

Course: Adsorption Science and Technology: Fundamentals and Applications

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Week 04

Lecture 20 | Slurry Adsorption

Hello everyone, welcome to this last lecture of this week on this adsorption diffusion models. Today we are going to talk about the slurry transport. So, slurry transport or slurry adsorption is particularly relevant for systems in batch or in stirred vessel, where the adsorbents are actually present in the solution phase as dispersed particles. So, typically there could be a batch mode of operation this is what normally any adsorption based equipment or you know experiments where equilibrium is studied or equilibrium based separation is done, or achieved one does a batch operation. It is also possible to have a continuous operation in the likes of similarly this continuous stirred tank reactor which many of you might have heard in the context of reaction engineering. So, in this case it is primarily assumed that the slurry is prepared by mixing the adsorbent particles within the solution phase, in such a way that it is very well agitated and stirred and is mixed it is almost like a fluidized bed which is contained within this vessel having a lot of this you know agitation by using you know propellers or baffles or you know this by this shearing action.

So, this is what is achieved both in the batch as well as in the continuous phase. So, here the transport phenomena which happens is primarily controlled by the external mass transfer rather than the intrinsic transport within the particle. So, the primary. So, the primary consideration in this slurry adsorption mode is that small particles are used in slurry or suspension and the relative velocity between particles and liquid in the stirred or agitated slurry is low (so small particles sorry small particles tend to move with the particle).

Primary consideration in the slurry adsorption mode,
→ small particles are used in slurry (suspension) &
the relative velocity between particles & liquid in
the stirred (or agitated) slurry is low (small particles
tend to move with the particle), the rate of
adsorption is controlled by external transport
(and NOT) internal mass transfer.

BATCH

CONTINUOUS



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So, it can be assumed that the relative velocity is almost 0. The rate of the rate of adsorption is controlled by external transport in this case and not internal mass transfer. So, this is the primary context of slurry adsorption where due to the high rates of mass transfer the external film transport is actually controlling the overall rates of this mass transfer. So, let us see two cases of this operation which is normally practiced in the industry one is the batch, one is the continuous mode.

So, first we will talk about the continuous sorry the batch mode of operation. So, in the batch mode of the operation the rate of solute adsorption that is $\frac{dC}{dt}$. So, we consider a lumped parameter system because this is very well mixed right. So, this is well mixed tank. So, the lumped approximation holds good is multiplied with the mass transfer coefficient in the tank multiplied with 'a' that is the external surface area of the adsorbent per unit volume of the liquid and this $C - C^*$.

So, C is of course, the concentration of adsorbate in the bulk liquid. C^* is of course, the equilibrium concentration with the specific or with the particular adsorbent particular adsorbent loading. K_c is the external liquid phase mass transfer coefficient and 'a' is the specific this external surface area of adsorbent, this is particularly important. the other because this is what determines the you know the level of adsorption per unit volume of liquid or I can say per unit volume of the amount of the liquid phase solution that it is

absorbed by this particular adsorbent. So, this is the transport equation or the overall lumped parameter model based transport equation in this case.

Now, we also have a mass balance equation or a material balance equation. So, this is same as the balance equation that we have already studied previously while calculating some equilibrium based models. This C_f represents the instantaneous bulk on this concentration. Q is the liquid volume. You can also consider it to be V .

BATCH

rate of solute adsorption, (well mixed tank)


$$-\frac{dc}{dt} = k_c a (c - c^*)$$

$-\frac{dc}{dt}$: conc. of adsorbate in the bulk liquid
 k_c : mass-transfer coefficient
 a : sp. ext. surf. area of adsorbent per unit vol. liquid
 $(c - c^*)$: equilibrium conc. with the particular liquid adsorbent loading

Material balance :

$$C_f Q = c(t) Q + q S$$

C_f : Feed conc.
 Q : Vol. of liq.
 $c(t)$: instantaneous conc @ t
 q : adsorbate conc. in adsorbent
 S : mass of adsorbent


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That is something gives you the total mass of the adsorbent, sorry, total mass of the adsorbate initially in the system. This is multiplied with the value of C at any time t , into the total volume. We assume the total volume remains unchanged due to this adsorption plus the amount that is adsorbed or in the solid phase multiplied with the S or the mass of the adsorbent. So, just to be clear this is the feed concentration or the concentration at t equal to 0, this is the volume of liquid which contains the dispersed adsorbent as well as the adsorbate species. This is the instantaneous concentration.

So, maybe I can write this as $C(t)$ instantaneous concentration at t , q is the adsorbate concentration in adsorbent and S is the mass. So, this is a simple mass balance at any time p which will hold as the adsorbate species is getting transferred from the solution phase to the solid phase. And then finally, you have the isotherm equation which relates the q with the c^* . So, we can write as q as $k \times C^*$ to the power n . One can also, so this

is a Freundlich type I have written. It can also be written as the Langmuir type or we can use the simple linear Henry's type.


Isotherm equation
 $q = K C^*{}^{1/n}$ (Freundlich isotherm)

For sake of simplicity (consider linear isotherm, $n=1$)

Analytical solution

$$C = \frac{C_F}{1 + (Q/KS)} \left[\exp \left\{ -K_C \frac{Q}{KS} \left(1 + \frac{Q}{KS} \right) t \right\} + \frac{Q}{KS} \right]$$

as $t \rightarrow \infty$, equilibrium is approached,

$$C^* \equiv C(t \rightarrow \infty) = \frac{C_F (Q/KS)}{1 + (Q/KS)} = \frac{C_F}{1 + \left(\frac{KS}{Q} \right)}$$


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So, these are the fundamentals fundamental equation the 3 major equation or the 3 equations that we have for the for this case of the batch adsorption that will be used to quantify the evolution of the concentration starting from an initial value to an equilibrium value. So, please note that the 3 you know unknown parameters sorry the unknown variables in this case one is of course, the C that is what we are trying to track one is C^* that is the equilibrium concentration. And of course, we have the q . So, we have three unknown variables and we have three equations that can be used to solve this system of equation. So, for the sake of simplicity, let us consider linear isotherm of course, you can also work out this for this non-linear type or when n is not equal to 1, but for the linear isotherm case when n is equal to 1.

The solution of this set of equation can be analytically obtained and this analytical solution can be obtained by coupling this value of C^* in from equation 3 you put this into equation 2 and then equation 2 can be substituted into equation 1 in terms of this C^* . So, on doing so the analytical expression is obtained as C is equal to C_F divided by $1 + Q$ by KS multiplied with exponential minus K_C q by KS again $1 + Q$ by KS into t . So, put this nicely inside the bracket plus q by KS . So, where K is of course, the equilibrium isotherm constant, S is the mass of the adsorbent and q is the amount of the volume. So, as the, so as this time t approaches to infinity, equilibrium is approached.

Continuous mode
 Liquid & solid flow continuously in a perfectly mixed vessel


$$\frac{C_F - C_{out}}{t_{res}} = K_c a (C_{out} - c^*)$$

residence time $\rightarrow t_{res}$

$$C_{out} = \frac{C_F + K_c a t_{res} c^*}{1 + K_c a t_{res}}$$

Mass conservation: $C_F Q = C_{out} Q + q_{out} S$

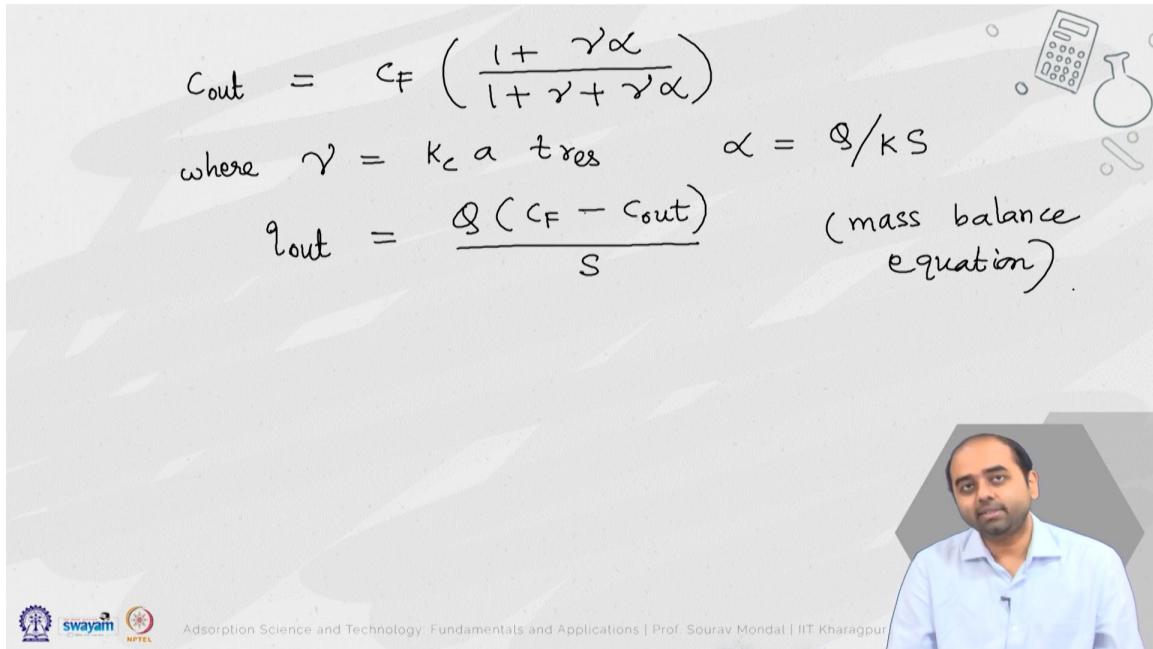
For linear isotherm: $c^* = q_{out} / K$



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And from this linear isotherm model, one can work out what would be the value of this C at, so c as t tending to infinity which is referred to as the c star is equal to c_F times or in other words, this can be related as c_F by this factor. So, it is clearly understood that it is reduced by 1 plus k into s by Q , where Q is the volume of this liquid and S is the mass of the adsorbent and k is of course, the equilibrium constant. So, this is the solution or the analytical solution for the simplified scenario when n is not equal to 1 . Of course, you can also work out for other scenarios where the isotherm is represented by Langmuir type or you know the classical Freundlich type, maybe analytical expressions is slightly complicated to obtain in that scenario. In the case of this continuous mode, So, when the liquid and solids flow continuously in a perfectly mixed vessel the previous equation that we have obtained for the batch is converted to a steady state scenario in terms of the residence time t .


So, we use the idea of the classical CSTR and we say that in this scenario, this design equation can be related as something like this. So the concentration at the outlet is same throughout the system as it attains steady state. And here the steady state operation is very important. All of the symbols has the same interpretation as the previous case. So on rearranging this equation, one can get the outlet equation as something like this.



$$C_{out} = C_F \left(\frac{1 + \gamma \alpha}{1 + \gamma + \gamma \alpha} \right)$$

where $\gamma = K_c a t_{res}$ $\alpha = Q/KS$

$$q_{out} = \frac{Q(C_F - C_{out})}{S} \quad (\text{mass balance equation})$$



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So, this is the design equation to relate the outlet concentration in this continuous mode of operation where C^* is the equilibrium concentration and t_{res} is the residence time. So, this is the residence time of the you know residence time of the adsorbate species in the vessel of volume Q . So, also we have the mass balance equation as this is the initial or the inlet in this case, this is the outlet, plus the value of q at the outlet. So, it is assumed that the time scale of the adsorption is smaller than the residence time or within this residence time the system does attain equilibrium. So, in this scenario one can obtain for linear isotherm for linear isotherm it suggests that C^* can be related as this form.

Slurry adsorption:

Aqueous solution \rightarrow 0.01 moles phenol/L
 adsorbent (AC) to reduce phenol conc. to 0.00057 $\frac{\text{mol}}{\text{L}}$


Isotherm: $q = 2.16 c^{1/4.35}$

$\Rightarrow c^* = \left(\frac{q}{2.16} \right)^{4.35}$ here q & c are in mmol/g & mmol/L

Converting in terms of mol/L (or kmol/m³)
 as well as mol/g (or kmol/kg)

$c^* = \left(\frac{q}{0.01057} \right)^{4.35}$

Batch & continuous mode of adsorption



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The overall expression of C out now looks something like this. I will define what do you mean by gamma and alpha. So, where of course, gamma is a $K_c a$ into the residence time and alpha is q by kS , where S is of course, the mass of the adsorbent and the expression of Q out can also be given here from the law of mass action or from the law of mass conservation something like this which is of course, we know is similarly simply by rearranging the mass balance equation. Of course, if you have a non-linear isotherm equation, it may not be practically possible to relate this result explicitly in terms of Q out, but it is highly possible in this linear case. Now, let us try to see a simple example problem using some numbers.

So, this problem of slurry adsorption. So, let us say we have an aqueous solution which contains 0.01 moles phenol per liter and this is to be the adsorbent treated with an adsorbent activated carbon to reduce the concentration, reduce phenol concentration to subsequently low values. So, in this case the Freundlich equation isotherm relation is non-linear in type. that is related as q is equal to 2.16 c to the power 1 by 4.35. So, if you rearrange in terms of C or C^* one can write this as q by 2.16 to the power 4.35. So, of course, here Q and C are in millimoles per gram and millimoles per liter.

Batch mode: Using 10 g/L of AC, what is the time needed to reduce the conc. to the desired value


Ext. mass transfer coefficient (K_c) $\equiv 5 \times 10^{-5}$ m/s
 sp. surf. area (a) $\equiv 5$ m²/kg

$S/Q = 10$ g/L $= 10$ kg/m³ $K_c a = 5 \times 10^{-5} \times 5 \times 10 \approx 2.5 \times 10^{-3}$ s⁻¹

$C_F = 0.01 \frac{\text{mol}}{\text{L}} \equiv 0.01 \text{ kmol/m}^3$

$q = \frac{C_F - C}{S/Q} = \frac{0.01 - C}{10}$

Substituting into the isotherm expression,
 $C^* = \left(\frac{0.01 - C}{10 \times 0.01057} \right)^{4.35}$



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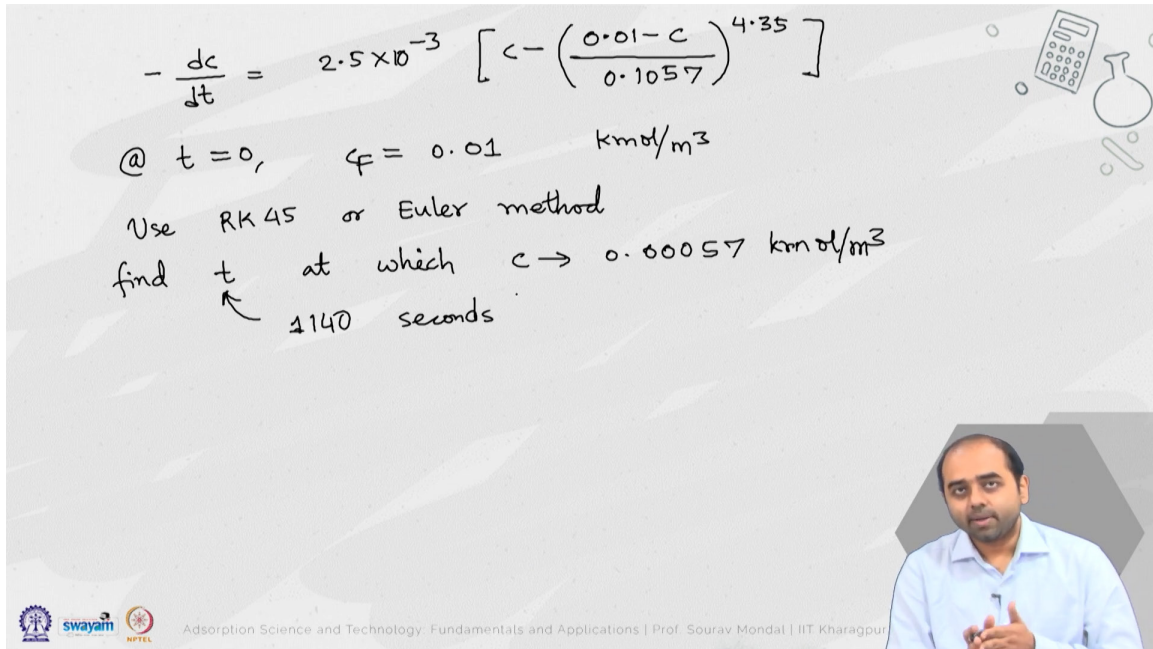
So, one should be of course, slightly careful with the units of moles and millimoles. Now, so if you convert this in terms of converting in terms of moles per liter or kilo moles per meter cube as well as moles per gram or kilo moles per kg in terms of q , one will get a slightly modified equation because the coefficient would change. Of course, the functional form would remain So, now the question is that what would be I mean you this for batch we have to study the operation in batch and continuous mode of adsorption. So, for the batch mode it is asked that using a value of 5 grams sorry. So, for batch mode I will state the problem clearly.

So, batch mode the question asked is using 10 grams per liter of activated carbon, what is the time needed to reduce the concentration to the desired value, that is mentioned desired value. Of course, we need the value of the external mass transfer coefficient. So, these are the coefficient which is K_c is 5 into 10 to the power minus 5 meters per second. Specific surface area, specific surface area or the particle surface area the value of a is given as 5 meter square per kg. So, now we have to find out the time.

So, let us work out and find out the relations here in batch mode. So, we can define this S by Q which is the mass of the adsorbent by the volume is nothing, but the sort of the concentration of the adsorbent in the solution. So, even though the total volume and the mass is not known, everywhere in the expression S by Q is used. So, this is 10 grams per liter or 10 kg per meter cube. The value of K_c into A is 5 into 10 to the power minus 5

cross 5 cross 10 because please note that you have to multiply the specific surface area which is given in terms of meter square per kg.

So, the amount of the adsorbent that is used here also needs to be multiplied. So, that is why 10 is multiplied here and this gives a value of 2.5×10^{-3} inverse. So, the value of initial concentration C_F is given as 0.01 moles per liter which is nothing but equal to 0.01 kilo moles per liter meter cube. The value of q from the mass balance is one can obtain as this. So, this relates to $0.01 - c$ by, of course, this is C^* , because there is the, sorry, this is C , I am slightly wrong here, divided by 10, which is the value of S by Q . Now, if this is substituted into the expression of the q So substituting into the isotherm expression we can get C^* as 0.01057, 10 multiplied with this value to the power sorry. So, using these values and substituting it into the differential equation you can get the differential equation taking the form something like this 2.5×10^{-3} multiplied with c minus 0.01 minus c divided by 0.1057 to the power 4.35. Now of course, to solve this you need the initial condition at t is equal to 0, C was given as 0.00057 kilo mole per meter cube. Now, please note that this is a non-linear differential equation which cannot be solved in this case analytically. So, you can use you know any of these Runge-Kutta 45 method or Euler's method to solve this initial value problem. You can use a small numerical technique and from this numerical you know calculations you can see that what is the time that is needed, time that is needed. Sorry, I wrote this value as wrong. This is 0.01. So, initial value is 0.01. Sorry, pardon my mistake. Initial value is 0.01. So, from this Euler method, you have to find the t at which C approaches to this reduced value of 0.0057 kilo mole per meter cube. And if you use this RK45 Euler method, you will see that this time comes close to around 1140 seconds. So, this is the part of the batch adsorption. Now, let us look into the continuous adsorption problem for this same system. So, in the continuous mode it is asked that determine the residence time needed in seconds for this operation. So, we can use the you know sorry we can use the residence time formula directly in the continuous mode as something like this.



$$-\frac{dc}{dt} = 2.5 \times 10^{-3} \left[c - \left(\frac{0.01 - c}{0.1057} \right)^{4.35} \right]$$

@ $t = 0$, $c = 0.01 \text{ kmol/m}^3$

Use RK45 or Euler method

find t at which $c \rightarrow 0.00057 \text{ kmol/m}^3$
 ↗ 1140 seconds

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Of course, the C^* has to be obtained at the, so where C^* is to be obtained from the relation that q is equal to q_{out} and you know that is something we have already worked out in this case so this is how the c star expression in this case of the non-linear you know isotherm model would actually look like so we will substitute that expression of C^* here in this case so then the final expression of the residence time takes this form so the numerator is 0.01 that is the inlet An outlet is the reduced concentration 0.00057 that is what we target for divided by K_c into 'a' is 2.5 into 10 to the power minus 3 and C_{out} value is 0.00057 and the C^* value is given from this expression that is 0.01 minus 0.00057, divided by 0.1057 that is 10 multiplied with 0.01057 to the power 4.35. So, if you work out the numbers, this will give you a value of 6950 second.

Continuous mode:

determine the residence time needed (in seconds)

$$t_{res} = \frac{C_F - C_{out}}{k_c a (C_{out} - C^*)}$$

where C^* is to be obtained from $q = q_{out}$



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Batch mode: Using 10 g/L of AC, what is the time needed to reduce the conc. to the desired value

Ext. mass transfer coefficient (k_c) $\equiv 5 \times 10^{-5}$ m/s
Sp. surf. area (a) $\equiv 5$ m²/kg

$$S/Q = 10 \text{ g/L} = 10 \text{ kg/m}^3$$

$$k_c a = 5 \times 10^{-5} \times 5 \times 10 \approx 2.5 \times 10^{-3} \text{ s}^{-1}$$

$$C_F = 0.01 \frac{\text{mol}}{\text{L}} \equiv 0.01 \text{ kmol/m}^3$$

$$q = \frac{C_F - C}{S/Q} = \frac{0.01 - C}{10}$$

Substituting into the isotherm expression,

$$C^* = \left(\frac{0.01 - C}{10 \times 0.01057} \right)^{4.35}$$



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So, it must be noted that this is appreciably. So, this t residence time is much larger than the t of the batch time to reduce I mean where in the batch case this is the time needed to reduce the concentration from 0.01 to 0.00057. And in the case of equilibrium in the case of continuous operation to achieve equilibrium the residence time has to be more you know in this case and it is found that for this operation the as residence time is almost you know six times six to almost six and half times larger than the residence time than the operational time in the case of the batch so this is this is very important to note that the residence time in continuous mode is generally larger than the batch mode so this is the

problem related to the batch value I can also you can also work out that at this value of the concentration sorry at this value of the time that is 6950 what is the batch level concentration so at t is equal to. So, this for the batch operation for batch operation you can do a comparative study and you can see that at t is equal to this t residence time that is if we equate the batch time and the residence time.


Continuous mode:
determine the residence time needed (in seconds)


$$t_{res} = \frac{C_F - C_{out}}{k_c a (C_{out} - C^*)}$$

where C^* is to be obtained from $q = q_{out}$

$$t_{res} = \frac{0.01 - 0.00057}{2.5 \times 10^{-3} \left[0.00057 - \left(\frac{0.01 - 0.00057}{0.1057} \right)^{4.35} \right]} = 6950 \text{ s}$$

$t_{res} > t_{batch}$




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The concentration or the outlet concentration in the batch mode at this case will be roughly equal to 0.000543. So, this is like if you are comparing the same time where the batch time is equal to the residence time of a continuous system, the concentration in the batch would reduce further than the desired value or the target value. So, I hope all of you have followed these two problems and the case of slurry transport in the case of batch and continuous mode. So, there is also something known as a semi continuous mode of the operation.

Continuous mode:

determine the residence time needed (in seconds)

$$t_{res} = \frac{C_F - C_{out}}{k_c a (C_{out} - C^*)}$$

where C^* is to be obtained from $q = q_{out}$

$$t_{res} = \frac{0.01 - 0.00057}{2.5 \times 10^{-3} \left[0.00057 - \left(\frac{0.01 - 0.00057}{0.1057} \right)^{4.35} \right]} = 6950 \text{ s}$$

for batch $t_{res} > t_{batch}$

@ $t = t_{res} (6950 \text{ s})$ $c(t)|_{batch} \sim 0.000543$



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In the semi continuous mode the adsorbent is essentially fixed within the vessel, whereas the liquid is flowing at a constant rate. So, there is batch process for the adsorbent and the adsorbent is not replaced or it is not in and out of the adsorbent, but the liquid is actually flowing continuously. So, thank you and see you everyone in the next week.