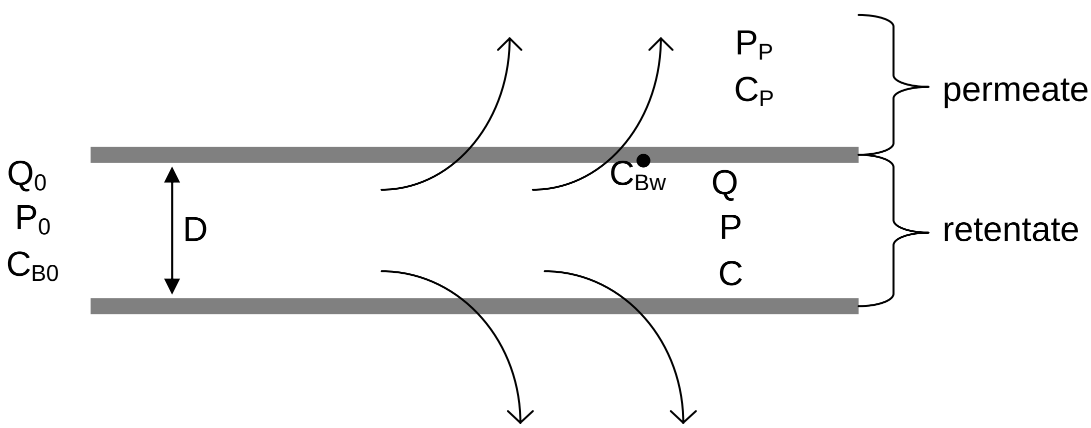
Solution to 10.32 Problem Set 3, Spring 2005

We are asked to concentrate Kraft Black Liquor (KBL) using a reverse osmosis process constructed of a parallel membrane tube bundle.

Given:
System operates at 82C
Initial KBL solids weight percentage in retentate, w_o=0.15
Final KBL solids weight percentage in retentate, w_f=0.20-0.25
Maximum salt weight percentage in permeate, $w_{P,max}$=0.4
Initial pressure, P_o=120 atm
Pressure in permeate, P_P=1 atm
Inlet flow rate, Q_o=1 L/s
Tube diameter, D=0.01 m
Permeation coefficient, $K_m=1.7\times10^{-6}$ m/s/atm
Osmotic pressure of KBL at 15 wt%, Π=70 atm
Kinematic viscosity of KBL, $\nu=1.2\times10^{-6}\,m^2/s$
Schmidt number, Sc=1000
Diffusivity of solids in water, Diff=$1.2\times10^{-9}\,m^2/s$
Constant density of all liquor solutions, $\rho=1.2\ g/cm^3$
Rejection coefficient of membrane, R=0.99
Definition of recovery, Recovery=(total amount of permeate)/(amount of KBL fed to system)



Part a.

We are asked to qualitatively sketch how the following parameters vary with tube length and to justify the shape of each curve:

1. solids concentration in retentate
2. flow rate in tube
3. flux through tube walls
4. solids concentration in permeate (before mixing)
5. recovery

We know that we are concentrating the solids in the retentate from 15wt% to 25wt%, so **the concentration of solids in the retentate must increase as the tube length increases.**

We can write an overall mass balance on a differential element of fluid in the permeate:

$$\rho Q - \left[\rho Q + \frac{d(\rho Q)}{dx}dx\right] - \rho N \pi D dx = 0 \qquad (1)$$

which simplifies to $\dfrac{dQ}{dx} = -N\pi D$ (2).

Therefore, **the flow rate in the tube decreases with the tube length.**

The flux of water through the membrane is related to the pressures in the retentate, permeate and the osmotic pressure as:

$$N = K_m\left(P - P_P - \Delta\Pi\right) \qquad (3)$$

where N is the flux, P is the pressure inside the tube, P_P is the pressure in the permeate and $\Delta\Pi$ is the osmotic pressure

From class, we can relate the pressure drop in the tube to the friction factor as

$$\frac{dP}{dx} = -\frac{0.316\rho V^2 D}{2\,Re^{0.25}} \qquad (4)$$

and, therefore the pressure in the tube decreases with tube length, therefore **the flux decreases with tube length.**

defined as:

$$\Lambda\Pi = k_{osm}\left(C_{Bw} - C_P\right) \qquad (4)$$

We know that the concentration of solids at the wall, C_{Bw}, increases along the tube length because the bulk concentration of solids in the tube, C_B, increases with length. From the definition of the rejection coefficient, R:

$$R \equiv 1 - \frac{C_P}{C_{Bwall}} \qquad (5)$$

where C_P is the solids concentration in the permeate before mixing and therefore

$$C_P = C_{Bwall}(1 - R) \qquad (6)$$

and we expect C_P to increases along the tube length because the solids concentrate in the permeate (and at the wall) should increase. However, the parameters in this problem cause a dramatic decrease in flux along the tube length, which causes both C_P and C_{Bwall} to decrease along the length of the tube.

Recovery is defined as (total amount of permeate)/(amount of KBL fed to system). The total amount of permeate, Q_P, is the initial flowrate, Q_0 minus the flowrate at a given distance x along the tube and the amount of KBL fed to the system is Q_0 so

$$\mathrm{Re\,cov\,ery}_{@\,x<L} = \frac{Q_0 - Q_x}{Q_0} = \frac{Q_P}{Q_0}$$

Since we know that the flow rate decreases with tube length, **Recovery must increase with tube length.**

Part (b).
We have learned in lecture that capital costs increase with the amount of material used to construct a separation device. Therefore we expect the capital costs to increase with tube length.

Since the recovery increases with tube length, the electric power required to pump the KBL through the tube decreases as the tube length (and hence the recovery) increases.

Therefore **we do expect an optimum tube length** that minimizes these costs, which have opposite trends as a function of tube length.

Part (c).
We are asked to derive a set of equations and devise a calculation system to determine the performance of the reverse osmosis system as a function of tube length.

From our overall mass balance in part a:

$$\boxed{\frac{dQ}{dx} = -N\pi D} \qquad (1)$$

We can also write a mass balance just on the solids within a differential element:

$$C_B Q - \left[C_B Q + \frac{d(C_B Q)}{dx}dx\right] - C_P N\pi D dx = 0 \qquad (2a)$$

where C_B is the concentration of solids and is related to the given weight fraction of solids by $C = w\rho$
Rearranging, we find

$$\boxed{\frac{dC_B}{dx} = \frac{-C_B \frac{dQ}{dx} - C_P N\pi D}{Q}} \qquad (2)$$

The equation for flux across the membrane is

$$\boxed{N = K_m\left(P - P_P - \Delta\Pi\right)} \qquad (3).$$

The equation for the osmotic pressure across the membrane is

$$\boxed{\Lambda\Pi = k_{osm}\left(C_{Bwall} - C_P\right)} \qquad (4)$$

where k_{osm} osmotic gradient mass transfer coefficient. We can quickly calculate

We can relate the concentration of solids at the wall, C_{Bwall} to the concentration of solids in the permeate by writing a flux balance on the solids at the wall:

$$NC_B = NC_P + k_{MT}\left(C_{Bwall} - C_B\right) \qquad (5a)$$

where the last term represents the flux of solids back into the permeate. Solving for C_B:

$$\boxed{C_{Bwall} = \frac{N(C_B - C_P)}{k_{MT}} + C_B} \qquad (5)$$

where k_{MT} is a mass transfer coefficient that is NOT given in the problem statement.

The relationship between C_{Bwall} and C_P is given from the definition of the rejection coefficient and

$$\boxed{C_P = C_{Bwall}(1-R)} \qquad (6)$$

For turbulent flow in a pipe,

$$\boxed{\frac{k_{MT}D}{Diff} = 0.023(Re)^{0.8}(Sc)^{0.33}} \qquad (7)$$

Where Diff is the diffusivity in the pipe given in the problem statement. The Reynolds number Re=DV/ν and the velocity V can be found from the volumetric flow rate and the pipe geometry:

$$\boxed{V = \frac{4Q}{\pi D^2}} \qquad (8)$$

The friction factor, f, is related to the pressure loss down the tube as

$$f = -\frac{\left(\frac{dP}{dx}\right)D}{\frac{\rho V^2}{2}} \qquad (9a).$$

At large Reynold's numbers the friction factor, f, is

$$f = \frac{0.316}{Re^{0.25}} \qquad (9b).$$

If we solve for the pressure drop along the length of the tube, we find

$$\boxed{\frac{dP}{dx} = -\frac{0.316\rho V^2 D}{2\,Re^{0.25}}} \qquad (9).$$

Equations 1,2 and 9 are the differential equations that we can use to find Q and C_B and P as a function of tube length.

To evaluate the Recovery= (total amount of permeate)/(amount of KBL fed to system) at a given distance along the tube length can be calculated from an overall mass balance on material flow through the tubes and through the membrane:

$$\boxed{Re\,cov\,ery_{@\,x<L} = \frac{Q_0 - Q_x}{Q_0} = \frac{Q_P}{Q_0}} \qquad (10)$$

where the term in the denominator represents the overall rate of permeate production, or Q_P.

The overall concentration of solids in the permeate is similarly calculated from a mass balance on the solids flowing through the membrane system:

$$C_{B0}Q_0 = C_{P,mixed}Q_P + C_{B,x}Q_x \qquad (11a)$$

and $\boxed{C_{P,mixed} = \dfrac{C_{B0}Q_0 - C_{B,x}Q_x}{Q_P}}$ (11)

So, our calculation scheme would proceed as follows:

1. Using the given parameters and initial values of P, Q and C_B given in the problem, determine the initial values of V, Re, k_{MT}, C_{Bwall}, C_P and $\Delta\Pi$ and N.
2. Numerically solve the differential equations (1), (2) and (9) from above to find Q, C_B and P over small differential increments in tube length, $x=\Delta x$.
3. Solve the algebraic equations above to calculate V, Re, k_{MT}, C_{Bwall}, C_P and $\Delta\Pi$ and N at $x=\Delta x$.
4. Calculate the Recovery at $x=\Delta x$ using the value of Q at $x=\Delta x$ using equation (9).
5. Calculate the concentration of solids in the permeate, or $C_{P,mixed}$ at $x=\Delta x$ using equation (10).
6. Repeat steps 2-5 at $x=x+\Delta x$, then at $x + 2\Delta x$, $x + 3\Delta x$, etc. until x=15meters.

Part (d).

We are asked to implement our calculation strategy outlined in part (c)

We begin by calculating the unknown osmotic pressure mass transfer coefficient, k_{osm}. We are given the value of $\Delta\Pi$ when there is pure water on one side of the membrane and the concentration of C_B is 15wt% so

$$k_{osm} = \frac{\Delta\Pi}{C_{Bwall} - C_P} = \left(\frac{\Delta\Pi}{C_{Bwall}}\right)_{15wt\%\,experiment}.$$

At the inlet of the membrane tube (x=0) we are given the initial flowrate, Q_0, so we can then calculate V_0, Re_0 and k_{MT0} using equations (7) and (8) and the definition of Re.

The remaining unknowns are C_{Bwall}, C_P and $\Delta\Pi$ and N. We have algebraic equations to describe them ((3), (4), (5) and (6) from above); however, they are all in terms of each other and need to be manipulated to calculate C_{Bwall}, C_P and N.

We can substitute the following expression for C_P into the equation for C_{Bwall} derived from the solids flux balance:

$$C_P = C_{Bwall}(1-R)$$

substitute into the C_{Bwall} flux equation:

$$C_{Bwall} = \frac{N(C_B - C_{Bwall}(1-R))}{k_{MT}} + C_B$$

We can also substitute our expression for flux, N:

$$N = K_m(P - P_P - \Delta\Pi)$$

into the same equation so that

$$C_{Bwall} = \frac{K_m(P - P_P - \Delta\Pi)(C_B - C_{Bwall}(1-R))}{k_{MT}} + C_B.$$

And we can then substitute our expression for osmotic pressure, $\Delta\Pi$:

$$\Lambda\Pi = k_{osm}(C_{Bwall} - C_P)$$

so that

$$C_{Bwall} = \frac{K_m\left(P - P_P - k_{osm}\left(C_{Bwall} - C_P\right)\right)\left(C_B - C_{Bwall}\left(1-R\right)\right)}{k_{MT}} + C_B\,.$$

We now have an expression for C_{Bwall} in terms of only constants and the quantities determined from the differential equations (P, C_P and C_B). If we rearrange this quadratic equation:

$$\begin{aligned}
0 &= C_{Bwall}^2\left[K_m k_{osm}\left(R - R^2\right)\right] \\
&+ C_{Bwall}\left(PRK_m + K_m P_P - K_m P - K_m P_P R - k_{osm} K_m C_B R - k_{MT}\right) \\
&+ \left[C_B\left(K_m P - K_m P_P + k_{MT}\right)\right]
\end{aligned}$$

We use the quadratic formula and determine the real, positive root and our expression for C_{Bwall}, which is how we must calculate C_{Bwall0} at the tube inlet.

We can then easily calculate C_P then $\Delta\Pi$ then N.

The following table summarizes the initial values computed using this approach:

Parameters			**Given Initial Values**		
D	0.01	m	Q_0	1	L/s
ν	1.20E-06	m^2/s	Q_0	0.001	m^3/s
Diff	1.20E-09	m^2/s	C_{B0}	1.8	g/cm^3
ρ	1.2	g/cm^3	C_{B0}	1800	kg/m^3
Sc	1000		P_0	120	atm
P_P	1	atm	P_0	12159000	Pa
P_P	101325	Pa	**Calculated**		
R	0.99		$\mathbf{k_{osm}}$	**3.9E+03**	$\mathbf{m^2/s^2}$
K_m	1.70E-06	m/s/atm	$\mathbf{V_0}$	**12.73**	**m/s**
K_m	1.68E-11	m/s/Pa	$\mathbf{Re_0}$	**106103**	
$\Delta\Pi_{15wt\%}$	70	atm	$\mathbf{k_{MT0}}$	**0.000282808**	**m/s**
$\Delta\Pi_{15wt\%}$	7092750	Pa	$\mathbf{C_{Bwall0}}$	**2176.366**	$\mathbf{kg/m^3}$
			$\mathbf{C_{Bwall0}}$	**18.136**	**wt%**
			$\mathbf{C_{P0}}$	**21.7637**	$\mathbf{kg/m^3}$
			$\mathbf{C_{P0}}$	**0.181**	**wt%**
			$\mathbf{\Delta\Pi_0}$	**8490033**	**Pa**
			$\mathbf{N_0}$	**5.986E-05**	**m/s**

To proceed with our calculation scheme, we first numerically solve the differential equations (eg using *ode45* or *ode15s* in MATLAB) then calculate C_{Bwall}, C_P, $\Delta\Pi$ and N. We would then calculate C_{Pmized} and Recovery at each incremental value of dx:

$$\mathrm{Re\,cov\,ery} = \frac{Q_0 - Q_x}{Q_0}$$

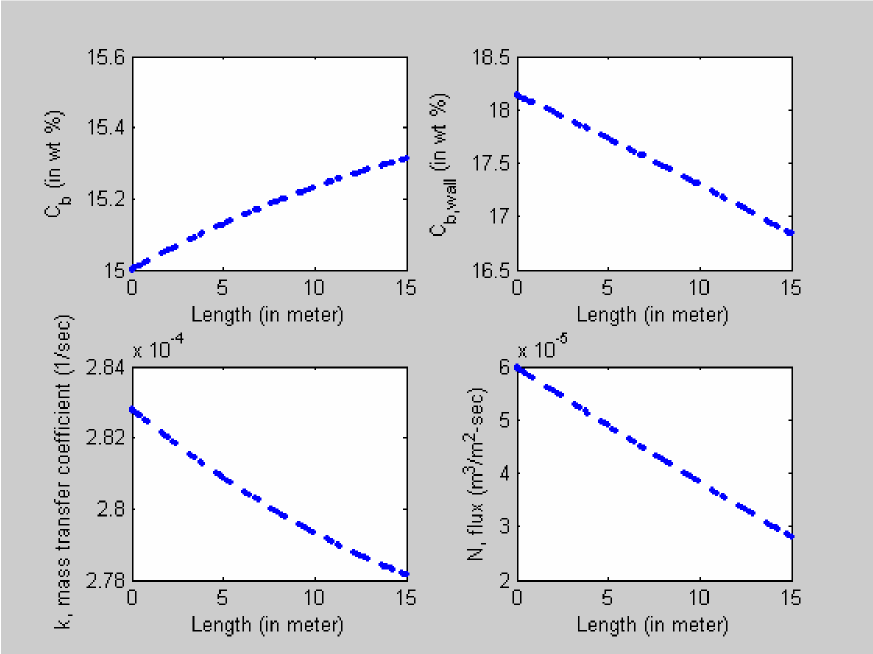
$$C_{P,mixed} = \frac{C_{B0}Q_0 - C_{B,x}Q_x}{Q_P}$$

The following script was used in MATLAB to generate plots of Recovery and C_{Pmized} as functions of tube length:

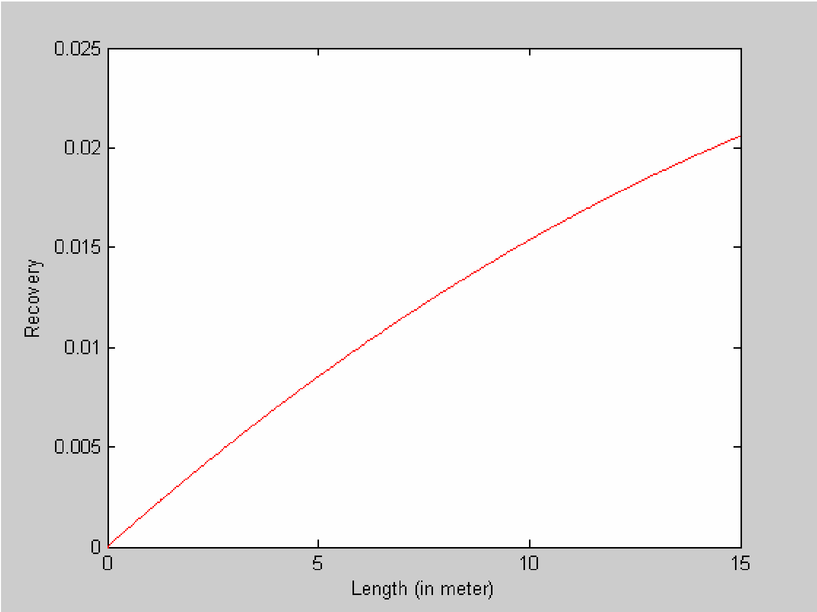
```
% 10.32 Problem Set #3

function [] = reverse_osmosis_quad()

%Initial Values
P_initial = 120;                %[atm]
Q_initial = 0.001;              %[m^3/sec]
Cb_initial = 15;                %[wt%]
initial = [Q_initial Cb_initial P_initial];

%Length Limits
length = linspace(0,15,1000);       %[m]

%Use ode15s to solve the set of differential equations
[L,y] = ode45(@rates, length, initial)
[a,b] = size(y);
recovery = (Q_initial - y(:,1))./Q_initial;
figure
plot(L,recovery,'r')
ylabel('Recovery')
xlabel('Length (in meter)')

Cp_mixed = ((y(1,2)*y(1,1))-(y(:,2).*y(:,1)))./(y(1,1)-y(:,1));
figure
plot(L,Cp_mixed,'r')
ylabel('C_p_,_m_i_x_e_d (in meter ^3)')
xlabel('Length (in meter)')

recovery_final = (Q_initial - y(a,1))/Q_initial
Cp_mixed_final = ((y(1,2)*Q_initial)-(y(a,2)*y(a,1)))/(Q_initial-
y(a,1))

function [d_dx,Cp] = rates(L,y)

Q = y(1); Cb = y(2); P = y(3);

%Variables
P_permeate = 1;               %Pressure of permeate [atm]
D = 0.01;                     %Diameter [m]
Km = 1.7E-6;                  %Permeation coefficient [m/s-atm]
nu = 1.2E-6;                  %Kinematic viscosity [m^2/sec]
Sc = 1000;                    %Schmidt number
D_solid = 1.2E-9;             %Diffisivity of solids in water [m^2/sec]
rho = 1200;                   %Density [kg/m^3]
osm_pressure_initial = 70;    %Osmotic pressure [atm]
Cb_initial = 15;              %Conc. of bulk at L = 0 meters [wt%]
K_osm = osm_pressure_initial/Cb_initial;  % [atm/wt%]
R = 0.99;                                 % Rejection Coefficient

%Calculation of values needed for differential equations
velocity = (4*Q)/(pi*(D^2));              % [m/sec]
Re = (D*velocity)/nu;                     % Reynold's Number
k = (D_solid/D)*0.023*(Re^0.8)*(Sc^0.33); % [1/sec]
```

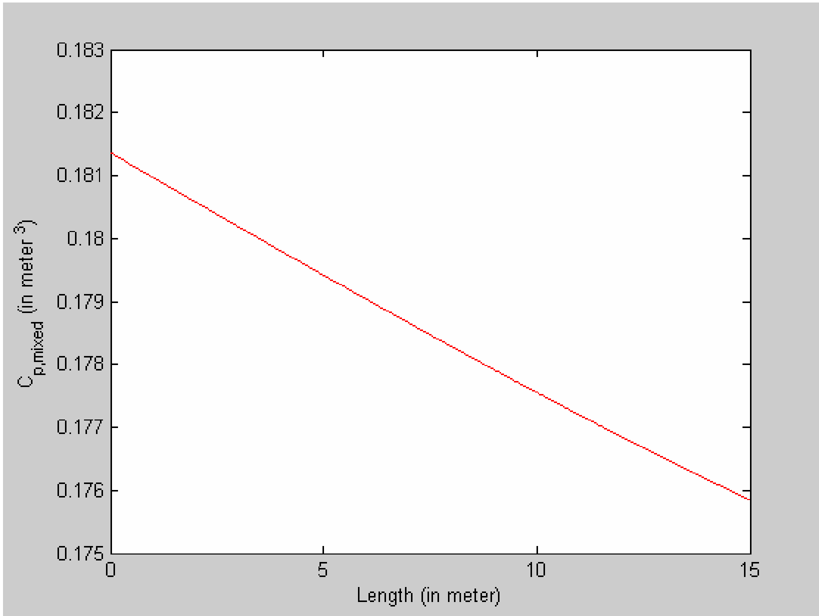
```
%Calculate quadratic coefficients for Cb
a = -Km*K_osm*R*(1-R);
b = k+(Km*K_osm*R*Cb)+(Km*P*(1-R))-(Km*P_permeate*(1-R));
c = (-Km*P*Cb)+(Km*P_permeate*Cb)-(Cb*k);
Cb_wall = (-b+((b^2)-(4*a*c))^0.5)/(2*a);

Cp = (1-R)*Cb_wall;
osm_pressure = K_osm*(Cb_wall*R);
N = Km*(P-P_permeate-osm_pressure);
f = 0.316/(Re^0.25);

subplot(2,2,1)
plot(L,Cb,'.')
xlabel('Length (in meter)')
ylabel('C_b (in wt %)')
hold on

subplot(2,2,2)
plot(L,Cb_wall,'.')
xlabel('Length (in meter)')
ylabel('C_b_,_w_a_l_l (in wt %)')
hold on

subplot(2,2,3)
plot(L,k,'.')
xlabel('Length (in meter)')
ylabel('k, mass transfer coefficient (1/sec)')
hold on

subplot(2,2,4)
plot(L,N,'.')
xlabel('Length (in meter)')
ylabel('N, flux (m^3/m^2-sec)')
hold on

%Differential Equations
d_dx(1,1) = -N*pi*D;
d_dx(2,1) = (-N*pi*D*Cp-Cb*d_dx(1,1))/Q;
d_dx(3,1) = -(rho*f*(velocity^2))/(2*101325*D);
return
```

The following graphs show the trends for C_B, k_{MT}, C_{Bwall} and N as a function of tube length. Note that C_{Bwall} decreases, contrary to our prediction in part (a). This is due to the large flux and the rejection coefficient that allows solids to leak throughout the tube.



The following graphs show Recovery and $C_{P,mixed}$ as functions of tube length. Note that C_P has a periodic trend that is sensitive to the size of dx.





Point Allocation (10 points total):

Part (a) (2 points total)
0.5 point each: correct trends (increasing/decreasing) for C_B, Q, N and Recovery
Both trends accepted for C_P (increasing, decreasing)

Part (b): (1 point total)
1 point: Recognizing that there is an optimum length because the capital and operating (pressure) costs have opposite trends; also accepted arguments using principle of diminishing marginal returns as tube length increases

Part (c) (5 points total)
2 points: correctly writing relationships (given in lecture) between R, C_P, C_{Bwall}, $\Delta\Pi$, k_{osm} N, P, P_P, k_{MT}, dQ/dx, dP/dx, D, Diff, Re, Sc and ν.
1 point: correctly deriving dC_B/dx from differential balance on solids in the tube
1 point: correct expression for Recovery
1 point: correct quadratic/algebraic expression for C_{Bwall}

Part (d) (2 points total)
1 point: successfully coding differential equations, showing various parameters as functions of tube length
0.5 point: graph of $C_{P,\ mixed}$ as a function of tube length with correct expression for $C_{P,mixed}$
0.5 point: graph of Recovery as a function of tube length