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Determination of the effect of cations and cationic polyelectrolytes on the characteristics and final properties of synthetic and activated sludge

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Abstract

This study has investigated in a comparative fashion the effect of cations and polyelectrolytes on the characteristics and final properties of both synthetic and activated sludge. Synthetic sludge was prepared according to established procedures; activated sludge was produced in a lab-scale, continuous-flow reactor which was fed with live activated sludge from a wastewater treatment plant. The results from experiments indicate that cations and polyelectrolytes could influence sludge floc characteristics as they relate to sludge conditioning. The relationship between polysaccharide concentration and cation concentration was examined at laboratory scale during flocculation with both synthetic and activated sludge; an increase in feed cation concentration led to a decrease in final polysaccharide concentration. An increase in cation concentration in the feed to the reactors was also associated with an increase in the bound biopolymer concentration. The changes in the bound biopolymer were explained according to the cation bridging model. The effects of a polyelectrolyte conditioner on sludge conditioning were determined. A qualitative link exists between polyelectrolyte conditioner dosage and sludge conditioning for both types of sludge. The two types of sludge also have very similar sludge conditioning after cationic polymer is added to the reactor. Thus synthetic and activated sludge behave very similarly in terms of their characteristics and sludge conditioning, and synthetic sludge can be used as a surrogate in activated sludge studies. The results of this work also indicate that the formation of cation-polymer complexes and polymer gelation are amongst the most important mechanisms for sludge coagulation–flocculation, and offer a means for optimisation of the activated sludge process.

Keywords: Activated sludge; Synthetic sludge; Calcium ions; Polysaccharide; Polyelectrolyte

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1. Introduction

Activated sludge is a heterogeneous mixture of particles, micro-organisms, colloids, organic polymers and cations, whose composition depends on the origin of the sample and the date of sampling [1]. It is a flexible, reliable process, capable of producing a high quality effluent. Soluble organic matter is reduced to low levels, and a clear effluent low in suspended solids is produced, due to the flocculant nature of the biomass [2]. The flocculated microbial aggregates, known as flocs, are the essential components of the system. Flocs typically vary in size from 10 to 1000 μm [3].

In general, the concept of the structure of activated sludge comprises three levels: bacteria, micro-colonies and flocs [4,5]. The first level of structure is made up of bacteria tightly bound together by a polymeric matrix to form the second level of structure called micro-colonies. The extracellular polymers arise from two origins, either from metabolism and cell lysis of micro-organisms or from incoming wastewater [6]. These extracellular polymers or extracellular polymeric substances (EPS) are typically made up of proteins, polysaccharides, humic compounds, nucleic acids, and lipids. Polymers and cations further link the micro-colonies to produce the third and final level: activated sludge flocs.

The flocculation of activated sludge is an active process, and depends on physical, chemical and biological factors. The basis of activated sludge floc formation lies in the ability of micro-organisms to stick to each other and to non-biological particles. Microbial adhesion mechanisms have been studied widely, but are still not understood. It appears that exocellular biopolymers form the bridges between micro-organisms; these biopolymers typically contribute 15 to 20% by weight of mixed liquor suspended solid (MLSS) [6]. At the approximately neutral pH values typical of activated sludge, these polymers carry net negative charges. It is thought that divalent cations such as Ca^{2+} and Mg^{2+} interact with negatively charged polymers to form bridges that allow the cells to adhere to each other. Many major operating problems in the process, such as those which occur in solid–liquid separation, can also be attributed to the properties of the flocs.

1.1. Bioflocculation

Biosolid–liquid separation by gravity settling in a clarifier is one of the most critical operations in the activated sludge process. Bioflocculation of activated sludge determines how the sludge will dewater, flow, and settle, all of which are obvious concerns in the operation of wastewater treatment plants. The identification and eventual control of bioflocculation mechanisms is therefore of major interest [7]. The formation of stable biological flocs is essential for the successful operation of the process. In many cases, the efficiency of the clarifier is the limiting factor in producing a high quality effluent, and it is often regarded as the bottleneck of the process in terms of upgrading or increasing the capacity of the treatment plant. The settling properties of sludge are determined primarily by the conditions prevalent in the aeration basin. The most notably adverse effect of poor or no flocculation is inefficient settling in the clarifier, resulting in a turbid effluent. Poorly flocculated sludge can also have an adverse effect on sludge dewatering. The thickened sludge that is produced as waste from the process is often dewatered to reduce the sludge handling costs. Sludge dewatering characteristics are influenced by biologically induced flocculation, and a well flocculating sludge will dewater easily.

1.2. The role of cations

Ions such as calcium and magnesium are commonly found in natural water systems, while iron and aluminium may be prevalent if these are used as conditioners. These metals, common to water and wastewater systems, are believed to exist predominantly in complexes with the extracellular polymeric materials. Even though calcium and magnesium ions have similar properties, findings indicate that their respective interactions with polymers are not similar. The addition of magnesium ions to sludge had been found to have no effect on the bound water content, whereas the addition of calcium ions was observed to reduce the bound water remarkably [8]. A column of precipitated polymer was packed with sand, and solutions containing calcium and magnesium ions were passed through it. The results showed that there was a remarkable removal of calcium ions by the column; however, magnesium ions were not removed [8]. Results like this clearly indicate that calcium ions are more preferentially bound to sludge polymers than magnesium ions. The findings of a more recent study have also demonstrated the deflocculation of activated sludge when the calcium ions are extracted from sludge flocs by several different methods [9]. This causes the sludge turbidity to increase, and filterability to decrease. The same research [9] proposes that sludge polymers could be alginate, or another polymer with properties very close to those of alginates. In later work, synthetic sludge flocs were formed from stable particles by adding calcium ions and alginate [10], further suggesting that one of the mechanisms of bioflocculation could be the interaction of alginate and calcium ions.

Cations have been shown to have a significant effect on the bulk properties of activated sludge. Novak and co-workers [11–13] have shown that, for both lab-scale and full-scale wastewater treatment systems, sludge settling and dewatering properties could be improved by the addition of cations to the influent wastewater. In each case, settling properties were improved with the addition of calcium or magnesium. Batch addition of cations to activated sludge also showed improvements in the sludge settling characteristic [11]. Multivalents such as aluminium (Al) and iron (Fe) salts are widely used in wastewater treatment plants (WWTP) as coagulating and phosphorous-removing agents. However, little is known regarding their influent source, the nature of the relevant chemical species in the influent wastewater or wastewater biomass, and their impact on bioflocculation, especially for Al. Although the role of Al and Fe in the floc structure has not been extensively studied, these multivalents are often found at high concentration in activated sludge.

1.3. Synthetic sludges

The living micro-organism consortium in activated sludge is complicated and unstable. It changes the sludge characteristics continuously, making it practically impossible to carry out controlled experiments during sludge studies. Sanin and Vesilind [14] developed a novel chemical surrogate for activated sludge, which they named synthetic sludge, to study sludge dewatering, settling and conditioning characteristics. Synthetic sludge is made up of non-living particles that resemble activated sludge components. The components of synthetic sludge include: polystyrene latex particles of bacterial size, which simulate individual bacteria; alginate simulates extracellular polymeric substances; and calcium ions are used as bridging cations. The results obtained by Sanin and Vesilind [14] have shown that it is possible to create a chemical sludge having close resemblance to biological sludge by using bacteria-like particles, polysaccharides, and cations common to activated sludge at quantities typical of those in activated sludge. In this work, preliminary tests show that synthetic sludge and activated sludge behave very similarly in terms of their filterabilities and their responses to a cationic conditioner. This stable, chemically well-defined and less complex system can thus be used as an analogue for real sludge during physical, chemical (and non-biological) tests.

The overall objective of this research is thus to investigate the relationship between the cation and polysaccharide content and their important role in floc formation and floc structure. Another objective is to evaluate the effect of cationic polyelectrolyte conditioner on the characteristics of both synthetic sludge and activated sludge, and its' relationship to final floc properties. In this fashion, we can establish the validity of using synthetic sludge as a physical and chemical analogue to the real, activated sludge.

2. Materials and methods

2.1. Bacteria simulating particles

The concentrated sulphate polystyrene latex particle solution was 5% by weight with a 0.5 μm mean particle diameter to simulate individual bacteria. The coefficient of variation of particle diameters was usually less than 5%. The procedure of preparing the sulphate latex particles followed previous guidelines [15]. About 20% of the surface area of particles is covered with sulphate groups, to give them the necessary stability and negative surface charge. The zeta potential was measured as −14 mV. The stock solution was diluted to 0.1%, to match the design particle concentration to that of bacteria in activated sludge.

2.2. Preparation of synthetic sludge

The creation of synthetic sludge follows the previously established procedure established by Sanin and Vesilind [16]. Sulphate polystyrene latex particles were suspended in deionised water. Samples of 500 mL with a pre-selected 0.1% particle concentration and an added alginate concentration of 100 mg/L were rotated horizontally in an incubator at 12 rpm and 25°C for 12 h. Alginate was adsorbed on the particles during the incubation period. When the incubation period was completed, Ca (II) was added to samples in varying concentrations to monitor flocculation dynamics.

2.3. Activated sludge

Four semi-continuous flow and two batch mode 6-L, bench-scale reactors were set up at the Environmental Engineering Laboratory, Virginia Tech, USA. The reactors were used to simulate the activated sludge process. The reactor configuration is shown in Fig. 1. The reactor consisted of a complete mixing zone and a settling zone, separated by a slanted baffle. An aeration stone provide air and mixing to the system.

The reactors were seeded with mixed liquor from the Blacksburg, Virginia, municipal wastewater treatment plant. After collection, the samples were returned to the laboratory (within 1 h) and stored at 4°C. Bactopeptone, a microbiological enzymatic digest of protein for use in culture media, was chosen as the food source for seeding to the reactor at a concentration of 500 mg/L. The concentration of several cations and nutrients in the bactopeptone seed are given in Table 1. The influent pH was consistently near 7 for all seed conditions. The hydraulic retention time (HRT) was 0.5 days, and the sludge age was maintained at 10 days.

2.4. Polysaccharide

Alginate (low viscosity, sodium form) from brown algae was supplied by Sigma Chemical Company. Polysaccharide in the supernatant was measured using the method of Dubois [17].

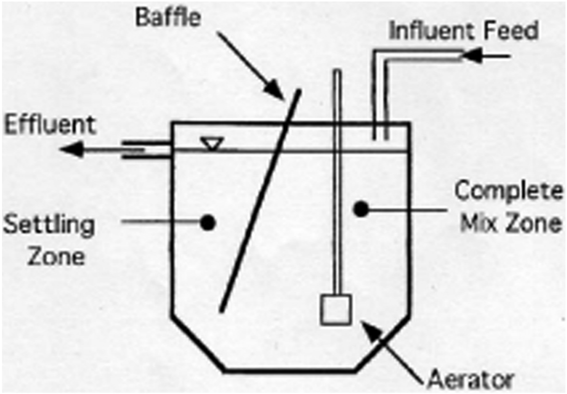

Fig. 1. Profile of laboratory scale activated sludge reactor.

Table 1
Cation and nutrient concentrations in bactopeptone seed used in laboratory activated sludge reactor

Constituent	mg/L	mM/L
Na^+	20.9	0.9
NH_4^+	0.5	0.03
K^+	2.1	0.05
Mg^{2+}	3.8	0.16
Ca^{2+}	10.0	0.25
PO_4^{3-}	2.3	0.024
NO_3^-	15.9	0.26
TKN	46.5	–
COD	500	–
Fe^{3+}	2.4	0.043
Al^{3+}	0.25	0.010

2.5. Settling and dewatering properties

Total suspended solids (TSS) were analyzed using method 2540D in Standard Methods (1998). The settling properties of biological suspensions were characterized by the sludge volume index (SVI), as described by method 2710D in Standard Methods (1998). The dewatering characteristics of biological suspensions were determined by capillary suction time (CST), using method 2710G in Standard Methods (1998) [18].

2.6. Conditioning

Cationic polyelectrolytes obtained from Clarifloc and Stockhausen were used for the conditioning of thickened sludges from the reactors. Polymer of 1 wt % in water stock solution was made to the final design concentration, by diluting the concentrated polymer with distilled water. During conditioning and dewatering, the polymer was added to a 100-mL sludge sample and mixed for 30 s in a beaker. The mixing speed was 250 rpm ($200\,s^{-1}$). After mixing, the CST was measured and the optimum dosage was considered as the dose which resulted in the minimum CST.

3. Results and discussion

3.1. Relationship between cations and polysaccharide on the flocculation behaviour of synthetic sludge

Two separate experiments were conducted to investigate the effect of calcium concentration alone and combined calcium together with aluminium ions on the flocculation behaviour of synthetic sludge, respectively. Calcium and aluminium in the form of $CaCl_2 \cdot 2H_2O$ and $AlCl_3 \cdot 6H_2O$ were dissolved in distilled water. The appropriate volume of concentrated salt solution was added to the samples to match the design calcium concentration for each experiment.

Standard synthetic sludges (0.05% latex particles, pH 7.5, 100 mg/L alginate) were prepared in 500 mL samples, and the calcium concentration of the samples was varied between 0 and 20 mM Ca(II) with fast (F) feeding for 10 min. There was no significant change in the pH of the sample after calcium addition. The results showed that no floc formation occurred without adding calcium ions. The experimental results provide valuable information about the flocculation behaviour of synthetic sludge. The normalized mass of polysaccharide in the supernatant is plotted as a function of the calcium ion concentration in the feed of the laboratory synthetic sludge system without and with low concentrations of iron and aluminium ions, as shown in Figs. 2 and 3.

The result from experiments by Nguyen et al. [19] stated that the rate of the flocculation increases initially with the addition of calcium concentration and then approaches a steady-state rate at the higher concentrations. This suggests that at a higher calcium concentration, saturation of the floc has occurred, and the rate of flocculation is independent of calcium concentration. It was also apparent that for the higher calcium concentrations, the rate of aggregation was faster. The concentration of calcium ions in the solution after flocculation was generally less than the initial feed concentration for each experiment.

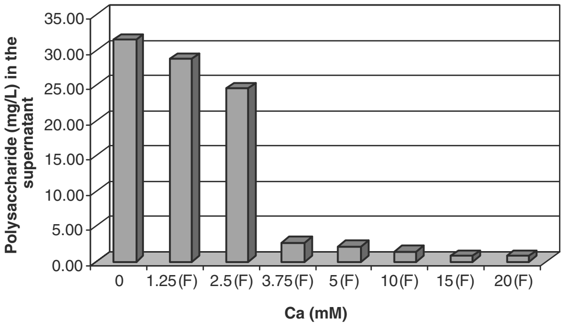

Fig. 2. Relationship between calcium ions fed and polysaccharide concentration in the supernatant of synthetic sludge.

This indicates that an uptake of calcium ions was occurring during the flocculation process, which confirms that calcium ions are used as a medium in the formation of synthetic activated sludge.

The relationship between calcium ions fed and polysaccharide concentration in the supernatant is shown in Fig. 2. It can be seen that, at lower concentrations of calcium added to the samples, the concentration of polysaccharide in the supernatant is higher. On the other hand, when a higher concentration of calcium is added, the concentration of polysaccharide in the supernatant is lower.

This result is in agreement with the work of Higgins and Novak [20]. They found that there was a relationship between exocellular biopolymer concentration and fed cation concentration when using laboratory scale activated sludge reactors with bactopeptone as a feed. An increase in the divalent cation concentration in the feed to the reactors was associated with a decrease in exocellular biopolymer concentration in the supernatant.

The relationship between calcium, aluminium ions and polysaccharide concentration in the supernatant is shown in Fig. 3. The conditions for these experiments were similar to the above experiments with calcium ions, except for the addition of a low concentration of aluminium ions to the sample to see whether the trivalent ions could effect the flocculation behaviour. Aluminium was added to the samples with a low concentration of 0.25 mg/L. From Fig. 3, it can be seen from comparison with Fig. 2 that, without calcium added to the sample, a small amount of polysaccharide was nevertheless adsorbed by flocculation. This implies that trivalent ions also play an important role in the floc formation. From Figs. 2 and 3, it can be seen in each case that the rate of aggregation depends on the cations existing in the samples. The combination of both divalent and trivalent ions could increase the rate of aggregation, resulting in the lower concentration of polysaccharide in the supernatant.

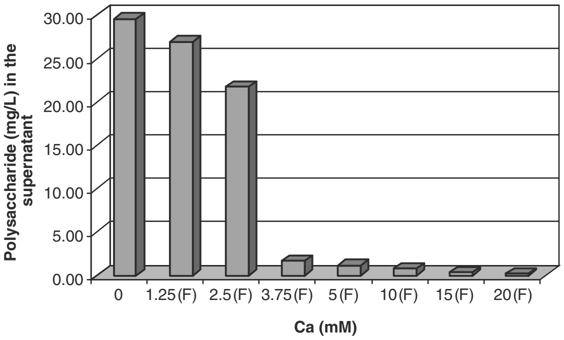

Fig. 3. Relationship between calcium, aluminium ions and polysaccharide concentration in the supernatant of synthetic sludge.

3.2. Relationship between cations and polysaccharide on the flocculation behaviour of activated sludge

Two separate sets of 6, 6-L reactor experiments were conducted to investigate the effect of cations on the flocculation behaviour of activated sludge. Each set experiment consisted of 6 reactors, of which the first 4 reactors were slow (S) for 5 h to simulate semi-continuous mode and the last 2 reactors were fast (F) feeding for 10 min to simulate a batch-mode reactor. Calcium and Aluminium in the form of $CaCl_2 \cdot 2H_2O$ and $AlCl_3 \cdot 6H_2O$ were dissolved in distilled water.

The appropriate volume of concentrated salt solution was added to the samples to match the design calcium concentration for each experiment. Laboratory reactors were operated until steady-state conditions were obtained. The feed to the reactor contained bactopeptone plus additional monovalent, divalent, and trivalent ions.

In the first set of experiments, the concentration of calcium ions was increased in both slow (S) and fast (F) feeding. The aluminium ions were fed to each reactor with a low concentration of 0.25 mg/L. The conditions applied for the second set of experiments were similar to the first one, except for changes in concentration of aluminium in the feeding regime: the concentration of aluminium was fed at the higher concentration of 0.5 mg/L. The normalized mass of polysaccharide in the supernatant is plotted as a function of calcium ion concentration in the feed of the laboratory activated sludge system with low and high concentrations of aluminium ions, as shown in Figs. 4 and 5.

The relationship between fed calcium ion concentration and polysaccharide concentration in the supernatant with low fed concentration of aluminium ions is shown in Fig. 4. From Fig. 4, it can be seen that, at the lower concentration of calcium added to the reactors, the concentration of polysaccharide in the supernatant is higher. On the other hand, a higher concentration of calcium added led to a lower concentration of polysaccharide in the supernatant. One interesting result from these experiments shows that for the same concentration of calcium (0.25 and 2.5 mM) added to the reactor but under a different feeding regime, the polysaccharide concentration in the supernatant was different. The polysaccharide concentration in the supernatant of the activated sludge with semi-continuous (S) feeding was higher when compared to the batch (F) mode with the same concentration of feeding. As seen in Fig. 4, it is suggested that the increase in calcium ions results in an increase in bound polysaccharide concentration. The interactions among micro-organism, polysaccharide, and cations are thus important for flocculation and depend on the feeding regimes.

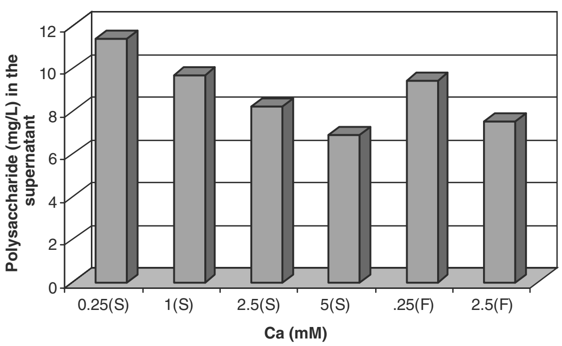

Fig. 4. Relationship between calcium ions and polysaccharide concentration in the supernatant of activated sludge.

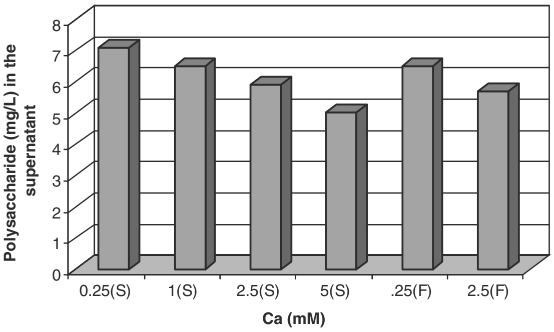

Fig. 5. Relationship between calcium, aluminium ions and polysaccharide concentration in the supernatant of activated sludge.

This finding could be explained by the work of Higgins and Novak [11,12]. Their work concluded that when cations were present in slow feeding, they could become incorporated within the microbe-biopolymer network into flocs as they form, resulting in a denser floc that is more resistant to shear. In contrast, during fast feeding, the cations may not become completely enmeshed in the biopolymer network; binding of cations would thus be decreased. This was supported by the lack of change in the floc density during batch tests, while floc density increased over time when cations were present in the semi-continuous test. Cations would thus have had more chance to bridge with polysaccharide in the supernatant during fast feed. As a result, polysaccharide in the supernatant during fast feed, batch mode had a lower concentration when compared to the semi-continuous slow feed mode, with the same concentration of cations fed to the reactors in each case.

It has been speculated that Al may have a better flocculating capability for activated sludge. Keiding and Nielsen [21] predicted that when sludge is deficient of Al, many organic compounds would remain unflocculated and washed out of the system. Since the conditions applied for the second set of experiments involved a higher concentration of aluminium at 0.5 mg/L, this can be clearly seen by comparing Fig. 4 with Fig. 5. The polysaccharide in the supernatant decreased as Al concentration increased in the biomass. Al has a positive effect on the flocculating capability of activated sludge. A similar trend to the previous one was found for the dependence of the flocculation behaviour of activated sludge on the feeding regime. This finding seems to agree with the view of Park et al. [22], which indicated that Al was an excellent collector of negatively charged organic matter, because as floc Al increased, biopolymer in solution decreased. Although Al in this form is known to function as an effective coagulant, it is not clear how Al in activated sludge flocs coagulates biopolymer during the flocculation process. Clearly, this area is worthy of further study.

3.3. Sludge conditioning

A conditioning was performed using thickened sludge samples, with 1 g/L of total suspended solid (TSS), for both synthetic and activated sludge. The sludge conditioning as a function of cationic polyelectrolyte addition is shown in Figs. 6 and 7. The value of capillary suction time decreased as a function of added cationic polyelectrolyte until the optimal cationic polyelectrolyte dosage was reached. Any further increase beyond the optimal dosage caused deterioration in dewaterability. The samples with higher added calcium concentration showed greater improvement during sludge conditioning and a lower optimal dose of polymer added, as seen in Figs. 6 and 7.

The result from Nguyen et al.'s work [19] also showed that the addition of calcium improves

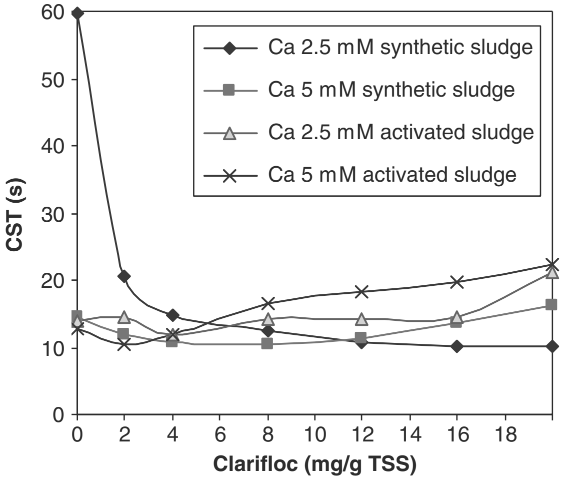

Fig. 6. Effect of clarifloc polymer on sludge conditioning of synthetic and activated sludge.

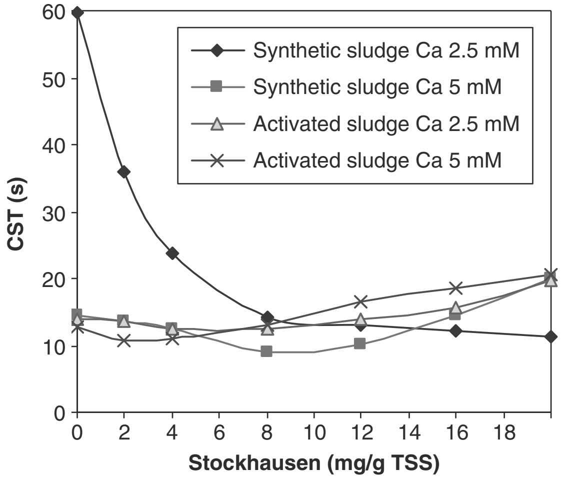

Fig. 7. Effect of Stockhausen polymer on sludge conditioning of synthetic and activated sludge.

the sludge conditioning of both synthetic and activated sludge. However, the sludge conditioning of activated sludge showed a greater improvement than that of synthetic sludge. Although the solid content was similar in both types of sludges, the variability associated with the sludge, such as viscosity and the surplus polyelectrolyte present in the sludge, could affect the CST values. The polyelectrolyte will increase the liquor viscosity and so increase the rate of absorption by the filter paper. Nevertheless, the Ca (II) ion strongly enhances the conditioning of industrial wastewater sludge, especially biological sludge. The good conditioning when calcium ion is added to the system could possibly result from the interaction of polysaccharide from the biological sludge with calcium ion [23].

The observation made in this study supports the finding by Mikkelsen and Keiding [24] that the CST decreased as the amount of polysaccharide in the supernatant decreased. This was particularly evident from the polysaccharide fraction of the biopolymer. It has been observed that the polysaccharide fraction in the biopolymer and in sludge is particularly important for the flocculation ability of the sludge [25]. Jin et al. [26] reported that the CST had good statistical correlations with the polymeric constituent measured in both the sludge and the extracted biopolymer. High amounts of the individual and total polymers measured in the extracted biopolymer corresponded to a good dewaterability determined by the CST.

The overdosing phenomenon associated with sludge conditioning chemical leads to increases in CST at high polymer dosages. Overdosing in dilute suspensions is attributed to a reduced ability to aggregate the colloidal solids, associated with saturation of the colloidal surfaces with polymer. Saturation of the colloidal surface with polymer is usually accompanied by a reversal of the surface charge. The optimal polymer dosage is commonly associated with partial coverage of the colloidal surface, accompanied by a minimum surface charge [27,28]. These results seem to support Eriksson et al.'s work [29,30]. They stated that polyelectrolyte is mainly consumed in the neutralization of biopolymers and the flocculation of colloids, and to a lesser extent in rebuilding floc fragments and improving existing flocs, which is especially evident with high degrees of stirring. This, however, depends strongly on sludge characteristics. The addition of calcium can also decrease polymer demand for the conditioning. Therefore, the soluble calcium content in synthetic activated sludge should be included in evaluations where flocculation, settling, and dewatering problems are evident.

4. Conclusions

- The strong relationship between cations and polysaccharides for both synthetic and activated sludge has been explored through the measurement of the concentration of polysaccharide in the supernatant with the changes of cation concentration fed to the reactor. The presence of cations decreases the polysaccharide concentration in the supernatant. An increase in cation concentration was also associated with an increase in the bound biopolymer concentration.
- The cations and polysaccharides play an important role in the formation of both synthetic and activated sludge. Calcium ions contribute to the floc formation by constructing calcium ion bridges between polysaccharides or biopolymer gel adsorbed on individual particles/bacteria; aluminium ions also seem to assist in floc binding and the flocculation of other organic material. The cations contribute significantly to the binding of the sludge flocs in both synthetic and activated sludge; this binding appears stronger for a 'slowly fed' sludge.
- The effects of calcium and cationic polyelectrolytes on the resulting final properties of sludge, such as sludge conditioning, have also been measured and characterized for both synthetic

and activated sludge. An optimum concentration exists for polyelectrolyte conditioner; higher concentrations of Ca^{2+} in the sludge contributed to a significant improvement in sludge dewaterability and lowered the optimum conditioner concentration.

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