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Desorption of Salicylic Acid from Modified Bentonite by Using Supercritical Fluids in Packed Bed Column

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ABSTRACT

Desorption of salicylic acid from organically modified bentonite by using supercritical fluids (SCFs) was studied. The parameters, such as pressure, temperature, SCF flow rate, and cosolvent (entrainer) concentration, were investigated. A desorption yield of 40 wt% salicylic acid was obtained by using supercritical CO_2 by operating at low pressure (300 bar), low temperature (40°C), and 2 mL CO_2/min, it reached up to 77 wt% in the presence of ethanol as cosolvent 10 vol%. Similarly, a maximum desorption yield of 76 wt% salicylic acid was obtained by using supercritical CO_2 by operating at high pressure (500 bar), high temperature (80°C),

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and 2 mL SC CO_2/min, it reached up to 98 wt% in the presence of ethanol as cosolvent 10 vol%. Hence, it was concluded that the mean contents in the desorbed solute are approximately 1.5–2-fold higher by addition of 10 vol% ethanol than only supercritical CO_2 desorption process.

Key Words: Adsorbent regeneration; Desorption; Supercritical fluids; Modified bentonite.

INTRODUCTION

Soil remediation and adsorbent regeneration using CO_2 in a supercritical fluid extraction (SFE) process is one innovative technique now available. This technology has been successfully applied to a variety of soil pollutants: hydrocarbons, pesticides, phenols, etc, in a word, persistent pollutants of difficult treatment. The properties of gases under supercritical conditions (31°C and 73 bar for CO_2) are considered ideal to extract substances from a solid matrix as is required for the regeneration of adsorbents. These supercritical fluids (SCFs) exhibit densities similar to those of liquids (high solvent strengths) and diffusion coefficients similar to those of gases (excellent transport characteristics), enabling them to effectively dissolve and/or desorb contaminants from the surface and to easily enter/exit even the smallest pores and carry away any released material.

The extraction and recovery a solute from a solid matrix can be regarded as a five-stage process: the desorption of the compound from the active sites of the matrix; diffusion into the matrix itself; solubilization of the analyte in the extractant; diffusion of the compound in the extractant; and collection of the extracted solutes. To obtain quantitative and reproducible recoveries, careful control and optimization of each step are required; in particular, the collection of the extract needs to be carefully controlled, as it is often neglected when compared with the extraction step. In practical environmental application (e.g., extraction of pollutants from solids and sediments), the first step is usually the rate-limiting step, as solute–matrix interactions are very difficult to overcome and to predict. However, for other matrices (e.g., plant materials), the rate maybe limited by either the solubilization or diffusion step. As a consequence, the optimization strategy will strongly depend on the nature of the matrix to be extracted.[29]

The SCF technologies, such as SFE and supercritical water oxidation (SCWO), are drawing much attention as emerging techniques for soil remediation and adsorbent regeneration due to the following attractive features:

a. Cleanness. A SCF process uses environmentally benign solvents (CO_2 and water) to extract/destroy pollutants in contaminated soils/sediments without destroying the structure and altering the major properties of the treated soils/sediments.

b. Quickness. The cleanup can be achieved in a relatively short processing time.
c. Wide range of application.[2]

Contaminated soils, wastewater, chemical industry sludges, and solid adsorbents are major environmental concerns. Salicylic acid and its derivatives are also toxic when consumed in large amounts.

Among the earliest applications of SCF technology was the regeneration of adsorbents, including activated carbon.[1,2] In the case of the activated carbon regeneration, researchers have showed that desorption processes under supercritical condition are hindered by a strong affinity between organic compounds and a carbon surface, which diminishes the recovery yield. In the past decades, extensive research has been conducted to develop innovative, effective, inexpensive, easy regenereable, and promising adsorbent materials for dealing with the treatment problem of contaminated wastewater. Organically modified clays are the adsorbent materials that generally have the potential of meeting this requirement.[3–8] Particularly, in the past 10 years, there has been much interest and advancement in the use of organoclays as adsorbants to remediate organic contamination.[7–14] Among the various organoclays, organobentonites are the most widely investigated by many researchers.[4,11,15–18] Organobentonites are produced by replacing exchangeable inorganic cations (e.g., Na^+, Ca^{2+}, H^+) on the internal and external mineral surfaces of bentonite with quaternary alkylammonium cations. Naturally occurring bentonite is not efficient as an adsorbent for the uptake of hydrophobic organic pollutants from aqueous solution primarily because of the electrically charged and hydrophilic characteristics of its surface. With this exchange treatment, the bentonite surfaces are drastically altered. As a result, the organobentonites are turned into strong adsorbents for nonionic organic pollutants compared with the natural one.[8] The sorption properties of organobentonites depend greatly on the characteristics of the exchanged organic cations. Smith and Galan[12] demonstrated that tetrachloromethane sorption to bentonite modified by exchanged small organic cations was characterized by nonlinear isotherms, strong solute uptake, and competitive sorption. In contrast, tetrachloromethane sorption to bentonites modified by relatively large organic cations ($C > 10$) was characterized by essentially linear isotherms, lower solute uptake, and noncompetitive sorption. The authors concluded that the differences between the two groups of organoclay sorbents were attributable to different sorption mechanisms: adsorption for bentonite modified with organic cations of small functional groups and partition for bentonite modified with organic cations of relatively large functional groups. The small organic cations (e.g., tetramethylammonium) create relatively rigid, nonpolar surface amenable to nonionic solute uptake by adsorption. The larger organic cations (e.g., hexadecyltrimethylammonium bromide) create an organic partition medium through the conglomeration of their flexible alkyl chains. Hence, the organobentonites are turned into strong adsorbents for nonionic organic pollutants compared with the natural one. Although, these organoclays find growing usage in environmental applications such as contaminant fixation and fuel spill control, systematic studies to achieve optimum adsorption parameters of adsorption of organic contaminants onto organobentonites have not been studied extensively, and there are minor studies in this subject.[6,18]

In addition, organically modified bentonites are adsorbents that easy regenereable under supercritical conditions. Park and Yeo[19] found that the extraction percentages of phenols reached up to 92.6 wt% in 3 hr of extraction with an ethanol cosolvent for an hexadecytrimethyleammonia-bentonite (HDTMA-B), and it was determined that HDTMA-modified montmorillonite exhibited undiminished adsorption power toward phenols after three regeneration cycles. Salgın et al.[20] also found that the maximum desorption of phenol approximately 98 wt% by using supercritical CO_2 (SC CO_2) was obtained by operating at 500 bar, 353 K, 3.33×10^{-8} CO_2 m^3/sec, and results showed that regenerated octadecyltrimethylammonia bromide-bentonite (ODTMA-B) exhibited undiminished adsorption power toward phenol after several regeneration cycles.

Salicylic acid was a key component of medical treatment throughout history. It also is used as a raw material for other pharmaceutical compounds, aromachemicals (for perfumes and fragrances), dyes, and as a pH regulator in the manufacture of phenolic resins and in potassium extraction. Various industrial and hospitals wastewater containing salicylic acid respect of public health and environment is a great concern. Methods such as aeration, biological degradation, chemical oxidation, photo oxidation, solvent extraction, and adsorption have been developed for the removal of this type of organic pollutants. Adsorption is preferred over all methods for the reason that it is nondestructive and recovery of the organics through regeneration is relatively easy.[21] The SFE process maybe expected to be favorable technology for the regeneration of the adsorbent as well as for the recovery of the adsorbed materials from the adsorbent.[19]

Studies about salicylic acid solubilities in pure SC CO_2 and various cosolvents were determined at different temperatures and pressures.[22,23] To determine supercritical desorption behavior of salicylic acid in contaminated soil and the regeneration of activated carbon, supercritical adsorption equilibria was studied at different temperatures and pressures ranges, 35–55°C and 90–250 bar, respectively.[24] Repeated adsorption of phenolic acids on clays, as an alternative adsorbent, also was studied.[30]

In this study, recovery of salicylic acid and regeneration of adsorbent was carried out in a SFE system at various pressures, temperatures, cosolvent concentration, and SCF flow rates.

MATERIALS AND METHODS

Materials

Na-bentonite from Çankırı in Turkey was used in this study. The chemical analysis of the bentonite is given in Table 1. Cation exchange capacity (CEC) of original bentonite was determined by the methylene blue test (ANSI/ASTM C 837-76). Total organic carbon analyses were performed by using TOC C-MAT 5500 (Strohlein, Germany).

XRD Analysis

The x-ray powder diagrams of the original and the organobentonites, prepared as random powder material, were obtained with a Rikagu D-max 2200 powder difractometer (Rikagu D-max 2200, Japan and Philips CuK_{α}, Netherlands). Montmorillonite was the main mineral in the samples. Minor amounts of quartz, α-cristobalite, albite also were identified in the raw materials.

Particle Size Analysis

The particle size distributions of the solid samples were determined by using a Malvern Mastersizer 2000 (Hydro 2000 MU) particle analyzer, which is based

Table 1. Chemical analyses of the original bentonite.

Sample	Na-B
MgO	0.85
Al_2O_3	15.50
SiO_2	70.74
CaO	0.46
Fe_2O_3	2.23
SO_3	0.17
K_2O	0.24
Na_2O	2.12
TiO_2	0.00
KK[a]	6.53

[a] Weight loss at 1000°C.

on the principle of laser ensemble light scattering. The particles are introduced to the analyzer beam in a sample presentation cell located in the optical unit.

Brauner–Emmet–Teller Analysis

Specific surface areas (BET) and pore-size distributions of the original and organobentonite samples were determined by using the Quantachrome NOVA 2200 series volumetric gas adsorption instrument. The determination is based on the measurements of the adsorption isotherms of nitrogen at −196°C. Before measurements were started, moisture and gases such as nitrogen, oxygen, which were adsorbed on the solid surface or held in the open pores, were removed under reduced pressure at 150°C for 5 hr.

Synthesis of Adsorbent (ODTMA-B)

For the exchange of organic cations with inorganic ions, (ODTMA, Fluka) was used.

Organically modified montmorillonite was synthesized by adsorbing a CEC equivalent amount of ODTMA on the clay. The amount of ODTMA-B equal to the CEC of sodium (85 meq/100 g clay) bentonite was dissolved in 1 L distilled water and added to bentonite suspension and agitated for 12 hr at 25°C. After mixing period, ODTMA-B suspensions were separated from water by centrifuging and washed by distilled water until little ODTMA was found in the washed solution. The synthesized organobentonite was freeze-dried and preserved in a brown bottle until use.

Preparation of Salicylic Acid Loading Bentonite

To prepare a salicylic acid loading sample, 1 L of prepared solution containing 500 mg/L salicylic acid was placed in a flask and 20 g of organobentonite was added. The flask was then placed in the constant temperature shaker, which was set at 150 rpm for 24 hr at 25°C. At equilibrium, the supernatant was centrifuged and the concentration was determined at 323 nm by using a UV/VIS spectrophotometer (UV-1601A, Shimadzu). Hence, salicylic acid loading samples containing 15.5 mg salicylic acid/g bentonite were obtained.

Supercritical Desorption Experiments

Desorption of salicylic acid from organobentonite by using SC CO_2 was performed with a semicontinuous SFE system (SFX System 2120, Isco Inc., Lincoln, NE).

In each desorption experiment, a known mass of adsorbent loaded with salicylic acid (about 0.25 g) was put in a 0.5-mL fixed-bed column and 0.5-μm filters were placed at both ends of the column to prevent any carryover of particles. Care was taken to ensure that the air was purged by using CO_2. The column was then placed into the temperate-controlled chamber of the SCF system. A preset operation temperature was reached; then CO_2 was then charged into the high-pressure syringe pumps from a CO_2 tank. The high-pressure syringe pump further compressed the CO_2 to the desired pressure. Then the valve between the high-pressure syringe pumps and the SCF system was opened and the SC CO_2 was allowed to flow at a constant rate. The supercritical phase at the outlet of the column was passed through the automatic valves to reduce the pressure slowly. The temperature of the restrictor was kept at 60°C (±5°C). The desorbed solute was collected in collection vials that contained ethanol.

The desorption experiments runs were carried out in the range of 0.5, 1, and 2 mL/min CO_2 flow rates; 40°C, 60°C, and 80°C temperatures; 300, 400, and 500 bar pressures; and 1, 2.5, 5, 10, and 20 vol% entrainer (ethanol) concentrations for 6 hr.

RESULTS AND DISCUSSION

Characterization of Adsorbent

Total organic carbon content, BET surface areas, and basal spacing [*d*(0 0 1)] of the original and the treated bentonite are presented in Table 2. The organic carbon content of the natural clay sample was very low in comparison with the ODTMA-B. The organic carbon in the ODTMA-B was almost entirely derived from the exchanged organic cations.

The x-ray diffraction basal spacings *d*(0 0 1) of the original bentonite was 12.4 Å (Table 2). The interlayer spacings of organobentonite increased with the quaternary ammonium cations used in synthesizing and it reached to 17.6 Å for ODTMA-B. These spacings for ODTMA-B correspond to formation of bilayers and paraffin complexes in which ODTMA ions are in direct contact with each other, leading to the formation of partition phases derived from the C_{18} hydrocarbon groups.

Table 2. Properties of original and organobentonite.

Sample	Total organic carbon content (%)	Surface area (m^2/g)	*d* (0 0 1)
Original	0.7	55.37	12.40
ODTMA-B	24.28	28.92	17.60

The BET surface areas of original Na-B was 55.37 m^2/g. This data decreased to 28.92 m^2/g for organobentonite (ODTMA-B); ODTMA-B was more aggregated and had lower surface areas than the natural clay. The relatively low surface areas of the ODTMA-B indicate external surface only, no internal surface area was accessible to nitrogen gas.[25]

For a textural characterization of any porous solid, the concept of surface area does not give a visual picture of it. Pore size and pore-size distributions are necessary if the material is to be fully characterized. The pore-size distribution in the mesopore region was obtained by applying the method of Barret–Joyner–Halena (BJH)[26] to the desorption branch of the isotherms of nitrogen at −196°C, assuming the pores to be cylindrical in shape. Figure 1 compares the change of pore-size distribution for the original and the ODTMA-B. As seen from the figure, the samples have almost mesopores of which diameters are between 20 and 500 Å. The original sample exhibited maxima in differential pore volumes at about 39.34 Å in pore diameter. However, ODTMA-B showed maximum differential pore volumes at about 27.64 Å. After that, the differential pore volumes for these samples tend to decrease as the pore diameter decrease. It should be considered that the pores were closed by adsorbed ODTMA cations.

Particle-size analysis of the original and organobentonites also were carried out. The particle-size distributions for both the original and the organobentonites were shown in Fig. 2(a) and (b). The distributions are presented

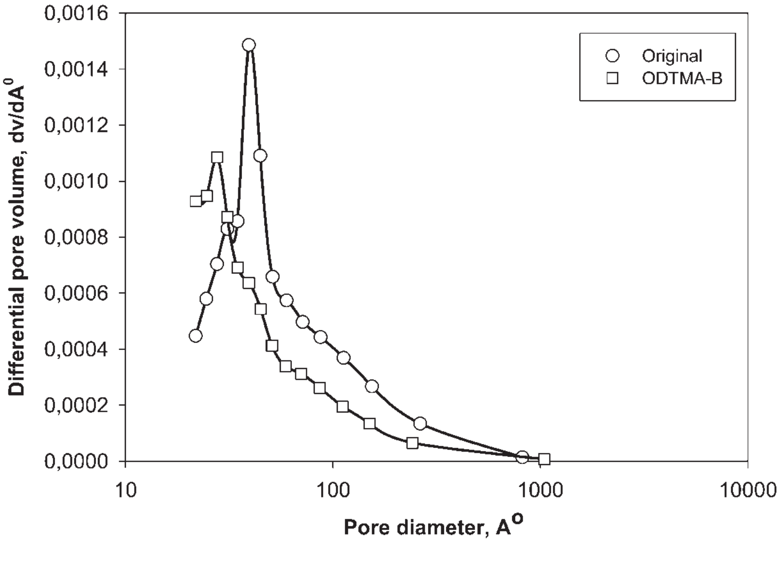
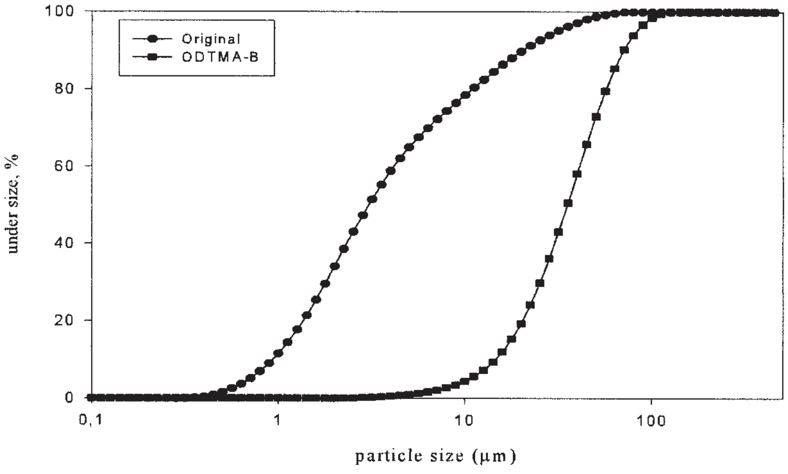
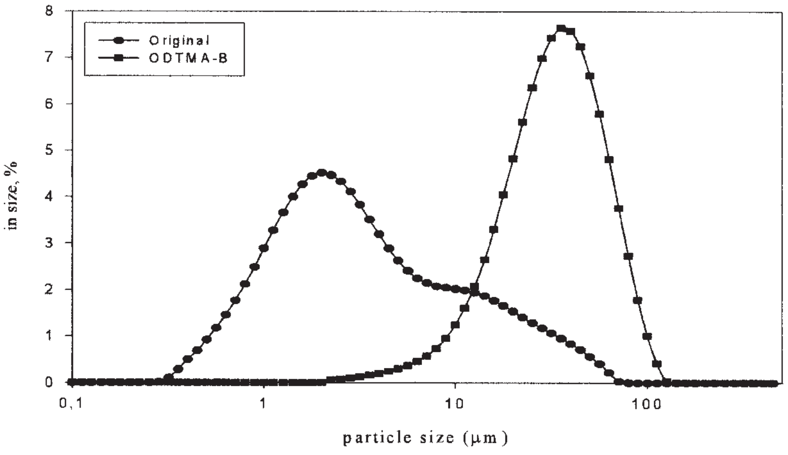


Figure 1. Pore-size distributions of original and ODTMA-B.



(a)



(b)

Figure 2. Particle-size distribution: (a) under size, (b) in size.

in terms of undersize [Fig. 2(a)] and in size [Fig. 2(b)]. Analysis of the original and organobentonites showed that the organobentonites contain more coarse particle than the original bentonite. It was obvious [Fig. 2(a) and (b)] that the whole size range of the original bentonite was finer than the organobentonite. As can be seen from Fig. 2(a) about 80% of the original bentonite is less than 10 μm, whereas, 5% of ODTMA-B is less than 10 μm. The distributions of the particles in the bulk obtained from organobentonite are more uniform than the original sample size distribution, as shown Fig. 2(b).

Analysis of Salicylic Acid Desorption from Organobentonite

The effect of desorption (extraction) parameters such as pressure, temperature, SCF flow rate, and cosolvent concentration was studied. Desorption yield (kg desorbed salicylic acid/kg sample) is defined as the mass of desorbed salicylic acid divided by the mass of the initial loaded salicylic acid on adsorbent. The cumulative amount of CO_2 is defined as the total mass of CO_2 passed through the packed bed column divided by the mass of sample.

The first set of the desorption experiments was designed to investigate the effect of desorption process temperature on desorption yield and rate. Desorption was carried out at constant pressures of 300, 400, and 500 bar, respectively, and by using SC CO_2 at 2 mL/min and temperatures varying from 40°C, 60°C and 80°C,. As seen in Fig. 3(a)–(b) that a general trend of increasing desorption yield with increasing temperature at especially medium-and high-pressure conditions.

However, increasing temperature leads to a decrease in density at constant pressure and lower solvent power of the SC CO_2, increasing temperature increases vapor pressure of the solute. Hence, the vapor pressure of the solute is dominant in this desorption process.

It is evident from these figures [Fig. 3(a)–(c)] that the initial desorption rate increased with temperature under all pressure conditions. However, it was observed that the change of the desorption rates is marked at 400 and 500 bar according to 300 bar.

The second set of the desorption experiments was designed to investigate the effect of desorption process pressure on desorption rate and yield. Desorption was carried out at constant temperatures of 40°C, 60°C, and 80°C and by using SC CO_2 at 2 mL/min and pressures varying from 300, 400, to 500 bar, respectively. As seen in Fig. 4(a)–(c), a general trend of increasing desorption yield with increasing pressure. The change of desorption yield depends on solvent power, which is related to solvent density. In general, solvent power of the SCFs increases with increasing density.[27] Solvent density is based on pressure and temperature.

At constant temperature, the increase in solvent density with pressure overcame the relatively small change of solute vapor pressure, resulting in favored desorption at a higher pressure. Roy et al.[28] explained that this crossover property due to the solubility is controlled by a balance between solvent density and solute vapor pressure change with the change of pressure and

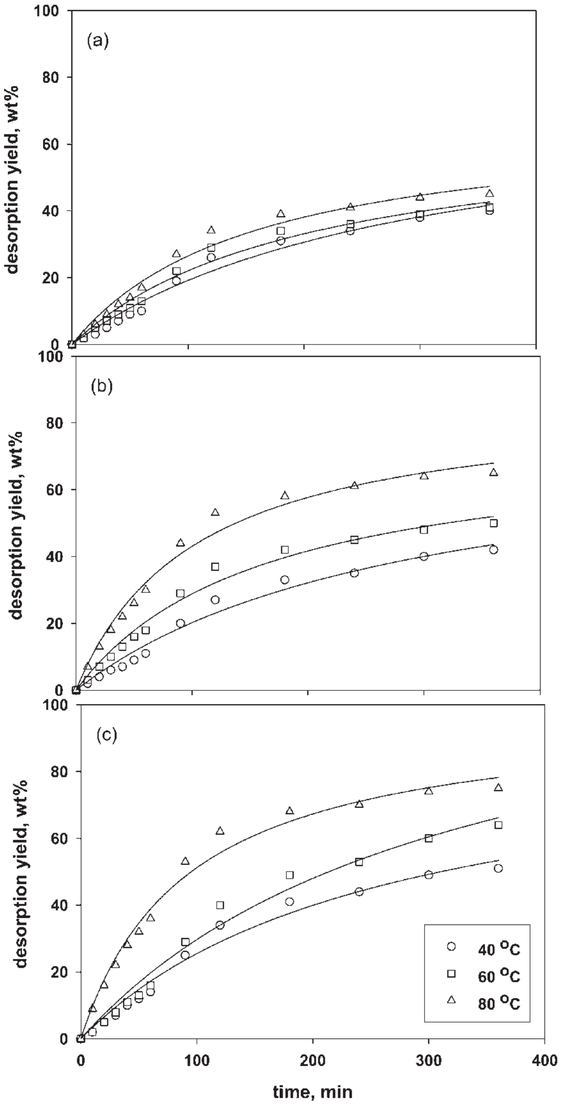


Figure 3. Effect of temperature on the desorption yield of salicylic acid, 2 mL CO_2/min, (a) 300 bar, (b) 400 bar, and (c) 500 bar.

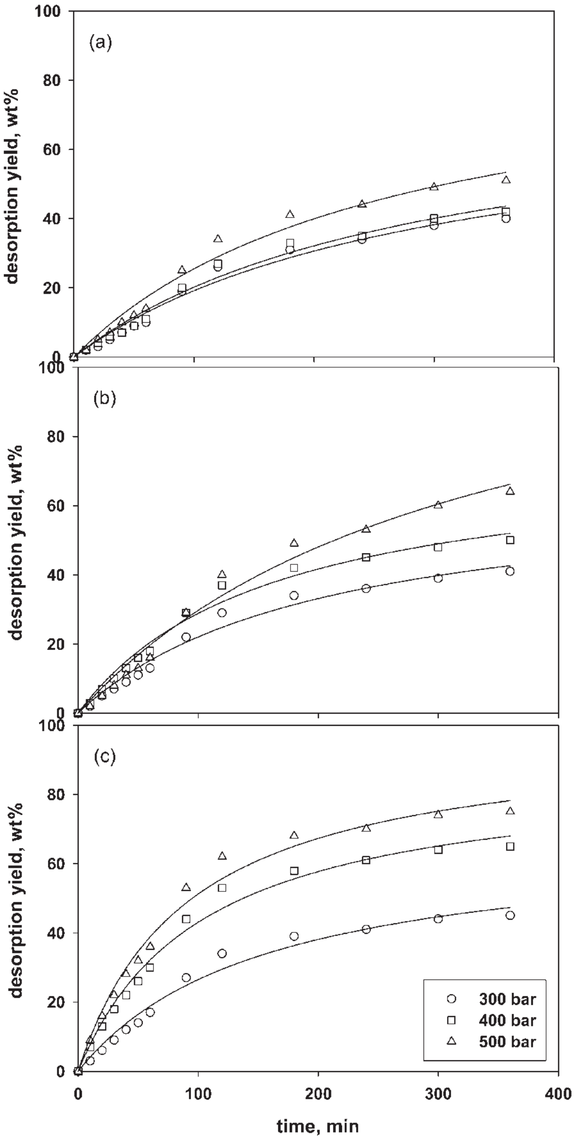


Figure 4. Effect of pressure on the desorption yield of salicylic acid, 2 mL CO_2/min, (a) 40°C, (b) 60°C, and (c) 80°C.

temperature. Similar results were obtained for desorption of phenol from ODTMA-B.[20]

It is evident from these figures that the initial desorption rate increased with pressure at all temperature conditions. However, it was observed that the change of the initial desorption rates at 80°C is marked according to 40°C and 60°C. As seen in Fig. 4(a) and (b), all initial desorption curves lie almost on a single line.

The third set of the desorption experiments was carried out at 400 bar and 60°C to investigate the effect of volumetric flow rate of SC CO_2 on desorption yield and initial desorption rate.

The effect of CO_2 flow rate is shown in Fig. 5(a) and (b). Increasing SC CO_2 flow rate provided a positive effect on the desorption yield. Desorption yield increases with increasing SC CO_2 flow rate, as in Fig. 5(a).

Figure 5(b) exhibits that desorption curve is not affected by the low (0.5 mL CO_2/min) and medium (1 mL CO_2/min) flow rates as both curves almost lie on a single line at the beginning. Roy et al.[28] studied extraction of essential oils with SC CO_2 and found similar effects. These effects were explained as follows: the exit concentration of the solute is independent of this flow rates, and, therefore, it is consider that desorption process is in equilibrium, and the intraparticle diffusion resistance is not dominant in this desorption process. However, at high (2 mL CO_2/min) flow rate, it was found that desorption rate decreased depending on intraparticle diffusion resistance. When intraparticle diffusion resistance and resistance time are important the slope of the desorption curve in the plot of yield vs. SC CO_2 become smaller for higher flow rates.

The last set of the desorption experiments was designed to investigate the effect of cosolvent concentrations on desorption yield and rate.

Desorption experiments were carried out at two different operation conditions. First, at a constant pressure of 300 bar, at temperature 40°C [Fig. 6(a)]; and the second at a constant pressure of 500 bar, at a temperature of 80°C [Fig. 6(b)], and at 2 mL CO_2/min flow rate and at 1, 2.5, 5, 10, and 20 vol% cosolvent concentration. Increasing cosolvent concentrations resulted in increasing desorption yield in spite of no marked change in the density of SC CO_2 + cosolvent (ethanol).

We compared the results of desorbed yield with SC CO_2 and SC CO_2 + ethanol mixtures. The most effective solvent system, SC CO_2 with 10 vol% ethanol, was able to reach approximately 98 wt% of the salicylic acid from ODTMA-B as compared with SC CO_2 at the same desorption conditions.

It was found that by increasing cosolvent concentration (20 vol%), the desorption yield decreased. This means that the excess cosolvent concentration resulted in remarkable changes in physical and mass transport properties of SCF.

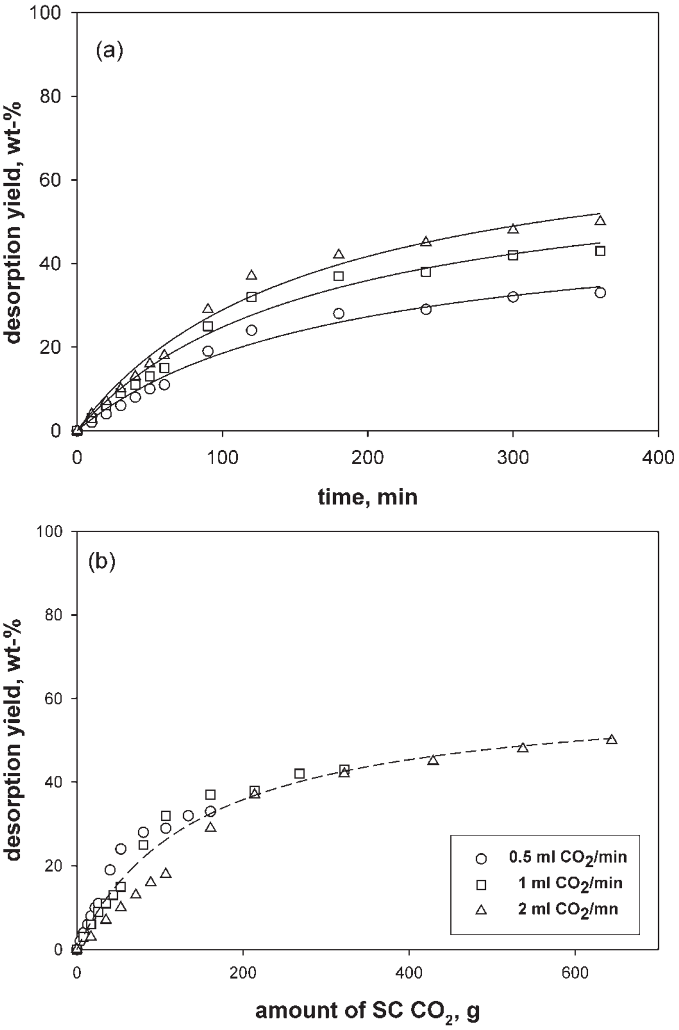


Figure 5. (a) Effect of CO_2 flow rate on desorption yield of salicylic acid at 40°C and 400 bar vs. desorption time. (b) Effect of CO_2 flow rate on desorption yield of salicylic acid at 40°C and 400 bar vs. cumulative amount of CO_2 passed.

CONCLUSIONS

The desorption yield of salicylic acid was evaluated by determining the desorption profiles in the presence of SC CO_2 and SC CO_2 + ethanol. It was

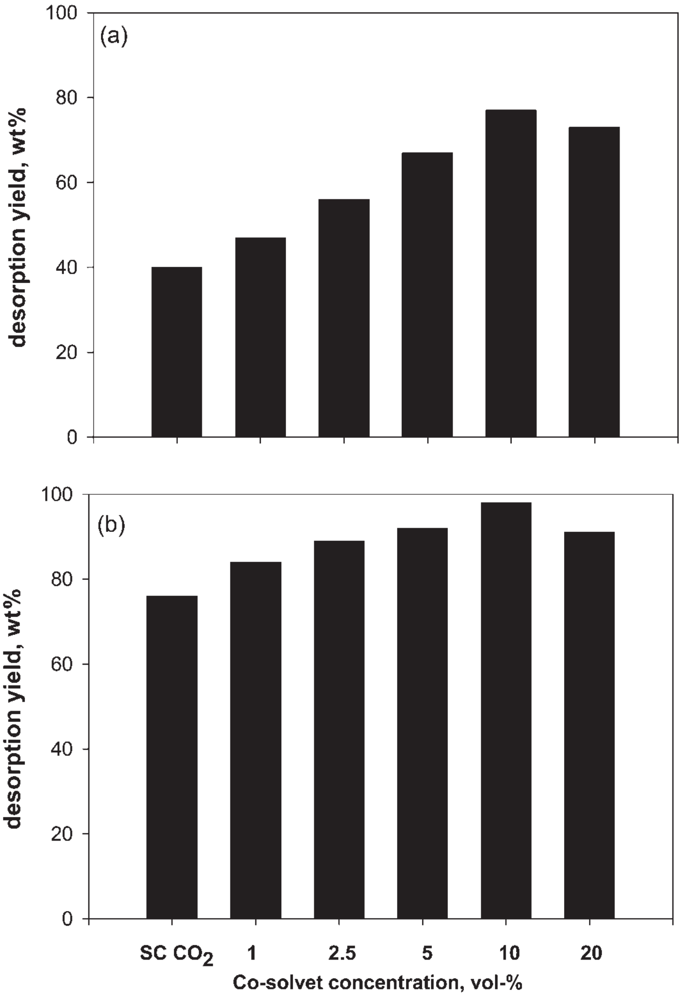


Figure 6. Effect of cosolvent concentration on desorption yield of salicylic acid at 6 hr and 2 mL CO_2/min, (a) 40°C and 300 bar (b) 80°C and 500 bar.

observed that the desorption yield of salicylic acid increased with increasing temperatures, pressures, SCF flow rates, and cosolvent concentrations. It obtained at approximately 76 wt% of desorption yield at high temperature (80°C) and pressure (500 bar) when using SC CO_2. However, SC CO_2 with 10 vol% ethanol was able to reach the desorption yield at approximately 98 wt% of salicylic acid from ODTMA-B as compared with SC CO_2. This result shows the advantages of using ethanol as cosolvent in SC CO_2. Hence, when organobentonites are used as alternative adsorbents toward organic compounds such as salicylic acid, SCF is a preferable technology for the regeneration of organobentonites, saving adsorbent costs and minimizing disposal problems as well as for recovery of the adsorbed compounds from an organobentonite.

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