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EFFECTS OF COLLOIDAL STABILITY ON CLARIFICATION AND DEWATERING OF ACTIVATED SLUDGE

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ABSTRACT

The effect of colloidal stability upon activated sludge properties for clarification and dewatering by filtration was investigated through controlled chemical manipulations of sludge in laboratory scale. The manipulations resulted in changes of the surface charge density and the shear sensitivity, the latter indicating a weakening of the sludge floc structure. The shear sensitivity was found to correlate with the residual turbidity after settling as well as with sludge filterability characteristics. The data strongly suggest the importance of blinding to increase with increasing shear sensitivity. The amount of fine particles present in the sludge was found to increase when sludge was exposed to a shear of similar magnitude to the shear in the employed filtration apparatus, indicating erosion of flocs during filtration to be important for blinding. Qualitatively similar results were obtained in full scale investigations of sludge from a treatment plant with varying inlet wastewater composition, indicating the possible importance of colloidal stability for solid/liquid separation processes in full scale wastewater treatment. Copyright © 1996 IAWQ. Published by Elsevier Science Ltd.

KEYWORDS

Activated sludge; blinding; colloidal stability; erosion; flocculation; floc strength; residual turbidity; shear sensitivity.

INTRODUCTION

Solid/liquid separation processes are of importance in the operation of activated sludge systems in order to achieve effluents of high quality and excess sludge containing a high solids fraction. The effluent quality is determined by the effectiveness of secondary clarifiers in separating solids from the liquid phase through settling of suspended solids, whereas the solids content in the excess sludge is determined by the ability of the sludge to yield water within a limited time scale by mechanical means such as filtration or centrifugation.

Activated sludge normally contains a fraction of non-settleable solids, which can be considered as the primary source of solids in the effluent from well-designed clarifiers. The concentration of non-settleable solids can be described by the residual turbidity of sludge water after settling (Wahlberg *et al.*, 1994). The residual turbidity of sludge water has also been found to correlate with the amount of free cells in sludge water and with the sludge filterability in experiments of anaerobic storage (Rasmussen *et al.*, 1994; Sørensen *et al.*, 1995). It has further been shown, that the amount of supracolloidal particles in the size range 1-100 μm seems to be an important factor for the filterability of activated sludge (Karr and Keinath, 1978; Barber and Veenstra, 1986). The reason for this is generally believed to be blinding of the sludge cake or filter medium due to clogging with fine particles. Given this background, it can be assumed that the amount of fine particles in a sludge will be of importance for both clarification and filterability.

The amount of fine particles present at a given shear in a turbulent flow system is expected to be dependent upon the sludge floc strength, as these particles presumably are produced by erosion of existing flocs (Parker *et al.*, 1971, 1972). Furthermore, the amount of fine particles is affected by the ability of these to flocculate upon collision with existing sludge flocs, which is described as the fraction of collisions that results in flocculation (Argaman and Kaufman, 1970). It can therefore be expected that the colloidal stability of the sludge system has an impact on the simultaneously occurring processes of particle erosion and flocculation, thereby controlling the amount of fine particles to be expected at a given shear intensity. Such considerations have been employed in the development of a "shear sensitivity" parameter as a means of characterizing the physical stability of a biological sludge (Mikkelsen and Keiding, in preparation a).

Even though controlled flocculation of activated sludge prior to settling has been found to improve effluent quality, some sludge waters tend to remain relatively turbid (Wahlberg *et al.*, 1994). Hence sludges possess varying flocculation properties. These properties have further been found to vary in time (Wahlberg *et al.*, 1994). Likewise, effluent quality has been observed to be poor during snow melting periods (Eriksson *et al.*, 1992) and in Danish treatment plants both effluent quality and excess sludge filterability have been observed to deteriorate during periods of heavy rainfall.

It is suggested that the colloidal stability of activated sludge particles at a given plant varies in time, hence leading to varying sensitivities to shear. Because the shear sensitivity is expected to be predictive of the amount of fine particles present in the sludge at any shear intensity, this parameter is also presumed to affect effluent quality as well as sludge filterability. The aim of this study was to produce evidence for the effect of changed colloidal stability upon clarification and filterability through controlled chemical manipulations of a given sludge in laboratory scale experiments. The findings were related to observations of changed sludge properties in full scale for a treatment plant known to be periodically receiving industrial wastewater.

MATERIALS AND METHODS

Laboratory tests were carried out using activated sludge from Aalborg East wastewater treatment plant. The plant is designed to perform biological nitrogen and phosphorus removal with supplementary simultaneous phosphorus precipitation through addition of ferro sulphate. The treatment plant is operated with a sludge age of approximately 30-35 days. Activated sludge was sampled in the aeration tank, stored at 4°C and used the same day. All tests were performed within three consecutive days to avoid changes other than those mediated by the controlled laboratory modifications.

Chemical manipulations were carried out using three different principles of surface charge modification, each principle tested within one day in a series of four sludge samples. The manipulations were (a) adjustment of pH through addition of concentrated HCl or 1M NaOH, (b) addition of the anionic detergent sodiumdodecylsulphate (SDS) followed by adjustment of pH with 1M HCl to the original pH and (c) replacement of sludge water with deionized water. Sludge samples were stirred in order to keep solids suspended during addition of chemicals. The pH was measured during sample preparation, the resulting pH, however, was measured immediately before performing tests. Exchange of sludge water with deionized water was realised after allowing sludge samples to settle for approximately two hours at 4°C. Sludge water equivalent to two thirds of the total sludge volume was decanted and replaced by deionized water. This procedure was repeated up to three times after shaking the sample to ensure mixing after each exchange.

The chemically manipulated sludges were kept suspended through gentle shaking for approximately 14 hours at 4°C in order to allow sufficient reaction time as well as standardised pretreatment of all samples.

Effects of changed colloidal stability for activated sludge in full scale were investigated for activated sludge from the Herning wastewater treatment plant for a two month period during which the composition of inlet wastewater was expected to change due to industrial vacation. The plant is designed to perform biological nitrogen removal and chemical removal of phosphorus through iron precipitation. The sludge age is approximately 30 days. Eight samples of sludge were investigated, four of which were taken in June 1994 before the vacation period to act as reference, and four of which were taken in July 2-3 weeks after the onset of the vacation period.

Surface charge density

In the controlled experiments the surface charge density was determined through a colloid titration procedure. The application of such a procedure has been investigated elsewhere (Mikkelsen and Keiding, in preparation b). The tests were performed by diluting a 1 ml sample of sludge to a total volume of 100 ml with deionized water, reacting the sludge with an excess amount (5 ml) of a 0.25 g/l Polydiallyl Dimethyl Ammonium Chloride (Cat-Floc) solution followed by back-titration with a 1.55×10^{-3} N Potassium Polyvinyl Sulphate (PVSK) solution to a colourimetric endpoint indicated by the change of 0.1 mg of Toluidine Blue from blue to red. The endpoint of the titration was determined from spectrophotometric absorbance measurements at 620 nm. The surface charge density was calculated from the difference in PVSK required to reach the endpoint of a sample titration and a blind titration.

The surface charge density for the sludge samples from the full scale investigations was characterized by the zeta potential calculated from the electrophoretic mobility.

Colloidal stability

In the controlled experiments colloidal stability was characterized by the shear sensitivity defined by Mikkelsen and Keiding (in preparation a) as k_B/k_A in the combined flocculation and deflocculation equation used in Wahlberg *et al.*, (1994):

$$n_t = \frac{k_B G}{k_A} + \left(n_0 - \frac{k_B G}{k_A}\right) e^{-k_A X G t} \tag{1}$$

where n_t is the number of primary particles at time t, k_B is the breakup rate coefficient, G is the root-mean-square (rms) velocity gradient, k_A is the aggregation rate coefficient, n_0 is the number of primary particles at time 0 and X is the sludge concentration.

A baffled reaction chamber with diameter 105 mm and 4 baffles of 11 mm depth was stirred with a paddle with a blade 50 mm wide and 12 mm high using a Heidolph RZR 2051 electronic stirrer at 1000 rpm. The sludge temperature was kept at approximately 4°C. Using a sample of 1 l sludge, the rms velocity gradient was determined as $G=530\ s^{-1}$. The number of primary particles at stirring times 0, 0.5, 1, 2, 3, 5, 10, 20 and 30 minutes was characterized by the modified CST defined by Christensen, (1992):

$$CST_{mod} = \frac{CST - CST_f}{\mu_{f/w} \cdot SS_{\%}} \tag{2}$$

where CST_{mod} is the modified CST, CST is the measured CST of a 5 ml sludge sample, CST_f is the CST of the filtrate, $\mu_{f/w}$ is the viscosity of filtrate relative to water, $SS_{\%}$ is the fraction (% w/w) of solids in the sludge. CST_{mod} was found to be directly proportional to residual turbidity (data not shown) and is therefore assumed to adequately quantify the true amount of primary particles. The shear sensitivity was determined by fitting data for CST_{mod} versus time to (1), k_A and k_B being the only unknown parameters.

In the full scale investigations an empirical method of measuring sludge floc strength as described by Eriksson *et al.*, (1992) was adopted. The floc strength is described by the parameter "CST-slope", being the slope of a plot of CST versus stirring time in a given reactor at 1000 rpm. The procedure was modified to a time scale of 60 minutes, and the modified CST as described above was used instead of CST.

Residual turbidity

The residual turbidity was characterized by CST_{mod} in the controlled experiments, this parameter having been found to correlate linearly with the turbidity (data not shown). In the full scale investigation the residual turbidity was measured at 650 nm on a spectrophotometer after two minutes of centrifugation at 600 g. The turbidity was converted to NTU units according to Standard Methods (1985).

Filterability

Filtration tests were carried out by filtering a sludge sample of 100-200 ml through a 5 cm diameter Whatman #41 filter under an applied pressure of 1 bar. Simultaneous recordings of filtrate volume and filtration time were automatically made by a computer throughout each test. From the data the specific resistance to filtration (SRF) was calculated from plots of dt/dV against V according to the equation (Sørensen *et al.*, 1995):

$$\frac{dt}{dV} = \frac{\mu}{P}(SRF \cdot C \cdot V + R_m) \tag{3}$$

where t is the filtration time, V is the filtrate volume per unit cross-sectional area, μ is the filtrate viscosity, P is the applied pressure, C is the deposited mass of solids per unit filtrate volume and R_m is the medium resistance. C was estimated as the total mass of cake solids in the dewatered sludge cake divided by the total filtration volume at the end of filtration, determined from the commencement of the expression phase.

A non-linear approach was adopted to describe the blinding during filtration according to the procedure suggested by Sørensen *et al.*, (1995). They proposed the filtration process to be described by the equation:

$$\frac{dt}{dV} = a_0 + a_1 V + a_2 V^2 \tag{4}$$

where a_0 is the initial medium resistance coefficient, a_1 is the cake filtration coefficient and a_2 is the blinding coefficient.

RESULTS AND DISCUSSION

Chemical manipulations of activated sludge

The chemical manipulations in the controlled laboratory experiments were expected to cause changes in sludge surface charge density, leading to changes in the electrostatic repulsion between sludge particles and hence altering the colloidal stability characterized by the shear sensitivity (k_B/k_A). The shear sensitivity is a descriptor of the ease with which fine particles are eroded from the sludge surface relative to the ability of such fine particles to be flocculated upon collision with sludge flocs. According to (1) the amount of fine particles present in a sludge at steady state is expected to be given by the product of the shear intensity (G) and the sludge shear sensitivity, a high shear sensitivity thereby indicating a high number of fine particles to be expected at any given shear. Increased electrostatic repulsion through increased surface charge density is expected to cause increased shear sensitivity, since according to the principles of DLVO-theory, increasing deflocculation and decreasing flocculation is the result of increased electrostatic repulsion, provided that only negligible change of attractive van der Waal's forces is concomitantly induced.

Results for the measured surface charge density and shear sensitivity for the sludge samples are shown in Table 1. All of the chemical manipulations brought about changes of these parameters in the expected manner. Adjustment of sludge pH was expected to cause changes of the surface charge density through changes of the dissociation of H^+ from functional surface groups. For these experiments the negative surface charge and the shear sensitivity were expected to increase with increasing pH, as is also seen to be the case. The positive surface charge for sludge with pH 3.2 indicates the isoelectric point of the sludge to be at a pH above this value. Addition of anionic detergent (SDS) to the sludge was expected to cause increased surface charge density and shear sensitivity due to adsorption of the detergent onto the sludge surfaces. Data given in Table 1 show that this was indeed the case, the addition of SDS having led to large alterations in the measured parameters. Finally, replacement of sludge water with deionized water was expected to increase the surface charge density and shear sensitivity due to desorption of cations and reduced ionic strength. The data show this to be the case, although effects were considerably smaller than those obtained through changed pH and addition of detergent.

Table 1. Surface charge density and shear sensitivity for sludge samples after chemical manipulations

Sludge sample	Surface charge density [meq/g SS]	Shear sensitivity (k_B/k_A) [s^2]
pH 3.2	0.25	0.025
pH 5.9	-0.07	0.045
pH 7.3	-0.27	0.062
pH 9.1	-0.29	0.170
Untreated sludge	-0.15	0.046
2 meq/l anionic detergent added	-0.21	0.113
5 meq/l anionic detergent added	-0.45	0.201
10 meq/l anionic detergent added	-1.44	0.275
Untreated sludge	-0.17	0.048
1 dilution *)	-0.18	0.056
2 dilutions *)	-0.21	0.083
3 dilutions *)	-0.24	0.080

*) Dilution: exchange of sludge water with deionized water.

The Figures 1-4 show the results of residual turbidity and filtration characteristics for the sludge samples as a function of the shear sensitivity. The measured parameters are seen to follow the same general trends, regardless of the chemical principle used for the sludge surface modification. The results of a first order regression analysis including all data points for each parameter is shown on each of the figures. In all cases there is a significant positive slope of the regression line. Hence, based on the present set of data, the statistical analysis indicates that a significant coherence exists between the shear sensitivity parameter and each of the measured sludge characteristics. At this point no inferences are made regarding the nature of these coherences.

Figure 1 shows that the residual turbidity (characterised by CST_{mod}) was found to increase with increasing sludge shear sensitivity. This was expected as a consequence of an increasing number of fine particles at any applied shear intensity according to (1). Figure 2 shows a similar dependence between shear sensitivity and specific resistance to filtration (SRF). The possible reasons for the increasing SRF are a generally increased resistance from the cake solids or increased blinding. Figure 3 shows a close to linear dependence between the shear sensitivity and the cake filtration coefficient, which can be interpreted as a result of less irregularly shaped sludge flocs, caused by erosion of the floc surface, leading to a less porous sludge cake. Figure 4 shows that the greater impact of the shear sensitivity was found on the blinding coefficient, indicating increasing importance of the blinding phenomenon with increasing shear sensitivity. The non-linear dependence of the blinding coefficient on the shear sensitivity can be explained from the impact of fine particles on the filter medium or sludge cake porosity. With a given initial porosity, deposition of a small number of fine particles will lead to a small decrease in the porosity. The relative effect of a given number of particles on the porosity will, however, increase as the porosity decreases. Hence, the effect of blinding will increase at a higher rate than the number of fine particles. Furthermore, a reduced initial porosity of the sludge cake can be expected when erosion causes more rounded flocs, leaving the sludge cake more vulnerable to blinding. The latter suggestion, however, will only be valid if blinding occurs in the sludge cake rather than in the filter medium. The resistance of the unblinded filter medium was found not to be significant (data not shown).

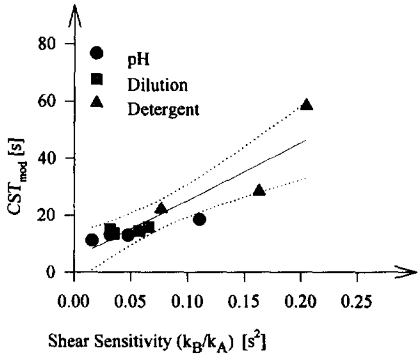

Figure 1. Relationship between the residual turbidity (CST$_{mod}$) and the shear sensitivity.
······· 99% confidence limits for 1. order regression.

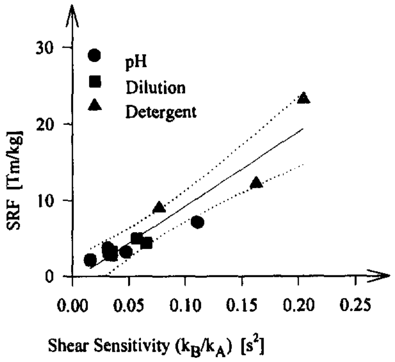

Figure 2. Relationship between specific resistance to filtration and the shear sensitivity.
······· 99% confidence limits for 1. order regression.

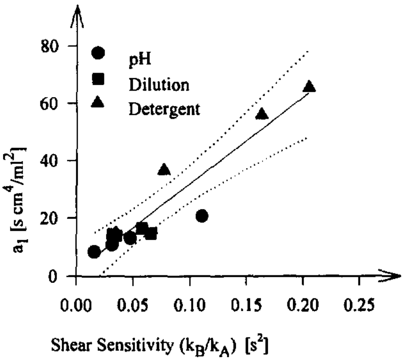

Figure 3. Relationship between the cake filtration coefficient (a_1) and shear sensitivity.
······· 99% confidence limits for 1. order regression.

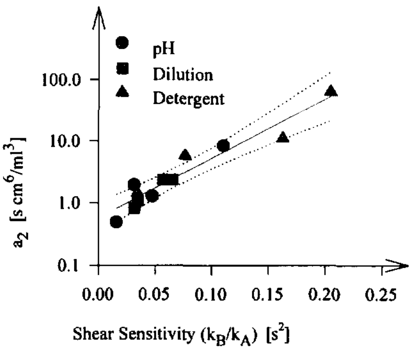

Figure 4. Relationship between the blinding coefficient (a_2) and the shear sensitivity.
······· 99% confidence limits for 1. order regression.

Similar observations for SRF have been reported by Karr and Keinath (1978) for changed pH and by Keiding and Nielsen (1995) for removal of Ca^{2+} through ion exchange. Karr and Keinath (1978) explained the changed filterability as an effect of changed particle size distribution, as the amount of supracolloidal particles was increased with increasing pH, an observation in accordance with the increased shear sensitivity observed in the present study.

As described above, correlations between SRF and the amount of fine particles present in a sludge described as turbidity, number of free cells, suspended solids in supernatant after settling or amount of particles of a given size have been found in various studies. According to the concept of shear sensitivity the amount of fine particles should, however, be expected to vary with the shear. Sludge particles will be exposed to larger shear intensities during filtration than under the quiescent conditions under which the residual turbidity is often measured. Hence, Novak and Lynch (1990) estimated a shear of G=500 s^{-1} to be realistic for filtration of sludge in a filtration apparatus with an applied pressure of 1 bar. This value is similar to the shear used for determination of the shear sensitivity in the present study, although the different geometries make direct quantitative comparisons unreasonable. During these tests the modified CST was found to increase significantly for all sludge samples. It is therefore suggested that the correlation between parameters measured at different shear intensities (such as the correlation between turbidity and SRF or CST and SRF) be considered as a correlation to the shear sensitivity of the sludge rather than a correlation to the actual measured parameters.

Full scale investigation

The full scale investigation was concerned with a treatment plant where poor sludge properties frequently have been observed. This was hypothesized to be a result of changes in the sludge surface charge density due to adsorption of anionic dyes, periodically discharged from textile colouring industries. Table 2 shows that the surface charge density (zeta potential) and shear sensitivity (CST-slope) decreased during the vacation period, leading to improved residual turbidity and sludge filterability. The greatest changes of individual parameters were found for the shear sensitivity (CST-slope), the residual turbidity and the blinding coefficient, the average of these parameters being approximately halved during the vacation period. Although some variations were observed, all changes in the measured parameters were significant. These results qualitatively match the results of the controlled experiments. The reduced surface charge is assumed to be a consequence of a reduced amount of negative charge in the inlet wastewater during this period (data not shown). The investigation supports the hypothesis that the colloidal stability can be of importance for the achievement of high quality effluents and good sludge filterability for full scale systems. In the present investigation the reduced inlet charge density and improved sludge properties during the vacation period was assumed to be a result of the lack of textile dyes in the inlet wastewater. However, the source of negative surface charges has not been proven to be these industries. Other industrial wastes could possibly explain the observations in a similar manner, since in Denmark it is normal for several industries to stop production for vacation at the same time. The assumed importance of colloidal stability, nevertheless, remains the same regardless of the source of negative charges.

Table 2. Results of full scale investigation for the reference period and the industrial vacation period. The results are based on four sampling days in each period

	Reference period		Vacation period	
	Average	Std. dev.	Average	Std. dev.
Zeta potential [mV]	-11.7	0.6	-9.7	1.1
CST-slope [s/min]	2.14	0.71	1.21	0.17
Turbidity [NTU]	3.1	1.6	1.1	0.2
SRF [Tm/kg]	5.4	1.4	3.4	0.6
a_1 [s cm^4/ml^2]	19.1	4.9	12.3	1.1
a_2 [s cm^6/ml^3]	1.17	0.65	0.45	0.09

CONCLUSIONS

From the present investigation the following conclusions can be drawn.

Colloidal stability is important for clarification of activated sludge, since the amount of suspended solids in the effluent was found to be directly proportional to the shear sensitivity.

Colloidal stability is important for the filterability of activated sludge, resulting in deteriorating filterability with increasing shear sensitivity.

The importance of blinding is rapidly increasing with increasing shear sensitivity, presumably due to an increasing number of fine particles in the sludge prior to filtration and erosion of fine particles during filtration.

Sludge shear sensitivity, residual turbidity after clarification and filterability can be altered through controlled chemical manipulations of activated sludge in order to change the colloidal stability.

Similar relationships can be expected to - at least in part - explain full scale observations on deteriorating sludge properties for clarification and filtration due to the presence of chemicals with an impact on sludge surface properties.

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