Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Sahle-Demessie, Endalkachew , Yi, Jung Seok , Levien, Keith L. and Morrell, Jeffrey J.(1997) 'Supercritical Fluid Extraction of Pentachlorophenol from Pressure-Treated Wood', Separation Science and Technology, 32: 6, 1067 — 1085

To link to this Article: DOI: 10.1080/01496399708000946

URL: http://dx.doi.org/10.1080/01496399708000946

SEPARATION SCIENCE AND TECHNOLOGY, 32(6), pp. 1067–1085, 1997

Supercritical Fluid Extraction of Pentachlorophenol from Pressure-Treated Wood

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ABSTRACT

The extraction of pentachlorophenol (PCP) from pressure-treated wood wafers with supercritical carbon dioxide (SC-CO_2) was studied in a continuous-flow extractor. PCP extraction rates were determined as a function of pressure (17.5–25 MPa), temperature (313–353 K), flow rate (1–3 mL/min at supercritical conditions), and sample size (0.8 × 10 × 50 mm and 2.2 × 10 × 50 mm) by measuring PCP concentrations in the extractor effluent intermittently. The rate of extraction increased with an increase in solvent pressure and a decrease in particle size. A fundamental model was developed which includes rates of intraparticle diffusion, external film mass transfer, linear desorption isotherms, and initial distribution of PCP between pore volume (cell lumen) and pore surfaces (cell wall) of wood wafers. The overall mass transfer coefficient and the rate of extraction increased with an increase in solvent pressure, temperature, and flow rate. The adsorption equilibrium coefficients of PCP with wood substance were very small, and more than 80% of the PCP was found to be in the cell lumen initially.

Key Words. Supercritical fluid; Extraction; Pentachlorophenol; Wood; Modeling

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INTRODUCTION

While preservative treatment significantly prolongs the service life of wood for utility poles and other products, such materials are increasingly becoming the subject of concern as they near the end of their useful life, since they require disposal. More than 1.6 million poles are replaced every year, creating the potential for three million cubic meters of PCP-contaminated wastes. These wastes are estimated to have PCP concentrations greater than 10 g/kg of wood and oil concentrations more than 10% v/v. While most poles are currently either given to adjacent landowners for reuse as posts, or placed in sanctuary landfills, there have been efforts to categorize PCP-treated wood as hazardous waste. While the regulations remain unchanged, and PCP-treated wood remains disposable in lined landfills, a reclassification would produce a volume of material that would quickly overwhelm the available hazardous disposal capacity. Conventional methods for disposing of these wastes, such as incineration or biodegradation, are either too expensive or as yet have not proven reliable, hence a cost-effective disposal method is demanded. Supercritical fluids (SCFs) offer an alternative as process solvents for remediating contaminated materials and in reducing the volume of toxins that must be destroyed by incineration or chemical oxidation (1).

Supercritical fluid extraction has been used for removal of toxic contaminants such as polycyclic aromatic hydrocarbons, polychlorinated dibenzo-*p*-dioxin, polychlorinated dibenzofurans, and PCP from soil, sludge, and ground water (2–10). The factors that can influence the mechanism of an SFE process include: 1) thermodynamic factors, such as the solubility of the extract; 2) kinetic factors that include the solvent–solid contact and the extraction time; and 3) the influence of the solid matrix on diffusion and the interaction of the extract with the solid, for example, effect of moisture or other solvents in the solid. Effective diffusion may involve molecular diffusion, bulk flow of dissolved solute, and replacement of the solute by solvent molecules from the solid surface.

The following mechanisms have been proposed for supercritical extraction of chemicals from solid matrices (1, 11):

1. A single-step process in which organic contaminants are dissolved and removed from the solid matrix (12, 13). The extraction rate depends mainly on the contaminant dissociation, solubility in the SCF phase, and the net flux out of the solid matrix.
2. A two-step process that includes desorption of contaminants from the solid matrix followed by dissolution. Examples include the use of

SCFs as desorbing solvents for regeneration of activated carbon loaded with pesticides such as alchlor and atrazine (14); organic chemicals like ethyl acetate, benzene, and toluene (15–17); or phenanthrene, hexachlorobenzene, and pentachlorophenol (18).

3. A two-step extraction that involves dissolution and reaction (mostly oxidation) of toxic materials that are normally difficult to dissolve (2, 19).

Modeling an extraction process should, therefore, be based on the type of extractive material and the interaction of the extractive with the solid matrix. Extraction of PCP from pressure-treated wood was assumed to follow the second type of mechanism discussed above.

The rate of a typical dynamic supercritical fluid extraction is initially rapid, but then slows down. The characteristic kinetics of SFE can be best understood by studying the influence of the various factors experimentally with the help of mechanistic models. A simple extraction model consisting of a differential mass balance equation and incorporating linear desorption kinetics was applied for the regeneration of activated carbon (15). A more comprehensive model that accounts for desorption, interparticle diffusion, and convective film mass transfer was developed by assuming a parabolic solute concentration profile in the pore fluid of the activated carbons (20). The use of reversible linear desorption kinetics using the same model showed better agreement of simulated values with experimental data (21). A similar modeling approach has successfully been adapted for caffeine extraction from wet coffee beans (22) and peppermint oil from peppermint leaves (23).

Although the application of SCFs has received increased interest in recent years, only a few of these applications have reached commercial scale. Further development of some applications are limited by the lack of sufficient experimental data and the need for reliable models for process design. The objective of this study was to understand the extraction of pentachlorophenol from pressure-treated wood using supercritical carbon dioxide. To understand the process kinetics, a mathematical model that incorporates extraction and reversible linear desorption was used with proper initial and boundary conditions.

As wood ages in service, there is a change in the distribution and bonding of PCP in the wood matrix (24), and a loss of the carrier solvent and the preservative. However, this study was done using recently treated wood samples to control the initial loading of PCP. Therefore, these samples may have PCP concentrations higher than commonly found in old utility poles.

EXPERIMENTAL

Materials

Samples of wood wafers were taken from Douglas-fir heartwood blocks and conditioned to 15% (w/w) moisture content. Two chip sizes were used: Size-A = 0.8 × 10 × 50 mm, and Size-B = 2.2 × 10 × 50 mm. The wafers were pressure treated by keeping them for 30 minutes at 0.96 MPa and 25°C in a treatment solution of P-9 Type A oil containing 5 wt% pentachlorophenol (PCP). The amount of PCP retained in the treated wood was determined by taking samples from each size group and grinding them to a particle size of about 1 mm. The dust was then analyzed using an x-ray florescence analyzer (Asoma 8620, Asoma Instruments, Austin, TX). The average initial concentrations of PCP in the wood wafers were 23.1 (± 1.8) kg/m^3 for Size-A wafers and 35.9 (± 1.3) kg/m^3 for Size-B wafers. The measured density of the wafers at 15% moisture content was 0.71 g/mL, and the porosity of the wafers was estimated to be 0.73 (25). Solvents, chemicals, and other reagents used in this study were all analytical grade (Sigma Chemicals, St. Louis, MO) and were used without further purification.

Supercritical Fluid Extraction

An Isco Series 2000 extraction apparatus consisted of a syringe pump, a pump controller, a dual extraction chamber module, a sampling valve, and a flow metering valve was used in these studies (Fig. 1). The syringe pump jacket was cooled to 12°C using a chiller (VWR model 1156) to liquefy the CO_2 and reduce density fluctuations. The pump has the capacity to deliver liquid CO_2 at a rate of 90 mL/min at pressures up to 50 MPa. The extraction module consisted of a 10-mL sample cartridge that had upper and lower metal frits, and end-caps to contain the sample.

The syringe pump was filled with liquid carbon dioxide from a CO_2 tank with a dip tube (99% pure, Industrial Welding Supply, Portland, OR). The extractor was heated to the desired temperature, then eight wood wafers were added to the extraction cartridge separated from one another with copper wire. The system was allowed to reach thermally equilibrate at the desired value (± 1°C) for the 30 minutes before the extractor was pressurized with CO_2 to the desired value. The pressure was allowed to stabilize for about 3 minutes, and a steady flow was established through the extraction vessel using a micrometering valve (Autoclave No. 10VRMM2812, Erie, PA). The variation in flow rates was less than 14% off the set values despite disturbances caused by sampling the effluent stream. The outlet flow was bubbled through an acetone cold-trap to cap-

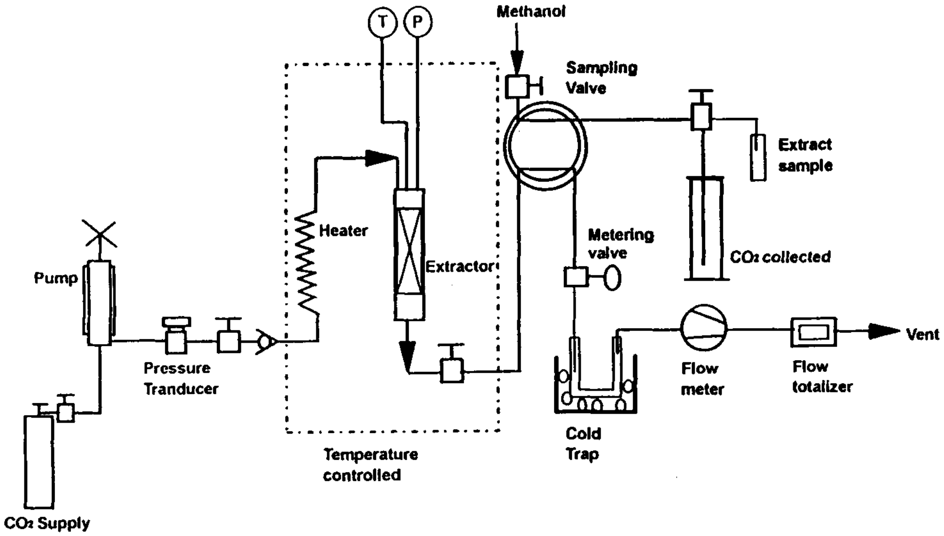

FIG. 1 Diagram of extraction apparatus.

ture the PCP from the exit flow. The effluent flow was frequently sampled using a six-port sampling valve (Valco No. C6U1380, Houston, TX) connected to a 2-mL sample loop. The concentration of PCP in the captured sample was measured using a Hewlett-Packard gas chromatograph equipped with a flame ionization detector (Hp 5840A). Because PCP is a nonvolatile compound, a derivatization agent, MSFTA (*N*-methyl-*N*-trimethyl-silytri fluorancet-amide), was added to each sample to form a detectable, volatile derivatives (26).

MODEL DEVELOPMENT

A mathematical model was developed to better understand the process kinetics. The model was based on differential mass balances describing transport of PCP through wood pores. The following simplifying assumptions were made to develop the model.

1. The solvent was assumed to rapidly fill the wood pores. Since the extractor is not large, it was approximated as a differential extractor with no axial concentration changes in the wood or fluid.
2. The wafers were assumed to be initially isothermal with a uniform PCP distribution.

3. The porosity, permeability, and humidity of the wood were assumed to be constant and did not vary with time.
4. Pure solvent fluid was assumed to flow to the extractor at a constant pressure and temperature.
5. The main diffusion flux was through the face of the wafer and across the half thickness.
6. The intraparticle concentration profile through wafer pores had a parabolic profile at all times (27, 28).

Such a simplified model is intuitive. However, researchers have found that the approximate solutions obtained by using the parabolic profile are simple and agree well with the exact solution except for the brief initial period (28, 29–31, 33). Similar assumptions have been used in supercritical extraction studies of ethyl acetate from activated carbon (21) and caffeine from coffee beans (22). A total of N wood wafers, having an initial PCP retention of, c_{T0}, were loaded in the extraction vessel. Since the thickness of the wafers (δ) was very small compared to their width (W) and length (L), it was assumed that much of the diffusion flux was in the x-direction across the half thickness ($\delta/2$). Therefore, diffusion fluxes in the y- and z-directions were neglected. The mass balance for the solute in the bulk fluid, $c(t)$, can be written as

$$\frac{dc}{dt} = -\frac{c}{\tau} + Ek_{\mathrm{p}}(c_{\mathrm{i}}|_{\delta/2} - c) \tag{1}$$

where τ is the residence time of solvent in the extractor, E is the ratio between wafer volume and the extractor void volume, k_{p} is the combined mass transfer coefficient, and $c_{\mathrm{i}|\delta/2}$ is the surface concentration. The differential mass balance for the solute in the pore volume of a wafer, $c_{\mathrm{i}}(t)$, can be written as

$$\epsilon \frac{\partial c_{\mathrm{i}}}{\partial t} = D_{\mathrm{e}} \frac{\partial^2 c_{\mathrm{i}}}{\partial x^2} - \frac{dc_{\mathrm{s}}}{dt} \tag{2}$$

where ϵ is the porosity of the wood wafer and c_{s} is the concentration of PCP adsorbed to the cell wall. It was assumed that c_{s} and the PCP in the pore fluid with concentration, c_{i}, are in equilibrium with a linear reversible adsorption isotherm, so that

$$\frac{dc_{\mathrm{s}}}{dt} = K \frac{dc_{\mathrm{i}}}{dt} \tag{3}$$

Because PCP has only a weak chemical affiliation to the cell walls (32), part of the PCP was initially in pore volume fluid within the wafer (cell lumen) and did not interact with the cell wall. Therefore, the total amount of PCP was assumed to be distributed between the cell lumen and cell wall of the wood wafers. The total initial PCP concentration is

$$c_{T0} = \epsilon c_{i0} + c_{s0} \tag{4}$$

The fraction of the initial amounts of PCP in the pore fluid of the wood out of the total amount, m, is defined as:

$$m = \frac{\epsilon c_{i0}}{c_{T0}} = 1 - \frac{c_{s0}}{c_{T0}} \tag{5}$$

The value of m is between 0 and 1. For $m \approx 0$, essentially all the PCP in the wood is on or within the wood cell wall. For $m \approx 1$, all of the PCP is in the cell lumen. The boundary conditions are

$$\frac{\partial c_i}{\partial x} = 0 \qquad \text{at } x = 0 \qquad \text{for } t > 0 \tag{6}$$

$$-D_e \frac{\partial c_i}{\partial x} = k_f(c_i - c) \qquad \text{at } x = \frac{\delta}{2} \qquad \text{for } t > 0 \tag{7}$$

the initial conditions at all locations in the wood become:

$$c = 0 \qquad \text{at } t = 0 \tag{8}$$

$$c_i = c_{i0} = \frac{m}{\epsilon} c_{T0} \qquad \text{at } t = 0 \tag{9}$$

$$c_s = c_{s0} = (1 - m)c_{T0} \qquad \text{at } t = 0 \tag{10}$$

Because of the inclusion of intraparticle diffusion in Eq. (2) with boundary conditions Eqs. (6) and (7), significant numerical effort is required to solve these differential equations. However, assuming that the interparticle PCP concentration profile has a parabolic shape simplifies the problem. So

$$c_i(s, t) = a(t) + b(t)x^2 \tag{11}$$

Equation (11) can be substituted into Eq. (2) and the boundary conditions to obtain volume-averaged mass balances:

$$\epsilon \frac{dc_i}{dt} = k_p(c - c_i) - \frac{dc_s}{dt} \tag{12}$$

The combined mass transfer coefficient was defined as $k_p = 3k_f/(\delta/2)(3 + \text{Bi})$, in which k_f is the convective film mass transfer coefficient and Bi is the Biot number expressed as $k_f(\delta/2)/D_e$, where D_e is the effective intraparticle diffusion coefficient. Assuming local equilibrium, Eq. (3) can be used to eliminate c_s from Eq. (2). The dimensionless quantities are then defined as follows:

$$C = c/c_{T0}, \qquad C_i = c_i/c_{T0}, \qquad \theta = t/\tau, \qquad \phi = k_p\tau$$

Equations (1) and (2) can then be rewritten in dimensionless variables:

$$\frac{dC_i}{d\theta} = \left(\frac{\phi}{\epsilon + K}\right)(C - C_i) \tag{13}$$

$$\frac{dC}{d\theta} = -C - E\phi(C - C_i) \tag{14}$$

where the initial conditions then become

$$C = 0 \quad \text{at } \theta = 0 \tag{15}$$

$$C_i = \frac{m}{\epsilon} \quad \text{at } \theta = 0 \tag{16}$$

Equations (13) to (16) can be solved using the appropriate Laplace transforms to yield $C(\theta)$ and $C_i(\theta)$. Therefore, the equation for $C(\theta)$ becomes

$$C(\theta) = \frac{mE\phi}{2\epsilon\alpha}\left(\exp\left(\frac{(-\beta + \alpha)}{2}\theta\right) - \exp\left(\frac{(-\beta - \alpha)}{2}\theta\right)\right) \tag{17}$$

where

$$\beta = 1 + \left(\frac{1}{\epsilon + K} + E\right)\phi > 0 \tag{18}$$

$$\alpha = \left(\beta^2 - \frac{4\phi}{\epsilon + K}\right)^{1/2}, \qquad \text{thus} \quad 0 < \alpha < \beta \tag{19}$$

Equation (17) shows that the effluent concentration responds as a second-order dynamic system with three unknown parameters: the desorption rate coefficient (K), the combined mass transfer coefficient (k_p), and the initial distribution PCP ratio (m). The combined mass transfer coefficient depends on the external mass transfer coefficient (k_f) and the effective intraparticle diffusion coefficient (D_e), and arises because of the parabolic concentration profile approximation for c_i as a function of location (x). The parameters of Eq. (13) were obtained by fitting the model with the experimental data PCP effluent concentration data.

RESULTS AND DISCUSSION

Model Parameters

The effluent extraction data was used to estimate the model parameters K, k_p, and m. Table 1 shows that the desorption rate coefficient (K) was

TABLE 1
Estimated Model Variables and Amount of PCP Extracted at Various Experimental Conditions

Pressure (MPa)	Temperature (K)	Flow rate[a] (cm^3/min)	Sample thickness[b] (mm)	$K \times 10^6$	$k_p{}^c \times 10^3$ (1/s)	$m \times 10^2$	$k_p{}^d \times 10^3$ (1/s)	% Extracted
			Pressure Variance					
17.5	353	2	0.8	3.38	0.21	28.7	0.34	43.0
20.0	353	2	0.8	0.00	1.03	20.7	1.07	57.5
22.5	353	2	0.8	0.01	2.17	21.6	2.40	70.9
25.0	353	2	0.8	1.20	3.12	20.1	3.14	72.9
			Temperature Variance					
22.5	313	2	0.8	4.00	1.35	20.1	1.36	63.5
22.5	333	2	0.8	1.00	3.04	15.8	2.16	60.0
22.5	353	2	0.8	0.01	2.17	21.6	2.40	70.9
			Flow Rate Variance					
22.5	353	1	0.8	0.80	1.80	13.2	0.83	60.7
22.5	353	2	0.8	0.01	2.17	21.6	2.40	70.9
22.5	353	3	0.8	0.10	3.12	21.0	3.31	63.4
			Sample Thickness Variance					
22.5	353	2	0.8	0.01	2.17	21.6	2.40	70.9
22.5	353	2	2.2	1.00	2.13	6.3	2.13	55.9

[a] Flow rate is at supercritical conditions (T, P).

[b] Sample size is thickness × 10 × 50 mm. For the 0.8-mm thick wafers, $E = 0.504$, and for the 2.2 mm thick wafers, $E = 0.787$.

[c] Estimated using a three-parameter model.

[d] Estimated using a one-parameter model.

always very small (less than 10^{-5}). This indicates that the rate of PCP desorption from the cell wall of the wood wafers was much smaller than the rate of concentration changes in cell lumen. The average value for the initial distribution ratio, m, was around 0.20 ± 0.05 for the Size-A samples, which shows that initially about 20% of the total PCP was in the cell lumen devoid of any interactions with the surface of the wood cell. Simulation studies showed that the initial extraction rate increased strongly with the increase in the distribution coefficient, m, and the time at which the maximum concentration occurs was independent of m. The concentration tailing increased with the increase in the desorption coefficient (34).

Based on the results shown in Table 1, the model was then simplified to a single parameter instead of three. Because the model was not sensitive for K values below 0.01, K was taken to be zero. This infers that the PCP extracted during these experiments was initially present in the pore fluid and the PCP bound to cell wall remained nearly constant. Since m represents the initial PCP distribution ratio, it may be taken to be constant for wafers of the same size and initial concentration.

Keeping the two parameters constant, $K = 0$ and $m = 0.20$, the optimum values of the k_p were recalculated for each run (Table 1). The average k_p value for the various conditions was 0.0021/s. Other researchers have reported combined mass transfer coefficients between 0.004/s and 0.022/s for caffeine extraction from coffee beans (22), and between 0.018/s and 0.055/s in the extraction of ethyl acetate from activated carbon (21). The combined mass transfer coefficient obtained in this work was of the same order of magnitude.

Effects of Pressure and Temperature

The effects of pressure (17.5 to 25 MPa) and temperature (313 to 353 K) were determined at a constant solvent flow rate (2 cm^3/min) using measured and simulated PCP concentration histories in the effluent stream. Measured values are given in Tables 2 and 3, and the curves in Figs. 2 and 3 show simulated values. The extraction rates were initially rapid, followed by a slow tailing period. Measured and computed values show that the rate of extraction increased with an increase in solvent pressure, but showed a crossover behavior with temperature. Extraction of 0.8 mm thick wafers at 353 K showed that as the solvent pressure

TABLE 2

Measured PCP Concentrations in the Effluent Stream at Selected Pressures

	At P = 17.5 MPa		At P = 20 MPa		At P = 22.5 MPa		At P = 25 MPa	
Conditions	Time (minutes)	Concentration (ppm)	Time (minutes)	Concentration (ppm)	Time (minutes)	Concentration (ppm)	Time (minutes)	Concentration (ppm)
T = 353 K	2	145.6	1	372.7	1	623.8	2	849.9
F = 2 cm^3/min	4	150.2	4	440.4	4	753.1	5	1026.6
δ = 0.8 mm	7	161.3	9	551.4	7	841.2	8	652.8
	10	177.0	13	355.1	10	579.1	11	313.5
	14	226.8	18	256.7	13	377.4	15	237.4
	17	249.4	21	204.2	16	232.9	19	140.7
	20	246.2	24	158.8	19	201.4	23	129.8
	24	241.1	29	135.2	23	140.6	26	101.6
	27	203.7	33	116.1	27	115.8	31	74.2
	30	182.2	40	92.3	33	83.9	42	68.3
	36	150.1	44	79.9	39	68.1		
	41	109.6	48	74.3	45	55.4		
	46	90.7						
	53	87.1						

TABLE 3
Measured PCP Concentrations in the Effluent Stream at Selected Temperatures

	At T = 313 K		At T = 333 K	
Conditions	Time (minute)	Concentration (ppm)	Time (minute)	Concentration (ppm)
P = 22.5 MPa	2	552.4	2	678.7
F = 2 cm^3/min	5	606.7	5	789.7
δ = 0.8 mm	8	541.1	8	444.6
	11	440.1	11	328.9
	15	319.2	14	184.4
	18	253.0	18	146.6
	21	198.6	21	126.2
	24	148.6	25	87.9
	27	124.1	28	74.9
	30	107.6	32	57.8
	34	92.0	38	56.9
	39	89.9	44	54.4
	45	73.7		
	53	67.4		

increased from 17.5 to 25 MPa, the extraction efficiency increased from 43 to 72.9%, respectively. For extraction of PCP from a 0.8-mm thick wafers at 22.5 MPa when the solvent temperature increased from 313 to 353 K, the extraction efficiencies increased from 63.5 to 70.9% (Table

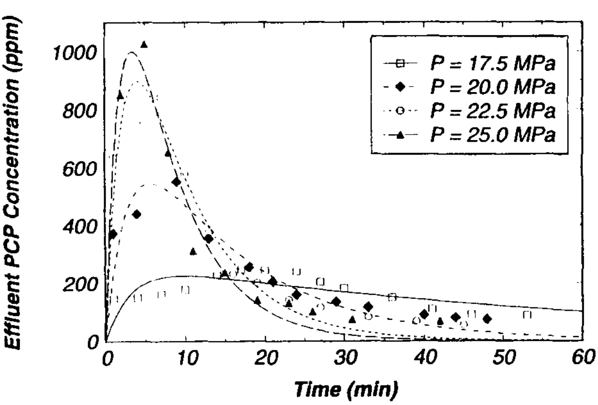

FIG. 2 Effect of pressure on PCP extracted at 353 K, 2 cm^3/min, from wafers 0.8 mm thick. Curves represent model fittings.

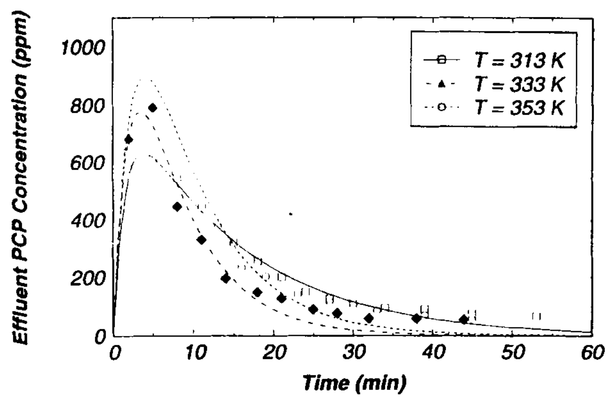

FIG. 3 Effect of temperature on PCP extracted at 22.5 MPa, 2 cm^3/min, from pressure-treated wafers 0.8 mm thick. Curves represent model fittings.

1). The combined mass transfer coefficient increased with an increase in pressure and temperature (Figs. 4 and 5). To check reproducibility, three runs were performed at each experimental condition. The variation increased with temperature and pressure, but the maximum was less than ± 10%. The bars in Figs. 4 to 5 show the 95% confidence intervals of estimated k_p values.

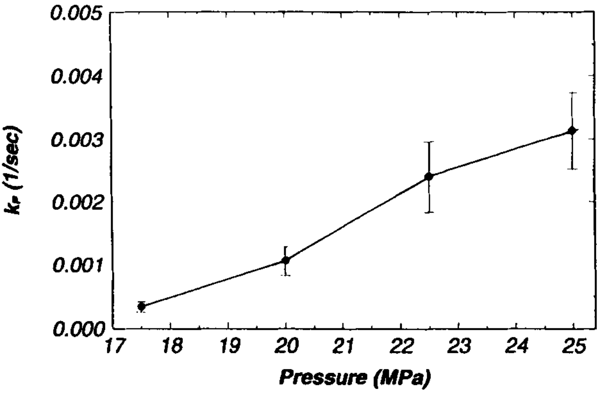

FIG. 4 Pressure effect on combined mass transfer coefficient.

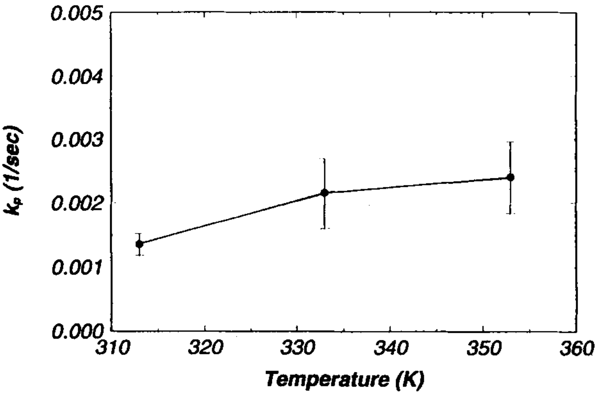

FIG. 5 Temperature effect on combined mass transfer coefficient.

Effect of Flow Rate

The effect of the solvent flow rate was determined using effluent concentration histories for extractions made at 22.5 MPa and 353 K (Table 4). Higher flow rates increased the extraction rates and created less tailing

TABLE 4
Measured PCP Concentrations in the Effluent Stream at Selected Flow Rates

	At F = 1 cm^3/min		At F = 3 cm^3/min	
Conditions	Time (minute)	Concentration (ppm)	Time (minute)	Concentration (ppm)
F = 22.5 MPa	2	533.2	2	806.1
T = 353 K	5	602.3	5	755.2
δ = 0.8 mm	8	688.7	8	386.3
	11	665.9	11	205.6
	14	510.9	14	171.8
	17	362.8	17	131.4
	20	280.7	20	75.7
	23	230.3	23	58.7
	27	175.2	26	39.3
	31	155.9	31	30.8
	37	105.0	36	22.1
	44	102.5	46	11.1
	50	78.8	51	4.2
	57	70.5		

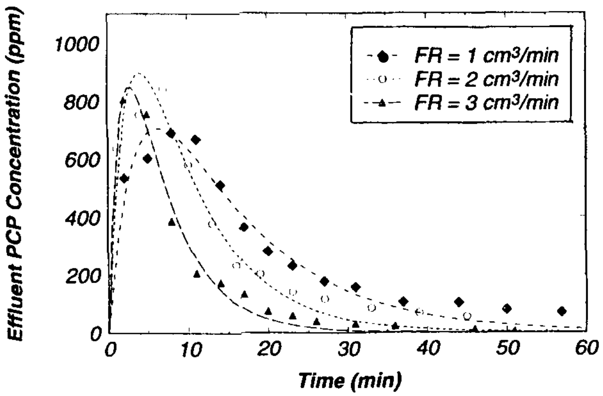

FIG. 6 Effect of flow rate on PCP extracted at 22.5 MPa, 353 K, from pressure-treated wafers 0.8 mm thick. Curves represent model fittings.

(Fig. 6). A solvent feed rate of 2 cm^3/min created a laminar flow of 1 cm/min superficial linear velocity in the extraction cell.

Solvent velocity mainly affected the convective mass transfer of PCP from the wood surface. Therefore, the combined mass transfer coefficient change plotted against the square root of the flow rates, based on the Nu = Re$^{1/2}$Sc$^{1/3}$ relationship of mass transfer on a flat plate, shows that the relationship between the two is linear over the conditions of the experiment (Fig. 7). The result shows that a lower flow rate allows slower mass

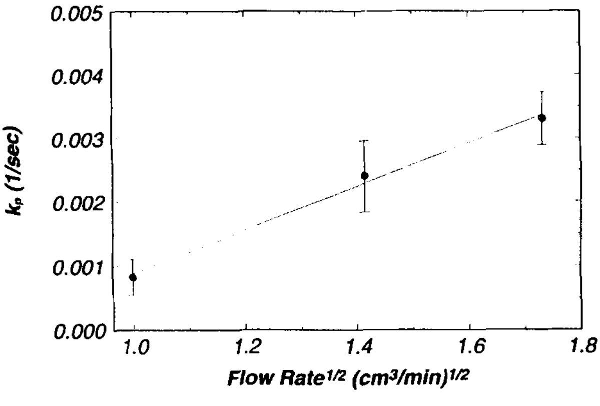

FIG. 7 Effect of flow rate on the combined mass transfer coefficient.

transfer, whereas higher flows yield less extraction per unit mass of solvent. A balance of these two opposing effects was also noted in other studies (21, 22).

Effect of Particle Size

The wood chip size has a strong influence on the rate of extraction. The effect of particle size is shown using measured and simulated PCP concentrations in the effluent stream (Table 5 and Fig. 8). Reduced particle sizes increase the surface area, decrease surface penetration path lengths, and result in significantly increased PCP transfer rates into the bulk of the SCF. As the wafer thickness increased from 0.8 to 2.2 mm, the extraction efficiency decreased from 70.9 to 55.9% (Table 1). Previous studies showed that PCP extraction efficiencies increased from 54 to 94% when wood particle size was reduced from 3 to 0.125 mm (35). These results suggest that intraparticle diffusion, which is directly proportional to the diffusivity of the solute and inversely proportional to the square of the diffusion distance, is the rate-limiting step in the extraction of PCP from large diameter wood chips.

Concentration Tailing

The PCP in a pressure-treated wood existed in a solution of a semivolatile organic solvent. During the extraction process the carrier solvent and

TABLE 5

Measured PCP Concentrations in the Effluent Stream for Selected Wood Chip Thickness

	For δ = 0.8 mm		For δ = 2.2 mm	
Conditions	Time (minute)	Concentration (ppm)	Time (minute)	Concentration (ppm)
P = 22.5 MPa	1	623.8	2	426.3
T = 353 K	4	753.1	5	364.5
F = 2 cm^3/min	7	841.2	8	234.1
	10	579.1	11	168.5
	13	377.4	14	141.4
	16	232.9	17	122.8
	19	201.4	20	104.5
	23	140.6	23	121.6
	27	115.8	27	95.6
	33	83.9	31	96.7
	39	68.1	36	88.6
	45	55.4		

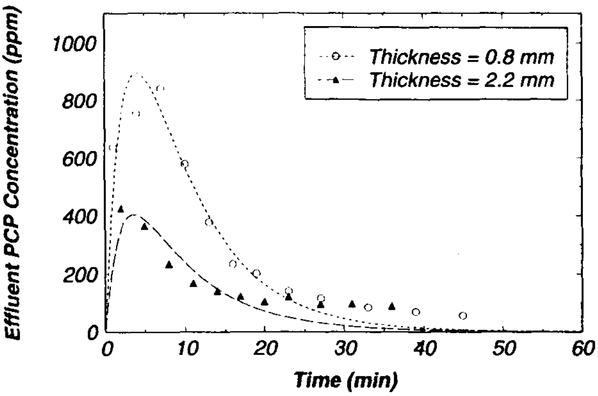

FIG. 8 Effect of wafer thickness on concentration histories of PCP extracted at 22.5 MPa, 353 K, and 2 cm^3/min. Curves represent model fittings.

most of the PCP in the cell lumen were extracted first. The residual PCP that was adsorbed to the cell wall was then extracted at a much slower rate. This residual PCP was analyzed using an x-ray florescent analyzer. The effect of the gradual loss of carrier solvents and the adsorption of the PCP to the cell wall are more significant in the extraction of PCP from old pressure-treated wood (24).

The PCP extraction process is hence limited by desorption from the wood matrix and by intraparticle diffusion. Polar cosolvents may reduce the desorption resistance by their effect on the desorption isotherm and by swelling the cellular matrix. Although the mathematical model describes well the time-dependent extraction process, it fails to predict the concentration tailing that might be caused by the slow desorption rate.

CONCLUSION

Supercritical fluid extraction of PCP from pressure-treated wood was experimentally studied, and the kinetic data were analyzed using a mathematical model. The model, which includes desorption equilibrium, intraparticle diffusion, and convective film mass transfer considering initial PCP distribution between cell lumen and cell walls, gave a good description of the experimental results. The desorption rate of PCP from the cell walls to the cell lumen of wood wafers was very small compared to the rate of mass transfer from the cell lumen to the bulk volume of the extractor. The rate of extraction increased with solvent pressure, temperature, and flow rate due to an increase in the combined mass transfer coefficient. As the wood chip size increased, the rate of extraction decreased significantly due to the slow intraparticle diffusion.

The model failed to predict the desorption tailing. Several mechanisms have been proposed to describe excessive tailing of SFE of solids including nonequilibrium adsorption, nonlinear adsorption isotherms, and nonsingularity (36, 37). The use of cosolvents has been shown to improve the extraction efficiency of PCP from pressure-treated wood (38), and the effects of cosolvents on both desorption and pore diffusion are currently being investigated. Further studies are needed to better understand adsorption characteristics of the PCP with the wood substance.

ACKNOWLEDGMENT

The authors thank Dr. Satish Kumar for providing the treated wood and for his assistance in retention analysis.

NOMENCLATURE

Bi	Biot number $= k_f(\delta/2)/D_e$
c	PCP mass concentration in CO_2 in the extractor (g/cm^3 of bulk fluid)
C	dimensionless PCP concentration in CO_2 in the extractor $= c/c_{T0}$
c_i	average PCP mass concentration in the pore volume of wafer (g/cm^3 of pore volume)
C_i	dimensionless average PCP concentration in the pore volume of wafer $= \langle c_i \rangle / c_{T0}$
c_{i0}	initial PCP mass concentration in the pore volume of wafer (g/cm^3 of pore volume)
c_{T0}	initial PCP mass concentration in the wafer (g/cm^3 of wafer volume)
c_s	adsorbed PCP mass concentration in the wafer (g/cm^3 of wafer volume)
c_{s0}	initial adsorbed PCP concentration of wood wafer (g/cm^3 of wafer volume)
C_s	dimensionless adsorbed PCP concentration in the wafer $= c_s/c_{T0}$
D_e	effective intraparticle diffusion coefficient for PCP in wood (cm^2/s)
E	(volume of wafer)/(volume of bulk fluid) in the extractor $= N(LW\delta)/V_b$
K	equilibrium adsorption coefficient

k_f	external mass transfer coefficient (cm/s)
k_p	combined mass transfer coefficient $= 3[k_f/(\delta/2)]/(3 + \mathrm{Bi})$ (1/s)
L	length of wood wafer = length of extractor, 5 cm
m	initial distribution ratio of PCP in the pore fluid to the total PCP in the wafer
N	number of wood wafers
Nu	Nusselt number $= k_f L/D_e$
Re	Reynolds number $= vL/\nu R^2\,\pi$
Sc	Schmidt number $= \nu/D_e$
t	time (second)
v	volumetric flow rate of solvent (cm^3/s)
V_b	volume of bulk fluid in the extractor $= \pi R^2 L - N\delta WL$ (cm^3)
W	width of wood wafer, 1 cm

Greek Letters

α	parameter defined in Eq. (19)
β	parameter defined in Eq. (18)
δ	thickness of the wood wafer (cm)
ϵ	porosity of wafer = (volume of pore)/(volume of wafer)
θ	dimensionless time $= t/\tau$
ν	kinematic viscosity (cm^2/s)
τ	residence time (bulk fluid volume of extractor)/(volumetric flow rate) (second)
ϕ	dimensionless mass transfer coefficient $= k_p\tau$

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Received by editor May 20, 1996
Revision received August 20, 1996