Controlling the selectivity of separation processes by pressure

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1. Summary

Braaß (2002) carried out experiments that proofed the pressure resistance of YADH. These results lead to the conclusion that pressure can be a suitable tool to control selectively adsorption/desorption equilibria.

For the utilization of high hydrostatic pressure for selective separation processes, an automated high-pressure plant for a continuous flow through a fixed bed was designed and constructed. The plant is computer controlled and can be operated at pressures of up to 360 MPa.

The surface of the silica gels XWP P005 and SP-60-20-P were modified and the effectiveness of the modification was proofed by means of kinetic investigations and isotherms. A modification of SP-60-20 P was utilized to record isotherms under high pressure conditions of up to 300 MPa, modifications of XWP P005 were used to investigate the dynamic behaviour by means of breakthrough curves and complete adsorption/desorption cycles. A strong pressure dependency of the adsorption capacity of the modified supports was found and it was shown that only by altering the pressure a desorption of Triton X-100 can be initiated. The amount of regained material is directly correlated to the pressure that is applied during the adsorption process. A maximum of 75% of the initial Triton X-100 concentration could be regained if the adsorption pressure was 300 MPa.

2. Introduction

In various applications pressure becomes more and more interesting as a parameter to control chemical equilibria and biotechnological processes. Areas of research include chemical reaction engineering (Klärner, 1989; Beuermann et al., 2002; Buback, Nelke, Vögele, 2003; Becker et al., 2004), food processing (Behsnilian, Regier, Stahl 2003; Weidner, 2004), and pharmaceutical and medical applications (Friedrich et al., 2002; Meyer-Pittroff, 2002). The effect of high pressure on the stability and activity of enzymes is elaborately examined (e.g. Morild, 1980; Hernandez, Cano, 1998; Cho, Northrop, 1999) and it is looked into possibilities to make use of high pressure to treat cancer cells (Diehl et al., 2003) and of pressure/temperature combinations to sterilise foodstuff (Knorr, Heinz, 1999). In the following, an approach is given to utilise pressure in a semi-continuous selective separation process.

To take advantage of high pressure in a semi-continuous separation process, joint results of researches in different branches are necessary. Since one focus for the separation process are biological molecules like enzymes it had to be assured that those molecules withstand the aimed working conditions unharmed (Braaß, Thiesen, Niemeyer, 2000; Braaß, 2002). An automated high-pressure plant for a continuous flow through a fixed bed at pressures of up to 360 MPa was designed and built and its hydrodynamic behaviour was investigated (Jansen, Niemeyer, 2005). Silica-based matrices were chemically modified to show a selective interaction with the aimed component to adsorb (Cartellierei et al., 2000; Rosenfeld et al., 2005) and were characterised by means of kinetic investigations and isotherms. To record isotherms at high pressure, a circulation plant for a maximum operational pressure of 360 MPa was built and isotherms at a pressure of up to 300 MPa were recorded utilizing a modification of the carrier matrix SP-60-20-P.

3. Experimental

3.1. Material

The silica gel XWP-P005 was delivered by Grace Davison, Worms, Germany. XWP-P005 provides a specific surface of 80 m²/g, an average pore diameter of 50 nm, a pore volume of 1 to 1.2 mL/g, a density of 2120 kg/m³, and a void fraction of 0.82. SP 60-20 P is from Daiso Co. Ltd., Japan und has a specific surface of 170 m²/g, an average pore diameter of 23 nm, a pore volume of 0,98 cm³/g, and a particle size of 18,9 μ m. 3-mercaptopropyl-trimethoxysilane, diethylene-glycoldiglycidylether, and 2,2,2-trifluoroethanesulfonylchloride are from Fluka (Fluka Chemie GmbH, Buchs, Switzerland); hydrochloric acid, sodium chloride, acetone, toluene, sulphuric acid, potassium permanganate (Titrisol) and Triton X-100 were purchased from Merck (Merck, Darmstadt, Germany). All not otherwise specified chemicals are of analytical-reagent grade.

3.2. Preparation of the adsorbents

The silica gels are covered with over molecular sieve dried toluene and 3-mercaptopropyltrimethoxysilane is added. This mixture is heated up to 80°C. After 90 minutes of reaction time the support is filtered and extracted with acetone (Rosenfeld et al., 2005). The result is a preliminary stage of the employed adsorbents, it is referred to as XWP-1 as it is only employed based on XWP P005. It is characterised to proof the efficiency of the further modifications.

Water and diethyleneglycoldiglycidylether are then added and the mixture reacts 24 h at a temperature of 45°C under constant rotation in a rotary evaporator. The supports are extracted with sodium chloride solution (1 mol/L) and water. Afterwards they are covered with hydrochloric acid (0.05 mol/L) and rotated for 24 h at 65°C in a rotary evaporator. The resulting substances are filtrated, extracted with acetone and dried at 60°C. This adsorbents are referred to as XWP-1.2.1 and SP-1.2.1, respectively.

3.3. The adsorbate Triton X-100

Triton X-100 is a non-ionic surfactant that is used as adsorbate as a model substance for amphiphilic substances such as glycolipides which provide large biological and pharmaceutical effects. Its formula is C_8H_{17} - C_6H_4 -(OCH₂-CH₂)_n-OH where n equals 8...10 and it has an average molecular weight of 600 g/mol. Its structural formula for n = 8 is given in Fig. 1.



Fig. 1: Structural formula of Triton X-100

To quantify Triton X-100 concentrations in aqueous solution, an easy and reliable photometric analysis method has been developed. 300 µL solution are added to 900 µL half-concentrated sulphuric acid and 300 µL potassium permanganate. The sulphuric acid consists of 2 parts sulphuric acid, 99%, and 3 parts water. The concentration of potassium permanganate is 0.02 mol/L. This solution reacts under constant shaking in 1.5 mL reaction caps at a temperature of 30°C. The resulting redox reaction gradually achromatises the potassium permanganate. After a reaction time of exactly 90 minutes, 300 µL of the solution are pipetted into a microtiter plate (HJ-Bioanalytik, Moenchengladbach, Germany). The absorption of light of a wavelength of $\lambda = 490$ nm is measured with a 1420 VICTOR²

Multilabel Counter (Perkin-Elmer Life Sciences – Wallac Oy, Turku, Finland) and compared to standard solutions.

3.4. High pressure plant

The high pressure plant (Jansen, Niemeyer, 2005) shown in Fig. 2 has been used to carry out the pressure-controlled fixed bed adsorption and desorption experiments with Triton X-100.



Fig. 2: Schematic diagram of the high pressure plant

The plant is fully automated and designed for a continuous flow through a fixed bed reactor at pressures of up to 350 MPa. The feed, for the experiments at hand an aqueous solution of Triton X-100 of various concentrations, is filled into the three vessels S1, S2, and S3. From there it is led into the pipe loop (SL), where it is pressurised by an MhR 150/7 (ProMinent Orlita, Giessen, Germany) motor driven diaphragm pump (P) to the desired pressure. The feed is conducted through the fixed bed reactor (S4) and is than depressurised by the pneumatic valve FV 24. A fraction sampler from Pharmacia (Amersham Biosciences Europe GmbH, Uppsala, Sweden) collects time-based up to 175 samples in caps of 1.5 mL size.

4. Results

4.1. Characterization of the adsorbents

Kinetic investigations

Adsorption kinetics for the carriers XWP-1 and XWP-1.2.1 and Triton X-100 were investigated by the batch method. 15 mg adsorbents were added to 1.5 mL Triton X-100 solution of a concentration of 0.32 g/L. Reaction temperature was 30°C and the reaction caps were constantly shaken. Samples were analysed after reaction times of 1, 3, 5, 10, and 15 minutes and thereafter every 15 minutes until a stable equilibrium was reached.

The results of these experiments are shown in Fig. 3. It can be seen that XWP-1 reaches a high maximum loading of about 30 mg/g but has a rather slow kinetic, equilibrium is reached

only after 30 minutes. The third value is assumed to be an analytical error. XWP-1.2.1 however has a maximum loading of about 3mg/g and no certain conclusions can be drawn concerning the kinetic.



Fig. 3: Adsorption kinetics; concentration of Triton X-100 is 0.32 g/L, reaction temperature 30°C

Isotherms

From the kinetic investigations it was found that after 60 minutes equilibrium is reached and further investigations showed that it remains stable for at least three hours. Hence, to determine adsorption isotherms an adsorption time of 120 minutes was chosen. The experimental set-up and the conditions were the same as for the kinetic investigations. The original Triton X-100 solutions utilised for the isotherms were of 15 different concentrations, ranging from 0.05 g/L to 0.61 g/L.



Fig. 4: Adsorption isotherms, adsorption temperature 30°C

The isotherms for XWP-1 and XWP-1.2.1 are presented in Fig. 4. Both isotherms reflect the results achieved from the kinetic investigations. XWP-1 has a large adsorption capacity, the part of its isotherm that was recorded is linear, has a steep slope and shows no saturation. The adsorption capacity of XWP-1.2.1 approaches zero, negative loading values are within the uncertainty of the analytical method.

Isotherms at high pressures were recorded utilizing SP-1.2.1, the results are presented in figure 5. The surface modification of SP-1.2.1 is the same as for XWP-1.2.1, hence a similar adsorption behaviour can be expected.



Fig. 5: Adsorption isotherms with SP-1.2.1 at various pressures

It can be seen that SP-1.2.1 does not show any significant adsorption at ambient pressure. The adsorption capacity, however, increases strongly with increasing pressure. The highest rises occur between ambient pressure and 100 MPa and between 100 MPa and 200 MPa, the rise above 200 MPa is much lower. With increasing pressure the isotherms become more favourable, showing a steeper slope at lower concentrations and hence a higher affinity towards the employed surfactant Triton X-100. The higher adsorption capacity is reversible. Rreducing the pressure leads to a significant desorption, as shown in figures 6 and 7.



Fig. 6: Effect of pressure decrease from 200 MPa to 120 MPa on the adsorption equilibrium



Fig. 7: Effect of pressure decrease from 300 MPa to 210 MPa on the adsorption equilibrium

Figures 6 and 7 show the effect of a reduction of pressure in the circulation plant on the adsorption equilibrium with SP-1.2.1 as adsorbents. It can be seen that the adsorption capacity of the adsorbents decreases with decreasing pressure. The capacity decrease is bigger if the pressure is reduced from 200 MPa to 120 MPa than it is for a reduction from 300 MPa to 210 MPa. These findings are in accordance with the results taken from the isotherms, the pressure dependence of the adsorption capacity becomes lower above 200 MPa.

4.2. Breakthrough curves

To research the pressure dependency of the adsorption capacity, breakthrough curves were recorded with XWP-1 and XWP-1.2.1 at various pressures, presented in figure 8.



Fig. 8: Breakthrough with XWP-1 and XWP-1.2.1 at various pressures

For these investigation the high pressure plant specified in Jansen and Niemeyer (2005) has been utilised. The column S4 has been filled with 0.61 g and 0.70 g of the adsorbents XWP-1 and XWP-1.2.1, respectively, making up the fixed bed. It was renewed after every experiment. The mass flow for all experiments was 1.2 mL/min. In Fig. 8 the Triton X-100 concentration of the fluid leaving the plant is plotted against the total volume of the fluid that has passed the plant.

Experiments carried out at a pressure of 0.8 MPa (blue squares) match the findings from the kinetic investigations and the isotherms. XWP-1 has a large adsorption capacity, leading to a late breakthrough. XWP-1.2.1 shows nearly no adsorption, the breakthrough occurs after 15 mL solution have passed the plant, almost immediately after the plant's dead volume of 9 mL (Jansen, Niemeyer, 2005). While the breakthrough does not change significantly with increasing pressure for the adsorbent XWP-1, a strong pressure dependence of the adsorption capacity is found for XWP-1.2.1. At a pressure of 125 MPa (red square) the Triton X-100 concentration begins to after 30 mL have passed the plant and at a pressure of 250 MPa (green triangle) the breakthrough begins at the 38 mL point. Its slope, however, is not as steep as that for the curves recorded at lower pressures. This indicates a pressure influence on adsorption kinetics and mass transfer that was observed by Jansen and Niemeyer (2005) in prior works.

4.3. Pressure controlled adsorption and desorption

Utilising the adsorbent XWP-1.2.1 a full separation process was investigated. For every experiment 0.70 g of the adsorbent were filled into the column of the high pressure plant. Breakthrough curves and the pressure-induced desorption were recorded at pressures of 50, 100, and 300 MPa, Fig. 8.

After the breakthrough had occurred, the feed was switched from the original Triton X-100 solution to water. The desorption was than initiated by stopping the high pressure pump (P in Fig. 2) after the plant was flushed with a sufficient amount of water to wash away any not-adsorbed Triton X-100 molecules under high pressure. Stopping the pump causes a pressure decrease at a rate of 15 MPa/min. All times at which the respective actions occurred are specified in table 1 by means of the volume that had passed through the plant at the time.

Pressure / MPa	Feed → Water at mL	Pump stopped at mL
50	80	140
100	120	190
300	130	250

Table 1: Volumes for feed-switch and pump-stop

In Fig. 9 a significant pressure dependency of the adsorption/desorption equilibrium can be seen. While for an adsorption at 50 MPa the maximum concentration that was reached during the desorption process is 1/3 of the initial concentration, it is more than 50% for the experiment at 100 MPa, and nearly 75% are obtained if a pressure of 300 MPa was applied during the adsorption.



Fig. 9: Adsorption-desorption process at various pressures

5. Discussion and Conclusion

From the kinetic investigations and isotherms it can be stated that the surface modification of the silica gel XWP P005 was effective and a good surface coverage was reached. The breakthroughs of the two modified supports again proofed their different behaviour.

XWP-1.2.1 and SP-1.2.1 showed only a marginal adsorption capacity under normal pressure conditions for the isotherm and the breakthrough (XWP-1.2.1 only) accordingly. However, a strong pressure dependence of their adsorption capacity was found during equilibrium and dynamic experiments. Furthermore, isotherms recorded with SP-1.2.1 as adsorbents became more favourable with increasing pressure, indicating a higher affinity towards the employed surfactant Triton X-100.

The pressure dependence of the adsorption capacity was found to be not linear with the pressure. It is high below 200 MPa and significantly lower above 200 MPa. Further experiments indicated that the strongest pressure dependence might be between 100 MPa and 200 MPa. Above 300 MPa the capacity increase is even less than between 200 MPa and 300 MPa (Jansen, 2005).

The low overall capacity of XWP-1.2.1 and SP-1.2.1 is very favourable for an effective separation process. For a pressure controlled adsorption/desorption equilibrium only the differences of the capacity at various pressures are of interest, since that makes up the fraction of the adsorbate that can be regained. In fact, a separation process benefits from an adsorption capacity that approaches zero under normal pressure conditions because it saves adsorbate that otherwise would be irreversibly bound to the adsorbent and by this enhances the overall efficiency of the process. That means the overall separation process would not gain but rather lose from an adsorbent with a higher capacity at ambient pressure, thus a high capacity does not stand for a good adsorbent in the process investigated.

From the experiments carried out it can be concluded that the adsorption/desorption equilibrium can be effectively controlled by pressure. A pressure decisively above 100 MPa

leads to more favourable isotherms and hence a stronger affinity towards the desired component. Beyond that it was found that there exists an optimum pressure for a given system, the pressure dependence of the adsorption capacity is not linear in pressure but decreases above 200 MPa. The highest concentration during the desorption phase was reached at a pressure of 300 MPa, so depending on the specific goal, the optimum adsorption pressure for the system investigated is between 200 MPa and 300 MPa.

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