

SUPERCRITICAL CO₂ EXTRACTION OF HEXACHLOROBENZENE AND PENTACHLOROPHENOL FROM SOIL AND ACTIVATED CARBON

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1. Introduction

Supercritical fluid extraction (SFE) may offer some advantages over conventional liquid extraction including the ability of supercritical fluids (SCFs) to dissolve organic contaminants from soil and the ability to vary the solvent power of SCFs near the critical point by small changes in temperatures and pressures. Furthermore, compared to liquid solvents, the low viscosities of SCFs combined with high solute diffusivities in SCFs result in superior mass transfer characteristics. Moreover, the low surface tension of SCFs enables facile penetration into microporous materials such as soils. These properties may result in faster rates of removal of organics from solid matrices such as soil or activated carbon. Among the SCFs, supercritical carbon dioxide (SCCO₂) is particularly attractive for extraction since it is non-toxic and environmentally acceptable. In addition, it is non-flammable and does not introduce a safety hazard during operation. SCCO₂ has a low critical temperature, 207.4 K, and a moderate critical pressure, 72.8 atm; it is cheap and readily available in large quantities. As a result of these properties, research and development work has already been conducted in various laboratories for removal of organic contaminants from soil by SCCO₂, and pilot plants have been constructed. These studies included removal of PCB's, DDT, toxophene^{2,3}, phenol and hexachlorobenzene^{4,5} from soil and certain PAHs and chlorinated benzenes from soil and carbon^{6,7}.

Extraction of soluble species (solutes) from solid matrices takes place through four different mechanisms. If there are no interactions between the solute and the solid phase (if the solid phase is a simple mixture) the process is simple dissolution of the solute in a suitable solvent which does not dissolve the solid matrix; such would be the case for separation of sugar and sand by dissolving sugar in water. If there are interactions between the solid and the solute, then the extraction process is desorption in presence of the solvent and the adsorption isotherm of the solute on the solid in presence of the solvent determines the equilibrium. Most solids extraction processes, such as activated carbon regeneration, fall in this category. A third mechanism is swelling of the solid phase or the destruction of solid texture by the solvent accompanied by extraction of the entrapped solute through the first two mechanisms such as extraction of essential oils. The fourth mechanism is reactive extraction where the insoluble solute reacts with the solvent and the reaction products are soluble hence extractable; such as extraction of lignin from wood. Extraction is always followed by another separation process where the extracted solute is separated from the solvent.

Although there are extensive work on the application of supercritical fluids for extraction of solid matrices, very few studies have concentrated on the understanding of the extraction process. In extraction from solid matrices, the adsorption equilibrium constant of the solute (equilibrium

distribution between the supercritical phase and the solid phase) determines the thermodynamic extent of extraction and dictates the feasibility of the process. Unfortunately very few studies report on the adsorption isotherms (or adsorption equilibrium constants) in supercritical systems although there are numerous studies on phase behavior in supercritical solutions. The rate of mass transfer, axial dispersion, and diffusion into the pores are the engineering parameters needed for the design of the extraction system. Data on these parameters or reliable prediction techniques are not available as well.

We have measured adsorption isotherms of hexachlorobenzene and pentachlorophenol on soil and carbon and developed a model to predict the desorption profiles. The model parameters were determined independently from literature data and/or correlations. Model predictions are excellent considering there are no adjustable parameters.

2. Experimental

The experimental technique is based on frontal analysis chromatography and the details of the experimental set-up are given elsewhere^{6,7}. A step change in concentration is introduced at the entrance of the soil or carbon column and the column breakthrough is obtained by on line measurement of the effluent concentration. Analyses of the breakthrough curve yields the adsorption isotherm.

3. Model Development

The mathematical formulation of the supercritical extraction systems is similar to the formulation of adsorbers and an extensive literature is available on adsorption processes^{8,9}. Mathematically, the overall adsorption/desorption of the contaminant from the solid particles can be described by a set of Partial Differential Equations (PDEs). The assumptions of the model are: (a) the system is isothermal, (b) the radial concentration gradients are neglected, (c) the physical properties of the fluid are constant, (d) the flow pattern is axially dispersed, and (e) local equilibrium in the pores. The relevant differential fluid phase mass balance is:

$$\frac{\partial C}{\partial \tau} - \frac{1}{Pe_b} \frac{\partial^2 C}{\partial z^2} + v \frac{\partial C}{\partial z} + \frac{1-\epsilon}{\epsilon} \frac{3L}{R_p} \frac{Bi}{Pe_p} (C-C_s) = 0 \quad (1)$$

The boundary conditions for this equation are given by:

$$\frac{\partial C}{\partial z} = Pe_b (C-C_0) \quad \text{at } z = 0 \quad (1a)$$

$$\frac{\partial C}{\partial z} = 0 \quad \text{at } z = 1 \quad (1b)$$

For desorption, the initial condition is given by,

$$C = C_0 \quad \text{when } t = 0 \quad \text{for all } z \quad (1c)$$

Assuming local equilibrium in the pores of the solid matrix, the relevant particle phase differential mass balance is:

$$\left[\epsilon_p + (1 - \epsilon_p) \frac{\partial q}{\partial C_p} \right] \frac{\partial C_p}{\partial \tau} = \frac{1}{Pe_p} \frac{L}{R_p} \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left[\rho^2 \frac{\partial C_p}{\partial \rho} \right] \quad (2)$$

The associated boundary conditions are :

$$Bi(C - C_s) = \frac{\partial C_p}{\partial \rho} \quad \text{at } \rho = 1 \quad (2a)$$

$$\frac{\partial C_p}{\partial r} = 0, \quad \frac{\partial q}{\partial r} = 0 \quad \text{at } r = 0 \quad (2b)$$

$$C_p = C_0, \quad q = q_0 \quad \text{when } t = 0 \quad \forall \rho \quad (2c)$$

where, q and C_p are related by the adsorption isotherm. Using the Freundlich isotherm,

$$q = K \left(\frac{C_p}{C_0} \right)^n \quad (3)$$

we have,

$$\frac{dq}{dC_p} = \frac{Kn}{C_0^n} \left(\frac{C_p}{C_0} \right)^{n-1} \quad (4)$$

The model equations are solved by orthogonal collocations on finite elements (10)

4. Results and Discussion

Figures 1-4 show the adsorption isotherms of hexachlorobenzene and pentachlorophenol on soil and on carbon. For adsorption on soil, the hexachlorobenzene isotherm is linear, the pentachlorophenol isotherm exhibits favored adsorption. Both isotherms can be fitted by the Freundlich isotherm. Although the solubility of pentachlorophenol in SCCO₂ is about five times that

of hexachlorobenzene, the amount adsorbed is about 70 times more. On the other hand the amount of pentachlorophenol adsorbed on carbon is only about double the amount for hexachlorobenzene. Isotherms on carbon are both favored isotherms (Type - I). Model predictions of the desorption profiles are presented in Figures 5-8.

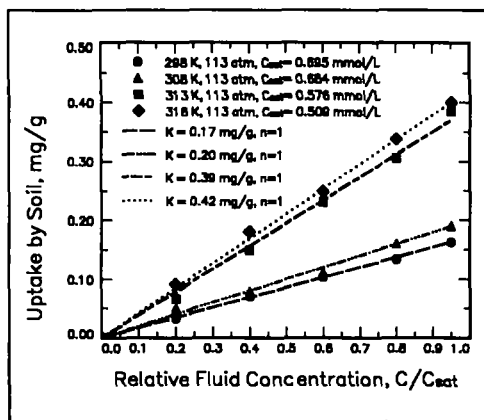


Figure 1: Adsorption isotherms of hexachlorobenzene on soil

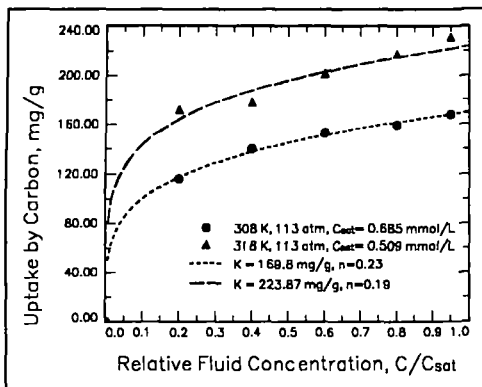


Figure 2: Adsorption isotherms of hexachlorobenzene on activated carbon

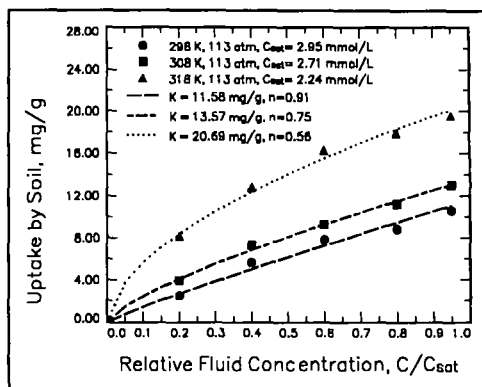


Figure 3: Adsorption isotherms of pentachlorophenol on soil

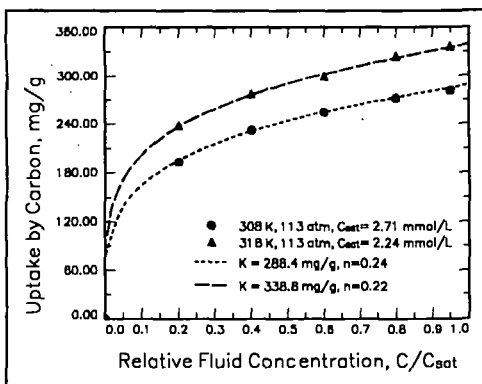


Figure 4: Adsorption isotherms of pentachlorophenol on carbon

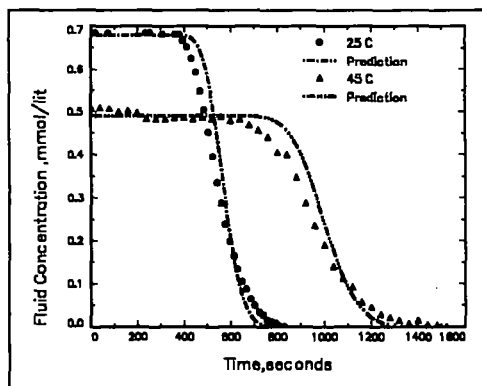


Figure 5: Desorption profiles of hexachlorobenzene from soil and model prediction

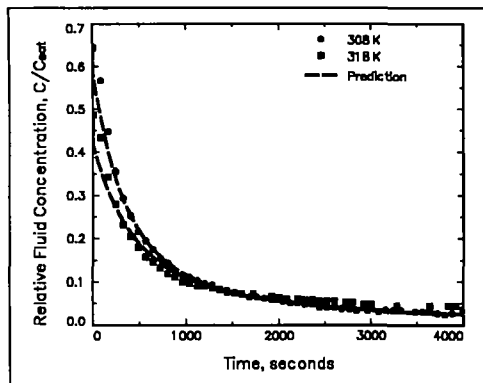


Figure 6: Desorption profiles of hexachlorobenzene from carbon and model predictions

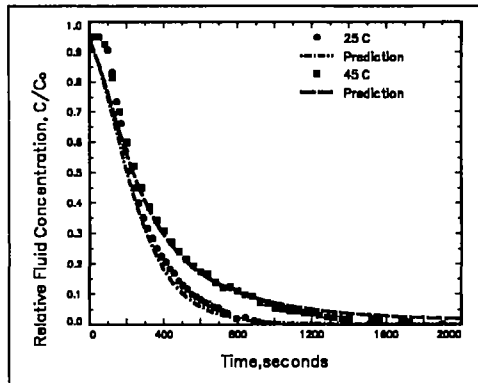


Figure 7: Desorption profiles of pentachlorophenol from soil and model predictions

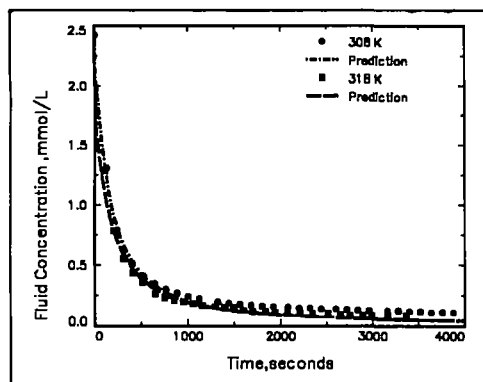


Figure 8: Desorption profiles of pentachlorophenol from carbon and model predictions

5. References

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