Breakthrough Curve for Adsorption of Thiol Functionalized Silica-Mixed Matrix Membranes for Silver Capture from Aqueous Solution

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Abstract

This study investigates the adsorption behavior of thiol functionalized silica mixed matrix membranes (MMMs) for silver ion removal as the effective capture of silver ions from aqueous solution is of great importance for environmental protection and resource recovery. A mathematical model based on partial differential equations was developed to explain the breakthrough curve and mass transfer dynamics by involving key parameters namely membrane flux, adsorption kinetics and silver affinity constant. Finite Difference Approximation was used for numerical simulation and Monte Carlo simulations were conducted in order to access the statistical distribution of breakthrough times. The consequent results highlighted a high adsorption efficiency of thiol functionalized silica MMMs with well-defined breakthrough behavior. The model predictions are compatible with experimental observations, thereby validating the proposed approach with the research successfully highlighting the effectiveness of silica based MMMs for silver ion capture and wastewater treatment applications

Keywords: silver ions, Monte Carlo Simulations, thiol functionalized silica MMMs, Finite Difference Approximations, silver affinity constant, adsorption kinetics

1 Introduction

Adsorption is the adhesion [6] 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 [4, 5], 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]. The dimensionless system of Partial

Differential Equations from literature are given as[1]:

$$\frac{\varphi L}{J_w T_s}\frac{\partial C}{\partial t} + \frac{\partial C}{\partial z} + (1-\varphi-\varphi_p)\frac{kL}{J_w}(\gamma C - q\frac{q_\infty}{C_o}) = 0 \tag{1}$$

$$\frac{\partial q}{\partial t} = \frac{kT_s C_o}{q_\infty}(\gamma C - q\frac{q_\infty}{C_o}) \tag{2}$$

where

$$C = \frac{C'}{C_o}, \qquad q = \frac{q'}{q_\infty}, \qquad z = \frac{z'}{L}, \qquad t = \frac{t'}{T_s} \tag{3}$$

Subjected to boundary conditions as:

$$C(0,t) = 1, \qquad q(z,0) = 0, \qquad C(z,0) = 0 \tag{4}$$

Symbol	**Description**
φ	Free volume fraction
φ_p	Polymer volume fraction
$(1-\varphi-\varphi_p)$	Fractional volume of silica particles
C'	Concentration of Ag^+ in bulk liquid phase (moles of Ag^+/m^3 of liquid)
q'	Concentration of silver in silica phase (moles of Ag^+/m^3 of silica particles)
q_{eq}	Maximum concentration of silver in silica phase for C' (moles of Ag^+/m^3 of silica particles)
J_W	Membrane flux (m/s)
t'	Time (s)
z'	Distance down the membrane thickness (m)
C_0	Inlet feed concentration of silver ion ($mole/m^3$)
q_∞	Maximum silver capture (moles of Ag^+/m^3 of silica)
L	Membrane thickness (m)
T_S	Time at which saturation of silver capture was observed and experiment was terminated (s)
γ	Silver Affinity Constant
k	Volumetric mass Transfer Rate (s^{-1})

Table 1: Definitions of Symbols Used in the Study

2 Mathematical Model

For the equations defined , Finite Difference Approximation is implemented for discretization of equations corresponding to the timestep and length step

$$\frac{dC}{dz} = \frac{C(i+1) - C(i-1)}{2\Delta z} \tag{5}$$

[1]These partial differential equations have been sourced from [7] along with the parameters and the experimental parameters which can be referred to in Tables 1 and 2

Symbol	Value	Unit
C_0	1.03	mole/m^3
L	150×10^{-6}	m
φ	0.63	-
φ_p	0.27	-
q_∞	4.62×10^3	mol/m^3
γ	5021.8	-
J_w	8.5×10^{-6}	ms^{-1}
k	0.00158	s^{-1}
T_s	60	s
q_o	4.62×10^3	

Table 2: Parameter Values with Units

$$C(end) = \frac{4C(Nz-1) - C(Nz-2)}{3} \tag{6}$$

```
    clc;
clear;
close all;

% Input Parameters
psi=input('Free Volume Fraction=');
psip=input('Polymer Volume Fraction=');
L=input('Thickness of Membrane= ');
Co=input('initial Concentration=');
gamma=input('Silver Affinity Constant=');
Jw=input('Membrane Flux=');
qinfinity=('Maximum silver Capture=');
Ts=input('Saturation Time='); %Saturation Time (From refernce paper)
qo=input('Initial Heat=');
K=input('Volumetric mass Transfer Rate=');

% For simplification of solution
a = psi * L / Jw / Ts;
b = (1 - psi - psip) * K * L / Jw;
e = q0 ./ C0;
d = K * Ts * C0 ./ q0;

% Initialization of Time Step
tt = 0:150:24000;
t = tt / Ts;

% Initialization of step for Length
Nz = 200;
zz = linspace(0, L, Nz);
z = zz ./ L;
dz = z(2) - z(1);

% Initialization of Initial Conditions
```

```
IC_A = zeros(1, Nz);
IC_B = zeros(1, Nz);
IC = [IC_A, IC_B];

% Solving ODE
[t, c] = ode15s(@(t, c) f(t, c, Nz, a, b, C0, e, d, dz, gamma), t, IC);

% Extraction of Values
C = c(:, 1:Nz);
q = c(:, Nz+1:2*Nz);

% Redefining the boundary conditions
C(:, 1) = 1;
C(:, end) = (4 * C(:, Nz-1) - C(:, Nz-2)) / 3;

% Plotting Concentration vs Time
figure(1)
plot(t, C(:, end), '--')
title('Jw=8.5e-6 and K=0.00150')
ylim([0 1.2])
grid on
xlabel('t*/Ts (Ts=60)')
ylabel('Concentration Ratio (C*/Co)')

% Plotting Concentration Profile
figure(2)
imagesc(z, t, C)
xlabel('z*/L')
ylabel('Time t*/Ts')
colormap jet
colorbar

% Function Definition
function dcqdt = f(t, c, Nz, a, b, C0, e, d, dz, gamma)
    dcqdt = zeros(2*Nz, 1);
    dcdt = zeros(Nz, 1);
    dqdt = zeros(Nz, 1);

    % Defining values
    C = c(1:Nz);
    q = c(Nz+1:2*Nz);

    % Boundary Conditions
    C(1) = 1;
    C(end) = (4 * C(Nz-1) - C(Nz-2)) / 3;

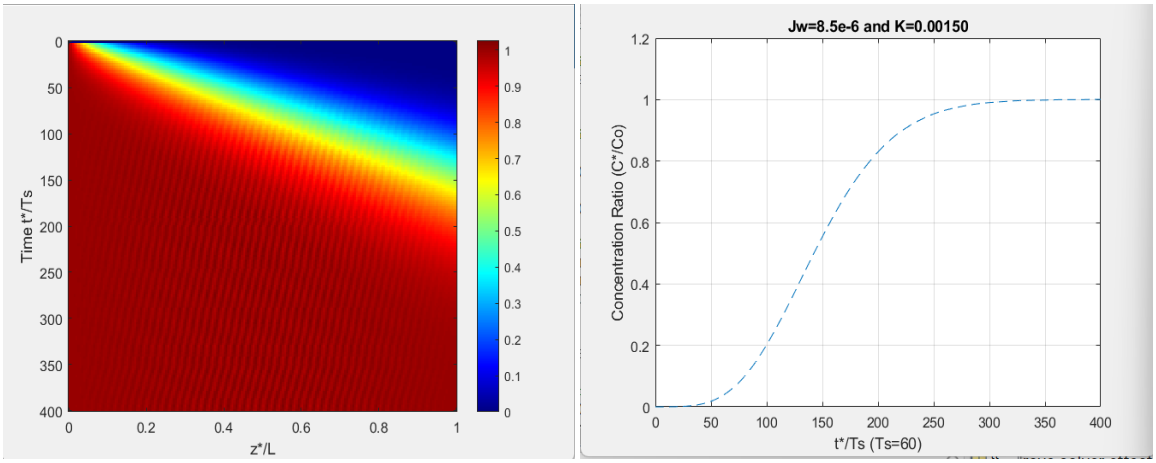
    % Initialize dcdz array
    dcdz = zeros(Nz, 1);

    % Loop for internal operations (Centered FDA)
    for i = 2:Nz-1
        dcdz(i) = (C(i+1) - C(i-1)) / (2 * dz); % FDA centered for first derivative
        dcdt(i) = (-1 / a) * (dcdz(i) + b * (gamma * C(i) - q(i) * e));
        dqdt(i) = d * (gamma * C(i) - q(i) * e);
    end

    % Output derivative
    dcqdt = [dcdt; dqdt];
```

```
end
```

Listing 1: Finite Difference Approximation Code for Breakthrough Curve



(a) Concentration Distribution Contour (b) Breakthrough Curve for Adsorption

Figure 1: Concentration Contour and Breakthrough Curve for Thiol Functionalized Silica-Mixed Matrix Membranes

3 Monte Carlo Simulation for Breakthrough Time

```
    clc;
clear;
close all;

% Number of Monte Carlo runs
N = 1000;

% Define system properties
Nx = 200; % Number of spatial grid points
L = 150e-6; % Column length (m)
dx = L / Nx;
Nt = 24000; % Number of time steps
dt = 0.01;
u = 0.01; % Flow velocity (m/s)
rho = 0.1; % Adsorbent density (g/L)

% Define mean values and standard deviations for key parameters
Jw_mean = 8.5e-6; Jw_std = 1e-6;
gamma_min = 4000; gamma_max = 6000;
k_mean = 0.00158; k_std = 0.0003;
qinf_mean = 4.62e3; qinf_std = 500;

% Generate random samples for parameters
Jw_samples = normrnd(Jw_mean, Jw_std, [N, 1]);
```

```
gamma_samples = unifrnd(gamma_min, gamma_max, [N, 1]);
k_samples = lognrnd(log(k_mean), k_std, [N, 1]);
qinf_samples = normrnd(qinf_mean, qinf_std, [N, 1]);

% Preallocate storage for results
breakthrough_times = zeros(N, 1);

for i = 1:N
    % Assign current random parameters
    Jw = Jw_samples(i);
    gamma = gamma_samples(i);
    k = k_samples(i);
    qinf = qinf_samples(i);

    % Solve adsorption PDE using Finite Difference Method
    C = zeros(1, Nx); % Concentration profile along the column
    q = zeros(1, Nx); % Adsorbed concentration profile
    C_in = 10; % Inlet concentration (mg/L)

    for t = 1:Nt
        % Apply inlet concentration
        C(1) = C_in;

        % Compute adsorption using Freundlich model
        q = qinf * C .^ (1 / gamma) ./ (1 + Jw * k);

        % Transport equation (upwind finite difference)
        for x = 2:Nx
            C(x) = C(x) - (u * dt / dx) * (C(x) - C(x-1)) - (rho * dt) * (q(x) - q(x
    -1));
        end

        % Extract breakthrough time (when C reaches 50% of C_in)
        if any(C >= 0.5 * C_in)
            breakthrough_times(i) = t * dt;
            break;
        end
    end
end

% Plot histogram of breakthrough times
figure;
histogram(breakthrough_times, 'Normalization', 'pdf');
xlabel('Breakthrough Time (s)');
ylabel('Probability Density');
title('Monte Carlo Simulation of Breakthrough Time');

% Compute statistical properties
mean_time = mean(breakthrough_times);
std_time = std(breakthrough_times);
disp(['Mean Breakthrough Time: ', num2str(mean_time), ' s']);
disp(['Standard Deviation: ', num2str(std_time), ' s']);
```

Listing 2: Monte Carlo Simulation Code

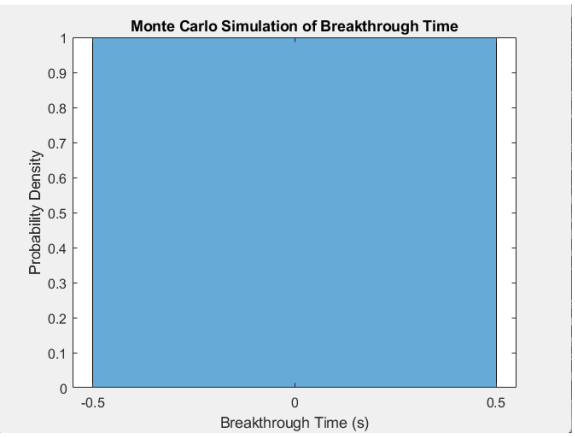


Figure 2: Monte Carlo Simulation for Breakthrough Time

Conclusion

Through the conducted study, mathematical models were successfully developed which effectively played an important role in analyzing the adsorption performance of thiol-functionalized silica mixed matrix membranes for silver ion removal. The mathematical framework successfully captures the breakthrough behavior, with numerical simulations aligning with the membranes' high efficiency in silver adsorption. The Monte Carlo simulation also verified the reliability of the findings by providing statistical information regarding the breakthrough time variability. These results highlight the potential of functionalized MMMs in industrial water treatment and precious metal recovery applications.

References

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