Studii şi Cercetări Ştiinţifice 2023, **24** (2), pp. 145 – 153
Chimie şi Inginerie Chimică, Biotehnologii, Industrie Alimentară

Scientific Study & Research
Chemistry & Chemical Engineering, Biotechnology, Food Industry *ISSN 1582-540X*

ORIGINAL RESEARCH PAPER

STUDY ON THE PREPARATION AND CHARACTERIZATION OF ALUMINUM-PILLARED CLAYS USING MONTMORILLONITE K10

Ana-Maria Georgescu[1*], Nicoleta Platon[1], Vasilica-Alisa Arus[1], Cosmin Jinescu[2], Françoise Nardou[3], Ileana-Denisa Nistor[1*]

[1]"Vasile Alecsandri" University of Bacău, Faculty of Engineering, Department of Chemical and Food Engineering, 157 Calea Mărăşeşti Street, 600115 Bacău, Romania
[2]Politehnica University of Bucharest, Department of Industrial Process Equipment, 313 Splaiul Independentei, 060042, Bucharest, Romania
[3]University of Limoges / CEC, SPCTS, UMR 7315 CNRS, 12 Rue Atlantis, 87068 Limoges Cedex, France

*Corresponding authors: ana.georgescu@ub.ro, dnistor@ub.ro

Received: May, 11, 2023
Accepted: June, 28, 2023

Abstract: Aluminum-pillared interlayered clays (Al-PILCs) were synthesized under various experimental conditions starting from commercial montmorillonite K10 (K10-Mt). The pillaring process involves several steps that are easy realized in laboratory. The effect of montmorillonite/NaCl solution mass ratio for cationic exchange, OH/Al molar ratio and the aging time of pillaring solution on physico-chemical properties and thermal stability of Al-PILCs were examined in this paper. The synthesized nanomaterials were characterized by textural analysis: specific surface area (using Brunauer-Emmett-Teller (BET) and Langmuir methods), micropore volume and micropore area by *t*-plot method. X-ray diffraction (XRD) analysis was used to determine the basal distance and mineralogy of the materials. The modified clays were characterized by thermal analysis using thermogravimetric (TGA) and differential thermal (DTA) analysis. The specific surface area values, the basal spacing and the thermal stability of the Al-PILCs were affected by the synthesis parameters. The modified products are intended to be used for the adsorption of organic pollutants from wastewater.

Keywords: *basal spacing, montmorillonite K10, pillaring, specific surface area, thermal analysis*

INTRODUCTION

Montmorillonite is the main constituent of bentonite produced by volcanic ash. Montmorillonite is a dioctahedral phyllosilicate, with an octahedral layer (AlO_6 units) sandwiched between two tetrahedral layers (SiO_4 units). Chemically it consists of hydrated sodium, calcium, aluminum, magnesium silicate hydroxide [$(Na, Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$]. Potassium, iron and other cations are the common substituents [1]. Through acid activation of montmorillonites, known in the literature as K10-Mt, the atoms from the octahedral sheets and the aluminum from the tetrahedral sheets are partially removed to displace them into the interlayers. Thus, the cation exchange capacity is reduced and the distance between the interlayers is increased [2, 3].
Montmorillonite K10 clay has been extensively used in catalytic processes for removing the moisture from air and gases or for the prevention of the leakages of fluids, in biodiesel production from waste cooking oil, esterification of levulinic acid, synthesis of parabens, nitration of chlorobenzene, isomerization and dimerization of pinenes, in chemical vapor deposition of multi-wall carbon nanotubes from methane [1, 3 – 9]. Due to its adsorption properties, K10-Mt was used as gaseous adsorbent, in removal of antibiotics or heavy metals, in immobilization of enzymes, in electrochemical hydrogen storage, as anti-caking agent in animal feed, drainage aid component, cosmetics, and also used in the base of some cat litter products [1, 10 – 14].
In recent years, Pillared InterLayered Clays (PILCs) have been widely used in several applications, especially in adsorption and catalysis. Intercalation of clays with polyhydroxycations through exchange of cations from the interlayer space of clay, followed by a thermal treatment, is an effective way to obtain adsorbents, catalysts or catalyst supports.
In this paper, we realized the synthesis of Al-pillared interlayered clays (Al-PILC) starting from commercial K10-Mt. For the pillared clays synthesis, we used the method that is essentially based on mixing of a dilute clay suspension with a dilute pillaring solution. This method involves the following steps: sodium-exchanged clay preparation, a dilute pillaring solution preparation, intercalation of Na-clay with Al-pillaring agent, repeated washing till all the chloride ions are removed, drying into an oven and finally, calcinations of the dried product to obtain the pillared clay. The obtained powders were characterized by textural analysis (Brunauer-Emmett-Teller / BET, *t*-plot), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and differential thermal analysis (DTA).

EXPERIMENTAL PART

Materials

The starting clay was a commercial K10-Mt provided from Sigma-Aldrich. The specific surface area is 220 - 250 $m^2 \cdot g^{-1}$ as described by the catalogue. The chemical composition in oxides was: SiO_2 (79.3 %), Al_2O_3 (13.6 %), MgO (1.48 %), Na_2O (0.206 %), Fe_2O_3 (2.73 %), CaO (0.378 %), K_2O (1.7 %), Ti_2O (0.506 %), MnO

(0.00726 %), which was determined using Wavelength-dispersive X-ray (WDX) technique [10].
All chemicals used in this work (aluminum chloride hexahydrate (Chimopar S.A.), sodium chloride (Lach-ner), sodium hydroxide pellets (Merck) and silver nitrate (Merck)) were of analytical grade reagents and were used without further purification.

Synthesis of Al-PILCs

The pillaring process consists in the following steps: ionic exchange of K10-Mt, preparation of Al-pillaring agent, intercalation of the exchanged montmorillonite (Na-K10-Mt) with pillaring agent and calcination.
To obtain Al-PILCs, the raw material was sodium-exchanged by its treating with 1 M NaCl, with different S:L mass ratios (1:50 and 1:100), by continuous stirring at 80 °C [15], for 2 h or 3 h (Table 1). The procedure was repeated three times for a complete sodium-exchanged obtaining. Between sodium-exchanged operations, after the complete decantation, the samples were washed with distilled water in order to remove all the chloride ions ($AgNO_3$, test) and filtered under vacuum. Further, the samples were dried into an oven at 110 °C for 24 h, and then were ground. The homoionic montmorillonite samples were denoted hereafter as *Na-K10-50* and *Na-K10-100*.
The dilute Al-pillaring agent was prepared by drop-wise addition of a 0.2 M NaOH solution to a 0.2 M $AlCl_3 \cdot 6H_2O$ solution [16], at 60 °C with vigorous stirring. The (OH/Al) molar ratios were varied from 2.0 – 2.4, as presented in Table 1. These pillaring agents were kept at room temperature (at dark), being used after different times (from 12 h to 8 days). This period of time is known as aging time.

Table 1. *Varied parameters for synthesized materials*

Material	Clay:NaCl mass ratio [g·mL^{-1}]	Temperature and duration for Na-K10-Mt obtaining	OH/Al molar ratio	Aging time of pillaring solution [h]
Al_{13}-K10-Mt-1	1:100	80 °C, 2 h	2.2	12
Al_{13}-K10-Mt-2	1:100	80 °C, 2 h	2	12
Al_{13}-K10-Mt-3	1:50	80 °C, 3 h	2.2	36
Al_{13}-K10-Mt-4	1:50	80 °C, 3 h	2.4	12
Al_{13}--K10-Mt-5	1:50	80 °C, 3 h	2.2	192

The suspensions of Na-exchanged montmorillonites (*Na-K10-50* and *Na-K10-100*) (2 wt %) were stirred for 1 h, at room temperature before intercalation. Further, these slurries were mixed with the pillaring solutions at 60 °C till the Al/g clay ratio was 4 mmol·g^{-1}. The rate of pillaring solution addition was 1 mL·min^{-1} for the uniform distribution of pillars into the PILCs structure.
The final solution containing clay and Al-pillaring agent was constantly stirred at the same temperature (60 °C) for 3 h and allowed to stand till the next day (about 20 h). The pillared clay was then washed with distilled water till all the chloride ions were removed ($AgNO_3$ test). The pillared clays were then dried into oven at 110 °C for 24 h, ground and heated at 400 °C for 2 h [17]. The pillared clays are further denoted as *Al_{13}-K10-Mt-x*, where *x* represents the five protocols used for the obtaining of synthesized materials.

Characterization methods

The mineralogical composition and basal distance of the obtained materials were investigated by XRD analysis. XRD powder patterns were collected on a Siemens Diffraktometer D5000 device, using Cu $K\alpha_1$ radiation (Ni filter, λ = 0.15401 nm, voltage 40 kV and current 30 mA).
Specific surface area was calculated using BET and Langmuir methods. The other textural parameters, as: volumes of micropores (V_μ) and mesopores (V_m) were calculated with *t*-Plot method, obtained from N_2 adsorption–desorption isotherm at 77 K, measured in a Micromeritics ASAP 2010. The samples were outgased at 473 K, for 14 h. The 0.1620 nm^2 value was taken for all samples as the N_2 molecular cross-section area.
Thermal behavior studies were performed using a LABSYS 400 device, at a heating rate of 10 °C·min^{-1} from room temperature to a maximum temperature of 1000 °C in the case of differential thermal analysis, and to 1100 °C in the case of thermogravimetric analysis. The thermal analyses were realized under argon atmosphere.

RESULTS AND DISCUSSION

In Figure 1 are presented X-ray diffraction patterns of K10-Mt, used as raw material in this paper, of homoionic montmorillonite samples (*Na-K10-50* and *Na-K10-100*) and of pillared clays.

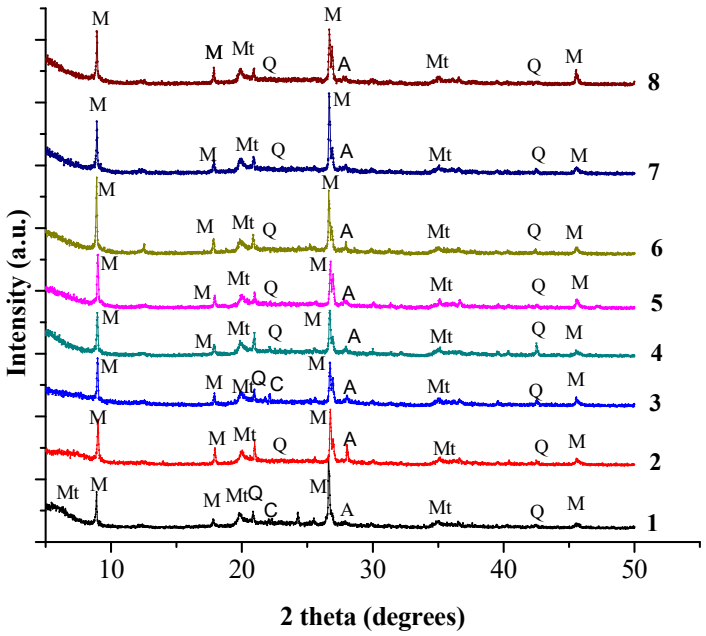

Figure 1. *X-ray diffraction patterns for K10-Mt (1), Na-K10-50 (2), Na-K10-100 (3), Al_{13}-K10-Mt-1 (4), Al_{13}-K10-Mt-2 (5), Al_{13}-K10-Mt-3 (6), Al_{13}-K10-Mt-4 (7), Al_{13}-K10-Mt-5 (8)*
(Mt – montmorillonite, M – muscovite, Q – quartz, C – cristobalite, A – albite)

It can be noted that K10 clay is constituted by montmorillonite (Mt), muscovite (M) quartz (Q) and traces of cristobalite (C) and albite (A) as impurities. Also, it can be observed that there are no major differences between raw material and the modified materials, except the intensities of the phases.
The values for the basal distance (d_{001}), specific surface area (using BET and Langmuir methods), and pore volume of the synthesized materials are presented in Table 2.

Table 2. *Physical and textural characteristics of synthesized materials*

Material	Basal distance [nm]	BET surface area [$m^2 \cdot g^{-1}$]	BET V_M [$cm^3 \cdot g^{-1}$]	Langmuir surface area [$m^2 \cdot g^{-1}$]	Langmuir V_M [$cm^3 \cdot g^{-1}$]	Micropore volume [$cm^3 \cdot g^{-1}$]	Micropore area [$m^2 \cdot g^{-1}$]	External surface area [$m^2 \cdot g^{-1}$]	Average pore diameter [nm]
K10	1.50	242.11	-	-	-	-	-	-	-
Al_{13}-K10-Mt-1	1.53	193.78	44.51	281.39	64.64	0.0196	40.30	153.48	0.40
Al_{13}-K10-Mt-2	1.51	204.69	47.02	297.45	68.33	0.0211	43.16	161.53	0.41
Al_{13}-K10-Mt-3	1.70	212.15	48.73	308.43	70.85	0.0214	44.12	168.03	0.40
Al_{13}-K10-Mt-4	1.55	219.40	50.39	322.08	74.11	0.0240	49.21	170.18	0.44
Al_{13}-K10-Mt-5	1.53	216.84	49.81	315.02	72.37	0.0228	46.70	170.14	0.42

As it can be shown from Table 2, the intensities of (001) reflection are different. It can be observed that the (001) reflection, characteristic to the parent clay, from $2\theta = 5.861°$, is shifted towards lower 2θ values in case of the modified samples (ionic exchanged and pillared clays). During the Na-ionic exchanged process, the basal distances increase from 15.067 Å, corresponding to parent clay, to 16.93 Å for *Na-K10-50* and to 16.21 Å for *Na-K10-100*, respectively. These results clearly indicate an enlargement of the clay interlayer space. During the calcinations process, the basal spacing is decreasing, fact that is indicated by the values obtained for d_{001}.
The specific surface area of the parent clay was 242.11 $m^2 \cdot g^{-1}$, which is close to the value described in the catalogue of the manufacturer. The material *Al_{13}-K10-Mt-4* exhibits the highest specific surface area, while the material *Al_{13}-K10-Mt-1*, the lowest surface area. By pillaring process, the values of the synthesized materials decreased, as described by other papers in literature [18, 19]. The average pore sizes are in the range of 0.40 - 0.44 nm, indicating that all the pillared clays are mostly microporous.
Thermal behavior of K10-Mt and of various modified clays, were evaluated by thermogravimetric and derivative thermogravimetric analysis (TG/DTG), the results being shown in Figures 2a and 2b.
The total mass losses of Al-PILCs prepared under different parameters were similar in the TG plots, except *Al_{13}-K10-Mt-2* material. Three major stages of mass loss were observed. The first loss of weight occurs between 20 and 90 °C. These transformations correspond to the evaporation of free water adsorbed between silicate layers and to dehydration of water molecules around the exchangeable cations such as Ca^{2+} and Na^{+}. The second loss of weight occurs between 190 and 520 °C, which can be attributed to dehydroxylation of Keggin cations; in this range the montmorillonite does not undergo thermal changes. The third weight loss from 520 to 900 °C corresponds to the total dehydroxylation of the hydroxyl groups in the aluminosilicate structure [20, 21].

a)

b)

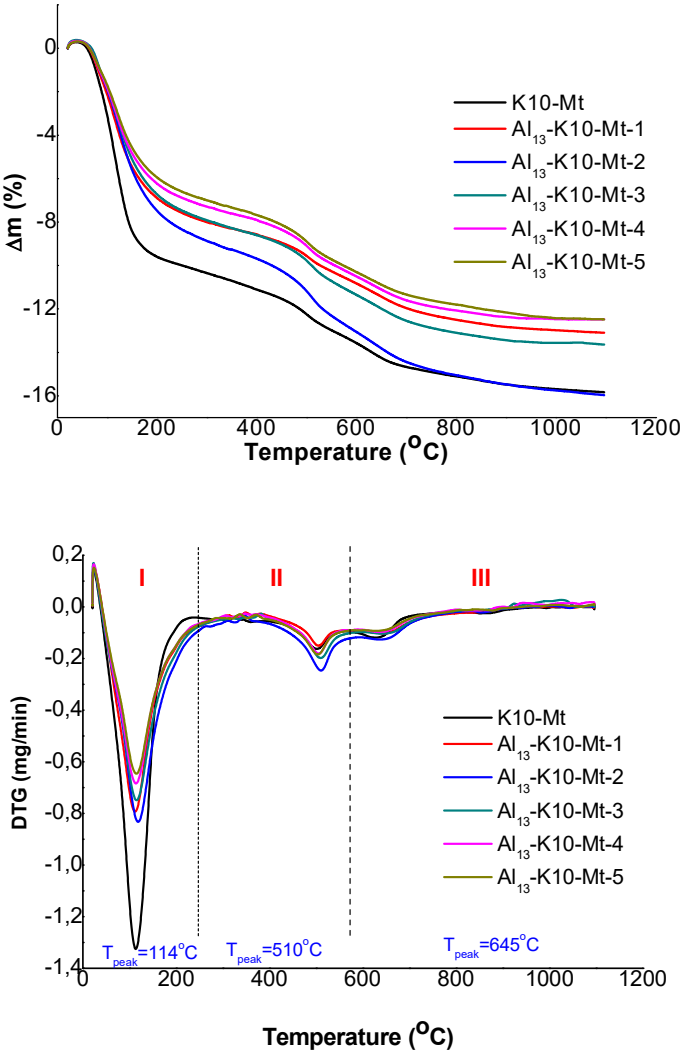

Figure 2. *TG (a) and DTG (b) analysis of K10-Mt and of pillared clays*

The TG analysis curves show that pillared clays lose less weight than raw material due to the calcination step till 400 °C. More specifically, the untreated montmorillonite loses 15.7 % in comparison with the pillared clays, which lose between 12.4 % and 13.6 %, except *Al13-K10-Mt-2* material.

The thermal stability of the studied materials was achieved through differential thermal analysis too. In Figures 3a and 3b are presented DTA analyzes of starting and modified clays, respectively.

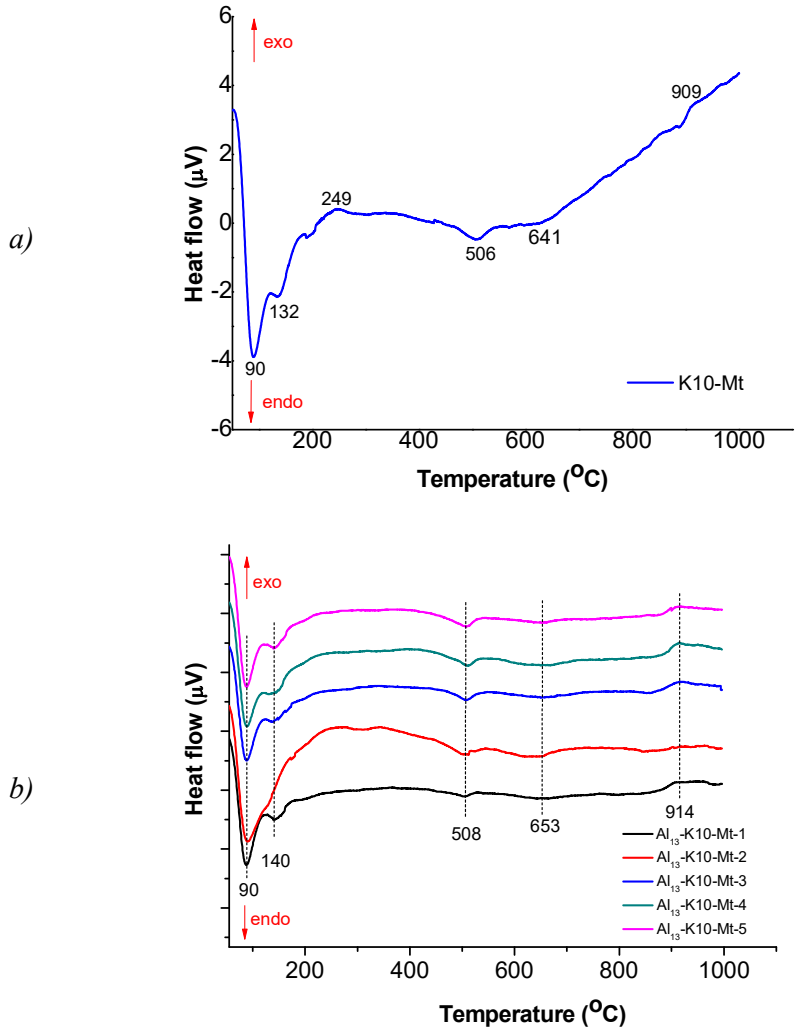

Figure 3. *TDA analysis of K10-Mt (a) and of pillared clays (b)*

The decomposition peaks of the pillared clays synthesized under different parameters were similar in the DTA plots. The results above indicate that the Keggin structure pillars can improve the thermal stability of pillared clays.

CONCLUSIONS

In this paper, Al-pillared clays were prepared starting from a commercial montmorillonite, K10. The materials were characterized by textural and thermal analysis, in order to evaluate the stability of synthesized materials at high temperature. The obtained results show that the thermal degradation of bentonite intercalated with polyhydroxycations of Al (III) occurs progressively, noting the presence of three stages.

These stages correspond to the progressive dehydroxylation of the clay, which progressively loses its crystallinity, forming new phases. The pillared montmorillonites had similar surface areas, indicating that the composition of the Al-pillaring solution did not cause significant changes in the final surface areas. BET surface area resulted were confirmed by *t*-plot method. Due to their good adsorption properties, the chemically and thermally modified materials will be used in environmental remediation.

ACKNOWLEDGEMENT

This paper was realized with the support of BRAIN project: "Doctoral scholarships as an investment in intelligence", financed by the European Social Found and Romanian Government (AM POS-DRU-ID 6681).
These results were achieved thanks to the support of SPCTS Laboratory from University of Limoges.

CONFLICTS OF INTEREST

The authors declare no conflict of interest.

REFERENCES

1. Reddaiah, K., Madhusudana Reddy, T., Subba Rao, Y., Raghu, P., Gopal, P.: Development of electrochemical sensor based on β-cyclodextrin/K_{10} montmorillonite towards the enhanced electro-catalytic oxidation of isoorientin: A voltammetric study, *Materials Science and Engineering: B*, **2014**, **183**, 69-77;
2. Gubernat, M., Zambrzycki, M.: Catalytic activity of K10 montmorillonite in the chemical vapor deposition of multi-wall carbon nanotubes from methane, *Applied Clay Science*, **2021**, **211**, 106178, https://doi.org/10.1016/j.clay.2021.106178;
3. Kurian, M., Kavitha, S.: A review on the importance of pillared interlayered clays in green chemical catalysis, *IOSR Journal of Applied Chemistry, International Conference on Emerging Trends in Engineering & Management*, **2016**, 47-54;
4. Yahya, S., Muhamad Wahab, S.K., Harun, F.W.: Optimization of biodiesel production from waste cooking oil using Fe-Montmorillonite K10 by response surface methodology, *Renewable Energy*, **2020**, **157** (12), 164-172;
5. Da Silva Junior, V.A., Shigueyuki Kanda, L.R., Zandoná-Filho, A., Corazza, M.L., Sutile de Lima, C.: Effect of supercritical carbon dioxide over the esterification of levulinic acid with ethanol using montmorillonite K10 as catalyst, *Journal of CO_2 Utilization*, **2020**, **39**, 101158, https://doi.org/10.1016/j.jcou.2020.101158;
6. Hazarika, M.K., Parajuli, R., Phukan, P.: Synthesis of parabens using montmorillonite K10 clay as catalyst: A green protocol, *Indian Journal of Chemical Technology*, **2007**, **14** (1), 104-106;
7. Choudary, B.M., Sarma, M.R., Kumar, K.V.: Fe^{3+} - Montmorillonite catalyst for selective nitration of chlorobenzene, *Journal of Molecular Catalysis*, **1994**, **87** (1), 33-38;
8. Harvey, B.G., Wright, M.E., Quintana, R. L.: High-density renewable fuels based on the selective dimerization of pinenes, *Energy Fuels*, **2010**, **24**, 267-273;
9. Al-nayili, A., Muhammad, N.J.: Perovskite's $LaNiMnO_6$/montmorillonite K10 nanocomposites: Synthesis and enhanced photocatalytic activity, *Materials Science in Semiconductor Processing*, **2023**, **155**, 107254, https://doi.org/10.1016/j.mssp.2022.107254;

10. Ursu, A.V., Gros, F., Nistor, D. I., Djelveh, G.: Characterization and utilization of a commercial clay for ammonia adsorption. Influence of operating parameters on gas retaining, *Revista de Chimie*, **2008**, **59** (10), 1067-1072;
11. Imanipoor, J., Mohammadi, M., Dinari, M.: Evaluating the performance of L-methionine modified montmorillonite K10 and 3-aminopropyltriethoxysilane functionalized magnesium phyllosilicate organoclays for adsorptive removal of azithromycin from water, *Separation and Purification Technology*, **2021**, **275**, 119256, https://doi.org/10.1016/j.seppur.2021.119256;
12. Dos Santos, V.C.G., Grassi, M.T., Abate, G.: Sorption of Hg(II) by modified K10 montmorillonite: Influence of pH, ionic strength and the treatment with different cations, *Geoderma*, **2015**, **237-238**, 129-136;
13. Sanjay, G., Sugunan, S.: Immobilization of α-amylase onto K-10 montmorillonite: characterization and comparison of activity in a batch and a fixed-bed reactor, *Clay Minerals*, **2005**, **40** (4), 499-510;
14. Samimi, F., Ghiyasiyan-Arani, M., Salavati-Niasari, M.: New avenue for preparation of potential hydrogen storage materials based on K10 montmorillonite and $Ca_2Mn_3O_8$/$CaMn_3O_6$ nanocomposites, *Fuel*, **2022**, **320**, 123933, https://doi.org/10.1016/j.fuel.2022.123933;
15. Azzouz, A., Ursu, A.V., Nistor, D., Sajin, T., Assaad, E., Roy, R.: TPD study of the reversible retention of carbon dioxide over montmorillonite intercalated with polyol dendrimers, *Thermochimica Acta*, **2009**, **496** (1-2), 45-49;
16. Georgescu, A.M., Nardou, F., Nistor, I.D.: Influence of synthesis parameters on morphological properties of aluminum(III)-pillared bentonites, *Scientific Study and Research-Chemistry and Chemical Engineering Biotechnology Food Industry*, **2016**, **17** (3), 261-269;
17. Georgescu, A.M., Nardou, F., Zichil V., Nistor, I.D.: Adsorption of lead (II) ions from aqueous solutions onto Cr-pillared clays, *Applied Clay Science*, **2018**, **152**, 44-50;
18. Platon, N., Siminiceanu, I., Miron, N.D., Muntianu, G., Zavada, R.M., Isopencu, G., Nistor, I.D.: Preparation and characterization of new products obtained by pillaring process, *Revue Roumaine de Chimie*, **2011**, **62** (8), 799-805;
19. Imanipoor, J., Ghafelebashi, A., Mohammadi, M., Dinari, M., Ehsani, M.R.: Fast and effective adsorption of amoxicillin from aqueous solutions by L-methionine modified montmorillonite K10, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **2021**, **611**, 125792, https://doi.org/10.1016/j.colsurfa.2020.125792;
20. Xi, Y.F., Frost, R.L., He, H.P., Kloprogge, T., Bostrom, T.: Modification of Wyoming montmorillonite surfaces using a cationic surfactant, *Langmuir*, **2005**, **21** (19), 8675-8680;
21. Park, Y., Ayoko, G.A., Frost, R.L.: Application of organoclays for the adsorption of recalcitrant organic molecules from aqueous media, *Journal of Colloid and Interface Science,* **2011**, **354** (1), 292-305.