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Sang-Do Yeo[a]; Kyung-Sik Kim[a]
[a] Department of Chemical Engineering, Kyungpook National University, Taegu, South Korea

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Supercritical Extraction of Phenol from Activated Carbon Fiber

Sang-Do Yeo* and Kyung-Sik Kim

Department of Chemical Engineering, Kyungpook National University,
Taegu, South Korea

ABSTRACT

Phenol was extracted from activated carbon fiber (ACF) using supercritical carbon dioxide in a fixed-bed extractor. Phenol was adsorbed to ACF from aqueous solutions at two different loadings, 277 and 402 mg phenol/g ACF. Supercritical extraction of the loaded ACF was carried out at temperatures of 30, 50, 70, and 90°C in a pressure range from 206.8 to 344.7 bar. The extraction percentage of phenol from ACF was recorded as function of carbon dioxide used, and the trend of experimental data was extended by using an extrapolation technique. We observed a crossover point at which the extended isotherms of different temperatures could possibly intersect. This result reflects the combined effect of pressure and temperature on carbon dioxide density and on the desorption rate of phenol from ACF. The desorption rate constant was estimated from extraction profiles, which decreased with increasing temperature and pressure.

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*Correspondence: Sang-Do Yeo, Department of Chemical Engineering, Kyungpook National University, Taegu, 702-701, South Korea; E-mail: syeo@knu.ac.kr.

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INTRODUCTION

Activated carbon fiber (ACF) has been used for adsorption of a wide variety of organic compounds from both gaseous and aqueous phases.[1] ACF has unique properties compared with granular activated carbons, exhibiting rapid external and intraparticle mass transfer kinetics and hence showing high adsorption rates. ACF is known to have rather well defined pore structures and surface characteristics, and fundamental research on adsorption and desorption behaviors has been performed in various aspects. The major compounds treated by ACF were environmental pollutants such as volatile organic compounds (VOCs) and phenolic mixtures, which were adsorbed from gas and aqueous phases, respectively.[2,3]

The applications of ACF on adsorption have been accompanied by investigation of the regeneration processes of the spent ACF. The regeneration methods include chemical extraction,[4] thermal desorption,[5] and supercritical fluid extraction.[6] Among these methods, supercritical extraction has been widely used to extract organic pollutants from various solid environmental matrices such as soil and many types of solid adsorbents.[7,8] Supercritical extraction shows unique characteristics resulting from versatile operational variables such as pressure, temperature, and adjustable solvent powder. Each of these individual factors influences the desorption behavior in different ways, and therefore the overall extraction capacity can be easily manipulated by regulating these variables.

In this study, we investigated the desorption behavior of phenol from ACF using supercritical carbon dioxide as an extraction medium. The extraction was performed in a fixed-bed column, with carbon dioxide continuously flowing through the phenol-loaded ACF bed. We focused on observation of the amount of phenol desorbed as a function of carbon dioxide used at various temperatures, pressures, and initial phenol loadings on ACF. Experimental data were extrapolated to predict the trend of extraction behavior, and as a result, we observed a crossover point at which the isotherms for extraction percentage appear to intersect.

EXPERIMENTAL METHODS

Materials

Activated carbon fiber was obtained from Toyobo Co. Ltd. (model KF-5000), Japan. The ACF was made from cellulose-based fiber and manufactured in felt form. The BET analysis and SEM photomicrograph showed that the physical properties of ACF are: fiber diameter (20 μm), surface area (1500 m^2/g), and pore volume (0.5 ml/g). ACF was kept in a dry oven for 24 hours at 100°C to remove any volatile organic compounds from the fiber surface. Phenol was purchased from Junsei Chemical Co., Japan, and used without further purifications. Carbon dioxide was used as a supercritical fluid.

Adsorption of Phenol

Phenol was adsorbed to ACF from aqueous solutions at different phenol concentrations. First, phenol was dissolved in water at concentrations of 2500–5000 mg/L. A known amount of ACF was added to 200 ml of the phenol solutions, and the mixtures were agitated for 2 hours at 25°C. During the adsorption process, an aqueous phase sample was taken every 1–10 minutes, and the concentration was determined using a UV spectrophotometer (HP model 8452A). Analysis showed that the adsorption equilibrium between ACF and the aqueous solution was reached in a very short time. At equilibrium, the uptake of phenol by ACF was calculated and the adsorption isotherms were prepared. The adsorption isotherm was well described by the classical form of the Langmuir isotherm equation: $C/S = (1/ab) + (C/b)$, where C is the equilibrium solution concentration, S is the uptake per unit mass of ACF, a is the affinity parameter or Langmuir constant, and b is the capacity parameter. The phenol-loaded ACF was dried in an oven to remove surface water and was kept in a sealed vessel.

Extraction of Phenol

Supercritical extraction of phenol from the loaded ACF was performed in a fixed-bed column. In this study, only pure carbon dioxide was used as an extraction medium, and any effect of co-solvent or entrainer was not investigated. Figure 1 shows the experimental apparatus used in this study. The extraction unit was purchased from Isco Co. (model SFX2-10). The system consists of a high-pressure syringe pump (Isco model 260D), an extraction column (2.5-ml volume), and a stainless steel capillary restrictor (300-μm OD). The syringe pump was used for carbon dioxide supply. This pump is pulseless and provides highly accurate flow rate so that it can precisely maintain the carbon dioxide flow rate inside the extraction column without any fluctuation. The system was designed to keep a constant pressure and flow rate during extraction.

Phenol extraction was performed using two ACF samples, which have different initial phenol loadings. The extraction column was charged with

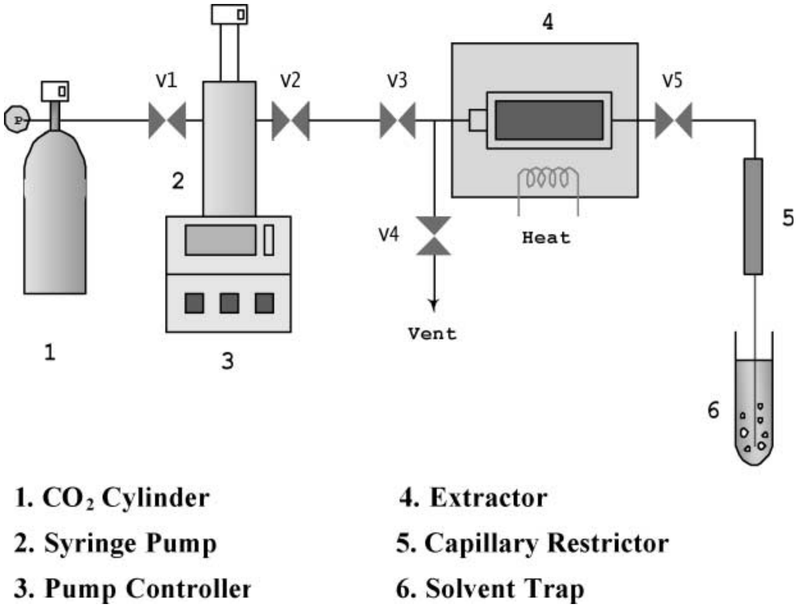

Figure 1. Experimental apparatus for supercritical extraction of phenol from activated carbon fiber.

0.38 g of the phenol-loaded ACF. Before extraction, the system was vented with gaseous carbon dioxide for 2 minutes to remove air from the extraction system. Carbon dioxide was charged to the head of syringe pump from the carbon dioxide cylinder. In order to charge the carbon dioxide as much as possible, the pump head was cooled using an ice pack. The amount of initially charged carbon dioxide in the syringe pump was the maximum amount of carbon dioxide that could be used in one set of experiments. In this experiment, the extraction was continued until the once-charged carbon dioxide was totally consumed. Phenol extraction was performed by continuously supplying carbon dioxide through the extraction column. The experiments were carried out at pressures of 206.8, 275.8, and 344.7 bar and at temperatures of 30, 50, 70, and 90°C. The flow rate of carbon dioxide was maintained at 1.3–2.3 ml/min at each temperature and pressure. The extract was collected in a solvent trap, which contained distilled water. The solvent traps were changed every 10 minutes to obtain the extraction profile with time. The aqueous solution in the solvent trap was analyzed using a UV spectrophotometer to measure phenol concentration.

RESULTS AND DISCUSSION

Adsorption of Phenol

Figure 2 shows the amount of phenol adsorbed from the aqueous solutions as a function of time. The legend represents the initial concentration of phenol in the aqueous solutions before adsorption takes place. The results indicate that the phenol adsorption to ACF is completed in less than 10 minutes, regardless of phenol concentration. This result reflects the small internal mass transfer resistance inside the pores of ACF.[9] The adsorption isotherm of phenol on ACF is shown in Fig. 3. The experimental data were well represented by the Langmuir adsorption isotherm with constants of $a = 0.7695$ and $b = 0.0017$. For the extraction experiments, phenol-loaded ACF with uptakes of 277 and 402 mg phenol/g ACF were prepared.

Extraction of Phenol

A feature of this experiment is that a pulseless syringe pump was used to supply carbon dioxide to a fixed-bed column. This generates an undisturbed steady flow of carbon dioxide inside the extraction column, and this provides

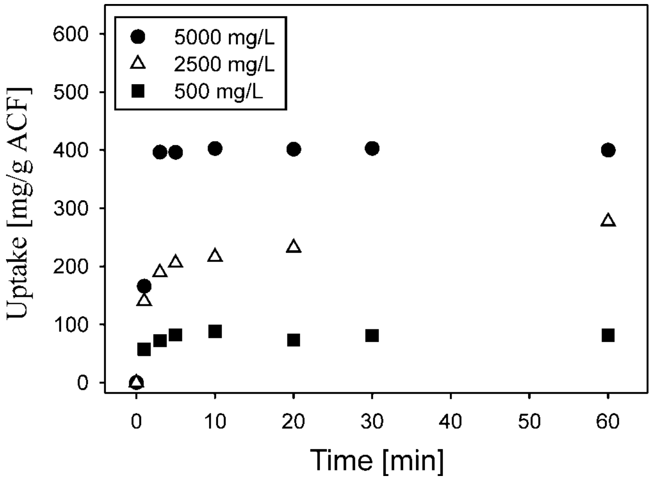

Figure 2. Phenol uptake on activated carbon fiber as a function of time measured at various concentrations of aqueous solutions.

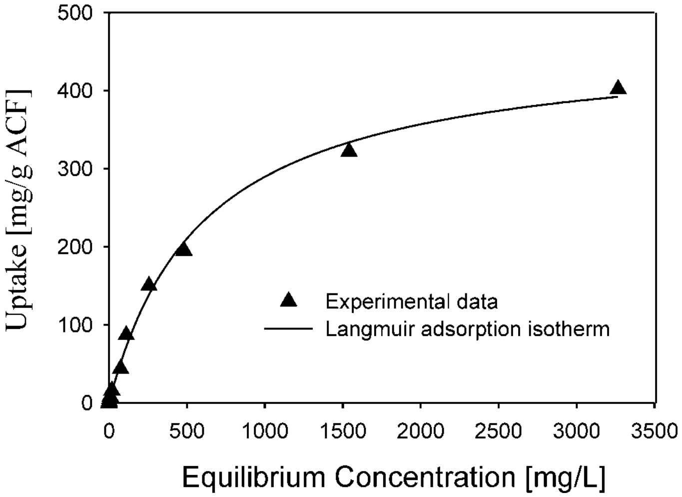

Figure 3. Adsorption isotherm of phenol on activated carbon. The curve represents the Langmuir adsorption isotherm.

highly precise experimental data. The total volume of the syringe pump is 260 ml, which is the maximum volume of carbon dioxide that can be delivered to extraction column. In the pressure range of this study, the amount of carbon dioxide initially charged inside the syringe pump was ca. 90 g. Therefore, in every experiment, extraction of phenol was performed by using 90 g of carbon dioxide, and the extraction was stopped when all the carbon dioxide inside the pump was consumed.

Figures 4 and 5 show the extraction percentage of phenol from ACF as a function of carbon dioxide used. In these figures, abscissa represents the amount of carbon dioxide passed through the extraction column, which definitely increases with time. The extraction percentage was calculated based on the initial loading on ACF and the amount of phenol extracted. Figure 4 shows the variation of extraction percentage measured at temperatures of 30, 50, 70, and 90°C. Initial loading of phenol prior to extraction was 277 mg phenol/g ACF, and the experiments were conducted at pressures of 206.8 (a), 275.8 (b), and 344.7 (c) bar. As previously mentioned, acquisition of experimental data was finished when the carbon dioxide contained in the syringe pump was used up. Based on these results, the trend of extraction was extended by extrapolation of a set of experimental data measured at a constant temperature. The curves in Figs. 4 and 5 represent the results of the extrapolation using an appropriate polynomial function. Overall,

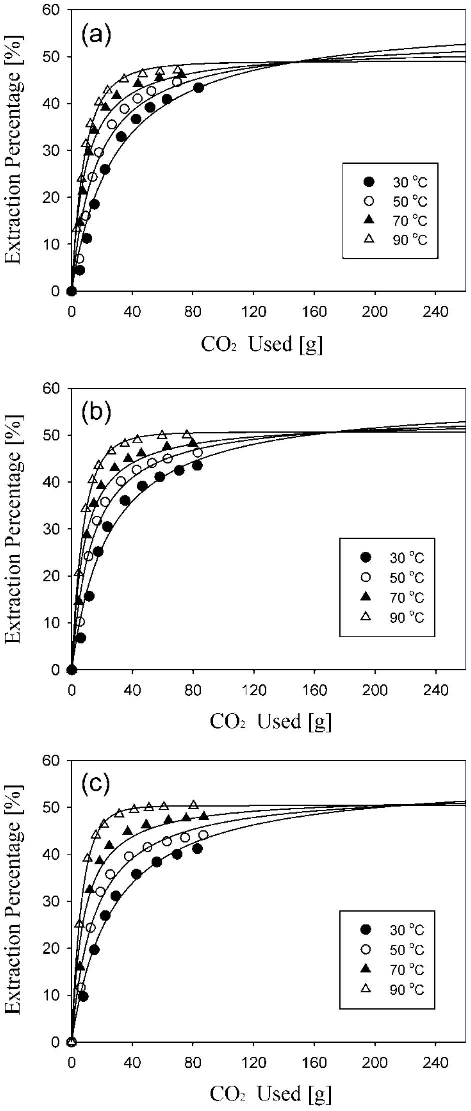

Figure 4. Extraction percentage of phenol as a function of carbon dioxide used, measured at various pressures (a) 206.8 bar, (b) 275.8 bar, (c) 344.7 bar. Initial phenol loading on activated carbon fiber is 277 mg phenol/g ACF. Experimental data were extrapolated and displayed in solid curves. The flow rates of carbon dioxide were (a) 1.3 ml/min, (b) 1.8 ml/min, (c) 2.3 ml/min.

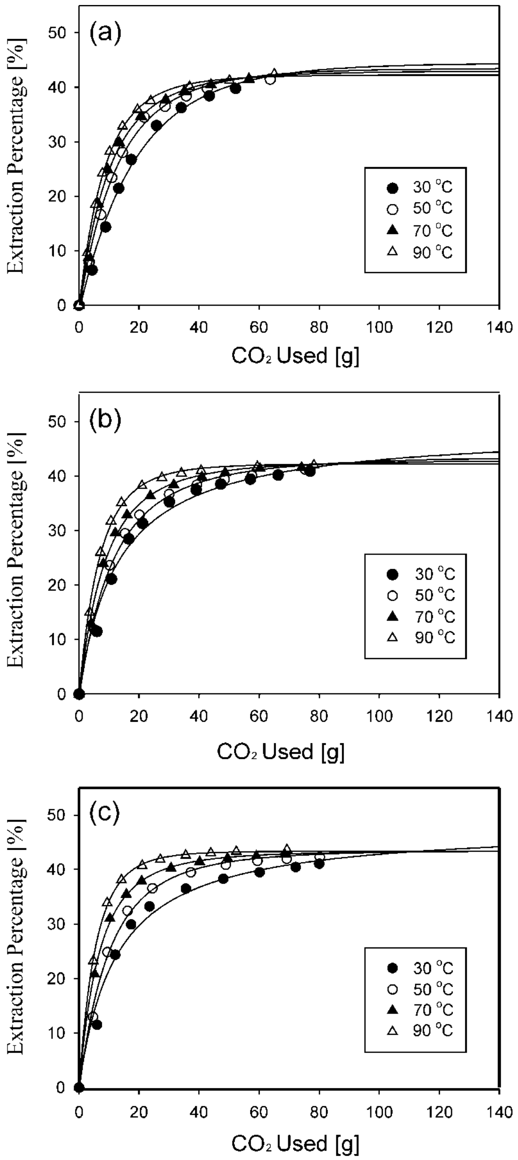

Figure 5. Extraction percentage of phenol as a function of carbon dioxide used, measured at various pressures, (a) 206.8 bar, (b) 275.8 bar, (c) 344.7 bar. Initial phenol loading on activated carbon fiber is 402 mg phenol/g ACF. Experimental data were extrapolated and displayed in solid curves. The flow rates of carbon dioxide were (a) 1.3 ml/min, (b) 1.8 ml/min, (c) 2.3 ml/min.

the extraction percentages were less than ca. 50% at all experimental conditions investigated. Generally, the low extraction percentages have been observed when supercritical carbon dioxide was used to extract phenol from activated carbon-based solid adsorbents.[10]

Our results suggest that there may exist a crossover point at which the extended isotherms of different temperatures intersect and eventually cross over. The crossover point represents the amount of carbon dioxide used when the extraction percentages become identical at all temperatures. We call this amount of carbon dioxide the 'crossover amount.' For example, the crossover amount in Fig. 4(a) is 148 g. Table 1 shows the crossover amount of carbon dioxide for two ACF samples with different initial phenol loadings. These numbers are described in Figs. 4 and 5. In these figures, the significance of the crossover point can be explained as follows. When the amount of carbon dioxide used is less than the crossover amount, the extraction percentage increases with increasing temperature when the same amount of carbon dioxide passes through the extractor. In case the amount of carbon dioxide used is more than the crossover amount, the effect of temperature becomes reversed. Moreover, it is meaningful to note that the crossover amount increases as the operating pressure increases from 206.8 to 344.7 bar, which can be seen by comparing Figs. 4(a–c). Regarding the effect of pressure, the extraction percentage increased with pressure at constant temperature. As the operating pressure increased, the influence of temperature on the extraction percentage became greater. In other words, the distance between each isotherm in Fig. 4 became larger at higher operating pressures. This crossover phenomenon was consistently observed in experiments performed with different phenol initial loadings on ACF (Fig. 5).

Table 1. Crossover amount of carbon dioxide when 0.38 g of ACF is charged in extraction column.

Phenol loading (mg/g)	Pressure (bar)	Crossover amount (g)
277	206.8	148
	275.8	171
	344.7	216
402	206.8	63
	275.8	87
	344.7	110

These results reflect the combined effect of pressure and temperature on carbon dioxide density or solubility (solubility control) and on the desorption rate of phenol from ACF (desorption control). At the initial stage of extraction (when the amount of carbon dioxide used is less then the crossover amount), it appears that extraction is determined by desorption control. In this region, the extraction percentage increased with temperature when the same amount of carbon dioxide was used for extraction. The enhanced extraction percentage at the elevated temperature indicates that the higher temperature accelerates desorption of phenol from ACF. At high temperatures, enhanced desorption of phenol dominates the diminished carbon dioxide density which, in turn, provides a higher extraction percentage. In fact, the concentration of carbon dioxide effluent stream from the extraction column was measured, and it turned out that the phenol concentration was much less than the saturated concentration.[11] This confirms that the present system is desorption-controlled extraction.

The desorption mechanism in supercritical regeneration of activated carbon-based adsorbents has been studied using various mathematical models such as 1) an equilibrium model, which assumes that mass-transfer resistances are negligible,[12] and 2) a surface and pore diffusion model that assumes equilibrium at a desorption site but includes intraparticle concentration gradients, and 3) a two-parameter model where mass transfer and first-order irreversible kinetics control the desorption process.[13] Among these theories, the simple equilibrium model that incorporated linear adsorption equilibrium has been successfully applied to analyze the desorption data of organic compounds from activated carbon fiber.[6] This theory was also used in this study as shown in Modeling of Extraction Profile section.

As can be seen in Figs. 4 and 5, when the carbon dioxide used exceeds the crossover amount, the extraction percentage tends to increase with decreasing temperature. This conclusion is based on the extrapolated curves in Figs. 4 and 5. In this range, most of the phenol should already be desorbed from ACF macropores and the extraction of residual phenol in micropores takes place, which may be affected mainly by carbon dioxide density. Therefore, the high-density carbon dioxide at low temperature provides an enhanced extraction percentage.

These results provide useful information on the relation of operating conditions and the necessary amount of carbon dioxide used in order to achieve a targeted extraction percentage. In this study, the crossover point was identified by extrapolation of the acquired experimental data. This finding is based on the acquisition of highly accurate experimental data and on the consistent extractional trend with the validity of extrapolation technique applied in present system. In this viewpoint, the existence of crossover point claimed in this paper should be confirmed by acquiring experimental data beyond the crossover point, which remains for our future work.

Modeling of Extraction Profile

The extraction profiles of phenol from ACF in a fixed column were modeled by adopting equations suggested by Tan and Liou.[14] The material balance in the extraction column can be written as,

$$\varepsilon\frac{\partial C}{\partial t}+u\frac{\partial C}{\partial z}=-(1-\varepsilon)\frac{\partial S}{\partial t} \tag{1}$$

where ε is the bed porosity, u is the superficial velocity of carbon dioxide, and S is the phenol concentration per unit volume of ACF. The initial and boundary conditions are at $t=0$, $C=0$ and at $z=0$, $C=0$. The linear desorption kinetics used is as follows,

$$\frac{\partial S}{\partial t}=-kS \tag{2}$$

where k is the desorption rate constant. This desorption isotherm has been used to model the desorption from solid adsorbents such as activated carbon and organoclays.[14,15] The initial condition is at $t=0$, $S=S_0$. The solution of Eqs. (1) and (2) with the initial and boundary conditions gives the expression for the concentration at the exit of extraction column C_e:

$$C_e=\frac{1-\varepsilon}{\varepsilon}S_0\left\{\exp\left[-k\left(t-\frac{\varepsilon L}{u}\right)\right]-\exp(-kt)\right\} \tag{3}$$

where L is the column length. The amount of extraction can be calculated by integrating C_e with respect to time. The desorption rate constant k is determined by regression of Eq. (3) with the experimental data.

Figures 6 and 7 display the extraction profiles, showing the amount of phenol extracted as a function of time. The profiles indicate that the amount of extraction is influenced by temperature mostly at the first stage of extraction, and the profiles tend to collapse to almost a single curve. These experimental data were regressed by using Eq. (3) with the desorption rate constant as an adjustable parameter. The curves in Figs. 6 and 7 represent the regression results of each isotherm. Figure 8 shows

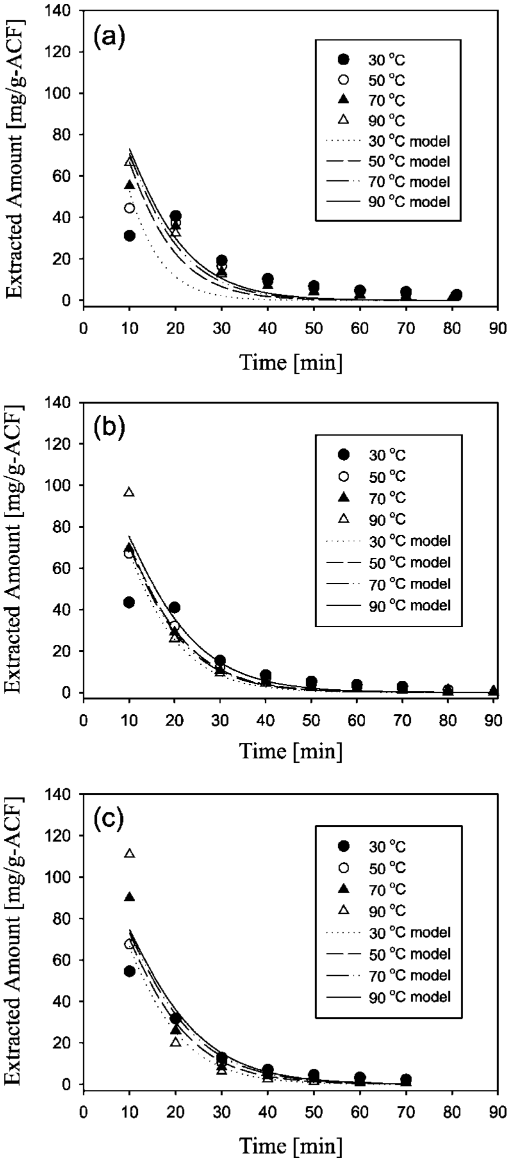

Figure 6. Extraction profile of phenol as function of time at various pressures, (a) 206.8 bar, (b) 275.8 bar, (c) 344.7 bar. Initial phenol loading on activated carbon fiber is 277 mg phenol/g ACF. The curves represent the result of regression using Eq. (3).

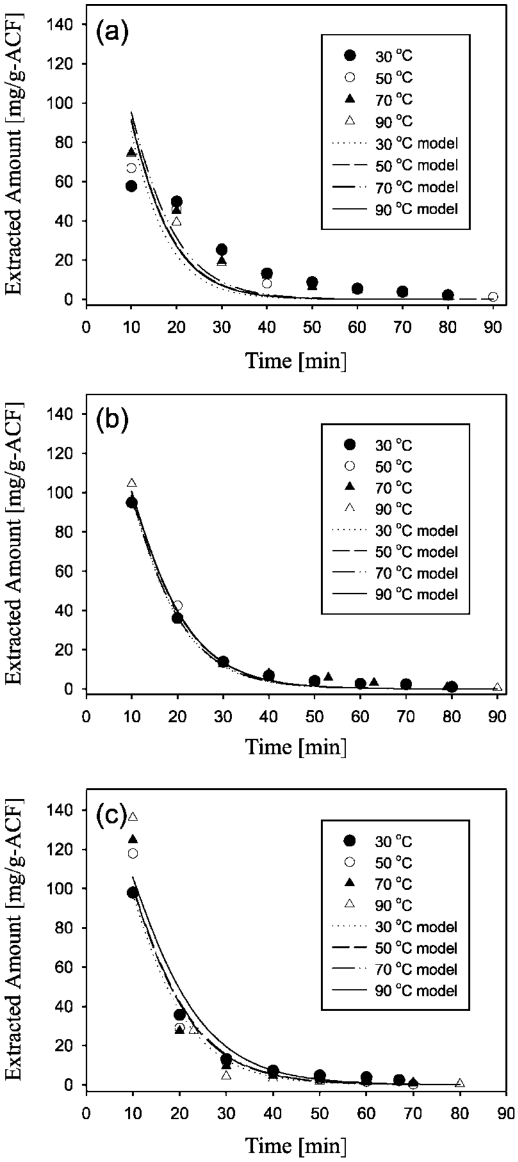

Figure 7. Extraction profile of phenol as function of time at various pressures, (a) 206.8 bar, (b) 275.8 bar, (c) 344.7 bar. Initial phenol loading on activated carbon fiber is 402 mg phenol/g ACF. The curves represent the result of regression using Eq. (3).

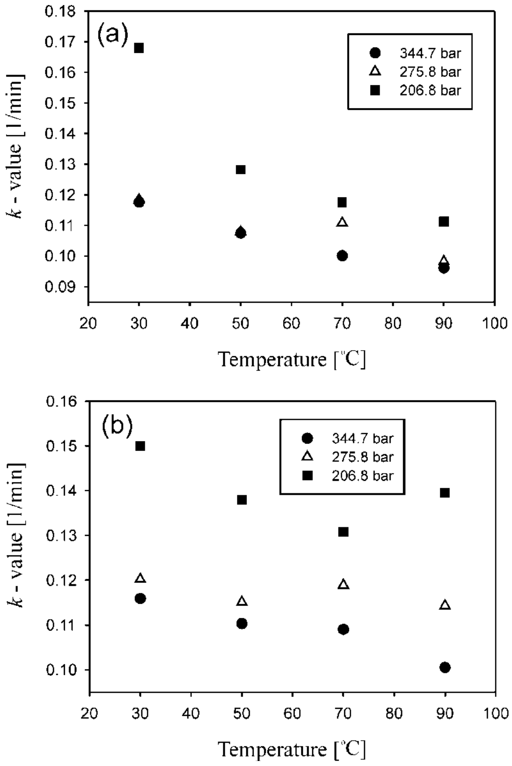

Figure 8. The desorption rate constant *k* as a function of temperature at various pressures. Initial phenol loading is (a) 277 mg phenol/g ACF, (b) 402 mg phenol/g ACF.

the adjusted values of desorption rate constant *k* as a function of temperature. From the figures, it turned out that the changes in *k* values with temperature and pressure are very little and are probably insignificant if one considers the error range of data.

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