

Flocculation efficiency of hybrid polymers with trivalent metal cations

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Acrylamide/acrylic acid copolymers (AAm/AA) have been synthesized by microemulsion polymerization in absence and presence of trivalent cations Al^{+3} and Fe^{+3} . Starch materials were obtained by introducing cations Al^{+3} and Fe^{+3} , in the form of aqueous solutions of sulphates(VI) (modif. starch/ Me^{+3}), into the oxidized starch (modif. starch). The flocculation performance of obtained polyacrylamide copolymers and the one based on the natural polymer was compared with the performance of the commercial AAm/AA flocculant (CF). All materials were characterized by capillary viscometry, FTIR and DSC methods. An aqueous suspension of talc was used for the flocculation studies. The flocculation effectiveness was evaluated on the basis of reduction of suspension extinction and the sludge volume. It was found that synthesized AAm/AA/ Me^{+3} copolymers and modif. starch/ Me^{+3} materials exhibit better flocculation properties for a model talc suspension than a commercially available flocculant.

Keywords: polyacrylamide copolymers, starch, hybrid polymers, trivalent metal cations, flocculants.

INTRODUCTION

Polyacrylamide is one of the most important water soluble polymers with many applications. In fact, almost all industrial “polyacrylamides” are copolymers of pure nonionic acrylamide and ionic acrylates e.g. acrylic acid. Polyacrylamide has such a wide usage for the following reasons: very high molecular weight, water solubility, forms strong hydrogen bonding with mineral particles and can be easily modified.

The acrylamide based polymers and copolymers find the greatest utility in waste water treatment and water clarification processes¹⁻⁵. In spite of a great number of available flocculant agents and research articles, the problem of natural water, industrial waste and waste water treatment has not been solved yet. Variability of characteristics and variety of sewage stimulate searches for new more effective or selective flocculants. Comparatively new and prospective flocculants are hybrid polyacrylamide and starch materials. Acrylamide copolymers modified by polyvalent metal cations may be obtained in polymerization processes in the presence of inorganic substances (*in situ*)^{6,7} or by the modification of already synthesized hydrophilic polymers^{8,9}.

Poly(acrylamide-co-acrylic acid) interacts with many metal cations in aqueous solutions¹⁰. Aluminium and iron(III) cations introduced into a copolymerization mixture of acrylamide and acrylic acid create a bonding with carboxylic or amide group. The cations can complex together polyacrylamide chains resulting in the growth and branching of a copolymer structure. Such a polymeric-metal cation hybrid is characterized by a high absorption surface effecting in higher flocculation effectiveness in comparison with unmodified polyacrylamide.

Polysaccharides^{11,12} are also an attractive research material for the production of new flocculating materials. In recent years, intensive research on flocculants combining synthetic and natural polymers^{13,14} is carried out. Starch is a natural, renewable, completely biodegradable¹⁵ plant reserve compound. Starch is a beneficial alternative to synthetic materials obtained from petroleum raw materials¹⁶⁻¹⁹. Starch can be modified chemically, physically and enzymatically²⁰⁻²³. The chemical modification of

starch can be carried out in many ways, e.g. cross-linking, esterification, etherification or oxidation. However, scientists confirm that chemical modification is the most effective to modify the structure of biopolymers and their properties²⁴.

In the present work, the characterization and flocculation efficiency of synthesized poly(acrylamide-co-acrylic acid), oxidized starch and their hybrid in the presence of trivalent metal cations like aluminium (Al^{+3}) and iron (Fe^{+3}) have been studied. The flocculation abilities of the obtained hybrids were compared to a commercially available flocculating agent CF. The AAm/AA/ Me^{+3} copolymers were prepared via *in situ* “water-in-oil” emulsion polymerization processes. The starch hybrids (modif. starch/ Me^{+3}) were obtained by the instillation of an aqueous solution of the aluminium or iron sulphates(VI) to the oxidized starch. The received materials and the commercial flocculant were characterised by capillary viscometry, FTIR and DSC methods.

EXPERIMENTAL

Synthesis of polyacrylamide copolymers

The (co)polymerizations of acrylamide (crystalline AAm, ~99%, Fluka) and acrylic acid (AA) (~98%, Aldrich) with trivalent metal cations Al^{+3} or Fe^{+3} (an aqueous solution of aluminium sulfate(VI) [$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$] or ferric sulfate(VI) [$\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$] – POCH SA) were carried out as heterogeneous, water-in-oil polymerization processes. The molar ratio of AAm/AA was 0.9:0.1 and the molar ratio of the metal cations to a carboxyl group of acrylic acid in acrylamide copolymer was 1:50. The reactions were carried out at $40 \pm 2^\circ\text{C}$ (by the end of the reaction the temperature was increased to 72°C for 20 minutes), under nitrogen atmosphere for 4 hours. AIBN-2,2'-azodiisobutyronitrile, purchased from POCh, in 0.1 wt.% was applied as a radical initiator. The mixture of toluene (399,5%, Chempur) and heptane (pure, POCH) (3:1 w/w) was used as the continuous phase. Reaction products were precipitated in methanol, isolated by vacuum filtration and allowed to air-dry.

Synthesis of starch hybrids

Starch materials were obtained by oxidation of potato starch from the potato industry plant "Nowamył" S.A., Poland (super-standard quality). The oxidation of starch (0.04 M) was carried out using a hydrogen peroxide (H_2O_2 , 0.3 M) – POCH Gliwice. The pH control during the reaction (pH=9) was regulated using an aqueous sodium hydroxide solution (20 wt.% NaOH, POCH Gliwice). Before starting the modification, the starch was gelatinized 80°C for 60 min. After cooling the gelatinized starch to 20°C , the 30% (w/v) H_2O_2 was added dropwise to the starch over a period of 1h with continuous stirring. The reaction was carried out at $30 \pm 2^\circ\text{C}$ for 3 h. The cations Al^{+3} or Fe^{+3} were entered into the system in the form of water solution of aluminum sulfate(VI) $[\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}]$ or ferric sulfate(VI) $[\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}]$. The assumed molar ratio of the metal cations to starch was 1:50. When the reactions were completed, the oxidized starch and modified starch/ Me^{+3} were precipitated in the large amount of ethanol and then separated. The products were dried for 24 h at 80°C .

Experimental procedure and techniques

Fourier transform infrared spectroscopy –FTIR. Infrared spectra for the synthesized AAm/AA, AAm/AA/ Me^{+3} copolymers, the commercial flocculant (dried powdered samples) and the raw and modified starch were obtained using Nexus FTIR spectrometer (Thermo Nicolet Corp., USA) with Golden Gate (ATR) attachment and OMNIC computer program. The FTIR spectra included scale normalization and the equalization of baseline. A low-anionic, powdered commercial flocculant from a local (Westpomeranian) factory was used as a comparative flocculant.

Differential Scanning Calorimetry –DSC. Q100 DSC (TA Instruments Inc., USA) was used for the polymer materials characterisation ($10^\circ\text{C}/\text{min}$, from 0 to 350°C for polyacrylamide materials, from 10 to 100°C for the gelatinization characteristic of starches products²⁵). Samples were weighed (~ 5 mg) on the aluminum pans and hermetically sealed before analyses.

Capillary viscometry. The intrinsic viscosity values of AAm/AA, AAm/AA/ Me^{+3} hybrids and a reference CF flocculant in aqueous solutions²⁶ were compared on a basis of capillary viscometric measurements. Ubbelohde's viscometer (constants $K = 0,0484$) was used; the measurements were carried out at $30 \pm 0,2^\circ\text{C}$ four times for each polyacrylamide samples. For the starch materials prepared in aqueous solutions, Ubbelohde's viscometer (constants $K = 0,005012$) was used; the measurements were carried out at $40 \pm 0,2^\circ\text{C}$ four times for each polymer solution. Intrinsic viscosity values were found using the following equation:

$$[\eta] = \lim_{c \rightarrow 0} [(t-t_0)/t]/c \quad [\text{cm}^3/\text{g}]$$

where: t_0 – solvent time of flow through the capillary; t – flow time of polymer solution with a concentration of c [g/cm^3]

Flocculation tests. To prepare a model talc suspension, 5 g of fine particle material was mixed with 1dm^3 of distilled water in a glass beaker. Talc (Alfa, II Quality, Slovakia) was used as an inorganic pollutant. Required

amount of the tested polymer material (the concentrations of flocculants were 0,75 and $4,5 \text{ mg}/\text{cm}^3$) was added to the beaker containing the model talc suspension while stirring. The stirring was continued for 10 s at 400 rpm after the addition of the polymer solution. The stirring rate was then reduced to 50 rpm and continued for 10 minutes. The entire suspension was then transferred to a calibrated Imhoff funnel and allowed to settle down. Extinction of the aqueous phase was measured using Specol 11 (Carl Zeiss Jena; wavelength 470 nm) every 10 minutes for 2 hours. The volume of the settled deposit was noted. Measurements under similar experimental conditions for untreated talc suspension were carried out for comparative purposes.

RESULTS AND DISCUSSION

The infrared spectra of AAm/AA, AAm/AA/ Me^{+3} hybrid acrylamide copolymers with Al^{+3} or Fe^{+3} and CF were recorded between $4000\text{--}450 \text{ cm}^{-1}$ (Fig. 1.). The bands located at 3350 , 3200 , 1670 and 1610 cm^{-1} were correlated to the NH_2 vibration, amide $\text{C}=\text{O}+\text{CN}$ and $\text{NH}+\text{CN}$ vibration respectively. Spectra exhibited a peak at 2900 cm^{-1} related to stretching oscillations of C-H group. The infrared spectra of all samples showed a characteristic stretching absorption band of the carbonyl group $\text{C}=\text{O}$ at 1700 , 1650 and 1450 cm^{-1} for C-H. Weaker bands associated with scissor and bending vibrations of $-\text{CH}_2-$ and $\text{CH}-\text{CO}$ groups were at $1450\text{--}1415 \text{ cm}^{-1}$. The bands at $1250\text{--}1175 \text{ cm}^{-1}$ might be related to OH and C-O stretching vibration of neighboring carboxyl groups²⁷. The examination of FTIR spectra of these copolymers showed that there were no significant observable changes in their spectral features apart from variations in the intensities of the absorptions bands. Therefore, it was concluded that a commercial flocculant (CF) is based on polyacrylamide copolymers and was correctly used as a reference material in application tests.

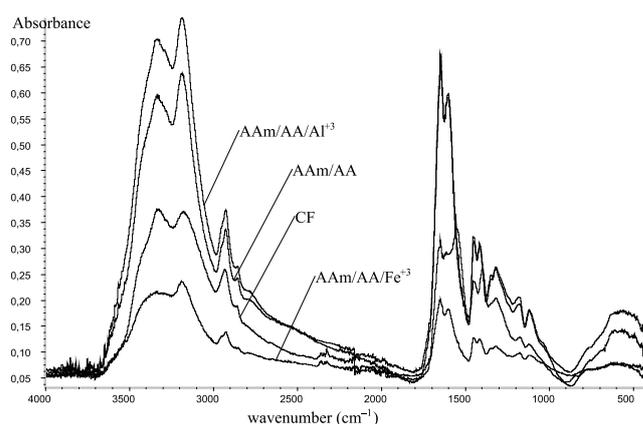


Figure 1. The FTIR spectra of the acrylamide copolymers-AAm/AA, modified by trivalent cations copolymers: AAm/AA/ Al^{+3} , AAm/AA/ Fe^{+3} and commercial flocculant CF

The confirmation of chemical modification of starch was made by the infrared spectroscopy. The FTIR transmission spectra of the raw potato starch and starch modified by oxidation are shown in Figure 2. A typical FTIR spectrum recorded for starch showed a wide band in the wavelength range $3650\text{--}3000 \text{ cm}^{-1}$, which indicated the presence of OH groups (stretching vibrations), and

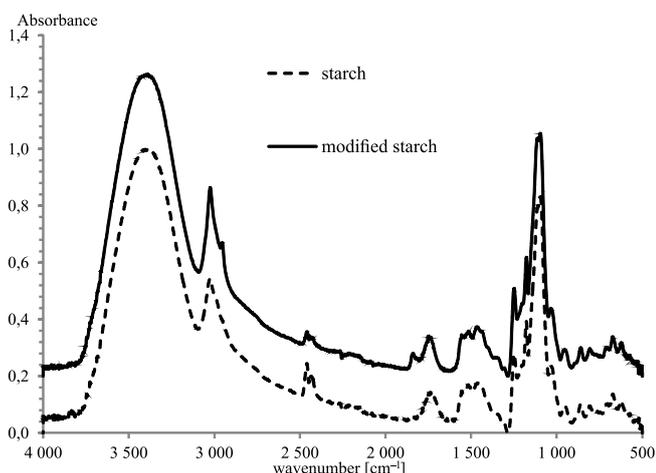


Figure 2. The FTIR spectra of the potato starch and modified starch by oxidation

at 2900 cm^{-1} corresponding to the C-H group stretch vibrations and symmetric CH_2 vibrations. The appearance of new bands – carbonyl moiety ($-\text{C}=\text{O}$, $1740\text{--}1725\text{ cm}^{-1}$), characteristic for the oxidized starch, confirms the modification of starch²⁸.

Figure 3 shows heat flow thermographs of synthesized AAm/AA copolymer, AAm/AA/ Me^{+3} hybrids and CF studied by DSC. Thermogravimetric studies of polyacrylamides show that thermal degradation starts at temperatures above 220°C ²⁹. There is every indication that temperatures $> 209^\circ\text{C}$, marked on DSC thermographs, show starting of degradation processes (especially for CF sample). Characteristic transition temperatures are function of various parameters e.g. charge density, counter-ion in a polyelectrolyte or complexing metal cations. Heat flow thermographs (Fig. 2.) show that the presence of trivalent cations in the copolymer AAm/AA (characteristic transition temperature 113°C) causes shift of exothermic peaks maxima to the lower temperature

of 101.4°C for P(AAm/AA)/ Al^{+3} ; and to the higher temperature of 117.5°C for acrylamide copolymer complex with Fe^{+3} . Flocculating agent, CF, has maximum of transition temperature at 122.3°C .

The gelatinization process of obtained starch materials was characterized by an endotherm observed in the results of differential scanning calorimetry (DSC). The temperature's parameters: at the onset of gelatinization – T_0 , the temperature at peak – T_p and the temperature at the end of gelatinization are shown in Table 1. The modified starch (oxidized) had gelatinization temperatures slightly lower than native, potato starch. The literature reports show that the temperature values for the modified starch can be lower^{25, 30} or higher³¹ than for the row starch materials. Variations in the thermal properties of starches from different sources may be related to the granule composition: the ratio of amylose/amylopectin, the residual lipids and protein, morphology and distribution of starch granules. The starch hybrids with trivalent metal cations show gelatinization temperatures of the onset of gelatinization similar to native starch, the temperatures at peak – similar to modified starch and the temperatures at the end of gelatinization slightly lower than potato starch. The gelatinization process of starch hybrids is shorter than for starch and modified starch.

The comparative studies of the obtained polymers and CF were made on the basis of capillary viscometry (Fig. 4. – AAm/AA, hybrids AAm/AA/ Me^{+3} and CF; Fig. 5. – a modified starch and modified starch/ Me^{+3} hybrids) and intrinsic viscosity values (Table 2.). All the tested materials obtained linear concentration extrapolation (see Fig. 4. and 5.). The intrinsic viscosity values for synthesized acrylamide copolymers were lower than for the commercial flocculant (CF) – $7535\text{ cm}^3/\text{g}$. There is an indication of shorter macromolecules chains forming AAm/AA and AAm/AA/ Me^{+3} copolymers comparing to the length of CF chains. Ferrous cations present in

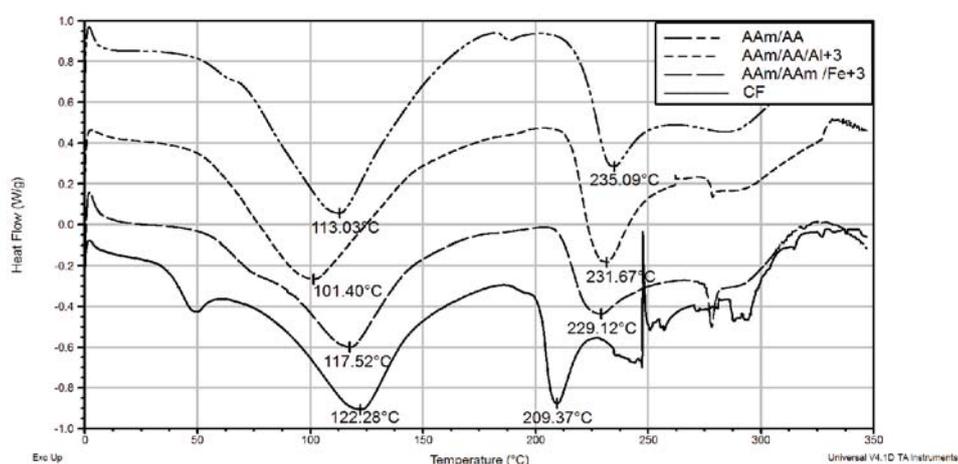


Figure 3. The DSC thermographs acrylamide copolymers-AAm/AA, by trivalent cations copolymers: AAm/AA/ Al^{+3} , AAm/AA/ Fe^{+3} and commercial flocculant CF

Table 1. Thermal properties of potato starch, modified starch and starch hybrids with trivalent cations Fe^{+3} and Al^{+3}

Polymer material	T_0	T_p	T_c
Potato starch	61.9	65.8	72.0
Modified starch	61.2	64.2	69.5
Modified starch/ Fe^{+3}	62.0	64.3	69.2
Modified starch// Al^{+3}	62.1	64.8	69.0

T_0 – temperature at onset of gelatinization. T_p – temperature at peak. T_c – temperature at the end of gelatinization

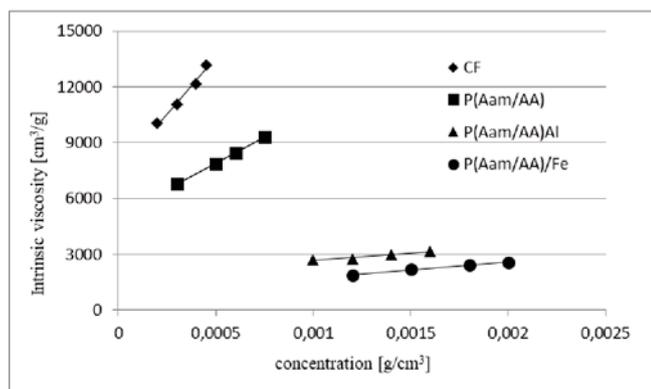


Figure 4. Dependence of reduced viscosity on concentration of an acrylamide copolymer-AAm/AA, hybrids AAm/AA/Me³⁺ and commercial flocculant CF solutions

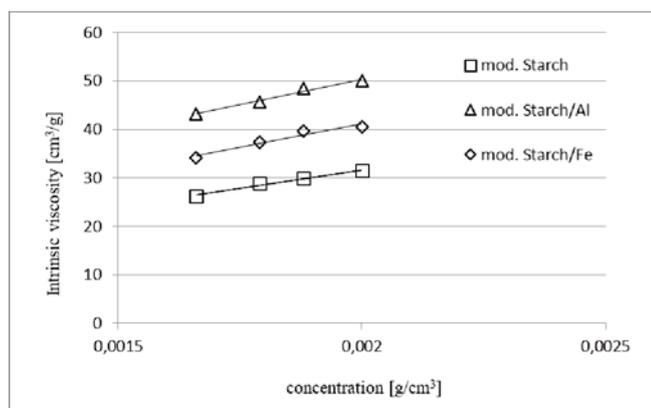


Figure 5. Dependence of reduced viscosity on concentration of a modified starch and hybrids modified starch/Me³⁺ solutions

Table 2. Intrinsic viscosity values of acrylamide copolymer, AAm/AA/Me³⁺ hybrids, commercial flocculant CF, modified starch and starch hybrids

Copolymer	Intrinsic viscosity at $c \rightarrow 0$ $[\eta]$ [cm ³ /g]
P(AAm/AA)	5090
P(AAm/AA)/Al ³⁺	1860
P(AAm/AA)/Fe ³⁺	810
Commercial flocculant CF	7535
Modified starch	1.56
Modified starch/ Fe ³⁺	2.75
Modified starch// Al ³⁺	8.65

acrylamide hybrid significantly reduce intrinsic viscosity values [810 cm³/g for P(AAm/AA)/Fe³⁺] in comparison with initial copolymers [5090 cm³/g for P(AAm/AA)]. A decrease of intrinsic viscosity of AAm/AA/Al³⁺ was observed in case of aluminum cation present in an acrylamide hybrid – 1860 cm³/g.

The obtained results from capillary viscometry for starch polymers indicate that the presence of trivalent cations affects the increase of intrinsic viscosity values compared to oxidized starch (modified starch – 1.56 cm³/g, modified starch/ Fe³⁺– 2.75 cm³/g and with Al³⁺ 8.65 cm³/g). This suggests that starch hybrids can form larger molecules than modified starch.

The flocculation efficiency of all copolymer samples was assessed by the extinction and the sludge volume measurements in the model talc suspension. The results of jar tests for the concentration of flocculant 0.75 mg/cm³ and 4.5 mg/cm³ are presented in Figure 6 and 7

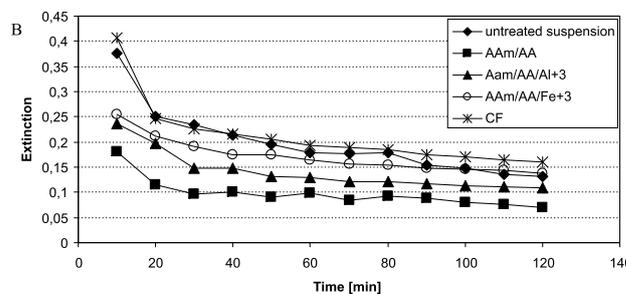
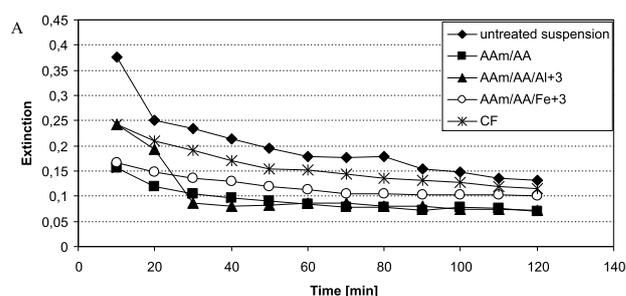


Figure 6. Dependence of extinction for talc aqueous suspension as a function of time for the tested acrylamide copolymers-AAm/AA, modified by trivalent cations copolymers: AAm/AA/Al³⁺, AAm/AA/Fe³⁺ and commercial flocculant CF; : A – concentration 0.75 µg/cm³, B – concentration 4.5 µg/cm³

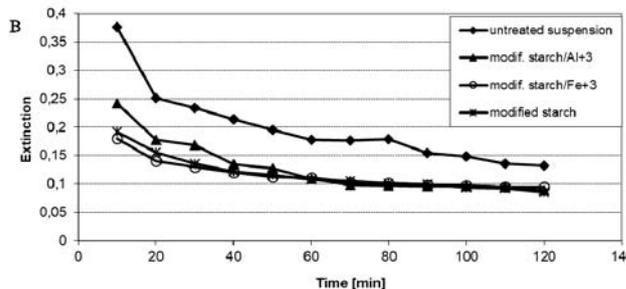
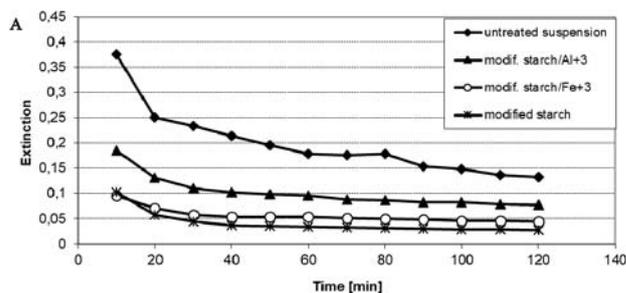


Figure 7. Dependence of extinction for talc aqueous suspension as a function of time for the tested modified starch and hybrids modified starch/Me³⁺ solutions; : A – concentration 0.75 µg/cm³, B – concentration 4.5 µg/cm³

Fig. 6. – AAm/AA, hybrids AAm/AA/Me³⁺ and CF; Fig. 7. – a modified starch and modified starch/Me³⁺ hybrids. Table 3 shows sludge volumes found during the same flocculation experiments.

The polyacrylamide copolymers show flocculation ability at both applied flocculant concentrations with the exception of the commercial agent that shows no flocculation ability at the higher concentration of 4,5 mg/cm³ (Fig. 6B). The best results in the extinction reduction of talc suspension were obtained for AAm/

Table 3. The sludge volumes changes during flocculation tests for talc aqueous suspension dependent on material type and dose

Flocculant concentration [$\mu\text{g}/\text{cm}^3$]	0.75						4.50					
Time [min]	10	20	30	60	90	120	10	20	30	60	90	120
Type of copolymer	Sludge volume [cm^3] after time											
Untreated suspension	6.0	7.5	7.5	8.0	8.0	8.0	6.0	7.5	7.5	8.0	8.0	8.0
P(AAm/AA)	16.0	16.0	16.0	15.0	15.0	15.0	18.0	17.0	17.0	17.0	17.0	17.0
P(AAm/AA)/Al ³⁺	16.0	15.0	15.0	15.0	14.0	14.0	15.0	15.0	15.0	15.0	15.0	15.0
P(AAm/AA)/Fe ³⁺	14.5	14.0	14.0	13.0	13.0	13.0	15.0	14.0	14.0	14.0	14.0	14.0
Commercial flocculant	16.0	15.0	13.0	13.0	13.0	13.0	4.0	6.0	7.5	9.5	11.0	12.0
Modified starch	10.5	11.0	11.0	11.0	11.0	11.0	10.5	11.0	11.0	11.0	11.0	11.0
Modified starch// Al ³⁺	9.0	9.5	9.5	10.0	10.0	10.5	9.5	9.5	9.5	10.0	10.0	10.5
Modified starch/ Fe ³⁺	10.0	10.0	10.5	10.5	10.5	11.0	12.0	12.0	12.0	12.5	12.5	12.5

AA/Al³⁺ and AAm/AA (Fig. 6A) and unmodified AAm/AA (Fig. 6B). The reduction in suspension turbidity was significant: from 0.38 for untreated suspension to 0.15 for AAm/AA copolymer after 10 minutes and 0.08 for AAm/AA/Al³⁺ hybrid after 30 minutes – Fig. 6A. The CF did not exhibit such a good flocculation effectiveness as synthesized copolymers. It is not necessary to use higher concentration than 0.75 mg/cm³ in the case of polyacrylamide flocculants.

The starches products show the flocculation effectiveness for all synthesized materials in both concentrations (Fig. 7). For the flocculant concentration of 0.75 mg/cm³ (Fig. 7A), the effectiveness of the flocculation action is as follows: modified starch, modified starch/Fe³⁺ and modified starch/Al³⁺. If the concentration of starch flocculants was 4.5 mg/cm³ (Fig. 7B), all used materials showed similar flocculating properties for the talc suspension. The oxidized starch and modified starch/Fe³⁺ (Fig. 7A) gives the best results in the extinction reduction of talc suspension. The reduction in turbidity of the suspension was significant: from 0.38 for the untreated slurry to 0.28 and 0.42 for the respective samples.

The sludge volume changes during flocculation tests depending on the material type and concentration have been compiled in Table 3. The volume of sludge for untreated talc suspension after 1h was 8 cm³. In all cases, after treating the suspension by the flocculant, the sediment volume was higher than for the untreated system with the exception of CF (Table 3, concentration 4.5 mg/cm³). The highest sludge volume for AAm/AA copolymer was received for both series after 120 minutes: 15 and 17 cm³ for 0.75 mg/cm³ and 4.5 mg/cm³ respectively, but the volume of sludge for AAm/AA/Al³⁺ hybrid decreased from 16 cm³ after 10 minutes to 14 cm³ after 120 minutes (0.75 mg/cm³) and was 15 cm³ after 120 minutes for 4.5 mg/cm³ concentration. The samples of AAm/AA/Fe³⁺ show 13 and 14 cm³ after 2h for 0.75 mg/cm³ and 4.5 mg/cm³ respectively. Taking into consideration similar results from extinction measurements for AAm/AA and AAm/AA/Al³⁺ (Fig. 6A), a hybrid AAm/AA/Al³⁺ is better flocculant because the sediment contained less water compared to the AAm/AA sample.

All starch flocculants show higher sludge volume than the untreated sample. The highest sludge volume (12.5 cm³) was observed for modify. starch/ Fe³⁺ for 4.5 mg/cm³ concentration of flocculant. For the oxidized starch and starch modified with aluminum cation, the sludge volume does not depend on the flocculant concentration used (similar results for both concentration in the same time).

CONCLUSIONS

Acrylamides and starch hybrids with trivalent cations: Al³⁺ and Fe³⁺ presented in these studies can be used as flocculants in wastewater treatment processes. The flocculants obtained by modification of a natural polymer such as starch should deserve the special attention. Starch is a natural, renewable, biodegradable and, the most important, cheap plant reserve. Such hybrid materials show similar or even higher flocculation efficiency as conventional acrylamide flocculants. It was found that synthesized AAm/AA/Me³⁺ copolymers and modify. starch/Me³⁺ materials exhibit better flocculation properties for a model talc suspension than a commercially available flocculant.

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