

REGENERATION OF GAC-F400 BY SCCO₂: EFFECT OF SYSTEM CONDITIONS ON DESORPTION STUDIES

C. S. Kalpage and B. Al-Duri^{*}, Dept of Chemical Engineering, University of Birmingham, Edgbaston – Birmingham B15 2TT, England – UK.
E-mail: B.Al-Duri@bham.ac.uk, Fax: +44 121 4145324.

The present work investigates regeneration of caprolactam-laden granular activated carbon Filtrasorb 400 (GAC-F400) used for wastewater treatment, by employing supercritical CO₂ (scCO₂) as the regenerating solvent. First, high affinity of GAC-F400 to adsorb caprolactam was experimentally proved by producing the adsorption isotherm, then solubility of caprolactam in CO₂ was investigated under several temperatures (40-60°C) and pressures (100–200 bars), and was found to be highly soluble (30 mg/g average). Then, caprolactam desorption studies were conducted in a fixed bed column under a range of desorption conditions including temperatures of 25–70°C, pressures of 80–285 bars, CO₂ flow rates of 1–5 L/min and initial caprolactam solution concentrations of 500–2000 mg/L. Results were shown in terms of kinetic data.

It was found that increasing the pressure enhanced both, desorption rate and the maximum desorbed material. Increasing the temperature favoured the desorption process at higher pressures (>200 bar), but had a negative effect at lower pressures. The desorption rate *increased* with scCO₂ flow rate increase and initial solute concentration increase.

In general, the studies showed that scCO₂ is feasible in the regeneration of GAC-F400, as it succeeded to regenerate 70% of the adsorbent capacity. Expectedly, 100% regeneration was not possible due to chemisorption and irreversible adsorption behaviour, which is inevitable in the case of GAC, and is responsible for its excellent adsorptive behaviour in the first place.

INTRODUCTION

Caprolactam is one of the most widely used chemical intermediates. Almost all of the annual world wide production (2.2x10⁶ MT in 1994) is consumed as the monomer for Nylon-6 fibre and plastics [1]. In the production of caprolactam, there is much wastewater containing 5-10% caprolactam, the factor that causes both a reduction in economic profit and an increase in the COD of the wastewater. In addition, caprolactam is known to have some toxic effects. Prolonged, heavy exposure in human can lead to dermatitis, fever and seizures. In several tests, caprolactam had a mutagenic effect, introducing DNA damage and chromosomal aberrations.

Granular activated carbon Filtrasorb 400 (GAC-F400) is an excellent adsorbent for the treatment of aqueous waste streams [2] due to its large surface area and well-developed internal structure and abundant active adsorption sites. For improved process economics and to reduce the adversity of landfills, activated carbon often requires re-generation due to its relatively high price (~ 50 euro per kg). Of the existing techniques are thermal regeneration, wet oxidation, acid washing and solvent regeneration. Supercritical fluid (SCF) regeneration can be carried at much lower temperatures than thermal regeneration [3], and has less power requirement than wet oxidation. Also, SCF's show significantly high solubility for organic

compounds and much reduced mass transfer limitations, hence they give much higher recovery in desorption, and less environmental impact than conventional solvent regeneration.

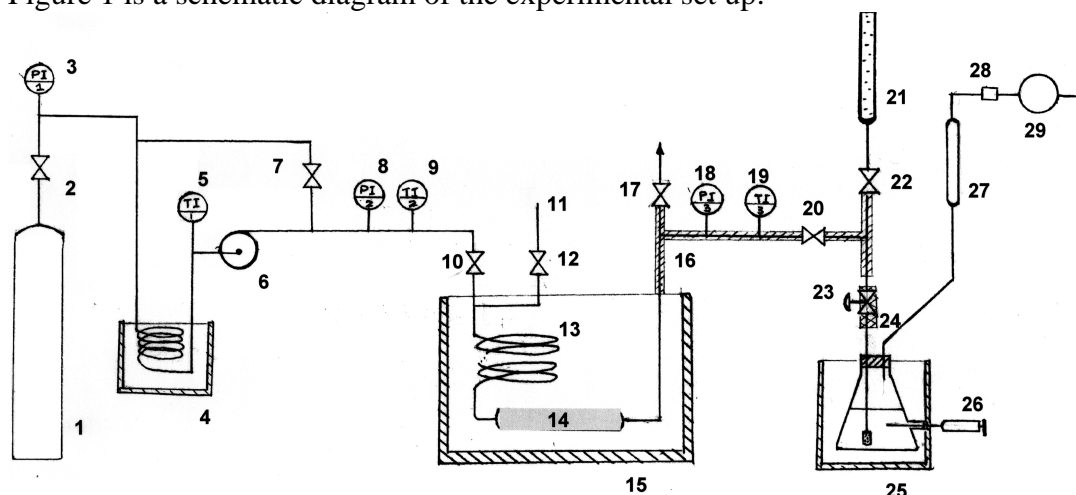
MATERIALS AND METHODS

Materials: Caprolactam ($C_6H_{11}ON$) is the adsorbate supplied by Sigma Chemicals UK. Granular activated carbon Filtrasorb 400 is the adsorbent, supplied by Chemviron carbon, UK Ltd. CO_2 of commercial grade is the regenerant (solvent) is supplied by BOC Ltd.

Preparation of system: GAC F-400 was first crushed using a rod mill and screened to a series of particle size ranges. Each fraction was repeatedly rinsed with distilled water to remove fines, dried at $110\text{ }^{\circ}C$ for 24 hours and stored in airtight containers. Aqueous solutions were prepared (using distilled water) and brought into contact with 3 g of activated carbon in 1L reactors and magnetically stirred overnight. The exhausted activated carbon was then filtered out and dried at $110\text{ }^{\circ}C$ for 24 hours. After drying, 2.5 g of prepared exhausted carbon was packed in a 0.8 cm ID stainless steel 316 tube with a height of 14 cm. The packed bed desorber was then fitted in the Test rig.

The operation rig:

Figure 1 is a schematic diagram of the experimental set up:



1.CO₂ cylinder, 4.Freezer unit, 6.Liquid pump, 11.Co-solvent injection, 13.Heat exchange coil, 14.Desorber, 16.Insulated tubing, 21.Solvent reservoir, 23.Micro metering valve, 24.Heating Tape, 25.Cold trap 26.Sampling point, 27.Rotameter, 28.Filter, 29.Dry test meter, 17.Bursting disk, 3, 8, 18 Pressure gauges, 5, 9, 19 Temperature gauges, 2, 7, 10, 12, 20, 22 Stop valves.

Figure 1: A schematic diagram of the operation rig.

Carbon dioxide withdrawn from the cylinder was chilled then compressed to the operating pressure, before passing through a heat exchanger coil where it was heated to the operating temperature. It then passed through the desorber unit, which are immersed in constant temperature water bath, maintaining the operating temperature within $\pm 1\text{ }^{\circ}C$. The exit from the desorber was then expanded across a micro metering valve. The flow rate in the desorber was determined by the volumetric flow rate of the expanded gas as it passed through the Rota-meter and the total flow by the Dry test meter.

The desorbed caprolactam was collected in a cold trap which contained Ethanol at $0\text{ }^{\circ}C$. Before withdrawing a 5-ml sample from the cold trap, the flow of CO_2 was temporarily stopped by the stop valve (6), and then the expansion zone was washed with 10 ml of Ethanol from the solvent reservoir.

Samples were analysed in a GC (Varian Factor Four capillary column) coupled with a Flame Ionisation Detector. In solubility tests, the desorber was packed with powder caprolactam, and CO₂ was passed for 45 minutes. Caprolactam in the expanded CO₂ was collected in a thimble filter through which the gas was released to the rotameter, wet test meter and finally to atmosphere.

RESULTS AND DISCUSSION

Adsorption studies: Figure 2 shows the adsorption isotherm for caprolactam on GAC-F400 using 355-500 μ m granules. Results showed the GAC-F400 capacity to be around 200 mg/g, which is high. The isotherm showed Redlich-Peterson behaviour. This indicated reversibility properties, i.e. possibility of regeneration; and heterogeneous surface behaviour, which is related to the energy of adsorption and adsorbate distribution on the GAC surface.

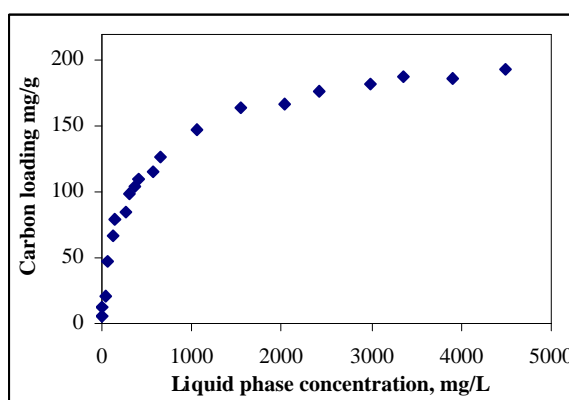


Figure 2: Adsorption equilibrium isotherm for caprolactam /GAC-F400 system, under atmospheric conditions.

Solubility studies: The solubility of Caprolactam was evaluated in scCO₂ at a range of pressures and temperatures. Table 1 shows the results:

Solubility of Caprolactam in scCO ₂ , g/kg					
Temperature	Pressure (bar)				
(° C)	100	125	150	175	200
40	13.33	27.35			163.8*
50	7.52	14.09	24.13		
60	2.63	3.44	15.73	30.07	

* With a recycle flow.

Table 1: Solubility of caprolactam in scCO₂ at various temperatures and pressures.

Results show good solubility in scCO₂, though values are rather low compared to literature [4]. It is clear that at lower pressures the solubility improved with temperature decrease, while the effect was reversed under higher pressures. This is related to the density of scCO₂, and the vapour pressure of solute. This will be further discussed in the following sections.

Desorption Studies:

The rate of desorption: Figures 3 and 4 show the kinetic plot of desorption for temperatures 25 and 40°C, respectively at various pressures. Generally, the rate of desorption increases with pressure at both temperatures, but it is observable that the effect of pressure is more prominent for pressures and temperatures around the critical region.

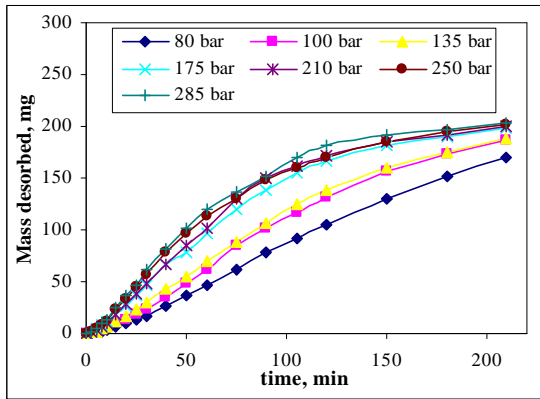


Figure 3: The effect of pressure on the supercritical desorption rate in caprolactam / GAC-F400, at 25 °C.

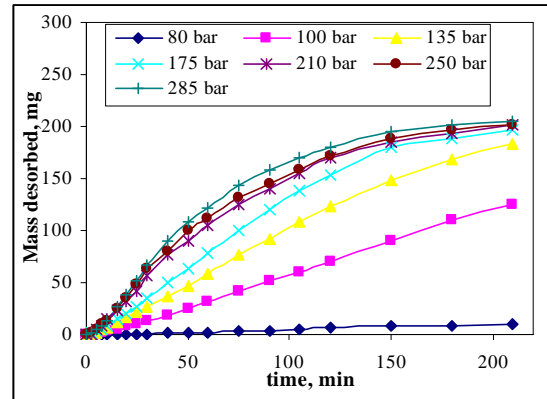


Figure 4: The effect of pressure on the supercritical desorption rate in caprolactam / GAC-F400, at 40 °C.

Clearly, at 25°C (subcritical T) the desorption rate is ‘less sensitive’ to pressure changes than at 40°C (supercritical). Above T_c (31°C), the CO_2 density (and hence solvating power) is highly sensitive to changes in pressure the factor that is responsible for the ‘tunability’ of SCF properties in that operation region. This is shown in the ‘wide spread’ of desorption rates in Figure 3. Typically, the desorption curves are not linear with time, indicating the effect of intraparticle diffusion within the GAC particles, which is a function of time *and* position or location of caprolactam molecules *within* the GAC particles.

The effect of temperature and pressure: Figures 5 and 6 show the maximum desorbed amount of caprolactam as function of pressure and temperature, respectively. For a given system, the maximum desorbed amount is a balance of two factors, namely the solvent density and the vapour pressure of the solute. At lower pressures, increasing the temperature reduces the solvent density and hence its activity (power). Higher pressures enhance the solute vapour pressure (volatility) to an extent that overcomes the reduction in solvent density inflicted by elevated temperatures. Hence the effect of temperature ‘reverses’ above a certain pressure, generally termed as the ‘crossover pressure’. Figure 4 shows that the crossover pressure is about 200 bars, below which low temperature operation is favoured, while high temperature operation is required above.

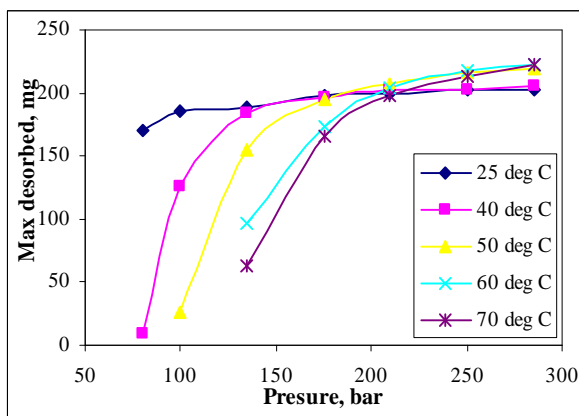


Figure 5: The effect of pressure on the maximum mass desorbed in caprolactam / GAC- F400 system at various temperatures.

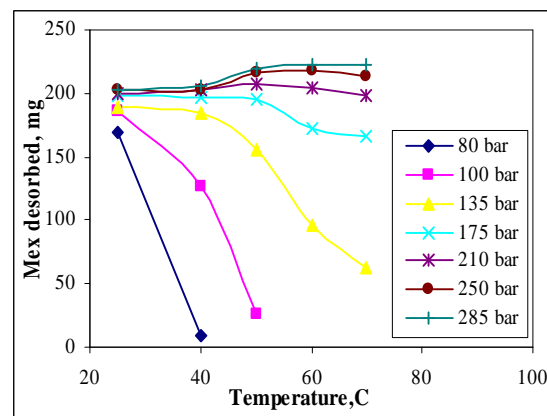


Figure 6: The effect of temperature on the maximum mass desorbed in caprolactam / GAC- F400 system at various pressures.

Figure 6 shows the same effects in a slightly different fashion. The maximum amount adsorbed greatly decreased with temperature at lower pressures up to about 200 bars where the effect began to reverse and total amount desorbed increased with temperature.

It is interesting to see that the same effects observed in SF extraction systems are observed in this desorption system. While extraction is a dissolution process, desorption is the breakage of solute-particle surface bonds originally formed during adsorption. While the use of SCF reduced mass transfer limitations, it would not totally eradicate them.

The effect of SCF flow rate: Figure 7 shows the effect of CO₂ flow rate on the rate of desorption. It is clear that increased SCF flow increased both the rate of desorption and the maximum amount of caprolactam desorbed. At 40°C and 250 bars and after three hours, the maximum amount desorbed was increased by 141% upon doubling the CO₂ flow from 1 to 2 L/min, and by 160% upon using 5 L/min. A detailed economic assessment is required to find the optimum CO₂ flow rate.

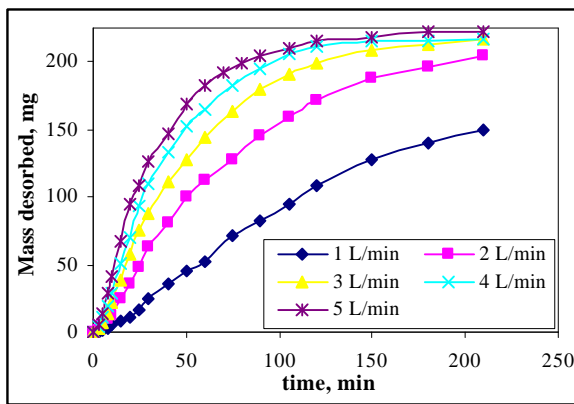


Figure 7: The effect of CO₂ flow rate on desorption of caprolactam /GAC-F400 system at 250 bars and 40°C.

At higher flows (> 3 L/min) the desorption rate curves became closer, as they showed a balance between two contradicting effects: higher solvent amounts in a unit time would enhance desorption, and increased solvent flow rate would reduce film mass transfer limitations, which increased desorption rate on the one hand. Whereas reduced residence time would naturally reduce the mass desorbed.

The net effect is enhanced desorption rate.

The effect of initial carbon loading: Figure 8 shows the effects of initial carbon loading with caprolactam on the rate of desorption using 2 L/min of CO₂, at 250 bars and 40°C.

It shows that at a given CO₂ flow rate, desorption rate increased with the initial concentration of caprolactam, which in turn affected the GAC loading. This would naturally increase the driving force for desorption. Yet, at 500 ppm initial concentration, 81.5% of the caprolactam was desorbed, while it reduced to 70.3% for a 1000ppm solution, and remained around 69% desorption at higher concentrations (1500 and 2000 ppm). This was due to the change in the solid/fluid ratio, which affects the internal resistance in the system. Besides, in systems with higher loading, part of the caprolactam would be resident in the micropores (inner pores with smaller diameter).

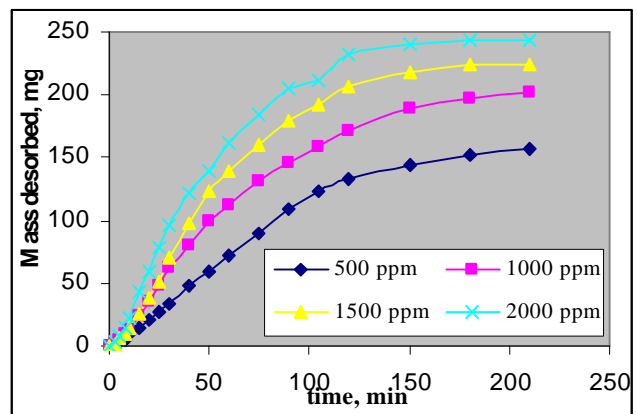


Figure 8: The effect of initial concentration and hence the carbon loading on the rate of supercritical desorption in caprolactam / GAC-F400 system, at 250 bars and 40°C.

In the micropores, the pore diameters would be of comparable sizes to the adsorbate molecular diameter, hence the adsorption mechanism is based on multidimensional interactions [5] forming bonds that are much harder to break, the factor that is responsible for irreversible adsorption no matter how powerful the regenerating solvent. Table 2 below shows the initial carbon loadings based on the caprolactam solutions that they were prepared from:

Initial solution concentration, ppm	Initial GAC-F400 loading, mg	Mass desorbed , mg	% desorbed in the run
500	193	157	82.5
1000	288	202	70.3
1500	325	224	69.05
2000	536	244	68.9

Table 2: Carbon loadings and mass of caprolactam desorbed, which are correspondent to various initial solution concentrations.

CONCLUSIONS

The present work has led to the following conclusions:

- Supercritical CO₂ can be successfully used to regenerate GAC-F400, originally used to remove caprolactam from aqueous waste streams, by recovering up to 70% of the caprolactam. The latter can be recovered if required, to 100% purity.
- Both the rate of desorption and maximum amount desorbed favoured higher operating pressures (= 200 bars).
- The optimum desorption temperature is 25°C for pressures = 200 bars, and 40°C for pressures > 200 bars.
- The rate of desorption increases with the solvent (regenerant) flowrate and initial solute concentration in the effluent stream.
- Complete economic assessment of the process is required before selecting the optimum overall operating conditions.

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