Equations of Transport of Multi-Component Adsorption with Langmuir Isotherm and Brunauer-Emmett-Teller Isotherm

Muhammad Abdullah Zafar Ghauri

April 2025

1 Introduction

Adsorption is the adhesion [7] of atoms, ions or molecules from some gaseous, liquid or dissolved solid from surface [3], which leads to the formation of film, called adsorbate on the surface of adsorbent. While the process differs from adsorption, in which fluid is dissolved by or permeates a liquid or solid. The phenomenon of adsorption often precede absorption, which involves the transfer of the absorbate into the volume of the absorbent material, alternatively, adsorption is distinctly a surface phenomenon, wherein the adsorbate does not penetrate through the material surface and into the bulk of the adsorbent [2]. The phenomenon of adsorption dominates in different natural, physical, biological and chemical phenomenon and is extensively used in industrial applications such as heterogeneous catalysts [5, 6], activated charcoal, the capturing of waste heat and utilizing for reverse air conditioning (in adsorption chillers), improving the storage capacity of carbide-derived carbons and most importantly water purification [1]. In general the transport of adsorption is given by following equations aided using Langmuir Isotherm:

$$\frac{\partial C}{\partial t} = De\frac{\partial^2 C}{\partial z^2} - u\frac{\partial C}{\partial z} - \frac{1-\epsilon}{\epsilon}\rho\frac{\partial q}{\partial t} \tag{1}$$

$$\frac{\partial q}{\partial t} = k_f(q^* - q) \tag{2}$$

Where ϵ refers to the porosity of film q^* refers to the Langmuir Model defined as:

$$q^* = \frac{q_m K_L C}{1 + K_L C} \tag{3}$$

The Langmuir adsorption model explains adsorption by assuming an adsorbate behaves as an ideal gas at isothermal conditions. According to the model, adsorption and desorption are reversible processes. This model even explains the effect of pressure at these conditions the adsorbate's partial pressure p_A is related to its volume V adsorbed onto a solid adsorbent. The adsorbent, as indicated in the figure, is assumed to be an ideal solid surface composed of a series of distinct sites capable of binding the adsorbate. The adsorbate binding is treated as a chemical reaction between the adsorbate gaseous molecule A_g and an empty sorption site S. This reaction yields an adsorbed species A_{ad} with an associated equilibrium constant K_{eq}:

$$A_g + S \rightleftharpoons A_{ad} \tag{4}$$

From these basic hypotheses the mathematical formulation of the Langmuir adsorption isotherm can be derived in various independent and complementary ways: by the kinetics, the thermodynamics, and the statistical mechanics approaches respectively. The final Langmuir adsoprtion equation in terms of partial pressure and not considering the haet flux is given as follows:

$$\theta_A = \frac{V}{V_m} = \frac{K_{eq}^A p_A}{1 + K_{eq}^A p_A} \tag{5}$$

where θ_A is the fractional occupancy of the adsorption sites, i.e., the ratio of the volume V of gas absorbed onto solid to the volume V_m of gas molecules monolayer covering the entire surface of solid.

1.1 Assumptions of Langmuir Model

Following are some important assumptions [8] taken into consideration for simplest Langmuir model, the adsorption of single adsorbate onto series of equivalent sites onto surface of solid:

1. The surface containing the adsorbing sites is a perfectly flat plane with no corrugations (assume the surface is homogeneous). However, chemically heterogeneous surfaces can be considered to be homogeneous if the adsorbate is bound to only one type of functional groups on the surface.
2. The adsorbing gas adsorbs into an immobile state.
3. All sites are energetically equivalent, and the energy of adsorption is equal for all sites.
4. Each site can hold at most one molecule (mono-layer coverage only).
5. No (or ideal) interactions between adsorbate molecules on adjacent sites. When the interactions are ideal, the energy of side-to-side interactions is equal for all sites regardless of the surface occupancy.

1.2 Assumptions of Brunauer-Emmett-Teller Model

The Brunauer-Emmett-Teller Isotherm is an extension of Langmuir Isotherm, where the Brunauer-Emmett-Teller theory [4] explains the physical adsorption of gas molecules on a solid surface and serves as basis for for analysis technique for the measurement of the specific surface area of materials. The theory applies fortosystems of multilayer adsorption which use some probing gas, referred to as adsorbate and is chemically inert and does not undergo any reaction with adsorptive material to quantify specific surface area. The BET thory is based on following assumptions;

1. Gas molecules physically adsorb on a solid in layers infinitely
2. Gas molecules only interact with adjacent layers and the Langmuir theory is applicable to each layer.
3. The enthalpy of adsorption for the first layer is constant and greater than the second (and higher).
4. The enthalpy of adsorption for the second (and higher) layers is the same as the enthalpy of liquefaction.

In terms of vapor pressure p_o, the BET equation can be written as without accounting for heat flux:

$$\theta = \frac{cp}{(1-\frac{p}{p_o})(p_o + p(c-1))} \quad \forall \quad \frac{\frac{p}{p_o}}{v[1-(\frac{p}{p_o})]} = \frac{c-1}{v_m c}(\frac{p}{p_o}) + \frac{1}{v_m c} \quad c = e^{\frac{E_1 - E_L}{RT}} \tag{6}$$

Where p and p_o are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, v is the absorbed gas quantity and v_m is the monolayer adsorbed gas quantity and c is the BET constant

2 Mathematical Model

As defined above the transport of adsorption is given by following equations aided using Langmuir Isotherm:

$$\frac{\partial C}{\partial t} = De\frac{\partial^2 C}{\partial z^2} - u\frac{\partial C}{\partial z} - \frac{1-\epsilon}{\epsilon}\rho\frac{\partial q}{\partial t} \tag{7}$$

$$\frac{\partial q}{\partial t} = k_f(q^* - q) \tag{8}$$

Where ϵ refers to the porosity of film q^* refers to the Langmuir Model defined as:

$$q^* = \frac{q_m K_L C}{1 + K_L C} \tag{9}$$

subjected to conditions and boundary conditions as:

$$C(z,t) = 0 \quad q(z,t) \quad \forall \quad t = 0 \tag{10}$$

$$C(0,t) = C_O \quad \forall \quad z = 0 \tag{11}$$

$$\frac{dC}{dt} = 0 \quad \forall \quad z = L \tag{12}$$

Symbol	Description
L	Length of column
ϵ	Porosity
u	Liquid flow velocity
k_f	Film mass transfer coefficient
C_0	Inlet concentration
ρ	Density
D_e	Effective diffusion coefficient
K_L	Liquid-phase adsorption coefficient
q_{max}	Maximum adsorption capacity

Table 1: Column Parameters and Their Descriptions

2.1 Implementation of Centered 2nd Order FDA

$$\frac{d^2C}{dz^2} = \frac{C(i+1) + C(i-1) - 2C(i)}{\Delta z^2} \tag{13}$$

2.2 Implementation of Centered 1st Order FDA

$$\frac{dC}{dt} = \frac{C(i+1) - C(i-1)}{2\Delta t} \tag{14}$$

2.3 Implementation of Backward 2nd Order FDA on Boundary Condition

$$C(end) = \frac{4C(end-1) - C(end-2)}{3} \tag{15}$$

```
    clc;
clear;
close all;
%Equation Parameters subjected to user input
L=input('Surface Length=');
epsilon=input('Porosity of Film=');
U=input('Flow Velocity (m/min)=');
kf=input('Film Mass Transfer Rate=');
Co=input('Initial Concentration of Absorbent=');
rho=input('Density of fluid=');
De=input('Effective Diffusion=');
Kl=input('Liquid-phase Adsorption Coefficient=');
qmax=input('Maximum Adsorption Capacity=');

%Discretization of Length
Nz=300;
z=linspace(0,L,Nz);
dz=z(2)-z(1);

%Discretization of Time
t=[0 2500]; %in minutes
ICA=zeros(1,Nz); %For PDE dC/dt........
```

```
ICB=zeros(1,Nz); %For PDE dq/dt........
IC=[ICA ICB];

%Solver for ODE
[t y]=ode15s(@f,t,IC,[],epsilon,U,kf,Co,rho,De,Kl,qmax,Nz,dz);

%Defination of values of Recalculation using Coding from function

C=y(:,1:Nz);
q=y(:,Nz+1:2*Nz);

%Implementation of Boundary Conditions using FDA Algorithms
C(:,1)=Co;
C(:,end)=(4*C(:,end-1)-C(:,end-2))./3; %Second order backward FDA

%Plotting of curves and contours
Cp=C(:,end)./Co; %Ratio Concentration
plot(t/60,Cp,'-o','LineWidth',2)%Conversion of time to hours from minutes
grid on
title('Breakthrough Curve')
xlabel('Time passed')
ylabel('C/Co')
figure(2)
imagesc(z.*100,t/60,C)
title('Distribution of Concentration')
xlabel('Length')
ylabel('Time passed in hours')
colormap jet
colorbar
grid on
%Defination of function
function dydt=f(t,y,epsilon,U,kf,Co,rho,De,Kl,qmax,Nz,dz)
dydt=zeros(length(y),1);
dCdt=zeros(Nz,1);
dqdt=zeros(Nz,1);

%Defination of values
C=y(1:Nz);
q=y(Nz+1:2*Nz);

%Implementation of Boundary Conditions using FDA Algorithms
C(1)=Co;
C(end)=(4*C(end-1)-C(end-2))./3; %Second order backward FDA

%Interior Conditions
for i=2:Nz-1
    qstar(i)=qmax.*Kl.*C(i)./(1+Kl.*C(i));%Langmuir Model
    dqdt(i)=kf.*(qstar(i)-q(i));
    dCdz(i)=(C(i+1)-C(i-1))./2./dz; %From Centered FDA Algorithm
    dC2dz2(i)=(C(i+1)-2*C(i)+C(i-1))./dz.^2; %Second order Centered FDA Algorithm
    dCdt(i)=De.*dC2dz2(i)-U.*dCdz(i)-rho.*((1-epsilon)./epsilon).*dqdt(i);
end
dydt=[dCdt;dqdt]
end
```

Listing 1: Solution for Equations of Transport of Adsorption with Langmuir Isotherm

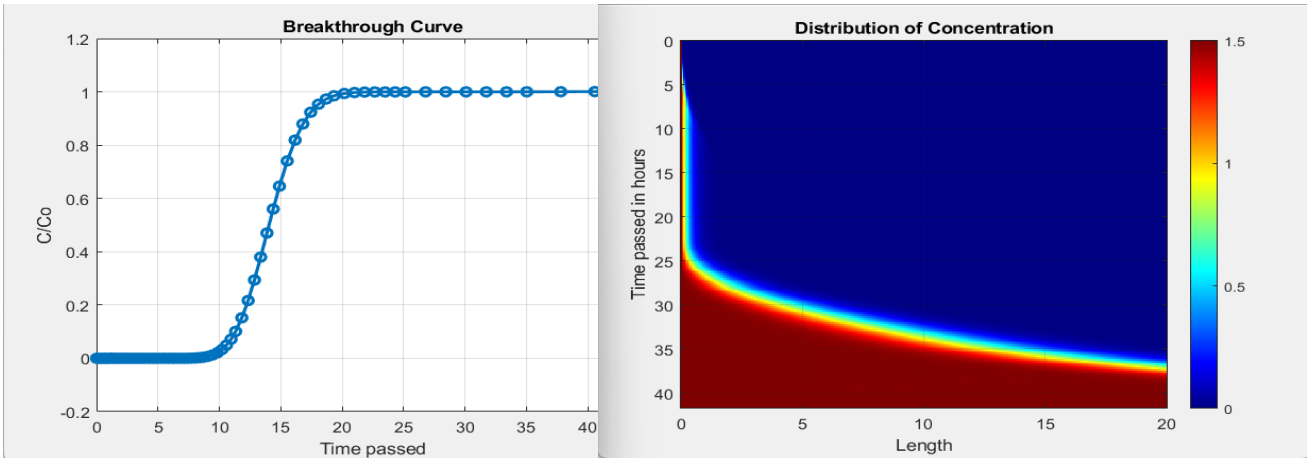
The following figure corresponds to the following experimental data as sourced from literature

3 Mathematical Model for Multilayer Adsorption System

For analysis of multilayer adsorption, the adsorption equation is coupled with Brunauer-Emmett-Teller isotherm while the boundary conditions and initial conditions remain the same with certain modifications.

$$\frac{\partial C_i}{\partial t} = De\frac{\partial^2 C_i}{\partial z^2} - u\frac{\partial C_i}{\partial z} - \frac{1-\epsilon}{\epsilon}\rho\frac{\partial q_i}{\partial t} \tag{16}$$

$$\frac{\partial q}{\partial t} = k_{f,i}(q_i^* - q_i) \tag{17}$$



(a) Breakthrough Curve (b) Concentration Distribution Curve

Figure 1: Breakthrough Curve for Langmuir Isotherm and Distribution of Concentration about Film

Symbol	Description	Value
L	Length of column	0.2 m
ϵ	Porosity	0.8
u	Liquid flow velocity	0.06 m/min
k_f	Film mass transfer coefficient	0.09 (1/min)
C_0	Inlet concentration	1.5 kg/m^3
ρ	Density	980 kg/m^3
D_e	Effective diffusion coefficient	1.2×10^{-9} m^2/min
K_L	Liquid-phase adsorption coefficient	0.00451 m^3/kg
q_{max}	Maximum adsorption capacity	231 kg/kg

Table 2: Column Parameters and Their Values

The Brunauer-Emmett-Teller Isotherm as q* is defined as follows:

$$q_i^* = \frac{q_{m,i} K_{BET} C_i}{(1 - K_{BET} C_i)(1 + (K_{BET} - 1)C_i)} \tag{18}$$

Subjected to conditions and boundary conditions as:

$$C(z,t) = 0 \quad q(z,t) \quad \forall \quad t = 0 \tag{19}$$

$$C(0,t) = C_O \quad \forall \quad z = 0 \tag{20}$$

$$\frac{dC}{dt} = 0 \quad \forall \quad z = L \tag{21}$$

3.1 Implementation of Centered 2nd Order FDA

$$\frac{d^2C}{dz^2} = \frac{C(i+1) + C(i-1) - 2C(i)}{\Delta z^2} \tag{22}$$

3.2 Implementation of Centered 1st Order FDA

$$\frac{dC}{dt} = \frac{C(i+1) - C(i-1)}{2\Delta t} \tag{23}$$

Symbol	Description
L	Length of column
ϵ	Porosity
u	Liquid flow velocity
k_f	Film mass transfer coefficient
C_0	Inlet concentration
ρ	Density
D_e	Effective diffusion coefficient
K_L	Liquid-phase adsorption coefficient
q_{max}	Maximum adsorption capacity
K_{BET}	Brunauer-Emmett-Teller Constant
C_i	Concentrate of absorbate i
$q_{m,i}$	Maximum monolayer adsorption capacity for species i

Table 3: Column Parameters and Their Descriptions

3.3 Implementation of Backward 2nd Order FDA on Boundary Condition

$$C(end) = \frac{4C(end-1) - C(end-2)}{3} \tag{24}$$

```
    clc;
clear;
close all;

% User Input for System Parameters
L = input('Surface Length= ');
epsilon = input('Porosity of Film= ');
U = input('Flow Velocity (m/min)= ');
kf = input('Film Mass Transfer Rate= ');
Co = input('Initial Concentration of Absorbent= ');
rho = input('Density of fluid= ');
De = input('Effective Diffusion= ');

% Multi-Component Adsorption (BET Isotherm)
Ns = input('Number of Adsorbates= ');

% Initialize BET Parameters
qmax = zeros(1, Ns);
K_BET = zeros(1, Ns);

for j = 1:Ns
    fprintf('For Adsorbate %d:\n', j);
    qmax(j) = input('Maximum Adsorption Capacity qmax= ');
    K_BET(j) = input('BET Constant K_BET= ');
end

% Discretization of Length
Nz = 300;
z = linspace(0, L, Nz);
dz = z(2) - z(1);

% Discretization of Time
t = [0 2500]; % in minutes
IC = zeros(1, 2 * Ns * Nz); % Initial Conditions for all species

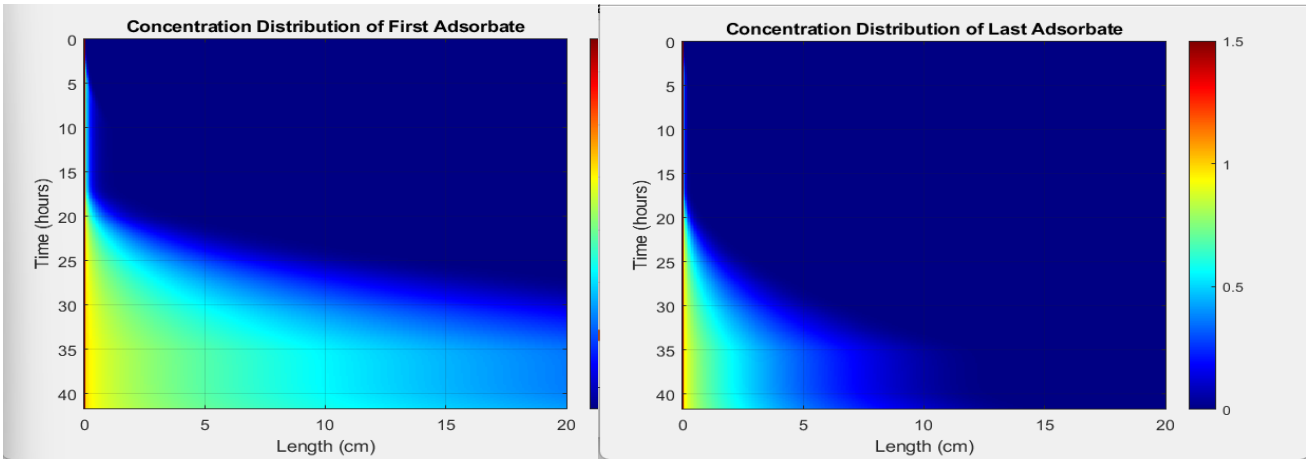
% Solve ODE System
[t, y] = ode15s(@f, t, IC, [], epsilon, U, kf, Co, rho, De, qmax, K_BET, Ns, Nz, dz);

% Extract Values
C = reshape(y(:, 1:Ns*Nz), [], Nz, Ns);
q = reshape(y(:, Ns*Nz+1:end), [], Nz, Ns);
```

```
42
43 % Implement Boundary Conditions using FDA
44 C(:, 1, :) = Co;
45 C(:, end, :) = (4 * C(:, end-1, :) - C(:, end-2, :)) / 3; % Second-order backward FDA
46
47
48
49 % Plot Breakthrough Curves for Each Adsorbate
50 figure(1);
51 hold on;
52 colors = lines(Ns);
53 for j = 1:Ns
54     plot(t/60, C(:, end, j) ./ Co, '-o', 'LineWidth', 2, 'Color', colors(j,:));
55 end
56 grid on;
57 title('Breakthrough Curve for Multi-Component Adsorption (BET)');
58 xlabel('Time (hours)');
59 ylabel('C/Co');
60 legend(arrayfun(@(x) sprintf('Adsorbate %d', x), 1:Ns, 'UniformOutput', false));
61
62 % Plot Concentration Distribution Contour for First Adsorbate
63 figure(2);
64 imagesc(z .* 100, t / 60, C(:,:,1)); % For first species
65 title('Concentration Distribution of First Adsorbate');
66 xlabel('Length (cm)');
67 ylabel('Time (hours)');
68 colormap jet;
69 colorbar;
70 grid on;
71 figure(3);
72 imagesc(z .* 100, t / 60, C(:,:,end)); % For first species
73 title('Concentration Distribution of Last Adsorbate');
74 xlabel('Length (cm)');
75 ylabel('Time (hours)');
76 colormap jet;
77 colorbar;
78 grid on;
79 % Function Definition
80 function dydt = f(t, y, epsilon, U, kf, Co, rho, De, qmax, K_BET, Ns, Nz, dz)
81     dydt = zeros(length(y), 1);
82     dCdt = zeros(Nz, Ns);
83     dqdt = zeros(Nz, Ns);
84
85     % Extract Values
86     C = reshape(y(1:Ns*Nz), Nz, Ns);
87     q = reshape(y(Ns*Nz+1:end), Nz, Ns);
88
89     % Implement Boundary Conditions using FDA
90     C(1, :) = Co;
91     C(end, :) = (4*C(end-1, :) - C(end-2, :)) / 3;
92
93     % Loop over all spatial points
94     for i = 2:Nz-1
95         for j = 1:Ns
96             % BET Isotherm for multi-component adsorption
97             qstar = (qmax(j) * K_BET(j) * C(i,j)) / ...
98                    ((1 - K_BET(j) * C(i,j)) * (1 + (K_BET(j) - 1) * C(i,j)));
99
100            % Rate of adsorption/desorption
101            dqdt(i,j) = kf * (qstar - q(i,j));
102
103            % Finite Difference Approximations
104            dCdz = (C(i+1,j) - C(i-1,j)) / (2 * dz);
105            dC2dz2 = (C(i+1,j) - 2*C(i,j) + C(i-1,j)) / dz^2;
106
107            % Modified transport equation
108            dCdt(i,j) = De * dC2dz2 - U * dCdz - rho * ((1-epsilon) / epsilon) * dqdt(
    i,j);
109        end
110    end
111
```

```
    % Reshape back into vector form
    dydt = [reshape(dCdt, [], 1); reshape(dqdt, [], 1)];
end
```

Listing 2: Solution of Multilayer Adsorption System using BET Isotherm



(a) Concentration Distribution for First Adsorbate (b) Concentration Distribution for Last Adsorbate

Figure 2: Concentration Distributions for Adsorbates

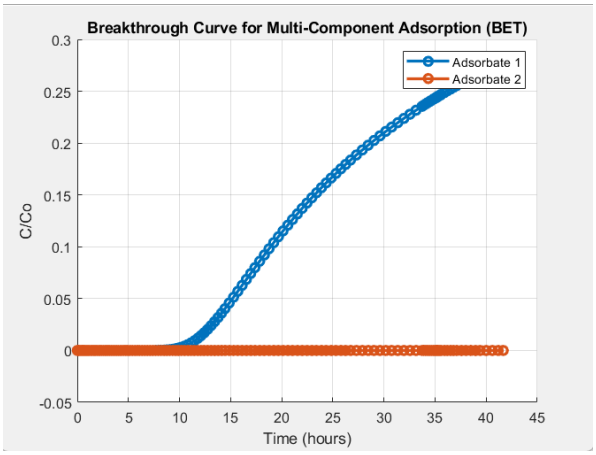


Figure 3: Breakthrough Curve for Multi-Component Adsorption (BET)

Conclusion

References

[1] Ali, S. M., Ashour, B., Farahat, M. G., and El-Sherif, R. M. Biomass-based perovskite/-graphene oxide composite for the removal of organic pollutants from wastewater. *Ceramics International 50*, 23 (September 2024), 49085–49094.

[2] Atkins, P. W., De Paula, J., and Keeler, J. *Atkins' Physical Chemistry*, eleventh ed. Oxford University Press, Oxford, United Kingdom, 2018.

[3] Brownsfields. Glossary. Archived from the original on 2008-02-18. Retrieved 2009-12-21.

[4] Brunauer, S., Emmett, P. H., and Teller, E. Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society 60*, 2 (February 1938), 309–319.

Symbol	Description	Value
L	Length of column	0.2 m
ϵ	Porosity	0.8
u	Liquid flow velocity	0.06 m/min
k_f	Film mass transfer coefficient	0.09 (1/min)
C_0	Inlet concentration	1.5 kg/m^3
ρ	Density	980 kg/m^3
D_e	Effective diffusion coefficient	1.2×10^{-9} m^2/min
N_s	Number of adsorbates involved	2

Table 4: Column Parameters and Their Values

Number of Adsorbate	Maximum Adsorption Capacity	$\mathbf{K_{BET}}$
1	231.0	0.00451
2	589.23	0.0084

Table 5: Values for maximum adsorption capacity of adsorbates and values of K_{BET}

[5] Czelej, K., Cwieka, K., Colmenares, J. C., and Kurzydlowski, K. J. Insight on the interaction of methanol-selective oxidation intermediates with au- or/and pd-containing monometallic and bimetallic core@shell catalysts. *Langmuir 32*, 30 (2016), 7493–7502.

[6] Czelej, K., Cwieka, K., and Kurzydlowski, K. J. Co stability on the ni low-index surfaces: Van der waals corrected dft analysis. *Catalysis Communications 80*, 5 (May 2016), 33–38.

[7] Guruge, A. R. Absorption vs adsorption. *Chemical and Process Engineering* (February 2021). Retrieved 2023-11-26.

[8] Masel, R. *Principles of Adsorption and Reaction on Solid Surfaces*. Wiley Interscience, 1996.