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The Impact of Aluminium Salt Dosing for Chemical Phosphorus Removal on the Settleability of Activated Sludge

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Abstract: The use of metal salts like aluminium in the precipitation of phosphorus in activated sludge plants has increased considerably in recent years due to the need to achieve tighter discharge consents for phosphorus in treated wastewater effluent. The impact of aluminium salt (Al^{3+}) dosing on the settleability of activated sludge as a function of zone settling velocity (ZSV) and stirred specific volume index (SSVI) were investigated in batch settleability tests over a three-year period. The results showed that ZSV increased with increasing dose of aluminium salt as SSVI decreased. This trend was observed for dosing concentrations of less than 100 mg/L. At a dose concentration >100 mg/L, the trend was reversed as ZSV decreased and SSVI increased. At dose concentrations of <100 mg/L, Al^{3+} helped in the bioaggregation of dispersed activated sludge flocs, thereby improving settleability. The surface morphology from the scanning electron microscope (SEM) images indicated that the initial potential of interfloc bridging, open floc formation, and spindly bulking noticed in the undosed activated sludge flocs were remarkably reduced as the flocs became more compacted after Al^{3+} treatment. At >100 mg/L of Al^{3+}, the sludge settleability started to disintegrate due mainly to surface charge reversal linked to the formation of aluminium hydroxides and the resultant disintegration of the activated sludge floc structure.

Keywords: activated sludge; aluminium; settleability; SSVI; ZSV

1. Introduction

Due to the increasingly stringent requirements for effluent quality, particularly the removal of nutrients (phosphates and nitrates), the activated sludge process (ASP) have become widely used in Europe for the treatment of wastewater. Old biofilters are being replaced by ASPs to help meet <1 mg/L phosphorus consents [1]. Phosphorus removal is achieved by either enhanced biological phosphorus removal (EBPR) or chemical phosphorus removal (CPR). The use of EBPR is limited by the requirement for strong wastewater with high readily biodegradable biological oxygen demand (BOD). Hence, CPR is the most widely used for phosphorus removal in wastewater treatment. In the UK, over 80% of WWTPs remove phosphorus by CPR [2]. The ASP process involves the removal of both the biological and non-biological particulate from its biological reactors by settling. The suspension is well mixed and aerated to provide the required oxygen level for microbial metabolism and reduce potential settling of the suspension. The bacteria (heterotrophic, nitrifying, denitrifying, poly-phosphate and glycogen accumulating) accounts for most pollutant removal from wastewater, but some other bacteria called filamentous bacteria negatively impacts activated sludge settling and affects the operational capacity of wastewater treatment plants through sludge bulking and foaming [3–5].

The three main factors that affect activated sludge settleability in wastewater treatment include particle size, particle structure, and particle densification. Particle densification is affected by microbial storage product content (MSP), polyhydroxyl butyrate (PHB), non-volatile suspended solids (NVSS), and chemical coagulants added in the reactors [6]. Other factors affecting settleability include extracellular polymeric substances (ECPS) and flocculating capability [7–9]. While sludge particle size and structure have received substantial consideration in the literature, there are limited studies on sludge densification and chemical precipitation.

Aluminium salt alongside ferric salts are the most widely used chemicals for the chemical precipitation of phosphorus. The impact of aluminium coagulants on activated sludge has been explained through charge neutralisation of negatively charged colloids by cationic hydrolysis products [10]. Urbain et al. [11] further commented that the overall activated sludge floc structures are negatively charged due to the physical and chemical interactions between floc bacteria, ECPS and multivalent cations. This explains why aluminium salts (Al^{3+}) have the potential to be strongly absorbed by the surface of sludge flocs since they produce positively charged metal hydroxides, which are responsible for the charge neutralization and reversal process during periods of aluminium overdosing. The ECPS also impacts activated sludge settling processes and physicochemical properties of activated sludge flocs due to the ability of its internal layer to tightly bind and adhere closely with strong stability to the cellular surface [12,13]. Earlier studies have also shown that the activated sludge flocs are embedded in the ECPS structure [7,14,15] and the amount of ECPS extractable from the activated sludge is positively related to stirred suspended volume index (SSVI). Wang et al. [16] also reported a similar linear relationship between loosely and tightly bound ECPS and SSVI.

According to Higgins et al. [17], multivalent cations like aluminium (III) ion (Al^{3+}) are an effective way to optimise activated sludge settleability. In support of this claim, Higgins and Novak [18] and Subramanian et al. [19] have also explained that aluminium (Al^{3+}) will promote activated sludge settleability performance due to its ability to neutralise the sludge surface charge. Nevertheless, Jin et al. [15] demonstrated that dense, strong, and large flocs are required for good activated sludge settleability and compaction. Li et al. [20] equally reported that aluminium supplements promote larger flocs. Also, aluminium has been used in wastewater treatment due to its higher valency and low solubility [21,22]. Despite these studies, there is no data available on how varying concentrations of aluminium used in CPR impact on the settleability parameters of ZSV and SSVI. The purpose of this paper is to evaluate the impact of varying aluminium dosing concentrations on the settleability of activated sludge as a function of ZSV and SSVI.

2. Materials and Methods

2.1. Materials

Activated sludge samples were regularly collected over a three years' period from a Wastewater Treatment Plant (WWTP) in the West Midlands in the United Kingdom. Mixed liquor suspended solids (MLSS) samples were collected at the beginning of the aeration zone before any chemical dosing. The WWTP is an activated sludge plant with an average design flow of 450 ML/D at flow to full treatment (FFT) of 1070 ML/D. The mixed liquor samples were collected in 32.5 L plastic containers and transferred to the laboratory-scale plant. All analyses were completed within 24 h of sampling. The MLSS concentration of the samples ranged from 2800 to 3500 mg/L, with the pH ranging from 6.5 to 7.5 and a phosphate concentration of 7 to 12 mg/L. All chemical used were of analytical grade and purchased from Sigma Aldrich (Dorset UK).

2.2. Jar Tests Protocol

SVI is the most common sludge settleability indicator used to measure the settling characteristics of suspended growth of activated sludge solids in ASPs. This is because of the simplicity with which the SVI (unstirred) test is performed. However, SVI suffers some major draw backs since there is no consistent relationship between SVI and suspended solids concentration in mg/L (MLSS) [23], but this challenge was addressed in a review conducted by Dick and Vesilind [23] suggesting the inclusion of a slow stirring regime (1–2 revolutions per minute), and this led to a proposed stirred specific volume index (SSVI) test using a 4 L settling column instead of the 1 L settling column in the unstirred SVI test [24]. The zone settling velocity (ZSV) and SSVI are the most commonly accepted measure of activated sludge settleability [25,26], and these were investigated in the jar test experiments in this study.

The mixed liquor samples were mixed gently by swirling the container in an air tight condition so that the flocs are not broken, and no air was entrapped into the sample container. 3250 mL of mixed sample was transferred into a 5 L beaker and afterwards, the content of one the 5 L beakers was used as a control without any chemical dosing (un-dosed) and then stirred for 10 min at 2 revolutions per minute (rev/min) using an overhead stirrer. The un-dosed sample was then transferred into the settlometer to reach both the 3250 mL scale for SSVI and 50 cm scale for ZSV, for the settling process to commence for 30 min interval at a maximum height of 50 cm. Furthermore, 3250 mL of the mixed sample was transferred into a 5 L beaker and treated with a varying concentration of aluminium sulphate measured as Al^{3+} (0, 10, 20, 30, 40, 50, 100, 150, 200, and 250 mg/L). The samples were stirred for 10 min at 2 (rev/min) using an overhead stirrer before being used for the settlometer test. The time was recorded for every 5 cm height ranging from 50, 45, 40, 35, 25, 20, 15, 10, 5, and 0 cm, respectively using a stop clock and at the end of the 30 min, settled solids volume (mL/), sludge height (cm), MLSS (g/L), $SSVI_{30}$ (mL/g) and ZSV (m/h) was estimated. The standard Water Research Council (WRc) settling test [27] was performed in a 3.25 L type 305 settlometer equipment (Triton Electronic Ltd., Essex, UK) with 100 mm diameter and 500 mm height, a slow speed stirrer (1 rev/min) was used to prevent any event of sludge bridging to the wall. The jar test process has been previously described by Clark and Stephenson [28].

The settled solid volume (SSV) (mL/L), mixed liquor suspended solids (MLSS) (g/L), SSVI (mL/g), and ZSV (m/h) result was obtained from the following equation:

$$\text{ZSV (m/h)} = \frac{(\text{H}_2 - \text{H}_1) \times 0.6}{(\text{T}_2 - \text{T}_1)} \tag{1}$$

$$\text{SSV (mL/L)} = \frac{\text{Volume of Settled Sludge after 30 min, mL} \times 1000\ \text{mL/L}}{\text{Sample Volume, mL}} \tag{2}$$

$$\text{SSVI (mL/g)} = \frac{\text{Volume of Settled Sludge after 30 min, } \frac{\text{mL}}{\text{L}} \left(\frac{1000\ \text{mg}}{\text{g}}\right)}{\text{MLSS Concentration, mg/L}} \tag{3}$$

where H_2 is the initial height of the settlometer cylinder (cm), H_1 is the height of the final point selected on the gradient (cm), T_2 is the time of the final point selected on the gradient (min), T_1 is 0 (min), and MLSS is the mixed liquor suspended solids (g/L).

When the initial height is equal to 50 cm, SSVI was calculated from Equation (4); when the initial height is not equal to 50 cm, Equation (5) was utilised. The 50 cm depth criteria was utilised to adjust the conventional 1 L settling column capacity to yield a total volume of 4 L settling column to include the required stirring regime (slow stirring of between 1–2 revolution/minute) in the existing SVI test procedure without stirring [23–25].

$$\text{SSVI (mL/g)} = \frac{\text{Final Height of the blanket (cm)} \times 20,000}{\text{MLSS Concentration (mg/L)}} \tag{4}$$

$$\text{SSVI}\left(\frac{\text{mL}}{\text{g}}\right) = \frac{\%\ \text{volume}}{\%\ \text{solid}} = \frac{\text{Initial Height of the blanket (cm)} \times 100}{\text{MLSS Concentration}\left(\frac{\text{mg}}{\text{L}}\right) \times 10,000} \tag{5}$$

$$\%\ \text{Solid} = \frac{\text{MLSS (g/L)}}{10,000} \tag{6}$$

$$\%\ \text{Volume} = \frac{\text{Final Height (cm)}}{\text{Initial Height (cm)}} \times 100 \tag{7}$$

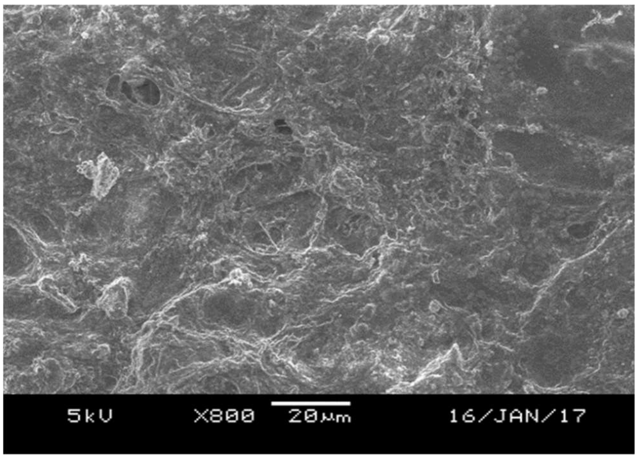
2.3. Scanning Electron Microscope

The variability in the morphology of the sludge floc quality in tested activated sludge sample in the laboratory-scale plant was examined using the SEM (JEOL-6060LV, JEOL Ltd, Hertfordshire, UK). The sludge morphological investigation was conducted for both the control and aluminium-treated sludge samples. The SEM was used due to the limitations of a light microscope, which is limited by the physics of light.

3. Results and Discussion

3.1. Effects of Aluminium Dosing on Activated Sludge Morphology

Microscopic analysis of sludge flocs for control sample (0 mg/L) and aluminium dosed (20, 50, 100, and 150 mg/L) in SEM-Joel JSM-6060LV showed initial evidence of interfloc bridging, open floc formation and spindly bulking potential in the control sample (Figure 1a), while in the aluminium-treated sample (20 mg/L), some reduced sludge porosity was observed with reduced interfloc bridging and improved sludge compaction (Figure 1b). However, a better improvement was noticed at a dosing concentration of 50 mg/L with not just reduction in the interfloc bridging but open floc formation and spindly bulking reduction with better sludge compaction (Figure 1c) compared to treatment with increased aluminium dosing concentration of 100–150 mg/L (Figure 1d,e).



(**a**)

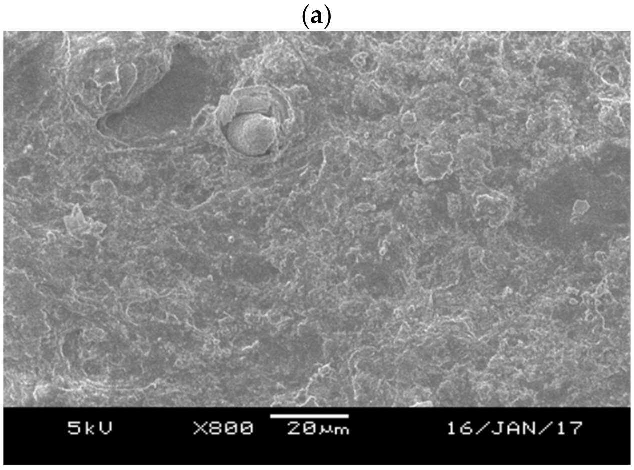


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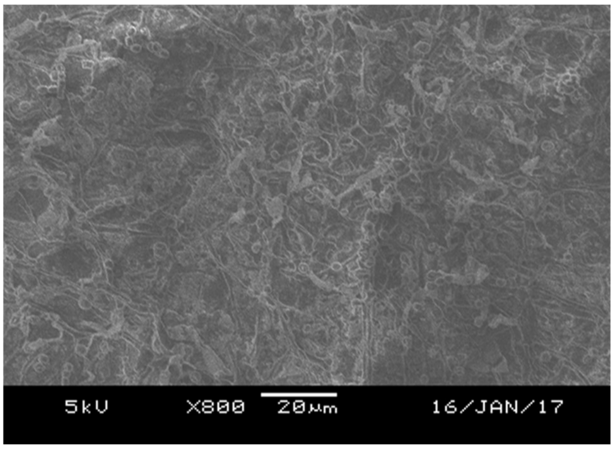
Figure 1. *Cont.*



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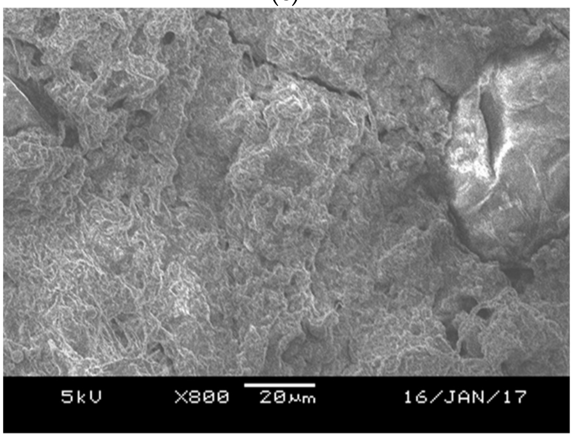

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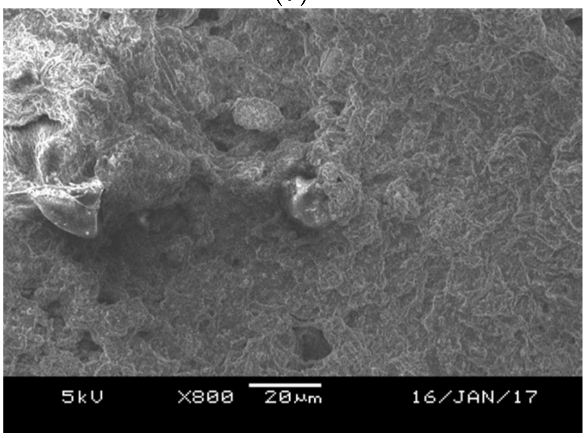


(**e**)

Figure 1. Scanning electron microscopy (SEM) of sludge floc (**a**) control (0 mg/L); (**b**) Al-Dosed (20 mg/L); (**c**) Al-Dosed (50 mg/L); (**d**) Al-Dosed (100 mg/L); (**e**) Al-Dosed (150 mg/L).

The control sludge floc exhibiting an interfloc bridging indicates interference with bioaggregation of floc particle leading to slow settling rate and reduced sludge compatibility and overall reduced activated sludge settleability. On the other hand, the aluminium-treated sludge floc showed the impact of aluminium in the reduction of the length of the filament into smaller filaments. We can therefore infer that aluminium-treated sludge floc (aluminium sludge) reduced the issues of extending filamentous organisms over floc forming bacteria in the entire sludge particle surface (interfloc bridging), scattering of floc-forming bacteria into smaller set along extended filamentous organism (open floc formation), and floc forming bacteria formed along filament length of filamentous organism (spindly bulking).

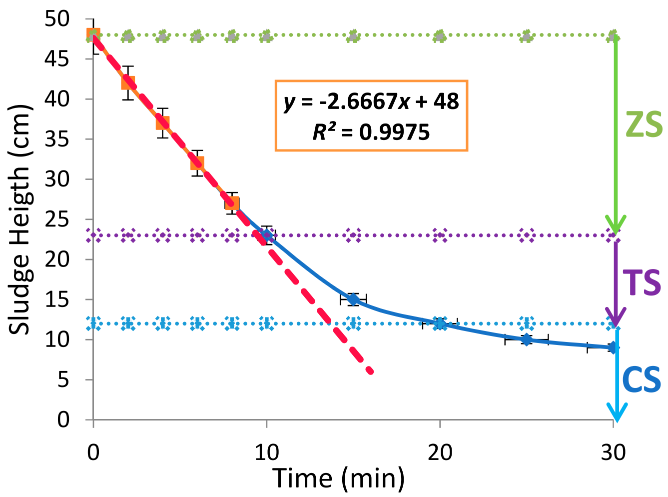
This agrees with findings of other researchers on sludge bio-flocculation and improvements in sludge settleability [29–33]. This also explains the observation of Ojo and Ifelebuegu [1] in the improvement of sludge settleability with increasing dose of aluminium in a full-scale activated sludge treatment plant.

3.2. Effects of Aluminium Dosing on ZSV and SSVI

The phosphorus concentrations of the undosed samples ranged from 7 to 12 mg/L for all batch sample collected over the three years period. The final concentrations after treatment with varying concentrations of aluminum salt ranged from 0.1 to 1.11 mg/L. The ZSV were estimated over a range of un-dosed and aluminium-dosed activated sludge concentrations (0, 20, 50,100,150, 200, and 250 mg/L) for five batch test regimes. The results from a typical ZSV test are shown in the zone settling curves (ZSC) (Figure 2a–g). They show that approximately 50% of the original sludge volume within the sludge depth of the settling column settled after 5–10 min for both the control and aluminium-treated sludge. It was observed from the zone settling curve (ZSC) that the initial faster settling is probably due to the absence of spaces between the sludge flocs causing free settling without interference. However, after the initial first 10 min of settling, it was noticed that the change in the sludge height with time (ZSV) began to decline. This agrees with the previous work by Vesilind [26] and can be explained by the floc to floc interaction based on their proximity and slowing down of their settling velocities.

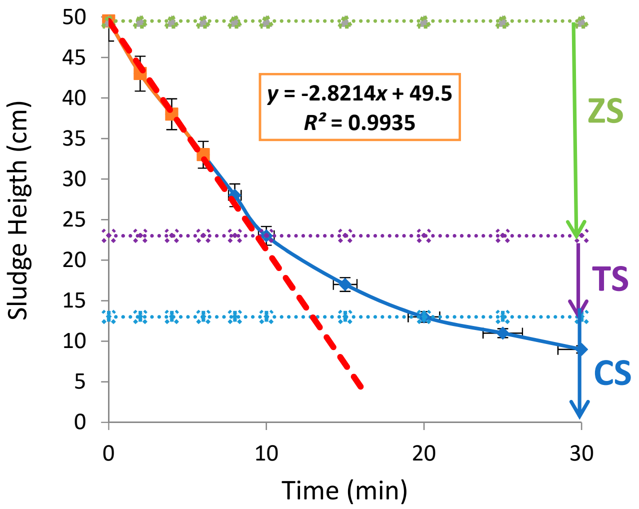
Consequently, within this zone settling regime (ZS), the agglomeration of floc bacteria tends to settle as a zone of blanket (sludge blanket), accounting for the decrease in the settling velocity and below this dilute settling zone is the transition zone (TS), in which the concentration of solids increased rapidly before entering the compression regime (CS) [34]. Moreover, as the settling velocity began to approach the zero axes, there was a possible dehydration of water from the sludge floc pore spaces due to the compressive forces acting on the floc bacteria as the sludge floc enters a compression settling regime (CS). In addition, the linear portion of the ZSC's (Figure 2a–g) represents the settling velocity of the sludge flocs as reported in previous work [35] and as such an increased sludge concentration will result in a decrease in the settling velocity due to increased resistance to water flow through the settling sludge column.

Below this dilute settling zone is the transition zone, in which the concentration of solids increases rapidly, and then the compression zone.



(**a**)

Figure 2. *Cont.*



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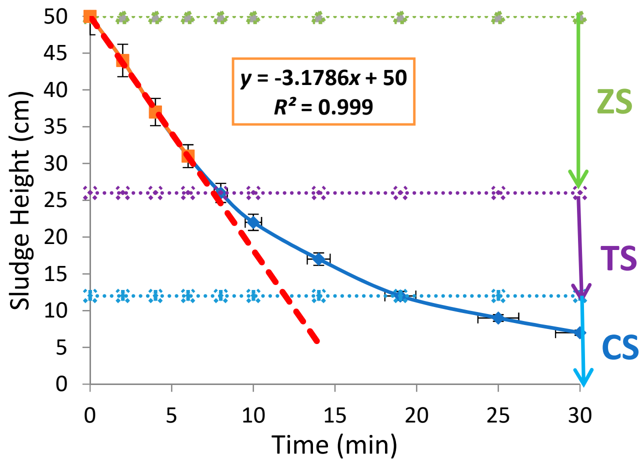

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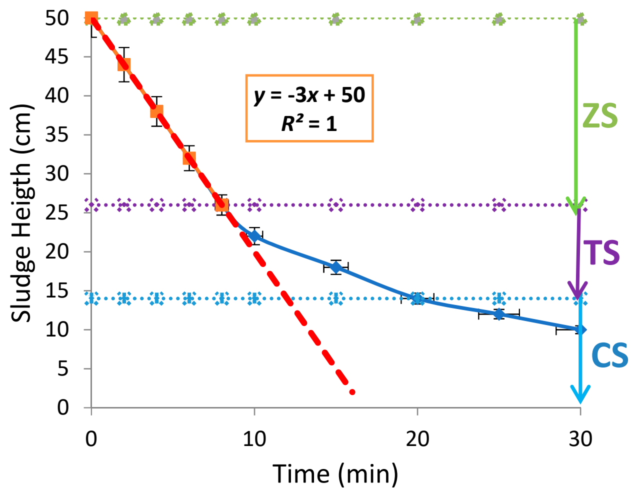

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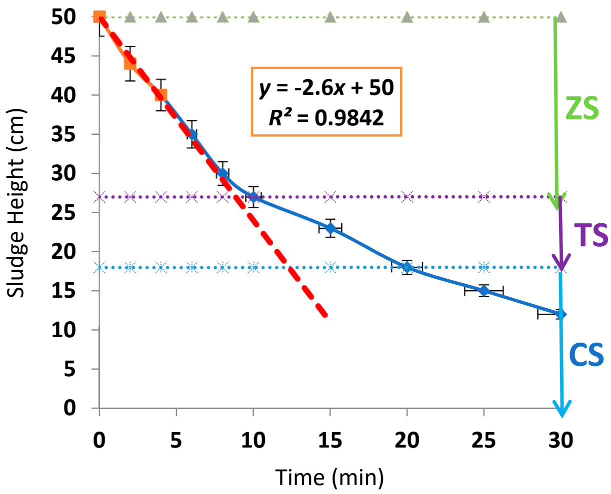
Figure 2. *Cont.*



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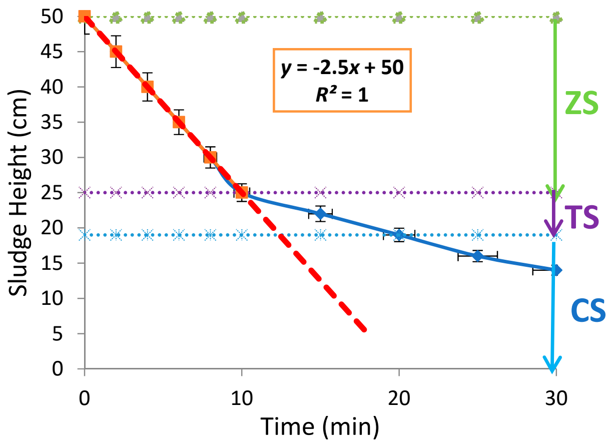

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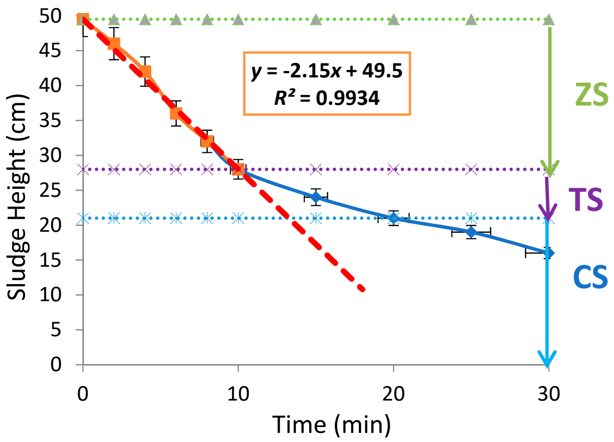

(**g**)

Figure 2. (**a**) Zone settling curve (ZSC) for undosed mixed liquor suspended solids (MLSS); (**b**) ZSC for 20 mg/L aluminium-dosed MLSS; (**c**) ZSC for 50 mg/L aluminium-dosed MLSS; (**d**) ZSC for 100 mg/L aluminium-dosed MLSS; (**e**) ZSC for 150 mg/L aluminium-dosed MLSS; (**f**) ZSC for 200 mg/L aluminium-dosed MLSS; (**g**) ZSC for 250 mg/L aluminium-dosed MLSS; (ZS = zone settling, TS = transition settling, CS = compression settling, error bars represent the standard deviation of the mean). The zone settling velocity (ZSV) was obtained from the slope of the linear graph.

The results of the impact of aluminium dosing on activated sludge settleability index (ZSV and SSVI) are summarised in Table 1. It was observed that the ZSV values increased at the beginning with increasing concentration of aluminium dose (10, 20, 30, 40, 50, 100 mg/L) and started to decrease significantly after 100 mg/L dose concentration (150, 200, and 250 mg/L) as shown in Table 1 and Figure 3. A reversed trend is observed for the SSVI, which decreased with increasing dose of aluminium up to a 100 mg/L dose rate, as shown in Table 1 and Figure 4. At a 100 mg/L dose rate, the SSVI had started to increase. A smaller SSVI value represented a faster settling rate of activated sludge and vice versa. This agrees with the work of Ojo and Ifelebuegu [1], who reported that increasing concentration of aluminium dose in a full-scale activated sludge plant resulted to improved settleability until an aluminium dose of about 145 mg/L, when settleability disintegrated and the sludge started to bulk.

Table 1. Mean and standard deviation data of zone settling velocity (ZSV) and stirred specific volume index (SSVI) for aluminium un-dosed and dosed sludge for five batch settling tests.

Parameter	Control	Dosing Concentration (mg/L)									
		Alum Dosed									
	0	10	20	30	40	50	80	100	150	200	250
Mean ZSV (m/h)	1.49	1.59	1.71	1.84	2	2.11	2.12	2.06	1.52	1.43	1.33
Mean SSVI (mL/g)	87.43	80.8	73.41	68.8	63.24	58.36	58.55	69.24	80.78	100.1	105.5
Mean X (g/L)	2.52	2.65	2.73	2.8	2.86	2.92	2.99	3.09	3.3	3.55	3.76
SD ZSV (m/h)	0.13	0.11	0.08	0.12	0.19	0.28	0.12	0.36	0.23	0.06	0.15
SD SSVI (mL/g)	32.95	29.01	27.04	24.02	21.95	19.4	22.33	23.74	24.1	14.64	15.5
SD X (g/L)	0.25	0.17	0.17	0.16	0.2	0.19	0.13	0.19	0.19	0.18	0.16

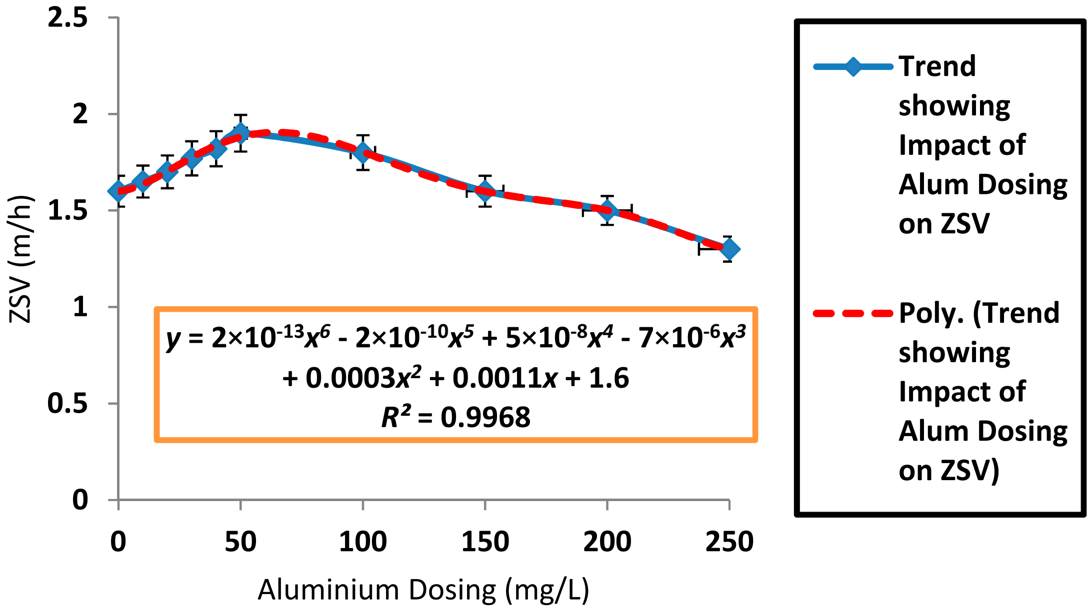

Figure 3. The impact of Al dosing (mg/L) on ZSV (m/h) (error bars represent standard deviation of the mean).

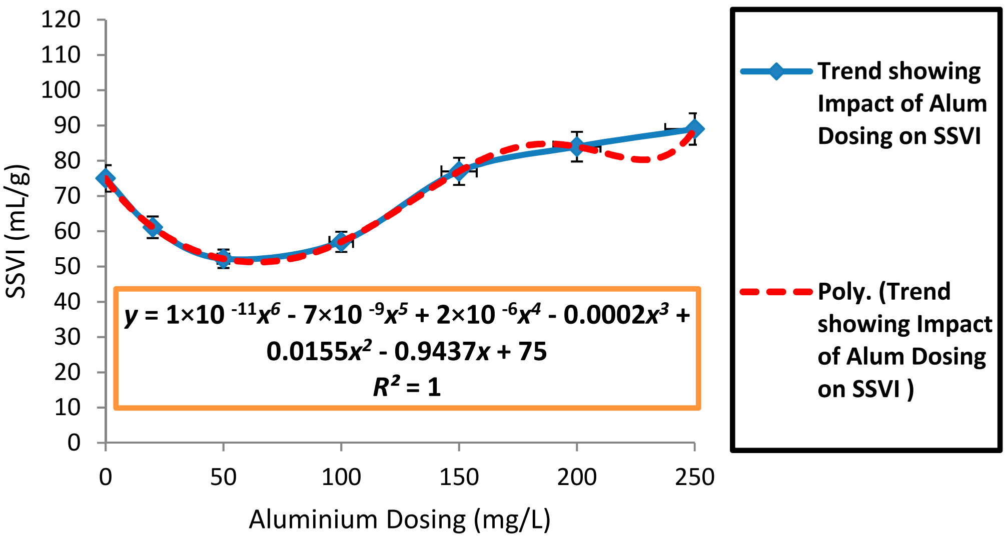

Figure 4. The impact of Al dosing (mg/L) on SSVI (mL/g) (error bars represent standard deviation of the mean).

The improvement noticed in activated sludge settleability (low SSVI and high ZSV) at initial aluminium dosage rates (10 to 100 mg/L) observed can be attributed to the surface charge theory of the activated sludge [24,30]. Forster [36] explained that the theory of bulking could be based on filamentous bacteria concept, but Urbain et al. [11] reported that filament content in activated sludge is not the only issue contributing to activated sludge settleability: other factors like surface chemistry of the sludge contributes to poor settling sludge within the FST. The impact of aluminium dosing can be further explained through charge neutralisation of negatively charged colloids by cationic hydrolysis products [10]. Previous studies by Urbain et al. [11] supported that the overall activated sludge floc structure is negatively charged due to the physical and chemical interactions between floc bacteria, extracellular polymeric substances (ECPS), and multivalent cations. It was posited that aluminium dosed salts have the potential to be strongly immersed by the surface of sludge flocs because of the produced positively charged metal hydroxides which account for the charge neutralisation process and charge reversal during periods of aluminium overdosing. In the present study, the observed behaviour of the SSVI that initially decreased at a dose rate of (10 to 100 mg/L) and started increasing significantly at 150 mg/L dose concentration may be due to charge reversal as a result of over dosed aluminium coagulant. Two competing reactions are predominantly involved in the precipitation of phosphorus by aluminium namely; formation of aluminium hydroxide and aluminium phosphate (Equations (8) and (9)) [37]. Although there are other more complex hydrolysis products that could be formed, the reaction in Equation (9) is more thermodynamically and kinetically favoured over the reaction in Equation (8). At the lower dosing concentration, the formation of $AlPO_4$ is predominant. However, at the higher dosing concentrations when the phosphates in the wastewater have been precipitated, the excess alum results in the formation of hydroxides as in Equation (8). This is responsible for the disintegration of the overall floc structure at higher alum concentration resulting in the drop in ZSV and increase in the SSVI.

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \quad (8)$$

$$Al^{3+} + PO_4^{3-} \rightarrow AlPO_4 \quad (9)$$

Researchers have also reported that ECPS could impact the activated sludge settling processes and physicochemical properties of activated sludge flocs (surface charge) due to the ability of its internal layer to tightly bound and adhere closely with strong stability to the cellular surface [13,38]. In support of this claim, Wang et al. [16] reported similar linear relationship between loosely and tightly bound

ECPS and SSVI since the activated sludge flocs are reported to be embedded in the ECPS structure and the amount of ECPS extractable from the activated sludge is positively related to SSVI [7,14,15]. In the current study, the observed trend in the SSVI with increasing chemical dosing could be explained through ECPS binding capacity to microbial cells through its bridging nature with aluminium and overall impact on the ECPS content in the activated sludge flocs [13,38,39]. This is supported by the observations in Figure 1a–e which showed improved bioaggregation at lower aluminium dosing concentrations compared to the undosed sludge. It has also been previously reported that negatively charged mineral and sludge particles can form flocs by cation bridging when multivalent cations are dosed into an ASP [40].

The improvement in settleability of the activated sludge at lower Al^{3+} concentations can also be attributed to ability of aluminium to neutralise the sludge surface charge [18,19], and decreased surface charge is related to decrease SSVI values [7,41,42] and ability to form larger flocs due to higher valence and low solubility [20]. The decrease in ZSV and increase in SSVI and hence decreased settleability at the higher dose concentrations are attributed surface charge reversal linked to high aluminium dosing rate and high surface charge which is a function of weaker bonding between the various sludge floc fractions resulting to the breakage of the general activated sludge floc structure [1,29,42,43]. The reduction in the ZSV values with increasing SSVI also indicates a sludge with a slow settling rate that may hinder the activated sludge compressibility and underflow concentration within the FST [30].

4. Conclusions

The impact of aluminium dosing for CPR on activated sludge settleability (ZSV and SSVI) was studied in batch settling tests over a three-year period using a type 305 settlometer. The surface morphology of the dosed and undosed sludge samples was also investigated using SEM. The results showed that ZSV increased while SSVI decreased with increasing dose of Al^{3+}. The best settleability was achieved at 50 mg/L dose of Al^{3+}. The improved settleability with increasing dose of Al^{3+} was attributed to the improve bioaggregation of the activated sludge with dosing as shown by the SEM and through ECPS binding capacity to microbial cells through its bridging nature with aluminium. The sludge settleability started to decline at about 100 mg/L dose concentration, completely disintegrating at 200 mg/L. The decrease in ZSV and increase in SSVI and hence decreased settleability at the higher dose concentrations are attributed to surface charge reversal linked to a high aluminium dosing rate and high surface charge which is a function of weaker bonding between the various sludge floc fractions resulting in the breakage of the general activated sludge floc.

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