Sepiolite functionalized with *N*-[3-(trimethoxysilyl)propyl]-ethylenediamine triacetic acid trisodium salt. Part I: Preparation and characterization

SLAVICA S. LAZAREVIĆ*, IVONA M. JANKOVIĆ-ČASTVAN, BOJAN M. JOKIĆ,
DJORDJE T. JANAĆKOVIĆ and RADA D. PETROVIĆ

*Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4,
11000 Belgrade, Serbia*

Abstract: Natural sepiolite from Andrici (Serbia) was functionalized by covalent grafting of *N*-[3-(trimethoxysilyl)propyl]ethylenediamine triacetic acid trisodium salt onto the Si–OH sepiolite groups. The functionalized material, MSEAS, was characterized by determination of the phase composition by X-ray diffraction (XRD) analysis, analysis of the morphological characteristics by scanning electron microscopy (SEM), using Fourier transform infrared (FTIR) spectroscopy, differential thermal analyses (DTA), determination of the specific surface areas and pore size distribution using the BET method and point of zero charge (pH$_{pzc}$) determination. The crystal structure of sepiolite did not change significantly upon surface modification. The FT-IR and DTA analyses confirmed that the modified sample maintained the basic structure of sepiolite and the presence of organic groups in the functionalized sepiolite sample. The point of zero charge of MSEAS in KNO$_3$ solutions of different concentrations, determined by the batch technique, was at pH 7.0±0.1.

Keywords: sepiolite; functionalization; *N*-[3-(trimethoxysilyl)propyl]ethylenediamine triacetic acid, trisodium salt.

INTRODUCTION

The variety of possible reactions of the active centres on the surface of clays allows the surface properties to be changed by introduction of new groups of atoms. Grafting is a process that links inorganic and organic components *via* strong bonds, such as covalent or ionic–covalent linkages, to obtain functionalized clays, *i.e.*, the formation organic–inorganic hybrid materials combining the mechanical stability of a clay framework and the reactivity of organofunctional groups. The alkoxysilane part of an organosilane molecule is capable of bonding

1193

with a variety of mineral or metal surfaces through complex hydrolysis/condensation reactions, whereby Si–O–metal bonds are ultimately formed.[1]

The reactions of clay minerals with reagents containing metal chelating functionalities have recently been explored in an effort to enhance the heavy metal binding capacities of clays and their selectivity to the type of metal considered.[2–9]

The surface of sepiolite has a great ability for grafting reactions with organosilanes due to its high content of silanol groups that are very susceptible to the reactions.[10] By hydrolysis, the alkoxy-groups of the organosilane ($R–SiX_3$, where X designates hydrolysable alkoxy groups (usually methoxy, $–OCH_3$, or ethoxy, $–OC_2H_5$)) are converted to silanol groups, which react with silanol groups of sepiolite forming Si–O–Si covalent bonds.[11] The most widely used functional silanes contain thiol ($–SH$) or amino ($–NH_2$) groups. The surface of sepiolite was previously functionalized using silane coupling agents: 3-mercaptopropyltrimethoxysilane (MPS),[2] triethoxy-3-(2-imidazolin-1-yl)propylsilane,[12] [3-(2-aminoethylamino)propyl]trimethoxy-silane).[13]

In previous papers, natural, acid activated and thermo-acid activated sepiolites were functionalized using (3-mercaptopropyl)trimethoxy-silane and [3-(2--aminoethylamino)propyl]trimethoxysilane and the capacities of the obtained sorbents for chromium(VI) sorption from aqueous solutions were investigated.[9,14,15] It was shown that adsorption capacities of the amine-functionalized sepiolites were much higher than those of mercapto-silane functionalized sepiolites under the same conditions, indicating that adsorption capacities of functionalized sepiolites depended on the type of groups covalently grafted to the sepiolite surface.

The present study is the first to investigate the modification of sepiolite with *N*-[3-(trimethoxysilyl)propyl]ethylenediamine triacetic acid trisodium salt in order to improve sorption capacity for metal ions from aqueous solutions. The silanation reagent *N*-[(3-trimethoxysilyl)propyl]ethylenediamine triacetic acid contains three methoxy groups, which could react with the OH groups on clays, and an EDTA group, which could chelate metals. This paper reports the preparation of the modified material and its characterization by XRD analysis, scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, differential thermal analyses (DTA), surface-area analysis and determination of the point of zero charge (pH_{pzc}). In the second part of this paper, the adsorption properties of the functionalized sepiolite sample, the sorption of Ni^{2+} on the MSEAS as a function of the initial metal concentration, the equilibration time, the pH value and temperature are discussed.

EXPERIMENTAL

Materials

The natural sepiolite (SEP) used for the modification was obtained from Andrici (Serbia). The chemical composition, specific surface area, pore volume, pore radius, X-ray diffraction, and FTIR analyses of the sample were reported previously.[16] The functionalization of sepiolite was performed from aqueous solution[6,17] by mixing a mechanically stirred suspension of 50 g of sepiolite in distilled water, pH of 7.1, with 22.5 mL of a 45 % aqueous solution of *N*-[3-(trimethoxysilyl)propyl]ethylenediamine triacetic acid trisodium salt $((CH_3O)_3Si(CH_2)_3N(CH_2COONa)N(CH_2)_2N(CH_2COONa)_2)$, MSEA, Gelest). The mixture was filtered after 2 h and the modified sepiolite sample, MSEAS, was washed with water.

Characterization of the modified sepiolite

The scanning electron microscopic (SEM) analysis of the sepiolite powder was realized on a Tescan Mira 3 microscope. The powder was fused with a Pd–Pt alloy. X-Ray diffraction (XRD) analysis of the sample was performed using an Ital Structures APD 2000 diffractometer with CuKα radiation, in the 2θ angle range from 5 to 60°, with a 0.02° step.

Infrared spectroscopy analysis was made on a MB Boman Hartmann 100 instrument in the wave number range from 4000 to 400 cm^{-1}. The sample was prepared by the KBr method at a ratio of sample:KBr of 1:75. Differential thermal analysis in air was realized using an AMINCO instrument with computer-controlled temperature, at a heating rate of 10 °C min^{-1}.

The specific surface areas and pore size distribution of the modified sample was estimated using nitrogen adsorption–desorption isotherms determined using a Micrometrics ASAP 2020 instrument. Before the sorption measurement, the sample was degassed at 150 °C for 10 h under reduced pressure. The specific surface area of sample (S_{BET}) was calculated according to the Brunauer–Emmett–Teller (BET) method from the linear part of the nitrogen adsorption isotherm.[18] The total pore volume (V_{tot}) was given at $p/p_0 = 0.998$. The volume of the mesopores and pore size distribution were analyzed according to the Barrett, Joyner and Halenda method from the desorption isotherm.[19] The volume of the microspores was calculated according to *t*-plot analysis[20] using the Harkins–Jura thickness curve.

The point of zero charge (pH$_{pzc}$) of the modified sepiolite was determined in KNO$_3$ solutions having concentration 0.1, 0.01 and 0.001 mol L^{-1}, using the batch equilibration method as described previously.[21] In order to determine the degree of dissolution of the modified sepiolite powder, the concentration of Mg^{2+} in the solutions after equilibration with a 0.01 mol L^{-1} KNO$_3$ solution was measured by atomic absorption spectroscopy (AAS, Perkin Elmer 730).

RESULTS AND DISCUSSION

Characterization of modified sepiolite

The characteristic peak positions in the XRD spectrum of the sepiolite sample had not changed after modification with *N*-[3-(trimethoxysilyl)propyl]-ethylenediamine triacetic acid trisodium salt (Fig. 1), indicating that the structure and crystallinity of sepiolite were maintained, which could be attributed to the functionalization occurring mainly on the surface or by the partial replacement of zeolitic water.
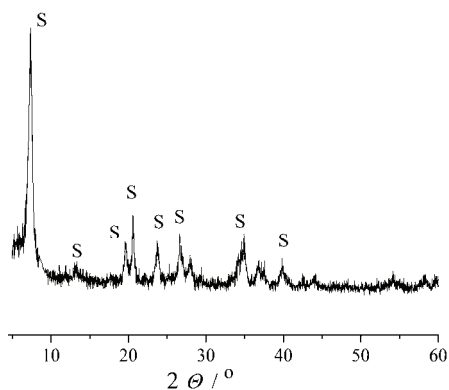
Fig. 1. XRD spectrum of the MSEAS sample (S – sepiolite).

The SEM micrograph of MSEAS is shown in Fig. 2. It could be seen that the modified sepiolite had a fibrous structure, as did the natural sepiolite.[22] The micrographs of natural sepiolite sample showed the fibres had needle morphology of 30–50 nm in diameter and 1 μm in length. After surface modification, the needle morphology was maintained but with reduced fibre length. The fibres of the functionalized sample formed bundle-like aggregates.
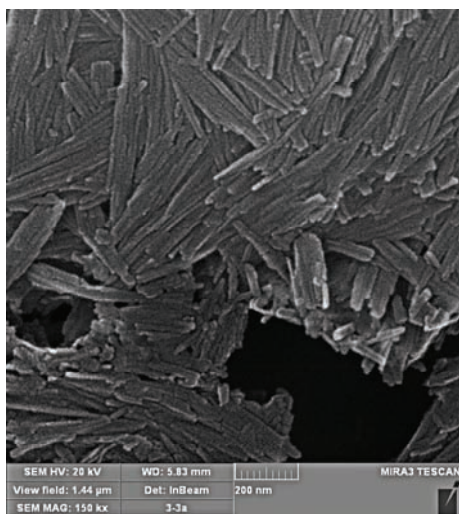

Fig. 2. SEM micrograph of the modified sepiolite.

The FTIR spectrum of the modified sample (Fig. 3) was generally similar to that of natural sepiolite, confirming that the modified material had maintained the basic structure of sepiolite. Three regions indicative for sepiolite[23,24] could be observed in Fig. 3: bands in the 4000–3000 cm^{-1} range corresponding to the vibrations of the Mg–OH group (3690 cm^{-1}), bound water coordinated to magnesium in the octahedral sheet (3570 cm^{-1}) and zeolitic water in the channels (at 3422 cm^{-1}); a band at 1658 cm^{-1} due to the vibration of zeolitic water; bands in

the 1200–400 cm^{-1} range characteristic of silicate: bands centred at 1016 and 467 cm^{-1} due to Si–O–Si vibration; bands at 1215 and 1078 cm^{-1} due to Si–O bonds; a band at 437 cm^{-1} originating from octahedral–tetrahedral bonds (Si–O–Mg bonds) and bands at 690 and 637 cm^{-1} corresponding to vibrations of the Mg–OH bond. The band at 1381 cm^{-1} corresponds to vibrations of C–H of the CH$_2$ groups. The C–H stretching vibrations of the methoxy (O–CH$_3$) and chain methylene (CH$_2$) groups could be observed at 2850 and 2930 cm^{-1}, respectively.[9,13] A band, assigned to symmetric COO$^-$ stretching vibrations,[25] could be clearly observed at 1407 cm^{-1}. The detected CH$_2$ and COOH groups belong to the units of the MSEA, clearly indicating the presence of the organic modifier in the sample.
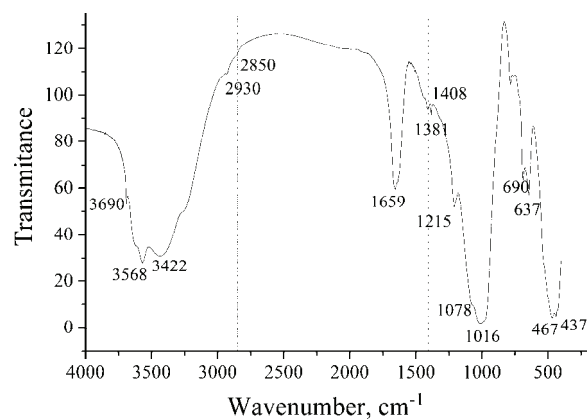

Fig. 3. FT-IR spectrum of the MSEAS sample.

The DTA curve of the modified sepiolite, shown in Fig. 4, revealed the decomposition of the aminocarboxylic group on the surfaces of MSEAS and dehydration of the sepiolite structure. The endothermic peak represents the loss
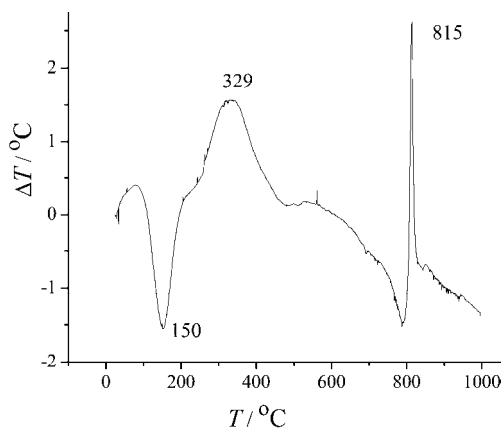

Fig. 4. DTA curve of the MSEAS sample.

of zeolite water (at 150 °C),[26] the exothermic peak at 815 °C represents the dehydratation of the octahedrically coordinated hydroxyl groups, *i.e.*, phase transformation of sepiolite into enstatite ($MgSiO_3$). The broad exothermic peak at ≈329 °C reveals the decomposition of the grafted silane ligand and clearly proves the presence of organic silane molecules on the modified material.

Textural properties of modified sepiolite

Adsorption–desorption isotherms at −196 °C for MSEAS, and the pore volume and pore size distribution are presented in Fig. 5a and b. The MSEAS shows a hysteresis pattern which is associated with the filling and emptying of the mesopores by capillary condensation, but does not show a plateau at high p/p_0 values, which is characteristic of a Type IV isotherm. The hysteresis loop is of Type H3. According to the classification of Rouquerol *et al.*,[18] such a shape of a nitrogen
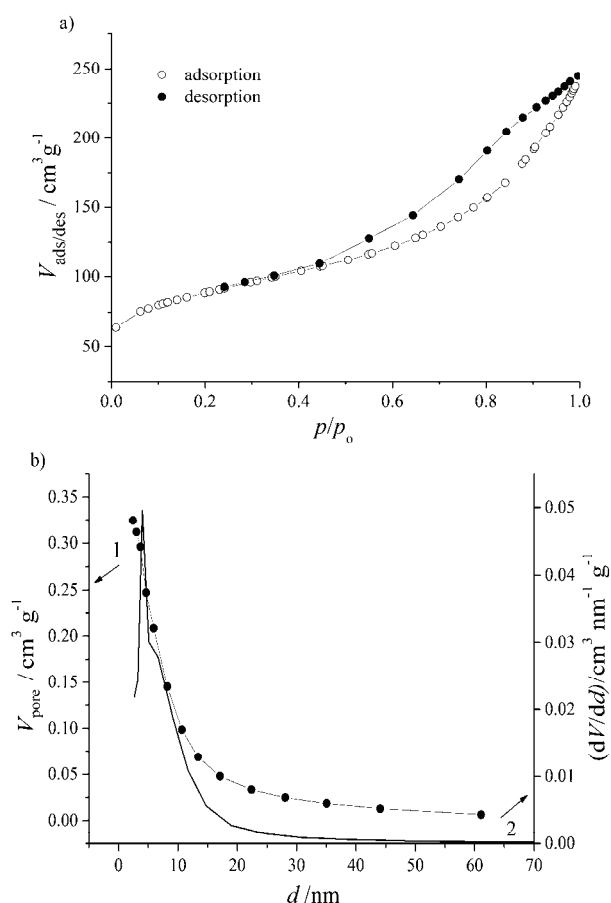

Fig. 5. a) Nitrogen adsorption/desorption isotherms; b) pore volume (1) and pore size distribution (2) of the MSEAS.

isotherm is characteristic for Type IIb indicating that the material contained both mesopores, which are responsible for the hysteresis, and macropores, which results in the absence of the plateau typical for mesoporous Type IV isotherms. The H3 hysteresis pattern indicates the presence of slit-like pores.[27]

From Fig. 5 and the data summarized in Table I (BET surface area, volume of mesopores, $V_{mesopore}$, and micropores, $V_{micropore}$, the overall pore volume, $V_{poretotal}$, and the maximum, d_{max}, and average, d, mesopore diameters) and data obtained for a natural sepiolite,[16] it could be noticed that the modification of the sepiolite with MSEA caused a small change in the specific surface area, an increase in the total pore volume, the micropore volume and the mesopore volume. Increases in the maximum and average mesopore diameters were observed for the modified sepiolite sample. It could be assumed that silane modification occurred almost exclusively on the external sepiolite surface, with only partial entry into the sepiolite channels, *i.e.,* that the pores of the sepiolite were not closed during the functionalization.

TABLE I. The textural properties of the MSEAS

S_{BET} / m^2 g^{-1}	$V_{poretotal}$ / cm^3 g^{-1}	$V_{micropore}$ / cm^3 g^{-1}	$V_{mesopore}$ / cm^3 g^{-1}	d_{max} / nm	d / nm
309.9	0.374	0.054	0.325	4.00	6.51

Determination of the point of zero charge of the modified sepiolite

The point of zero charge (pH_{pzc}) is an important interfacial parameter, extensively used in characterizing the ionization behaviour of a surface. It is very important for the determination of the acid–base characteristics of the surface functional groups and their interactions with ions from aqueous solutions. The surface potential exists as a direct result of the presence of surface charge. The solution pH value at which the surface charge density of the solid phase is equal to zero ($\sigma_0 = 0$, $\psi_0 = 0$), is called the point of zero charge (pH_{pzc}). The solid phase surface is positively charged if $pH < pH_{pzc}$ and negatively if $pH > pH_{pzc}$.

The point of zero charge of MSEAS in KNO_3 solutions of different concentrations, determined by the batch technique from the plateaus, *i.e.*, the curve inflexions, from the dependences pH_f *vs.* pH_i, (Fig. 6) was at pH 7.0±0.1. The pH_{pzc} determined in KNO_3 solutions of different concentrations were independent of the ionic strength of the KNO_3 solutions, indicating that KNO_3 was an inert electrolyte, *i.e.*, specific sorption of K^+ and NO_3^- did not occur at the surface.

The slight change in the point of zero charge of MSEAS compared with the pH_{pzc} of the natural sepiolite sample (7.4±0.1)[16] indicates an insignificant decrease in the basicity of the sepiolite surface after functionalization.

The dependence of the quantity of Mg^{2+} released into the solution during equilibration of 0.05 g of the MSEAS with 25 cm^3 0.01 mol L^{-1} KNO_3 solution

is also shown in Fig. 6 in order to determine the degree of dissolution of the modified sepiolite powder. In the investigated pH range, the quantity of Mg^{2+} present in the solution as a result of the dissolution of sepiolite was almost constant and equal to 0.05 mmol g^{-1} MSEAS.
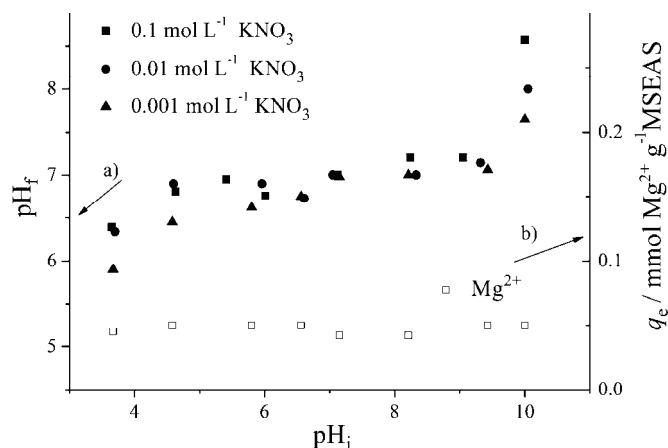

Fig. 6. a) Determination of the pH_{pzc} of MSEAS in KNO_3 solutions of different concentrations; b) dependence of the quantity of Mg^{2+} released into the solution per unit mass of MSEAS on pH_i during equilibration with 0.01 mol L^{-1} KNO_3 solutions.

CONCLUSIONS

The obtained results showed that natural sepiolite from the Andrici deposit could be modified by treating with *N*-[3-(trimethoxysilyl)propyl]ethylenediamine triacetic acid trisodium salt in the presence of an aqueous solution. The surface modification of the sepiolite involved chemical reaction of the silanol groups on the sepiolite surface with the alkoxy groups of the organosilane molecule. The signs of modification of the sepiolite surface were: the presence of new exothermic peaks in the DTA spectrum for modified sepiolite, the detection of carboxylic functional groups present on modified sepiolite by FTIR spectroscopy. The point of zero charge of MSEAS in KNO_3 solutions of different concentrations, determined by the batch technique, was pH 7.0±0.1.

И З В О Д

ФУНКЦИОНАЛИЗАЦИЈА СЕПИОЛИТА ПРИМЕНОМ СОЛИ НАТРИЈУМА
N-[(3-ТРИМЕТОКСИ)ПРОПИЛ]ЕТИЛЕНДИАМИНТРИАЦЕТАТНЕ КИСЕЛИНЕ.
ПРВИ ДЕО: ПРИПРЕМА И КАРАКТЕРИЗАЦИЈА

СЛАВИЦА С. ЛАЗАРЕВИЋ, ИВОНА М. ЈАНКОВИЋ-ЧАСТВАН, БОЈАН М. ЈОКИЋ, ЂОРЂЕ Т. ЈАНАЋКОВИЋ
и РАДА Д. ПЕТРОВИЋ

Технолошко-металурски факултет Универзитета у Београду, Карнегијева 4, 11000 Београд

Природни сепиолит из налазишта Андрићи је функционализован применом соли
натријума *N*-[(3-триметокси)пропил]етилендиаминтриацетатне киселине успостављ-
њем ковалентне везе између модификатора и Si−OH површинских група сепиолита.
Карактеризација функционализованог узорка означеног са MSEAS извршена је одређи-
вањем морфолошких карактеристика применом скенирајуће електронске микроскопије
(SEM), одређивањем фазног састава рендгенско-дифракционом анализом (XRD) и при-
меном инфрацрвене спектроскопске анализе (FT-IR) и диференцијално-термијске ана-
лизе (DTA), као и одређивањем специфичне површине и расподеле величина пора BET
методом и тачке нултог наелектрисања (pH$_{pzc}$). Кристална структура сепиолита није
битно промењена поступком функционализације. Резултати FT-IR и DTA анализе
потврдили су присуство основне сепиолитске структуре у узорку MSEAS, као и при-
суство карбоксилних група органског модификатора. Тачка нултог наелектрисања
узорка MSEAS, одређена у растворима KNO$_3$ различитих концентрација применом
методе уравнотежавања посебних проба, износи 7,0±0,1.

(Примљено 19. фебруара, ревидирано 11. маја, прихваћено 14. маја 2015)

REFERENCES

1. Y. Xie, C. A. S. Hill, Z. Xiao, H. Militz, C. Mai, *Composites, A* **41** (2010) 806
2. R. Celis, M. C. Hermosin, J. Cornejo, *Environ. Sci. Technol.* **34** (2000) 4593
3. I. P. Blitz, J. P. Blitz, V. M. Gunko, D. J. Sheeran, *Colloids Surfaces, A* **307** (2007) 83
4. K. F. Lam, C. M. Fong, K. L. Yeung, G. McKay, *Chem. Eng. J.* **45** (2008) 185
5. A. M. F. Guimaraes, V. S. T. Ciminelli, W. L. Vasconcelos, *Appl. Clay Sci.* **42** (2009) 410
6. A. N. Vasiliev, L. V. Golovko, V. V. Trachevsky, G. S. Hall, J. Khinast, *Micropor. Mesopor. Mat.* **118** (2009) 251
7. X. Liang, Y. Xu, G. Sun, L. Wang, Y. Sun, Y. Sun, X. Qin, *Chem. Eng. J.* **174** (2011) 436
8. X. Liang, Y. Xu, X. Tana, L. Wang, Y. Sun, D. Lin, Y. Sun, X. Qin, Q .Wang, *Colloids Surfaces, A* **426** (2013) 98
9. V. Marjanović, S. Lazarević, I. Janković-Častvan, B. Potkonjak, Dj. Janaćković, R. Petrović, *Chem. Eng. J.* **166** (2011) 198
10. M. Alkan, *Micropor. Mesopor. Mat.* **84** (2005)75
11. O. Demirbas, M. Alkan, M. Dogan, Y. Turhan, H. Namli, P. Turan, *J. Hazard. Mater.* **149** (2007) 650
12. Y. Turhan, P. Turan, M. Dogan, M. Alkan, H. Namli, O. Demirbas, *Ind. Eng. Chem. Res.* **47** (2008) 1883
13. M. Dogan, Y. Turhan, M. Alkan, H. Namli, P. Turan, O. Demirbas, *Desalination* **30** (2008) 248
14. V. Marjanović, S. Lazarević, I. Janković-Častvan, B. Jokić, A. Bjelajac, Dj. Janaćković, R. Petrović, *Hem. Ind.* **67** (2013) 715

15. V. Marjanović, S. Lazarević, I. Janković-Častvan, B. Jokić, Dj. Janaćković, R. Petrović, *Appl. Clay. Sci.* **80**–**81** (2013) 202

16. S. Lazarević, I. Janković-Častvan, D. Jovanović, S. Milonjić, Dj. Janacković, R. Petrović, *Appl. Clay Sci.* **37** (2007) 47

17. J. F. Bringley, Y. J. Lerat, U.S. Pat. Appl. 2005276862

18. F. Rouquerol, J. Rouquerol, K. Sing, *Adsorption by Powders and Porous Solids,* Academic Press, London, 1975

19. E. P. Barrett, L. G. Joyner, P. P. Halenda, *J. Am. Chem. Soc.* **73** (1951) 373

20. B. C. Lippens, J. H. De Boer, *J. Catal.* **4** (1965) 319

21. S. Milonjic, A. Ruvarac, M. Susic, *Thermochim. Acta* **11** (1975) 261

22. S. Lazarević, Ž. Radovanović, Dj. Veljović, A. Onjia, Dj. Janaćković, R. Petrović, *Appl. Clay Sci.* **43** (2009) 41

23. F. R. Cannings, *J. Phys. Chem.* **72** (1968) 1072

24. C. Serna, J. L. Alrichs, J. M. Serratosa, *Clay Clay Miner.* **23** (1992) 452

25. R. De Palma, S. Peeters, M. J. Van Bael, H. Van den Rul, K. Bonroy, W. Laureyn, J. Mullens, G. Borghs, G. Maes, *Chem. Mater.* **19** (2007) 1821

26. A. Singer, W. F. A. Kirsten, C. Buhmann, *S. Afr. J. Geol.* **95** (1992) 165

27. U. Kuila, M. Prasad, *Geophys. Prospect*. **61** (2013) 341.