

KAUNAS UNIVERSITY OF TECHNOLOGY

EDITA LEKNIUTĖ-KYZIKĖ

**MODIFIED STARCH FLOCCULANTS WITH QUATERNARY
AMMONIUM GROUPS**

Summary of Doctoral Dissertation

Technological Sciences, Chemical Engineering (05T)

2017, Kaunas

This doctoral dissertation was prepared at Kaunas University of Technology, Faculty of Chemical Technology, Department of Polymer Chemistry and Technology during the period of 2012–2017. The studies were supported by Research Council of Lithuania.

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Editor: Dovilė Dumbrasuskaitė (Publishing Office “Technologija”)

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The official defence of the dissertation will be held at 10 a.m. on 6 September, 2017 at the public meeting of Dissertation Defence Board of Chemical Engineering Science Field in Rectorate Hall at Kaunas University of Technology.

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Summary of doctoral dissertation was sent on 5th August, 2017.

The doctoral dissertation is available on the internet <http://ktu.edu> and at the library of Kaunas University of Technology (K. Donelaičio St. 20, 44239 Kaunas, Lithuania).

KAUNO TECHNOLOGIJOS UNIVERSITETAS

EDITA LEKNIUTĖ-KYZIKĖ

**KETVIRTINĖS AMONIAGRUPĖS TURINTYS MODIFIKUOTO
KRAKMOLO FLOKULIANTAI**

Daktaro disertacijos santrauka

Technologijos mokslai, chemijos inžinerija (05T)

2017, Kaunas

Disertacija rengta 2012-2017 metais Kauno technologijos universiteto Cheminės technologijos fakultete Polimerų chemijos ir technologijos katedroje. Mokslinius tyrimus rėmė Lietuvos mokslo taryba.

Mokslinis vadovas:

Doc. dr. Joana BENDORAITIENĖ (Kauno technologijos universitetas, Technologijos mokslai, Chemijos inžinerija, 05T).

Redagavo: Dovilė Dumbruskaitė (leidykla “Technologija”)

Chemijos inžinerijos mokslo krypties disertacijos gynimo taryba:

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Disertacija bus ginama viešame chemijos inžinerijos mokslo krypties disertacijos gynimo tarybos posėdyje 2017 m. rugsėjo 6 d. 10 val. Kauno technologijos universiteto rektorato salėje.

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Disertacijos santrauka išsiųsta 2017 m. rugpjūčio 5 d.

Su disertacija galima susipažinti internetinėje svetainėje <http://ktu.edu> ir Kauno technologijos universiteto bibliotekoje (K. Donelaičio g. 20, 44239 Kaunas).

INTRODUCTION

Relevance of work. Nowadays, one of the biggest problems is urban wastewater, its recycling and utilization. On the basis of data provided by the Environmental Protection Agency in 2012, the natural environment has been released with 179.5 million m³ of household, industrial and municipal sewage in Lithuania. In 2012, at the time of wastewater treatment, over 45 thousand tons of sludge¹ (according to the dry materials) were produced, and only a small proportion (about 40%) of it is used purposefully (composting and fertilization, etc.). The remaining sludge is accumulated in the sludge storage sites. The Council of the European Union has adopted directives (No. 91/271/EEB² and No. 86/278/EEB³), on urban wastewater treatment and the protection of environment, in particular of the soil, using sewage sludge in agriculture, whose main objective is to protect the environment from the harmful effects of wastewater.

The separation of liquid-solid particles or the stabilization of system processes determines the efficiency of production technology of the paper, metal, food industries, wastewater treatment, water preparation, biotechnology, etc. By adding a flocculant to the disperse system, the particles are combined to a large flocculus which settles down fast and thus is separated from the liquid. A few kilograms of soluble synthetic flocculant per tonne of dry solids is enough for the flocculation and separation of the phase of the disperse system. However, due to the inherent resistance of carbon chains of the macromolecules, synthetic flocculants are not degradable and remain in purified water, treated sludge and hereby complicates its further processing and use. In addition, using the synthetic flocculants, optimal and reliable phase separation takes place in a narrow minimum and maximum effective flocculant dose interval, also called the flocculation window.

Another important aspect – the fact that synthetic flocculants are derived from petroleum products, mostly from acrylamide, which is toxic, classified as an extremely hazardous substance (EPCRA, 42 U.S.C. 11002)⁴ and included in the list of carcinogenic substances⁵. Therefore, is important to find an alternative to synthetic flocculants which would have the same or similar efficiency as synthetic, but was obtained from renewable resources and harmless to the surrounding environment. One potential natural polymer used for the preparation of such flocculants is starch, which is biodegradable, its decomposition products are environmentally friendly, and it is produced from renewable sources, such as wheat, potatoes, maize, etc. Therefore, the modified starch flocculants could be a suitable alternative for the used synthetic ones.

Eco-innovation contributes to the achievement of sustainable development by reducing negative environmental impact of production, as well as a more efficient and responsible use of natural resources in a more sustainable business, dealing with climate change, resource scarcity and biodiversity loss.

The aim of the work was to develop an effective biodegradable modified starch flocculant with quaternary ammonium groups which would be suitable for removing negatively charged pollutants and for thickening the municipal sewage sludge.

The tasks proposed to achieve the aim were:

1. To synthesize starch derivatives of various chemical composition containing quaternary ammonium groups;
2. To evaluate the biodegradability of the starch derivatives;
3. To produce an effective flocculant from ionogenic starch;
4. To identify the influence of physico-chemical factors on the efficiency of ionogenic starch flocculant;
5. To verify the suitability of the ionogenic starch flocculant for model kaolin disperse systems and for thickening and dewatering the municipal sewage sludge;
6. To propose a technological scheme for obtaining ionogenic starch flocculant and make its prototype with the existing.

Scientific novelty of the work. A novel hydromechanical method for obtaining starch flocculants was proposed and the conditions of obtaining an efficient and biodegradable optimal structure ionogenic starch flocculant were selected. The dependence of biodegradability on the degree of substitution (DS) of cationic starch derivatives was determined. According to the model systems and municipal wastewater destabilization studies, the flocculation mechanism of new modified starch derivatives was proposed.

Practical value. It was determined that the sheared cross-linked cationic starch derivative is the most suitable for thickening municipal sewage sludge; the flocs resistant to mechanical stress are obtained when using this derivative. The ionogenic starch flocculant prototype was made in the pilot of equipment and tested in Water Treatment Company of Lithuania. Although the amounts of an effective dose are higher when compared to normal use of synthetic cationic flocculant in wastewater treatment, the new modified starch derivatives have a number of advantages:

- flocculant is obtained from renewable natural resources;
- biodegradable raw material;
- wasteless production of flocculant;
- flocculant is effective in a wide interval of doses;
- flocculant is biodegradable, the thickened biomass decomposes easily during processing and does not pollute nature, therefore, the biomass can be used as a fertiliser;

- during the processing of thickened biomass, a higher yield and quality biogas (a lower amount of hydrogen oxide and a higher amount of methane) are obtained.

The main statement of the dissertation. An effective biodegradable modified starch flocculant suitable for thickening and dewatering of municipal sewage sludge is obtained by mechanical processing with the use of shear forces of swollen starch microgranules, containing quaternary ammonium groups with a degree of substitution by cationic groups, not higher than 0.30, to a submicron particle size.

Validation and publication of research results. The results on the topic of this dissertation are presented in three publications in Clarivate Analytics databases indexed in the Web of Science journals with Impact Factor. Five publications are published in other indexed journals without Impact Factor and six publications – in the proceeding of international conferences. One patent was registered (EU patent application) at the International Patent Office (EPO) and two were registered in the national patent office. An industrial test was done in the water treatment system of Kauno vandenys Ltd company. Proposed the product obtaining technology was proposed and its prototype was made in KTU “Biopolymer Research Laboratory”.

1. RESEARCH METHODOLOGY

Materials and chemicals used in this work were chemically or analytically pure reagents, not purified additionally before use.

The synthesis of cationic starch derivatives. Cationic starch (CS) derivatives were prepared by etherification of native potato starch with 2,3-epoxypropyltrimethylammonium chloride (GTAC) in the presence of NaOH as a catalyst, thereby connecting the quaternary ammonium groups⁶. The amount of cationic groups shows the degree of substitution (DS_{cat}), obtained derivatives are marked CS_{DScat} . Amphoteric starch (AMS) derivatives with different content of cationic and anionic groups characterized by substitution degree DS_{cat} and DS_{an} , respectively, were prepared by a two-step procedure⁷. First of all, cationic starch with DS_{cat} 0.29 ($CS_{0.29}$) and preserved granular morphology were obtained by etherification of potato starch with GTAC. Further, $CS_{0.29}$ was treated with succinic anhydride to form the half ester – cationic starch succinate. Non-stoichiometric ionic complexes (NIC) with an excess of cationic groups were formed between CS with DS_{cat} of 0.47 ($CS_{0.47}$) and 4-sulfophthalic acid (SPH), both in acid and ionized forms⁸. Before complex formation, $CS_{0.47}$ had been dispersed in cold water by mechanical shearing and used in the form of colloidal gels. The amount of SPH added to the $CS_{0.47}$ colloidal suspension was 5 mol%, 10 mol% or 25 mol% depending on the amount of $CS_{0.47}$ cationic groups present in a

colloidal suspension. The obtained complexes were marked as $NIC_{DS_{Scat}/SPH_{mol}\%}$. Cross-linked cationic starch (CLCS) derivatives can be obtained using two methods: one and two-stages⁹. In producing the CLCS with a one-stage method, an etherification mixture is prepared by mixing the solution of NaOH with GTAC and adding a cross-linking agent, epichlorohydrin (EPI), to the mixture. In producing the CLCS by a two-stage method, cross-linked starch is produced first and then cationized. The obtained derivatives are marked as $CLCS_{DS_{Scat}/EPI}$, EPI – the amount of cross-linking agent, mol/mol_{AGU}.

Modified starch microgranules (1% w/w) were swollen to the equilibrium state in distilled water (20°C) and then processed by mechanical shearing at 15,000 rpm with an Ultra-Turrax T25 digital (IKA, Germany) device at room temperature to obtain a **colloidal disperse system**.

The characterization of starch and its derivatives. The degree of substitution of cationic groups (DS_{cat}) was calculated from the nitrogen content of cationic starch derivatives and estimated by the Kjeldahl method. The number of anionic groups (DS_{an}) was determined according to the method described by Stojanovic, et al.¹⁰. The **molecular weight** of cationic starch samples was determined with the size exclusion chromatography SEC system (Viscotek 270 Dual Detector, Malvern Instruments Ltd.) which contains a refractive index (RI) and light scattering (RALS and LALS) detection. The eluent was DMSO with 0.05 M LiBr and two Viscotek-A columns (A2500 and A5000) were used in a series. Data were recorded and the molecular weights were calculated with the Malvern OmniSEC software version 4.7. The **enzymatic hydrolysis** of native and modified starches was performed using an α -amylase (Liquozyme® Supra from Novozymes) preparation. Water suspension (3%) of starch or cationic starch derivatives was mixed with the α -amylase and then investigated by using Brabender Micro-Viscoamylograph®. The value of dextrose equivalent (DE) was determined by using the Schoorl method¹¹. The biodegradability of starch and its derivatives was determined by **aerobic degradation** in liquid and solid media, according to the ISO 14851¹² and ISO 14855-2:2007¹³ standards, respectively. The **dynamic viscosity** [η] of CS aqueous slurry and colloidal suspensions was measured with the rotational viscometer Rheotec RC02-R (Germany) at 20°C, using a TR8 spindle. The measurements were performed with 1% w/w (by dry basis) of cationic starches. To determine the **accessibility** (A) of modified starch derivatives cationic groups (%) to polyanions, the polyelectrolyte titration was done^{7,14}. The **particle size** and the **ζ -potential** of sheared CS particles and destabilised kaolin floccules in aqueous medium were measured by using DelsaNano C instrument (Beckman Coulter, Japan). The **optical observations** were carried out using an Olympus CX31 optical microscope (Philippines) under 100-time magnification. The photograph of CS slurry in water was taken with an

Olympus camera. For the **SEM analysis**, the freeze-dried native and modified starches were examined on a FEI Quanta 200 FEG.

The **flocculation experiment** with a model kaolin suspension was performed and the residual turbidity (RT, %) of kaolin suspension after the addition of cationic starch flocculant was evaluated^{6,7}. Suspensions of kaolin were prepared by ultrasonic treatment of the finely dispersed aqueous kaolin suspension of 1 g/l concentration for 15 minutes. Destabilization treatment with kaolin suspensions is performed at room temperature. The light absorption of the upper fraction of destabilized kaolin suspension is measured at the wavelength of 500 nm (*A500*) with the spectrophotometer UNICAM UV3 UV/Vis and **residual turbidity** (RT) was calculated from the obtained data. The **quality** of modified starch flocculants is characterized by the **minimum amount (dose) of the flocculant** C, mg/g of kaolin, in the presence of which the suspension destabilization occurs up to 10% of RT and by the width of the **flocculation window** (W). W is defined as a difference between maximum and minimum (C) amounts of flocculant, at the presence of which the residual turbidity (RT) is less than 10%.

The experiment of **destabilization of sewage sludge** suspension was carried out at room temperature. 400 ml of the suspension was poured to a 600 milliliter beaker, followed by dosing the required amount of the flocculating agent and the resulting disperse system mixed. After the destabilized sludge is filtered and measured in 200 ml of filtrate flow time – the **filtration rate**, ml/s, is calculated. The **filtration efficiency** of destabilized disperse systems (kaolin, sewage sludge) was determined by a standard 304M CST apparatus (Triton Electronics Ltd., England), which measures the capillary suction time. The capillary suction pressure generated by a standard filter paper is used to ‘suck’ water from the sludge.

Experimental studies of **sludge digestion** were carried out at Aleksandras Stulginskis University biogas laboratory. Stands with vertical laboratory biogas reactors and their control and parameter measurement system¹⁵ were used for the research.

2. RESULTS AND DISCUSSION

2.1. Ionogenic starch derivatives

Ionogenic starch derivatives: cationic starch (**CS**), amphoteric starch (**AMS**), non-stoichiometric ionic complexes (**NIC**) and cross-linked cationic starch (**CLCS**), were obtain by a modifying the native starch (Fig. 1). All of them are united by the fact that the group has a strong base – quaternary ammonium – $N^+(CH_3)_3$.

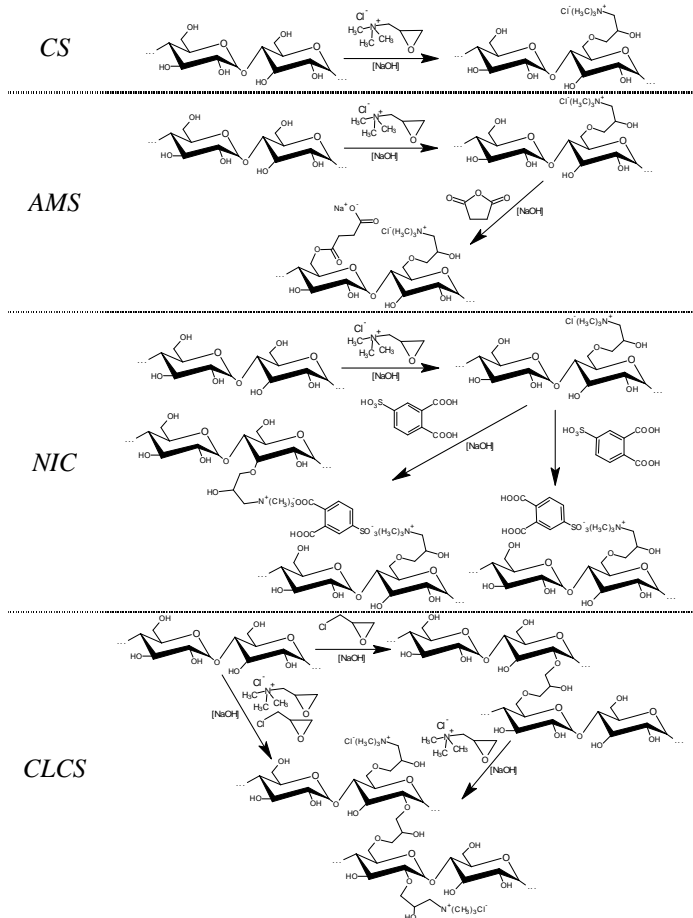


Fig. 1. Synthesis scheme of ionogenic starch derivatives

CS, AMS and CLCS preserved the microgranular state and oval shape characteristic of the native starch¹⁶ after the chemical modification (Fig. 2). According to Vihervaara, et al.¹⁷ granular form is not affected by cationization.

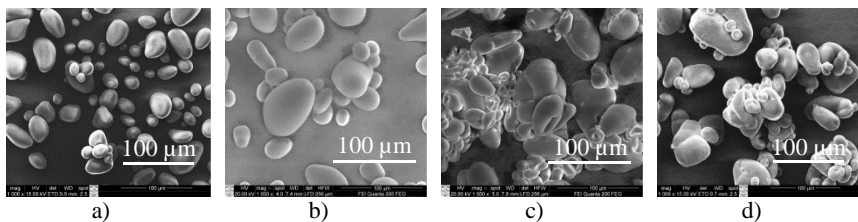


Fig. 2. SEM pictures of native starch (a), CS_{0.30} (b), AMS_{0.29/0.22} (c) and CLCS_{0.28/0.0005} (d)

2.2. Biodegradability of starch and its chemically modified derivatives

The influence of cross-linking and cationization of starch for its biodegradability were evaluated. For such purpose the enzymatic (using α -amylase) and aerobic (in liquid and solid media) degradation of native and modified starches were done.

The dextrose equivalent (DE), the molecular weight (M_w) and the viscosity $[\eta]$ of water solutions of modified starches were evaluated after **enzymatic hydrolysis (degradation)** (Table 1). By increasing the amount of α -amylase, the degree of destruction of starch and its modified derivatives increases; however, a slight decrease of DE is notable with increasing DS_{cat} . The low amount of enzyme CS derivatives have significantly lower DE values compared to its natural starch. When the amount of enzyme was 0.2 mg/g, the DE of CS_{0.10-0.30} derivatives was 3–6 times lower, respectively, and when $DS_{cat}=0.54$, the degree of destruction was very low, $DE \leq 1\%$. Even after a 100-fold increase in enzyme levels, up to 20 mg/g, the DE value of CS_{0.54} changed to a minor extent. A similar relationship was observed for the case of cross-linking the starch – the destruction degree decreases with an increasing amount of EPI, mol/mol_{AGU}.

Table 1. The characteristics of starch and its modified derivatives after enzymatic hydrolysis

Sample	DE, %, when α -amylase amount is:			M_w^* , kDa	$[\eta]^*$, dl/g
	0.2 mg/g	2 mg/g	20 mg/g		
Starch	13	27	30.8	3.2	0.117
CS _{0.10}	2.4	11.8	17.9	8.7	0.194
CS _{0.19}	3.5	9.5	10.4	42.8	0.277
CS _{0.30}	2.1	5.3	6.2	79.7	0.575
CS _{0.54}	0.4	0.8	1.2	528.0	3.473
CLS _{0.005}	12.3	25.3	-	-	-
CLS _{0.10}	5.5	14.6	-	-	-

* when α -amylase amount 0.2 mg/g

The **aerobic degradation** tests of the non-modified and modified starch samples **in liquid media** were performed using manometric respirometric equipment OxiTop[®] OC110 control system. The biodegradability of natural starch

and the dependence on DS_{cat} and cross-linking level (EPI content) are presented in Fig. 3.

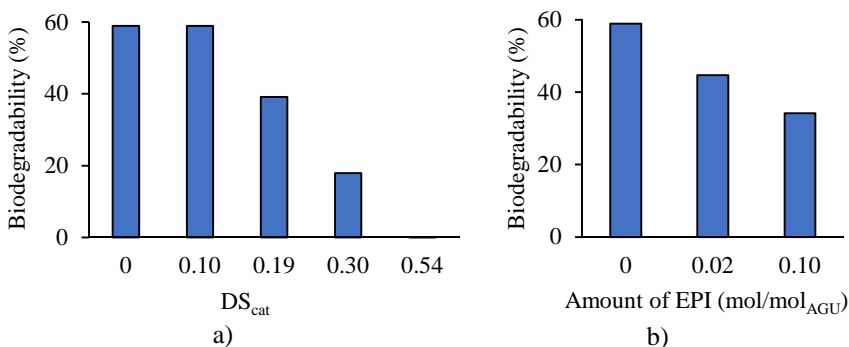


Fig. 3. The dependence of starch biodegradability on the cationic groups (a) and the cross-linking agent (b) amount after 28 days in the model liquid media

The graphs show that the chemically modified starch derivatives are less biodegradable compared to natural starch – biodegradability gradually decreases with the increasing degree of substitution of starch. Starch and $CS_{0.10}$ disintegrated about 59% within 28 days. Meanwhile $CS_{0.19}$ and $CS_{0.30}$ biodegradation values were 39% and 18%, respectively, and $CS_{0.54}$ – only 1%. Insoluble CLS derivatives are less biodegradable. When the biodegradability values of $CS_{0.10}$ and $CLS_{0.10}$ are compared, the samples show that cross-linking has a greater negative impact on the starch biodegradation than cationization – $CLS_{0.10}$ biodegradation value is only 34%.

The **aerobic degradation** of the non-modified and modified starch samples

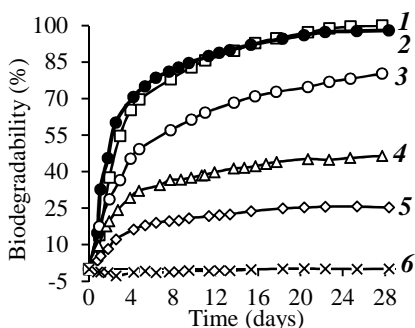


Fig. 4. Starch biodegradability in compost dependence on the duration of the test and DS_{cat} : 1 – 0; 2 – 0.10; 3 – 0.14; 4 – 0.19; 5 – 0.30; 6 – 0.54

in solid media was investigated by Microbial Oxidative Degradation Analyzer (MODA) apparatus. The microgranules of natural starch, various DS_{cat} of CS and cross-linking level of CLS were maintained in compost for 28 days. During the first 5 days, intensive decomposition was maintained and the biggest change in CO_2 evolution was recorded (Figs. 4 and 5). Natural starch and $CS_{0.10}$ disintegrate completely within 20 days, as it is shown in the graphs. These data confirm previous findings – natural

starch and $CS_{0.10}$ are readily biodegradable, then the low degree of substitution CS derivatives when $DS_{cat} \leq 0.10$, naturally break down completely and such derivatives could reasonably be called biodegradable, apart from the fact that the enzymatic hydrolysis of $CS_{0.10}$ under laboratory conditions with pure enzyme α -amylase is more difficult (Table 1). The biodegradability of higher DS_{cat} CS derivatives when DS_{cat} sequence varies 0.14–0.19–0.30, respectively, are 82%–47%–26% after 28 days.

Meanwhile, cationic starch with $DS_{cat} \geq 0.54$ is equivalent to synthetic, non-biodegradable polymers. The influence of cross-linking on biodegradability of starch is analogous – increasing the amount of EPI declines the biodegradation value. However, to compare the $CS_{0.10}$ and $CLS_{0.10}$ samples, the biodegradability of $CS_{0.10}$ reaches 98%, while the value of $CLS_{0.10}$ – 1.3 times smaller, only 77%, again confirming that the influence of starch cross-linking on biodegradability is higher.

The results of the biodegradation test obtained by two methods in different media correlated with each other, suggesting that both methods are adequate for evaluating the biodegradability of starch and its derivatives. However, this can not be said of the research data regarding the digestion of starch derivatives with α -amylase enzyme. Thus, studies with α -amylase do not reflect the modified starch biodegradation taking place in nature.

The fact that the linked cationic quaternary ammonium groups can reduce the biodegradability of starch derivatives was not a surprise, but it was unexpected that cross-linking which creates alkyl bridges between polysaccharide macromolecules, has a greater impact than the attached cationic groups ($CS_{0.10}$ and $CLS_{0.10}$ samples).

2.3. Novel hydromechanical processing method of starch flocculant

The objective of this part of work was to investigate the influence of the mechanical treatment on the state and properties of cationic starch derivatives. Chemically modified starch microgranules without the application of external heat were treated with water and processed using shear forces (shearing). During this process, the swollen microgranules began to rupture and break down, yielding a low viscosity opalescent colloidal disperse system (sheared suspension) composed of dissolved macromolecules and submicroparticles of cationic polysaccharide.

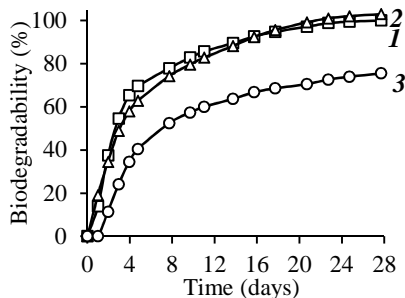


Fig. 5. The dependence of starch biodegradability in compost on the duration of the test and the amount of EPI, mol/mol AGU: 1 – 0; 2 – 0.02; 3 – 0.10

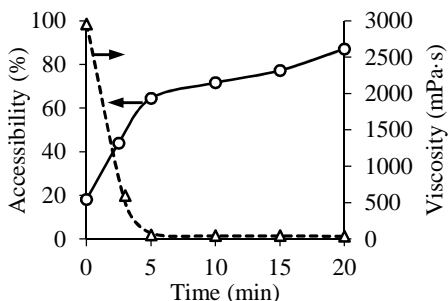


Fig. 6. Dynamic viscosity and the accessibility of cationic groups to polyanions of CS_{0.19} slurry / suspension dependence on shearing time

The mechanical treatment initiated huge changes in the dynamic viscosity of the aqueous CS slurry and in the accessibility of CS cationic centres to polyanions (Fig. 6). A sharp reduction in dynamic viscosity of CS slurry occurred during the first five minutes of shearing (from 2960 to 49 mPa·s) and did not further reduce with additional shearing time, which indicates that a stable colloidal suspension was formed. Not all cationic groups in CS microgels can be reached easily by the macroions, presumably, due to the steric hindrance. The accessibility (A) of cationic centres of the CS_{0.19} slurry was only 18%, but during the first 5 minutes of the mechanical treatment it increased 3.5 times – to 64% and reached 87% after 20 minutes of shearing. A comparison of the accessibility and the dynamic viscosity in the graph indicates the same characteristic reflection point at 5 min in the time-dependence curves. The only difference is that the viscosity values after such a point lies on the plateau, meanwhile the accessibility continuously increases with increasing shearing time. It may be suggested that some qualitative changes in the sheared CS suspension take place during intense mechanical treatment. Presumably, when the microgel particles of CS are subjected to a shearing force, the weak hydrogen bonds and covalent ones are disrupted. The sheared product is non-homogeneous and is composed of swollen microgranule fragments, submicroparticles of CS and dissolved CS macromolecules.

The average molecular weight in kDa of CS_{0.19} before and after shearing is given in Table 2. The molecular weight of the sheared CS_{0.19} by weight (M_w) decreased by half compared to the non-sheared CS. This means that after mechanical treatment the size of CS macromolecules varies and their hydrodynamic volume is smaller; the molecules with a higher molecular weight during shearing are disrupted more. This can be explained by the destruction of

Table 2. The average molecular weight of CS_{0.19} before (1) and after (2) shearing

CS _{0.19}	Molecular weight, kDa			M_w/M_n
	M_n	M_w	M_z	
1	4932	15288	66716	3.10
2	3521	7493	23243	2.13

the large-branched amylopectin macromolecules due to the disruption of covalent bonds and, as a result, the formation of new macromolecules with a lower molecular weight. It is reasonable to suggest that such a

process increases the mobility of the polymer chains and, therefore, facilitates the

approach for the oppositely-charged macroions to certain centres or the structure domains.

The mechanical treatment of cationic starch in cold water causes the changes of slurry – a colloidal opalescent suspension is obtained with smaller particle size which varies from 1 μm to 500 nm (submicroparticles). Submicroparticles of sheared CS have the polydispersity index value (PI) greater than 0.3, which indicates a wide size distribution. In all cases, the positive ζ -potential value of the particles has been determined (Table 3). These submicroparticles are visualised in the SEM picture of freeze-dried CS (Fig. 7).

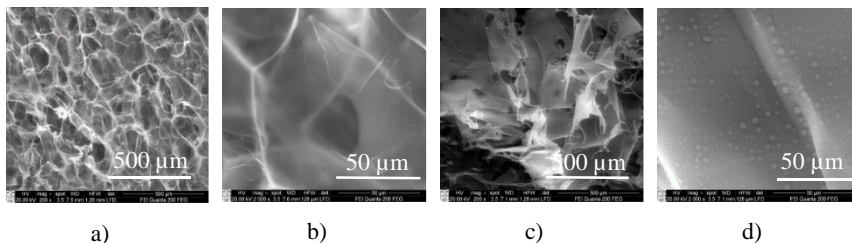


Fig. 7. SEM pictures of freeze-dried CS_{0.19} before (a, b) and after shearing (c, d)

Table 3. The characteristics of cationic starch derivatives before and after shearing

CS sample	Amount of cationic groups in CS, mg-equ/g			Particles of sheared CS in suspension		
	Theoretical according to DS	Accessible to polyanions (experimental value)		Size, nm	PI	ζ -potential, mV
		Slurry	Sheared suspension			
CS _{0.10}	0.564	0.055	0.421	1119 \pm 31	0.41	+34 \pm 2
CS _{0.19}	1.040	0.190	0.803	747 \pm 20	0.34	+41 \pm 1
CS _{0.30}	1.446	0.265	1.232	563 \pm 7	0.36	+46 \pm 1
CS _{0.54}	2.215	0.411	1.915	534 \pm 21	0.33	+51 \pm 1

The conditions of flocculant preparation change after the cross-linking of starch, i.e. to achieve larger accessibility of the cationic group values, greater shearing duration is required (Fig. 8). As in the case of CS, the CLCS accessibility to polyanions increases with increasing shearing duration. It appears that CLCS_{0.19/0.0005 A} is only 4%, and after 30 minutes of shearing – as much as 40%, an

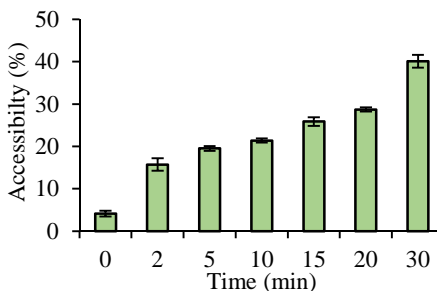


Fig. 8. Accessibility to polyanions of CLCS_{0.19/0.0005} dependence on shearing time

increase of 10 times. The optical microscopy pictures (Fig. 9) show that swollen CLCS microgranules in water after shearing are decomposed to submicron-sized particles.

In summary, two modified starch derivatives can be identified – CS and CLCS and their starch-water mixture composition scheme is presented in Fig. 10. Cationic

starch microgranules in water produce a slurry which contains swollen granules and dissolved macromolecules. In some cases, the CS solutions can be obtained and the A value reaches 100%. CLCS granules in water form microgels and soluble fraction is not available, A is up to 5%. The size of the microgel depends on the cross-linking level, when the amount of EPI is higher, the microgels are denser and take up a smaller hydrodynamic volume. Processing the swollen CLCS microgranules using shear stress (\vec{F}_x), the microgranules are crushed and the higher surface area of microgels is reached, so the A value increases. Meanwhile NIC and AMS derivatives occupy an intermediate state between CS and CLCS flocculants mixtures because the macromolecules of these polysaccharides have the opposite charge of ionogenic groups (Fig. 1). They participate in intermolecular and intramolecular interactions, thus reducing the hydrogel and macromolecular hydrodynamic volume and solubility. In some cases, SPH forms ionically bonded (cross-linked) cationic polysaccharide macromolecules (Fig. 1, NIC).

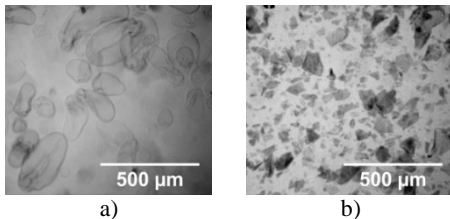


Fig. 9. Optical microscopy pictures of $CLCS_{0.19/0.0005}$ microgranules before (a) and after shearing (b)

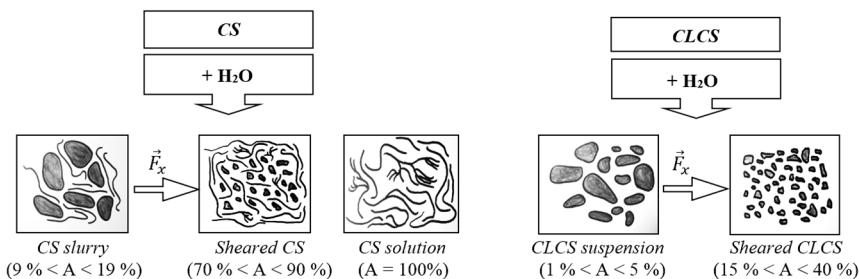


Fig. 10. A scheme of CS, CLCS and water mixtures before and after processing with shear stress (\vec{F}_x)

2.4. Flocculation efficiency of cationic starch derivatives

In order to obtain exhaustive information on the flocculating performance of sheared cationic starch derivatives, the flocculation of fine-particle kaolin suspension has been examined. The quality of ionogenic starches as flocculants after their mechanical treatment is characterized by the minimum dose of the flocculant (C, mg/g) and by the width of the flocculation window (W), which shows that the range of flocculant concentrations where the residual turbidity upon sedimentation is less than 10% can be reached. The lower the C and the wider the W, the more effective flocculation can be expected.

The data of flocculation efficiency of various **degrees of substitution** of cationic starch derivatives are presented in Table 4. It can be seen that the minimum dose of the flocculant decreases with increasing the DS_{cat} from 0.10 to 0.54, meanwhile the flocculation window narrows. This tendency is characteristic of both non-sheared and sheared CS, only the C and W values are much lower in the case of sheared CS. C of sheared CS derivatives is 5–20 times lower and W is 4–10 times narrower than that of non-sheared CS, respectively, when the DS_{cat} increases from 0.10 to 0.54. Taking into account the high affinity of CS to a substrate and the correlation between cationic starch DS_{cat} and the required C, the electrostatic interactions are the main driving force in the flocculation of kaolin suspensions. The different flocculation performance of non-sheared and sheared cationic starches might be explained bearing in mind the peculiarities of their water slurries/suspensions. It is possible to conclude that the sheared cationic starch colloidal dispersion consists of the dissolved linear and branched cationic starch macromolecules of various molecular weights and of CS submicroparticles of various size.

The influence of chemical composition of **cross-linked** cationic starch on the flocculation efficiency was evaluated (Table 5). The flocculation efficiency of CLCS with DS_{cat} increased from 0.19 to 0.28 significant changes were not visible; however, when it increased to 0.39, C reduced from 14.5 to 9 mg/g. This flocculant minimum dose reduction could be adopted as an advantage if there was no negative effect – the width of the flocculation window is

Table 4. Flocculation efficiency of CS before (1) and after (2) shearing

Sample	Flocculation efficiency			
	C, mg/g		W, mg/g	
	1	2	1	2
CS _{0.10}	70	3.5	96	9.5
CS _{0.19}	28	2.5	35	8.5
CS _{0.30}	18.5	2.3	32	7.4
CS _{0.54}	5.3	1.1	18.2	4.7

Table 5. Flocculation efficiency of CLCS derivatives

Sample	Flocculation efficiency	
	C, mg/g	W, mg/g
CLCS _{0.19/0.0005}	14.5	49.5
CLCS _{0.28/0.0005}	14	49
CLCS _{0.39/0.0005}	9	25
CLCS _{0.19/0.01}	383	-
CLCS _{0.19/0.002}	87	-
CLCS _{0.19/0.001}	62	-
CLCS _{0.19/0.0001}	5	8.5

halved. Also, the influence of EPI amount was evaluated and it is visible that C decreases from 383 to 5 mg/g with lowering the EPI amount from 0.01 to 0.0001 mol/mol_{AGU}, respectively. In case of CLCS_{0.19/0.0001}, the density of cross-linking is so low that it behaves almost like CS_{0.19} (Table 4). When the amount of EPI is higher than 0.0005 mol/mol_{AGU}, the microgranules of CLCS swell insufficiently and their density is high, making it more resistant to mechanical stress, i.e. they are not crushed enough after shearing. This greatly reduces the effectiveness of CLCS flocculant: the C values are very large and W is difficult to assess because it has not been determined due to the large quantities. The data shows that the optimal amount of EPI is 0.0005 mol/mol_{AGU} for the CLCS flocculant.

The flocculation properties of cationic flocculant based on starch from various **botanical origins** were examined (Table 6). The differences in flocculation were observed only for gelatinized CS_{0.19}, meanwhile, sheared CS_{0.19} of various origins flocculated in similar way and A is higher than 80% in all cases.

Table 6. Flocculation efficiency and the accessibility of the cationic group to polyanions of various botanical origin CS_{0.19} slurries before (1) and after (2) shearing

CS _{0.19} botanical origins	Flocculation efficiency				A, %	
	C, mg/g		W, mg/g		1	2
	1	2	1	2		
Potato	28	3	35	10	18 ± 2.2	80 ± 2.5
Wheat	19	3	32	10	22 ± 2.3	83 ± 1.4
Maize	11	3	26	9	27 ± 1.2	87 ± 1.6
Rice	9	4	21	12	28 ± 0.8	88 ± 1.1

The incorporation of **anionic groups** to CS structure led to a wider flocculation window (Fig. 11, Table 7). As the figures show, the anionic groups improved the CS flocculation efficiency only when DS_{an} is optimal – AMS_{0.29/0.22}. When DS_{an} is lower, the flocculation efficiency is worse than CS_{0.29} – C needs to be higher and W is narrower. An increase of DS_{an} to 0.34 does not offer any improvement either, because a large dose of an AmS (12 mg/g) is needed to flocculate the kaolin suspension sufficiently. Meanwhile, anionic starch (AS_{0.19}) does not clarify the kaolin suspension sufficiently,

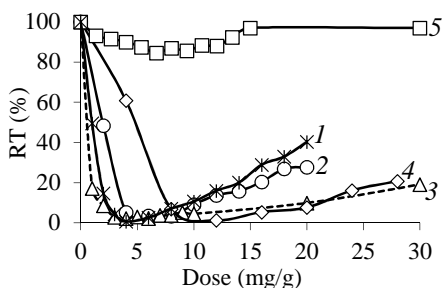


Fig. 11. The residual turbidity of kaolin suspension dependence on flocculant dose, using a sheared flocculant: 1 – CS_{0.30}; 2 – AMS_{0.29/0.13}; 3 – AMS_{0.29/0.22}; 4 – AMS_{0.29/0.34}; 5 – AS_{0.19}

while larger quantities stabilize the suspension due to electrostatic repulsion forces.

The flocculation efficiency of ampholytes obtained by ionic forces (NIC) depend on the amount of SPH introduced during complex formation (Table 7). There was no difference between the flocculation efficiency of the NIC_{0.47/5} or NIC_{0.47/10} and the CS_{0.47} alone. Meanwhile, the NIC_{0.47/25} presented a broader W at the optimal dose than CS_{0.47}. Meanwhile, NIC_{0.47/25+NaOH} destabilized the kaolin suspension in another manner: C decreased 1.87 times and W is wider in comparison with NIC_{0.47/25}. With regards to NIC obtained from CS with DS_{cat}=0.47 and 25 mol% SPH, the degree of substitution after complex formation can be expressed: DS_{cat}=0.35 and DS_{an}=0.24.

It must be mentioned that the **molecular weight** (M_w) of the flocculating agent is one of the most significant factors that influence the flocculating performance. The influence of M_w was evaluated using enzyme-destructed (α -amylase, 0.2 mg/g) CS derivatives with various DS_{cat} (Fig. 12). The enzymatic hydrolysis of CS macromolecules significantly reduced the M_w : 9 kDa, 43 kDa, 80 kDa and 528 kDa, respectively by DS_{cat}: 0.10,

0.19, 0.30 and 0.54, while the initial value of M_w over 15,000 kDa. It is evident that lower molecular weight gives worse flocculation performance and when M_w is lower than 9 kDa the flocculant is ineffective. So the conclusion can be drawn that molecular weight of flocculant must be optimal; in this case, it must be equal or higher than 528 kDa to get good results of flocculation efficiency: C=1.8 mg/g and W=6.8 mg/g. When discussing these results, it should be noted that all investigated samples were soluble, due to the high degree of destruction.

In summary, it is possible distinguish several effective ionogenic starch flocculants and compare them with the widely used synthetic cationic flocculants (SCF₁ – PRAESTOL 859 and SCF₂ – Unafloc 4963) (Table 8). The data shows that effectively bind pollutants required very small amounts of SCF, but the W

Table 7. Flocculation efficiency of AMS and NIC derivatives

Sample	Flocculation efficiency	
	C, mg/g	W, mg/g
AMS _{0.29/0.13}	3.7	6.6
AMS _{0.29/0.22}	1.7	18.3
AMS _{0.29/0.34}	7.7	13.6
NIC _{0.47/5}	2.3	6.7
NIC _{0.47/10}	2.3	6.2
NIC _{0.47/25}	2.8	7.9
NIC _{0.47/25+NaOH}	1.5	8.7

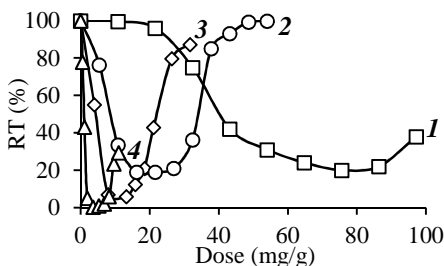


Fig. 12. Residual turbidity of the dependence of kaolin suspension on flocculant dose, using enzyme-destructed (0.2 mg/g) flocculant: 1 – CS_{0.10}; 2 – CS_{0.19}; 3 – CS_{0.30}; 4 – CS_{0.54}

value is also small – it is easy to overdose such flocculant and the suspension can be quickly restabilized. The optimum composition of ionogenic starch flocculant W value is significantly higher. This is one of the main advantages of these flocculants, while the C values are similar or up to 10 times higher.

Table 8. Flocculation efficiency of various flocculants

Sample	Flocculation efficiency	
	C, mg/g	W, mg/g
SCF ₁	1.7	3.1
SCF ₂	1.2	7.8
CS _{0.19}	2.5	8.5
AMS _{0.29/0.22}	1.7	18.3
CLCS _{0.19/0.0005}	14.5	49.5

2.5. Models of flocculation mechanism for destabilizing the kaolin suspension

Ionogenic starch flocculants consisting of shorter linear and longer branched macromolecules and those of different size hydrogels containing cationic and/or anionic groups. Ionogenic groups are involved in the electrostatic interaction and compose ionic bonds with the opposite charge-branded compounds or solid particles, for example, kaolin. The particles of kaolin have negative charge, therefore, they interact easily with ionogenic starch flocculants which have quaternary ammonium groups. The mechanism of interaction and the ratio of kaolin and flocculant's structural elements involved in the interaction depend on the composition of flocculant, if it is composed of soluble macromolecules and/or hydrogels.

Derivatives containing cationic groups adsorb on the surface of kaolin particle. Short macromolecules and small hydrogels involved in close interaction with negative charge of kaolin particle. The thickness of the adsorbed macromolecule and particle layer is smaller than Debye radius $1/\kappa$ of kaolin particle; consequently, it can not be involved in the "bridge" formation with other particles because of high potential repulsion¹⁸. As a result, positive charge "patches" are formed, which decrease the initial charge of kaolin particles and further electrostatically interact with the uncovered parts of a particle surface – compose associates and, subsequently, aggregates. Flocculation occurs in accordance with a mosaic ("charge patch") mechanism. When the flocculant macromolecules are long enough (high molecular weight) and hydrogels are larger in sizes, they come out beyond the diffuse layer of the kaolin particles and extend beyond the Debye radius, the repulsive force between particles is weak, therefore the macromolecules or hydrogels of a flocculant can form a "bridge" between two or more particles with opposite charge – they aggregate, form floccules and settle down because of higher weight of floccules. Flocculation occurs in accordance with the "bridges" mechanism.

The predominant mechanism of the flocculation model can be seen from ζ -potential values of flocculus obtained after the destabilization process (Fig. 13). Flocculus ζ -potential dependence on the dose of flocculant was determined using various DS_{cat} sheared CS derivatives and synthetic flocculant. The curves show that higher DS_{cat} -sheared CS rather fully replaces the charge of kaolin particle surface from a negative to positive value. A flat curve segment can be associated with the flocculation window width – efficient flocculation begins minimal change of ζ -potential of the flocculus, and when the ζ -potential becomes high, the positive value initiates the restabilization process. Increasing the solubility of CS, e.g. increasing the amount of

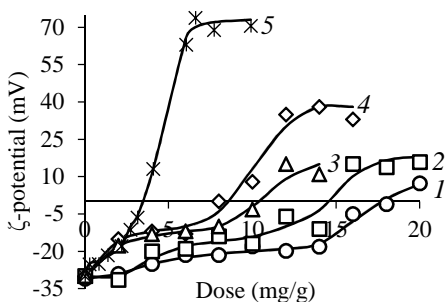


Fig. 13. ζ -potential of flocculus dependence on flocculant dose: 1 – $CS_{0.10}$; 2 – $CS_{0.19}$; 3 – $CS_{0.30}$; 4 – $CS_{0.54}$; 5 – SCF_1

soluble macromolecules, the density of cationic groups and decreasing the particle size (Table 3), the CS adsorbs into the denser surface of the kaolin particle and takes up more surface area during the flocculation. Therefore, the flocculus ζ -potential values of destabilized kaolin suspension with $CS_{0.54}$ show a sharp rise of the positive value. Destabilizing the kaolin suspension with SCF_1 composed entirely of soluble macromolecules also produced a sharp change of flocculus ζ -potential; there is no horizontal segment and the disperse system is restabilized faster. This is due to the fact that SCF_1 act solely on the “bridges” consisting of macromolecules flocculation mechanism.

In summary, the results obtained from destabilizing the kaolin suspension with ionogenic starch flocculants, the scheme of destabilized kaolin disperses phases, flocculant structural elements and possible flocculation mechanisms can be suggested. (Fig. 14). The flocculation mechanisms of CS derivatives are mentioned above thus the mechanisms of amphoteric starch derivatives should be explained in more detail. The presence of counterion macromolecules enables to create more opportunities for interactions. Polyampholytes (AMS, NIC) can react with each other thus extending the involvement of intramolecular interaction (Fig. 14, D, 1) and creating an additional opportunity to flocculate by the “bridges” mechanism (Fig. 14, D). Insoluble AMS and NIC derivatives (higher DS_{an}) adsorbed on the surface of kaolin particles form “patches” and are followed by the possibility of a “bridge” formation between the other kaolin particles directly or through ampholyte with an opposite charge fragment (Fig. 14, E, 2), as in the case of CLCS. When flocculants are used in non-sheared ionogenic starch slurries or suspensions, their swollen hydrogels are generally higher than 100 μm , the

flocculation process takes place in the reverse order – contaminants adsorbed on the surface of the hydrogel form negatively charged “patches” (Fig. 14, F).

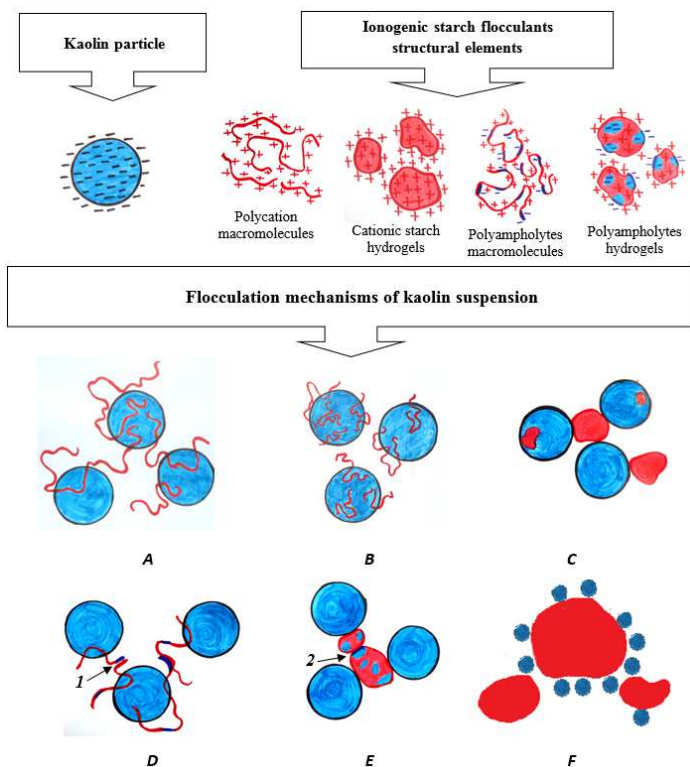


Fig. 14. Disperse phases of destabilized kaolin, structural elements of flocculants and flocculation mechanisms: *A* – “bridges”, flocculant – soluble high molecular weight macromolecules; *B* – “patch charge”, flocculant – soluble low molecular weight macromolecules; *C* – “bridges”, “patch charge”, flocculant – sheared hydrogel particles (submicron-sized); *D* – “bridges”, “patch charge”, flocculant – soluble amphoteric starch macromolecules; *E* – “bridges”, “patch charge”, flocculant – amphoteric starch hydrogel particles (submicron-sized); *F* – “patch charge”, kaolin particle adsorption onto ionogenic starch hydrogels.

2.6. Municipal wastewater sludge treatment

This section discusses the suitability of the optimal efficiency ionogenic starch flocculants (sheared CS_{0.19} and CLCS_{0.19/0.0005}) for municipal sewage sludge

thickening and their effectiveness is compared with the widely used synthetic cationic flocculants.

2.6.1. Thickening the surplus activated sludge

The efficiency of SCF and sheared CS and CLCS was determined by measuring the filtrate flow time of the destabilized kaolin suspension (Fig. 15). Figure 15 shows that CS_{0.19} is not effective, as the filtration rate of the thickened sewage sludge does not even reach 10 ml/s. Meanwhile, in the case of SCF, the filtration rate reaches 400 ml/s, but with an increasing dose of flocculant the rate suddenly decreases; it indicates that the flocculating agent is overdosed and the restabilization of the disperse system takes place. In the case of CLCS_{0.19/0.0005}, a large dose of flocculant is needed to achieve higher filtering values (≥ 100 ml/s): 50 mg/g or more. Although the effective dose of CLCS is much higher than SCF, as many as 10 times; however, using this flocculant, the system is not restabilized and a wide flocculation window is clearly visible.

Another important parameter is that the flocculus would be readily and rapidly dewatered after the destabilization process. The filtration efficiency results were obtained using a standard CST apparatus (Fig. 16) and it can be seen that SCF, CS and CLCS filtration efficiency (the dewaterability) of the surplus active sludge is similar: SCF₁ – 69%, CS_{0.19} – 67% and CLCS_{0.19/0.0005} – 72%. However, the flocculant is overdosed (in higher doses) when filtration efficiency decreases, which is particularly notable in the case of synthetic flocculant. The suitability of the flocculant for sewage sludge thickening can be determined from the dewatered

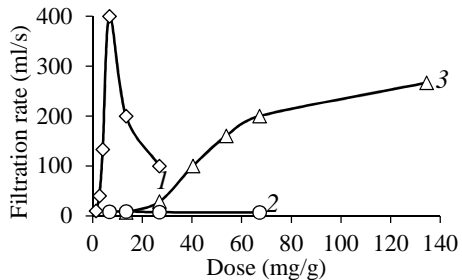


Fig. 15. Filtration rate dependence on flocculant dose thickening surplus activated sludge of Kauno vandenys Ltd: 1 – SCF₂; 2 – sheared CS_{0.19}; 3 – sheared CLCS_{0.19/0.0005}

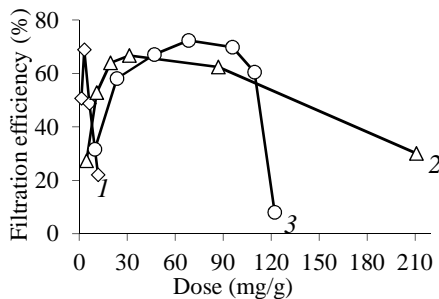


Fig. 16. Filtration efficiency of dewatering of thickened surplus activated sludge of Kauno vandenys Ltd dependence on flocculant dose: 1 – SCF₁; 2 – sheared CS_{0.19}; 3 – sheared CLCS_{0.19/0.0005}

flocculus pictures (Fig. 17). The optimal the flocculus must be large and strong, as in cases of SCF and CLCS (Fig. 17, b and d).

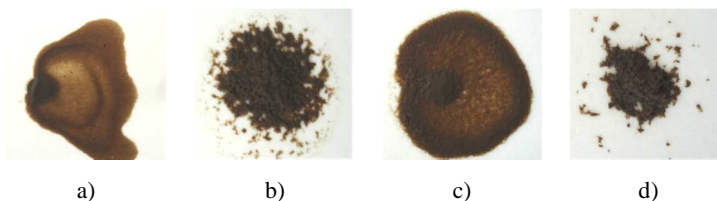


Fig. 17. Pictures of dewatered thickened surplus activated sludge (Kauno vandenys Ltd) flocculus: raw sludge (a) and thickened with SCF₁ (b), sheared CS_{0.19} (c) and CLCS_{0.19/0.0005} (d)

The flocculus formed during flocculation must be not only large, but durable and resistant to mechanical stress as well. The strength of the flocculus is determined in accordance with filtration efficiency, with different mixing intensity (Fig. 18). When the mixing intensity is low (≤ 500 rpm) the flocculus is not destroyed. However, when the mixing intensity increases to 1200 rpm, the observed filtration efficiency decreases; the strength of the flocculi by using different flocculant can be ranked in the following order: SCF₁>CS>CLCS. It can be concluded that the flocculus obtained with CLCS flocculant is most resistant to mechanical stress than others. Comparing the flocculus resistance of SCF and CLCS to mechanical stress, it can be related to the dominant mechanism of flocculation. Considering that soluble macromolecules adsorb on the surface of

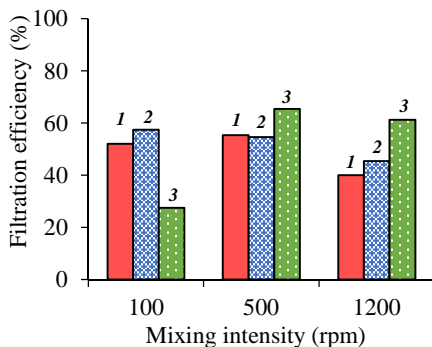


Fig. 18. Filtration efficiency of thickened surplus activated sludge of Kauno vandenys Ltd dependence on mixing intensity when flocculant dose is optimal: 1 – SCF₁; 2 – sheared CS_{0.19}; 3 – sheared CLCS_{0.19/0.0005}

contaminants under “bridges” consisting of macromolecules mechanism (Fig. 14) it can be readily destroyed by affecting them with external forces as compared to CLCS when the “bridges” consist of particles and the formed “bridge” is not easily broken due to a smaller distance and thus stronger forces of interaction. In the case of CS, the “patch charge” flocculation mechanism is predominant, which results in smaller flocculus and weaker interaction between the pollutants, thus it is easier to disrupt it mechanically.

2.6.2. Production of biogas from surplus activated sludge in a methane tank

Biogas is produced during the digestion process when anaerobic microorganisms digest the organic matter in the methane tank. The experiment was done in the biogas laboratory of Aleksandras Stulginskis University. The impact of biogas production on synthetic flocculant and ionogenic starch flocculant (CS_{0.30}) was evaluated digesting the thickened surplus activated sludge under anaerobic conditions in the vertical biogas reactors. The yield and composition of the biogas (methane and hydrogen sulphide concentration) were investigated during digestion. The average yield of biogas from the control of raw material (sludge thickened with SCF) was 14.2 l/kg_{raw material} (B_M) or 379.0 l/kg_{dry material} (B_{SM}) and 493.4 l/kg_{dry organic material} (B_{SOM}). Meanwhile, in the case of CS_{0.30}, 1 kg of raw material produced a higher yield of biogas: 6% by B_M, 19% by B_{SM} and even 21% by B_{SOM}. The composition of the biogas is also better – 0.6% higher methane concentration, 133 ppm less hydrogen sulphide and higher energy value. The pH of the substrate throughout the entire experiment in the reactor was about 7.4, suggesting that anaerobic process of sewage sludge was stable. The obtained results suggest that when using CS_{0.30} instead SCF, the digestion process is easier and more efficient, and the ionogenic starch flocculants, unlike the synthetic one, are biodegradable and decompose during the digestion process.

2.7. Technological scheme of ionogenic starch production

The cross-linked cationic starch flocculant can be produced as both “liquid” and “solid” forms, depending on the needs and technical possibilities. The production of the CLCS flocculant consists of 7 phases. First, the modifying solution consisting of cationization, cross-linking agents and aqueous hydroxide solution is prepared. All is well-mixed at room temperature. The starch solution is modified and intensively mixed and the mixture is left at 45°C for 48 hours. After the reaction ends, the reaction mixture is neutralized in order to avoid the destruction of modified starch and equipment corrosion. During the preparation of “**liquid**” form of CLCS flocculants, its particles are swollen in water and then sheared using shear stress reducing the particle size and increasing the surface area, which increases the accessibility of cationic groups to polyanions. Finally, CLCS is preserved, for example, with sodium metabisulphite (Na₂S₂O₅), and then the product can be packaged to sealed containers. The first three stages of preparing the “**solid**” form of CLCS flocculant are analogous. Then the resulting reaction product is sieved in order to homogenise the semi-finished product so that the next extruding process run smoothly and steadily. CLCS is treated with shear stress and high temperature. The resulting product – an extrudate, is crushed to granules of the chosen size and/or powdered. Since the resulting product is dry, its preservation is not necessary, therefore, it can be immediately packaged in moisture-proof bags.

According to the CLCS flocculant production stages a technological scheme is offered (Fig. 19). The manning, equipment size and capacity of the technological scheme depend on the form and content of the product.

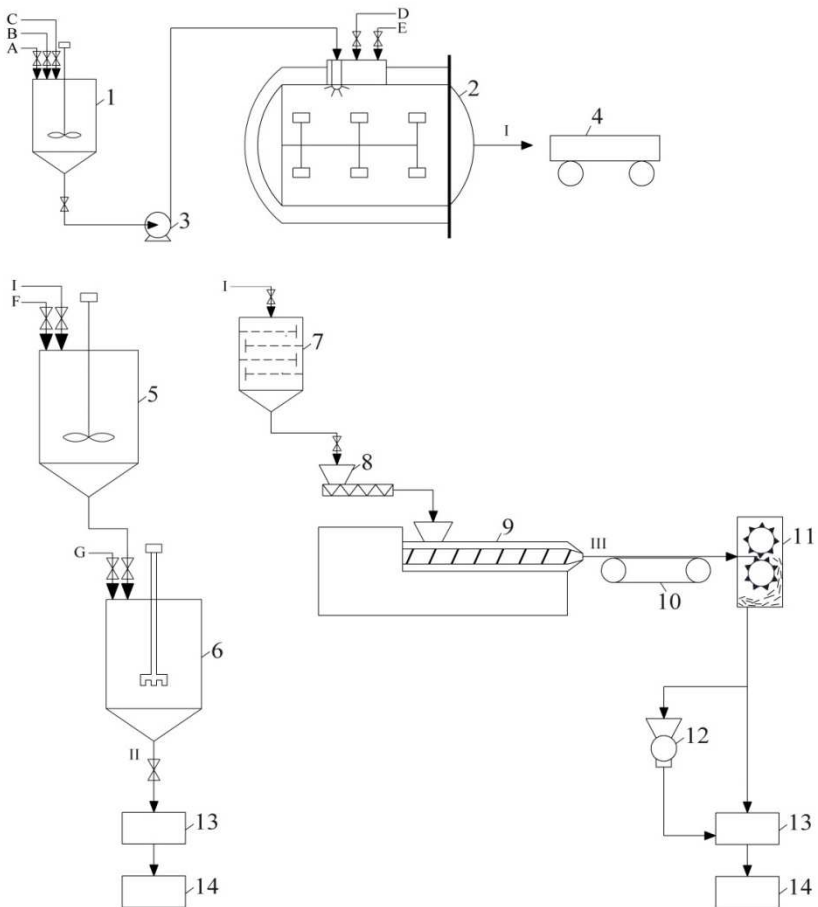


Fig. 19. A technological scheme of CLCS flocculant production: 1, 5 – mixer; 2 – reactor; 3 – pump; 4 – trolley; 6 – dispersator; 7 – sieve; 8 – screw conveyor; 9 – extruder; 10 – belt conveyor; 11 – cutter; 12 – mill; 13 – product packaging; 14 – product storage. I – semi-finished product; II – Sheared CLCS suspension; III – CLCS extrudate

3. CONCLUSIONS

1. Etherification of natural starch with 2,3-epoxypropyltrimethylammonium chloride produced N-(2-hydroxy)propyl-3-trimethylammonium starch chloride in the form of microgranules – cationic starch with a degree of substitution by quarternary ammonium groups is from 0.10 to 0.54; it is further used in the synthesis of different ionogenic starch derivatives of chemical composition and structure for the production of potential flocculants: limited swelling cross-linked cationic starch, amphoteric starch with carboxylic and predominant quaternary ammonium groups and the non-stoichiometric ionic complexes.
2. Cationic starch derivative with a degree of substitution by cationic groups of 0.1 or smaller is biodegradable, i.e. completely decompose within 28 days. The increasing degree of substitution of cationic starch decreases the biodegradability accordingly, and the biodegradability of cationic starch with a degree of substitution of 0.54 is only 1% after 28 days.
3. The swollen microgranules of cationic starch treated with shear forces decreases the particle size, molecular weight, viscosity of slurries of the ionogenic starch and increases the accessibility of cationic groups to polyanions.
4. The efficiency of ionogenic starch flocculants depends on its chemical composition and spatial structure of macromolecules, the ratio of amount of cationic and anionic groups, the molecular weight of modified starch and its preparation method.
 - 4.1. The larger the amount of cationic groups in the derivative is, the lower the minimum effective dose of flocculant and the narrower the flocculation window.
 - 4.2. A higher flocculation efficiency of amphoteric starch is observed when the amount of anionic and cationic groups is optimal, i.e. the ratio of cationic and anionic groups is 0.29/0.22 in the case of amphoteric starch and 0.35/0.24 in the case of non-stoichiometric ionic complexes.
 - 4.3. The minimum effective dose of non-sheared ionogenic starch flocculants of different botanical origin decreases and the flocculation window narrows depending on the starch particle size in a range: potato>wheat>maize>rice, while, the efficiency of sheared ionogenic starch flocculants is independent on the botanical origin of the raw material.
 - 4.4. A Cross-linked ionogenic starch flocculant consists of a higher mechanical strength of flocculus during the flocculation, compared with the flocculus obtained using modified starch flocculant composed from linear and branched macromolecules or synthetic cationic flocculant.

5. Modified starch flocculant with quaternary ammonium groups consisting of linear and branched macromolecules and submicron-size hydrogels, interacts with particles of kaolin suspension. It reduces the negative potential of kaolin suspension and creates the opposite charge “patches” on its or primary compounds, which consist of the opposite charge hydrogels and particles of suspended matter. The initiating association and aggregation of substituted and unsubstituted particles during the macromolecules of flocculant form “bridges” or the hydrogels of flocculant – hydrogel “bridge”.
6. Sheared cross-linked cationic starch is the most suitable for thickening municipal sewage sludge. Despite the fact that the dose of cross-linked cationic starch to reach an effective flocculation is high compared to the dose of synthetic cationic flocculant normally used in water treatment, it is effective in a significantly broader range of flocculant amount: the flocculation window is as much as 15 times wider. In addition, in further anaerobic digestion processes, a higher amount of biogas is produced from the thickened sewage sludge with modified starch flocculant.
7. A technological scheme for the production of modified starch flocculant was invented. According to this scheme, a prototype of cross-linked cationic starch flocculant was produced in the pilot of equipment and tested in the water treatment company of Lithuania.

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REZIU MĖ

Temos aktualumas

Viena iš didžiausių šių dienų problemų – miesto nuotekos, jų perdirbimas ir utilizavimas. Aplinkos apsaugos agentūros pateiktais duomenimis, Lietuvoje per 2012 m. į gamtinę aplinką išleista 179,5 mln. m³ valytinų buitinių, gamybinių ir komunalinių nuotekų. 2012 m. nuotekų valymo metu susidarė per 45 tūkstančius t dumblo [1] (pagal sausas medžiagas), kurio tik nedidelė dalis (apie 40 proc.) yra panaudojama tikslingai (tręšti, kompostuoti ir kt.), visas likęs dumbblas yra kaupiamas dumblo saugojimo aikštelėse. Europos Sąjungos Taryba yra priėmusi direktyvas Nr. 91/271/EEB [2] ir Nr. 86/278/EEB [3] dėl miesto nuotekų valymo ir aplinkos, ypač dirvožemio, apsaugos naudojant žemės ūkyje nuotekų dumblą, kurių pagrindinis tikslas yra apsaugoti aplinką nuo žalingo nuotekų poveikio.

Skysčio ir kietos medžiagos dalelių atskyrimo, arba sistemos stabilizavimo, procesai lemia produkcijos gamybos technologijų efektyvumą popieriaus, metalų, maisto pramonėje, vandenvaloje, paruošiant vandenį, biotechnologijoje ir kt. Pridedant į dispersines sistemas flokulantų, jose esančios dalelės sujungiamos į dideles greitai sėdančias flokules ir taip yra atskiriamos nuo skysčio. Flokuliacijai ir dispersinės sistemos fazėms atskirti pakanka kelių kilogramų tirpaus sintetinio flokulianto tonai sausų kietų medžiagų. Tačiau dėl prigimtinio angliagrūdinių makromolekulių atsparumo sintetiniai flokuliantai nesuyra, lieka valytame vandenyje, sausintame dumble ir komplikuoja jo tolimesnį perdirbimą bei panaudojimą. Be to, naudojant sintetinius flokuliantus, optimalus ir patikimas fazių atskyrimas vyksta siauru mažiausios ir didžiausios veiksmingų flokulianto dozių intervalu, kitaip dar vadinamu „flokuliacijos langu“.

Kitas svarbus aspektas – tai, kad sintetiniai flokuliantai gaunami iš naftos produktų, dažniausiai iš akrilamido, kuris yra toksiškas, klasifikuojamas kaip ypač pavojinga medžiaga (EPCRA, 42 U.S.C. 11002) [4] ir yra priskiriamas prie kancerogeninių medžiagų [5]. Todėl labai svarbu rasti tokį atitikmenį sintetiniams flokuliantams, kad prilygtų savo efektyvumu, būtų gaunamas iš atsinaujinančių gamtos išteklių ir nebūtų kenksmingas supančiai aplinkai. Vienas iš potencialių tokiems flokuliantams gauti naudojamų gamtinių polimerų yra krakmolai – jo skilimo produktai draugiški aplinkai, jis bioskaidus ir yra gaunamas iš atsinaujinančių šaltinių, pvz., iš bulvių, kviečių, kukurūzų ir kt. Todėl modifikuoto krakmolo flokuliantai gali būti tinkama alternatyva pramonėje naudojamiems sintetiniams flokuliantams.

Tokios ekologinės inovacijos padeda pasiekti darnaus vystymosi tikslą, mažinant neigiamą gamybos poveikį aplinkai, taip pat efektyviau ir atsakingiau naudojant gamtos išteklius, vykstant labiau aplinką tausojantį verslą, sprendžiant klimato kaitos, išteklių trūkumo ir biologinės įvairovės nykimo problemas.

Disertacinio darbo tikslas

Šio darbo tikslas yra sukurti efektyvų bioskaidų ketvirtinių amoniograpių turintį modifikuoto krakmolo flokuliantą, kuris tikėtų neigiamo paviršiaus krūvio teršalams pašalinti ir komunalinių nuotekų dumbalui tankinti.

Darbo tikslui pasiekti suformuluoti šie uždaviniai:

1. Susintetinti įvairios cheminės sudėties krakmolo darinius, turinčius ketvirtinių amoniograpių;
2. Nustatyti krakmolo darinių bioskaidumą;
3. Gauti efektyvų jonogeninio krakmolo flokuliantą;
4. Nustatyti fizikinių-cheminių veiksnių įtaką jonogeninio krakmolo flokulianto efektyvumui;
5. Patikrinti jonogeninio krakmolo flokulianto tinkamumą tiek modelinėms kaolino dispersinėms sistemoms, tiek realiam komunalinių nuotekų dumblo tankinimui ir sausinimui;
6. Pasiūlyti jonogeninio krakmolo flokulianto gavimo technologinę schemą ir pagaminti jo prototipą esamoje įrangoje.

Mokslinis darbo naujumas

Pasiūlytas naujas hidromechaninis krakmolo flokuliantų gavimo būdas, parinktos sąlygos gauti efektyvų ir bioskaidų tinkamos struktūros jonogeninio krakmolo flokuliantą. Pirmą kartą nustatyta katijoninio krakmolo darinių bioskaidumo priklausomybė nuo pakeitimo laipsnio. Remiantis modelių sistemų ir komunalinių nuotekų destabilizavimo tyrimų rezultatais, pasiūlytas naujų modifikuoto krakmolo darinių flokuliacinis mechanizmas.

Praktinė darbo vertė

Nustatyta, kad komunalinių nuotekų dumbalui tankinti geriausiai tinka disperguotas tinklinio katijoninio krakmolo darinys, kurį naudojant susidaro stambios mechaniniam poveikiui atsparios flokulės. Pilotinėje įrangoje pagamintas jonogeninio krakmolo flokulianto prototipas, kuris išbandytas Lietuvos vandenvalos įmonėje. Nors tokio flokulianto efektyvi dozė didesnė, palyginti su įprastai nuotekoms valyti naudojamu sintetiniu katijoniniu flokuliantu, tačiau naujasis modifikuoto krakmolo flokuliantas turi šiuos privalumus:

- flokuliantas gaunamas iš atsinaujinančių gamtos išteklių;
- žaliava bioskaidi;
- naudojama flokulianto gamyba be atliekų;
- flokuliantas veiksmingas plačiu dozių intervalu;
- flokuliantas bioskaidus, perdirbant sutankintą biomasę, lengvai suyra, neteršia gamtos, todėl toliau gauta biomasė gali būti naudojama kaip trąša;

- perdirbant sutankintą biomasę, gaunama didesnė biodujų išeiga ir geresnė jų kokybė (mažesnis divandenilio sulfido ir didesnis metano kiekis).

Ginamasis disertacijos teiginys

Komunalinių nuotekų dumbliui tankinti ar sausinti tinkamas efektyvus bioskaidus modifikuoto krakmolo flokulantas yra gaunamas šlyties jėgomis iki submikroninio dydžio dalelių disperguojant išbrinkintą ketvirtinių amoniograpių turinčio mikrogranulių pavidalo krakmolą, kurio pakeitimo laipsnis pagal prijungtas katijonines grupes yra ne didesnis negu 0,30.

Darbo aprobavimas ir publikavimas

Doktorantūros studijų metu „Clarivate Analytics Web of Science“ duomenų bazės žurnaluose, turinčiuose citavimo indeksą, disertacijos tema paskelbtos 3 publikacijos. 5 publikacijos paskelbtos kituose recenzuojamuose leidiniuose ir 6 publikacijos – tarptautinių konferencijų pranešimų medžiagoje. Įregistruotas 1 patentas (EU patento paraiška) tarptautinėje patentų tarnyboje (EPO) ir įregistruoti 2 patentai nacionalinėje patentų tarnyboje. Atliktas gamybinis bandymas įmonėje UAB „Kauno vandenys“, nuotekų valykloje. Pasiūlyta produkto gavimo technologija ir esamoje pilotinėje įrangoje pagamintas jo prototipas.

IŠVADOS

1. Eterinant gamtinį krakmolą 2,3-epoksipropiltrimetilamonio chloridu gautas mikrogranulių formos 2-hidroksipropiltrimetilamonio krakmolo chloridas – katijoninis krakmolas, kurio pakeitimo laipsnis pagal ketvirtines amoniogrupes yra 0,10–0,54, toliau jis panaudotas sintetinant įvairios cheminės sudėties ir struktūros jonogeninio krakmolo darinius, potencialius flokulantus: riboto brinkumo tinklinį katijoninį krakmolą, amfoterinį krakmolą su karboksi- ir vyraujančiomis ketvirtinėmis amoniogrūpėmis bei nestechiometrinius joninius kompleksus.
2. Katijoninio krakmolo darinys, kurio pakeitimo laipsnis pagal katijonines grupes yra 0,1 ir mažesnis, yra bioskaidus, t. y. visiškai suyra per 28 paras. Toliau didinant katijoninio krakmolo pakeitimo laipsnį, bioskaidumas atitinkamai mažėja, ir po 28 parų katijoninio krakmolo, kurio pakeitimo laipsnis yra 0,54, jis siekia tik 1 proc.
3. Išbrinkusias katijoninio krakmolo mikrogranules paveikus šlyties jėgomis, sumažėja jonogeninio krakmolo dalelių dydis, molekulinė masė, kleisterių klampa, padidėja katijoninių grupių prieinamumas polianijonams.
4. Jonogeninių krakmolo flokulantų efektyvumas priklauso nuo flokulianto cheminės sudėties ir jo makromolekulių erdvinės struktūros, katijoninių ir anijoninių grupių kiekio santykio, modifikuoto krakmolo molekulinės masės bei jo paruošimo būdo.

- 4.1. Kuo didesnis prieinamų katijoninių grupių kiekis darinyje, tuo mažesnis minimalus efektyvus flokulianto kiekis, o flokuliacijos langas – siauresnis.
- 4.2. Amfoterinio krakmolo didžiausias flokuliacijos efektyvumas yra esant optimaliam katijoninių ir anijoninių grupių santykiui, kuris amfoteriniame krakmole yra 0,29/0,22, o nestechiometriniuose joniniuose kompleksuose – 0,35/0,24.
- 4.3. Nedisperguotų skirtingos botaninės kilmės jonogeninio krakmolo flokuliantų efektyvi flokuliacijos dozė mažėja ir flokuliacijos langas siaurėja, priklausomai nuo krakmolo dalelių dydžio, tokia seka: bulvių > kviečių > kukurūzų > ryžių, o disperguotų jonogeninio krakmolo flokuliantų efektyvumas nuo žaliavos botaninės kilmės nepriklauso.
- 4.4. Tinklinės struktūros jonogeninio krakmolo flokuliantai flokuliacijos metu sudaro didesnio mechaninio atsparumo flokules, palyginti su flokulėmis, gautomis naudojant modifikuoto krakmolo flokuliantus, sudarytus iš linijinių ir šakotų makromolekulių, ar sintetinį katijoninį flokuliantą.
5. Ketvirtinių amoniograpių turintis modifikuoto krakmolo flokuliantas, sudarytas iš linijinių, šakotų makromolekulių ir submikroninio dydžio hidrogelių, sąveikauja su destabilizuojamos kaolino suspensijos dalelėmis, mažina jų neigiamą potencialą ir sukuria ant jų priešingo krūvio „dėmes“ arba pirminius darinius iš priešingo krūvio ženklų hidrogelių ir suspenduotos medžiagos dalelių, taip inicijuojama pakeistų ir nepakeistų dalelių asociacija ir agregacija per flokulianto makromolekulių „tiltelius“ arba flokulianto hidrogelio daleles – hidrogelio „tiltelius“.
6. Komunalinių nuotekų dumbliui tankinti geriausiai tinka disperguotas tinklinis katijoninis krakmolas. Nepaisant to, kad tinklinio katijoninio krakmolo flokulianto dozė efektyviai flokuliacijai pasiekti reikalinga didesnė, palyginti su vandenvalyje naudojamo sintetinio katijoninio flokulianto doze, tačiau jis veiksmingas esant įvairiam flokulianto kiekiui: flokuliacijos langas net 15 kartų platesnis. Be to, tolimesniame anaerobinio nuotekų dumblo pūdymo procese iš apdoroto nuotekų dumblo, tankinto naudojant modifikuoto krakmolo flokuliantą, susidaro didesnis biodujų kiekis.
7. Sukurta bioskaidaus modifikuoto krakmolo flokulianto gavimo technologija. Pagal ją naudojant pilotinę įrangą pagamintas tinklinio katijoninio krakmolo flokulianto prototipas ir išbandytas Lietuvos vandenvalos įmonėje.

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UDK 664.2 (043,3)

SL344. 2017-06-22, 2,5 leidyb. apsk. I. Tiražas 50 egz.

Išleido Kauno technologijos universitetas, K. Donelaičio g. 73, 44249 Kaunas
Spausdino leidyklos „Technologija“ spaustuvė, Studentų g. 54, 51424 Kaunas