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Impacts of morphological, physical and chemical properties of sludge flocs on dewaterability of activated sludge

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Abstract

This study examined how the floc characteristics affect dewaterability of activated sludge. The floc properties were characterized by morphological parameters (floc size distribution, fractal dimension and filament index), physical properties (flocculating ability, surface charge, relative hydrophobicity and viscosity), and chemical constituents in sludge and extracted extracellular polymeric substances (EPS), including the polymeric compounds protein, humic substances, carbohydrates and the ions Ca^{2+}, Mg^{2+}, Fe^{3+} and Al^{3+}. The dewaterability was defined in terms of the bound water content and capillary suction time (CST). The bound water and CST corresponded to a similar indication with respect to dewaterability of activated sludge. The floc physical parameters were the most important factors which effect significantly on the water binding ability of the sludge flocs. The morphological characteristics had relatively weak impact on the dewaterability. The polymeric components protein and carbohydrate had a significant contribution to enhance the water binding ability of the sludge flocs. The effect of humic substances in the sludge on the dewaterability was, however, insignificant. The CST had good statistical correlations with the polymeric constituents measured in both sludge and the extracted EPS, and the bound water was only correlated well with the individual polymers measured in the sludge. High concentration of Ca^{2+}, Mg^{2+}, Fe^{3+} and Al^{3+} had significant improvement for dewaterability.

Keywords: Activated sludge; Dewaterability; Bound water; CST; Floc size; Fractal dimension; Filament index; Viscosity; Flocculating ability; Hydrophobicity; Surface charge; Polymer constituents; Metallic ions; EPS

1. Introduction

A key aspect of the operation of activated sludge systems is the separation of the biological solids from the liquid phase and the subsequent dewatering of these biosolids. Separation results from settling of spontaneously aggregated bacteria into flocs. A subsequent dewatering step is usually necessary to obtain a reduction in sludge volume to facilitate transport and handling, or to minimize the space or energy needed in case of drying or incineration. Dewatering is one of the most difficult and costly processes in wastewater treatment [1–3]. Generally, the dewatering is done by physical means with mechanical methods such as vacuum filtration, belt filter presses, drying beds and centrifugation [4]. The choice of technique is mainly based on the type of sludge and space available. The efficiency of the dewatering process is highly dependent on the nature of the sludge. In many cases, chemical conditioning agents are required to improve the dewaterability [5].

It is know that activated sludge flocs have a complex and heterogeneous composition and the floc characteristics, e.g. size, micro-structure, surface properties and density, can be very different depending on variations in the surrounding environment, e.g. due to changing wastewater composition and operational conditions [1,6,7]. Previous studies show that the characteristics of the flocs affect the dewaterability, especially the size distribution and the presence of small particles [8–10]. Surprisingly little is, however, known about the impact of the floc properties on the dewaterability of activated sludge. Apart from bacteria, the flocs contain extracellular polymeric substances (EPS) and various inorganic and organic molecules [11]. Water represents the main component of the microbial aggregates, followed by the EPS and biomass [12]. The EPS originate either from the metabolism or lysis of microorganisms or adsorbed compounds from the wastewater [13]. The precise function of the EPS is not fully known but they retain exoenzymes near the cell surfaces [11,14]. The EPS can bind organic and

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inorganic matter and ions, in particular Ca^{2+}, and assist in the attachment of bacteria to surfaces [2]. They are believed to improve floc formation, but high concentrations may lead to poor settling and compaction properties [13,15,16]. Although a part of the water in activated sludge is intracellular and thus trapped by the cell walls, most of the water is bound by the EPS [12,17]. Keiding et al. [12] pointed out that since the polymer network contains high concentrations of negative charges surrounded by counterions, the osmotic gradient may lead to high water uptake (swelling). The EPS represent a highly hydrated matrix with water content up to 98% [18]. Previous work has shown that the concentration of EPS has an effect on the dewaterability [19,20]. Mikkelsen and Keiding [20] found that the dry matter content of the filter cake decreased as the concentration of EPS increased.

The dewaterability of sludge can be defined in two ways: either as rate of filtration or as bound water content of the sludge cake after dewatering. The bound water is not a well-defined parameter and various methods, such as drying, centrifugal settling and dilatometric measurements, have been used to characterize it [21–23]. The water content of the sludge can be divided into two categories: "free" water and "bound" water [21,24]. The free water can be easily removed by thickening or weak mechanical means, and behaves thermodynamically as pure water. The bound water, on the other hand, is held firmly in the floc matrix, bound to the sludge or trapped between sludge particles and cannot be removed by mechanical means, and represents a small proportion of the total water. Furthermore, the bound water has a different chemical potential compared to the one in the bulk water. The bound water can be divided into chemically or physically bound water which can only be removed by thermal drying at temperature above 105 °C; and mechanically bound water which is bound by capillary forces in micro- and macro-capillaries [24]. Bound water and capillary suction time (CST) have been used previously for the characterization of the dewaterability of activated sludge. The CST method has been widely accepted and used due to the simple equipment required. However, there is no information available in the literature, indicating how the CST relates to the water content of the sludge.

The objective of this study was to assess how the sludge floc characteristics, including: (1) morphological aspects (size distribution, filament index, fractal dimension); (2) physical properties (flocculating ability, hydrophobicity, surface charge and viscosity); (3) and chemical constituents of polymeric substances (protein, humic substances and carbohydrate) and metallic ions (Ca^{2+}, Mg^{2+}, Fe^{3+} and Al^{3+}), affect the dewaterability of the activated sludge. The bound water and CST methods were used to evaluate the dewaterability. The investigations were carried out in full-scale wastewater treatment plants (WWTPs). The experimental results were evaluated by statistical data analysis.

2. Materials and methods

2.1. Activated sludge samples

Activated sludge samples were taken from seven different full-scale activated sludge WWTPs in Brisbane, Australia, including five sewage treatment plants (STPs) and two industrial activated sludge treatment processes for oil refinery and leachate effluent. The process descriptions of the WWTPs are given in Table 1. The sludge samples from each WWTP were collected from the aeration tanks and maintained in filled plastic containers placed in ice cooler during the transportation from WWTP site to laboratory. Sample tests started immediately and were completed within 20 h, while being kept in a refrigerator at 4 °C. Sludges from each WWTP were generally examined twice with up to 4 months in between.

2.2. Dewaterability

The dewaterability of the activated sludge was determined by CST and bound water. The CST has been widely accepted and used for the evaluation of dewaterability of activated sludge due to the simple equipment required. It measures the time when the filtrate requires to travel a fixed distance on a specific filter paper, reported in seconds. A high value of CST usually implies a poor filterability and dewaterability [25,26]. The CST was measured by a CST instrument as detailed in Standard Methods [27] with a Whatman No. 17 chromatography grade paper. The CST for distilled water was stable at 2 s. Mikkelsen and Keiding [20] stated that for a specific sludge, the CST and viscosity were related and dependent on the suspended solids concentration. In the present

Table 1
Process descriptions of the wastewater treatment plants (carbon removal (C); nitrogen removal (N); and phosphorus removal (P))

Treatment plant	Source of wastewater	Biological process	Chemical dosage	SRT[a] (days)
Wacol (A)	Domestic 50%; industrial 50%	C, N, P		35
Oxley Creek (B)	Mainly domestic	C		4
Gibson Island (C)	Mainly domestic	C, N		18
Thorneside (D)	Mainly domestic	C, N, P	Lime and alum	12
Capalaba (E)	Mainly domestic	C, N, P	Alum	15
Caltex (F)	Oil refinery effluent	C		30
Tip (G)	Leachate	C, N (sequencing batch reactor)	$Mg(OH)_2$	20

[a] Solids retention time (SRT) or sludge age.

study, these two parameters were measured at a mixed liquid suspended solids (MLSS) concentration approximately 4 g/l and should, therefore, be comparable with each other. The test was made in triplicate with a standard deviation of 5%.

A simplified centrifugation method was used to measure the water content of the activated sludge cake after centrifugation. When the sludge is centrifuged, the flocs are first quickly settled since the centrifugal acceleration is much higher than the gravitational acceleration. As the centrifugal force is increased, the sludge cake is gradually compressed. The centrifugation removes the bulk water and some free water from the activated sludge tested. A 10 ml volume of sludge with a MLSS approximately 4 g/l was placed in a centrifugal tube. The previously weighed tubes were centrifuged at 1200, 2000 and 3000 rpm for 10 min, which corresponds to 181, 768 and 1132 g, respectively. Subsequently, the supernatant was removed and the tubes were weighed. By subtracting the weight of removed supernatant from the total sludge sample, the water content of the sludge after centrifugation could be calculated. The bound water in this study was expressed as percentage of water content in the centrifuged sludge cake (%, kg water/kg MLSS). The bound water was measured in triplicate with a standard deviation of 6%. According to Smollen [28], the water content measured in the sludge after the centrifugation may include the so-called physically bound water and the chemically bound water. In the present paper, the bound water is defined as the sum of the interstitial water, i.e. water trapped in capillaries and voids between and inside sludge flocs, internal water in bacterial cells and chemically/physically bound in the sludge, and surface water that is adhered or adsorbed onto the wet sludge.

2.3. Floc size distribution

The size distributions of the flocs were determined by a Malvern Mastersizer/E instrument with a 300 mm lens which enables the measurement of particles in the range 0.9–546 μm. This instrument measures the size of particles by means of light scattering. The samples were diluted in filtrated effluent (0.45 μm millipore filter) to avoid multiple scattering. The activated sludge suspension was then continuously recycled through the sample cell of the Malvern with a peristaltic pump to be exposed to a 2 mW He–Ne laser (wavelength 633 nm). Each sample was measured three times with a standard deviation 0.1–4.5%. The scattered light is detected by means of a detector that converts the signal to a size distribution based on volume. The average size of the flocs was given as the mean based on the volume equivalent diameter (D) [4,3].

2.4. Fractal dimension

The structure of the flocs was quantified in terms of fractal dimensions (D_f), The D_f corresponds to the space filling capacity of an object and is thus a measure of the aggregate structure. The D_f was calculated from the raw light scattering data from the Malvern Mastersizer instrument according to the method by Spicer et al. [29]. Guan et al. [30] used this method to calculate the fractal dimensions for activated sludge. This technique is based on a power law relationship between the total scattering intensity of the light from the aggregates and the magnitude of the scattering vector. The scattering intensity at each detector was calculated from the raw scattering data by means of information from the Malvern Mastersizer/E. By plotting the log of the light scattering intensity as a function of the log of the light scattering vector, the linear slope is the D_f. The D_f varies between 1 and 3. The high value of the D_f is related to compact and dense flocs.

2.5. Filament index

The sludge flocs were examined by light microscopy and images were captured on a Nikon Microphot FXA microscope via a charge-coupled device connected to a PC. Filamentous organism content was quantified as filament index using the method by Jenkins et al. [31]. The numbers of filamentous organisms were rated on a scale of 1–5, where 1 corresponds to no filamentous organism presented and 5 corresponds to excessive growth of filamentous organisms, according to Eikelboom and van Bijsen [32].

2.6. Sludge viscosity

The apparent viscosity was determined using a rotational viscosity meter (Model LVDVII, Brookfield, England). Due to the non-Newtonian nature of the sludge flow, the viscosity depends on shear rate gradient under certain pressure and temperature [33,34]. The viscosity, expressed as mPa s, was measured at the shear rate $100\,s^{-1}$ for 5 min to keep the sludge in suspension. The measurements were carried out at MLSS concentration of approximately 4 g/l at 20 °C. The apparent viscosity of the sludge is a reflection of internal and external interaction forces occurring within the sludge flocs and fluids, and describes the deformation of the flocs under the influence of stresses [33,35].

2.7. Physical and chemical parameters

The measurement procedures for sludge floc physical parameters: flocculating ability, relative hydrophobicity and surface charge, and chemical constituents: protein, humic substances, carbohydrate and metallic ions, as well as EPS extraction were given in detail by Wilén et al. [6]. The EPS were extracted from the activated sludge by mixing with a cation exchange resin according to the method by [11]. The flocculating ability of activated sludge was determined as the reflocculation ability of sludge flocs after disruption [36]. The measurement of surface charge of the sludge flocs was performed by colloidal titration [37]. The relative hydrophobicity of the sludge flocs was measured as adherence to hydrocarbons [38]. All analyses were carried out in triplicate. Mixed liquid suspended solids and volatile suspended solids (VSS) were measured according to Standard Methods [27].

2.8. Statistical analysis

The statistical analysis was performed to identify major determining factors. To simplify the analysis, univariate linear correlations were used where the values of bound water and CST were paired with each of the measured sludge floc properties. This analysis provided an initial estimate of the strength of the correlations. All statistical analysis was carried out with the software *Statistica* (Statsoft, Tulsa, OK, USA). Since a normal distribution was not obtained for many of the properties examined, a distribution-free statistical method was used. The Pearson's product momentum correlation coefficient (r_p) was used to estimate linear estimations. The Pearson's r_p coefficient is always between -1 and $+1$, where -1 means a perfect negative correlation and $+1$ a perfect positive correlation while 0 means absence of relationship. Correlations were considered statistically significance at a 95% confidence interval ($P < 0.05$).

3. Results and discussion

3.1. Variation in bound water content with centrifugation rate

Fig. 1 shows that the bound water contents measured by centrifugation at 1200, 2000 and 3000 rpm for 10 min correspond to linear correlations. Furthermore, the water content was linearly correlated with the *g*-value increased in the range 181–1132 g (data not shown).

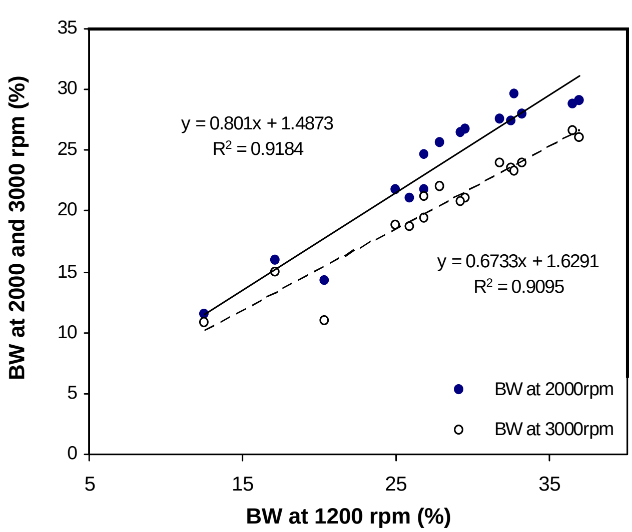

Fig. 1. Variation of bound water (BW) with centrifugation rate.

Clearly, the measured bound water content is dependent on the measurement technique used. The centrifugal settling method was originally utilized for measuring the "packed cell volume" by extrapolating the sludge sediment height at N (centrifugation speed) $\rightarrow$ 8 limit [22]. When a sludge suspension is centrifuged at a high speed, the sludge flocs are compressed towards the bottom of the centrifugal tube and the sludge and the bulk water are separated. Since the sludge flocs are deformed under the influence of a centrifugal force, the sludge gets more compact when the centrifugal force increases. At a certain centrifugation speed, the sludge cannot be compressed any more and it contains only the solid phase and the bound water [21]. The equilibrium sediment height for an activated sludge is found to vary linearly with N^{-1} when rotational speed ranges from 500 to 3500 rpm [22,35]. However, as the rotational speed increases further, the relationship is non-linear and it is thus not accurate to calculate the bound water content from linear regression of the sediment height versus N^{-1} from the intercept as $N \rightarrow \infty$ [21]. It was therefore suggested that the centrifugal method mainly gives information about the compressibility of the filter cake. In the present study it was found that for all sludges investigated, the bound water per unit of dry solids was linearly correlated to the reciprocal of the rotational speed (data not shown). Since the height of the sediment and the amount of water in the sludge are related parameters, the results obtained with the two methods should be interpreted in the same way. Because the centrifugal force at $N \rightarrow$ 8 limit should be infinitely large, and bound water is recognized as the portion of the moisture that is hard to remove via mechanical means, it is proposed that the sediment in equilibrium with infinite rotational speed limit contains only the solid phase and the bound water [22,24]. The capacity of activated sludge to bind water depends upon the chemical, physical and electrical properties of the sludge. Based on this information and some physical interpretations, a classification of the moisture in the sludge can be constructed accordingly. Consider a sludge made of particles, finite void space always exists between these particles in centrifugal settling tests at high rotational speed. The water content (the bound water) within the sludge cake is the sum of interstitial water, surface water and internal water [22,39]. Bound water represents a very small proportion of the total water contained in the sludge. The aim of this study was not to study the centrifugal method as such but it was chosen to find a simple method to be able to compare the water binding capacity of different sludges. Therefore, the measurements of the bound water content at the highest centrifugation rate tested (3000 rpm) was used to define the bound water content. Since the rotational speed was kept at 3000 rpm in which the bound water content vary linearly with *g*-value, the total bound water may include chemically, physically and mechanically bound water as classified by Colin and Gazbar [24]. It has, however, to be stressed that the bound water measured by the centrifugation method may be an inaccurate value, which is higher than what

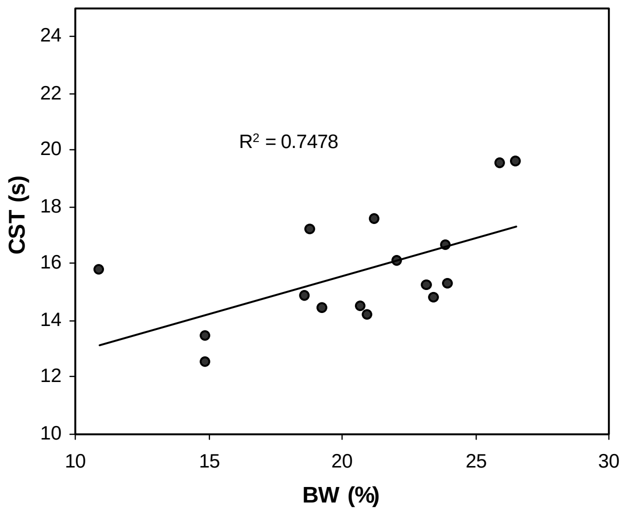

Fig. 2. Relationship between bound water and CST.

would be expected if infinite rotational speed had been used.

3.2. Relationship between bound water and capillary suction time

For all samples studied, the bound water tested at the centrifugation rate 3000 rpm was in the range of 10–27%, and CST was between 12 and 20 s. Fig. 2 illustrates how the CST and bound water were related to each other. A low value of CST corresponded linearly to a low content of bound water ($r_p = 0.7489$, $P = 0.0306$). This finding reveals that the measurements of both CST and bound water correspond to a similar indication in terms of dewaterability of activated sludge. Sludges containing higher amounts of bound water demonstrated a longer CST, indicating poorer dewaterability. It has been widely accepted that short CST is associated with good dewaterability of the sludge [3,28,39,40]. However, the difficulty is that the CST test does not quantify a particular, fundamentally based physical parameter of the sludge. While efforts to correlate the CST measurement with the basic physical properties of the sludge and solid–liquid separation process continue, the CST test has been assigned a specific protocol in the US [27], and there is no assurance that this measurement will either assist in making fundamental advancements in the conceptual understanding of separation processes, or that it will invariably predict the efficiency of a specific dewatering device [33]. Although both bound water and CST have been widely used for determining dewaterability of activated sludge, to date, little attention has been given to determine the relationship between the bound water and CST. Smollen [28] concluded that no correlation was found between the sludge bound water content and CST. On the other hands, even if the water passes through the filter cake quickly, the water content inside small pores and capillaries, as well as water bound inside the floc matrix in the EPS and cells, may remain high. Therefore, the CST may strongly related to the “free” water in the activated sludge, whereas the bound water content may be related to the firmly bound water existing in the sludge flocs.

3.3. Effect of sludge floc properties on dewaterability

The characteristics of the sludge flocs are summarized in Tables 2 and 3, and have previously been described in detail [16]. To facilitate statistical analysis, correlation coefficients were calculated by statistically pairing the values of bound water and CST with each of the measured sludge floc properties. This analysis provided an initial estimate of the strength of the correlations. The results of the statistical analysis calculated by Pearson’s correlation and P-values are summarized in Table 4. The effects of the sludge floc characteristics and properties on the dewaterability are discussed in the following sections.

3.3.1. Floc morphological characteristics

The morphological properties were characterized by floc size, filament index and fractal dimension. The statistical results reveal that these parameters had relatively weak impacts on the bound water and CST (Table 4). In general, sludges with large size of flocs contained high bound water and displayed long CST. With the exception of two sludges (C and G), sludge floc size corresponded to significant correlations with bound water and CST (Fig. 3a). The different sludges had not only different floc size but also different morphology. For instance, flocs with a high number of filaments were also large and had relatively lower values of fractal dimensions (D_f). An increase in quantity of filamentous microorganisms in the sludge tended to increase the bound water content. The impact of the filament index on the CST was statistically insignificant. No recognizable correlation was found between D_f and the bound water, whereas D_f had a weak, but statistically significant correlation with CST (Fig. 3b), indicating that highly compact flocs behaved high dewaterability measured by CST. It was notable that sludges C and G demonstrated somehow different dewaterability evaluated by both bound water and the shortest CST, comparing with other sludges, as indicated in Figs. 3 and 4. The C-sludge contained the highest numbers of filamentous microorganisms (filament index 5), resulting in large floc size and loose floc structure ($D_f = 2.1$) [7]. The G-sludge from leachate treatment plant had an almost granule-like structure, which contained relatively large and very compact flocs with no filaments [7], and demonstrated the lowest bound water and CST. The sludge with high filament index had relatively high water binding ability, leading to high values of bound water and CST. However, the correlation between filament index and CST was insignificant.

Higgins and Novak [40] reported that the “supracolloidal” particles in the range 1–100 μm had the greatest affect on the dewaterability of sludges, and as the concentration of the particle in this size range increased, dewaterability decreased.

Table 2
Summary of floc characteristics of the sludge flocs and physical properties of the activated sludge

Parameter	Unit	Activated sludge sample						
		A	B	C	D	E	F	G
Floc size	μm	122 ± 2	311 ± 2	176 ± 3	122 ± 5	63 ± 3	55 ± 2	124 ± 3
D_f	–	2.16 ± 0.23	1.96 ± 0.06	2.12 ± 0.02	2.15 ± 0.01	2.30 ± 0.04	2.44 ± 0.04	2.09 ± 0
Filament index	–	2	4–5	5	3–4	2–4	1	1
Flocculating ability	%	60 ± 1	55 ± 3	55 ± 1	56 ± 2	37 ± 4	69 ± 1	32 ± 5
Hydrophobicity	%	65 ± 2	68 ± 3	70 ± 2	60 ± 2	60 ± 6	64 ± 6	48 ± 1
Negative surface charge	meq./g MLSS	0.26 ± 0.07	0.54 ± 0.02	0.34 ± 0.06	0.32 ± 0.12	0.30 ± 0.01	0.19 ± 0.03	0.13 ± 0.05
Viscosity	mPa s	4.75 ± 0.13	4.59 ± 0.43	10.5 ± 0.46	5.19 ± 0.38	4.53 ± 0.13	4.96 ± 0.02	3.97 ± 0.12
Bound water (at 3000 rpm)	%	21.4 ± 2.1	22.1 ± 1.2	26.3 ± 0.3	23.7 ± 0.3	19.0 ± 0.2	21.6 ± 0.6	12.8 ± 2.1
CST	s	16.9 ± 0.3	14.7 ± 0.6	19.6 ± 0.0	15.1 ± 0.2	14.7 ± 0.2	16.8 ± 0.7	13.0 ± 0.4
Volatile fraction (VSS/MLSS)	%	80 ± 2	73 ± 5	80 ± 5	79 ± 3	71 ± 2	84 ± 4	59 ± 1

Table 3
Summary of chemical constituents (mg/g MLSS) in the sludge and the extracted EPS of the activated sludge

Parameter	Activated sludge sample						
	A	B	C	D	E	F	G
Polymer							
Protein (sludge)	217 ± 3	353 ± 35	254 ± 7	302 ± 11	224 ± 11	336 ± 7	191 ± 18
Protein (EPS)	45 ± 3.6	56 ± 4.5	41 ± 11	55 ± 2.2	45 ± 6.5	30 ± 4.0	28
Humic substances (sludge)	195 ± 45	191 ± 54	127 ± 3	131 ± 1	111 ± 18	73 ± 3	183 ± 17
Humic substances (EPS)	28 ± 9.0	48 ± 6.8	23 ± 2.8	43 ± 12	33 ± 1.0	17 ± 0.2	51
Carbohydrate (sludge)	83 ± 8.3	64 ± 6.3	89 ± 2.1	93 ± 3.5	61 ± 1.2	64 ± 1.2	55 ± 0.2
Carbohydrate (EPS)	7.8 ± 0.6	11 ± 0.5	7.0 ± 1.9	9.8 ± 0.04	9.2 ± 1.8	5.7 ± 1.1	40
Total extracted (EPS)	81 ± 14	114 ± 12	71 ± 15	108 ± 14	87 ± 9	52 ± 5	119
Cations in sludge							
Al^{3+}	2.9 ± 0.9	5.8 ± 1.9	1.4 ± 0.1	16 ± 0.4	17 ± 2.3	3.2 ± 0.5	2.7 ± 0.1
Fe^{3+}	6.0 ± 1.6	11 ± 0.3	6.5 ± 0.1	3.9 ± 0.1	3.0 ± 0.4	16 ± 0.1	76 ± 1.7
Ca^{2+}	13 ± 1.1	13 ± 1.5	11 ± 0.2	14 ± 0.5	15 ± 1.3	6.2 ± 0.1	7.9 ± 0.5
Mg^{2+}	5.0 ± 0.5	3.8 ± 0.7	4.4 ± 0.7	3.5 ± 0.8	5.9 ± 0.4	2.6 ± 0.3	19 ± 2.7

An opposite relation between bound water and floc size was established by Liao et al. [41] and they stated that bound water contents decreased linearly as floc size increased in the range 20–100 μm. From the correlations observed in this study in association with the measurement principles, it may hypothesize that (1) the bound water and the CST may have different indications with respect to the dewaterability of the sludge flocs, (2) the CST may be strongly influenced by the free water since it constitutes a large portion of the water and can be easily released on the filter paper, (3) the bound water contents may not reflect the dewaterability of the bulk sludge due to the strongly binding characteristics of the bound water and its small portion compared with the free water. The two procedures of measuring the dewaterability may reflect different part of the water existed in the sludge, resulting in the different water binding mechanisms and capacities. The CST appears to reflect the macro-structure of the sludge flocs, whereas the bound water reflects the micro-structure and the chemical and colloidal properties of the flocs. Therefore, a misleading result may come up when the bound water and CST are used to determine the dewaterability of the activated sludge. This problem would call for further investigation to identify the physical interpretations with respect to dewatering ability associated with the measurement methods.

3.3.2. Flocculating ability and surface properties

The flocculating ability measured in this study reflects overall internal and external mechanisms of binding biopolymers and water. It is therefore rather probable that the flocculating ability also reflects the water binding properties of the sludge. The results presented in Table 4 and Fig. 4 indicate that a sludge with high flocculating ability had a high

Table 4
Summary of Pearson's correlation coefficient (r_p) and P-value between floc characteristics and bound water and CST

Parameters	Unit	Bound water (%)		CST (s)	
		r_p	P	r_p	P
Floc size	μm	0.9229**	0.0002	0.8248**	0.0066
D_f	–	0	0	0.6277*	0.0274
Filament index	–	0.7772	0.0192	0.2654	0.1451
Flocculating ability	%	0.7497	0.0352	0.6921*	0.0329
Relative hydrophobicity	%	0.8478	0.0129	0.5253	0.0389
Negative surface charge	meq./g MLSS	0.5607	0.0370	0.5381**	0.0403
Viscosity	mPa s	0.6367	0.01435	0.7560	0.0017
Protein (sludge)	mg/g MLSS	0.6415	0.0372	0.5730*	0.0429
Protein (EPS)	mg/g MLSS	0.5858	0.0434	−0.5616	0.0359
Humic substances (sludge)	mg/g MLSS	0	0	0	0
Humic substances (EPS)	g/g MLSS	0	0	−0.6072	0.0348
Carbohydrate (sludge)	mg/g MLSS	0.7264	0.0038	0.7065*	0.0098
Carbohydrate (EPS)	g/g MLSS	0	0	−0.6018	0.0428
Total extracted (EPS)	mg/g MLSS	0	0	−0.6803	0.0299
Ca + Mg	meq./g MLSS	−0.8612	0.0005	−0.6591*	0.0312
Al + Fe	meq./g MLSS	−0.8445	0.0006	−0.7943	0.0218

* Sludge C excluded.
** Sludge C and G excluded.

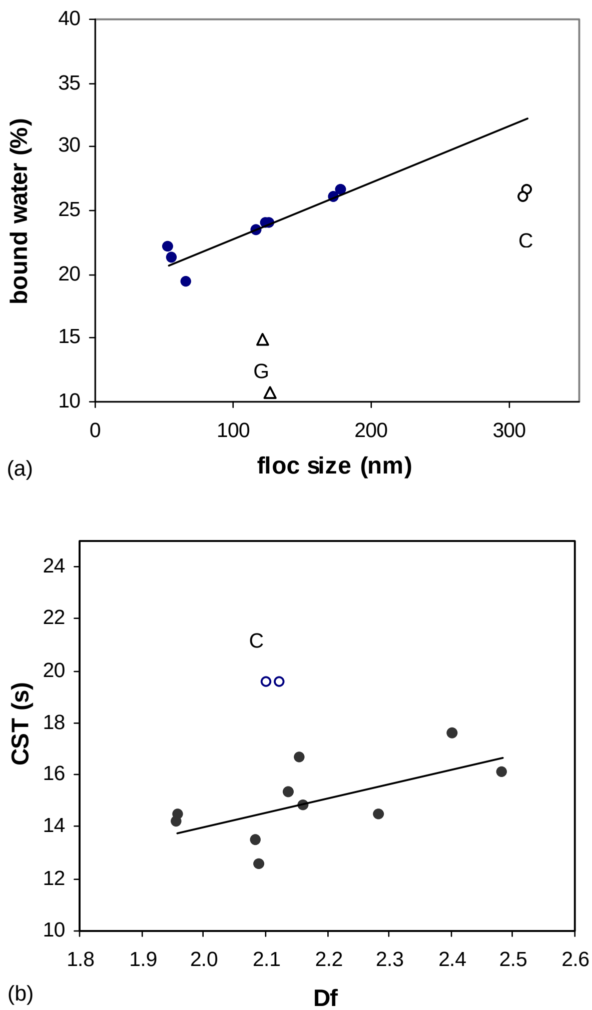

Fig. 3. Correlationship (a) between floc size and bound water and (b) between fractal dimension and CST.

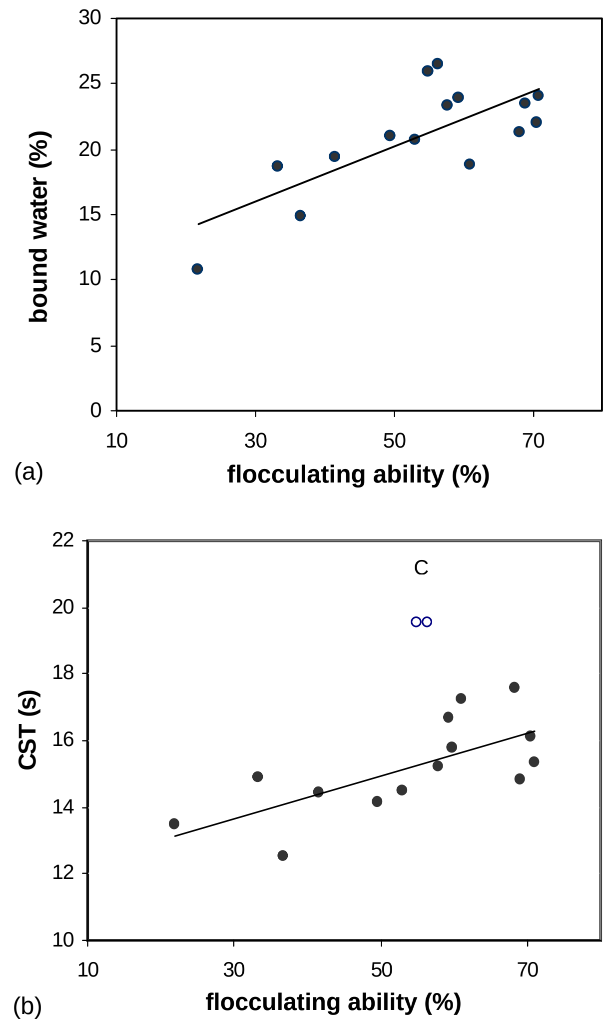

Fig. 4. Effect of flocculation ability on (a) bound water and (b) CST.

capacity to bind water. In other words, high flocculating ability was associated with high values of the bound water and the CST.

From the statistical results shown in Table 4 and Fig. 5, it can be found that the surface properties measured by the relative hydrophobicity and surface charge had significant impacts on the dewaterability. High values of relative hydrophobicity and negative surface charge corresponded to high bound water content and long CST. The correlations associated with bound water were, however, stronger than the CST. This indicates that the physico-chemical properties of the sludge has a more important effect on the binding of the water rather than affecting the resistance to filtration.

Previous studies into the effect of flocculating ability of sludge flocs have shown that strongly flocculated flocs has higher degrees of compressibility of the activated sludge determined as sludge volume index [16]. The results reveal that the flocculation mechanism, or the internal forces generated by the molecular and electrostatic interactions, have a strong impact on binding water within the activated sludge matrix and may be a dominant factor in the dewaterability. It was interesting to find that with increasing values of flocculating ability, hydrophobicity and negative surface charge, both bound water and CST tended to increase. Forster and Dallas-Newton [42] found that the electrophoretic mobility of the sludge was proportional to the bound water content. Liao et al. [41] stated that surface charge determined as electrophoretic mobility had no correlation with bound water, and surface charge may not be a dominating factor that influences bound water content in sludge. The surface charge measured by electrophoretic mobility represents only the surface of single cells and small clumps of cells, or fine flocs, because of the retention of large flocs by filtration effects associated with the method [42]. Colloid titration used in this study, on the other hand, determines the surface charges of all floc particles in the suspension and consequently yields an average value of surface charge. The basis for relating surface charge to bound water and the dewaterability of sludge rests with an interpretation of the DLVO theory. According to the DLVO theory, a decrease in surface charge

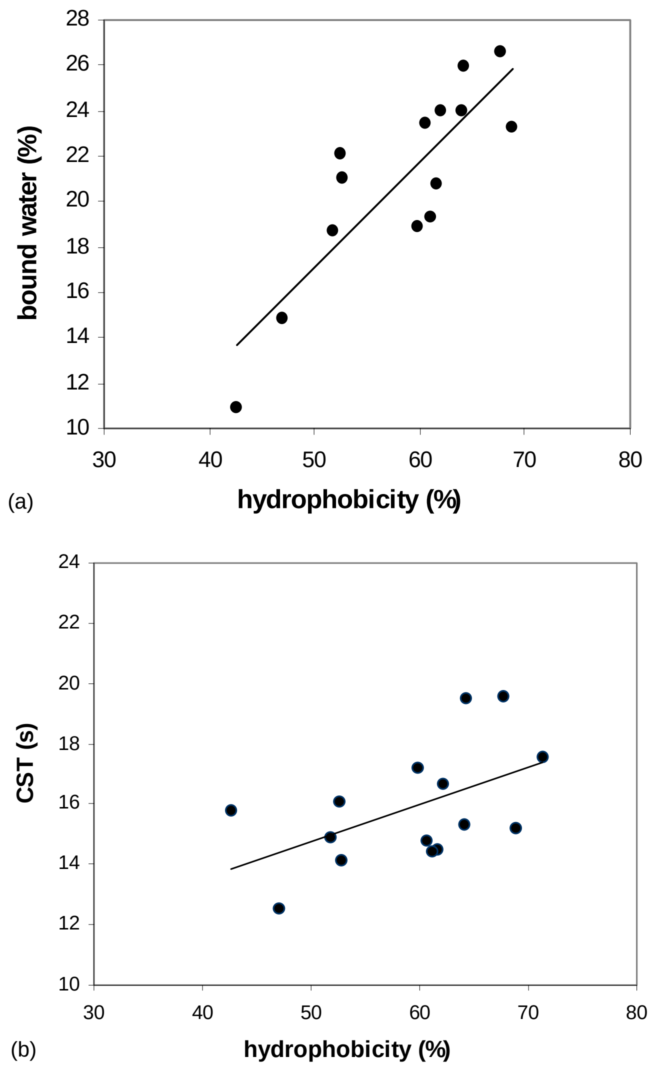

Fig. 5. Effect of hydrophobicity on (a) bound water and (b) CST.

could result in a decrease in repulsive electrostatic interactions and enhance flocculation of fine flocs, thus lowering bound water content and improving dewaterability [41].

3.3.3. Sludge viscosity

The apparent viscosity is a reflection of the magnitude of particle interaction in a suspension [35]. The results shown in Table 4 reveal that the viscosity of the sludge suspension exhibited clear correlations with both bound water content and CST. Both the bound water content and CST increased as the viscosity of the bulk sludge increased from 3.8 to 11.0 mPa s. These results indicate that the sludge viscosity could be a good variable to assess dewaterability. The measurement and assessment of viscosity is simple and could be applied on-line [43].

3.3.4. Chemical constituents

The chemicals in the sludge samples were tested as the polymeric compounds (protein, carbohydrates and humic substances), and the metallic ions (Ca^{2+}, Mg^{2+}, Fe^{3+} and Al^{3+}). In this study, the polymeric compounds were classified in terms of total polymers measured in the sludge and the extracted EPS (Table 3). As summarized in Table 4, the polymeric compounds protein and carbohydrate in the sludge had significant contribution to water binding capability determined by both bound water and CST, whereas no correlation between the amount of humic substances and CST or bound water was observed. It was interesting to note, however, concentrations of the individual polymers and total EPS measured in the extracted EPS had negative correlations with CST, and the amount of protein measured in the total sludge and the extracted EPS corresponded oppositely to the CST (Fig. 6), relating to different water binding aspects. The bound water content had a significant positive correlation with amount of protein measured in the extracted EPS. No recognizable correlations were found between the bound water and the amount of humic substances, carbohydrate and total EPS measured in the extracted EPS. These results indicate that high amount of the total extracted EPS was associated with low CST.

In previous study [22] it was found that sludges containing high concentrations of EPS demonstrated high resistance to break up when they were exposed to shear. Furthermore, this was associated with a better filterability. During filtration, the sludge flocs are exposed to high shear and small primary particles may be released to the bulk water and these may increase the resistance to filtration by clogging the filter cake [10]. The observations made in this study support the findings by Mikkelsen and Keiding [22] in that the CST decreased as the amount of total extractable EPS increased. This was particularly evident for the protein fraction of the EPS. It has been observed that the protein fraction in the EPS and in the sludge is particularly important for the flocculation ability of the sludge [6]. The opposite correlations for the polymer fractions in sludge and extracted EPS indicate that the easily extractable EPS has a different function in the sludge and its presence in the sludge is beneficial for the filterability. For the water binding ability of the sludge, the EPS appear to have a positive effect. This is probably due to the gel-like structure of the polymers and their high concentration of charged sites [6,38] attract counterions. This leads to swelling, or uptake of water, by the polymers to reduce the osmotic pressure [12,44]. This finding may further reveal that the extractable EPS demonstrated a relatively weak capacity to bind not only the floc constituents but also the water in the bulk sludge system. The CST can be significantly related to the easily extracted EPS, consequently to the weakly bound "free" water in the bulk activated sludge. It can be hypothesized that the extractable part of the polymers in the activated sludge may have an important impact on the dewaterability of activated sludge.

Although a part of the water in the sludge is intracellular, and thus trapped by the cell walls, most of the water is bound by EPS. It is well known that the EPS form a matrix in which the microorganisms are immobilized by keeping

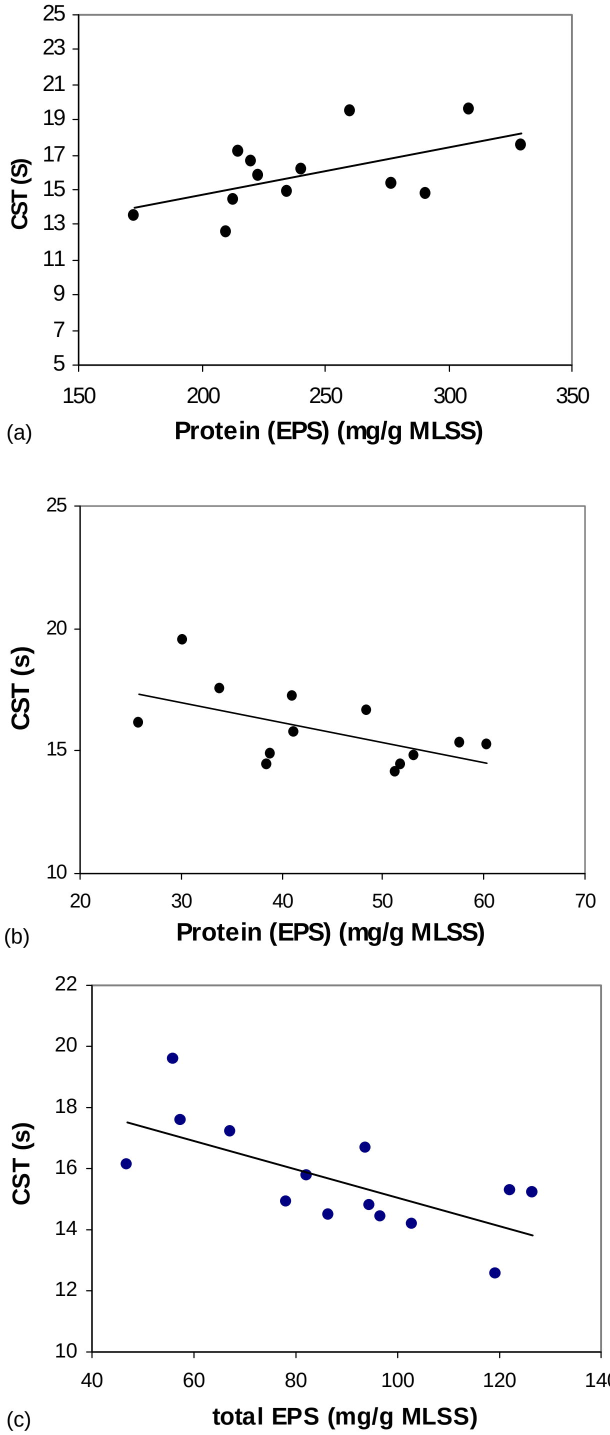

Fig. 6. Variation in CST with polymer concentration of (a) protein in sludge (b) protein in the extracted EPS and (c) total amount of extracted EPS.

them in their three-dimensional arrangement, allowing the formation of stable microconsortia [12,39]. The components in the EPS influence the water binding properties, and thus also influence the dewaterability of the sludge. The water is bound by a few mechanisms in the sludge, such as hydrophilic interactions and hydrogen bond forces. It has been proved that the water bonds are considered as the contribution of other molecules with hydrogen-bond, such as –OH and –NH bonds. Important molecules in this respect are the proteins and polysaccharides in the activated sludge [45]. The current study show that: (1) the biopolymers, such as protein and carbohydrate, in the sludge contribute to the water binding capability of the sludge floc matrix; (2) the polymeric substances may contribute to two different water binding aspects for bound water and "free" bulk water; and (3) the CST was significantly related to the "free" bulk water which is bound by the weakly bound and mechanically extracted polymeric substances, while bound water was strongly influenced by the relatively firmly bound polymers. Work related to the chemical nature of the sludge polymers is not widely reported in the literature. Liao et al. [44] reported that the total amount of EPS was positively correlated to the bound water content of sludge from bench-scale studies, but the correlation between total EPS and bound water content of sludge from full-scale systems was inconclusive. Kang et al. [14] investigated the effects of the extracellular polymer content in sludge on the dewatering characteristics

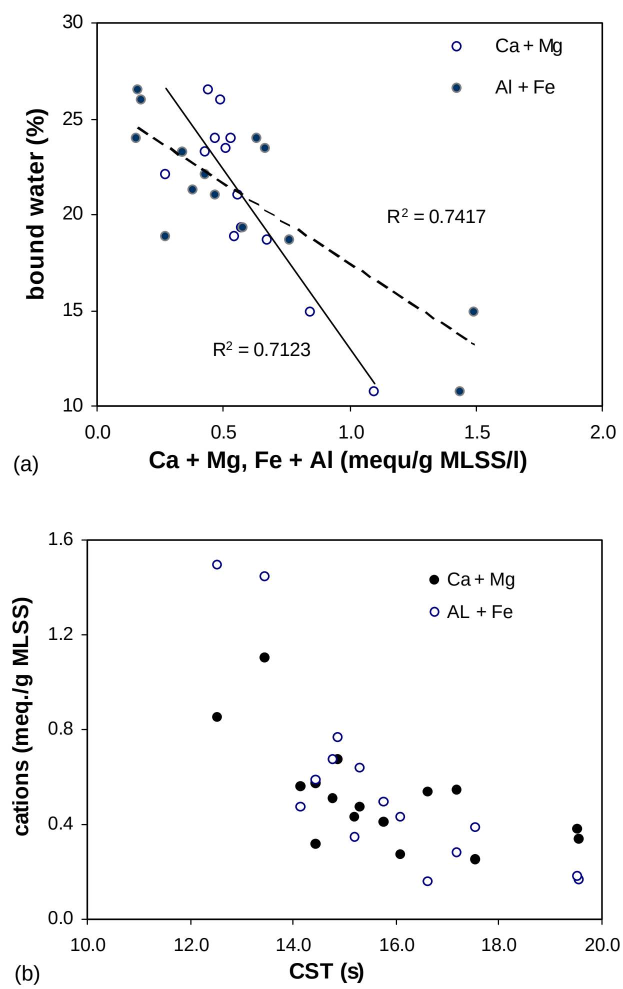

Fig. 7. Variation in (a) bound water and (b) CST with concentration of metallic ions in the sludge.

by addition of the extracted EPS, and found that the EPS had a negative effect on the dewatering process.

It was expected that increased concentrations of the divalent and trivalent metallic ions Ca^{2+}, Mg^{2+}, Al^{3+} and Fe^{3+} in the activated sludge would improve dewaterability since theses cations contribute to the floc formation by binding polymeric chains in the flocs together and by decreasing the net negative floc surface charge [6,40,46]. The statistical results in Table 4 indicate that the bound water content and CST were significantly influenced by the concentration of the divalent and trivalent cations. High concentration of these multivalent cations was related to low values of bound water contents and CST (Fig. 7). Improvement of dewaterability by addition of multivalent cations has been demonstrated by many previous researchers [1,24,26,46], and is a common practice in the activated sludge process.

4. Conclusions

This study examined how morphological, physical and chemical properties of sludge flocs influence the dewaterability of activated sludge. The bound water content after centrifugation and the capillary suction time have been used to describe the sludge dewaterability. A variety of full-scale activated sludges was studied. The main conclusions are:

- Both bound water and CST corresponded to a similar indication with respect to dewaterability. Therefore, they may be interchangeable parameters for describing sludge dewatering properties under certain conditions. However, the bound water content and CST reflect somewhat different water binding properties of the activated sludge. The CST reflects more the weekly bound water in the sludge flocs, and/or “free” bulk water in activated sludge. The bound water was significantly affected by the physical and chemical properties of the sludge flocs.
- The floc physical properties flocculating ability, hydrophobicity, surface charge and sludge viscosity, were important factors which significantly affect the water binding ability of the sludge flocs. High values of flocculating ability, hydrophobicity, negative surface charge and viscosity corresponded to high bound water content and long CST, indicating poor dewaterability.
- The morphological characteristics determined by sludge floc size, fractal dimension and filament index had statistically weak correlations with the values of bound water and CST. Sludge containing compact and large flocs containing high numbers of filaments had high capacity for water binding.
- The polymeric components protein and carbohydrate contributed significantly to the water binding ability of the sludge flocs, whereas no effect of humic substances was observed. The CST had good statistical correlations with the polymeric constituents measured in both sludge and the extracted EPS, and the bound water was only correlated well with the individual polymers measured in the sludge. High amount of the individual and total polymers in the extracted EPS corresponded to a good dewaterability determined by the CST. High concentration of Ca^{2+}, Mg^{2+}, Fe^{3+} and Al^{3+} in the sludge contributed a significant improvement for sludge dewaterability.

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