

Q1: An amberlite IR-20 ion-exchange resin with a maximum ion-exchange capacity of 4.9 meq/g of dry resin is used to remove cupric ion from a waste stream containing 9.75 mM CuSO₄ (~ 19.5 meq Cu²⁺/L solution). The equilibrium ion-exchange reaction is:



As ion exchange takes place, the meq of cations in the aqueous solution and in the resin remain constant. The following equilibrium data for cupric ions with 19.5 meq/L solution is obtained:

c (meq Cu ²⁺ /L solution)	0.022	0.786	4.49	10.3
q (meq Cu ²⁺ /g resin)	0.66	3.26	4.55	4.65

The equilibrium constant, $K_{Cu^{2+}, H^+} = 2.0$

- (a) From the data compute the resin capacity Q , in eq/L of bed volume
- (b) Predict the meq of Cu²⁺ exchanged at equilibrium from 10L of 20 meq Cu²⁺/L, using 50 g of dry resin

[10]

Q2. An aqueous solution containing 20 mol/m³ each of glutamic acid (GA), glycine (G) and valine (V), is to be separated using Dowex 50W-X8 column of 470 mm in length. The bed porosity is 0.374. All the three solutes follow a linear isotherm, $q_i = K_i c_i$, where the values of K are 1.18 for GA, 1.74 for G and 1.64 for V. The superficial velocity is 0.025 cm/s.

Find (a) pulse duration to achieve complete separation

- (b) Time duration of the elution needed before the second pulse
- (c) If external mass transfer is significant, will the pulse duration and / or elution time change? Explain your answer.

[10]

Q3: Water containing 0.223 mg/L of chloroform (CF) is to be removed using activated carbon (AC) by adsorption. The activated carbon particle diameter is 1.5 mm (external surface area is 5 m²/kg) and follows a Freundlich isotherm, $q = 10 c^{0.564}$ where q is mg CF adsorbed / g AC and c is mg CF/L solution. The Sherwood number is 30, and the diffusivity is 1.13×10^{-5} cm²/s. The mass transfer resistance in the pores is negligible compared to external resistance. For an effluent of 0.01 mg CF/L,

- (a) Minimum amount of adsorbent needed per L of feed solution?
- (b) For batch with twice the minimum amount of adsorbent, what is the contact time?
- (c) For continuous mode with twice the minimum amount of adsorbent, the required residence time?

[10]

Solution of class Test QP 2 (11 Nov 2023)

Q1: In this problem, the max. Ω is mentioned in the (a) problem, but actual $\Omega \leq \Omega_{\text{max}}$.

The ion-equilibrium relation in this case is

$$K_{\text{Cu}^{2+}, \text{H}^+} = \left(\frac{\bar{c}}{\Omega}\right) \frac{y_{\text{Cu}^{2+}}(1-x_{\text{Cu}^{2+}})^2}{x_{\text{Cu}^{2+}}(1-y_{\text{Cu}^{2+}})^2}$$

where $\bar{c} = 0.0195 \text{ eq/L}$ and Ω is unknown.

$$x_{\text{Cu}^{2+}} = C_{\text{Cu}^{2+}} / 19.5 \quad \text{and} \quad y_{\text{Cu}^{2+}} = q_{\text{Cu}^{2+}} / \Omega$$

Using the above data in the problem:

<u>c</u>	<u>q</u>	<u>x</u>	<u>y</u>	<u>Ω (all roots)</u>
0.022	0.66	0.00113	0.66/ Ω	3.0, -1.67
0.786	3.26	0.0403	3.26/ Ω	6.105, 0.415
4.49	4.55	0.230	4.55/ Ω	8.58, 0.517
10.3	4.65	0.528	4.65/ Ω	8.77, 0.528

Here $K=2$ is given, so Ω can be found out

$$\text{as } K = \frac{\bar{c}}{\Omega} \frac{(q/\Omega)(1-x)^2}{x(1-q/\Omega)^2}$$

$$\Rightarrow \Omega^2(1-\frac{q}{\Omega})^2 = \frac{\bar{c}}{K} q \frac{(1-x)^2}{x}$$

$$\Rightarrow \Omega^2 - 2q\Omega + q = \frac{\bar{c}}{K} q \frac{(1-x)^2}{x}$$

$$\Rightarrow \Omega^2 - 2q\Omega + q \left(1 - \frac{\bar{c}}{K} \frac{(1-x)^2}{x}\right) = 0$$

$$\therefore \Omega = q \pm \sqrt{q^2 - q \left(1 - \frac{\bar{c}}{K} \frac{(1-x)^2}{x}\right)}$$

Clearly the for the + sign, $\Omega > \Omega_{\text{max}}$ in the last case (also in the last case $\Omega < 0$).

So taking average of all values for $0 < \Omega \leq \Omega_{\text{max}}$,

$$\Omega \approx 1.114 \text{ eq/L} \quad [\text{Here } \Omega_{\text{max}} = 4.9 \text{ meq/g}]$$

or 4.9 eq/L b.d

considering resin density $\approx 1 \text{ kg/L}$

(b) The total concentration (given in the problem)

$$c = 0.02 \text{ eq/L}$$

In this case, the capacity ~~is~~ can be considered as 1.114 eq/L (you can also take 4.9 meq/L as mentioned in part (b))

So, the equilibrium equation becomes,

$$2 = \frac{0.020}{1.114} \frac{y(1-x)^2}{x(1-y^2)}$$

Initially solution contains $(0.02)(10) = 0.2 \text{ eq Cu}^{2+}$ with $x_{\text{Cu}^{2+}} = 1.0$

Say $a \equiv \text{eq. of Cu exchanged.}$

Then @ equilibrium, from material balance

$$x_{\text{Cu}^{2+}} = \frac{0.02 - (a/10)}{0.02}$$

$$y_{\text{Cu}^{2+}} = \frac{a/50}{1.114 \times 10^{-3}}$$

Substituting these into equilibrium relation,

$$2 = 0.0179 \frac{\left[\frac{a/50}{0.00114} \right] \left[1 - \frac{0.02 - (a/10)}{0.02} \right]^2}{\left[\frac{0.02 - (a/10)}{0.02} \right] \left[1 - \frac{(a/50)}{0.00114} \right]^2}$$

Solving the non-linear by equation by successive iteration or in programmable calculator,

$$a = 0.199 \text{ eq of Cu exchanged.}$$

Thus $\frac{a}{(0.02)(10)} = 0.995$ (or 99.5% of Cu^{2+} exchanged)

Q2.

$$\text{Interstitial velocity } u = u_s/\epsilon_b = \frac{0.025}{0.374} = 0.0668 \text{ cm/s}$$

(a) Solute wave velocity $\equiv u_i = \frac{u}{1 + \left(\frac{1 - \epsilon_b}{\epsilon_b}\right) k_i'}$

(no diffusion effects)

$$= \frac{0.0668}{1 + \left(\frac{1 - 0.374}{0.374}\right) k_i'} = \frac{0.0668}{1 + 0.674 k_i'}$$

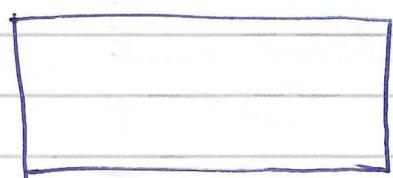
So,	Solute	K_i	$u_i (\text{cm/s})$
	C _A	1.18	0.0225
	G	1.74	0.0171
	V	2.64	0.0123

Since K of V is highest, it will be most strongly adsorbed. Therefore, solutes will leave the column in the order of C_A followed by G, then V. (first)

Thus, @ the end of the column, the trailing edge of C_A peak will coincide with the leading edge of G. So, the input can be injected till the time when the mean residence time between (max.) for difference between the two solute peaks.

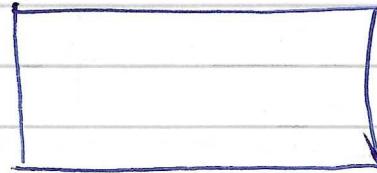
$$t_p = \frac{47}{0.0171} - \frac{47}{0.0225}$$

$$= 660 \text{ s}$$



So, the time needed for the trailing edge of C_A to reach end of the column @ 47 cm

$$= t_p + \frac{47}{0.0225} = 2749 \text{ s}$$



At that time, trailing edge of G wave will be @ $(47/0.0225)(0.0171) = 35.7 \text{ cm}$, while the leading edge of V wave will be

@ $(2749)(0.0123) = 33.8 \text{ cm}$. Therefore, C & V waves will be separated.

(b) Elution time,

the time needed for the trailing edge of the slow V wave to reach end of column (47 cm)

$$\Rightarrow t_p + \frac{47}{0.0123} = 4481 \text{ s}$$

Time for the leading edge of the second pulse of GA to reach end of column (47 cm) so that V & GA are just separated = $\frac{47}{0.0225} = 2089 \text{ s}$

The difference is $4481 - 2089 = 2392 \text{ s}$ before the second pulse starts. But ~~is~~ $t_p (= 660 \text{ s})$ of it is the first pulse.

$$\begin{aligned}\text{Therefore elution time} &= 2392 - 660 \\ &= 1732 \text{ s}\end{aligned}$$

1 Pulse (step input for) : 660 s

Elute : 1732 s

2 Pulse : 660 s

- Elute : 1732 s

:

Q3 : (a) The min. amt. of adsorbent corresponds to equilibrium with a solution of the effluent concentration of 0.01 mg/L. From Freundlich isotherm relation,

$$q = 10 (0.01)^{0.564} = 0.745 \text{ mg CF/g AC}$$

By material balance on CF, $c_i q = c_e q + q s_{\min}$

eq. conc. of CF vol. of solution
 in solution

min. amt. of A

Solving for 1 L basis of solution,

$$s_{\min} = \frac{q(c_i - c_e)}{q} = \frac{1(0.223 - 0.01)}{0.745} = 0.28 \text{ g AC}$$

for 1 L solution

(b) In the batch mode, the \$ rate of solute adsorption is controlled by external (solution phase) mass transfer, (adsorption kinetics is fast here)

$$\text{so, } -\frac{dc}{dt} = k_L a (c - c_e) \quad (\text{linear driving force model})$$

Now from material balance, $c_i q = c q + q s$

From isotherm, $c_e = (q/k)^{1/n}$ this is not c_e

[Freundlich isotherm is $q = k c_e^n$]

\therefore Combining these equations,

$$-\frac{dc}{dt} = k_L a \left\{ c - \left[\frac{q(c_i - c)}{s k} \right]^{1/n} \right\}$$

Here $a =$ external surface area of adsorbent per unit volume of liquid (cm^2/cm^3)

$k_L =$ external liq. phase mass transfer coefficient (cm/s)

$$\therefore a = \frac{5}{kg} \frac{\text{m}^2}{\text{kg}} (s/q) = 5 \left(2 \frac{s_{\min}}{q} \right) = 5 \left(2 \times 0.286 \right)$$

given in problem $\Rightarrow = 2.86 \text{ m}^2/\text{m}^3$ (or $0.0286 \text{ cm}^2/\text{cm}^3$)

$$\text{Here } Sh = \frac{k_L}{D_{AB}} \Rightarrow k_L = \frac{Sh D_{AB}}{dp} = \frac{30 (1.13 \times 10^{-5})}{0.15} = 0.00226 \text{ cm/s}$$

Thus,

$$-\frac{dc}{dt} = (0.00226 \times 0.0286) \left\{ c - \left[\frac{1(0.223 - c)}{(2 \times 0.286)(10)} \right]^{1/0.564} \right\}$$

$$= 6.46 \times 10^{-5} \left\{ c - \left[\frac{0.223 - c}{5.72} \right]^{1.773} \right\}$$

where c is in mg CF/L solution & t in seconds.

The equation (ODE) can be solved by Euler method

$$c^{j+1} = c^j + (\Delta t) \frac{dc}{dt}$$

$$\Rightarrow c^{j+1} = c^j - (\Delta t) 6.46 \times 10^{-5} \left\{ c^j - \left[\frac{0.223 - c^j}{5.72} \right]^{1.773} \right\}$$

Tabulating the values, (can choose $\Delta t = 500 \text{ s}$)

Time (s) c^j

0 0.223

500 0.216

1000 0.209

1500 0.202

!

!

↓ c is decreasing

(you can choose
large Δt for
quick calculation)

so, to reach 0.01 mg CF/L solution, the time needed would be 51500 (or 14.3 h).

The above problem can also be solved graphically.

(c) when both solid & liquid flows continuously, (in a perfectly mixed vessel), the ODE converts to a algebraic equation, & since the system is in ~~ss~~ steady-state.

In terms of residence time t_{res}

$$\frac{C_{in} - C_{out}}{t_{res}} = K_L a (C_{out} - C_e)$$

rearranging, $t_{res} = \frac{C_{in} - C_{out}}{K_L a (C_{out} - C_e)} = \frac{0.223 - 0.01}{6.46 \times 10^{-5} (0.01 - 0.00292)}$

Now from mass balance,

$$C_{in} Q = C_{out} Q + q|_{out} S$$

$$\Rightarrow q|_{out} = \frac{Q (C_{in} - C_{out})}{S} = \frac{1 (0.223 - 0.01)}{0.572} = 0.372 \text{ mg/g}$$

$$\therefore C_e|_{out} = \left(\frac{q}{10}\right)^{1/0.564} = \left(\frac{0.372}{10}\right)^{1.773} = 0.00292 \text{ mg/L}$$

$$\therefore t_{res} = \frac{0.223 - 0.01}{6.46 \times 10^{-5} (0.01 - 0.00292)} = 466000 \text{ s} \quad (\text{or } 130 \text{ h})$$