

The synthesis of poly(acrylic acid)-bentonite and polyacrylamide-bentonite composites for adsorption applications

Piotr NATKAŃSKI, Anna BIAŁAS, Piotr KUŚTROWSKI – Faculty of Chemistry, Jagiellonian University, Kraków, Poland

Please cite as: CHEMIK 2012, 66, 7, 742-749

Introduction

Clay minerals are added to polymers to improve their thermal and mechanical properties. The challenge in the synthesis of this kind of composites is combining a hydrophilic layered material with a hydrophobic organic part. Frequently, in aim to ensure the contact between the components a surfactant is added (e.g. quaternary alkylammonium salts). Its functional groups interact electrostatically with clay layers and a hydrocarbon chain facilitates polymer introduction. In the case of the macromolecules containing carboxylic groups ion exchange between them and the cations balancing the negative charge of clay layers can occur – this eliminates the necessity of surfactant using [1].

To the synthesis of composites layered aluminosilicates are applied - the most often from the bentonite group, abundant in nature. The main component of bentonite, montmorillonite is the clay mineral composed of the layers containing two sheets built of silicon oxide tetrahedrals and placed between them the sheet of aluminum oxide octahedrals, where one third of oxygen atoms form hydroxyl groups. Al^{3+} ions are partly replaced by the cations with lower valence, which results in the negative charge of the whole layer. This charge is balanced by cations, the most often Na^+ , K^+ , Ca^{2+} or Mg^{2+} , situated in interlayer spaces. Extra-framework cations can take part in the ion exchange or a chemical reaction enabling the introduction of organic substances into galleries. The structure of montmorillonite is presented in Figure 1.

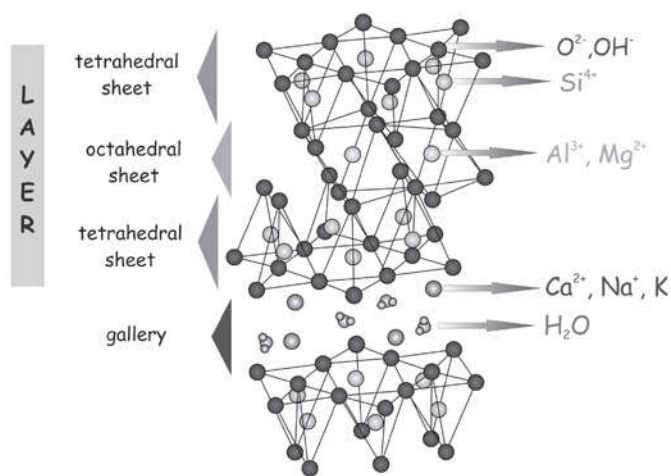


Fig. 1. Montmorillonite structure

There are three main ways of the synthesis of polymer-aluminosilicate composites based on the introduction of organic part into the interlayer spaces of a clay mineral: (i) *in situ* polymerization, (ii) intercalation of a polymer from its solution or (iii) its molten

form. In the case of solution using, layered silicate must swell in the solution of monomers or polymers. The introduction of a molten polymer into a clay mineral does not require any solvent, which is an advantage in the case of the necessity of the application of toxic organic solvents. The limitation of this method is the amount of an introduced clay mineral (usually to 4 wt.%) and the possibility of using only thermoplastic polymers [2].

One of the polymer groups, which can be applied to the synthesis of composites are hydrogels exhibiting hydrophilic properties and swelling in water. These features with the chemical structure of hydrogels cause that they can be used in many applications including the adsorption of cationic pollutants. The composites based on hydrogels were successfully applied, among others, to the removal of heavy metal cations from water [3].

The detrimental influence of an iron excess on the human body causes that an efficient adsorbent of $Fe(III)$ cations is searched for the remediation of drinking water [4]. In the presented paper the hydrogel-bentonite composites were used for this purpose. They were based on acrylic acid or acrylamide, used as monomers in the process of intercalation polymerization, and raw aluminosilicate.

Experimental

Materials

Bentonite (BZ), from the deposits in Jelsovy Potok, Slovakia, (BENTONIT SPECJAL, ZGM Zębiec) containing min. 75 wt.% of montmorillonite, was used to the synthesis of examined composites. Acrylic acid (AA) (Arkema, Poland) and acrylamide (AAM) (Sigma-Aldrich) were used as monomers. N,N' -methylenebisacrylamide (MBA) (Sigma-Aldrich) and ammonium persulfate (POCH) were used as a crosslinker and an initiator, respectively. Iron(III) nitrate (POCH) was applied in adsorption tests.

Synthesis

Hydrogel-bentonite composites based on non-crosslinked acrylamide (BZ-PAAM) and acrylic acid (BZ-PAA) as well as on their crosslinked forms, denoted in the paper as BZ-PAAM-MBA and BZ-PAA-MBA, were synthesized by the *in situ* intercalation polymerisation. In all syntheses the identical weight ratio of polymer to inorganic part equal to 1:1 and a constant amount of the initiator (1 mol.% in respect of monomers) were maintained. N,N' -methylenebisacrylamide in the amount of 1 mol.% was applied to the preparation of the crosslinked forms of polymers based on acrylic acid and acrylamide.

The dispersion of montmorillonite containing 10 wt.% of monomers (including in chosen cases the linking monomer) was stirred at room temperature for 24 hours. Before the beginning of polymerisation process oxygen was removed from the system by purging it with argon for 10 min, subsequently ammonium persulfate

was added. The polymerization reaction was carried out at 60°C for 3 hours. The obtained composites were cut into pieces, and then milled in an agate ball mill.

Methods

The structural investigation of bentonite and the obtained composites were conducted using a powder X-ray diffractometer - Bruker D2 Phaser, equipped with a Cu anode ($\lambda = 1.54056 \text{ \AA}$) in the range of 2θ from 3 to 40°, with a step of 0.02°. IR spectra were recorded by means of a FT-IR Nicolet 6700 spectrometer equipped with a MCT-a detector and an accessory for the measurement of Attenuated Total Reflectance (ATR). The spectra were collected for the powder samples in the wavenumber range of 4000-650 cm^{-1} , doing 200 scans with 2 cm^{-1} resolution.

The composite materials were examined as adsorbents of iron(III) cations from water nitrate solutions at a constant temperature of 30°C. In this purpose Fe^{3+} solutions (50 ml) were prepared in the range of concentrations from 48 mg/l to 1120 mg/l. To these solutions 0.1 g of an adsorbent was added. The sorption process was carried out for 5 days. The changes in iron(III) ion concentrations were determined by the rhodanate method by means of a Merck Spectroquant Pharo 100 VIS spectrophotometer. The sorption capacity of composites in respect of Fe^{3+} ions was calculated from the following equation:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m}$$

where: q_e – sorption capacity in respect of Fe^{3+} ions (mg/g), C_0 – the initial concentration of Fe^{3+} ions in a solution (mg/l), C_e – the concentration of Fe^{3+} ions at equilibrium (mg/l), V – the volume of a iron (III) nitrate solution (l), m – adsorbent mass (g).

Results and discussion

Powder X-ray diffraction patterns recorded for raw bentonite (BZ) and the obtained composites are presented in Figure 2. The shift of the (001) reflection, characteristic of the montmorillonite (MT) phase - dominant in the examined bentonite, towards the lower values of 2θ angles is observed after introducing hydrogel. This confirms the successful intercalation of polymer chains into the interlayer spaces of montmorillonite. On the basis of Bragg's law expressed as:

$$n \cdot \lambda = 2d \cdot \sin \theta$$

the interplanar distances were calculated and are demonstrated in Table I.

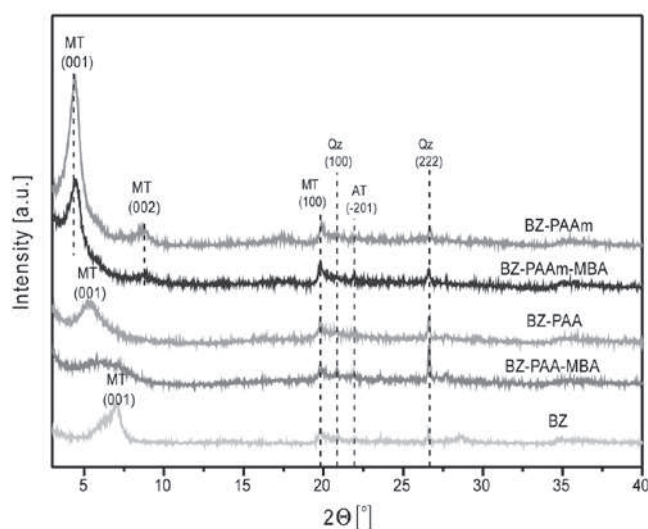


Fig. 2. X-ray diffraction patterns of raw bentonite (BZ) and composites (BZ-PAAm, BZ-PAA, BZ-PAAm-MBA and BZ-PAA-MBA)

In the case of the composite based on crosslinked poly(acrylic acid) along with the intercalation partial delamination of aluminosilicate layers occurred, which is confirmed by a significantly lower intensity as well as by broadening the (001) reflection. This brought about that the determination of the exact position of the maximum is not possible. In contrast to the composites based on PAA, in the materials containing polyacrylamide an increase in layer ordering is visible, which is proven by the appearance of the (002) reflection. Also the diffraction peaks characteristics of other crystalline phases present in raw bentonite are observed in the collected patterns. The relatively high intensity of reflections enables the identification of quartz (Qz) and albite (AT).

A profounder insight into the structure of raw and modified bentonite was gained by means of IR spectroscopy. FT-IR spectra of all examined materials are collected in Figure 3.

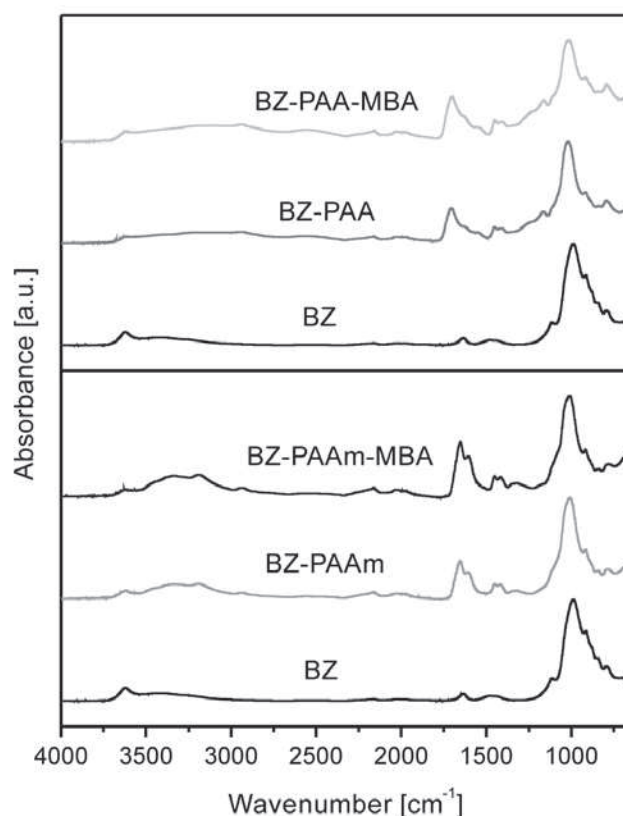


Fig. 3. FT-IR spectra of raw bentonite (BZ) and composites (BZ-PAAm, BZ-PAA, BZ-PAAm-MBA and BZ-PAA-MBA)

For pristine bentonite bands typical of stretching vibration of OH groups present in silanol groups (Si-OH) (3620 cm^{-1}) and stretching and bending vibrations of H-OH in water molecules adsorbed on the surface of aluminosilicate at 3430 and 1635 cm^{-1} , respectively, are observed. The bands corresponding to asymmetric stretching vibration in SiO_2 tetrahedrals (990 and 1115 cm^{-1}) as well as bending vibrations of O-H bonds in Al_2OH (915 cm^{-1}) and MgAlOH (842 cm^{-1}) groups are also visible [5 ÷ 7]. The band at 795 cm^{-1} confirms the presence of quartz in the tested bentonite.

The bands typical of the montmorillonite structure as well as originating from a polymer part were observed in FT-IR spectra recorded for the hydrogel-bentonite composites. For all hydrogel matrixes the bands corresponding to bond vibrations in the backbone chain: 2950 cm^{-1} (C-H stretching), 1460 cm^{-1} (C-H deformation), 1316 cm^{-1} (C-C stretching) and 1117 cm^{-1} (C-H in plane bending) are visible. Observed in the spectra of BZ-PAAm and BZ-PAAm-MBA, absorption maxima at 1650 and 1606 cm^{-1} , are ascribed to stretching vibrations of C=O bonds and in plane bending vibrations of N-H bonds in amide groups, respectively [8]. In spectra of the

composites based on poly(acrylic acid), the band at 1706 cm^{-1} is connected with the stretching vibrations of $\text{C}=\text{O}$ in carboxyl group. Absorption maxima at 1552 and 1410 cm^{-1} are characteristic of asymmetric and symmetric stretching vibrations of $\text{C}-\text{O}$ bonds in carboxyl groups [9].

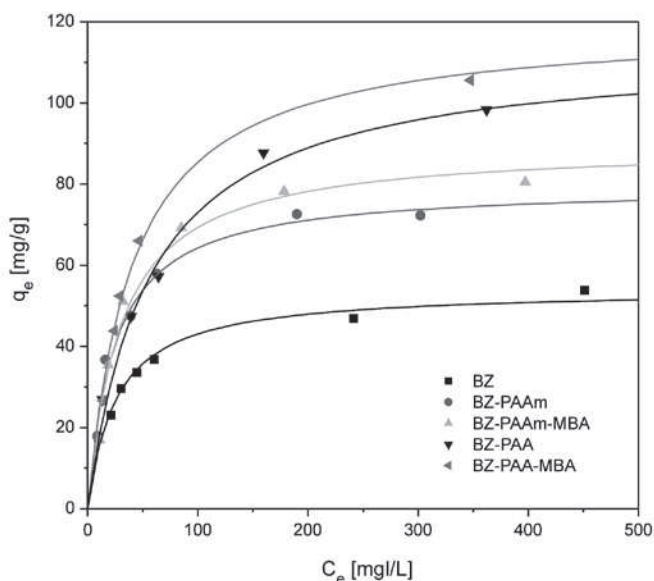


Fig. 4. Adsorption isotherms of Fe^{3+} cations for bentonite and hydrogel-bentonite composites determined at 30°C

In Figure 4 the results of the adsorption of Fe^{3+} cations from iron(III) nitrate solutions are presented for the raw material and the obtained composites. The values of sorption capacity at equilibrium (q_e) were measured after 5 days of the contact of an adsorbent with a solution at 30°C . Model adsorption isotherms were fitted to experimental points using the equations postulated by Langmuir and Freundlich, expressed as following:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

where: q_m , K_L and C_e denote the value of adsorption corresponding to a monolayer, adsorption equilibrium constant and the equilibrium concentration of iron(III) ions in a solution, respectively,

$$q_e = K_f C_e^{\frac{1}{n}}$$

where: C_e is the equilibrium concentration of iron(III) ions in a solution, and K_f and n are the constants characteristic of an adsorbate and adsorbent at a temperature.

In Table I the results of fitting the experimental points to the above presented adsorption model are compared.

On the basis of the presented data one can state that the introduction of a hydrogel modifier to a raw layered aluminosilicate significantly increases its sorption capacity in respect of Fe^{3+} ions. Also crosslinking of the composite has a positive influence on the performance of the examined composites. The composite material based on crosslinked poly(acrylic acid) exhibited the highest sorption capacity. This effect could be caused by the strong interaction between COO^- and Fe^{3+} cations, which is confirmed by better fitting the Langmuir model in comparison to Freundlich isotherm. Partial delamination of montmorillonite layers, which occurs in the case of the discussed composite, additionally favors an increase in the activity of surface in the adsorption of metal ions.

Table I

Interplanar distances and fitting parameters of adsorption models for examined materials

Sample	Interplanar distance $d(001)$ [\AA]	Langmuir model			Freundlich model		
		q_m ($\times 10^{-3}\text{ g g}^{-1}$)	K_L ($\times 10^3\text{ l mol}^{-1}$)	R^2	K_f	n	R^2
BZ	12.6	54.1	0.039	0.9750	12.15	4.05	0.9600
BZ-PAAm	19.8	79.5	0.042	0.9797	15.91	3.58	0.8910
BZ-PA-Am-MBA	20.1	89.7	0.034	0.9760	16.73	3.57	0.8340
BZ-PAA	16.4	113.6	0.018	0.9870	13.22	2.86	0.9546
BZ-PAA-MBA	-	119.6	0.025	0.9942	16.51	3.05	0.9166

Conclusions

Pristine layered aluminosilicate can be relatively easily modified, excluding the preliminary stage of organophilisation, by introducing the hydrogel chains of poly(acrylic acid) or polyacrylamide to interlayer galleries. The successful intercalation was confirmed complementary by powder X-ray diffraction (the shift of the (001) reflection coming from the montmorillonite phase proving an increase in the interplanar distance) as well as by IR spectroscopy (the appearance of the vibrations characteristic of introduced organic macromolecules). The performed modification results in a significant increase in the sorption capacity of the material in respect of Fe(III) cations, which allows to assume, that the developed composites can be applied as adsorbents of cation pollutants from water solutions.

Acknowledgment

The work was financed by the Polish National Science within the grant N N507 217640. Piotr Natkański thanks to Scholarship Program DOCTUS, co-financed by European Social Funds, for support. The experiments were carried out using the equipment bought from the means of European Regional Development Funds within the Polish Innovation Economy Operational Program (contract no. POIG.02.01.00-12-023/08). The authors express their gratitude to Zakłady Górniczo-Metalowe Zębiec for pristine bentonite as well as to Ms. Krystyna Fajfer for help during the adsorption tests.

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Piotr NATKAŃSKI – M.Sc., graduated from the Faculty of Chemistry, Jagiellonian University (2009). Nowadays he is a Ph.D. student at Environmental PhD Study IMIM Polish Academy of Sciences – Jagiellonian University, in the field of material engineering. Research topics: polymer chemistry, composite materials. He is co-author of 3 scientific papers and 17 oral and poster presentations at Polish and international conferences.

e-mail address: piotr.natk@gmail.com. phone: (12) 663 2096

Anna BIAŁAS – Ph.D., graduated from the Faculty of Chemistry, Jagiellonian University (1994). She obtained her Ph.D. degree from the Faculty of Chemistry JU (2004). Nowadays she works as an adjunct at the Department of Chemical Technology JU. Research topics: chemistry of solid state and environmental catalysis. She is a co-author of 32 scientific papers and 60 oral and poster presentations at Polish and international conferences.

e-mail address: anbias@chemia.uj.edu.pl. phone: (12) 663 2286

Piotr KUŚTROWSKI – Sc.D., (prof. UJ), graduated from the Faculty of Chemistry, Jagiellonian University (1995). Ph.D. (2000) and habilitation (2007) he obtained from the Faculty of Chemistry JU. Awarded for his scientific achievements by the Minister of Science and Higher Education and the Rector of JU. Nowadays he works as a professor at the Department of Chemical Technology JU heading the Group of Organic Technology and Faculty Laboratory of Photoelectron Spectroscopy ESCA. Research topics: synthesis and modification of porous materials, catalysis. He is co-author of 104 scientific papers and 219 oral and poster presentations at Polish and international conferences.

e-mail address: kustrows@chemia.uj.edu.pl. phone: (12) 663 2006

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