

INFLUENCE OF DISSOLVED ORGANIC MATTER ON COAGULATION/ FLOCCULATION OF WASTEWATER BY ALUM

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ABSTRACT

The influence of different humic substances and linear alkylbenzene sulfonate on chemical treatment of a synthetic wastewater was investigated at pH=6-6.5. In soft water, humus significantly inhibited particle destabilization. The additional coagulant dosages needed for efficient coagulation corresponded to the dosages required for humus removal from pure solutions. Adsorption of humus onto precipitated hydroxide was regarded as being the major mechanism of interaction here. In hard water, high concentrations of humus seemed to impair aggregation of microflocs. This was attributed to the formation of soluble calcium humate complexes in raw water that may adsorb more slowly on precipitated hydroxide than dissolved humus. Precipitation of phosphate was not affected by humus in a definite way. A clear influence of LAS on coagulation was not found.

KEYWORDS

Wastewater treatment; alum; coagulation; phosphate precipitation; flocculation; humic substances; LAS; removal mechanisms

INTRODUCTION

Chemical treatment of domestic wastewater is applied for two major reasons: precipitation of phosphate and coagulation/flocculation of particles and colloids. So far, phosphate precipitation was usually considered as being the process which determines coagulant demand. With respect to an advanced process design, however, more attention should be directed towards destabilization/flocculation of particulate material.

Flocculation studies conducted with suspensions of mineral particles have shown that macromolecular organic substances can severely impair the formation and separation of flocs. Klute *et al.* (1979) demonstrated the inhibiting effect of humic acid on destabilization of silica particles. Gibbs (1983) found that increased colloid stability in river water was due to coatings by natural organic substances. Jekel (1986) investigated the influence of different fractions of humic material on the stability of silica and kaolinite particles. He showed that high-molecular-weight species were favourably adsorbed on the particle surfaces. Their stabilization potential was attributed to steric rather than to charge effects.

Bernhardt *et al.* (1985, 1986) studied the impairment of flocculation of silica particles by allogenetic organic substances which were isolated from algal cultures. The effects were explained as being due to adsorption of these substances on the particles as well as formation of ligand complexes between dissolved organics and both metal ions and hydroxide precipitates. A reduction of the impairment of flocculation observed in hard water was attributed to the formation of complexes between calcium ions and the allogenetic material.

Studies by Novak and Haugan (1981) indicated that polymeric species produced by microorganisms in activated sludge may play an important role for sludge conditioning. Bantz *et al.* (1989) showed that these biopolymers strongly inhibited flocculation of silica suspensions.

Humic substances from the local drinking water supplies are also present in wastewaters. Moreover, humus-type substances are formed during biodegradation processes in the sewer system and the biological treatment stage, respectively (Link *et al.*, 1989), as are biopolymers. On the other hand, the particulate material in wastewater consists first of all of organic compounds like proteins, fat and polysaccharides (Metcalf and Eddy, 1979; Koppe and Stozek, 1986), while mineral particles are a minor portion only. Therefore, an experimental study was done to show whether humic substances also affect coagulation of medium-concentrated wastewater.

In industrialized countries, linear alkylbenzene sulfonate (LAS) is the most widely used detergent, resulting in concentrations up to 10 mg/l in raw domestic wastewater (Brunner *et al.*, 1988; Korber, 1989). According to Smith *et al.* (1956) alkylbenzene sulfonate concentrations less than 25 mg/l do not disturb coagulation of clay particles. Domestic wastewater, however, contains 40-100 mg/l of fat compounds, most of them being colloidal and particulate (Koppe and Stozek, 1986). Since the latter's stability could be affected by detergents, the influence of LAS on coagulation of wastewater was also evaluated here.

MATERIALS AND EXPERIMENTAL METHODS

A synthetic wastewater prepared 2 h prior to each experiment was used in order to maintain constant boundary conditions. It was prepared by adding the compounds listed in Table 1 to Trondheim tapwater which is a soft water with low content of salts and organics. Two different hardness levels were compared: 0,2 mmol/l corresponding to a water type often found in Scandinavia, and 2,5 mmol/l being typical for Central Europe.

TABLE 1 Compounds Used to Prepare the Synthetic Wastewater

Compound	Soft testwater	Hard testwater
CaCl ₂ , mg/l	0	255
NaHCO ₃ , mg/l	60	400
NaCl, mg/l	400	0
NH ₄ Cl, mg/l	100	100
K ₂ HPO ₄ , mg/l	50	50
Dry milk*, mg/l	300	300
Potato starch**, mg/l	60	60
Latex***, mg/l	10	10
Bentonite, mg/l	80	80
Humus, mg/l	0-50	0-50

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The composition of the testwater in terms of group parameters is shown in Table 2 together with data considered typical for domestic wastewater (Metcalf and Eddy, 1979). Hence, it can be assumed that the testwater represents most of the characteristics of real wastewater with respect to coagulation and precipitation.

TABLE 2 Composition of the Testwater Compared to Domestic Wastewater

Compound	Soft/Hard Testwater	Domestic wastewater
Proteins, mg/l	80	100-220
Fat, mg/l	85	40-100
Carbohydrates, mg/l	160	90-180
Other organic material, mg/l	15	?
Total organic matter	340	365
Clay, mg/l	80	} 65
Other inorganic material, mg/l	-	
Salts, mg/l	640/830	> 290*
Total inorganic matter, mg/l	720/910	> 355*
Alkalinity, mmol/l	1.7/5.7	> 2*
Ortho-P, mg/l	9.1/7.3	5
Suspended material, mg/l	170/260	220
Colloidal material, mg/l	180/ 90	50

*To be increased by the amount in local drinking water

Humic material was taken from two sources: One type was isolated from Lake Hyllvannet in Mid-Norway by means of a strong-base anion exchange resin (Lewatit MP 500 A). 1 mg of humus was assumed to correspond to 0.5 mg of TOC. The other type was a commercial product (Roth No 7824). LAS was a technical-grade product with a molecular weight of 344 g/mol. Aluminium sulfate was the technical product ALG provided by Kemira Kemi AB, Sweden.

A jar test apparatus equipped with an in-line mixing unit was used, with 1 min of rapid mix, 10 min of slow mix and 20 min of settling. Alum was dosed from a 20 g/l stock solution. The wastewater's initial pH was 7.9. If necessary, pH was adjusted by adding HCl or NaOH during the rapid mix stage. After sedimentation the supernatant was analyzed with respect to residual turbidity (Ratio-turbidimeter 18900, Hach Co), pH (SA 520 pH-meter, Orion Research Inc.), total-P and ortho-P (Norwegian Standard Methods). In addition, UV-absorbance at 254 nm was measured in samples filtered through 0.2 µm membranes (Hitachi 100-20 spectrophotometer).

EXPERIMENTAL RESULTS

Coagulation of particulate material

In an earlier study pH-dosage domains for efficient removal of colloids and particles from phosphate-free testwater had been established (Fettig *et al.*, 1990). Between pH=5.5 and pH=7.5 the dosage needed in soft water increased with increasing pH while it was almost constant in hard water. For pH<5.5 the dosages needed were quite small, because the zero point of charge for protein and fat compounds in the testwater is in the pH-range 4-4.5. On the other hand, restabilization effects were observed for pH<5.5 at high dosages.

The effect of simultaneous phosphate precipitation on particle removal has also been investigated in detail. As a result, precipitation of phosphate consumed an additional amount of alum in soft water, but did not affect much the dosage necessary for particle removal in hard water. This phenomenon has been discussed earlier (Fettig *et al.*, 1990). In this study, the influence of dissolved organic matter on removal of both particles and phosphate was evaluated.

Effect of lake humus

Residual turbidity values for different concentrations of lake humus are shown in Figures 1 and 2 as a function of alum dose. According to Fig. 1 the dosages required for efficient coagulation differ by a factor of about 2 between soft water containing no humus and water containing 50 mg/l of humus. This increase is clearly dependent on the humus concentration, as can be seen from the results obtained with 5, 10 and 20 mg/l of humic substances, respectively.

In hard wastewater, the effect of humus looks different (Fig. 2). About 70-80% turbidity reduction is achieved by relatively small alum doses. Removal of the remaining portion of particulate material then requires significantly higher dosages which again depend on the initial humus concentration.

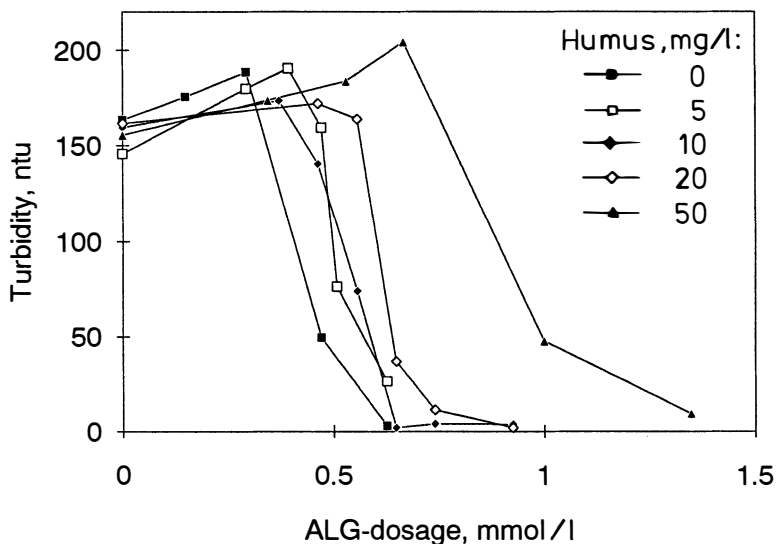


Fig. 1. Effect of lake humus on particle removal in soft testwater.

Effect of commercial humus

The effects obtained with commercial humus were similar to those found with lake humus, although less pronounced. Fig. 3 shows residual turbidity values for soft testwater as a function of alum dosage. Here, 50 mg/l of humus increase the alum dose needed by about 40% compared to the humus-free water.

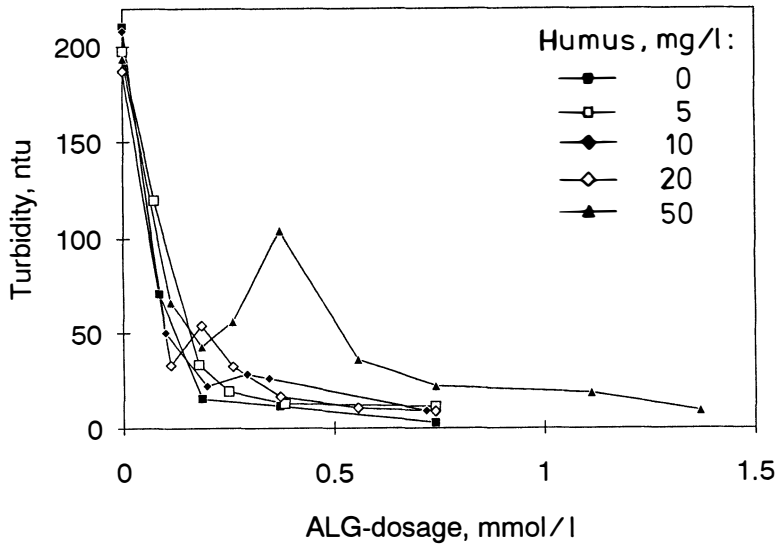


Fig. 2. Effect of lake humus on particle removal in hard testwater.

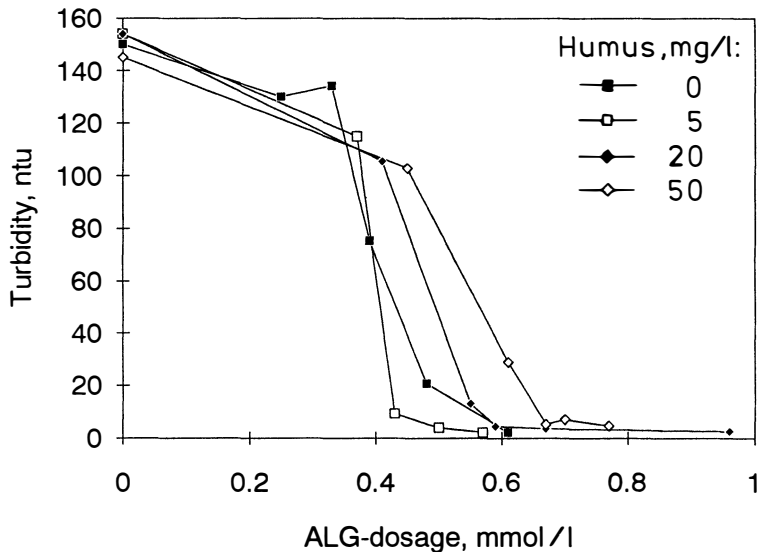


Fig. 3. Effect of commercial humus on particle removal in soft testwater.

UV-absorbance data measured in soft and hard testwater are shown in Figures 4 and 5. In both types of water certain compounds besides humus give a background value of about 0.08 1/cm. However, the initial concentrations of dissolved humus were significantly lower in testwater than in pure humus solutions and again lower in hard testwater than in the soft water type. This can be attributed to partial adsorption of humus onto particles that might be enhanced by calcium ions (Jekel, 1986), and to formation of calcium humate precipitates. With increasing alum dosage the amount of dissolved humus then gradually decreases. From

the turbidity removal data (Fig. 3) it can be concluded that this humus type inhibits flocculation as long as the humus-related UV-value is higher than about 0.12 1/cm corresponding to 5-6 mg/l of dissolved humic substances.

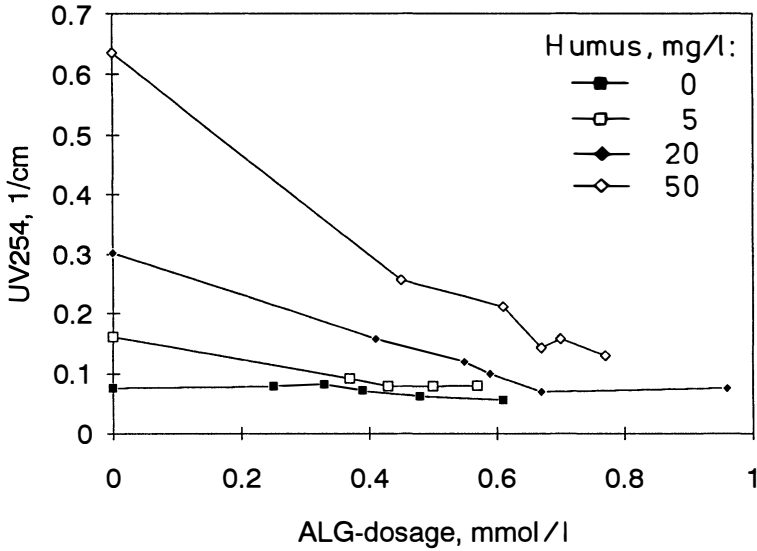


Fig. 4. Removal of dissolved humus in soft testwater.

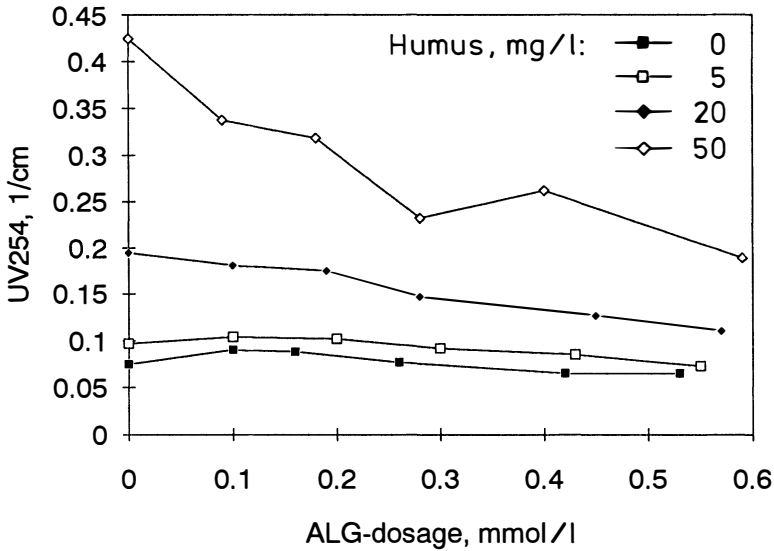


Fig. 5. Removal of dissolved humus in hard testwater.

Ortho-P removal in soft testwater is shown in Fig. 6 as a function of alum dose. Although the data differ somewhat, the initial humus concentration does not seem to have a clear influence on phosphate precipitation. However, removal of total-P (not shown) was inhibited to the same extent as removal of particles and colloids.

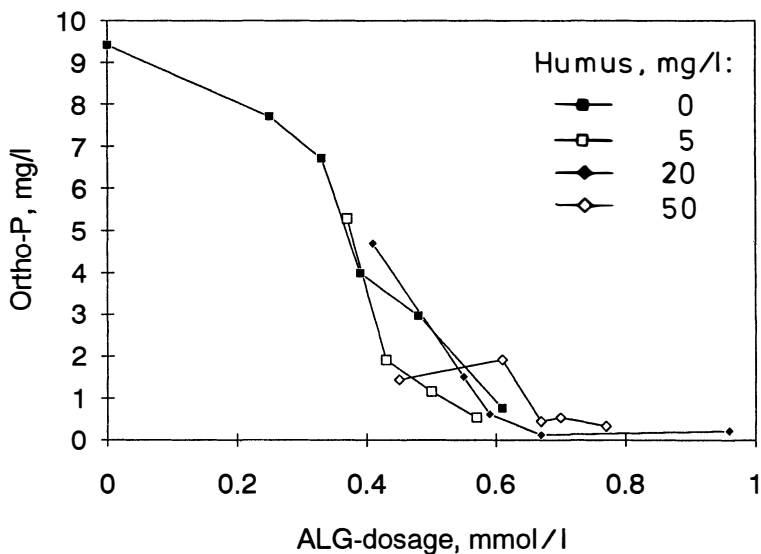


Fig. 6. Effect of commercial humus on phosphate precipitation in soft testwater.

Effect of LAS

In testwater about 80% of the total fat content is colloidal and particulate, respectively. The possible influence of LAS on flocculation and floc separation was studied by adding 10 mg/l LAS to soft testwater during the preparation period. Residual turbidity values as a function of alum dose are shown in Fig. 7. Although coagulation begins at a slightly higher dosage when LAS is present, it is concluded that the detergent had no significant effect, either on coagulant dose needed for maximum particle removal or on removal efficiency.

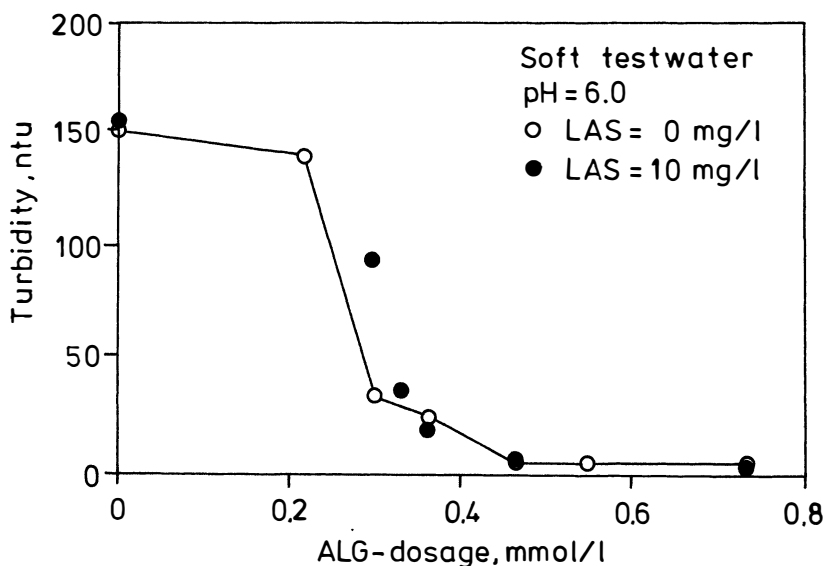


Fig. 7. Effect of LAS on particle removal in soft testwater.

DISCUSSION

It has been demonstrated that flocculation is inhibited by humic substances in both soft and hard wastewater where the majority of particles is organic. With respect to the mechanisms involved the distribution of humus in the raw water is an important factor. In soft water most of the humic material is dissolved while a certain portion is adsorbed on the particles. In hard water, formation of calcium humate precipitates and soluble calcium humate complexes must also be accounted for (Jekel, 1985). The amount adsorbed could not be determined here because it was not possible to apply DOC-analysis in this system. UV-absorbance was considered an unsuitable surrogate parameter for that purpose.

According to Edzwald (1986), formation of aluminium hydroxide is kinetically favoured over direct complexation of humic substances for pH=6-8 when alum is added to a pure humus solution. Humus removal is then primarily caused by adsorption onto precipitated hydroxide. The coagulant dosage needed increases with increasing humus concentration, the average Al/humus-ratio being about 0,25 mg/mg.

Jar test data with pure humus solutions containing 5 mmol/l of NaHCO_3 -buffer are shown in Fig. 8. The experimental conditions were 1 min of rapid mix, 30 min of slow mix and 60 min of sedimentation. The data reveal that commercial humus is more easily removed by alum than lake humus. In soft water the dosages needed are about 0.1 mmol Al per 10 mg of lake humus (0.27 mg/mg) and 0.05 mmol Al per 10 mg of commercial humus (0.14 mg/mg). The difference is attributed to better removal characteristics of commercial humus, as can be expected from its high colour/TOC-ratio of 23 (mg-Pt/l)/mg C, compared to the ratio of 8.5 (mg-Pt/l)/mg C for lake humus (Eikebrokk and Fettig, 1990). In hard water, however, about 35% of the humic material in terms of UV-254 are already precipitated by calcium ions and can be removed by membrane filtration. As a result, the alum dosage needed for removal of the remaining humics is lower than in soft water (Fig. 8). Aggregation of the microflocs formed in hard water seemed to be a relatively slow process.

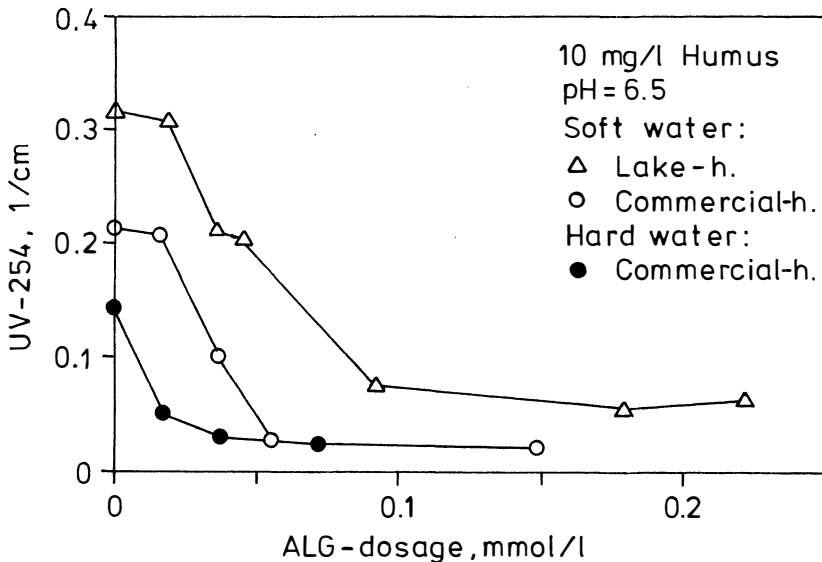


Fig. 8. Removal of humus from pure solutions by alum (filtered samples).

In soft wastewater the particulate material first aggregates when most of the dissolved humus is removed (Figures 1, 3, and 4). Assuming the mechanism referred to before to be predominant, the humics adsorb onto aluminum hydroxide that is precipitated either on particle surfaces or in solution. As a result, the destabilization potential of the coagulant is lower than in humus-free systems, and a higher coagulant dose is needed for efficient particle destabilization. Humus adsorbed onto the particles before coagulant addition would have a similar effect, that is, higher coagulant dosages were required then because of increased particle stability.

When the dosages needed for 90% turbidity removal in soft testwater are correlated with humus concentrations, it is found that the average increase is about 0.1 mmol Al per 10 mg of lake humus and 0.05 mmol Al per 10 mg of commercial humus, respectively. Thus, the specific dosages are the same as in pure humus solutions. This finding supports the assumed mechanism of interaction in soft water.

In hard testwater most of the particulate material is coagulated by alum dosages close to that found with humus-free water (Fig. 2). For humus concentrations >10 mg/l residual turbidity then increases with increasing dosage before optimum removal is achieved. This is interpreted as an indirect effect of humus: Dissolved humic substances are forming soluble complexes with calcium ions that may adsorb poorly on aluminium hydroxide (Jekel, 1985). If it is furthermore assumed that adsorption of these complexes is a slow process, it will not be finished within that period of time needed for formation of microflocs. Consequently it will interfere with flocculation rather than with particle destabilization. Thus, a coagulant surplus will be required to remove the complexes efficiently. There is no clear indication, however, that the amount of humus precipitated as calcium humate or adsorbed onto the particles before coagulant addition is significantly affecting the flocculation process.

CONCLUSIONS

1. Humic substances inhibit coagulation/flocculation of medium-concentrated wastewater that primarily contains organic particles and colloids. The extent of interference is dependent on type and concentration of the humic material and on the water's hardness.
2. In soft water, humic substances are assumed to adsorb on precipitated hydroxide, thus reducing its destabilizing potential and impairing coagulation. The additional coagulant dosage needed to compensate for the humus effect corresponds to the coagulant dosage required for humus removal from pure solutions.
3. In hard water, humus is partially precipitated as calcium humate before coagulant addition. Interference is assumed to be caused by slow adsorption of soluble calcium humate complexes on precipitated hydroxide during the flocculation period, resulting in slow aggregation of microflocs.
4. LAS has no significant effect on coagulation/flocculation of wastewater containing colloidal and particulate fat compounds, either with respect to dosage or regarding removal efficiency.

ACKNOWLEDGEMENT

The experiments were conducted in part while the authors were affiliated with the Norwegian Hydrotechnical Laboratory in Trondheim. The promotion of our work by Prof. Hallvard Ødegaard is gratefully acknowledged.

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