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The Influence of the Addition of Polymers on the Physico-Chemical Properties of Bentonite Suspensions

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Abstract:

Bentonite clays have many applications in industries ranging from construction to cosmetics. Addition of polymers can profoundly influence the properties of bentonite suspensions and we now describe the influence of a range of different polymers. Whereas polyvinyl pyrolidone and soy isolate only slightly influenced the pH and the electrical conductivity of bentonite polymers in suspension, Carbopol solution caused decreases in both pH and electrical conductivity. As expected, strong electrolytes like sodium chloride caused big changes in the electrical conductivity of the suspensions. When the temperature of the bentonite suspensions was increased, the pH was almost unchanged, but the electrical conductivity increased. Bentonite treated with polymer suspensions can be used in purifying polluted water; for example, our results suggest that high pH caused by phosphorous salts can be addressed using bentonite modified with Carbopol.

Keywords: *Bentonite, Carbopol, k30, Purine.*

1. Introduction

Bentonite is a remarkable material, with wide-ranging applications in the geochemical, building and pharmaceutical industries. Clay minerals, including bentonite, are key components in the formulation of ceramics, cements and modeling sand. They are also used as fillers and thixotropic agents in dyes, lubricants, adhesives, pharmaceutical products and many other dispersive systems. Bentonite has applications in the cosmetic industry as an agent for firming, in products like shampoos, calamine lotions, facial creams and lipsticks. It makes them homogenous and moisturizing, without leaving fatty deposits. This is possible because of the strong colloidal properties of bentonite [1, 2]. Sodium bentonite is able to absorb several times its own mass in water. For this reason, it is an important component of anti-diarrheal preparations and is also used in the production of oils, creams and toothpastes. It has application in the identification and isolation of vitamins, enzymes and crystals as disintegrators [3]. For example, an improvement of polyribosome preparation was achieved using RNAase inhibitors (bentonite, polyvinyl pyrrolidone). Bentonite improves the

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polyribosome profile by removing unwanted proteins, although non-specific adsorptive properties results in low yields of polyribosomes [4]. The negatively charged surface of bentonite particles attracts impurities in wine, and bentonite is used to remove proteins and tannins.

Bentonites are clays made by degradation of volcanic tuffs (that is, rock composed of consolidated volcanic ash) and they contain above 70% of the mineral montmorillonite. Montmorillonite has the chemical formula sodium calcium aluminium magnesium silicate hydroxide $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2{\cdot}nH_2O$. Other cations, including potassium and iron may substitute. In montmorillonite, layers consisting of $[SiO_4]$-tetrahedrons enclose layers of octahedra with the formula $[M(O_5, OH)]$, where M is usually Al or Mg, but Fe is also often found. The silicate layers have a slight negative charge that is compensated by exchangeable ions in the intercrystallite region. The charge is so weak that the cations (in the natural bentonite, predominantly Ca^{2+}, Mg^{2+} or Na^+ ions) can be adsorbed in this region with their hydrate shells [1].

Aggregation of clay particles in different conditions of temperature, pH and electrolyte concentration lead to variations in the characteristics of bentonite suspensions. These changes can compromise the industrial use of bentonite suspensions, which need to be very homogeneous if they are to be effective in petroleum drilling, civil engineering (underground constructions, geosynthetic clay liners for waste disposal management, nuclear waste barrier), catalysis, environmental remediation and animal feed [5, 6]. Homogeneity is normally achieved by the addition of polymers or other substances capable of stabilizing clay particles and preventing aggregation [7].

The aim of this work was to prepare surfactant-modified clay and to investigate the effect of surfactants on the electrokinetic properties, especially electrical conductivity and pH of the clay. Surfactant modification of clays has been used to improve their properties and gives those significant hydrophobic characteristics and higher organic content for the adsorption of toxicants through partitioning [8]. In this study, three different surfactants (Carbopol, k30 polivinylpirrolidone, and soybeans isolate - purine) were used to modify the properties of clay and their electrokinetic properties were investigated. The inhibition of swelling of the clay by amphoteric water-soluble cellulosic polymers has previously been studied, using similar preparations of cationic polymers and bentonite in different ratios. Four different cationic polymers were used in the investigation which varied in type, cation density and molecular weight. It was shown that clay-polystyrene complexes had a similar uptake of toluene (model system) and their association with toluene is of similar stability as complexes of the clay with a double-chain alkyl ammonium cation. Polymers prepared as amphoteric, water-soluble cellulose derivatives suppress the swelling of bentonite and it was found that their inhibitive effect depends on the degree of quaternization, the molecular conformation and the type of counterions [9, 10].

2. Experimental

The polymers used in these experiments were: polyvinyl pyrolidone (k30) (BASF/Germany), carbomers (Carbopol®) (The Lubrizol Corporation), purine (soy isolate with more than 90% protein) (The Solae Company/Producer of Soy Protein/France).

2.1. Preparation of bentonite suspensions

Bentonite (montmorillonite clay of the first quality with Ca^{2+} and Na^+ as the principal cations) was sourced from Minerali. Co. (The clay came from Vranjska banja, a spa in the southeast region of Serbia where the water temperature in the springs is 78 ^{0}C). Suspensions were made by dispersion of 1 g, 2 g and 5 g of bentonite in 100 mL of water at temperatures of 20 ^{0}C, 40 ^{0}C, 60 ^{0}C and 80 ^{0}C, making a total of 12 suspensions. Modified bentonite was prepared by dispersion of 1 g, 2 g and 5 g in 100 mL of water with 5 mL polyvinyl pyrolidone, soy isolate and Carbopol at temperatures of 20 ^{0}C, 40 ^{0}C, 60 ^{0}C and 80 ^{0}C (together 36 suspensions). The suspensions (all 48) were mixed by stirring for 5 min, using a magnetic stirrer.

2.2. Determination of the chemical compositions of the clay

It was weighted out 1 g of the sample (m_1) and put in a drier at temperature 105 - 110 °C, around 2h. After cooling in a dessicator, it was measured the mass m_2. The content of moisture was determined according to the equation:

% moisture = 100 x $(m_1 - m_2)/ m_1$

Loss of water on ignition was determined by gradual heating (20 °C/ min) of 1 g of the sample (m_1) in the electrical oven to 1000 °C and keeping at this temperature for 1 h. After cooling in a dessicator, it was determined:

Loss of water on ignition = $(m_1 - m_2)/ m_1$

For the determination of chemical composition of bentonite, it was prepared 1 g of dry sample in the mixture of *conc* HF and *conc* HCl. In order to remove HF, thus prepared solution was evaporated several times with HCl and afterwards dry residue was dissolved in 100 cm^3 normal flask with deionized water. Concentration of Fe, Al, Mg, Mn, Ca, K and Na was determined using spectrophotometric method on ICP-OES spectrometer. The Si content was determined gravimetrically [11].

2.3. pH Measurements

pH was measured using a pH-meter (HANNA). Firstly, bentonite suspensions in water were prepared and then polymer solutions made in water were added. Bentonite suspensions were made by intense mixing using a magnetic stirrer over 5 minutes: 1 g, 2 g and 5 g bentonite in 100 mL water at temperatures: 20^{0}C, 40^{0}C, 60^{0}C and 80^{0}C. After homogenization of bentonite in water and pH and electrical conductivity measurements, aqueous solutions of polymers were added with intense mixing using a magnetic stirrer for 5 min. After mixing, the suspensions were allowed to stand for 24 h and the pH and electrical conductivity of the aqueous solution standing above the suspension was measured. The pH of each suspension was measured in the solution immediately above the solid. Measurements were performed at room temperature (~20^{0}C).

Electrical conductivity was measured using a HANNA conductometer.

2.4. Effects of polymers

To determine the effects of various polymers on the properties of the bentonite suspensions, the following polymer solutions replaced water in the experiments above: 1) Carbopol 940 (5 g) in 100 mL water; 2) Polyvinyl pyrolidone k30 (8 g) in 100 mL water; 3) Soy isolate (purine) (5 g) in 100 mL water.

2.5. Effect of electrolyte on the properties of bentonite

The second part of the experiment was the measurement of the influence of added electrolyte (sodium chloride) on the electrical conductivity and pH of bentonite suspensions. Suspensions were obtained by dispersion of different quantities of bentonite in 100 ml of water at 20 ^{0}C, as described above. After pH and electrical conductivity measurements, sodium chloride (2 g) was added into suspensions and measurements were repeated three times.

2.6. Preparation of samples for SEM analysis

Scanning electron microscope JSM-5300 (JEOL, Japan) was used for the investigation of organoclay samples. Preparations of samples were performed by putting organoclay dry samples on a base of alumina using glue. The device used for the spreading of conductive layer on sample surface is JFC-1100 ION SPUTTER (JEOL Co., Japan). The difference of potential of electronic acceleration was 30kV, and magnification of samples was 350, 1500, 2000, 7500, 10000 and 15000 times.

3. Results and Discussion

The bentonite clays investigated came from the Prisjan region of Serbia, close to the border with Bulgaria. The southeast region of Serbia represents the wine-growing region from Roman times.

The chemical compositions of these clays were investigated at The Institute for Mineral and Nuclear Raw Materials, Belgrade. The results of the analysis are shown in Tab. I. As expected, silicate and aluminate dominate the analysis.

Tab. I Results of the analysis of the clay expressed in % of compounds.

Compound	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	SO_3	H_2O (110^{0}C)	H_2O (1100^{0}C)
Percentage/ %	51.82	0.34	26.86	2.30	0.10	1.27	1.44	0.75	2.07	trace	5.56	7.20

Morphological properties of the clay were evaluated by SEM (scanning electron microscopy), JOEL-5300 (JEOL, Japan) (Fig. 1).

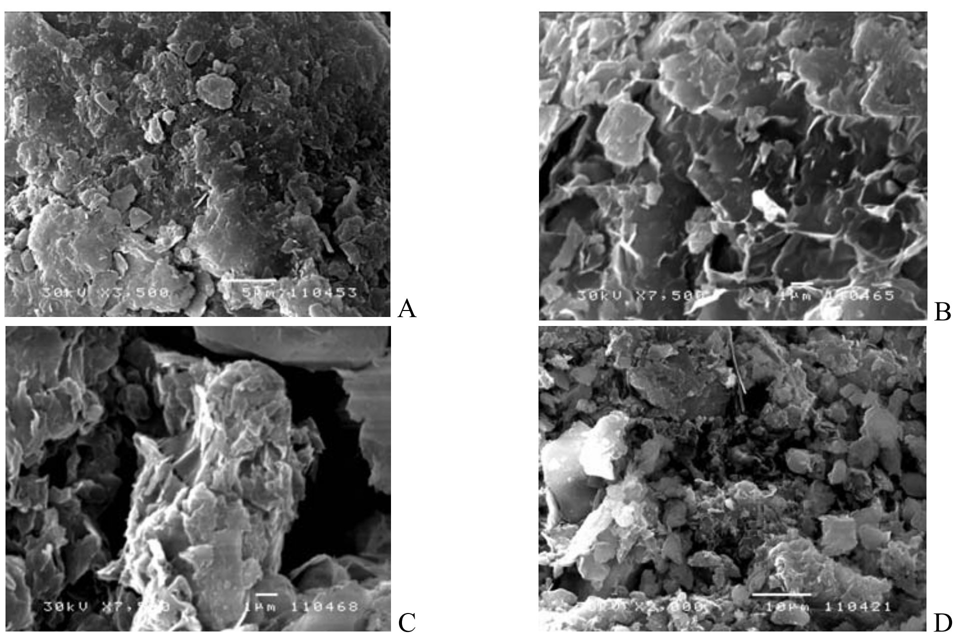


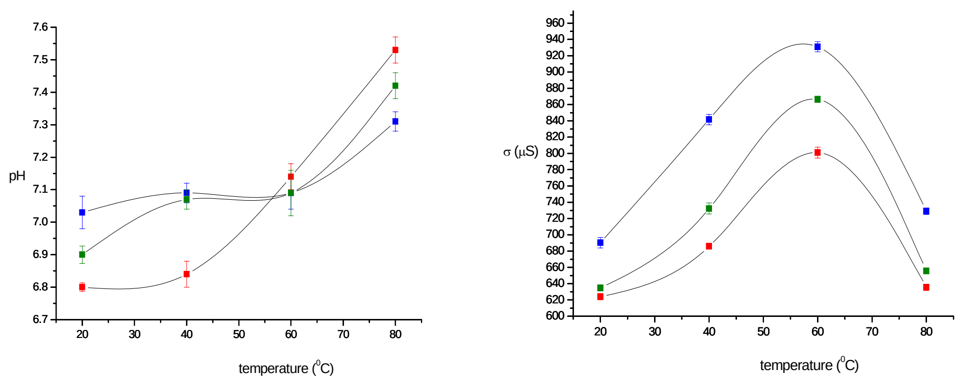
Fig. 1. SEM microscopy of dried samples of bentonite **A** and with **B** Carbopol, **C** polyvinyl pyrolidone, **D** soy isolate.

In order to identify the changes in composite structures, a sample of pure bentonite was first investigated. From the SEM record (Fig. 1A), it can be seen that the clay structure is layered, the particles are small and there is inhomogeneity, the particles having different sizes and shapes and being unevenly distributed.

Upon the modification of clay (Fig. 1B, C and D), the distance between layers increases. This is most readily observed in Fig. 1B. Particle size increases and this results in increased porosity. The polymer molecules insert between the layers of clay resulting in this change in the observed changes in structure.

3.1. Properties of pure bentonite solutions

Fig. 2 shows that for pure bentonite suspensions, the pH value was highest for suspensions of 5 g of bentonite in 100 mL of water at ambient temperature. The pH of this suspension changed very little with increasing temperature of the dispersion, varying quite linearly between 7.03 at 20 ^{0}C and 7.31 at 80 ^{0}C. The less concentrated suspensions (with 1g and 2g bentonite in 100 mL water) showed more complex behavior, over a wider pH range. The 1 g in 100 ml suspension showed a pH variation from 6.8 at 20 ^{0}C to 7.53 at 80 ^{0}C. At all concentrations of bentonite, the electrical conductivity increased with temperature from 20 ^{0}C, reaching a maximum at 60 ^{0}C and then falling sharply. The most concentrated suspension (5 g in 100 mL) showed higher conductivity at all temperatures (Fig. 2).



a) b)

Fig. 2. Dependance of a) pH and b) electrical conductivity of aqueous suspensions of 1g■, 2g■ and 5g■ of bentonite on different temperatures of dispersion.

On the basis of pH measurement, it can be concluded that montimorillonite from Vranjska banja is slightly alkaline. Electrical conductivity depends on concentration of ions in solutions, their ability to dissociate, their charges and their speed of diffusion. It means that in the temperature region 60-80 ^{0}C, the bentonite becomes more soluble.

Fig. 3 shows that the addition of polyvinyl pyrolidone and soya isolate made quite small differences to the pH and electrical conductivity characteristics of bentonite. In particular, the temperature dependence of electrical conductivity was retained, and the pH remained close to neutral.

Fig. 4, however, shows that the addition of Carbopol has a more profound effect on characteristics of the suspension. The pH falls by nearly 3 units and the electrical conductivity by approximately 250 units, although the characteristic maximum at 60 ^{0}C remains. Carbopol forms acidic solutions (pH around 3) and in the combination with almost neutral bentonite gives acidic solutions. Carbopol has a tendency to form gels, increasing the viscosity of solutions and decreasing the concentration of ions thus causing a decrease in electrical conductivity. At 60 ^{0}C, equilibrium of the system was achieved.

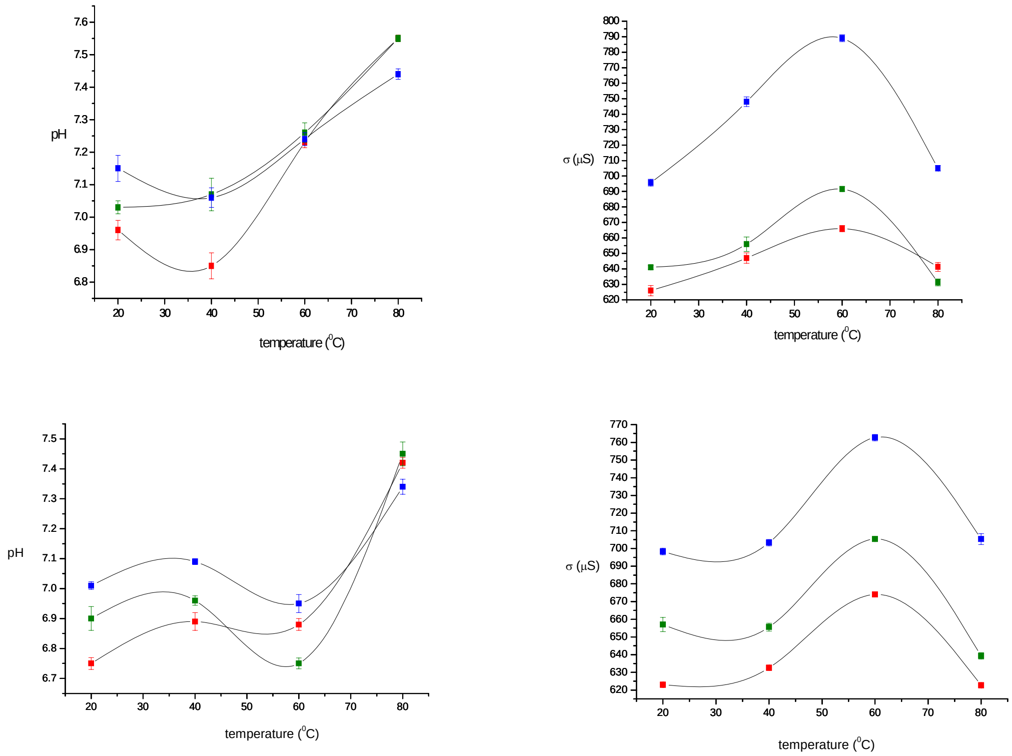


Fig. 3. Dependence of pH and electrical conductivity with temperature of aqueous suspensions of 1g, 2g and 5g of bentonite in the presence of (top) polyvinyl pyrolidone (5 ml solution) And (bottom) soya isolate (5 mL).

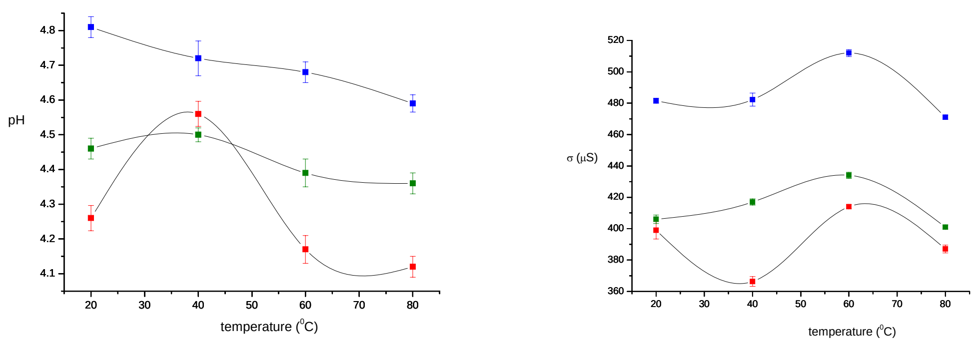


Fig. 4. Dependance of pH a) and electrical conductivity b) of aqueous suspensions of 1g, 2g and 5g (Carbopol solution was added) of bentonite on different temperatures of dispersion (5 mL).

Mixtures of bentonite and sodium chloride were prepared by keeping the sodium chloride concentration constant and adding different amounts of bentonite. The sodium chloride solutions showed small changes in pH in response to different amounts of bentonite, with the pH reaching a maximum when 5 g bentonite was added to 2 g sodium chloride. The electrical conductivity of sodium chloride solution is, as expected, high compared with the conductivity of bentonite suspensions. Bentonite reduced the conductivity of the sodium chloride solutions in a non-linear fashion.

Tab. II pH and electrical conductivity of aqueous suspensions of pure bentonite and with the addition of 2g of NaCl on room temperature of dispersion (~20^{0}C).

The content of bentonite	1g			2g			3g			4g			5g			6g			8g			10g		
	7.01	7.02	7.05	7.12	7.09	7.11	7.14	7.21	7.18	7.22	7.17	7.21	7.21	7.26	7.23	7.22	7.20	7.22	7.26	7.29	7.27	7.32	7.27	7.29
pH	7.03±0.02			7.1±1.1			7.18±0.02			7.20±0.02			7.23±0.02			7.21±0.01			7.27±0.01			7.29±0.01		
	7.17	7.15	7.21	7.26	7.24	7.29	7.26	7.27	7.25	7.41	7.38	7.42	7.45	7.47	7.48	7.43	7.45	7.48	7.39	7.40	7.35	7.39	7.42	7.45
pH (NaCl)	7.18±0.02			7.27±0.02			7.26±0.01			7.40±0.02			7.47±0.01			7.45±0.02			7.38±0.02			7.42±0.02		
	596	599	586	599	603	598	621	622	626	631	637	629	643	638	645	666	674	669	725	722	724	743	745	732
σ (μS)	593,3±5.1			600±2.0			623±2.0			632.3±3.1			642±2.7			669,7±2.9			723.7±1.1			739±4.1		
	25221	25201	25189	25410	25415	25382	22608	22605	22592	21809	21802	21788	21622	21635	21573	21120	21112	21084	19123	19118	19081	12060	11955	11988
σ (μS) (NaCl)	25203±11.5			25402±13.5			22601±6.4			21800±.7.8			21610±24.0			21105±14.2			19107±17.5			12001±39.3		

Solutions of bentonite can have application in fermentation processes, the processes of clarification and stabilization of wine and juices [12, 13], bioremediation processes [14] as well. However, the effect of the addition of polymers (Carbopol, polyvinyl pyrolidone, soy isolate) on these processes has not been investigated.

Our results suggest different applications for the different polymer-bentonite mixtures. Neutral bentonite suspensions are useful in the removal of organic compounds and phosphate from water [15]. The addition of either the natural polymer soy isolate purine or the synthetic polyvinyl pyrolidone improves the properties causing emulsification (soy isolate) or decreasing ionic strength (polyvinyl pyrolidone) by binding to the bentonite surface making it less polar without significantly affecting the pH. Similarly, Carbopol modification can be used for purifying polluted solutions showing high pH values (for example the presence of phosphorous in waste waters).

In order to explain the influence of pH causing visible changes of bentonite structure on molecular level, we can use the investigations performed in case with high bentonite concentration and low electrolyte content. It was found that the plates in bentonite can bend depending of their relative position and relative size of their surfaces, as well as the potentials on their edges. When edges are positive, plates getting bent towards the negative face. When edges are negative, the plates are orientated parallel with one another [16].

It was shown that the clay and the polymer interactions are driven by entropy (condition for the spontaneous process) and it can be said that following interactions are possible between clay and polymer: 1) ion-dipole; 2) hydrogen bonding and 3) van der Waals interactions [17]. Ion-dipole interactions are characteristic for interaction between the charged species, in this case the polar surface of bentonite and polymer.

4. Conclusions

Properties of bentonite suspensions can be changed upon the addition of polymers. Values of pH and electrical conductivity of pure suspensions were increased with increasing of bentonite concentrations. It was noticed that the addition of two polymers into suspensions – k30 and soy isolate only slightly influenced the changes in pH and the electrical conductivity. Addition of Carbopol solution caused decreses in pH and in electrical conductivity. As expected, strong electrolytes like sodium chloride caused big changes in values of the electrical conductivity of the suspensions. Experiments show that pH remained almost unchanged and electrical conductivity was higher when the temperature was increased.

The influence of the acid polymer-Carbopol and the neutral polymers, soy isolate and polyvinyl pyrolidone, on pH and electrical conductivity of bentonite solutions has not previously been investigated. The addition of soy isolate-purine causes emulsification and polyvinyl pyrolidone decreases the ionic strength by binding to the bentonite surface making it less polar with significant influence on pH. We propose the use of Carbopol modification for the treatment of polluted solutions with higher pH (e.g. the presence of phosphorous in waste waters). The neutral polymers improve the physical properties of bentonite solutions and they may prove to be of interest in fermentation and bioremediation processes.

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Садржај: *Бентонитне глине имају велику примену у индустрији, од грађевинарства до козметике. Додатак полимера може доста да утиче на особине бентонитних суспензија, и у овом раду ми дајемо опис утицаја низа различитих полимера. Док поливинил пиролидон и изолат соје само незнатно утичу на pH и електричну проводљивост бентонитних полимера у суспензији, раствор Карбопола узрокује смањење како pH, тако и електричне проводљивости. Као што се и очекује, јаки електролити као натријум хлорид узрокују велике промене у електричној проводљивости суспензија. Када је температура бентонитне суспензије била повећана, pH се готово није ни променио, али се вредност електричне проводљивости увећала. Бентонит третиран суспензијама полимера се може користити у пречишћавању отпадних вода; на пример, наши резултати сугеришу да се висока pH вредност узрокована фосфатима може неутралисати коришћењем бентонита модификованог Карбополом.*
Кључне речи*: бентонит, карбопол.*