Separation Processes, ChE 4M3, 2012

Assignment 4

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Objectives: Understanding membrane separation processes.

Question 1 [5; already answered as pop-quiz in class; do not re-submit a solution]

A microfiltration membrane operating with pure feed of water produces a flux of 0.06 kg.s^{-1}.m^{-2} when operated with a TMP of 30 kPa.

1. What is the resistance due to the membrane? Specify the units.

2. If operated with a protein-water mixture at a 20 kPa pressure difference, a flux of 216×10^{-6}kg.s^{-1}.m^{-2} is measured at steady state. What is the resistance due to cake build-up? Specify the units.

Solution

The general equation is:

$$J = \frac{\Delta P}{\mu \left(R'_c + R'_m \right)}$$

1. When pure water is being filtered, the resistance due to cake build up is zero, so solve the equation for R'_m. Using/assuming water viscosity to be $\mu = 1 \times 10^{-3}$ Pa.s, then $R'_m = 5 \times 10^8$ m^2.kg^{-1}.

2. This membrane resistance remains the same when filtering the protein, so solving the general equation gives $R'_c = 9.2 \times 10^{10}$ m^2.kg^{-1}.

Question 2 [20; but please see the next paragraph though]

Please answer part A **or** part B. Part A was the class submission you handed in on 16 October. If you handed in at class, and want to keep that as your submission (i.e. less work for you in this assignment), then please indicate that in your assignment submission. If you prefer to do part B (i.e. because you feel you can do a better job than part A you handed in earlier) please submit the answer only to part B. We will either grade part A or part B, but not both. My suggestion is to do part B, mainly so you get practice on a different problem.

Part A

An asymmetric ultrafiltration membrane is used with the aim of separating dyes from a liquid stream and to achieve a more concentrated dye-water mixture. The feed waste stream arrives at a flow rate of 2.2 m^3.hour^{-1} with concentration of 1.2 kg.m^{-3}. The membrane's operating characteristic was calculated from various experiments:

$$J_v = 0.04 \ln \left(\frac{15}{C} \right)$$

where the bulk concentration C has units of kg.m^{-3} and flux is measured in m^3.hour^{-1}.m^{-2}.

If two membrane modules, each of area 25 m^2, are simply placed in series, give reasonable estimates of:

1. the dye concentration from the first membrane module?

2. the permeate flow rate from the first membrane module?

3. the dye concentration from the final membrane module?

4. the permeate flow rate from the final membrane module?

5. Then explain whether the above answers seem reasonable.

Please show all calculations, assumptions and relevant details.

Part B

An asymmetric ultrafiltration membrane is used with the aim of separating dyes from a liquid stream and to achieve a more concentrated dye-water mixture. The feed waste stream arrives at a flow rate of $3.0\,\mathrm{m^3.hour^{-1}}$ with concentration of $0.5\,\mathrm{kg.m^{-3}}$. The aim is to achieve a dye-water concentration leaving the membrane of $20\,\mathrm{kg.m^{-3}}$, so that it can be reused to dye fabric. The membrane's operating characteristic was calculated from various experiments:

$$J_v = 0.04 \ln\left(\frac{25}{C}\right)$$

where the bulk concentration C has units of $\mathrm{kg.m^{-3}}$ and flux is measured in $\mathrm{m^3.hour^{-1}.m^{-2}}$.

We have tubular membranes available from a supplier, but only as $30\ \mathrm{m^2}$ modules. The modules are placed in parallel, so the effectively can be treated as one large membrane.

1. What is the flow rate of the cleaned water from the system (we can use it elsewhere in our process)?

2. What number of modules would we have to purchase if operated in a single-stage feed-and-bleed configuration?

3. What would be the *optimal* module arrangement if operated with two stages of feed-and-bleed in series? (*hint*: optimal should be taken to be the smallest number of modules per feed-and-bleed stage; each stage may have a different area).

4. For the optimal arrangement you choose: specify what will be the total flow of cleaned water (*hint*: think carefully!)

5. What are your thoughts on putting four feed-plus-bleed stages in series?

Please note: it is in your interest to solve this problem as if it were in a test or exam; i.e. don't use computer software.

Solution

Part A: see solutions to the 2012 midterm on the course website.

Part B

1. A single membrane unit is being used: the aim is calculate the total area provided by the parallel modules. As shown in the solutions developed in class:

    - From a mass balance around the unit, assuming no dye leaves in the permeate (a reasonable assumption for ultrafiltration): $Q_0 C_0 = Q_{R1} C_{R1}$

    - From a volume balance we have $Q_0 = Q_{P1} + C_{R1}$

- The given flux equation $J_v = \dfrac{Q_{P1}}{A_1} = 0.04 \ln\left(\dfrac{25}{C}\right)$

- When solving the above equations we find that: $Q_{R1} = \dfrac{Q_0 C_0}{C_{R1}} = \dfrac{(3)(0.5)}{20} = 0.075\,\mathrm{m^3.hr^{-1}}$

So the flow of clean water from the single unit is $Q_{P1} = 2.925\,\mathrm{m^3.hr^{-1}}$.

2. Use the flux equation and solve for $A_1 = 327.7\,\mathrm{m^2}$, provided by 11 modules.

3. We require to find the areas of the two units to determine this. As with the single module system, set up the mass and volume balances for both units. Substitute these into the flux equation for each unit:

$$
\begin{aligned}
Q_0 &= Q_{P1} &+\; Q_{R1}\\
3.0 &= 0.04 A_1 \ln\left(\dfrac{25}{C_{R1}}\right) &+\; \dfrac{1.5}{C_{R1}}\\
Q_{R1} &= Q_{P2} &+\; Q_{R2}\\
\dfrac{1.5}{C_{R1}} &= 0.04 A_2 \ln\left(\dfrac{25}{C_{R2}}\right) &+\; \dfrac{1.5}{20}
\end{aligned}
$$

These 2 equations involve 3 unknowns: A_1, A_2 and C_{R1}. As is the case with optimization, there are always spare degree(s) of freedom to adjust. In this case we adjust C_{R1} to different values and find the result of A_1 and A_2 so their total sum is at a minimum.

Some values that were tried:

C_{R1} [kg.m^{-3}]	A_1 in m^2	A_2 in m^2
8	61.7 [3 modules]	12.6 [1 module]
12	97.9 [4 modules]	5.60 [1 module]
4	35.8 [2 modules]	33.6 [2 modules]
5	41.9 [2 modules]	25.2 [1 module]

This tables makes sense: as we increase the intermediate retentate concentration, C_{R1}, the area required in the first unit to achieve that concentration increases, meaning that less area is required in the second unit.

There will be a broad range of valid solutions around $C_{R1} = 5\,\mathrm{kg.m^{-3}}$, corresponding to 2 modules in the first unit and 1 module in the second unit.

4. Let the optimal arrangement be the last row in table 5 (note there are many possible, similar solutions), then the total flow of cleaned water is found by calculating the permeate flows from both units.

Note however, that the area of the first unit, $41.9\,\mathrm{m^2}$, is not actually achieved, it is $A_1 = 60\,\mathrm{m^2}$. So solve the membrane mass and volume balance equations for this new area to calculate C_{R1} (requires an iterative solution, as in the midterm). Then calculate the permeate flow rate $Q_{P1} = 0.04 A_1 \ln\left(\dfrac{25}{C_{R1}}\right)$.

Repeat this for the second unit using $A_2 = 30\,\mathrm{m^2}$ to calculate Q_{P2}. Sum the two for the final solution of clean water flow.

Note that C_{R2} will exceed the specifications of 20 kg.m^{-3} from the overall system.

5. Using more than 2 feed-plus-bleed units will be counterproductive for 3 or more stages. We are already using 3 modules in 2 units, so at best a 3-unit system will use a module each, but at significantly increased capital cost.

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Question 3

At 25 °C in a lab membrane with area $A = 2 \times 10^{-3}\,\text{m}^2$ we feed a solution of 10 kg NaCl per m^3 solution so well mixed that essentially it has the same strength leaving.

The permeate is measured as 0.39 kg NaCl per m^3 solution at a rate of $1.92 \times 10^{-8}\,\text{m}^3.\text{s}^{-1}$ when applying a constant pressure difference of 54.42 atm.

Calculate:

1. the permeance constants for the solvent

2. the permeance constants for salt (these type of constants are previously given, but this question shows how they may be calculated experimentally)

3. the rejection coefficient.

Solution

This question shows how permeance constants, A_{solv} and A_{salt}, which are normally given, may be calculated.

1. The solvent flux is given by $J_{\text{solv}} = A_{\text{solv}}\left(\Delta P - \Delta \pi\right) = \dfrac{1.92 \times 10^{-8}\,\text{m}^3.\text{s}^{-1}}{2 \times 10^{-3}\,\text{m}^2}.$

$$C_{\text{F}} = C_{\text{R}} = 10000\frac{\text{g}}{\text{m}^3} \times \frac{\text{mol}}{58.5\text{g}} = 170.9\frac{\text{mol}}{\text{m}^3}.$$

$$C_{\text{P}} = 390\frac{\text{g}}{\text{m}^3} \times \frac{\text{mol}}{58.5\text{g}} = 6.67\frac{\text{mol}}{\text{m}^3},$$

So now the osmotic pressure difference can be found from

$$\Delta \pi = \left(C_{\text{F}} - C_{\text{P}}\right) RT \times 2\frac{\text{ions}}{\text{mol of NaCl}}$$
$$= (170.9 - 6.67)\left(8.2057 \times 10^{-5}\right)(298)(2) = \mathbf{8.0}\ \text{atm}$$

Solving for $A_{\text{solv}} = \dfrac{1.92 \times 10^{-8}\,\text{m}^3.\text{s}^{-1}}{2 \times 10^{-3}\,\text{m}^2} \cdot \dfrac{1}{(54.42 - 8.0)\,\text{atm}} \times \dfrac{1000\,\text{kg}}{\text{m}^3} = 2.07 \times 10^{-4}\,\dfrac{\text{kg solvent}}{\text{s.atm.m}^2}.$

2. The permeance constant for salt is found from $J_{\text{salt}} = A_{\text{salt}}\left(C_{\text{R}} - C_{\text{P}}\right)$; and $J_{\text{salt}} = J_{\text{solv}}C_{\text{P}}$.

$$A_{\text{salt}} = J_{\text{solv}}\frac{C_{\text{P}}}{(C_{\text{R}} - C_{\text{P}})} = \frac{1.92 \times 10^{-8}\,\text{m}^3.\text{s}^{-1}}{2 \times 10^{-3}\,\text{m}^2} \cdot \frac{0.39\,\text{kg NaCl.m}^{-3}}{(10 - 0.39)\,\text{kg NaCl.m}^{-3}} = \mathbf{3.9 \times 10^{-7}}\,\text{m.s}^{-1}.$$

3. The rejection coefficient is $R = 1 - \dfrac{C_{\text{P}}}{C_{\text{F}}} = 1 - \dfrac{0.39}{10.0} = 0.961$ or **96.1 %**.

Question 4 [5]

Why did we not take osmotic pressure in account for microfiltration and ultrafiltration? Perform a representative calculation to prove your answer.

Solution

Thanks to Xin and Sean

In microfiltration and ultrafiltration, the membrane can only retain very large particles, while the smaller ions can freely pass through pores and equilibrate on both sides of the membrane. As a result, larger particles

are the only contributor to the molar concentration difference across the membrane, which will be very small due to large molecular weight of these particles. Since osmotic pressure is purely generated by molar concentration difference across membrane, it is likely negligible compared to the positive pressure applied in the case of MF and UF.

Representative calculation In seawater, the salt concentration is 3.5 wt%, which generates an osmotic pressure of 25.2 atm against pure water in RO applications. In UF applications, the typical molecular weight is 1 to 1000kDa. Assume a molecular weight of 100 kDa and the same solid concentration as seawater. The molar concentration in feed is, $C_F = 3.5 \dfrac{\text{g solid}}{100\,\text{g water}} = \dfrac{35\,\text{kg solid}}{1\,\text{m}^3\,\text{water}} \times \dfrac{1\,\text{mol}}{100\,\text{kg}} = 0.35\,\text{mol.m}^{-3}$.

Assuming negligible solid concentration on permeate side, the osmotic pressure at 25 °C is $\Delta\pi = (C_F - C_P)\,RT = (0.35 - 0)\,\text{mol.m}^{-3}(8.2057 \times 10^{-5}\,\text{atm.m}^3\text{mol}^{-1}.\text{K}^{-1})(298\,\text{K}) = 8.56 \times 10^{-3}\,\text{atm}$.

Typical transmembrane pressures for UF application are about 1 to 10 atm. The osmotic pressure generated in this example is less than 0.1% of the applied TMP. Therefore osmotic pressure can be safely ignored in UF and MF applications.

Question 5

Reverse osmosis with an NaCl-water feed, 2.5 g/L NaCl (note, a previous version of the assignment had 2.5 wt%, which was corrected on the course website midway during the assignment) is being separated into a permeate and retentate stream using a TMP of 27.2 atm at 25 °C.

Through lab experiments (e.g. see a previous question in this assignment), the permeance of the membrane with respect to salt is $4.2 \times 10^{-7}\,\text{m.s}^{-1}$ and solvent is $5.0 \times 10^{-4}\,\text{kg.s}^{-1}.\text{m}^{-2}.\text{atm}^{-1}$. The membrane is operated so the cut is unusually low, at 10%, producing a permeate stream of 0.38 m^3 per hour.

Calculate the permeate concentration, retentate concentration, rejection coefficient, and separation factor. It is not reasonable to assume that the feed and retentate concentration are the same in this problem: we require accurate estimates.

Solution

The feed concentration, $C_F = 2.5$ g/L NaCl $\equiv 0.0427\,\text{mol.L}^{-1}$. A solution of this concentration has an osmotic pressure of 2.09 atm.

We are told the cut $= \theta = \dfrac{Q_P}{Q_F} = 0.1$, from which we can calculate (see course notes) that $C_F = (1-\theta)C_R + \theta C_P$, or that $C_P = \dfrac{C_F - (1-\theta)C_R}{\theta}$.

Solving for the permeate and retentate concentrations requires iteration. Pick a value of $C_R > C_F$, so about 2.8 g/L, which leads to calculated value of $C_P = \dfrac{2.5 - (1-0.1)(2.8)}{0.1} = -0.2$ g/L. This is not possible, but it indicates to us a rough upper bound on C_R.

So we need to reduce our initial guess: try $C_R = 2.7$ g/L leads to $C_P = 0.7$ g/L. At this level, the rejection coefficient is $R = 1 - \frac{C_P}{C_F} = 0.72$, which is very low for a membrane. We should possibly use a different (higher C_R) so we can get this recovery value around 90%, which is typical for membranes.

Using these values anyway, we can calculate $\Delta\pi = (C_R - C_P)RT = 1.67$ atm (making sure you convert the concentration units and use a factor of 2 for NaCl ions).

Next the solvent flux is calculated as $J_{\text{solv}} = A_{\text{solv}}\,(\Delta P - \Delta\pi) =$

$J_{\text{solv}} = 5.0 \times 10^{-4}\,\text{kg.s}^{-1}.\text{m}^{-2}.\text{atm}^{-1}\,(27.2 - 1.67\,\text{atm})\,\dfrac{\text{m}^3}{1000\,\text{kg}} = 1.28 \times 10^{-5}\,\text{m}^3.\text{s}^{-1}.\text{m}^{-2}.$

This is equal to $J_{\text{solv}}C_{\text{P}} = J_{\text{salt}} = A_{\text{salt}}\,(C_{\text{R}} - C_{\text{P}}) =$

$J_{\text{salt}} = 1.28 \times 10^{-5}\,\text{m}^3.\text{s}^{-1}.\text{m}^{-2} \times 0.7\,\text{g.L}^{-1} \cdot \dfrac{1000\,\text{g.kg}^{-1}}{1000\,\text{L.m}^{-3}} = 8.9 \times 10^{-6}\,\text{kg NaCl.m}^{-2}.\text{s}^{-1}.$

Equating that to $A_{\text{salt}}\,(C_{\text{R}} - C_{\text{P}})$ and solving for $C_{\text{R}} = 21.97\,\text{kg NaCl.m}^{-3} = 21.97\,\text{g NaCl.L}^{-1}$. This number is higher than our original guess, which indicates our picked value of C_{R} was too low. Now we know that $2.7 < C_{\text{R}} < 2.8$ g/L.

If during your iterations you get a negative osmotic pressure, because $C_{\text{R}} < C_{\text{P}}$ then you must stop and question what's going on: in this case you cannot have $C_{\text{R}} < C_{\text{P}}$, so select other starting values and begin again.

So you may complete the rest of the question on computer, if you wish, or by hand for another iteration or so.

There is very poor numeric conditioning, so answers roughly in the range of the following are OK: $C_{\text{R}} = 2.75$ g/L, $C_P = 0.08$ g/L are acceptable.

From this the rejection coefficient is $R = 1 - \frac{C_{\text{P}}}{C_{\text{F}}} = 1 - \dfrac{0.08}{2.75} \approx 0.96.$

Separation factor is $S_{ij} = \dfrac{x_{i,1}/x_{j,1}}{x_{i,2}/x_{j,2}} = \dfrac{x_{\text{NaCl,R}}/x_{\text{water,R}}}{x_{\text{NaCl,P}}/x_{\text{water,P}}} = \dfrac{2.75}{0.08} \approx 31$, where i and j are selected so that $S_{ij} \geq 1$.

Question 6 [5]

Self-directed learning question : write no more than 0.5 page (i.e. 2 paragraphs) that answer **all** of the following questions in that space.

1. Where are membrane bioreactors used?

2. What do they separate?

3. What material(s) is/are they made from?

4. What is the advantage over the usual separation step that MBRs replace?

5. Who are the main manufacturers of MBRs?

6. What is the typical lifetime of an MBR unit?

For those in the class not familiar with self-directed learning: it is a valuable skill, that you will require in your future career, to be able to extend your existing knowledge into a new area and potentially apply that knowledge.

Solution

From Sean and Xin

Membrane bioreactors (MBR) are widely used in municipal and industrial wastewater treatment plants. They separate suspended solids from wastewater in the activated sludge process, which uses biological microorganisms to remove dissolved organic matter. The majority of MBRs are manufactured using micro-filtration (MF) and ultrafiltration (UF) hollow fibre or flat sheet membranes, which are made with common

materials such as polysulfone, polyvinylidene fluoride (PVDF), polyethylene, as well as other proprietary polymers [1]. Major manufacturer of MBRs include General Electric Water & Process Technologies (formerly Zenon Environmental), Siemens (formerly US Filter), Kubota and Mitsubishi-Rayon [1]. MBRs are able to replace sedimentation and other downstream unit operations, such as granular filtration and disinfection, in a conventional wastewater treatment process. The main advantage of MBR over conventional sedimentation process is reduction of footprint, as the latter separates suspended solids in wastewater by gravity, which requires considerable footprint to achieve similar capacity using MBRs. MBRs can also provide superior effluent quality compare to conventional processes to meet more stringent discharge requirements [2]. Membrane life in MBR depends on design flux through the membrane, but an average life of 10 years is typically expected provided that membranes are normally operated at design flux and are properly cleaned [2].

1. Yang, Cicek, and Ilg, "State-of-the-art of membrane bioreactors: Worldwide research and commercial applications in North America," *Journal of Membrane Science*, **270**, pp. 201-211, February 2006.

2. Cote, Alam, and Penny, "Hollow fiber membrane life in membrane bioreactors (MBR)," *Desalination*, **288**, pp. 145-151, March 2012.

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