THE EQUILIBRIUM OF ADSORPTION PROCESSES OF SULPHUR DIOXIDE ON ZEOLITES

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Lucrarea prezintă un studiu al echilibrului adsorbției SO_2 pe zeoliții de tip Y, caracterizați prin spectrele de difracție cu raze X. S-au determinat izotermele de adsorbție a dioxidului de sulf pe doi zeoliți NaY şi HY în funcție de presiunea şi temperatura adsorbatului. Au fost calculate izotermele de adsorbție folosind modelele Langmuir şi Freundlich, care apoi au fost comparate cu izotermele experimentale. S-a constatat că adsorbția SO_2 pe zeoliți Y pote fi descrisă de modelul Freundlich, iar zeolitul NaY, este mai bun sorbent decât cel HY.

This paper presents a study of the equilibrium of SO2 adsorption on Y type zeolites, for which the the X-ray diffraction spectra were also carried out. The adsorption isotherms of sulphur dioxide on two HY and NaY zeolites were determined depending on the pressure and temperature of the adsorbate. The adsorption isotherms were calculated using Langmuir and Freundlich models, which were subsequently compared to the experimental isotherms. It was found that SO2 adsorption on Y zeolites can be described by the Freundlich model, and that the NaY zeolite is a better sorbent than HY.

Keywords: sulphur dioxid, adsorption, Y zeolites, XRD spectra

1. Introduction

The effective decrease of SO_2 content in gases resulting from the combustion of fuels containing sulphur is one of the most important environmental challenges. SO_2 removal through adsorption onto an adsorbent is a potential alternative to conventional technologies based on wet or dry removal. The latter are technologies with high operational cost and low efficiency in removing SO_2 and which do not solve the issue of capitalizing on the SO_2 [1].

The adsorption processes can occur with a high degree of retention, but require large amounts of adsorbent and high energy consumption for adsorbent regeneration. These problems can be solved using an adsorbent material with high sulphur dioxide adsorption capacity.

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A great variety of adsorbents were tested in the adsorption process of SO_2 [2-10] of which natural or synthetic zeolites appear to have the most extensive activity. Therefore, with the exception of relatively low SO_2 adsorption capacity at high temperatures, the utilization of zeolites for the adsorption of SO_2 from residual combustion gases is an increasingly attractive idea.

The most common adsorption isotherms used to estimate the influence of the various parameters are the Langmuir and Freundlich isotherms.

Langmuir's model is based on an adsorbent on the surface of which are active sites with residual valences [11]. He applies the hypothesis holding that covalent bonds are formed between the surface of the adsorbent and the molecules of the adsorbed component and there is no interaction among the molecules of the adsorbed component.

The model is described by the following formula:

$$q = \frac{K \cdot P \cdot q_{\max}}{1 + K \cdot P} \qquad (1)$$

The Langmuir adsorption equation can be represented in the liniar form: $\frac{1}{q} = \frac{1}{K \cdot P \cdot q_{\max}} + \frac{1}{q_{\max}}$

making the changes in variable $\frac{1}{q} = y$ and $\frac{1}{P} = x$ a linear equation is obtained:

$$y_c = A \cdot x + B$$

where q, q_{max} - sulphur dioxide content at equilibrium and the maximum adsorption capacity of sulphur dioxide (mg/g);

P - sulphur dioxide pressure at equilibrium (mmHg)

K – the equilibrium constant of the model

The Freundlich model assumes that chemical equilibrium is achieved when there is a dynamic exchange between the adsorbed phase molecules and the ones remaining in the solution [12]:

$$q = K \cdot P^m \qquad (2)$$

Equation (2) can be linearized by taking the logarithm:

$$\ln q = \ln K + m \ln P$$

In the end a linear regression which is solved using the method of least squares is reached.

The objectives of the present study were primarily to model the processes of sulphur dioxide adsorption on NaY and HY zeolites using the classic Langmuir and Freundlich isotherms and to understand the influence of pressure and temperature on these processes.

2. Experimental

The diffractograms were carried out at Institute de Recherches sur la Catalyse, Villeurbanne, France on a Siemens D5 diffractometer, using CuKα radiation, shown in Fig. 1 for the NaY zeolite and in Fig. 2 for the HY zeolite and interpreted by comparison with simulated X-ray diffraction patterns found in literature [13-15].

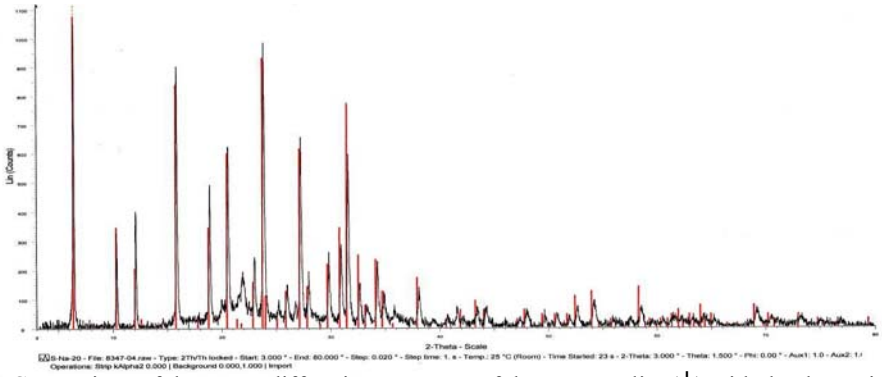

Fig. 1. Comparison of the X-ray diffraction spectrum of the NaY zeolite (|) with the theoretical model (|)

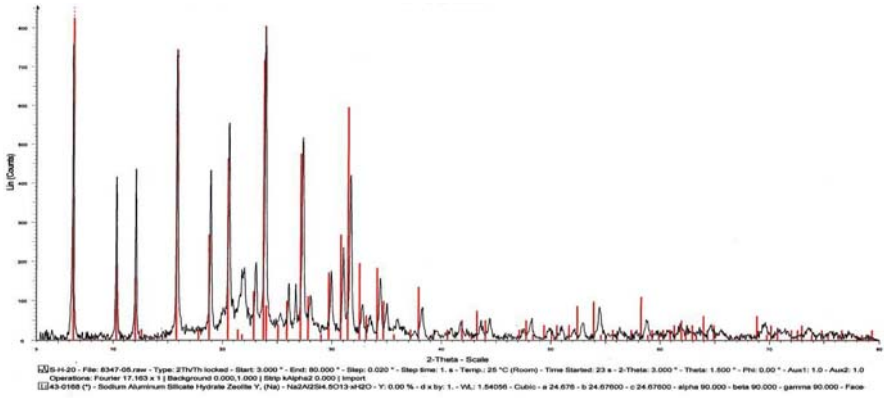

Fig. 2. Comparison of the X-ray diffraction spectrum of the HY zeolite (|) with the theoretical model (|)

The zeolites used have a well-defined crystalline structure, in accordance with the models from literature.

According to literature data for the NaY zeolite, the composition can be expressed using the formula:

$Na_xAl_xSi_{192-x}O_{384} \cdot zH_2O$

By analysing the X-ray diffraction spectrum, the value of both x and the Si/Al and SiO_2/Al_2O_3 ratios are determined and presented in Table 1.

Table 1.

Zeolite composition

Zeolite / *Size*	*NaY*	*HY*
a(Å)	24.676	24.676
x	59.08	56.47
Si/Al	2.25	2.40
SiO_2/Al_2O_3	4.50	4.80

In order to characterize the adsorption systems from a thermodynamic viewpoint, the adsorption isotherms were experimentally determined using the apparatus in Fig. 3.

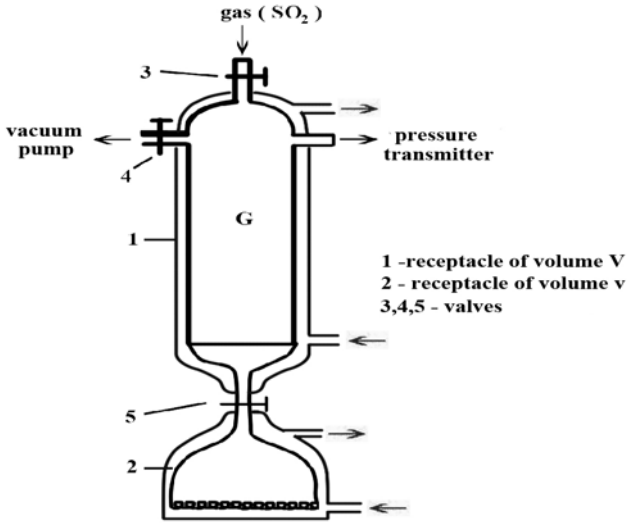

Fig. 3. Experimental apparatus for determining the adsorption isotherms

Experimentally obtained data for the two adsorbents were interpreted following the variation in adsorption capacity depending on the nature of the adsorbent, the adsorption temperature, the concentration of the adsorbed gas, but were also used to check to what extent they correspond to the theoretical models developed in literature, namely the Langmuir and Freundlich models [16-17].

3. Results and Discussion

The experimental results establish the equilibrium curves for determining the adsorption capacity of sulphur dioxide on the zeolites' surface (NaY and HY) using the Langmuir and Freundlich isotherms at three temperatures 25°C, 50°C and 100°C. Using the adsorption isotherm, which represents the relationship between the adsorbed sulphur dioxide and the equilibrium pressure (Langmuir and Freundlich equation), the maximum adsorption value (q_{max}) and the constant (K) referring to the adsorption energy can be calculated, measurements necessary for comparing the zeolites in terms of their adsorption properties of the gas being studied. Resulting from the regression calculations are the following values of the interpolation line parameters for the Langmuir and Freundlich model. The relevant parameters are listed in Tables 2 and 3.

Table 2

Thermodynamic parameters for SO_2 adsorption on NaY zeolite

Temperature	***Langmuir***			***Freundlich***		
(°C)	***K***	***q_{max} (mg/g)***	***R^2***	***K***	***m***	***R^2***
25	0.069	118.527	0.9814	12.048	0.581	0.9902
50	0.043	87.435	0.9789	5.344	0.668	0.9932
100	0.092	31.090	0.9551	4.137	0.521	0.9860

Table 3

Thermodynamic parameters for SO_2 adsorption on HY zeolite

Temperature	***Langmuir***			***Freundlich***		
(°C)	***K***	***q_{max} (mg/g)***	***R^2***	***K***	***m***	***R^2***
25	0.086	63.661	0.9516	7.629	0.563	0.9889
50	0.0434	53.788	0.9782	3.299	0.676	0.9891
100	0.0581	18.593	0.9484	1.653	0.587	0.9712

It can be seen from the presented values that the Freundlich model provides the best approximation of the sulphur dioxide adsorption isotherms (R^2 = 0.97÷0.99) for both types of zeolites, as compared to the Langmuir model (R^2 = 0.94÷0.98).

The Langmuir model provides a better approximation for the NaY type zeolite, in other words, adsorption is more pronounced for this zeolite than for the HY zeolite at a temperature of 25°C. The square values of the correlation coefficients are lower for the HY zeolite due to low adsorption explained by the HY zeolite's composition, which contains less sodium and aluminium and more silicon than the NaY zeolite.

The influence of temperature is also felt on the exchange's intensity. Thus, from the Freundlich model, the A = 1/n slope offers information on the

adsorption's intensity and ordinate B = lnK is indicative of the adsorption capacity, the values of A and B being presented in Table 4:

Table 4

Straight line interpolation parameters A and B for the Freundlich model

Temperature	***NaY Zeolite***		***HY Zeolite***	
(°C)	***A***	***B***	***A***	***B***
25	0.581	2.488	0.563	2.032
50	0.668	1.676	0.676	1.194
100	0.521	1.420	0.587	0.503

The adsorption of sulphur dioxide on NaY and HY zeolites at equilibrium at different temperatures resulted in the experimental values P_e and q_e represented in the curves in Figs. 4-7 along with the Langmuir and Freundlich models.

With the help of the model's parameters, which were calculated by linear regression, the Langmuir and Freundlich isotherms were drawn.

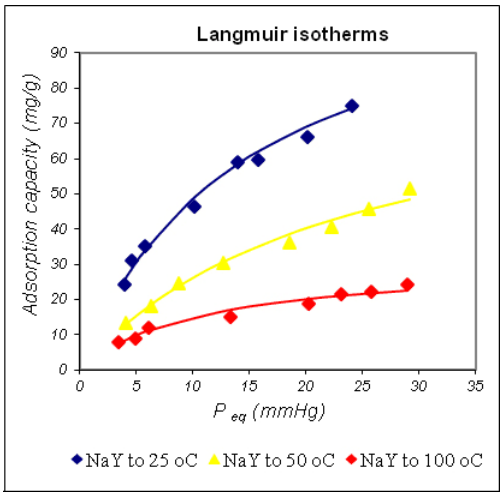

Fig. 4. The SO_2 adsorption Langmuir isotherms for NaY zeolite

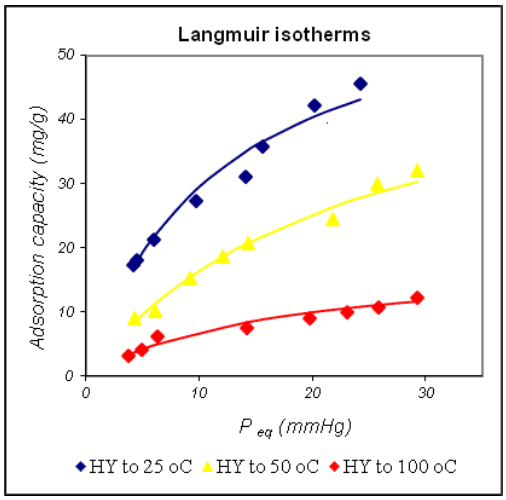

Fig. 5. The SO_2 adsorption Langmuir isotherms for HY zeolite

Figs. 4-7 illustrate the adsorption process of sulphur dioxide on the two zeolites (NaY and HY), where the points are experimental data and the line is the result of the model used.

By comparing the isotherms represented centrally, it is found that the adsorption equilibrium of sulphur dioxide on NaY and HY type zeolites type can be mathematically described by the Langmuir and Freundlich thermodynamic models. However, it can be seen that temperature significantly affects the

adsorption of sulphur dioxide on the NaY type zeolite, compared to the HY zeolite and the most significant growth is achieved, as expected, at low temperatures (25°C).

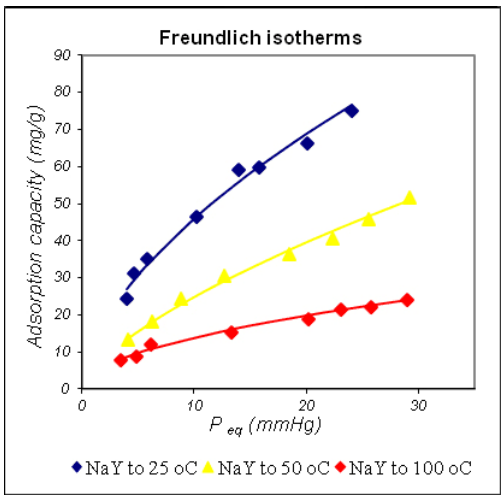

Fig. 6. The SO_2 adsorption Freundlich isotherms for NaY zeolite

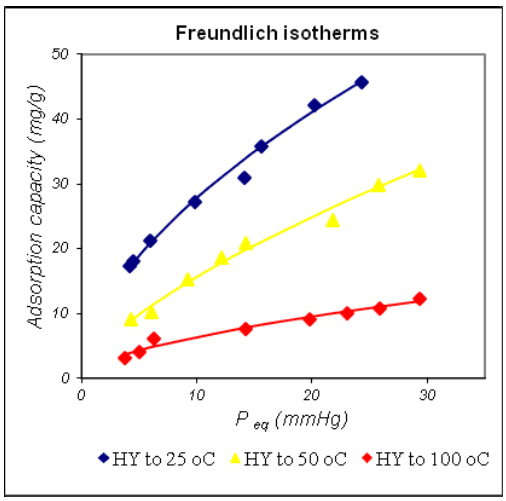

Fig. 7. The SO_2 adsorption Freundlich isotherms for HY zeolite

It is noted that upon increasing the sulphur dioxide pressure the adsorption capacity increases and upon increasing the temperature, the SO_2 adsorption on NaY and HY zeolites capacity decreases, the adsorption-desorption equilibrium shifting in favor of the desorption process. The HY zeolite is found to have lower adsorption capacity than the sodium form, which indicates the involvement of sodium in SO_2 adsorption.

4. Conclusions

- the Y zeolites utilized have a very good crystallinity, virtually copying theoretical models;
- in relation to sulphur dioxide, NaY and HY zeolites prove to be good adsorbents;
- the adsorption capacity decreases for both zeolites as the temperature increases;
- the NaY zeolite has greater adsorption properties than those of the HY zeolite;
- the experimental isotherms of sulphur dioxide adsorption are Freundlich type;
- Y type zeolites can be used to remove sulphur dioxide from combustion gases that pollute the atmosphere.

R E F E R E N C E S

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