Flocculation efficiency of cationic potato starch in the presence of coagulants

Dorota ZIÓŁKOWSKA, Alexander SHYICHUK, Piotr CYSEWSKI, Agnieszka ORGANIŚCIAK - Division of General Chemistry, Faculty of Chemical Technology and Engineering, University of Technology and Live Sciences, Bydgoszcz

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Introduction

Flocculants synthesized on the basis of water-soluble natural polymers are the subject of increasing attention because of their non-toxicity and biodegradability [1÷3]. Among them cationic modifications of starch have many the very important advantages such as solubility in cold water not mentioning of the relatively low price. Pure starch consists of two polymers: amylose (up to 20 %) of linear structure and low molecular mass as well as amylopectin (up to 95%) of highly branched structure and high molecular mass. Modification of polysaccharides to enlarge their flocculation activity in general is performed via graft-polymerization of acrylamide [2] resulting in nonionic copolymers. However, natural suspensions composed of colloidal particles with high negative charge are more effectively flocculated with polysaccharides possessing positively charged groups, as amino, imine, amonium etc. [1]. Cationized polysaccharides are effective flocculants towards negatively charged organic and inorganic substances in wide range of suspension pH values.

The previous work [3] was concentrated on flocculation abilities of cationized wheat and potato starches produced in Poland [4]. The studied products proved to accelerate effectively the sedimentation of aluminosilicates suspensions. The flocculation effectiveness is increased with the increase of the substitution degree of both potato and wheat cationic starches [3]. Moreover it was proved, the flocculation efficiency of the examined kinds of cationic starches proved to be somewhat less effective as compared with polyacrylamide-derived flocculants [3]. Additional increase of sedimentation rate can be obtained through mutual application of the flocculant and a coagulant. Typically, a clarification process consists generally of two stages, namely: neutralization of the negative surface charge of the suspension particles performed with the aid of a cationic coagulant is followed by the particle bridging performed with the aid of non-ionic flocculants (mainly polyacrylamide) [5]. In the present work typical commercial coagulants (both ferric or aluminum ones) have been tested for their ability for improvement of the flocculation efficiency of the cationic starch.

Methods

The model suspensions have been prepared with the industrial kaolin KOM (SURMIN-KAOLIN, Poland). The size of the kaolin particles do not exceed 15 μm, whereas equivalent diameter of 62% of them is less then 2 μm [6]. The cationic potato starch BORCET SZ 2000 (BOCHEM, Poland) with substitution degree 0.180-0.200 [4] and solubility 20% [3] has been used as a flocculant. The coagulants were the commercial ones: ferric PIX-123 and aluminum PAX-XL19 (KEMIPOL, Poland) [7].

Measurements have been performed at 22°C in capped test cylinders containing kaolin suspensions of 4 g/dm^3 concentration. At first a dose of diluted solution of coagulant has been added to the test cylinder and mixed. Secondly a dose of starch flocculant solution (of 150 mg/dm^3) has been added. The component volumes have been selected so that the final volume of the mixture has been equal to 500 cm^3. Then the cylinder has been mixed for 10 times by vortex for 180° with 1 turn/sec. Next the test samples were periodically collected from the top layer. Turbidity of the samples was determined with the spectrophotometer Spekol 10 in the nephelometric mode at the wavelength 555 nm and results have been expressed in relative units. The directly measured parameter was the signal of the nephelometric set, I [mV], which increases proportionally to the increase of suspension turbidity.

Results

The preliminary experiments have been performed on kaolin sedimentation in the presence of the BORCET, PIX and PAX aids separately. The obtained results have been presented in Table 1.

Table 1

Sedimentation of kaolin in the presence of the flocculant and coagulants. Suspensions turbidity has been expressed as the nephelometric signal value, I. Doses of flocculant and coagulants towards the kaolin mass are equal to: BORCET SZ 2000 – 0.75 mg/g , PIX-123 - 1 mg Fe^{3+}/g , PAX-XL19 – 0.1 mg Al^{3+}/g

reagent		the signal of the nephelometric set, mV				
coagulant	flocculant	after 5 min.	after 10 min.	after 60 min.	after 120 min.	after 240 min.
none	none	619	542	330	271	126
none	BORCET	225	153	85	52	41
PIX	none	215	144	60	20	18
PAX	none	244	158	36	31	29
PIX	BORCET	156	100	24	20	16
PAX	BORCET	167	103	52	37	20

Based on above data it is evident that the cationic starch BORCET SZ 2000 accelerates sedimentation of kaolin suspension as well as it improves final clarity of suspension. Similar result has been obtained with the coagulants PIX-123 and PAX-XL19. Moreover, it was proved that clarification of kaolin suspension could be further improved through application of the coagulant and the flocculant, in the sequence. The synergistic effect is visible especially at the initial stage of the sedimentation process. The application of the composition „ferric coagulant + cationic starch" caused sedimentation efficiency has been increased by 31-35% during first 5-10 min. In the same time range the composition of „aluminum coagulant + cationic starch" has improved the sedimentation process by 26-33% only. The time necessary for obtaining the best clarity of the supernatant has been registered to be equal to about 90 min in the case the cationic starch has been applied alone and to be equal to about 60 min in the case the single coagulants has been applied. However, the mentioned time has been reduced to 20 min in the case the composition of „ferric coagulant + cationic starch" has been applied.

Since both the cationic starch and the coagulants bind to the kaolin particles due to electrostatic attraction to the negative charged surface the multivalent cations of coagulants adsorbed onto mineral particles neutralize their negative surface charges leading to destabilization of the suspension. Consequently, the flocculant macromolecule is adsorbed simultaneously on several particles causing their bridging, what leads to creating of heavy, easily drooping agglomerates (so-called „flocks") [8]. Applying coagulant and cationic starch in sequence causes the synergistic result, which is confirmed by the data presented in Table 1. However, one should remember that application of two species of cationic nature causes a risk of their overdosage resulting in the change of the surface charge of kaolin particles into the positive one and causing decrease of sedimentation rate. Therefore, in the second stage of investigation the sedimentation of kaolin suspension in the presence of composition „coagulant + flocculant" with different quantitative ratios of components has been performed. Figures 1 and 2 present dependences of suspensions turbidity changes (expressed as the signal, I) on quantity of cationic starch used in the presence of different doses of coagulants PIX (Fig. 1) and PAX (Fig. 2).

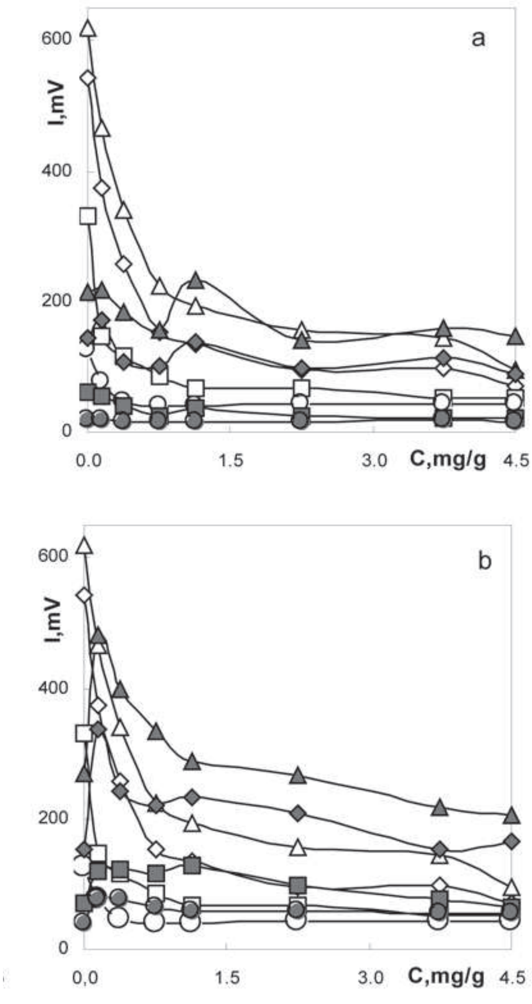

Fig. 1. Dependence of turbidity of kaolin suspension on the concentration of cationic starch BORCET SZ 2000 after 5 (▲), 10 (◆), 60 (■) and 240 (●) min. from initiation of the process. Conditions corresponding to lack of coagulant were denoted by white symbols, while results of the PIX-123 coagulant presence were denoted by gray symbols. Two concentrations of Fe^{3+} were tested: 1 mg Fe^{3+}/g (a) and 20 mg Fe^{3+}/g (b) per kaolin mass

Figures 1a and 2a demonstrate that flocculation effect of the BORCET SZ 2000 starch increases in presence of low concentrations of coagulants, especially in the range of 0-1 mg/g. At short sedimentation times addition of small amount of ferric coagulant (about 1 mg Fe^{3+}/g) improves the flocculation activity of the starch, when its dose does not exceed 0.875 mg/g (Fig. 1a). At more long sedimentation time the little amount of PIX increases activity of starch in all the range of its concentrations. Greater concentrations of the PIX coagulant (about 20 mg Fe^{3+}/g) accelerate the clarification of suspension under the condition that the used dose of the starch flocculant is lower than 0.125 mg/g, otherwise they stabilize the suspension (Fig. 1b).

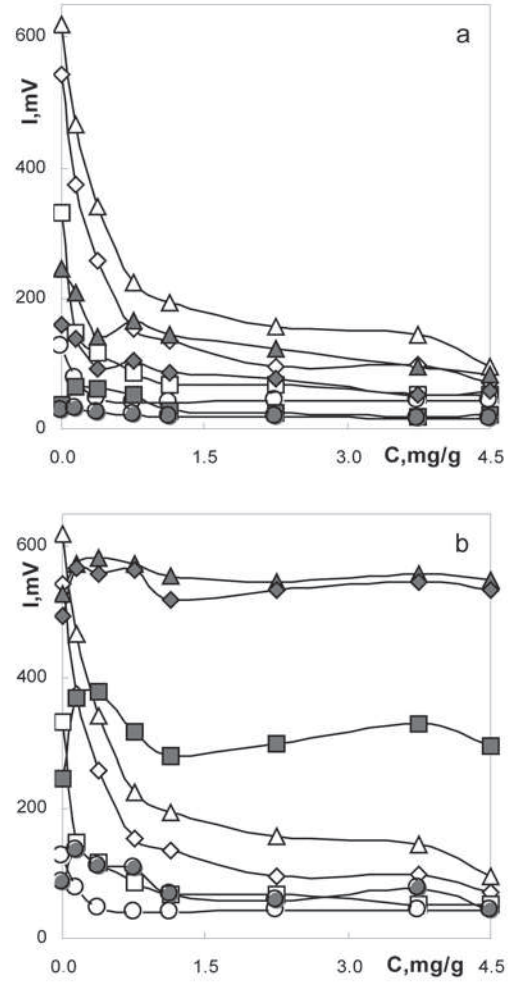

Fig. 2. Dependence of turbidity of kaolin suspension on concentration of cationic starch BORCET SZ 2000 after 5 (▲), 10 (◆), 60 (■) and 240 (●) min. from initiation of the process. Conditions corresponding to lack of coagulant were denoted by white symbols, while results of the PAX-XL19 coagulant presence were denoted by gray symbols. Two concentrations of Al^{3+} were tested: 0.1 mg Fe^{3+}/g (a) and 2 mg Fe^{3+}/g (b) per kaolin mass

Addition of the PAX-XL19 coagulant applied in the amount of about 0.1 mg Al^{3+}/g increases flocculation activity of the cationic starch in all the range of examined concentrations, independently on the sedimentation time (Fig. 2a). Greater doses of aluminum coagulant (about 2 mg Fe^{3+}/g) definitely spoiled the flocculation effect of the cationic starch, independently on the sedimentation time (Fig. 2b). Additionally, comparison of data presented in Figures 1b and 2b lead to the conclusion that excess of aluminum coagulant stabilizes kaolin suspension in a greater extent then that of ferric coagulant.

The most probable reason of the suspension stabilization in the presence of the greater doses of coagulant can be that they neutralize too much negative charges on the surface of kaolin particles. In these conditions adsorption of starch macromolecules takes place in a less extent or become impossible resulting in reduced bridging of suspension particles. Adsorption of cations or cationic macromolecules in an excess can also "reverse" the surface charge of kaolin, which doesn't favor suspension destabilization, as well.

Conclusions

1. The dose of the cationic starch BORCET SZ 2000 ensuring the best clarification of kaolin suspension equals about 1 mg/g, i.e. it is typical for flocculants of polyionic character [9].

2. The ferric and aluminum coagulants increase the flocculation effect of the cationic starch under the condition that they are used at low doses (i.e. PIX-123 of about 1 mg Fe^{3+}/g as well as PAX-XL19 of about 0,1 mg Al^{3+}/g). The most effective proved to be composition: PAX-XL19 (0.1 mg Al^{3+}/g) + cationic starch (at least 0.375 mg/g).
3. Application of greater doses of the coagulants leads to stabilization of the kaolin suspension.

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Dorota ZIÓŁKOWSKA, Ph.D.- graduated from Department of Technology and Chemical Engineering, University of Technology and Live Sciences (earlier Technical and Agricultural University) in Bydgoszcz (1990). Her doctoral degree she obtained at Department of Chemistry, Nicolaus Copernicus University in Toruń (1995). Currently, she works in the Department of Technology and Chemical Engineering, University of Technology and Live Sciences in Bydgoszcz. Scientific interests: adsorption and flocculation processes in water and wastewaters purification technologies. She is the author or co-author of monograph, 25 articles in scientific journals and 12 posters and oral presentations at national and international conferences.

Alexander SHYICHUK, (Sc.D.), Professor – graduated from the University of Chernivtsi, Ukrainie (1983). He obtained the doctoral degree in chemistry at Lvov Polytechnic Institute (1988) and earned habilitation at Institute of Chemistry of High Molecular Compounds of National Academy of Sciences of Ukraine (Kiev, 1998). At the time he affiliated at University of Technology and Life Sciences in Bydgoszcz. His scientific interests concern polymer modification, adsorption and flocculation as well as macromolecule simulation. He authored ca. 100 scientific papers and delivered ca. 50 lectures and posters at scientific conferences.

Piotr CYSEWSKI, (Ph.D.) Professor- graduated from Nicolaus Copernicus University in Toruń (1984). His PhD dissertation was presented in Institute of Chemistry of his mother Institution in 1989. His scientific interests are now concentrated on *in silico* experiments characterizing the properties of free radical modified nucleic acid bases resulting from oxidative stress. He is the author of over 80 publications presented in peer-reviewed scientific journals and many presentations of domestic and international conferences.

Agnieszka ORGANIŚCIAK, M.SC.- graduated from the Department of Technology and Chemical Engineering, University of Technology and Live Sciences in Bydgoszcz (2009).

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