

<sup>1\*</sup>Yessengeldi A.M., <sup>1</sup>Yessengulova A.A., <sup>1</sup>Kayralapova G.Zh.,  
<sup>1</sup>Iminova R.S., <sup>2</sup>Beysbekov M.M.

<sup>1</sup>Al-Farabi Kazakh National University, Almaty, Kazakhstan

<sup>2</sup>Kazakh Head Architectural and Construction Academy, Faculty of Building Technologies,  
Infrastructure and Management, Almaty, Kazakhstan

\*e-mail: yess.assem@mail.ru, yessengulova02@gmail.com

### Obtaining of surface-active substance sorbents based on acrylate-clay polymers

**Abstract:** In this work the problem of sewage treatment containing surface-active substance (SAS), using polymer-bentonite clay (BC) was discussed and sorbent synthesized. The sorption capacity of obtained polymer-clay composites in relation to surfactant in different environments and conditions was estimated. The used bentonite clay of the Manyrak deposit (East Kazakhstan region) was purified with the help the method of Salo by repeated washing with distilled water. Chemically cross-linked composite gels based on bentonite clay and polycarboxylic acids – polyacrylic (PAA) and polymethacrylic acids (PMAA) in ratio 1:10, 3:10 and 5:10 were synthesized with adding cross-linking agent methylene-bis-acrylamide (MBAA) 1 mole %, dinitrile of azo-bis-isobutyric acid (DAA) 0.5 mole % by weight of the monomer at a temperature of 70 °C for 2 hours. The kinetics of swelling of obtaining composites in solutions of and cationic surfactants – cetylpyridinium bromide (CPB), cetyltrimethylammonium bromide (CTAB) were studied; the influence of internal factors: the content of clay, concentration of surfactants, temperature and pH of the medium, on the swelling of composites in surfactant solutions was examined. These studies were carried out on a scanning electron microscope Quanta 3D 200i Dual system, Leica DM 6000 M (Switzerland) digital optical microscope for obtaining the morphological structure of dry and swollen samples of the obtained compositions, IR spectrometer «Satellite» FTIR Mattson (USA), and Radwag AS 220/X (Poland) for measuring the density.

**Key words:** bentonite clay, polyacrylic acid, polymethacrylic acid, composite material, sorbent, ions of surface-active substance (SAS).

#### Introduction

The main reason of accumulation of surface-active agents in water objects, especially in the lower parts, is their resistance to biochemical oxidation. In turn, it reduces a possibility of self-purification of natural water resources and leads to secondary pollution of a water surface. Therefore surfactants belong to the group of the most dangerous and harmful substances which are found in sewage. Currently, protection of sewage from surfactants is an extremely important and global problem.

Requirements requested by polymer carriers are determined based on the forms and methods of testing. The most important condition is that their homogeneous and constituent components be co-located. To do this, it is important to select the component compositions correctly.

To obtain a composite carrier on the basis of polymer and clay, BC was selected from the East

Kazakhstan region and polycarboxylic acid (PCA). Their choice as a composite composition was made for the following reasons:

1. Polycarboxylic acid refers to polyanions has a negative charge. If we rely on literature sources and the results of the research it is known that bentonite clay consists of negative particles, and this in turn means that both components have the same negative charge. If they have antipodal charges, then with electrostatic interaction a complex of salt will result and this would lead to the creation of insoluble compounds. This would destroy the homogeneity of the composition. And the same-named charged components of the composition are connected with each other by means of non-nucleon forces like hydrogen bonds and hydrophobic interactions. Such a system should retain the ability to swell and be homogeneous and interconnected in the ability to swell and be homogeneous and interconnected.

2. Like bentonite clay, polycarboxylic acids (PCA) individually have functional groups (-COOH, -OH) capable of binding surfactants and hydrophobic groups. These qualities make it possible to assume that it is possible to bind surfactants and composite materials [1].

In this connection, in this work, the possibility of obtaining materials of composite carriers based on bentonite clay and polycarboxylic acids will be investigated. To determine the optimal conditions for the synthesis of bentonite clay-polycarboxylic acid composite gels (BC-PCA), the influence of various internal and external factors, such as the amount of bentonite clay (BC) the synthesis route, temperature and were studied in two surfactant solutions.

### Materials and methods

To produce polymer-clay composite gels, domestic bentonite clay of the Manyrak deposit (East Kazakhstan region) and polyacrylic and polymethacrylic acid monomers were used, which were subjected to initial purification. The used bentonite clay was cleaned with the help of the method of Salo. Only

after three washings the investigated clay is separated from large parts and impurities of sand, the content of these components reaches up to 48 % [2].

The chemical content of natural and purified bentonite clays determined by the diffraction spectral analysis (DFS-13) method is presented in Table 1. Based on the results, the clay studied, consisting of alumina and silicon oxides, refers to aluminosilicates. In this composition, the predominance of montmorillonite is evident.

Chemically cross-linked composite gels based on bentonite clay and polycarboxylic acids – polyacrylic (PAA) and polymethacrylic acids (PMAA) in ratio 1:10, 3:10 and 5:10 were synthesized. A cross-linking agent methylene-bis-acrylamide (MBAA) 1 mole %, dinitrile of azo-bis-isobutyric acid (DAA) 0.5 mole % by weight of the monomer was added. 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 hours. The completeness of the washing of the composite gels PAA-BC and PMAA-BC was controlled by a qualitative reaction to the double bond of  $\text{KMnO}_4$  [3].

**Table 1** – X-ray analysis of clay

Example of clay	Phase			
	Intensive		Amorphous, C <sup>0</sup>	
	SiO <sub>2</sub> 3.3 Å <sup>0</sup>	montmorillonite 4.6 C <sup>0</sup>		
Natural	62.0	92.0	3.50	2.20
Purified	35.0	130.0	3.63	2.20

### Results and their discussion

The composition and physicochemical parameters of the composite gels obtained are shown in Table 2. Based on the data of the table, one can observe a general pattern observed for all acrylate-clay gels, as the amount of bentonite clay in the composition increases, the yield of gels increases accordingly. Since, as the amount of bentonite clay increases, the bond between polycarboxylic acids and polymers increases, and as a result, a favorable condition is established for increasing the density and yield of the composite. The similarity of the ash content of BC-PAA and BC-PMAA gels may be due to the amount of bentonite clay in the composition. It is known that organic substances in the composition of the com-

posite burn and remain inorganic substances. To be more precise, bentonite clay remains in the ash as unburned inorganic matter.

To obtain the exact composition it was interesting to obtain figures of acrylate-clay gels in a scanning electron microscope (SEM). Based on the obtained results, the size of the BC-PAA complex amounted to about 1-3 mm of the same world composition units [4].

Based on the data of the table, one can observe a general pattern observed for all acrylate-clay gels, as the amount of bentonite clay in the composition increases, the yield of gels increases accordingly. Since, as the amount of bentonite clay increases, the bond between polycarboxylic acids and polymers increases, and as a result, a favorable condition is es-

established for increasing the density and yield of the composite. The similarity of the ash content of BC-PAA and BC-PMAA gels may be due to the amount of bentonite clay in the composition. It is known that

organic substances in the composition of the composite burn and remain inorganic substances. To be more precise, bentonite clay remains in the ash as unburned inorganic matter.

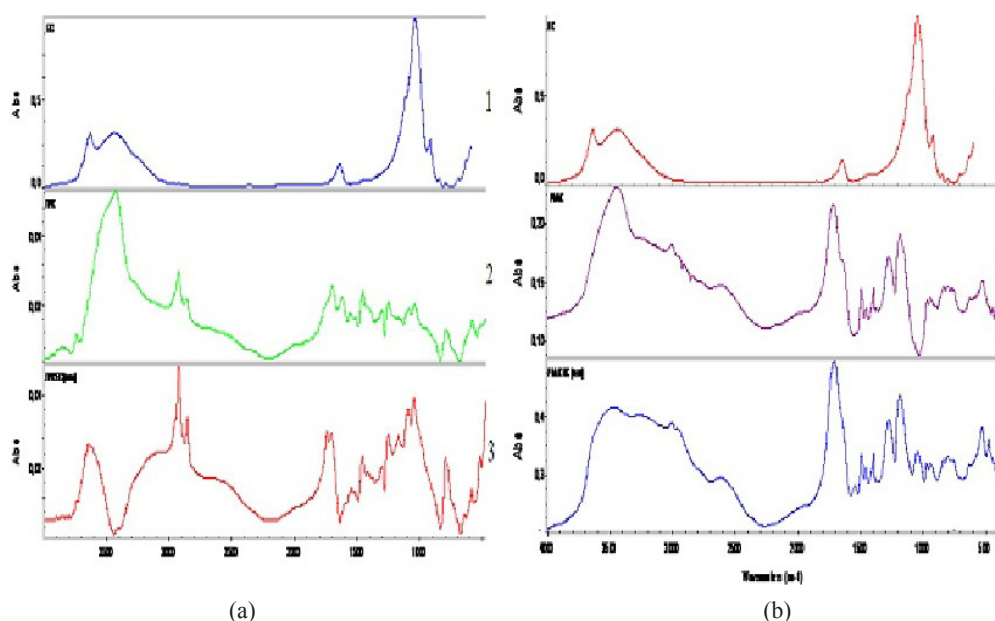
**Table 2** – Physicochemical characteristics of gels

Composite	BC-PAA			BC-PMAA		
	3:10	5:10	7:10	3:10	5:10	7:10
Composition, weight %	3:10	5:10	7:10	3:10	5:10	7:10
G, %	84.80	98.40	102.31	84.11	86.83	73.53
A <sup>a</sup> , %	18.24	29.94	38.19	18.24	29.94	37.89
$\rho$ , g/cm <sup>3</sup>	1.34	1.361	1.37	1.49	1.54	1.56
S, %	7.06	3.70	1.20	12.32	9.70	7.70
j, %	2.80	2.13	1.93	3.59	3.15	2.89

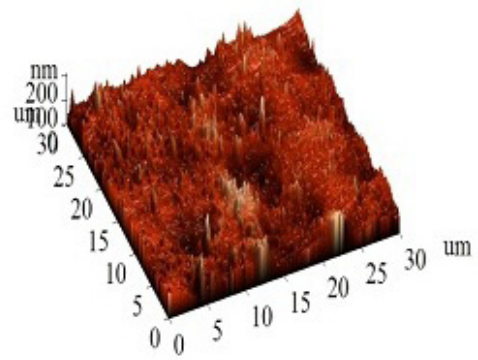
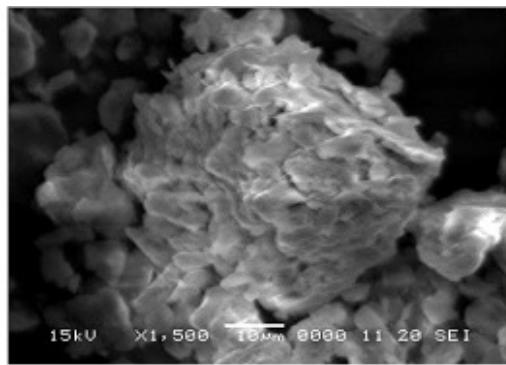
G – yield of the fraction of the composite gel, %; A<sup>a</sup> – ash content of composite gels, %; P – density of composite gel, g/cm<sup>3</sup>; S – yield of the fraction sol, %; J – degree of crosslinking, %

To confirm the composition of acrylate-clay BC-PCA gels, the IR spectrum was removed. The results of IR spectroscopy show the formation of the BC-PCA complex. In the spectrum, one can see the bands inherent in both carbon and bentonite clay (Figure 1). In the spectra of acrylate-clay gels, the vibration of carboxylate ions is prescribed in the interval 1705, 1699, 1706 cm<sup>-1</sup>, 1539, 1540, 1549 cm<sup>-1</sup>, the connection of the tetrahedron net of bentonite clay 3648 cm<sup>-1</sup>

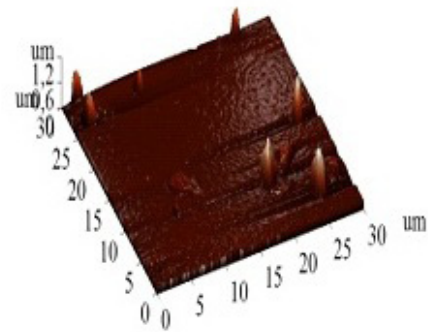
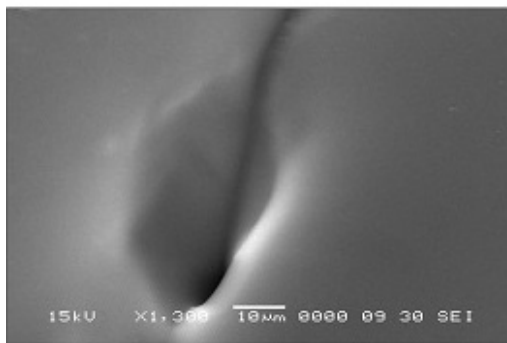
bathochromic shift and in the form of a wide band 3650-2800 cm<sup>-1</sup>. In all these bands, one can observe a significant increase in intensity proving the formation of hydrogen bonds. The Si-O-Si bond is prescribed in area 1044; 1092 cm<sup>-1</sup>, C-C ( $\delta$ ) 797, 795 cm<sup>-1</sup>, and the Si-O bond in 5885, 516, 552, 468, 521, 416 ( $\delta$ ) cm<sup>-1</sup>. A strand can be seen broad bands of increased intensity inherent in the hydrogen bond chelate type in the spectra of 3200-2500 cm<sup>-1</sup>.



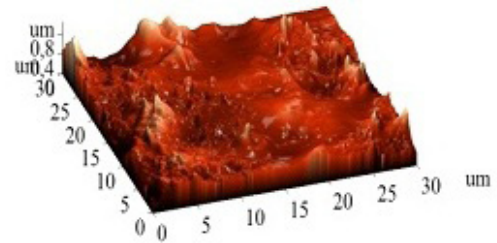
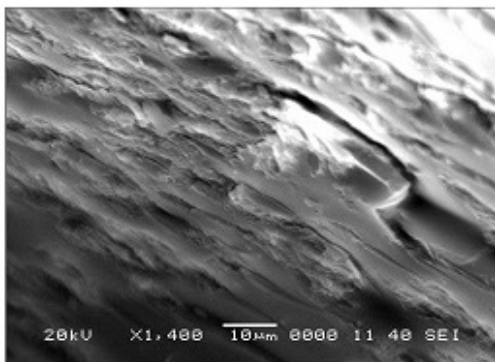
**Figure 1** – IR spectra of the BC-PCA; where: a) bentonite clay (1); PAA gel (2); BC-PAA gel (3)  
b) bentonite clay (1); PMAA gel (2); BC-PMAA gel (3)



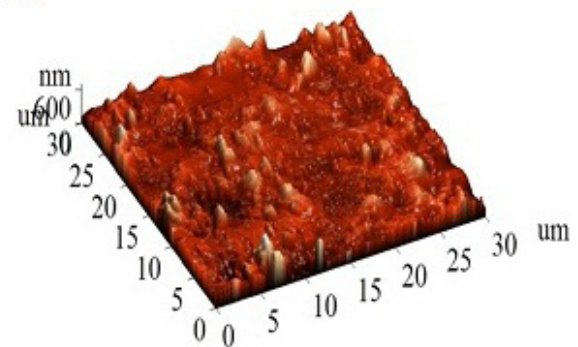
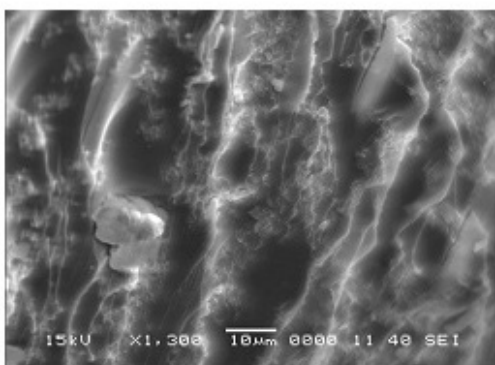
(a)



(b)



(c)



(d)

**Figure 2** – Pictures of scanning electron microscopy and atomic-force microscopy; where: BC (a); PAA (b); BC-PAA(c); BC-PMAA (d)



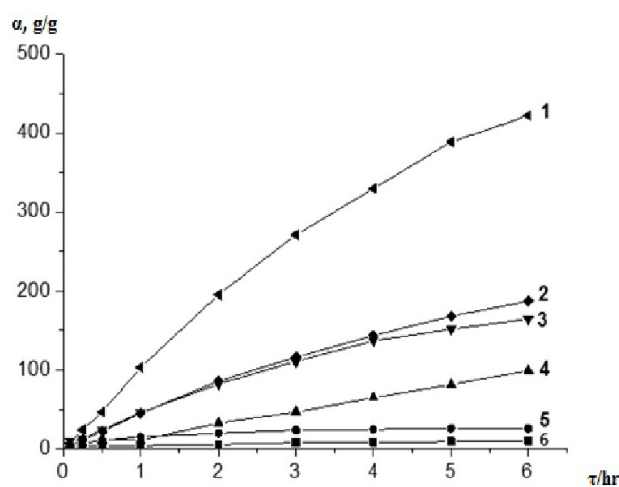
To obtain a difference in the surface structure of the obtained composite gels based on BC-PAA, pure gel PAA and BC. These differences can be seen in the pictures of the composition taken with an atomic force microscope. It is noticeable from the pictures that with the addition of bentonite clay, the surface of the gel becomes smooth, this indicates that the particles of bentonite clay penetrate the polymer and produce a uniform gel. The principle of the atomic force microscope is based on recording the force interaction between the surface of the sample and the probe, by recording the magnitude of the bend, one can obtain an image of the surface relief [5].

According to the results of the research, the components of the obtained composite BC-PCA gels together form a complex with the help of hydrogen bonds and are chemically crosslinked by cross-linking agent.

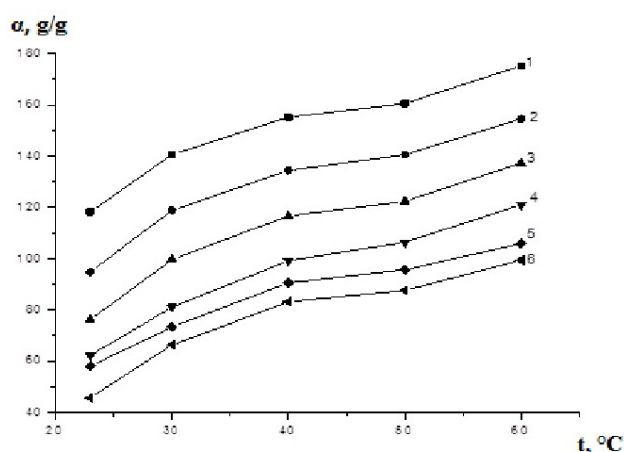
Before evaluating and regulating the sorption capacity of composite gels, one should know about the swelling of gels in a CPB and CTAB solution. Therefore, the degree of swelling of synthesized clay polymer compositions is determined by the methods of swelling equality [5]. Based on the results of the study, the effect of the pH of the medium on the swelling kinetics of competing gels in the CPB solution (Figure 3) can be seen that as the pH of the medium increases, the swelling of the composite gels increases significantly, because the degree of dissociation of the weak PAA depends on the pH medium. For example, for BC-PAA gels the swelling ratio at pH = 1 is about 10 g/g, and at pH = 11, it will increase to about 422 g/g.

Figure 4 shows the change in the swelling characteristics of composite gels as a function of temperature, as well as the change in the volume of bentonite clay in the composite. With the increase in the volume of bentonite clay, the swelling capacity of the composite decreases. The swelling capacity of pure bentonite clay in the CPB solution is significantly low, resulting in the properties of the composite in which the volume of bentonite clay is closer to the swelling of pure bentonite clay. For example, the degree of swelling for the composite BC-PAA gel [1:10] at 25 °C is about 119.03 g/g, and for the BC-PAA [5:10] gel, about 82.09 g/g. With increasing temperature, the movement of molecules in the CTAB solution increases and leads to an increase in swelling of the gel. At the same time, an increase in temperature leads to a weakening of the hydrogen bond between the composite and the CTAB, as a result of which the swelling properties increase. For example, at a temperature of 25 °C for BC-PAA G (1:10), the de-

gree of swelling is 119.03 g/g, and at a temperature of 60 °C, the degree of swelling of the composite increases and is about 175.19 g/g. Thus, the composite gels obtained with a negatively charged cationic surfactant-CTAB through an electrostatic bond form a complex. For various internal and external factors, in particular, the volume of BC in the composition of the composite and the concentration of the CTAB solution, the pH of the medium and the relationship with the temperature change shows different swelling capacities.



**Figure 3** – Kinetics of swelling of composite gels at different pH values; where:  $\tau = 6$  hours;  $T = 25$  °C; BC-PAA (1:10); [DAA] = 0.5 %; CA = 1 %; pH = 11 (1), 9 (2), 7 (3), 5 (4), 3 (5), 1 (6)



**Figure 4** – Dependence of the swelling degree of compilation gels on temperature; where:  $\tau = 6$  hours;  $T = 25$  °C; [CTAB] =  $1 \cdot 10^{-4}$  M; BC-PAA [1:10] (1); [3:10] (3); [5:10] (5); BC-PMAA [1:10] (2); [3:10] (4); [5:10] (6)

## Conclusions

Protection of sewage from surfactants is an extremely important and global problem. This situation determined the intensive development of serious scientific research into the study of the specific features of this type of pollution and the search for ways to prevent it.

The following conclusions were made to the results of the study:

1) acrylate-clay gels on the basis of bentonite clay and polycarboxylic acid (acrylic and methacrylic acids) were obtained by radical polymerization, optimal synthesis conditions were identified, physicochemical characteristics of the gels were determined; It was found that the components of acrylate-clay gels are linked together by hydrogen bonding and form a uniform, water-swallowable polyelectrolyte gel, that the components of acrylate-clay gels are linked together by a hydrophobic bonds;

2) the kinetics of swelling of obtaining composites in solutions of anionic and cationic surfactants – cetylpyridinium bromide (CPB), cetyltrimethylammonium bromide (CTAB) were studied; the influence of internal factors: the content of clay, concentration of surfactants, temperature and pH of the medium, on the swelling of composites in surfactant solutions was examined by the method of equilibrium swelling. The results of morphological structure studies were obtained.

## References

- 1 Shachneva E.U. Methods for determination of non-ionic surfactants // *Water purification, management and supply*. – Rus. 2015. – Vol. 6. – No. 90. – P. 18-23.
- 2 Volkova G.A., Smorotun N.Y. Methods of sewage treatment, containing surface-active agents // *Herald of Brest State Technical University*. – Rus. 2012. – Vol. 2. – P. 38-41.
- 3 Kinetic research on the sorption of aqueous lead by synthetic carbonate hydroxyapatite / H. Xu, L. Yang, P. Wang, Y. Liu, M. Peng // *J. Environ. Manag.* – 2008. – Vol. 86. – P. 319–328
- 4 Glazunova I.V., Martynenko N.P. Complex sorbent for sewage treatment from oil products and heavy metals // *Herald of Agrochemistry*. – Rus. 2008. – Vol. 4. – P. 38-39.
- 5 Bakajin, O. Microfluidic sieve using intertwined, free-standing carbonnanotube mesh as active medium / O. Bakajin, A. Noy // Patent US No. 7290667. – 06.11.2007.
- 6 Erlan D.E, Kayralapova G.Zh, Zhaksybaev Zh.S, Sarshesheva A.M. Bentonite clay changed Bentonite clay and polycarbon acids based chemically cross-linked gels on the patterns of surface-active substances. International Conference for students and young scientists “World of Science”, Almaty, 2012. – P.54.