

Process Engineering Laboratory II

Chromatography

Introduction

Chromatography refers to a broad range of separation techniques used to separate complex mixtures. It involves a sample (or sample extract) being dissolved in a mobile phase (which may be a gas, a liquid or a supercritical fluid). The mobile phase is then forced through a bed or column packed with an immobile, immiscible stationary phase. The phases are chosen such that the components of the sample have different affinities for each phase. A component with high affinity for the stationary phase will take longer to travel through the packed bed than a component with lower affinity for the stationary phase. As a result of these differences in mobilities, sample components will become separated from each other as they travel through the stationary phase.

Chromatography can be preparative or analytical. Preparative chromatography seeks to separate the components of a mixture for further use (and is thus a form of purification). Analytical chromatography operates only with small amounts of material with the aim to measure the relative proportions of distinct analytes in a mixture.

Chromatographic processes are based on two major physicochemical phenomena namely (physical) adsorption and ion exchange. Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid (adsorbent), forming a film of molecules or atoms (the adsorbate). The exact nature of the bonding depends on the details of the species involved. The adsorption process is generally classified as physisorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding). Ion exchange chromatography utilizes ion exchange mechanism to separate analytes. For this a charged stationary phase is used to separate charged compounds including amino acids, peptides, and proteins. In conventional methods the stationary phase is an ion exchange resin that carries charged functional groups which interact with oppositely charged groups of the compound to be retained.

The aim of this practicum is to refresh your theoretical knowledge and to investigate a separation process in a small scale chromatographic column. One of the goals of this practicum is also to explain physically correct the phenomena you observed in a well written report. In the following sections a description of the chromatographic column is given, your theoretical knowledge is refreshed and the practical tasks are discussed. The final section provides a guideline for the report you are expected to hand in to pass the practicum. The report is an important part of the practicum as it trains your ability to present results in a scientific way.

Theoretical background

Adsorbent materials and ion exchange resins

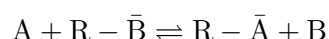
Technical adsorbent materials are generally porous materials with a high specific surface. This is important as the thickness of the adsorbed layer is usually only a few molecular diameters due to the limited influence of the van der Waals forces. Typical adsorbent materials for different applications are activated carbon, silica gel, alumina or molecular sieves, for instance zeolites.

Ion exchange resins consist of an insoluble, mostly organic matrix with integrated charged functional groups acting as exchange centers. Depending on the type of these functional groups, anions or cations from acid or basic solutions can be removed.

Within this practicum a highly acidic cation exchange resin (Dowex 50W-8X) is used and characterized further in section "Description of the Experimental setup".

Equilibrium behavior

The equilibrium behavior of an ion exchanger can be described by the following equation with R describing the ion exchange resin and \bar{A} or \bar{B} the adsorbed state:



The **equilibrium loading** is defined as the mass of adsorbed species (adsorbate or ions) per mass of stationary phase (adsorbent or ion exchange resin) at a given temperature and concentration or partial pressure:

$$q = \frac{\text{mass of adsorbed species}}{\text{mass of stationary phase}}$$

The knowledge of the equilibrium behavior is essential for the process layout. These data are usually determined performing batch experiments and represented by isotherms giving the quantity q at different concentrations or partial pressures, respectively, at a specified temperature. In figure 1 an isotherm for copper sulfate on Dowex 50W-X8 at room temperature, as used in this practicum, is shown. Different isotherm models exist for the mathematical description of the adsorption equilibria. The simplest model is a linear isotherm $q = kc$. A comparably simple model of high practical relevance has been described by **Langmuir** (1918) originally for the adsorption of gas phase species:

$$q = q_{\max} \frac{k_L c}{1 + k_L c}$$

In figure 1 a Langmuir isotherm is used to describe the experimental data. In the literature various improvements compared to the Langmuir model are proposed, e.g. the isotherms according to Fowler, Radke-Prausnitz, Freundlich or Brunauer-Emmet-Teller (BET isotherm), respectively (3).

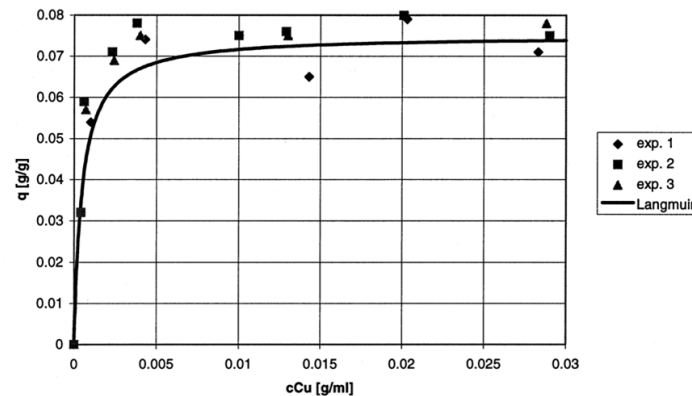


Figure 1: Experimentally measured isotherms of copper sulfate on Dowex 50W-X8 at room temperature (symbols) and description with Langmuir isotherm (line): $K = 2100$; $q_m = 0.075$ g/g.

Process kinetics

For the process design, apart from the equilibrium behavior, also the kinetics are crucial. In most cases an experimental determination of these data is required as the layout and operation method of the equipment influences it. Kinetics are mainly affected by the following variables:

- flow conditions.
- mass transfer from the fluid phase to the surface of the stationary phase.
- diffusion inside the pores of the stationary phase.
- size of the stationary phase particles.

Regeneration

In order to use the stationary phase (adsorbent material or ion exchange resin) several times, a regeneration of the material has to be feasible. Different options for regeneration of adsorbent materials exist and are used (1):

- temperature increase ("thermal swing").
- pressure decrease ("pressure swing").
- decreasing the partial pressure of the adsorbate by flushing with inert gas.
- replacement of the adsorbed species.

For the regeneration of ion exchange resins the adsorbed ions are again replaced by the original ones. This is done by flushing with a mineral acid or a concentrated salt solution for cation exchangers and with a base for anion exchangers. In this practicum a highly acid cation exchanger is used which is regenerated by hydrochloric acid.

The fixed bed process

Chromatographic processes are done mostly in columns with the stationary phase as fixed bed. During the process three different regions inside the column can be distinguished:

1. the zone in which equilibrium is already achieved.
2. the active mass transfer zone (adsorption zone or exchange zone) in which the material exchange takes place at the moment.
3. the zone with fresh stationary phase.

The active zone travels slowly through the fixed bed. The faster the equilibrium is achieved and the diffusion takes place, respectively, the smaller this zone is. As soon as the mass transfer zone reaches the end of the bed the adsorbed species breaks through and the stationary phase has to be regenerated. With the assumption of instantaneous equilibrium, isothermal conditions and negligible axial dispersion, the mass balance for the fluid phase for a column with constant flow through it can be described by the following partial differential equation:

$$u \frac{\partial c}{\partial z} + \frac{\partial c}{\partial t} + \frac{(1 - \varepsilon_{\text{total}})}{\varepsilon_{\text{total}}} \frac{\partial q}{\partial t} = 0$$

$\varepsilon_{\text{total}}$ describes the overall void fraction of the bed and q the loading per volume of adsorbent material given by the corresponding isotherm. The velocity of the mass transfer zone $v(c)$ can then be calculated:

$$v(c) = \frac{u}{1 + \frac{(1 - \varepsilon_{\text{total}})}{\varepsilon_{\text{total}}} \left(\frac{\Delta q}{\Delta c} \right)}$$

Description of the Experimental setup

The feed stream to the column is defined by the multiway valve V1, see Figure 2. During the experiment a copper sulfate solution is fed to the column whereas for the regeneration diluted hydrochloric acid is used to replace the copper ions by H^+ ions. After the regeneration the column is flushed with water. The piston pump which is used to pump the fluid to the column contains an air bleed valve to remove the air in the tubes. The two glass columns are packed with the ion exchange resin Dowex 50W-8X (a highly acidic cation exchange resin) which is fixed by porous frits at both end of the columns.

The ion exchange process can be observed by the color change of the solution. The copper sulfate solution loses its blue color after releasing the copper ions, therefore the concentration of the copper ions can be monitored by an UV-Vis spectrometer. After calibrating the spectrometer the uv-light absorption can be correlated to the concentration.

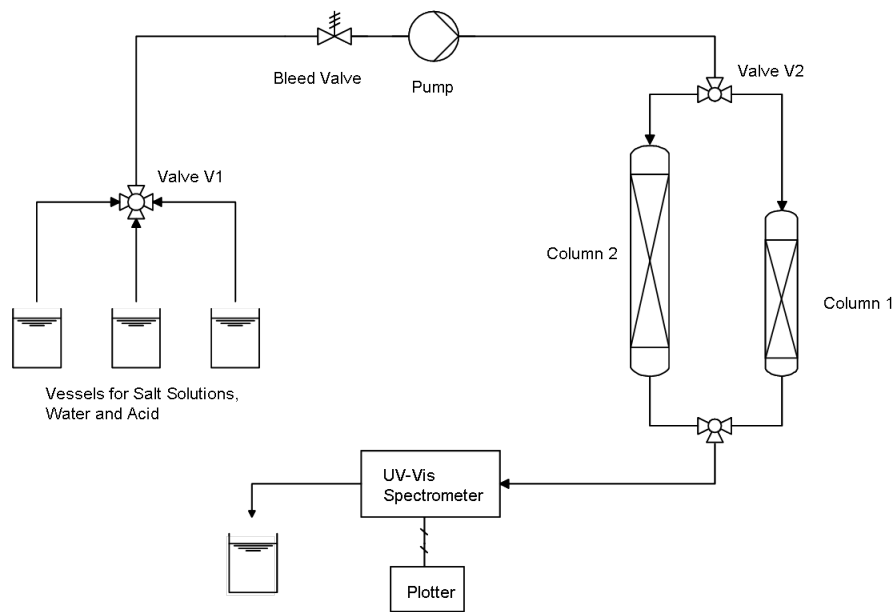


Figure 2: Scheme of the experimental setup.

Table 1: Data

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|--------------------------------|-----------------------|-------|--|
| Column 1: | | | |
| Length | L_1 | 7.5 | cm |
| Diameter | d_1 | 1 | cm |
| Mass of the ion exchange resin | m_1 | 5.4 | g |
| Column 2: | | | |
| Length | L_2 | 17.0 | cm |
| Diameter | d_2 | 1.5 | cm |
| Mass of the ion exchange resin | m_2 | 25.6 | g |
| General data: | | | |
| Porosity | ε_{total} | 0.71 | - |
| Particle size Dowex 50W-8X | d_p | 40-80 | μm |
| Solutions: | | | |
| Copper Sulfate | — | 0.02 | $\text{g}_{\text{Cu}_2^+} / \text{g}_{\text{solvent}}$ |
| HCl | — | 1.5 | M |

Experimental Tasks

The general task is to find the process parameters, i.e. the flow rate, for column 2, for a given breakthrough time of 30 minutes.

1. First experimental run on column 1 using an arbitrary flow rate (between 1 to 10 ml/min). During the first run you should think about the regeneration, what kind of concentration profiles based on the equilibrium theory do you expect?

2. Regeneration of column 1. During the regeneration of column 1: Define process parameters, i.e. flow rate, for column 2 in order to obtain a breakthrough time of 30 minutes.
3. Second experimental run on column 2 with the calculated parameters.
4. Simulate chromatographic process using a given Fortran program.

Assignments

The following questions need to be properly answered within the report:

1. Explain using a schematic drawing how the different void fractions $\varepsilon_{particle}$, ε_{bed} and ε_{total} are defined and show their mathematical relation.
2. Calculate the pressure drop in column 2 using the Ergun equation.
3. Which profile do you expect for the regeneration of the column loaded with CuSO_4 ? Explain why?
4. Fix suitable operating parameters for column 2, namely the flow velocity for a 30 min loading time. Are there additional phenomena to be considered?
5. Compare the printouts of the simulated and the experimental runs and explain the differences.

Report

A report has to be written containing all the important information of the experiments carried out. The report should include, but is not limited to, the following items:

- title page: the title page includes a title (obviously), your names, your email addresses, the date you handed the report in and a small abstract.
- introduction: a small introduction that explains what experiment you are doing and what insight you want to gain.
- theory section: the theory section includes all the equations you are going to use to interpret your results. **Complete** derivations of all equations **do not** have to be included, but you should shortly state the principles behind the equations used and draft the basic maths to derive them. If assumptions have to be made for an equation to be valid, they have to be **clearly** stated.
- experimental part which includes **what** you did, **why** you did it and **how** you did it.
- results and discussion: in this part your results are included. Your measurement results have to be explicitly given, so that any calculations are reproducible. This part also includes the discussion of your experimental as well as simulated results. In the discussion you state if the results you obtained were expected. If they were not expected, give explanations why they are not what you expect. This section is the most important

section of your report because it gives the indication if you understood what you were doing. All the figures you are implementing in the report have to be commented (**what** can be seen and **why** do you think it is important to show?).

- the assignments have to be answered properly.

You have three weeks time to hand in a report that meets these standards, which includes possible corrections you have to make. Therefore, it is recommended to hand in the first version of the report earlier, so that you have time to correct possible mistakes. The time the assistant takes to correct your report is **not** included in the three weeks. The report can be handed in either digitally or as hard copy directly at the assistant's office.

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References

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