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SYNTHESIS AND PHYSICAL-CHEMICAL STUDY OF ORGANOBENTONITE-BASED NANOCOMPOSITES

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***Abstract**: A series of experiments was conducted to obtain a nanocomposite based on organo-bentonite and a synthetic polymer polyvinylpyrrolidone by a hydrothermal method. Octadecilaminacetate-processed bentonite was used as organoclay. Obtained samples were investigated by X-ray, IR spectroscopic methods of analysis. It found that samples can also be used as adsorbents.*
***Keywords:** bentonite, polymer, hydrothermal synthesis, nanocomposite*
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Introduction

In recent years, the problem of synthesis, studying the structure and properties of polymer nanocomposites (PNC), based on layered silicates, is - great interest to researchers as a promising direction in industry.

One of the advantages of clay minerals is that their structure allows for targeted modification to control surface properties and adsorption characteristics of natural aluminosilicates [1]. An increase in the adsorption characteristics of natural aluminosilicates is possible by ion exchange, their treatment with acids, alkalis, salts of various metals and organic compounds which lead to rise in the concentration of acid and basic centers, changes in transfer energy, and facilitate electronic transitions and ion mobility [2].

The analysis of literature data showed that completely new prospects were revealed in the development of polymeric composite materials by using layered silicates as fillers with montmorillonite structure (MMT).

But, due to the fact that outer and inner surfaces of montmorillonite are hydrophilic and polar, their compatibility with the organic polymer matrix is impossible. This problem can be solved by modifying montmorillonite with organic compounds [3-7].

Experiment

The use of organo-bentonite as a nanocomposite filler (3-5%) in the composition of polymeric materials makes it possible to regulate rheological properties of the system in a wide range which significantly improves physicomechanical properties of polymeric materials. Organoclays are better combined with polymers to form layered polymeric nanocomposites which are well dispersed in the polymer matrix [8-9].

In this regard, for the hydrothermal method of synthesis the initial reagents were taken in different molar ratios (synthetic polymer polyvinylpyrrolidone as polymer matrix, and bentonite treated and untreated with octadecylamine of acetate as organic clay, the duration of the experiments varied from 24 up to 144 hours, in the temperature range of 110-130^{0}C, the percent of occupancy of the autoclave was 70-75%, respectively.

After the end of the experiment, the product was poured into a Petrik cup and the mother liquor was separated by decanting the next process to dry product completely. The results of hydrothermal synthesis were investigated by X-ray (XRD-based apparatus D2-Phaser “Bruker”) and IR-spectroscopic

(IR- on FTIR spectroscopy Nicolefisio VSA) analysis methods.

Results and its discussion

Initially, we obtained octadecylamine of acetate (ODAA) using glacial acetic acid which was heated in a flask heater (or in a water bath) to a temperature of 40-50^{0}C with constant stirring. Next, the calculated amount of amine was introduced until the pH of the medium reached 7. The resulting solution was filtered and evaporated.

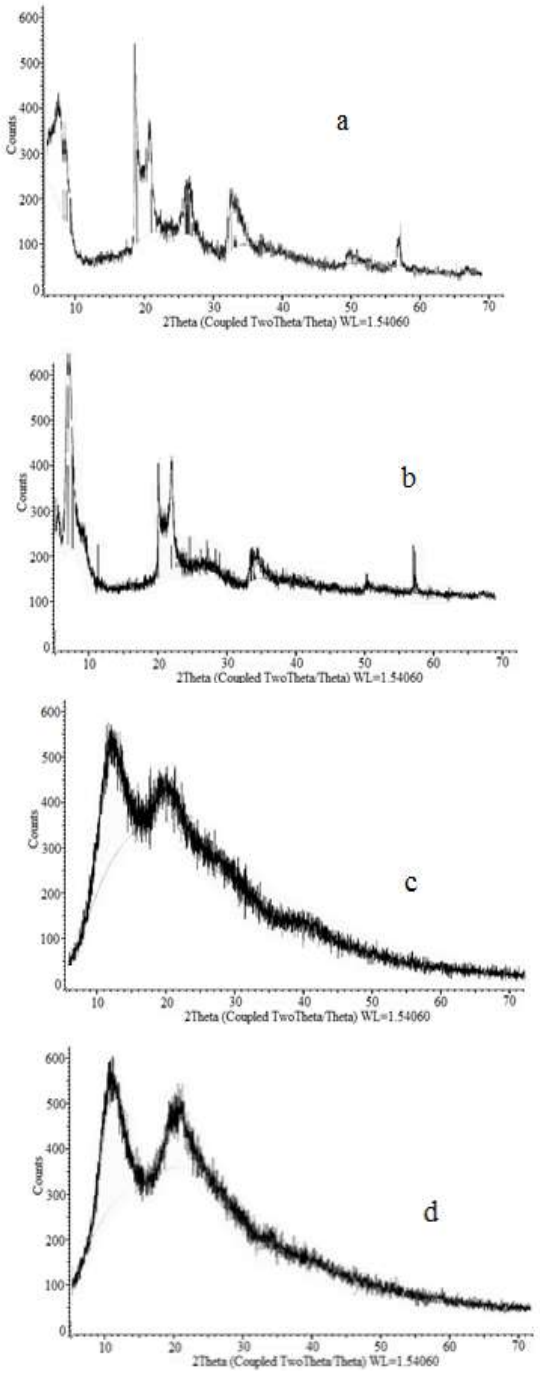

Fig. 1. Diffraction of a) starting montmorillonite; b) montmorillonite treated with octadecylamine of acetate; c) starting polyvinylpyrrolidone; d) polyvinylpyrrolidone/organo-bentonite nanocomposite

The treatment of bentonite with octadecylamine of acetate in a solvent medium was carried out with stirring of the laundered rock of bentonite, containing 80% of MMT Dash-Salakhly deposit of the Republic of Azerbaijan, with amine salt at a ratio of MMT: octadecylamine = 70:30 in the environment of 90% ethyl alcohol for 30 min., with the

subsequent by evaporation of excess alcohol in a water bath and drying the product to obtain a homogeneous, powdery modified organoclay. The results of X-ray analysis showed that the following phases can be distinguished in clay samples: montmorillonite, low-temperature quartz, illite, etc. (Fig. 1 a).

The main rock-forming mineral in the Dash-Salahlinsky deposit is montmorillonite. It is known that montmorillonite when heated it loses water and swells again when it enters a humid environment. As temperature rises, the mineral retains its properties to a certain limit. At high temperatures, irreversible changes in the structure of the mineral up to complete destruction are possible which adversely affects the sorption properties of clay. Therefore when using MMT, the temperature factor is taken into account. MMT has a crystalline structure with low crystallinity which is due to the content of impurities in the composition of bentonite. After processing and purifying MMT from ODAA admixtures its crystallinity increases (Fig. 1 b).

In the figure polyvinylpyrrolidone is characterized by two diffusion reflections (Fig. 1 c), which indicates the mesomorphic nature of the mutual packing of this polymer' chains, a nanocomposite based on polyvinylpyrrolidone and organo-bentonite (Fig. 1d) had two strongly pronounced reflex's which was due to the introduction of organo-bentonite into the composition of polymer which in turn has a crystalline structure.

Using IR spectroscopic analysis, the structures of the starting, modified of layered silicate, polymer and polymer nanocomposite were also studied. The method of IR-spectroscopy is currently one of the most common methods for identification of polymers and polymer composite materials and their structural analysis.

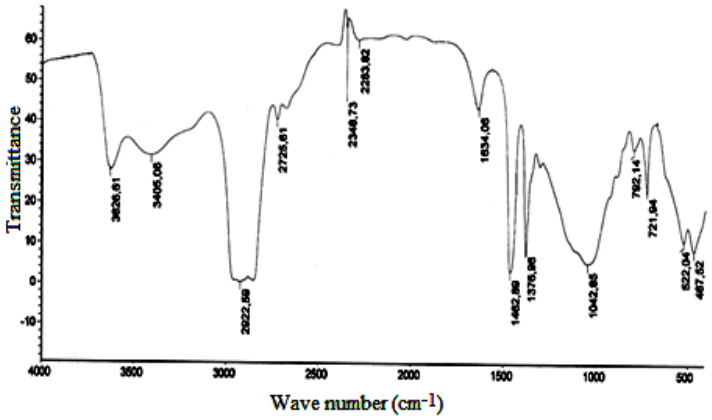

Fig. 2. IR spectrum of starting montmorillonite

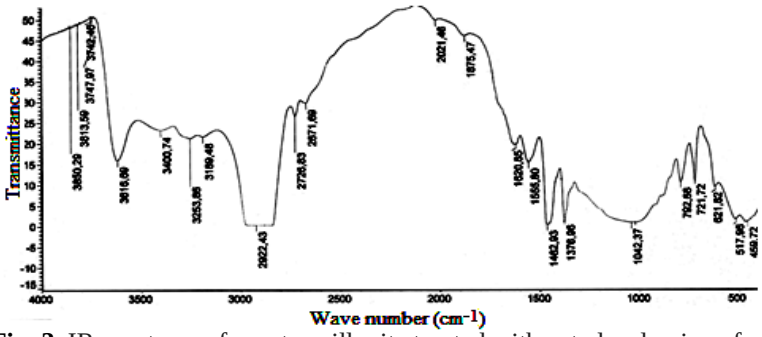

Fig. 3. IR spectrum of montmorillonite treated with octadecylamine of acetate

According to IR spectroscopy (Fig. 2), characteristic absorption bands 2348, 3405, 3626 cm^{-1} were observed in the spectrum of the initial MMT of the free and associated forms of Si – OH; the band at 1634 cm^{-1} refers to OH- stretching vibrations. The bands

1000–1100 and 460–500 cm^{-1} are caused by vibrations of the Si – O– bond in the SiO_4^{4-} - tetrahedral. Bands in the range of 3000-3400 cm^{-1} relate to OH- stretching vibrations of free or bound water.

On IR spectra of samples treated with organic compounds, these bands are absent (Fig. 3). This is due to the fact that the molecules of organic compounds are distributed in the into interlayer space and displaced the water from there. The absorption bands in the regions of 1555–1620 cm^{-1} and 1868 cm^{-1} characterize the vibrations of the C – H bond, which indicates the presence of organic compounds in the structure. The absorption bands 3189-3253 cm^{-1}, 1875 cm^{-1}, appearing in the IR spectrum, belong to the amino groups and acid residues.

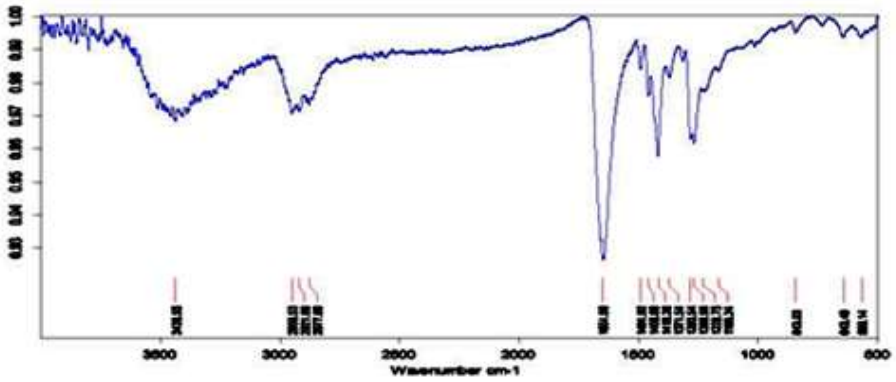

Fig. 4. IR spectrum of the starting polyvinylpyrrolidone

In contrast to natural bentonite, in the IR spectrum of organo-bentonite there is an increase in the absorption bands in the region of 2672-3254 cm^{-1} and 1555-1620 cm^{-1}, associated with asymmetric stretching and deformation vibrations, which form a covalent bond with aprotic centers of the surfaces of aluminosilicate sorbents by the donor-acceptor mechanism. The absorption bands of 2800-3000 cm^{-1} belong to the asymmetric and symmetric valence vibrations of the CH_2 group of the adsorbed surfactant.

An important role in the analysis of polymers is played by structurally sensitive bands in the IR spectra, which are excellent importance in establishing the “structure-property” relationship.

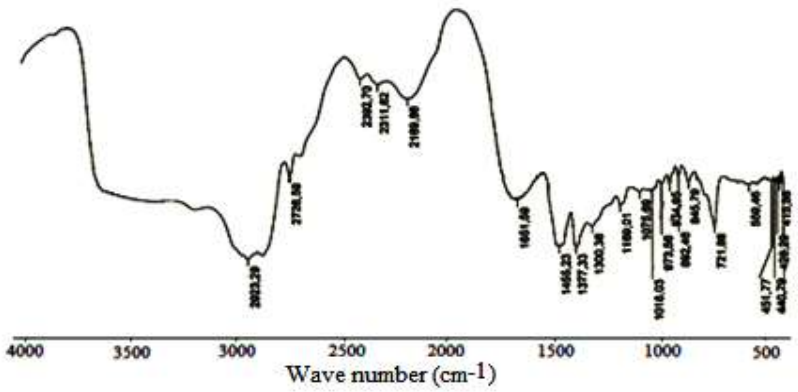

Fig. 5. IR spectrum of polyvinylpyrrolidone/organo-bentonite nanocomposite

Comparing the IR spectra of the initial polymer (Fig. 4) with the IR spectrum of the obtained composite (Fig. 5) makes it possible to reveal appearance of new absorption bands. It can be seen that the IR spectrum of the studied polymer systems contains several

characteristic bands; these are stretching vibrations of the OH group in the range O-H = 3400-3415 cm^{-1} and stretching vibrations of the aliphatic CH group 2041, 2955 cm^{-1}.

Thus, on the basis of the studies, the optimal condition for obtaining a nanocomposite at a temperature of 125^0C and a holding time of 72 hours was found. In the course of the research, the experimentally obtained (organoclay, nanocomposite) samples were studied by physicochemical methods. Also, explorations were conducted to study sorption properties of the obtained nanocomposite. The study into sorption properties of the obtained product was carried out under static conditions using model aqueous solutions of metal salts such as lead, molybdenum, tungsten with a concentration of 1 g/l. Results obtained made it possible to establish that nanocomposites based on polymer and organo-bentonite can be used in the process of heavy metal ion extraction from model aqueous solutions (in this case, from wastewater). More details of the studies will be reported in future work.

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ÜZVİ BENTONİT ƏSASINDA NANOKOMPOZİTLƏRİN SİNTEZİ VƏ FİZİKİ-KİMYƏVİ TƏDQİQİ

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Hidrotermal üsulla üzvi gil və sintetik polimer polivinilpirrolidon əsaslı nanokompozitin alınması istiqamətində bir sıra təcrübələr aparılmışdır. Üzvi gil kimi oktadesilaminasetatla işlənmiş bentonit istifadə edilmişdir. Alınan nümunələr rentgenoqrafik və İQ spektroskopik analiz üsulları ilə tədqiq edilmişdir. Müəyyən edilmişdir, ki nümunələr həm də adsorbent kimi istifadə edilə biləllər.

Açar sözlər: *bentonit, polimer, hidrotermal sintez, nanokompozit.*

СИНТЕЗ И ФИЗИКО-ХИМИЧЕСКОЕ ИССЛЕДОВАНИЕ НАНОКОМПОЗИТОВ НА ОСНОВЕ ОРГАНОБЕНТОНИТА

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Была проведена серия экспериментов по получению нанокомпозита на основе органоглины и синтетического полимера поливинилпирролидона гидротермальным способом. В качестве органоглины был использован бентонит, обработанный октадециламинацетатом. Полученные образцы исследовали методами рентгеновского и ИК-спектроскопического анализа. Было установлено, что образцы также могут быть использованы в качестве адсорбентов.
***Ключевые слова**: бентонит, полимер, гидротермальный синтез, нанокомпозит.*