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Separation of Phenolic Pollutants from Dilute Solutions Using Supercritical Carbon Dioxide and Nitrous Oxide

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ABSTRACT

In recent years supercritical fluid extraction has been investigated for the removal of hazardous pollutants from wastewaters, especially those contaminated with trace amounts of toxic organic compounds. A semicontinuous flow system was employed here, using supercritical CO_2 and N_2O, for the extraction of phenolic pollutants from dilute aqueous solutions. This study showed the extent of extraction as a function of time. The equilibrium distribution coefficients of phenol and *p*-chlorophenol between aqueous and supercritical fluid phases were determined at 311 and 323 K and at pressures ranging from 10.34 to 24.13 MPa.

INTRODUCTION

In recent years supercritical fluid extraction has had renewed interest in extraction as a viable separation technique for removing organic compounds from water because of the increased extraction efficiency it sometimes provides over liquid–liquid extraction. There has been much research on the use of supercritical fluid (SF) as an extraction media, but few applications of this technology have reached the commercial stage (1–5). A major factor limiting the commercial success of this technology is the high costs associated with the lack of reliable data for the design of separation units for this high pressure extraction, especially in specialty chemicals processing and hazardous waste treatment where many species are difficult to separate and require continuous adaptation in downstream separations. To design large-scale commercial units for this separation process, it is necessary to have reliable supercritical phase–liquid phase equilibrium data such as solubility and the distribution coefficient of the solute. These data, however, are scarce in the literature, and few adequate methods for predicting the equilibrium behavior are available. Roop and Akgerman (4) investigated the extraction of phenol from water using supercritical carbon dioxide with various entrainers. Ghonasgi et al. (5) reported experimental vapor–liquid equilibria for CO_2 with phenol/water, *p*-chlorophenol/water systems.

A very common group of groundwater contaminants is the chlorinated phenols, which have widespread use in a variety of industries as starting materials (6, 7). Of this group, phenol and *p*-chlorophenol are frequently detected in the treated effluents of fine chemicals processing, oil refinery, steel plant, dyeing industries, polymer manufacturing, etc. (8). The aim of this article is to provide extraction data showing the effectiveness of supercritical CO_2 and N_2O in removing these contaminants from water. We also report the determination of equilibrium distribution coefficients of these solutes in the SF–water system from the experimental extraction fraction.

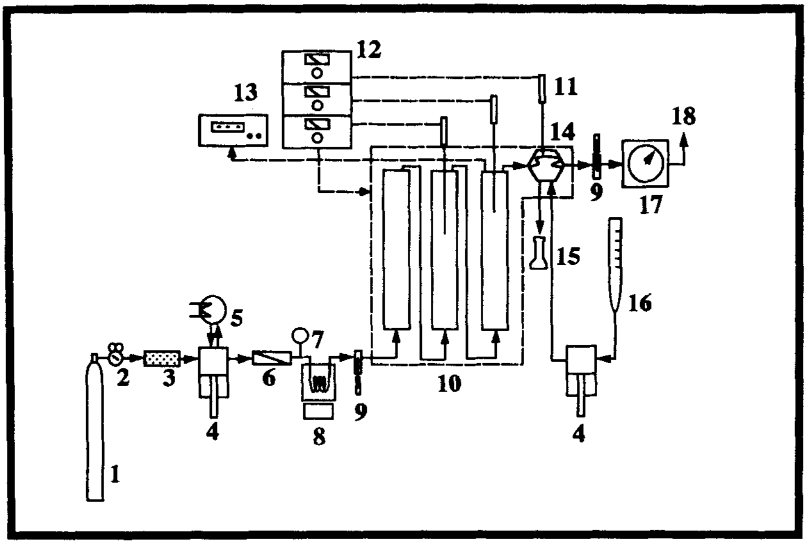
EXPERIMENTAL METHODOLOGY

Materials

A synthetic wastewater was used in this study. Analytical grade materials of phenol (99.5%+), *p*-chlorophenol (98%), and methanol (99.9%) were purchased from Merck Chemical Company and used without further purification. Deionized water was generated from a reverse osmosis water purifier (Millipore, Milli-RO60 and Milli-QSP). Liquefied CO_2 and N_2O were purchased from a local gas supplier.

Procedure

A diagram of the experimental apparatus is shown in Fig. 1. Supercritical fluid was fed by a duplex piston metering-pump (Milton Roy, NSI-33R) into the extractor established with three stainless steel seamless tubes (30 cm in length, 1.2 cm in inside diameter). The extractor was initially filled with stainless steel wire-mesh rings (200 mesh) as packing to improve the mass transfer between the supercritical CO_2 and the aqueous solution. A digital pressure transducer (Druck, PDCR-910) was employed for monitor-



1	**gas cylinder**	**9**	**metering valve**
2	**regulator**	**10**	**constant temperature extractor**
3	**filter**	**11**	**thermocouple**
4	**metering pump**	**12**	**temperature controller**
5	**cooler**	**13**	**digital pressure transducer**
6	**check valve**	**14**	**six-port valve with a 100μL loop**
7	**pressure gauge**	**15**	**sampling flask**
8	**pre-heater**	**16**	**glass burette**
		17	**wet gas meter**
		18	**vent**

FIG. 1 Schematic flow diagram of semicontinuous supercritical fluid extraction system.

ing the pressure in the extractor. Temperatures in the extractor were measured with K-type thermocouples. The extraction system was heated by three separate heating elements (Glas-Col, CC-10), and the temperature was controlled by three proportional and integral controllers. A wet gas meter (Shinagawa, W-NK-1A) was utilized for measuring the flow rate and the total volume of CO_2 that flowed through the extractor. CO_2 flow rate and system pressure were controlled via a micrometering valve (Alltech, 2-way SSI valve) located between the six-port sampling valve and the wet gas meter. The pressure was controlled within 0.05 MPa.

Aqueous solutions (60 mL) containing 10,000 ppm phenol (or 2500 ppm *p*-chlorophenol) were placed in the extractor. These feed solutions were prepared and equilibrated at room temperature. The first two columns were individually filled with 25 mL aqueous solutions, and the last column was filled only with 10 mL aqueous solution to prevent the aqueous solution from overflowing the extractor.

Three extractive columns, a 100 μL internal sampling loop, the six-port sampling valve (Rheodyne, 7010), and the micrometering valve were kept at constant temperature by means of three controllers. Once the temperature of the extractive system had reached the desired point, CO_2 was pumped into the extractor by turning on the metering pump. Approximately 90 minutes was required for the system to reach the desired temperature and pressure. After stable state was reached, 30 minute was allowed prior to the batch extraction tests to dampen any remaining thermal gradients. Following this period, the micrometering valve was then slowly opened for manually controlling the CO_2 flow rate at 60 ± 5 mL/min during the semicontinuous flow extraction tests. The uptake of water by the supercritical fluids is less than 1 mL during the extraction; it was checked by the mass balance of aqueous solution before and after experiments. There is no significance in the uptake of water by SF CO_2 and by SF N_2O.

Analytical Techniques

Samples were collected using a six-port sampling valve which was equipped with a calibrated internal loop of 100 μL. Samples were taken every 30 minutes. The solute inside the loop was rinsed with 25 mL distilled water, and the rinsing solution was collected into a 25-mL volumetric flask.

Four grams of each liquid sample was first weighed with a digital balance (Mettler, AJ100), and 1 g of 100 ppm standard solution (phenol or *p*-chlorophenol) was added to prepare the sample for HPLC analysis. The concentration of the sample was determined by a high pressure liquid chromatograph (Waters, 510) equipped with a reverse phase Nova-Pak C-18 column (i.d. 0.39 cm; length 12 cm, Merck), a deuterium lamp, and a UV/Vis detector. The HPLC system consisted of a single piston solvent delivery system for the injection of a 3-μL sample via a manually operated injection valve. The eluant was monitored at 270 nm for phenol and 280 nm for *p*-chlorophenol, corresponding to the maximum wavelengths of phenol and *p*-chlorophenol, respectively. The mobile phase for *p*-chlorophenol was 50:50 (v/v) for the methanol and water mixture, and for phenol 220:50 (v/v) for the methanol and water mixture. The flow rate of the mobile phase was set at 1.0 mL/min. The analog signal was recorded by an integrator which permitted adjustment of the chromatographic baseline integration.

Mole Fraction of Solute in SF Phase

A few milligrams of solute collected within the 100-μL internal loop can be determined from HPLC analysis. Known CO_2 densities at supercritical and standard (STP) conditions as well as the mole fraction of solute in the SF phase could be calculated for the extraction conditions. The solute concentration in this 100 μL loop could be estimated from the weight of the solute per unit of CO_2 volume under STP conditions. This solute concentration was measured as a function of time.

RESULTS AND DISCUSSION

Calculation of Extraction Fraction of Solute

Because the solute concentration in the internal loop equals the solute concentration of the SF phase, this concentration in the internal loop was plotted against STP volume of CO_2 measured by the wet gas meter to obtain a polynomial curve which could fit the experimental data with a confidence limit greater than 95%. Then the total moles of solute extracted into the SF phase was calculated as the sum of the following two quantities. The first, an area generated from the integration of the polynomial curve with respect to STP volume of CO_2, represents the cumulative weight of the solute passing through that internal loop during a given period, and the second is the amount of solute existing with the SF gas above the 10-mL aqueous solution in the last column, and it represents the residue of solute remained in the SF phase. The extraction fraction of the solute, ϕ, was then obtained with the following equation in which all N's represent the moles in the third column.

$$\phi = \left(\frac{N_3^{\mathrm{v}}}{N_3^{\mathrm{t}}}\right) \times 100\% \qquad (1)$$

where N_3^{v} = cumulative moles of solute extracted into the SF phase
N_3^{t} = moles of solute originally present in the aqueous phase

Due to flow configuration of three columns in series and unsaturated extraction prior to the semicontinuous flow extraction tests, all curves of ϕ versus time exhibited an S shape and approached being flat after 300 minutes. An explanation is as follows. In the beginning of semicontinuous flow extraction, the unsaturated SF gas, passed through the previous two columns, continued flowing into the third column, and ϕ was increasing; after longer extraction at a smaller flow rate of supercritical fluid, the SF gas becomes saturated with solute before entering the third column and is in equilibrium with the solute in the SF phase, and then ϕ ceases to increase. In other words, moles of solute in the SF phase start diffusing back into the solution and equilibrate with moles of solute in the aqueous phase. This is similar to SF recirculating through the solution until it reaches equilibrium. The above explanation was also evidenced by the experimental data, which show that moles of solute in the aqueous phase stop decreasing after 300 minutes.

Figures 2 to 5 represent the extraction fractions of phenol and *p*-chlorophenol at 311 and 323 K with respect to time. For the same pressure, the extraction of *p*-chlorophenol at 311 K was more rapid than extraction at 323 K. This might be explained by the larger influence of the solvent density (denser at 311 K) than the vapor pressure of the solute (higher at 323 K). For all five isobaric curves in a given period shown in Figs. 2–5,

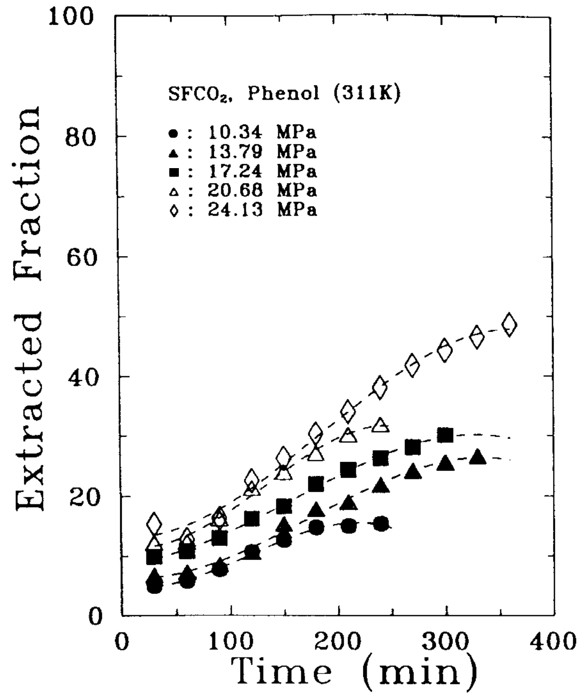


FIG. 2 SF CO_2 extraction fraction of phenol versus time at 311 K.

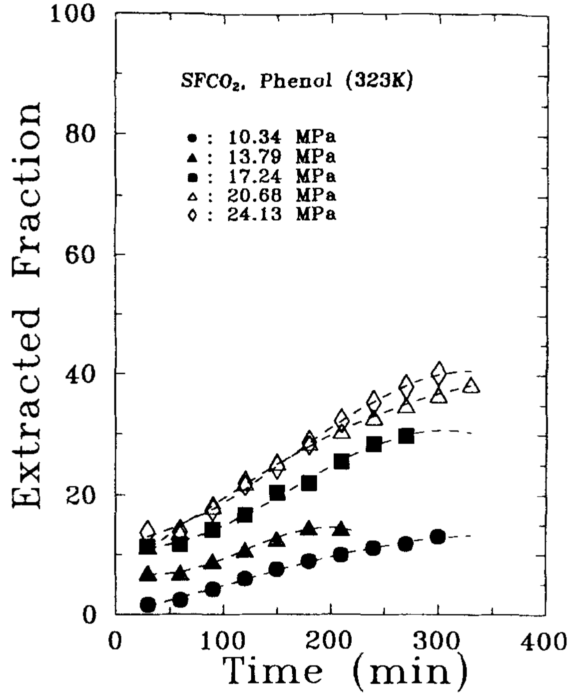


FIG. 3 SF CO_2 extraction fraction of phenol versus time at 323 K.

the extraction fraction of *p*-chlorophenol is higher than that of phenol. Longer extraction times resulted in higher extraction fractions, but the extraction rate decreased, approaching zero after 300 minutes. However, the maximum extraction fraction was obtained at zero extraction rate. The average maximum of *p*-chlorophenol was about two times that of phenol. It is obvious that the influence of solvent density, caused by the change of temperature, on the maximum fractions of *p*-chlorophenol is larger than in the case of phenol. There might be two major factors dominating the extraction of solute from the aqueous solution under supercritical fluid extraction. The first factor is the intermolecular force between the solute and water molecules, and the second factor is the intermolecular force between the solute and CO_2 molecules. The smaller average maximum extraction fraction of phenol might be attributed to the more hydrophilic affinity of phenol than of *p*-chlorophenol. In other words, the first factor is more important than the second factor for the supercritical fluid extraction of phenol from its aqueous solution.

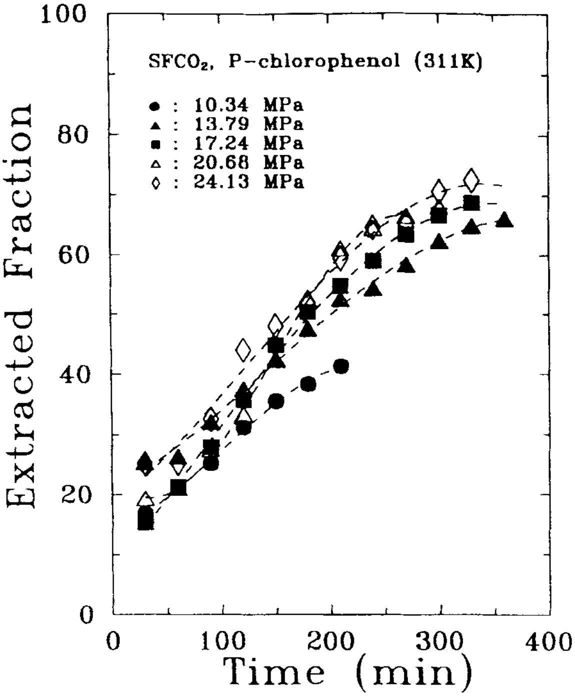


FIG. 4 SF CO_2 extraction fraction of *p*-chlorophenol versus time at 311 K.

Determination of Equilibrium Distribution Coefficient of Solute

Supercritical fluid extraction of a solute from an aqueous solution forms two phases: a supercritical phase and an aqueous phase. The ratio of the mole fraction of solute in the supercritical phase to the mole fraction of solute in the aqueous phase is the distribution coefficient, which provides a measure of the solvent power of different supercritical fluids for the same solute. For the same supercritical fluid used as the solvent, this ratio also provides a measure of chemical affinity of the solvent to the solutes for comparison. In this study the extraction system of three columns in series was designed to provide the saturated extraction (i.e., equilibrium state) attained in the third column. The equilibrium distribution coefficient, K, is represented as a function of the maximum extraction fraction, ϕ_{max}, using the following equations: The mole fraction of the solute in

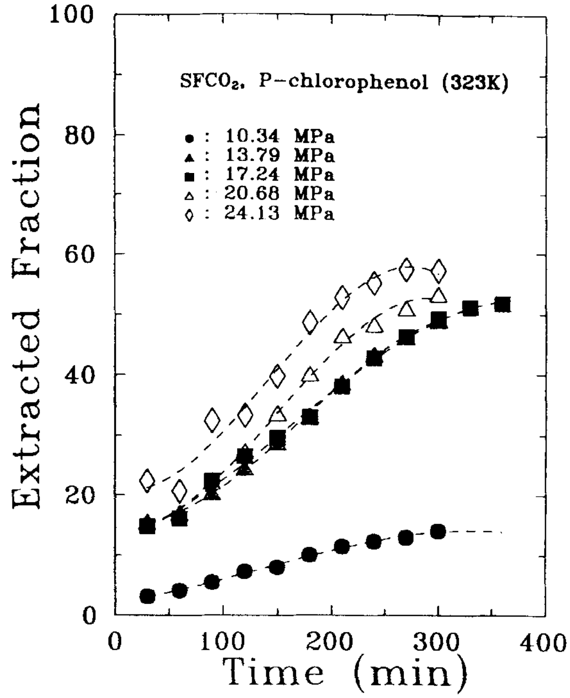


FIG. 5 SF CO_2 extraction fraction of *p*-chlorophenol versus time at 323 K.

the SF phase, y_3, can be expressed by

$$y_3 = \frac{N_3^V}{N_1^V + N_2^V + N_3^V} \doteq \frac{N_3^V}{N_1^V} \tag{2}$$

where N_3^V = cumulative moles of solute extracted into the SF phase, $\ll N_1^V$

N_2^V = moles of water in the SF phase, $\ll N_1^V$

N_1^V = moles of CO_2 in the SF phase

According to the definition of extraction fraction as given in Eq. (1), y_3 becomes

$$y_3 = \left(\frac{N_3^t}{N_1^V}\right)\phi \tag{3}$$

The mole fraction of the solute in the aqueous phase, x_3, can similarly be shown as

$$x_3 = \frac{N_3^L}{N_1^L + N_2^L + N_3^L} \doteq \frac{N_3^t - N_3^V}{N_2^L} = \left(\frac{N_3^t}{N_2^L}\right)(1 - \phi) \tag{4}$$

where N_3^L = moles of solute remaining in the aqueous phase, $\ll N_2^L$
N_2^L = moles of water in the aqueous phase
N_1^L = moles of CO_2 in the aqueous phase, $\ll N_2^L$

Then, the equilibrium distribution coefficient of the solute can be calculated by

$$K = \lim_{t=\infty}\left(\frac{y_3}{x_3}\right) = \lim_{t=\infty}\left(\frac{\phi}{1 - \phi}\right)\left(\frac{N_2^L}{N_1^V}\right) = \left(\frac{\phi_{max}}{1 - \phi_{max}}\right)\left(\frac{N_2^L}{N_1^V}\right) \tag{5}$$

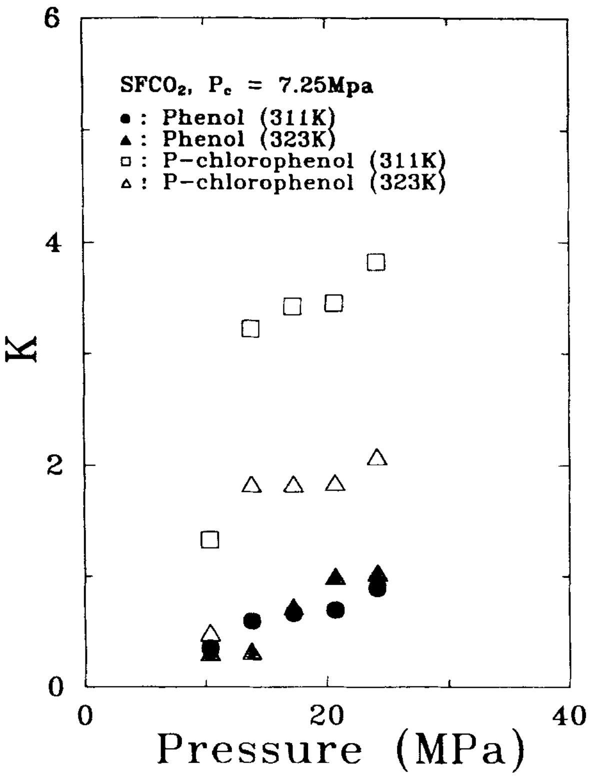


FIG. 6 Effect of temperature on equilibrium distribution coefficients of phenol and *p*-chlorophenol at various pressures in SF CO_2 extraction.

Figure 6 shows equilibrium distribution coefficients of phenol and *p*-chlorophenol at 311 and 323 K. There is a similar trend between the maximum extraction fraction and equilibrium distribution coefficient. Again, CO_2 molecules have a stronger chemical affinity for *p*-chlorophenol molecules than for phenol molecules.

Comparison between SF CO_2 and SF N_2O Extractions

Nitrous oxide has a critical temperature (36.5°C) and critical pressure (72.5 atm) similar to CO_2 but is highly polar, like water. Figure 7 shows an increase of the extraction fraction of phenol with SF N_2O at 323 K. Compared with Fig. 3, it shows higher extraction fractions with SF N_2O than with SF CO_2 under the same conditions.

Figure 8 illustrates the higher distribution coefficients with SF N_2O, especially in the lower pressure region (i.e., less than 20 MPa).

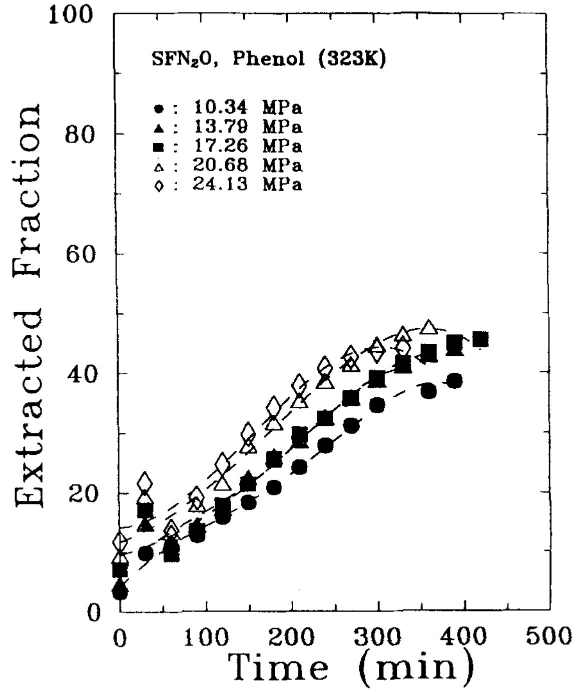


FIG. 7 SF N_2O extraction fraction of phenol versus time at 323 K.

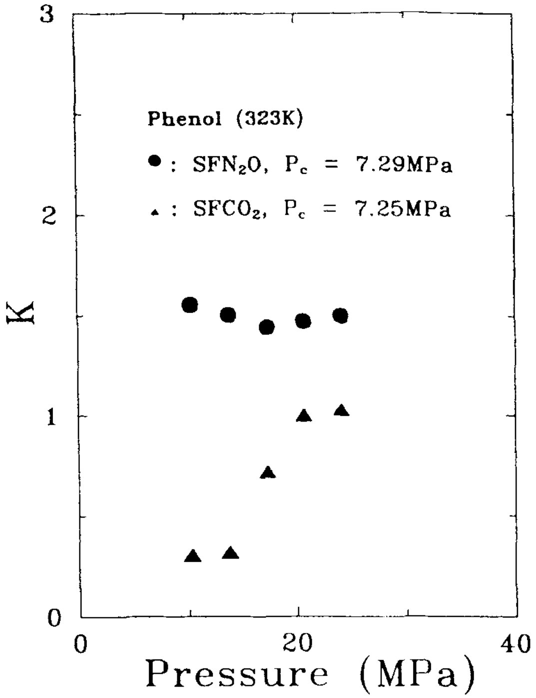


FIG. 8 Comparison of equilibrium distribution coefficients of phenol in SF CO_2 and SF N_2O extractions at 323 K.

CONCLUSIONS

Supercritical CO_2 extraction for the removal of phenol and *p*-chlorophenol from water has been studied using a semicontinuous flow cell. The extraction fraction and equilibrium distribution coefficient for both phenol and *p*-chlorophenol were measured at two temperatures, 311 and 323 K, for the 10.34–24.13 MPa pressure range. In the pressure range studied, the effect of temperature on the equilibrium distribution coefficient was prominent for *p*-chlorophenol but not for phenol because of the smaller equilibrium distribution coefficient of phenol compared to that of *p*-chlorophenol. In comparison with supercritical CO_2, supercritical N_2O, with its more polar characteristics, gave a better extraction fraction (larger equilibrium distribution coefficients) with phenol.

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