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ORIGINAL CONTRIBUTION

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Influence of humic acid on the flocculation of clay

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Abstract The aim of this study was to improve the flocculation of wastewater from gravel pits, especially the separation of the finely dispersed inorganic particles and the removing of humic acid. Clay was used as a model to investigate the influence of humic acid on the flocculation with two different types of polycation. The dependence of the sedimentation behaviour on time was investigated as well as the turbidity of the supernatant and the light absorption as a measure for humic acid removal. Bridging of particles remained the dominant mechanism of particle destabilisation by treating the clay in water with cationic polyacrylamides of very high molecular mass (CPAM). Poly(diallyldimethylammonium chloride) (PDADMAC) of lower molar mass (35 000 g/mol) was found to act by charge neutralisation. In this case the so-called flocculation window was very small. This behaviour is the same for systems containing humic acid. However, the need for cationic flocculant increases because humic acid as a weak polyanion can interact with the polycation. By using CPAMs with low charge this interaction does not play a significant role. The optimum flocculation concentration is relatively high. The flocs are larger and the velocity of sedimentation is higher than for the short-chain and highly charged polycation PDADMAC. However, because the latter is more effective in removal of humic acid at the point of optimum flocculation it is more advantageous to combine the highly charged polycation with a high molecular weight polyanion (dual system).

Keywords Humic acid · Clay · Wastewater · Dual flocculation · Complexation

Introduction

The separation of finely dispersed particles by flocculation is a well-known and widely used process, for instance in the paper industry, in wastewater treatment, and in mineral processing industries. While the flocculation of inorganic model systems in water is well investigated, there is still a lack of understanding for systems in practice. So the separation of finely dispersed particles from washing water in the gravel industry is not effective owing to the small size of the particles and also the influence of organic matter in natural water. This problem is very complex because a lot of "different" interactions are involved. In the literature in most cases you can find investigations of separate parts of this complex process, such as clay–humic interactions, the flocculation of inorganic particles in water, or the complexation between humic acid and cationic flocculants, as we will show in the following.

The flocculation of clay suspensions in water with polycations was intensively studied, for instance by Gill and Herrington [1, 2, 3]. They investigated the flocculation of kaolin slurries with cationic polyacrylamides of varying molar mass but the same cationic character as well as the influence of charge density of the polyacrylamides or polyethyleneimines. In our previous work [4, 5, 6] we showed that a so-called dual system (highly charged polycation prior to a high molecular weight polyanion) also has many advantages compared with monoflocculation for the separation of clay. These effects are obtained by a combination of charge patch formation and bridging. The behaviour depends especially on the concentration of polycation according to the anionic character of the suspension and the molar ratio of anionic and cationic charges.

The situation becomes much more complicated under the condition that natural organic matter (NOM) is in the suspension to be flocculated because the cationic flocculant can interact not only with the particle but also with the organic matter. Humic acid or polysaccharides are well-known examples of NOM [7, 8, 9, 10].

The effectiveness of water treatment processes in removing NOM was also extensively studied. Humic substances can be removed from water by a number of different processes, such as sorption processes, adsorption on activated carbon, or membrane filtration [11]. The conventional treatment is coagulation/floc separation. Bolto et al. [8] and Edzwald and Tobiason [12] found synergistic benefits from combinations of cationic polymers with other components, for instance, alum or clay.

The interaction between humic acid with a series of synthetic cationic polyelectrolytes (without inorganic particles) was studied by Kam and Gregory [7] to investigate the charge density of some commercial humic acids. Systematic differences in the apparent humic charge density were found, depending on the charge density of the cationic polyelectrolytes used. The best removal of humic acid (in water) was found with polycations of high charge density.

Aggregates such as clay minerals are effectively stabilised in the presence of some organic polymers. Several excellent reviews can be consulted for additional information about surface properties of clays and the clay–humic acid interaction [13, 14, 15, 16, 17]. The results of this research provide a better understanding of how organic matter affects the behaviour of particles in natural water. One example is wastewater from gravel pits which contain clay as well as humic acid. They are known to be difficult to flocculate. One of the problems is the small size of the particles that causes low efficiency of separation because of the very low sedimentation rate. Further, the interaction between organic matter and the cationic flocculant influences the process and leads to a higher consumption of flocculant compared with model systems.

In the following investigations the flocculation of wastewater from gravel pits is reported for model systems. Because the main components are kaolinite (35–45%), illite (25–35%), feldspar (5–10%) and quartz (10%) as found by X-ray analysis we used clay (90% kaolinite) as a model. Humic acid was chosen as a model for NOM. The flocculation of clay in water is compared with the same process in the presence of humic substances. In addition the interaction between humic acid and the polycations (without clay) was investigated as well as the interactions between humic acid and clay (without polycation).

Experimental

Materials

Two types of clay (Amberger Kaolinwerke, Germany) with different particle size were selected for flocculation experiments. The particle size of clay FKS 84 is higher than that of the other clay TEC FF 840. The particle size distribution is very broad with a high content of fine particles for both types (about 90% of all particles are smaller than 2 μm). Because it was shown [18] that the particle size distribution of clay TEC FF 840 is more familiar to the wastewater this type of clay was used in most of the experiments.

Humic acid, obtained as s sodium salt from Aldrich, was dissolved in deionised water (Millipore Q) and used as a model for NOM.

For calculating the amount of humic acid adsorbed the clay particles were stirred in humic acid of certain concentration on a magnetic stirrer for 20 h and then separated by centrifugation (10,000 rpm, 10 min). The supernatant was characterised by polyelectrolyte titration.

For the flocculation experiments the clay (10 g/l) was stirred in Millipore water or in a solution of humic acid (50 or 25 mg/l) in water for 20 h to reach equilibrium.

Flocculation experiments

In most experiments a conventional test apparatus with six graduated cylinders (50-ml volume) was used for visual characterisation of sedimentation behaviour and clarification. After the preparation of the model suspension 50 ml was filled in each cylinder. Certain amounts of polymer(s) were added quickly. The apparatus was gently turned five times to ensure complete mixing. The flocs were allowed to settle for 30 min before about 10 ml was withdrawn from the top of the supernatant for turbidity measurements (2,100 AN IS turbidimeter, Hach, Germany). The removal of humic acid in the supernatant was quantified by measuring the light absorption of the flocculated suspension after filtration at a wavelength of 500 nm (Lambda 800 UV/vis spectrophotometer, PerkinElmer, UK).

Polyelectrolyte solutions

Two different types of polycations were used. The cationic polymer poly(diallyldimethylammonium chloride) (PDADMAC) with high cationic charge and relatively low molecular weight (35,000 g/mol according to the manufacturer) was obtained from Katpol Chemie, Bitterfeld, Germany, as a 20 wt% aqueous solution. The polymers of the other type of polycation—the high molecular weight cationic polyacrylamides (CPAM)–were obtained from Degussa/Stockhausen, Krefeld, Germany and differed in their charge density. The properties of these high molecular weight products (polymers A–D) are summarised in Table 1.

The anionic polyelectrolyte (Praestol 2530) used as the second component of the dual system was also a modified polyacrylamide [poly(acrylamide-*co*-sodium acrylate)] with about 30% of anionic charges and very high molecular weight (several million), provided as a powder by Degussa/Stockhausen, Krefeld, Germany.

The initial polymer solutions ($c_{\mathrm{PDADMAC}} = 0.01$ mol/l, $c_{\mathrm{Praestol}} = 0.1\%$ for all polymers of the polyacrylamide type) were prepared with deionised water (Millipore Q). They were gently stirred for 24 h and characterised by polyelectrolyte titration before use.

Methods

Polyelectrolyte titration

To determine the charge of the initial polymer solutions polyelectrolyte titration with a PCD 02 particle charge detector from Mütek, Herrsching, Germany, was used. This method is based on the generation of a streaming potential.

Determination of carbon content

The carbon concentration in the supernatants was determined using a total organic carbon analyser (TOC 5,000, Shimadzu).

Particle size

The size of the particles (distribution by volume) was measured with a HELOS (Sympatec, Clausthal–Zellerfeld, Germany) based on the principle of laser diffraction. The particles were measured in the wet state directly after the flocculation process. About 30 ml sample was removed from the flocculation cylinder and stirred slowly by using the SUCELL unit for dispersion. Each floc sample was measured three times for reproducibility.

Results

First, the interaction between clay and humic acid was investigated for our model substances. As known from the literature [19, 20, 21] and also shown in Fig. 1 for our system, the humic acid is adsorbed on clay. Saturation is not reached at our maximum concentration of humic acid. The anionic character of the clay suspensions increases with the concentration of humic acid added. By calculating from the charge of the supernatant (without clay) one can say that about 40% of the humic acid is adsorbed under these conditions. Further, the negative charge of the clay particles increases owing to the adsorption of humic substances. This was confirmed by polyelectrolyte titration of the separated and dried particles (Table 2).

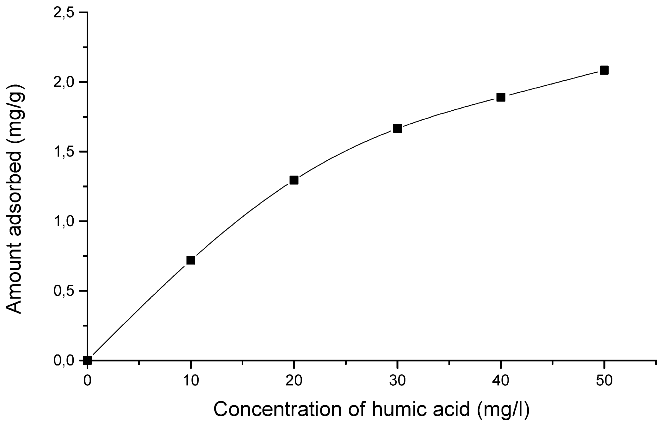

Fig. 1 Adsorption isotherm of humic acid (sodium salt) on clay FKS 84 (10 g/l) in water; the pH of the clay suspension without adjustment was between 7 and 8 and slightly increased with increasing amount of humic acid; 20 °C

The monoflocculation of clay in water with polycations was presented already in Refs. [5, 6]. The high molecular weight polycations of the polyacrylamide type act by bridging (broad flocculation window), whereas the strong polycation PDADMAC (with relatively low molecular weight) shows typical patching behaviour. We found that the size of the particles stays relatively low for PDADMAC, but it strongly increases with dosage for the products of high molecular weight. As also found by Gill and Herrington [22] the number of larger particles increases with increasing amount of the flocculant. The largest flocs were obtained with the product of the lowest charge density (polymer A). The size of the flocs is shown later.

The aim of this work was to study intensively the flocculation of clay suspensions in humic substances. Because the particle size distribution of clay TEC FF 840 is more familiar to the wastewater from the gravel pit, this type was used in most of the experiments. As expected from the results in Fig. 1 and Table 2 the amount of polycation necessary for flocculation is larger for suspensions with humic acid as shown in Fig. 2 for

Table 1 Characterisation of cationic polyacrylamide (*CPAM*)–polycations (polymers A–D)

Polymer	Product "Praestol"	Activity[b]	Charge (mmol/l)[a]	pH 0.1% solution[b]	Viscosity 0.1% (mPa s)[b]
A	610 BC	Slightly cationic	(+) 0.51	7	≈35
B	630 BC	Medium	(+) 1.33	7	≈50
C	644 BC	Strong	(+) 2.54	7	≈70
D	690 BC	Very strong	(+) 3.46	7	≈70

[a] 0.1% solution; charge determined by polyelectrolyte titration
[b] According to the manufacturer [23]

Table 2 Properties of particles

Material	Average particle sizex_{50} (μm)	Charge of the unaffected material (C/g)[a]	Charge after interaction with humic acid(C/g) [a,b]
Clay FKS 84	19.0	−0.4	−0.8
Clay TEC FF 840	7.3	−0.96	−1.3
Particles in the effluent from the gravel pit (for comparison)	7.9	−0.54	–

[a] Determined by polyelectrolyte titration of the aqueous dispersion
[b] Humic acid 50 mg/l

two examples. However, the principal behaviour is the same: broad flocculation window for polyacrylamide polymers, whereas the turbidity is significantly reduced only at certain concentrations of PDADMAC. The flocculation behaviour of CPAM with very high charge density (polymer D) is similar to PDADMAC (also very high charge density, but low molecular weight); see Fig. 3. On the logarithmic scale in Fig. 3 one can also see very well that the supernatant is not really clear for this type of clay in humic acid (after a sedimentation time of 30 min). Further, a lot of the supernatants are brown, demonstrating that humic acid is still in the supernatant and not in the sediment. So two different problems have to be solved: the separation of the clay particles and the removal of humic acid. When we compare the turbidity of flocculated suspensions after 30-min sedimentation with the absorption of light (as a measure for the content of humic acid) the different behaviour for the two types of polycations is also found (Fig. 4). For PDADMAC we get a small flocculation "window". Turbidity and also the absorption (500 nm) after flocculation—not shown here–are significantly reduced only at a special amount of polycation. For the high molecular weight polycation with low charge density we get a very broad flocculation window with respect to turbidity; however, the result is not good. To characterise the removal of humic acid in detail, the supernatants of the flocculated suspensions were analysed after filtration to remove clay particles and also "agglomerates" which are not able to precipitate. It is seen in Fig. 4 that the absorption of the filtrates decreases with increasing amount of polycation. We need only 1.6 mg/g highly charged PDADMAC for the reduction of the absorption, but much more polymer for the removal of humic acid with CPAM. Owing to the filtration of "agglomerates" (complexes between humic acid and the polycation) the flocculation window with respect to removal of humic acid becomes broader for PDADMAC, but it is not as effective for CPAM of low charge density. Humic acid is removed to a large extent only with PDADMAC and with CPAM of high charge density, independent of their molecular weight. CPAM of low charge density is not successful in removing humic acid, demonstrating that the formation of a complex between the polyanion in solution with the cationic charge of the flocculant is responsible for the separation process. These results are in good agreement with those for the removal of humic acid with polycations (without clay) [7]. In our experiments up to 95% reduction of NOM was obtained. The polymers with lower charge

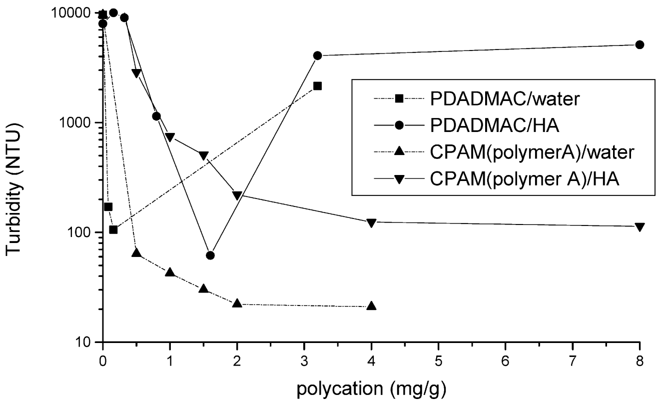

Fig. 2 Flocculation of clay TEC FF 840 (10 g/l) with poly(diallyldimethylammonium chloride) (*PDADMAC*) and cationic polyacrylamides (*CPAM*)–polymer A. Dependence of the turbidity of the supernatant on the amount of polycation. Comparison between systems in water and in humic acid (50 mg/l)

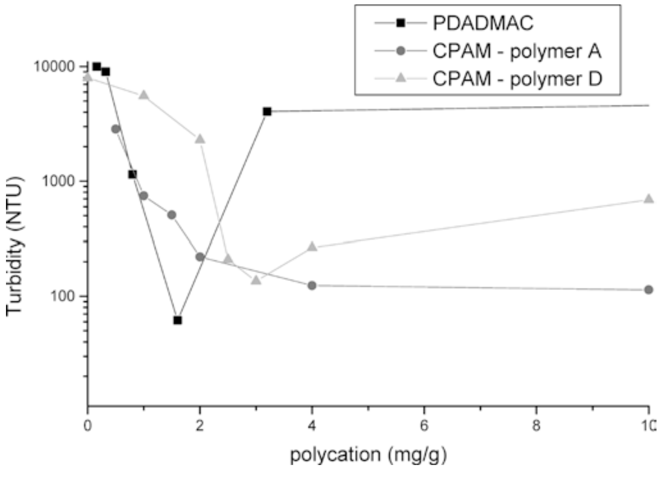

Fig. 3 Flocculation of clay TEC FF 840 (10 g/l) in humic acid (50 mg/l) with polycations. Dependence of the turbidity of the supernatant on the amount of polycation

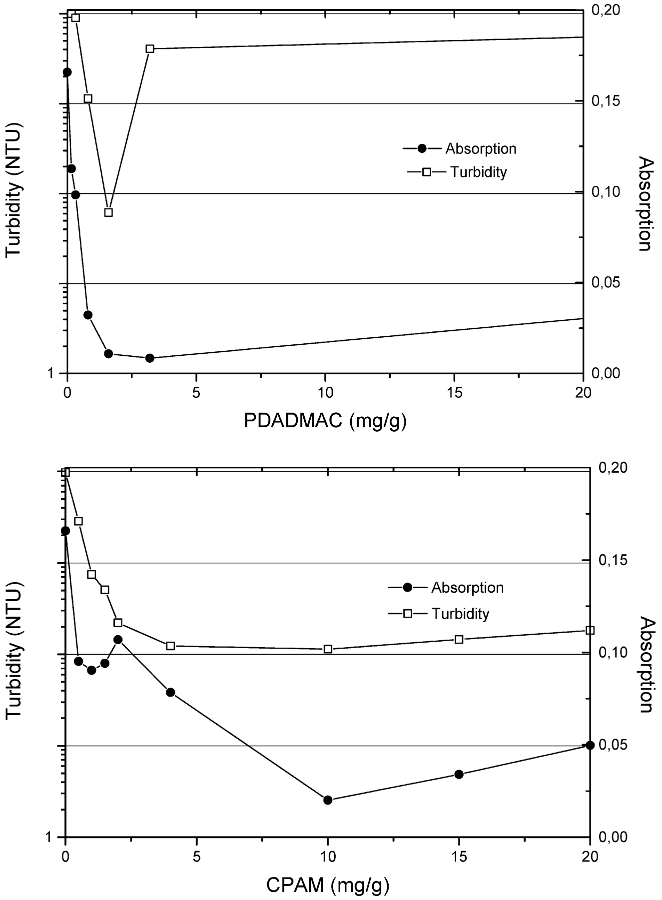

Fig. 4 Flocculation of clay TEC FF 840 (10 g/l) in humic acid (50 mg/l) with PDADMAC or CPAM–polymer A. Dependence of the turbidity of the supernatant and absorption after filtration on the amount of polycation

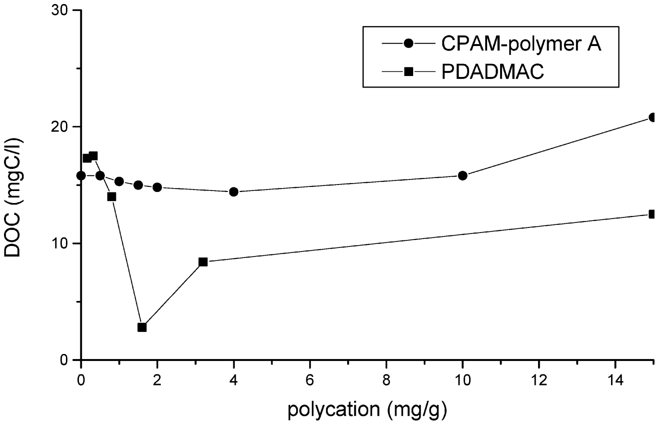

Fig. 5 Flocculation of clay TEC FF 840 (10 g/l) in humic acid (50 mg/l). Dependence of the dissolved organic carbon in the supernatant on the amount of polycation

density seem to be unable to remove the humic substances effectively. This is also confirmed by the results of the carbon content of the supernatant.

In Fig. 5 it is demonstrated that the decreasing carbon content in the supernatant also indicates the removal of humic acid, for instance, for PDADMAC. In case of CPAM–polymer A the dissolved organic carbon is always relative high, indicating that precipitation of the complex with humic acid did not occur. For the other polymers with higher charge density we find a minimum in the carbon content and a minimum in the turbidity. The filtrates are clear and colourless at this point (examples in Table 3), demonstrating that the complex formation between humic acid and the polycation is also responsible for the effective separation of very fine clay particles. However, by comparing the different polycations we agree with Kam and Gregory [7] that PDADMAC is especially effective in removing humic acid over a fairly narrow range of dosage also for clay suspensions. As the charge density of the polyelectrolyte decreases the zone of optimum flocculation concentration becomes broader and the removal becomes worse.

The dramatic reduction of the carbon content for flocculation with strong polycations at certain concentration is expected to occur by the complexation of polycations with humic acid and precipitation of the complexes. This was confirmed for PDADMAC without clay (Fig. 6). By dropwise addition of this polycation to humic acid (50 mg/l) and stirring, the turbidity in the mixture increases owing to complex formation. Simultaneously the cationic charge in the dispersion decreases. At a certain composition precipitation can be noticed. At this point (with the ratio of anionic to cationic charges n^{-}/n^{+} of about 0.85) the supernatant becomes colourless. This effect is found for PDADMAC and also for CPAM with very high charge density (polymer D).

On the basis of these results, the following conclusions can be drawn:. The flocculation of suspensions including very fine particles and also NOM is very complex. By using polycations with high molecular weight but low charge the optimum flocculation concentration is relatively high and the removal of humic acid is not complete. But the flocs are larger and the separation is better than for the short-chain polycation PDADMAC. However, because the latter is more effective in removal of humic acid at the point of optimum flocculation, it is more advantageous to combine the two different principles of flocculation. By using an optimum concentration of PDADMAC in a first step–it depends on the anionic character of the system and has to be found—and by adding only a small amount of a high molecular weight polyanion we are able to improve the flocculation process significantly. It is clearly shown in Fig. 7 that the efficiency of separation at low polymer content is much higher than in comparison with monoflocculation and the flocculation window becomes

Table 3 Properties of supernatants after flocculation with different types of CPAMs

Polymer	Polycation (mg/g)	Supernatant	Dissolved organic carbon (mgC/l)	Turbidity (NTU)[a]
Without	0	Brown, slightly turbid	16.5	13.1
B	1	Brown, slightly turbid	15.3	14.8
B	2	Brown, clear	11.2	21.5
B	3	Brown, clear	12.6	8.30
B	3.5	Almost colorless, clear	10.2	4.75
B	4	Almost colorless, clear	11.2	4.95
B	10	Colorless, clear	6.7	1.69
C	1	Light brown, clear	15.7	8.7
C	1.5	Light brown, clear	10	19.5
C	2	Light brown, clear	10.5	4.0
C	2.5	Light brown, clear	11.8	12.3
C	3.5	Colorless, clear	7.2	4.1
C	4	Colorless, clear	7.0	3.8
C	10	Almost colorless, clear	11.6	7.1
D	1	Light brown, turbid	9.6	20.1
D	2	Colorless, clear	7.5	5.9
D	2.5	Colorless, clear	8.0	1.7
D	3	Colorless, clear	6.0	0.5
D	10	Brown, turbid	21.3	48.6

[a] Turbidity measured 24 h after flocculation

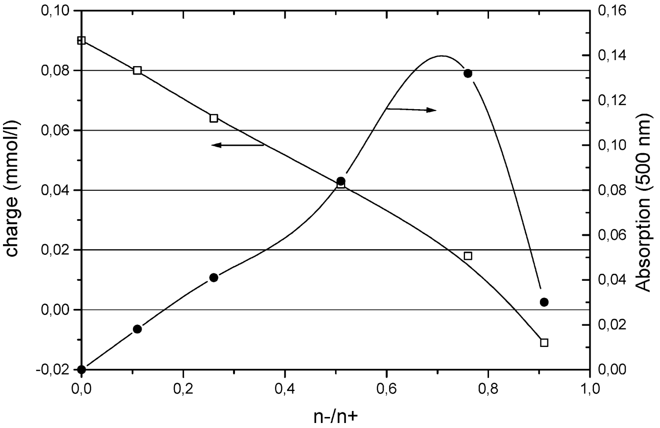

Fig. 6 Interaction between humic acid and PDADMAC (without clay). Dependence of the charge of the mixture (measured by polyelectrolyte titration) and absorption (500 nm) on the ratio of anionic to cationic charges n^-/n^+ in the mixture

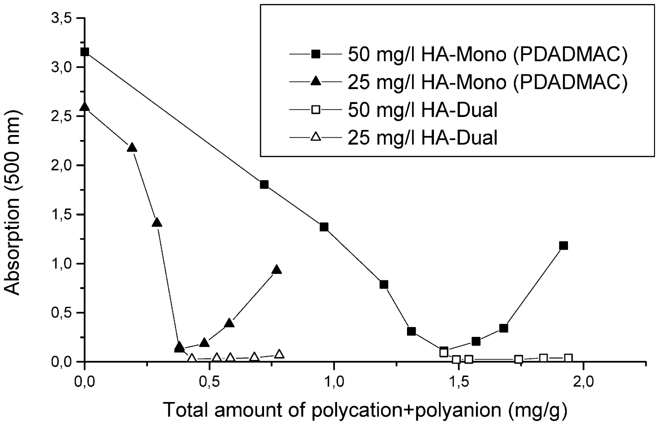

Fig. 7 Monoflocculation or dual flocculation of clay FKS 84 (10 g/l) in water/humic acid (50 or 25 mg/l). Dependence of the absorption (500 nm) of the supernatant on the total amount of polymer used; PDADMAC in case of monoflocculation, polycation plus polyanion in case of dual flocculation

broader. Further, effective removal of NOM is also achieved for high humic acid concentration (50 mg/l). The size of the flocs is shown in Fig. 8. As already mentioned at the beginning for systems which are free of humic acid the size of the flocs increases with the amount of polymer. The flocs obtained with PDADMAC are much smaller than those obtained with the high molecular weight polycations. For the CPAM polymers, bridging is the predominant mechanism, resulting in relatively large flocs [22]. The largest ones are obtained with the polymer of the lowest charge density (polymer A) owing to the very long loops and tails formed by the molecules after adsorption on clay. In case of the polymer with very high charge density (polymer D) neutralisation also plays a contributory role. These flocs are not much greater than those obtained with the highly charged but short PDADMAC. For flocculation with the dual system mentioned earlier the size of the flocs increases with the amount of the polyanion added (not shown here). For an "optimum" dual system the flocs are relatively large, causing a high sedimentation rate.

Conclusion

The separation of inorganic particles such as kaolinite is influenced by the presence of humic compounds. Owing to their adsorption on clay and the higher anionic charge of the system to be flocculated the optimum concen-

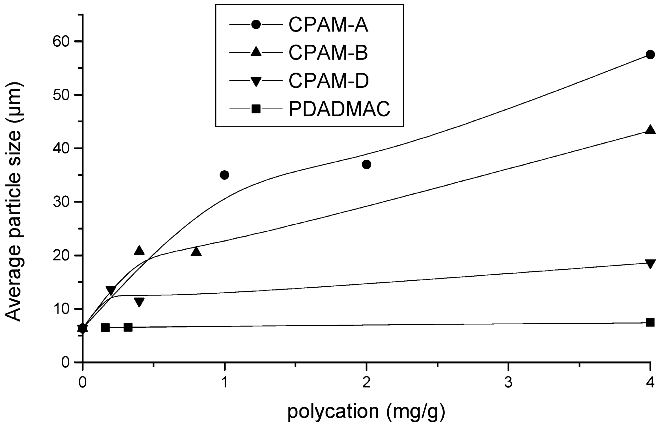

Fig. 8 Flocculation of clay TEC FF 840 (10 g/l) with PDADMAC and CPAM polymers. Dependence of the size of the particles on the amount of polycation

tration of the cationic flocculant increases compared with clay in water. Therefore polycations with high charge density are effective, but only at the optimum flocculation concentration (small flocculation window). The supply is rather high for polymers with low charge density; however, such flocs are very large, causing a high sedimentation rate. Polymers with high charge density, which form only small flocs, are more effective in removing humic acid owing to complex formation and precipitation. It was shown that the complexes formed by the highly charged polycation PDADMAC and the weak polyanion humic acid are also able to collect the fine clay particles. So excellent clarification and also effective removal of humic acid are obtained, but only for a certain concentration of polymer. The best results were obtained with a combination of the highly charged polycation (even of low molecular weight) and small amounts of a high molecular weight polyanion. In this case, a broad flocculation window is obtained as well as larger flocs compared with monoflocculation.

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