The Determination of Mass Transfer Characteristics of a Column for Sulphur Dioxide Adsorption in 13 X Zeolite Working in Unsteady-State Regime

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In the present work, the mass transfer characteristics such as the length of mass transfer unit (LMTU), the break through time and column saturation time have been studied in the case of sulphur dioxide adsorption on 13 X zeolite. The adsorption column was working in unsteady-state conditions. For these determinations a chromatographic method has been used, permitting the direct inregistration of breakthrough curves, whose shape depends on adsorption conditions (gas concentration, temperature, the size of adsorbent grains, gas velocity). The method is very sensitive, reflecting all changes of adsorption parameters.

Keywords: zeolites; adsorption in unsteady-states regime; mass transfer unit; breakthrough curves

Large combustion plants contribute greatly to emissions of sulfur dioxide, nitrogen oxides and dust, so it is necessary to reduce these emissions to the requirements of the best available techniques [1, 2].

In a previous paper [3, 4] a chromatographic method has been presented permitting the direct obtention of breakthrough curves. The main advantages of this method are his sensitivity and the possibility to reflect continously all the changes of adsorption parameters.

The determination of breakthrough curve has been studied using theoretical models [3-14] and practical methods as well [15-24].

Theoretical models developed for determination of breakthrough curves in adsorption columns working in unsteady-state regime are generally based on the following assumptions:
- the temperature remains practically constant throughout the adsorption bed;
- the pressure-drop along the bed is negligible under the experimental conditions;
- there is a constant fluid velocity throughout the bed.

Different adsorption models are presented in literature: pore diffusion model, surface diffusion model and bidispersed diffusion model.

In the surface diffusion model the diffusing molecules can not escape the force field of adsorbent surface. The surface diffusivity coefficient is generally much smaller than the other diffusivities.

In the bidispersaed diffusion model the macropore and micropore diffusion control the mass transfer simultaneously.

In the literature has been also proposed the pore diffusion with kinetic isotherm. This model is the same as pore diffusion model except that no equilibrium exist between pore and solid.

In all adsorption studies the two cases have been taken in consideration: single component adsorption and multicomponent adsorption. In the first case all mentioned models have been used. In the second case the extended Langmuir isotherm model has been also applied.

Large combustion plants contribute greatly to emissions of sulfur dioxide, nitrogen oxides and dust, so it is necessary to reduce these emissions to the requirements of the best available techniques [1, 2].

The most difficulties in using the mentioned theoretical model consist in adoption of a lot of simplifying assumption. That is why the theoretical breakthrough curves do not reflect exactly all changes of adsorption parameters.

The chromatografic method used in the present work put in evidence continuously all the adsorption conditions and the accidentaly changes of adsorption parameters [4].

Experimental part

In this work the 13X zeolite have been used as adsorbent. Two electronic controllers have been used for measure the flowrates of SO2 and N2. The two individual streams were mixed in a mixing chamber.

After mixing chamber, the gas having the concentration C0 passes through the adsorption column (being of 2 cm diameter and 40 cm high). The proposed physical model is based on the assumption that the gas adsorption occurs till the saturation of a limited zone L, defined as mass transfer unit (LMTU), whose length depends on adsorption conditions (gas concentration, temperature, adsorbent granule size, gas velocity). When the mass transfer unit attains the final outlet position, the gas concentration is continously increased from C = 0 to C = C0 in accordance with breakthrough curve 4 (fig. 1). That she is why the
breakthrough curve characterizes the adsorption process in unsteady-state conditions, permitting the calculation of all characteristic parameters (the length of mass transfer unit, the adsorption degree in dynamic conditions, the optimum number of LMTU and therefore the optimum adsorption column length).

The breakthrough curve is continuously recorded using the chromatographic device presented in figure 2 [4].

The gas containing sulfur dioxide, whose initial concentration is C₀, enters successively the aluminum channel 4 containing the electrical resistance R₀, adsorption column 2 and aluminum channel 5 containing the resistance R₅. Due to continuous SO₂ adsorption in column 2, its concentration continuously diminished, modifying the thermal conductivity of gas. This modification is recorded by the recorder 3, resulting the breakthrough curve.

Although the thermal conductivity of SO₂ is relatively small one (the thermal conductivity l of sulfur dioxide, at 25 C, is 2.08 x 10⁻⁵ cal/cm·s·grd) the chromatographic device is sensitive enough for breakthrough curve recording. It is evident that the sensitivity of device increases with the increasing of SO₂ concentration.

In the present work the following data have been used: C₀ = 0.25, 0.5 and 1%SO₂; the temperature was about 25 C; the grain size was about 1 mm and the gas velocity 0.4 m/s. The adsorbent was a commercial 13X zeolite.

Results and discussions

Using the chromatographic device presented in figure 2 the breakthrough curves have been obtained for different parameters, permitting the calculation of the length of mass transfer unit (LMTU) the adsorption degree θ in dynamic conditions, the breakthrough time tₚ, the column saturation time tₛ and the adsorption coefficient f = \( \frac{a}{a_0} \) (fig.1).

In order to determine the length of mass transfer unit (LMTU) the following relation has been used [1].

\[
L_{MTU} = \frac{t_E - t_S}{t_S - t_F} L = \frac{t_E}{t_S - t_F (1 - f)} \quad (1)
\]

where: L represents the length of adsorption column, cm
tₕ - the necessary time for column saturation, min
tₚ - the breakthrough time, min
tₛ - the time of displacement of LMTU, min
tₕ - the formation time of LMTU, min
f - the adsorption coefficient

Knowing the LMTU, the adsorption degree θₚ in breakthrough time tₚ can be determined, according to the relation:

\[
θₚ = \frac{Gₚ}{a_0 L}
\]

where:
Gₚ represents the quantity of SO₂ retained in breakthrough time, kmol
aₚ - the linear concentration of SO₂ adsorbed in time tₚ, kmol/cm

The data contained in the breakthrough curve put in evidence that:

\[
θₚ = \frac{a_0 L_S + a_0 L_{MTU} - a_0 (L_S + L_{MTU})}{a_0 (L_S - L_{MTU} (1 - f))}
\]

In these conditions:

\[
θₚ = \frac{L_{MTU} (1 - f)}{a_0 L} = \frac{1 - 1 - f}{n L_{MTU}}
\]

The relation (3) puts in evidence the dependence of adsorption degree \( θₚ \) on adsorption coefficient f and LMTU. The adsorption conditions (the initial gas concentration C₀, the temperature, the size of adsorbent grains, the gas velocity) must ensure a big value of f and a small one for LMTU, as results from equation (3) written as follows:

\[
θₚ = \frac{L_{MTU} (1 - f)}{a_0 L} = \frac{1 - 1 - f}{n L_{MTU}}
\]

where: n represent the number of LMTU in a column having the length L.

The figure 3 represents the dependence of adsorption degree \( θₚ \) on the number of LMTU for two adsorption coefficients f (0.4 and 0.6).

In order to obtain big values for \( θₚ \) the number of LMTU must be sufficiently high. According to the relation \( L = n L_{MTU} \) the adsorption conditions must ensure small values for LMTU. That is very important from economical and technical reasons, because increasing the number of LMTU the pressure drop increases as well.

The influence of initial gas concentration C₀ on LMTU

\[
C₀ = \frac{a}{a_0} \quad (a < 0.43)
\]

where: C₀ = 0.25% SO₂

Fig. 3. Variation of the degree of adsorption \( θₚ \) on the number of LMTU for two adsorption coefficients f (0.4 and 0.6).

Fig. 4. The shape of breakthrough curve when C₀ = 0.25% SO₂.

1 - chromatographic device; 2- adsorption column; 3- recorder; R₀-platinum electric resistance; R₅-reference platinum electric resistance; Rₖ-variable manganine electric resistance;
In order to put in evidence the influence of $C_0$ on $L_{MTU}$, the breakthrough curves have been obtained for $C_0 = 0.25; 0.5$ and 1% SO$_2$. These curves are represented in the figures 4, 5 and 6 respectively.

In all cases the experiences have been performed in a column where the adsorbent length $L = 40$ cm (diameter = 3 cm).

The gas velocity was $w_g = 0.2$ m/s. The grain diameter of adsorbant $d_a = 1$ mm.

For the initial gas concentration $C_0 = 0.25$ %, the column saturation time $t_s = 155$ min and the breakthrough time $t_R = 113$ min.

For the initial concentration $C_0 = 0.5$, the data are the following: $t_s = 125$ min; $t_R = 111$ min; $t_e = 125-111 = 14$ min; $t_f = 14 \times (1-0.52) = 6.7$ min.

One obtain:

$$L_{MTU} = \frac{t_e}{t_s - t_f} = \frac{14}{125 - 6.7} = 0.11 \text{ cm}$$

As aspected, the $L_{MTU}$ increases when the initial concentration $C_0$ decreases. That why the purification of very diluted gases may become very expensive, the big pressure drop becoming unacceptable.

Conclusions

The aim of this work is the determination of mass transfer characteristics, such as the length of mass transfer unit ($L_{MTU}$), the breakthrough time $t_b$ and the column saturation time $t_s$, which permit finally the calculation of adsorption coefficient in unsteady-state conditions $d_{sp}$, and of the optimum number $n$ of $L_{MTU}$. In this purpose a chromatographic method has been used, permitting the direct inregistration of breakthrough curves, whose shape depends on adsorption parameters like gas concentration, temperature, the size of adsorbent grains and the gas velocity.

References

1. BUMBAC, G., BOMBOS, D., Rev. Chim. (Bucharest), 66, no. 11, 2015, p. 1891
2. CAPATINA, C., CIRITIKA, D., Rev. Chim. (Bucharest), 68, no. 10, 2017, p. 2248
3. ORBULET, O.D., PINCOVSCHI, I., MODROGAN, C., Rev. Chim. (Bucharest), 67, no. 5, 2016, p. 829
4. PINCOVSCHI, I., MODROGAN, C., Rev. Chim. (Bucharest), 65, no. 8, 2014, p. 876

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