Application of membrane filtration for the treatment of copper containing test wastewaters using a CM CELFA P-28 test apparatus

1 Theoretical background

Membranes have gained an important place in chemical technology and are used in a broad range of applications. The key property that is exploited is the ability of a membrane to control the permeation rate of a chemical species through the membrane. In separation applications, the goal is to allow one component of a mixture to permeate the membrane freely, while hindering permeation of other components. The membrane separation processes can be categorized based on the driving force of the process. Microfiltration, ultrafiltration, nanofiltration and reverse osmosis belong to the group of **pressure-driven membrane processes** while in case of dialysis, gas separation the driving force is the concentration difference between the two sides of the membrane. Pervaporation and membrane distillation belong to the third group, where the partial pressure difference and temperature play a great role in permeation.

Microfiltration, Ultrafiltration, Nanofiltration and Reverse Osmosis altogether are called membrane filtration.

Nanofiltration (NF) membrane rejects only ions with more than one negative charge, such as sulfate or phosphate, while passing single charged ions. NF also rejects uncharged, dissolved materials and positively charged ions according to the size and shape of the molecule in question. The rejection of sodium chloride with NF varies from 0-50 percent depending on the feed concentration.

This effect has proven desirable for a number of applications where moderate salt removal is acceptable since operating pressures and power consumption are significantly lowered.

Reverse Osmosis (RO) is the tightest possible membrane process in liquid/liquid separation. Water is in principle the only material passing through the membrane; essentially all dissolved and suspended material is rejected.

1.1 Filtration techniques

Particle filtration is usually investigated by conventional dead-end filtration. The bulk flow is to be treated flows perpendicular to the filter medium and filtrate flows in the same direction, i.e. perpendicularly away from the filter media. The filtered particles remain on the surface of the filter media forming a cake, which increases the total resistance of filtration. Contrary the conventional filtrations, the membrane separation processes apply mainly cross-flow filtration. The feed fluid flows parallel the membrane surface; meanwhile the permeable components pass through the membranes perpendicularly due to the driving force. The turbulent flow of the bulk solution over the surface minimizes the accumulation of particulate matter on the membrane, and facilitates continuous operation of the system. Therefore the concentration polarization can be minimized and the fouling of the membrane can be avoided. A schematic drawing of the comparison of **dead-end** and **cross-flow filtration** can be seen in Figure 1.
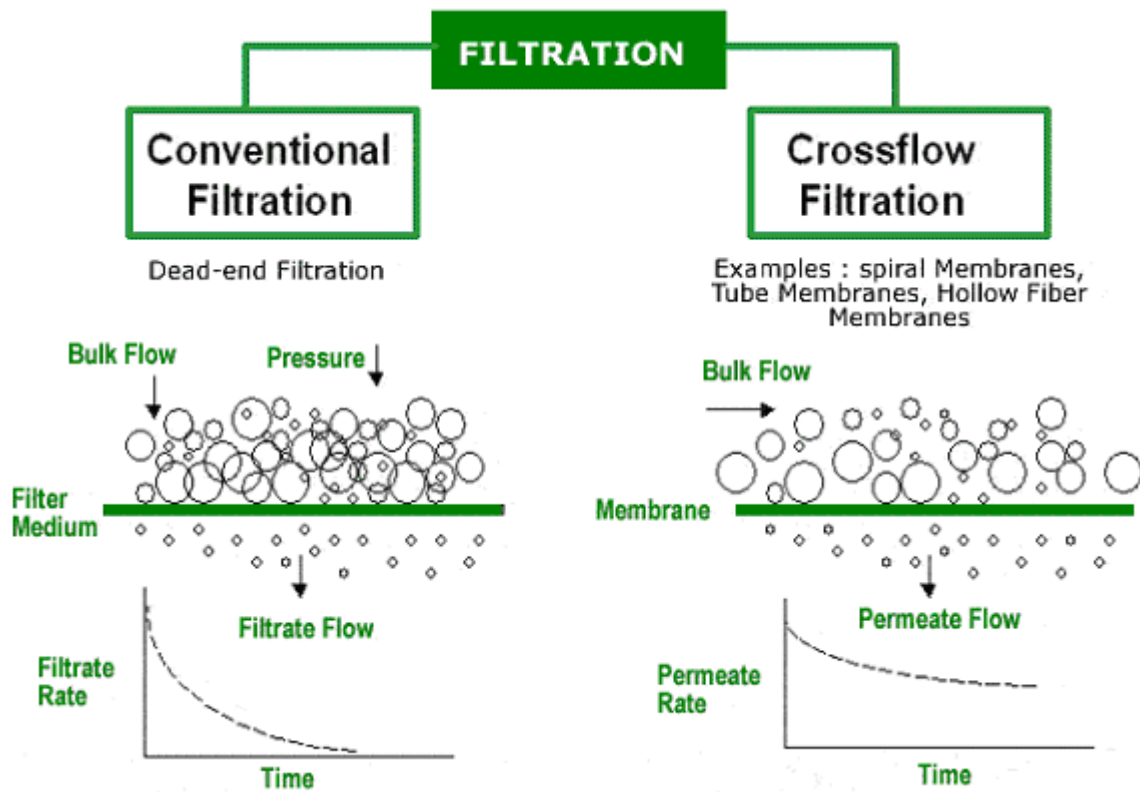
Figure 1 Comparison dead-end and cross-flow filtration

1.2 Module types and characteristics

Modules are designed to achieve improved membrane properties, i.e. higher flux and rejection or selectivity, and better stability, and reduced concentration polarization. Based on these considerations different modules are designed. The simplest module is the **flat sheet** (see Figure 2), which is mainly used for test experiments. When applying cross-flow filtration on a flat sheet membrane, the characteristic of the feed flow (temperature, concentration etc.) changes along the membrane surface. These changes can be neglected in case of a bench scale membrane, but not in industrial scale. Attaining better efficiency, flat sheet membranes are built into **plate and frame module**. In this module membranes sitting on a plate that provides a porous support for the permeate outlet, and they are connected serial or parallel. Membranes are separated from each other by a spacer.

Higher flux can be achieved using membranes larger in area. If the flow is to be treated contains suspended solids, it is very important not to damage the membranes by fouling. **Tubular membranes** can offer a good choice for the treatment of high suspended solids containing solutions. Tubular membranes are generally constructed as a membrane layer cast on a sturdy backing material. This backing material supports the thin inside membrane layer. Tubular membranes operate inside-to-outside: the pressurized feed stream flows through the inside of the tube, while the water permeates through the membranes on the outside of the tube. **Capillary module** is a special class of tubular membrane, in which the diameter of a tube is as wide as capillary tube. Flat sheet membrane, tubular module and capillary module can be seen in Figures 2, 3 and 4, respectively.

Figure 2 Flat sheet module
(**www.sterlitech.com**)

Figure 3 Tubular module
(**www.kochmembrane.com**)

Figure 4 Capillary module
(**www.enwa.no**)

Hollow fiber modules (**Error! Reference source not found.**) are membranes that are self supporting, i.e., the walls are strong enough to avoid collapse. The outer diameters are typically less than 1.0 mm. Hollow fiber modules contain thousands of fibers arranged in a 'bundle' and potted by epoxy in an outer shell. Conceptually the design is similar to the capillary and tubular design, but can be operated with shell side or lumen side feed depending on the membranes and application. **Spiral wound membrane** (**Error! Reference source not found.**) uses flat sheets wound around a central tube. The membranes are glued along three sides to form leaves attached to permeate channel (tube) along the unsealed edge of the leaf. The internal side of the leave contains a permeate spacer designed to support the membrane without collapsing under pressure. This permeate spacer is a porous and conducts the permeate to the permeate tube.
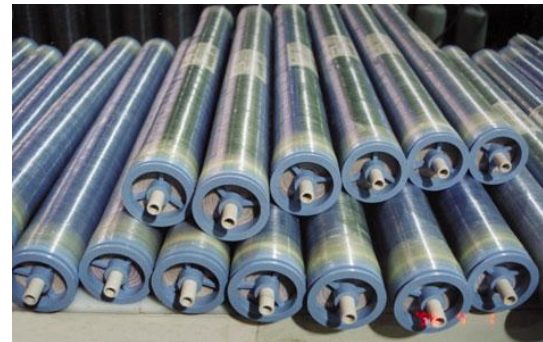

Figure 5 Hollow fiber module
(**www.kochmembrane.com**)

Figure 6 Spiral wound module
(**www.kochmembrane.com**)

1.3   Characterization of membrane filtration

1.3.1   Permeate flux

During the experiments, permeate flux (*J*) can be calculated according to the Eq.1:

$$J = \frac{1}{A} \cdot \frac{dV_P}{dt}$$

(1)

where A (m^2) is the membrane surface, V_P (m³)is the volume of the permeate and t (s) is the time.

The measurement unit for permeate flux in SI is $m^3/(m^2 s)$, but usually $L/(m^2 h)$ is used.

1.3.2 Rejection

The rejection of a compound is calculated according to Equation (2):

$$R = \left(1 - \frac{c_p}{c_f}\right) \times 100 \qquad (2)$$

where R is the rejection (%), c_p and c_f are the concentrations of the permeate and the feed regarding the same compound, respectively.

Membrane filtration is a spreading technique in wastewater treatment because of its efficiency of elimination multivalent ions. It is important especially in the electrochemical and electroplating industry. This laboratory work is focused on the elimination of copper(II) and ion. A circle-shaped flat sheet membrane is used in the test membrane apparatus (CELFA P-28).

2 Experimental

This laboratory work is focused on the filtration of copper(II) ion containing test solution. A circle-shaped flat sheet membrane is used in the test membrane apparatus (CELFA P-28).

2.1 Experimental apparatus

The applied laboratory set-up is shown schematically in Figure 7. The feed solution is kept at constant temperature in a stainless steel tank (1). In order to supply the driving force of the membrane filtration, gauge pressure is used on the feed side of the membrane. The constant gauge pressure in the tank is ensured by a reducer (8) using an inert gas, in our case nitrogen gas. The feed solution that is circulated by a pump (2), contacts one side of the membrane (3). Due to the circulation cross-flow experiments can be achieved. The effective area of the membrane is 28 cm^2.
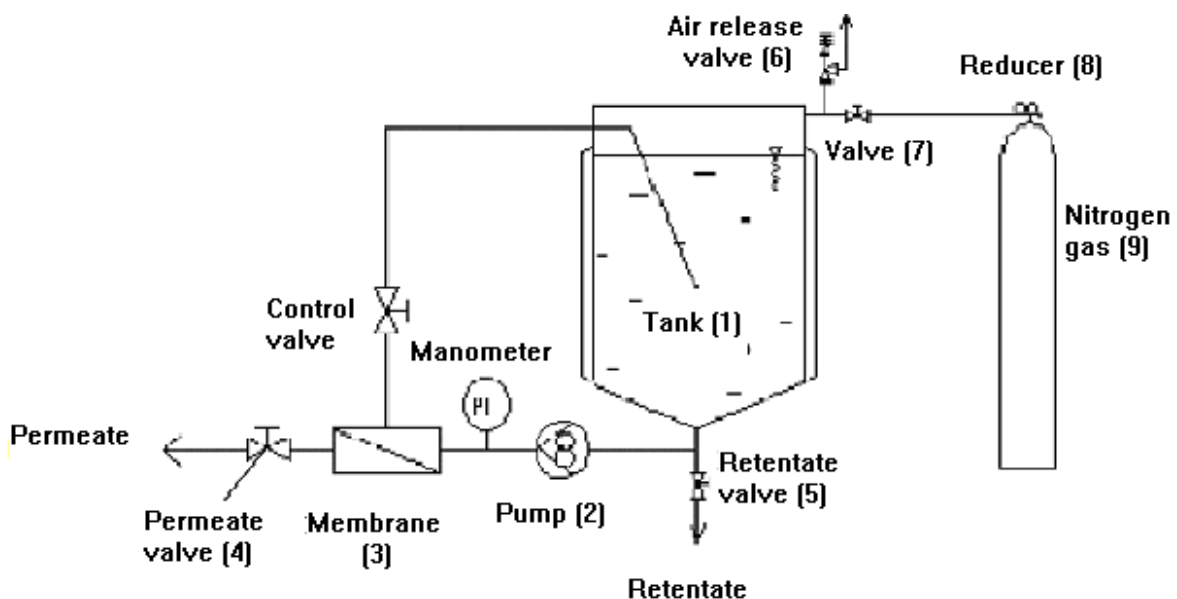

Figure 7 Schematic drawing of the CELFA P-28 test membrane apparatus

2.2 Measurement method:

1. Measure 500 ml from the previously prepared copper-containing solution. Use a cylinder. This is the initial feed solution.
2. Place glass pots under the permeate and retentate valves.
3. Check the state of the valves number (4) (5) (7) whether they are closed. If yes, then check the reducer (8) to be closed (If you turn the pressure regulator of the reducer to the left, it should be totally to the end. In this case if the valve on the top of the gas cylinder is open, there will not be overpressure in the tube which connects the reducer to the tank.)
4. Check the state of the speed regulator on the pump (2). It should stand at 300.
5. Pour about 50 ml distilled water into the tank (1) then switch on the pump (2) (press the small button next to the speed regulator; it gives light when switched on). The membrane is now washed.
6. After about 2-3 minutes washing, switch off the pump (2) and open the retentate valve (5) in order to let the washing water flow out of the device. Then close the retentate valve (5).
7. Pour the copper-sulfate solution into the tank (1), switch on the pump (green button), and after 2-3 minutes circulation, switch off the pump and open the retentate valve (5), so let the solution flow out. Then close the valve (5). (This step is important, because about 10 g of distilled water remain in the dead space of the apparatus, which has effect on the dilution of the initial concentration.)
8. Measure the conductivity of the modified/diluted feed solution.
9. Take 5 ml sample from the modified feed solution using a pipette. Then weigh the mass of the feed solution.
10. Pour the feed solution into the tank (1).
11. Place the cap onto the tank (1) and close it tight.
12. Switch on the pump (2) (green button).
13. Open the valve number (7).
14. Adjust the gauge pressure from the nitrogen gas cylinder: open the valve of the gas cylinder, then adjust the gauge pressure by turning slowly the pressure regulator of the reducer. The gauge pressure in the tank is shown by the manometer.
15. After adjusting the gauge pressure, open the permeate valve (4) and start measuring the operating time
16. Measure the operating time until the end of the experiment. During this, measure the flow rate of the permeate: record the time moments at each 10 ml of permeate.
17. Measure the flux, i.e. record the time, and conductivity of every 10 ml of permeate.
18. End of experiment: Take away 100 ml of permeate, then stop measuring time and close the permeate valve (4).
19. Switch off the pump (2) (press the green button) and close the nitrogen valve (at the top of the gas cylinder).
20. Wear protective glasses.
21. Hold the plastic tube of the retentate valve (5) very tight, and open the valve (5) very slowly. Attention, the apparatus spits when all the retentate flow out. Weigh the mass and record the volume of the retentate.
22. If the gauge pressure is disappeared, close the valve number (7), and turn the pressure regulator of the reducer to the left.
23. Remove the cap of the tank (1).

24. Wash the membrane with distilled water according to points 5-6. Repeat the washing until the conductivity of the removed washing water is about kb. 10 μS/cm.
25. At the and of washing, pour about 50 ml into the tank, in order to avoid the
26. Take 5 ml sample from the retentate and analyze the copper concentration of the feed and the retentate samples by iodometric titration.
27. Regard the copper concentration of the permeate equal to 38 mg/l. (The copper concentration of the permeate is lower than the detection limit of the titration. It could be determined by atomic absorption.)

Solution is to be filtrated:
$CuSO_4.5H_2O$ solution (about 10 g/l concentration)
Applied membrane:
Effective area: 28 cm^2
Type: *given by the practice leader*
Circumstances:
Transmembrane pressure: 30bar
Temperature: 25°C
Operating time: time, which is needed to collect 100 ml permeate
Results and diagrams:
1. Table including the circumstances, operating time and permeate volume.
2. Mass and component balance regarding the copper ion.
3. Rejection of the membrane regarding the copper ion (According to Eq.2.)
4. Diagram: Permeate flux versus operating time Flux=[l/m^{2}h], time=[min]
5. Diagram: permeate conductivity versus operating time.

# Analysis of copper (II) ions by iodometric titration

Principle: copper(II) ions oxidize the iodine ions to iodine while forming copper(I) ions. These copper (I) ions form copper-iodine, which precipitates from the solution. The reaction is as follows:

$$2Cu^{2+} + 4I^- \longrightarrow 2CuI + I_2$$
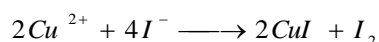
The precipitate shifts the reaction to the formation of iodine. Since the equilibrium constant of the gross reaction is not too high, therefore iodine is needed in excess.
Having iodine in appropriate excess, the quantity of ion is practically equal to the quantity of copper (II) ions. The copper(I)-iodine precipitates totally when the reaction takes place in acidic environment. For that acetic acid is used. Strong acids solve the precipitates

Ioidine can be analyzed by sodium-thiosulfate solution, in presence of starch indicator:

$$i_2 + 2S_2O_3^{2-} = S_4O_6^{2-} + 2I^-$$
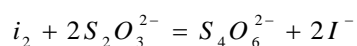
1 ml sodium-thiosulfate solution with a concentration of 0.1 mol/litre measures 1 mmol, i.e. 63.54*0.1=6.354 mg copper(II) ion.

Reagents:
  0.1 mole/litre $Na_2S_2O_3$ solution
  5% acetic acid
  potassium-iodine
  starch indicator

Process:
Place the sample into a 100 cm³ Erlenmeyer-glass. Dilute it to about 50 cm³. Add 5 cm³ of acetic acid and about 1 g KI, then close the Erlenmeyer-glass. After 5 minutes reaction time, titrate the formed iodine with 0.1 mole/litre $Na_2S_2O_3$ solution. Near to the equilibrium point, add 1cm³ starch indicator into the solution. At the end of titration the solution contains white precipitation.