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# PERFORMANCE EVALUATION OF ANIONIC POLYMER-CATIONIC SURFACTANT COMPLEX COAGULANTS IN WATER TREATMENT

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## Abstract

The performance of some complex coagulants derived from weak and medium anionic polymers and medium cationic surfactant in coagulation-flocculation process for water treatment was experimentally investigated by carrying out kinetic studies and by determining the optimum coagulant dose. The complex coagulants were prepared from weak anionic and medium anionic copolymers of acrylamide and sodium acrylate with the commercial names Praestol 2515 and Praestol 2540, and medium cationic surfactant derived from triethanolamine with the commercial name Tetranyl AT-7590. The coagulation-flocculation process was studied for suspensions of kaolin particles in tap water. The electro-kinetic studies revealed that the addition of surfactant leads to a significant decrease of coagulant concentration for which the electro-kinetic potential of the dispersion medium becomes zero. The favorable influence of the addition of surfactant also resulted from the kinetic studies. Thus, the formation of some large flocks leads to shortening the flocculation period. These results are consistent with those obtained for sedimentation velocity, sludge volume and separation efficiency.

*Key words:* anionic polymer, cationic surfactant, coagulation – flocculation, complex coagulant

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## 1. Introduction

Currently, coagulation-flocculation is widely used in water and wastewater treatment (Simate et al., 2012; Wang et al., 2011). There are a large number of chemicals that may be used as coagulants and flocculants in treating many types of waters and wastewaters. These include inorganic-based coagulants, organic-based flocculants and some hybrid materials (Păcală et al., 2012). Some of them are both technically and economically feasible, however, there is still of interest to improve their performance and develop some new materials with superior properties (Aguilar et al., 2005; Lee et al., 2012). In addition, some of classical coagulants (i.e., aluminum sulfate) have received special attention due to their negative impact on both environment and human health (Li et al., 2013).

Water soluble organic polymers such as polyacrylamide polymers or polyacrylamide copolymers are currently widely used in coagulation-flocculation process due to their advantages such as the increasing the settling rate of the formed flocks, providing better dewatering characteristics of the sludge, decreasing of sludge volume, increasing quality of treated water, availability, environmental properties, as well as their acceptable cost (Lee et al., 1998). The polymers used in coagulation-flocculation processes should be selected depending on the properties of the colloidal suspension that will be destabilized, and on the process conditions (i.e., pH, temperature) (Zahrim et al., 2010). The main two action mechanisms of these polymers are charge

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neutralization and polymer bridging, which are heavily dependent on the adsorption of polymers on the particle surfaces (Bolto and Gregory, 2007).

The polymer-surfactant systems were developed and used in a wide range of applications such as the production of paints, detergents, and cosmetics, in the food sector and in recent years in water and wastewater treatment (Petzold et al., 2007; Yang et al., 2013). The specific interactions that occur between a surfactant and an oppositely charged polymer lead to formation of a polymer-surfactant system which will have all the physical and chemical properties of these combinations making it more effective as coagulant (Lee, 1999).

Therefore, the objective of this study was to evaluate the performance of some complex coagulants derived from the weak and medium anionic polymers and medium cationic surfactant in coagulation-flocculation process for water treatment by carrying out kinetic studies and by determining the optimum coagulant dose.

## 2. Experimental

The complex coagulants were prepared from weak anionic and medium anionic copolymers of acrylamide and sodium acrylate with commercial names of Praestol 2515 and Praestol 2540 (purchased from Evonik-Degussa, Bucharest, Romania), and medium cationic surfactant derived from triethanolamine with commercial name of Tetranyl AT-7590 (KAO Chemicals Europe, Barcelona, Spain). The preparation procedure and the properties of these coagulants were described in a previous paper (Bobirică et al., 2012). All experiments were performed with solutions of complex coagulants having the surfactant concentration higher than its critical aggregation concentration.

The coagulation-flocculation process was studied for suspensions of kaolin particles in tap water. The experiments were conducted as follows: the kaolin particles were contacted with tap water (corresponding to a concentration of 0.1 g/L) and then dispersed by blade stirrer for five minutes. Next, both coagulant solution and a suspension of calcium oxide were added to the kaolin suspension. The calcium oxide (purchased by Merck) was added to achieve an optimum pH value of 11.5.

The pH was measured by a Fisher Scientific Accumet 25 pH meter. The obtained mixture was then subjected to the coagulation-flocculation process using a Flocculator SW5 manufactured by Stuard Scientific, Staffordshire, United Kingdom. The coagulation-flocculation process was conducted in two stages as follows: dispersion stage (3 minutes) and maturation stage (6 minutes).

The electro-kinetic potential ($\zeta$) was measured by a Burton device manufactured in our laboratory. The schematic drawing of the Burton device and its electrical scheme are presented in a previous paper (Mihai et al., 2010).

The kinetic studies were performed by using a microscopic image technique. In this respect, a series of samples were sampled from flocculator and put on microscope slide (Motic AE 30/31 Inverted Microscope manufactured by GMI, Inc. Ramsey, USA). The pictures from the eyepiece microscope were taken with Canon G9 digital camera. The flocks were measured by using Sigma Scan Pro5 trial version software.

The sedimentation velocity was measured by using a settling tube and the settleable solids were measured using an Imhoff cone. The turbidity measurements were performed by using a spectrophotometer UV-VIS Cintra 5 manufactured by Dandenong, Australia.

## 3. Results and discussion

Previous studies (Mihai et al., 2010) emphasized that the kinetic potential of kaolin aqueous suspension is about -60 mV.

This means that the kaolin particles in the suspension are negatively charged and, their hydrophobic surface could be loaded with positive charged counter ions. Also, the optimum pH of kaolin suspension for coagulation-flocculation process it was found to be 11.5. In this respect, all experiments were carried out at this pH value of the kaolin suspension and at a temperature of kaolin aqueous suspension of 20±0.2 ºC. The experimental results obtained from the electro-kinetic studies, are presented comparatively in Fig. 1.

As can be seen, although Praestol 2540 is a medium anionic polymer stronger than Praestol 2515, which is a weak anionic polymer, the kaolin suspension treated with these two different polymers reaches the zero zeta potential at approximately the same concentration, which is about $10^{-3}$ %. The addition of surfactant leads to a significant decrease of coagulant concentration for which the electro-kinetic potential of the dispersion medium becomes zero (corresponding to the optimum dose). Thus, when the complex Praestol 2515- Tetranyl AT-7590 and complex Praestol 2540- Tetranyl AT-7590 were used, the optimum coagulant dose ($c_\zeta$) was $7.10^{-6}$ %, a value which is about two orders of magnitude smaller than that associated with the use of polymers Praestol 2515 and Praestol 2540.

It may be also noted that when the optimal complexes dose is exceeded, the electro-kinetic potential of kaolin suspension is stronger modified than when the optimal polymers dose is exceeded. These results suggest that when the coagulant optimal dose was exceeded (especially in the case of complex coagulants) the polarity of kaolin particles was changed and a new colloidal suspension was formed.

The experimental results obtained from kinetic studies showed that the rate formation of flocks depends on the nature of coagulant and operating conditions.

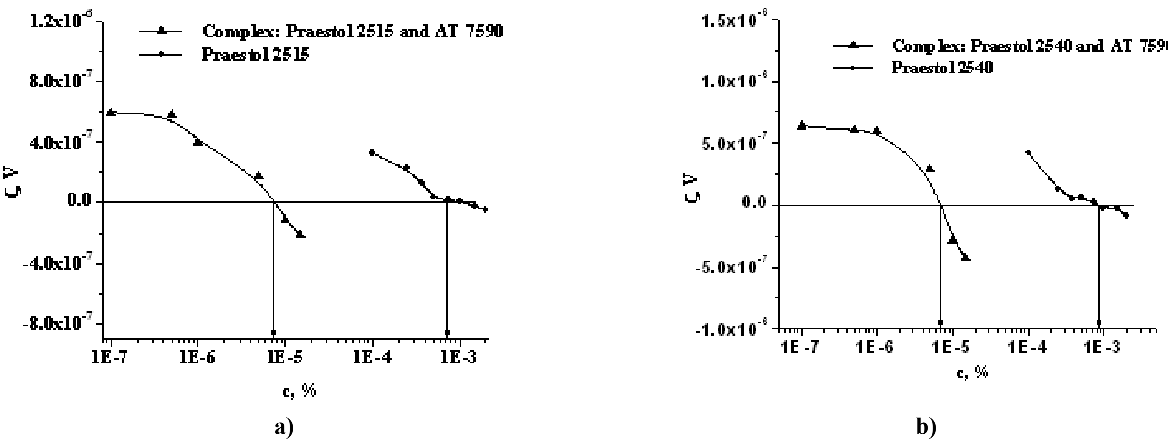



**Fig. 1.** Variation of zeta potential of kaolin suspension as a function of coagulant concentration (a – comparison between the complex coagulat derived from Praestol 2515 and AT 7590, and the anionic polymer Praestol 2515; b – comparison between the complex coagulat derived from Praestol 2540 and AT 7590, and the anionic polymer Praestol 2540)

In this respect, when complex coagulants were used the dispersion and maturation phases of the flocks formation are shorter than when only corresponding polymers complex were used as coagulants. When complex are used both consolidated flocks and early associations of particle-macromolecule type there are in the same time. This demonstrates that the stages of destabilization of suspension, macromolecule adsorption and aggregates formation have different kinetic from the initial polymer. Finally, the individual compacted flocks have sedimentation velocity much higher than in the case of classical coagulants. The evolution of average diameter (derived from microscopic image technique) of the flocks during the flocculation time is presented in Fig. 2. As it can be seen from this figure, the average diameter of the flocks is higher when complex coagulants are used than in the case when only their polymers are used. The formation of some large flocks leads to shortening the flocculation period. The flocks grow fast in the first three minutes corresponding to the first fast mixing stage (the dispersion stage) and then tend to stabilize. In the second stage, the average diameter of the flocks tends to stabilize after approximately six minutes when the maturation stage was completed (the maturation stage).

The images of the flocks formed during the flocculation time at optimum coagulant dose are presented in Fig. 3. During the flocculation process the particles tend to attach to the chain of the complex, and subsequently, between these aggregates occurring bridges that lead to the growing of the flocks. Thus, it can be said that the main destabilization mechanisms of the colloidal suspension are: charge neutralization and polymer bridging which are preceded by adsorption of coagulant on the particles surface.

The efficiency of a coagulant can be verified based on the properties of the flocks formed during coagulation-flocculation process. In this respect, the flocks must have a high stability, must settle slightly and must generate a small volume of sludge. The experimental results regarding the sedimentation velocity of flocks, presented in Fig. 4, highlights that the addition of surfactant lead to high values of sedimentation velocity, than those obtained when only their polymers were used as coagulants, but at lower surfactant concentration this time.

Therefore, when the complex Praestol 2515-Tetranyl AT-7590 was used, a maximum sedimentation velocity of $8.56 \cdot 10^{-2}$ mm/s was obtained corresponding to an optimum coagulant dose of $2 \cdot 10^{-6}$ % while when only Praestol 2515 was used, the maximum sedimentation velocity was $2.78 \cdot 10^{-2}$ mm/s corresponding to an optimum coagulant dose of $0.5 \cdot 10^{-3}$ %. When the complex Praestol 2540-Tetranyl AT-7590 was used, a maximum sedimentation velocity of $5.98 \cdot 10^{-2}$ mm/s was obtained corresponding to an optimum coagulant dose of $2 \cdot 10^{-6}$ % while when only Praestol 2540 was used, the maximum sedimentation velocity was $8.5 \cdot 10^{-3}$ mm/s corresponding to an optimum coagulant dose of $2 \cdot 10^{-3}$ %. The volume of sludge is always smaller when the complex coagulants were used (Fig. 5).

In addition, the results obtained concerning the influence of coagulant dose on the sedimentation velocity of flocks and on the resulted volume of sludge, are consistent with those obtained from electro-kinetic studies. Thus, the highest sedimentation velocity and the smallest sludge volume were found at a coagulant dose close to the coagulant concentration corresponding to the zero value of the electro-kinetic potential (the coagulant dose considered as optimum).

The turbidity measurements showed that the removal efficiency of colloidal suspensions of kaolin (relative to both particle concentration in suspension after the sedimentation of flocks and optimum coagulant dose) is higher when the complex coagulants were used compared with the efficiency recorded when only their polymers were used. The results obtained are presented in the Fig. 6 in terms of initial and final turbidity ratio.

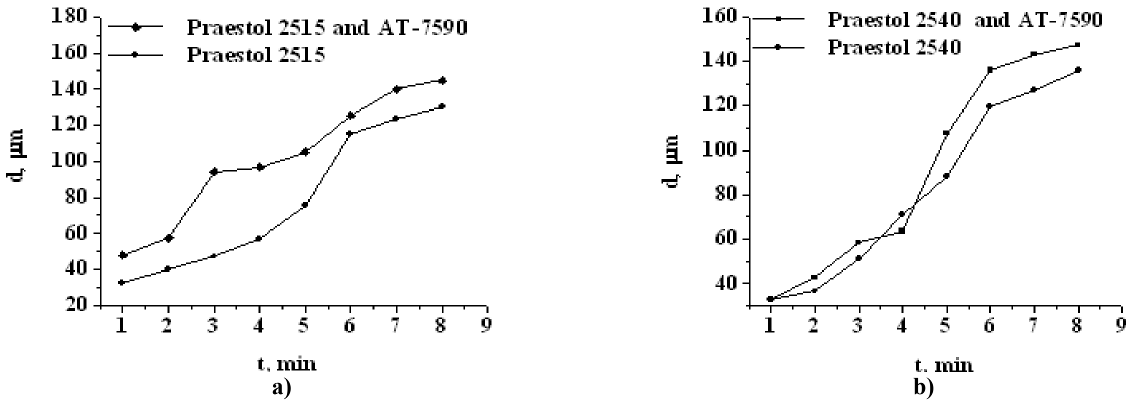
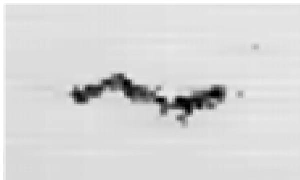
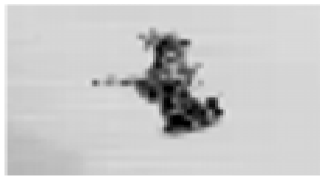



**Fig. 2.** Flocculation kinetic of kaolin particles at optimal coagulant dose (a – comparison between the complex coagulat derived from Praestol 2515 and AT 7590, and the anionic polymer Praestol 2515; b – comparison between the complex coagulat derived from Praestol 2540 and AT 7590, and the anionic polymer Praestol 2540)

| *Time, min* | *Praestol 1540* | *Complex: Praestol 1540 and AT-7590* |
|---|---|---|
| 1 |  |  |
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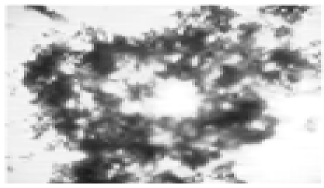
| 6 |  |  |

**Fig. 3.** Images of the flocks at optimal coagulant dose

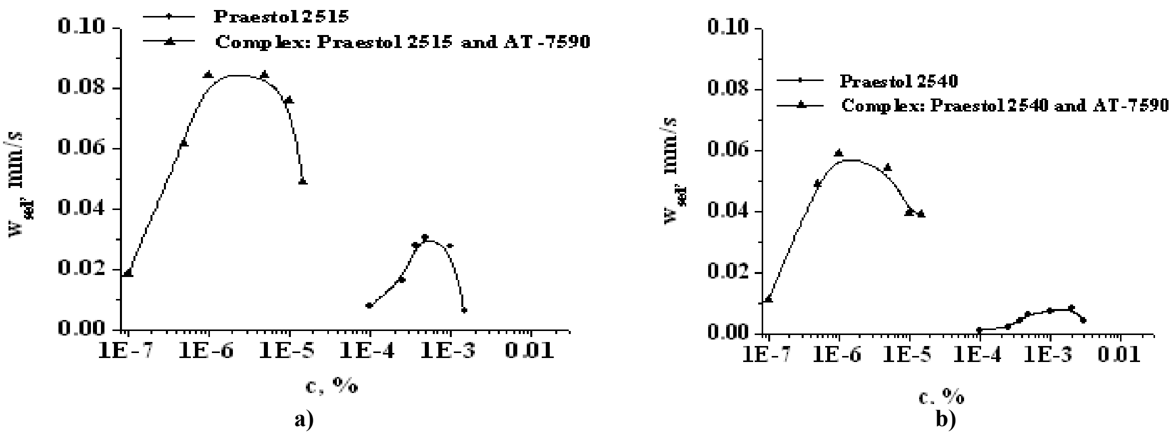
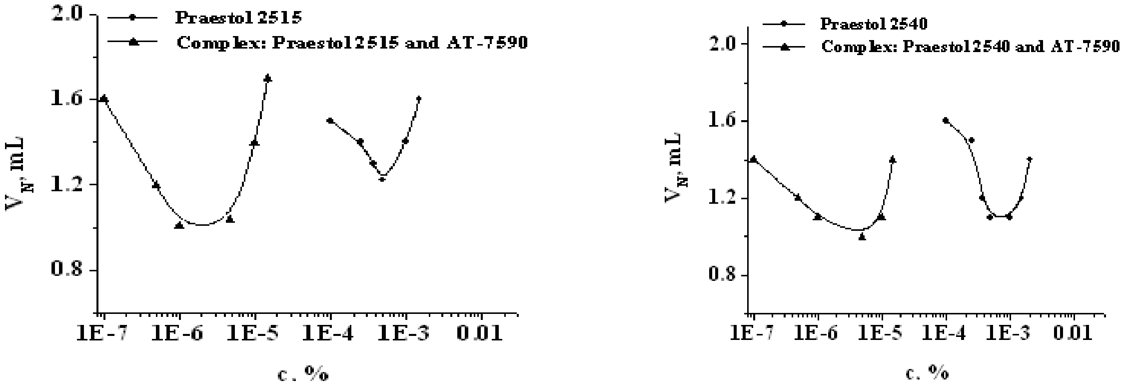
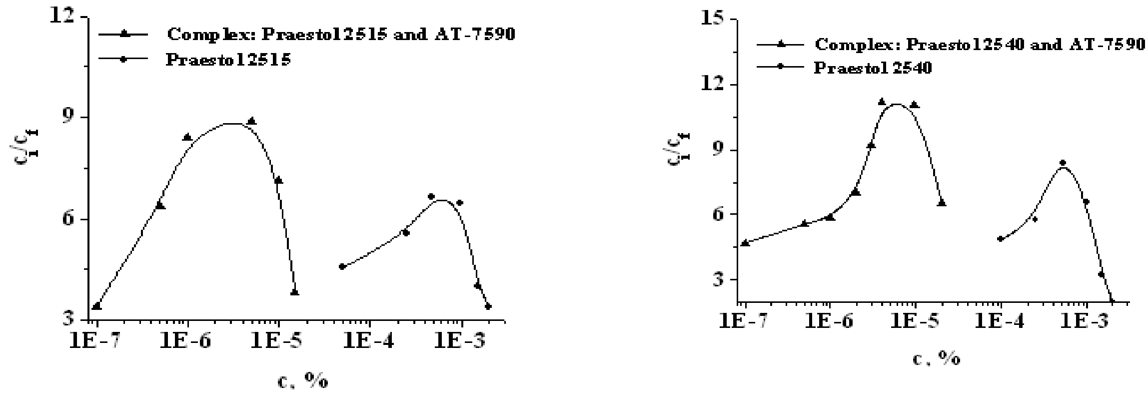



**Fig. 4.** Sedimentation velocity of flocks as a function of coagulant dose (a – comparison between the complex coagulat derived from Praestol 2515 and AT 7590, and the anionic polymer Praestol 2515; b – comparison between the complex coagulat derived from Praestol 2540 and AT 7590, and the anionic polymer Praestol 2540)




a) b)

**Fig. 5.** Sludge volume resulted after sedimentation of the flocks as a function of coagulant dose dose (a – comparison between the complex coagulat derived from Praestol 2515 and AT 7590, and the anionic polymer Praestol 2515; b – comparison between the complex coagulat derived from Praestol 2540 and AT 7590, and the anionic polymer Praestol 2540)




a) b)

**Fig. 6.** Separation efficiency as a function of coagulant dose dose (a – comparison between the complex coagulat derived from Praestol 2515 and AT 7590, and the anionic polymer Praestol 2515; b – comparison between the complex coagulat derived from Praestol 2540 and AT 7590, and the anionic polymer Praestol 2540)

As it was expected, a higher efficiency was obtained by using the complex coagulants. These results are consistent with those obtained from the kinetic studies which were presented and explained above.

## 4. Conclusions

The objective of this paper was to investigate the performance of some complex coagulants derived from the weak and medium anionic polymers (Praestol 2515 and Praestol 2540) and medium cationic surfactant (Tetranyl AT-7590) in coagulation-flocculation process for water treatment. The results obtained by carrying out kinetic studies and by determining the optimum coagulant dose highlighted as follows:

- the results of electro-kinetic studies revealed that the addition of surfactant leads to a significant decrease of coagulant concentration for which the electro-kinetic potential of the dispersion medium becomes zero (corresponding to the optimum dose);
- the results of kinetic studies showed that when complex coagulants were used the dispersion and maturation phases of the flocks formation are shorter than when only corresponding polymers complex were used as coagulants.
- two main destabilization mechanisms of the colloidal suspension were identified when complex coagulants were used, namely charge neutralization and polymer bridging which are preceded by adsorption of coagulant on the particles surface;
- the experimental results regarding the sedimentation velocity of flocks highlights that the addition of surfactant lead to a higher values of sedimentation velocity, than those obtained when only their polymers were used as coagulants, but at lower surfactant concentration this time. These results are consistent with those obtained for volume of sludge and separation efficiency.

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