

Investigating the Performance of Amine-Grafted Silica-Base Adsorbents in CO₂ Removal from a Natural Gas Stream Using a Diffusion Based Mathematical Model

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Abstract: In this study a diffusion based mathematical model was developed to compare the performance of amine-grafted adsorbents with that of 13X zeolite in a fixed-bed adsorption tower which is used to capture CO₂ from both humid and dry nitrogen stream under industrial conditions. The results show that the performance of amine-grafted adsorbent and 13X zeolite is almost the same in the dry conditions. However, amine grafted adsorbents show better outcome when the gas stream is humid. Using amine-grafted adsorbents can reduce the expenses as a result of eliminating the pre-drying unit. Also the results of this simulation indicate that the economical breakthrough time is less than 30 minutes. This breakthrough time indicates that traditional TSA (Thermal Swing Adsorption) processes are uneconomical for regeneration of the adsorbents. Thus, a modified version of TSA process with lower regeneration time, i.e. RTSA (Rapid Thermal Swing Adsorption), must be employed for this case.

Keywords: Amine Grafted Adsorbent, Mathematical Modeling, TSA, RTSA

1. Introduction

Adsorption is one of the processes which have been attracted a lot of attentions in gas processing industries. The first application of the adsorption process dates back to 1940 (Khale, 1942); however, it had not hold such appeal until A and X type zeolites were synthesized in 1950 (Ruthven, 1984). Although these types of zeolite have been commercialized to be applied in natural gas dehydration and olefin/paraffin separation units, their application in natural gas sweetening was not successful because of simultaneous presence of CO₂ and H₂S in natural gas streams. The cationic sites of these zeolites act as a catalyst

and convert H₂S and CO₂ into H₂O and COS (Maddox and Sheerar, 1982). Another obstacle for the application of these zeolites in acid gas removal is that the presence of even small amount of water in gas stream prevents the adsorption of any other components as a result of strong tendency of water molecules to adsorb on these types of adsorbent (Ruthven, 1984).

In 1992, by developing mesoporous structures, a new horizon was opened up in the field of adsorption and catalytic reaction (Kresge et al., 1992). Compared with other kinds of zeolite, the most significant characteristic of mesoporous structures is their higher pore size.

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Table 1. Summary of support materials, amine groups of well-known adsorbents, and CO₂ adsorption capacity in dry and humid conditions

Support material	Amine group	CO ₂ capacity for dry streams (mmol/gr)	CO ₂ capacity for wet streams (mmol/gr)	References
Silica gel	3-Aminopropyl groups	0.41	0.89	(Leal et al., 1995)
MCM-41	Diethanolamine (DEA)	2.36	Insensitive to moisture	(Franchi et al., 2005)
MCM-41	3-[2-(2-Aminoethylamino)ethylamino]propyl trimethoxysilane (TRI)	1.41	1.52	(Harlick and Sayari, 2006b)
MCM-41	3-[2-(2-Aminoethylamino)ethylamino]propyl trimethoxysilane (TRI)	2.65	2.94	(Harlick and Sayari, 2006a)
SBA-12	3-Aminopropyl	1.04	-	(Zelenak et al., 2008)
	3-(Methylamino)propyl	0.98		
	3-(Phenylamino)propyl (PAP)	0.68		
MCM-41	3-[2-(2-Aminoethylamino)ethylamino]propyl trimethoxysilane (TRI)	2.05	2.25	(Belmabkhout and Sayari, 2009)
MCM-41	Mono aminosilane	0.39-2.7	3.06	(Chang et al., 2009)
SBA-15	Di aminosilane			
PE-SBA-15	Tri aminosilane			
SBA-15	Poly(ethyleneimine) (PEI).	2.4	-	(Yan et al., 2011)
Nanocomposite sorbent	Polyethylenimine, PEI, and tetraethylenepentamine, TEPA	-	7.9	(Qi et al., 2011)
MCM-41	3-Aminopropyltriethoxysilane	1.15	-	(Mello et al., 2011)
MCM-48	3-Aminopropyltriethoxysilane	0.52-1.14	-	(Gil et al., 2011)
SBA-15	3-Aminopropyltriethoxysilane	1.18	1.45	(Huang et al., 2013)
SAPO-34	3-Aminopropyltrimethoxysilane	1.25	-	(Kim et al., 2013)
MCM-41	Ethylenediamine	1.25-2.7	-	(Liu et al., 2013)
	Tetraethylenepentamine			
	Polyethylenimines			
Double-walled silica nanotubes	(3-Aminopropyl) trimethoxysilane	0.12-2.23	-	(Ello et al., 2013)
13X	-	2	0.09	(Harlick and Sayari, 2006a)

The largest pore size of industrial adsorbents which is about 1.3 nm belongs to 13X zeolite (Ruthven, 1984). However, by applying the appropriate synthesis procedure, one can synthesize the mesoporous particles with the pore size between 2 to 50 nm (Sayari and Yang, 1999). Implanting appropriate functional group on the pore sides enables us to provide the adsorbents with the desirable adsorptive and catalytic characteristics. In order to make functional groups span throughout the porous particles uniformly, the adsorbent pore size must be adequately large, i.e. more than 2 nm. Many attempts have been made to impregnate the mesoporous adsorbents with amine materials or graft functional groups inside mesoporous structure. These modified structures have been applied to remove acid gases such as CO₂ from a gas stream (Belmabkhout et al., 2009; Huang et al., 2002)

Table 1 summarizes the support materials, amine groups and CO₂ adsorption capacity of such adsorbents. As it is shown in this table, the amine grafted mesoporous structures show acceptable adsorption capacity for CO₂. In contrast to molecular sieves such as 13X and 5A zeolite, the presence of water vapor enhances CO₂ adsorption capacity of amine grafted adsorbents (Belmabkhout and Sayari, 2009).

Although it has been shown that amine-grafted mesoporous adsorbents outperform 13X zeolite in CO₂ adsorption, their performance for industrial applications has not been examined yet. Adsorption processes are arranged based on different strategies for regeneration of adsorbent including PSA¹, TSA², VSA³, VPSA⁴, RPSA⁵ and RTSA⁶. The criterion that can be used to select the optimum strategy depends on breakthrough time of the adsorption process and equilibrium isotherm. In this regard, mathematical models are powerful and inexpensive approach that can be used to calculate breakthrough times. In this study the performance of an amine-grafted adsorbent in CO₂ removal for a natural gas stream is investigated based on the results of a mathematical model. Also, the optimum strategy for regeneration process is investigated. By using the developed model, the performance of the amine-grafted adsorbent is compared with that of the 13X zeolite.

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- 1 - Pressure Swing Adsorption
 - 2 - Temperature Swing Adsorption
 - 3 - Vacuum Swing Adsorption
 - 4 - Vacuum Pressure Swing Adsorption
 - 5 - Rapid Pressure Swing Adsorption
 - 6 - Rapid Temperature Swing Adsorption

2. Mathematical Model

2.1. Assumptions

The porous volume of the amine-grafted adsorbent pellet can be classified into two parts of mesopore and macropore based on their pore sizes. The large pore network (macropore) inside the adsorbent pellets provides a means to transport adsorbate molecules to the interior where they are adsorbed into the tiny particles of amine-grafted adsorbent crystals (mesopores). Thus, when a pellet is exposed to a moving fluid, the mass transfer from bulk of fluid into the volume mesopores occurs through the bulk of fluid to the surface of pellet, the macropore volume and the macropore volume to the mesopore volumes. These mass transfer rates were calculated based on the fact that the controlling step of mass transfer is the mass transfer through mesopores. Based on this fact the following assumptions were made:

1. The adsorbate concentration at the edge of pellet is equal to that at the bulk of fluid.
2. Molecular diffusion model is valid in macropore volume.
3. The local adsorbate concentration at the macropore is in equilibrium with the corresponding adsorbate concentration in the mesopore.

The other assumptions made to develop the model were as follows:

1. Radial temperature, concentration, and velocity gradients within the bed are negligible.
2. There is no pressure distribution along the bed.
3. The gas stream is assumed to be a binary mixture.
4. CH₄ has negligible adsorption capacity compared with CO₂.
5. Gas phase behave as an ideal gas mixture.

2.2. Governing Equations

With the above mentioned considerations, the concentration change of the adsorbing component through the bed length can be described by the following equation.

Writing CO₂-component material balance over the gaseous phase of a differential control volume of the adsorption fixed bed yields:

$$\frac{\partial}{\partial z} \left(D_{ax} \frac{\partial C_b}{\partial z} \right) - \frac{\partial (UC_b)}{\partial z} - \frac{1 - \varepsilon_b}{\varepsilon_b} \frac{\partial q_p}{\partial t} = \frac{\partial C_b}{\partial t} \quad (1)$$

In this equation q_p is the total amount of CO₂ accumulated inside the pellet per unit volume of the pellet as a result of adsorption. By integrating the mass adsorbed into the mesopore volume over the spherical pellets and dividing the result by the volume of that pellet the following equation is obtained:

$$\frac{\partial q_p}{\partial t} = \frac{3}{R_p^3} \int_0^{R_p} r^2 \frac{\partial q_c}{\partial t} dr \quad (2)$$

Where q_c is the mass of CO₂ adsorbed into mesopore volume at r position per unit volume of the pellet. The following equation expresses the CO₂ mass balance in gas phase over a differential spherical shell inside adsorbent particle:

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(D_{eff} r^2 \frac{\partial C_p}{\partial r} \right) - \frac{1 - \varepsilon_p}{\varepsilon_p} \frac{\partial q_c}{\partial t} = \frac{\partial C_p}{\partial t} \quad (3)$$

This equation is used to determine the CO₂ concentration distribution inside the pellet.. q_c which varies radially inside the particles was obtained by using equilibrium isotherm, as follows:

$$q_c = \left(q_{s1} \frac{b_1 p}{1 + b_1 p} + q_{s2} \frac{b_2 p}{1 + b_2 p} \right) \rho_s \quad (4)$$

The constants $b_{1,2}$ and $q_{s1,2}$ depend on the temperature in the following ways:

$$b_{1,2} = b_{01,2} \exp \left(\frac{E_{1,2}}{T} \right) \quad (5)$$

$$q_{s1,2} = \frac{A_{1,2}}{T} + A_{1,2} \quad (6)$$

Thermal regeneration of the adsorbents is done via passing a hot gas through the bed. The regeneration consists of heating step and desorption step. The temperature of hot gas directly affect the regeneration time. To calculate the time needed for both steps it is necessary to develop the conservation equation of thermal energy in the bed. Because the heat transfer is far faster than mass transfer inside the pellet, the local temperature equilibrium can be assumed. The following equation was obtained by writing the differential energy balance in the bed:

$$\frac{\partial}{\partial z} \left(k_{ax} \frac{\partial T_b}{\partial z} \right) - \frac{\partial (\rho_g UC_{pg} T_b)}{\partial z} - \Delta H^{ads} \frac{\partial q_p}{\partial t} = \frac{\partial}{\partial t} (\rho_g C_{pg} T_b + \rho_s C_{ps} T_b) \quad (7)$$

2.3. Initial and Boundary Conditions

The initial and boundary conditions for all governing equations are summarized in Table 2.

Four other parameters which are required in the model are calculated using the following equations:

$$D_{ax} = \gamma_1 D_m + \gamma_2 d_p U \quad (\text{Ruthven, 1984}) \quad (8)$$

$$D^{eff} = \frac{1}{\tau} \left(\frac{1}{D_m} + \frac{1}{D_k} \right)^{-1} \quad (\text{Poling et al., 2000}) \quad (9)$$

$$\frac{k_{ax}}{k_f} = \frac{k_e^0}{k_f} + 0.5 \text{Re}_p \text{Pr} \quad (\text{Wen and Ding, 2006}) \quad (10)$$

$$Nu = 2 + 1.1 \text{Pr}^{\frac{1}{3}} \text{Re}^{0.6} \quad (\text{Ruthven, 1982}) \quad (11)$$

2.4. Equilibrium Parameters

The parameter of CO₂ equilibrium isotherm on amine grafted adsorbent and 13X zeolite are listed in Table 3. These parameters were obtained by regression the experimental data of pure CO₂ on these two adsorbents.

3. Result and discussion

3.1. Model Validation

In order to verify the proposed model the experimental data of Mohamadinejad et al. (Mohamadinejad et al., 2000) were used. In this experiment the data of single-component breakthrough curve (CO₂) at atmospheric pressure and ambient temperature on 5A zeolite were collected. The model results and experimental data are compared in Figure 1. The comparison shows good agreement between the experimental data and calculated results and indicates the capability of diffusion model in predicting mass transfer between phases.

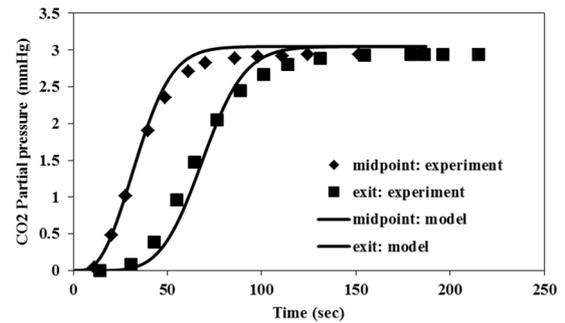


Figure 1. Comparison between the results of developed model and experimental data of Mohamadinejad et al. (Mohamadinejad et al., 2000)

Table 2. Initial and boundary equations for governing equations

Governing equation	Initial and boundary condition
Mass conservation of CO ₂ in bed {gas phase, equation(1)}	$C_b _{z,t=0} = C_b^0, \quad \frac{\partial C_b}{\partial z} \Big _{z=L,t} = 0, \quad C_b _{z=0,t} = C_{in}$
Mass conservation of CO ₂ in pellet {gas phase, equation(3)}	$C_p _{r,t=0} = C_b^0, \quad \frac{\partial C_p}{\partial r} \Big _{r=0,t} = 0, \quad C_p _{R_p,t} = C_b$
Energy conservation {equation(7)}	$T_b _{z,t=0} = T_b^0, \quad \frac{\partial T_b}{\partial z} \Big _{z=L,t} = 0, \quad T_b _{z=0,t} = T_{in}$

Table 3. The adsorption equilibrium parameter of CO₂ on amine grafted and 13X adsorbents fitted on DSL model

Adsorbent	A_{11} (mmol K/gr)	A_{12} (mmol/gr)	A_{21} (mmol K/gr)	A_{22} (mmol/gr)	References
Amine grafted adsorbent	1222.6000	-2.5539	10.7510	1.1448	(Belmabkhout and Sayari, 2009)
13X	630.2800	-0.0981	1282.4000	-3.2647	(Lee et al., 2002)
	b_{01} (1/bar)	E_1 (K)	b_{02} (1/bar)	E_2 (K)	
Amine grafted adsorbent	0.0037	4039.1000	0.1156	1304.4000	
13X	0.0491	1626.4000	0.0432	3016.0000	

3.2. The Investigation of the Amine-Grafted Adsorbent Performance in Industrial Scale

Natural gas fed to a refinery usually contains up to 3 percent CO₂. Thus, the maximum value of 3 percent was considered for CO₂ content of natural gas in these calculations. The computations were stopped at breakthrough time when the concentration of CO₂ in the gas stream leaving the bed reached 3 ppm. The characteristics of the adsorption bed, adsorbent and gas flow are shown in Table 4.

Table 4. The characteristics of adsorption bed, sorbent pellet and gas flow

Inlet gas composition	
Component	mole fraction
CO ₂	0.03
CH ₄	0.97
Initial values of gas composition in the bed	
Component	Mole fraction
CO ₂	0
CH ₄	1
Inlet gas characteristics	
Molar gas flow rate, kmol/h	23929
Inlet gas Temperature, K	295.5
Inlet gas Pressure, bar	64
Bed characteristics	
Bed diameter, m	3.5
Bed length, m	5.5
Bed porosity	0.34
Pellet characteristics	
Pellet porosity	0.36
Pellet-Solid density, kg/m ³	1500
Pellet Diameter, m	0.002
Mean macro-pore diameter, m	1.7 e-7

Figure 2 shows the CO₂ concentration in the gas phase versus time at midpoint of the bed. The variations of CO₂ concentration in the pellets along the bed is shown in Figure 3. As it is obvious in these figures, due to having higher capacity, the 13X zeolite shows a better performance than the amine-grafted adsorbent in dry condition. As it can be seen in table 1, the ability of zeolite 13X to capture CO₂ diminishes when the gas mixture is wet. However, for amine-grafted silica-base adsorbents the presence of water vapor has beneficial effect on CO₂ adsorption capacity. It is the main advantage of amine-grafted silica-base adsorbents over zeolite types.

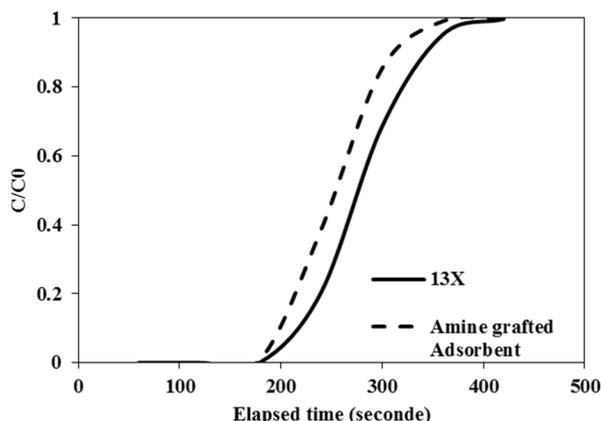


Figure 2. Relative concentration distribution of CO₂ in gas phase versus time at midpoint of the bed

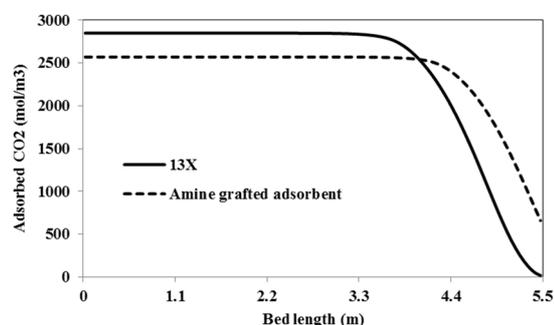


Figure 3. Concentration distribution of CO₂ along the bed at breakthrough time for dry gas

The values of the main parameters which are required for adsorption bed design are shown in Table 5. These parameters were obtained through solving the governing equations of the mathematical model. As shown in this table the values of these parameters are very close together for both types of adsorbent in dry condition. These values were attained for a 5.5-m fixed bed. As it is shown in this table, the unused length of the bed at breakthrough time is about 1 meter which is acceptable for an industrial-scale bed with the length of 5.5 meter (Ruthven, 1984). However, having the breakthrough time of 7 minutes indicates that TSA strategy is not economical to be used as the regeneration method.

Table 5. Calculated breakthrough time, unused length and length of mass transfer zone

	Amine grafted adsorbent	13X zeolite
Breakthrough time (min)	7	7
Length of mass transfer zone (m)	2.1	2.15
Unused length (m)	1.05	1.075

In PSA and VSA strategies, pressure reduction is utilized as a means of regenerating adsorbents. However, due to strong attachment of CO_2 molecules to amine groups, amine-grafted adsorbents need a minimum temperature of 70°C to be regenerated using pressure decrease (Huang et al., 2002; Serna-Guerrero et al., 2010). Figure 4 shows the variation of regeneration time versus temperature for these two adsorbents. These data were calculated by solving equations 1 through 8 using appropriate boundary conditions. This figure shows that the time required for regenerating the adsorbent bed at 70°C is 700 min which is too much more than 7-minute time of adsorption process. Consequently, in order to employ this type of adsorbent in an industrial adsorption fixed bed, one needs to use at least 101 parallel beds simultaneously. As a result, 100 beds are work in regenerating mode while merely 1 bed is at adsorption mode. It makes this process so uneconomical that could not be considered as an industrial operation.

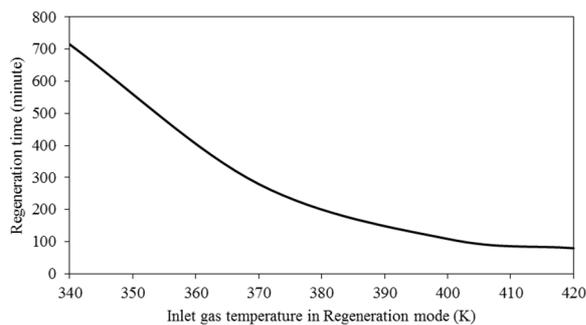


Figure 4. The effect of regeneration temperature on regeneration time

In order to use TSA strategy as the regeneration method, the temperature should increase to the temperature higher than 70°C . However, when the temperatures rises higher

than 150°C , the amine groups are detached from the surface of silicate and it degrades the structure of the adsorbent. As it is apparent from figure 4, even at temperature of 150°C the regeneration time is undesirably high compared to the adsorption time. Thus, a thermal regeneration method in which the regeneration time is less than 7 minutes is required for industrial conditions. A new TSA method called Rapid Thermal Swing Adsorption (RTSA) have recently developed to overcome this problem (Lively et al., 2012; Lively et al., 2011; Rezaei et al., 2013; Yu et al., 2012). The main benefit of RTSA is low regeneration time. By doping the amine-grafted silica in hollow fibers, Lively et al. has developed a RTSA with approximate cycle time of 300 seconds. A schematic diagram of this process is shown in Figure 5. As it can be seen in this figure, the process is performed in four steps through four pieces of shell-and-tube equipment as adsorption and regeneration beds. In these pieces of equipment the doped hollow fibers were utilized as tubes. During the adsorption step, CO_2 -containing gas flows into the shell side, while cooling water running through the tubes removes the heat generated by adsorption process. In the next step, the bed is heated using hot water running through the pipes while closing the shell side which creates a high pressure zone because of CO_2 desorption. Then, a N_2 stream sweeps CO_2 desorbed from the bed. In this way, a plug of high purity CO_2 is captured. At final stage, the hollow fibers are cooled to the adsorption temperature using cooling water driving through the tubes (Lively et al., 2012). A full cycle including the four steps is performed in 300 seconds.

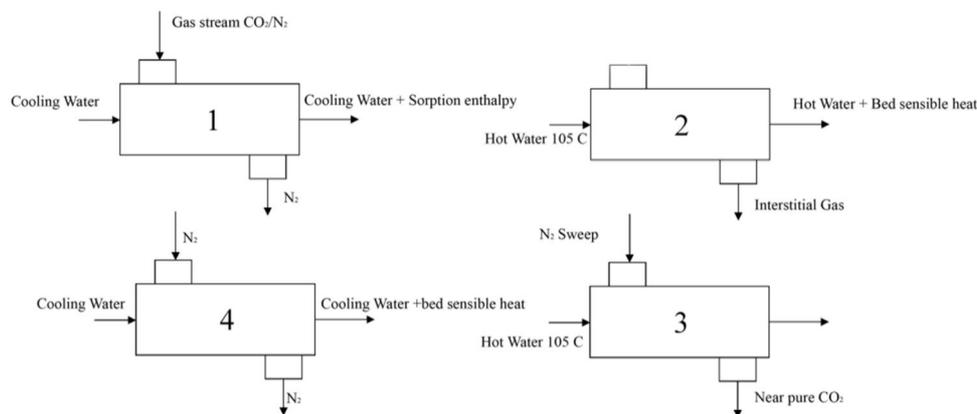


Figure 5. The overview of RTSA adsorption operation using hollow fibers (Lively et al., 2012)

4. Conclusion

In this study a mathematical model was developed to investigate the performance of amine grafted-adsorbents for capturing CO₂ from a gas stream in industrial scale and to compare their performance with 13X zeolite. The results showed that the performance of amine-grafted adsorbents and 13X zeolites are almost the same in dry condition, but the amine-grafted adsorbents demonstrate too much better performance when the gas stream is humid. Another important result is that the conventional TSA process is not an appropriate method for adsorbent regeneration. The predicted breakthrough time of 7 minutes indicates that a quick version of TSA such as RTSA will be a suitable method to regenerate amine-grafted adsorbents which are employed to separate CO₂ from a natural gas stream.

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Nomenclature

b	adsorption affinity parameter (kPa ⁻¹)
C_b	adsorbing component concentration in the bed space (mole/m ³)
C_p	adsorbing component concentration in within the intra-particle space (mole/m ³)
C_{in}	inlet concentration of Adsorbing component in gas phase (mole/m ³)
C_b^0	initial concentration of adsorbing component in the bed space (mole/m ³)
C_{pg}	Gas heat capacity (j/kg K)
C_{ps}	Solid heat capacity (j/kg K)
D_{ax}	axial dispersion (m ² /s)
D^{eff}	effective diffusivity in particle (m ² /s)
D_m	molecular diffusivity (m ² /s)
D_k	knudsen diffusivity (m ² /s)
d_p	particle diameter (m)
K_{ax}	Axial thermal conductivity (W/m K)
P	partial pressure of adsorbing component (kPa)
q_e	equilibrium concentration of adsorbing component in solid phase (mole/m ³)
q_p	average adsorbing component concentration in solid phase (mole/m ³)
q_s	maximum equilibrium capacity of adsorbing component in solid phase (mole/m ³)

r	particle radius (m)
T_b	Temperature (K)
t	time (s)
U	interstitial velocity (m/s)
z	bed length (m)

Greek letters

ϵ_b	bed porosity
ϵ_p	pellet porosity
ΔH^{ads}	Adsorption enthalpy (j/mol)
ρ_g	Gas density (kg/m ³)
ρ_s	particle skeleton density (kg/m ³)
Y	axial dispersion correlation coefficient
τ	tortuosity factor

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