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INFLUENCE OF ALGAE AND THEIR EXUDATES ON REMOVAL OF HUMIC SUBSTANCES AND OPTIMAL DOSE OF COAGULANT

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ABSTRACT

There is still not enough information about the influence of several important variables, which occur in natural systems, on the coagulation of humic substances. One of these rarely studied variables is type and concentration of algal exudates. This paper presents the results of research of the influence of alga Scenedesmus quadricauda and its exudates on the results of coagulation experiments with model humic water. The arrangement of experiments should simulate one possible way how algae might influence natural water systems and water treatment.

The results demonstrate that both the residual concentration of humic substances and residual aluminium are influenced during the time which elapses after the addition of the washed algae to the model humic water. But the influence of algae on residual colour is partly different from their influence on residual aluminium. Early after the algae addition to the model humic water, they influence the system predominantly with their surfaces, because the concentration of their exudates is low. This increases the residual concentration of aluminium. On the other hand, longer "algal residence time" in model humic water decreases the residual aluminium concentrations. Systems with algae are sensitive to overdosing with respect to both residual humic substances and residual aluminium.

KEYWORDS

Coagulation; drinking water; water treatment; humic substances; algae; extracellular organic matter; colour; aluminium; centrifugation.

INTRODUCTION

In the research of drinking water treatment most attention was paid to the coagulation of inorganic particles (turbidity). Thus, most theories were developed with this type of pollution in mind. Processes of coagulation and the removal of natural organic matter (e.g. humic substances-HS) and organisms attracted less attention.

With respect to humic substances, research was oriented into their isolation and characterization in the nineteen sixties (Black and Christman 1963 a,b; Chalupa 1963; Packham 1964; Gjessing 1965).

An overview of methods of physical and chemical characterization of aquatic humic substances is presented in Gjessing's book (1976). Further research focused on the implications of various properties of HS (e.g. their fractions and origin) for their removal during water treatment (Edzwald, 1979; Jekel, 1983, 1986; Dempsey et al., 1984; Vik et al., 1985; Dolejs, 1986; Collins et al., 1986; Hundt and O'Melia, 1989).

Research into and practical experience in the processes of removal of various organisms from surface waters in drinking water treatment is still relatively scarce. Several earlier papers which addressed this problem were published by Orlita (1960), Bernhardt (1967), Bernhardt and Clasen (1967) and Svorcova (1970). Only recently, have Legionella, Giardia, and Cryptosporidium, been considered as organisms of general interest. All others are probably often taken for "particles" only. Rarely, in most monographies on drinking water treatment, can one complete paragraph be found on removal of different organisms from raw water. Because eutrophication is still a problem of many water sources, both researchers and practicioners in this field are in debt. Enough data is usually not available, about the numbers of organisms, like algae, in treated water. Corresponding to the great variety of planktonic species, organisms differ in a number of features which are important from a water treatment point of view. An inspiring attempt to present an overview of characteristics concerning interference of various organisms in water treatment was published by Janssens et al. (1986).

There remains a lack of information about the influence of several important factors, which occur in natural systems, on the coagulation of humic substances. One of these rarely studied variables is the influence of algal exudates, also called extracellular organic mater (EOM). Most papers dealing with the influence of EOM on coagulation were published by H. Bernhardt and his co-workers, and research performed at the Wahnbach Reservoir. The first paper in this field from the Wahnbach laboratory was published by Bernhardt and Wilhelms (1972). At that time only bioflocculation (Tenney and Stumm, 1965) in wastewater treatment had been mentioned in a water treatment monograph like Weber's (1972) and studies such as electrokinetic phenomena of algae (Ives, 1960, 1956) were often overlooked.

Over the course of the last twenty years the Wahnbach group published 20 papers which dealt fully or partly with the influence of algal exudates on drinking water treatment. The most important publications are probably those of Bernhardt et al. (1985a,b), Hoyer et al. (1985), Lüsse et al. (1985), Bernhardt et al. (1986), Kunikane et al. (1986) and Hoyer et al. (1987) and Lüsse (1988). Experiments were done mostly with model waters containing quartz flour graded to contain particles 2-12 µm. Recently the influence of EOM was studied also by Akiba et al. (1990) who used kaolin in their model water.

It has been shown by Kaplan and Bott (1982) and Hino (1988 a,b) that the excretion of EOM continues in a decreased rate in the dark as well as in different cellular phosphorus content and physiological state of algae. Important are also the interactions of metals and protons with algal surfaces, which were studied by Han-Bin Xue et al. (1988) and Crist et al. (1988).

The aim of this work was to investigate whether the results reported in literature about the influence of EOM on the coagulation of mineral suspensions are similar to results gained with model humic water. On the other hand, the aim was not to study the removal of algae. They were introduced into the system as "donors" of EOM, but the influence of their surfaces upon the experimental system was not eliminated. Additionally to the field of drinking water treatment, the results might contribute to our knowledge of origins of coagulation in lakes (O'Melia and Bowman, 1984).

MATERIALS AND METHODS

Model humic water. The experiments were carried out with model humic water. Tap water was diluted with distilled water to the desired concentration of Ca+Mg ions. A stock of humic substances concentrate was taken from a peatbog. The concentrations were COD_{Cr}=210 mg/l, COD_{Mn}=118.4 mg/l, pH=3.72, absorbancy at 254nm=4.67 (1cm) and at 387nm=0.924 (1cm) and contained a predominantly high molecular humic acid fraction. The acid neutralizing capacity to pH=4.5 (ANC) was adjusted by $NaHCO_3$ or HCl. After the addition of all components, the model humic water was left overnight to reach equilibrium. The main parameters of the model humic water were:

A_{254} = 0.23 (1cm)	A_{387} = 0.165 (5cm)
pH = 6.85	ANC = 0.30 meq/l
COD_{Cr} = 9.90 mg/l	COD_{Mn} = 3.85 mg/l
Ca+Mg = 0.30 mmol/l	$Fe_{tot.}$= 0.085 mg/l
Colour= 40 Pt mg/l	

Cultivation of algae. Alga *Scenedesmus quadricauda* was cultivated in the mineral medium made of dechlorinated tap water by the addition of:

125 mg/l KNO_3	10 mg/l $MgSO_4$
10 mg/l K_2HPO_4	1.25 mg/l $FeCl_3$

Algae were exposed to scattered day light in a room with windows facing north-west. Growth was limited by the diffusion of CO_2 through a cotton-wool filled plug. The reason for this arrangement was to carry out experiments with algae which possess practically the same physiological state. The concentration of algae was measured spectrophotometrically at 560 nm (A_{560}) (Lüsse, 1985) and also at 820 nm (see Fig.1.). A coefficient 403.10^3 was estimated experimentally and used to transform A_{560} to cell counts. Algae between the 20th and 34th day of cultivation were used for the experiments.

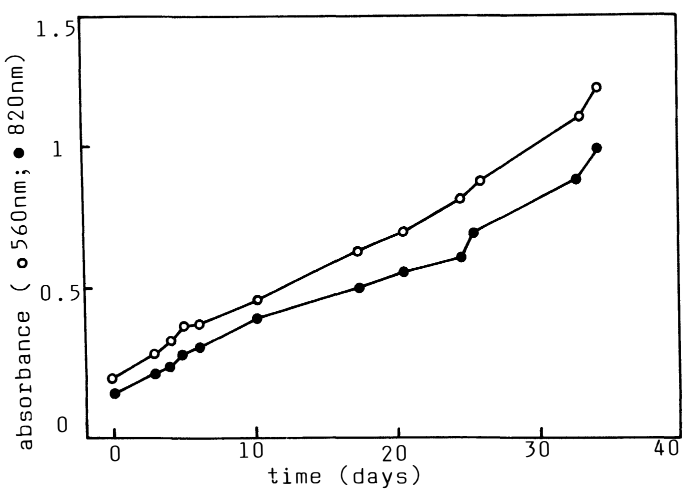


Fig. 1. Growth curve of alga *Scenedesmus quadricauda*

Coagulants. Two coagulants were used in the experiments. Aluminium sulphate (alum = $Al_2(SO_4)_3.18H_2O$) and partially neutralized aluminium sulphate (PNAS) in 15 mmol/l solution. The degree of PNAS neutralization r (r = OH/Al) is an important feature of all partially neutralized coagulants. Further information about the PNAS use and its performance is in Dolejs (1989). r=0.9 was used in the experiments reported here.

Coagulation experiments. Algae were separated from the mineral medium by ultrafiltration using low underpressure, and washed several times with model humic water. After filtration, they were gently transferred into a beaker with model humic water and resuspended. The desired amount of this concentrated suspension was added to model humic water. The aim of this procedure was to avoid the influence of the cultivation medium, as wal as EOM which was already present in it, on coagulation. This arrangement should simulate e.g. processes which accompany sedimentation of algae into the hypolimnion of a reservoir.

Time which elapsed after the addition of the concentrate of washed algae to the model humic water until commencement of the coagulation experiment was also considered as one variable ("algal residence time"). This was a surrogate parameter for changes of EOM concentrations in model humic water aimed to avoid laborious isolation of EOM from mineral medium.

Coagulation experiments were carried out according to the procedure described by Dolejs (1986, 1990). They were focused on perikinetic phase of aggregation of humic substances only. This procedure uses centrifugation for separation of destabilized molecules of humic substances which aggregate (together with the coagulant dosed) by Brownian motion as the only transport mechanism.

250 ml volumetric cylinders are first dosed with the appropriate amount of coagulant. The desired amount of raw water (100-250 ml) is then quickly injected from a large-volume syringe into the cylinders. Homogenization with the coagulant is achieved immediately and completely. After a certain period of time, which should reflect the residence time of water in the real system (between coagulant dosing point and the last separation unit), samples are transferred to centrifugation cells and centrifuged. Residual concentrations of coagulant, colour, COD etc. are determined. The value of the product g.t (g=gravity acceleration, t=time) used in this series of experiments was 640.10^3 m/s.

RESULTS AND DISCUSSION

To simulate the processes in most real treatment plants, pH was not controlled in the experiments. It changed simultaneously with the change of the coagulant dose (see Fig.2.). The reduced acidity of PNAS is apparent in comparison with alum. The presence of algae decreased the pH of coagulation, especially at higher doses of both types of coagulants.

Figures 3 a,b show results of coagulation experiments with alum used as coagulant. Different concentrations of algae were added to model humic water samples in different time periods before the start of each coagulation experiment.

All chosen combinations of algae counts and algae residence times in model humic water decreased the removal efficiency of humic substances expressed as colour. There was only one exception (the lowest dose of coagulant and experiment with 8000 cells/ml of algae which were present for 3 days in the model humic water). The same, i.e. the best removal efficiency, was valid for the same combination of experimental conditions, also with respect to the residual aluminium (see Fig. 3b).

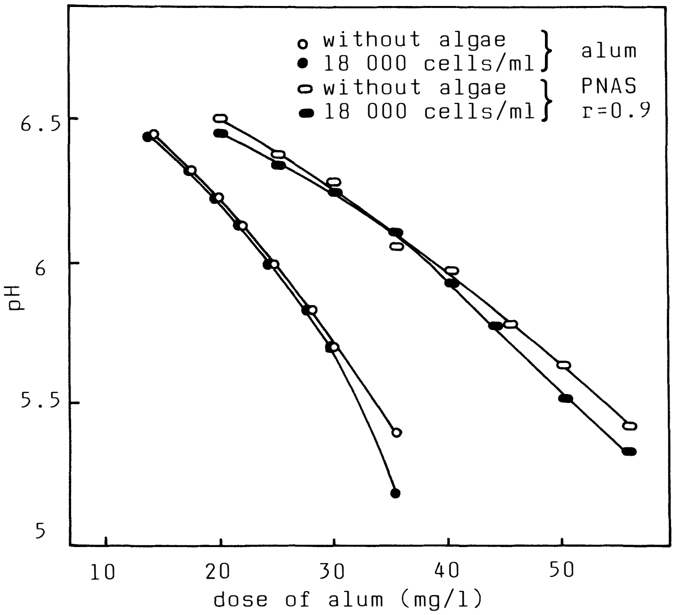


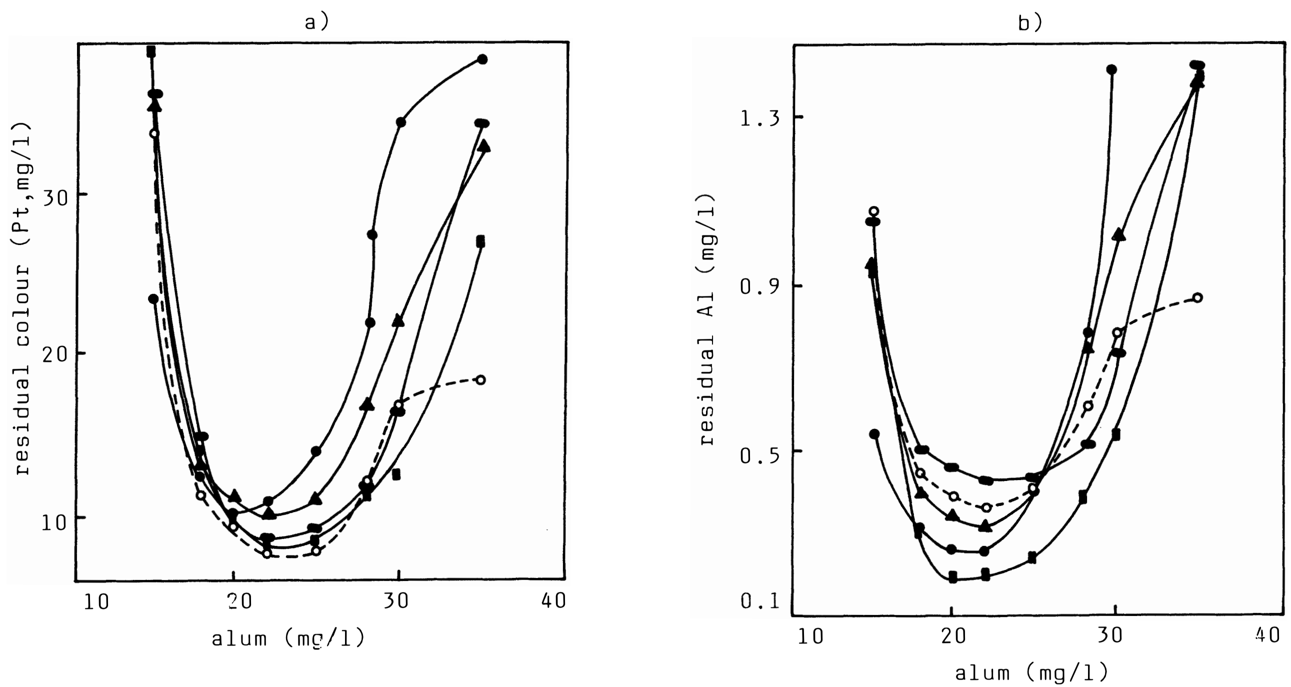
Fig.2. Influence of coagulant dose on the coagulation pH

Fig. 3a also shows the high sensitivity to overdosing of systems containing either high numbers of algae added to model humic water a few hours before the experiment (18 000 cells/ml, 4 hours) or lower numbers which were allowed to stay in the model humic water for several days (8 000 cells/ml, 3 days).

Residual concentrations of aluminium in coagulation experiments are shown in Fig. 3b. The lowest concentration of algae present for the shortest period of time in the model humic water (4 000 cells/ml, 1 hour) decreased the removal efficiency of aluminium and increased the optimal dose of alum. The lowest residual aluminium was achieved in the experiment with 8 000 cells/ml and 15 hours residence time. The same algae counts and 3 days residence time decreased the removal of Al, and caused a "sensitizing effect" to overdosing.

These results can be explained in the same way as Bernhardt et al. (1985a,b)and Kunikane et al. (1986) have already done for waters containing turbidity. After the addition of washed algae to model water, they influence the system predominantly by their surfaces. Production of EOM continues in time, after washing the algae. Low concentrations of EOM, which occur in the model water first, could act as a coagulation aid. This is probably the case in the experiment with 8 000 cells/ml and 15 hours residence time (see Fig.3b). On the other hand, higher concentrations of EOM, which are produced after 3 days residence time, decrease the removal efficiency at the "optimal dose" (optimal dose with respect to the experiment without algae), but also increase the Al removal in the underdosed system.

Fig. 4. shows results of two experiments with PNAS, coagulation experiment without algae and the experiment with 18 000 cells/ml and 1 hour algal residence time in model humic water. In comparison with



o without algae; ▬ 4000 cells/ml (1h); ▲ 18000 cells/ml (4h);
■ 8000 cells/ml (15h); ● 8000 cells/ml (3 days)

Fig. 3 a,b. Influence of alum dose and presence of algae on residual colour and residual Al

Fig.3 a,b, an approximately three times broader zone of optimal PNAS doses is apparent. This feature of prepolymerized coagulants is sometimes favourable for keeping the stability of treatment process.

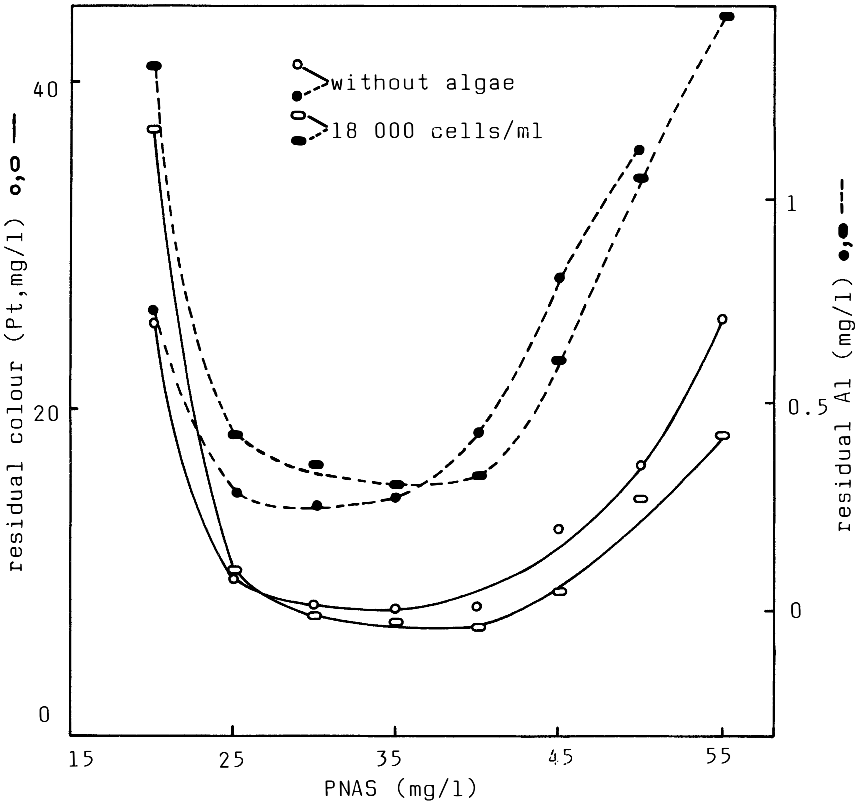


Fig. 4. Influence of PNAS dose and presence of algae on residual colour and residual aluminium

There are also differences in residual colour and Al between experiments with and without algae. The second feature of PNAS is its higher coagulation efficiency, which, on one hand, is able in comparison with alum to decrease concentrations of both residual colour and Al. On the other hand, it is able to cope with higher algal counts than in Fig 3. Algae increase the optimal dose from 30 to 38 mg/l of PNAS, which corresponds with with the same tendency in Fig 3.a,b.

The results presented in this paper are based on extensive work by H. Bernhardt and his co-workers who pioneered the field of EOM influence on water treatment. This is the first part of an experimental study on the influence of EOM on coagulation and treatment of humic waters. Although the setup of experiments, type of pollutant and experimental procedure in this paper was different from experiments done by the research team at the Wahnbach Reservoir, which were carried out with waters containing inorganic particles, the results are in agreement.

CONCLUSIONS

The addition of alga Scenedesmus quadricauda into model humic water influences both the residual concentration of humic substances and residual aluminium. Freshly washed algae added to model humic water decrease the removal of aluminium and require a higher optimal dose of coagulant.

Certain "algae residence times" and algal counts in model humic water produce a suitable concentration of EOM, which decreases the residual aluminium concentrations. As an example, concentration of algae = 8000 cells/ml and 15 hours algae residence time had a positive effect of algal EOM which was similar to the positive influence of properly dosed polyelectrolyte.

A longer "algae residence time" in the model humic water system causes better removal in the underdosed system, and sensitivity to overdosing with respect to both residual humic substances and residual aluminium. This is clearly demonstrated in the experiment with 8000 cells/ml and 3 days algae residence time (Fig. 3 a,b).

Partially neutralized aluminium sulphate (PNAS) gives better results than alum with respect to Al and colour removal, and the influence of algae on coagulation of humic substances by PNAS is the same . PNAS gives an approximate three times broader spectrum of suitable doses than alum.

REFERENCES

Akiba, M., Gotoh, K. and Satoh, A. (1990). The influence of algogenic organic matter on coagulation under pre-chlorination. Water Supply, 8, Jönköping, 103-109.

Bernhardt, H. (1967). Uber die Entfernung von Oscillatoria rubescens aus einem Telsperrenwasser durch Flockung und Filtration. Arch. Hydrobiol., 61, 311-327

Bernhardt, H. and Clasen, J. (1967). Probleme der Entfernung von Mikroorganismen durch Flockung in der Trinkwasseraufbereitung. Veröff. d. Abt. u. d. Lehrstuhls für Wasserchem. d. Univ. Karlsruhe, 3, 294-338.

Bernhardt, H. and Wilhelms, A. (1972). Einfluß von Algenstoffwechsel- und Abbauprodukten auf den Flockungsprozeß. Gewässerschutz-Wasser-Abwasser, 8, 111-138.

Bernhardt, H., Hoyer, O. and Lüsse, B. (1985a).Untersuchungen zur Beeinflussung der Flockung und Flockenabtrennung durch algenbürtige organische Substanzen. Z. Wasser-Abwasser- Forsch., 18, 6-17.

Bernhardt, H., Hoyer, O. Schell, H. and Lüsse B. (1985b).Reaction mechanisms involved in the influence of algogenic organic matter on flocculation. Z. Wasser- Abwasser- Forsch., 18, 18-30.

Bernhardt, H., Lüsse, B. and Hoyer, O. (1986). The addition of calcium to reduce the impairmant of flocculation by algogenic organic matter. Z. Wasser- Abwasser- Forsch., 19, 219-228.

Black, A.P. and Christman, R.F. (1963a). Chemical characteristics of fulvic acids. J. Amer. Water Works Assoc., 55, 753-770.

Black, A.P. and Christman, R.F. (1963b). Characteristics of colored surface waters. J. Amer. Water Works Assoc., 55, 897-912.

Chalupa, J. (1963) Humic acids in water. 1. Methods of preparation and determination. Sci. Papers of Prague Inst. of Chemical Technol., Ser. Fuel and Water, 7(1), 17-55.

Crist, R.H., Oberholser, K., Schwartz, D., Ryder, D. and Crist, D.R. (1988). Interactions of metals and protons with algae. Environ. Sci. Technol., 22, 755-760.

Collins, M.R., Amy, G.L. and Steelink, C. (1986). Molecular weight distribution, carboxylic acidity, and humic substances content of aquatic organic matter: implications for removal during water treatment. Environ. Sci. Technol., 20, 1028-1032.

Dempsey, B.A., Ganho, R. and O'Melia, C.R. (1984). The coagulation of humic substances by means of aluminium salts. J. Amer. Water Works Assoc., 76, 141-150.

Dolejs, P. (1986). Centrifugation study of humic waters coagulation by Brownian motion. In: Chemistry for Protection of the Environment 1985, L. Pawlowski, G. Alaerts and W.J.Lacy (Eds). Elsevier, Amsterdam, pp. 297-310.

Dolejs, P. (1989). Treatment of low alkalinity humic waters with partially neutralized aluminium sulphate. Environ. Technol. Lett., 10, 41-48.

Dolejs, P. (1990). A simple test for determination of optimal doses in the treatment of humic waters. In: Chemical Water and Wastewater Treatment, H.H. Hahn and R. Klute (Eds). Springer-Verlag Berlin Heidelberg., pp.377-390.

Edzwald, J.K. (1979). Coagulation of humic substances. AICHE Symp. Ser. Water, 75, 54-72.

Gjessing, E.T. (1965). Use of "Sephadex" gel for the estimation of molecular weight of humic substances in natural water. Nature, 208, 1091-1092.

Gjessing, E.T. (1976). Physical and Chemical Characteristics of Aquatic Humus. Ann Arbor Science Publ., Ann Arbor, Mich.

Hino, S. (1988a). Variations in physiological states corresponding to cellular phosphorus content in freshwater phytoplankton - Correlations with adenylate energy charge and photosynthetic activity. Arch. Hydrobiol., 113, 295-305.

Hino, S. (1988b). Extracellular release of organic matter associated with the physiological state of freshwater blue-green algae. Arch. Hydrobiol., 113, 307-317.

Hoyer, O., Lüsse, B. and Bernhardt, H. (1985). Isolation and characterization of extracellular organic matter (EOM) from algae. Z. Wasser- Abwasser- Forsch., 18, 76-90.

Hoyer, O., Bernhardt, H. and Lüsse, B. (1987). The effect of ozonation on the impairment of flocculation by algogenic organic matter. Z. Wasser- Abwasser- Forsch., 20, 123-131.

Hundt, T. R. and O'Melia,C.R. (1989). Aluminium-fulvic acid interactions: Mechanisms and applications. J. Amer. Water Works Assoc., 80(4), 176-186.

Ives, K.J. (1960). The significance of surface electric charge on algae in water purification. J. Biochem. Microbiol. Technol. Engn., 1, 37-47.

Ives, K.J. (1956). Electrokinetic phenomena of planktonic algae. Proc. Soc. Wat. Treat. Exam., 5, 41-58.

Janssens, J.G., Van Dijck, H., Meheus, J. and Waeterschoot, H. (1986). Investigation of the relationship between plankton counts, particle counts, and modified fouling index. In: Chemistry for Protection of the Environment 1985, L. Pawlowski, G. Alaerts and W.J.Lacy (Eds). Elsevier, Amsterdam, pp. 571-597.

Jekel, M. (1983). The complexation of aluminium ions with humic acids in the flocculation process. Vom Wasser, 61, 349-361.

Jekel, M. (1986). Interactions of humic acids and aluminium salts in the flocculation process. Wat. Res., 12, 1535-1542.

Kaplan, L.A. and Bott, T.L. (1982). Diel fluctuations of DOC generated by algae in a piedmont stream. Limnol. Oceanogr., 27, 1091-1100.

Kunikane, S., Lüsse, B., Hoyer, O. and Bernhardt, H. (1986). Flocculation and filtration of the green algae Chlorella sp. and Dictyosphaerium sp. under selected conditions. Z. Wasser- Abwasser- Forsch., 19, 145-151.

Lüsse, B., Hoyer, O. and Soeder, C.J. (1985). Mass cultivation of planktonic freshwater algae for the production of extracellular organic matter (EOM). Z. Wasser- Abwasser- Forsch., 18, 67-75.

Lüsse, B. (1988). Physiologically caused changes of the separability of algal cells by flocculation and filtration. Vom Wasser, 70, 11-20.
O'Melia, C.R. (1984). Origins and effects of coagulation in lakes. Schweiz. Z. Hydrol., 46, 64-85.
Orlita, A. (1960). Chemical flocculation and its influence on microorganisms (in Czech). Vodní Hosp., 10(2), 69-71.
Packham, R.F. (1964). Studies of organic colour in natural water. Proc. Soc. Wat. Treat. Exam., 13, 316-334.
Svorcova, L. (1970). Biological evaluation of laboratory coagulation experiments (in Czech). Vodní Hosp., 20(3), 1-6.
Tenney, M. and Stumm, W. (1965). Chemical flocculation of microorganisms in biological waste treatment. J. Water Poll. Con. Fed., 37, 1370-1388.
Vik, E.A., Carlson, D.A., Eikum, A.S. and Gjessing E.T. (1985) Removing aquatic humus from Norwegian lakes. J. Amer. Water Works Assoc., 77(3), 58-66.
Weber, W.J.,Jr. (1972). Physicochemical Processes for Water Quality Control. Wiley-Interscience, New York, p.86.
Xue, Han-Bin, Stumm, W. and Sigg, L. (1988). The binding of heavy metals to algal surfaces. Wat. Res., 22, 917-926.