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

IRINA PINCOVSCHI[1], CRISTINA MODROGAN[2]*

[1]University Politehnica of Bucharest, Department of Hydraulics, Hydraulic Machinery and Environmental Engineering,1-7 Gh. Polizu Str., 011061, Bucharest, Romania

[2]University Politehnica of Bucharest, Department of Analytical Chemistry and Environmental Engineering, 1-7 Gh. Polizu Str., 011061, Bucharest, Romania

In the present work, the mass transfer characteristics such as the lenght of mass transfer unit (L_{MTU}), 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, permiting 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 permiting 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].

The 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.

The pore difusion model can be considered when diffusion occurs in the macro and mesoporous adsorbents.

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.

The most difficulties in using the mentioned theoretical model consist in adoption of a lot of simplifying assumption. That is why the theoretical breakthroug 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 SO_2 and N_2. The two individual streams were mixed in a mixing chamber.

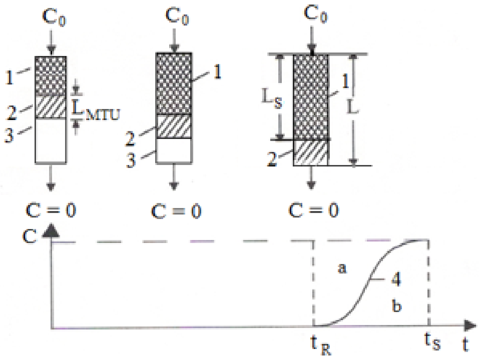

Fig. 1. The physical model used for the gas adsorption process in unsteady-state regime. 1 - the saturated zone; 2- the length of the mass transfer unit (L_{MTU}); 3- the free zone; 4- the breakthrough curve; t_R -the breakthrough time; t_S - column saturation time; C_0 -initial gas concentration

After mixing chamber, the gas having the concentration C_0 passes through the adsorption column (being of 2 cm diameter and 40 cm high). The proposed physical model is based on the asumption that the gas adsorption occurs till the saturation of a limited zone L, defined as mass transfer unit (L_{MTU}), whose lenght depends on adsorption conditions (gaz 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 = C_0 in accordance with breakthrough curve 4 (fig. 1). That she is why the

---

*email: c_modrogan@yahoo.com

breakthrough curve characterizes the adsorption process in unsteady-state conditions, permitting the calculation of all characteristic parameters (the lenght of mass transfer unit, the adsorption degree in dynamic conditions, the optimum number of L_{MTU} and therefore the optimum adsorption column lenght.

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

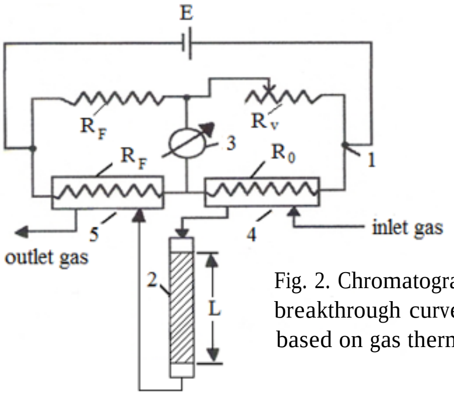

Fig. 2. Chromatographic device for breakthrough curve determination based on gas thermal conductivity

1 - chromatographic device; 2- adsorption column; 3- recorder; R_0-platinum electric resistance; R_r - reference platinum electric resistance; R_F - fixed manganine electric resistance; R_v-variable manganine electric resistance

The gas containing sulfur dioxide, whose initial concentration is C_0, enters successively the aluminium chanel 4 containing the electrical resistence R_0, adsorption column 2 and aluminium chanel 5 containing the resistence R_F. Due to continue SO_2 adsorption in column 2, its concentration continously diminished, modifying the thermal conductivity of gas. This modification is recorded by the recorder 3, resulting the breakthrough curve.

Although the thermal conductivity of SO_2 is relatively small one (the thermal conductivity l of sulfur dioxide, at 25 C, is 2.08×10^{-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 SO_2 concentration.

In the present work the following data have been used: C_0 = 0.25, 0.5 and 1%SO_2; 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 (L_{MTU}) the adsorption degree θ_R in dynamic conditions, the breakthrough time t_R, the column saturation time t_s and the adsorption coefficient $f=\frac{a}{a+b}$ (fig.1).

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

$$L_{MTU} = L\frac{t_S - t_R}{t_S - t_F} = L\frac{t_E}{t_S - t_E(1-f)} \qquad (1)$$

where: L represents the lenght of adsorption column, cm

t_S – the necessary time for column saturation, min

t_R – the breakthrough time, min

t_E – the time of displacement of L_{MTU}, min

t_F – the formation time of L_{MTU}, min

f – the adsorption coefficient

Knowing the L_{MTU}, the adsorption degree θ_R in breakthrough time t_R can be determined, according to the relation:

$$\theta_R = \frac{G_R}{a_m L} \qquad (2)$$

where:

G_R represents the quantity of SO_2 retained in breakthrough time, kmol

a_m -the linear concentration of SO_2 adsorbed in time t_S, kmol/cm

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

$$G_R = a_m L_S + a_m f L_{MTU} = a_m(L_S + f L_{MTU}) = a_m[L - L_{MTU}(1-f)]$$

where: $L_S = L - L_{MTU}$ and (fig. 1)

In these conditions:

$$\theta_R = \frac{G_R}{a_m L} = \frac{a_m[L - L_{MTU}(1-f)]}{a_m L} = 1 - \frac{L_{MTU}(1-f)}{L} \qquad (3)$$

The relation (3) puts in evidence the dependence of adsorption degree θ_R on adsorption coefficient f and L_{MTU}. The adsorption conditions (the initial gas concentration C_0, the temperature, the size of adsorbent grains, the gas velocity) must ensure a big value of f and a small one for $L_{MTU,}$ as results from equation (3) written as follows:

$$\theta_R = 1 - \frac{L_{MTU}(1-f)}{nL_{MTU}} = 1 - \frac{1-f}{n} \qquad (3')$$

where: n represent the number of L_{MTU} in a column having the length L.

The figure 3 represents the dependence of adsorption degree θ_R on the number of L_{MTU} for two adsorption coefficients f (0.4 and 0.6).

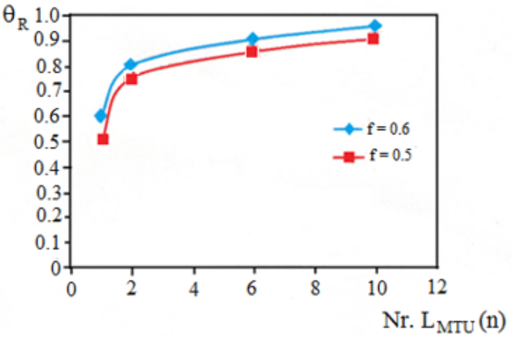

Fig. 3. Variation of the degree of adsorption θ_R on the number n of mass transfer units at different values of the coefficient of adsorption

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

The influence of initial gas concentration C_0 on L_{MTU}

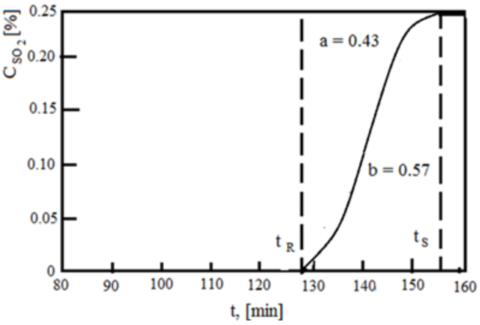

Fig. 4. The shape of breakthrough curve when C_0 = 0.25% SO_2

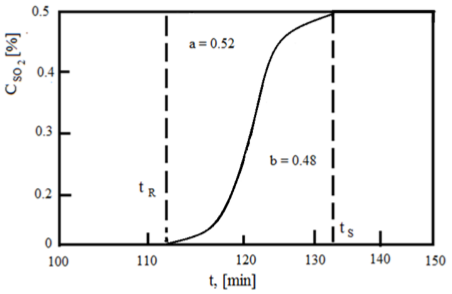

Fig. 5. The shape of breakthrough curve when C_0 = 0.5 % SO_2

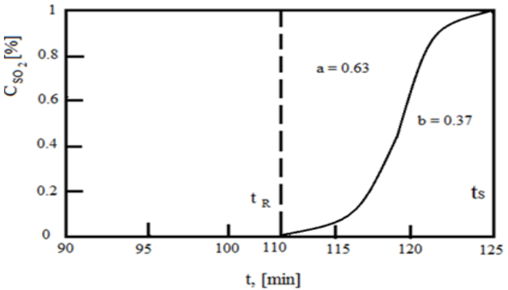

Fig. 6. The shape of breakthrough curve when C_0 = 1 % SO_2

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 lenght L = 40 cm (diameter = 3 cm).

The gas velocity was w_g = 0.2 m/s. The grain diameter of adsorbant d_p = 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 = 127 min.

In this case the displacement time of L_{MTU}, $t_E = t_s - t_R$ = 155-127=28 min and the formation time of L_{MTU}, $t_F = t_E(1-f)$ = 28 (1-0.38) = 17 min.

In these conditions:

$$\theta_R = \frac{G_R}{a_m L} = \frac{a_m \left[L - L_{MTU}(1-f)\right]}{a_m L} = 1 - \frac{L_{MTU}(1-f)}{L}$$

For the initial concentration C_0 = 0.5 % the data are the following: t_s = 132 min; t_R = 113 min; $t_E = t_s - t_R$ = 132-113=19 min

$$t_F = t_E(1\text{-}f) = 19'''(1\text{-}0.42) = 11$$

In these conditions:

$$L_{MTU} = L\frac{t_E}{t_s - t_F} = 40\frac{19}{132 - 11} = 7.4\,\text{cm}$$

Finaly, when C_0 = 1 % the data are the folllowing: t_s = 125 min; t_R = 11 min; t_E = 125-111 = 14 min; t_F = 14 x (1-0.52) = 6.7 min.

One obtain:

$$L_{MTU} = L\frac{t_E}{t_s - t_F} = 40\frac{14}{125 - 6.7} = 4.6\,\text{cm}$$

As aspected, the L_{MTU} increases when the initial concentration C_0 decreases. That why the purification of very diluted gases may become very expensiv, the big presure drop becoming inacceptable.

The variation of L_{MTU} with C_0 is represented in figure 7.

The experiments made in order to put in evidence the infuence of temperatures, gas velocities and the size of adsorbent grains on L_{MTU} confirm the previsible facts that small temperatures, gas velocity and grain dimensions are favorable to obtain small values for L_{MTU}. Unfortunately small values of these parameters are prohibitive from practical point of view.

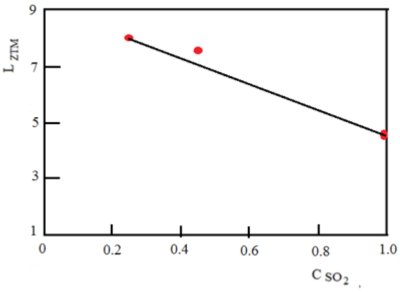

Fig. 7. The variation of mass transfer unit length with the concentration of SO_2

Conclusions

The aim of this work is the determination of mass transfer characteristics, such as the lenght of mass transfer unit (L_{MTU}), the breakthrough time t_R and the column saturation time t_S, which permit finally the calculation of adsorption coefficient in unsteady-state conditions q_R, 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., CIRTINA, 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
5.GUPTA, A., GAUR, V., VERNA, N., Chem. Eng. And Processing, **43** (2004), p.9
6.SIAHPOOSH, M., FAYTEMI, S., VATANI, A., Iran. J. Chem. Chem Eng., **28** (2009), p. 25
7.YOON, Y., NELSON, J.H., An. Ind. Hyg. Assoc. J., 45 (1994), p. 509
8.CARTA, G., CINCOTTI, A., Chem. Eng.Sci., **53** (1998), p. 3483
9.ZHANG, R., RITTER, J.A., Chem. Eng. Sci. **52** (1977), p. 3161
10.SCRBEZOV, A., SOTIRCHOS, J.A., Chem. Eng.Sci., **54** (1999), p. 5647
11.WAKAO, N., FUNAZKRI, T., Chem. Eng.Sci., **33** (1978), p. 1375
12.FAROOK, S., RUTHVEN, M., AICh. Journal, **37** (1991) p. 299
13.THIBAUT-ERKEY, C., GUO, Y., ERKEY, C., AKGERMAN**, A.,** Environ. Sci. Technol. **30** (1996) p. 2127
14.KOPAC, T., Chem. Eng. and Process.**, 38** (1999) p. 45
15.MIHALY, M., ANDREIADIS, E.S., PINCOVSCHI, E., UPB Sci. Bull., Series B, vol. **67** (2005), p. 57
16.CHANG, C.L., CHIANG, P.C., CHANG, E.E., Chemosphere, **53** (2003) p. 17
17.SANKARARAO, B., GUPTA, S.K., Comp. Chem. Eng., **31** (2007), p. 1282
18.VERMULEN, T., QUILICI, I., Ind. Eng. Chem. Fundam. **9** (1970), p. 179
19.CHANG, H., YUAN, X., TIAN, H., ZENG**, A.,** Chem. Eng. and Process, **45** (2006) p. 747
20.TANTET, J., EIC, M., DESAI, R**.,** Gas. Sep. Purif. **9** (1995) p. 233
21.GAUR, V., SHARMA, A., VERMA, N**.,** Chem. Eng. and Process., **45** (2006) p. 1
22.KOPAC, T., KOCABAS, S., Chem. Eng. and Process.**, 41** (2002) p. 223
23.LEE, Y.W., PARK, J.W., CHOUNG, J.H., CHOI, D.K., Environ. Sci. Technol., **36** (2002) p. 1086
24.IGHIGEANU, D., MARTIN, D., CALINESCU, I., BULEARCA, A., MANAILA, E., CRACIUN, G., Rev. Chim.(Bucharest), **63**, no. 2, 2012, p. 187

Manuscript received: 23.11.2017