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Possibilities of composite materials use on the basis of polivinilipirrolidon and bentonite clay as sorbents of heavy metals ions

Abstract: The chemically crosslinked gels based on bentonite clay of the Manyrak deposit (East Kazakhstan region) and nonionic polymer polyvinylpyrrolidone were synthesized with using the process of intercalation of the monomer in the aqueous suspension of bentonite. Swelling degree, sorption capacity of the obtained polymer-clay composites to metal cation ions are evaluated. It is shown that with increasing the concentrations of bentonite clay in gels the sorption capacity to metal ions increases significantly.
Key words: bentonite clay, gel polymer-clay composites, sorption.

Introduction

Interest to polymer-clay composite materials, and also to researches of reactions of a complex formation with their participation is caused by that such complexes, along with valuable properties of components have improved thermal, mechanical and sorption properties. Polymer-clay compositions on the basis of natural and synthetic polymers are available carriers of medicinal substances and sorbents [1]. One of ways of polymer-clay compositions obtaining is radical intercalation polymerization «*in situ*» of monomer on a surface of clay silicates [2]. As a result, are formed more uniform material with uniform distribution of a mineral in all volume of a polymeric matrix. A continuous phase in composites can be synthetic polymers, and as a filler the bentonite clays (BC), with a predominant content of the mineral montmorillonite [3]. It is known that Kazakhstan is rich in deposits of this valuable mineral. Therefore, in the present study offers new perspectives for the using of composite materials based on non-ionic polymer – polyvinylpyrrolidone (PVP) and BC of deposit Manyrak as environmentally friendly and cost-effective sorbents of heavy metal ions.

Experimental part

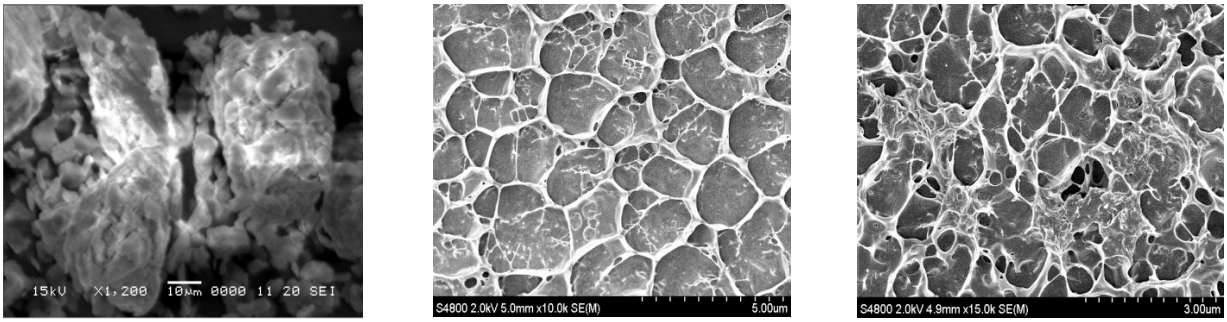
Composite gels of PVP-BC were synthesized by «*in situ*» intercalation radical polymerization of an aqueous monomer solution with incorporated purified bentonite clay particles. N,N-methylene-bis-acrylamide (MBAA) was used as the crosslinking agent without further purification, and 2,2-azo-bis-isobutyronitrile (AIBN) was used as initiator which has undergone several times recrystallization. Conditions of carrying out synthesis and the characteristic of initial components of composite gels are described in early works [4]. The morphology of bentonite clay, reference and composite gel samples were examined by high-resolution scanning and cryo-scanning electron microscopy (SEM, cryo-SEM) by using the scanning electron microscope S-4800 from Hitachi (Japan). The respective samples were rapidly frozen in melting nitrogen and fractured in a cryo chamber at -145ºC. After etching for 45s at -98 ºC, the samples were sputtered with a thin platinum layer. The degree of swelling of gels and bentonite clay was investigated by method of equilibrium swelling. Amount of sorption ions of metals by obtained composites was determined by atomic adsorption ASS Shimadzu 6200 microscope.

Results and their discussion

It is known that indisputable the conditions of carrying out polymerization affect on physical and chemical properties of polymer-clay compositions. As a result of carrying out series of experiences and research of an exit of gel-fraction and the swelling ability, the optimum ratio monomer-solvent, equal to the content of water 70, and monomer – 30 vol.% is established with the different maintenance of a mineral complex. In early works [5, 6] data polymer-clay compositions were offered as the carrier of medicinal substance of a rikhlokain with the maintenance of BC

of 1-3 mas.% monomer volume, and in this work we consider possibility of application of these compositions as sorbents of metal ions, and for improvement the sorption properties we changed the maintenance of concentration of BC of 1-4 mas.% of the total volume, which in turn should have a beneficial influence on the quantitative values of sorption. By results of the previous works [5, 6] it was also established that increase of concentration of crosslinking agent and BC promotes increase in an exit of gel-fraction, the ash content and densities of the gels.

The scanning microscopy is used for research of morphology of a surface of composite gels [7]. Apparently from figure 1, bentonite clay (a) has flaked layered structure. Figure 1 (b) shows the formation of polymeric matrix as a result gel formation of PVP homogels, and polymer-clay compositions of PVP-BC with represent varying degrees intercalated structure due to the penetration of the monomer into the interlayer space of the clay and uniform distribution of the clay particles in the polymer matrix. The result is the formation of homogeneous compositions.



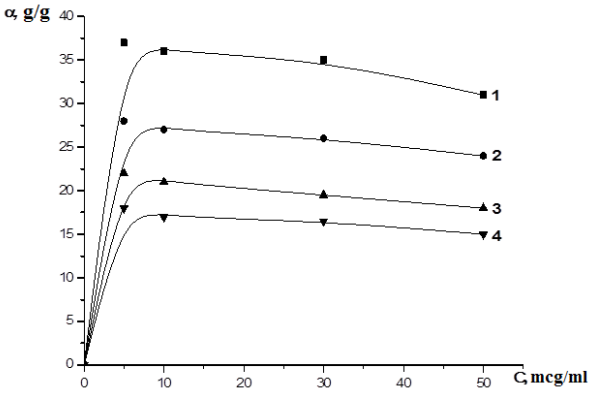
a b C

Figure 1 – Cryo-SEM snapshots of BC (a), cryo-SEM snapshots of PVP homogels (b), and composite gels of PVP-BC (b).

By results of the previous works [5, 6] at research of the swelling capacity, morphology and structure it is established that compositions of PVP-BC combine properties of initial components and are characterized by biocompatibility and homogeneity. It was revealed that with increasing content of the crosslinking agent, concentration of BC and in the presence of electrolyte degree of swelling of the PVP-BC composite gels considerably decreases. Increase in temperature and pH environment leads to reduction of volume of composite gel that testifies about incentive susceptibility of gels. These characteristics of clay compositions of polymer can expired by the non-Coulomb nature of interaction, formation of through hydrogen bonds and hydrophobic interactions, and also greatly influenced by negatively charged particles of BC.

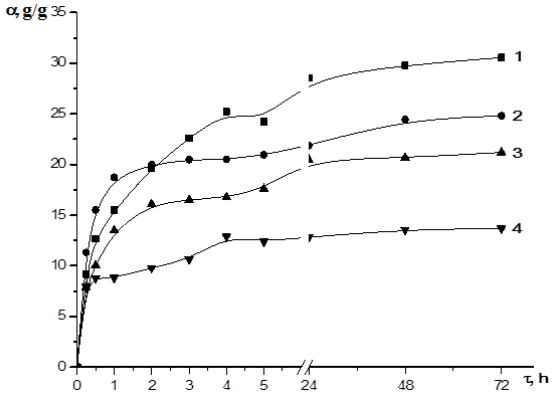
Polymer-clay materials, due to high sorption and complexing ability, are excellent sorbents of cations of metals. Therefore one of the most important branches of possibility of application of clay polymeric composites can note the purification of industrial sewage of heavy metals [8]. In this connection and to evaluate the sorption ability of the obtained polymer composites was studied sorption Pb^{2+}, Zn^{2+}, Cd^{2+} by gels. Studies were carried out by atomic adsorption spectroscopy using the spectrometer AAS Shimadzu 6200. For clarification of the nature of interaction of ions of metals with composites the swelling ability of gels in solutions of metals was studied. Swelling ability of gels in solutions of metals was studied for clearing up of the nature of interaction of ions of metals with composites. The results of studies of the effect of concentration solution of metals on the swelling behavior of the gels (Figure 2, for example, a solution of Pb^{2+}), found that increasing of the concentration of Me^{2+} ions in the solution decreases the volume of composite gels.

With increasing content of bentonite clay swelling capacity of the gels naturally decreases, as can be seen from the data in Figure 3, which shows the swelling kinetics of the composite gels in solution Cd^{2+} (30 mcg/ml) containing bentonite clay 1, 2 and 4% by weight. Probably, the gradual contraction of the gel in a solution of the metal occurs due to the ionic strength of the last, however, is compacted mesh with the content of bentonite, which further prevents to increase in the net.



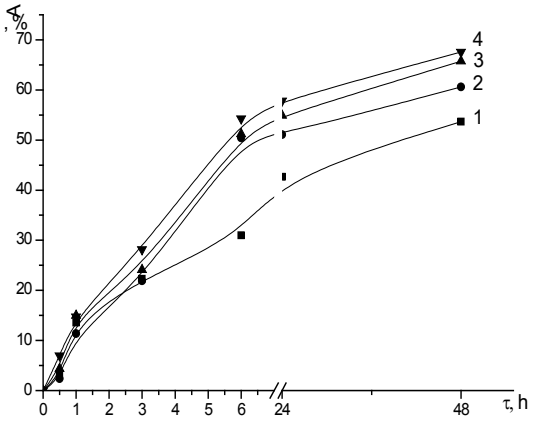
t=25˚C; PVP–1; PVP-BC: BC,
1% – 2; BC, 2% – 3; BC, 4% – 4;
[AIBN]=0,5 mol.%; [MBAA]=1 mol.%

Figure 2 – The dependence of the degree of swelling of gels on the concentration of Pb^{2+}



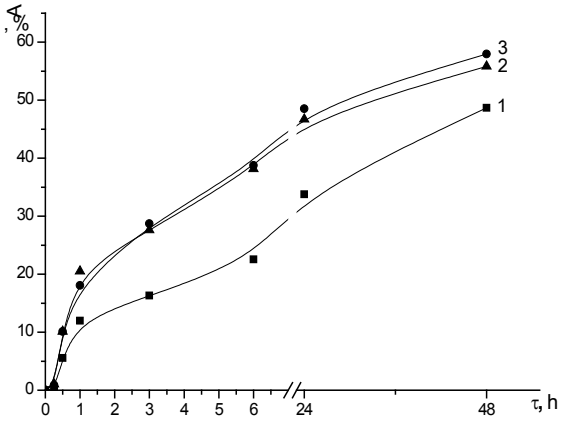
t=25˚C; [Cd^{2+}]= 30 mcg/ml; PVP–1; PVP-BC: BC,
1% – 2; BC, 2% – 3; BC, 4% – 4;
[AIBN]=0,5 mol.%; [MBAA]=1 mol.%

Figure 3 – Kinetics of gels swelling in the sample solution Cd^{2+}



t=25˚C; [Cd^{2+}]= 10 mcg/ml;
PVP–1; PVP-BC: BC, 1% – 2; BC, 2% – 3; BC,
4% – 4; [AIBN]=0,5 mol.%; [MBAA]=1 mol.%

Figure 4 – Kinetics of sorption Cd^{2+} on the gels PVP-BC



t=25˚C; 1-[Pb^{2+}], 2-[Zn^{2+}], 3-[Cd^{2+}]
[AIBN]=0,5 mol.%; [MBAA]=1 mol.%

Figure 5 – The kinetics of sorption of metal ions on the gel PVP-BC (BC, 1%) of the combined solutions

As a result of the analysis of sorption of cations of metals the obtained composite gels are revealed some regularities. So, the limit values are set the sorption during the day. And with the increase in the content of bentonite clay composites there is a significant increase in the amount of adsorption of metal ions, that testifies to a primary role of clay in sorption of cations of metal (Figure 4). In general, it is possible such interactions of metal ions with composite gels as a coordination bond and electrostatic binding between the lone pairs of the polymer, the active centers of bentonite clay and free orbitals of the metal lattice. Increasing the concentration of Me^{2+} in the solution leads to a decrease in the sorption, for example the value of the sorption of Cd^{2+} ions on gels PVP-BC 1% per day in a solution of 10 mcg/ml up to 57%, 30 and 50 mcg/ml 45 and 42%, respectively.

Also, for research of selectivity of composite gels was prepared combined solution of heavy metals. The results showed that polymer-clay gels can adsorb simultaneously some metals complex solution. Figure 5 shows the adsorption of ions of metals in com-

position of PVP-BC (BC, 1%) in complex solution. Numerical values of sorption of ions of metals from complex solution it is much less, than in solutions of ions of metals separately. It is connected with that metals compete among themselves, so in 24 hours the composition of PVP-BC (BC, 1%) absorbs of lead 31%, of zinc 42%, of cadmium 48%.

Thus, chemically cross-linked homogeneous, water-swellable polymer-clay compositions based on BC of deposit Manyrak (East Kazakhstan region) and nonionic polymer PVP are obtained through the formation of complex by hydrogen bonds and hydrophobic interactions. It was estimated the sorption capacity of chemically cross-linked polymer-clay composite gels PVP-BC in relation to heavy metal cations. Swelling, sorption properties and morphology of the gels was established. With increase in the content of bentonite clay in gels their swelling ability naturally decreases, and the number of sorption of ions of metal significantly increases. It is shown that with increasing of concentration of Me^{2+} sorption ability of composite gels decreases. Results of further research of composite gels on the basis of PVP and BC gives the chance of perspective use as sorbents of cations of heavy metals.

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