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Influence of crosslinking degree on Cu(II) and Fe(III) adsorption capacity of hydrogel/montmorillonite composites^{**)}

This article is dedicated to Professor Edgar Bortel on the occasion of his 85th birthday

Summary — Intercalation of polyacrylamide (PAAm) and poly(acrylic acid) (PAA) into interlayer spaces of natural montmorillonite by the *in situ* polymerization technique was studied. The modifications were carried out with using both the raw and pre-treated clay. It was shown that no initial modification of the layered mineral (by ion-exchange with Na⁺ cations or organophilization) is needed for the successful introduction of hydrogels into the interlayer gallery. The effect of kind of polymer and its crosslinking degree (with *N,N'*-methylenebisacrylamide, MBA) on the structure of the obtained composites was investigated. The polyacrylamide-containing materials exhibited a tendency to the formation of exfoliated structure. Finally, the composites were tested in a role of adsorbents in an elimination of transition metal cations (Cu²⁺ and Fe³⁺) from aqueous solutions. The highest adsorption capacity was achieved on the poly(acrylic acid)/montmorillonite composite with the hydrogel crosslinked with MBA at the MBA/monomer molar ratio of 0.01.

Keywords: hydrogel, polyacrylamide, poly(acrylic acid), montmorillonite, polymer composites.

WPLYW STOPNIA USIECOWANIA NA POJEMNOŚĆ SORPCYJNĄ KOMPOZYTÓW HYDROŻELOWO-MONTMORYLONITOWYCH WZGLĘDEM KATIONÓW Cu(II) i Fe(III)

Streszczenie — Badano interkalację do przestrzeni międzywarstwowych naturalnego montmorylonitu (MMT), polimerów hydrożelowych otrzymywanych w wyniku polimeryzacji *in situ*. Polimerową matrycę stanowił poliakrylamid (PAAm) lub poli(kwas akrylowy) (PAA). Określano wpływ wstępnej modyfikacji MMT na przebieg procesu interkalacji. Stwierdzono, iż przygotowanie naturalnego montmorylonitu na drodze wymiany jonowej na dominujący rodzaj kationów międzywarstwowych bądź jego modyfikacja polegająca na wprowadzeniu środków powierzchniowo czynnych (operacje sugerowane w literaturze naukowej jako konieczne do uzyskania interkalowanego kompozytu polimerowo-glinokrzemianowego) nie jest niezbędne. Oceniano strukturę dwóch serii materiałów PAAm/montmorylonit oraz PAA/montmorylonit, różniących się stopniem usieciowania matrycy polimerowej. Jako czynnik sieciujący posłużył *N,N'*-metylenobisakrylamid (MBA), wprowadzany do kompozytów w stosunku molowym MBA/monomer = 0,00; 0,01; 0,02 oraz 0,05. Zaobserwowano zmniejszanie się odległości międzywarstwowej montmorylonitu wraz ze zwiększaniem stopnia usieciowania polimeru bazowego. Gęsto usieciowane materiały na bazie poliakrylamidu wykazywały ponadto tendencję do eksfoliacji. Przygotowane kompozyty zastosowano w procesie eliminacji jonów metali przejściowych (Cu²⁺ i Fe³⁺) z roztworów wodnych. Stwierdzono wyraźnie większe pojemności sorpcyjne preparatów opartych na poli(kwasie akrylowym), co powiązano z obecnością aktywnych w wiązaniu kationów, grup karboksylowych. Najlepsze wyniki odnotowano w przypadku materiału zawierającego poli(kwas akrylowy), usieciowany MBA w ilości odpowiadającej stosunkowi molowemu MBA/monomer = 0,01.

Słowa kluczowe: hydrożel, poliakrylamid, poli(kwas akrylowy), montmorylonit, kompozyty polimerowe.

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INTRODUCTION

In recent years there has been a rapid growth of interest in hydrogel polymers. They are three-dimensional networks of hydrophilic polymers, exhibiting the presence of various functional groups, which allow them swelling in polar solvents as well as adsorbing organic molecules (*e.g.* drugs, dyes) [1] and heavy metal cations (*e.g.* Fe^{3+} , Cr^{3+} , Pb^{2+} , Hg^{2+}) [2–4]. Due to the high swelling ability, high adsorption capacity, and biodegradability, these materials are successfully used in medical, pharmaceutical, agricultural and adsorption applications.

In order to improve the functional characteristics of hydrogels (such as mechanical strength, thermal stability, biodegradability and adsorption capacity) inorganic particles are often introduced to the polymeric matrix. Layered silicates, known as clays, are the most popular fillers in such composite materials. Among them, montmorillonite (MMT) has the widest applicability for the production of polymer composites because of its ease availability and well known intercalation/exfoliation ability [5]. Raw montmorillonite used in the synthesis of polymer/clay composites is usually pre-treated to minimize the surface energy of clay layers. The interlayer cations (*e.g.* Ca^{2+} , Mg^{2+} , Na^+ , K^+) occurring in the natural MMT are predominantly exchanged by sodium ions, which improve the swelling ability of the pristine clay in polar solvents and consequently facilitate the intercalation of hydrophilic monomers into the MMT galleries. The inner surface of aluminosilicate can be also organophilized by the introduction of cationic surfactant chains. This modification leads to weakening the forces between adjacent layers. Moreover, the presence of surfactant improves compatibility of the organic and inorganic phases in a composite and therefore various types of polymers can be easily incorporated into the MMT structure [6]. One of the groups of polymer/montmorillonite composites are superabsorbent materials, in which hydrogels form the polymer matrix. The intercalation of the hydrophilic polymers [*e.g.* poly(acrylic acid), poly(itaconic acid), polyacrylamide and their copolymers] into the MMT structure allows to obtain composites with enhanced sorption properties compared to an unmodified clay. Such materials are effective adsorbents of heavy metal cations [7, 8] and dyes [9, 10] from aqueous solutions. We suppose that the hydrogel/montmorillonite composites characterized by high sorption capacity of transition metal cations can be also used in preparation of new type of catalyst precursors. An introduction of metal cations to the hydrogel located in the interlayer spaces of aluminosilicate, and subsequent thermal decomposition of the composite at oxidizing atmosphere could lead to the formation of highly dispersed metal oxide on the mineral surface.

In this work we have discussed the influence of the montmorillonite form (pre-treated and unmodified) used in the composite synthesis on intercalation of hydrogel

chains into the clay gallery. Furthermore, the effect of the type of hydrogel forming the composite material and its crosslinking degree on the sorption capacity of transition metal cations (Fe^{3+} , Cu^{2+}) was investigated.

EXPERIMENTAL

Materials

Natural Wyoming montmorillonite (CEC = 90 meq/100 g) with the following chemical composition: 47.8 % O, 32.3 % Si, 13.6 % Al, 2.5 % Fe, 1.9 % Mg, 0.9 % Na, 0.7 % Ca, 0.2 % K, was used for the syntheses. Organophilization of the clay was performed with using hexadecyltrimethylammonium chloride (HDTMAC) (Fluka). Acrylamide (AAm), ammonium persulfate (APS) and *N,N'*-methylenebisacrylamide (MBA) were purchased from Sigma-Aldrich. Acrylic acid (AA) was supplied by Arkema (France), whereas copper(II) nitrate [$\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$], iron(III) nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$] and potassium thiocyanate (KSCN) by POCh (Poland).

Syntheses

Hydrogels

Two types of hydrogel polymers based on acrylamide and acrylic acid were synthesized by radical polymerization. Aqueous solutions of each monomer (10 wt. %) were prepared separately. *N,N'*-methylenebisacrylamide (MBA) was used as a crosslinking agent at the MBA/monomer molar ratio of 0.01. The obtained monomer solutions were purged by argon for 10 minutes in order to remove oxygen from the reaction system. Subsequently, the APS initiator (APS/monomer molar ratio = 0.01) was added and the mixtures were kept in water bath at 338 K for 3 h. After polymerization, the solid products were cut to small pieces, dried in air at 333 K and milled into powder.

Sodium-exchanged montmorillonite

MMT was initially pre-treated with an aqueous solution of NaCl in order to exchange pristine interlayer cations by Na^+ . 100 g of the clay was suspended in 4 dm³ of 1 M NaCl solution. The slurry was stirred at 343 K for 24 h, and then the solid was isolated by filtration and washed several times with distilled water until Cl^- ions were removed. The presence of chloride anions was tested by an addition of AgNO_3 solution (0.1 M). Finally, the obtained material, denoted as MMT(Na), was dried at 333 K overnight.

Organophilized montmorillonites

The raw montmorillonite and its sodium form were organophilized using the C_{16} surfactant (hexadecyltri-

methylammonium chloride). In 500 cm³ of distilled water, 10 g of the clay was suspended and stirred for 1 h at 353 K. 0.05 M solution of surfactant (500 cm³) was slowly added and the obtained mixture was agitated at 343 K for further 24 h. The modified clay was filtered, washed with distilled water for several times until no chloride ions were detected. The product was dried at 333 K for 24 h and then ground into powder in a mortar. The organophilized MMT(Na) is denoted as MMT(C16)-a, whereas the MMT sample after modification with the surfactant – MMT(C16)-b.

Hydrogel/montmorillonite composites

The first series of hydrogel/clay composites was synthesized using acrylamide and various forms of montmorillonite [MMT, MMT(Na), MMT(C16)-a and MMT(C16)-b] by the *in situ* polymerization technique. For all materials, the constant mass ratio of monomer to clay equal to 1:1 was used. 10 g of the clay was dispersed in an aqueous solution of monomer (10 wt. %). The cross-linking agent was additionally introduced at the MBA/monomer molar ratio of 0.01. The mixture was stirred at room temperature to obtain homogeneous suspension. Before polymerization, the slurry was purged by argon for 10 min to remove oxygen and then the APS initiator (at the APS/monomer molar ratio of 0.01) was added. The polymerization was carried out at 338 K for 3 h. The product was isolated, comminuted and dried at 333 K. All the dried composites were ground in an agate mortar to obtain powder. The synthesized samples are denoted as MMT-PAAm (synthesis with MMT), MMT(Na)-PAAm [from MMT(Na)], MMT(C16)-PAAm-a and MMT(C16)-PAAm-b [from MMT(C16)-a and MMT(C16)-b, respectively].

Moreover, two series of the polyacrylamide/montmorillonite and poly(acrylic acid)/montmorillonite composites with various crosslinking degree (the MBA/monomer molar ratio = 0.00, 0.01, 0.02 and 0.05) were synthesized by the same method using the raw clay (MMT) as a starting material. The sample codes are MMT-*x*-MBA-*y*, where *x* is the kind of hydrogel introduced (PAA or PAAm), and *y* – the content of crosslinking agent in relation to monomer.

Methods of testing

– X-ray diffraction (XRD) experiments were performed at room temperature by means of a Bruker D2 Phaser X-ray powder diffractometer (30 kV, 10 mA) equipped with a copper lamp ($\lambda = 0.15406$ nm) in the 2 θ range of 2–50° with a step size of 0.02° and at a scanning rate of 1 s/step.

– The real polymer content in the synthesized composites was investigated using a TA Instruments SDT Q600 thermoanalyzer. The measurements were carried out for samples of about 12 mg in a temperature range of

303–1273 K at a heating rate of 10 K/min in flowing dry air (100 cm³/min).

– The synthesized hydrogels and hydrogel/clay composites were tested in adsorption of Fe³⁺ and Cu²⁺ cations. The adsorbent (0.3 g) was immersed in 150 cm³ of 0.01 M iron(III) nitrate or 0.01 M copper(II) nitrate solution. The obtained slurry was stirred at 303 K for 27 h with an agitation rate of 200 rpm. The adsorption study was performed at constant pH (2.0 for Fe³⁺ and 5.0 for Cu²⁺). pH was measured on-line during the adsorption experiments and controlled by adding suitable amounts of 0.1 M HNO₃ and 0.1 M/1 M KOH. 5 minutes before collecting a sample to an analysis, stirring was stopped in order to separate the composite particles from the solution by sedimentation. 0.25 cm³ of iron(III) nitrate solution and 1 cm³ of copper(II) nitrate solution were taken to determine the concentration of Fe(III) and Cu(II) cations. The changes in the metal ion content were studied by means of a Merck Spectroquant Pharo 100 VIS spectrophotometer. The concentration of Fe³⁺ cations in the studied solutions was determined by complexation with thiocyanate anions (20 wt. % solution of KSCN), whereas Cu²⁺ ions by complexation with ammonia (3 M NH₄OH). The amount of adsorbed metal ions was calculated from the following equation (1):

$$q_t = \frac{(C_0 - C_t) \cdot V}{m} \quad (1)$$

where: q_t – the amount of metal cations adsorbed by a unit amount of adsorbent after time t (mmol/g), C_0 and C_t – the concentrations of metal ions in the solution before adsorption and after time t , respectively (mmol/cm³), V – the volume of the solution containing metal cations (cm³), and m – the mass of composite (g).

The V value was corrected by the volume of samples withdrawn to the spectrophotometrical analyses. The fitting of kinetic curves as well as the determination of kinetic constants and adsorption capacity at equilibrium were performed using Mathcad 15 software.

RESULTS AND DISCUSSION

Effect of montmorillonite form on intercalation of hydrogel

In the first step of our study we investigated the effect of form of montmorillonite on intercalation of polymer chains into the interlayer spaces of clay. Four different synthesis paths, presented schematically in Fig. 1, were proposed. Acrylamide crosslinked by *N,N'*-methylene-bisacrylamide (1 mol. %) was chosen as the studied polymeric matrix, which was introduced into the raw montmorillonite, the sodium-exchanged clay and the products of their organophilization [MMT(C16)-a and MMT(C16)-b].

The structure of the obtained composite materials was examined by means of XRD analysis. The diffraction patterns recorded for the raw clay and the modified samples

are collected in Fig. 2. For each material, the diffraction lines corresponding to the layered structure typical of montmorillonite and some additional, natural impurities (mainly quartz – QZ) were identified. The interlayer distance in the clay was calculated based on the position of (001) diffraction line according to the Bragg equation.

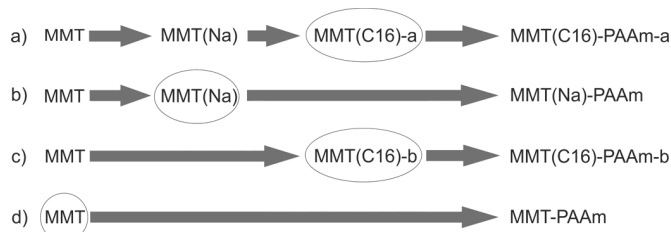


Fig. 1. The proposed paths of synthesis of the hydrogel/montmorillonite composites

The raw montmorillonite shows the $d(001)$ -spacing of 1.22 nm. Regardless of the form of montmorillonite used, the introduction of the polyacrylamide chains resulted in an increase in the interlayer distance to 1.96–2.07 nm,

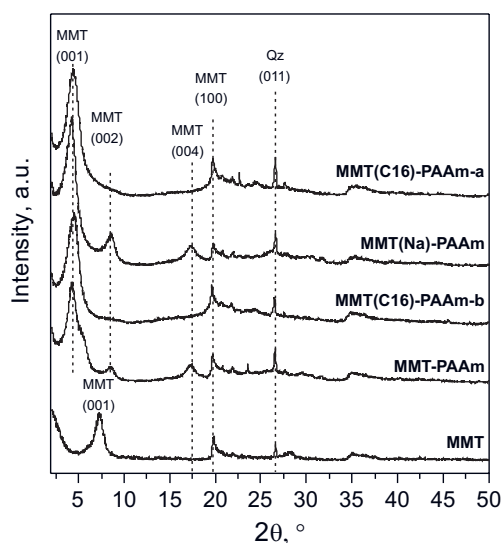


Fig. 2. The XRD patterns of the unmodified clay and the polyacrylamide/montmorillonite composites synthesized based on different MMT forms

which evidences the successful intercalation of polymer into the interlayer gallery. For the MMT(Na)-PAAm and MMT-PAAm samples, the appearance of (002) and (004) diffraction lines is observed, which confirms additional ordering the aluminosilicate layers. Taking into account the presented results and searching the simplest way of hydrogel/clay composite synthesis, the path based on direct intercalation of polymer into raw montmorillonite was selected for further investigations.

Composition and structure of PAA/MMT and PAAm/MMT composites

The optimized synthesis method was applied to obtain two series of hydrogel/montmorillonite composites based on poly(acrylic acid) and polyacrylamide, respectively. The content of the crosslinking agent varied in the samples in the range from 0 to 5 mol. %. The real content of hydrogel in the synthesized materials was determined by thermogravimetric analysis (Table 1). It can be found that the amounts of PAA and PAAm introduced are very close to the intended ones (50 wt. %). The insignificant differences in the hydrogel content, measured by TG, can be explained by a non-ideal distribution of the polymer part in the obtained composites.

Table 1. Real polymer content and $d(001)$ -spacings calculated for PAA/MMT and PAAm/MMT composites

Sample	$d(001)$ -spacing nm	Polymer content wt. %
MMT	1.22	—
MMT-PAA	1.77	50.0
MMT-PAA-MBA 1%	1.74	51.2
MMT-PAA-MBA 2%	1.73	47.0
MMT-PAA-MBA 5%	1.71	47.7
MMT-PAAm	2.06	51.0
MMT-PAAm-MBA 1%	2.02	48.9
MMT-PAAm-MBA 2%	1.72	45.7
MMT-PAAm-MBA 5%	—	49.6

The structural differences of the synthesized materials were investigated by the XRD method. Figs. 3 and 4 show

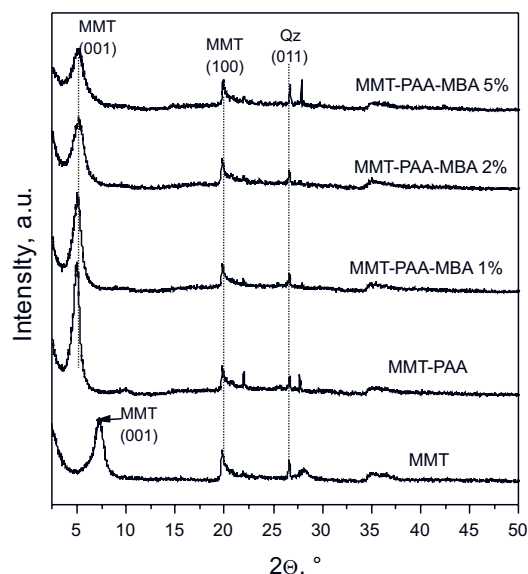


Fig. 3. The XRD patterns of the PAA/MMT composites with various crosslinking degree

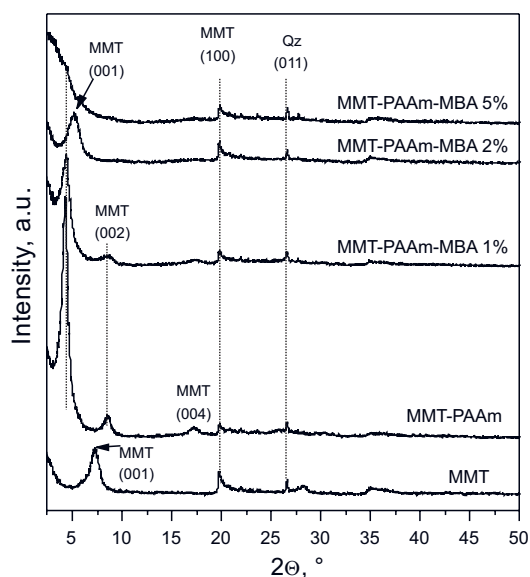


Fig. 4. The XRD patterns of the PAAm/MMT composites with various crosslinking degree

the diffraction patterns recorded for the poly(acrylic acid)/MMT and polyacrylamide/MMT composites, respectively. It should be noticed that the intercalation of polymer chains into interlayer spaces of montmorillonite was achieved regardless to the content of the crosslinking agent and the type of used hydrogel. The calculated d -spacings (001) for all composites are summarized in Table 1. For both series, the effect of the MBA content on the composite structure is confirmed by a decrease in the distance between the clay layers. For the poly(acrylic acid)/MMT composites the value of $d(001)$ changes from 1.77 (0 wt. % MBA) to 1.71 (5 wt. % MBA), whereas in the case of the polyacrylamide-containing materials the increase in the MBA content results in delamination of clay layers and finally exfoliation of montmorillonite structure observed for MMT-PAAm-MBA-5%.

Adsorption capacity of hydrogels and hydrogel/MMT composites

Initially, we tested adsorption capacity of pure poly(acrylic acid) and polyacrylamide as adsorbents for removal of copper(II) and iron(III) cations from aqueous nitrate solutions. The experimental data were fitted using the pseudo-first-order kinetic equation (2) [11]:

$$\ln(q_e - q_t) = \ln q_e - k_f t \quad (2)$$

where: q_e (mmol/g) — the amount of metal ions adsorbed at equilibrium, q_t (mmol/g) — the amount of metal cations adsorbed at time t , k_f — the adsorption rate constant for the first-order adsorption,

and pseudo-second-order kinetic equation (3) [12]:

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{t}{q_e} \quad (3)$$

where: k_s — the adsorption rate constant for the second-order adsorption.

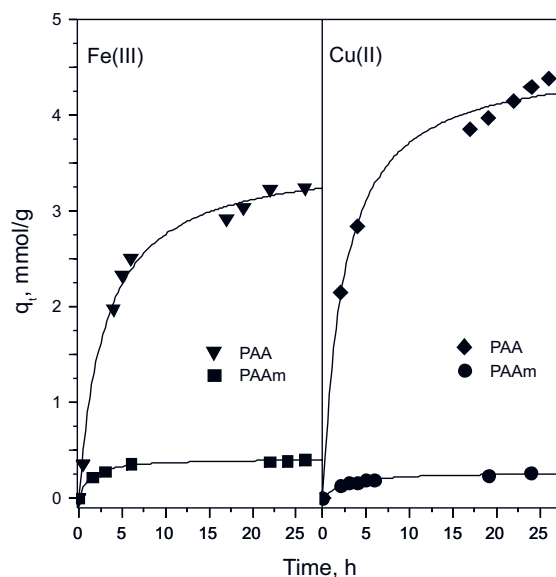


Fig. 5. Kinetics study of adsorption of Cu(II) and Fe(III) cations by polyacrylamide and poly(acrylic acid) hydrogels

The experimental q_t points with the fitted kinetic curves are presented in Fig. 5, and the calculated kinetic parameters are listed in Table 2.

Table 2. Adsorption parameters of PAA and PAAm hydrogels in Cu^{2+} and Fe^{3+} sorption

Sample	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	Cu ²⁺ sorption					
	k_f h ⁻¹	q_e mmol/g	R_1^2	k_{s_1} g· mmol ⁻¹ ·h ⁻¹	q_e mmol/g	R_2^2
PAA	0.323	4.134	0.9851	0.090	4.610	0.9943
PAAm	0.306	0.248	0.9828	1.465	0.280	0.9958
	Fe ³⁺ sorption					
PAA	0.260	3.135	0.9943	0.092	3.593	0.9941
PAAm	0.483	0.391	0.9913	1.814	0.419	0.9936

Huge differences in the effectiveness of removal of Cu^{2+} and Fe^{3+} cations by the prepared hydrogels are noticed. The high sorption capacity of PAA can be attributed to high efficiency of carboxylic groups in adsorption of metal cations by ion exchange with protons. In case of polyacrylamide, the free electron pair located on nitrogen atom in amide group exhibits lower tendency to bonding metal cations.

The achieved results disposed us to focus on the series of the hydrogel/MMT composites based on poly(acrylic acid) as more promising adsorbents of transition metal cations. Kinetic data for the sorption of Fe^{3+} and Cu^{2+} ions on the PAA/MMT materials are shown in Figs. 6 and 7 as well as in Table 3. It can be pointed out that the adsorption process (especially in the case of Cu^{2+} elimination) is better described by the model of pseudo-second order

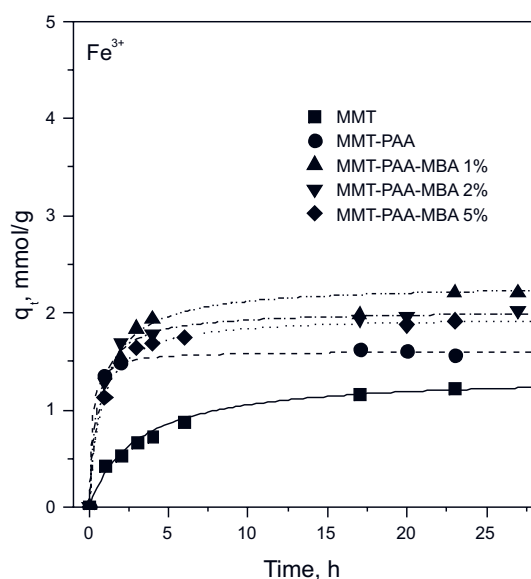


Fig. 6. The effect of the crosslinker content in the PAA/MMT composites on adsorption capacity of Fe^{3+}

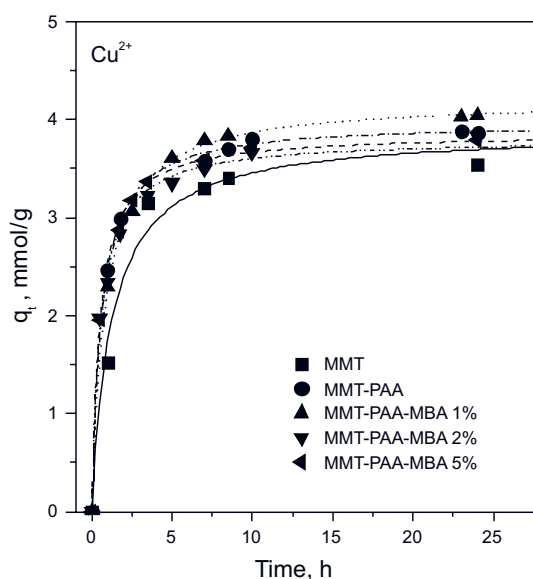


Fig. 7. The effect of the crosslinker content in the PAA/MMT composites on adsorption capacity of Cu^{2+}

adsorption. The studied poly(acrylic acid)/montmorillonite composites exhibit higher sorption capacities in Cu^{2+} adsorption than in Fe^{3+} ions. Thus, Cu^{2+} cations reveal a stronger tendency to the formation of complex with poly-anions in contrary to the Fe species. This effect can be attributed to lower valency of Cu^{2+} ions, which demand a smaller number of adjacent COO^- groups to be adsorbed. The highest sorption capacity of both metals cations was

CONCLUSIONS

The *in situ* polymerization technique can be applied for intercalation of polyacrylamide and poly(acrylic acid) into the montmorillonite structure. Raw clay, without any initial modification by ion-exchange or organophilization, can be used as the starting material in this synthesis. The intercalation of hydrogel into the interlayer spaces of

Table 3. Adsorption parameters of PAA/MMT and PAAm/MMT series of composites in Cu^{2+} and Fe^{3+} sorption

Sample	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	Cu ²⁺ sorption					
	<i>k_f</i> , h ⁻¹	<i>q_e</i> , mmol/g	<i>R</i> ₁ ²	<i>k_s</i> , g mmol ⁻¹ h ⁻¹	<i>q_e</i> , mmol/g	<i>R</i> ₂ ²
MMT	0.609	3.462	0.9963	0.207	3.886	0.9847
MMT-PAA	0.990	3.766	0.9935	0.416	3.976	0.9991
MMT-PAA-MBA 1%	0.765	3.867	0.9856	0.281	4.197	0.9994
MMT-PAA-MBA 2%	1.222	3.497	0.9641	0.427	3.805	0.9941
MMT-PAA-MBA 5%	1.242	3.550	0.9724	0.497	3.859	0.9973
	Fe ³⁺ sorption					
MMT	0.289	1.179	0.9790	0.251	1.361	0.9928
MMT-PAA	1.883	1.580	0.9973	3.553	1.605	0.9987
MMT-PAA-MBA 1%	0.593	2.196	0.9987	0.511	2.298	0.9976
MMT-PAA-MBA 2%	1.054	1.933	0.9923	0.952	2.026	0.9964
MMT-PAA-MBA 5%	0.899	1.815	0.9894	0.715	1.967	0.9985

achieved for the MMT-PAA-MBA 1% composite. It means that a low crosslinking degree favors the adsorption capacity of the PAA/MMT composites. An increase in the MBA content leads to the formation of highly linked structure, in which penetration of transition metal ions present in water solvent is strongly limited.

montmorillonite is manifested by the significant increase in the $d(001)$ value. The clay modified with polyacrylamide shows higher tendency to exfoliation than that modified with poly(acrylic acid). Nevertheless, the composites containing poly(acrylic acid) are more promising adsorbents of cations from water. The highest adsorption

capacities are achieved for the materials in which PAA is crosslinked by relatively low amount of MBA (1 mol. % in relation to PAA).

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