right)\frac{\partial q(z,t)}{\partial t} \tag{19}$$

Mass balance for phenol on the carbon:

$$\frac{\partial q(z,t)}{\partial t} = k_o a_s [q_y(y,T,P) - q(z,t)] \tag{20}$$

The initial and boundary conditions are:

$$\begin{aligned} y(z,0) &= 0 \\ y(0,t) &= 0 \\ q(z,0) &= q^o \end{aligned} \tag{21}$$

where q_y, equilibrium carbon corresponding to the mole fraction of phenol in the fluid phase, is evaluated as a function of fugacity of phenol at given temperature, pressure, and composition from the previously derived density-dependent isotherm given by Eq. 17. The initial uniform carbon loading, q^o, is calculated from Eq. 1 (at 36°C, in this work).

The overall mass transfer coefficient, k_0, is calculated from:

$$\frac{1}{k_o(T,P)} = \frac{1}{k_f(T,P)} + \frac{d_p}{10 D_e(T,P)} \tag{22}$$

The fluid-to-particle mass transfer coefficient, k_f can be obtained from Wakao-Kaguei correlation (1985):

$$\frac{d_p k_f(T,P)}{D(T,P)} = 2 + 1.1\left[\frac{d_p u \rho(T,P)}{\mu(T,P)}\right]^{0.6}\left[\frac{\mu(T,P)}{\rho(T,P)\,D(T,P)}\right]^{1/3} \tag{23}$$

The effective diffusivity, D_e, is given by:

$$\frac{1}{D_e(T,P)} = \frac{\tau}{\epsilon_p}\left[\frac{1}{D(T,P)} + \frac{1}{D_\kappa(T)}\right] \tag{24}$$

The Knudsen diffusion coefficient, D_κ, is obtained from:

$$D_\kappa(T) = 9.7\times 10^{+3}\Gamma\left(\frac{T}{M}\right)^{1/2} \tag{25}$$

The thermophysical properties are calculated as a function of fluid-phase composition as follows: The supercritical fluid phase density, ρ, is obtained from the Peng-Robinson equation of state with mixing rules given by Eqs. 12 to 14; however, the binary interaction parameters are derived from experimental solubility data of phenol in supercritical carbon dioxide at 60°C (Van Leer and Paulaitis, 1980). The viscosity of the fluid phase, μ, is calculated by the method of Chung et al. (Reid et al., 1987). The infinite dilution binary diffusion coefficient of phenol in supercritical carbon dioxide, D, is obtained from the correlation of Takahashi (1974), with the required low-pressure diffusion coefficient as calculated from the Fuller

Table 1. Parameters Used in Fixed-Bed Desorber Model

$L = 29.21$ cm	$\epsilon_p = 0.43$
$u = 1.47$ cm/s	$\tau = 9$
$\epsilon = 0.55$	$\Gamma = 18 \times 10^{-8}$ cm
$\rho_s = 0.455$ g/cm^3	$d_p = 0.10$ cm
$q^0 = 1.017 \times 10^{-2}$ mol/g	$a_s = (6/d_p)$ cm^{-1}

et al. correlation (Reid et al., 1987). The constants associated with the type of activated carbon modeled, column length, and the superficial fluid phase velocity used in the simulations are given in Table 1. The temperature and pressure dependence of the thermophysical properties at supercritical conditions are well known. The temperature and pressure dependence of overall mass transfer coefficient, k_o, is given in Figure 5. For the temperature and pressure ranges studied, the overall mass transfer coefficient is very close to the particle mass transfer coefficient imbedded in Eq. 22, which justifies the use of the solid film resistance model in Eq. 20.

Results and Discussion

The partial differential equations describing the desorption in a fixed bed are discretized in the spatial domain by using five-point biased-upwind finite difference formulas, which are fourth-order accurate. The resulting set of stiff ordinary differential equations is integrated in the time domain with the LSODES. The fraction of phenol desorbed from activated carbon is calculated from Eq. 26 by evaluating the integral as an additional ordinary differential equation introduced into the primary set.

$$\text{Fraction desorbed} = \frac{\rho(u/\epsilon)}{q^o \rho_s \left(\dfrac{1-\epsilon}{\epsilon}\right) L} \int_0^t y(L,t)\, dt \qquad (26)$$

Figure 6 shows the effect of temperature on the fraction of phenol desorbed at four different pressures. At 75 atm, regeneration increases with increasing temperature. At this pressure and at 36°C (in the vicinity of the critical point of the supercritical carbon dioxide) the regeneration is very slow, and little is desorbed even after a long period of desorption. At 60°C, on the other end, the regeneration is much more rapid. Most of the regeneration occurs in the very early stages of the operation; after approximately 1,000 s there is not much to gain by continuing the operation. When the pressure is increased to 100 atm the situation begins to change; the crossover of the regeneration curves occurs, and at long desorption times the regeneration obtained at 48°C exceeds that at 60°C. The regeneration occurs more rapidly at 48°C than at 36°C at the onset of the desorption. At 100 atm, the optimal regeneration temperature is 36°C with a relatively long period of desorption since the fraction of phenol desorbed persists to increase with increasing desorption time. However, at this pressure, if the cycle time for desorption is important, operation at 60°C may be the choice since the regeneration occurs more rapidly at the beginning. When the pressure is increased to 135 atm the crossover behavior still exists. However, at 135 atm, 48°C becomes the optimal regeneration temperature. The regeneration at 36°C, which was favorable at 100 atm, turns out to be the least favorable. When the pressure is further increased to 185 atm, the situation completely changes; the crossover behavior disappears and the regeneration efficiency increases with increasing temperatures.

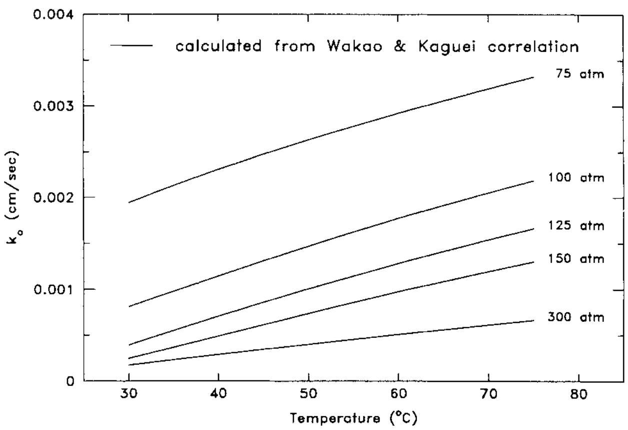

Figure 5. Temperature and pressure dependence of the overall mass transfer coefficient.

As can be seen from Figure 6, when the conventional fixed-bed desorber model is coupled with an equation-of-state-based sorption isotherm, experimentally observed phenomena, as to the existence of pressure-dependent optimal regeneration temperature are predicted. The entity of a pressure interval, in which the crossover of regeneration curves at different temperatures is revealed, can be explained in terms of the temperature and pressure effects on the solvency power of the supercritical carbon dioxide. Figure 7 depicts the experimental (Van Leer and Paulaitis, 1980) and calculated (using the Peng-Robinson equation of state) solubilities of phenol in supercritical carbon dioxide. When Figures 6 and 7, which are based on two independent sets of experiments, are compared, it becomes obvious that there is a unique relationship between regeneration efficiencies and the solvency power of supercritical carbon dioxide. The pressure interval in which the crossover of the regeneration curves occurs matches the pressure interval where solubility reversals with respect to temperature take place. The very same relationship exists between the carbon loadings and the solubility as well. As an overall conclusion, it can be stated that as the solvency power of the supercritical fluid increases, the equilibrium carbon loadings decrease (i.e., sorption equilibrium becomes more favorable for desorption); hence the regeneration efficiencies increase.

Figure 8 shows the effect of pressure on the fraction of phenol desorbed at three different temperatures. It can be seen that the regeneration efficiencies increase with increasing pressure. The speed of regeneration increases with temperature at all pressure levels. At constant temperatures, the existence of an optimal regeneration pressure is not seen, which is also confirmed by experimental findings.

Figure 9 shows the effect of the supercritical fluid density on the fraction of phenol desorbed at three different temperature levels. The strong dependence of the regeneration efficiency on the density is clear. At each density the fraction of phenol desorbed increases with increasing temperatures. At carbon dioxide density corresponding to 0.2 g/cm^3 almost none of the phenol can be desorbed at 36°C, even after a very long desorption period. The pressure corresponding to these operating conditions is below the critical pressure of the carbon

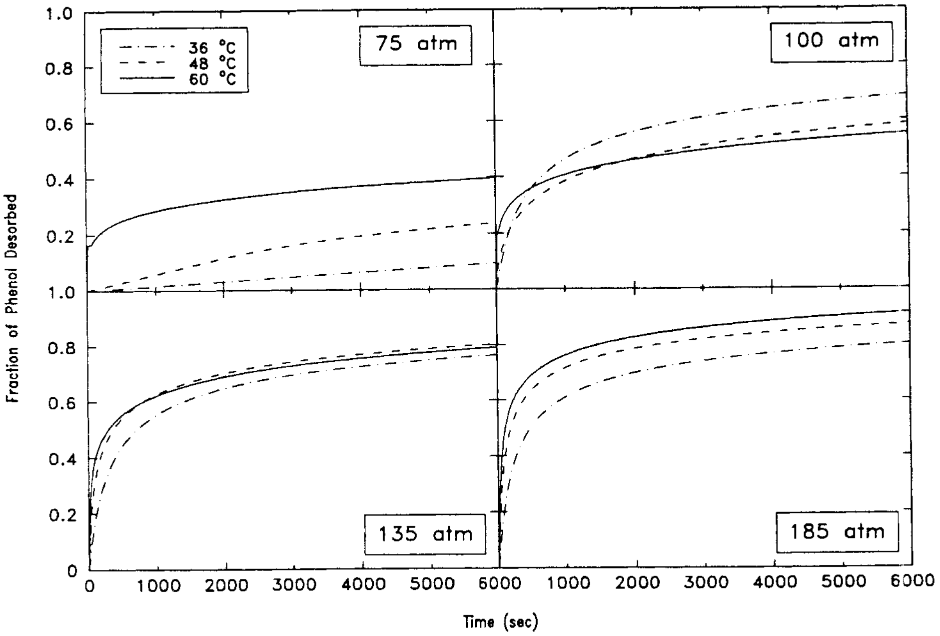

Figure 6. Temperature effect on regeneration at constant pressures.

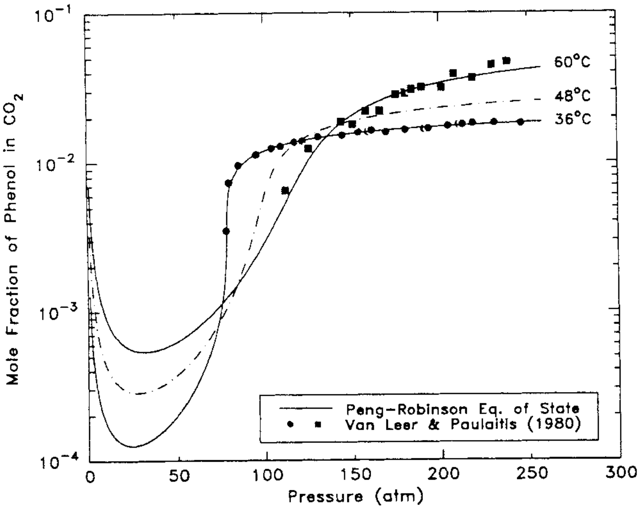

Figure 7. Solubility of phenol in supercritical carbon dioxide.

dioxide, and very sharp changes are observed as the pressure approaches and exceeds the critical pressure. At constant density, an optimal regeneration temperature does not exist, as confirmed by experimental observations. At 60°C/256 atm, which corresponds to a density of 0.8 g/cm^3, almost 100% regeneration can be achieved at sufficiently long desorption times, with more than 80% of the regeneration being accomplished in the very early stages of the operation. These overall results are closely related to the changes in the shape of the sorption isotherm with temperature and pressure; at higher temperatures and densities the equilibrium sorption isotherms become less favorable for adsorption, hence, more favorable for desorption, as can be seen from Figure 3.

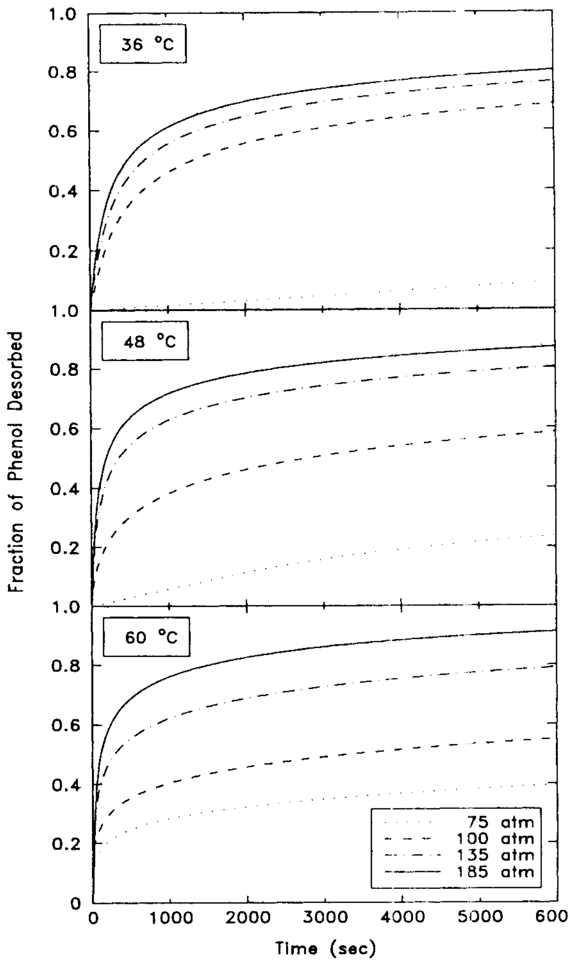

Figure 8. Pressure effect on regeneration at constant temperatures.

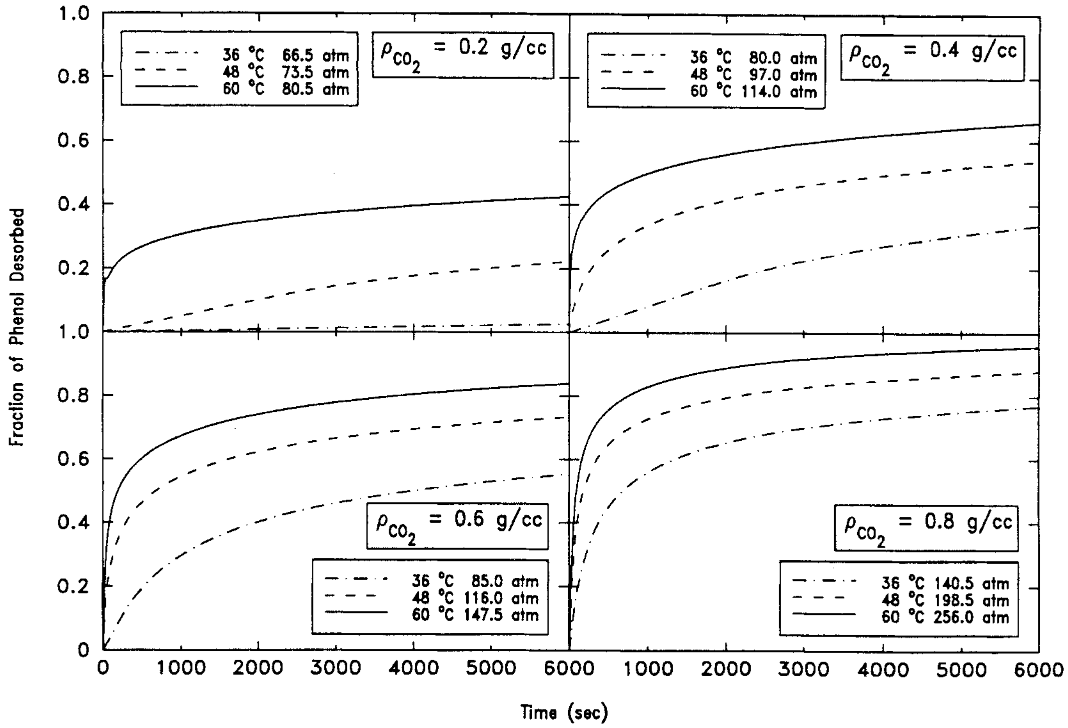

Figure 9. Effect of supercritical fluid density on regeneration efficiency.

To fully appreciate the predictive power of the method and corroboration of the results with the experimental findings, Figures 6 and 8, with regard to the temperature and pressure dependence of the regeneration efficiency, should be compared with the findings of Tan and Liou (1989b), and Figure 9 should be compared with the results of the same investigators concerning the effect of supercritical fluid density (Tan and Liou, 1989c).

It is known that when a small amount of entrainer (e.g., benzene or toluene) is used, the solubility of phenol in supercritical carbon dioxide increases (Roop and Akgerman, 1989). Hence, based on the previously discussed solubility–regeneration efficiency relationships, an appropriate cosolvent can be utilized in increasing the regeneration efficiency, while keeping the operating pressure comparably low, possibly to further increase the economical incentives of supercritical desorption process. This naturally results in more complicated solvent recovery. It should be clear that the method developed can also be used to predict the cosolvent enhancements to regeneration efficiencies of supercritical desorbers, if the necessary cosolvent solubility data exist. The method should also predict the dynamics of nonisothermal supercritical desorption in fixed beds where the interactions between thermal and mass fronts under supercritical conditions may play an important role in regeneration efficiencies.

Conclusions

An equation-of-state-based, density-dependent sorption isotherm, which is a function of adsorbate fugacity in the supercritical fluid phase, was developed. When the supercritical sorption isotherm was coupled with a conventional fixed-bed desorber model, the experimentally observed characteristics of supercritical fluid desorption process, such as the existence of a pressure-dependent optimal regeneration temperature, and high-density-favored desorption, were predicted. It was shown that the enhancements in solvency power of the supercritical fluid is responsible for higher regeneration efficiencies. The temperature, pressure, and density effects on the regeneration efficiencies and on the solubilities encountered in supercritical fluids were shown to be closely related. This approach provides a thermodynamic framework for modeling supercritical fluid desorption process, and thus facilitates development of mechanistic models which are at least as reliable as in the case of conventional adsorption/desorption processes.

Notation

a_s = specific surface area of carbon particles, cm^{-1}
a, b = pure-component parameters
a_m, b_m = mixture parameters
c = aqueous phase phenol concentration, mmol/L
c^* = concentration corresponding to T^*, mmol/L
D = molecular diffusion coefficient of phenol, cm^2/s
D_e = effective diffusion coefficient of phenol, cm^2/s
D_κ = Knudsen diffusion coefficient for phenol, cm^2/s
d_p = mean particle diameter, cm
f_x = fugacity of phenol in aqueous phase
f_y = fugacity of phenol in supercritical fluid phase
ΔH_{st} = isosteric heat of adsorption, kJ/mol
k_f = fluid side mass transfer coefficient, cm/s
k_{ij}, k_{ji} = binary interaction parameters
k_o = overall mass transfer coefficient, cm/s
L = length of desorption column, cm
M = molecular weight of phenol, g/mol
M_w = molecular weight of water, g/mol
P = pressure, atm
P^s = vapor pressure of pure phenol
q = solid phase concentration, mol/g
q^0 = initial solid phase concentration, mol/g

q_x = equilibrium carbon loading of phenol adsorbed from aqueous solution, mol/g
q_y = equilibrium carbon loading of phenol adsorbed from supercritical fluid, mol/g
T = temperature, K
T^* = reference temperature, K
u = supercritical fluid phase velocity, cm/s
V = molar volume, cm^3/mol
x = mole fraction of phenol in aqueous phase
y = mole fraction of phenol in supercritical fluid phase

Greek letters

Γ = mean pore radius, cm
β = conversion factor, Eq. 6
γ = activity coefficient of phenol in aqueous solution
γ^∞ = infinite dilution activity coefficient of phenol in aqueous solution
ϵ = bed voidage
ϵ_p = particle porosity
θ_i = parameters of Toth isotherm
μ = viscosity of supercritical fluid, g/cm·s
ρ = density of supercritical fluid, mol/cm^3
ρ_s = density of activated carbon, g/cm^3
ρ_w = density of water, g/cm^3
τ = tortuosity factor

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