# ADSORPTION OF WATER VAPOUR ON MONTMORILLONITE SATURATED WITH MONO AND BIVALENT CATIONS

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A b s t r a c t. The process of adsorption of water vapour at T= 293 K on montmorillonite (Wyoming Bentonite) saturated with $Li^+$, $Na^+$, $K^+$, $Mg^{++}$, $Ca^{++}$ and $Ba^{++}$ cations was studied. The experimental measurement were carried out by using the vacuum microbalance technique. Additionally, porosity of the samples were investigated by using the mercury porosimeter. The experimental adsorption isotherms were described by the so-called exponential adsorption equation. The coefficients of this equation define the energy distribution function, which characterizes energetic heterogeneity of adsorbing surfaces. These functions provide additional characteristics of adsorbing systems and are useful while discussing adsorption properties.

## INTRODUCTION

The problem of a proper choice of an analytical form of the isotherm equation to describe adsorption of gases on soils and clay minerals has been the subject of numerous investigations.

In the case of monolayer adsorption, several equations such as Langmuir, Hill-DeBoer, Harkins-Jura are considered [1,4,18,17,19]. The multilayer adsorption, however, is most often interpreted in terms of the classical BET theory [9,10,13,14]. Unfortunately, in general, none of the above listed equations can accurately describe experimental data for a wide range of pressures [14]. One of the main reasons for that is the fact, that at surface coverages lower than the monolayer capacity, energetic heterogeneity of adsorbing sites plays a very

important role, whereas all the above equations were derived assuming that adsorbing sites possess the same value of adsorption energy. In the case of higher surface coverages, however, the structure of soil adsorbents may change, e.g., some of the clay minerals may swell. Obviously, the above theories do not also take into account any possibility of such changes [14].

At low and moderate adsorbate pressures, the role of energetic heterogeneity of adsorbing surfaces seems to be more important than possible modifications of the adsorbent by the already adsorbed phase. Therefore, in this note we present an application of the theories of adsorption of gases on energetically heterogeneous surfaces [5,6,7,8] to describe adsorption of water vapour on montmorillonite, saturated with mono and bivalent cations.

### THEORY AND METHODS

#### Adsorption isotherm equation

In the case of energetically heterogeneous solid surfaces, the adsorbing potential changes randomly and cannot be described by any analytical equation. These random changes are obviously connected with the physical nature of real surfaces. The exsistence of pores of different shape and size, different chemical species present on the surface and

irregularities of its structure cause quite random and rather big changes in the adsorbing field. Thus, any attempt to describe adsorption on energetically heterogeneous surfaces (i.e. on real surfaces) cannot neglect the real energetic character of adsorbing centers.

Denoting by $\varepsilon_i$ the energy of interactions of a single adsorbate molecule with the adsorbing site $i$ of the adsorbent surface, the energetic surface heterogeneity can be characterized by invoking the distribution function $\chi(e)$, definded in such a manner, that $\chi(\varepsilon)d\varepsilon$ represents the ratio of all adsorbing sites having adsorbing energies from the range $[\varepsilon, \varepsilon+d\varepsilon]$ [6,7,8]. Next assuming that the adsorption equilibrium on a model homogeneous surface, for which all adsorbing sites have the same adsorption energy $\varepsilon$, is described by the so-called local adsorption isotherm $\Theta_l$, the total adsorption $\Theta_t$ can be described by

$$\Theta_t(p) = \frac{N(p)}{N_m} = = \int_\Omega \chi(\varepsilon)\, \Theta_1(p, \varepsilon)\, d\varepsilon$$

(1)

where $p$ is the pressure, $N(p)$ is the amount of adsorbed gas, $N_m$ is the monolayer capacity and $\Omega$ is the range of adsorption energies $\varepsilon$. Thus, an analytical evaluation of the total adsorption equation requires the knowledge of both: the local adsorption isotherm $\Theta_1(p,\varepsilon)$ and the energy distribution function $\chi(\varepsilon)$. On the other hand, for a given local adsorption model, the energy distribution function can be evaluated by solving integral Eq. (1), providing that the total adsorption isotherm is known (e.g., it has been determined from experimental measurements) [6,7,8]. In other words, from experimentally measured adsorption isotherms, one can get some additional information concerning the energetic character of the surface by solving the integral Eq. (1). Obviously, the shape of the evaluated distribution function will depend slightly upon the

assumed local adsorption model, but this effect is rather small. The last problem was discussed in details elsewhere [8].

Previous studies [2,6,7,8,12] have shown, that in the case of the Langmuir model of local adsorption

$$\Theta_1(p,\varepsilon) = \frac{p}{K\exp(-\varepsilon/RT) + p},$$

(2)

the total adsorption isotherm

$$\Theta_t(p) = \exp\left[\sum_{l=1}^{M} B_l\, (RT\,\ln(p/p_O))^l\right],$$

(3)

corresponds to the following energy distribution function

$$\chi(\varepsilon) = \left(\sum_{l=1}^{M} lB_l(\varepsilon_0-\varepsilon)^{l-1}\right)\exp\left(\sum_{l=1}^{M} B_l(\varepsilon_0-\varepsilon)^l\right).$$

(4)

In the above $T$ is the temperature, $R$ is the gas constant, $K$ is a constant, connected with the minimum adsorption energy $\varepsilon_0$ on a given surface by the relation: $\varepsilon_0 = RT\,\ln(K/p_0)$.

In the case of multilayer adsorption, the formation of the subsequent adsorbed layers is very often treated as the process similar to condensation of gaseous adsorbate. In other words, the adsorbent-adsorbate interactions are effectively screened by the first adsorbed layer. In such a case, the minimum adsorption energy $(\varepsilon_0)$ is identified with the energy of condensation of the gaseous adsorbate $(\varepsilon_c)$ and the pressure $p_0$ with the saturated vapor pressure. Thus assuming that the local adsorption isotherm is described by the BET equation

$$\Theta_1(p,\varepsilon) = \frac{\partial\ln y}{\partial\ln(p/p_0)}$$

$$\frac{(p/p_0)\exp[(\varepsilon-\varepsilon_c)/RT]}{1+(p/p_0)\{\exp[(\varepsilon-\varepsilon_c)/RT]-1\}}$$

(5)

where

$$y = \sum_{i=1}^{r} (p/p_0)^i$$

$$\lim_{r \to \infty} \frac{\partial \ln y}{\partial \ln (p/p_0)} = \frac{1}{1 - p/p_0}, \qquad (6)$$

and $r$ is the number of adsorbed layers, one can show that the energy distribution function $\chi(\varepsilon)$ given by Eq. (4) corresponds now to the following form of the total isotherm equation

$$\Theta_t (p) = \frac{\partial \ln y}{\ln (p/p_0)} \exp$$

$$\left[ \sum_{l=1}^{M} B_l \left( RT \ln \frac{p/p_0}{1 - p/p_0} \right)^l \right]. \qquad (7)$$

The coefficients $\{B_l\}$, $l \geq 1$ determine the shape of the energy distribution function and are called 'the heterogeneity parameters'. The lowest-order parametr $B_0$, however, is connected with the monolayer capacity $N_m, N_m = \exp (B_0)$. We also note that Eq.(3) and Eq.(7) are commonly known as the mono- and multilayer exponential adsorption isotherms [8].

According to the above equations, the problem of evaluation of the energy distribution function from experimentally measured adsorption isotherms is reduced to the problem of the approximation of the adsorption data $N = N(p)$ by Eq. (3), or by Eq. (7), depending on the mono- or multilayer character of adsorption. Numerical methods of such an approximation are described in papers [2,6,7,8,12].

The Eq. (4) defining the energy distribution function is very flexible and can describe that functions $\chi(\varepsilon)$ exhibiting single, as well as, multiple maxima. In the simplest case of $M=1$ it reduces to an exponential distribution, whereas for $M=2$ and $B_{1=0}$ it leads to a quasi-gaussian distribution. In the latter case, the total adsorption isotherm Eq. (3) is identical with the Dubinin-Radushkevich isotherm, whereas in the former case it leads to the well-known Freundlich formula [8].

We have stressed above, that the energy distribution functions evaluated from solutions of the integral adsorption equation are rather insensitive to the choice of the local adsorption model. Thus, the energy distributions obtained from the above described procedure can be considered as good approximations, reflecting real energetic heterogeneity of the investigated samples.

As numerous investigations have indicated (cf. the review article [8]), the adsorption isotherm Eqs (3) and (7) can describe experimental data very precisely. Thus, they can also be considered as a useful tool in investigations of several aspects of adsorption phenomena, e.g., in studies of surface diffusion coefficients, the definition of which involves the derivative $\partial \Theta_t (p)/ \partial p$ [4].

Obviously, all thermodynamic quantities, characterizing the adsorption process (e.g., isosteric heats of adsorption) can be next evaluated from both equations (2) or (7) by using the standard methods, described in ref. [12]. For example, the heat of immersion is defined by [3,11]

$$Q_W = W + \tilde{\varepsilon} \qquad (8)$$

where $W$ is the work connected with the creation of a liquid surface and is independent of the nature of the adsorbent, whereas $\tilde{\varepsilon}$ is the average energy of interactions of the adsorbed monolayer with the surface and is given by

$$\tilde{\varepsilon} = N_m \int \varepsilon \chi (\varepsilon) d\varepsilon . \qquad (9)$$

The term $W$ can be evaluated from the theories of liquid state [11]. Thus, a comparison of the results computed according to Eq. (9) with experimental values of $Q_W$ provides an additional test of accuracy of the energy distribution evaluation.

### Experimental

Experimental measurements were carried out for samples of Wyoming Bentonite, saturated with $Li^+$, $Na^+$, $K^+$, $Ca^{++}$, $Mg^{++}$

and $Ba^{++}$ cations. All samples were obtained from the Macauley Institute, Scotland.

Adsorption-desorption isotherms were measured using the classical vacuum microbalance technique, as described in paper [15]. The results of the experiments performed are shown in Fig. 1.

Moreover, additional measurements of porosity of all investigated soil samples were carried out using a mercury porosimeter. The results of the last measurements are collected in Table 1.

## RESULTS AND DISCUSSION

Our calculations indicated, that in the case of all systems under investigations, the classical BET equation provides a poor description for both a finite (r=3) and an infi-

**T a b l e 1.** The results of porosimetric measurements for montmorillonite saturated with $Na^+$, $K^+$, $Ca^{++}$ and $Mg^{++}$ cations

| Property | Cation | | | |
|---|---|---|---|---|
| | $Na^+$ | $K^+$ | $Mg^{++}$ | $Ca^{++}$ |
| S, $m^2$/g | 19.6 | 25.0 | 26.9 | 25.31 |
| Porosity, $cm^3$/g | 0.179 | 0.197 | 0.197 | 0.203 |

nite number of adsorbed layers. Some selected examples of the BET plots, obtained for montmorillonite non-treated and treated with $K^+$ cations are displayed in Fig. 2. Considering the region of relative pressures $p/p_0 \in [0.15, 0.4]$, we have evaluated the parameters of the BET equation. The values of monolayer capacities $N_m$ were next used
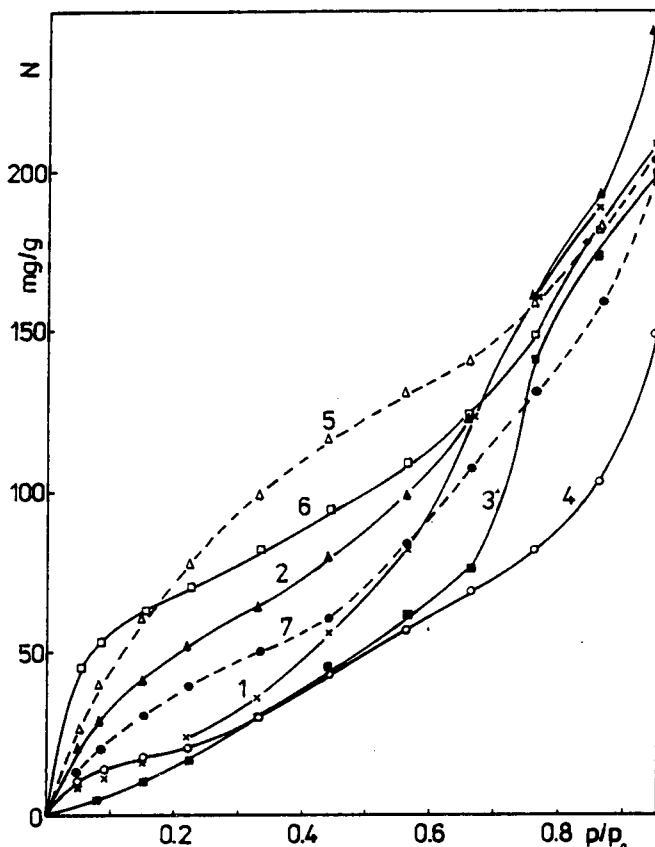


**Fig. 1.** Adsorption isotherms of water vapour on non-treated and on treated montmorillonite. The line (1) denotes the non-treated solid, the subsequent numbers denote the following cations: 2 - $Li^+$, 3 - $Na^+$, 4 - $K^+$, 5 - $Mg^{++}$, 6 - $Ca^{++}$ and 7 - $Ba^{++}$. The temperature is equal to 293 K.

T a b l e 2. Parameters c, monolayer capacities $N_m$ and surface areas S, evaluated from the BET isotherm for pressures from the range $p/po \in [0.15, 0.4]$

| | | | | Adsorbent | | | |
|---|---|---|---|---|---|---|---|
| | $n^*$ | $Li^+$ | $Na^+$ | $K^+$ | $Mg^{++}$ | $Ca^{++}$ | $Ba^{++}$ |
| c | 8 | 15.2 | 8.66 | 7.8 | 11.4 | 12 | 12.7 |
| $N_m$, $cm^3/g$ | 0.042 | 0.062 | 0.10 | 0.038 | 0.097 | 0.072 | 0.049 |
| S, $m^2/g$ | 122 | 180 | 290 | 110 | 281 | 207 | 143 |

*The symbol n denotes the nontreated montmorillonite. The treated samples are labelled by the chemical symbols of the saturating cations.

toevaluate the specific surface area of the samples $(S)$. The cross-sectional area of a single water molecule was assumed to be equal to $10.8 \text{ Å}^2$ [19].

The values of $c = \exp[(\varepsilon - \varepsilon_c)/RT]$, $N_m$ and S evaluated from the BET equation for an infinite number of adsorbed layers $(r = \infty)$ for all studied adsorbents are collected in Table 2.

The results of porosity measurements (Table 1) indicate that all investigated samples exhibit a rather small porosity. The ratio $(R_a)$ of the amount of desorbed to the amountof adsorbed water (see Fig. 3) is almost constant over a wide range of relative pressures $p/p_0$, except for the region of very

small and very high pressures. This feature is common for all samples, except for the montmorillonite saturated with $Na^+$ cations, and it indicates that the hysteresis loops on the adsorption/desorption isotherms are not connected with capillary condensation, but are rather caused by changes in the interlayer of soil samples [14].

The experimentally determined adsorption isotherms were next approximated by Eq. (3) (in the region of submonolayer adsorption) and by Eq. (7) (in the whole range of pressures), using the method of least squares [14]. Table 3 contains the results of our numerical calculations, together with the mean square deviations between the experimental and approximated data. The en-
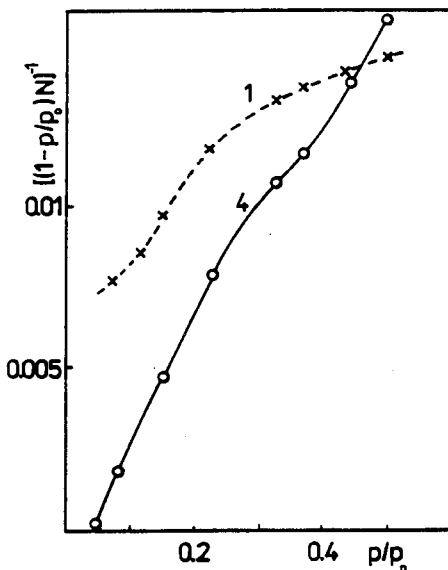


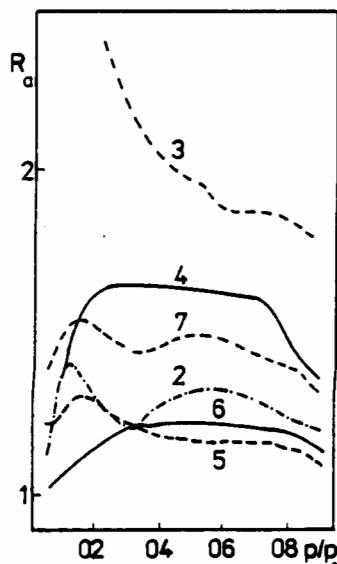Fig. 2. Examples of the BET plots for systems 1 and 4. The abbreviations are the same as in Fig. 1.

**Fig. 3.** The ratio $R_a$ of the amount of desorbed to adsorbed water. The abbreviations are the same as in Fig. 1.

**T a b l e  3.** The coefficients $B_i' = B_i (RT)^i$ of the exponential adsorption isotherm (7) and the sum of the squared deviations $\Sigma$

| Adsorbent* | Coefficient | | | | | $\Sigma$ |
|---|---|---|---|---|---|---|
| | $B_0'$ | $B_1'$ | $B_2'$ | $B_3'$ | $B_4'$ | |
| n | 4.093 | 1.637 | 0.606 | -0.0876 | -0.2209 | $0.31 \times 10^{-5}$ |
| $Li^+$ | 4.408 | 0.6125 | -0.721 | -1.458 | -0.917 | $0.13 \times 10^{-4}$ |
| $Na^+$ | 4.022 | 1.2688 | -0.4621 | -0.3607 | 0 | $0.15 \times 10^{-3}$ |
| $K^+$ | 3.940 | 1.384 | -0.3216 | -0.1657 | 0 | $0.19 \times 10^{-4}$ |
| $Mg^{++}$ | 4.823 | 0.4586 | -0.2252 | -0.1347 | 0 | $0.95 \times 10^{-5}$ |
| $Ca^{++}$ | 4.631 | 0.6807 | 0.4289 | 0.2035 | -0.008 | $0.17 \times 10^{-4}$ |
| $Ba^{++}$ | 4.195 | 0.7433 | 0.2851 | 0.1992 | -0.001 | $0.15 \times 10^{-4}$ |

*The non-treated montmorillonite is denoted by n, the saturated samples are labelled by using the chemical symbol of the corresponding cation.

ergy distribution functions, obtained by using the coefficients $\{B_i\}$ listed in Table 3, however, are shown in Fig. 4. We stress that, for all considered cases, the exponential adsorption equation describes the experimental data quite satisfactory.

Almost all evaluated energy distributions exhibit two wide maxima (except for non-treated montmorillonite). The position of the second maximum on the energy axis is shifted towards higher energies, according to the series $Na < K < Mg < Ca < Ba < Li$. This series differs from the series of energies of hydratation of the considered cations in an infinitely diluted solu-

tion: $K < Na < Li < Ba < Ca < Mg$ [17]. However, for the series of increasing heats of immersion [19]: $Mg < K < Ca < Ba < Li$ much better coincidence with our series was observed.

Obviously, the different maxima on the $\chi(\varepsilon)$ curves correspond to different groups of adsorption centers. A sharp high maximum corresponds to a well-distinguished group of adsorbing sites, whereas a wide maximum is probably a superposition of several, physically distinct centers. Unfortunately, in any case, physical interpretation of subsequent peaks on the $\chi(\varepsilon)$ curve is difficult and requires some
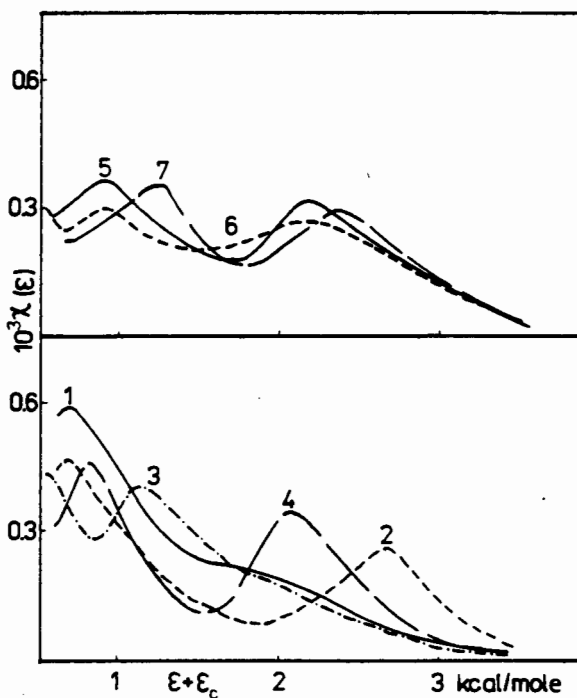
**Fig. 4.** The energy distribution functions $\chi(\varepsilon)$. The abbreviations are the same as in Fig. 1.

**Table 4.** Monolayer capacities ($N_m$), average energies of adsorption $\varepsilon$, and specific surface areas (s) evaluated from the exponential adsorption isotherm

| | Adsorbent | | | | | | |
|---|---|---|---|---|---|---|---|
| | n | $Li^+$ | Na+ | $K^+$ | $Mg^{++}$ | $Ca^{++}$ | $Ba^{++}$ |
| $N_m$, $cm^2/g$ | 0.074 | 0.101 | 0.069 | 0.064 | 0.154 | 0.127 | 0.082 |
| $(\varepsilon)$, kcal/mol | 12.3 | 12.8 | 11.8 | 12.2 | 12.4 | 12.5 | 12.6 |
| S, $m^2/g$ | 214 | 292 | 199 | 185 | 436 | 367 | 237 |

Abbreviations are the same as in Table 3.

additional information, which could be, for example, obtained from spectroscopy measurements [19].

Let us now compare the values of heats of desorption $E_d$ at T=573 K, obtained from derivatographic measurements, with the evaluated distribution functions. Fig. 5 shows the dependence of $E_d$ versus the amount of adsorbed water on montmorillonite saturated with $Na^+$, $K^+$, $Ca^{++}$, $Mg^{++}$ cations. All plots are exponential, although at some points also a subtle structure can be seen. It should be stressed, however, that

the curves $E_d$ were evaluated from desorption, not from adsorption branches. Also, the temperature of the experiments was significantly higher than the temperature of adsorption studies. Table 4 collects the values of average energies of adsorption

$$(\varepsilon) = \tilde{\varepsilon}/N_m \qquad (10)$$

where $\tilde{\varepsilon}$ was evaluated according to Eq. (9). Additionally, the values of the monolayer capacities, evaluated from the exponential adsorption isotherm, according to the relationship $N_m = \exp(B_0)$, as well as the specific
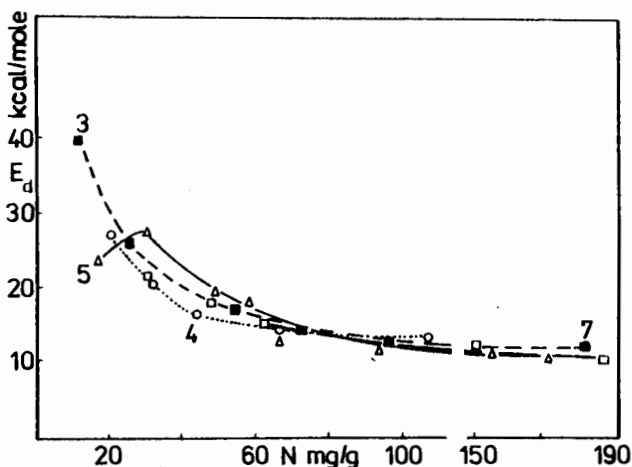
Fig. 5. Energies of desorption of water vapour, evaluated from derivatographic measurements. Abbreviations are the same as in Fig. 1.

of the BET isotherm (Table 2). Moreover, the values of the surface area given in Table 4 are remarkably greater than the values obtained from the BET equation.

The energy distribution functions presented here do not contain information about the most energetic centers on the surface. The evaluation of these contributions to $\chi(\varepsilon)$ requires the knowledge of adsorption at extremely low temperatures. Also, as we noted above, the theory applied here does not take into account changes in the structure of the adsorbent during the adsorption process.

Nevertheless, the presented theory seems to be a promising approach solution to describe sorption processes occurring on soils and on clay minerals.

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## ADSORPCJA PARY WODNEJ NA MONTMORYLONICIE WYSYCONYM KATIONAMI JEDNO- I DWUWARTOŚCIOWYMI

Badano proces adsorpcji pary wodnej na montmorylonicie wysyconym jonami $Li^+$, $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Ba^{2+}$. Pomiary prowadzono przy użyciu próżniowej mikrowagi sorpcyjnej, w temperaturze 293 K. Do opisu doświadczalnie otrzymanych izoterm adsorpcji zastosowano uogólnione równanie adsorpcji. Równanie to pozwala na wyznaczenie parametrów charakteryzujących niejednorodność energetyczną powierzchni adsorbentów. Dla badanych próbek montmorylonitu przeprowadzono też pomiary porozymetryczne. Dyskutowano związek pomiędzy niejednorodnością energetyczną powierzchni, porowatością i rodzajem kationu wysycającego a adsorpcją pary wodnej na montomorylonicie.