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Influence of the dextran-acrylamide copolymer structure on the sedimentation rate of a kaolin suspension has been examined. The flocculation efficiency has been evaluated, by measuring the turbidity of a suspension top layer by nephelometry. The size of kaolin clusters is estimated by means of microphotographs. It is found that dextran-backbone copolymers obtained by grafting long polyacrylamide chains possess the best flocculation abilities. Doses of dextran-graft-polyacrylamide copolymers sufficient for the effective sedimentation of low-concentrated kaolin suspensions are higher than those for high-concentration kaolin suspensions.

Keywords: flock size; graft length; kaolin suspension; turbidity

INTRODUCTION

Flocculation is one of the generally used techniques for industrial processes of mineral processing, wastewater clarification, sludge dewatering, etc. In the last years, many investigations are focused on replacing the non-biodegradable and costly polyacrylamide flocculants with natural polymers. Many authors prove that graft copolymers of polyacrylamide possess a better flocculation efficiency than that of linear polyacrylamide because of peculiarities of their macromolecular structure in a solution, which results in the better approachability of the side-chains to suspension particles [1,2].

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Moreover, the copolymers obtained by grafting the acrylamide chains on natural polymers are easily biodegradable [1,3].

It has been recently proved that graft-copolymers of dextran and polyacrylamide possess good flocculation abilities towards kaolin suspensions with high concentration ($30\,g/dm^3$) [3]. However, to obtain a full characteristic of the new flocculants, it is required to determine their flocculation abilities towards suspensions in a wide range of concentrations. For that reason, the present work concerns the flocculation of kaolin suspensions of low concentrations ($4\,g/dm^3$) with the mentioned copolymers.

Another important task in flocculation technology appears to be the optimization of a flocculant dosage. The flocculant loading should be minimal from both environmental and economic reasons. In the present study, the optimum dosage range has been determined for the grafted polysaccharides of different macromolecular structures considering the sedimentation rate and the supernatant clarity as indicative parameters.

MATERIALS AND METHODS

Two samples of dextran from Serva (Sweden) with molar masses of $2 \cdot 10^4$ and $7 \cdot 10^4$ g/mol (designated as D20 and D70, respectively) were used for the synthesis as a copolymers backbone. The grafting reaction was carried out via the red-ox initiation method mediated by cerium (IV) ions [3]. The required numbers of polyacrylamide (PAA) chains were obtained by adjusting the molar ratio of a cerium initiator to dextran. Lengths of PAA chains (short and long) were controlled by the quantity of acrylamide used. Characteristics of the obtained copolymers are presented in Table 1. A linear polyacrylamide with molecular mass equal to $1 \cdot 10^6$ g/mol (i.e., very close to those

TABLE 1 Structural and Flocculation Characteristics of the Studied Copolymers

Copolymer	Average number of grafts	Molecular mass $M_w \cdot 10^{-5}$ [g/mol]		Dextran content [%]	Sufficient dose [mg/dm^3]
		Dextran	Copolymer		
D20-PAA-short	6	0.2	8.7	2.3	5.0
D20-PAA-long	6	0.2	69.0	0.3	1.0
D70-PAA-short	6	0.7	9.2	7.6	5.0
D70-PAA-long	6	0.7	47.0	1.5	2.0

for copolymers with short PAA chains – see Table 1) has been used as a reference flocculant. All the flocculants have been applied as stock solutions with a concentration of 20 mg/dm^3. Suspensions for the flocculation tests have been prepared by the thorough mixing of 1 g of kaolin KOM (Surmin-Kaolin, Poland) with 150 cm^3 of distilled water during 10 min at 22°C. After the mixing, the suspensions have been put into test cylinders and completed with a certain volume (1, 2, 4, 8, 16, 32, 64, or 96 cm^3) of the flocculant stock solution and distilled water up to a volume of 250 cm^3. The cylinders were turned 10 times by 180°, and samples for the microscopic investigations have been taken immediately. Samples for the turbidity measurements have been taken from the top layer after 5 min of sedimentation. The sample turbidity has been measured by nephelometry at 555 nm, and the obtained results have been presented as the intensity of a signal, *I* [mV]. Photographs have been obtained with a microscope Nikon Eclipse E400POL and analyzed by means of the SigmaScan Pro programme.

RESULTS

Both the visual observations and the turbidity measurements indicated that the examined graft-polyacrylamide copolymers accelerate the kaolin suspension sedimentation to a great extent. Figure 1 shows

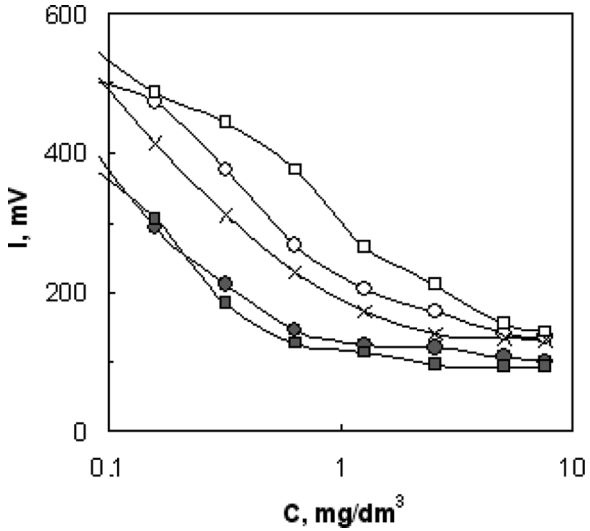

FIGURE 1 Turbidity of a kaolin suspension versus the concentration of flocculants: PAA (×), D20-PAA-short (○), D20-PAA-long (●), D70-PAA-short (□), D70-PAA-long (■).

the dependence of the suspension turbidity on the flocculant concentration. There are no minima on the plots in the wide concentrations range, i.e., from 0.08 to 8 mg/dm^3. This observation remains out of accordance with minima revealed on the plots for both star-shaped and linear polyacryamides [3,4]. Instead of this, a constant value of suspension turbidity has been registered, when the flocculant concentration increases beyond a certain value. The values of the flocculant sufficient for obtaining the best suspension clarity are listed in Table 1. The lowest values of the sufficient dose have been noticed for the copolymers D20-PAA-long and D70-PAA-long. This observation suggests that the flocculation abilities of copolymers are related to the length of grafted polyacrylamide chains. The copolymers with short PAA chains (i.e., with lower molecular masses – see Table 1) are characterized with worse flocculation abilities than those with long PAA chains (see Fig. 1). Both the D20-PAA-long and D70-PAA-long copolymers possess a better efficiency as compared with linear PAA. It is worth to notice that the length of grafted PAA chains in both mentioned copolymers is approximately the same as that for the referring linear PAA chain. Apparently, the registered differences in flocculation abilities concern the macromolecule structure and the chain conformations in an aqueous solution.

A comparison of the present results with those reported earlier [5] leads to the inference that the flocculation ability of dextran-graft-polyacrylamide copolymers depends on the suspension concentration as well. When the kaolin loading was high (i.e., 30 g/dm^3), the copolymers with short PAA chains appeared to be as efficient as linear polyacrylamide, even at low flocculant doses (i.e., below 1 ppm). The presented results (for the kaolin suspension of 4 g/dm^3 – see Fig. 1) prove that the linear PAA appeared to be a more efficient flocculant than copolymers with short PAA chains (when used in low doses). The concentrations above 5 mg/dm^3 are required for both the D20-PAA-short and D70-PAA-short copolymers in order to obtain the flocculation efficiency comparable with that of linear PAA. Moreover, in highly concentrated suspensions, the short distances between grafted PAA chains always caused improving the clarifying abilities of the copolymers under study. In kaolin suspensions of low concentrations, such a dependence was observed only for copolymers with short PAA chains. On contrary, when long PAA chains have been grafted in the same quantity to dextrans of different molar masses, the flocculation performance of the copolymers revealed to be independent of the dextran backbone length (Fig. 1).

The analysis of the kaolin flock dimensions has been also performed to justify the differences in flocculation behavior of the

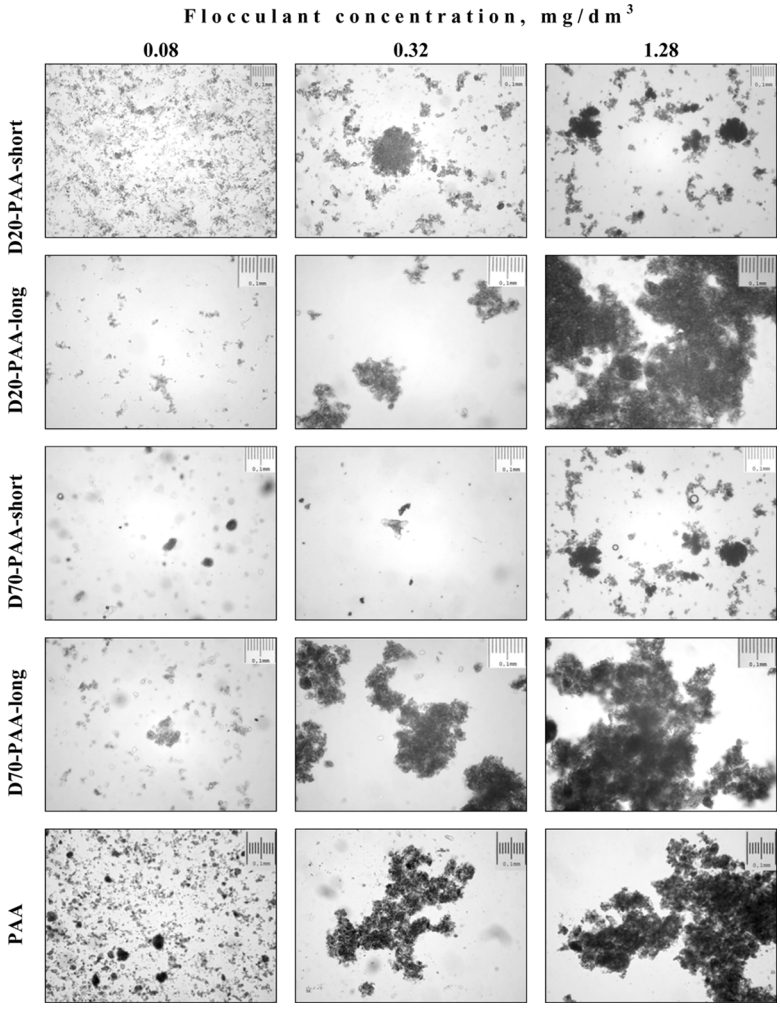

FIGURE 2 Microphotographs of flocks in kaolin suspensions containing flocculants.

dextran-graft-polyacrylamide copolymers. The microphotographs illustrate clearly that flock dimensions increase when the copolymer concentration increases (Fig. 2). The increase of the flock volume and mass accelerates the suspension particle sedimentation and causes an improvement of the suspension clarity. The clearly different dimensions of flocks observed for the copolymers with short and long PAA chains confirm that the higher molecular mass of a copolymer

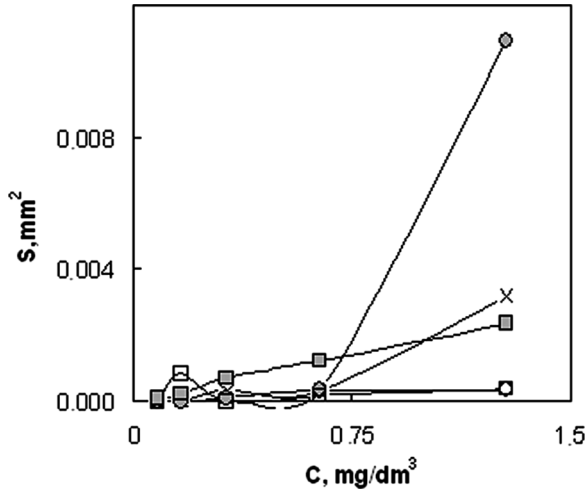

FIGURE 3 Flocks surface areas versus the concentration of the flocculants. Notations as in Figure 1.

leads to an increase in the flocculation efficiency. In addition, the comparison of the flocks created by means of the D20-PAA-short and D70-PAA-short copolymers (Fig. 3) allows us to conclude once more that a higher molecular mass of the dextran backbone results in worse flocculation properties.

CONCLUSIONS

Flocculation abilities of dextran-graft-polyacrylamide copolymers depend on both the dextran backbone length and the PAA graft length.

The flocculant performances are different in suspensions of different concentrations. In low-concentration kaolin suspensions, the best flocculation efficiency has been registered for copolymers with long PAA chains. The mentioned flocculants are more efficient in the creation of large kaolin flocks than linear polyacrylamide.

Increase of the dextran-based flocculant concentration up to a certain value results in improving the kaolin suspension clarity. Higher copolymer loadings do not change the supernatant turbidity.

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