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Environmental friendly flocculants for drinking water treatment

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Abstract
Coagulation-flocculation is an important step for the treatment of drinking water obtained from surface water sources. Various types of flocculants are available in the drinking water treatment market but only some of them are friendly for the environment due to their specific structure, which includes natural compounds. Starch-based flocculants are included in this category and some types of them were tested in our research work, in similar conditions with ordinary polyelectrolytes, in order to prove their efficiencies for turbidity and organic load (COD-Mn) removal. Five types of flocculants based on starch and acrylamide were tested during the classic treatment flow coagulation-flocculation-settling with aluminum sulfate as coagulant (1-10 mg Al/L) and 0.5-10 mL/L flocculant dose (0.2% active substance). Better removal efficiencies of turbidity and organic load (COD-Mn) in case of flocculants based on starch and acrylamide copolymers: over 99% for turbidity and ~90% for COD-Mn in case of 300-400 NTU initial surface water turbidity were registered.

Keywords: *coagulation-flocculation, flocculants, polyelectrolyte, starch*

INTRODUCTION

Coagulation-flocculation process is a common process for the treatment of drinking water (surface water) and wastewaters being used as a treatment phase before settling. Coagulation is referring to the destabilization process during the compression of two electric layers of colloidal particles, which make possible their aggregation, and flocculation is defined as destabilization by adsorption of long chain polymeric molecules, which create bridges between particles [1-3].

In addition to this water clarifying effect, coagulation-flocculation removes some organic and inorganic pollutants and microorganisms by their adsorption on the precipitates that are formed.

The best-known model that explains the interactions on the surface of colloidal systems is the double layer model: the interface consists of one electronegative layer on the surface of solid particles and one electropositive layer that form together Stern double layer and a diffuse layer consisting of ions and counterions [3-5]. The double electric layer action is only up to 10^{-8} m from colloidal surface such as two particles must be closer than $2x10^{-8}$ m in order to have an interaction between their double electric layers and the generation of attraction - rejection forces [5-8].

Coagulation-flocculation phases are [7]:

- destabilization of colloidal system (coagulant hydrolysis and polimerization of hydrolyzed products leading to mono and polynuclear complex compounds);
- diffusion of hydrocomplex compounds to the surface of colloidal particles and their interaction.

The flocculation mechanism has four steps: adsorption on polymer macromolecules, creation of the bridges, charges neutralization and the end of flocculation (longer time and lower mixing speed toward coagulation) [9-11].

Organic (polyelectrolytes) and inorganic polymers are used for the creation of the bridges between colloidal particles and to increase the efficiency/speed of phases separation (e.g., settling, filtration, flotation). The organic polymers can be cationic (tertiary amines polymers), anionic (acrylic acid polymers, polyacrylamide, sulfonated polystyrene, etc.) or non-ionic (polyacrylamide) [8].
Classic coagulants-flocculants are classified within three main categories [12-15]: hydrolysed metal salts (ferric chloride, ferric sulphate, magnesium chloride, and aluminium sulphate), prehydrolized metal salts (aluminium polychloride, ferric polychloride, ferric polysulfate) and synthetic polymers (aminomethyl-polyacrylamide, polyamines, etc.)
In recent years, there is concern for application of natural polymers in coagulation-flocculation processes [16-19]. These natural polymers can be classified taking into account their origin (*plants* - guar gum, Arabic gum, cactus extract, starch from potato or corn, *animal* - chitosan, *microorganisms* - based on a polysaccharide produced by Xantomonas compestris - Xantan gum) and the electric charge of active groups (*cationic* - chitosan, starch, *anionic* - sulfonated polysaccharides, sulfonated lignin, *non-ionic* - starch, cellulosic derivates. microbial polisaccharides, gelatine, glue).
The starch was well studied because it is a biodegradable compound, harmless for human health and able to be associated with synthetic polymers in order to diminish the amount of classic flocculant doses and therefore decreasing secondary pollution of drinking water [20].

EXPERIMENTAL PART

The experimental was performed in two main phases. First, testing of two types of flocculants (F1 and F2 polyelectrolytes) recommended by a Romanian manufacturer in order to select the best one and second, improving characteristics of selected flocculant on phase A and test the new products for drinking water treatment were performed.
There were performed coagulation-flocculation experiments (Jar tests) based on the following steps: sample homogenization, addition of coagulant, pH correction (with NaOH solution), coagulation, flocculation and settling.
Coagulation-flocculation experiments were performed using water samples from Arges River, which is the main surface water source for drinking water of Bucharest. The main physical-chemical characteristics of surface water were pH = 7.93, turbidity = 366 NTU, COD-Mn = 6.5 mg O_2/L, conductivity = 232 μS/cm.
The aim of these tests was to remove turbidity and organic load by coagulation with aluminum sulfate (solution 434 mg Al/L) and flocculation with a new Romanian flocculant (0.2% active substance) based on starch and acrylamide.
Laboratory tests were performed in three steps for both flocculants:

- coagulation tests (only aluminum sulfate adding);
- flocculation tests (only polyelectrolyte adding);
- coagulation-flocculation tests (coagulation with aluminum sulfate followed by flocculation with F1/F2 polyelectrolytes).

Coagulation, flocculation and settling time were kept constant for all experiments corresponding to 15 min., 5 min. and 60 min. respectively. Mechanical stirring was to 150 rpm for coagulation and 100 rpm for flocculation step.

RESULTS AND DISCUSSION

Preliminary tests of F1 and F2 flocculants based on starch and acrylamide copolymer

Table 1 shows the results of coagulation tests with $Al_2(SO_4)_3$: 1÷10 mg Al/L

Table 1. Coagulation tests results

Sample	Coagulant dose, mg Al/L	Turbidity, NTU	η Turbidity %	COD-Mn, mg O_2/L	η COD-Mn, %
Initial	-	366	-	6.5	-
C1	1	80.9	78	2.7	58
C2	2	37.3	90	2.4	63
C3	5	11.4	97	1.4	78
C4	10	11.7	97	1.2	82

The removal efficiencies of turbidity and organic load (COD-Mn) were 78-97% and 58-82% respectively, the best yields being for 5-10 mg Al/L doses.

Experimental tests with F1 Flocculant

The efficiencies of turbidity and organic load removal in case of flocculation with F1 polyelectrolyte are presented in table 2.

Table 2. Flocculation tests results using polyelectrolyte F1

Sample	Flocculant dose, mL/L	Turbidity, NTU	η Turbidity %	COD-Mn, mg O_2/L	η COD-Mn, %
Initial	-	366	-	6.5	-
F1a	0.5	66.3	82	2.6	60
F1b	1.25	47.2	87	3.4	48
F1c	2.5	73.1	80	3.4	48
F1d	5	100.1	73	3.4	48
F1e	7.5	126.2	66	3.7	43
F1f	10	137.2	63	5.9	9

The best efficiencies of turbidity and organic load removal were registered for small doses of flocculant (0.5-2.5 mL/L): 80-82% and 48-60% respectively.

Table 3 presents experimental conditions and removal efficiencies of turbidity and organic load by coagulation-flocculation. The selection of coagulant and flocculant doses was based on previous tests.

Table 3. Coagulation-flocculation tests results using polyelectrolyte F1

Sample	Coagulant dose, mg Al/L	Flocculant dose, mL/L	Turbidity, NTU	η Turbidity %	COD-Mn, mg O_2/L	η COD-Mn, %
Initial	-	-	366	-	6.5	-
F1g	5	0.5	2.8	99	2.4	63
F1h	5	1.25	3.4	99	2	69
F1i	5	2.5	1.6	99	2.6	60
F1j	10	0.5	0.2	99	0.9	86

The coagulation-flocculation tests emphasized turbidity and COD-Mn removal with efficiencies over 99% and 60-86% respectively, residual values being situated below admitted limits (1 NTU and 5 mg O_2/L) just with ordinary settling.

Experimental tests with F2 Flocculant

Similar conditions with flocculant F1 were used also for polyelectrolyte F2.

The variation of turbidity and organic load removal in case of flocculation with F2 (0.5-10 mL/L) are presented in table 4. No aluminum sulfate was added.

Table 4. Flocculation tests results using polyelectrolyte F2

Sample	Flocculant dose, mL/L	Turbidity, NTU	η Turbidity %	COD-Mn, mg O_2/L	η COD-Mn, %
Initial	-	366	-	6.5	-
F2a	0.5	49.1	87	1.9	71
F2b	1.25	60.9	83	2.4	63
F2c	2.5	71.8	80	3	54
F2d	5	111.1	70	3.4	48
F2e	7.5	141.9	61	2.9	55
F2f	10	153	58	4.48	31

The best removal efficiencies for turbidity and organic load were found in case of F2 for the same small doses of flocculant F1 (0.5-10 mL/L) but a little higher: 80-87% and 54-71% respectively.
Table 5 is centralizing experimental conditions and removal efficiencies of turbidity and organic load by coagulation-flocculation with flocculant F2.

Table 5. Coagulation-flocculation tests results using polyelectrolyte F2

Sample	Coagulant dose, mg Al/L	Flocculant dose, mL/L	Turbidity, NTU	η Turbidity %	COD-Mn, mg O_2/L	η COD-Mn, %
Initial	-	-	366	-	6.5	-
F2g	5	0.5	1	>99	1.4	78
F2h	5	1.25	3	>99	2.4	63

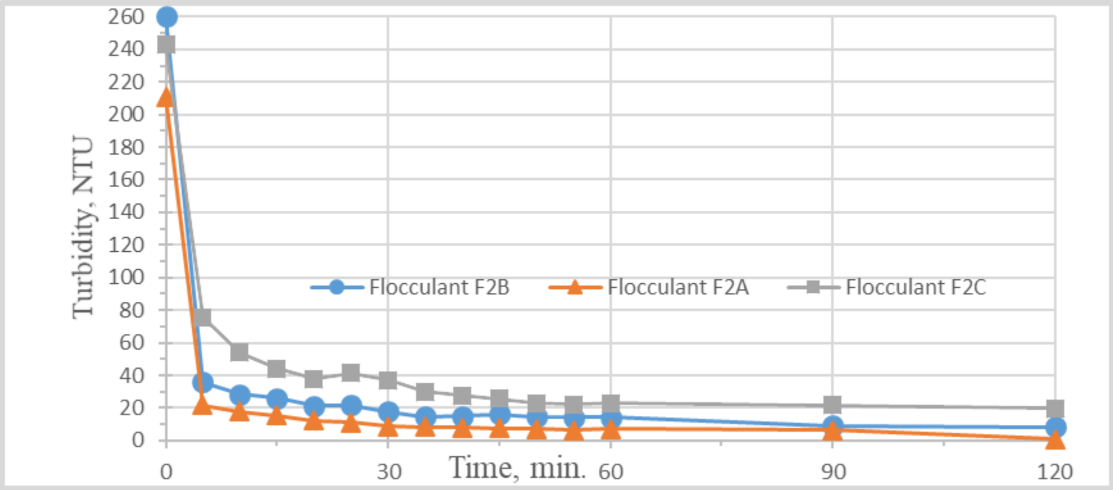
The results of coagulation-flocculation tests emphasized that turbidity removal efficiency over 99% and COD-Mn removal efficiency of max, 78% were obtained for small flocculant doses (0.5-1.25 mL/L) lower values compared with F1 coagulation-flocculation tests. Sample F2g had the best results. For this reason, it was tested again with a modified settling time of 15 minutes in order to verify if is possible to accelerate the treatment flow in case of pilot scale application.
The last test proves that 15 minutes of settling led to a residual turbidity (0.97 NTU) and organic load (2 mg O_2/L) below the admitted limit.

Tests with F2 improved flocculants (F2A, F2B, F2C)
Based on preliminary tests A, the manufacturer of flocculants decided to improve F2 flocculant properties (more stable chemical bond between starch and acrylamide in order to keep turbidity below the limit, silver adding in order to increase settling efficiency and to add an antibacterial effect).

Table 6. Coagulation-flocculation tests results using polyelectrolyte F2A (with Ag), F2B and F2C

Sample	Flocculant	Flocculant dose, ml/L	Turbidity, UNT	η Turbidity %	COD-Mn, mg O_2/L	η COD-Mn, %
Initial	-	-	279	-	12.7	-
A1	**F2A**	**1.25**	**1.1**	**>99**	**1.4**	**89**
A2	F2A	2.5	2.7	99	1.4	89
B1	F2B	1.25	3.2	99	2	84
B2	F2B	2.5	2.3	>99	1.74	86
C1	F2C	1.25	4.6	98	4	68
C2	F2C	2.5	2.6	99	2.78	78

Fig. 1. Settling curve for F2A, F2B and F2C flocculants



Three new flocculants (F2A with silver, F2B, F2C) were tested in similar conditions and the data were shown in table 6. Coagulant dose was similar for all tests - 5 mg Al/L.

In case of sample A1 for the flocculant dose of 1.25 mL/L there was an improve of turbidity and COD-Mn removal comparing with sample F2h. Turbidity was close to and organic load, below admitted limit. The increase of flocculant dose did not increase the turbidity removal.

Settling curve for 120 minutes (figure 1) show a better settling in case of F2A polyelectrolyte with silver (the decrease of turbidity was faster compared with other flocculants).

CONCLUSIONS

The experimental results of new environmental friendly flocculants with possible application in the field of drinking water treatment emphasized some conclusions.

Taking into consideration the coagulation-flocculation processes with classic polyelectrolytes we found comparative or better removal efficiencies of turbidity and organic load (COD-Mn) in case of flocculants based on starch and acrylamide copolymers: over 99% for turbidity and ~90% for COD-Mn. These results were obtained for the same usual doses of coagulant (aluminum sulfate) and classic flocculant (polyacrylamide). The silver content of starch-based flocculants improve the settling properties. The application of this new flocculant led to more biodegradable sludge after settling step due to decrease of acrylamide content.

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