Modeling and Simulation of Non-isothermal Adsorption Separation Systems

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Extended Abstract

Adsorption phenomena are operative in most natural physical, biological, and chemical systems, and adsorption operations employing solids such as activated carbon and synthetic resins are used widely in industrial applications and for purification of wastewaters. The process of adsorption involves the preferential portioning of substances from gaseous or liquid phase onto the surface of the solid substrate. The adsorption isotherms play a crucial functional role in predictive modeling procedures for analysis and design of adsorption systems. For the transport of adsorbate from the bulk of the fluid to the interior of a pellet before adsorption takes place, the following mass transfer steps may be considered: transport of adsorbate species within the homogeneous phase, transport to the adsorbent pellet, and transport inside the pellet (intra-particle mass transfer).

In order to assess the importance of these underlying phenomena as well as to acquire predictive capabilities of the adsorption process, modeling and simulation of adsorption phenomena can be done under certain set of simplifying assumptions. Predictions of the simulations will help understand the adsorber dynamics. Most of the work in literature has either been done to obtain analytical solution for the breakthrough curves for linear isothermal plug and/or dispersed plug flow by Anzeliu(1926), Walter(1945), Furnas(1930), Nusselt (1930), Klinkenberg(1954), Lapidus and Amundson(1952), Levenspiel and Bischoff(1963), Rosen(1952), Ramuson and Neretnicks(1983), Kwazoe and Takeuchi(1974). Bohart and Adams(1920), Cooper(1965), Liberman(1965,1970), Weber and Chakravorti(1974) have found analytical solutions for breakthrough curves for systems with irreversible isotherms. Carter and Husian(1974) , Zwiebel(1975) , Liapis and Rippin (1978), Balzi, Liapis and Santacesaria(1978), have worked on Numerical solutions for isothermal multicomponent systems using Crank Nicolson and Forward Finite difference techniques. Carter(1966,1968,1978) , Barrett, Meyerand Weber (1967,1969), Cooney(1974), Marcussen(1979), Ruthven (1983) have done numerical solutions for adiabatic ,adsorption columns with finite mass transfer resistance. Industrial adsorption columns are generally operated under non-isothermal conditions. Heat of adsorption evolves in the column and there is always a heat loss occurring in the column through column wall. Performance of the adsorption column for non-isothermal conditions should be tested properly. In fact, a considerable amount of work has been made on the non- isothermal adsorption columns. Most of work has been limited to the constant pattern regime. Wakao and Kaguei (1976,1985,1987,1989) have found analytical solutions for the dispersed plug flow model.

Proposed model equations have been solved numerically. The necessary assumptions were done and mathematical formulation of the mass and heat balance were made. The proposed equations were coupled partial differential equations. The model equations have been solved to obtain the concentration and temperature profiles of adsorbate in bulk fluid and inside the pellet numerically using 'Backward Implicit Scheme'. Finite difference numerical scheme provided the tridiagonal banded matrix(TDM). These m x m matrix has been converted to m*3 matrix. The program in FORTRAN-77 has been made to obtain the value of concentration and temperature profiles at various axial distances in column and inside of the particles located at various axial distances for various times. Also parametric studies have been done to study the sensitivity of the parameters on the dynamics of non-isothermal adsorption system. Adsorption equilibrium constant, heat of adsorption, and overall heat transfer coefficient were found to be the important parameters to which the model predictions are found to be sensitive. Parameters like axial fluid dispersion coefficient, particle to fluid heat transfer coefficient, thermal conductivity of adsorbent particle, effective diffusivity in adsorbent particle are found less important and particle-to-fluid mass transfer coefficient, axial fluid dispersion coefficient were found not to affect the predictions at all. The equations, their parameters and the diagrams showing the results are given in what is hoped to be a comprehensive way to facilitate the comparison of various parameters in an adsorption column. The results obtained using this finite difference scheme has been compared with the analytical solutions available in literature, as well as with the results of the experiments in the literature.

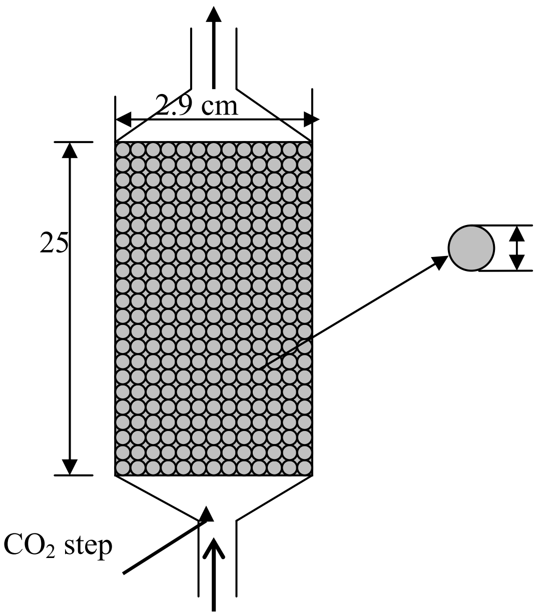
Modeling

Theory-Adsorption/Thermal waves Advancing in the adsorption column with a concentration step input

Packed adsorption column containing spherical activated carbon particles is taken and as step input of CO_2 with inert gas N_2 is given. Fig.1 shows the experimental set up taken for modeling and Table 1 shows the experimental conditions.

The theoretical developments are made with the ***assumptions*** listed below:

1. Intra-particle diffusion rate is expressed in terms of effective diffusivity and the gradient of adsorbate concentration in the intra-particle fluid phase.
2. The effective diffusivity is constant.
3. Concentration and temperature profiles have centre symmetry in adsorbent particle.
4. Fluid is with dispersed-plug flow.
5. Adsorbate concentration and temperature in the bulk fluid is uniform at any cross-section of the bed.
6. Heat loss rate through the column wall may be expressed in terms of the temperature difference between the bulk fluid in the bed and the room temperature outside the column.
7. All the parameters involved in heat and mass transfer processes in the adsorption column are temperature independent



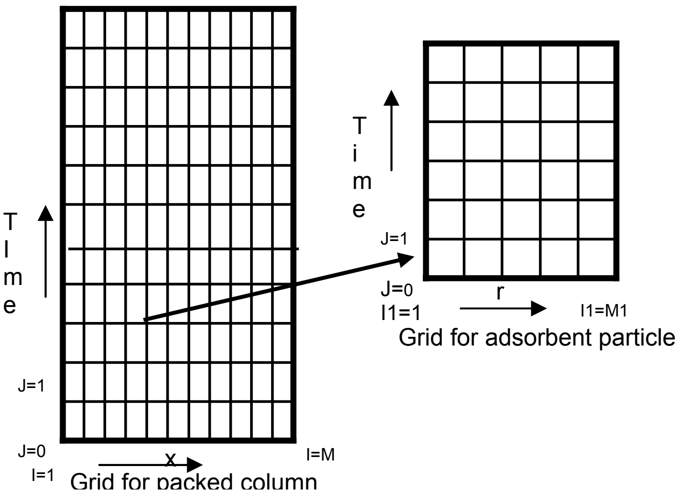


Fig1. Packed Adsorption column

Fig.2. Grid for packed bed and adsorbent particle

Table 1: Experimental conditions (Ref: Wakao, 1985)

COLUMN	Cylinder with ID=2.9 cm ,
ADSORBENT	0.26 cm activated carbon spherical particles, $Cs\rho s = 0.84E6\ Jm^{-3}K^{-1}$, $ks=0.4\ Wm^{-1}K^{-1}$, $\varepsilon_b=0.60$
ADSORPTION BED	Length = 25 cm, $\varepsilon_p=0.38$
CARRIER GAS	Nitrogen, $C_F\rho_F=1.2E3\ Jm^{-3}K^{-1}$, $k_F=0.026\ Wm^{-1}K^{-1}$
ADSORBATE GAS	Carbon dioxide imposed in a carrier gas, in the mole ratio of CO_2 to N_2 = 0.0184 ;$C0=0.75 mol/m^3$
ROOM TEMPERATURE	20^oC
FLOW RATE	Superficial gas velocity based on the empty column= 0.033 ms^{-1}; Re=5.6
ADSORPTION ISOTHERM	Linear; $g(Ci)=K_ACi$

The ***mass balance*** then gives:

- Bulk concentration of fluid at any axial distance x along the column:

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - U\frac{\partial C}{\partial x} - \frac{a}{\varepsilon_b} D_e \left(\frac{\partial Ci}{\partial r}\right)_R$$

- Concentration inside particle at any radial distance r is given by:

$$\varepsilon_p \frac{\partial Ci}{\partial t} = D_e \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial Ci}{\partial r}\right) - \rho_s \frac{\partial c_{ad}}{\partial t}$$

- At r=R, we have

$$D_e\left(\frac{\partial Ci}{\partial r}\right)_R = k_f\left(C - Ci\right)$$

- Adsorption Isotherm is assumed to be linear:

$$c_{ad} = K_A Ci$$

The ***Energy balance*** then gives:

- The temperature at the axial distance x along the column length is given by:

$$\frac{\partial Tf}{\partial t} = \alpha_{ax}\frac{\partial^2 Tf}{\partial x^2} - U\frac{\partial Tf}{\partial x} - \frac{a}{\varepsilon_b C_F \rho_F} k_s \left(\frac{\partial Ts}{\partial r}\right)_R - \frac{2h_0}{R_T \varepsilon_b C_F \rho_F}\left(Tf - To\right)$$

- The temperature inside the particle at a radial distance r from centre is given by:

$$C_s \rho_s \frac{\partial Ts}{\partial t} = k_S \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial Ts}{\partial r}\right) + (-\Delta H)\rho_s \frac{\partial c_{ad}}{\partial t}$$

- At

$$k_s\left(\frac{\partial Ts}{\partial r}\right)_R = h_p\left(Tf - Ts\right)$$

r=R, we have

Initial conditions and Boundary conditions:

At x=0 C=Co ,T=To
and At x=L dC/dx=0
dT/dx=0
At t=0 Ci=0, Tf=To, Ts=To
t=0 and x>0 C=0

This set of equations has been solved through finite difference numerical scheme which provides the coefficient matrix as tridiagonal-banded matrix. Here matrix of order m x m has been transformed into matrix of order m x 3 and is solved using Srivatava's subroutine(1983). The program in FORTRAN-77 computer language has been made to obtain the values of concentration and temperature at various axial and radial distances in column and along the radius of the particles located at various axial distances for various times.

Results and Discussion

Breakthrough curves (fig.3) clearly show the breakpoint at which regeneration or replacement of the adsorbent particles is made necessary. The fluid temperature (fig. 4) at any axial distance first increases till the adsorption can take place and beyond the breakpoint it starts decreasing with time due to transfer of heat to lower temperature region. Parametric studies indicate that adsorption equilibrium constant, heat of adsorption, and overall heat transfer coefficient are important parameters to which the model predictions are found to be sensitive. With the increase in adsorption equilibrium constant the bulk fluid concentration decreases (Fig.5) indicating that more adsorption is taking place on the solid surface and hence the temperature increases (fig.6). With the increase in heat of absorption there is no effect on the bulk fluid concentration (fig.7) but the temperature of the bulk fluid rises(fig.8). With the increase in over all heat transfer coefficient there is no effect on the concentration of the bulk fluid, but the temperature of the bulk fluid decreases, indicating more heat loss to the surroundings.

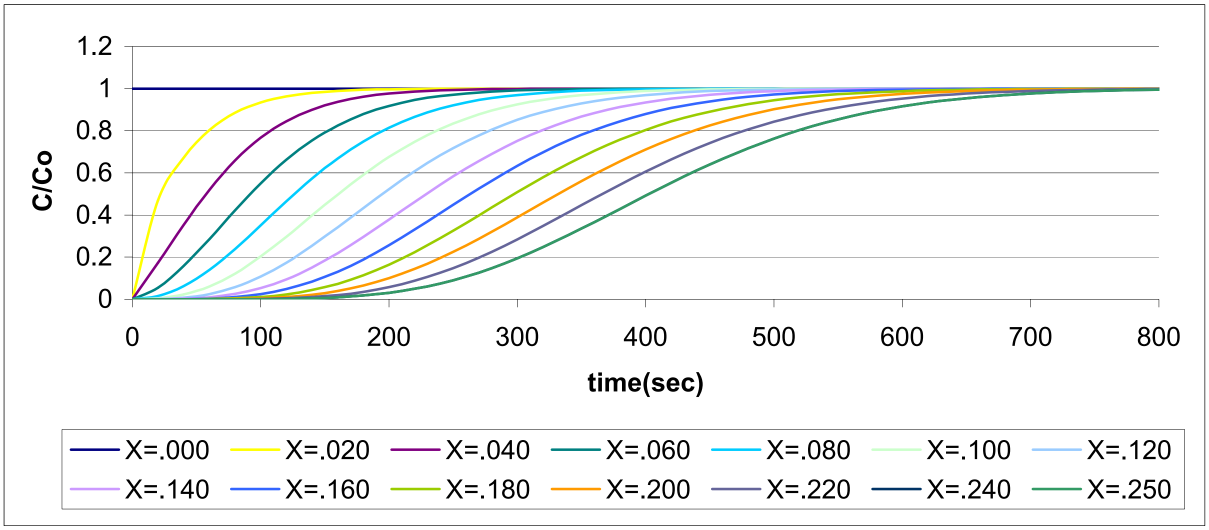


Fig 3: Bulk fluid concentration at various axial distances

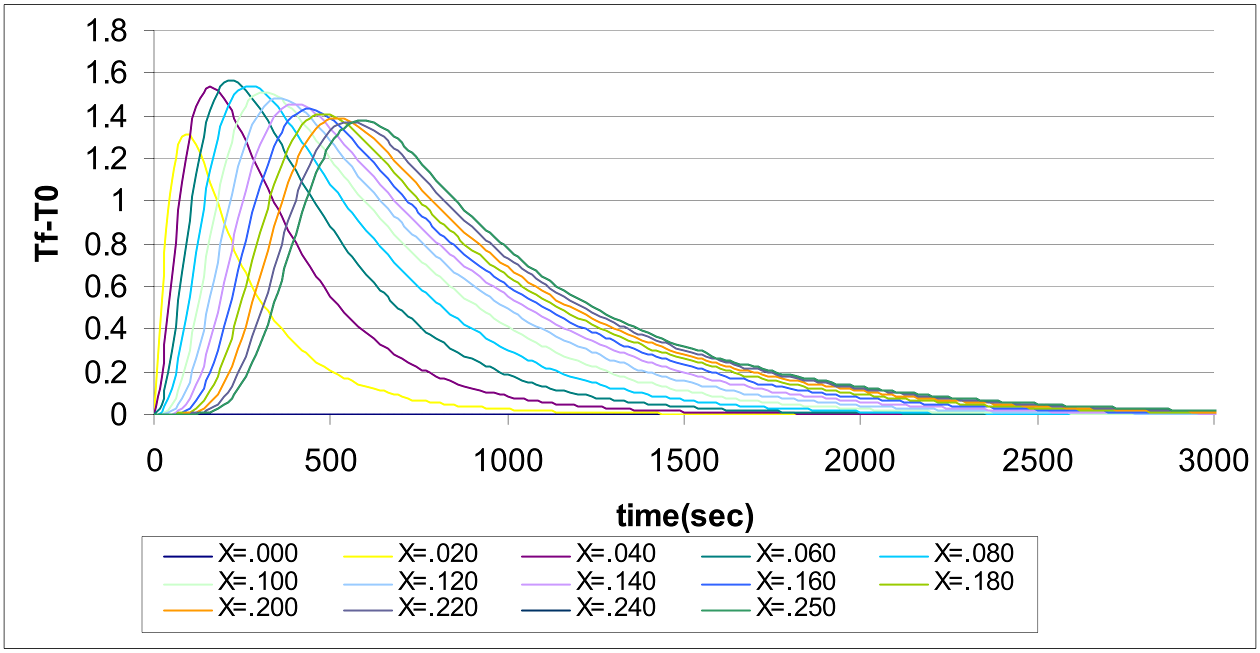


Fig 4: Bulk fluid temperature at various axial distances

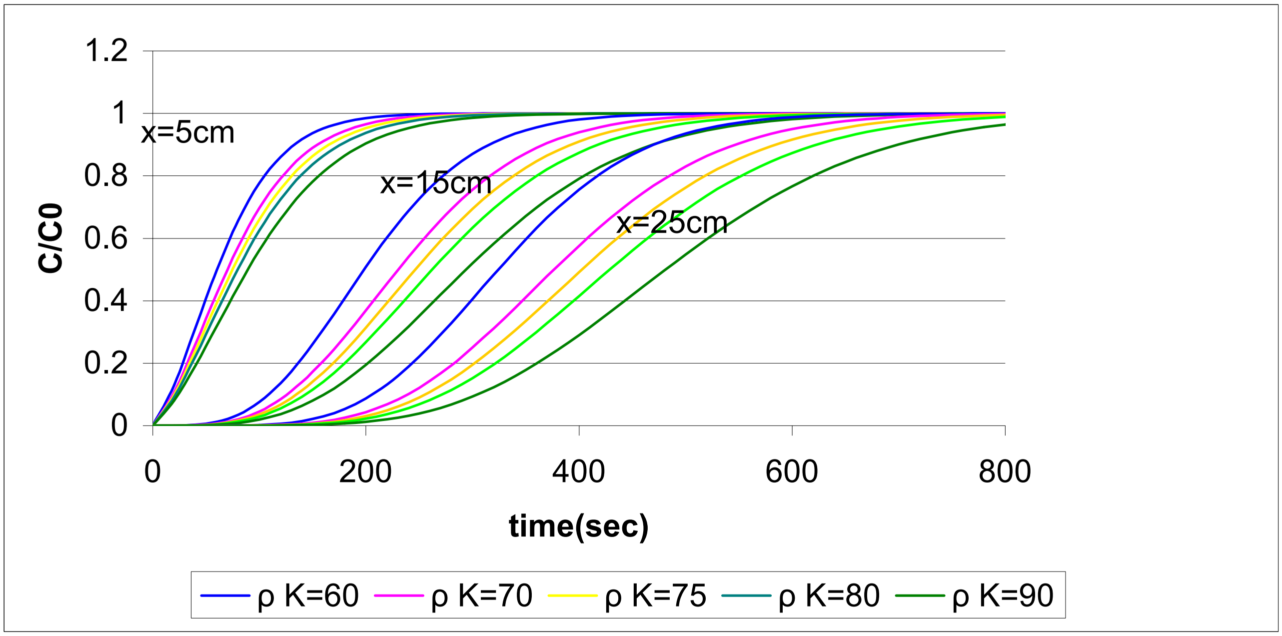


Fig5: Effect of change in Adsorption Equilibrium constant on bulk fluid concentration

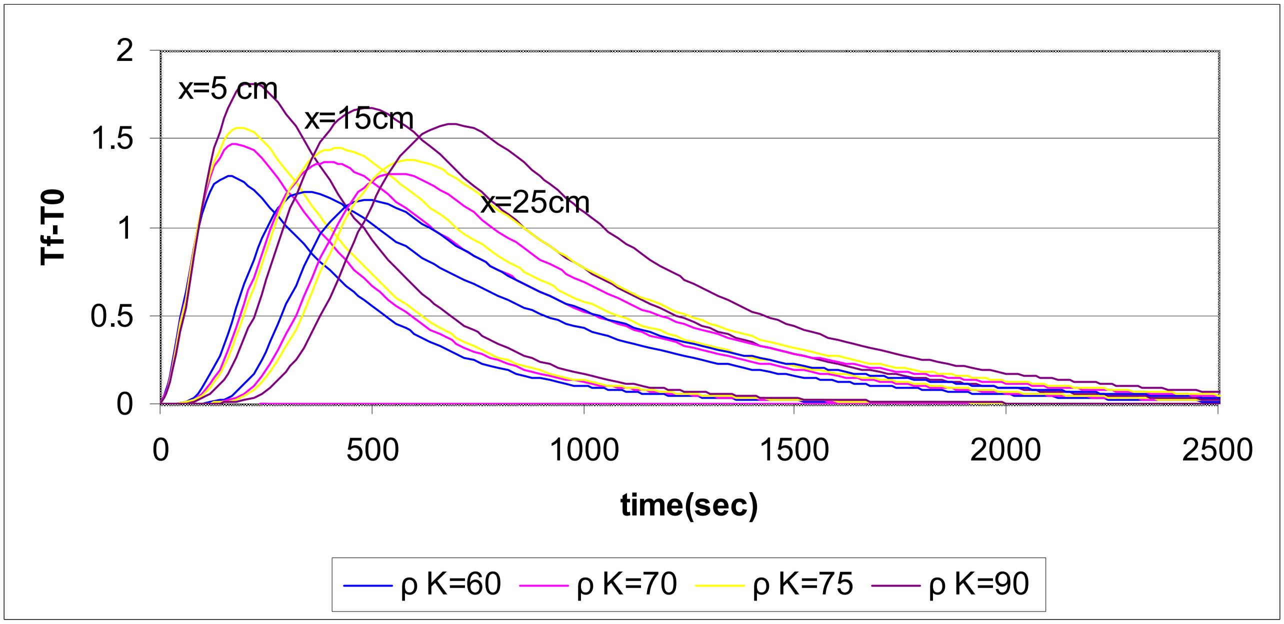


Fig6: Effect of change in Adsorption Equilibrium constant on bulk fluid temperature

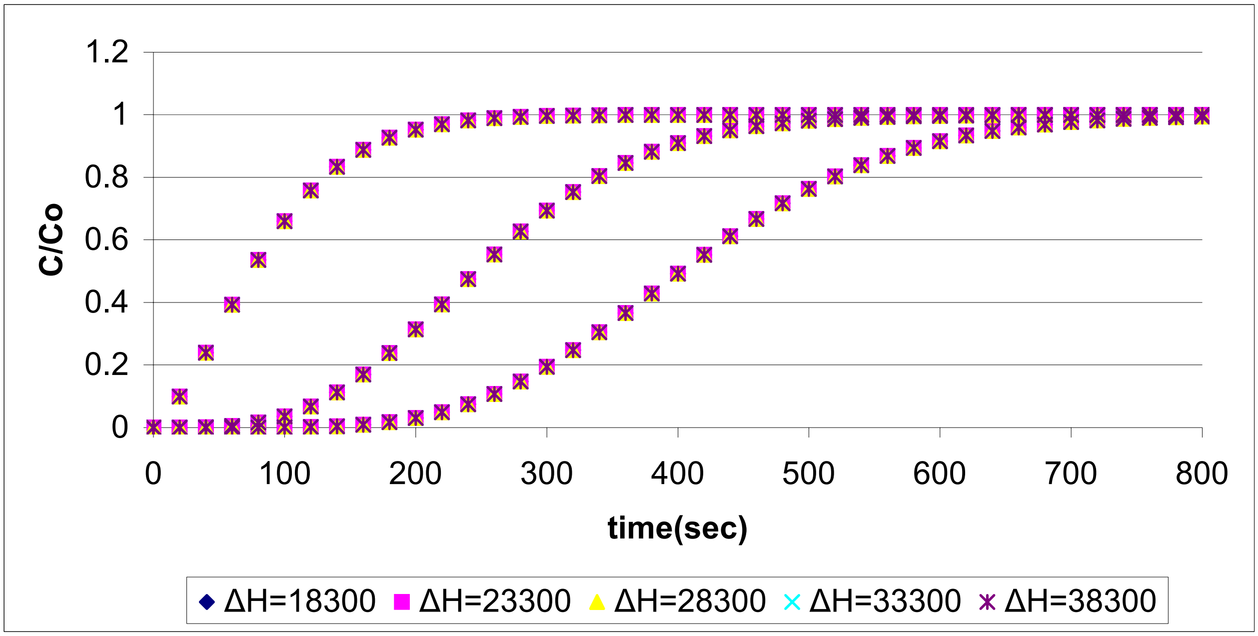


Fig7: Effect change in Heat of Adsorption on bulk fluid concentration

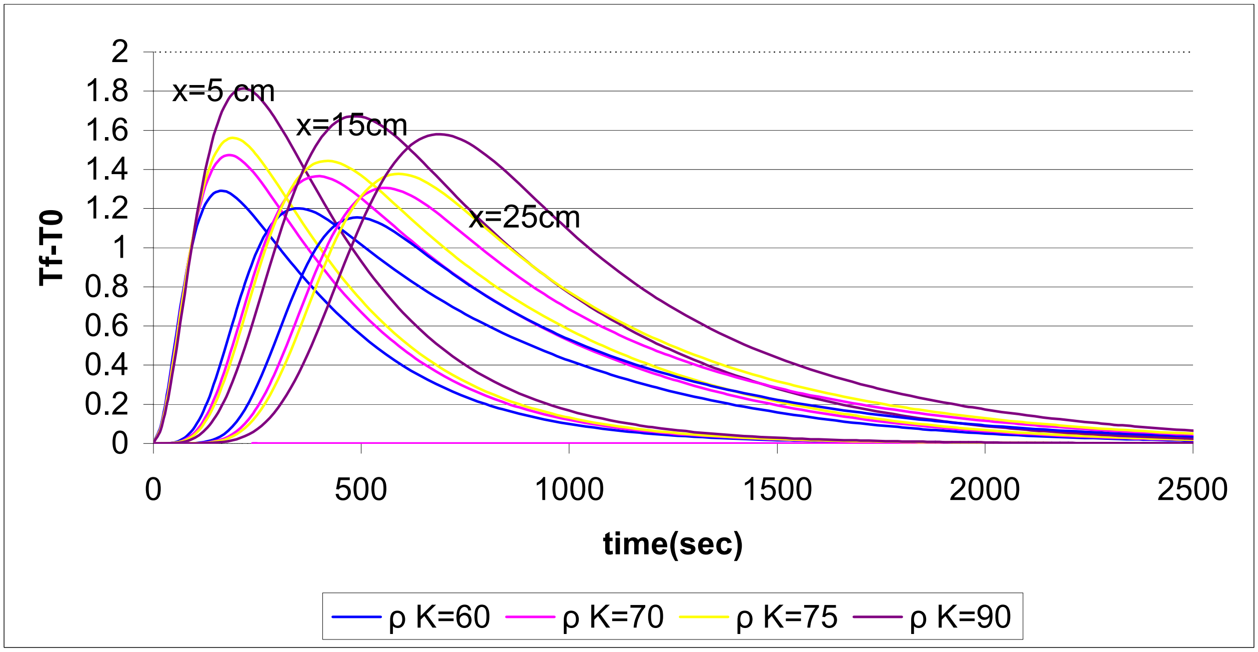


Fig8: Effect of change in Heat of Adsorption on bulk fluid temperature

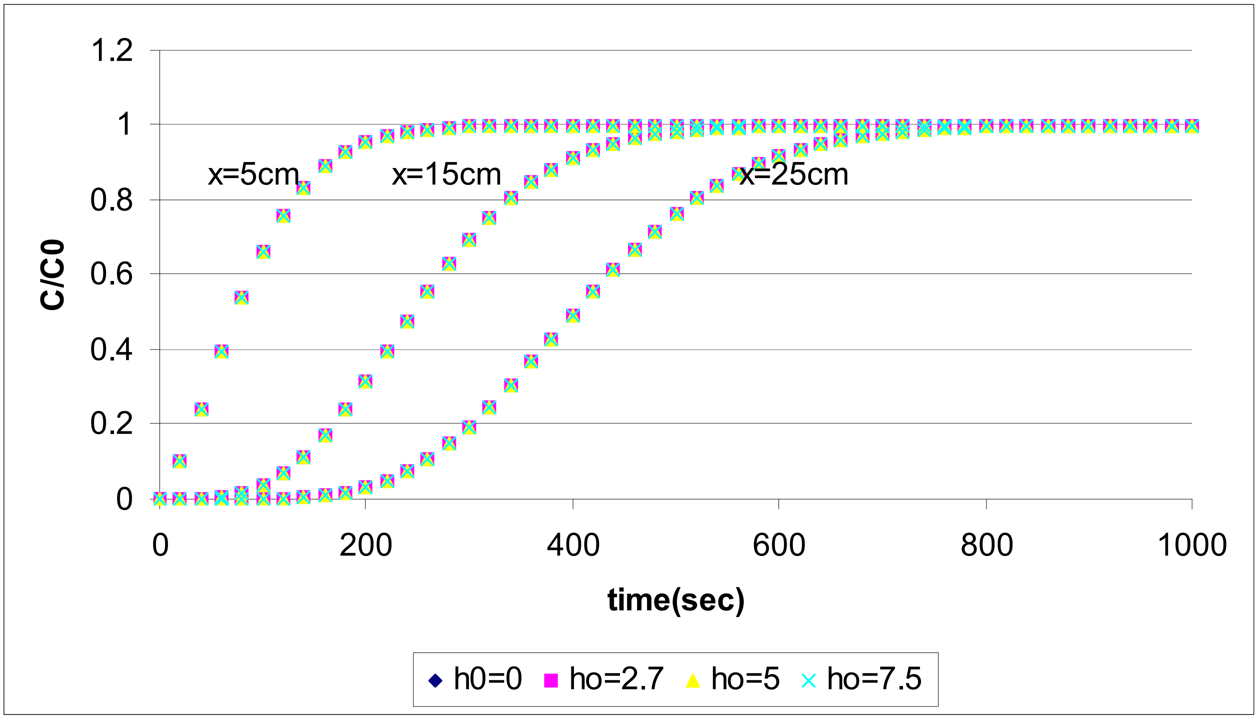


Fig9: Effect change in overall heat transfer coefficient on bulk fluid concentration

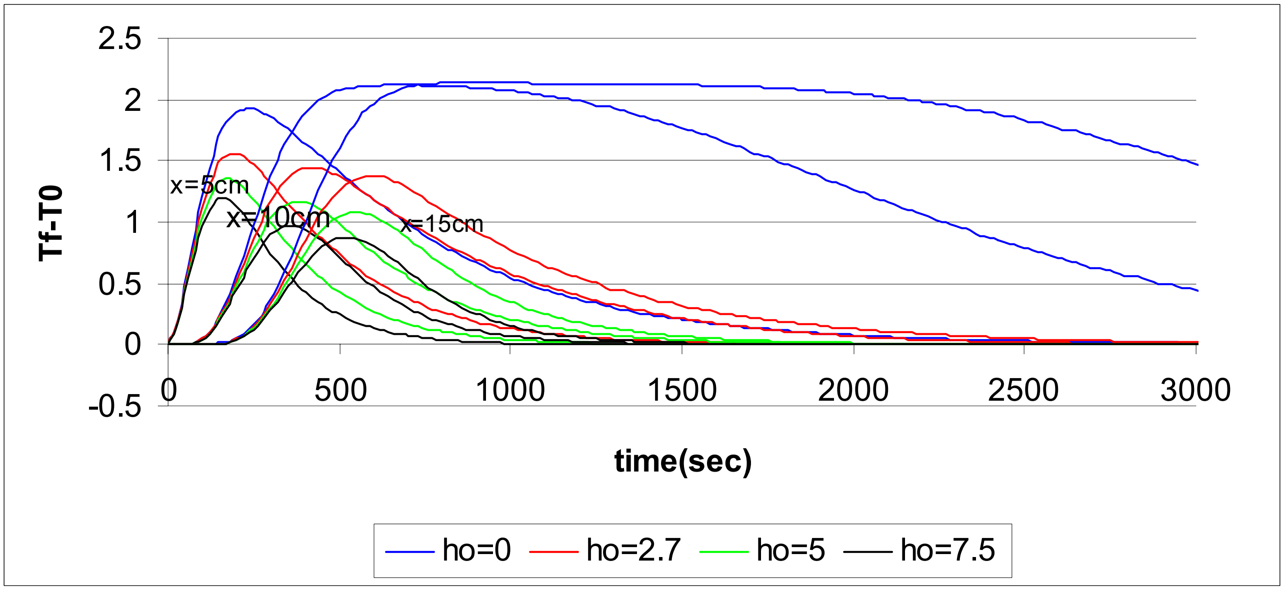


Fig10: Effect of change in overall heat transfer coefficient on bulk fluid temperature

Validation of numerical method

The simulated numerical solution of the model has been compared (fig.11) with the results published in literature(Wakao,1985). Also comparison is made with the analytical solution provided by Wakao(1985).

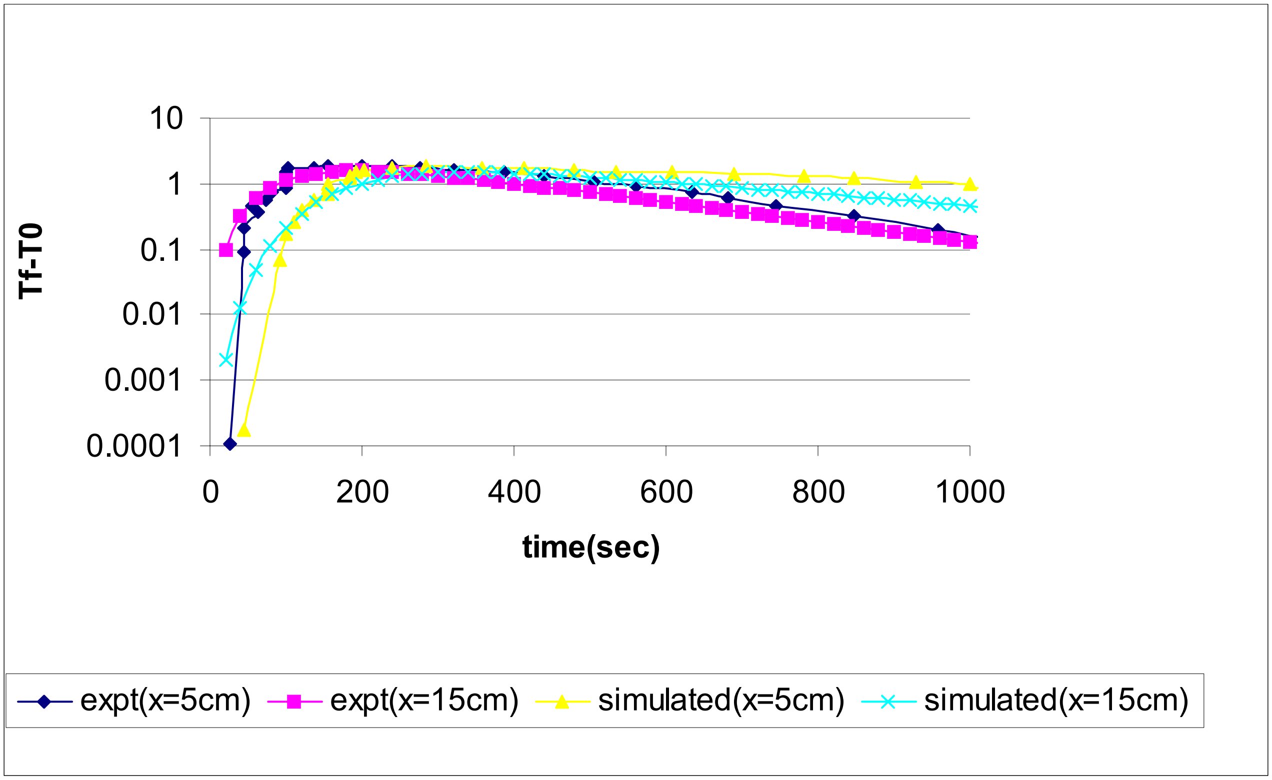


Fig11: Comparison with experimental data[Wakao(1985)]

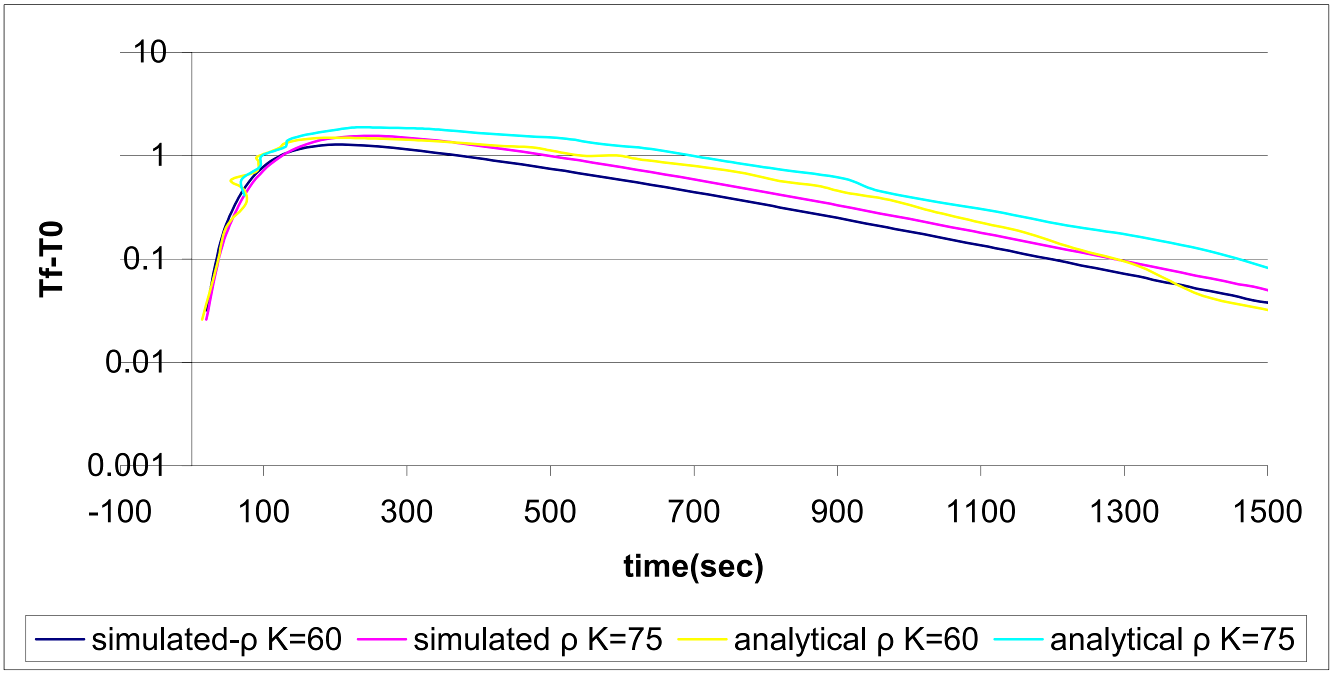


Fig12:Comparison with analytical data[Wakao(1985)]

Conclusion

The existing model(Wakao1985) for non-isothermal adsorption has been solved numerically for computing temperature and concentration profiles outside and inside the pellets. The results obtained matched with the analytical solution of model(1983) and also the experimental results.

Nomenclature

A	Particle surface area per unit volume of packed bed, m^{-1}
C	Adsorbate concentration in bulk fluid phase, $mol.m^{-3}$
C_F	Specific heat of fluid, $J\ kg^{-1}K^{-1}$
Cs	Specific heat of adsorbent particles, $J\ kg^{-1}K^{-1}$
C_0	Adsorbate concentration imposed as a step function, $mol\ m^{-3}$
c_{ad}	Amount adsorbed in particle,$mol\ kg^{-1}$
Ci	Adsorbate (gas) concentration in intraparticle pore volume, $mol.m^{-3}$
D_x	Axial fluid dispersion coefficient,m^2s^{-1}
D_e	Effective diffusivity in adsorbent particle. m^2s^{-1}
h_p	Particle to fluid heat transfer coefficient $Wm^{-2}K^{-1}$
h_o	Overall heat transfer coefficient, $Wm^{-2}K^{-1}$
ΔH	Heat of adsorption, $j.mol^{-1}$
K_A	Adsorption equilibrium constant. m^3 .kg
k_F	Thermal conductivity of fluid, $W.m^{-1}.\ K^{-1}$
k_f	Particle-to-fluid mass transfer coefficient. $m.s^{-1}$
Ks	Thermal conductivity of adsorbent particle, $Wm^{-1}K^{-1}$
R	Particle radius,m
R_T	Column radius,m
R	Radial distance variable in a particle, m
Tf	Temperature in bulk fluid phase,K
T_R	Reference temperature,K
Ts	Temperature in adsorbent particle,K
T_0	Room temperature ;temperature of the fluid flowing into an adsorption bed , K
T	Time, s
U	Interstitial fluid velocity, ms^{-1}
X	Axial distance variable,m
A	$\varepsilon_p+\rho sK_A$

Greek Symbols

α_{ax}	Axial fluid thermal dispersion coefficient, m^2s^{-1}
ε_b	Void fraction in adsorption bed
ε_p	Intraparticle void fraction
μ	Fluid viscosity, Pa s
ρ_F	Fluid density , $kg.m^{-3}$
ρ_s	Density of adsorbent particle, $kg.\ m^{-3}$

References

1. J.E.walter, J.Chem.Phys.13,229 and 332(1945).
2. A. Anzelius, Z. Angew. Math.Mech.6,291(1926).
3. C.C.Furnas, Trans.Am.Inst. Chem Eng. 24, 142(1930).
4. W.Nusselt, Tech. Mech. Thermodynam.1,417(1930).
5. A. Klinkenberg, Ind.Eng.Chem. 46,2285(1954).
6. L. Lapidus and N.R. Amundson, J.Phys.Chem.56,984(1952).
7. O.Levinspeil and K.B. Bischoff, Advances in Chemical Engineering, vol. 4,95,academic press, New York, (1963).
8. J.B.Rosen,J.Chem.Eng.Phys.20,387(1952).
9. J.B.Rosen, Ind.Eng.Sci.37,787(1982).
10. A. Ramuson and I. Neretneiks, AIChE J.29,922(1983).
11. K. Kwazoe and Y.Takeuchi, J.Chem.Eng.Japan 7,431(1974).
12. G.Bohart and E.Adams, J.Am.Chem.Soc.42,523(1920).
13. R.S.Cooper, Ind.Eng.Chem.Fund. 4,308(1965).
14. R.S. Cooper and D.A. Liberman, Ind.Eng.Chem.Fund. 9, 620(1970).
15. T.W. Weber and R.K.Chakravorti, AIChE. J.20,228(1974).
16. J.W. Carter And H. Husain, Chem.Eng.Sci. 29,267(1974).
17. R.L. Gariepy and I. Zwiebel, AIChE Symp. Ser. 71, (152)59(1975).
18. A.I.Liapis, and D.W.T.Rippin, Chem. Eng.Sci. 33,593(1978).
19. M.W. Balzi, A.I. Liapis, and D.W.T.Rippin, Trans.I.Chem.Eng. 56,145,(1978).
20. E.Santacesaria,M.Mobidedlli,a.Servida,G.Storti, and S.Carra, Ind.Eng.Chem.Proceeses Design Develop. 21,446(1982).
21. J.W.Carter,Trans.I.Chem.Eng.44.T253(1966).
22. J.W.Carter,Trans.I.Chem.Eng.46.T213(1968).
23. J.W.Carter,Trans.I.Chem.Eng.51.T75(1973).
24. O.A. Meyer and J.W. Weber, AIChE J. 13,457(1967).
25. O.A.Meyer and J.W. Weber, Can.J.Chem.Eng.47,60,(1969).
26. D.O.Cooney, Ind.Eng.Chem. Proc. Design Develop, 13,368(1974).
27. K.Ikeda,Chem.Eng.Sci.34,941(1979).
28. L.Marcussen, Chem.Eng.Sci.34,941(1979).
29. H. Yoshida and D.M.Ruthven, Chem Eng.Sci.36,877-884(1983)
30. S. Kaguei, Q .yu and N. Wakao, Chem. Eng. Sci.,40,7,1985 (1069-1076).
31. S. Kaguei, M. Nishio and N. Wakao, Chem.Eng.Sci.,42,12,1987(2964-2966)
32. N. Wakao, K.. Tanaka and H. Nagao, Chem.Eng. Sci., 31, 12, 1976 (1109-1113)
33. S. Kaguei, N. Ono and N. Wakao, Chem. Eng, Sci.,44,11,1989(2565-2570)
34. S. Kaguei, L.W.Shemilt and N. Wakao, Chem. Eng. sci.44,3,1989, (483-491)
35. Srivasatva,V.K(1983),”The thermal cracking of benzene in a pipe reactor.”Ph.D. University of Wales, Swansea,U.K.