

Mathematical Modelling for the Adsorption Process of CO₂ in Nanopores of Catalytic Particles in a Fixed Bed Reactor Using Numeral Inverse Laplace Transform

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Theoretical analysis on the CO₂ adsorption on NaX has been carried out in fixed bed reactor. In the proposed process, CO₂ was passed through a stationary adsorbent bed allowing continuous operation. A one-dimensional and isothermal model was proposed to describe the adsorption process of CO₂. Attention has been focused on a mathematical model to simulate the transient behavior of dissolved CO₂ within the gas phase and then adsorbed into the nanopores of the solid phase (adsorbent). The simulation results were compared to the one experimental case. After, it was performed a sensibility analysis in relation to CO₂ concentration within of the nanopores of the solid phase as well as accounting for the amount of adsorbed CO₂ in the nanopores of the solid phase.

1. Introduction

It well know that fossil fuel is still the world's primary energy source and its combustion is one of the major sources of the greenhouse gas carbon dioxide. CO₂ has been know as one of the causes of global warming, but the purified and concentrated CO₂ stream can be used as an important carbon source to synthesize clean fuels and fine chemicals. Serious preoccupations have been raised with respect to the impact of the increasing concentration of CO₂ in the atmosphere on the environment. Therefore, it's evident that the strategic importance of pos-combustion capture systems are required to prevent emissions from the existing fleet of power plants when considering the abundant sources of CO₂ emissions (Oliveira and Silva, 2012).

The adsorption process to capture CO₂ on NaX has been widely applied in chemical engineering and environmental engineering. Computer simulation became an increasingly important optimization tool in continuous adsorption-based process such as in the fixed bed reactor. The mathematical explanation for the fixed bed reactor of component systems has been developed. Usually, an analytical solution is not possible for non-linear component model. Although the adsorption process has some restrictions, this technique is attractive since it provides information in relations to concentration dependence of micropore diffusivities.

NaX has presented promising results for separating CO₂ form gas mixtures and can potentially be used in the adsorption processes. Based on the advanced analysis of several important studies with respect to CO₂ adsorption using NaX, it shows that the surface basicity and size of NaX as well as the strength of the electric fields caused by the presence of exchangeable cations in the frameworks and cavities of NaX are the essential factors for the CO₂ adsorption on NaX.

A crucial problem of the adsorption process is CO₂ adsorbent performance (Ding and Alpay, 2000). Based on the capacity of CO₂ adsorption, the adsorbents with high capacity are considered ideal. On the other hand, the adsorbents with low capacity are clearly inappropriate. Therefore, the objective of the present work has been to carry out a sensibility analysis regarding CO₂ concentration within of the nanopores of the solid phase as well as accounting for the adsorbed amount of CO₂ in the nanopores of the solid phase.

2. Mathematical modelling

2.1 Process detail

The process consists in a fixed bed reactor (FBR) with stationary catalytic adsorbent. The main approach of this process is the use of mobile CO₂ (concurrent downward) flowing through the FBR with the stationary adsorbent phase. The adsorbent pellets were of spherical shape of 0.156cm diameter and 0.748 ncm nanopore.

2.2 Governing equation

A mathematical model of the accountancy has been developed to describe the isothermal adsorption process of CO₂ on a small-scale FBR. CO₂ adsorption model assumptions were summarized such as axially dispersed plug flow, perfect gas behaviour, no radial concentration gradient and an adsorbent section of uniform voidage and particle size. Based on the above assumptions, mass balance of CO₂ could be written as follows (Silva et al, 2003).

$$\frac{\partial C_{CO_2}(z,t)}{\partial t} + \frac{4Q_g}{\pi d_c^2} \frac{\partial C_{CO_2}(z,t)}{\partial z} = D_{z,CO_2} \frac{\partial^2 C_{CO_2}(z,t)}{\partial z^2} - k_{gs} \frac{3}{r_a} (1-\varepsilon_s) \left[C_{CO_2}(z,t) - C_{CO_2}(r,t) \right]_{r=R} \quad (1)$$

Where C_{CO₂}(z,t) is the molar concentration of CO₂ into the gaseous phase in mol/cm³, t is the time in sec, Q_g is the flow of the gaseous phase in cm³/sec, d is the diameter of the reactor in cm, z is the axial distance in the FBR in cm, D_{z,CO₂} is the dispersion coefficient of CO₂ in cm²/sec, k_{gs} is the gas-solid mass transfer coefficient in cm/sec, r_a is the adsorbent radius in cm, ε_s is the internal porosity and C_{CO₂}(r,t) is the molar concentration of CO₂ in the nanopore spaces at r = R of the solid particles in mol/cm³.

The initial and boundary conditions for the Eq. (1) are given as allow;

$$\text{for } t > 0, C_{CO_2}(z,t) \Big|_{t=0} = C_{CO_2,0} \text{ for all } z \quad (2)$$

$$\text{for } t \geq 0, D_{z,CO_2} \frac{\partial C_{CO_2}(z,t)}{\partial z} \Big|_{z=0^+} = \frac{4Q_g}{\pi d_c^2} \left[C_{CO_2}(z,t) \Big|_{z=0^+} - C_{CO_2}(z,0) \right]; \text{ as } z \rightarrow \infty, \frac{\partial C_{CO_2}(z,t)}{\partial z} = 0 \quad (3)$$

A mathematical model adopted to describe the intraparticle diffusional mass transfer (IDMT) of CO₂ at the adsorbent nanopores has been considered. It is important to note that the IDMT involves two different phenomena (diffusion at the nanopores of the solid particles and diffusion at the surface of the solid particles). In the diffusion of the nanopores, it is assumed that the adsorbate (CO₂) diffuses into the nanopores according to the model of the Eq (4). The diffusion at the surface reports the diffusion of the adsorbate (CO₂) through the external film to the outer surface of the solid particles; at this surface, adsorption occurs instantaneously and equilibrium is assumed to be established between adsorbate (CO₂) in the fluid and that on the surface as follows the Eq (8) see Ramachandran and Smith (1979).

$$\frac{\partial C_{CO_2}(r,t)}{\partial t} = D_{e,CO_2} \left(\frac{\partial^2 C_{CO_2}(r,t)}{\partial r^2} + \frac{2}{r} \frac{\partial C_{CO_2}(r,t)}{\partial r} \right) - \frac{\partial q_{CO_2}(r,t)}{\partial t} \quad (4)$$

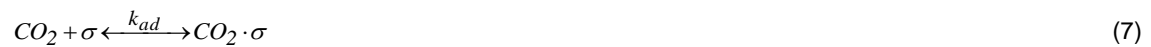
Where D_{e,CO₂} is the Effective diffusivity coefficient of CO₂ in cm²/s, r is the nanopore radius in ncm, C_{CO₂}(r,t) is the molar concentration of CO₂ in the nanopores space of the solid particles in mol/cm³ and q_{CO₂}(r,t) is the adsorbed concentration of CO₂ on the solid particles in mol/cm³.

The initial and boundary conditions for the Eq (4) are presented as;

$$\text{for } t \leq 0, C_{CO_2}(r,t) \Big|_{t=0} = 0 \text{ for all } r \quad (5)$$

$$\text{for } t > 0, D_{e,CO_2} \frac{\partial C_{CO_2}(r,t)}{\partial r} \Big|_{r=R} = k_{gs} \left[C_{CO_2}(z,t) - C_{CO_2}(r,t) \right]_{r=R}; \text{ for } t > 0, \frac{\partial C_{CO_2}(r,t)}{\partial r} \Big|_{r=0} = 0 \quad (6)$$

Adsorption reversible occurs at the sites (σ) into an adsorbent particle according to first-step mechanism below.



Based on this first-step mechanism, the adsorption rate of CO₂ can be written as allow:

$$\frac{\partial q_{CO_2}(r,t)}{\partial t} = k_{ad} \left(C_{CO_2}(r,t) - \frac{q_{CO_2}(r,t)}{\rho_s K_{ed}} \right) \quad (8)$$

The initial condition for the Eq (8) has been described as;

$$\text{for } t \leq 0, q_{CO_2}(t) \Big|_{t=0} = 0 \text{ for all } r \quad (9)$$

2.3 Application of the Laplace transformation on the mathematical model

The Laplace transformation method has been used for transforming partial differential equations (PDEs) in ordinary differential equations (ODEs) according to Silva and Oliveira (2012). PDEs (1) to (9) and their restricted conditions can be transformed easily using the Laplace transformation according to the Equation (10) as follow.

$$\bar{C}_i(z,s) = \int_0^{\infty} C_i(z,s) e^{-st} dt; \bar{C}_i(z,s) = \bar{C}_{CO_2}(z,s), \bar{C}_{CO_2}(r,s) \text{ and } \bar{q}_{CO_2}(r,s) \quad (10)$$

Initially, Eqs (1) to (9) and their initial and boundary conditions were obtained in the Laplace domain using the above Eq (10) as follows.

- Mass balance for the gas phase in the Laplace domain;

$$D_{z,CO_2} \frac{d^2 \bar{C}_{CO_2}(z,s)}{dz^2} - \alpha_1 \frac{d \bar{C}_{CO_2}(z,s)}{dz} - \alpha_2(s) \bar{C}_{CO_2}(z,s) + \alpha_3 \bar{C}_{CO_2}(r,s) \Big|_{r=R} - \bar{C}_{CO_2,0} = 0 \quad (11)$$

- The Eq (11) is restricted the following initial and boundary conditions in the Laplace domain;

$$\text{for } s > 0, \bar{C}_{CO_2}(z,s) = \frac{C_{CO_2,0}}{s} \text{ for all } z \quad (12)$$

$$\text{for } s \geq 0, D_{z,CO_2} \frac{d \bar{C}_{CO_2}(z,s)}{dz} \Big|_{z=0^+} = \frac{4Q_g}{\pi d_c^2} \left[\bar{C}_{CO_2}(z,s) \Big|_{z=0^+} - \frac{C_{CO_2,0}}{s} \right]; \text{ as } z \rightarrow \infty, \frac{d \bar{C}_{CO_2}(z,s)}{dz} = 0 \quad (13)$$

- Mass balance for the solid phase in the Laplace domain;

$$\frac{d^2 \bar{C}_{CO_2}(r,s)}{dr^2} + \frac{2}{r} \frac{d \bar{C}_{CO_2}(r,s)}{dr} - \beta_1(s) \bar{C}_{CO_2}(r,s) = 0 \quad (14)$$

- The Equation(14) is restricted the following initial and boundary conditions in the Laplace domain;

$$\text{for } s \leq 0, \bar{C}_{CO_2}(r,s) \Big|_{s=0} = 0 \text{ for all } r \quad (15)$$

$$\text{for } s \geq 0, D_{e,CO_2} \frac{d \bar{C}_{CO_2}(r,s)}{dr} \Big|_{r=R} = k_{gs} \left[\bar{C}_{CO_2}(z,s) - \bar{C}_{CO_2}(r,s) \Big|_{r=R} \right]; \text{ for } s > 0, \frac{d \bar{C}_{CO_2}(r,s)}{dr} \Big|_{r=0} = 0 \quad (16)$$

- The adsorption rate of CO₂ in the Laplace domain;

$$\bar{q}_{CO_2}(r,s) = \beta_2(s) \bar{C}_{CO_2}(r,s) \quad (17)$$

- The initial condition in the Laplace domain for the Equation (17);

$$\text{for } s \leq 0, \bar{q}_{CO_2}(r,s) \Big|_{s=0} = 0 \text{ for all } r \quad (18)$$

The spatial domain was discretized using centred finite differences of second order over a uniform grid. This approach was found to give a converge solution in which a value of 1.0×10^{-6} for absolute tolerance (Silva, 2012). The coefficients [α_{1g} , $\alpha_{2g}(s)$, α_{3g} , $\beta_1(s)$ and $\beta_2(s)$] of Eqs (11), (14) and (17) are defined in the appendix (A).

Table 1: Input values of operating conditions, properties of the gas and solid phases used in the simulation were extracted of the following references (Ding and Alpay, 2000 and also Xiu et al, 2002)

Categories	Properties	Numerical Values
Operation Conditions	Operation temperature of the gas phase, T_g K	390-570
	Operation pressure, P_{op} atm	70-160
	Gas flow rate, Q_g cm^3/sec	1.12×10^{-6}
	Initial concentration of CO_2 in the gaseous phase, $C_{\text{CO}_2,0}(z,t)$ mol/cm^3	0.102
	Initial concentration of CO_2 in the nanopores space of the solid particles, $C_{\text{CO}_2,0}(r,t)$ mol/cm^3	0.000
	Initial adsorbed concentration of CO_2 on the solid particles, $q_{\text{CO}_2,0}(r,t)$ mol/cm^3	0.000
	Catalytic reactor diameter, d_r m	0.260
Gas properties	Dispersion coefficient of CO_2 , D_{z,CO_2} cm^2/s	0.712-1.054
	Gas-solid mass transfer coefficient, k_{gs} cm/s	7.568-8.579
	Effective diffusivity coefficient of CO_2 , D_{e,CO_2} cm^2/s	1.863×10^{-6}
	Adsorption rate coefficient, k_{ad} $1/\text{s}$	1.231×10^{-3}
	Adsorption equilibrium coefficient, K_{ed} cm^3/mol	0.851
Properties of the solid phase	Void fraction of the solid phase, ε_s (-)	0.463
	Density of the solid phase, ρ_s g/cm^3	1.162
	Adsorbent radius, r_a cm	0.078
	Nanopore radius, r_n nm	0.370

3. Results and discussions

3.1 Performance of the fixed bed reactor

Here the FBR has been used for CO_2 adsorption on NaX adsorbent. We consider a 1m FBR with one - subsections which is packed with flowing mixture of $\text{CO}_2 + \text{N}_2$ on NaX. The main parameters of the mathematical model have been shown in the above Table (1). These parameters were offered to feed the computer code. The simulations have been carried out for completing a cycle length of 20s with a tolerance of 1.0×10^{-6} . Experimental data with respect to CO_2 , obtained in the Environmental and Energetic Technology Laboratory of Polytechnic School – UPE, were used for the validation of the model. Only one set of experimental results were obtained owing to the project is in initial phase. In future works, we can present more experimental results. The experimental results and predicted values of the proposed model provided a good correlation at tested flow rate according to the Figure 1.

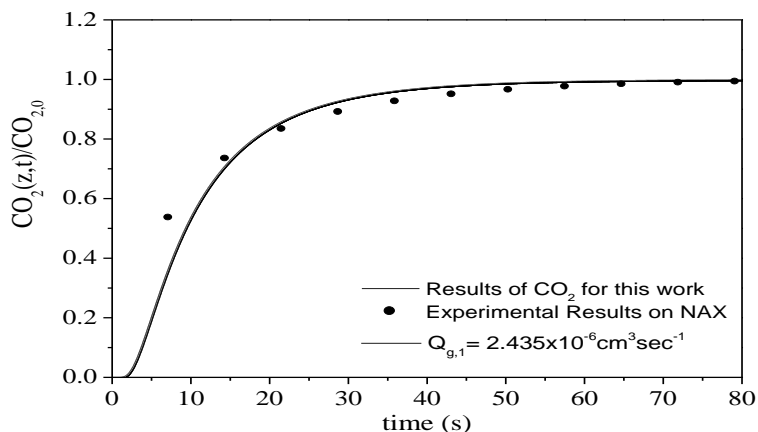


Figure 1: The experimental and predicted breakthrough curves for adsorption of CO_2 on NaX for one flow rate in the gas phase.

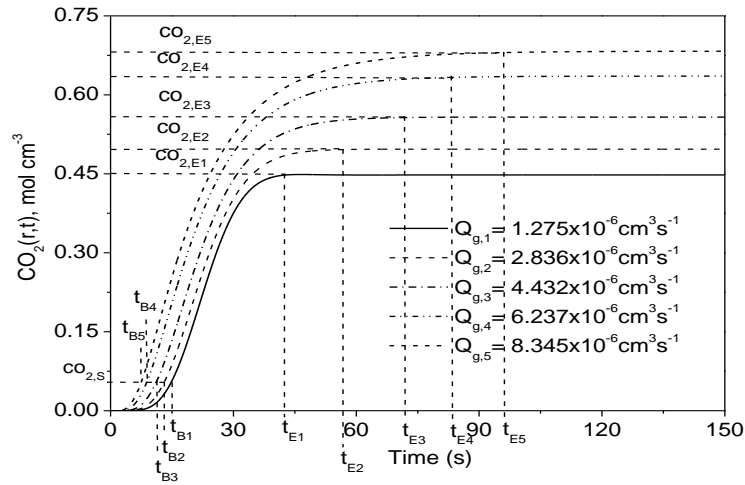


Figure 2: Effect of different flow rates on breakthrough curves at different breakthrough time in the solid phase

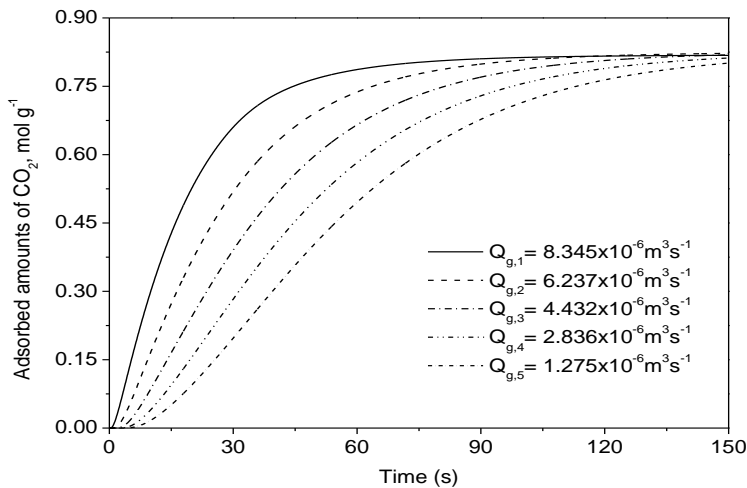


Figure 3: Effect of different flow rates on adsorbed amounts of CO_2 in the solid phase ($\text{CO}_{2,0} = 0.56 \text{ kg m}^{-3}$, adsorbent size = 0.156 cm and nanopores diameter = 0.748 ncm)

As can be seen in the Figure 2, the breakthrough curves of CO_2 have shown a growth with the increase in flow rate along the time with the physical properties fixed. Breakthrough time for the curve 1 is t_{B1} ; t_{B2} -breakthrough time for the curve 2, t_{B3} -breakthrough time for the curve 3, t_{B4} -breakthrough time for the curve 4 and t_{B5} -breakthrough time for the curve 5; t_{E1} -exhaustion time for the curve 1, t_{E2} -exhaustion time for the curve 2, t_{E3} -exhaustion time for the curve 3, t_{E4} -exhaustion time for the curve 4 and t_{E5} -exhaustion time for the curve 5; $\text{CO}_{2,E1}$ -exhaustion concentration of CO_2 for the curve 1, $\text{CO}_{2,E2}$ -exhaustion concentration of CO_2 for the curve 2, $\text{CO}_{2,E3}$ -exhaustion concentration of CO_2 for the curve 3, $\text{CO}_{2,E4}$ -exhaustion concentration of CO_2 for the curve 4 and $\text{CO}_{2,E5}$ -exhaustion concentration of CO_2 for the curve 5). According to Figure 3 the adsorbed amounts of CO_2 increased with growth in flow rate (1.275 - 8.375) $\times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$.

4. Conclusions

It has been shown that zeolite NaX with large nanopore diameter of 0.74 ncm is one of the most suitable zeolite adsorbents for the recovery and capture of CO₂ due to its high adsorption capacity and high selectivity according to the Figure 1. On the other hand, the mathematical modelling for the adsorption process in the fixed reactor was developed in relation to CO₂ on NaX. The simulations of this model carry us to the following conclusions:

- The validation process was shown by comparison with the experimental and simulated results of CO₂, in the gas phase, as follows the Figure 1. The simulated curve has shown an excellent agreement in comparison with the experimental points. This is a good indication that there is no systematic discrepancy between model and experiments for the point set as a whole;
- It was allowed by the developed model a sensibility analysis with respect to CO₂ concentration within of the nanopores of the solid phase for different flowing rates (Q_g). As can be seen in the Figure (2), the concentrations of CO₂ increase when the flowing rates (Q_g) increase;
- It was shown the behaviour of the accountancy for the adsorbed amount of CO₂ in the nanopores of the performed simulations using different flowing rate (Q_g). Other variables can be tested to check the effect on adsorbed concentration of CO₂ such as the Initial adsorbed concentration of CO₂ on the solid particles q_{CO₂,0}.

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Appendix A

$$\alpha_1 = \frac{4Q_g}{\pi d_c^2}; \alpha_2(s) = s + k_{gs} \frac{3}{r_a} (1 - \varepsilon_s) \quad (A1)$$

$$\alpha_3 = k_{gs} \frac{3}{r_a} (1 - \varepsilon_s) \quad (A2)$$

$$\beta_1(s) = \frac{s}{D_{z,CO_2}} \left(1 + \frac{\rho_s k_{ad} K_{eq}}{s \rho_s K_{eq} + k_{ad}} \right) \quad (A3)$$

$$\beta_2(s) = \frac{\rho_s k_{ad} K_{eq}}{s \rho_s K_{eq} + k_{ad}} \quad (A4)$$

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