Biological Process Design for Wastewater Treatment

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Lecture – 12

Reaction Kinetics

Welcome to this NPTEL online certification course on biological process design for wastewater treatment. So, in today's lecture, we are starting another section on reaction and bacterial growth kinetics in the biological treatment processes that can happen, and we will try to understand that how we can model the biological treatment processes using various reaction kinetic equations, and growth kinetic equation for a microorganism. We will begin with some basic understanding of various reaction types and their reaction kinetics.

So, in the previous lecture, already, we have understood that stoichiometry of the growth kinetics we understood; but we have only written the reactions. We tried to find out the stoichiometric coefficient. So starting today, we will try to understand how to model the reactions actually happening during the sewage or wastewater treatment, and how we can model the overall growth kinetics.

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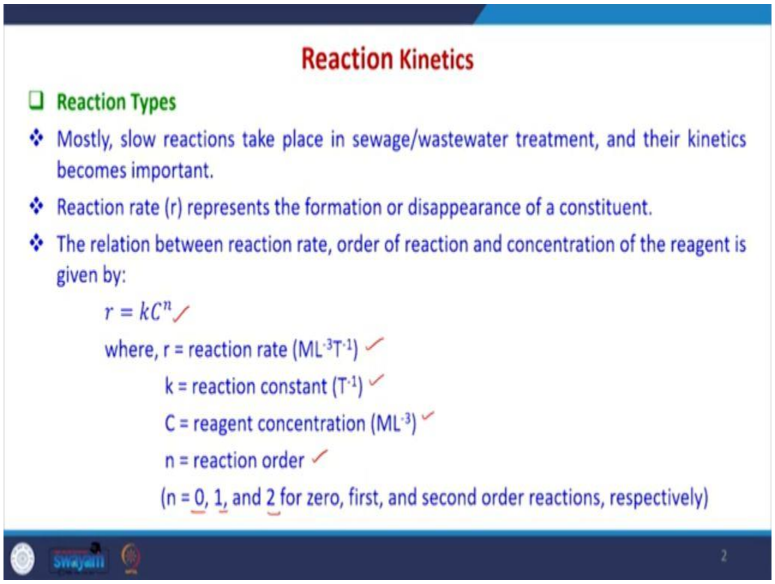

Reaction Kinetics

- ☐ Reaction Types
- ❖ Mostly, slow reactions take place in sewage/wastewater treatment, and their kinetics becomes important.
- ❖ Reaction rate (r) represents the formation or disappearance of a constituent.
- ❖ The relation between reaction rate, order of reaction and concentration of the reagent is given by:

$$r = kC^n$$

where, r = reaction rate ($ML^{-3}T^{-1}$)
k = reaction constant (T^{-1})
C = reagent concentration (ML^{-3})
n = reaction order
(n = 0, 1, and 2 for zero, first, and second order reactions, respectively)

So, reaction rate actually represents in general, the reaction rate represents the formation or disappearance of any of the constituent of a reaction; that may be a reactant that may be a product. Now, the relationship between the reaction rate, and the order of reaction, and the concentration of the reagent is generally written by this particular equation, where rate is equal to kC^n, where r is the reaction rate. k is the reaction rate constant, and C is the reagent concentration in terms of appropriate unit, and n is the reaction order which may be 0, 1, 2, zero, first, second order reactions respectively.

It need not be integer, it can be any other value also. So, it is not particular that it should be 0, 1, 2; but it can be any in the intermediate value also.

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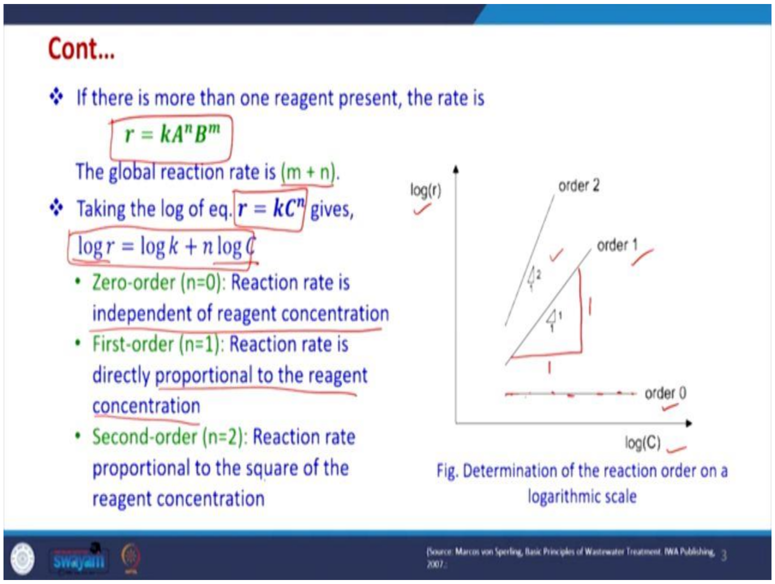

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- If there is more than one reagent present, the rate is

  $\boxed{r = kA^nB^m}$

  The global reaction rate is (m + n).
- Taking the log of eq. $\boxed{r = kC^n}$ gives,

  $\boxed{\log r = \log k + n \log C}$

  - Zero-order (n=0): Reaction rate is independent of reagent concentration
  - First-order (n=1): Reaction rate is directly proportional to the reagent concentration
  - Second-order (n=2): Reaction rate proportional to the square of the reagent concentration

Fig. Determination of the reaction order on a logarithmic scale

(Source: Marcos von Sperling, Basic Principles of Wastewater Treatment. IWA Publishing, 2007.)

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$$r = kA^nB^m$$

Taking the log of eq.

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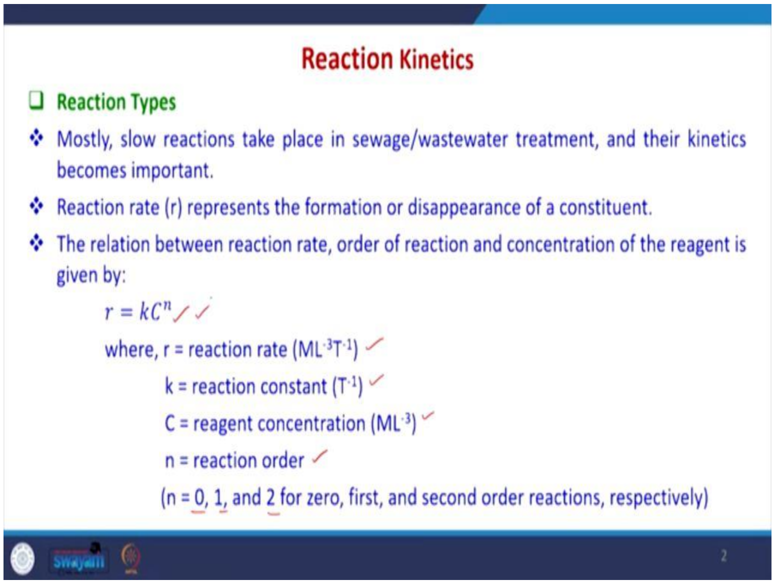

Reaction Kinetics

❑ Reaction Types

- ❖ Mostly, slow reactions take place in sewage/wastewater treatment, and their kinetics becomes important.
- ❖ Reaction rate (r) represents the formation or disappearance of a constituent.
- ❖ The relation between reaction rate, order of reaction and concentration of the reagent is given by:

$r = kC^n$ ✓✓

where, r = reaction rate ($ML^{-3}T^{-1}$) ✓
k = reaction constant (T^{-1}) ✓
C = reagent concentration (ML^{-3}) ✓
n = reaction order ✓
(n = 0, 1, and 2 for zero, first, and second order reactions, respectively)

Now, if there is more than one reagent present, the overall reaction can be written like this, where A and B are two different reagents. And thus, the overall growth reaction rate can be written as m plus n. So, we have the order of this particular reaction is m plus n. Now, for in general, where only the reaction rate is dependent upon one of the reagents; the reaction can be more easily be written as reaction is equal to kC^n, which was like given earlier in this particular case.

Now, taking the log of this equation on both sides, we can write log r is equal to log k plus n log C. So, that means if we can write the value of log r, plot a graph of log r versus log C; the slope of the curve will give the reaction order. So, like here, we can for log r versus log C, and the data is represented by this particular line. So, we can see the there is not much difference, there is no slope in particular; the order of the slope is 0. So, under this condition, the reaction is of 0 order.

If the order of slope is 1; that means the change in the y is equal to change in the x value. So, that means this is y, this is 1, this is both are same; so that means the order of reaction is 1. In the other case, it may be possible that y is changing double the value of the change in x. So, that means the order of reaction is 2.

So, in this way we can find out experimentally the order of reactions of various types of equations. For 0 order, the reaction rate is independent of the reagent concentration; for the first order, the reaction rate is directly proportional to the reagent concentration. For the second order, the reaction rate is directly proportional to the square of the reagent concentration. So, this is how we go ahead.

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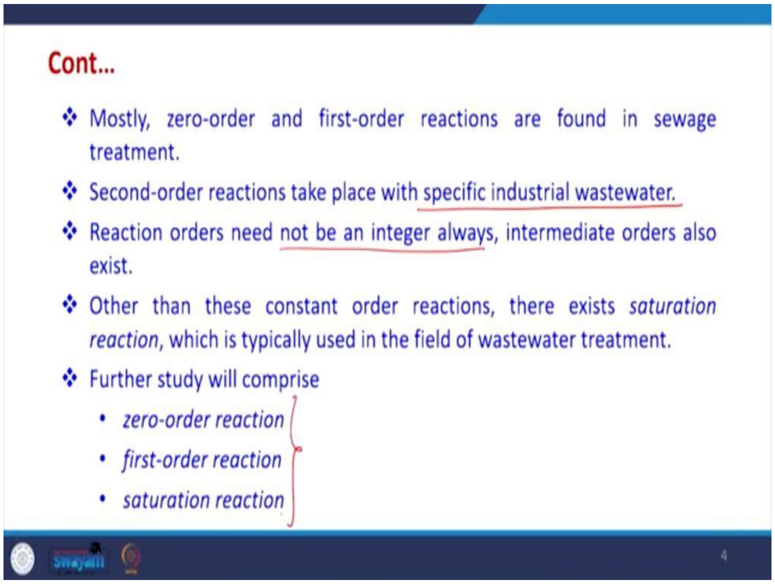

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- Mostly, zero-order and first-order reactions are found in sewage treatment.
- Second-order reactions take place with specific industrial wastewater.
- Reaction orders need not be an integer always, intermediate orders also exist.
- Other than these constant order reactions, there exists *saturation reaction*, which is typically used in the field of wastewater treatment.
- Further study will comprise
  - *zero-order reaction*
  - *first-order reaction*
  - *saturation reaction*

Mostly, in sewage treatment in the wastewater treatment, the reaction orders are either zero-order or first-order. So, in very seldom some cases only will be the second-order reaction that will be finding; and those second-order reactions are generally for industrial wastewater treatment. For serious treatment, generally, the zero-order and first-order reactions are good enough; and we can always represent the reaction kinetics by zero-order or first-order. Reaction orders need not be an integer always. They can be intermediate also like 0.5, 1.5, 1.4; all those values can also exist.

Other than these constant order reactions, there exist some saturation reactions also, which typically are used in the wastewater treatment. And will be studying those saturation reactions in today also. Further, study that will be finding that how to further understand this zero-order, first-order and saturation reactions. So, zero-order reactions, the reaction rate already is independent of the reagent concentration we have found.

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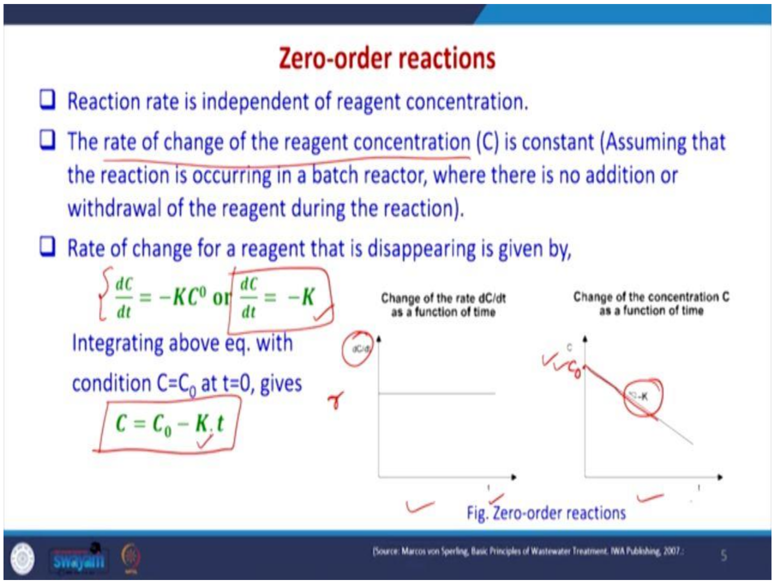

Zero-order reactions

- ☐ Reaction rate is independent of reagent concentration.
- ☐ The rate of change of the reagent concentration (C) is constant (Assuming that the reaction is occurring in a batch reactor, where there is no addition or withdrawal of the reagent during the reaction).
- ☐ Rate of change for a reagent that is disappearing is given by,

$$\frac{dC}{dt} = -KC^0 \text{ or } \boxed{\frac{dC}{dt} = -K}$$

Integrating above eq. with condition $C=C_0$ at $t=0$, gives

$$\boxed{C = C_0 - K.t}$$

Fig. Zero-order reactions

(Source: Marcos von Sperling, Basic Principles of Wastewater Treatment, IWA Publishing, 2007.)

Rate of change for a reagent that is disappearing is given by,

$$\frac{dC}{dt} = -KC^0 \text{ or } \frac{dC}{dt} = -K$$

$$C = C_0 - K.t$$

The rate of change of reagent concentration is constant, assuming that the reaction is occurring in a batch reactor, where there is no addition or withdrawal of reagent. So, in this case, the reaction the rate of change of any reagent concentration is constant. So, that means the rate of change of the reagent concentration is directly proportional for this case to K value, and there is no integrating. If we integrate this particular equation, we can find out the C_0 will be equal to C_0-Kt. And we can represent this equation via these two graphs. So here, the rate of change is written with respect to r, r is written with respect to t.

So, we can see that this is constant, and this constant value will be some K value. And in the second case, we can write with respect to C. So, we can see that the initially the concentration is C_0; but with time, it is decreasing linearly with time. So, this is and this linear slope is K value. So, we can see the C when plotted against time; so this will start from C_0 and decrease with time. And the decrease rate is with respect to this proportionality constant or reaction rate constant. The reaction rate is proportional to concentration of reagent for the first order reaction.

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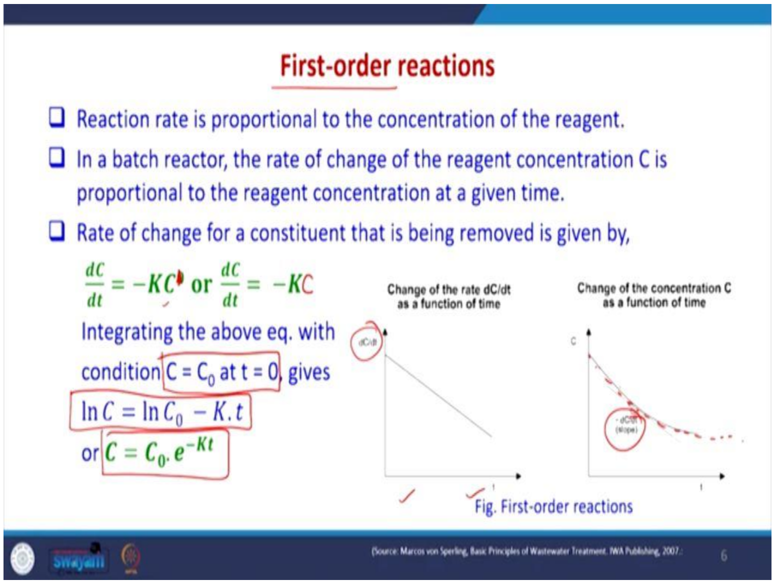

First-order reactions

- ☐ Reaction rate is proportional to the concentration of the reagent.
- ☐ In a batch reactor, the rate of change of the reagent concentration C is proportional to the reagent concentration at a given time.
- ☐ Rate of change for a constituent that is being removed is given by,

$\frac{dC}{dt} = -KC^{0}$ or $\frac{dC}{dt} = -KC$

Integrating the above eq. with condition $\boxed{C = C_0 \text{ at } t = 0}$, gives

$\boxed{\ln C = \ln C_0 - K.t}$

or $\boxed{C = C_0 . e^{-Kt}}$

Fig. First-order reactions

(Source: Marcos von Sperling, Basic Principles of Wastewater Treatment. IWA Publishing, 2007.)

$$\frac{dC}{dt} = -KC^{0} \text{ or } \frac{dC}{dt} = -K$$

$$\ln C = \ln C_0 - K.t$$

$$\text{or} \quad C = C_0 . e^{-Kt}$$

So, for first order reaction, we have; this is wrong, this is 1. So, we have for first-order reaction, the reaction can be written like this. In a batch reactor, the rate of change of the reagent concentration C is proportional to the reagent concentration at a given time. So, dC/dt is equal to minus KC. And the integrating the above equation with the condition that the concentration is C_0 at time t is equal to 0 will give this particular equation, ln C is equal to ln C_0 minus Kt; or C is equal to C_0, e raise to minus Kt. So this is the equation. So, we can again represent this equation by this graph, where dC/dt.

So, here we can see the slope is continuously decreasing, because the concentration is decreasing with time. Now, if we plot with respect to concentration wise versus time graph, so it will first decrease linearly; and then it will like go up to a saturation value. The slope will be at some particular value minus dC/dt. The slope is changing with time for the first-order reaction.

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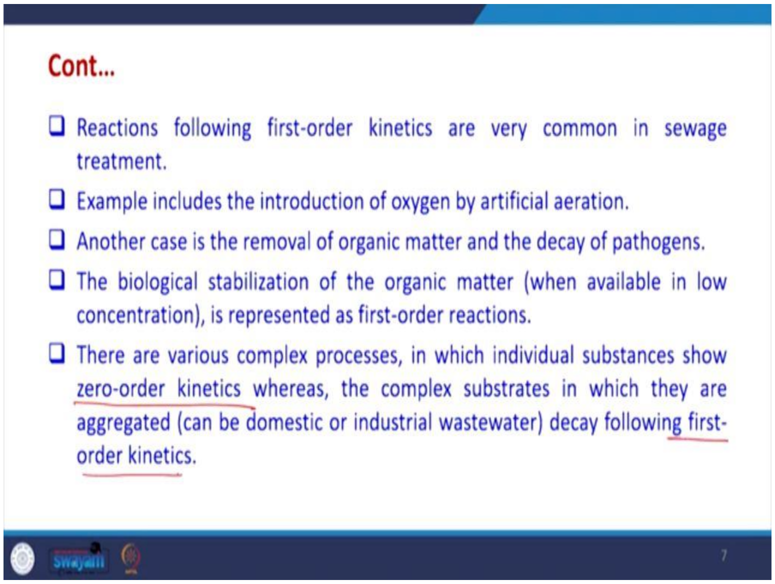

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- ☐ Reactions following first-order kinetics are very common in sewage treatment.
- ☐ Example includes the introduction of oxygen by artificial aeration.
- ☐ Another case is the removal of organic matter and the decay of pathogens.
- ☐ The biological stabilization of the organic matter (when available in low concentration), is represented as first-order reactions.
- ☐ There are various complex processes, in which individual substances show zero-order kinetics whereas, the complex substrates in which they are aggregated (can be domestic or industrial wastewater) decay following first-order kinetics.

Now, reactions following first-order kinetics are very very common during the wastewater treatment or sewage treatment. Examples include the introduction of oxygen by artificial aeration, there are many cases. Another case is the removal of organic matter and the decay of pathogens; this is also followed by first-order reactions. The biological stabilization of organic matter is also represented by first-order reactions, and we can easily find out the value of K for different types of organic matter.

There are various complex processes in which the individual substances, so either zero-order kinetics, and or the aggregated following first-order kinetics. So, there will be many reactions in which combination of both zero-order and first-order kinetics happens; so, will be trying to understand those reactions also.

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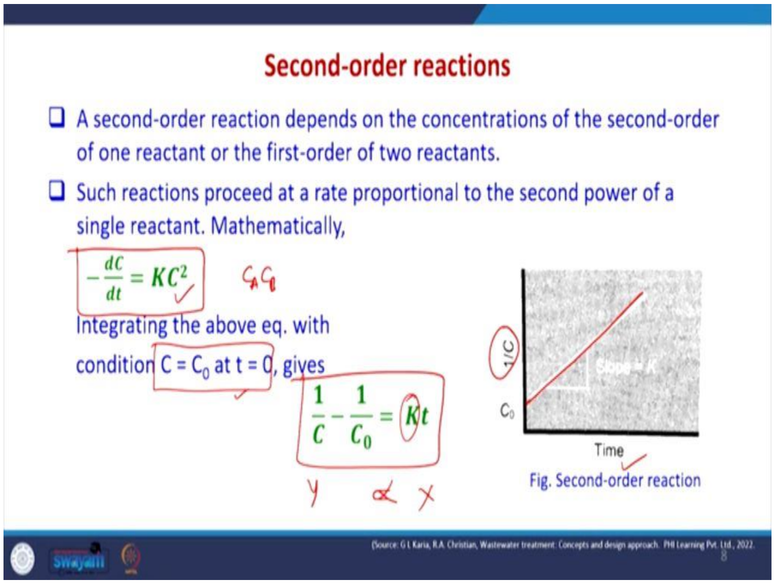

Second-order reactions

- ☐ A second-order reaction depends on the concentrations of the second-order of one reactant or the first-order of two reactants.
- ☐ Such reactions proceed at a rate proportional to the second power of a single reactant. Mathematically,

$$\boxed{-\frac{dC}{dt} = KC^2} \checkmark \qquad C_A C_B$$

Integrating the above eq. with condition $\boxed{C = C_0 \text{ at } t = 0}$, gives

$$\boxed{\frac{1}{C} - \frac{1}{C_0} = Kt}$$

$$y \quad \propto \quad x$$

Fig. Second-order reaction

(Source: G L Karia, R.A. Christian, Wastewater treatment: Concepts and design approach. PHI Learning Pvt. Ltd., 2022.

Mathematically,

$$-\frac{dC}{dt} = KC^2$$

$$\frac{1}{C} - \frac{1}{C_0} = Kt$$

Then, there are second order reactions. In the second order reaction the concentration of the second-order, it is like the rate is proportional to the square of the concentration of the one of the reactant, or the first-order of two reactants. So, it is possible that we may have two reactants and both are having first order; so overall order is second. Now, if we are following the first case where only one reagent is there, but the rate is proportional to the square of concentration of the one reagent. So, overall, this equation can be integrated for the condition C is equal to C_0 that the concentration is C_0, at time t is equal to 0; and we can obtain this particular equation.

And for this particular equation, if we plot 1/C versus time, the slope will be K. So, here we can see, the y is taken this and x is the time. So, the slope we can see here is easily K; and from this slope we can cross check whether second-order reaction is there or not. So this, this is the for this equation represents the second-order reaction. Now, before going further, we will try to solve a problem; and try to determine the reaction order of a reactant removal process for the data which is given here.

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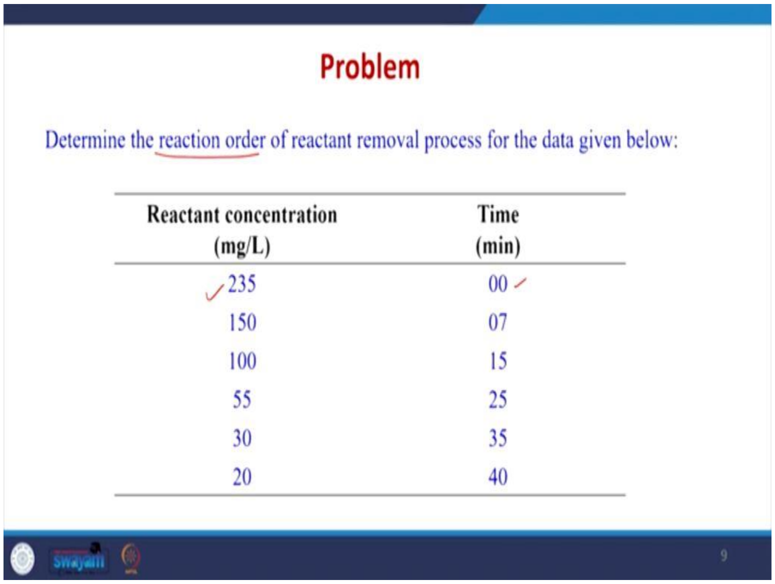

Problem

Determine the reaction order of reactant removal process for the data given below:

Reactant concentration (mg/L)	Time (min)
235	00
150	07
100	15
55	25
30	35
20	40

So, we have a reaction which is happening in a batch reactor and the reactant concentration is decreasing with time. And so, initially the concentration is 235 milligram per liter; and it is decreasing with minute and the values are noted with minute. Now the, what we need is we have to determine the reaction order, whether it is zero-order, first-order, or second-order reaction. So, this is what is meant to be determined from this particular problem.

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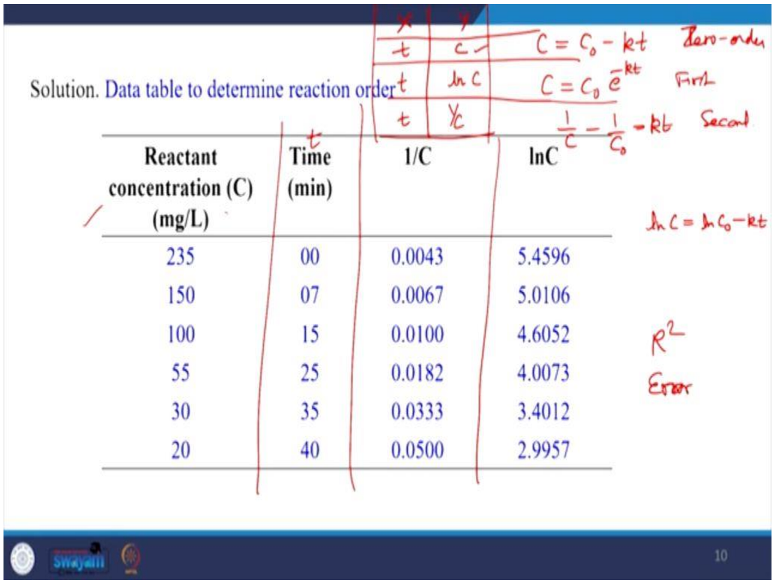

Solution. Data table to determine reaction order

x	y		
t	C	$C = C_0 - kt$	Zero-order
t	ln C	$C = C_0 e^{-kt}$	First
t	1/C	$\frac{1}{C} - \frac{1}{C_0} = kt$	Second

Reactant concentration (C) (mg/L)	Time (min)	1/C	lnC
235	00	0.0043	5.4596
150	07	0.0067	5.0106
100	15	0.0100	4.6052
55	25	0.0182	4.0073
30	35	0.0333	3.4012
20	40	0.0500	2.9957

$\ln C = \ln C_0 - kt$

R^2

Error

Now, data table used to determine the reaction order can further be written like this. So if, what we see that we try to use the different reaction equations that were determined; so, we have one equation where C is equal to C_0 minus Kt. So, one reaction is this C is equal to C_0 minus Kt; this is for zero-order reaction; this is one reaction that we have. Then, C is equal to C_0, e raise to minus Kt, this is the for first-order; and then there is another 1 by C minus 1 by C_0 is equal to Kt, this is first second-order. So, we have three equations, which are known to us for first, second and third order.

Now, from here what we do is that we try to find out three curves, and which curve is better representing the data we can find out. Now, so for plotting the curve, we that means we require some values of x and some values of y; and from this these equations, what we can see is that for the zero-order reaction, the x value will be t; all the values of t and the y value can we C. So, this is known from here. Second is that this first order equation can be converted into linear form. So, if we convert that into linear form, so we can easily see that x value can be t, and the y value can be ln C.

So, because from this first-order equation, we can write that ln C is equal to ln C_0 minus Kt. So, this equation first-order equation can also be written like this. So, that means we have y, ln C and x value is again the time value. For the third case, we can write 1 by C versus t. So, that means if we can draw these three curves, we can cross check, which curve is better represented. And that we can find out using the R square value, or some error values we can find out using the statistical mathematics, and then we can represent. So, from here, that means we require three types of data; time is already known to us, so that means time is already present.

So, we require C; C is already known to us. So, C versus t, graph can be easily drawn to check whether zero-order is fitting or not. Now, we for first order we require ln C, the ln C has been calculated here. Similarly, for second-order, we have to find out 1 by C; so, 1 by C value has been calculated here. Now, we will plot three curves for checking whether the reaction data which is given here, it is zero-order, first-order, or second-order.

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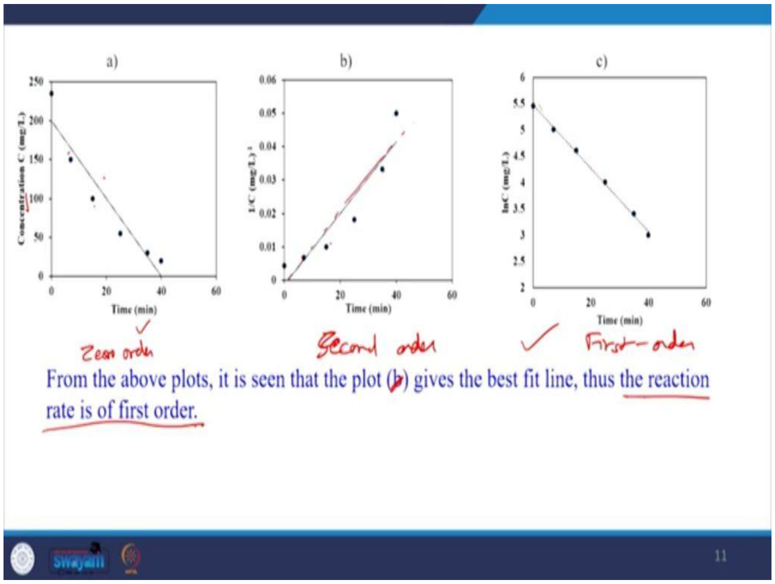

From the above plots, it is seen that the plot (b) gives the best fit line, thus the reaction rate is of first order.

So, for doing so, we can see here the curves have been plotted; the concentration C versus time. This is the first curve, for this is for zero-order. Now, for second, we can see that we can for second order, we can plot this 1/C versus t to this is for second-order; this is the second-order, and this is for first-order, the graphs are different. Now, we can easily see that here the line is straight line is not represented, and they are not for concentration versus time; this is not a very good fitting representing the data. Similarly, for second-order also, we can see the data is not, the line is not well representing the data; because (like) these values are scattered.

Whereas, for the first-order graph, we can easily see; there the line is perfectly representing the data points. So, that means overall it is seen that the plot which gives the this particular plot which is the third plot, actually best represents the data. And so, the overall reaction rate is of first-order; so, from here we can find out that the data is being represented well. And thus, we can find out and cross check that the data which was given; it is representing first-order kinetics. Now, going further we have saturation reactions.

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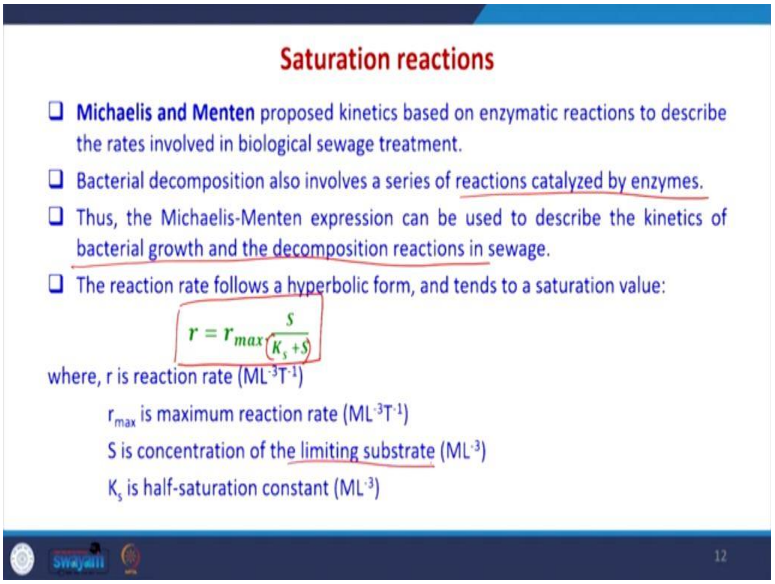

Saturation reactions

- **Michaelis and Menten** proposed kinetics based on enzymatic reactions to describe the rates involved in biological sewage treatment.
- Bacterial decomposition also involves a series of reactions catalyzed by enzymes.
- Thus, the Michaelis-Menten expression can be used to describe the kinetics of bacterial growth and the decomposition reactions in sewage.
- The reaction rate follows a hyperbolic form, and tends to a saturation value:

$$\boxed{r = r_{max} \cdot \frac{S}{(K_s + S)}}$$

where, r is reaction rate ($ML^{-3}T^{-1}$)

r_{max} is maximum reaction rate ($ML^{-3}T^{-1}$)

S is concentration of the limiting substrate (ML^{-3})

K_s is half-saturation constant (ML^{-3})

The reaction rate follows a hyperbolic form, and tends to a saturation value:

$$\boldsymbol{r = r_{max} \cdot \frac{S}{K_s + S}}$$

So, one of the saturation reaction which is very commonly written is the Michaelis-Menten equation. The Michaelis-Menten proposed kinetics based on enzyme reactions to describe the rates involved in the biological sewage treatment, or the biological wastewater treatment. The bacterial decomposition also involves a series of reactions catalyzed by enzymes. Thus, the Michaelis-Menten expression can be used to describe the kinetics of the bacterial growth and the decomposition reaction both in the sewage and wastewater. The reaction rate follows a hyperbolic form and tends towards the saturation value.

So, overall, the Michaelis-Menten equation is written like this, r is equal to r max into S, divided by K_s plus S. So, r represents the reaction rate, r max is the maximum reaction rate that is possible. S is the concentration of limiting substrate; the substrate which will be utilized first in the reaction, or which limits the overall reaction rate. And K_s is the half saturation constant. So, this is the Michaelis-Menten equation.

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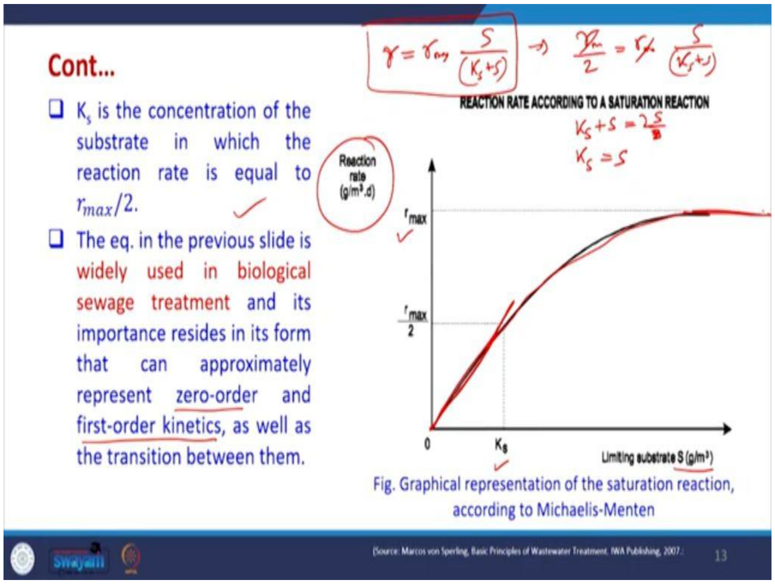

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- K_s is the concentration of the substrate in which the reaction rate is equal to $r_{max}/2$. ✓
- The eq. in the previous slide is widely used in biological sewage treatment and its importance resides in its form that can approximately represent zero-order and first-order kinetics, as well as the transition between them.

$$\boxed{r = r_{max}\frac{S}{(K_s+S)}} \rightarrow \frac{\cancel{r_m}}{2} = \cancel{r_m}\frac{S}{(K_s+S)}$$

$$K_s + S = 2S$$

$$K_s = S$$

Fig. Graphical representation of the saturation reaction, according to Michaelis-Menten

(Source: Marcos von Sperling, Basic Principles of Wastewater Treatment. IWA Publishing, 2007.)

And K_s actually if we plot the curve like r. What we do is that we try to plot the reaction rate by which is given by like gram of gram per meter cube per day, with respect to limiting substrate concentration, which is in gram per meter cube. And now, if you plot this r versus S, the curve will be represented by this. Now, in this case, the case value represents the condition, where r is equal to r_{max}. So, under that condition we present the case is the concentration of substrate in which the reaction rate is equal to $r_{max}/2$. So, we can easily see from the this particular equation itself how it is defined, r is equal to this r equal to r_{max}, S upon K_s plus S.

So, if we write r is equal to $r_{max}/2$, is equal to r_{max} S, K_s plus S; under that condition this goes off. So, we have K_s plus S is equal to S by 2, 2S; and that means K_s is equal to S. So, that means the, when the rate of reaction is equal to $r_{max}/2$, the K_s is equal to substrate concentration; so, this is what is defined here. This equation in the previous slide is widely used; this Michaelis-Menten equation is widely used in the biological sewage treatment.

And it is important resides in its form that can be approximately represented by both zero-order and first-order kinetics, and the transition between them. At least this rate where we can from here we can see that in this particular equation, this when the K_s value is like much much greater than S. So, under that condition the r is like directly proportional to S; so, we have first-order reaction.

When the S value is greater than much much greater than Ks, like under this condition; so, in this condition, this goes to r max that means zero-order reaction. So, this state actually represents the first-order kinetics, and this state represents the second-order kinetics which is given later on.

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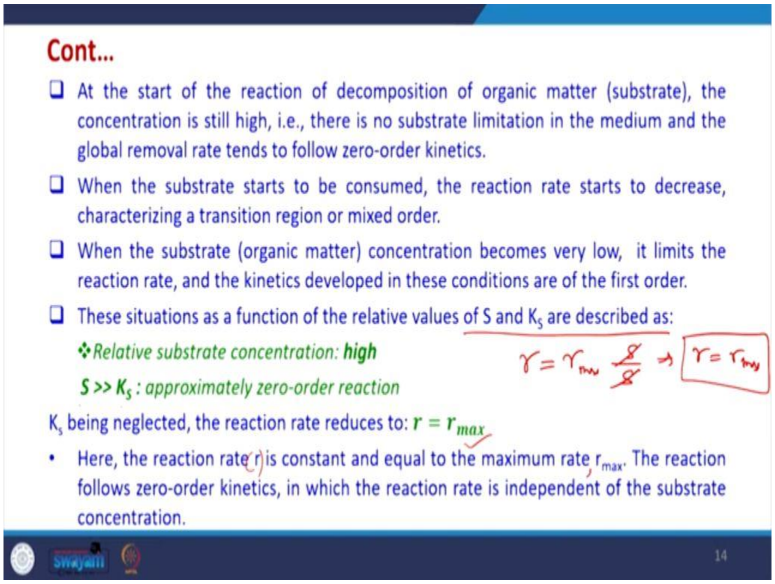

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- ☐ At the start of the reaction of decomposition of organic matter (substrate), the concentration is still high, i.e., there is no substrate limitation in the medium and the global removal rate tends to follow zero-order kinetics.
- ☐ When the substrate starts to be consumed, the reaction rate starts to decrease, characterizing a transition region or mixed order.
- ☐ When the substrate (organic matter) concentration becomes very low, it limits the reaction rate, and the kinetics developed in these conditions are of the first order.
- ☐ These situations as a function of the relative values of S and K_S are described as:

❖ *Relative substrate concentration:* ***high***

$S >> K_S$: approximately zero-order reaction

$$r = r_{max} \frac{\cancel{S}}{\cancel{S}} \rightarrow \boxed{r = r_{max}}$$

K_s being neglected, the reaction rate reduces to: $r = r_{max}$

- Here, the reaction rate (r) is constant and equal to the maximum rate r_{max}. The reaction follows zero-order kinetics, in which the reaction rate is independent of the substrate concentration.

At the start of the reaction of decomposition of organic matter that is substrate, the concentration is high. That means there is no substrate limitation in the medium and we have very high substrate. The global removal rate then tends to follow the zero-order kinetics. When the substrate starts to be consumed, the reaction rate starts to decrease, and characterizing a transition region or mixed order. When the substrate concentration becomes very low, it limits the reaction order; and the kinetics developed in these conditions is of the first order. So, these situations as a function of the relative value of S and Ks are described as relative substrate concentration is high.

So, when S is very high, so, that means r is equal to r_{max} and S upon S. So, that means, it becomes like r is equal to r_{max}; and this is the first order reaction, where the concentration dependence is eliminated. Now, when K_s is being neglected, the reaction order reduces to this which is given here. Here the reaction order is reaction rate is r is constant, and is equal to maximum rate r_{max}. And the reaction for the zero-order kinetics in which the reaction rate is independent of the substrate concentration.

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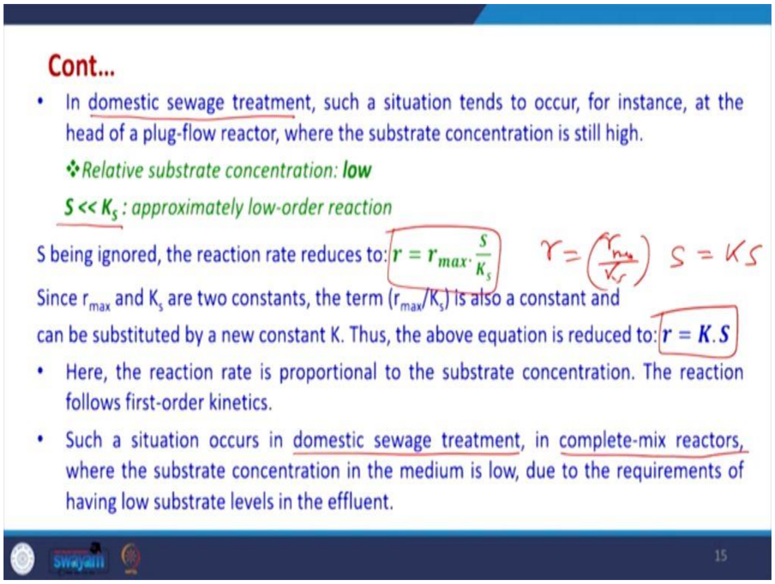

Cont...

- In domestic sewage treatment, such a situation tends to occur, for instance, at the head of a plug-flow reactor, where the substrate concentration is still high.

❖ *Relative substrate concentration:* ***low***

$S << K_S$ *: approximately low-order reaction*

S being ignored, the reaction rate reduces to: $\boxed{r = r_{max} \cdot \frac{S}{K_s}}$

$r = \left(\frac{r_{max}}{K_s}\right) S = KS$

Since r_{max} and K_s are two constants, the term (r_{max}/K_s) is also a constant and can be substituted by a new constant K. Thus, the above equation is reduced to: $\boxed{r = K.S}$

- Here, the reaction rate is proportional to the substrate concentration. The reaction follows first-order kinetics.
- Such a situation occurs in domestic sewage treatment, in complete-mix reactors, where the substrate concentration in the medium is low, due to the requirements of having low substrate levels in the effluent.

In the second case, in that like domestic sewage treatment, such as situation tends to occur, for instance, at the head of the plug-flow reactor, where the substrate concentration is still high. Now, when the relative substrate concentration is low; that means, S is much less than K_s. And so, under that condition, the overall reaction can be written like this, r is equal to r_{max} upon K_s which are fixed. And this is a function of substrate concentration or we can write this as new K_s. So, in this way, the reaction is like this.

And here the reaction or rate is proportional to the substrate concentration, and the reaction follows first-order kinetics. So, such a situation occurs in the domestic sewage treatment, in complete-mix reactors. In the complete-mix reactor like CSTRs, this condition will come, and where we have a first-order kinetics which is followed. So, overall this way we can write.

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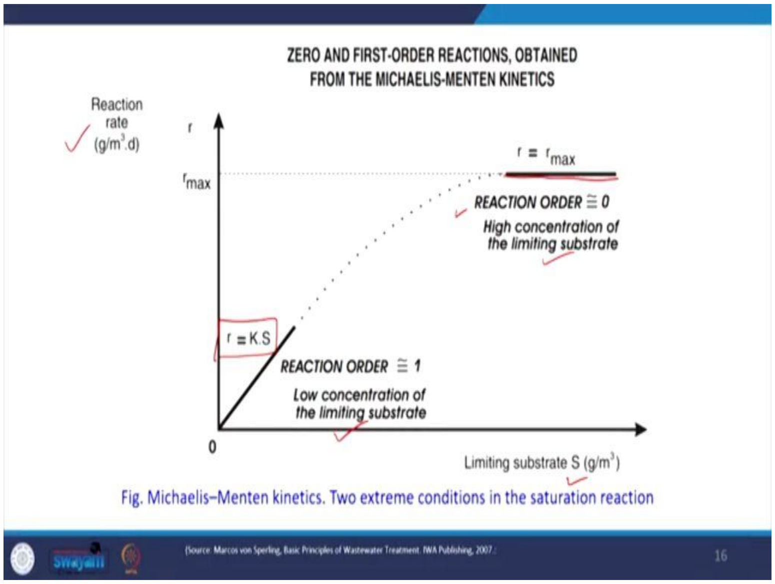

ZERO AND FIRST-ORDER REACTIONS, OBTAINED FROM THE MICHAELIS-MENTEN KINETICS

Fig. Michaelis–Menten kinetics. Two extreme conditions in the saturation reaction

(Source: Marcos von Sperling, Basic Principles of Wastewater Treatment. IWA Publishing, 2007.)

The reaction rate is plotted versus limiting substrate S. And initially we have r is equal to Ks at the low concentration of limiting substrate. At very high concentration of limiting substrate, the reaction order is zero; and it is operational at r is equal to r_{max}. So, we can see, both the zero and first order reactions are in-situ present inside the Michaelis-Menten kinetic expression itself. And Michaelis-Menten kinetic expression can represent both zero-order and first-order reaction, depending upon the limiting substrate concentration. So, this is any other possibility may be present during the wastewater conditions at a various condition.

Now, this particular again a second equation is given here and we will try to solve this problem, so as to understand further. The conditions are given here.

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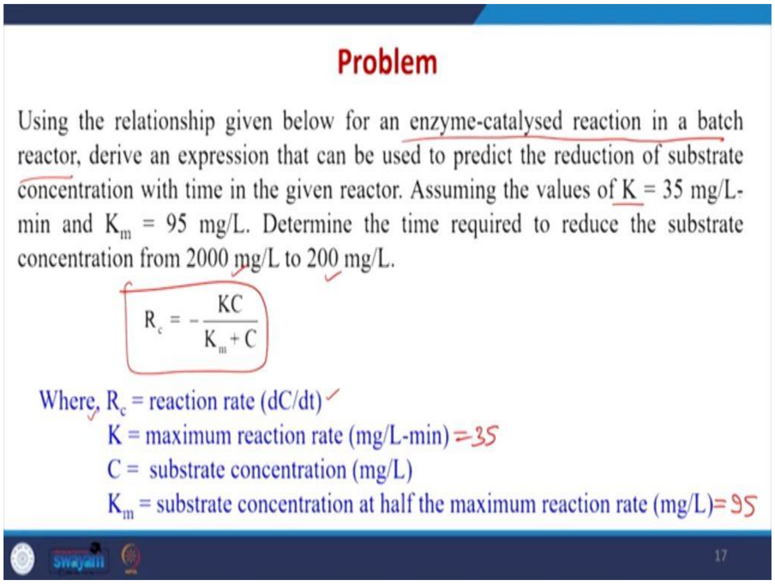

Problem

Using the relationship given below for an enzyme-catalysed reaction in a batch reactor, derive an expression that can be used to predict the reduction of substrate concentration with time in the given reactor. Assuming the values of K = 35 mg/L-min and K_m = 95 mg/L. Determine the time required to reduce the substrate concentration from 2000 mg/L to 200 mg/L.

$$\boxed{R_c = -\frac{KC}{K_m + C}}$$

Where, R_c = reaction rate (dC/dt) ✓
K = maximum reaction rate (mg/L-min) = 35
C = substrate concentration (mg/L)
K_m = substrate concentration at half the maximum reaction rate (mg/L) = 95

Using the relationship which is given below; so, this is the relationship which is given here. For an enzyme-catalysed reaction in a batch reactor, derive an expression that can be used to predict the reduction of substrate concentration with time in the given reactor. So, in this case, we have to find out an expression, where we can represent the concentration with time. And assuming that the value of f is equal to 35 milligram per liter per minute; and then the K_m value is 95 milligram per liter. Determine the time required to reduce the substrate concentration from 2000 milligram per liter to 200 milligram per liter; so, this is here.

So, Rc here represents the reaction rate, K is the maximum reaction rate in milligram per liter per minute, whose value is given as 35. C is the substrate concentration it is not given, K_m is the substrate concentration at half the maximum reaction rate; and its value is given as 95. So, we have K and K_m which is given. Now, we have to find out the equation of C with respect to time, and then we have to find out the time required to reduce the substrate concentration from 2000 milligram per liter to 200 milligram per liter.

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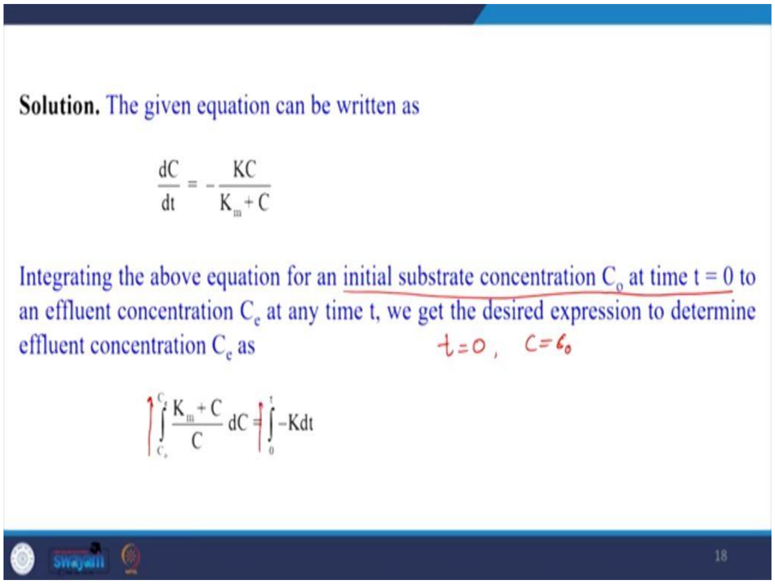

Solution. The given equation can be written as

$$\frac{dC}{dt} = -\frac{KC}{K_m + C}$$

Integrating the above equation for an initial substrate concentration C_0 at time t = 0 to an effluent concentration C_e at any time t, we get the desired expression to determine effluent concentration C_e as

$t = 0, \quad C = C_0$

$$\int_{C_0}^{C_e} \frac{K_m + C}{C}\, dC = \int_0^t -K dt$$

The given equation can be written as:

$$\frac{dC}{dt} = -\frac{KC}{K_m + C}$$

$$\int_{C_o}^{C_e} \frac{K_m + C}{C}\, dC = \int_0^t -Kdt$$

So, the equation can be written like this dC/dt is equal to minus KC upon K_m plus C. What we do is that we integrate this equation from initial substrate concentration C_0 at time t is equal to 0. So, we have at time t equal to 0, C is equal to C_0; so, we can integrate using this, and assuming that the effluent concentration is C at time t. So, the concentration is decreasing from C_0 to C, when the time is increasing from 0 to t. So, we try to solve this equation.

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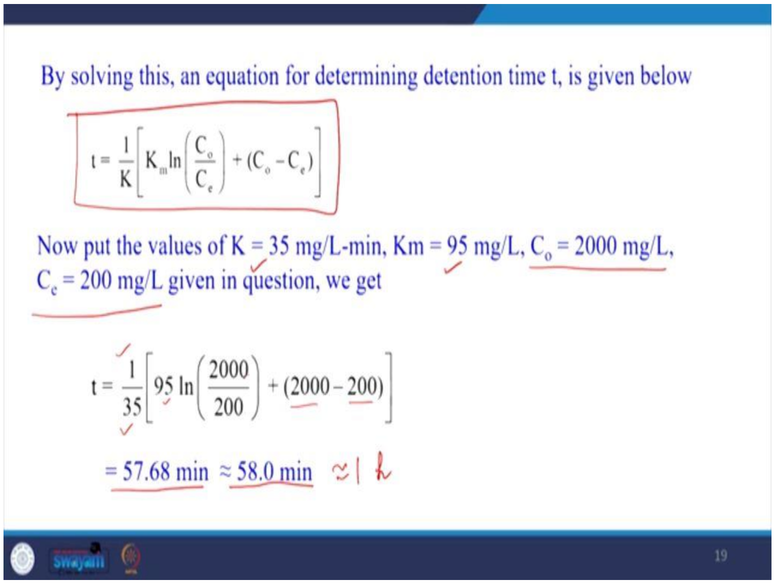

By solving this, an equation for determining detention time t, is given below

$$\boxed{t = \frac{1}{K}\left[K_m \ln\left(\frac{C_o}{C_e}\right) + (C_o - C_e)\right]}$$

Now put the values of K = 35 mg/L-min, Km = 95 mg/L, C_o = 2000 mg/L, C_e = 200 mg/L given in question, we get

$$t = \frac{1}{35}\left[95 \ln\left(\frac{2000}{200}\right) + (2000 - 200)\right]$$

$$= 57.68 \text{ min} \approx 58.0 \text{ min} \approx 1\ h$$

$$t = \frac{1}{K}\left[K_m \ln\left(\frac{C_o}{C_e}\right) + (C_o - C_e)\right]$$

$$t = \frac{1}{35}\left[95 \ln\left(\frac{2000}{200}\right) + (2000 - 200)\right]$$

And if we integrate by solving, we can easily find out the equation can be written like this. So, we can try and go on and solve this. Now, what we have to do is that we have to put the value of K and K_m. So, K was 35 milligram per liter and K_m is 95 milligram per liter. And now, in the further question it was given that initial concentration is 200 milligram per liter, which is getting reduced to 200 milligram per liter in the this particular question. So, we substitute the all the values, so K is equal to 35, K_m is equal to 95 200, 2000 to 200, 2000 minus 200; and we solve, it will be 57.68. Appropriately, 58 minute will it will require to reduce the concentration from 2000 milligram per liter to 200 milligram per liter, if the reaction kinetics is given by this particular equation.

So, this problem tells that if we report the reaction kinetics in the form of this; because for any reaction kinetics, we have to report the values of all the rate constants. So, in this case the rate constants were K and K_m, and both were reported previously. And since the rate was given, rate equation was given, the values of rate constants were given, we can use this rate constant to determine the time required for our design purpose; and it was found to be 58 minute.

And using this residence time which may be considered as 1 hour, we can design our reactor, if we have to reduce the concentration from 2000 milligram per liter to 200 milligram per liter. So, this is the usefulness of representing the reaction kinetics. Now, this is the last section of this particular lecture.

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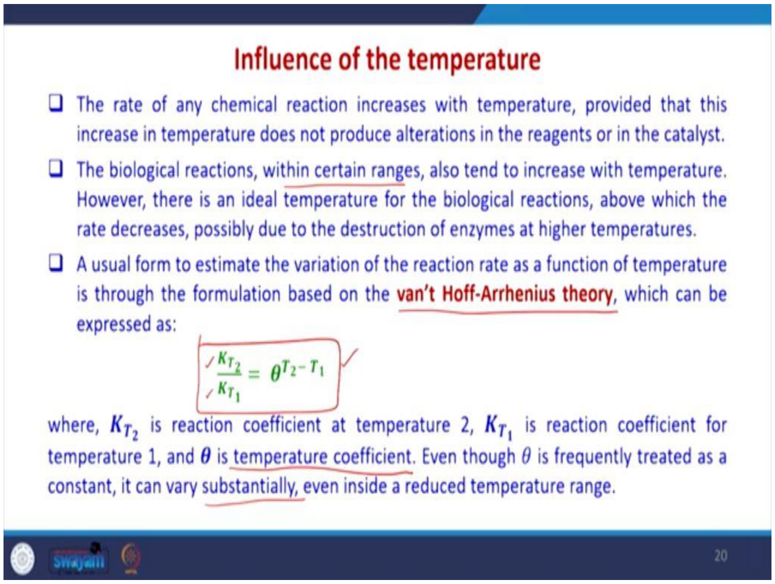

Influence of the temperature

- ☐ The rate of any chemical reaction increases with temperature, provided that this increase in temperature does not produce alterations in the reagents or in the catalyst.
- ☐ The biological reactions, within certain ranges, also tend to increase with temperature. However, there is an ideal temperature for the biological reactions, above which the rate decreases, possibly due to the destruction of enzymes at higher temperatures.
- ☐ A usual form to estimate the variation of the reaction rate as a function of temperature is through the formulation based on the **van't Hoff-Arrhenius theory**, which can be expressed as:

$$\boxed{\frac{K_{T_2}}{K_{T_1}} = \theta^{T_2 - T_1}}$$

where, K_{T_2} is reaction coefficient at temperature 2, K_{T_1} is reaction coefficient for temperature 1, and θ is temperature coefficient. Even though θ is frequently treated as a constant, it can vary substantially, even inside a reduced temperature range.

$$\frac{K_{T_2}}{K_{T_1}} = \theta^{T_2 - T_1}$$

Always the reaction rate or rate of any chemical reaction increases with increase in temperature, or and similar is the case for all the biological reactions also. And it is we know very well that we increase in temperature, the rate of any chemical reaction increases. The biological reactions also within certain ranges, they increase the reaction rate increases with increase in temperature. However, there is an ideal temperature for the biological reactions to occur, above which the rate decreases; so, there is some difference. In usual chemical reactions, the increase in temperature, the reaction rate always increases.

Whereas, for biological reaction, there is a optimum temperature; after which the reaction rate may not increase, it may actually decrease. But, within that limit, still the reaction may increase. The usual form to estimate the variation of reaction rate as a function of temperature is based upon various theories; it may be van’t Hoff-Arrhenius theory. And under that theory, the reaction rate at two temperatures can be defined using this type of equations. The equations may vary a little bit, but these types of equations are very common. So, reaction rate K at temperature T_2 divided by reaction rate at temperature T_1.

So, this can be defined as theta raised to T_2 minus T_1, where theta is the temperature coefficient. And KT_2 and KT_1 are the reaction coefficients for the temperature. And even though the theta is frequently treated as constant, it can vary substantially for different types of wastewater, different conditions et-cetera. So, this theta value may also change. And this already we have used such equation is when we try to find out the effect of temperature on the VOD. So, already we have used such equation in the previous lecture.

And this type of equation can be used for understanding the biological kinetics also under various temperature conditions. So, we will be using such equations, whenever desired for studying the effect of temperature on the biological reaction kinetics. So, with this we will end today's lecture; we will continue further with the reaction kinetics, and other types of differences between various types of reactions, and the growth kinetics, et-cetera. We will continue further. Thank you very much.