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Regeneration of Activated Carbon Loaded with Toluene by Supercritical Carbon Dioxide

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Abstract

Activated carbon loaded with toluene was regenerated by supercritical carbon dioxide. The adsorptive capacities after several regeneration cycles were still close to that of virgin carbon and remained stable. The effects of temperature, pressure, and flow rate on regeneration efficiency were studied. It was found that the operations at higher pressures were more favorable for regeneration, but the optimal operating temperature depended on pressure. The interphase mass transfer resistance was insignificant during regeneration. A one-parameter mathematic model assuming linear desorption kinetics is proposed which agrees well with the experimental data. The adsorption rates of activated carbon regenerated by the supercritical regeneration method and the steam regeneration method are compared in this study. It was found that the supercritical regeneration method is superior to the steam regeneration method.

INTRODUCTION

Supercritical fluid extraction has received widespread attention in recent years. One of the applications of this technology is to regenerate activated carbon (*1*, *2*). Kander and Paulaitis (*3*) studied the desorption of activated carbon loaded with phenol by supercritical carbon dioxide. They found that the supercritical carbon dioxide offered no significant thermodynamic advantage for regenerating carbon loaded with phenol, but they believed that carbon dioxide may be a powerful desorbent for

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other organic compounds which are not adsorbed strongly on activated carbon. DeFilippi et al. (*4*) studied the regeneration of activated carbon loaded with pesticides by supercritical carbon dioxide. They observed that the supercritical regeneration method was economical even though the operating temperature and pressure were above 387 K and 150 atm, respectively. A local equilibrium model using the Freundlich isotherm was propsed by them, and it was able to explain the experimental data.

Toluene is an important solvent used in petrochemical and polymer industries and is commonly emanated from industrial plants. To recover it from the effluent gas streams, activated carbon is generally employed. Since toluene is soluble in supercritical carbon dioxide (*5*, *6*) and is not strongly adsorbed on activated carbon as compared with phenol, to regenerate activated carbon by supercritical carbon dioxide seems to be a promising method according to the observation of Kander and Paulaitis (*3*). Hence, the main objective of this paper is to study the regeneration of activated carbon loaded with toluene by supercritical carbon dioxide at different operating conditions. A second objective is to propose a mathematical model which is plausible to describe the desorption phenomena in a packed column under supercritical operations.

Because the steam regeneration method is customarily employed to regenerate activated carbon (*7*, *8*), the third objective of this study is to compare the supercritical regeneration method with the steam regeneration method.

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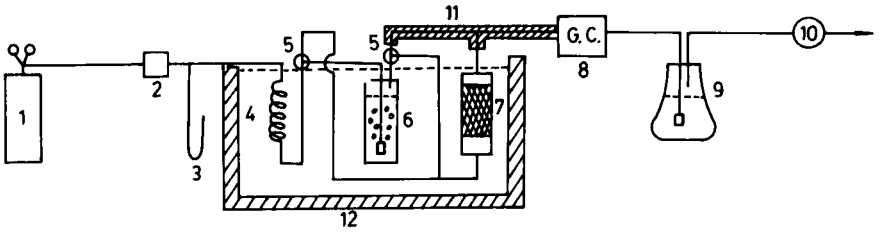
EXPERIMENTAL

Toluene was used as the adsorbate in this study since it is frequently used as the solvent in petrochemical and polymer industries and is often a constitutent of exhausted streams. A gas stream containing 1.74×10^{-3} mol/L toluene concentration was employed through this study by passing nitrogen through a container filled with about 12 cm of toluene (Fig. 1).

Virgin activated carbon (Merck 2514) was first screened to obtain a 18 to 20 mesh fraction (the average particle size was 0.1 cm). This fraction was boiled in deionized water to remove fines and was then dried in an oven at 393 K. After drying, about 5.3 g of activated carbon was packed in an i.d. 4.1 cm glass tube for adsorption experiments (Fig. 1). In order to achieve uniform flow distribution and to avoid possible end effects, glass beads of 0.1 cm diameter were packed in the regions above and below the activated carbon packing, both with heights about 4.0 cm. Platinum wires were used to support the packing in the column.



1. N_2 Cylinder
2. Mass Flow Controller
3. Manometer
4. Preheating Coil
5. Three Way Valve
6. Saturator
7. Adsorber
8. Gas Chromatograph
9. Collector
10. Wet Test Meter
11. Heating Tape
12. Constant - Temperature Bath

FIG. 1. Schematic diagram of apparatus used for adsorption experiments.

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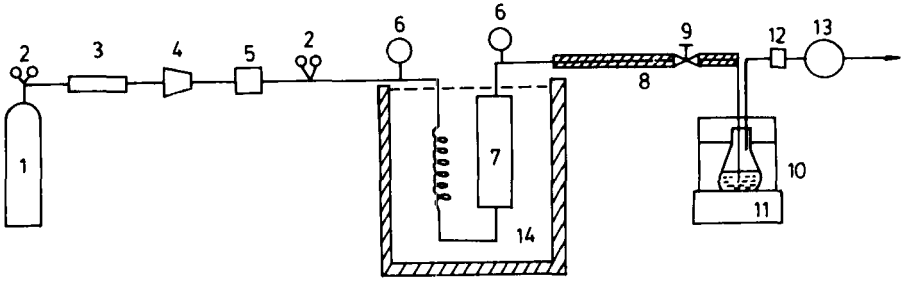
To execute the adsorption, the prepared gas stream was passed through the carbon column at 308 K. The flow rate was kept constant at 0.25 cm^3/s. A portion of the effluent was sent to a gas chromatograph (Varian 3700, FID detector) to analyze for the toluene concentration. The experiment was stopped when toluene breakthrough was achieved. The adsorptive capacity could then be obtained by measuring the weight differences of activated carbon before and after adsorption, which was about 0.20 (g of toluene)/(g of activated carbon). This amount was also checked with that obtained by integrating the breakthrough curve. The deviation was no more than 6.0%.

After the adsorption experiment the loaded activated carbon was taken out of the adsorber and was packed in a S.S. 316 tube (regenerator) with i.d. 2.12 cm. In order to make the supercritical fluid uniform in the packed bed, glass beads of 0.1 cm diameter were also packed in the regions above and below the activated carbon packing to heights of about 4.0 cm. Then the packed column was put into the regeneration apparatus shown in Fig. 2. Carbon dioxide of 99.7% purity was used as the desorbent. It first passed through a silica gel bed in order to remove possible water vapor and then was compressed and sent to a surge tank by a diaphragm compressor (Superpressure Inc.) with a minimum charge pressure of 47.6 atm. In each desorption experiment the pressure was controlled to within 1.0% of the desired value. The temperature was controlled in a constant-temperature bath whose accuracy was within 0.5 K. A preheating coil of 0.3 cm diameter and about 110 cm length was immersed in the constant-temperature bath to make the carbon dioxide reach the desired temperature. The gas coming out of the extractor was



1. CO_2 Cylinder
2. Regulator
3. Silica Gel Bed
4. Compressor
5. Surge Tank
6. Pressure Guage
7. Regenerator
8. Heating Tape
9. Metering Valve
10. Cold Trap
11. Magnetic Stirrer
12. Filter
13. Wet Test Meter
14. Constant-Temperature Bath

FIG. 2. Schematic diagram of apparatus used for supercritical regeneration experiments.

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expanded across a metering valve. The flow rate in the extractor was then determined by measuring the volume of the expanded gas as it passed through a cold trap and a wet test meter. The accuracy for the volume measurement was within 1.0%.

The desorbed toluene was collected in a cold trap which contained 1 L isopropanol. Samples of 2.0 μL were frequently taken out for gas chromatograph (FID detector) analysis in order to obtain the desorption curves. After about 190 L carbon dioxide had passed through the column bed, the desorption experiment was stopped. Then the subsequent adsorption experiment was executed to obtain the adsorptive capacity. This capacity was compared with the desorption amount in the previous desorption experiment. The agreements were satisfactory with a deviation of less than 3.0%.

EXPERIMENTAL RESULTS AND DISCUSSION

In the present study each adsorption experiment and the subsequent desorption experiment were considered as a cycle. In Fig. 3, each cycle included the adsorption taking place at 308 K for 1.74×10^{-3} mol/L

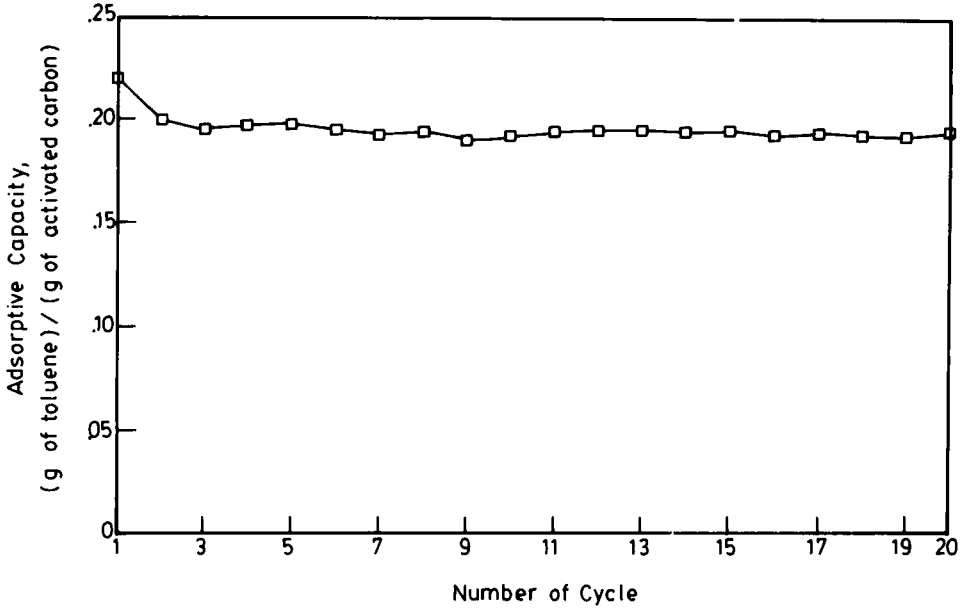

FIG. 3. Adsorptive capacities of regenerated activated carbon during the beginning cycles.

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toluene and the desorption occurring at 318 K and 119 atm. The total volume of carbon dioxide used for regeneration was about 190 L, lasting around 3 h. The average residence time of carbon dioxide in the packed activated carbon bed was about 1.2 min. Figure 3 shows that the adsorptive capacity of the regenerated activated carbon after the first cycle dropped to 88.0% that of the first cycle and remained stable. This phenomenon was also observed by Kander and Paulaitis (*3*).

When the carbon dioxide regeneration flow rate was fixed at 4.5 cm^3/min (calculated based on the operating temperature and pressure rather than on the normal conditions of 298 K and 1 atm), the effects of temperature at operating pressures of 87, 136, and 157 atm on the regeneration efficiency are shown in Figs. 4 to 6. Though the regeneration period in each experiment was more than 3 h, only the regeneration data at the beginning times are reported in these figures. Nevertheless, it can be seen that more than 50% regeneration for most of the runs could be achieved within the first hour. The reproducibility tests were executed at several operating conditions, and it was found that the average deviation of dynamic data was less than 3.0%, with a maximum deviation of about 5.0%.

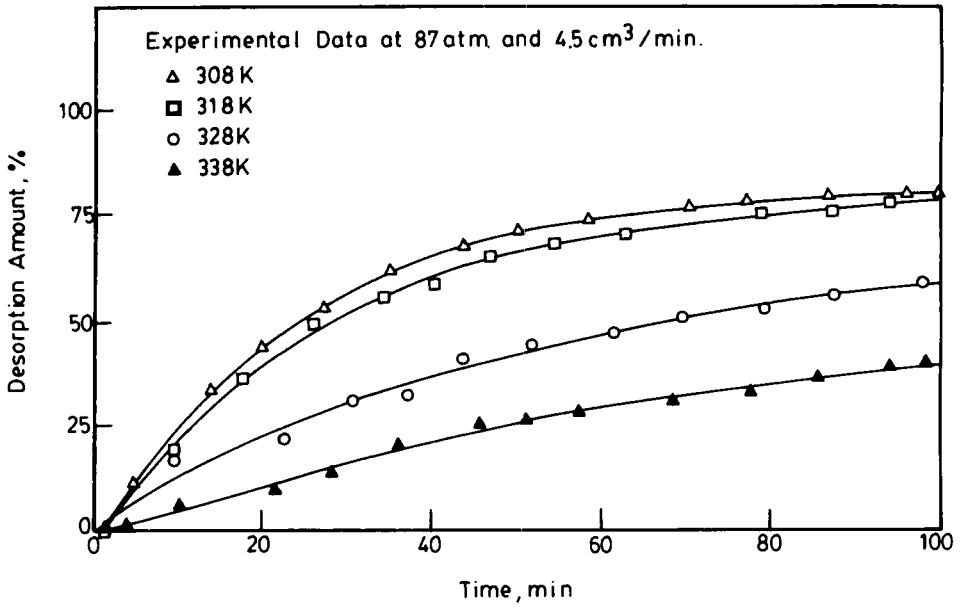

FIG. 4. Temperature effects on regeneration at 87 atm.

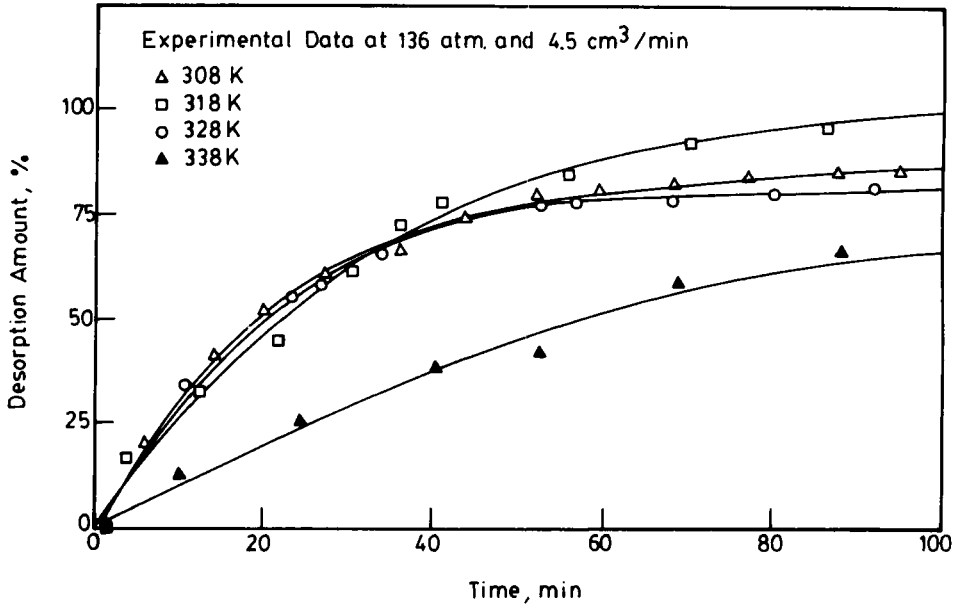

FIG. 5. Temperature effects on regeneration at 136 atm.

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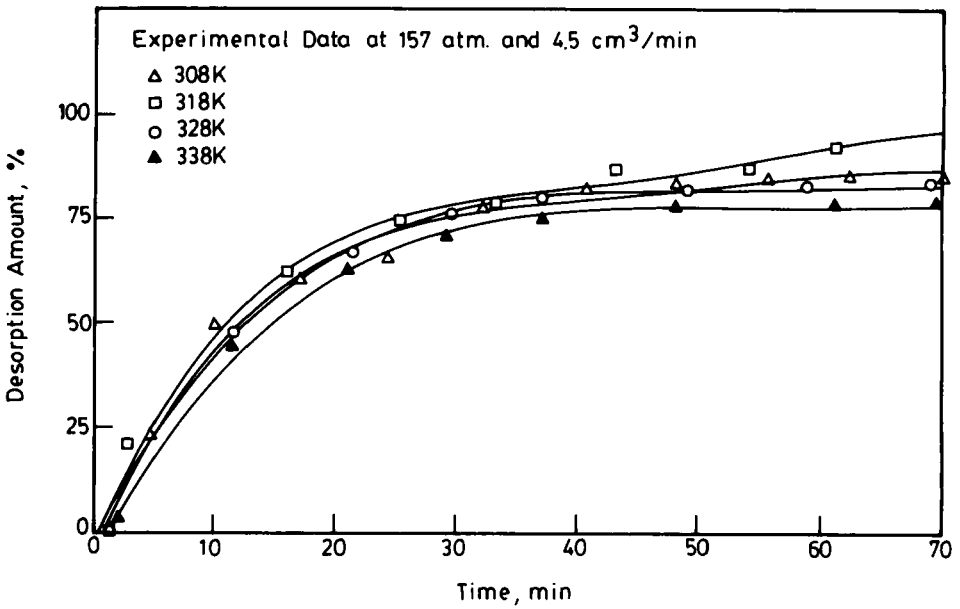

FIG. 6. Temperature effects on regeneration at 157 atm.

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Figure 4 indicates that the regeneration efficiency decreases with temperature at 87 atm. But when the regeneration pressures were raised to 136 and 157 atm, an optimal operating temperature existed, as shown in Figs. 5 and 6. Table 1 gives the density and viscosity of carbon dioxide at different oeprating conditions. In general, higher density may enhance the solubility of a solute in a supercritical fluid, but higher viscosity may have an adverse effect on the diffusion rate. At the lower operating pressure, 87 atm, the density effect seems more important, therefore the optimal regeneration condition is at the lowest temperature. But at the higher operating pressures, 136 and 157 atm, it seems that both the density and viscosity effects are important, hence an optimal temperature lies somewhere in the supercritical region. At the present time a general rule for obtaining the optimal temperature has not been found.

By comparing the desorption breakthrough curves within the first 60 min. from Figs. 4 and 6, it can be seen that the higher the operating pressure, the higher the regeneration efficiency. A representative illustration is given in Fig. 7, which shows the regeneration at different pressures at 318 K and 4.5 cm^3/min. This pressure effect may be due to an increase

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TABLE 1
Density and Viscosity of Carbon Dioxide at Various Conditions

Temperature (K)	87 atm		136 atm		157 atm	
	Density (g/cm^3)	Viscosity ($g/cm \cdot s \times 10^4$)	Density (g/cm^3)	Viscosity ($g/cm \cdot s \times 10^4$)	Density (g/cm^3)	Viscosity ($g/cm \cdot s \times 10^4$)
308	0.60	4.47	0.78	6.74	0.82	7.03
318	0.34	2.75	0.66	5.42	0.75	6.27
328	0.24	2.29	0.53	4.29	0.67	5.27
338	0.21	2.11	0.46	3.51	0.56	4.36

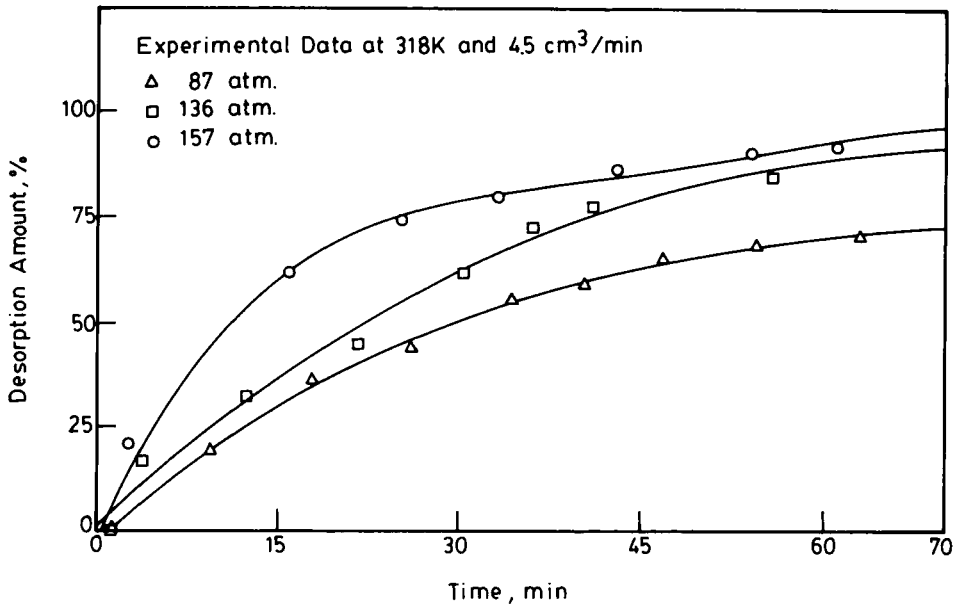

FIG. 7. Pressure effects on regeneration at 318 K.

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in density. Numerous studies have indicated that the solubility of a solute in a supercritical solvent increases with density (*2*, *9–11*). Therefore, desorption may occur more easily at higher fluid densities or at higher regeneration pressures.

The adsorption breakthrough curves for the regenerated activated carbon are shown in Figs. 8 and 9. It is seen that the better adsorptive capacities within a certain period of time were obtained for the better regeneration cases shown in Figs. 6 and 7. This consistency indicates that the results obtained in this study were reliable, and the optimal regeneration conditions might be sought from either the adsorption or the desorption dynamic data.

Since the interphase mass transfer coefficient is a hydrodynamic property, regeneration may be influenced by the flow rate of the regenerating fluid. Figure 10 illustrates that the desorption amounts at 4.5 and 17.5 cm^3/min were quite close. This idnicates that the interphase mass transfer resistance during regeneration under supercritical operations was relatively insignificant. Hence, the transport resistance in activated carbon particles might come from intraparticle diffusion and adsorption equilibrium.

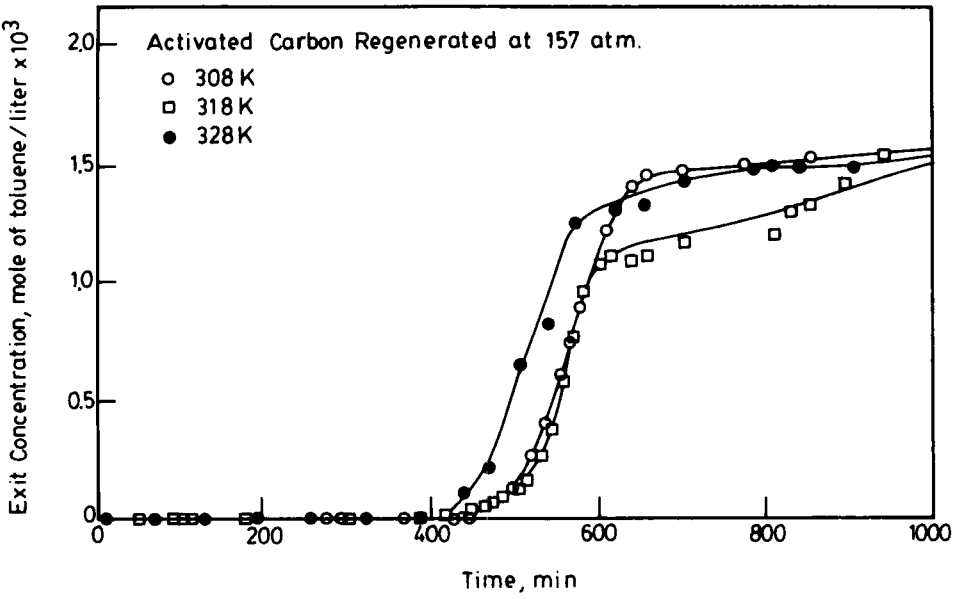

FIG. 8. Adsorption breakthrough curves for activated carbon regenerated at different temperatures at 157 atm.

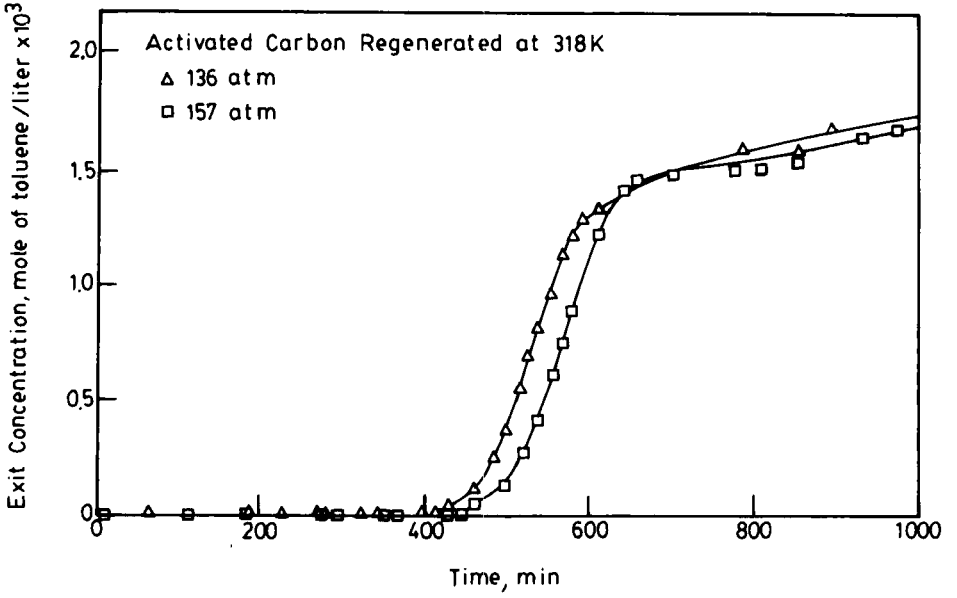

FIG. 9. Adsorption breakthrough curves for activated carbon regenerated at different pressures at 318 K.

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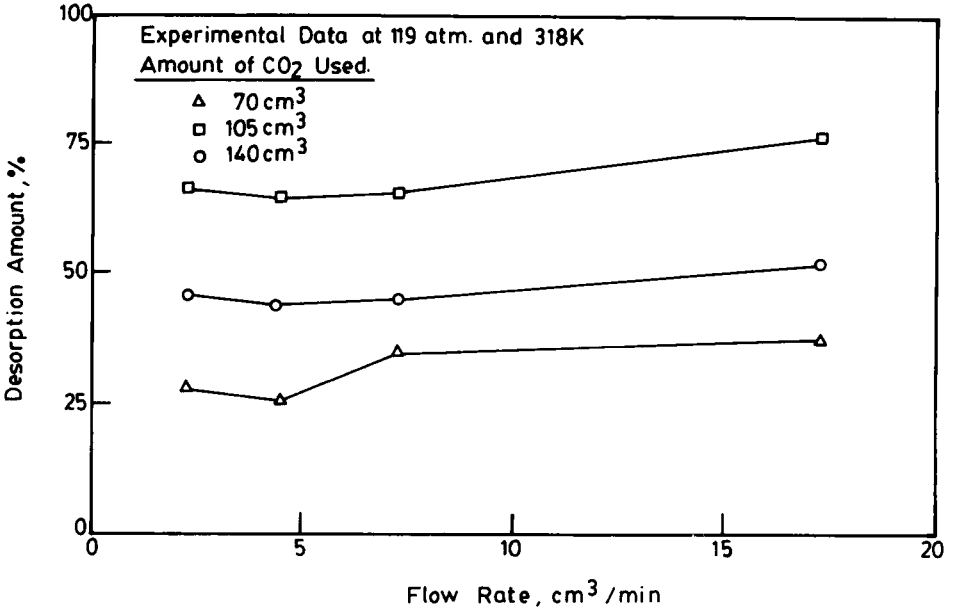

FIG. 10. Flow rate effects on regeneration at 318 K and 119 atm.

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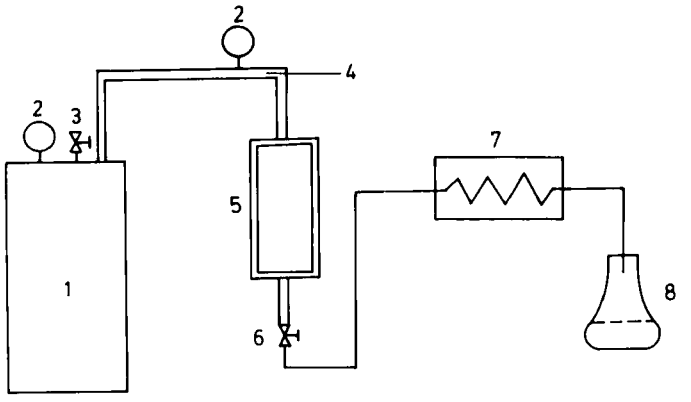
For most industrial plants, steam is used to regenerate activated carbon for the recovery of organic solvents. It is therefore of interest to compare the regeneration efficiencies using steam and supercritical carbon dioxide as desorbents. The apparatus used for the steam regeneration method in this study is illustrated in Fig. 11. The adsorption and desorption procedures were the same as described for the supercritical regeneration method. The temperature and pressure of the steam were 400 K and 4.5 atm, respectively. The flow rate was about 46.5 g/min, and the operating period lasted around 2 h. Figure 12 shows the adsorption data for the regenerated activated carbon from these two methods when the supercritical method was operated at 313 K and 136 atm. It is seen that the adsorptive capacities of the regenerated activated carbon using steam as the desorbent dropped greatly after the first cycle and that there was a large difference in breakthrough times between these two methods. The quick appearance of the breakthrough time in the steam regeneration method was probably due to the increase of the transport resistance in activated carbon caused by the condensed water. From the results shown in Fig. 12 it is concluded that the supercritical regeneration



1. Steam Generator
2. Pressure Gauge
3. Safety Valve
4. Thermocouple
5. Regenerator
6. Metering Valve
7. Condenser
8. Collector

FIG. 11. Schematic diagram of apparatus used for steam regeneration experiments.

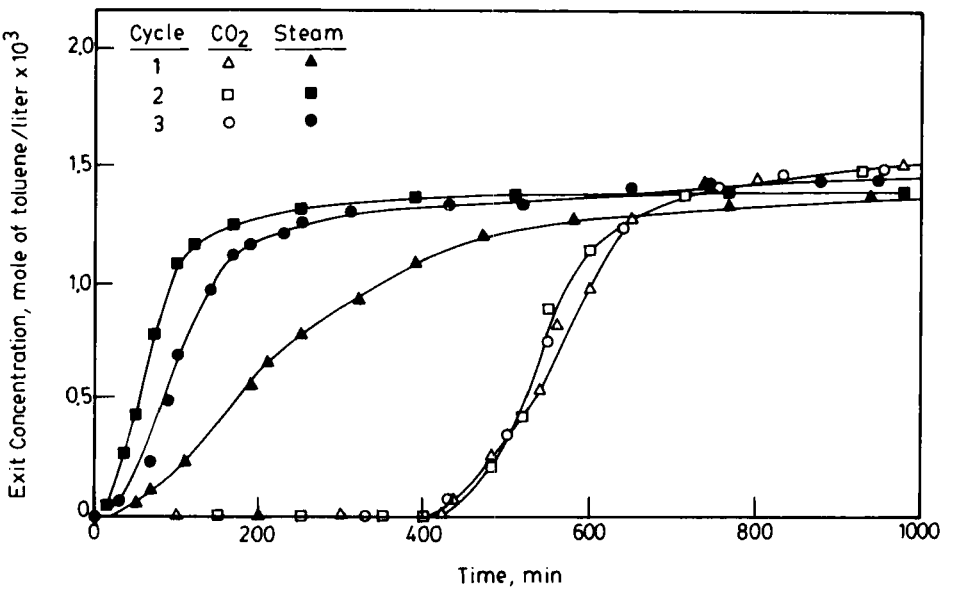


FIG. 12. Adsorption data for activated carbon regenerated by steam and supercritical carbon dioxide.

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method is superior to the stream method for adsorptive capacity in a certain period of time.

MODEL DESCRIPTION

Since there are many mathematical models available in the literature for adsorption in a packed column (*8*, *12*, *13*), and the main purpose of this study was to examine the regeneration efficiency by supercritical carbon dioxide, attention is paid here only to the development of a model for regeneration. The development is based on the mass conservation of toluene.

Suppose the axial dispersion effect can be neglected. The mass balance in the bulk phase in the column may be written

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

The initial and boundary conditions are

$$t = 0, C = 0 \tag{2}$$

$$z = 0, C = 0 \tag{3}$$

Because of the insignificance of the interphase mass transfer resistance, only the intraparticle diffusion resistance and the adsorption equilibrium need to be considered to construct the mass balance for an activated carbon particle. But due to the lack of information on the effective diffusivity of toluene in supercritical carbon dioxide and the adsorption isotherm, the mass balance for an activated carbon particle using linear desorption kinetics was proposed for this study. It may be expressed by

$$\partial S/\partial t = -kS \tag{4}$$

The initial condition is

$$t = 0, S = S_0 \tag{5}$$

By using Eqs. (4) and (5), the concentration at the exit of the column can be obtained by solving Eqs. (1) to (3). It is expressed by

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$$C_e = \frac{1-\varepsilon}{\varepsilon} S_0 \left[\exp\left(-k\left(t - \frac{\varepsilon L}{u}\right)\right) - \exp(-kt) \right] \qquad (6)$$

The total amount of desorbed toluene can then be calculated by integrating C_e with respect to time.

DISCUSSION

The adsorption rate constant k was evaluated by fitting Eq. (6) with the experimental data. The IMSL subroutine ZXSSQ was employed to achieve this fit. With the calculated k, the simulated results matched well with the experimental data for all operating conditions; some are shown in Figs. 13 and 14. The maximum deviation was no more than 10%, and the average deviation was about 6.0%. These agreements indicate that it is plausible to explain the mass transfer process in the regeneration stage by the one-parameter model.

If the desorption rate constant follows the Arrhenius law, the following linear relation exists:

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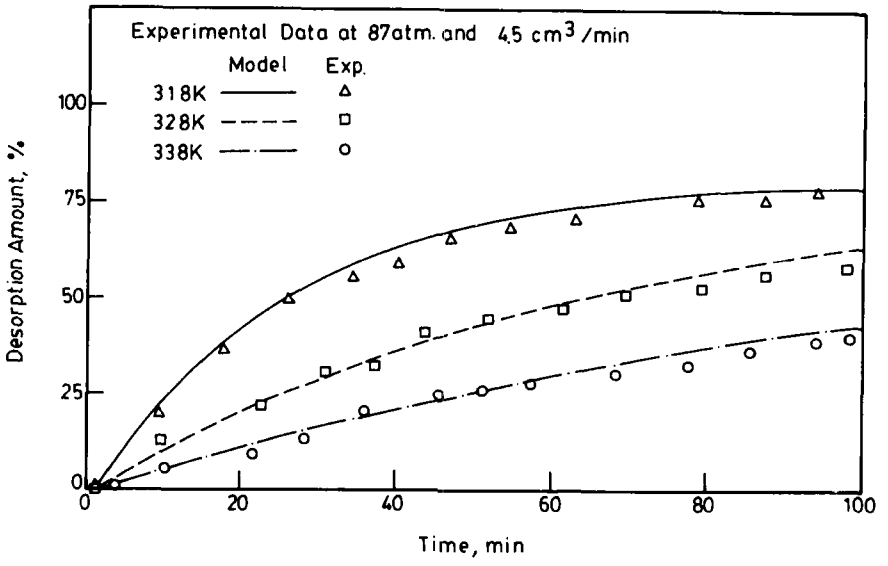

FIG. 13. Comparison of simulated results with experimental data at 87 atm.

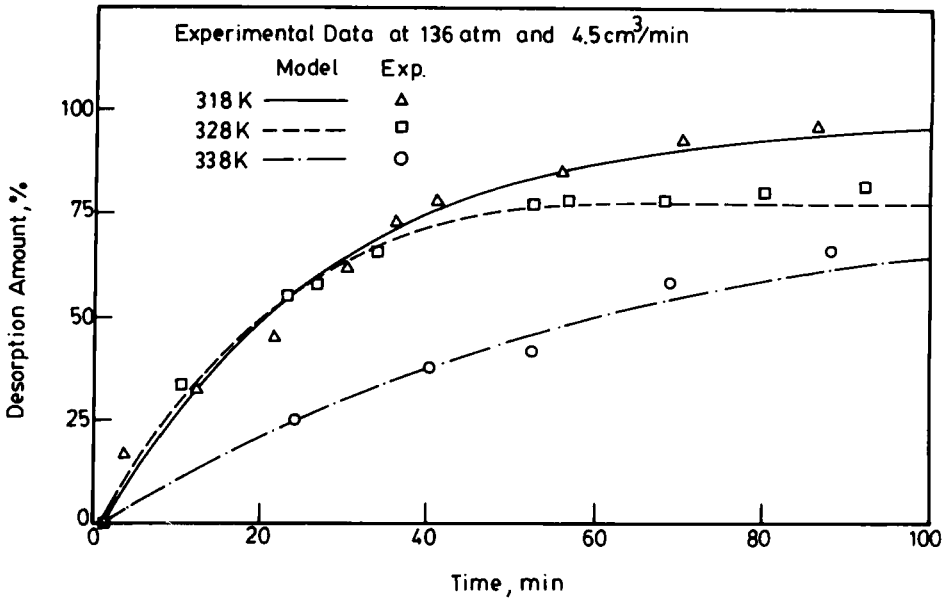

FIG. 14. Comparison of simulated results with experimental data at 136 atm.

$$\ln k = \ln k_0 - \frac{E}{RT} \tag{7}$$

Although this assumption may not be correct because an optimal temperature was observed under supercritical operations, it gives us an idea of how easy it is to regenerate activated carbon loaded with toluene. Suppose this assumption is allowed. Then, from the slope of the plot of ln k vs $1/T$, the desorption activation energy can be calculated. This plot is shown in Fig. 15, from which the activation energies were found to be 17, 15, and 10 kcal/mol for 87, 136, and 157 atm, respectively. The smaller desorption activation energy at higher pressure may be evidence that operations at higher pressures are more favorable for regeneration.

CONCLUSIONS

Regeneration of activated carbon loaded with toluene by supercritical carbon dioxide had been experimentally studied and mathematically analyzed.

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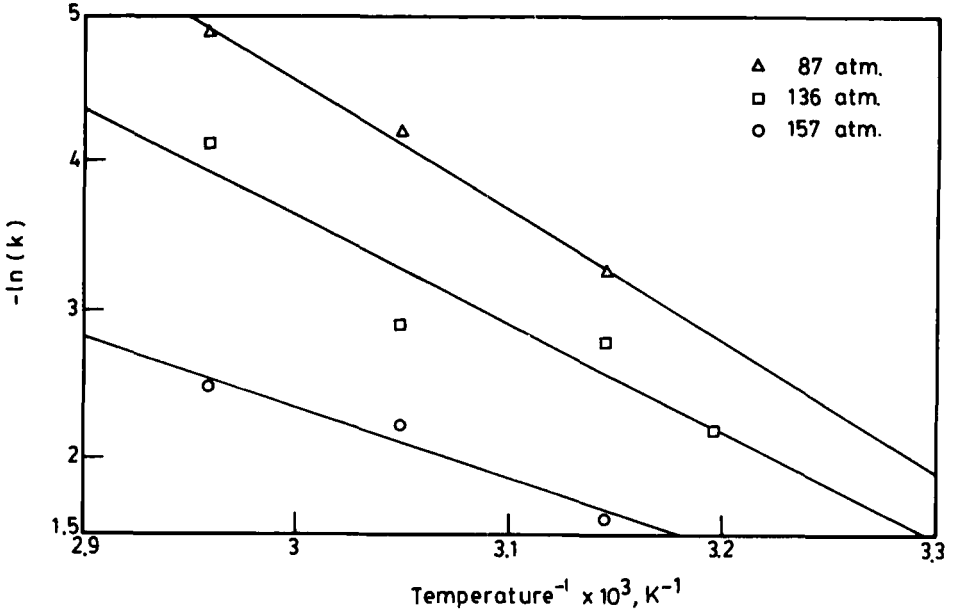

FIG. 15. Plot of ln k vs $1/T$.

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The adsorptive capacity of the regenerated activated carbon was found to be close to that of the virgin carbon and remained stable after several regeneration cycles. The effects of temperature, pressure, and flow rate of carbon dioxide on regeneration efficiency were studied. It was found that the higher operating pressures were more favorable for regeneration; this is probably due to the increase of density. Besides density, viscosity may also play an important role. These two properties determine the optimal operating temperatures at different pressures. A general rule, however, has not yet been found. The interphase mass transfer reistance was found to be unimportant, hence the transport resistances in activated carbon particles may come from intraparticle diffusion and adsorption equilibrium.

A one-parameter mathematical model using linear desorption kinetics was proposed. The simulated results by this model matched well with the experimental data for all operating conditions.

NOTATION

C concentration of toluene (mol/cm^3)
C_e exit concentration of toluene (mol/cm^3)

E activation energy (kcal/mol)
k desorption rate constant
k_0 desorption rate constant at the reference state
S loaded toluene on activated carbon (mol/cm^3)
S_0 initially loaded toluene on activated carbon (mol/cm^3)
T temperature (K)
t time (s)
z axial position in column (cm)

Greek Symbols

ε void fraction in the packed column

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Acknowledgment

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