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Synthesis of cryogels based on bentonite clay-polyacrylic acid and research their physical-chemical properties

Abstract: In this paper, we present ways of synthesizing sorbents based on bentonite clay-polyacrylic acid used in industrial wastewater and studying their physico-chemical properties. Cryogels were synthesized by radical polymerization based on bentonite clay (BC), brought from the East Kazakhstan region of Tarbagatai region, and polyacrylic acid (PAA), characterized by porosity by the definition of physico-chemical properties. 1 %, 3 % and 5 % of bentonite clay, 0,25 % ammonium persulfate and 0,25 % sodium metabisulphite as initiator, 10 % acrylic acid, 10 % sodium hydroxide were used of synthesis of cryogels based on BC-PAA. The optimal temperature is -30°C and 24 hours. In addition, the physico-chemical properties of obtained cryogels based on BC-PAA are investigated, and their density is about 1,5531 g/cm^3, yield 95 %. This shows the economic efficiency of cryogels. Morphological structure of composite cryogels were carried out on a Leica DM 6000M optical microscope, Ntegra THERMA atomic force microscope and Quanta 3D 200i Dual system scanning electron microscope, which resulted in porosity, chemically crosslinked, homogeneous and negatively charged composite cryogel. Sorption properties of cryogels in relation to ions of heavy metals are considered.
Key words: bentonite clay, polyacrylic acid, composite material, sorbent, heavy metal ions.

Introduction

The results of saving natural resources and anthropogenic conditions, as well as environmental problems of maintaining a balance in the environment, are increasing day by day. One of such environmental problems is the problem of pollution of industrial wastewater, non-compliance with the established requirements of water quality.

One such composite material that meets these requirements is cryogels. Cryogels have several special properties, the main of which is porosity. This property makes it possible to apply them in all branches of science and technology.

In the development of the science of chemistry for the purification of industrial wastewater sorption methods differed. Recently, for this purpose, according to the correspondence of organic and inorganic polymers, the importance of the use of composite materials in which the mechanical, physico-chemical and sorption properties have improved is growing.

The following are the causes, for which clay and polyacrylate were chosen:

1) polyacrylic acid does not belong to the colonies of the polyanions, that is, it is an ion with an negative spell. Bentonite clay conjoin from particles with detrimental spells, that is, two two-component gel are identical sponges. If they were illegal, then, in the result of the electro-tactical action, a saline complex would appear, and then an unequal connection. Components of displacement with the same name can connect with one another with non-circular forces, such as water links, hydrophobic activities. Such a system is characterized by the following features: the collected crucifixes are single-handed and protect the important of their creatures – a whirling cope.

2) cryogel has active centers (-COOH, -OH) and hydrophobic groups that support the binding of metal ions. In connection with these objects, it is possible to suggest that the materials on their basis can bind ions of heavy metals.

For these reasons, in this work, the possibility of obtaining cryogels based on polyacrylic acid and bentonite clay at different times and in different ratios of the original components was investigated. The influence of various external factors was considered:

the amount of bentonite clay (1, 3, 5 mol.), temperature, concentration of the medium.

It can be argued that the reason for introducing bentonite clay into the PAA cryogel is to increase the coping resistance of cryogels. Therefore, bentonite clay is a good sorbent, it copes heavy metal ions up to 100 %. Therefore, due to the growth of PAA cryogels and the high coping efficiency of BC, it is possible to receive a sorbent with a high sorbent cope.

Materials and methods

In this work cryogels were synthesized based on bentonite clay, brought from the East Kazakhstan region of Tarbagatai region and polyacrylic acid.

For studying interaction of bentonite clay with organic polymer for the beginning have prepared and have purified bentonite clay. Clay represents itself mix of particles of various sizes and contains, except clay, numerous impurity of other minerals. The used bentonite clay of the field Manyrak (East Kazakhstan region) of pink color was purified with the help of Salo method. Fat repeated washing by the distilled water.

Three phases are determined by results of X-ray-phase analysis (DRON-4-07) in composition of the studied bentonite clay: α-quartz SiO_2, montmorillonite $Al[OH]_2\{Si_4O_{10}\}\cdot mH_2O$ and amorphous phase. In this structure montmorillonite prevails.

The most optimal condition was chosen by changing and observing several times the condition of obtaining and composition of the cryogel. Synthetic cryogels were synthesized based on 10% polyacrylic acid (PAA) by the method of polymerization. As a result, the crosslinking agent used N, N'-methylene-bis-acylamide (MBAA), initiate-ammonium sulfate (APC) and sodium methabisulfite (SMBS), used sodium hydrate and water. At the time of bentonite clay content of 1 %, 3 % and 5 %, 10 % PAA, 10 % hydrochloride of total mass, 1 % N, N'-methylene-bis-acylamide, 0,25 % ammonium peroxide and 0,25 % sodium methabisulfite from the scale of the monomer. The cryogels PAA and BC-PAA were obtained with a radial polymerization at a temperature of -30 °C for 24 hours [1].

Results and discussion

The physicochemical properties of synthesized cryogels based on BC-PAA have been studied. For studying of the density, kinetics of swelling and the morphology of the gelled gels an optical microscope, scanning electronic microscope, an atom-force microscope was used.

Composition and the physico-chemical characteristics of the produced composite gels are shown in Table 1.

Table 1 – Physicochemical characteristics of composite cryogels

Structure (weight. %)	G, %	S, %	j, %	ρ, г/см³
Gel PAA	57,7	42	6,52	1,2070
Cryogel PAA	90,3	10	3,21	1,5974
Cryogel BC-PAA (1:10)	90,8	9	3,14	1,5781
Cryogel BC-PAA (3:10)	91,7	8	3	1,5677
Cryogel BC-PAA (5:10)	95,9	4	2,27	1,5531
G – yield of cryogels, %; S – the output of the sol fraction, %; j – degree of cross-linking, %; CA = 1 %.				

As can be seen from the table, for all comedy cryogels there is one common sign: when the clay is increased in size, the yield of cryogels increases, and the yield, the role of the fraction and the degree of reduction decrease [2]. The output of the fraction of the solution is peppered to the output of the clay, that is, it decreases. Sol fraction shows quantity not polymerized monomers in clarification time cryogels. With the decrease of this value, the output of clay increases, so that it may be suppressed that polycrystalline substances enter into polimerization. The reason for the decrease in the degree of crosslinking from the clay, as the clay increases in the composite, is that the quantity of the polimeral agent in according decreases, so the degree of cross-linking decreases.

The density of cryogels based on BC-PAA was measured on the basis of the Radwag AS 220/X. The component of the synthesized cryogels, that is, when the quantity of BC increases in size, and increases in size, in proportion, the density decreases. The reason for this is the coexistence of BC, in which the molecules of monomers are introduced, forming single, well-built composite cryogels [3].

When studying the properties of the collected cryogels, you must first pay attention to the disintegration and the morphological structure of the clay in composite. The literal review shows that the process of formation of emotions occurs on many intermediate stages. At the first stage, the tactoid appears, that is, the polymer disposes of the agglomerates of the organoclay. In the second stage, there is a transition of the polymer to the interstitial space of the organoclay, in the course of which they are exposed to 2-3 nm. On the third stage, the disintegration of the clay layers of the organoclay. On the next stage there is a crumbling with a thin layer. But, in the formation of polymeric nanocomposites, higher structures may be higher than this, which is linked to the degree of clay pumping. Because of the higher quantities and the low degree of clay in the polymeric material, there may be agglomerates of minerals.

On the results of the studies of cryogels with the help of an optical and an atomic-force microscope, it is possible to see that the upper layer of the structure of the body is slightly spoiled. This proves that the particles of BC are introduced into the polymeric grids, and a one-way interconnected gel is formed (Figure 1).

PAA cryogel BC-PAA cryogel

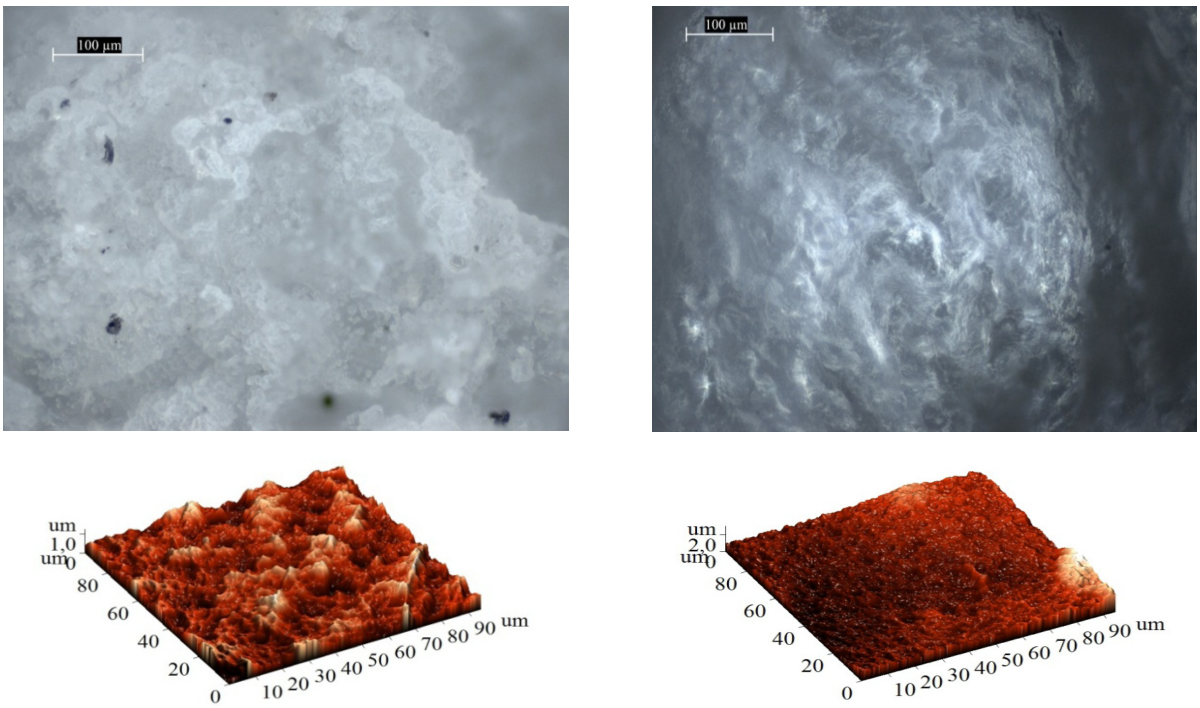
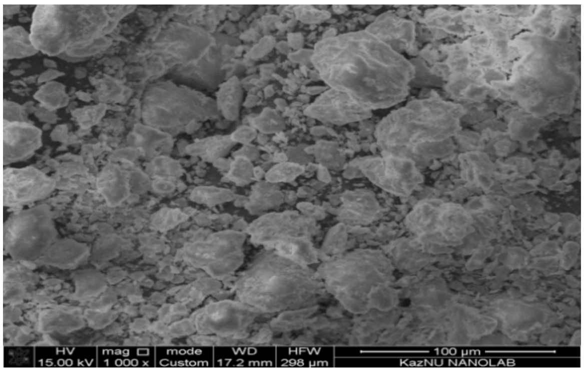
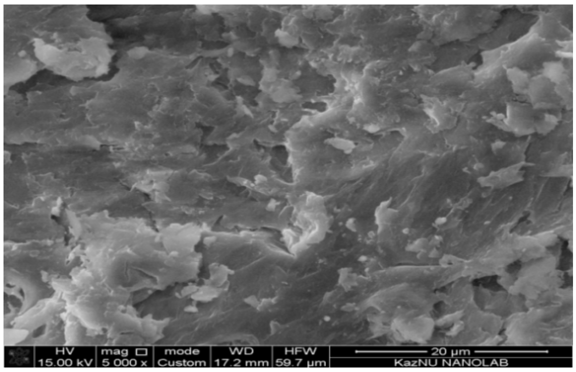


Figure 1 – Figures of cryogels obtained by optical microscope and an atomic-force microscope (AFM)

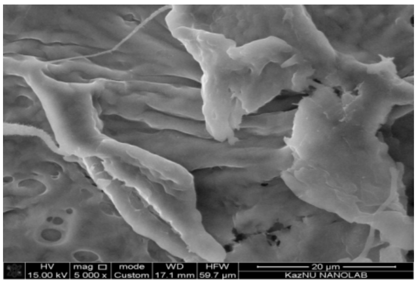
Interest to the microstructure of the gel is associated with the possibility of using them in the catalysis at the rate of the source, on electronic microequipment. In physical gels, polymer chains, when linked, form microstructures such as aggregates, micelles, multiplets, crystallites [4]. The size of these microstructures, as indicated by the avtop, is in the range of 1-100 nm [5]. The formation of crystalline gels is indicated in the examples in the complexes sodium yellow-alginate, PAA gels. In the opinion of detectors, the smallest dimensions of these crystals are 1 nm, in the range 4,6-7,1 nm, and they fulfill the role of cross-linked sites of networks from polymer networks. For the further establishment of the morphological structure of BC-PAA cryogels with the method of scanning electron microscopy, studies were carried out (Fig. 2) [6]. From the received information, it is possible to observe that the cryogels are composed of microstructural units with a size of 5-10 nm.



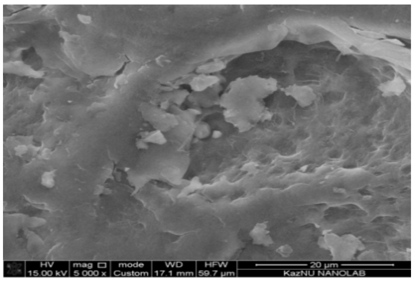
Bentonite clay



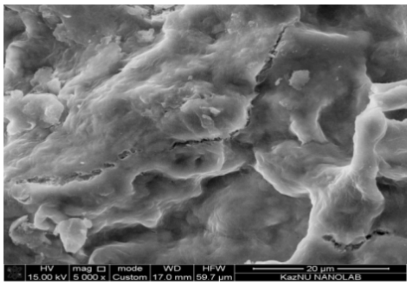
PAA cryogel



BC-PAA cryogel (1:10)



BC-PAA cryogel (3:10)



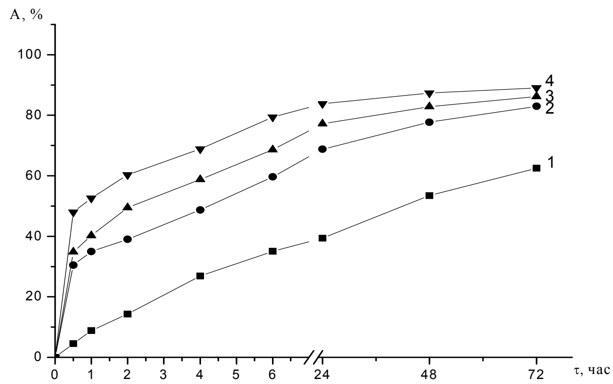
BC-PAA cryogel (5:10)

Figure 2 – Figures SEM of the BC-PAA cryogel

Sorption is one of universal methods in purification of the dissolved organic substances, an also of ions of heavy metals. In the same purposes, artificial and natural sorbents are much used. Therefore that, sorbents belong to effective, easily available materials in sorption of ions of heavy metals. Researches of sorption of ions of heavy metals by cryogels for an assessment of their sorption ability are conducted.

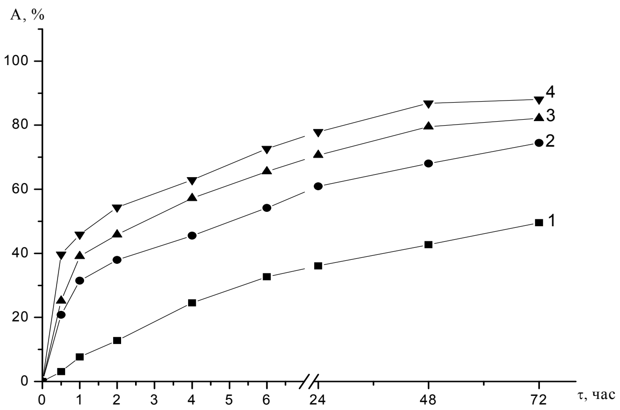
Results of sorption of cryogels based on BC-PAA in solutions of ions of metals are given in figures 3-4. By results of a research, sorption of cryogels BC-PAA on 3 days was in limits ~ 80-90%.

First, if cryogels based on bentonite clay and polyacrylic acid compare with PAA cryogel, it is visible that sorption values high (figures 3-4). It can be explained with presence of bentonite clay at structure of cryogel. High sorption ability of bentonite clay are investigated in many works. Increase in sorption value with increase in content of bentonite clay is connected with electrostatic interaction.



Crygel BC-PAA; NaOH = 10%; CA = 1,0%;
Initiator = 0,5%; C_{Pb2+} = 10 mkg/ml; τ = 72 h
PAA – 1; [BC:PAA] = [1:10] – 2; [3:10] – 3; [5:10] – 4.

Figure 3 – Sorption kinetics of cryogels in lead solution



Crygel BC-PAA; NaOH = 10%; CA = 1,0%;
Initiator = 0,5%; C_{Cd2+} = 10 mkg/ml; τ = 72 h
PAA – 1; [BC:PAA] = [1:10] – 2; [3:10] – 3; [5:10] – 4.

Figure 4 – Sorption kinetics of cryogels in cadmium solution

Conclusion

Composite cryogels have been synthesized based on bentonite clay-polyacrylic acid at different time and temperature by radical polymerization. Among these was selected the most optimal – the received cryogel at a temperature of -30 °C for 24 hours.

The physicochemical properties of the produced cryogels based on BC-PAA are studied, their density is approximately 1,5531 g/cm^3, the yield is 95 %. It shows that, cryogels – economic favorable. Morphological structures composite cryogels are investigated and in result of what existence of a time and education, uniform and mutually compatible, negatively loaded composite cryogels have been revealed. Physico-chemical studies have shown that the components of the formation form a complex in terms of the water connections stabilized by hydrophobic interactions. Values of sorption of BC-PAA composite cryogels from PAA cryogel is considerable in difference high (~90 %).

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