Anionic Polymer - Cationic Surfactant Complex Used in the Coagulation and Flocculation Processes

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The removal of kaolin fine particles from water by precipitation with polyelectrolyte and surfactant complex of polyacrylamide and hexadecyl trimethyl ammonium bromide (HTAB) was experimentally studied. The experiments have been carried out with a complex solution having the surfactants concentration higher than the critical aggregation concentration - cac, and the amount added corresponded to the potential ζ equal with zero. By using video microscopy and image analysis method, the kinetics of the flocculation process has been studied. The results showed the optimal duration of the flocks to be formed. The sedimentation velocity of the flocks, the sludge volume as well as the initial and final turbidity of the suspension samples has been measured. The efficiency of the process when the complex reactant was used as coagulant is compared with that obtained in same conditions in which only Praestol 2515 polyelectrolyte was used. The experimental results show that both coagulants fulfill the standard turbidity conditions for drinking water. In both cases, the separation efficiency and the sludge volume are the same. The coagulant doses showed a significant reduction when the complex is used as coagulant. In comparison with the case when only the Praestol 2515 was used, the polymer-surfactant complex formed large flocks, greater sedimentation rate and shortened flocculation duration.

Keywords: kaolin, polyacrylamide, hexadecyl trimethyl ammonium bromide (HTAB)

The coagulation-flocculation process is an important part of surface water treatment. It has an impact on the reliability of operation and water quality. Coagulation-flocculation process is influenced by raw water physical, chemical and bacteriological parameters, treatment device structures, as well as coagulant types and dosages.

Colloids of water are very fine particles, typically ranging from 10 nm to 10 μm. There are two types of colloids: hydrophilic colloids which are unstable and hydrophilic colloids that are stable. Generally, the solid particles from surface water have negative electrical charges, are unstable and can be easily destabilized. The magnitude of the zeta potential ζ is usually used to indicate colloidal particle stability.

Coagulation is the destabilization of colloidal particles by the addition of a chemical reagent. The optimum dosage of coagulant corresponds to ζ which is near zero. A further increase in coagulant dose will cause restabilization of the particles due to charge reversal on the colloids [1]. The control of *p*H is an essential aspect of coagulation and flock formation and an optimum pH exists for each system [2]. Coagulation can be accomplished through any of following mechanisms [3, 16]:

-the mechanism of double-layer compression relying on compressing the diffuse layer surrounding a colloid when an electrolyte is added and so the ζ decreases,

-the mechanism of adsorption and charge neutralization: coagulants with an opposite charge are used, they are adsorbed on the colloidal particles and neutralize surface charge;

-the mechanism of enmeshment by a precipitate consisting in adding of chemical compounds which precipitate and physically entrap the suspended colloidal particles as they settle;

-the mechanism of inter-particle bridging: synthetic polymeric compounds having large molecular sizes and multiple electrical charges along the molecular chain of carbon atoms are applied.

Flocculation is the agglomeration of destabilized particles.There are three major mechanisms of flocculation [4, 12-15]:

-perikinetic flocculation is the aggregation of particles caused by random Brownian motion and it occurs when the most particles are less than 1 μm in diameter;

-orthokinetic flocculation is the aggregation of particles caused by induced energy in the fluid and it occurs when both particles are larger than 1 μm in diameter and similar in size;

-differential settling is caused by different settling velocities of particles and it occurs when at least one of the particles is larger than 10 μm in diameter and the other is significantly different in size [5].

When the polymer is used as coagulation-flocculation agent, the major mechanism includes both adsorption and inter-particle bridging [6]. The adsorption process is accomplished by transport of particles close to the polymer chain, collision between particles and polymer and adhesion. Collision and adhesion are fast reaction processes, and the transport process governs the rate of polymer adsorption. As follows, the orthokinetic flocculation is the dominant mechanism in polymer flocculation with mixing input. The rate of particle transport is dependent on the mixing intensity, as mixing has an impact on both the length of the segment of the polymer chain and the conformation of the long chain polymer. Mixing determines chemical dispersion rate, the kinetics and degree of flocculation and flock size distributions. Higher mixing promotes flock formation, but it may also break up the flock.

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The use of polymers in coagulation – flocculation process increases the rate of flocculation, produce larger and denser flock that settles faster and strengthen the flock which improve mechanical separation. Synthetic water soluble polyacrylamide polymers or polyacrylamide copolymers are preferred to use in coagulation – flocculation process due to their availability, environmental properties, as well as their acceptable price [1, 7]. Cationic polymers can be effective in coagulating negatively charged particles; they do not require a large molecular weight to be effective in destabilization. Electrostatic forces or ion exchange is the process by which the polymers become attached to the surface particles. Anionic polymers of large molecular weight or size are able to bridge the energy barrier between two negatively charged particles, thereby effectively enhancing the coagulation efficiency. Generally speaking, anionic polymers can only assist in the physical process of flocculation.

In the last ten years, it was showed that it is possible to obtain polymer-surfactant complexes with certain properties for different applications, such as surface modification of disperse systems, sorption of organic molecules from wastewater or uses them as flocculants [8]. The physical models of polymer and polymer – surfactant complex adsorption on the solid surfaces sketched in figure 1 suggest that in the case of complex, the coagulant dose is reduced significantly. The paper [9] reports the experimentally results of using complexes to remove the dyes and colloids from surface water and concludes that the most important advantages of their using in water treatment were the high sedimentation velocity and a very broad range of the optimum flocculation concentration similar conclusions were drawn in [10-11, 17-23].

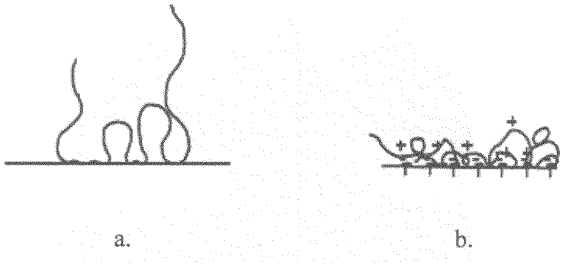

Fig. 1. Physical model of polymer (a) and polymer-surfactant complex (b) adsorption on the solid charged surface

In the present paper are presented the results of the kaolin fine particles removal from a synthetic aqueous colloidal suspension by coagulation – flocculation process with a complex formed between a weak anionic polyelectrolyte and a medium cationic surfactant. For this purpose, the results of a study on this complex formation and their properties, presented in a previous paper [24], were used. The efficiency of the coagulation-flocculation with complex agent is compared with that obtained in same conditions in which only Praestol 2515 polyelectrolyte was used, in order to put in evidence the advantages of polyelectrolyte – surfactant complex. The subject treated in this paper represents one of the constant concerns to improve the performances of waste water treatment installations [25-31].

Experimental part

In the experimental investigation the coagulation of dispersed kaolin particles in tap water was studied. As coagulant-flocculant was used a complex formed between a weak anionic polyelectrolyte consisting in a copolymer of acrylamide and sodium acrylate polyacrylamide, marketed under the name Praestol 2515 produced by Evonik - Degussa and hexadecyl trimethyl ammonium bromide, HTAB, purchased from Aldrich Chemical Co, as medium cationic surfactant. The complex properties were studied in a previous paper [24]. The experiments have been carried out with complexes having the surfactants concentration higher than the critical aggregation concentration, c_{ac} and the optimum dose was considered to be those that achieved a ζ potential of approximately zero.

A Flocculator SW5 manufactured by Stuard Scientific, Staffordshire, United Kingdom is used to perform the coagulation-flocculation process. The experimental parameters are listed in the table 1. An experiment was conducted as follows: first, the kaolin particles are added and dispersed by blade stirrer for 5 min, then the complex solution and calcium oxide suspension was added and the flock formation can be quickly observed and 10 min later a stationary flock size distribution appears. The process is conducted in two stages: dispersion stage (3 min) and maturation stage (7 min).

Table 1
EXPERIMENTAL PARAMETERS

Perikinetic stirrer Reynolds number	6250
Orthokinetic stirrer Reynolds number	1260
Kaolin concentration	0,1 g/l
Suspension volume	1 l
pH	11.5

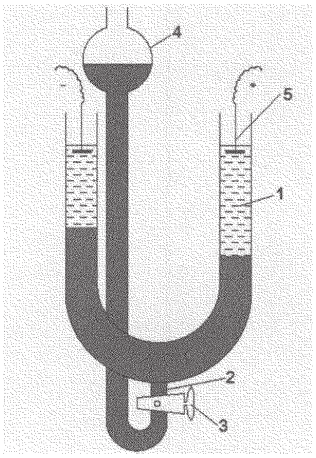

Fig. 2. Burton device, 1. U-shaped graded glass tube, 2. feeding tube, 3. tap, 4. funnel, 5. platinum electrodes

The zeta potential was measured with the Burton device presented in figure 2 whose electrical scheme is detailed in figure 3. The device was manufactured in order to perform this research. The device measures electrophoretic mobility of kaolin particles and the zeta potential is calculated with relation (1):

$$\zeta = 9 \cdot 10^4 \cdot \frac{4 \cdot \pi}{81} \cdot \frac{x}{t} \cdot \frac{L}{E} \qquad (1)$$

where:

x – suspension interface displacement within the branches of Burton device, m;

t - length of time corresponding to x, s;

E - potential, V;

L- distance between the electrodes, m,

ζ - zeta potential, V.

The alkaline *p*H necessary to achieve optimal coagulation conditions was obtained by adding calcium

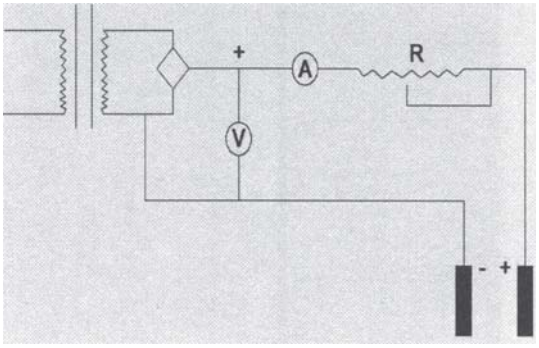

Fig. 3. The electrical scheme of the experimental installation for zeta potential measurement.

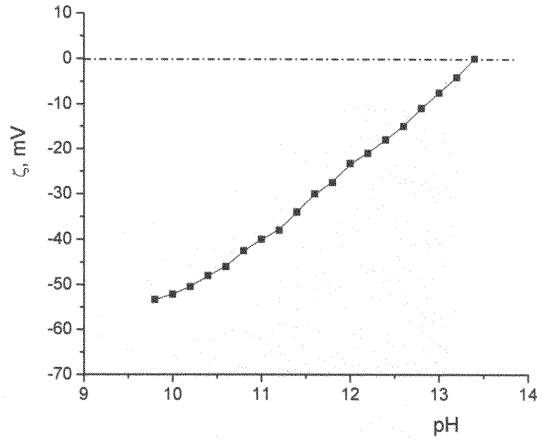

Fig. 4. Dependence of zeta potential of kaolin suspension on the *p*H

oxide, purchased by Merck. The *p*H was measured with a Fisher Scientific Accumet 25 pH meter. The pH meter was calibrated using *p*H = 4, *p*H = 7 and *p*H = 10 standard buffer solutions provided by Fisher Scientific. Calibration was performed on a daily basis.

A microscopic image technique has been used to study the flocculation kinetic [32]. Samples of suspension are drawn from flocculator by the aid of a pipette and put on a microscope slide. The flocks' pictures from the eyepiece microscope were taken with Canon G9 digital camera. The microscope was Motic AE 30/31 Inverted Microscope produsedby GMI, Inc. Ramsey, Minnesota, USA.

The flocks were measured with Sigma Scan Pro5 trial version software. This procedure provided a convenient means of gathering data to calculate flocks size distribution. Once the size distribution was calculated, the flocks growth and flocks size change in the aggregation process could be analyzed.

It was also measured the sedimentation rate and the sludge volume using the Imhoff cones, as a standard method for this category of measurement [17-18].

The turbidity of the kaolin suspension samples was determined using a Spectrofotometer UV-VIS Cintra 5, produced by Dandenong, Australia**.** The device was calibrated using manufacturer supplied formazin suspension standards prior to the measurement and between each measurement, as suggested by the supplier. The initial and final water turbidity ratio was the main criteria for establishing the coagulant efficiency.

Dynamic light scattering have been applied to measure the initial particle size distribution of kaolin in aqueous suspension by Mastersizer 2000 from Malvern Instruments Ltd, Worcestershire, U. K.

Results and discussion

The zeta potential of kaolin aqueous suspension was about -60mV meaning that the particles are negatively charged. The diagram of kaolin – tap water zeta potential at different *p*H is presented in figure 4. The results show that kaolin is one of the few hydrophobic particles whose surfaces are loaded with positive charges counterions. The coagulant concentrations in kaolin suspension corresponding to ζ equal to zero, c_ζ, were determined with Burton device and the results are shown in figure 5. One may notice that c_ζ for the Praestol 2515 is equal to 1×10^{-3} % while the Praestol 2515 – HTAB complex has this concentration of 2×10^{-6} % meaning a significant reduction in consumption if the complex is used as coagulant. The physical model from Figure 1 anticipated this result. This confirms the results reported in [23] that shown that the higher the charge of the complex, the lower the necessary amount for colloid destabilization.

The kaolin particles had a d(50) diameter of about 3.0 μm with a relatively narrow size distribution as showed the distribution curve from figure 6.

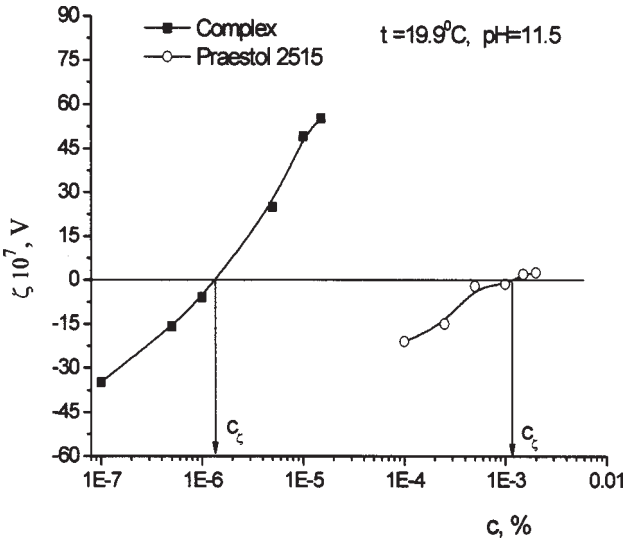

Fig. 5. Dependence of zeta potential of kaolin suspension on the coagulant concentration.

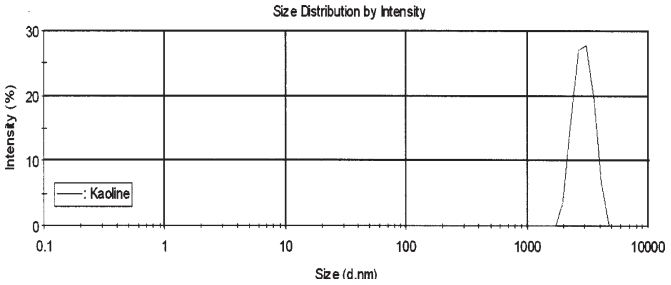

Fig. 6. Particle size distribution of initial kaolin suspension.

The microscopic image technique used to study the kinetic of the coagulation – flocculation process provides evolution with increasing time of the flocks' size distribution curves. The distribution curves with long tails towards large diameters from figures 7 show that the association and the aggregation were the main mechanism for flock's growth. The mode of the flocks' size distribution curves, defined as the value that occurs the most frequently in a data set or a probability distribution, decreases in time and the corresponding value of diameter remains practically constant until the end of the process. This indicates that almost all particles were destabilized and formed into flocks during the first minute of fast mixing period. This means that, the duration of coagulation is extremely short.

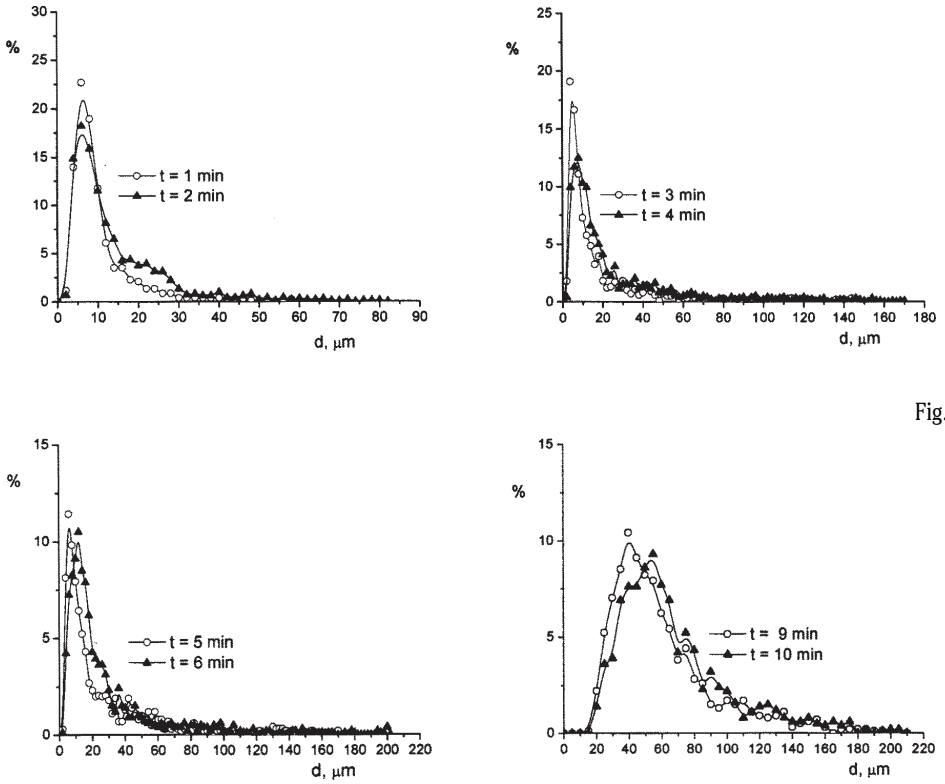

Fig. 7. Curves of flocks size distribution with Praestol 2515 and HTAB complex as coagulant-flocculant at optimal dosage

It could be seen on the photos from figure 8 that after 30 seconds the particles had been attached to the complex chains and between them occurred bridges and so the flocks growth. Consequently, the shape of the flocks was more filamentous than spherical, as shown in figures 8. The average shape factor, measured experimentally, is presented in figure 9. The shape factor is defined, in this case, as the quotient of the area of a sphere equivalent to the volume of a solid flock divided by the actual surface of the flock. The average value around 0.4 confirms the experimental observations. The photos from figure 8 highlight that the destabilization of the colloids appears by adsorption and charge neutralization mechanism too and by inter-particle bridging mechanism.

The growth of flocks' average diameter in time is shown in figure 10. In comparison with the case when only the Praestol 2515 was used, the polymer-surfactant complex formed large flocks and shortened flocculation time. The flocks quickly grew within 2 min of fast mixing. After 2 min, the average diameter of the flocks began to level off and this stage was completed. In the second stage, the average diameter tended to level off after 6 min when the maturation stage was ended.

As it is well known, an efficient flocculant produces flocks with a maximum sedimentation rate and a minimum sludge volume. The experimental results presented in the diagrams from figures 11 and 12 show the performances, from this point of view, of the Praestol 2515 and of the complex proposed by us. As seen, the maximum sedimentation velocity, respectively the

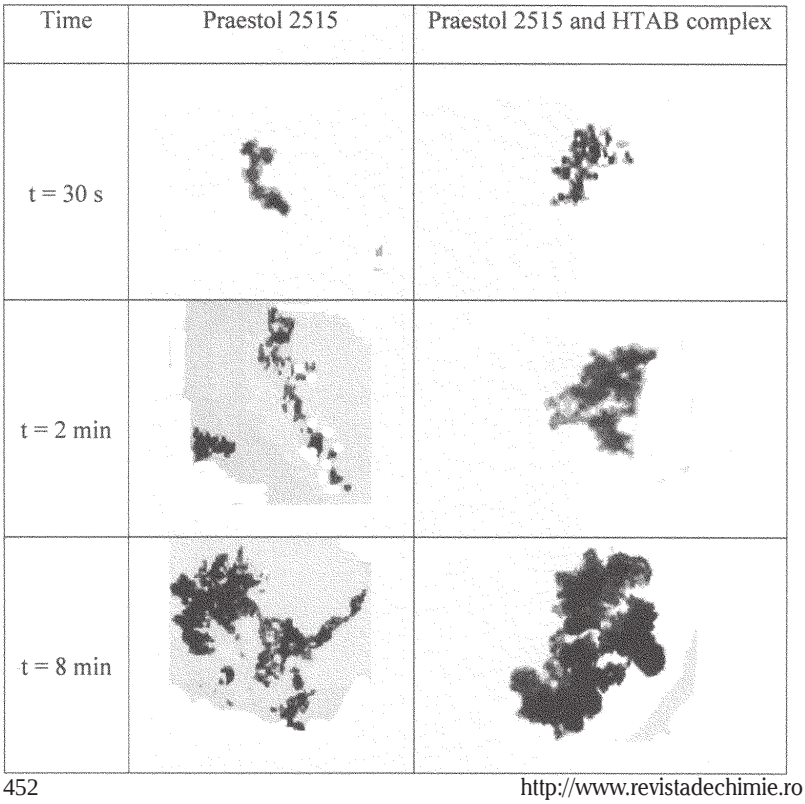

Fig. 8. Images of the flocks obtained at optimal dosage of coagulant.

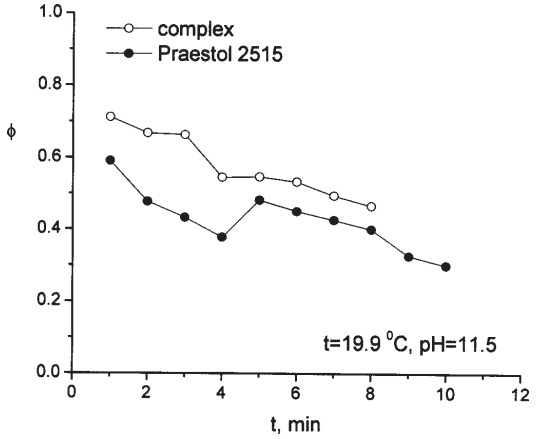

Fig. 9. Comparison of the medium shape factor of flocks produced with: Praestol 2515 and Praestol 2515 and HTAB complex.

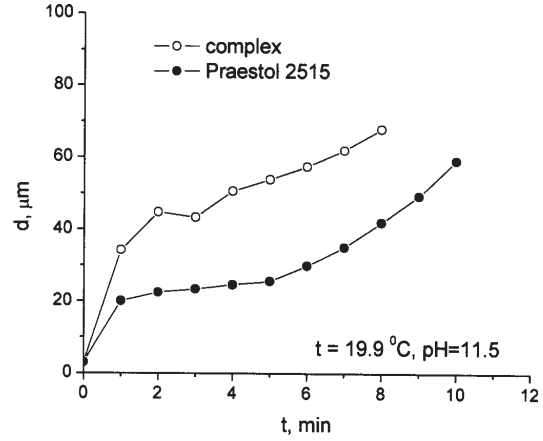

Fig. 10. Comparison of the flocculation kinetics of kaolin particles by: Praestol 2515 and Praestol 2515 and HTAB complex.

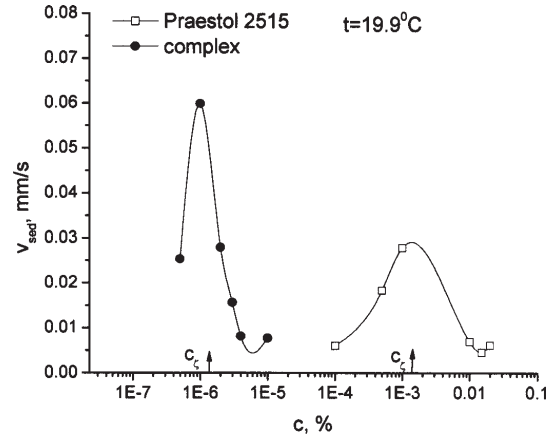

Fig. 11. Dependence of global sedimentation velocity of flocks formed with Praestol 2515 and Praestol 2515 and HTAB complex on the coagulant concentration

minimum volume of sludge obtained in both cases to c_ζ. The flocks' sedimentation velocity formed with complex coagulant – flocculant is greater than corresponding velocity of flocks obtained with Praestol 2515. This result is in good agreement with experimental data presented in figure 10.

The separation efficiency of the kaolin from suspension is analyzed in figure 13 in terms of initial and final turbidity ratio, c_i/c_f. As can be seen, for both coagulants is obtained the same efficiency at c_ζ.

Conclusions

In this paper are presented the results of the kaolin fine particles removal from a synthetic aqueous colloidal

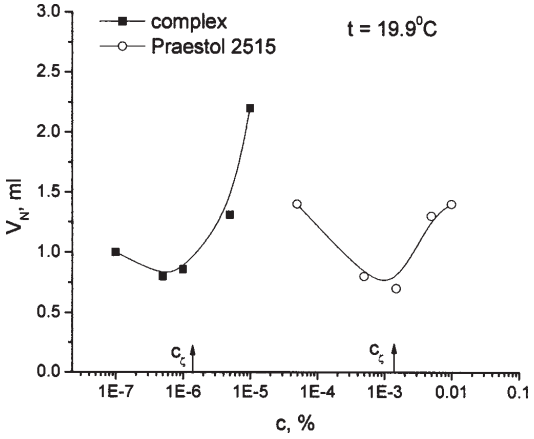

Fig. 12. Dependence of the sludge volume on the coagulant concentration

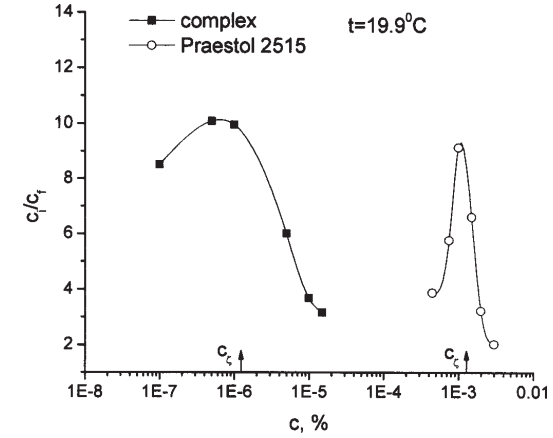

Fig. 13. Dependence of separation efficiency on the coagulant concentration

suspension by coagulation – flocculation process with a complex formed between a weak anionic polyelectrolyte Praestol 2515 and a medium cationic surfactant HTAB. The efficiency of the coagulation-flocculation with complex agent is compared with that obtained in the same conditions in which only Praestol 2515 polyelectrolyte was used, in order to put in evidence the advantages of polyelectrolyte – surfactant complex. The experiments have been carried out with complexes having the surfactants concentration higher than the critical aggregation concentration, c_{ac} and the optimum dose was considered to be those that achieved a ζ potential of approximately zero. The process is conducted in two stages: dispersion stage (3 min) and maturation stage (7 min).

The zeta potential was measured with the Burton device that was manufactured especially for this research. The alkaline *p*H necessary to achieve optimal coagulation conditions was obtained by adding calcium oxide. A microscopic image technique has been used to study the flocculation kinetic. The sedimentation rate of flocks and the sludge volume were measured with the Imhoff cones. The initial and final water turbidity ratio was the main criteria for establishing the coagulant efficiency.

The both coagulants fulfill the standard turbidity conditions for drinking water and have the same efficiency in studied case. The optimal dose corresponding to c_ζ showed a significant reduction in consumption if the complex is used as coagulant. In comparison with the case when only the Praestol 2515 was used, the polymer-surfactant complex formed large flocks and shortened flocculation time.

The experimental results show that the flocks obtained with complex coagulant have higher sedimentation rate and produced less sludge than the flocks from system with Praestol 2515 coagulant. As seen, the maximum sedimentation velocity and the minimum volume of sludge are obtained, in both cases, when the coagulant dose corresponds to c_ζ.

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