ETHANOL VAPOURS ADSORPTION BY NATURAL CLINOPTILOLITE

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ABSTRACT

An experimental study of the adsorption of ethanol vapours on Bulgarian natural clinoptilolite had been done. The experiments were carried out by dynamic breakthrough curves method. During the investigation the gas velocity, initial ethanol concentration in the gas mixture and the bed length were varied. The data concerning hydrodynamic parameters of the bed were obtained: the relationship between the bed length and the pressure drop was found; the breakthrough curves of the adsorbent beds were derived. The adsorption capacity of the adsorbent was investigated both by static and dynamic method and compared with similar experimental data available in literature concerning other types of adsorbents. Comparing it is evident that the adsorption capacities obtained with Bulgarian natural clinoptilolite are comparable with those found in literature for various modified forms of natural zeolites. Therefore the Bulgarian natural clinoptilolite is a promising material for adsorption of ethanol vapours mixed with air. The conditions when the external mass transfer resistance could be neglected were also determined.

Keywords: adsorption, natural zeolite, ethanol, dynamic conditions.

INTRODUCTION

There are many cases in the industrial practice when the air in the working environment is saturated with vapours of different types of solvents (e.g., alcohols). So, it is necessary to find a method to remove them using relatively cheap materials. That is why the adsorption of vapours of saturated alcohols had been extensively studied [1-17]. The following materials have been studied: activated carbon [5], similar to zeolites aluminium phosphates [4] or zeolites [1-3, 6-17]. The latter have the advantage of heteropolar structure, quite useful for adsorption of polar compounds. Their other characteristics are the pore uniformity turning them into the molecular sieves, their pores being available just for molecules with kinetic diameters smaller than the pores’ diameters. The molecular sieve action of zeolites and the presence in their structure of delocalized negative and localised positive electric charges is used for the separation of mixtures with different dimensions and dipole moments. That is the reason for some of the researchers to study the possibility of separation of alcohol mixtures [14] or of alcohol-in-water solutions [9,11,15]. The kinetic diameter of water is 0.265 nm, of the methanol - 0.376 nm, of the ethanol - 0.446 nm [18]. The latter is similar to zeolite pores [19]. Their dipole moments are 1.84, 1.7, 1.69 D respectively [20]. There are other studies concerning the adsorption equilibrium [1-4, 8, 10], adsorption kinetic parameters [3, 5], adsorption heat [7], desorption conditions [15], etc.
The experimental study of adsorption can be carried out at static or dynamic conditions. Adsorption by dynamic method gives the possibility to study the breakthrough curves, to find the adsorption capacity of the material, the length of the working zone (the one with the constant concentration profile), the breakthrough time (lifetime of the bed), as well as the velocity at which the external mass transfer resistance can be neglected. The dynamic experimental results are used for obtaining the values of the diffusion coefficients; the different domains of influence of the mass transfer resistances can be described and, as a result the different mathematical models describing the adsorption can be tested.

The aim of the present work is the study of ethanol vapours adsorption by natural zeolite - clinoptilolite by dynamic method and to define the main parameters of the dynamic experiment.

**EXPERIMENTAL**

**Materials and methods**

During the experiments the natural clinoptilolite from north-east Rodopa mountain - Bulgaria was used. Their mineral content was found to be about 87.2 %. The chemical analysis showed high contents of K⁺ and Ca²⁺ (Table 1). The bed bulk density was 780 kg m⁻³ and the porosity - 0.4.

The clinoptilolite is a natural zeolite with high silica contents. The molar ratio (silica modulus) of the sample was \( n = SiO_2 / Al_2O_3 = 9.73 \).

The experiments were carried out according to the dynamic breakthrough curves method using the standard experimental set-up (Fig.1) with packed bed adsorption column. The column inner diameter was 14 mm and height 50 cm. The column was closed in a jacket to maintain isothermal conditions. According to experimental data [21] for columns with outer water cooling the isothermal conditions can be maintained for maximal diameters of 16 cm. As a packed bed the adsorbent with sieve fraction 1.6 - 2 mm was used. The wall effect can be eliminated by use of column to particle diameter ratio between 6 and 10 [21, 22]. For our experiments this ratio was 7.8. A manometric tube was used to measure the pressure drop in the column filled with adsorbent beds with different heights. The experiments were carried out at temperature of 20°C. The model gas mixture was prepared when the preliminary dried air passed through ethanol. The quantity of the vapours was varied by changing the gas velocity, the position of the sparger in the volume and the temperature. The ethanol concentration at the inlet and at outlet of the column was found analytically; the capacity of the zeolite (the solid phase concentration) - gravimetrically and by integrating of the breakthrough curve. Before reaching a stable stationary operational regime (ethanol concentration, gas velocity and temperature) the gas mixture passed through a bypass line with the same re-

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**Table 1. Chemical content of the natural clinoptilolite, % mass.**

<table>
<thead>
<tr>
<th>sample</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>Loss of ignition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural zeolite</td>
<td>67.1</td>
<td>17.7</td>
<td>1.2</td>
<td>3.8</td>
<td>0.6</td>
<td>1.9</td>
<td>4.0</td>
<td>9.1</td>
</tr>
</tbody>
</table>

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Fig. 1. Experimental set-up.
sistance as the packed bed adsorption column. Before the experiments the adsorbent samples were treated for elimination of the water vapours and gases from the pores. The procedure was done by purging the bed with dry air with flow rate of 27 dm³ h⁻¹. In the same time the bed was heated with velocity of 5°C min⁻¹ until 200°C and this temperature was maintained during 2 hours. For this purpose the adsorption column in the set-up was replaced by a desorption one wrapped with electric heater with possibility of continuous temperature increase. The capacity of the zeolite to adsorb ethanol vapours was determined also at static conditions by the desiccator method. The zeolite samples were heated in a furnace for 3 hours at 200°C, and then cooled to room temperature in air-free atmosphere.

RESULTS AND DISCUSSION

To find the pressure drop in the column the experiments with superficial gas velocity of 0.094 m s⁻¹ were carried out, bed height being varied in the interval 5 to 22 cm. These experiments were purely hydrodynamic, not connected with the adsorption capacity of the zeolite. That is the reason not to account the ethanol concentration in the gas flow. The results obtained are given in Fig. 2. It could be seen that the pressure drop for the conditions studied was relatively low. These results can be used for the calculation of hydraulic resistance coefficient (friction factor).

For the case of fluid flow through packed bed of some particulate material (catalyst or adsorbent), the losses could be calculated by the equation [22]:

\[
h_{\text{loss}} = \frac{3 \cdot (1 - \varepsilon)}{2 \cdot \varepsilon^3 \cdot \varphi} \cdot \frac{\lambda \cdot L \cdot w_o^2}{d_e \cdot 2 \cdot g} \tag{1}
\]

\[d_e = \frac{4 \cdot \varphi \cdot \varepsilon \cdot d}{3 \cdot (1 - \varepsilon)} \tag{2}\]

where:

\(\lambda\) - drag coefficient of the bed;
\(L\) - bed height, m;
\(\varepsilon\) - bed porosity, \(\varepsilon = 0.4\) m³ m⁻³;
\(w_o\) - superficial flow velocity, in this case \(w_o = 0.094\) m s⁻¹;
\(d_e\) - equivalent sphere diameter, found by eq. (2) [22], m;
\(d\) - mean particles’ diameter, m, in this case \(d = 0.0018\) m;
\(\varphi\) - form factor for the particles, for the dimensions used \(\varphi = 0.75\) [24].

Using the measured pressure drop values a mean drag coefficient \(\lambda\) of 23.03 was calculated by eq. (1). In Table 2 the hydrodynamic data for energy losses calculations are presented. The drag coefficient could be also calculated from the Reynolds number values [25]:

\[\lambda = \frac{133}{\text{Re}} + 2.34 \tag{3}\]

The Reynolds number for packed bed can be found [22]:

\[\text{Re} = \frac{2 \cdot \varphi \cdot \varepsilon \cdot w_o \cdot d_e \cdot \rho}{\mu} \tag{4}\]

where

\(\rho\) - the fluid density, kg m⁻³;
\(\mu\) - fluid viscosity, Pa s⁻¹.

For Re numbers of 6.29 for our operational conditions a drag coefficient of \(\lambda = 23.49\) was found. These data are important element for the fluid velocity choice. For equipment used for solvent recuperation is recommended to maintain operational conditions assuring pressure losses less then 5 kPa per 1 m granulated bed [21]. For our experimental conditions this corresponds to velocity of 0.149 m s⁻¹.

In order to find the dynamic adsorption parameters the experiments were carried out at bed height from 5 to 22 cm. The ethanol concentration in gas mixture was \(p_o = 19\) Pa, the adsorption temperature was 20°C and the superficial gas velocity was \(w = 0.094\) m s⁻¹. For these conditions was determined the bed lifetime of the bed or the breakthrough time of the outlet adsorption curve \(\tau_b\) (time necessary to obtain a relative concentration in gas flow after the bed of \(p/p_o = 0.1\)). The data obtained are presented as a relationship between \(\tau_b\) and the bed height in Fig. 3. From the graph of the
breakthrough time vs. bed height the length of working zone is determined (it is the part of the bed with constant concentration profile). For the data presented in Fig. 3 it was found to be 9 cm.

The linear part of the graph can be described by Shiloff equation eq. (5):

$$\tau_b = k \cdot (L - h)$$  \hspace{1cm} (5)

Where: \( k \) - lifetime coefficient of the bed, min cm\(^{-1}\), \( h \) - unused height of the bed (dead zone), m.

For the experimental conditions the Shiloff equation coefficients had been calculated, as follows:

$$\tau_b = 1.404 \cdot (L - 5.625)$$

The \( L_o \) value can be calculated for the cases of already formed adsorption front that moves with constant velocity, i.e. for the cases of stationary conditions, from the breakthrough adsorption curve using the Michaelis-Treybal equation (6) [21]:

$$L_o = L \cdot \frac{\Delta \tau}{\tau_s - (1 - f)\Delta \tau}$$  \hspace{1cm} (6)

Here \( \tau_s \) - saturation time, min, i.e. the time necessary for the relative concentration in the gas phase after the bed to reach a value of \( p / p_o = 0.9 \).

\( \tau_b \) - breakthrough time, min

\( \Delta \tau = \tau_s - \tau_b \), min

\( f \) - the breakthrough curve symmetry coefficient.

In Fig. 4 the breakthrough adsorption curve for the following working conditions is presented: ethanol concentration in the gas phase \( p_o = 19 \) Pa; adsorption temperature \( t = 20^\circ C \); superficial gas velocity \( w_o = 0.094 \) m s\(^{-1}\); bed height \( L = 15 \) cm. For these conditions the following parameters were found: \( \tau_s = 27 \) min; \( \tau_b = 14.5 \) min; \( f = 0.45 \); \( \Delta \tau = 27-14.5 = 12.5 \) min. Their values were used to determine \( L_o = 9.32 \) cm using eq. (6).

The bed lifetime coefficient in Shiloff equation is used to calculate the velocity of the concentration front with constant profile by the relationship (7).

$$U = \frac{1}{k} = \frac{1}{(1.404 \cdot 60 \cdot 100)} = 0.000119 \text{ m s}^{-1}$$  \hspace{1cm} (7)

On the other hand the velocity of the concentration front with constant profile for isothermal adsorption can be calculated from the equilibrium capacity by Wilson equation (8) [21]:

$$U = w_o \cdot \frac{C_o}{(a_o + C_o)}$$  \hspace{1cm} (8)

Here \( a_o \) is the adsorption capacity, equilibrium to gas phase concentration \( C_o \). For the gas phase concentration of \( C_o = 0.025 \) cm\(^3\) cm\(^{-3}\) (19 Pa) the equilibrium capacity is \( a_o = 17.672 \) cm\(^3\) cm\(^{-3}\) (1.057 mmol g\(^{-1}\)), for gas velocity value of \( w_o = 0.094 \) m s\(^{-1}\), the front velocity is \( U = 0.000133 \) m s\(^{-1}\), a value higher with 11 % than that calculated by eq. (7).

It must be accounted for the fact that the change of the velocity, the particles’ diameters and the concentration in the gas phase leads to changes in Shiloff equation parameters. It was found experimentally that for the same system adsorbent-adsorbate the following dependencies can be used [23]:

$$k_1 \cdot w_1 = k_2 \cdot w_2 = const$$  \hspace{1cm} (9)

$$\frac{\tau_1 \cdot \sqrt{w_1}}{d_1} = \frac{\tau_2 \cdot \sqrt{w_2}}{d_2} = const$$  \hspace{1cm} (10)

$$\tau_1 \cdot C_{o1}^{m} = \tau_2 \cdot C_{o2}^{m} = const$$  \hspace{1cm} (11)

Here \( \tau = k \cdot h \) is the time loss for the constant profile zone formation or the time loss for breakthrough of the bed.

To derive the adsorption capacities of the natural clinoptilolite for the ethanol experiments with fol-
lowing operational conditions were carried out: adsorption temperature \( T = 20^\circ C \); superficial gas mixture velocity of \( w'_o = 0.094 \) m s\(^{-1}\); bed length \( L = 15 \) cm. The ethanol concentration in the gas mixture varied up to \( p'_o = 44 \) Pa. The adsorption was determined gravimetrically by the difference in the weight of the dehydrated sample after the adsorption and before the beginning. Other method to find the capacity was by solving the material balance after the integration of the breakthrough curve, presented in Fig. 4. The capacity derived from the breakthrough curve is so-called dynamic adsorption capacity. A comparison between the capacity values obtained in the column and in the desiccator was done. Its results are summarised in Table 3 and in Fig. 5 in the form of the adsorption isotherm.

It can be concluded from the data that the adsorption capacity derived at static conditions by the desiccator method was about 17 \% higher compared to those obtained by the dynamic method.

The data presented in Table 4 showed that the adsorption capacities for Bulgarian natural clinoptilolite are comparable with those found in literature for different modified forms of natural zeolites. Therefore the Bulgarian natural clinoptilolite is a promising adsorbent for the ethanol vapours from their mixtures with air.

The parameters of the adsorbent bed are highly dependent on the time of formation of the constant pattern, on its length and shape and its velocity. On the other hand these parameters at a given hydrodynamic regime and adsorption isotherm are defined by the mass transfer rate. It is well established that for different adsorption experimental conditions (gas phase flow rate, particles’ dimensions, the adsorbate concentration, etc.) the mass transfer limiting stage can be external or internal mass transfer. It is possible the process to be limited by both processes as well. For appropriate process management it is necessary to know the conditions of so-called internal and external hydrodynamic problem.

Because of the fact that the gas flow velocity is the determining parameter for the external mass transfer coefficient only the breakthrough curves (at the same other experimental conditions) will change until the moment when the internal diffusion becomes a limiting stage of the mass transfer process. This suggestion is based on the methods available in literature for \( W_f \) determination.
Table 3. Adsorption capacities.

<table>
<thead>
<tr>
<th></th>
<th>Dynamic breakthrough curves method</th>
<th>Desiccator method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gravimetrically (run 1)</td>
<td>Breakthrough curve (run 2)</td>
</tr>
<tr>
<td></td>
<td>$p_0$</td>
<td>$a_o$</td>
</tr>
<tr>
<td>Pa</td>
<td>mmol.g$^{-1}$</td>
<td>Pa</td>
</tr>
<tr>
<td>2.10</td>
<td>0.506</td>
<td>19</td>
</tr>
<tr>
<td>3.75</td>
<td>0.709</td>
<td></td>
</tr>
<tr>
<td>10.15</td>
<td>0.938</td>
<td></td>
</tr>
<tr>
<td>17.39</td>
<td>1.048</td>
<td></td>
</tr>
<tr>
<td>17.98</td>
<td>1.053</td>
<td></td>
</tr>
<tr>
<td>19.04</td>
<td>1.043</td>
<td></td>
</tr>
<tr>
<td>1925</td>
<td>1.060</td>
<td></td>
</tr>
<tr>
<td>19.13</td>
<td>1.057</td>
<td></td>
</tr>
<tr>
<td>24.85</td>
<td>1.074</td>
<td></td>
</tr>
<tr>
<td>32.99</td>
<td>1.093</td>
<td></td>
</tr>
<tr>
<td>39.45</td>
<td>1.136</td>
<td></td>
</tr>
<tr>
<td>43.91</td>
<td>1.171</td>
<td></td>
</tr>
</tbody>
</table>

The possibility to vary the velocity during the breakthrough curves dynamic method experiments was used to find the critical velocity at which the influence of the external mass transfer resistance became negligible. For this purpose a run of experiments at following working conditions was carried out: adsorption temperature $T=20^\circ$C, bed height $L=13.5$ cm, ethanol concentration in the gas mixture $p_o=19$ Pa. The superficial gas velocity was varied in the interval $w_o=0.043$ to $0.15$ m s$^{-1}$. The results of these experiments are presented in Fig. 6.

As a simple criterion for the elimination of the external mass transfer resistance can be used the interruption of the linear form of the graph $w_o=f(\tau_b)$. It can be seen from the figure, that for the working conditions this critical value is $=0.0615$ m s$^{-1}$.

CONCLUSIONS

Adsorption experiments have been done by the dynamic breakthrough curves method in a fixed bed adsorption column. During the investigation the gas velocity, the initial ethanol concentration in the gas mixture and the bed length were varied. The data concerning hydrodynamic parameters of the bed were obtained: the relationship between the bed length and the pressure drop was found; the breakthrough curves of the adsorbent beds were derived. The adsorption capacity of the adsorbent was investigated and compared with similar experimental data from the literature concerning other types of adsorbents. The adsorption capacities found for Bulgarian natural clinoptilolite are comparable with those found in literature for different modified forms of natural zeolites. Therefore the Bulgarian natural clinoptilolite is a promising adsorbent for ethanol vapours from their mixtures with air. The conditions when the external mass transfer resistance can be neglected were also determined. The data obtained can be used for prediction of adsorption capacities of Bulgarian clinoptilolite and for design of adsorption equipment.
Table 4. Comparison between the adsorption capacities obtained in this study with literature data.

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>a, mmol g(^{-1})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol vapours adsorbed with natural clinoptilolite at static conditions for 20 °C and (p_v = 44) mm Hg</td>
<td>1.391 mmol g(^{-1})</td>
<td>Present study</td>
</tr>
<tr>
<td>Ethanol vapours adsorbed with natural clinoptilolite at dynamic conditions (20 °C and (p_v = 44) mm Hg)</td>
<td>1.171 mmol g(^{-1})</td>
<td>Present study</td>
</tr>
<tr>
<td>Ethanol vapours adsorbed with dealuminated DAY at 25 °C; capacity calculated for (p_v = 44) mm Hg</td>
<td>4.4 mmol g(^{-1})</td>
<td>[3]</td>
</tr>
<tr>
<td>Ethanol vapours adsorbed with silicalite at 25 °C; capacity calculated for (p_v = 44) mm Hg</td>
<td>2.6 mmol g(^{-1})</td>
<td>[3]</td>
</tr>
<tr>
<td>Ethanol vapours adsorbed with zeolitelike aluminium phosphates AlPO(_4)-5 at 25 °C, capacity (q_o) found by Langmuir equation.</td>
<td>1.66 mmol g(^{-1})</td>
<td>[4]</td>
</tr>
<tr>
<td>Ethanol vapours adsorbed with different types of activated carbons at 20 °C, capacity calculated for (p_v = 44) mm Hg</td>
<td>4.147 - 7.19 mmol g(^{-1})</td>
<td>[5]</td>
</tr>
<tr>
<td>Ethanol vapours adsorbed with natural mordenite during a 35 min period at (p_v = 33) Pa</td>
<td>1.201 mmol g(^{-1})</td>
<td>[7]</td>
</tr>
<tr>
<td>Ethanol vapours adsorbed with reacciónated natural mordenite during a 35 min period at (p_v = 33) Pa.</td>
<td>1.972 mmol g(^{-1})</td>
<td>[7]</td>
</tr>
<tr>
<td>Ethanol vapours adsorbed with dealuminated DAY at 21 °C capacity calculated for (p_v = 44) mm Hg</td>
<td>3.696 mmol g(^{-1})</td>
<td>[8]</td>
</tr>
<tr>
<td>Ethanol vapours adsorbed with NaA (Si/Al=23) at 75 °C for (p_v = 10.5) mm Hg</td>
<td>0.752 mmol g(^{-1})</td>
<td>[9]</td>
</tr>
<tr>
<td>Ethanol vapours adsorbed with silicalite1 at 75 °C for (p_v = 10.5) mm Hg</td>
<td>0.465 mmol g(^{-1})</td>
<td>[9]</td>
</tr>
<tr>
<td>Ethanol vapours adsorbed with Na form of natural stilbite at при 25 °C for (P/P_s=0.5)</td>
<td>1.029 mmol g(^{-1})</td>
<td>[10]</td>
</tr>
</tbody>
</table>
REFERENCES