

STUDY OF GAS SEPARATION PROCESS BY DYNAMIC ADSORPTION IN FIXED BED

Stelian Petrescu^{*}, Marius Sebastian Secula, Maria Spiridon,
Ioan Solomon

„Gheorghe Asachi” Technical University Iași, Faculty of Chemical Engineering and Environmental Protection, Department of Chemical Engineering, 71 D. Mangeron Blvd., 700050 Iași, Romania

*Corresponding author: spetresc@ch.tuiasi.ro

Received: July 13, 2010

Accepted: July 30, 2010

Abstract: An experimental study of mass transfer at gas separation by dynamic adsorption in fixed bed of impregnated silica gel is presented in this work. By means of a mathematical model based on constants and coefficient easy to evaluate, the distributions of adsorbate concentration in gas and solid phases were determined as a function of time and throughout the height of the fixed bed, under isothermal conditions.

With this aim, water vapors from air were adsorbed in a fixed bed of impregnated silica gel. The values of the volumetric mass transfer coefficient, K_v , were determined experimentally at several values of air superficial velocity, an air relative humidity of 69%, at 38 °C.

The influence of the gas flow velocity and initial water concentration in adsorbent on the distribution of water concentration in both phases was established as a function of time and throughout the height of the fixed bed. The results obtained allow one to determination of the local adsorption rate.

Keywords: *dynamic adsorption, impregnated silica gel, fixed bed, mathematical model, volumetric mass transfer coefficient.*

INTRODUCTION

In practice, separation of mixtures by adsorption is a process of major importance. The most commonly gas separation by adsorption is achieved in fixed bed of particles. For this reason, the gas-solid mass transfer at adsorption processes in fixed bed is extensively studied concerning both theoretical and experimental aspects [1 – 25]. Results are of significant importance regarding on the first hand the design and adsorber unit operation and on the other hand modeling of catalytic heterogeneous processes.

In reference [7] Nutter and Burnet applied the diffusion model developed by Acrivos and Vermuelen for water vapor adsorption from air on molecular sieves. Experimental data were obtained and used to highlight the effect of gas flow velocity, shape and size of adsorbent particles on mass transfer and diffusion coefficients.

Cooney [2] presented a simple method to calculate the adsorbate concentration profiles in an adsorbent fixed bed when the process takes place under dynamic conditions.

Chumakova et. al. [16] proposed a mathematical model for non-isothermal adsorption of water vapor from air in fixed bed of composite material (grains of silica gel impregnated with calcium chloride). The model does not take into account nor the intraparticle diffusion neither heat transfer through conductivity in interior grain and that there are some discrepancies between the experimental and predicted data.

Dell'Osso and Winnick [17] established a mathematical model for the adsorption and desorption of two adsorbates in a fixed bed of composite material. The solution of equation system that describes the process was determined by finite difference method while the coefficients and constants required to use the mathematical model were experimentally determined.

Pentchev, Paev and Seikova [19] investigated the dynamic adsorption in fixed bed under non-isothermal conditions. The established mathematical model takes into consideration the radial temperature gradients effect. Axial and radial temperature profiles were determined experimentally.

In general, mathematical models reported in literature for adsorption processes in fixed bed of particles are very complicated and contain constants and coefficients difficult to evaluate. The use of models like these ones is awkward for adsorber unit design and operating calculation.

In the present paper is studied the mass transfer at gas separation by dynamic adsorption in fixed bed of particles. Using a previously established mathematical model containing constants and coefficients easy to evaluate, the distribution of adsorbate concentration in both phases as a function of time and throughout the height of the fixed bed was determined at isothermal adsorption of water vapor from air on MCSS1 composite material. In order to solve the system, it is necessary to determine experimentally the mass transfer coefficient K_v , while the equilibrium constant μ is considered from literature.

K_v coefficient was experimentally determined at atmospheric pressure and 38 °C, using for this aim MCSS1 material (silica gel grains impregnated with calcium chloride) and humid air with $u = 69\%$ and at several values of gas flow velocity.

Using the mathematical model we established the influence of air superficial velocity and initial water concentration in solid phase on distribution of concentration in both phases as a function of time and throughout the height of the fixed bed.

MATHEMATICAL MODEL

The separation process of a component from a gas mixture using dynamic adsorption in fixed bed of particles, considering the gas phase flow with ideal flow and isothermal regime, can be mathematically described by the mass balance equations of adsorbate for the gas phase, respectively solid and by the equilibrium equation:

$$\frac{\partial C}{\partial t} + v_z \cdot \frac{\partial C}{\partial z} + \frac{1-\varepsilon}{\varepsilon} \cdot \rho_s \cdot \frac{\partial X}{\partial t} = 0 \quad (1)$$

$$\frac{\partial X}{\partial t} = \frac{1}{1-\varepsilon} \cdot K_v [C - C^*(X)] \quad (2)$$

$$C^* = \mu \cdot X^n \quad (3)$$

Initial and limiting conditions are as follows:

$$t = 0, z > 0, X = X_0 \quad (4)$$

$$t > 0, z = 0, C = C_0 \quad (5)$$

Given $n = 1$, the analytical solving the equation system that describes the process leads to the following equation:

$$X = \frac{C_0 + (\mu \cdot X_0 - C_0) \cdot e^{-\phi}}{\mu} \quad (6)$$

$$\phi = \frac{K_v \cdot \mu \cdot t}{(1-\varepsilon) \cdot \rho_s} \exp\left(-\frac{K_v \cdot z}{\varepsilon \cdot v_z}\right) \quad (7)$$

$$C = \mu \cdot X + (C_0 - \mu \cdot X) \exp\left(-\frac{K_v \cdot z}{\varepsilon \cdot v_z}\right) \quad (8)$$

In order to be used, the suggested mathematical model requires the values of mass transfer coefficient, K_v , and equilibrium constant, μ .

MATERIALS AND METHODS

The experiments were carried out using the set-up described in Fig. 1.

The installation consists of one cylindrical vertical column (1), heat exchanger (2), thermostat (3), air wetting chamber (4), ventilator (5), digital technical balance (6), valves for air and water flow velocity adjustment and devices of measuring and control for temperature, flow velocity and air relative humidity.

Column (1) represents the adsorption column, made in PVC and equipped at the endings with caps provided with a stainless steel sieve (1a) for supporting the adsorbent bed. For sealing the column at both endings, two rubber rings (1c) and (1d) were employed. The adsorption column is fixed on a support made in copper.

The air heating is performed by means of the heat exchanger (2) made of thermo-resistant glass. The interior of heat exchanger is equipped with a coil where hot water circulates from thermostat (3). The air wetting chamber (4) is a cylindrical recipient made of stainless steel adjusted with heating jacketed where hot water circulates from thermostat (3). On the cap two connectors are fixed for air input and output. The air is transported in installation by means of fan (5).

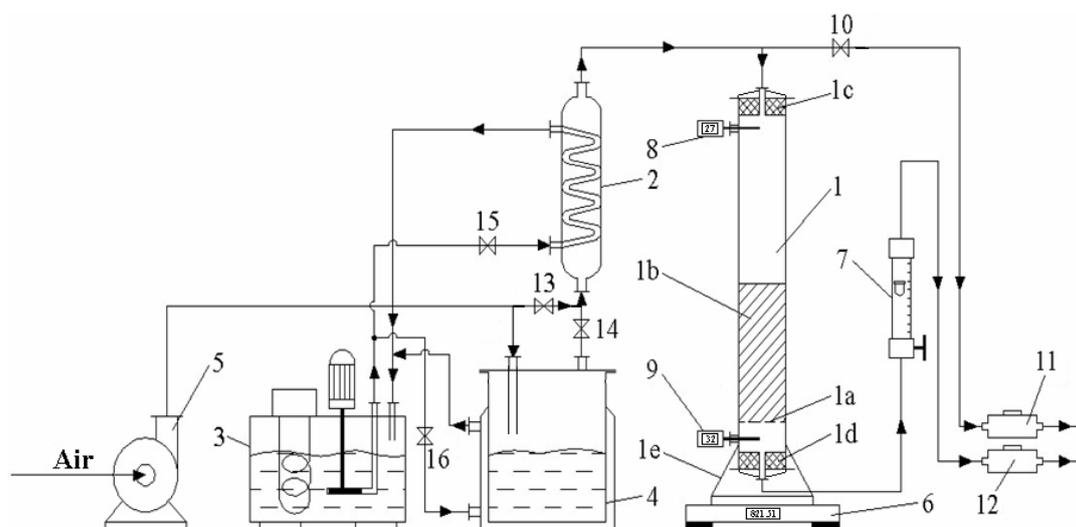


Figure 1. Experimental setup: 1-adsorption column, 2-heat exchanger, 3- thermostat, 4-air wetting chamber, 5-fan, 6-digital technical balance, 7-flowmeter, 8,9-digital thermometer, 10,13,14,15,16-valves, 11,12-chambers for fixing psychrometer probes at the column inlet and outlet

The determination in time of adsorbed water quantity was performed by means of digital technical balance (6) having an accuracy of ± 0.01 g. Gas flow velocity control is performed by means of the flowmeter (7) and measurements of air temperature at entrance and exit from the packed bed were made using digital thermometers (8) and (9).

To measure air humidity at the column entrance, the installation is provided with a bypass route adjusted by means of valve (10) and chamber (11) for fixing the psychrometer probe. The measurement of air humidity at the exit column was realized by means of another psychrometer with probe fixed in chamber (12). Air temperature adjustment is made using valve (15) and air humidity using valves (13), (14) and (16).

The experiments were carried out at atmospheric pressure and at $38\text{ }^{\circ}\text{C}$ using as gas phase wet air at two values of relative humidity: 69 and 97.75 %, and several values of air flow rate: 0.3; 0.6; 0.9; 1.2; $1.5\text{ m}^3\cdot\text{h}^{-1}$.

Adsorption process was realized in fixed bed of composite material MCSS1 under dynamic conditions. The geometrical parameters of fixed bed were: $H = 0.15$ m and $D = 2.95 \cdot 10^{-2}$ m.

In the investigations as adsorbent was used silica gel grains (purchased from Lach-Ner, Neratovice, Czech Republic) having an equivalent diameter of $3.57 \cdot 10^{-3}$ m.

The selective water composite material was synthesized by impregnating silica gel with calcium chloride followed by thermal drying at $200\text{ }^{\circ}\text{C}$.

Certain amounts of silica gel were dried in an oven at $160\text{ }^{\circ}\text{C}$ for four hours and then cooled to the room temperature in a desiccator. 15 wt% calcium chloride solutions were prepared dissolving calcium chloride (Merck analytical reagent) previously dried in oven for two hours, at $120\text{ }^{\circ}\text{C}$, and distilled water.

Further, the impregnation of silica gel was achieved using 15 wt% calcium chloride solutions. After 12 hours of impregnation, the composite material was separated by filtration under vacuum, at room temperature. Grains of impregnated material retained

on the filter material were dried for four hours in the oven at 160 °C, and then cooled in a desiccator.

The salt content in the composites was determined by weighing samples before and after impregnation and drying. Thus it was determined the concentration of salt in solid of 5.57 wt% CaCl₂.

By means of an ASAP 2020 Micromeritics the nitrogen adsorption-desorption isotherm of the synthesized impregnated silica gel was obtained. In Table 1 are shown the main characteristics of the synthesized mesoporous material.

Table 1. CaCl₂-silica gel (MCSS1) characteristics

Characteristic	Value
Mesoporous volume, cm ³ ·g ⁻¹	0.3626
Mean pore size, nm	2.21
BET specific surface, m ² ·g ⁻¹	645.1

RESULTS AND DISCUSSION

Using the experimental installation presented in Fig. 1, the evolution in time of relative humidity and temperature at column exit was determined at different periods: 10, 20 ... 120 min. Based on relative humidity and temperature values read at psychrometer, water vapor concentration in air values at column exit were determined. Using mass balance equation (9) for the adsorbate component, the water concentration in adsorbent was calculated:

$$M_s dX = M_v \cdot \int_0^t (C_0 - C) dt \quad (9)$$

Values obtained for X are presented in Fig. 2.

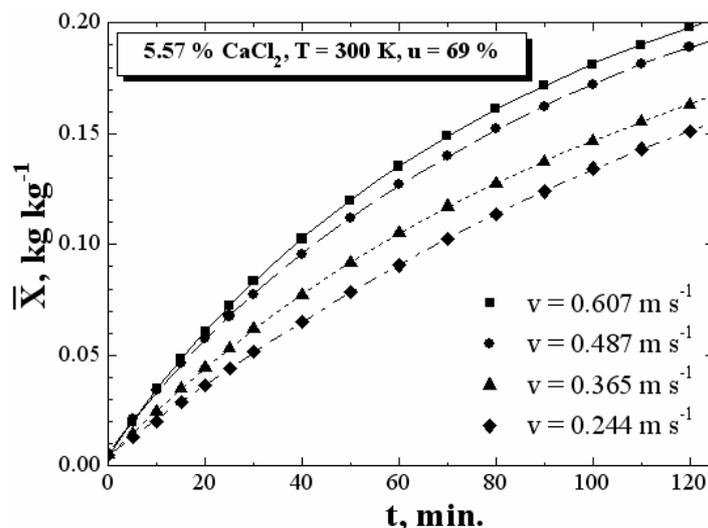


Figure 2. Water concentration variation in MCSS1 adsorbent at several values of air superficial velocity

According to the dependencies in Fig. 2, water adsorbed increases with air flow rate. In order to calculate the adsorption rate, the following relationship was used:

$$v_a = \rho_s \cdot \frac{dX}{dt} \quad (10)$$

Data regarding the adsorption rate were used to calculate the volumetric mass transfer coefficient by means of the following equation:

$$v_a = K_V \cdot (C - C^*)_{mean} \quad (11)$$

Average driving force $(C - C^*)_{mean}$ was calculated with the relationship:

$$(C - C^*)_{mean} = \frac{(C_0 - C^*) - (C - C^*)}{\ln \frac{C_0 - C^*}{C - C^*}} \quad (12)$$

Equilibrium concentrations for MCSS1 composite material-water vapor system were considered from literature [25].

The values obtained for mass transfer coefficient are represented in Figure 3.

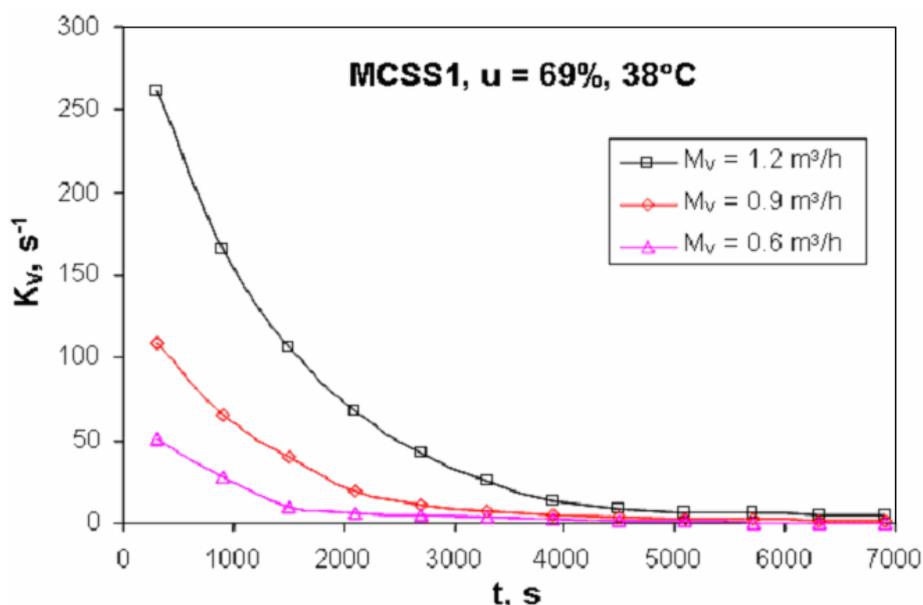


Figure 3. Volumetric mass transfer coefficient variation as a function of time

Dependencies in Fig. 3 reveal a decreasing in volumetric mass transfer coefficient with adsorption time. The flow rate and velocity respectively influence positively the mass transfer coefficient. This influence is more significant at higher values of gas flow velocity as described in Fig. 4.

Using the values obtained for K_V at different times, the average volumetric mass transfer coefficient was calculated within the time range of 0 – 120 min with the equation:

$$\overline{K_V} = \frac{1}{t} \cdot \int_0^t K_V(t) dt \quad (13)$$

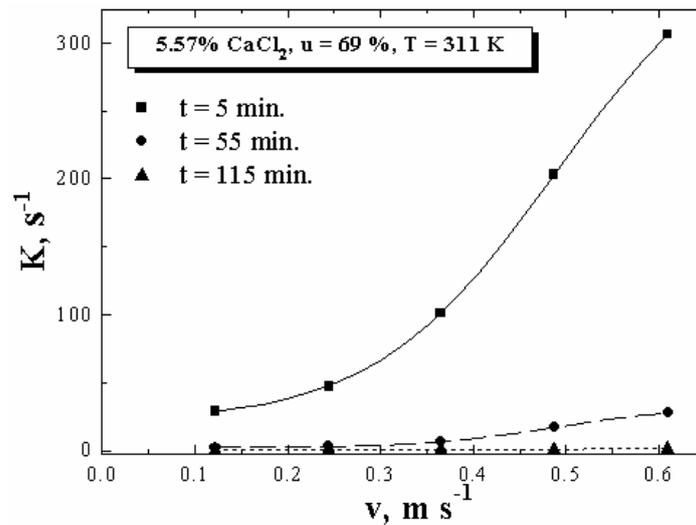


Figure 4. Mass transfer coefficient variation as a function of gas flow rate.

Having determined the experimental values for \overline{K}_v coefficient, water concentration distributions for both phases, gaseous and solid, were determined as a function of time and throughout the height of the fixed bed using equations (6) ÷ (8). In calculations, the following variable values were taken into account:

$$z: 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1 \text{ m}$$

$$t: 300, 600, 3600, 7200, 14400 \text{ s.}$$

The equilibrium constant μ was determined using data from literature [25] for the MCSS1 composite material (silica gel spherical impregnated with CaCl_2) – water vapor system at 38 °C. For air flow rate the following values were considered: 0.3; 0.6; 0.9; 1.2; 1.5 $\text{m}^3\cdot\text{h}^{-1}$, that correspond to the following values of gas flow velocity: 0.122; 0.244; 0.365; 0.487; 0.607 $\text{m}\cdot\text{s}^{-1}$.

The results obtained are shown in Fig. 5, 6 and 7. In Fig. 5a and Fig. 6a is presented the distribution of water concentration in gas phase (air) throughout the height of the fixed bed at several values of time at two different values of air flow rate.

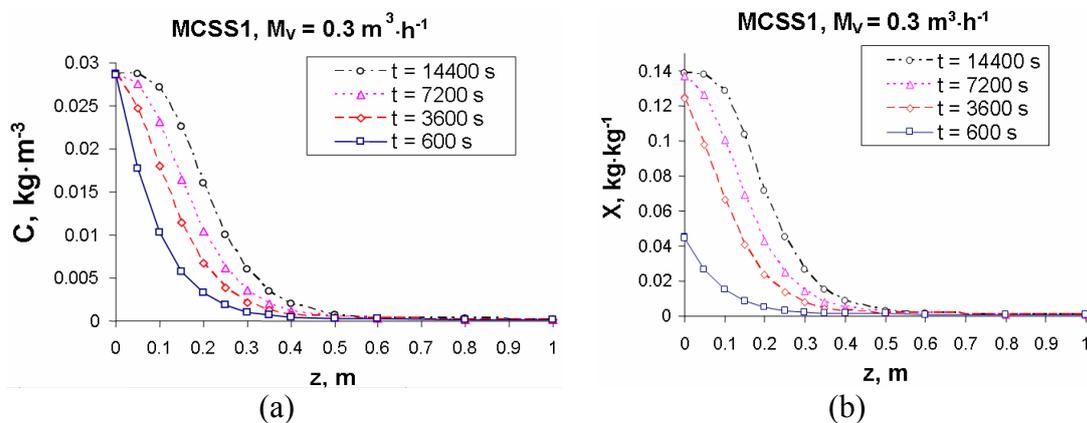


Figure 5. Distribution of water vapor concentration in air (a), respectively, water concentration in solid (b) throughout the height of the adsorbent bed at $0.3 \text{ m}^3\cdot\text{h}^{-1}$

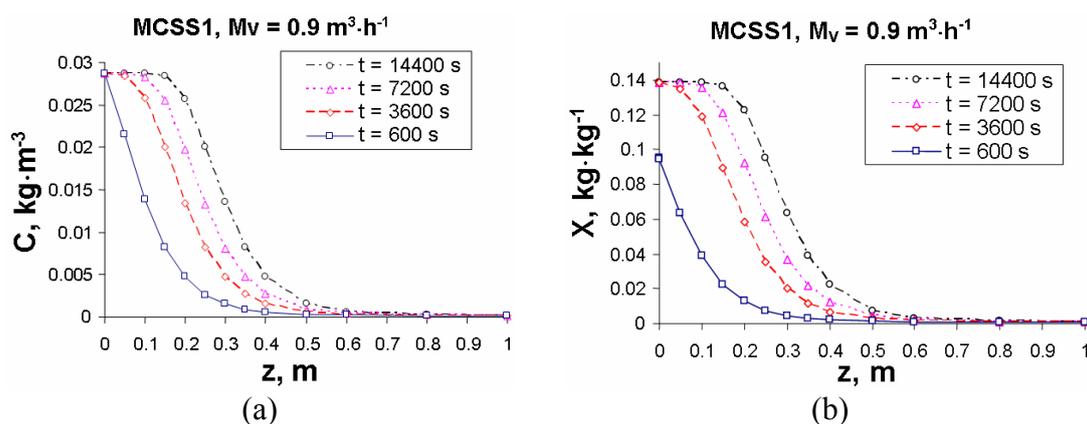


Figure 6. Distribution of water vapor concentration in air (a), respectively, water concentration in solid (b) throughout the height of the adsorbent bed at $0.9 \text{ m}^3 \cdot \text{h}^{-1}$

It can be noted a decreasing of water vapor concentration in air throughout the height of the fixed bed due to a gradual water adsorption as the air flows through the entire height of the adsorbent bed. The decrease of water concentration in air will determine a continuous diminishing of the mass transfer driving force and a decrease of adsorption rate throughout the height of the bed.

Also, it can be observed an increase of water vapor concentration in air with flow rate. Diagrams in Fig. 5b and Fig. 6b underline water vapor concentration variation from solid throughout the height of the fixed bed at several values of time for gas flow rate values of 0.3 and $0.6 \text{ m}^3 \cdot \text{h}^{-1}$ respectively.

As can be seen, at short adsorption times, throughout the height of the fixed bed there are two distinct areas: an area where mass transfer takes place followed by another one where there is no mass transfer.

At longer adsorption times, throughout the height of the fixed bed, it can be noted the presence of three areas: in the first region we have an equilibrium area saturated with water vapors, further is the area where mass transfer takes place and finally a free-adsorbate area. Increasing air superficial velocity, mass transfer area moves on the height of the fixed bed so that at longer adsorption times, occur two areas throughout the height of the fixed bed: the water vapor saturated one and the mass transfer one.

Fig. 7 emphasizes the influence of the adsorption time on the water concentration in MCSS1 adsorbent material. Increasing period increases water concentration in solid phase. At large distance from the top fixed bed, dependencies $X = f(t)$ are practically linear. It can observe the positive influence of aqueous phase rate on adsorbate concentration in solid phase. At high values of period, gas phase rate have a little influence on X concentration, but at low values of period, gas rate determine substantial modification of water concentration in adsorbent.

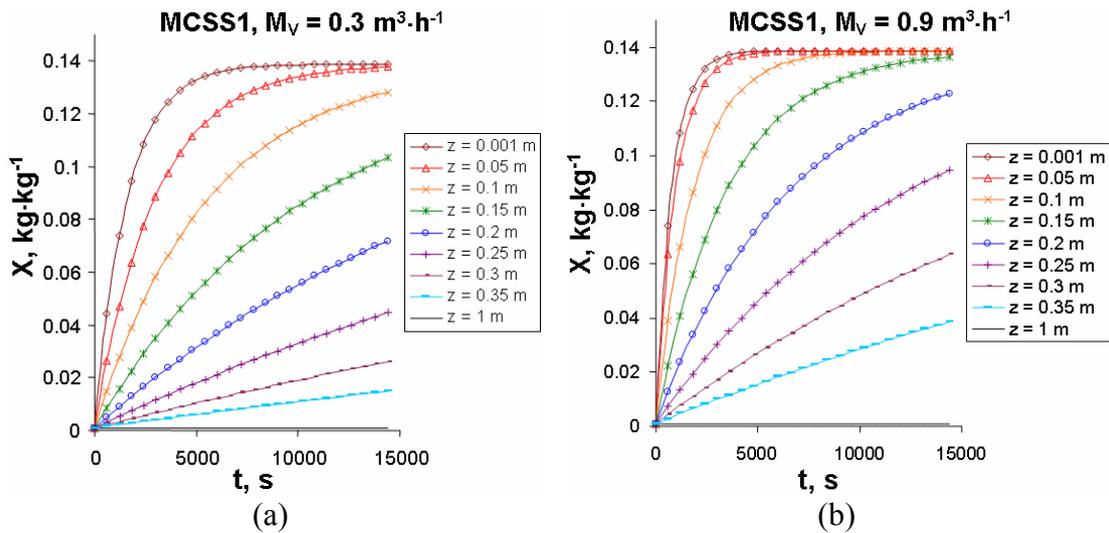


Figure 7. Evolution in time of water concentration in MCSS1 at different heights of bed at $0.3 \text{ m}^3\cdot\text{h}^{-1}$ (a) and $0.9 \text{ m}^3\cdot\text{h}^{-1}$ (b)

In Fig. 8 is presented the distribution of water vapor concentration throughout the height of the adsorbent bed at different values of initial concentration (X_0) of water in solid, for $M_V = 0.6 \text{ m}^3\cdot\text{h}^{-1}$, $t = 14400 \text{ s}$.

Dependencies in Fig. 8 show that the variation curves of water vapor concentration, at the exit from adsorption column, throughout the height of the fixed bed have similar shape for different X_0 . At higher values of X_0 , water vapor concentration at column exit, C , is higher in areas where mass transfer takes place and in the area where there is no mass transfer.

According to Fig. 9 it results that at relatively short adsorption times, the water concentration in solid phase presents higher values as X_0 concentration increases.

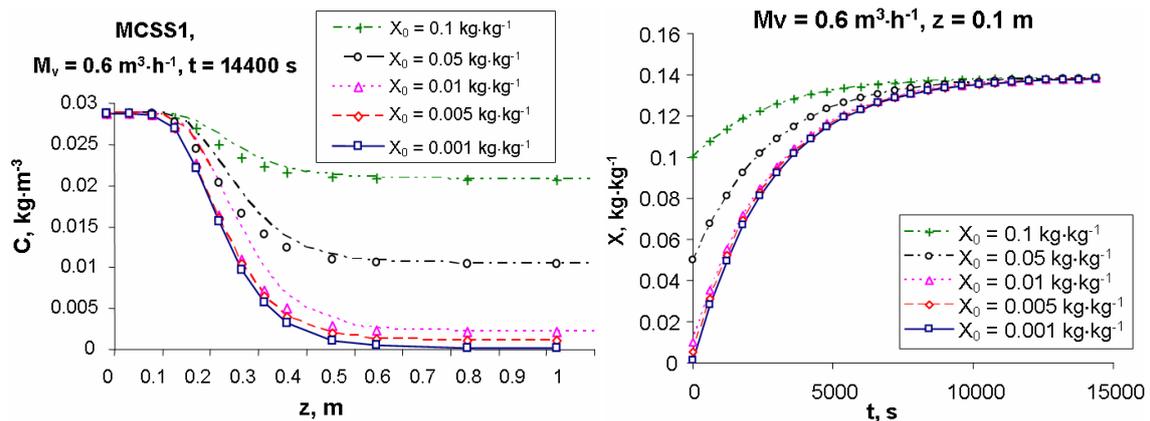


Figure 8. Distribution of water vapor concentration throughout the height of adsorbent bed at different initial water concentration in solid

Figure 9. The dependence $X=f(t)$ at different values of X_0 concentration

CONCLUSIONS

In this paper, based on a mathematical model previously established, available for dynamic adsorption of one component in granular fixed bed, the distribution of water vapor concentration from both phases was determined as a function of time and throughout the height of the adsorbent bed, at air drying by adsorption on MCSS1 composite material. The composite material was prepared by impregnating spherical grains of silica gel with calcium chloride.

Due to the mathematical model requires the values of volumetric mass transfer coefficient K_v , these were determined experimentally at 38 °C and several values of air superficial velocity. Air relative humidity was kept constant at 69 %.

Based on the mathematical model, it was established the influence of the gas flow velocity and initial water concentration in adsorbent on the distribution of water concentration in both phases as a function of time and throughout the height of the fixed bed.

The areas forming throughout the height of the fixed bed, while air drying process by adsorption takes place were emphasized.

The results obtained allow one to determination of the local adsorption rate.

ACKNOWLEDGEMENTS

Financial support for this work was provided by CNCSIS-UEFISCSU, in the framework of PN-II/IDEI PROGRAM (PN-II-ID-PCE-2007-1, Grant No. 63/01.10.2007, Cod 608). *Maria Spiridon* wants to thank for the financial support provided by BRAIN “Doctoral scholarships as an investment in intelligence” project, financed by the European Social Found and Romanian Government. *Ioan Solomon* wants to thank for the financial support provided by EURODOC “Doctoral Scholarships for research performance at European level” project, financed by the European Social Found and Romanian Government.

LIST OF NOTATIONS

C – adsorbate concentration in gas phase, $\text{kg}\cdot\text{m}^{-3}$;

C^* – equilibrium concentration of adsorbate in gas phase, $\text{kg}\cdot\text{m}^{-3}\cdot\text{s}^{-1}$;

C_0 – adsorbate concentration in gas phase at column inlet, $\text{kg}\cdot\text{m}^{-3}$;

K_v – volumetric coefficient of mass transfer, s^{-1} ;

M_S – dry solid phase mass, kg;

M_V – volumetric flow velocity of gas phase, $\text{m}^3\cdot\text{s}^{-1}$;

t – adsorption time, s;

u – air relative humidity, %;

v – air superficial velocity, $\text{m}\cdot\text{s}^{-1}$;

v_a – adsorption rate, $\text{kg}\cdot\text{m}^{-3}\cdot\text{s}^{-1}$;

v_z – gas flow rate in fixed bed on axial direction, $\text{m}\cdot\text{s}^{-1}$;

X – adsorbate concentration in solid phase, $\text{kg}\cdot\text{kg}^{-1}$;

X_0 – adsorbate concentration in solid phase at $t = 0$, $\text{kg}\cdot\text{kg}^{-1}$;

z – axial coordinate, m.

Greek letters

ε – porosity of fixed bed, dimensionless;

μ – equilibrium constant, $\text{kg}\cdot\text{m}^{-3}$;

ρ_s – solid density, $\text{kg}\cdot\text{m}^{-3}$.

REFERENCES

1. Ruthven, D.M.: *Principles of Adsorption and Adsorption Process*, J. Wiley, New York, **1984**;
2. Floarea, O., Dima, R.: *Processes of mass transfer and specific units*, Editura Didactică și Pedagogică, Bucharest, **1984**;
3. Motoyuki, S.: *Adsorption Engineering*, Elsevier, Amsterdam, **1990**;
4. Coulson, J.M., Richardson, J.F.: *Chemical Engineering*, vol. 2, Pergamon Press, Oxford, **1993**;
5. Jinescu, G., Lavric, V., Iordache, C.: Mathematical Model of Bulk Separation of Gas Mixtures by Pressure Swing Adsorption, *The 14th Int. Congress Chem. Process Eng.*, CHISA, Praga, **2000**;
6. Toth, J.: *Adsorption*, M. Dekker, New Jersey, **2002**;
7. Nutter, J.I., Burnet, G.: Fixed-bed drying of air using molecular sieves, *Industrial and Engineering Chemistry Process Design and Development*, **1968**, 5 (1), 28-36;
8. Wang, R., Farooq, S., Tien, C.: Maxwell-Stefan theory for macropore molecular-diffusion-controlled fixed-bed adsorption, *Chemical Engineering Science*, **1999**, 54 (18), 4089-4098;
9. Garg, D.R., Ruthven, D.M.: Linear driving force approximations for diffusion controlled adsorption in molecular sieve columns, *AIChE J.*, **1975**, 21 (1), 200-202;
10. Hand, D.W.J., Critenden, J.C., Thacker, W.E.: *Journal of Environmental Engineering, ASCE*, 1984, 110 (2), 440-456;
11. Perry, R.H., Green, D.W.: *Perry's Chemical Engineers' Handbook*, McGraw-Hill, New York, **1985**, 16-48;
12. Cooney, D.O.: Rapid approximate solutions for adsorption bed concentration profile and breakthrough curve behavior: favorable isotherms and both phase resistances important, *Chemical Engineering Communications*, **1990**, 91 (1), 1-9;
13. Frey, D.D.: Mixed-gas adsorption dynamics of high-concentration components in a particulate bed, *AIChE J.*, **1992**, 38 (10), 1649-1655;
14. Chuncai, Y., Chi, T.: Approximations of uptake rate of spherical adsorbent pellets and their application to batch adsorption calculations, *Chemical Engineering Science*, **1993**, 48 (1), 187-199;
15. Croitoru, C., Pop, F., Stanciu, V.: Mass Transfer modeling at selective adsorption of oxygen from air on carbon molecular sieve, *Rev. Chim.*, **1998**, 49 (4), 285-289;
16. Chumakova, N.A., Vermikovskaya, N.V., Tokarev, M.M., Koptyug, I.V., Ilyina, L.Yu, Aristov, Yu.I.: Water vapor sorption-desorption in fixed bed of composite sorbent: the refinement of transfer parameters and sorption kinetics, *Chemical Engineering Technology*, **2001**, 73, 776-784;
17. Dell'Osso, L., Winnick, J.: Mixed-Gas Adsorption and Vacuum Desorption of Carbon Dioxide on Molecular Sieve. Bed Design for Use in a Humid Atmosphere, *Industrial and Engineering Chemistry Process Design and Development*, **1969**, 8 (4), 469-467;
18. Wolborska, A.: External film control of the fixed bed adsorption, *Chemical Engineering Journal*, **1999**, 73 (2), 85-92;
19. Pentchev, I., Paev, K., Seikova, I.: Dynamics of non-isothermal adsorption in packed bed of biporous zeolites, *Chemical Engineering Journal*, **2002**, 85 (2-3), 245-257;
20. Todd, R.S., Webley, P.A.: Limitation of the LDF/echimolecular counterdiffusion assumption for mass transport within porous adsorbent pellets, *Chemical Engineering Science*, **2002**, 57 (19), 4227-4242;
21. Dawoud, B., Aristov, Yu.I.: Experimental study on the kinetics of water vapor sorption on selective water sorbent, silica gel and alumina under typical operative conditions of sorption heat pumps, *International Journal of Heat and Mass Transfer*, **2003**, 46 (2), 273-281;

22. Delgado, J.A., Uguina, M.A., Soleto, J.L., Ruiz, B.: Modeling of fixed-bed adsorption of methane/nitrogen mixtures on silicalite pellets, *Separation and Purification Technology*, **2006**, 50 (2), 192-203;
23. Petrescu, S., Galben, I., Cozma, R.: Study of binary gaseous mixtures separation by dynamic adsorption in fixed bed, *Revista de Chimie*. **2006**, 57 (2), 202-206.
24. Petrescu, S., Secula, M.S.: Mathematical Modeling of gas drying by adsorption, *Environmental Engineering and Management Journal*, **2008**, 7 (3), 179-191;
25. Mămăligă, I., Baciuc, C., Petrescu, S.: Adsorption equilibrium study for wet air-composite material systems, *Environmental Engineering and Management Journal*, **2009**, 8 (2), 253-257.