

Sorption kinetic of water vapour of MX80 bentonite submitted to different physical–chemical and mechanical conditions

G. Montes-H*, Y. Geraud

UMR 7517 ULP-CNRS, CGS, 1 rue Blessig, F-67084 Strasbourg, France

Received 25 April 2003; accepted 12 January 2004

Abstract

The clay materials are widely used in industrial processes. One significant application is as a solid desiccant agent or as a dehydrator of gases. In this case, it is fundamental to investigate on the sorption kinetics of water vapour. The main aim of the current study has been to present an experimental–theoretical study on the sorption kinetics of water vapour, using as reference material MX80 bentonite. This clay mineral was submitted at different physical, chemical and mechanical conditions. Then 0.5 g of the modified-sample previously dried for 24 h at 110 °C was placed in plastic desiccators (2 l) under isothermal conditions and atmospheric pressure, here the relative humidity was controlled by a supersaturated salt solution. This instrumental system allowed us to study the sorption kinetics of water vapour of MX80 bentonite where the control parameters were the interlayer cation (bentonite exchanged with Na, Li, K, Mg, Ca), mechanical compaction (uni-axial system at 21, 35 and 63 MPa), drying temperature of sample (110, 150, 250 and 500 °C), relative humidity (61, 75, 87 and 95%) and the amount of the sample (0.5, 1, 2, 3, 4 and 5 g).

Thanks to a kinetic model of second order it was possible to estimate that the sorption kinetic of water vapour of MX80 bentonite depends directly on the relative humidity, the interlayer cation and amount of the sample. In contrast, the sorption kinetics of water vapour was lightly affected by the mechanical compaction. Finally, the sorption kinetics of water vapour was modified by the drying temperature of sample exclusively when this is very high (for example, 500 °C).

© 2004 Elsevier B.V. All rights reserved.

Keywords: MX80 bentonite; Water sorption; Kinetic; Mechanical compaction; Cation saturation

1. Introduction

The industrial and environmental uses of clays are expanding every year. For example, it is estimated that about 8 million tons of the bentonites were used in 1992 throughout the world. One of the principal applications for bentonite is in drilling muds. However, it is widely used as a suspending and stabilizing agent, and as an adsorbent or clarifying agent, in many industries [1]. Frequently, the bentonites are also recommended as a desiccant agent or as dehydrator of gases, due to their excellent ability to adsorb water vapour. This process involves exposing the desiccant material to a high relative humidity. In these conditions a portion of water vapour is removed by the desiccant [2,3]. The water adsorption phenomena on the bentonites is a very complex process because of their textural and physical–chemical properties

[4,5]. Certainly, at the present time the numerous studies on the water adsorption of the bentonites under equilibrium conditions are reported in the literature. However, the kinetic studies on the water adsorption of bentonites are still insufficient.

A large number of solid materials take up water vapor from gases (such as silica gel, activated alumina, lithium chloride salt, molecular sieves, activated clays, etc.); some by actual chemical reaction, others because of loosely hydrated compounds, and a third group by adsorption [3]. Solid desiccant dehydration is an adsorption process, where the water molecules are bonded by surface forces on the desiccant agent. In this case, it is fundamental to investigate on the sorption kinetics of water vapour, because it is always necessary to regenerate the solid desiccant agent. The main aim of the current study has been to present an experimental–theoretical study on the sorption kinetic of water vapour, using as reference material the MX80 bentonite “commercial material”. This clay mineral was submitted at different physical, chemical and mechanical

* Corresponding author. Fax: +33-388367235.

E-mail addresses: german_montes@hotmail.com, montes@illite.u-strasbg.fr (G. Montes-H).

conditions. Then 0.5 g of the modified-sample previously dried for 24 h at 110 °C was placed in plastic desiccators (21) under isothermal conditions and atmospheric pressure, here the relative humidity was controlled by a supersaturated salt solution. This instrumental system allowed us to study the sorption kinetics of water vapour of MX80 bentonite where the control parameters were the interlayer cation (bentonite exchanged with Na, Li, K, Mg, Ca), mechanical compaction (uni-axial system at 21, 35 and 63 MPa), drying temperature of sample (110, 150, 250 and 500 °C), relative humidity (61, 75, 87 and 95%) and the amount of the sample (0.5, 1, 2, 3, 4 and 5 g).

Finally, a kinetic model of second order was used to fit the experimental data in order to describe physically the sorption kinetics of water vapour of MX80 bentonite submitted at several physical–chemical and mechanical conditions.

2. Materials and methods

2.1. MX80 bentonite

A Na/Ca-bentonite (commercial clay) was used for the study. Bentonite contains montmorillonite (80%), quartz (6%), K-feldspars (2%), plagioclases (4%), carbonates (4%), mica (3%) and other minerals (1%) [6]. Bulk sample is composed by 86.1% of particles in a size range less than 2 µm, 8.8% in the 2–50 µm range and 5.1% for sizes higher than 50 µm [5]. The specific surface area of bulk sample was estimated at 37.8 m²/g (±1 m²/g) by applying the Brunauer–Emmet–Teller (BET) equation and by using 16.3 Å² for a cross-sectional area of molecular nitrogen. For this estimation, a Sorptmatic 1990 instrument was performed.

2.2. Samples preparation

To study the adsorption kinetic of water vapour, the bulk samples (MX80-raw bentonite) were submitted at several physical–chemical and mechanical conditions.

2.2.1. Cation saturation

The bulk samples of MX80 bentonite were treated separately with five concentrated solutions (1N concentration) of sodium, lithium, calcium, magnesium and potassium chlorides. All salts have the same ionic force ($I = 2$).

Twenty grams of MX80 bentonite were dispersed into 1 l of salt solution (1N) at 60 °C. This suspension was vigorously stirred with magnetic agitation for 1 h at 60 °C. Then, the cation-saturated clay was separated by centrifugation (15 min at 13,000 rpm) and decanting the supernatant solutions. This process was repeated three times. The cation-saturated bentonite was then washed three to four times with distilled water until the AgNO₃ test for chloride

is negative. This method was used by Lee and Kim [7] and Rytwo [8].

The cation-saturated bentonite was subsequently dried for 48 h at 60 °C and finally ground for two minutes.

The samples here obtained were labelled MX80-Na, MX80-Li, MX80-Ca, MX80-Mg and MX80-K.

2.2.2. Sample drying

Four bulk samples were dried for 24 h at 110, 150, 250 and 500 °C. These samples were labelled MX80-110, MX80-150, MX80-250, MX80-500.

2.2.3. Mechanical compaction

Three bulk samples were mechanically compacted by an uni-axial system to different pressures (21, 35 and 63 MPa.) in order to obtain three different physical densities. Here the samples were labelled as MX80-21 MPa, MX80-35 MPa and MX80-63 MPa.

2.3. Isothermal sorption of water vapour

This equipment allows us to study the sorption kinetics of water vapour of the bulk and modified samples. An amount of 0.5 g of sample previously dried for 24 h at 110 °C (except for MX80-150, MX80-250, MX80-500 samples) was placed in plastic desiccators (21) where the relative humidity was controlled with an over-saturated salt solution. In order to keep constant relative humidity of air in the plastic desiccators and surrounding sample contained in glass jar. The desiccators were kept in a constant temperature room (23 °C) and atmospheric pressure (about 1 atm). To study the sorption kinetics of water vapour, the weighing of sample as a function of time was done by a digital balance (accuracy = 0.0001) until equilibrium was reached.

In order to estimate the influence of relative humidity on the sorption kinetics of water vapour, four bulk samples, i.e. without physical–chemical or mechanical treatment, were submitted at different relative humidities (61, 75, 87 and 95%). The others experiences were realised at 87 or 95% of relative humidity.

It is obvious that the sorption kinetics of water vapour depends directly on the sample weigh. Then, in order to study the influence of the amount of sample on the sorption kinetic of water vapour, five different weigh of the bulk sample were considered (1, 2, 3, 4 and 5 g).

2.3.1. Water content

The amount of adsorbed water in a sample as a function of time was calculated using the following formula:

$$W = \frac{w_t - w_s}{w_s} \quad (1)$$

where w_t represents the weight of the humid sample at a t instant time (g) and w_s represents the weight of the dry sample (g).

2.3.2. Measurements precision

This essentially depends on the instrument quality (balance and thermal regulation system) and also on the attention taken during weighing. Here, only the weighing accuracy was considered. The absolute error on the amount of adsorbed water was calculated using the following formula:

$$\Delta W = \frac{\Delta w}{w_s} (2 + W) \quad (2)$$

Δw being the balance accuracy (0.0001 g).

2.3.3. Curve fitting

2.3.3.1. Adsorption kinetic of water vapour. The experimental data were fitted using a kinetic model of the second order:

$$\frac{dW}{dt} = k_a (W_M - W)^2 \quad (3)$$

This kinetic model represents the amount of adsorbed water as a function of time up to an asymptotic maximum of time. The integral form is represented by a hyperbolic equation:

$$W = \frac{W_M t}{(1/k_a W_M) + t} \quad (4)$$

where W_M is the maximal amount of water adsorbed (g/g_{dry clay}), k_a kinetic coefficient of water adsorption. In order to simplify the experimental data fitting a novel constant was defined “ $(1/k_a W_M) = b$ ”. Physically this novel constant represents the time to which the half of the maximal amount of adsorbed water was reached ($0.5W_M$). Here, constant b is called “half-adsorption time”.

2.3.3.2. Desorption kinetic of water vapour. The experimental data of water desorption were also fitted using a kinetic model of the second order; in this case expressed as:

$$\frac{dW}{dt} = -k_d W^2 \quad (5)$$

The integral form is represented by a hyperbolic decay equation:

$$W = \frac{W_M}{1 + k_d W_M t} \quad (6)$$

where W_M is the maximal amount of water adsorbed (g/g_{dry clay}), k_d kinetic coefficient of water desorption. In order to simplify the theoretical interpretation, a novel constant was defined “ $(1/k_d W_M) = d$ ”. Physically this novel constant represents the time to which the half of the maximal amount of adsorbed water was desorbed ($-0.5W_M$). Here, constant d is called “half-desorption time”.

The parameters in the Eqs. (4) and (6) were estimated by non-linear regression using least-squares method.

3. Results and discussion

It is obvious that the sorption kinetics of water vapour of a solid desiccant depends on the numerous factors such as the chemical composition, texture, the physical–chemical properties, etc. In this paper, the physical (relative humidity, amount of the sample and drying temperature of sample), chemical (interlayer cation) and mechanical (physical density “mechanical compaction”) parameters were considered to study the sorption kinetic of water vapour of MX80 bentonite. In this section each parameter was separately discussed.

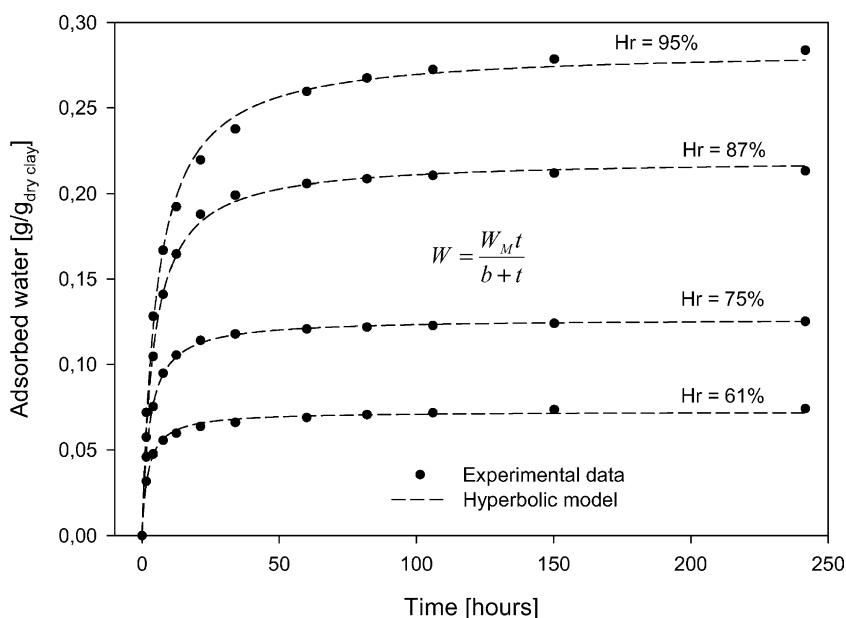


Fig. 1. Experimental data and fitting curves. Adsorption kinetic of water vapour of MX80 bentonite at four relative humidities. Hyperbolic model.

Table 1
Fitting kinetic parameters [9]

Relative humidity [%]	Fitting parameters		Correlation factor, R_c
	W_M (g/g _{dry clay})	Half-adsorption time "b" (h)	
0 → 95	0.2842 ± 0.0029	5.4057 ± 0.2931	0.9982
0 → 87	0.2199 ± 0.0012	4.2634 ± 0.2931	0.9989
0 → 75	0.1266 ± 0.0004	2.6597 ± 0.0535	0.9997
0 → 61	0.0725 ± 0.0007	2.2021 ± 0.1549	0.9973

Adsorption kinetic of water vapour of MX80 bentonite at four relative humidities. Non-linear regression by least-squares method.

Table 2
Fitting kinetic parameters [9]

Relative humidity (%)	Fitting parameters		Correlation factor, R_c
	W_M (g/g _{dry clay})	Half-desorption time "d" (h)	
95 → 0	0.2896 ± 0.0049	0.7228 ± 0.0595	0.9989
87 → 0	0.2153 ± 0.0036	0.9619 ± 0.0676	0.9989
75 → 0	0.1267 ± 0.0025	0.8229 ± 0.0753	0.9985
61 → 0	0.0761 ± 0.0020	1.1827 ± 0.1522	0.9972

Desorption kinetic of water vapour of MX80 bentonite at four relative humidities. Non-linear regression by least-squares method.

3.1. Relative humidity

The experimental data show that the adsorption kinetics of water vapour depends directly on the relative humidity (Fig. 1). In fact, the maximal amount of adsorbed water " W_M " increases when the relative humidity increases (Table 1). In addition, the half-adsorption time "b" increases proportionally with relative humidity augmentation (Table 1). In contrast, the desorption kinetic of water vapour depends lightly on the relative humidity (Fig. 2). Here,

Table 3
Fitting kinetic parameters [9]

Sample	Fitting parameters		Correlation factor, R_c
	W_M (g/g _{dry clay})	Half-adsorption time "b" (h)	
Influence of interlayer cation (Hr = 95%)			
MX80-Na	0.3706 ± 0.0068	6.2735 ± 0.8414	0.9983
MX80-Li	0.3517 ± 0.0099	7.3040 ± 1.2901	0.9962
MX80-K	0.1825 ± 0.0019	2.6625 ± 0.1804	0.9980
MX80-Ca	0.2501 ± 0.0028	1.7653 ± 0.1468	0.9973
MX80-Mg	0.2625 ± 0.0026	2.0943 ± 0.1993	0.9980
Influence of the amount of sample (Hr = 87%)			
MX80-1 g	0.2130 ± 0.0006	3.9570 ± 0.8414	0.9997
MX80-2 g	0.2180 ± 0.0008	8.2752 ± 1.2901	0.9998
MX80-3 g	0.2215 ± 0.0009	10.2427 ± 0.1804	0.9997
MX80-4 g	0.2269 ± 0.0011	12.7009 ± 0.2832	0.9996
MX80-5 g	0.2215 ± 0.0010	16.3826 ± 0.3173	0.9997
Influence of sample drying temperature (Hr = 87%)			
MX80-110	0.2066 ± 0.0009	3.0424 ± 1.2901	0.9995
MX80-150	0.2089 ± 0.0009	3.2077 ± 0.1804	0.9996
MX80-250	0.2069 ± 0.0008	3.7179 ± 0.2832	0.9996
MX80-500	0.1694 ± 0.0008	6.3822 ± 0.3173	0.9997
Influence of mechanical compaction (Hr = 95%)			
MX80-21 MPa	0.2822 ± 0.0016	11.2758 ± 0.4600	0.9988
MX80-35 MPa	0.2895 ± 0.0020	13.6420 ± 0.6339	0.9984
MX80-63 MPa	0.2910 ± 0.0020	14.1416 ± 0.6633	0.9985

Adsorption kinetic of water vapour of MX80 bentonite submitted to different physical-chemical and mechanical conditions. Non-linear regression by least-squares method. Hr: relative humidity (%).

the water desorption is extremely rapid in all cases (see half-desorption time values "d" in the Table 2). In conclusion, the speed of water vapour adsorption of MX80 bentonite "bulk samples" is always inferior than the speed of water vapour desorption.

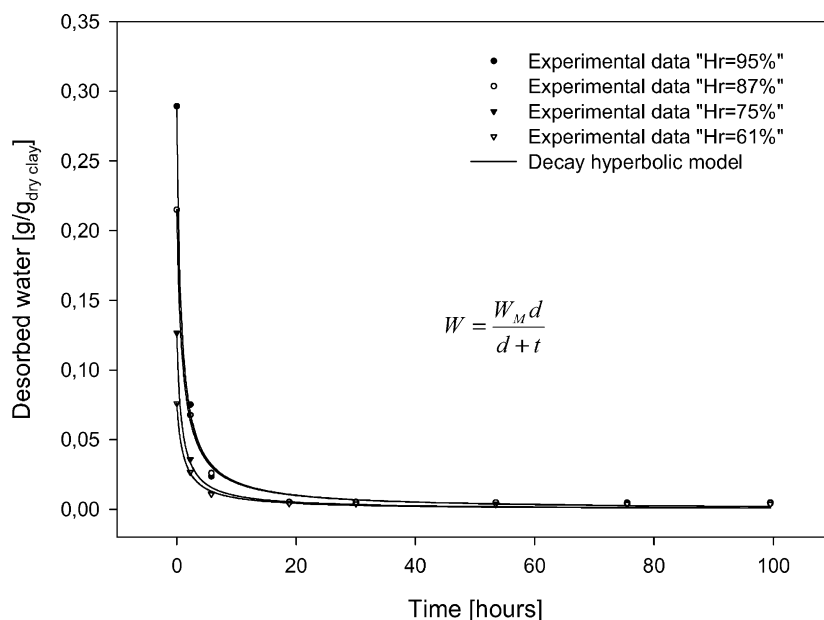


Fig. 2. Experimental data and fitting curves. Desorption kinetic of water vapour of MX80 bentonite at four relative humidities. Decay hyperbolic model.

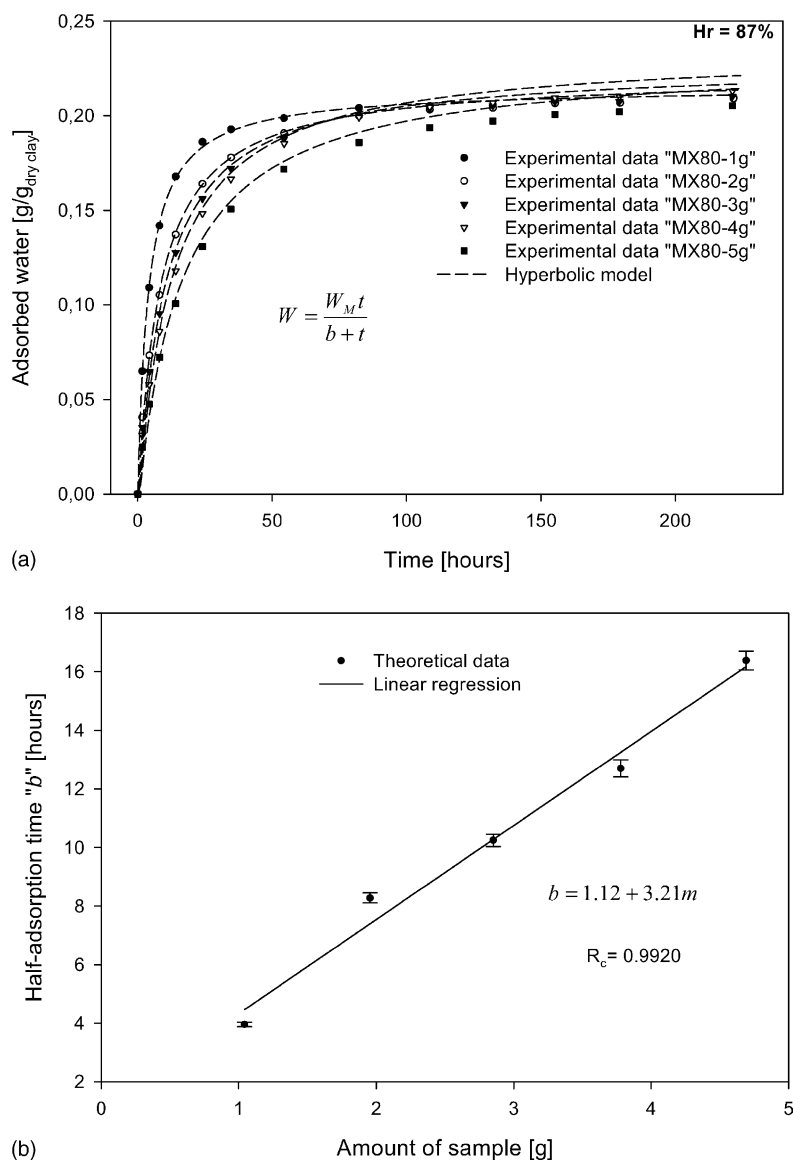


Fig. 3. Adsorption kinetic of water vapour of MX80 bentonite as a function of amount of the sample. (a) Experimental data and fitting curves "hyperbolic model". (b) "b" half-adsorption time and amount of sample correlation "linear model".

3.2. Amount of the sample

It is obvious that the speed of water vapour adsorption decreases when the amount of the sample increases. This hypothesis was confirmed because the half-adsorption time increases proportionally when the amount of sample increases (see Fig. 3; Table 3).

3.3. Drying temperature of sample

The drying temperature of sample does not play an important role in the water adsorption kinetics. However, when this temperature is very high (ex. 500 °C), the water adsorption phenomena was severely affected, i.e. the maximal amount of adsorbed water decreases and the speed of water

adsorption decrease because the half-adsorption time was about two times more superior (see Fig. 4; Table 3).

3.4. Interlayer cation

The Fig. 5 shows that the adsorption kinetic of water vapour of MX80 bentonite depends directly on the interlayer cation. Here, the maximal amount of adsorbed water " W_M " was more significant with interlayer cation of small size (Na and Li). In contrast, the maximal amount of adsorbed water was less significant for K-saturated bentonite. The Ca- and Mg-saturated bentonite present a similar behaviour on the adsorption kinetic of water vapour. In fact, the maximal amount of adsorbed water " W_M " between these samples was very near (see Fig. 5; Table 3). Concerning the

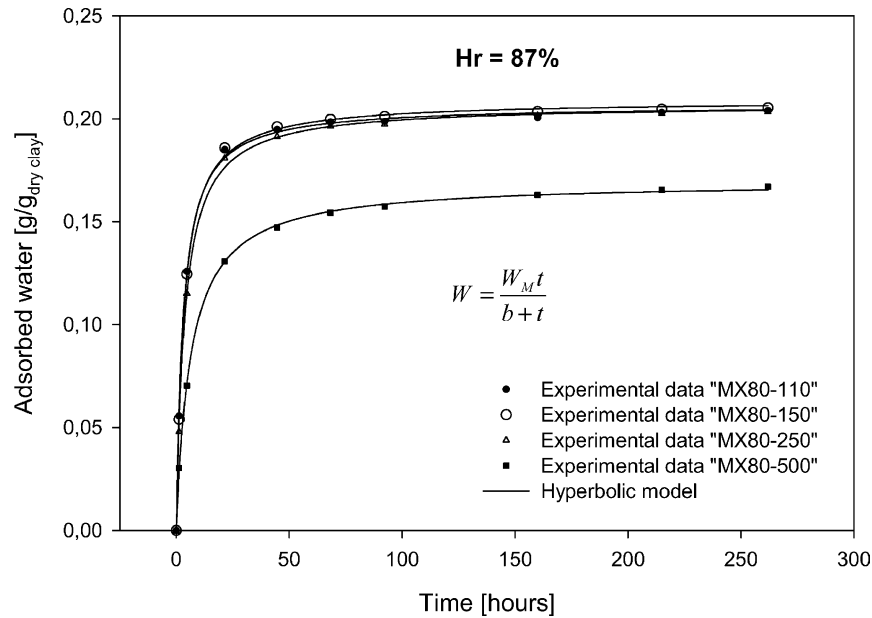


Fig. 4. Experimental data and fitting curves “hyperbolic model”. Influence of sample drying temperature on the adsorption kinetic of water vapour of MX80 bentonite.

speed of water vapour adsorption, it was observed that Ca- and Mg-saturated bentonite samples reach more rapidly the adsorption equilibrium because the half-adsorption time estimated was less than the half-adsorption time estimated for Li-, Na- and K-saturated bentonites samples (see Table 3).

3.5. Mechanical compaction

The mechanical compaction influences lightly on the adsorption kinetics of water vapour of the MX80 bentonite. In fact, the maximal amount of adsorbed water was not

modified with mechanical compaction. This signifies that the micro-porosity was not affected by the mechanical compaction. However, the first state of mechanical compaction (21 MPa) produces a significant augmentation of half-sorption time. After the first state of mechanical compaction, the half-sorption time increases lightly with the mechanical compaction (see Fig. 6; Table 3).

Finally, the absolute error (estimated by Eq. (2)) remains relatively low during adsorption and/or desorption kinetics of water vapour. The total error interval lies between 0.00015 and 0.00050 ($\text{g}_{\text{H}_2\text{O}}/\text{g}_{\text{dry clay}}$). This signifies that the

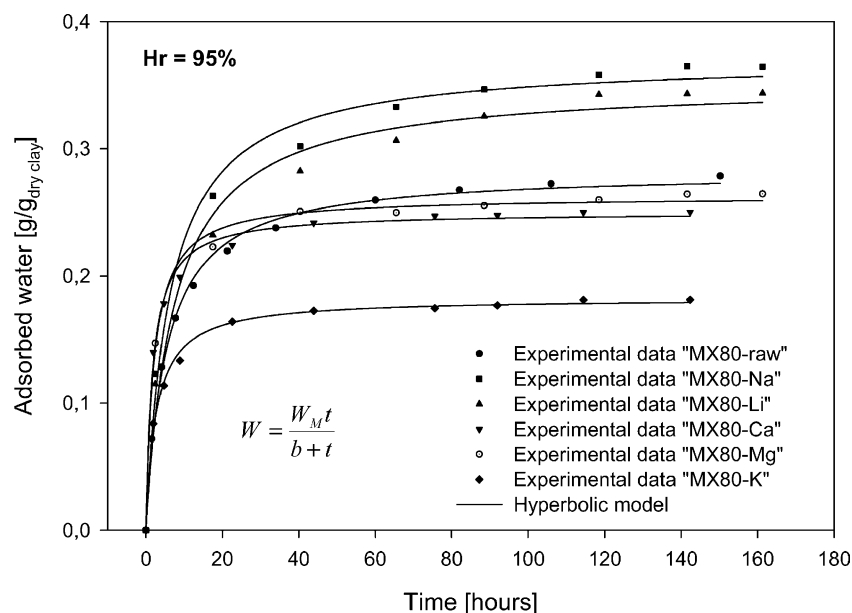


Fig. 5. Experimental data and fitting curves “hyperbolic model”. Influence of interlayer cation on the adsorption kinetic of water vapour of MX80 bentonite.

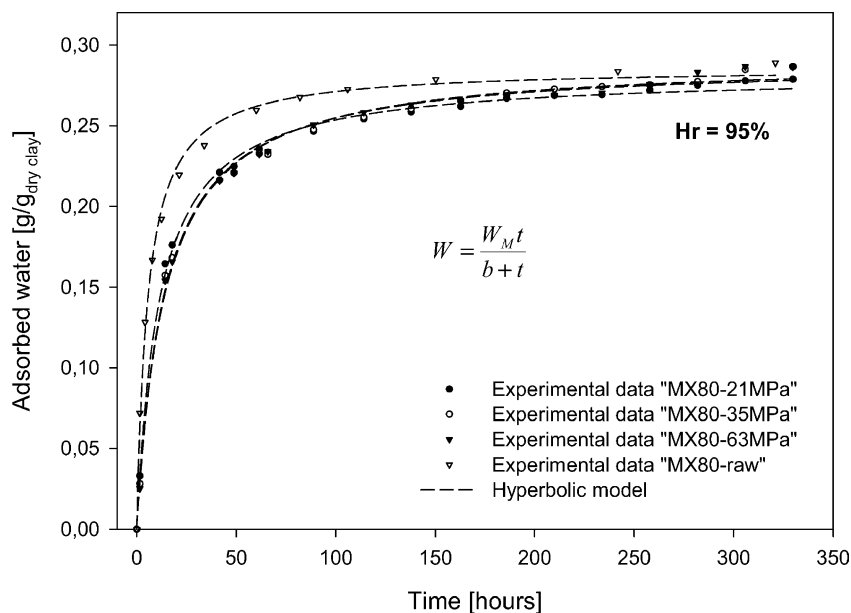


Fig. 6. Experimental data and fitting curves “hyperbolic model”. Influence of the mechanical compaction on the adsorption kinetic of water vapour of MX80 bentonite.

maximum error represents only about 7% of the amount of adsorbed water in the worst case.

4. Conclusion

The kinetic study realised in this paper allows us to conclude that the adsorption kinetic of water vapour of the MX80 bentonite depends directly on the relative humidity, the interlayer cation and amount of the sample. In contrast, the mechanical compaction influences only slightly on the water adsorption kinetics of the MX80 bentonite. Except for, the first state of mechanical compaction (21 MPa) because this produces a significant augmentation of half-sorption time. After the first state of mechanical compaction, the half-sorption time increases slightly with the mechanical compaction. Finally, the adsorption kinetics of water vapour was modified by the drying temperature of sample exclusively when this is very high (for example, 500 °C).

The kinetic models of second order here considered to describe the adsorption of water vapour (hyperbolic model) and desorption of water vapour (decay hyperbolic model) fitted well the experimental data.

Acknowledgements

The authors are grateful to National Council of Science and Technology, Mexico, and Louis Pasteur University, France, for providing a financial grant for this work.

References

- [1] H.H. Murray, *Appl. Clay Sci.* 17 (2000) 207.
- [2] J.C. Gonzalez, Molina-Sabio, F. Rodriguez-Reinoso, *Appl. Clay Sci.* 20 (2001) 111.
- [3] P. Gandhidasan, A. Abdulghani, Al-Farayehdi, A. Al-Mubarak Ali, *Energy* 26 (2001) 855.
- [4] D. Koch, *Appl. Clay Sci.* 21 (2002) 1.
- [5] A. Neaman, M. Pelletier, F. Villieras, *Appl. Clay Sci.* 22 (2003) 153.
- [6] E. Sauzeat, D. Guillaume, A. Neaman, J. Dubessy, M. François, C. Pfeiffert, M. Pelletier, R. Ruch, O. Barres, J. Yvon, F. Villeras, M. Cathelineau (Eds.), *Caractérisation minéralogique, cristalochimique et texturale de l’argile MX80. Rapport ANDRA No. CRP0ENG 01-001*, 82p.
- [7] S.Y. Lee, S.J. Kim, *J. Colloid Interf. Sci.* 248 (2002) 231.
- [8] G. Rytwo, *Clays Clay Miner.* 44 (2) (1996) 276.
- [9] G. Montes-H, *Etude expérimentale de la sorption d’eau et du gonflement des argiles par microscopie électronique à balayage environnementale (ESEM) et analyse digitale d’images*, PhD Thesis, Louis Pasteur University, Strasbourg I, France, 2002.