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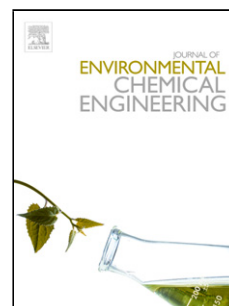
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Modelling the effects of ferric salt dosing for chemical phosphorus removal on the
settleability of activated sludge

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Highlights

- The effects of Fe^{3+} salt dosing on the settleability of activated sludge was modelled
- ZSV increased and SSVI decreased with increasing dose of Fe^{3+} up to 50 mgL^{-1}
- New settleability models for ZSV and SSVI for Fe^{3+} dosed sludge were proposed
- Proposed models correlated with experimental data from a full-scale ASP plant.

Abstract

There is a growing utilisation of ferric salts (Fe^{3+}) for precipitation of phosphorus from wastewater due to tighter regulatory limits for wastewater effluent discharge. The effect of Fe^{3+} dosing on activated sludge settleability indicators; zone settling velocity (ZSV) and stirred specific volume index (SSVI) were examined in laboratory-based batch settleability tests over a three years period. The experimental data revealed that ZSV increased with increasing dose of ferric salt as SSVI decreased with the highest changes obtained at a dose rate of 50 mgL^{-1} . Fe^{3+} facilitated the agglomeration of the activated sludge flocs, thereby improving settleability. At $>50 \text{ (mgL}^{-1})$ of Fe^{3+} , there was a slight breakdown in sludge settleability due mainly to surface charge reversals. The modelling of the settleability of ferric sludge in recent wastewater engineering practice for design and improvement purposes is presently based on conventional empirical sludge settleability models. This paper proposed a new activated sludge

settleability model that describes the effects of Fe^{3+} dosing on the ZSV and SSVI of activated sludge. The exponential form of the Vesilind equation was optimised and validated to include ferric chemical dosing parameters. The proposed ferric settleability equations were found to effectively describe the settling characteristics of ferric sludge.

Keywords

Activated sludge, Settleability, Zone Settling Velocity, Ferric salt, stirred sludge volume index.

1. Introduction

Increasing economic development and continuous rise in the human population are adding to the burden of phosphorus (P) discharges into our receiving waters leading to eutrophication problems [1,2,3]. To achieve the increasingly stringent effluent P consents of 1 mgL^{-1} or less as a result of the EU Water Framework Directive, the activated sludge plants (ASP) is predominantly used by water companies in the EU [4,5, 6]. The ASP comprises of both a biological and solid-liquid separation processes and the efficiency of the ASP depends on effective liquid-solids separation within a quiescent environment of the final sedimentation tank (FST) [7]. To achieve effluent P removal in ASPs, chemical phosphorus removal with ferric and aluminium salts is predominantly used [6].

Ferric salts have merit over other coagulants used in phosphorus removal and are effective in the removal of P from wastewater and also being a low cost product [3,8,9]. The most obvious impact of ferric salt on wastewater treatment plant (WWTP) is the hydrolysis reactions of the ferric salts during P-removal process [10] and the potential surface charge neutralisation of negatively charged colloids by cationic hydrolysis products [11,12]. The presence of a high concentration of iron resulting from the CPR process alters the overall sludge characteristics and likely to impact the activated sludge settleability.

Activated sludge settleability is a very complex and not yet fully understood [13]. The FST produces a full clarified effluent overflow and determines the level of effluent quality in the ASP [14, 15, 16]. Also, the increasing use of ferric and ferrous salts for CPR has changed the traditional sludge characteristics. Therefore, an adequate understanding of the effects of CPR on activated sludge settleability characteristics is vital for proper design and operation of the FST [17].

Empirical models have been developed to describe the settling characteristics of activated sludge. The solid flux theory was developed by Kynch [18] to evaluate the performance of FSTs. Other models have described a correction between activated sludge concentration (X) and zone settling velocity (ZSV) [19, 20]. However, the most suitable empirical model for forecasting the sludge settleability characteristics within the FST is the Vesilind 1968 model expressed in Equation (1).

$$\mathbf{ZSV = v_0 \exp(-kX)} \quad (1)$$

Where,

ZSV = zone settling velocity

X = activated sludge concentration (gL^{-1})

v_0 = sludge settleability constant (mh^{-1})

k = sludge settleability constant (Lg^{-1}).

The settleability constants k and v_0 from Equation (1), can be gotten from the gradient of batch test settling curves. Haandel & Lubbe [21], described the relationship between ZSV (Vesilind 1968 equation) and sludge volume index (SVI), diluted sludge volume index (DSVI), and stirred sludge volume index (SSVI) using empirical models. Nonetheless, studies have explained the effect of settling velocity with varying sludge concentrations and density [22]. Results obtained were in agreement with Vesilind [20] who reported that as activated sludge concentration increased in zone settling test, settling velocities reduces but a non-linear relationship between the settling velocity and buoyant density was observed. A new model that included the buoyant density parameter was also proposed [23].

The modelling of the design and optimisation of activated sludge settleability in the industry today, is based on the Pitman and White settleability model. The Pitman and White [24, 25] model is based on Vesilind [20] equation. The Pitman & White model is shown in **Equation (2)**. The SSVI (mL/g) is the volume of a unit mass of suspended solids after 30 min of settling and v_0 and k are sludge settleability constants.

$$v_0/k = 68\exp(-0.016SSVI) \quad (2)$$

Where,

SSVI = Stirred sludge volume index (mLg^{-1}).

The Pitman and White model was designed mainly on the settling behaviour of conventional activated sludge (CAS), but with the increasing usage of ferric salts in the precipitation of phosphates today, the rheology of conventional sludge on which the pitman and white model was built has changed significantly due to high metal contents [6]. Therefore, there is a need to develop a new model that describes the settling properties of chemically dosed activated sludge (CDAS). This paper is an attempt to develop a new CDAS model that describes the effects of the varying concentration of ferric dosing on activated sludge settleability indicators. The proposed new model equation will address the limitation of Pitman and White model for the modelling of the settleability of CDAS and describe the effects of the varying concentration of ferric dosing on activated sludge settleability indicators.

2. Materials and Methods

2.1 Activated sludge sampling and analysis

Samples were collected over a three years period from a full-scale wastewater treatment plant (WWTP) in the West Midland of the United Kingdom. The mixed liquor samples were collected in plastic containers from the distribution chambers prior to any chemical addition for the settleability experiments. The mixed liquor suspended (MLSS) solid samples ranged from 2800 to 3500 mgL^{-1} , with the pH ranging from 6.5 to 7.5 and a phosphate concentration of 7 to 12 mgL^{-1} . All analysis was

completed within 24 hours of wastewater sampling. The detailed methodology was recently described in Ojo & Ifelebuegu [6].

2.2 Settler Tests and Scanning Electron Microscope

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 the mixed sample was transferred into a 5 L beaker and treated with a varying concentration of a Fe^{3+} (0, 10, 20, 30, 40, 50, 100 and 150 mgL^{-1}) to mimic the CPR process. The samples were stirred for 10 minutes at 2 revolutions per minute (rev/min) using an overhead stirrer before being used for the settler test.

The standard Water Research Council (WRC) settling test [26] was performed in a 3.25 L type 305 settler equipment (Triton Electronic Ltd, Cambridge, UK) with 100 mm diameter and 500 mm height, a slow speed stirrer (1 rev min^{-1}) used to prevent any event of sludge bridging to the wall. The settleability process has been previously described [27]. The equations used to estimate the settled solid volume (SSV) (mLL^{-1}), mixed liquor suspended solids (MLSS) (gL^{-1}), SSVI (ml/g) and ZSV (mh^{-1}) results have been reported in previous studies [28]. Scanning electron microscope of the sludges was carried out using SEM (Joel-6060LV, Japan).

2.3 Data Analysis and Model validation

The measured ZSV and SSVI from the three years batch settling tests were used in modelling new ferric dosed activated sludge settleability. The results of the batch tests were analysed using the Minitab 17 software and solver optimisation tool. The solver parameter in the solver optimisation tool was used to set for a target objective of a reduced sum of square deviation (SSD) value so that the model fits the experimental data while the Minitab allows the design of an experimental model for investigation of the impact of input variables on the response variable at the same time. Results were also analysed using the non-linear regression in the software and R^2 (coefficient of determination), residual plot, probability plot and interval plot was used to validate how the ZSV model fits the ZSV experimental data.

3. Results and Discussion

3.1 Effects of Ferric dosing on activated sludge morphology

The structure of the sludge flocs for the control sample (0 mgL^{-1}) and ferric dosed ($50, 100$ and 150 mgL^{-1}) were evaluated using SEM and the result showed interfloc bridging, open floc formation and spindly bulking potential in the control sample (Fig. 1a) whereas in the Ferric treated sample (50 mgL^{-1}) some decrease in interfloc bridging, sludge porosity, and some enhanced sludge compaction was noticed (Fig. 1b). However, a more enhanced sludge compactibility was observed when the ferric dosing concentration increased from 100 to 150 mgL^{-1} (Fig. 1c and d). This result (Fig. 1c and d) when compared to 50 mg/l treated sludge sample demonstrated better sludge compaction (Fig. 1b). It can be concluded that the sludge floc with enhanced compactibility will improve activated sludge settleability and produce the best effluent quality. This result findings in ferric dosed sludge microscopic analysis agree with previous results [29,10,28] on sludge bio-flocculation and improvements in sludge settleability.

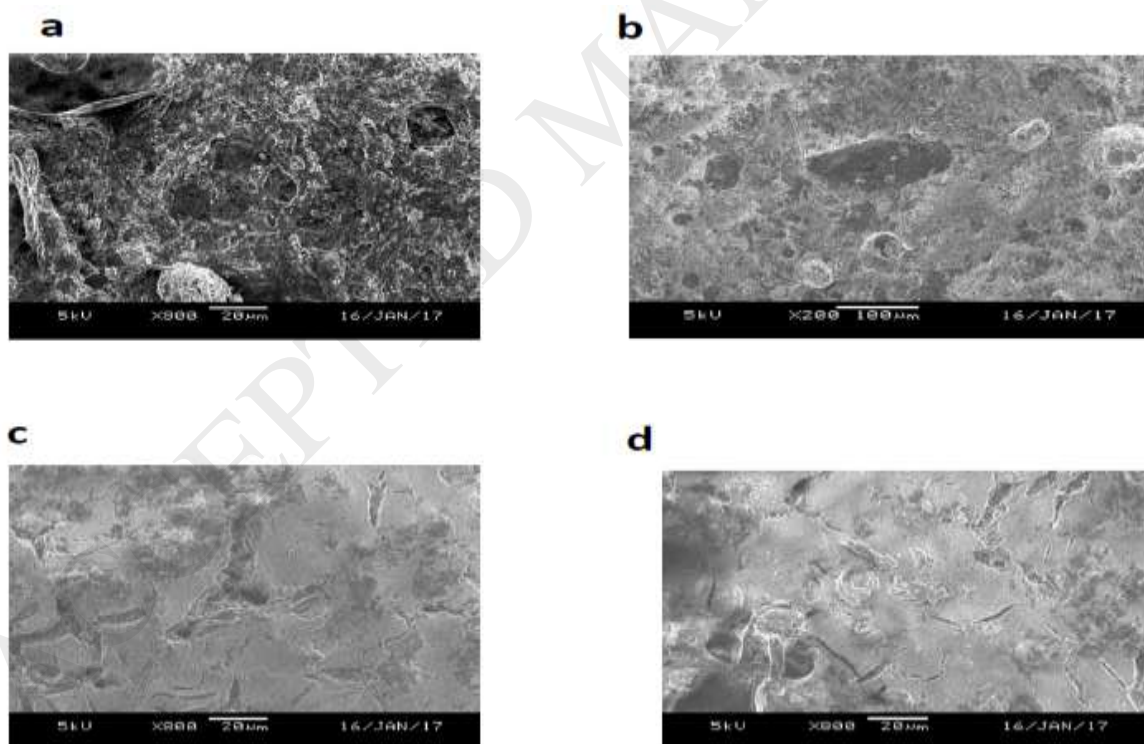


Fig. 1. SEM of sludge floc (a) control (0 mgL^{-1}); (b) Fe-Dosed (50 mgL^{-1}); (c) Fe-Dosed (100 mgL^{-1}); (d) Fe-Dosed (150 mgL^{-1}).

Besides, wet samples were dosed with 50mgL^{-1} ferric and investigation was conducted and comparison was made between the un-dosed wet sludge sample and 50mgL^{-1} ferric dosed sludge using a light microscope. It was observed in the control sample (0 mgL^{-1}) that filament extended into the bulk solution before treatment with ferric (Fig. 2a) but when treated with the addition of ferric (50 mgL^{-1}), the length of the filament was reduced to smaller length (Fig. 2b) and further improvement was noticed in Fig. (2c-d). The results in Fig. 2b-d agreed with previous result [13]. This is an indication that Fe^{3+} dosed sludge has the capacity to impact the length of the filament in filamentous organism present in activated sludge (Fig. 2c) and reducing them to smaller filaments that may be washed away in the settling column (Fig. 2d).

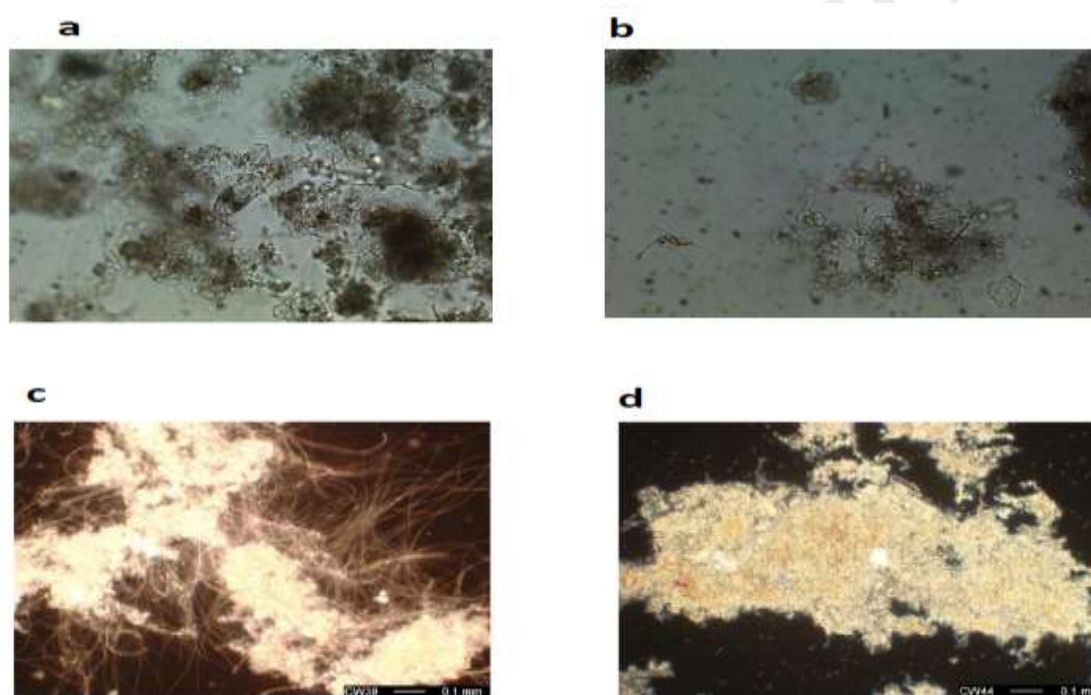


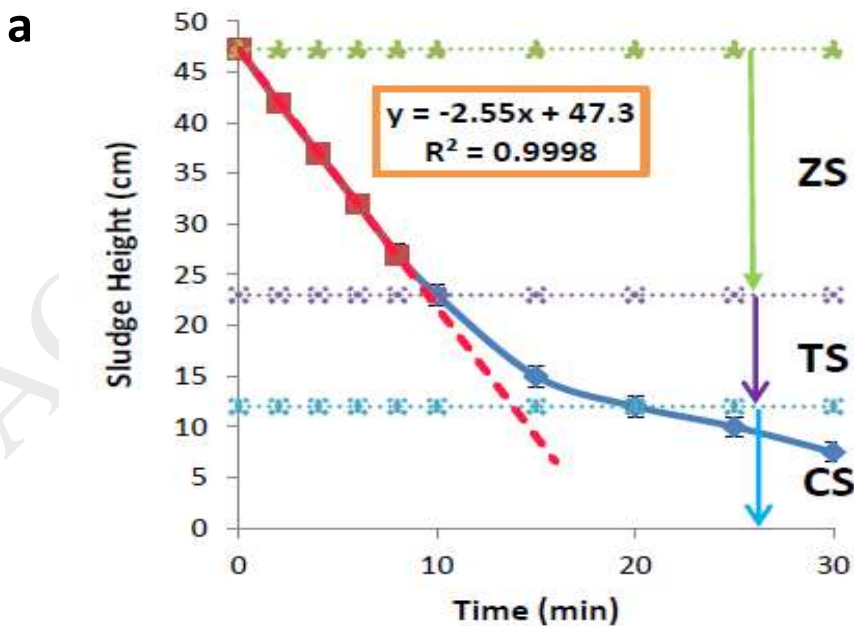
Fig. 2. Light Microscope of sludge floc on wet basis (a) control (0 mgL^{-1}); (b) Ferric -Treatment (50 mgL^{-1}); (c) Control (0 mgL^{-1}); (d) Ferric Treatment (150 mgL^{-1}).

3.2 Effects of Ferric Dosing on ZSV and SSVI

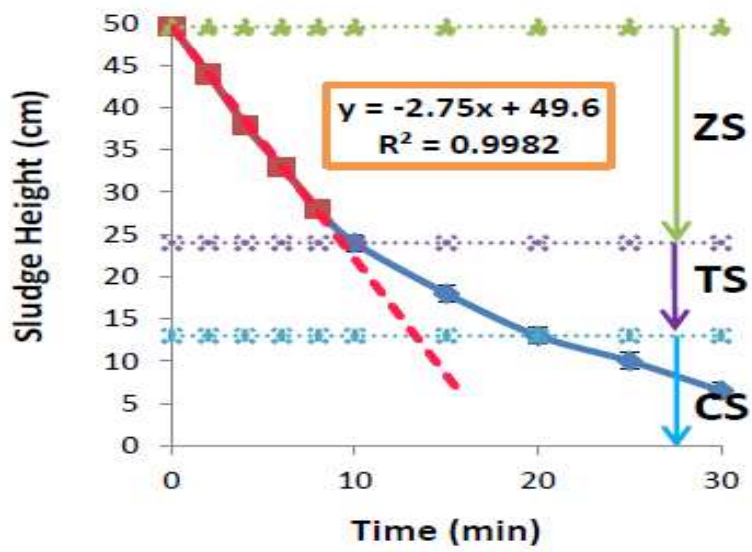
The ZSV were investigated over a range of un-dosed and ferric dosed activated sludge concentrations ($0, 10, 20, 30, 40, 50, 100$ and 150 mgL^{-1}) for 3 batch experiments. The results from a representative ZSV test are shown in Fig. 3a-g which shows that about 50% of the initial sludge volume within the

sludge depth of the settlometer settled after 5 to 10 minutes for both the control and ferric treated sludge. It was observed from zone settling curve (ZSC) that at first the activated sludge settleability was quicker due to an uninterrupted free settling within the settling column. On the other hand, after the first 10 mins of settling the change in the sludge height with time (ZSV) began to drop. This is in agreement with the observation in previous work [20, 28], the reason can be attributed to the individual sludge particles slowing down their individual settling velocities and because of the sludge floc to floc collaboration based on their close proximity. Consequently, within the zone settling regime, the observed bioaggregation of sludge flocs tends to settle as a zone of sludge blanket. This explains the decrease in the settling velocity [30].

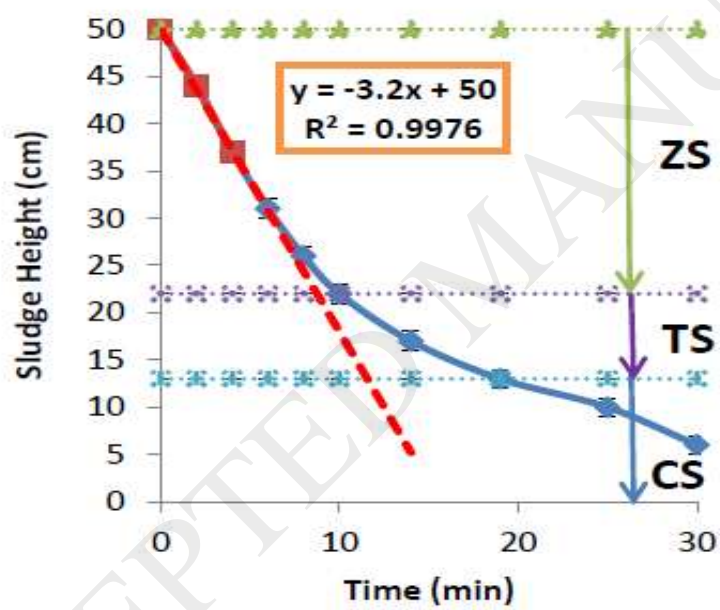
Furthermore, as the settling velocity began to approach the zero axes, there was observed dehydration of water from the sludge floc pore spaces and this was attributed to the compressive forces acting on the sludge flocs since the sludge floc has entered a compression settling regime. The linear portion of the ZSC's (Fig. 3a-e) represents the settling velocity of the sludge flocs and it was further explained in previous work [31] that there is a relationship between the sludge concentration and settling velocity. It was affirmed that a rise in the sludge concentration will result in a lower settling velocity due to greater resistance to water flow as the sludge passes through the settling sludge column.



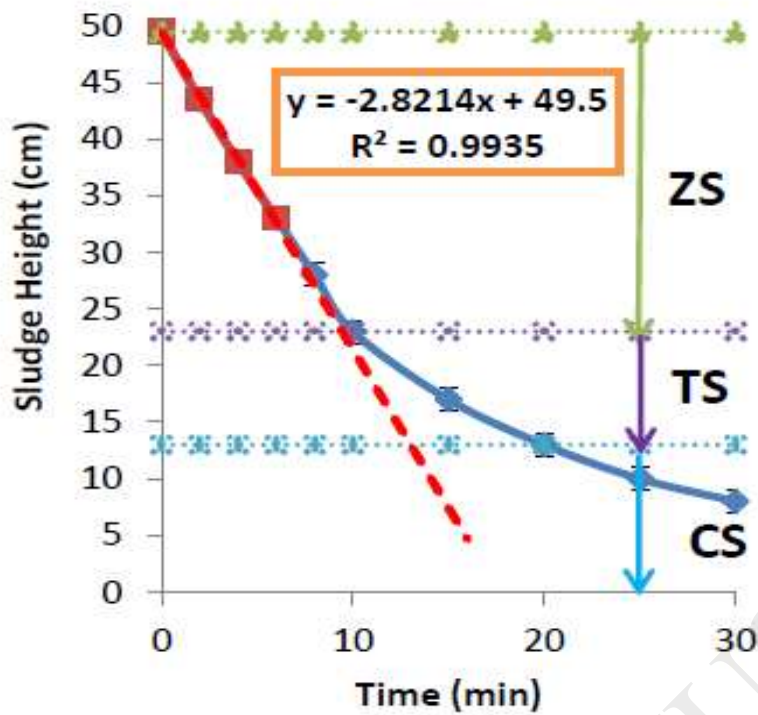
b



c



d



e

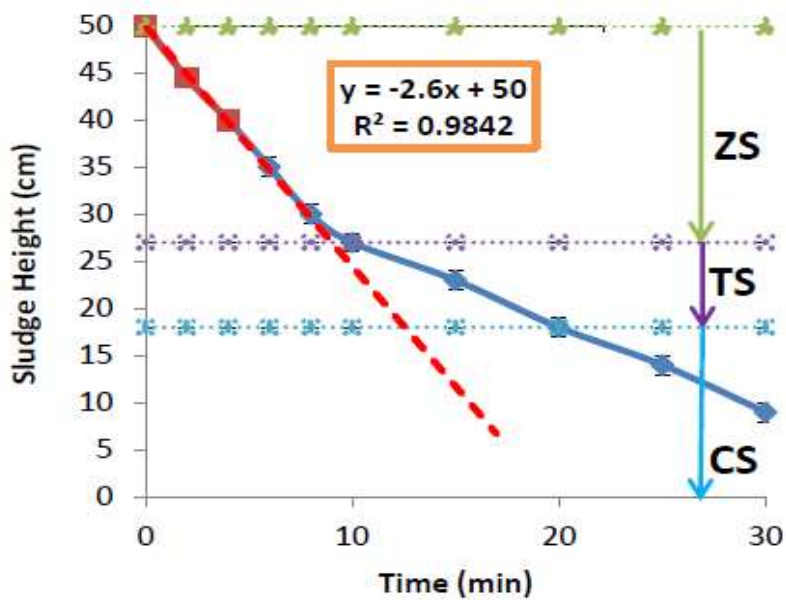


Fig. 3. ZSC for MLSS (a) Undosed 0 mgL⁻¹ (b) Ferric dosed 20 mgL⁻¹ (c) Ferric dosed 50 mgL⁻¹ (d) Ferric dosed 100 mgL⁻¹ (e) Ferric dosed 150 mgL⁻¹ (ZS = zone settling, TS = transition settling, CS = compression settling, error bars represent the standard deviation of the mean). The ZSV was obtained from the slope of the linear graph.

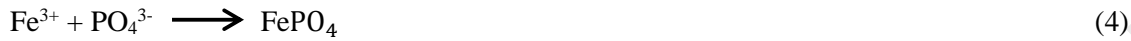
Table 1. Mean and Standard deviation (SD) data of ZSV and SSVI for ferric undosed and dosed sludge for three batch settling test

Parameters	Dosing concentration (mgL^{-1})							
	Control	Ferric dosed						
	0	10	20	30	40	50	100	150
Mean &SD								
ZSV(mh^{-1})	1.54± 0.05	1.63±0.03	1.71±0.03	1.80±0.06	1.90±0.08	1.94±0.11	1.79±0.08	1.66±0.05
Mean &SD								
SSVI(mLg^{-1})	67.71±8.72	63.45±7.36	59.47±6.53	54.84±5.64	50.89±5.27	47.11±5.05	58.31±3.74	63.27±4.5
Mean &SD								
(X) (mgL^{-1})	2.43±0.08	2.57±0.06	2.66±0.10	2.74±0.11	2.79±0.10	2.82±0.07	2.96±0.22	3.08±0.18

The enhancement observed in the activated sludge settleability with a decreasing SSVI and increasing ZSV between ferric dosage rates (10 and 50mgL^{-1}) (Table 1) can be ascribed to surface charge chemistry of the activated sludge [9]. It was reported filament that content in activated sludge causes sludge bulking [32] but, it was added that charge neutralisation of negatively charged colloids by cationic hydrolysis products also affects the sludge settleability [15]. The further relationship has also been observed between floc bacteria, extracellular polymeric substances (ECPS) and multivalent cations.

Nevertheless, the hypothesis was made that ferric dosed salts have the capacity to be sturdily absorbed by the surface of sludge flocs because of the released positively charged metal hydroxides which explain the charge neutralisation process and charge reversal during periods of ferric overdosing [33]. In the current study, the observed characteristics of the SSVI that first reduced at a dose rate of (10 and 50mgL^{-1}) and then began to rise at 100mgL^{-1} dose concentration (100 to 150mgL^{-1}) may be linked to charge reversal as a result of over dosed ferric coagulant. Equations 3 and 4, shows the two competing chemical reaction that takes place during precipitation of phosphorus by ferric, namely formation of

ferric hydroxide and ferric phosphate. The higher dosing concentrations of ferric when the phosphates in the waste water have been precipitated, the excess ferric results in the formation of hydroxides as in Equation 3. This is accountable for the fragmentation of the overall floc structure at a higher ferric concentration resulting to drop in ZSV and increase in the SSVI.



The activated sludge settleability processes and physicochemical properties of activated sludge flocs are affected by another key process parameter called EPS due to the ability of its internal layer that is tightly bound and adhere closely with strong stability to the cellular surface [30]. In the current study, the pattern observed in the plot of SSVI with increasing ferric dosing (Fig 3) may possibly be described by the EPS binding capacity to microbial cells and its bridging nature with ferric and its overall effect on the EPS content in the activated sludge particulate [34]. This is reinforced by the observations in Fig. 1a-d which exhibited improved bioaggregation with increasing lower ferric dosing concentrations when related to the control sludge. The enhancement in activated sludge settleability at increasing Fe^{3+} concentrations have been attributed to the ability of ferric to neutralise the sludge surface charge. The reduced surface charge has equally been related to decrease SSVI values and ability to form bigger flocs due to higher valence and low solubility [35]. The decrease in ZSV and increase in SSVI and hence decreased activated sludge settleability at the greater ferric dose concentrations are ascribed to surface charge reversal linked to high ferric 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 structure [36, 9].

4.2 Model development and Model validity for Ferric dosed sludge

SVI is one of the sludge settleability parameter used to evaluate the settling characteristics of activated sludge in activated sludge processes. The reason due to the simplicity with which the SVI (unstirred) test is been conducted. Conversely, previous research studies have addressed some key issues relating to SVI since there is no consistent relationship between SVI and suspended solids concentration in mg/l (MLSS) [30]. Further investigations suggested a gentle stirring regime (1 -2 revolution per minute)

which led to the proposed stirred specific volume index (SSVI) test using a 4L-settling column instead of the 1L-settling column in unstirred SVI test. Since SVI is defined as the volume occupied per unit mass of sludge particulate (mLg^{-1}) after 30 minutes of settling; it suggests that SVI is a function of settling velocity all through the settling column where the activated sludge vary with respect to time (t) and settling height (H). Nevertheless, using the SVI as a variable in the evaluation of the real settling in FSTs is argumentative because the test relies on the initial sludge concentration before it is being realised, which refutes the expectation of a true process parameter for sludge settleability.

Since FST plays a vital role in the efficiency of activated sludge plant, and its design and operation requirement is based on the developed solid flux theory (solid -liquid separation process under the influence of the downward force of gravity) [18], the evaluation of ZSV in the modelling and design of the FST becomes paramount [37]. This is because the applicability of the solid flux theory is based on the solid flux curve, in which the solids flux (product of sludge concentration and zone settling velocity-ZSV) is plotted against the sludge concentration (X, mgL^{-1}). Given the limitations of SVI, the zone settling velocity test (ZSV) approach was introduced that allows settling velocities to be evaluated over a range of activated sludge concentrations (X) and the rate of zone settling in the settling column where flocs are in proximity to each other are deduced. The resultant ZSV values are then used to regulate various models relating the settling velocity and solids concentration.

Although, other researchers have utilised the empirical relationship with the sludge settleability parameters such as SVI, diluted sludge volume index (DSVI) and SSVI to obtain the Vesilind v_0 and k parameter [38,39]. The research conducted involving analysis of six years full scale study resulted in the development of an empirical relationship between the constants of Vesilind's equation and SSVI. The correlation obtained was expressed in Equation (2) ($v_0/k = 68 \exp(-0.016\text{SSVI})$). Further studies were conducted [40-41] and the finding of Dick and Young [41] revealed the correlation between zone settling velocity and sludge index(SVI) in Equation 5:

$$\text{ZSV} = V_0 X^K \quad (5)$$

The capital V_0 and K are Dick and Young sludge settleability constants. The V_0 explains the impact of sludge settleability on the actual settling velocity while the K explains the effect of sludge settleability on sludge compaction (SVI). Further researches along with other researchers [40-43], came up with the findings that Pitman's empirical expression in Equation 2 resulted in a good description for all and that a relationship exists between V_0/K and k . This was expressed as in Equation 6:

$$K = 0.88 - 0.393 \log(v_0 k) \quad (6)$$

However, since the value of k is known then the value of v_0 can be computed as follows using Equations (2 and 6).

$$V_0 = (V_0/K)k \quad (7)$$

However, it is challenging to investigate settling behaviour of activated sludge at low concentrations specifically below 1 kg/m^3 due to no interaction with the sludge particles and no clear relationship exist with the concentration of activated sludge particles at low sludge concentration. Therefore, the settling velocity will be a function of individual floc properties. This challenge was resolved by other researchers by utilising Vesilind functions in different ways to determine the settling process at low concentration namely; modelling directly the functions [44] and defining particles with different velocities [45-46]. Previous studies reported the investigation of their own data from unit processes in South Africa [47] and concluded that Vesilind's equation gave a better description of the actual settling performance of activated sludge. Following a further result from research conducted by [48- 49], rearranging Equations (5)-(7) will make it possible to express k and v_0 as a function of SSVI which can be expressed as follows:

$$k = 0.16 + 0.0027SSVI \quad (8)$$

$$v_0 = (10.9 + 0.18 SSVI) \exp(-0.016SSVI) \quad (9)$$

The empirical coefficient v_0 and k are obtained by performing ZSV test over a range of mixed liquor suspended solids (MLSS) concentration for sludge samples. Upon substituting Equations (8 and 9) into Equation 2 and Equation (10) is obtained:

$$v_0 = (11.2 - 0.06SSVI) \quad (10)$$

It can be concluded that [48-49] findings agree with the earlier mentioned researchers view and that Equation (8 and 10) can be utilised to compute the constants k and v_0 directly from the SSVI values without conducting a ZSV test. Therefore, Vesilind equation has been adopted as the foundation for describing activated sludge settling in an FST.

In the present study, the batch settling test measurements (Zone Settling Curve (ZSC)) of ZSV reveals ZSV as a linear representation (Fig. 3a-g) of sludge height as a function of time (m/h) for ferric dosed sludge but a non-linear representation of ZSV and SSVI as a function of ferric dosing concentration was observed in Fig. 4 and Fig. 5. In Fig.4 there was an initial increase in the ZSV values with increasing ferric dosing concentrations (10, 20, 30, 40 and 50 mgL^{-1}) and began to decline beyond 50 mg/L dose concentration. The opposite effect was noticed in Fig.5 with the SSVI, which reduced with rising ferric dosing rate of up to 50 mgL^{-1} . However, it was further noticed that the SSVI started to rise at a dosing concentration of 100 and 150 mgL^{-1} . This provided an insight into the modification of the conventional empirical model of ZSV (Equation 1) to include a new ferric dosing parameter. It further reveals the impact ferric (Fe) dosing concentration on ZSV and SSVI as a non-linear correlation which is contrary to empirical Vesilind deduction of ZSV.

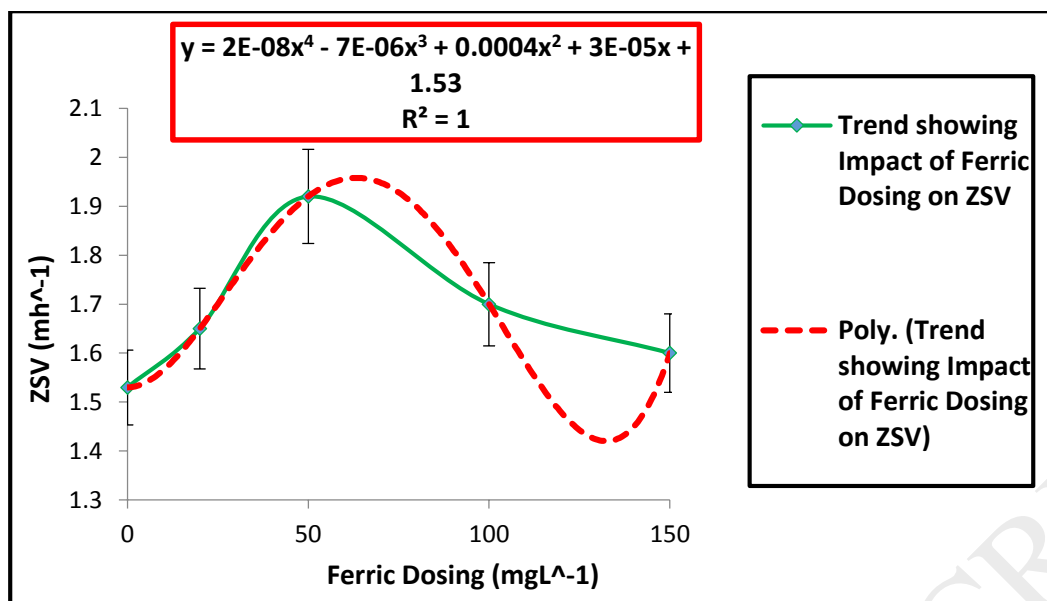


Fig. 4. The Impact of Fe Dosing (mgL⁻¹) on ZSV (mh⁻¹)

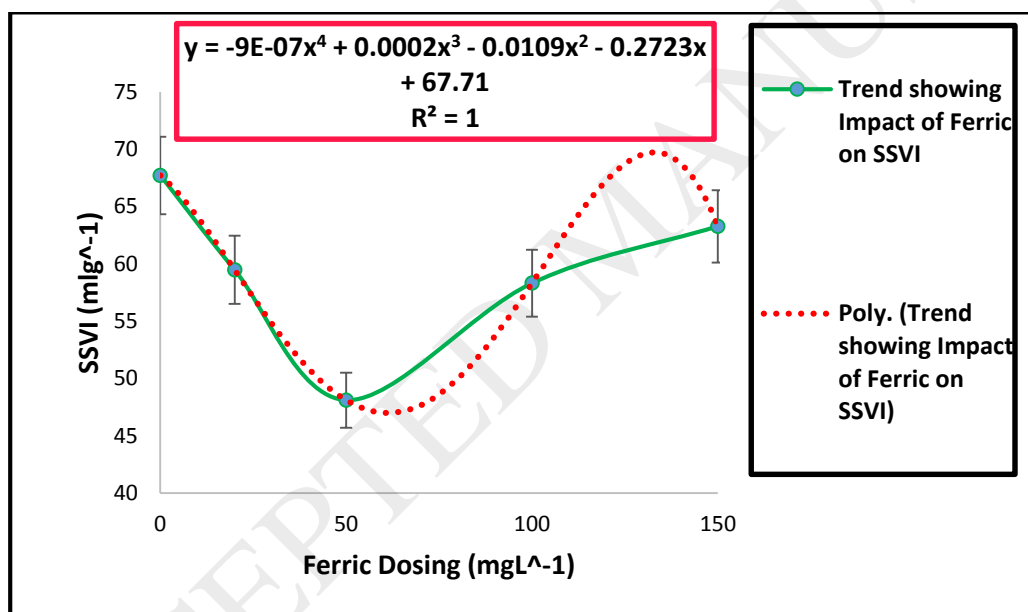


Fig. 5. The Impact of Fe Dosing (mgL⁻¹) on SSVI (mLg⁻¹)

The conventional empirical model for sedimentation in FST's expressed as a function of solid concentration, termed Vesilind equation is illustrated in Equation 1. The empirical coefficient v_0 and k are obtained by performing ZSV test over a range of mixed liquor suspended solids (MLSS) concentration for both un-dosed and ferric dosed sludges as mentioned earlier and applying linear regression to the linearized form of the vesilind equation to obtain a new expression in Equation 11.

$$\ln ZSV = -kX + \ln v_0 \quad (11)$$

The plot of the natural log of ZSV (mh^{-1}) against un-dosed and the ferric dosing concentration for the average data from the various batch test (Table 1) is shown in Fig 6. The negative of the gradient of each linear regression for the batch test is the Vesilind K value while the intercept is the Vesilind v_0 parameter. However, because it is a ferric dosed sludge, then Vesilind v_0 and k expression becomes re-defined as ZSV_0 and K_d for Fe dosed sludge. There is a need to define that there is a relationship between ferric dosing concentration and ZSV which was not accounted for in the conventional Vesilind model equation in Equation 3. This can be achieved by the transformation of data in the Vesilind exponential relationship and back tracking to calculate the values of the Vesilind exponential constant parameter. Thus, the linearised ZSV was plotted against Fe dosing up to 150 mgL^{-1} (Fig 6) However, it was observed from Fig.6, that the relationship between ferric dose concentrations and the settleability can be accurately described for up to 50 mgL^{-1} dose concentration (Fig. 7) and the gradient and intercept accounted for the Vesilind coefficients for Fe ($K_d = -0.0042$ and $ZSV_0 = 1.534 \text{ mh}^{-1}$). It can be concluded that the calculated ZSV_0 and K_d parameter for Ferric and dosed sludge from the graph of $\ln ZSV$ against Fe dosing concentration is a function of ferric dose concentrations up to 50 mg/L .

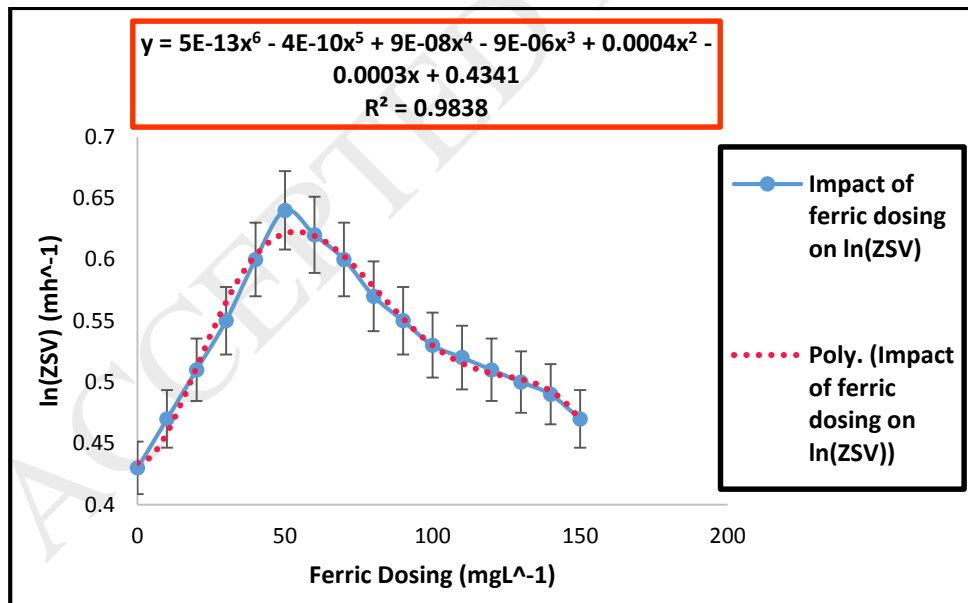


Fig. 6. Natural log of ZSV against Ferric Concentration (up to 150 mgL^{-1})

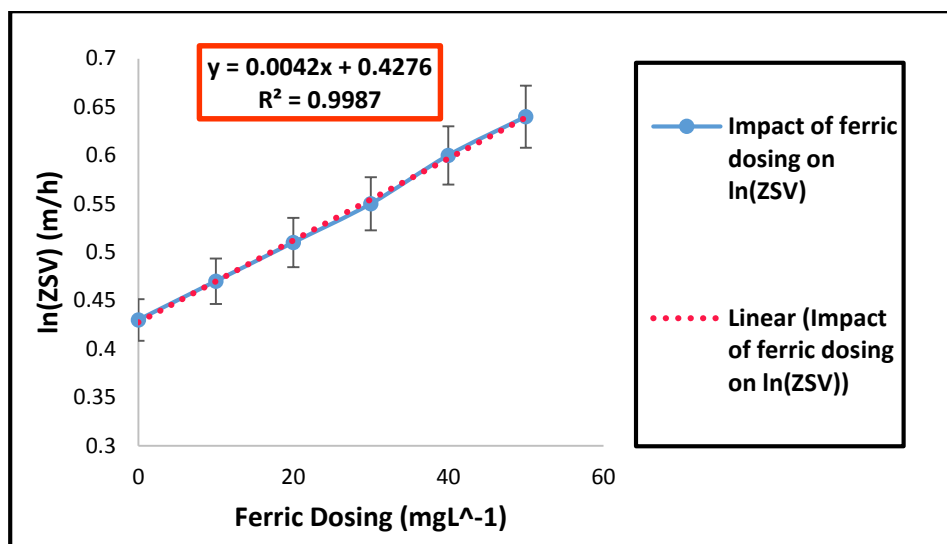


Fig. 7. Natural log of ZSV against Ferric Concentration (up to 50mgL^{-1})

The natural logarithm of SSVI was plotted against the Ferric dosing concentration up to 150mgL^{-1} (Fig 8). Nevertheless, a linear relation existed up to 50mgL^{-1} (Fig. 9) and the gradient and intercept of the plot accounted for the coefficients for Fe ($K_d = -0.0074$ and $ZSV_0 = 68.10\text{ml/g}$).

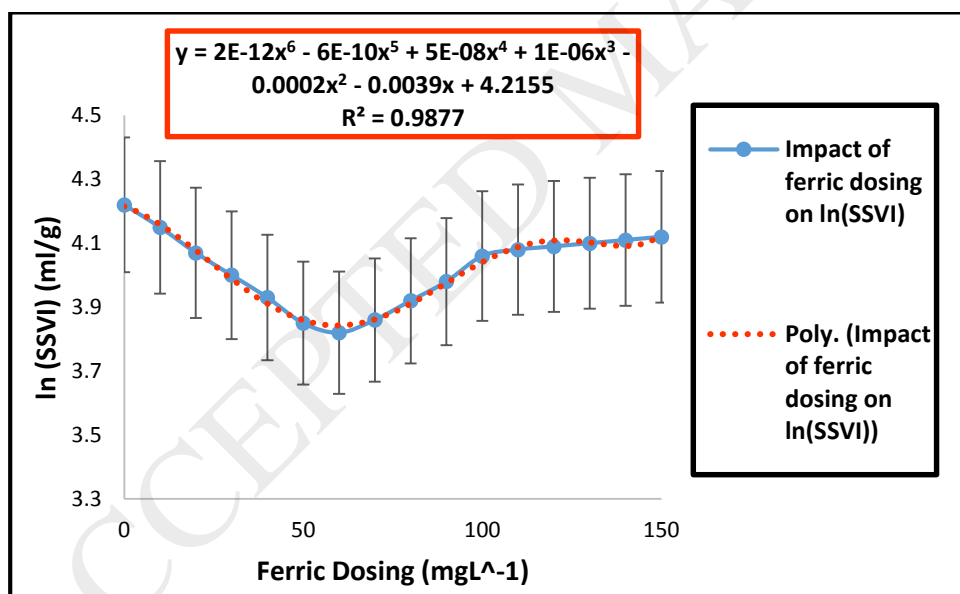


Fig. 8. Natural log of SSVI against Ferric Concentration (up to 150mgL^{-1}) (The error bars represent the standard deviation of the mean)

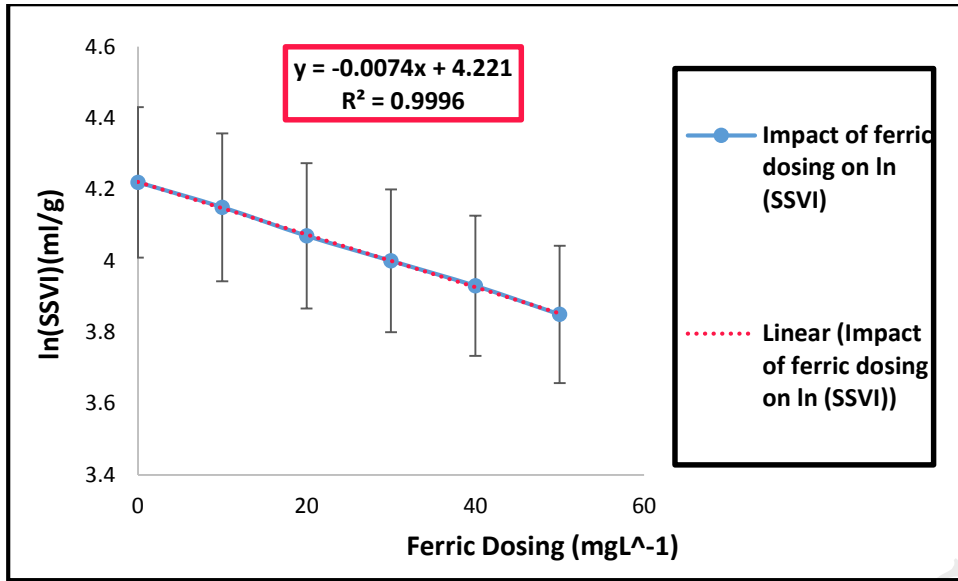


Fig. 9. Natural log of SSVI against Ferric dosing concentration (up to 50mgL⁻¹)

4.3 New Model Calibration to Include Ferric Dosing Parameter

The modelling and control of settling in final settling tanks (FST) in wastewater treatment depends on calibrated models [50]. Model calibration will inform whether or not the proposed new model equation describes accurately the settling behaviour of ferric (Fe³⁺) sludge. The procedure is to check whether the new model fits the laboratory batch test data. The exponential form of the Vesilind equation (Equation 1) can be optimised to include chemical dosing parameter by investigating a new model equation for settling velocity. The investigated ZSV₀ and K_d parameter for Ferric dosed sludge from the graph of ln ZSV and ln (SSVI) against ferric dosing concentration (mg/l) (Fig 6) shows a linearised correlation between ZSV and SSVI with Ferric dosing concentrations. The new empirical model for settling velocity for a Ferric dosed activated sludge can take the form of a decay equation ($A = A_0 \exp(-\lambda t)$) (Equation 12) that obeys the exponential law of decay.

$$A = A_0 \exp(-\lambda t) \quad (12)$$

Where

A = Activity (the number of unstable nuclei remaining), Bq

A₀ = Original number of unstable nuclei, Bq

$e = \text{Constant} = 2.718$

$\lambda = \text{Decay constant, s}^{-1}$

$t = \text{time, s}$

The new equation in Equation 13 shows the inclusion of a new dosing protocol (D_c) that follows the decay equation.

$$ZSV = (C_0 D_c + ZSV_0) \exp - (K_d - C_K D_c) X \quad (13)$$

Where,

$ZSV = \text{Actual settling velocity (m/h)}$

$(ZSV_0)_{Fe} = \text{Maximum settling velocity (m/h) for ferric dosed sludge}$

$(K_d)_{Fe} = \text{Empirical ferric dosed sludge settling parameter relating to sludge compaction}$

$(C_0)_{Fe} = \text{Empirical ferric dosing constant related to stokes settling velocity}$

$(C_K)_{Fe} = \text{Empirical ferric dosing constant related sludge compaction}$

$(D_c)_{Fe} = \text{Ferric dosing concentration (mgL}^{-1}\text{)}$

$(X) = \text{Ferric dosed MLSS concentration (mgL}^{-1}\text{)}$

Equation 13 obeys the exponential law of decay and both the additive and multiplicative rule of exponentials. The empirical coefficients in Equation 13 ZSV_0 and k_d are typically determined by performing zone settling velocity (ZSV) batch tests over a range of ferric dosing concentrations (0, 10, 20, 30, 40, 50, 100 and 150 mgL⁻¹) and applying regression analysis and linear approximation to Equation 10 by taking the natural log.

For a clearer comprehension of the new empirical heuristic expression for settling velocity for a dosed activated sludge, the comparison of terms in the new ferric dosed sludge expression and conventional decay equation becomes vital. The version of terms in Equation 12 compared with Equation 13 is as

follows; $A_0 = (C_0 D_C + ZSV_0)$, $\lambda = (K_d - C_K D_C)$ and $t = X$. This shows below that applying the additive rule with e as a common factor in Equation 13 then Equation 14 is obtained:

$$(C_0 D_C e + ZSV_0 e) = (C_0 D_C + ZSV_0) e \quad (14)$$

On the other hand, applying the multiplicative rule with X as a common factor in Equation 13, the expression in Equation 15 was realised.

$$-(K_d - C_K D_C)X = (\exp - K_d X)(\exp - C_K D_C X) = \exp(-(K_d - C_K D_C)X) \quad (15)$$

The constants ZSV_0, K_d, C_0 and C_K helps in shifting the ZSV model to predict the observed values in ferric dosed sludge. However, the experimentally estimated ZSV data have been universally used for regulating settling models in wastewater industry (Vesilind 1968: $ZSV = v_0 e^{-kX}$). Since it is common practice to deduce the Vesilind empirical constants (v_0 and k) through conducting batch laboratory ZSV test over a range of concentrations and applying linear regression evaluation to a linearized form of Vesilind equation ($\ln V = -kX + \ln v_0$), it becomes paramount to apply the same principle to the new ferric dosed activated sludge model.

We can consider defining F_1 and F_2 from Equation 13 as follows: $F_1 = (ZSV_0 D_C)$ and $F_2 = (K_d - C_K D_C)$ as two functions of ZSV and this gives Equation 16

$$ZSV = F_1 \exp(-F_2 X) \quad (16)$$

As earlier mentioned that there exists an exponential relationship between the ZSV and Fe dosing (Fig. 4) but because the relationship is a non-linear relationship, calculating the value of the new empirical coefficient (ZSV_0, K_d, C_0 and C_K) of ferric dosed activated sludge model can be realised by linearizing Equation 13 to become 16

Therefore, below is the linear approximation (Equation 17) obtained by taking the natural log of Equation 13.

$$\ln(ZSV) = \ln(C_0 D_C + ZSV_0) - (K_d - C_K D_C)X \quad (17)$$

The Equation 17 also follows the equation of a straight line ($Y = MX + C$), $M =$ Slope while $C =$ Intercept and hence Equation 17 can be modified as Equation 18 by re-defining $\ln(ZSV) = Z$; $(\ln C_0 D_C + ZSV_0) = P$ and $(K_d - C_K D_C) = Q$ respectively.

$$Z = P - QX \quad (18)$$

The transformation of Equation 13 to 17 allowed establishing a linear relationship between Z and X (Equation 18) and not between ZSV and X since it is already an exponential model. This transformation allows back tracking the constant of the new model for ferric dosed sludge (ZSV_0, k_d, C_0 and C_K) to predict the ZSV experimental data. Therefore, once a linear relationship is established between Z and X ($Z = P - QX$), the value of the ferric dosed settleability constants (ZSV_0, k_d, C_0 and C_K) can be evaluated and the experimental value of ZSV and dosing concentrations (D_C) without performing a ZSV batch experiment. A new expression (19 and 20) was obtained from Equation 18 for calculating the value of D_C as it relates to ferric when the four constants (ZSV_0, k_d, C_0 and C_K) for ferric dosed sludge are known.

$$D_C = (e^P - ZSV_0) / C_0 \quad (19)$$

$$D_C = (Q + K_d) / C_K \quad (20)$$

The results of regression analysis using Equation 17 showed that all the coefficient of determination (R^2) were close to 1 (Fig 6). This suggests that the exponential function in Equation 13 was suitable to model the ferric dosed activated sludge settleability process (ZSV).

However, the $SSVI$ expression for ferric dosed activated sludge can be derived from the new empirical ferric dosed activated sludge model for settling velocity in Equation 13. The k and V_0 parameter calculated from the expression in Catunda et al. [48] in Equation 8 and 9 becomes re-written as ZSV_0 and k_d parameter for Ferric dosed sludge computed in Equation (21) and (22)

$$k_d = 0.16 + 0.0027SSVI \quad (21)$$

$$ZSV_0 = (10.9 + 0.18 SSVI) \exp(-0.016SSVI) \quad (22)$$

Where,

k_d = Empirical ferric dosed activated sludge settling parameter related to sludge compaction (L/g)

ZSV_0 = Maximum settling velocity for ferric dosed activated sludge related to stokes settling velocity (m/h)

In deriving a new expression for ferric dosed SSVI, Equation (21) and Equation (22), was compared with the existing Pitman [24] and White [25] expression in Equation (2) ($C^V/k = 68 \exp(-0.016SSVI)$) and the Equation (2) can be re-written in the form of ZSV_0 and k_d parameter as follows:

$$ZSV_0 = 68K_d \exp(-0.016SSVI) \quad (23)$$

The new SSVI expression (Equation (24)) was obtained by substituting Equation (21)-(23) into Equation 13 is as follows:

$$SSVI_{Fe}(\text{mlg}^{-1}) = -\ln \left[\left(\frac{ZSV}{68K_d X + C_K D_C X} \right) - \left(\frac{C_0 D_C}{68K_d} \right) / 0.016 \right] \quad (24)$$

The results of regression analysis for the impact of ferric dosing on SSVI using the experimental data in the batch test conducted showed that all the coefficient of determination (R^2) were close to 1 (Fig 7). This suggests that the linearized expression in **Equation 24** was suitable to model the impact of ferric dosing on activated sludge settleability (SSVI) process.

4.4 Validation of Novel Model for Impact of Ferric Dosing on ZSV and SSVI

4.4.1 Novel ZSV Model

The heuristic expression used for derivation of the New model for Ferric dosed sludge expressed in **Equation 13** ($ZSV = (C_0 D_C + ZSV_0) \exp - (K_d - C_K D_C) X$) and its linear approximation is $\ln(ZSV) = \ln(C_0 D_C + ZSV_0) - (K_d - C_K D_C) X$. The experimental data of three batch (Ferric) settling

velocity test can be classified into two groups. The first group (Fig 3-7) were used to develop the model while the second group (Table 2-3, Fig. 10 and Fig. 11) are used to validate the model. The model was validated using a solver optimisation Tool and Minitab 17. Although, the batch settling test measurements revealed ZSV as a linear representation (sludge height as a function of time) (Fig 3), but on the contrary a non-linear representation was observed in Fig 6 and 7, showing ZSV and SSVI as a function of ferric dosing concentration. This also allows the inclusion of a new ferric dosing parameter (D_C) in the existing Pitman [24] and White [25] model reported in Equation 2 and Catunda et al. [47] in Equation 8 and 9 which are both in agreement with the Vesilind (1968) expression.

The solver optimisation tool and Minitab 17 was utilised to fit non-linear model data to actual experimental data for ferric dosed sludge (Table 2-3). Table 3 and Fig 10-11 shows a comparison of the experimental and predicted zone settling velocities using Equation 13. It was observed that the model results were valid for ferric concentration ranging from 0 to 50 mgL⁻¹. The Non-Linear Fitting, Interval Plot, Residual Plot and Probability plot (Fig. 10) further establishes the validity of the model using Minitab 17. The probability plot creates estimated cumulative distribution function from ferric dosed sample data by plotting the value of each observation against its estimated cumulative probability and a scale transformation allows the fitted distribution to form a straight line.

A good distribution fit is one where the observations are near the fitted line. The data in Fig.10 are near the fitted line hence it indicates a good distribution fit between the model and experimental data. The residual shows how far the model data from the experimental data is and the residual plot in Fig.10 shows a good fit. The coefficient of determination (R^2) was 0.998 in Table 2, shows that the difference between the observed experimental value and the model predicted values are small and unbiased. The interval plot (Fig. 10) shows that at 95% CI, the mean value of ZSV model and experimental is significant as the 95% confidence interval bar do not overlap.

Table 2. Model Validation Minitab and Solver optimisation tool result

Parameters	Estimated values
ZSV ₀	0.740
C ₀	0.0089
K _d	-0.290
C _K	-0.0025
α	0.05
R ²	0.998
SSD	0.1410

R²-R Squared, α -significance level, CI-Confidence Interval

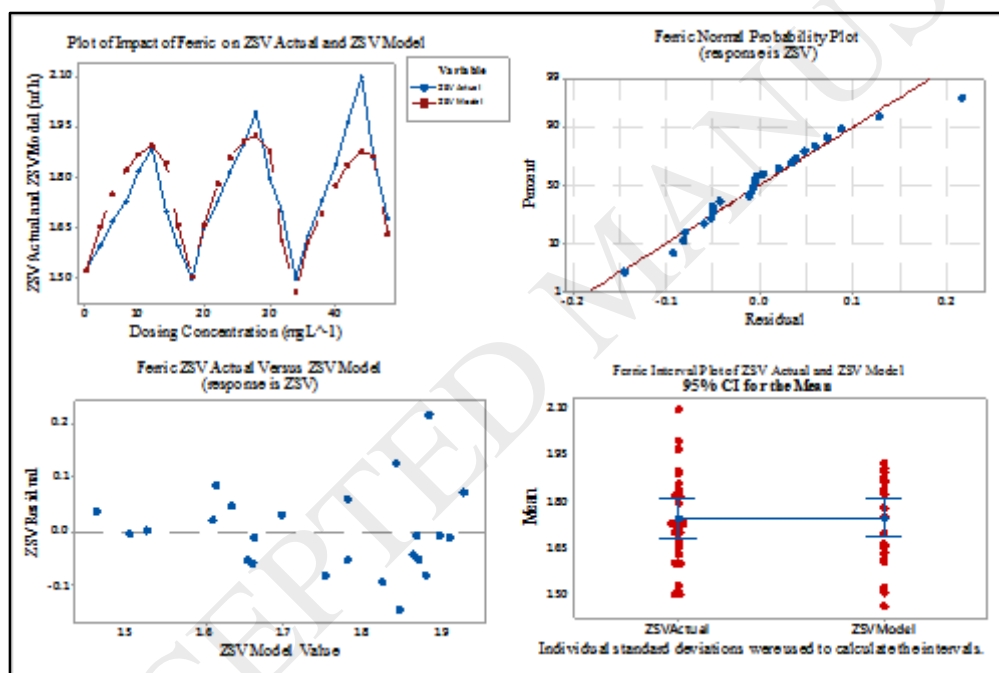


Fig. 10. Non-Linear Fitting, Interval Plot, Residual Plot and Probability plot (Ferric)

The solver optimisation tool allows the solver parameter to be set for the target objective of a reduced sum of square deviation (SSD) value so that the model fits the experimental data. In Table 2 and Fig. 11, a significant SSD value of 0.141 was reported and it indicated the ZSV model fits the actual ZSV value.

Table 3- ZSV experimental and ZSV model comparison using Solver optimisation and Minitab 17

MLSS (gL^{-1})	ZSV (mh^{-1})	ZSV Model(mh^{-1})	Fe- Dosing (mgL^{-1})	SD	Residual	Squared Residual	Squared ZSV
2.50	1.53	1.53	0.00	1.00×10^{-5}	3.44×10^{-3}	1.00×10^{-5}	2.34
2.60	1.60	1.65	10.00	2.79×10^{-3}	-5.29×10^{-2}	2.79×10^{-3}	2.56
2.68	1.67	1.75	20.00	6.65×10^{-3}	-8.16×10^{-2}	6.65×10^{-3}	2.79
2.74	1.73	1.82	30.00	8.73×10^{-3}	-9.34×10^{-2}	8.73×10^{-3}	2.99
2.78	1.82	1.87	40.00	2.55×10^{-3}	-5.05×10^{-2}	2.55×10^{-3}	3.31
2.80	1.89	1.89	50.00	4.00×10^{-5}	-5.93×10^{-3}	4.00×10^{-5}	3.57
2.72	1.70	1.84	100.00	2.1×10^{-2}	-1.45×10^{-1}	2.1×10^{-2}	2.89
2.90	1.60	1.66	150.00	3.47×10^{-3}	-5.90×10^{-2}	3.48×10^{-3}	2.56
2.45	1.50	1.50	0.00	2.00×10^{-5}	-4.64×10^{-3}	2.00×10^{-5}	2.25
2.62	1.65	1.66	10.00	1.40×10^{-4}	-1.16×10^{-2}	1.40×10^{-4}	2.72
2.75	1.73	1.78	20.00	2.63×10^{-3}	-5.13×10^{-2}	2.63×10^{-3}	2.99
2.84	1.82	1.86	30.00	1.87×10^{-3}	-4.31×10^{-2}	1.86×10^{-3}	3.31
2.89	1.90	1.91	40.00	1.10×10^{-4}	-1.02×10^{-2}	1.10×10^{-4}	3.61
2.90	2.00	1.93	50.00	5.21×10^{-3}	7.23×10^{-2}	5.22×10^{-3}	4.00
3.15	1.80	1.88	100.00	6.39×10^{-3}	-7.99×10^{-2}	6.38×10^{-3}	3.24
3.25	1.70	1.61	150.00	7.45×10^{-3}	8.64×10^{-2}	7.46×10^{-3}	2.89

2.35	1.50	1.46	0.00	1.47×10^{-3}	3.83×10^{-2}	1.46×10^{-3}	2.25
2.50	1.63	1.61	10.00	4.20×10^{-4}	2.03×10^{-2}	4.10×10^{-4}	2.67
2.55	1.73	1.70	20.00	1.04×10^{-3}	3.23×10^{-2}	1.04×10^{-3}	2.99
2.63	1.84	1.78	30.00	3.52×10^{-3}	5.93×10^{-2}	3.52×10^{-3}	3.39
2.70	1.97	1.84	40.00	1.64×10^{-2}	1.28×10^{-1}	1.64×10^{-2}	3.88
2.76	2.10	1.88	50.00	4.70×10^{-3}	2.17×10^{-1}	4.70×10^{-3}	4.41
3.00	1.86	1.87	100.00	6.00×10^{-5}	-7.64×10^{-3}	6.00×10^{-5}	3.46
3.10	1.68	1.63	150.00	2.22×10^{-3}	4.71×10^{-2}	2.22×10^{-3}	2.82

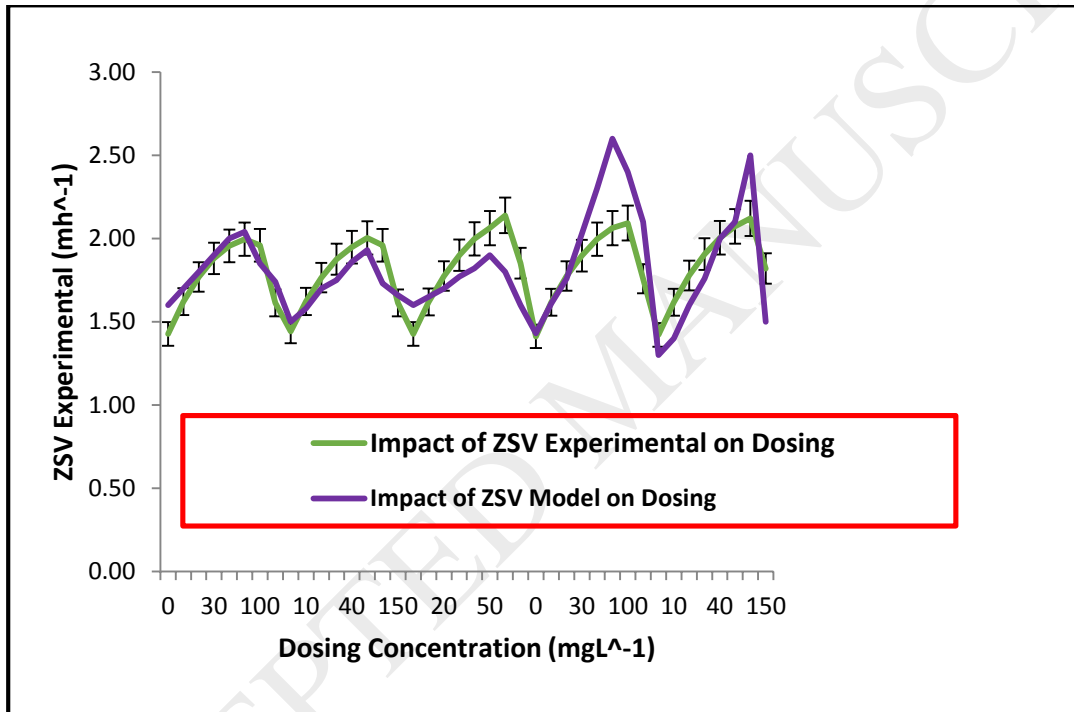


Fig. 11 - Non-Linear Curve Fitting of Impact of Ferric on ZSV

$$\mathbf{ZSV_{Fe} = (0.0089 D_C + 0.740)exp - (0.290 + 0.0025D_C)X} \quad (24)$$

The values of C_0 , ZSV_0 , K_d and C_K for ferric dosed sludge (Table 2) used to validate the numerical model in Equation 24 are the same at different dosing concentration (0, 10, 20,30,40,50 and 100 mgL^{-1}) and approximate to 0.0089, 0.740, -0.290 and -0.0025 respectively. Therefore, the new model for ferric dosed sludge is expressed as Equation 24.

The new SSVI expression for ferric dosed activated sludge (Equation 24) was derived from substituting the compared K_d and ZSVo parameter calculated from the redefined expression in Catunda et al. [48-49] with the Pitman [24] and White [25] expression in Equation 2 ($V_0/k = 68 \exp(-0.016SSVI)$) and substituting into the new ferric dosed activated sludge model for settling velocity in Equation 13.

$$SSVI_{Fe}(\text{mLg}^{-1}) = -\ln \left[\left(\frac{ZSV}{68K_d X + C_K D_C X} \right) - \left(\frac{C_0 D_C}{68K_d} \right) / 0.016 \right] \quad (25)$$

5. Conclusion

The impact of Ferric dosing on activated sludge settleability (ZSV and SSVI) was studied in batch settling tests over a three years 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 Fe^{3+} . The best settleability was achieved at 50 mg/l dose of Fe^{3+} . The improved settleability with increasing dose of Fe^{3+} was attributed to the improve bioaggregation of the activated sludge with dosing and through EPS binding capacity to microbial cells through its bridging nature with ferric. The sludge settleability started to decline between >50 mg/l to 150 mg/l dose concentrations. 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 ferric 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. A new activated sludge settleability model was proposed to analyse the effects of ferric dosing on activated sludge settleability indicators using the linear transformation of exponential functions to achieve replication of a non-linear correlation between the ferric dosing concentrations and settleability indicators (ZSV and SSVI). The new empirical model that describes the relationship between ferric dosing concentration and the ZSV and SSVI were further validated using non-linear parameterization. The results showed that the settleability indicators of Fe^{3+} dosed sludges can be described by the equations:

$$\text{ZSV}_{Fe}(\text{mh}^{-1}) = (0.0089 D_C + 0.740) \exp - (0.290 + 0.0025 D_C) X$$

$$\triangleright \text{SSVI}_{\text{Fe}}(\text{mLg}^{-1}) = -\ln \left[\left(\frac{\text{ZSV}}{68\text{K}_d\text{X} + \text{C}_K\text{D}_C\text{X}} \right) - \left(\frac{\text{C}_0\text{D}_C}{68\text{K}_d} \right) / 0.016 \right]$$

The proposed new models showed a good fit to the experimental data up to a dose range of 50 mgL^{-1} of Fe^{3+} . The new model equations will find application in the water industry for the modelling and optimization of Fe^{3+} dosed activated plants.

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