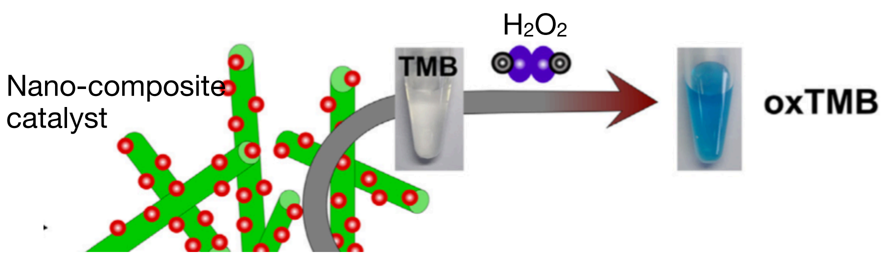
CBE 20255
Spring 2019
Final Exam
5/8/19

1. (Mimicked) Enzyme kinetics in batch reactors and CSTRs. (60 points)

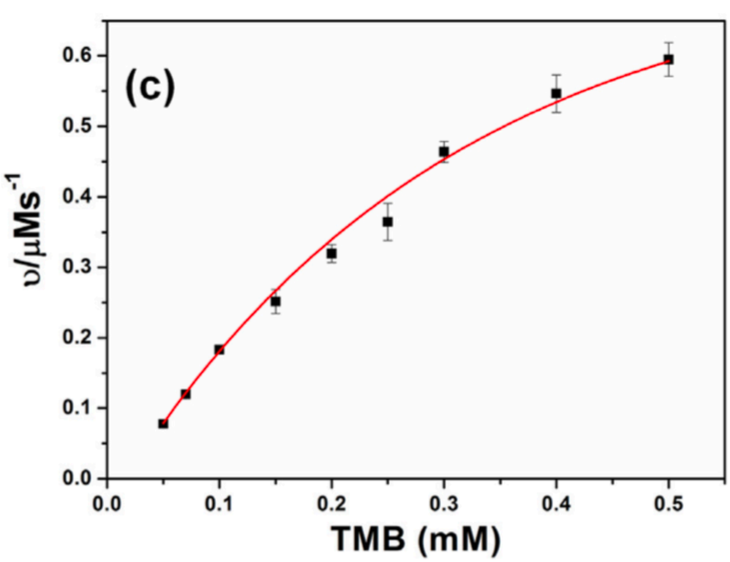


A recent paper in *Applied Surface Science* (2019) by Liu et al. describes the use of Pt/CeO_2 nano-composite (Pt particles on CeO2 rods — add in "nano" as a modifier as desired!) to mimic the catalytic behavior of the peroxidase enzyme. They state that the reaction of TMB to "oxTMB" was found to follow Michaelis-Menten kinetics of the form:

$$\frac{dC_{TMB}}{dt} = r = \frac{v_{max}\, C_{TMB}}{K_m + C_{TMB}} \quad ,$$

where C_{TMB} is the concentration of the reactant that we are tracking in this problem. The term v_{max} is the maximum rate of the reaction and K_m is the so-called Michaelis-Menten constant. The authors of the paper used (apparently) flow reactor measurements at steady state to get the rate as a function of the concentration of C_{TMB}. The fit to this data produced values of

Vmax = 0.885 μM/s (micromoles/s and K_m = 0.408 mM (millimoles/liter). The original data were plotted as rate versus TMB concentration:



Careful perusal of this information suggests that for the correct range of concentration, the prescribed reaction will follow first order kinetics,

$$\frac{dC_{TMB}}{dt} = k\, C_{TMB}$$

with a value of k = 0.0022/s.

a. Find an algebraic expression for the concentration of TMB as a function of time for a batch reactor if it is operating in the range where first order kinetics is valid.
b. How long will it take for an initial concentration of TMB to be reduced to 1/2 of its original value?
c. How long will it take to reduce the initial TMB concentration to less than 2% of its original value?
d. For what range of concentrations of TMB will first order kinetics be a good representation?
e. Presumably, the Michaelis-Menten kinetic expression has a second "limit". What is this relation and for which range of TMB concentrations will it be a good representation?

Now consider CSTR behavior for the reaction when it is first order. (There is nothing to be gained by trying to make all of the numbers into just moles or M as the exponents would always be 10^{-3} (milli) or 10^{-6} (μ).)

f. Find an expression for the exit concentration of TMB in terms of the volumetric flow rate (q), the reactor volume, V and all relevant concentrations and reaction rate information.
g. If a CSTR has a volume of 0.01liters (10 ml) and an input flow of 0.01 ml/s, what is the ratio of output TMB concentration input TMB concentration?
h. What residence time would be necessary to reduce the initial TMB concentration to 1/2 of its initial value
i. What residence time would be necessary to reduce the initial TMB concentration to just 2% of its initial value?

Answer this using the <u>complete kinetic expression</u>:

j. Suppose that the feed to the 10 ml reactor is 0.1 ml/s with an initial concentration of 0.55 mM, what is the exit concentration from the CSTR and how many moles of oxTMB are produced?

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$$\frac{dC_A}{dt} = -k C_A$$

$$\frac{dC_A}{C_A} = -k\,dt$$

$$\ln\left(\frac{C_A}{C_{A0}}\right) = -kt$$

(5)

$$\frac{C_A}{C_{A0}} = \exp(-kt)$$

$$\frac{\ln 1/2}{k} = t$$

(5)

$$\frac{C_A}{C_{A0}} = .02 \Rightarrow \exp(-4)$$

$$t = \frac{4}{k}$$

(5)

d) $<$ .1 mM

e) $r =$ CONST $= V_{MAX}$

$C_{TMB} \gg K_m$

$\sim > 1\,mM$

(J)

MATCHES FIGURE 1

f) $0 = q\,C_{Af} - q\,C_A - k\,C_A\,V$

$$0 = 1 - \frac{C_A}{C_{Af}} - k\frac{C_A}{C_A}\frac{V}{q}$$

$$\frac{C_A}{C_{Af}} = \frac{1}{1+k\theta} \qquad \theta = \frac{V}{q}$$

g) $\theta = 1000\,s \quad k = .0022$

$$\frac{C_A}{C_A} = \frac{1}{1+2.2} = \frac{1}{3.2}$$

h) $$1/2 = \frac{1}{1+k\theta} \qquad \theta = \frac{1}{k}$$

τ $\quad \theta = \frac{4q}{k}$

$$0 = q C_{Af} - q C_A - \frac{V_m C_A}{K_m + C_A} \quad \checkmark$$

$$= (.1)(.55) - (.1)(C_A) - \frac{.885 \times 10^{-3} C_A}{(.408) + C_A} \quad \checkmark$$