

Supercritical Carbon Dioxide Sorption Processes on Various Sorbent Materials

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Adsorption and desorption experiments of oleic acid on selected adsorbents (silicagel, neusilin, two aerogels) and ion exchange resin (Amberlite IRA 420) were performed. The conventional adsorption-desorption process was performed on glass chromatographic column using gravity flow. Experiments were performed at room temperature using organic solvents (methanol, acetone, acetonitrile, methanol+acetic acid). The supercritical CO₂ adsorption-desorption experiments were performed on high pressure chromatographic column at 40°C and pressures 130 and 300 bar.

INTRODUCTION

Aplicability of supercritical fluids (SCF) in sorption processes such as extraction from solid matrices, regeneration of adsorbents, SCF chromatography in analytical and preparative scale and adsorptive separations was extensively researched over the past years and several advantages over conventional processes were verified due to favourable transport and solvent properties of SCF. Some of important advantages of using SCF instead of liquids as solvents are products that are free of organic solvents, possibility of simple regeneration of solvent and simple recovery of product by isothermal decompression or isobaric heating, possibility to reduce the size of process volumes and to accelerate the chemical process. Another advantage of using SCF in sorption processes is the opportunity to change the selectivity and capacity of the solvent simply by varying the pressure/density, which influences the solid/solute and solvent/solute interactions. Furthermore, since adsorption/desorption process is related to solute solubility, the addition of entrainers to solvent (CO₂) also influences the sorption equilibria.

For the design and analysis of sorption separation process the adsorption and desorption isothermal data are crucial. In this work experimental data are presented for adsorption and desorption of oleic acid (OA) on various solid matrices using conventional and SCF techniques. The capacity of adsorbents for OA loading and efficiency of its subsequent desorption has been studied by using organic solvents or SC CO₂ as mobile phase.

MATERIALS AND METHODS

Materials.

Silica gel 60 was obtained from Merck (Germany), Neusilin S2 from Fuji Chemicals Industry (Japan), anion exchange resin Amberlite IRA 420 was obtained from Rohm & Haas (France), and both aerogels were prepared in our laboratory [1]. The properties of the adsorbents are reported in Table 1. The oleic acid was technical grade (90%) and was obtained from Aldrich (Germany). Methanol, acetone and acetonitrile were obtained from Fluka (Germany). Carbon dioxide was 99,5 % pure and supplied by Messer (Slovenia).

Table 1: Some physicochemical properties of the adsorbents.

		Silica gel 60	Neusilin S2	Amberlite IRA 420	Silica aerogel hydrophobic	Silica aerogel hydrophilic
particle size	(μm)	63 – 200	44-250	300 - 1200	-	-
mean surface area (method BET)	(m^2/g)	480 – 540	110	-	-	783
pore volume (N_2)	(cm^3/g)	0.74 – 0.84	-	-	-	-
loose on drying	(%)	at 150°C 7	at 110°C 5	-	at 100°C 2	at 100°C 10

Methods

High pressure equipment. SCF chromatography system (Figure 1) consists of: a the reservoir for mobile phase (CO_2 tank), a unit for establishing, maintaining and controlling pressure (NWA PM-101 and PR-102), an optional unit for adding a modifier (High pressure syringe pump, Gilson 305, type 5SC), rheodyne switching valve, steel column (4,6 mm ID, 100 mm length) with electrical heating, detector (UV-VIS diode array detector, Agilent 1100 with high pressure micro flowcell) for determining concentration of substance in the outlet stream, an unit for expansion of mobile phase (NWA PE-103) and a flow meter.

Adsorption experiments were performed at 130 bar and 40°C. The CO_2 from the tank was cooled to a liquid state and compressed. The pressure of CO_2 was controlled and maintained constant during the proces with regulation valve. The flow of CO_2 through the column was regulated with expansion valve. Adsorbent was transferred into the steel column and the column was weigted. In the first step the CO_2 was passed over the adsorbent bed for 15 min at 40 °C and 130 bar whereas no adsorption of CO_2 was detected. In the following adsorption step, the OA was charged into the stream of CO_2 . The concentration of the OA in CO_2 was aproximatelly constant in all experiments and was in the range from 0.002 to 0.003 mole fraction, which is below the saturated concentration [2, 3, 4]. The breakthrough of OA, i.e. the end of the adsorption process, was detected by the UV-VIS detector. Desorption was performed duing the third step at 300 bar and 40°C. The mass of column containing the adsorbent was determined after each step. The amount of OA in the outlet stream during the entire process was monitored with on-line UV-VIS detector at 230 nm.

Conventional equipment. Adsorption and desorption experiments were performed in a glass chromatographic column using gravity flow. The adsorbent dispersed in methanol was

transferred into a column of 1 cm internal diameter and 20 cm height. A solution of 20 % (v/v) OA in methanol was prepared. The process was carried out at room temperature. The flow rate of mobile phase through the column was maintained at 1 mL/min or was less due to lower permeability of the stationary phase (adsorbent). The concentration of the OA in the outlet stream after evaporation of the solvent was determined gravimetrically in time intervals. The capacity of adsorbent was calculated from the concentration difference of inlet and outlet stream and was expressed as loading (q_{adsorbed}) in g OA / g of adsorbent. Desorption experiments were performed successively with methanol, acetone, acetonitrile or methanol+acetic acid and the results are presented as desorbed amount in % (q_{desorbed}).

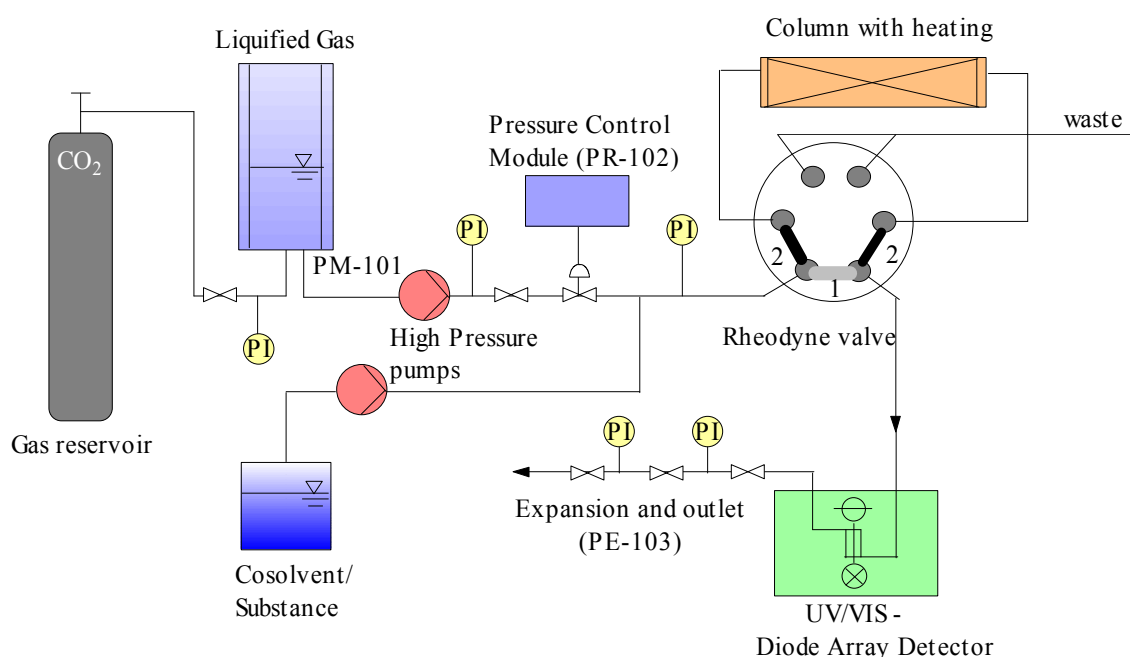


Figure 1: SCF chromatography system.

RESULTS

In Table 2 and 3 the results of the conventional adsorption and desorption experiments of OA on selected adsorbents are listed. The conventional adsorption of OA on hydrophilic aerogel using gravity flow could not be performed because the bed of adsorbent was not permeable for the methanol and therefore there was no free flow through the bed.

In Table 4 and 5 the results of SC CO₂ adsorption and desorption experiments are reported. Results show that the capacity of silica gel, neusilin and silica aerogel hydrophil for OA was higher in the case of SC CO₂ adsorption process at 130 bar and 40 °C compared to conventional adsorption of methanolic solution under gravity flow. In addition, adsorption time is much lower for high pressure process. The high pressure adsorption process was performed without any problems also in the case of hydrophilic aerogel, which was not permeable for the mobile phase under gravity flow. In the future, the low pressure experiments with forced flow of mobile phase of organic solvents have to be performed in order to compare the adsorption time.

Table 2: Conventional adsorption of oleic acid (OA) with methanol.

	q_{adsorbed} (g OA /g adsorbent)	Q_v (ml/min)	t (min)
silicagel	0.3771	1.59	39.7
neusilin	1.1228	0.336	110.1
Aerogel-hydrophob	0.2315	0.109	84.2
Aerogel-hydrophil	—	—	—
IRA 420	0.4556	0.920	102.7

Table 3: Conventional desorption of oleic acid with various solvents.

	Methanol			Aceton			Acetonitrile		
	q_{desorbed} (%)	t (min)	Q_v (ml/min)	q_{desorbed} (%)	t (min)	Q_v (ml/min)	q_{desorbed} (%)	t (min)	Q_v (ml/min)
Silicagel	92.03	21.2	2.39	93.72	14.9	3.48	94.23	14.2	3.55
Neusilin	95.58	148.0	0.50	96.41	68.9	0.74	97.10	80.1	0.75
Aerogel-hydrophob	100	65.5	0.02	—	—	—	—	—	—
Aerogel-hydrophil	—	—	—	—	—	—	—	—	—
	Methanol			Methanol + acetic acid					
IRA 420	65.42	104.0	0.65	100	131.7	1.02			

Table 4: SC CO₂ adsorption of oleic acid (OA) at 40°C and 130 bar.

	q_{adsorbed} (g OA /g adsorbent)	Q_v (L/min)	t (min)
Silicagel	0.4490	1.29	9.3
Neusilin	1.9469	1.05	11.7
Aerogel-hydrophob	0.0598	0.99	2.3
Aerogel-hydrophil	2.5269	1.05	10.3
IRA 420	0.1683	0.97	1.5

Table 5: SC CO₂ desorption of oleic acid at 40°C and 300 bar.

	q_{desorbed} (%)	Q_v (L/min)	t (min)
silicagel	97.70	1.33	86.0
neusilin	87.14	1.12	94.0
Aerogel-hydrophob	100	1.1	14.5
Aerogel-hydrophil	96.4	1.06	42.5
IRA 420	100	1.15	8.0

The capacity of silica aerogel-hydrophob doped with methyl groups and anion exchange resin Amberlite IRA 420 was lower in the case of SC CO₂ adsorption, compared to conventional process.

The SC CO₂ desorption process without cosolvents was effective for all adsorbents; the desorbed capacity was above 96.4 % whereas for neusilin it was somewhat lower (87.14 %).

CONCLUSION

Adsorption and desorption measurements of OA in methanol and SC CO₂ on and from selected adsorbents at 40°C were determined in pressure range from 130 – 300 bar. Further investigations will be performed in the future in order to investigate and understand how process parameters are influencing kinetics of sorption processes in various systems and mass transport and adsorption/desorption equilibria will be studied.

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