

Żaneta Kurleto-Kozioł, Beata Grabowska

Study on the activation of calcium montmorillonite (Ca-MMT) by sodium cations

Badania nad procesem aktywacji montmorylonitu wapniowego Ca-MMT kationami sodu

Abstract

The results of spectral research (IR, UV-Vis) on the activation process of calcium montmorillonite Ca-MMT by sodium cations are presented in this article. The modifications of Ca-MMT were carried out by a modifier in the form of sodium carbonate by keeping different times of activations. On the basis of received sodium modifiers MMT (Na-MMT) analytical cycle of research was done, including structural (IR) and spectrophotometric (UV-Vis) research, in order for the designation of ion exchange ability (CEC). There was observed that the method of processing modification (changing activation time) does not affect on ion exchange ability Na-MMT. Application of modified MMT used as a binding material in greensand will be described in the next part of our planned research.

Keywords: montmorillonite, activation of montmorillonite, cation exchange capacity, UV-Vis, IR

Streszczenie

W artykule przedstawiono wyniki badań spektralnych (IR, UV-Vis) procesu aktywacji montmorylonitu wapniowego Ca-MMT kationami sodu. Modyfikację Ca-MMT prowadzono z udziałem modyfikatora w postaci węglanu sodu przy zachowaniu różnych czasów aktywacji. Dla otrzymanych modyfikatorów sodowych MMT (Na-MMT) przeprowadzono cykl badań analitycznych, w tym strukturalnych (IR) oraz spektrofotometrycznych (UV-Vis), w celu oznaczenia ich zdolności wymiany jonowej (CEC). Stwierdzono, że sposób prowadzenia modyfikacji (zmiana czasu aktywacji) nie wpływa istotnie na zdolność do wymiany jonowej Na-MMT. Zastosowanie zmodyfikowanego MMT jako materiału wiążącego w masach klasycznych zostanie określone w następnej części zaplanowanych prac badawczych.

Słowa kluczowe: montmorylonit, aktywacja montmorylonitu, zdolność do wymiany jonowej, UV-Vis, IR

1. Introduction

Montmorillonite (MMT) belongs to the group of natural phyllosilicates from clay minerals. Each MMT layer is composed of an aluminum-oxygen octahedral sublayer located between two silicate-oxygen tetrahedral sublayers. Hence, montmorillonite is classified as the layered aluminosilicates of the 2:1 layer structure. The lack of full compensation of charges in the layer causes the appearance of a negative charge in the structure. This negative charge is compensated by the presence of metal cations (for example, Ca^{2+} , Na^+ , K^+) in the interlayer surfaces next to the water particles. These cations could easily be replaced by other cations by their ion exchange ability, thus changing the determined properties of MMT (for example, their adsorption and absorption abilities). Montmorillonite contained in the interlayer surface cations of calcium (Ca-MMT) appears in nature as an ingredient of calcium bentonite and is widely used as an absorbent, a catalytic carrier, an adhesive agent, an addition for medications and food, and (more recently) a polymeric nanofiller [1–6]. Literature data also shows the existence of many possibilities of modifying the MMT structure by physical or chemical means [1, 2, 4–7]. These processes are mostly performed in order to improve the thermostable and adhesive preferences of the material, and also to increase its sorption abilities [1, 2, 6, 7]. In casting technology, activated bentonite containing sodium cations (Na-MMT) obtained from ion exchange is used. Na-MMT shows greater binding abilities for sand grains, which is important for applications in molding-sand technology [8, 9].

The purpose of the research described in this paper was to elaborate the binding materials used in greensands as a result of Ca-MMT modification by sodium cations. Ca-MMT modification was processed with the sodium carbonate modifier by keeping different times of activations.

2. Methodology

2.1. Materials

The materials used in this study were:

- activated bentonite (Bentonite Specjal, ZGM “Zębiec”),
- non-activated bentonite (Bentonite SN, ZGM “Zębiec”),
- sodium carbonate (Na_2CO_3) by POCH,
- triethylenetetramine by Aldrich,
- CuSO_4 (sulfate [VI], copper [II], anhydrous) by MERCK,
- potassium bromide (KBr) by ACROS ORGANICS,
- distilled water by POCH.

2.2. Aparature

The aparature used in this study were:

- Spectrometer IR, Digilab Excalibur FTS 3000 Mx with detector DTGS, electrically cooled,
- VIS ODYSSEY DR/2500 spectrophotometer with automated wave length calibration Hach industry, range of wave length: 365–880 nm, resolution 1 nm,
- Microcomputer CP-251 pH-meter with automatic temperature compensation system Elmetron industry, equipped with combined pH electrode OSH 10-00 type.

2.3. Research methods

- Structural research by Fourier transform infrared spectroscopy (FTIR) – a bentonite sample (2 mg) was added to the weighed KBr (200 mg). Then, this compound was precisely mixed and placed in a hydraulic press (200 bars of pressure). A spectroscopic description of the prepared sample was made by an IR spectrometer in relation to the KBr sample as spectrum references. The transmission spectra of the investigated samples were recorded in a range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1} . A number of scans were selected dependent on the level of the obtained signal (within 32–64 scans).
- UV-Vis spectrophotometric measurement – water in a ratio of 1:20 was added to the weighed bentonite sample (200 mg). Then, this compound was dispersed by ultrasound. To received suspension, 10 ml 0.01M of Cu(II)-triethylenetetramine was added and by 50 ml of water was fulfilled, after everything was centrifuged until a clear solution required for photometrical measurement was received. The spectrophotometric description of the received solution was prepared in a 10-mm absorption cell when the length of the wave was equal to 620 nm in relation to water as a zero probe [10].

3. Results and discussion

3.1. The activation process Ca-MMT

The Ca-MMT modifications were prepared by the cation exchange of metals existing in the interlayer surfaces. In Figure 1, the schema of the prepared process of activated Ca-MMT using cation exchange is shown.

Ca-MMT modification was based on preparing a ternary mixture that consisted of calcium montmorillonite (60 g), distilled water (12 cm^3), and calcium carbonate (1.86 g). The mixture was subjected to preliminary homogenization (30 min). Then received mixture by mortar separate and next displace to ceramic crucible, and after that was put to dry (105°C; 1 h) or was put down for required time (activation time: 30 min; 1 h; 1.37 h; 2 h; 2.5 h; 3 h; 24 h).

Demanded activation time, 1.37 h, was the result of data contained in the patent about the activation of calcium bentonite [11]. After passing the required time of activation, the samples were placed to dry (105°C, 1 h). Dried samples of MMT were located to analytic research. The scheme of action for MMT modification is shown in Figure 2.

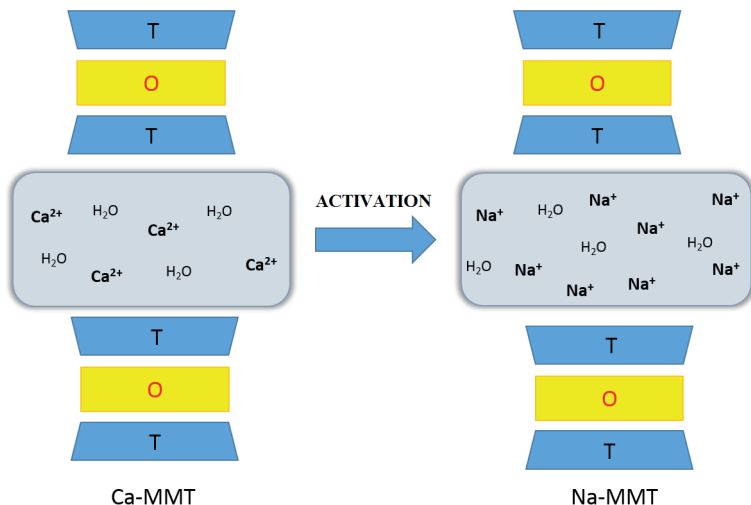


Fig. 1. Schematic idea of ion exchange

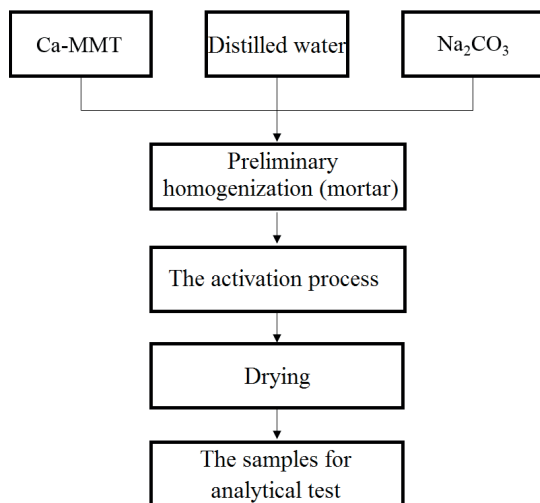


Fig. 2. Schema of Ca-MMT modification process

In the first phase change of pH for MMR before and after modification was defined and also compared received results with the value of commercial sodium bentonite Specjal (Na-MMT_{Specjal}) pH. All of the received in the result of activation MMT samples were characterized by approximated results of pH (approximately 11). In Table 1, the results of the research of pH for Ca-MMT and for the selected Na-MMT samples are presented.

Table 1. The pH test results

Sample labeling	Ca-MMT	Na-MMT _{0h}	Na-MMT _{1.37h}	Na-MMT _{24h}	Na-MMT _{Specjal}
Sample description	Calcium bentonite containing Ca-MMT	Sodium bentonite comprising Na-MMT, obtained without the activation process	Sodium bentonite obtained in the activation process, the activation time: 1.37 h	Sodium bentonite obtained in the activation process, the activation time: 24 h	Sodium bentonite prepared in the form of Zębiec (no accurate records of the time of activation)
pH	10.82	11.02	11.06	11.13	10.98

3.2. Structural research FTIR

In order to define the changes in the MMT structure after the activation process by ion exchange, spectroscopes research IR were made. A series of spectrums were carried out for inactivated bentonite contained Ca-MMT and activated samples of bentonites, including commercial activated bentonite Specjal (Na-MMT_{Specjal}). In Figure 3, shown spectrums of chosen samples of Na-MMT and compared them with spectrums Ca-MMT and Na-MMT_{Specjal}. Bands in the approximately 1600 cm⁻¹ wavenumber range are connected with stretching vibrations Al-OH and Si-OH bonds. Wideband with approximately 3400 cm⁻¹ maximum correspond with stretching vibrations in -OH group from water located in interlayer surface, and 1640 cm⁻¹ approximated band is result of the vibrations in -OH group in adsorbed water. Stretching vibrations in Si-O was assigned the band of approximately 1030–1040 cm⁻¹. Below 900 cm⁻¹ wavenumbers occurs bands characteristic for: AlAlOH, AlFeOH, AlMgOH and for bending vibrations. On the received spectrums could be noticed that in 3400 cm⁻¹ wavenumber for modifier samples bands are shifted. This fact shows occurring reactions with water in interlayer surface. Furthermore, all bands after modification changing its intensity. In the case of a sample-MMT_{24h} in the IR spectrum, all frequencies are characterized by higher intensity (spectrum 4) compared with the course of the spectra for other samples Na-MMT (spectrum 2, 3, and 5). This fact is related to the occurrence of ionic reaction in the interlayer space of MMT.

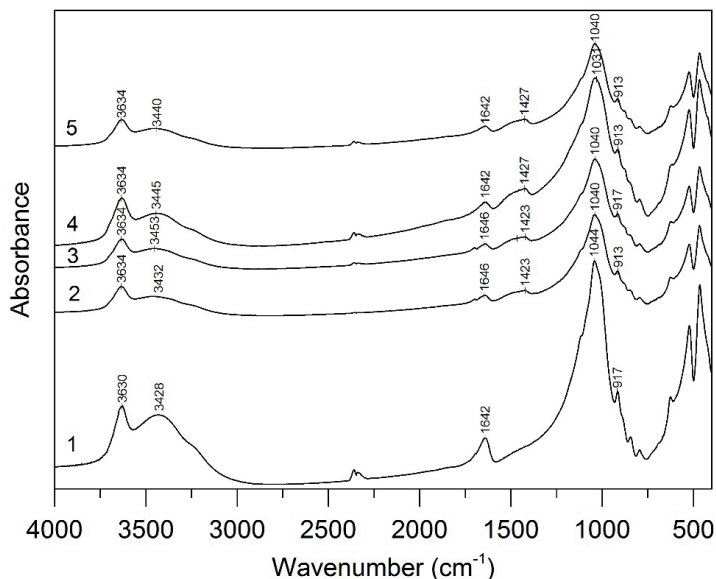


Fig. 3. IR Spectra: 1 – Ca-MMT; 2 – Na-MMT_{0h}; 3 – Na-MMT_{1.37h}; 4 – Na-MMT_{24h}; 5 – Na-MMT_{Special}

Characteristic absorption bands observed in the IR spectra of the investigated system are given in Table 2.

Table 2. Characteristic bands in the IR spectra of the investigated system

Ca-MMT	Na-MMT _{0h}	Na-MMT _{1.37h}	Na-MMT _{24h}	Na-MMT _{Special}	Ascription
cm ⁻¹					
3630	3634	3634	3634	3634	v-OH vibrations occurring minerals of 2: 1 in an environment octahedral Al
3428	3432	3453	3445	3440	v(H-O-H)
–	1423	1423	1427	1427	The presence of carbonate ions CO ₃ ²⁻
1044	1040	1040	1031	1040	v(Si-O) in SiO ₄ tetrahedron
917	913	917	913	913	δ(Al-Al-OH)

v – tensile, δ – bending

3.3. UV-Vis spectrometric research

Characteristic for the taken aluminosilicate charge of the layer and also a varying compensating cation charge are determined mainly by superficial preferences including free swelling capacity (FSC) and also by cation exchange capacity (CEC). The CEC is determined by various analytical methods, but currently, the spectrophotometric technique is widely used. This method consists of the measurement of absorbance in measuring analytes that contain samples of the described substance. Currently, the CEC spectrophotometric description is carried out with the methylene blue or Cu(II)-triethylenetetramine complex. In the given methods, the analytic base is the adsorption effect of methylene blue or Cu-TET on the aluminosilicate particles. It also turns out, however, that the adsorption of Cu-TET occurs easier; this is why this method is less time-consuming as compared to the method with methylene blue. CEC is the parameter that defines the binding preferences – the higher the CEC, the better the binding preferences are for MMT. In Figure 4, the results of the CEC are shown for selected samples of Na-MMT, and these are compared with the results of Ca-MMT and Na-MMT_{Spezial}. From the shown figure, we can see that the lowest value CEC was in the case of natural non modified Ca-MMT (65.99 mmol/100 g). Therefore, the highest value of CEC was in the case of Na-MMT_{24 h}, which is comparable with the value for Na-MMT_{Spezial} (78.89 mmol/100 g). Activation time does not significantly change the ability of the ion exchange. Cation exchange reaction occurs practically throughout the one-hour activation, although the highest ion exchange capacity has the Na-MMT_{24 h} sample that correlates to the underlying structural analysis (IR). Within 24 h of activation, it comes to the structural changes associated with the ion-exchange.

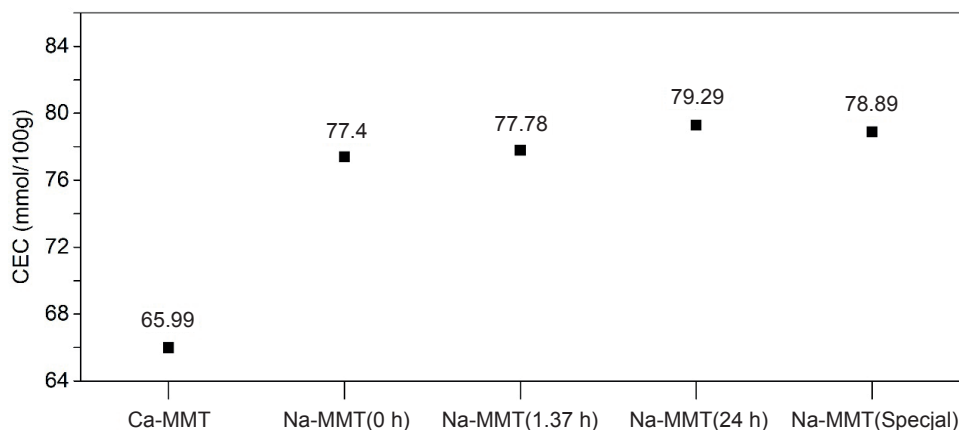


Fig. 4. Cation exchange capacity (CEC): Ca-MMT; Na-MMT_{0h}; Na-MMT_{1.37 h}; Na-MMT_{24 h}; Na-MMT_{Spezial}

4. Conclusion

The activation process of calcium montmorillonite was carried out while maintaining different activation times. For the obtained Na-MMT modifiers, analytical tests (pH, IR, UV-Vis) were conducted. Based on the obtained results, it was found that the ion exchange reaction takes place during the first hour of activation, as evidenced by structural changes (IR) and the value of ion exchange capacity (CEC). However, the maximum capacity of the ionic exchange has the Na-MMT_{24h} sample that correlates to the underlying structural analysis (IR). In the next stage, the obtained modifier Na-MMTs will be used as binders in the masses of classic and will be studied for their selected technological properties. The results obtained from this research will allow for the determination of the relationship between the activation time, ion exchange capacity, and technological properties of the mass.

Acknowledgement

The work was supported by the Project AGH No 11.11.170.318/13.

References

- [1] Kuczyńska H., Kamińska-Tarnawska E., Majkrzak P.: Wpływ modyfikacji montmorylonitu na właściwości reologiczne organicznych układów powłokotwórczychz jego udziałem. *Polimery*, 53, 7–8 (2008), 551–558
- [2] Pagacz J., Pielichowski K.: Modyfikacja krzemianów warstwowych do zastosowań w nanotechnologii. *Czasopismo Techniczne Chemia*, 1-Ch (2007), 133–147
- [3] Rybiński P., Janowska G.: Palność oraz inne właściwości materiałów i nanomateriałów elastomerowych – cz. I: Nanokompozyty elastomerowe z montmorylonitem lub haloizytem. *Polimery*, 58, 5 (2013), 325–341
- [4] Sarbak Z.: Wykorzystanie sorbentów w procesach oczyszczania gruntów. *Metrologia*, 15, 1 (2010), 77–92
- [5] Chang J., Ma J., Ma Q., Zhang D., Qiao N., Hu M., Ma H.: Adsorption of methylene blue onto Fe₃O₄/activated montmorillonite nanocomposite. *Applied Clay Science*, 119 (2016), 132–140
- [6] Veiskarami M., Sarvi M.N., Mokhtari A.R.: Influence of the purity of montmorillonite on its surface modification with an alkyl-ammonium salt. *Applied Clay Science*, 120 (2016), 111–120
- [7] Chmielarz L.: Naturalne krzemiany warstwowe jako materiały do syntezy katalizatorów dla procesu DeNOx. *Nauka dla Gospodarki*, 2 (2001), 7–29
- [8] Grabowska B., Holtzer M., Kot I., Kwaśniewska-Królikowska D.: Spectrophotometry application for the montmorillonite content determination in moulding sands with bentonite. *Metallurgy and Foundry Engineering*, 37, 1 (2011), 73–79
- [9] Kurlęto Ź., Szymański Ł., Kaczmarska K.: Glinokrzemiany stosowane w przemyśle odlewniczym – część I: Budowa, właściwości, zastosowania. In: Leśny J., Nyćkowiak J. (red. nauk.): *Badania i rozwój młodych naukowców w Polsce: nauki techniczne i inżynieryjne*, cz. 4. Monografie nr 24. Młodzi Naukowcy, Poznań 2016, 14–20
- [10] Grabowska B., Kaczmarska K., Bobrowski A., Kurlęto Ź., Mrówka N., Żymankowska-Kumon S.: Zdolność wymiany jonowej (CEC) attapulgitu – glinokrzemianu z grupy pałygorskitów. *Archives of Foundry Engineering*, 15, 4 (2015), 43–46
- [11] Harasowski J., Paczek H.: U.S. Patent No. 3,240,616. Kraków, D.C.: U.S. United States Patent Office (1966)