ABSTRACT

Natural clinoptilolite is a suitable adsorbent for polar molecules such as water, alcohols and many other adsorptive components and it is also very selective in removing sulfur dioxide at low concentrations from gaseous mixtures such as the undesired industrial waste gases. This paper investigates the fixed bed adsorption of sulfur dioxide by natural clinoptilolite in laboratory scale in order to determine the Intra Particle Mass Transfer Resistance of the process. Several experimental adsorption runs at different fixed bed lengths and gas flow velocities were made to achieve the Constant Pattern (CP) behavior and the CP–Breakthrough Curves (BTC) were further examined through their Breakthrough Points and statistical characteristics (1st absolute and 2nd central statistical moments) by means of the Intra Particle Linear Driving Force Model (LDFQ) and the simple linear Shilov’s relation in order to estimate the Intra Particle Mass Transfer Resistance. The results were quantitatively discussed in comparison to the Macro Pore Mass Transfer Resistance, using the binary molecular and Knudsen diffusivities and in accordance with the bi-porous structure of the zeolite as well. A comparison was also made to the Intra Particle Mass Transfer Resistance from the Intra Particle Diffusion Model (DMQ) at Langmuir and at linear equilibrium.

Keywords: fixed bed adsorption, breakthrough curves, natural zeolite, clinoptilolite, sulfur dioxide, LDFQ model, Shilov’s equation.

INTRODUCTION

Due to the specific breakthrough behavior the fixed bed adsorption is one of the highly successful technological methods to separate gaseous mixture or to remove waste gases contaminants such as sulfur dioxide at low concentration levels. Beside of the influence of the film diffusion and the axial dispersion in industrial scaled fluid-solid processes, the fixed bed breakthrough time is strongly connected with the Intra Particle Mass Transfer Resistance, which in gaseous phase is usually determined from laboratory column experiments, where the influence of the hydrodynamics could be significantly reduced in the experimental set up. Different mathematical models such as the Intra Particle Diffusion Model (DMQ), the Intra Particle Linear Driving Force models (LDFQ) or other more detailed diffusion or non-linear kinetic models or combined diffusion-kinetic models can be used to examine the experimental fixed bed laboratory data [1-10]. The estimation of the Mass Transfer Resistances (diffusion coefficients) is usually made either by direct Curve Fitting (CF) or by means of some specific elution curve characteristics such as statistical moments, HETP, Curves slope, Length of the Mass Transfer Zone etc. [2, 3, 5, 6, 10 - 12].

One of the most useful mathematical techniques at linear adsorption equilibrium is the statistical moment’s method, which was firstly introduced by Kubin [12] and...
which was very successful applied to fixed bed curves examination of different adsorption systems. Especially useful is the method, if more than one Local Intra Particle Mass Transfer Resistances are important, as for example during the adsorption in the bi-porous zeolite particles, where beside the Macro Pore Diffusion, also the Intra Crystalline Diffusion plays a significant role [3, 5, 6]. Also, there are many well known analytical solutions of the concentration time behavior, which are used to examine quantitatively the Intra Particle Mass Transfer Resistance from fixed bed adsorption data [13 - 15]. At non–linear adsorption equilibrium the quantitative examination of the fixed bed elution curves is mostly restricted by Curve Fitting (CF) of the experimental data to different kind of numerical solutions. In some special cases, such as at extremely concave, or Langmuir, or Freundlich type of equilibrium and at Constant Pattern (CP) conditions, simple analytical solutions are also well known [16 - 22], which strongly simplify the mathematical examination. Because of their simplicity these solutions are preferably recommended [1 - 10] for the examination of such complex experimental data as the fixed bed Breakthrough Curves (BTC). A quite simple non - linear analytical solution of the Linear Driving Force Model (LDF) is also known [5] for the combined case of simultaneous Intra Particle and External Mass Transfer Resistances at Langmuir equilibrium.

Under CP conditions a very promising combination could be outlined between the simplest linear analytical solution [1, 2] of Shilov [16] on the one side, which does not distinguish whether on the non-linearity type of the adsorption isotherm nor on the type of the Mass Transfer Resistances (overall, internal or external diffusion, or another local type) and on the other - the CP analytical solutions of LDFC [1, 2, 5, 8 - 10], which was originally derived by JZT – Michels [18, 19] and also of LDFQ [5, 8 - 10] originated from Hall et al. [20].

The aim of the present work was to examine mathematically a set of experimental Breakthrough Curves (BTC), derived for the SO$_2$ adsorption on natural clinoptilolite by means of the simple Intra Particle Linear Driving Force model (LDFQ) at Non-Constant (Non-CP) and at Constant Pattern (CP) conditions and to apply it to the linear Shilov’s equation in order to derive the quantitative value of the dominant Intra Particle Mass Transfer Resistance of the SO$_2$ adsorption on natural zeolite clinoptilolite.

Modeling equations

**Constant Pattern Velocity**

When traveling through the fixed bed at non-linear concave equilibrium, the real concentration profile of the adsorbed substance passes through two main time periods. In the first time period (Non-Constant Pattern) the concentration profile changes its shape continuously in accordance with the opposite action of two factors - the concavity factor of the adsorption isotherm on the one side and the overall mass transfer resistance (including film diffusion and axial dispersion) on the other. The concavity factor causes a shrinking and the overall mass transfer resistance - a flattering of the concentration profile. Therefore in this period each point of the concentration profile travels with its own velocity, according to the particular slope of the adsorption isotherm. In the second time period (Constant Pattern) the influence of these two factors becomes balanced and the shape of the concentration profile maintains constant regardless of the residence time in the fixed bed and all concentrations points of the concentration profile travel with a constant velocity - the Constant Pattern Velocity ($w_C$). There is only one point from the concentration profile - the point of the Center of Gravity (CG), which travels with a unique constant velocity in both periods and which is connected only with the overall equilibrium mass balance of the adsorption process. The CP-velocity ($w_C$) is therefore the traveling velocity of the Center of Gravity. The time needed by the Center of Gravity to reach the outlet of the fixed bed, i.e. to pass the fixed bed length ($L$) is the Mean Residence (Retention) Time ($t_R$) and the relation between ($t_R$) and ($w_C$) will be given by eq. (1):

$$t_R = \frac{L}{w_C} \quad (1)$$

where:

- $w_C$ CP-velocity of the concentration profile, ($cm \ s^{-1}$)
- $t_R$ Mean Residence (Retention) Time of the concentration front in the bed, ($s$)
- $L$ Fixed Bed Depth (length) (cm).

If all points of the concentration profile would reside in the fixed for a time ($t_R$) the concentration profile will be rectangular and the full static adsorption capacity ($q_a$), according to the inlet gas concentration ($C_0$) will be reached. Therefore ($t_R$) is connected to the overall equilibrium mass balance by means of eq. (2) and eq. (3), respectively:

$$V C_0 t_R = V_e C_0 + q_a V_{adv} \quad (2)$$
\[ t_R = \frac{L}{w} [\varepsilon + (1 - \varepsilon)K_o] \]  
(3)

\[ \varepsilon = \frac{V_c}{V} \quad 1 - \varepsilon = \frac{V_{ads}}{V} \]  
(4)

\[ K_o = \frac{q_o}{C_o} \]  
(5)

where:

- \( t_R \) is Mean Residence (Retention) Time, (s)
- \( V \) is Overall volume of the fixed bed, (\( cm^3 \))
- \( V_c \) is Volume of the particle free fixed bed space, (\( cm^3 \))
- \( V_{ads} \) is Fixed bed particle volume, (\( cm^3 \))
- \( V \) is Gas flow rate, (\( cm^3/s \))
- \( L \) is Fixed bed depth (length) (\( cm \))
- \( w \) is Gas flow velocity in the full square section of the fixed bed column (\( cm/s \))
- \( \varepsilon \) is Fixed bed porosity,
- \( K_o \) is Equilibrium phase distribution constant
- \( C_o \) is Initial (column inlet) gas phase concentration; (\( g/cm^3 \))
- \( q_o \) is Equilibrium (volume average) particle concentration related to the initial (column inlet) gas phase concentration \( C_o \) – static capacity; (\( g/cm^3 \)).

Therefore according to eq. (1) and eq. (3) the CP-velocity (\( w_c \)) will be:

\[ w_c = \frac{w}{\varepsilon + (1 - \varepsilon)K_o} \]  
(6)

**Breakthrough Time and Mass Transfer Resistance**

Due to the mass transfer the real concentration profile will not be rectangular and a Mass Transfer Zone (MTZ) along the bed will be formed, where the actual adsorption process takes place. Therefore the concentration profile points, which are in front of the Center of Gravity, will reach the outlet of the bed (\( L \)) earlier that the CG point and these one, which are behind him - later. The time, needed by the first point of the front part of the real concentration profile to reach the outlet of the fixed bed (\( L \)) is the Breakthrough Time or the Bed Service Time (\( t_B \)). At this time only a part of the adsorption equilibrium capacity will be reached, the dynamic adsorption capacity and the rest part of the equilibrium adsorption capacity maintains unused. The higher the overall mass transfer resistance - the wider the MTZ, the smaller the dynamic capacity, the wider the difference between the Mean Residence Time (\( t_R \)) and Breakthrough Time (\( t_B \)).

The time difference (\( t_0 \)) - eq. (7) is the time equivalent of the mass transfer resistance is characterized as the Time Delay due to the mass transfer.

\[ t_0 = t_R - t_B \]  
(7)

At Constant Pattern (\( t_0 \)) will also be constant, regardless of (\( L \)). Therefore, taking into account Eqn. (1), (\( t_B \)) can simply be determined by the linear relation - eq. (8) and eq. (9), respectively, the last one known as the Shilov’s equation [1, 2, 16].

\[ t_B = \frac{L}{w_c} - t_0 \]  
(8)

\[ t_B = kL - t_0 \]  
(9)

\[ k = \frac{1}{w_c} \]  
(10)

where:

- \( t_B \) is Breakthrough Time, (s)
- \( \mu_1 \) was characterized by Shilov’s [16] as the Fixed Bed Protection Time, (\( t_0 \)) - as Loss on Fixed Bed Protection Time and (\( k \)) - as the Fixed bed Protection Coefficient.

Therefore making experiments at different fixed bed lengths (\( L \)) at CP, one can simply estimate the values of (\( t_B \)) and determine by means of the Shilov’s equation the mass transfer time equivalent (\( t_0 \)). (\( t_0 \)) can be further connected with the particular mass transfer resistance, which is acting under the particular experimental conditions is the fixed bed adsorption process.

In taking into account, that for a real (non-rectangular) concentration profile (\( t_R \)) is equivalent to the value of the 1st absolute statistical moment of the Breakthrough Curve (\( \mu_1 \)). - eqs. (11) and (12), the Shilov’s relation can finely be expressed by means of eq. (13).

\[ t_R = \frac{1}{\mu_0} \int_0^C \rho dC \]  
(11)

\[ \mu_0 = C_o \]  
(12)
where:
\[ \mu_1 \] 1st absolute statistical moment (s)
\[ \mu_0 \] 0th absolute statistical moment, (g cm\(^{-3}\));
\[ C \] Current time gas phase concentration at the column outlet (g cm\(^{-3}\)).

\[ t_B = \mu_1 - t_0 \] (13)

In contrast to the original Shilov’s equation - eq. (9), which gives a various slope of the linear dependence at different flow rates \((w)\), the slope in eq. (13) is \((1)\), regardless of the flow rate. Further more, if the flow rate \((w)\) does not affect the overall mass transfer resistance, i.e. if it does not influence the Time Delay \((t_0)\), as for example is the case of negligible External Mass Transfer Resistance (or axial dispersion), and if the Intra Particle Mass Transfer Resistance \((\delta_S)\) is the only one dominant mass transfer parameter, then the experimental values for \((t_B)\) and \((\mu_1)\), derived from the BTC at different flow rates \((w)\), will coincide on a unique linear dependence with a slope of \((1)\) and a time constant \((t_0)\), which is strongly proportional to Intra Particle Mass Transfer Resistance \((\delta_S)\).

**Analytical Solution of LDFQ**

The ordinary form of the phase mass balance equations, including the Intra Particle Linear Driving Force Model (LDFQ) at Langmuir equilibrium can be expressed by eqs. (14) - (18):

\[ \varepsilon \frac{\partial C}{\partial t} + (1-\varepsilon) \frac{\partial q_m}{\partial t} = -w \frac{\partial C}{\partial z} \] (14)

\[ \frac{\partial q_m}{\partial t} = k_s (q^* - q_m) \] (15)

\[ q^* = q_{mon} \frac{bC}{1+bC} \] (16)

\[ z = 0 \quad \rightarrow \quad C = C_o \] (17)

\[ t \geq 0 \quad \rightarrow \quad C = C_o \] (18)

\[ z \] Fixed bed length coordinate (cm)

\[ t \] Time coordinate (s)

\[ q_{mon} \] Particle (volume averaged) concentration, (g cm\(^{-3}\))

\[ q_{mon} \] Mono layer adsorption capacity, (mol cm\(^{-3}\))

\[ b \] Adsorption equilibrium constant, (cm\(^3\) mol\(^{-1}\))

\[ q^* \] Equilibrium (volume average) particle concentration, corresponding to the surrounding gas phase concentration \(C_o\), (g cm\(^{-3}\));

\[ k_s \] Intra Particle Mass Transfer Coefficient, (s\(^{-1}\)).

At CP this model obeys an analytical solution [5, 8, 10], which was originally derived by Hall et al. [20] and which can be expressed in terms of the Intra Particle Mass Transfer Resistance \((\delta_S)\) as follows:

\[ t = \mu_1 - \delta_S \left[ \frac{1}{\varphi_o} Ln(1 - C / C_o) - \frac{(1-\varphi_o)}{\varphi_o} Ln(C / C_o) + 1 \right] \] (19)

\[ \delta_S = \frac{1}{k_s} \] (20)

\[ \varphi_o = \frac{q_o}{q_{mon}} = \frac{bC_o}{1+bC_o} \] (21)

where:

\[ t \] Process duration for reaching \(C / C_0\) at the fixed bed outlet, (s)

\[ \delta_S \] Intra Particle Mass Transfer Resistance, (s)

\[ \varphi_o \] Concavity factor of the Langmuir isotherm.

In comparing the Shilov’s eq. (12) with the analytical solution (19) at \((t_B)\) and taking \((t_B)\) as the corresponding time coordinate of \((0/\varphi_o)\), then the mass transfer time \((t_0)\) can be expressed in terms of \((\delta_S)\) for the case of dominant Intra Particle Mass Transfer Resistance.

\[ t_0 = \delta_S \left[ \frac{1}{\varphi_o} Ln(0.9) - \frac{(1-\varphi_o)}{\varphi_o} Ln(0.1) + 1 \right] \] (22)

Therefore, if after the initial period of Non-CP behavior, where the Breakthrough Time \((t_B)\) is non - linearly proportional to \((\mu_1)\), the further data coincide with Shilov’s line, a stationary concentration wave is build and the Constant Pattern behavior is established. \((t_B)\) would give the value of the Intra Particle Mass Transfer Resistance \((\delta_S)\). Eq. (22) was used in the present work to estimate the Intra Particle Mass Transfer Resistance \((\delta_S)\) from the \((t_B)\) - \((\mu_1)\) data of different experimental elution curves at Constant Pattern.

**Breakthrough Curve Dispersion**

The establishing of Constant Pattern behavior can
checked by the constancy of Breakthrough Curve dispersion, using the 2nd central statistical moment \( \mu_2 \) [2, 23] - eq. (23)

\[
\mu_2 = \frac{1}{\mu_0} \int_0^c (t - \mu')^2 dC = \text{const}
\]  

(23)

where \( \mu_2 \) is 2nd central statistical moment of the breakthrough curve, \( \mu \), and it is given by eq. (30):

\[
\mu_2 = 2 \mu'_1 \delta_S^{ll}
\]  

(30)

There are some quasi-empirical quantitative distinguishing criteria for the Non - CP and the CP behavior on the base of \( \mu_2 \), which were examined by Radeke et al. [23] by means of numerical simulations on the Intra Particle Diffusion Model (DMQ) at Langmuir type equilibrium - eq. (24) - (29).

1st Non-CP Zone - eq. (24) of linear proportionality - eq. (25) between \( \mu_2 \), \( \mu'_1 \) and the Intra Particle Mass Transfer Resistance at linear adsorption equilibrium(\( \delta_S^{ll} \)):

\[
\frac{\mu_2}{2(\mu'_1)^2} > 0.2
\]  

(24)

\[
\mu_2 \approx 2 \mu'_1(\delta_S^{ll})(1 - \varphi_0 / 2)
\]  

(25)

2nd Non-CP Zone - eq. (26) - of non-linear proportionality - eq. (27) between \( \mu_2 \), \( \mu'_1 \) and \( \delta_S^{ll} \):

\[
0.06 \varphi_0^2 > \frac{\mu_2}{2(\mu'_1)^2} > 0.2
\]  

(26)

\[
\mu_2 \approx 2 \mu'_1(\varphi_0 / (\delta_S^{ll})^{1 + \varphi_0})
\]  

(27)

3rd CP Zone - eq. (28), where \( \mu_2 \) maintains constant regardless of \( \mu'_1 \) - eq. (29). It is also parabolic proportional to \( \delta_S^{ll} \).

\[
\frac{\mu_2}{2(\mu'_1)^2} < 0.06 \varphi_0^2
\]  

(28)

\[
\mu_2 \approx 2(\delta_S^{ll})^2 \varphi_0^{-2}
\]  

(29)

At a given Intra Particle Mass Transfer Resistance \( \delta_S^{ll} \) and at a given isotherm concavity factor \( \varphi_0 \) all three zones coincide to a unique dependence between \( \mu_2 \) and \( \mu'_1 \), which leads to a plateau corresponding to the CP value of \( \mu_2 \). In the relations (25), (27) and (29) the Intra Particle Mass Transfer Resistance \( \delta_S^{ll} \) corresponds to the value at linear equilibrium, at which the relation between \( \mu_2 \), \( \mu'_1 \) and \( \delta_S^{ll} \) is also linear and it is given by eq. (30):

\[
\mu_2 = 2 \mu'_1 \delta_S^{ll}
\]  

(30)

Numerical LDFQ solution in the Non-CP Zone

In the Non-CP zone a numerical solution can be applied to describe the Breakthrough Curves. The transferred dimensionless form of LDFQ, which is derived from the original mass balance equation - eqs. (14) - (18) and which is used for the numerical solutions, is given by Eqs. (31) - (35).

\[
\frac{dX}{dZ} = -\left(1 - \frac{\varepsilon}{\varepsilon_0}\right) \varepsilon \frac{dY_m}{d\theta}
\]  

(31)

\[
\frac{dY_m}{d\theta} = k_s(Y^* - Y_m)
\]  

(32)

\[
Y^* = \frac{\alpha X}{1 + (\alpha - 1)X}
\]  

(33)

\[
Z = 0
\]

(34)

\[
\theta > \frac{z}{w} \rightarrow X = 1
\]  

(35)

where:

\( X \), \( Y_m \) and \( Y^* \) – new dimensionless concentrations - eq. (36);

\( \theta \) and \( Z \) – new dimensionless time and space coordinates - eq. (37);

\( \alpha \) – selectivity coefficient - eq. (38);

\[
X = \frac{C}{C_o}, \quad Y_m = \frac{q_m}{q_o}
\]  

(36)

\[
\theta = t - \frac{z}{w} \quad Z = \frac{z}{w}
\]  

(37)

\[
\alpha = 1 + bC_o = \frac{1}{1 - \varphi_0}
\]  

(38)

In contrast to \( \varphi_o \), which varies between 0 (for the non-selective linear equilibrium) and 1 (for the most
highly selective rectangular equilibrium), \( \alpha \) varies from (1) to \((\infty)\), respectively. In the present work, the dimensionless LDFQ model was solved by the extended predictor-corrector method of Euler and was used for calculating some of the Breakthrough Curves (BTC) in the Non-CP region.

Fluid Velocity – External Mass Transfer

If, as mentioned, the Intra Particle Mass Transfer \( \delta_f = \delta_f \) is dominant, the gas flow velocity \( w \) will cause only a lowering of the slope in the Shilov’s eq. (8) and eq. (9), respectively, although it would not affect the Mass Transfer Time Daley constant \( t_f \). In contrast, in the form of eq. (13) the gas velocity should not affect whether the slope \((1)\) nor \((t_f)\). If the External Mass Transfer Resistance would play a role, it would affect \((t_f)\) and even at CP conditions eq. (13) would not give a straight line, if the variation of \((\mu_f)\) is due to the fluid velocity \( w \). Therefore the Shilov’s straight line at CP in eq. (13) could be used as a criterion for checking the dominance of the Intra Particle Mass Transfer Resistance over the External Mass Transfer Resistance.

In comparison to the LDFQ analytical solution - eq. (19) - the corresponding analytical solution - eq. (39) - of the External Linear Driving Force Model (LDFC) - eq. (40) at Constant Pattern [1, 6, 8, 10] gives a quite different Breakthrough Curve distribution (The LDFC analytical solution was first derived by JZT [18] and Michels [19]).

\[
t = \mu_i - \delta_f \left[ \left(1 - \frac{\varphi_o}{\varphi_f}\right) \ln(1 - C/C_o) - \frac{1}{\varphi_f} \ln(C/C_o) - 1 \right]
\]

\[
\frac{\partial q_m}{\partial t} = k_j a (C - C^*)
\]

where:
\( k_j \) is External Mass Transfer Coefficient, according to the Sh - number, \((cm \ s^{-1})\), \((s_p = \frac{k_j}{D_{so}})\),
where:
\( \delta_f \) External Mass Transfer Resistance, according to \((k_f)\), \((s)\), \(\delta_f = \frac{k_j}{k_f}a\);
\( a \) Specific external surface area of the particles, \((cm^{-2})\).

Eq. (39) was used in the present work to illustrate the difference of both Linear Driving Force Models - LDFQ and LDFC.

**EXPERIMENTAL**

In the present work several fixed bed experiments were made and several Breakthrough Curves were measured at different flow rates \((\dot{V})\) and fixed bed lengths \((L)\) in order to achieve different Mean Residence Times \((\mu_i)\), (Table 1). The experiments were done at room temperature \((~20^\circ C)\) in a laboratory glass column of 16 mm in diameter, where a certain amounts \((G_{\text{ads}})\), between 20 and 40 \((g)\), of thermal activated zeolite particles of 1.6 - 2.0 mm sieve size were filled in.

The activation of the zeolite was achieved prior to each experiment by heating for 3 h to about 380°C in a separate thermally resistant glass column in order to evacuate the adsorbed water molecules from the fresh zeolite samples. During the heating a dry air flow was also supplied to the activation column. Before entering the adsorption column the carrier gas, atmospheric air, was dried in a second adsorption column, filled with dehydrated and activated zeolite particles. Then the air was mixed with \(SO_2\) (obtained from a high-pressure bottle) in a separate glass pearls column, so that an initial \(SO_2\) gas phase concentration of about 0.8 - 0.9 \((Vol\%)\) was achieved. The \(SO_2\) concentration at the inlet of the column and at the current outlet concentration was checked iodimetrically.

The natural zeolite samples originate from the Eastern Rhodopes region in Bulgaria with a mineralogical clinoptilolite content of about \(~87\%\). The apparent particle density and the specific internal surface areas by BET were measured to be about \(1.3 \,(g \,cm^{-3})\) and 20 \((m^2 \,g^{-1})\), respectively [24].

**RESULTS AND DISCUSSION**

Equilibrium Adsorption Capacity

The equilibrium mass balance data are shown in Fig. 1. There the experimental values of \((\mu_i)\), which were determined by the simple Simpson numerical integration of the BTC using eq. (11) with a constant integration step of \((0.05 \,C/C_o)\), are plotted as a linear function of the \((G_{\text{ads}}/\dot{V})\) parameter of each fixed bed experiment (Table 1). From the slope of the line \((N = 4392.6)\) the integral value of the adsorption equilibrium capacity of the zeolite was determined \((a_{so} = 105.2 \,mg \,g^{-1})\) according to eq. (41):

\[
\mu_i \approx \frac{G_{\text{ads}}}{\dot{V}} \frac{a_0}{y_{0\rho_{SO_2}}}
\]
where:

- $y_0$: Column inlet concentration of SO$_2$ (vol %);
- $a_0$: Equilibrium capacity of the zeolite at $y_0$, (g g$^{-1}$);
- $\rho_{SO_2}$: SO$_2$ vapor density at 20°C, (g cm$^{-3}$).

A more detailed investigation of the SO$_2$ adsorption equilibrium in a wider concentration and temperatures range was made in an earlier work [24], where also the co-adsorption of SO$_2$-water mixtures are summarized. The single adsorption equilibrium relation was found to be of the Langmuir type

$$a_0 = 107.7 \text{ mg g}^{-1}$$

According to this relation at $y_0 = 0.9$ Vol%, the equilibrium adsorption capacity $a_0 = 107.7$ mg g$^{-1}$ and this value is quite close to the integral value mentioned above. Therefore, at the present experimental conditions the concavity factor ($\varphi_0$) of the adsorption isotherm is approximately 0.7.

**Intra Particle Mass Transfer Resistance**

The experimental BTC and their mass transfer characteristics - Breakthrough Points at $C / C_0 = 0.1$ ($t_B$) and at $C / C_0 = 0.9$ ($t_{end}$) and curve dispersion ($\mu_1$) are shown in Figs. 2 - 6 and also in Table 1. The values of ($\mu_2$) were calculated by the above simple numerical integration as well, using eq. (23).

In Fig. 2 are shown some real BTC in order to illustrate qualitatively the transition of the BTC shape by varying the Mean Residence Time ($\mu_1$). In Fig. 3 and 4 the same Breakthrough Curves are shown in the reduced time scale ($t - \mu_1$) in order to illustrate more clearly the transition of the curve shape to a constant one at higher Mean Residence Times ($\mu_1$). In Fig. 5 are shown the BTC dispersion characteristics ($\mu_2$) for all experimental BTC in order to illustrate clearly the CP establishing as well. In Fig. 6 are shown the experimental Breakthrough Points at $C / C_0 = 0.1$ ($t_B$) and at $C / C_0 = 0.9$ ($t_{end}$) in the

<table>
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<th>$N$ of exp.</th>
<th>$V$, l h$^{-1}$</th>
<th>$G_{ads}$, g</th>
<th>$\mu_1$, min</th>
<th>$\mu_2$, min$^{-2}$</th>
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<tr>
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<td>11.5</td>
<td>3.5</td>
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<tr>
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<td>1044</td>
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<td>6.7</td>
<td>9.9</td>
<td>3.5</td>
<td>11.5</td>
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</tbody>
</table>

Table 1. Experimental conditions.
Shilov’s plot of eq. (13). According to eq. (19) the data for \( t_{\text{end}} \) will correlate to a different Mass Transfer Time Daley constant \( t_0 \). In all these figures the transition from Non-CP to CP is clearly indicated, although Fig. 5 shows the most pronounced indication of the CP region.

The experimental runs, which belong to the CP region according Fig. 5 were taken in the Shilov’s plot (Fig. 6) in order to extrapolate from the \( t_0 \) and \( t_{\text{end}} \) data the corresponding Mass Transfer Time Daley constants \( t_0 = 9.8 \text{ min} \) \( \rightarrow \) \( t_0^\text{end} = 5.1 \text{ min} \) and \( t_0 = 11.8 \text{ min} \) \( \rightarrow \) \( t_0^\text{end} = 5.0 \text{ min} \), respectively. From these constants a nearly equal Intra Particle Mass Transfer Resistance \( \delta_s \approx 5 \text{ min} \) was estimated according to eq. (22) and eq. (42), respectively.

\[
 t_{\text{end}}^0 = \delta_s \left[ \frac{1}{\varphi_o} \ln(0.1) - \frac{(1-\varphi_o)}{\varphi_o} \ln(0.9) + 1 \right] \quad (42)
\]

As a comparison to the values of \( \delta_s \), estimated above on the base of the Linear Driving Force Model (LDFQ) from the Shilov’s plot, the linear Intra Particle Mass Transfer Resistance can also be determined from the CP-data of \( \mu_1 \) – Fig. 5 using eq. (29) by means of the Intra Particle Diffusion Model (DMQ) [23]. For Langmuir type equilibrium the Intra Particle Mass Transfer Resistances of both models LDFQ \( - \delta_s \) and DMQ \( - \delta_s^{\text{DMQ}} \) are connected [5] by the semi-empirical relation - eq. (43):

\[
 \delta_s^{\text{DMQ}} = (1 - 0.192 \varphi_o^3) \delta_s
\]

(43)
The corrected value of the Intra Particle Mass Transfer Resistance, estimated by means of eq. (29) on the base of the Intra Particle Diffusion Model from the experimental $(\mu )$ – CP-data in Fig. 5 is $\delta_{S}^{\text{exp}} \approx 4.5 \text{ min}$ and it is in very good agreement with the value $\delta_{S} \approx 5 \text{ min}$, determined from the Shilov’s plot in Fig. 6.

In Figs. 2 - 4 are also shown the analytical LDFQ solutions - eq. (19) of the BTC by setting $\delta_{S} = 5.0 \text{ min}$ and it is evident from these data, that the coincidence of the whole BTC plot with the analytical LDFQ solution is quite well. In contrast, the LDFC analytical solution - eq. (39) reproduces a quite different BTC distribution in comparison to the LDFQ model, Fig. 7. This plot, as well as the consolidated Non-CP and CP regions in Figs. 5 and 6 are an evidence for supporting the dominance of the Intra Particle Mass Transfer Resistance ($\delta_{S}$) over the External Mass Transfer Resistance ($\delta_{p}$) in the present fixed bed process conditions.

Local Macro Pore Diffusion Resistance

As known, the zeolite particles are bi-porous. Therefore the estimated Intra Particle Mass Transfer Resistance ($\delta_{S}$) will represent the Local Macro Pore ($\delta_{p}$) and the Local Intra Crystalline ($\delta_{z}$) Resistances as a whole and at linear equilibrium will be connected to ($\delta_{p}$) and ($\delta_{z}$) by eq. (44) [3].

$$\delta_{S} = \delta_{p} + \delta_{z}$$  \hspace{1cm} (44)

where ($\delta_{p}$) and ($\delta_{z}$) can be explained by means of eq. (45) and (46), respectively [3]:

$$\delta_{p} = \frac{R_{z}^{2}K_{p}}{15\varepsilon_{p}D_{p}}$$  \hspace{1cm} (45)

$$\delta_{z} = \frac{R_{z}^{2}}{15D_{z}}$$  \hspace{1cm} (46)

where:

- $\delta_{p}$ Local Macro Pore Diffusion Resistance, $(s)$
- $D_{p}$ Macro Pore Diffusion Coefficient, $(cm^{2}s^{-1})$
- $\varepsilon_{p}$ Particle porosity
- $\delta_{z}$ Local Intra Crystalline Diffusion Resistance, $(s)$
- $R_{z}$ Mean crystal radius, $(cm)$
- $D_{z}$ Intra Crystalline Diffusion Coefficient, $(cm^{2}s^{-1})$.

Although eq. (44) is strongly fulfilled for a linear phase equilibrium, it was experimentally illustrated by the authors [25, 26], that the linear additive relation between ($\delta_{p}$) and ($\delta_{z}$) to ($\delta_{S}$) is also evident for the strongly non-linear equilibrium system of the Pb$^{2+}$ ion exchange on clinoptilolite [25], as well in the case of the alcohol vapors adsorption (methanol, propanol, butanol) on the same adsorbent [26]. The quantitative distinguishing of both Local Intra Particle Mass transfer Resistances can easily be done by varying the particle size - eq. (45).

In this study no experimental runs were done by varying the particle size, therefore the Macro Pore Diffusion Coefficient ($D_{p} \approx 0.04 \text{ cm}^{2}\text{s}^{-1}$) was approximately estimated by eq. (47), using the binary ($D_{AB} = 0.1 \text{ cm}^{2}\text{s}^{-1}$) [27] and the Knudsen ($D_{K} = 0.065 \text{ cm}^{2}\text{s}^{-1}$) diffusion coefficients [28] - eq. (48).

$$\frac{1}{D_{p}} = \frac{1}{D_{AB}} + \frac{1}{D_{K}}$$  \hspace{1cm} (47)

where:

- $D_{K}$ Knudsen diffusivity, $(cm^{2}s^{-1})$
- $D_{AB}$ Binary molecular diffusivity, $(cm^{2}s^{-1})$
- $D_{K} = 9700 \frac{r_{p}^{2}}{M} \sqrt{T} x 10^{-8}$  \hspace{1cm} (48)

$M$ Molecular mass, $(g\ mol^{-1})$;
$T$ Temperature, $(K)$;
$r_{p}$ Mean pore radius, $(A)$.

The mean pore size ($r_{p} \approx 307.4$), used in eq. (48), was estimated [28] by eq. (49) by means of the values of the internal pore surface area $(S = 20 \text{ m g}^{-1})$ and of the apparent particle density ($\rho_{ap} = 1.3 \text{ g cm}^{-3}$), mentioned above. The particle porosity ($\varepsilon_{p} = 0.4$) was calculated by the values of the apparent and the true zeolite densities ($\rho_{s} = 2.2 \text{ g cm}^{-3}$) [29] - eq. (50).

$$\rho_{ap} = \rho_{z} - \rho_{s}$$  \hspace{1cm} (49)

$$\varepsilon_{p} = \frac{\rho_{ap} - \rho_{s}}{\rho_{s}}$$  \hspace{1cm} (50)
Table 2. Numerical data for (δ_S) in the Non-CP region.

<table>
<thead>
<tr>
<th>Exp. N</th>
<th>Exp. 15</th>
<th>Exp. 11</th>
<th>Exp. 8</th>
<th>Exp. 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>μ₁, min</td>
<td>6.7</td>
<td>17.4</td>
<td>31.4</td>
<td>57.2</td>
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<tr>
<td>δ_S, min</td>
<td>1.9</td>
<td>3.3</td>
<td>4.5</td>
<td>4.8</td>
</tr>
</tbody>
</table>

\[ r_p = \frac{2ε_p}{Sρ_{ads}} \times 10^4 \]  
(49)

\[ ε_p \approx 1 - \frac{ρ_{ads}}{ρ_z} \]  
(50)

where:
- \( ρ_{ads} \): Apparent particle density, \((g \text{ cm}^{-3})\);
- \( S \): Internal pore surface area, \((m^2 \text{ g}^{-1})\).

The Local Macro Pore Diffusion Resistance \((δ_p = 3.2 \text{ min})\) determined by the value of \( D_s = 0.04 \text{ cm}^2 \text{s}^{-1}\) confirms quite well with the value of the overall Intra Particle Mass Transfer Resistance \((δ_S)\), mentioned above, being only a part of it. The Intra Crystalline Mass Transfer Resistance \((δ_z)\) will approximately correspond to the difference of \((δ_S)\) and \((δ_p)\).

**Intra Particle Mass Transfer Resistance at Non-Constant Pattern**

In Figs. 2, 3, 5 and 6 only a part of the BTC belongs to the CP region. In the Non-CP region the numerical solution of the LDFQ model was used to adjust the Intra Particle Mass Transfer Resistance \((δ_S)\) to the experimental BTC – data, Table 2.

In Table 2 the value for Exp. 1, which belongs to the CP region, is quite close to the value, derived above from the Shilov’s plot, whereas the other Non-CP values of \(δ_S\) - Exp. 8, 11, 15 - deviate in a decreasing non-linear tendency with \(μ_1\), which is similar to the Langmuir type. Therefore Non-CP Intra Particle Mass Transfer values at Non-CP should be understood only as effective non-linear quantitative parameters, which can not be directly connected to the real values of the Intra Particle Diffusion Coefficients. In contrast the CP-value of \(δ_S\), which was derived by the Shilov’s plot, is quite close to the value at linear equilibrium, as examined above by the relation of Radeke [23] by means of eq. (29).

**CONCLUSIONS**

A simple experimental and mathematical procedure was derived in the present work to examine quantitatively the Intra Particle Mass Transfer Resistance during the fixed bed adsorption in a laboratory column of SO\(_2\) from gaseous mixtures on natural zeolite - clinoptilolite using Breakthrough Curves in the Constant Pattern region. A modified linear Shilov’s plot was applied in the investigation, which includes the 1st absolute statistical moments of the BTC and which consolidates the slope of the Shilov’s line to unity (1) and the line intercept - to the analytical CP – solution of the Intra Particle Linear Driving Force Model (LDFQ). Also, the estimated quantitative value of the Intra Particle Mass Transfer Resistance is quite reasonable in comparing it to the Macro Pore Diffusion Resistance, extrapolated from the values of the binary molecular and Knudsen diffusivities for SO\(_2\) in a mixture with air. It was also illustrated, that the CP–LDFQ Intra Particle Mass Transfer Resistance is quite close to the CP-DMQ Intra Particle Mass Transfer Resistance, which is correlated to the Intra Particle Mass Transfer Resistance at linear equilibrium as well. And finely, under Non-CP conditions only a formal non – linear model parameter can still be examined in accordance to the Intra Particle Mass Transfer Resistance, which could not serve as a meaningful physical characteristics for the mass transfer mechanisms in the zeolite particles.

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