The adsorption characteristics and porous structure of bentonite adsorbents as determined from the adsorption isotherms of benzene vapor

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Abstract: The adsorption of benzene vapor on natural and acid activated bentonites was treated by the theory of volume filling of micropores. The micropore volume and characteristic values of the free energy of adsorption were determined from the adsorption isotherms. The Dubinin–Radushkevish–Stoeckli and Dubinin–Astakhov equations were used for this purpose. The results showed that natural bentonite has a more homogeneous micropore structure than the acid activated ones. The characteristic values of the free energy of adsorption for the natural bentonite were higher than those of the acid activated bentonite. This is due to differences in its structure and the pore size.

Keywords: adsorption, bentonite, chemical activation, Dubinin–Radushkevich–Stoeckli and Dubinin–Astakhov equations.

INTRODUCTION

It is known that natural bentonites become effective adsorbents and active catalysts just after acid activation.

The acid treatment replaces the exchangeable cations with hydrogen ions. Hydrogen ions also attack the Me–O bond in the fragment Me–O–Si in the octahedral sheets, probably at the site of the oxygen atom, which possesses electron donor characteristics. This results in the breaking of the Me–O bond and the transfer of metal ions (Al^{3+}, Fe^{3+}, Mg^{2+}) to exchangeable positions. The negative charge is balanced by hydrogen ions. As acid treatment proceeds, the adsorption properties of the activated bentonites change.[1–4]

Montmorillonite, the basic mineral in bentonite, belongs to a group of microporous adsorbents.[5,6]

Adsorption by microporous adsorbents is described by the theory of volume filling of micropores developed by Dubinin and his co-workers.[7] The fundamental relations are the Dubinin-Radushkevich and Dubinin-Astakhov equations. They are given, respectively, in the following forms:

$$W = W_0 \exp[-B(T/\beta)^2 \log^2(P_0/P)] \tag{1}$$

and

$$W = W_0 \exp[-(A/\beta E_0)^n] \tag{2}$$

In Eqs. (1) and (2), W represents the volume of liquid-like adsorbate filling the micropores at temperature T and relative pressure P/P_0, W_0 is the volume of the micropores, B is a parameter characterizing the microporous structure, β is the affinity coefficient of the characteristic curves, E_0 is the characteristic energy of adsorption, n is an equation parameter and A is the differential molar work of adsopriton *i.e.*, the differential Gibbs energy of adsorption, ΔG, defined by

$$A = -\Delta G = RT \ln(P_0/P) \tag{3}$$

Stoeckli attempted to generalize the Dubinin–Radushkevich equation to heterogeneous microporous adsorbents.[8] He assumed that the distribution of the micropore volume W_0 with respect to parameter B of the Dubinin–Radushkevich equation could be expressed by a Gaussian distribution function.

$$f(B) = \frac{dW_0}{dB} = \frac{W_0^\circ}{\Delta(2\pi)^{1/2}} \exp\left[-\frac{(B-B_0)^2}{2\Delta^2}\right] \tag{4}$$

where W_0° is the total volume of the micropores, B_0 is the value of the Dubinin–Radushkovich parameter B for the maximum of the distribution curve and Δ is the dispersion. By integrating the contribution of the micropores with the corresponding structural parameter B, each of which can be described by the Dubinin–Radushkevich equation and invole the function $f(B)$, Stoeckli derived the following equation

$$W = W_0^\circ \exp(-B_0 y) \exp(y^2\Delta^2/2) 0.5 [1-\text{erf}(z)] \tag{5}$$

where

$$y = [(T/\beta) \log P_0/P]^2 \tag{6}$$

$$z = (y - b_0/\Delta^2) \Delta/(2)^{1/2} \tag{7}$$

and efr(z) is an error function.

In this work this equation was applied for the determination of the porous characteristics of bentonites.

Useful information concerning the energetic characteristics can be provided from the differential distribution of the volume filling of the micropores, W, with the free energy of adsorption. The distribution function can be derived from the Dubinin–Astakhov equation

$$\frac{dW}{dA} = -\frac{W_0 n A^{n-1}}{(\beta E_0)^n} \exp[-(A/\beta E_0)^n] \tag{8}$$

For this distribution, the characteristics values of the free enrgy of adsorption (mode and mean) can be determined[9,10]

$$A_{\text{mode}} = \beta E_0 [(n-1)/n]^{1/n} \tag{9}$$

$$A_{\text{mean}} = \beta E_0 \Gamma(1/n + 1) \tag{10}$$

were Γ is the gamma function. The affinity coefficient β for benzene is 1.

The present study was an attempt to determine the adsorption and porous characteristics of natural bentonite from Macedonia and its forms acidoactivated with 10 % and 15 % solutions of hydrochloric acid.

EXPERIMENTAL

The natural bentonite from Ginovci, Macedonia (in the text labeled as B) has the following chemical composition: SiO_2 68.22 %, Al_2O_3 21.32 %, Fe_2O_3 3.21 %, MgO 4.15 %, CaO 2.03 %, Na_2O 0.40 %, K_2O 0.40 %, $H_2O + CO_2$ 8.06 %. The montmorillonite content of the bentonite is around 85 % and it has a monoclinic structure. Mg^{2+} and Ca^{2+} are the most abundant natural interlayer cations.[2]

Bentonite, with a particle size of less than 0.2 mm and dried at 105 ºC, was treated with 10 % and 15 % hydrochloric acid (labeled as B10Cl and B15Cl) by a standard procedure.[5]

Chemical and X-ray analysis of the activated bentonites show that acid activation besides leaching cations from the montmorillonite structure and replacing the exchangeable cations with hydrogen ions also dissolves impurities such as calcite, dolomite, *etc*. The changes are more expressed for the sample that had been treated with 15 % HCl.[11]

Adsorption isotherms of benzene on the natural and acid activated bentonites were determined by a modified flow method. Prior to the adsorption measurements, the samples were heated for 3 h at 393 K. The adsorption isotherms were determined at 298 K. The adsorption of benzene vapor was performed from the stream of nitrogen used as the carrier gas. The partial pressure of benzene vapor in the gas mixture was calculated from the flow of nitrogen. The amount of adsorption was measured gravimetrically.

RESULT AND DISCUSSION

The parameters of the Dubinin–Radushkevich–Stoeckli equation (Eq. (5)) can be determinated from its linear form:

$$\ln W^* = \ln W_0^\circ - B_0 y \tag{11}$$

where

$$W^* = \frac{W}{\exp{(y^2 \Delta^2 / 2)} 0.5 [1 - \text{erf}(z)]} \tag{12}$$

The values of y and z were calculated using Eqs. (6) and (7), the parameter B was accepted from the Dubinin–Radushkevich equation as a first approximation for the value of B_0. Using different values of Δ, the data of W^* were calculated. The value of Δ which gave the best accordance between the experimental data and the Dubinin–Radushkevich–Stoeckli equation was selected.[12] The micropore volume W_0° and the proper value of the parameter B_0 were evaluated from the intercept and the slope, respectively, of the plot of ln W^* against y (Eq. (11)), using the least squares method.

In order to determine the parameters of the Dubinin–Astakhov equation, its linear form was used

$$\ln W = \ln W_0 - A^n / E_0^n \qquad (13)$$

The micropore volume W_0 and the characteristic energy of adsorption E_0 were evaluated from the intercept and the slope of the resulting straight line by means of the least squares method.

The values of the parameters of the Dubinin–Radushkevich–Stoeckli and Dubinin-Astakhov equations determined using the described procedures are listed in Tables I and II.

TABLE I. Parameters of the Dubinin–Radushkevich–Stoeckli equation

Bentonite	$W_0^{\circ}/cm^3\ kg^{-1}$	Δ/K^{-2}	B_0/K^{-2}
B	162.55	1.4×10^{-6}	5.0×10^{-6}
B10Cl	144.60	1.6×10^{-6}	6.1×10^{-6}
B15Cl	110.06	2.4×10^{-6}	5.2×10^{-6}

TABLE II. Parameters of the Dubinin–Astakhov equation

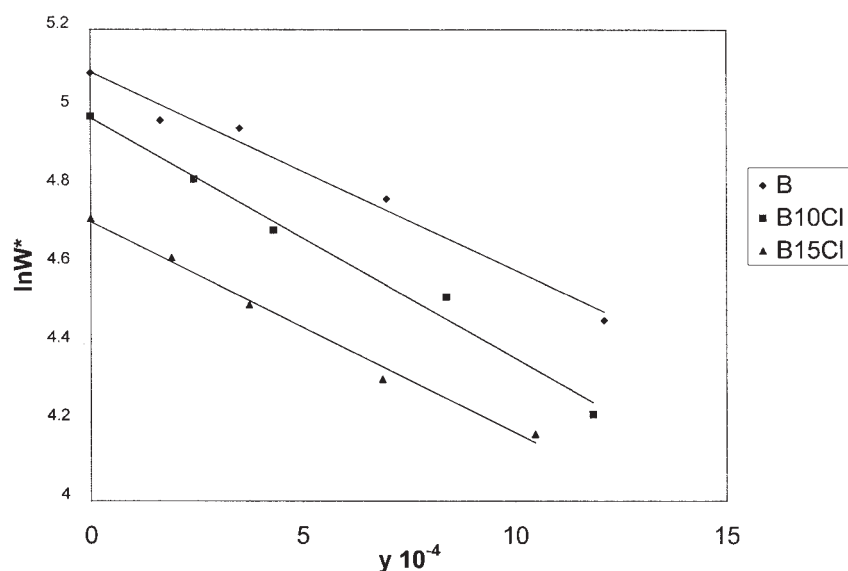| Bentonite	n	$E_0 / kJ\ mol^{-1}$
B	3.3	8.09
B10Cl	3.0	7.74

Fig. 1. Adsorption isotherms of benzene vapor on bentonites, plotted according to the Dubinin–Radushkevich–Stoeckli equation.
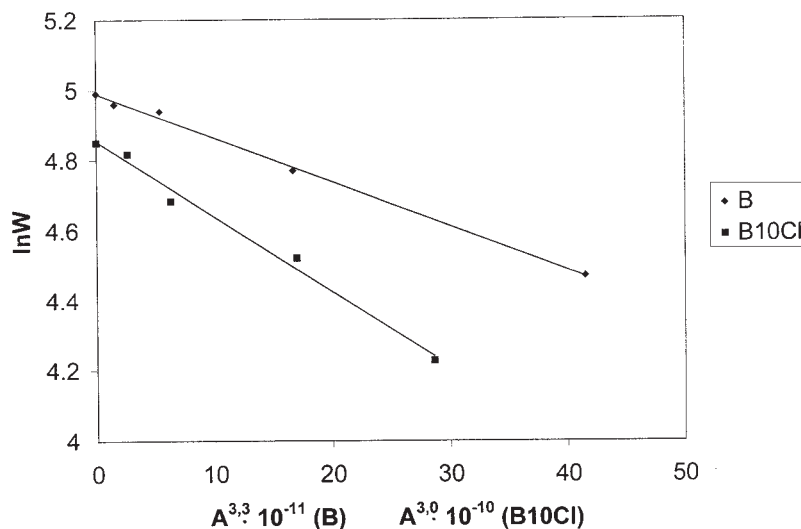
Fig. 2. Adsorption isotherms of benzene vapor on bentonites, plotted according to the Dubinin–Astakhov equation.

It can be seen from Table I that the dispersion Δ increases from B to B15Cl which means that the degree of microporous heterogeneity increases in the same direction.

The plots resulting from the Dubinin–Radushkevich–Stoeckli and Dubinin–Astakhov equations are presented in Figs. 1 and 2, respectively.
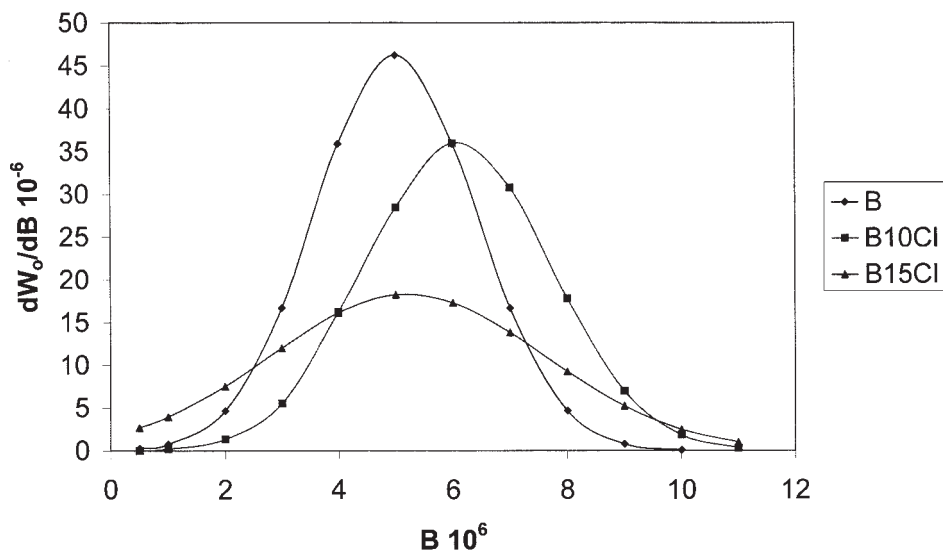

Fig. 3. Differential distribution of micropore volume with parameter B.

The adsorption isotherms for B15Cl are not presented in the linear form of the Dubinin–Astakhov equation (Fig. 2) because the differential distribution of micropore volume with free energy of adsorption is non-modal.
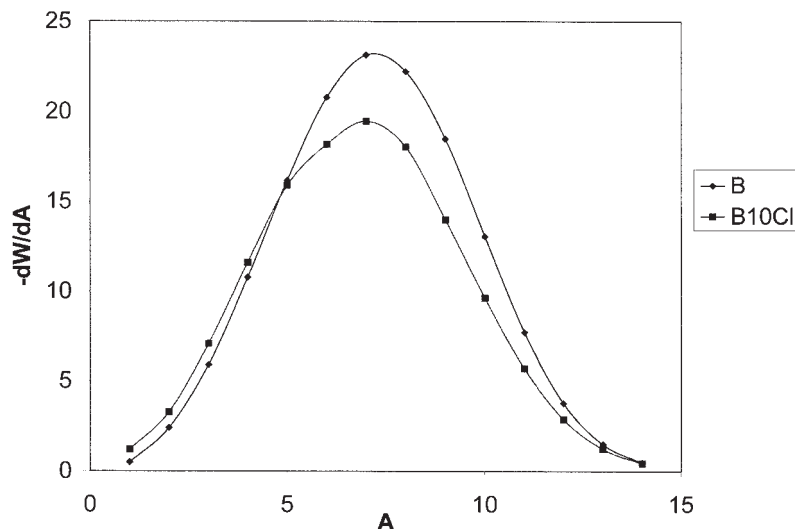
Fig. 4. Differential distribution of micropore volume with free energy of adsorption.

Natural bentonite has a more homogeneous micropore structure than the acid activated ones. This is illustrated by the differential distribution of the micropore volume with respect to the parameter *B*, Fig. 3, determined from Eq. (4).

From Fig.3 it can be seen that the size of the pores of adsorbent B10Cl is bigger than of B (the value of B_0 for B10Cl is higher than for B, Table I). The differential distribution of the micropore volume for B10Cl is moved in the direction of the bigger pores. Montmorillonite dried at temperatures below l50 °C contains the water which enables the penetration of the benzene molecules into the montmorillonite interlayer space.[13] The change in the montmorillonite structure during acid activation can be the reason for the decrease in the amount of residual water after drying and thus the limited penetration of benzene molecules, which is more remarkable for B15Cl.

The energetic characteristics of B and B10Cl, obtained from its differential distribution of micropore volume, *W*, with free energy of adsorption are presented in Fig. 4.

The broad distributions indicate that natural and acid activated bentonites have high degrees of energetic heterogeneity.

The mode, A_{mode} and mean, A_{mean}, values of the free energy of adsorption in these distributions were evaluated from Eq. (9) and Eq. (10) and are given in Table III.

TABLE III. Values of A_{mode} and A_{mean}

Bentonite	A_{mode}	A_{mean}
B	7.25	7.26
B10Cl	6.76	6.91

The decrease of the values of E_0, A_{mode} and A_{mean} for B10Cl (Tables II and III) is due to the increase of the pore size and to the absence of exchangeable cations and also to par-

tially removed cations from octahedral sheets, which results in weaker interaction of the benzene molecules with the adsorption centers.

CONCLUSION

After chemical activation, bentonites have different structures and pore sizes.[5,6,11] This was confirmed by adsorption of benzene vapor on natural and acid activated bentonites. The change of the montmorillonite structure during acid activation can be the reason for the decrease in the amount of residual water after drying and thus the limited penetration of benzene molecules. The result is a decrease of the values of the micropore volume for the acid activated bentonites (144.60 and 110.06 cm^3 kg^{-1}) in comparison with that for natural bentonite (162.55 cm^3 kg^{-1}), as determined by the adsorption of benzene vapor.

ИЗВОД

АДСОПРЦИОНА СВОЈСТВА И ПОРОЗНА СТРУКТУРА БЕНТОНИТСКИХ АДСОРБЕНАТА ОДРЕЂЕНИХ ИЗ АДСОРПЦИОНИХ ИЗОТЕРМИ БЕНЗЕНОВИХ ПАРА

СНЕЖАНА БРЕЗОВСКА, БИЉАНА МАРИНА, БИЉАНА ПАНОВА, ДОНЧО БУРЕВСКИ, ВАСА БОШЕВСКА И ЛЕПА СТОЈАНОВСКА

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Адсорпција бензенових пара на природном бентониту и бентониту после његове хемијске обраде раствором HCl, испитивана је теоријом запреминског попуњавања микропора. Запремина микропора и карактеристичне величине слободне енергије адсорпције одређиване су из адсорпционих изотерми. Коришћење су Dubinin–Radushkevich–Stoeckli и Dubinin–Astakhov једначине. Резултати ових испитивања указују на то да природни бентонит има хомогенију микропорозну структуру у односу на киселоактивирани бентонит. Карактеристичне величине слободне енергије адсорпције за природни бентонит су веће од оних за киселоактивирани бентонит, што је резултат разлика у њиховим порозним структурама.

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