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A comparative study of the flocculation behaviour and final properties of synthetic and activated sludge in wastewater treatment

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Abstract

In this study, we have investigated in a comparative fashion the flocculation behaviour 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 novelty of our approach lies in the attempt to use the former as a key to characterising the physical and chemical properties of the latter. The effects of calcium ion concentration on flocculation dynamics for both sludges were measured on-line using the photometric dispersion analyser; the effects of calcium, polyelectrolyte conditioner and shear rate on final sludge properties were determined, including settleability, turbidity of supernatant, sludge volume index and dewatering, sludge conditioning, and floc strength and structure. It was thus possible to link the flocculation dynamics to the final sludge properties. The results indicate that calcium ions play an important role in the floc formation and the final floc size for both types of sludge by the construction of calcium bridges, and hence played a significant role in determining the final properties of the sludge. A qualitative link exists between the flocculation dynamics and the final properties for both types of sludge, and between the floc dynamics and properties of synthetic sludge on the one hand and those of activated sludge on the other. The two types of sludge have very similar settling and dewatering characteristics after cationic polymer conditioning. However, there are quantitative differences in the calcium concentration required for flocculation, the supernatant turbidity, the sludge-volume index and the floc strength. This difference is believed to be due to the absence of filamentous

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material in the synthetic sludge which is present in the activated sludge. The stable and well-defined nature of synthetic sludge makes it useful as a non-complex analogue for the physical and chemical properties of activated sludge, but filamentous cellulose should be added to improve quantitative agreement with activated sludge.

Keywords: Synthetic sludge; Activated sludge; Wastewater treatment; Flocculation; Floc strength; Sludge properties; Sludge conditioners; Settleability; Dewatering

1. Introduction and review of sludge floc formation

Activated sludge is an aerobic, suspended growth process, in which microorganisms are grown in a variety of bioreactor configurations for the purpose of removing soluble organic matter. 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 [1]. The flocculated microbial aggregates, known as flocs, are the essential components of the system. Flocs typically vary in size from 10 to 1000 μm [2]. In the activated sludge process, the flocs remove both colloidal matter and soluble BOD (biochemical oxygen demand) by absorption and biodegradation, and their settling characteristics must be such that the discharge standards of the final effluent are met to a high degree of consistency [3].

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 abilities 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 15–20% by weight of mixed liquor suspended solid (MLSS) [4]. 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.

When built up by biopolymer bridging of relatively spherical micro-organisms, the flocs themselves will be roughly spherical in shape. To form the irregularly-shaped flocs often seen in activated sludge, other ingredients — filamentous organisms — are required. The filamentous organisms provide networks or “backbones” for the flocs. The networks direct floc growth into shapes other than spherical, and allow the flocs to grow larger [5]. The schematic structure of activated sludge is shown in Fig. 1. Since floc strength depends on the integrity of the biopolymer bridging, it is possible for strong and weak flocs to exist both with and without filamentous organisms. Due to the

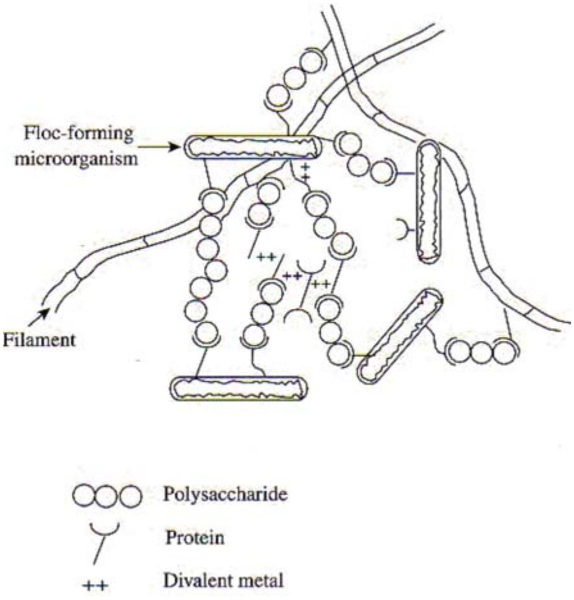


Fig. 1. Schematic structure of activated sludge.

complex nature of the flocs, they display a wide variation in physical, chemical and biological properties [6]. 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. An understanding of the flocs and their formation is therefore critical to the optimum operation of the activated sludge process.

1.1. Bonding theory

1.1.1. Double layer or DLVO (Derjaguin, Landau, Verwey, and Overbeek) theory

DLVO theory, named after its developers Derjaguin, Landau, Verwey, and Overbeek, is a classical colloidal theory in which the surface charge of the particles and the counter-ion charge in the adjacent solution form a double layer surrounding the particle. The first layer of surface charge, including adsorbed ions, is often referred to as the Stern layer [7], and the second layer as the diffuse layer. The concentration of ions in the counter-ion layer decreases with distance from the particle surface, until the concentration of ions equals that of the bulk solution. This results in an electrical potential which develops around the particle. The double layer results in osmotic repulsion of adjacent particles and inhibits aggregation. As the ionic strength increases, the size of the double layer decreases, which in turn decreases the repulsion between the particles and allows short-range Van der Waals attractive forces to promote aggregation. However, Sobeck and Higgins [8] state that results from monovalent cation addition in their reactor study conflict with the DLVO theory. According to DLVO, the addition of any ions such as Na^+ and Cl^- will increase the ionic strength and compress the double layer, thereby improving bioflocculation and the settling and dewatering properties. On the contrary, as results from this trial indicated, increasing the concentration of sodium in the system results in a substantial deterioration in settling and dewatering properties, as well as floc strength.

1.1.2. Divalent cation bridging (DCB) theory

The role of divalent cations has been demonstrated in experiments that examined floc formation during the growth of monocultures, finding that calcium and magnesium were important to the bioflocculation process [9]. A depiction of the divalent cation bridging (DCB) model is shown in Fig. 2. According to the DCB theory, divalent cations bridge negatively charged functional groups within the EPS, and this bridging helps to aggregate and stabilize the matrix of biopolymer and microbes and therefore promote bioflocculation. The DCB theory can be used to explain the results of sodium trials. Previous research has shown that high concentrations of sodium displaced divalent cations from within the floc by ion-exchange type reactions [10,11]. The replacement of divalent cations from within the floc by monovalent cations results in a deterioration in floc properties, due to the lack of bridging by the now monovalent cations.

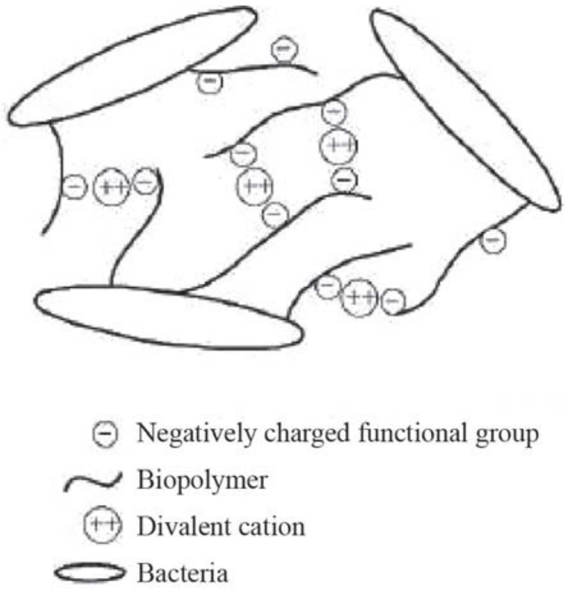


Fig. 2. Depiction of divalent cation bridging within floc matrix.

1.2. The role of cation ions

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 be predominantly complexed by the extracellular polymeric materials. Even though calcium and magnesium ions have similar properties, findings indicate that their 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 [12]. 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 [12]. 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 [10]. This causes the sludge turbidity to increase, and filterability to decrease. The same research [10] 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 [13], 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 [11,14,15] 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 improvement in the sludge settling characteristic [11].

1.3. 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 [16]. 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 term 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. Changes in the composition of activated sludge will lead to changes in the nature of the flocs, which can result in poor formation of biological flocs. 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.

1.4. 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 [13] 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 to simulate extracellular polymeric substances; and the use of calcium ions as bridging cations. The results obtained by Sanin and Vesilind [13] have shown that it is possible to create a chemical sludge having close resemblance to a 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 study of flocculation processes requires a method of assessing the state of aggregation of suspensions, preferably one which is rapid and does not cause significant disturbance of the sample. There are several methods available to determine the coagulation dose, based on either turbidity measurements or particle counting. Turbidity measurements are relatively easy to carry out, but fail in characterizing the size of the flocs as well as the state of aggregation. Particle counting is effective only for highly diluted suspensions, but fails to provide real-time responses during the operation. An optical method has already been developed for flocculation monitoring [17]. This method has been found to give a sensitive indication of floc formation, using a rather simple technique which is very well-suited to online application. The novelty of the technique lies in the fact that large numbers of particles can be simultaneously present in the sensing zone, and in the method of processing the fluctuating signal.

The overall objective of this research is to monitor and investigate the flocculation behaviour 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

Polystyrene sulphate latex particles were used to form a stock solution of concentration 5% by weight. Such mini-spheres of 0.5 μm mean particle diameter are intended 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 [18]. 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 –14mV. The stock solution was diluted to 0.05%, 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 [13]. Sulphate polystyrene latex particles of concentration 0.05% were suspended in distilled, deionised water. Samples of 500 mL, with an added alginate concentration of 100 mg/L, were stirred at 12 rpm in a 25ºC incubator for 12 h. Alginate was adsorbed onto the particles during the incubation period, and this simulated extracellular gel. When the incubation period was completed, Ca (II) was added to the samples in varying concentrations to monitor flocculation dynamics. Calcium is known to act as a sludge conditioning agent.

Numerous preliminary experiments were conducted to determine the minimum, or slight excess, concentrations of alginate and calcium required for floc formation in synthetic sludge. Alginate concentration was varied between 0 and 125 mg/L. The minimum concentration of alginate required for floc formation was observed to be 100 mg/L. Calcium concentration was varied from 0 to 25 mM Ca(II). Tiny flocs were formed after reaching 15 mM Ca(II) concentration in synthetic sludge, and larger flocs were observed at 20 mM Ca(II). A standard sludge was therefore defined as 20 mM Ca(II), 100 mg/L alginate, and 0.05% latex particles. The standard synthetic sludge was used as a bench mark to compare the changes that occur in the flocculation behaviour and final properties of synthetic sludge.

2.3. Activated sludge

2.3.1. Laboratory activated sludge system setup and operation

A five-litre, continuous-flow, bench-scale reactor was used to simulate the activated sludge process. The reactor configuration is shown in Fig. 3. The reactor consisted of a complete mixing zone and a settling zone, separated by a slanted baffle. An aeration stone provides air and mixing to the system.

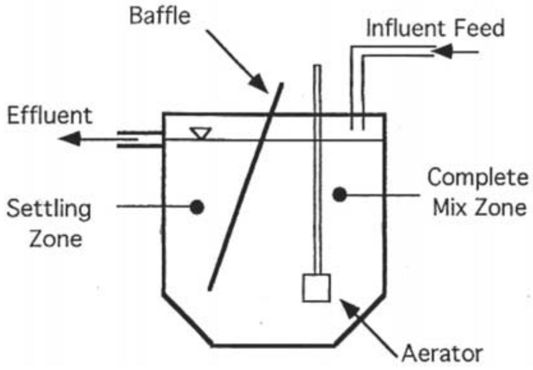


Fig. 3. Profile of laboratory scale activated sludge reactor.

2.3.2. Steady state determination

Wastewater and activated sludge were obtained from Stoke Bardolph municipal wastewater treatment plant in Nottingham, UK. After collection, the samples were returned to the laboratory (within 1 h) and stored at 4ºC. All the samples were kept for a maximum of five days. 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 300 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 sludge age was maintained at 10 days.

The activated sludge in the reactor was first fed with mixed liquor from Stoke Bardolph. The activated sludge reactor was operated until steady state was achieved, typically after 20 days of operation. Measured treatment efficiency parameters were plotted as a function of time to determine the steady state period. The reactor was considered to be at steady state when the variability in treatment efficiency was less than 20% between sampling periods. The steady-state values of each parameter were calculated as the average of values during the steady-state period. The sampling

Table 1
Cation and nutrient concentration 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+}	13.7	0.34
PO_4^{3-}	2.3	0.024
NO_3^-	15.9	0.26
TKN	46.5	—
COD	300	9.38

Table 2
Sampling results from activated sludge reactor at steady state

Determinant	mg/L	mM/L
COD	220	3.44
BOD_5	154	—
Nitrate	0.1	0.0016
Phosphate	9.0	0.095
MLSS	1148	—
Ca^{2+}	20.8	0.52
Mg^{2+}	16.32	0.68
Na^{+}	81.88	3.56
K^{+}	5.46	0.14

results of activated sludge from the reactor at steady state are given in Table 2.

Examples of steady state determination, as a function of time for the reactor, are plotted in Figs. 4 and 5.

2.4. Settleability and turbidity

Settling was measured in 100 mL graduated cylinders. The height of the interface was recorded after 60 min of settling. The small size of the cylinder was thought to produce an unwanted wall effect, but the cost of producing larger quantities of various types of synthetic sludge would have been prohibitive. The low solids concentration would also minimize the effect of the small cylinder diameter. The turbidity of the supernatants was measured using a Hach 2100AN turbidimeter after 60 min of settling.

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 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).

2.6. Conditioning

Cationic polymer polydiallyldimethyl ammonium chloride (PDADMAC) was used for the conditioning of thickened sludges from the reactors. Polymer of 20 wt % in water stock solution was made to the final design concentration, by mixing the concentrated polymer with distilled water. During conditioning and dewatering, the polymer

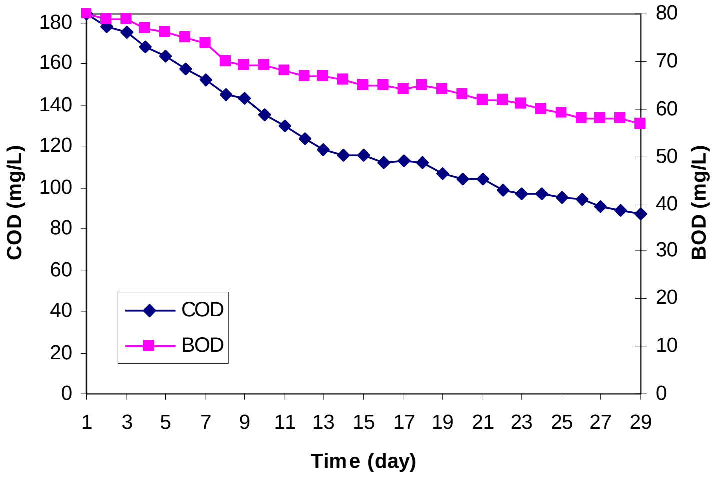


Fig. 4. COD and BOD of the effluent from the activated sludge reactor seeded with bactopeptone.

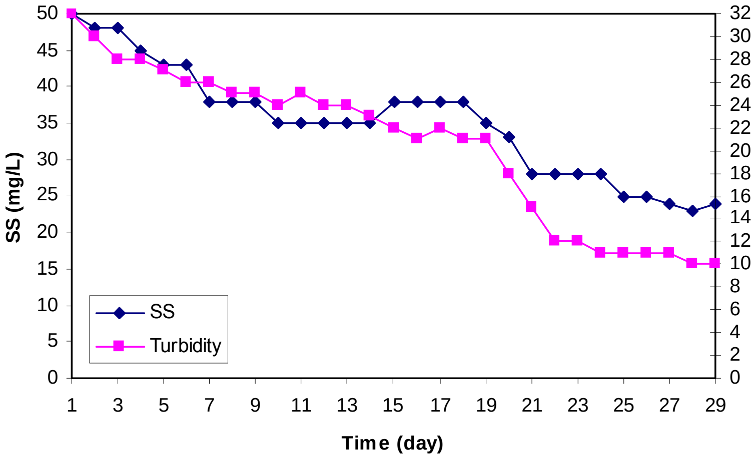


Fig. 5. SS and turbidity of the effluent from the activated sludge reactor seeded with bactopeptone.

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.

2.7. Floc strength and floc structure

Floc strength was analyzed by measuring CSTs following every 30 s interval of stirring, using a Triton-WRC (Essex, England) stirrer/timer. The floc structure of sludge was examined through a scanning electron microscope (SEM).

2.8. Filamentous organism quantification

Microscopic observations of the biological suspensions were performed periodically to assess the culture characteristics, and also to quantify the filamentous organism content. Filamentous organism content was quantified using the method of Jenkins et al. [19], in which the number of filamentous organisms was rated on a scale of 0–6, where 0 corresponds to no filamentous organisms present and 6 corresponds to excessive growth of filamentous organisms. All data reported in this study represent studies with a filamentous count less than or equal to 2.

2.9. Cation analysis

Calcium used in this investigation was added as chloride salt. Analysis of the cations Ca^{2+}, Mg^{2+}, K^{+}, Na^{+} was carried out by a Flame Atomic Absorption Spectrometer, using method 3111 in Standard Methods (1998).

2.10. Monitoring the dynamics of flocculation

A simple but sensitive optical technique, the photometric dispersion analyser (PDA), has been developed to monitor the state of aggregation of colloid suspensions [20,21]. In this instrument, light scattering in a flow-through detector is used to monitor the dynamics of coagulation. The PDA 2000 is intended as a monitor of flowing suspensions and emulsions, both in laboratories and in industrial applications. It provides an indication of changes in the state of aggregation of suspensions — either aggregation (flocculation) or disaggregation (dispersion, de-flocculation). It is applicable over a wide range of suspension concentrations and particle sizes. The output value of PDA can accurately reflect the state of formation of flocs. A schematic description of the experimental setup for monitoring the dynamics of coagulation by the PDA 2000 is shown in Fig. 6.

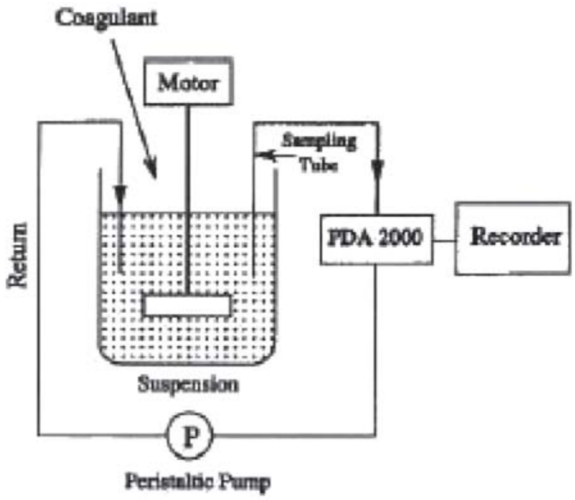


Fig. 6. Schematic description of the experimental set up for monitoring the dynamics of coagulation by PDA 2000.

On-line analysis of floc size has been performed previously during the flocculation of activated sludge [22]. The flocculation dynamics were described in terms of two keys mechanisms, aggregation and breakage. Initially, aggregation was controlling, resulting in a rapid increase in floc size. Breakage became more dominant as the floc size increased. Eventually, equilibrium was reached between aggregation and breakage, and steady state floc size was maintained.

A 500 mL synthetic sludge and a real activated sludge were used in the flocculation dynamic experiments. When calcium ions were added to the suspension, rapid mixing was performed with a stirrer in a batch reactor at a speed of 250 rpm (200 s^{-1}) for 30 s, in order to provide blending of calcium ions with the synthetic sludge and activated sludge, and this was followed by slow mixing at a speed of 100 rpm (50 s^{-1}) for 100 s to promote flocculation. The term “Flocculation Index (FI)” in this paper refers directly to the state of flocculation.

3. Results and discussion

3.1. Effect of calcium on flocculation dynamics

Two separate experiments were conducted to investigate the effect of calcium concentration on the dynamics of synthetic and activated sludge flocculation, respectively. Calcium in the form of $CaCl_2.2H_2O$ was 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. The results from both experiments are shown in Fig. 7 and Fig. 8 as the flocculation index (directly related to aggregation) vs. the time, for different calcium ions concentrations.

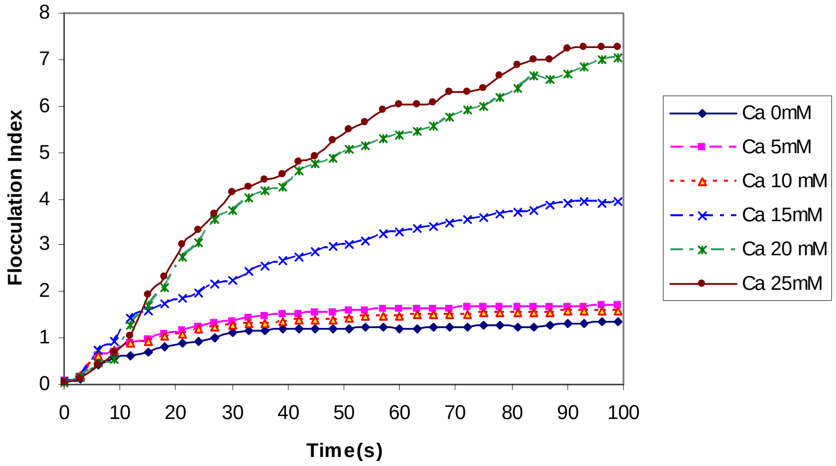


Fig. 7. Synthetic sludge flocculation dynamics via PDA with varying concentration of calcium.

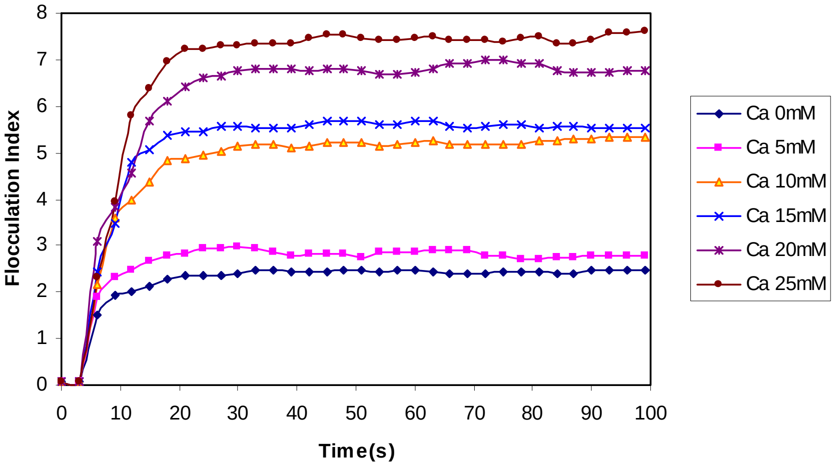


Fig. 8. Activated sludge flocculation dynamics via PDA with varying concentration of calcium.

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 25 mM Ca(II). 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 floc formation occurred when Ca (II) ion concentration increased to 15 mM, and was readily apparent for 20 mM Ca(II) and above (see Fig. 7). The flocculation index (FI) dramatically increased at 20 mM Ca (II) ions.

For all experiments, activated sludge was withdrawn from the five-litre, continuous-flow bench-scale reactor at the steady state. For each experiment, 500 mL of sample were withdrawn, containing a concentration of total suspended solids (TSS) of 1 g/L. This concentration remained constant for all experiments, and was similar to the concentration of particles in synthetic sludge. The results showed that some floc formation started to occur without the addition of calcium ions. This phenomenon results from the natural characteristic of activated sludge collected from a wastewater treatment plant; at the beginning, a certain amount of calcium ions already exists in the sample. The floc formation was readily apparent for 10 mM Ca(II), and above (see Fig. 8). The flocculation index (FI) dramatically increased at 20 mM Ca (II) ions.

Visual observation showed that, at higher concentrations of calcium (>20 mM), larger flocs were formed, and sludge started to settle to the bottom of the stirred batch reactor at the slow mixing speed of 100 rpm (50 s^{-1}). At lower concentrations of calcium, the slower floc dynamics led to a lower FI.

The results from the experimental technique provide valuable information about the flocculation dynamics of synthetic and activated sludge. From Fig. 7 and Fig. 8, it can be seen that, in each case, the rate of aggregation increases rapidly until a steady state of flocs is reached. It is also apparent that, for the higher calcium concentrations, the rate of aggregation is faster, but approaches a limiting value. Cousin and Ganczarczyk [23] investigated the effect of calcium on specific floc properties, such as size and density. It was found that the addition of calcium (>2 mM) resulted in an increase in floc size, and a decrease in porosity. A minimum addition of 2 mM was thought to be necessary to overcome the ion exchange between competing ions, such as sodium. The increase in floc size was then speculated to be due to the formation of calcium bridges among microbial aggregates and particles.

These results are in agreement with the work of Biggs et al. [24]. They found that the initial rate of change of floc size increases initially with the addition of calcium concentration, and then approaches a steady-state value at the higher concentrations. This suggests that, at a higher calcium concentration, saturation of the floc has occurred, and the rate of change of floc size is independent of calcium concentration. The experimental investigation reported here supports the model that cations are involved in flocculation, most likely through cationic bridging. The flocculation dynamic behaviour of synthetic sludge is qualitatively similar to that of activated sludge. This supports the idea that synthetic sludge is useful as a less-complex analogue for the study of activated sludge flocculation.

3.2. Settleability and turbidity

The results for the settling of synthetic activated sludge are illustrated in Fig. 9. No sludge settling was observed until the Ca (II) concentration reached 10 mM in both synthetic and activated sludge. All the flocs were dispersed in a turbid environment below 10 mM. When the calcium concentration exceeded 10 mM, a sudden improvement in the settleability of synthetic activated sludge was observed. However, settleability of activated sludge was improved beyond that of synthetic sludge when Ca (II) ion was beyond 10 mM. This phenomenon is thought to be due to the lack of filamentous micro-organisms in synthetic sludge. It has been observed that the presence of filamentous organisms in activated sludge has an effect on the structure of the flocs; according to one theory, it is probable that the filamentous organisms’ network provides a “backbone” for the build up of the floc, which is subsequently formed with the additional assistance of various polymer bridges between primary particles and smaller flocs [5].

This finding seems to agree with the view of Örmeci [25] that the addition of cellulose fibres to simulate the filamentous micro-organisms found in activated sludge also ensured good settling and compaction of synthetic sludge. The settling ability of synthetic sludge was greatly improved upon increasing the cellulose concentration.

The results for the turbidity of the supernatant of synthetic activated sludge after settling are illustrated in Fig. 10. The turbidity of supernatant after settling was decreased significantly when the calcium concentration reached 15 mM for syn-

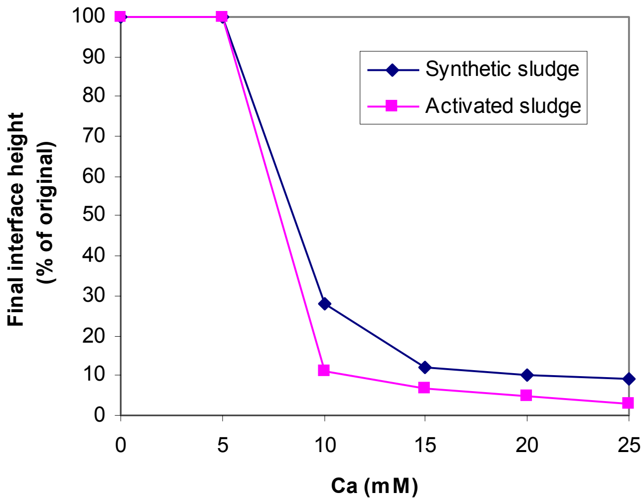


Fig. 9. Synthetic activated sludge settleability increases with increasing concentration of calcium.

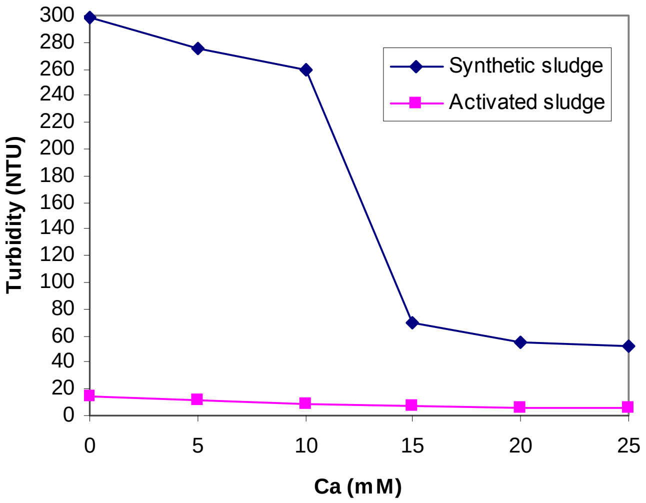


Fig. 10. Supernatant turbidity decreases with increasing concentration of calcium.

thetic sludge. There was a much smaller decrease in the already low turbidity of the supernatant of activated sludge after Ca (II) ion addition. This phenomenon could again be due to the lack of filamentous micro-organisms in synthetic sludge samples. This seems to agree with Örmeci's work [25]. This stated that the turbidity of supernatant also started to improve after the addition of cellulose to synthetic sludge.

Jenkins's work [19] concluded that when a filamentous, bulking activated sludge settles, it produces a very clear, low turbidity supernatant, because the filamentous organism network filters out the small particles that can cause turbidity. Sanin and Vesilind [16] demonstrated that the removal of calcium ions from the sludge floc matrix causes the sludge flocs to disintegrate, as indicated by a decrease in filterability and particle size, an increase in turbidity and solution carbohydrate concentration. This result would also seem to support the divalent cation bridging theory. Thus, Ca (II) ions may not only improve floc formation and synthetic activated sludge settleability, but also decrease the turbidity of supernatant. In real sludge, filamentous material plays a significant role, and this should therefore be borne in mind when Ca (II) ions are used as an indicator during the monitoring and prediction of activated sludge settling properties.

3.3. Settling and dewatering properties

The effect of calcium concentration on the settling and dewatering properties of synthetic activated sludge are shown in Figs. 11 and 12. When no Ca(II) ions were added to the synthetic sample, no floc formation occurred; all the particles were dispersed in the liquid solution. For the activated sludge sample, a non-filamentous bulking occurred. However, the settling improved in both synthetic and activated sludge as the calcium concentration in the feed was increased.

As can be seen in Fig. 12, the dewatering property measured by CST followed a trend similar to that of the SVI. The CST values indicated a relatively poor dewatering at the lowest calcium concentration, but the dewatering property improved as the calcium concentration increased. Most of the improvement in SVI and CST occurred after the first incremental addition of Ca(II) ion, with a modest improvement beyond this level.

This result is in agreement with the work of Higgins and Novak [11]. They demonstrated that the cation content in a wastewater could have a

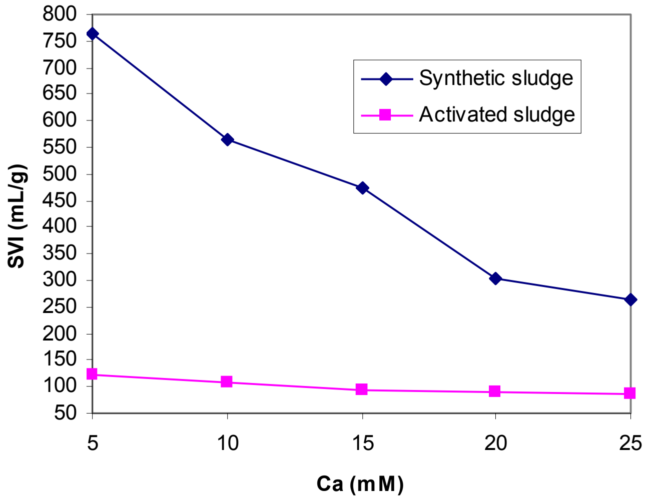


Fig. 11. Synthetic activated sludge settling increases with increasing concentration of calcium.

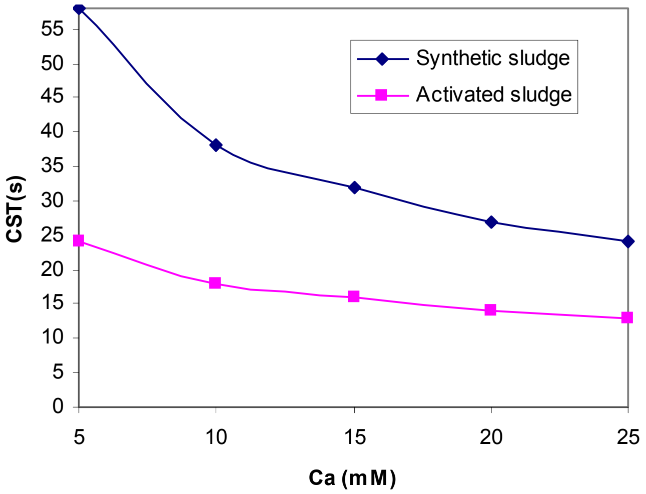


Fig. 12. Sludge dewatering of synthetic activated sludge.

major impact on the settling and dewatering characteristics of an activated sludge. In our work, there is a similarity in behaviour between the settling and dewatering characteristics of both synthetic and activated sludge when calcium is added. However, the settling and dewatering of activated sludge is improved more than that of synthetic sludge after calcium concentration addition. This phenomenon can be explained by the existence of filamentous organisms in activated sludge. Filamentous organisms also cause an improvement in the compaction and settling of synthetic sludge. The types of compaction and settling effects depend on the causative filamentous organism involved [19]. In addition, it should be noted that there are interactions between cations and biopolymers in activated sludge. An ion-bridging model has been proposed to explain the effect of cation on biological sludge properties [9]. This model proposes that divalent cations act as a bridge between negatively charged sites on exocellular biopolymer (gel). Therefore, improvements in settling and dewatering due to increased particle sizes should correlate to an increase in the bound exocellular polymer content involved in the aggregation process.

3.4. Sludge conditioning

A conditioning was performed using thickened sludge samples with 1 g/L of total suspended solid (TSS), in both synthetic and activated sludge. The sludge conditioning as a function of calcium addition is shown in Fig. 13 and Fig. 14, with and without conditioning polymer addition. The CST of the samples with added calcium decreased over time, but the samples with polymer added showed a better improvement of sludge conditioning, as indicated in Fig. 13 and Fig. 14.

The addition of calcium improves the sludge conditioning of both synthetic and activated sludge. However, the sludge conditioning of activated

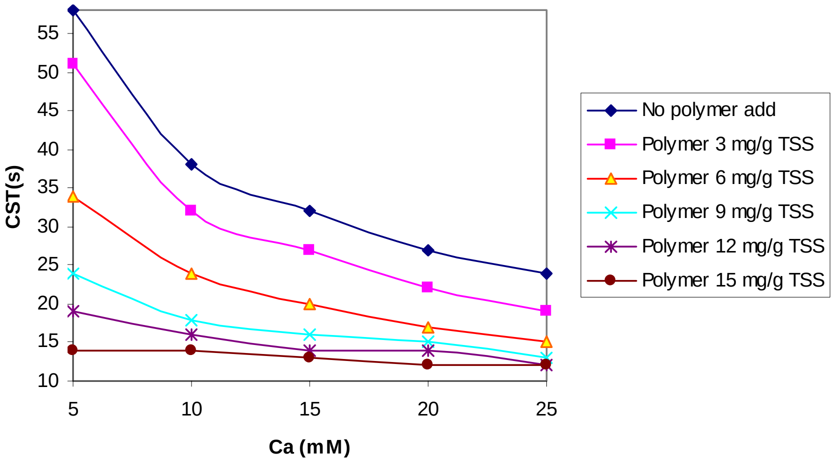


Fig. 13. Synthetic sludge conditioning with polymer.

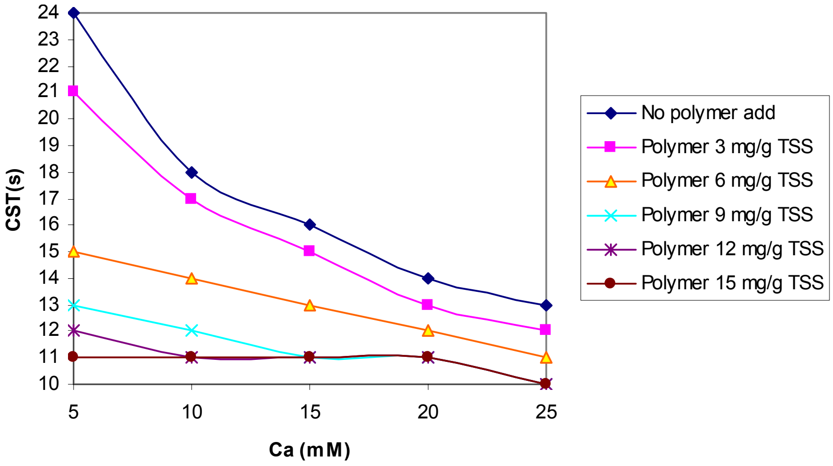


Fig. 14. Activated sludge conditioning with polymer.

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 [26].

These results seem to support Eriksson et al.'s work [27,28]. 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.

3.5. Floc strength and floc structure

Floc strength measurements indicated that flocs are more resistant to shear at higher calcium concentrations. The floc strength was analyzed by imparting a constant shear rate at the mixing speed of 250 rpm (200 s^{-1}) to a mixing liquor sample, and measuring CST over time. The CST measurement was made at every 1 min interval. The results from CST measurement over time are shown in Fig. 15 and Fig. 16 for both synthetic and activated sludge. Weak flocs are characterized by an increasing CST, due to floc break up during mixing, whereas stable flocs show a much smaller increase in CST with mixing. As can be seen in Fig. 15 and Fig. 16, the strongest flocs were those with the highest calcium concentration.

The results show that activated sludge flocs exhibit greater floc strength than synthetic sludge flocs. The reason for this is believed to be the absence of a backbone structure of flocs formed by the filamentous microorganisms in the synthetic sludge, and this makes these flocs more susceptible to shear. This seems to be in agreement with Wen et al [29]. They stated that for the present synthetic sludge system, there exists no "backbone" to strengthen the floc. Only after a finite

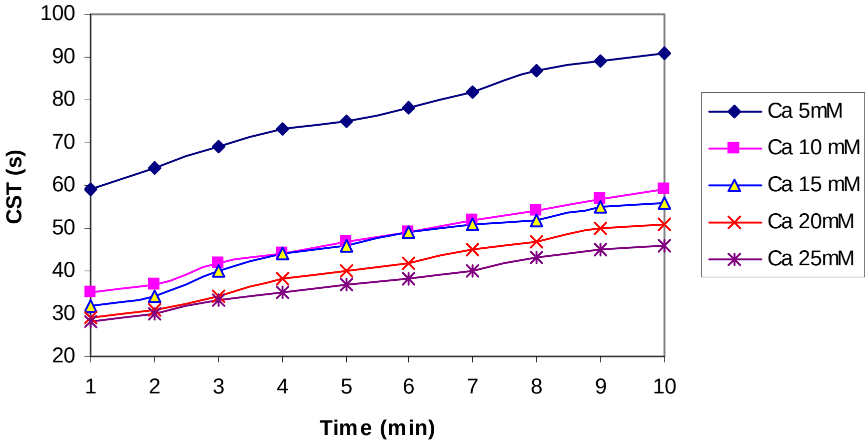


Fig. 15. Floc strength of synthetic sludge.

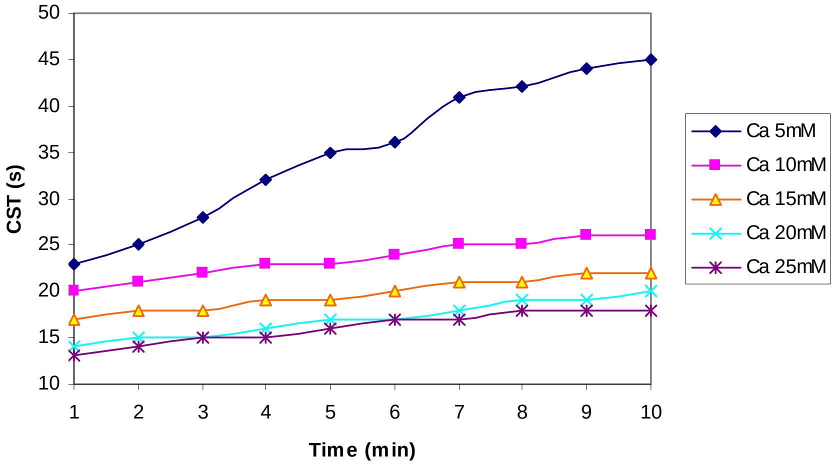
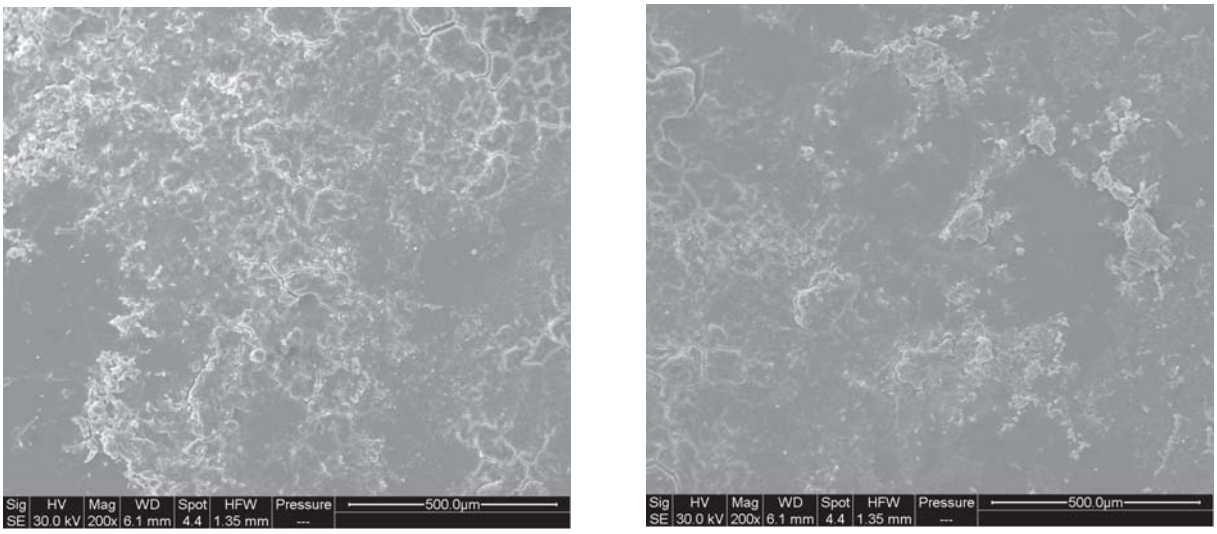


Fig. 16. Floc strength of activated sludge.

amount of polymer flocculants had been added could larger flocs with sufficient strength form, and then the flocculation process could take over.

The chemically produced synthetic sludge flocs created by using components and systems similar to that found in activated sludge also looks physically very similar to activated sludge flocs. The striking similarity in general appearance is exhibited in Fig. 17, in the micrograph of both synthetic and activated sludge.

The typical floc size of synthetic sludge was examined through a scanning electron microscope



(a) (b)

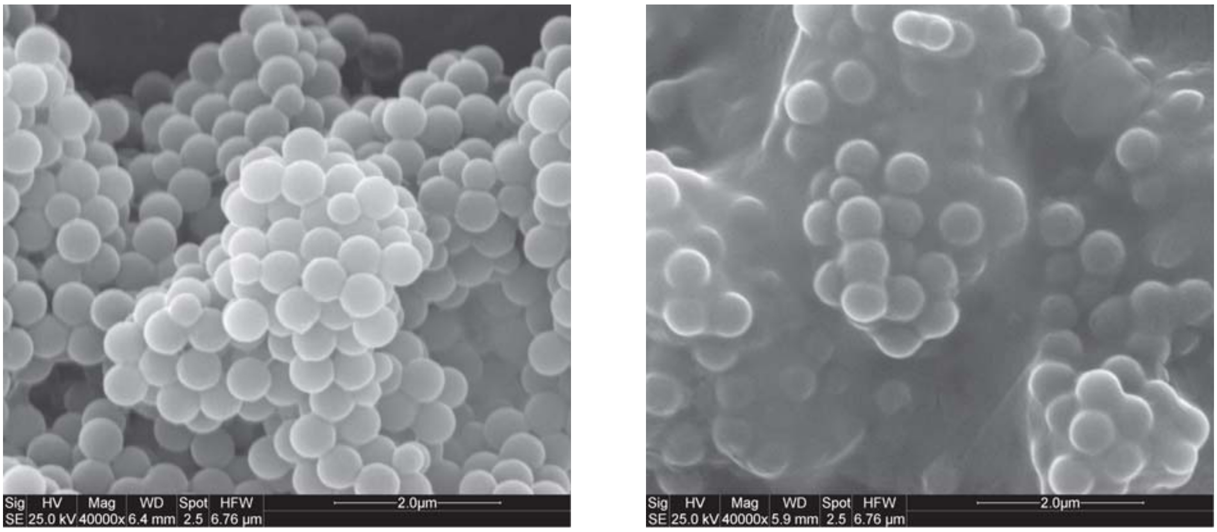
Fig. 17. Scanning electron microscope (SEM) comparison of synthetic sludge (a) and activated sludge (b). 200× magnification.

(SEM) with and without calcium addition. When calcium ion was added at 20 mM to the sample, the sizes of flocs of synthetic activated sludge were found to be in the range 10–60 µm. The characteristics of synthetic sludge flocs are shown schematically in Fig. 18. The structural results from this study suggest that calcium ions are effective in a two-stage floc formation. The latex-particle flocculation is the initial stage of 2–3 micron floc formation (a), and once the flocs are formed, calcium ions further bridge the flocs to each other to form larger 10–60 micron flocs (b).

The results from Cousin's work [23] also showed that calcium ion could have an effect on the physical characteristics of activated sludge flocs, such as floc size and size distribution. The addition of Ca(II) ion led to increased flocculation, and thus to an increase in floc size.

4. Conclusions

- The effects of an increasing calcium ion concentration on the flocculation dynamics of synthetic activated sludge have been explored through an on-line monitoring technique. The effects of calcium, cationic polyelectrolyte, and shear rate on the resulting final properties of sludge, such as settleability, turbidity of supernatant, sludge volume index and dewatering, sludge conditioning, and floc strength/structure, have also been measured and characterized for both synthetic and activated sludge.
- Calcium ions play an important role in the formation of both synthetic and activated sludge.Calcium contributes to the floc formation by constructing calcium ion bridges between alginate or biopolymer gel adsorbed on individual particles/bacteria. The calcium ion content in wastewater can have a major impact on the settling and dewatering characteristics of both synthetic and activated sludge.
- In this work, the PDA has been developed for the first time to monitor synthetic activated sludge flocculation. The technique of PDA has proven to be a useful tool for monitoring the flocculation of both synthetic and activated



(a) (b)

Fig. 18. Structure and size of synthetic sludge: (a) without calcium; (b) with calcium ion concentration at 20 mM. 40000× magnification.

sludge. Monitoring of the flocculation index by the PDA has established a qualitative link between the flocculation dynamics and the final properties, for both synthetic and activated sludge.

- There is also a good qualitative agreement between both the flocculation dynamics and final properties of synthetic sludge on the one hand, and those of activated sludge on the other. Nevertheless, there are notable quantitative differences: the concentration of calcium above which significant flocculation occurs, the supernatant turbidity, the sludge volume index and (to a lesser degree) the sludge dewatering, and the floc strength. It is hypothesized that such a discrepancy is due to the absence of a filamentous, backbone structure in synthetic sludge which is often present in activated sludge. Where such quantitative studies are carried out, the inclusion in synthetic sludge of a filamentous material such as cellulose is thus recommended. In addition, synthetic and activated sludge behave in qualitatively similar ways in terms of their settling and dewatering after cationic polymer conditioning.
- The stable and physically/chemically well-defined nature of synthetic sludge makes it very useful as a non-complex analogue for the physical and chemical (i.e. non-biological) properties of activated sludge, but filamentous cellulose should be added to improve quantitative agreement with activated sludge.

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