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Composite Polymer-Clay Hydrogels Based on Bentonite Clay and Acrylates: Synthesis, Characterization and Swelling Capacity

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Abstract

Clay minerals, especially montmorillonite, as well as bentonite minerals with a high content of montmorillonite, have the highest ability to adsorb various organic compounds. In the East Kazakhstan region, the Manyrak deposit has huge deposits of “pink” bentonite clay (BC) with 70% of montmorillonite, extensively studied back in the 70-80-s. Now it is successfully useful in the organo-polymer composition as a mineral filler of polymer composite materials (PCM) and finds the application as domestic sorbents for the group extraction of non-ferrous ions in the purification of industrial sewage and drinking water. This article presents the results of research of creating polymer-clay composite materials based on domestic bentonite clay with improved sorption characteristics. The polymeric matrix of the composites consists of acrylates – polyacrylic and polymethacrylic acids (PAA and PMAA). BC-PAA and BC-PMAA gels were obtained by radical polymerization “in situ” using the intercalation method (and without it). Preliminary intercalation forms more homogeneous and interconnected composite gels. An increase in the content of the clay component and the cross-linking agent in the starting mixture results in a higher cross-linking rate and compaction of the composite gels. The behavior of the swelling of gels under the influence of temperature, pH, ionic strength indicates their polyelectrolyte character with dominant hydrogen bonds and partial hydrophobic interactions (the latter is improved in the case of BC-PMAA). The preparation of composite gels based on local BC and PAA and PMAA expands the range of composite materials and can be used as sorbents for wastewater treatment.

1. Introduction

Specificity of the chemical structure and properties of the matrix in PCM, chemistry and technology of production and methods of research allow us to consider the Material science of PCM as a new field, developed based on existing concepts and methods of the polymer science, chemistry and physic of surface, and other sciences [1]. Composite hydrogels are the subject of intensive research as domestic authors [2–4], and foreign ones [5–8]. A lot of scientific review articles and monographs analyzed and generalized the main results of the research in field of composite materials [9–11]. There are generally accepted concepts, terms, methods of obtaining, mechanisms of interaction and structure formation in PCM systems of various polymer nature. The principles of application of various spectral methods (SEM, TEM, ACM, Cryo-SEM, XRD, etc.) allow establishing the morphological structure of the material and the range of applications of PCM, depending on the manifested physicochemical properties in medicine, engineering, construction, industry on cleaning plants, etc. Composite polymer hydrogels consist of at least two components and have a synergistic effect. In this case, the unique characteristics of the composite hydrogel are due not only to the physicochemical properties of the individual components, but also to the structure of the final material.

Inorganic component in composition hydrogels modifies the properties of conventional hydrogels.

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It provides the strength characteristics of the gel matrix, which makes it possible to make full use of the potential of stimulus-sensitive polymers [12]. The inorganic component in composite hydrogels can be metallic nanoparticles, oxides or clays containing natural minerals such as kaolin, bentonite and their modified forms. Clay minerals are relatively stable aqua silicates of aluminum, iron and magnesium with layered, layered-tape and mixed-layered structures. Due to this structure, they differ from other silicates by their high dispersity, hydrophilicity, sorption ability, ion exchange. Montmorillonite, as well as minerals with a high bentonite content are more preferable [13, 14]. Montmorillonite has the highest ability to adsorb various organic compounds, catalyze organic reactions. Some of its salts can swell unlimitedly in water and form inclusion compounds. These properties make montmorillonite, as well as bentonite, the most promising for use in the synthesis of both typical composite materials and in the development of reliable methods for the synthesis of high-tech nanostructured polymer-inorganic composites [15, 16]. This is because the properties of the filler nanoparticles, as well as the interfacial interactions at the interface of the polymer matrix with the filler, determine the properties of the nanocomposites. Polymeric nanocomposites with layered silicates, in addition to enhanced strength properties, have a number of other special properties already at low filling degrees [17]. At the same time, it is necessary to take into account the need for purity and high-fluidity, and often the nano size of the clay fraction.

In the East Kazakhstan region, the Manyrak deposit has huge deposits of "pink" bentonite clay (BC) with a montmorillonite content of 70%. The content, physicochemical properties, structure and sorption characteristics of the clay of the Manyrak deposit were thoroughly studied back in the 1970s and 1980s by the Soviet scientist Sh.B. Batalova and set forth in the monograph "Physical and Chemical Basis for the Preparation and Use of Catalysts and Adsorbents from Bentonites" [18]. Now this pink bentonite clay has a demand mainly in oil production at drilling rigs, wells, construction sites, partly in medicine and at home. At the same time, it is useful in both individually and in the organo-polymer composition as a mineral filler and find application as domestic sorbents for the group extraction of non-ferrous ions in the purification of industrial waste and drinking water, or as carriers of surfactants, prolonged forms of drugs and nanomaterials in technology.

Currently prof. K. Musabekov [19] conducts research on the physicochemical and operational properties of bentonite clays and the possibility of their use in the production of building materials. For several years, prof. J.A. Abilov and M.K. Beisebekov [2, 20–22] make attempts to create gel and film polymer and composite forms as carriers of domestic medicinal substances – alchidine, rihlokain, sorbents of ions of heavy metals and surface-active substances. As polymeric systems such polymers are used: natural – gelatin, agar, synthetic – polyacrylic and polymethacrylic acids (PAA, PMAA), polyacrylamide (PAA), poly2-hydroxyethyl acrylate (PHEA), polyvinyl alcohol (PVA), etc. As the filler – inorganic mineral is used – it is the bentonite clay (BC) of the Manyrak deposit [23]. Here is set out a part of the research on the possibility of creating polymer-clay composite materials based on domestic bentonite clay with improved sorption characteristics. The results of purification of natural bentonite clay, synthesis and research of the structure and basic physic-chemical characteristics of gels based on bentonite clay and acrylates – polyacrylic and polymethacrylic acids are received and discussed.

2. Experimental

Acrylic acid (AA), 99%, produced by Aldrich Chemistry, was subjected to a two-stage vacuum distillation under a nitrogen atmosphere, a fraction with a boiling point of 305 K/10 mm Hg. n_d^{20} = 1.4220.

Methacrylic acid (MAA), 99% of the production of Aldrich Chemistry, was subjected to a two-stage vacuum distillation under reduced pressure, a fraction with a boiling point of 331 K/10 mm sb, n_d^{20} = 1.4320.

N, N'-methylene-bis-acrylamide (MBAA) with the general formula $C_7H_{10}N_2O_2$, with a molecular weight of 154.2, manufactured in Belgium, purified in advance, was used as a crosslinking agent.

Dinitrile of azo-bis-isobutyric acid (AIBN), which was recrystallized and used as an initiator.

Purification of bentonite clay. Clay is a mixture of particles of different sizes and contains, in addition to clay, numerous admixtures of other minerals. The used bentonite clay of the Manyrak deposit was purified by the D.P. Salo method – repeatedly decantation of a muddy clay suspension with distilled water [24]. After three washings, the purified clay was dried in a vacuum oven at a temperature of 40–50 °C, then ground to a «powder» state with an

Table 1
Chemical composition of natural and purified clay

Sample of clay	Content, %								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	H_2O	others
Natural	65	13	1	0.5	1.5	1.5	0.5	11	6.5
Purified	60	9	0.5	0.5	1	0.8	0.5	7	20.3

Table 2
X-ray analysis of clay

Example of clay	Phase			
	Intensive		Amorphous	
	SiO_2 3.3 A^0	montmorillonite 4.6 C°		
Natural	62.0	92.0	3.5 C°	2.2 C°
Purified	35.0	130.0	3.6 C°	2.2 C°

average particle size of 0.0063 mm. The chemical composition of natural and purified bentonite clay, determined by diffraction spectral analysis (DFS-13), presented in Table 1. By results, the studied clay consisting of aluminum and silicon oxides, refers to aluminosilicates. X-ray diffraction analysis (DRON-4-07) showed the presence of three phases: α-quartz SiO_2, montmorillonite $Al[OH]_2\{Si_4O_{10}\}.mH_2O$ and amorphous phase with 70% predominance of montmorillonite (Table 2).

Synthesis of composite gels of polyacrylates with bentonite clay (BC-PAA, BC-PMAA). The hydrogels of polyacrylic and polymethacrylic acids (PAA G, PMAA G) are formed as a result of three-dimensional radical polymerization of acrylic/methacrylic acid monomer, in proportion with distilled water 90:10, with the participation of MBAA crosslinking agent (1 mol.%) and AIBN initiator (0.5 mol.%) in an ampoule lowered in a thermostat heated to 70 °C, isolated from air by a laboratory film “Parafilm”. Composite gels containing bentonite clay were obtained by radical in situ polymerization using the intercalation method (and without it) as follows: a suspension of bentonite clay and water was stirred for 2 h with a magnetic stirrer, then the monomer was added to the suspension and stirring continued within 6 h. Leave the mixture for a day and the next day continue to mix for 2 h. Further, cross-linking agent MBAA 0.1–1 mol.% by weight of the monomer. Then, AIBN 0.5 mol.% was added by weight of the monomer. The polymerization was carried out in an ampoule lowered in a thermostat heated to 70 °C and isolated from the air by a laboratory film “Parafilm”, at a temperature of 70 °C for 2 h. The content of bentonite clay varied between 1 and 5 wt.% of the total content.

The yield of the gel fraction (G) of the gels studied was calculated according to the formula:

$$G = m_{dry}/(m_{fresh.syn})*100\%,$$

where, m_{dry} – weight of dried gel, g; $m_{fresh\ syn.}$ – mass of freshly synthesized gel, g.

The degree of crosslinking (j) of the gels studied was calculated by the formula:

$$j = \frac{1}{S} + \sqrt{S}$$

where, S is the yield of the sol fraction: $S = 100 - G$.

The nature of the interaction of the compositions components obtained are determined by the method of equilibrium swelling and confirmed by the IR spectroscopy method using a Fourier spectrophotometer with the FTIR Satellite transformation of Mattson (USA) using KBr.

The density of the obtained polymer-clay gels was determined using analytical weights RADWAG 26-600 Radom 2004/108 AS series complete with a density measuring kit (Poland). Determination of the density of gels was carried out in a solution of benzene V = 300 ml, $\rho = 0.8745$ g/cm^3 at $t = 24$ °C.

Ash content of A^α% of samples was calculated according to the formula:

$$A^\alpha = m_{ash}/m_0 \cdot 100\%,$$

where: A^α is the ash content of the gel, m_0 is the initial mass of the gel, and mols is the mass of the ash.

The morphology and structure of bentonite clay and synthesized gels were examined using scanning electron microscopy images taken with a scanning electron microscope JEOL JSM-6380A with an EDS detector (Japan) [25], topographic images on an atomic force microscope Ntegra THERMA (Russia) (AFM). Using the images taken with a digital optical microscope Leica DM 6000 M, the structure of dry and swollen samples of the obtained compositions was investigated.

The swelling degree was determined by the gravimetric method of equilibrium swelling and was calculated from the mass of the swollen sample to the mass of the dry sample by the formula:

$$\alpha = \frac{m - m_0}{m_0}$$

where, m – mass of the swollen sample; m_0 – the mass of the dry sample; α – swelling degree.

3. Results and discussion

3.1. Synthesis and physicochemical characteristics of gels of polycarboxylic acids (PAA) and their compositions with bentonite clay

Gels based on PAA G and PMAA G and their compositions with bentonite clay (BC-PAA G and BC-PMAA G), as noted in the experimental part, were obtained by three-dimensional radical polymerization in aqueous solution. To obtain more homogeneous polymer-clay composite gels, the intercalation process was used [26]. The essence of the process consists in prolonged mixing of the monomer in an aqueous suspension of clay, as a result, of which a gradual swelling and additional dispersion of clay particles occurs, penetration of the monomer molecules (intercalation) into their interlayer space. During polymerization, a uniform fusion of clay particles and a polymer matrix

Table 3
Physical and chemical properties of gels

BC-PCA G (mas. %)	CA (MBAA) mol.%	Time of intercalation, h	ρ, g/cm^3	A$^\alpha$, %	G,%	S,%	j,%
BC-PAA G 1:10	0.1	24	1.254	-	47.99	52.01	7.25
		-	1.196	-	47.54	52.46	7.26
	0.5	24	1.348	8.67	92.94	7.060	2.80
		-	1.276	-	66.27	33.73	5.83
	1	24	1.361	-	94.98	5.22	2.47
		-	1.335	-	62.57	37.43	6.15
BC-PAA G 3:10	0.5	24	1.361	18.24	84.8	3.70	2.13
BC-PAA G 5:10	0.5	24	1.370	29.94	98.4	1.20	1.93
PAA G	0.5	-	1.207	-	57.73	42.27	6.52
BC-PMAA G 1:10	0.1	24	1.309	-	34.85	65.15	8.08
		-	1.303	-	32.15	67.85	8.25
	0.5	24	1.490	8.67	87.68	12.32	3.59
		-	1.323	-	77.11	22.89	4.82
	1	24	1.505	-	95.40	4.60	2.36
		-	1.530	-	75.13	24.87	5.03
BC-PMAA G 3:10	0.5	24	1.543	18.24	84.1	9.7	3.15
BC-PMAA G 5:10	0.5	24	1.562	29.94	85.8	7.7	2.89
PMAA G	0.5	-	1.063	-	50.00	50.00	7.09
Note: G is the yield of the gel fraction, %; P is the density, g/cm^3; A$^\alpha$ – ash content, %; S is the yield of the fraction sol, %; j – degree of crosslinking, %.							

occurs due to the development of polymerization inside the clay galleries during the intercalation of the monomer into gradually swelling clay particles. Table 3 shows the conditions for obtaining gels and the physicochemical characteristics of the obtained samples. As can be seen, an increase in the concentration of bentonite clay contributes to an increase in the yield of gel fractions and the density of gels, which is quite natural. As can be seen from the presented data, an increase in the concentration of bentonite clay contributes to an increase in the yield of the gel fraction and the density of the gels studied. This is quite natural, since mineral particles compact polymer network of polyacrylates. The nature of the interaction between the polymer and the mineral filler of the composite gel is hydrogen bonds and hydrophobic interactions. According to these indices, the density and yield of the gel increase with the increase of the cross-linking agent. This is due to that the crosslinking of the polymeric skeleton becomes more frequent with increasing amount of the cross-linking agent. The ash content of BC-PAA and BC-PMAA gels is the same, depends on the amount of clay in the composition.

Visually, the formation of a transparent gel of PCA homo-polymers in full and a pale pink homogeneous gel of BC-PAA compositions with 1–5 wt.% content of bentonite clay as well in full without any delamination of the system. This indicates the good compatibility of the original components of the composition with each other. IR spectra of BC-PAA and BC-PMAA are characterized by a complex of absorption bands corresponding to the initial components of the composition and the presence of shallow broad bands of intermolecular hydrogen bonds in the composite (Fig. 1). For example, at 1705, 1699, 1706 cm^{-1}, 1539, 1540, 1549 cm^{-1}, bands characteristic of carboxylate ions are observed, with a bathochromic shift due to interaction with the tetrahedral lattice of bentonite clay, and broad bands of carboxyl and hydroxyl groups are prescribed in the 3650 region -2800 cm^{-1}. It should be noted the high intensity of the observed peaks, which confirms the formation of hydrogen bonds. Si-O-Si bonds are prescribed in the 1044 region; 1092 cm^{-1}, C-C (δ) 797, 795 cm^{-1}, Si-O in the region of 5885, 516, 552, 468, 521, 416 (δ) cm^{-1}. At the same time, there are in the spectrum in the 3200-2500 cm^{-1} region, high-intensity wide bands characteristic of chelated hydrogen bonds. One can assume the formation of homogeneous composite gels due to hydrogen bonds and hydrophobic interactions of polymer chains.

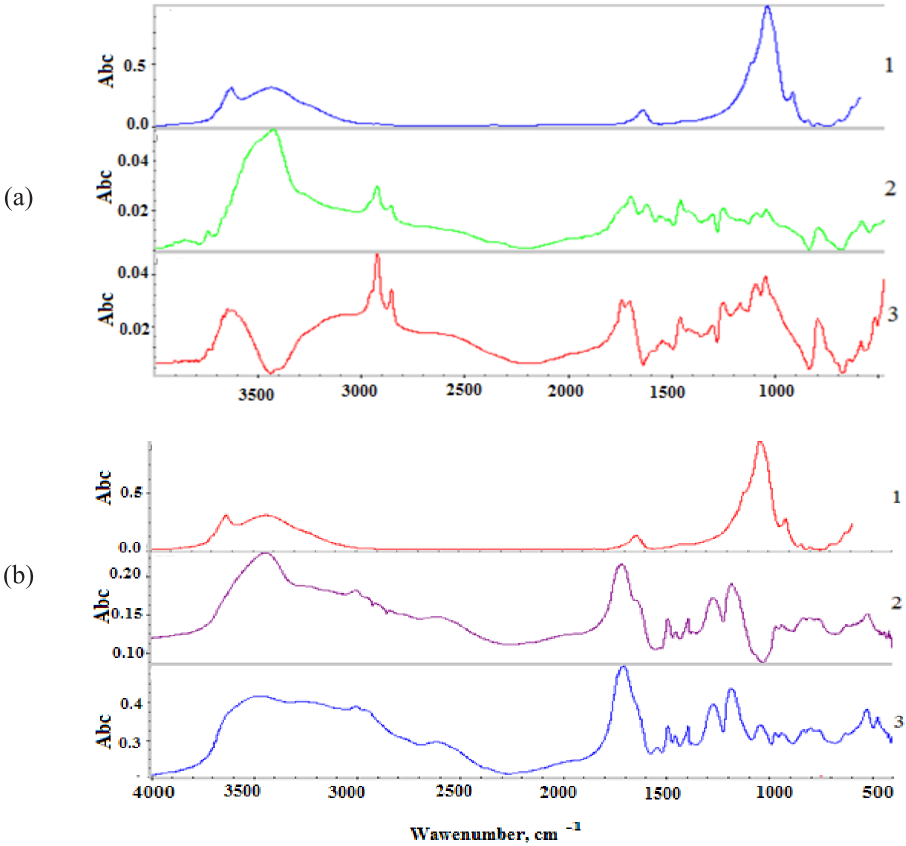
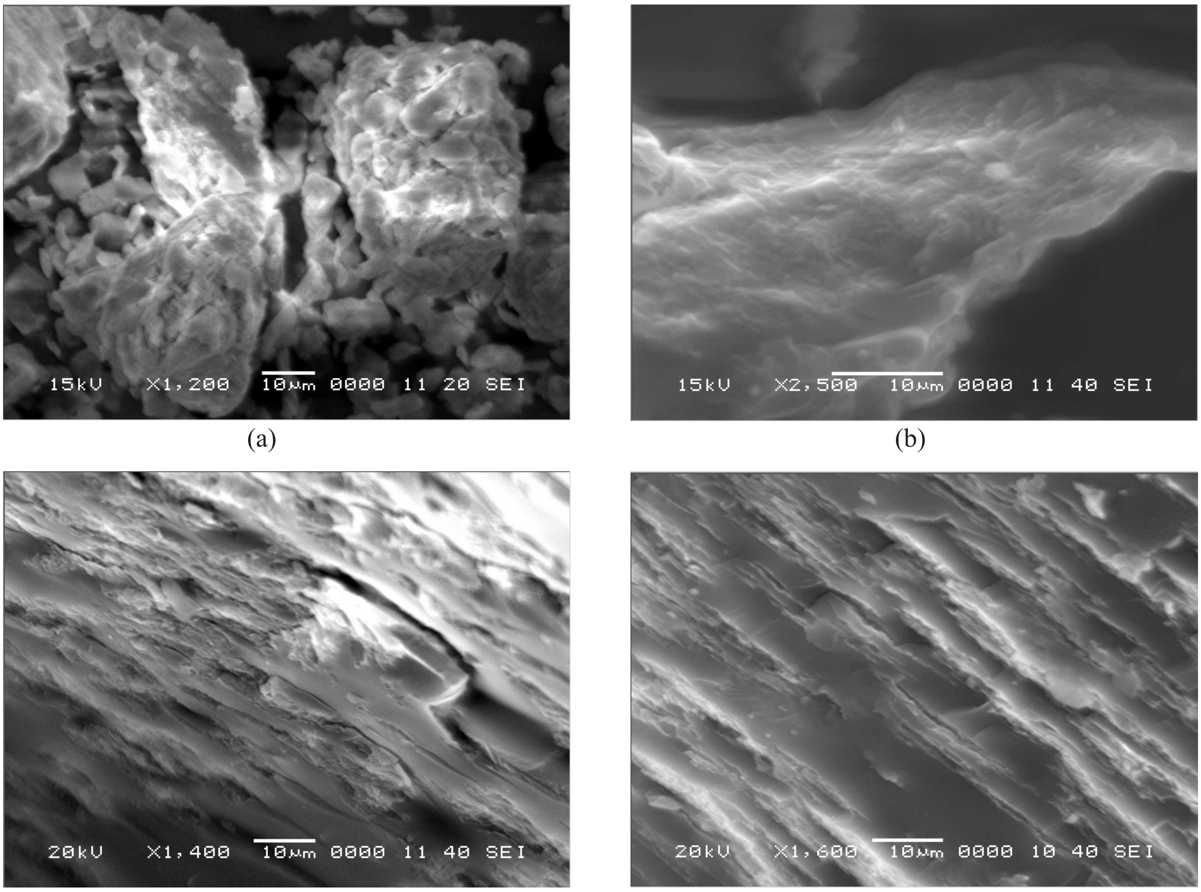


Fig. 1. IR-spectra of gels and compositions: (a) 1 – BC, 2 – PAA G, 3 – BC-PAA G; (b) 1 – BC, 2 – PMAA G, 3 – BC-PMAA G.

Based on the literature data and the results of studies on the synthesis of composite gels based on PCA and BC using the process of intercalation in situ, it is possible to suggest the formation of an intercalated morphological structure of the obtained composite sorbents. However, as is known, depending on the degree of distribution of clay particles in the polymer matrix of the composite, three basic structures are distinguished. There are micro composite (polymer surrounds agglomerates of clay), intercalated composite (penetration of the polymer into the interlayer space of the clay, expansion of the layers to 2–3 nm, partial stratification) and exfoliated composite (complete exfoliation of clay layers) [27]. At the same time, the formation of a composite with a mixed structure often occurs, and with an excess of clay and a poor degree of dispersion, the presence of mineral agglomerates in the polymer matrix is possible. Scanning electron microscopy (SEM) allows investigating the morphology of materials with nanometer resolution. According to the data of scientific studies of adding smectite into the polymer [28], there are the formation of three different morphological structures. The first structure is a typical composite, the second and third structures are the intercalated or exfolieted structure of the composite, resulting from the intercalation process. Intercalation is the intensive introduction of monomer molecules into the inter-packet spaces of layered bentonite and increasing the distance of the interlayer slats during of the polymeric skeleton forming. Consequently, ions of oxygen with charges of 1.5 or -0.5, capable of binding via hydrogen bonds or electrostatic interactions, become available in the crystal lattice of montmorillonite. Figure 2 shows photographs of SEM (at a voltage of 15 kV, solubility of 10 μm) of the surface of pure bentonite clay (a), the homo-polymer of PAA (b) and cut, clay compositions BC-PAA (B) and BC-PMAA (g) with elemental analysis of the BC surface -PAA with a component ratio of 1:10. The size of their structural units lies in the range of 1–10 μm. The chains of PAA and PMAA penetrate the clay layers, expanding the interlayer space and separating the tactoids from the laminated packets of plates, resulting in the formation of a composition with an ordered intercalated (BC-PAA) and exfolieted (BC-PMAA) structure.

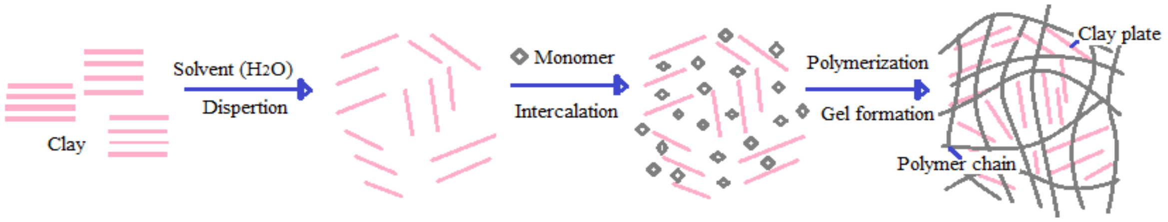


(a) (b)

(c) (d)

Fig. 2. Photographs of scanning electron microscopy of bentonite clay (a), PAA homopolymer (b), BC-PAA (c) and BC-PMAA (d).

The increase in the distance between the silicate plates (galleries) and the growth of polymer chains during the synthesis leads to an ordered distribution of the clay dispersion in the composite. World scientific literature well proves and describes such assumptions and often represents the following scheme for the formation of a polymer-clay composite:



3.2. *Swelling behavior of PCA gels and their compositions with bentonite clay*

Studying the influence of various factors on the swelling capacity of gels, one can judge the nature of the interaction of polycarboxylic acids in a composition with bentonite clay. It is clear, gel of an ionic nature has non-Coulomb interactions, the latter include van der Waals forces, hydrophobic interactions, and hydrogen bonds. In the case of the composite BC-PCA gel, it is necessary to consider the formation of a polyelectrolyte complex stabilized mainly by hydrogen bonds and hydrophobic interactions [29]. The latter are more pronounced in the case of a composition based on a more hydrophobic PMAA. A feature of hydrogels of polycarboxylic acids is a high swelling capacity [30], which in turn is an important criterion affecting the sorption capacity of the sorbents obtained. Investigating the influence of various internal and external factors on the swelling capacity of the compositions, one can predict the prospects of the proposed gels as sorbents. To clarify the nature of the binding of the components of the composition, the influence of such factors as ionic strength, the concentration of the mineral component, temperature, pH environment on the swelling kinetics of gels is considered.

The results of the equilibrium swelling studies of polycarboxylic acids homo gels and their compositions with clay (Fig. 3a and b) show that the equilibrium in the system occurs within 5–6 h, while homo gels of PAA and PMAA in comparison with their compositions have a much higher degree of swelling. When the mineral component is added, the degree of increase in the polymer network is significantly reduced, which is due to the compaction of the composite gel frame due to the presence of dispersed bentonite clay particles having a low swelling capacity (α of bentonite clay is about 8–10 g/g). Observing low swelling values of PMAA-based composite gels (BC-PMAA 1:10 α is equal to 100 g/g), compared to the gels of polyacrylic acid (BC-PAA with the ratio 1:10 α is equal to 170 g/g), due to the more hydrophobic nature of the polymeric chain of PMAA.

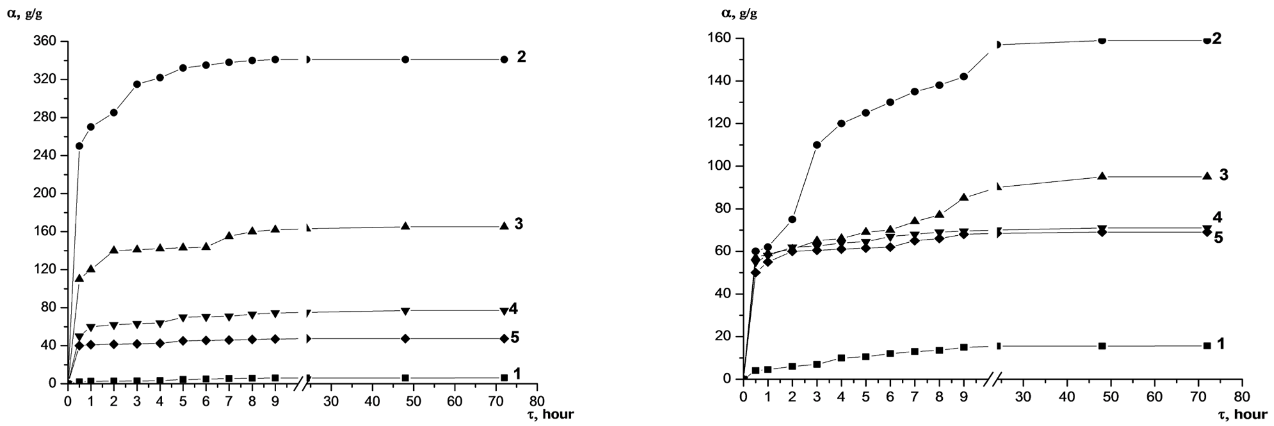


Fig. 3. Kinetics of swelling of PCA gels and their compositions with BC: (a) t = 25 °C, MBAA = 0.5 mol.% ; 1 – BC; 2 – PAA G; BC-PAA G – (1:10) (3); (3:10) (4); (5:10) (5); (b) t = 25 °C, MBAA = 0.5 mol.%; 1 – BC; 2 – PMAA G; BC-PMAA G – (1:10) (3). (3:10) (4); (5:10) (5).

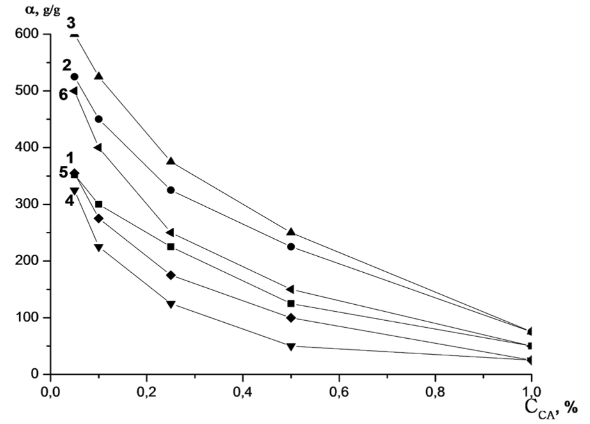


Fig. 4. Dependence of the degree of swelling of BC-PCA compositions (1:10) on the content of the cross-linking agent: τ = 7 h, BC-PAA G (1-3), BC-PMAA G (4-6); t = 25 °C (1, 4); 37 °C (2, 5); 60 °C (3, 6).

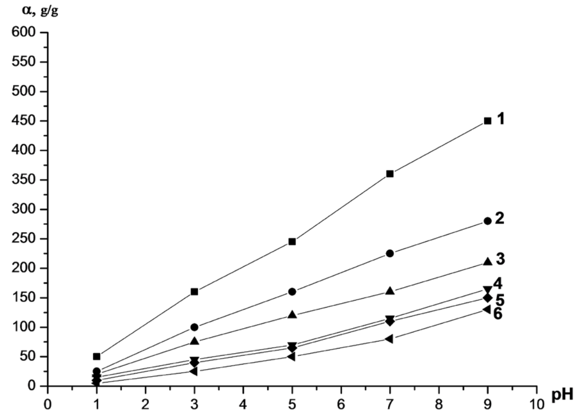


Fig. 6. Dependence of the degree of swelling of the compositions of BC-PCA (2:10) on the pH medium: t = 25 °C; BC-PAA G (1:10) (1, 3, 5); BC-PMAA (1:10) (2, 4, 6); CA = 0.25 mol.% (1, 2); CA = 0.5 mol.% (3, 4); CA = 1 mol.% (5, 6).

An increase in the temperature of the medium promotes a strong increase in the volume of the polymeric and polymer-clay network, and the increase in the cross-linking of the carcass results in a significant decrease in the swelling capacity of these systems (Figs. 4 and 5). The latter fully corresponds to the literary data. Increasing the temperature increases the degree of swelling of the gel by weakening and breaking the hydrogen bonds of hydroxyl and carbonyl groups PCA and Si-OH bentonite clays in the composite. There is a strong contraction of the BC-PAA (MBAA = 0.5 mol.%) composition in the ratio (1:10): at 60 °C and 25 °C it has *α* equal to 600 g/g and 350 g/g, respectively; and for a gel with a degree of crosslinking equal to 1 mol.%, at the same temperatures, *α* is 140 g/g and 70 g/g, respectively. In 0.16 M NaCl solution, appreciable contraction of gel volumes occurs as compared to the results of swelling in water and does not undergo significant changes with increasing temperature of the medium. A strong electrolyte compresses the polyelectrolyte framework of composites in view of the shielding effect [31]. As a result, the charged functional groups are solvated, and the composite gels retain a low degree of swelling as the temperature rises.

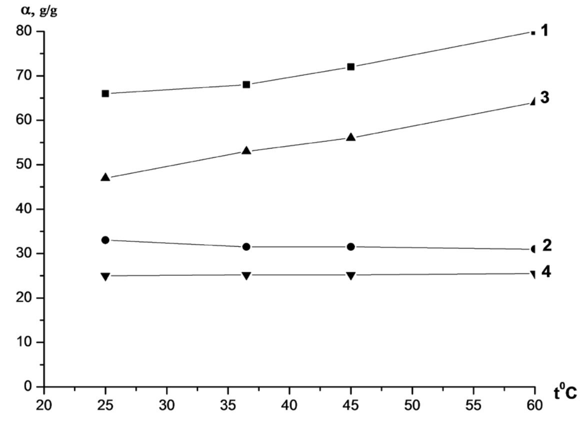


Fig. 5. Dependence of the degree of swelling of BC-PCA compositions (2:10) on temperature: CA = 0.5 mol.%; τ = 6 h; BC-PAA G (1, 2); BC-PMAA G (3, 4); water (1, 3); solution of NaCl (2, 4).

PCA-based gels belong to pH-sensitive gels: in an acidic environment, PCA molecules are stable, and their degree of dissociation increases in an alkaline medium [32]. Therefore, for BC-PAA G and BC-PMAA G compositions in an acidic medium, the gels are compressed, the formation of a compact structure and due to the enhancement of hydrogen bonds, and with an increase in the pH environment, an increase in the gel volume as the degree of dissociation of carboxyl groups of the PCA (Fig. 6). Analyzing the obtained data, shows that the interaction between the components of the composition is due to hydrogen bonds between hydroxyl groups on the surface of bentonite clay and undissociated carboxylic groups of polyacids and the IR spectroscopy data confirm it (Fig. 6).

4. Conclusions

Based on the results of the study of the influence of various factors – temperature, degree of cross-linking, clay mineral content, ionic strength, nature of polycarboxylic acids, we can conclude that the interaction between the components of the composition is due to hydrogen bonds between hydroxyl groups on the surface of bentonite clay and undissociated carboxylic groups of polyacids. IR spectra confirmed it. In the stabilization of BC-PCA compositions, hydrophobic interactions of hydrocarbon chains play an important role, more pronouncing in the case of a composition based on a more hydrophobic PMAA. The resulting composite gels based on PCA and BC expand the range of composite materials and are able to use them as sorbents for wastewater treatment.

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