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On-line monitoring of floc formation in various flocculants for piggery wastewater treatment

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ABSTRACT

In this study photometric dispersion analyzer (PDA) was used to monitor floc size variation during the flocculation process for piggery wastewater treatment. Three types of flocculants, alum, $Fe_2(SO_4)_3$ and $FeCl_3$ were used to investigate the effects of flocculant type and dosage, mixing intensity and temperature on floc formation. From the analysis of the floc size index (FSI) at the optimum dosage, $FeCl_3$ was proved to produce the larger floc formation and better settling efficiency than $Fe_2(SO_4)_3$ or alum. It took 7.5 min in $FeCl_3$, 18.5 min in $Fe_2(SO_4)_3$ and 22.0 min in alum for complete floc settlement. $FeCl_3$ produced the most easily settled flocs. As the mixing intensity increased from 200 to 400 rpm, FSI value reduction rate was 50% in alum, 21% in $Fe_2(SO_4)_3$ and 10% in $FeCl_3$. As well, floc formation produced by $FeCl_3$ had lower degree of disaggregation at high mixing intensity. Alum and $Fe_2(SO_4)_3$ were less effective in floc settling at low temperature while $FeCl_3$ showed no significant effect related to temperature. It could be concluded that $FeCl_3$ flocs did not affect from high shear force and low temperature due to the unaltered characteristics of turbulent flocculation, fluid dynamics and solubility of $FeCl_3$. It made $FeCl_3$ a better flocculant compared to alum and $Fe_2(SO_4)_3$. In terms of particle removal, turbidity and TP removals increased with the decrease of mixing intensity and with the increase of temperature. Mixing intensity and temperature have shown no significant effect on the removals of COD and NH_3-N in piggery wastewater.

Keywords: Photometric dispersion analyzer (PDA); Floc size index (FSI); Mixing intensity; Temperature; Piggery wastewater

1. Introduction

Pig production industries have been growing as the demand for pork has increased. As a result, the piggery wastewater management problem will become more serious in the future [1]. Generally, piggery wastewater contains high amount of solid particles and most of particles are in the stable forms of colloids. These colloids are suspended in a liquid and do not settle due to their negative electric charges on the surface [2]. Piggery wastewater treatment requires effective solid-liquid separation. The flocculation process involves the chemical destabilization of particulates and the physical transport of these destabilized particles to form flocs which are large enough to settle or be filtrated. Several researchers have found that the flocculation process could give high particle removal efficiencies in terms of the organic compounds, nitrogen and phosphorus in piggery wastewater [3–5]. However, the flocculation process is dependent on several factors such as flocculant type and concentra-

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tion of metal ion, pH of solution, turbidity, mixing rate, temperature and the presence of other constituents that may affect on the physico-chemical reactions. The choice of a suitable flocculant is the critical point when maintaining an efficient flocculation scheme under widely varying conditions. For example, higher mixing intensity is likely to break the aggregated flocs and result in the formation of smaller particles which leads to lower removal efficiencies [6]. It was reported that under low shear rate conditions, particles tended to aggregate while aggregated break-up was observed under an increased shear rate [7]. When the shear rate increases above critical level, aggregated flocs will break until a new steady state is reached. In some cases, because of the irreversible nature of floc breakage, flocs are unable to reform at a higher shear rate [8]. Mixing time had also a significant effect on floc formation and a short duration of high intensity mixing often gives better results. Flocculation mechanisms at various rapid-mixing times indicated that mixing time had a significant effect on charge neutralization and sweep flocculation. The rises in residual turbidity in sweep flocculation lead to the breakage of microflocs [9]. Another factor that affects the flocculation process is low temperature. It leads to reduce the rate of chemical reaction of added flocculants and to increase in water viscosity [10]. Some researchers have reported that the rate of flocculation at low temperature is slow and flocs are smaller than those at a high temperature [11]. Flocs at low temperature were vulnerable to break up due to fluid shear. Previous study on floc formation between alum and $Fe_2(SO_4)_3$ at various temperature has shown that alum flocs has more variation in size and strength than those of $Fe_2(SO_4)_3$ [12,13]. Design and operation of piggery wastewater treatment demand the proper understanding of ways in which flocs affect the treatment systems and how their properties can be manipulated to increase treatment efficiency. In this experiment, a photometric dispersion analyzer (PDA) was used for online monitoring of floc size and its formation. It is reported to be an effective and an easy-to-use comparative tool showing qualitative changes in floc aggregation [14]. The base line information from PDA experiment could predict and compare the effectiveness of flocculants under various conditions. The main objective of this study was to investigate the effects of flocculant type and dosage, mixing intensity and temperature variations on floc formation for piggery wastewater treatment using PDA. Three types of flocculants, alum, $Fe_2(SO_4)_3$ and $FeCl_3$ at concentration ranging from 500 mg/L to 3,000 mg/L, were used. Mixing intensity and temperature were varied in the range of 200–400 rpm and 5–35°C respectively while optimum flocculant dosage was maintained throughout the experiment. Particle removal was monitored at various operating conditions from several water quality parameters such as turbidity, COD, NH_3-N and TP.

2. Materials and methods

2.1. Photometric dispersion analyzer (PDA)

The PDA is an instrument used for monitoring of flowing suspensions and emulsions. It provides a sensitive indication of changes in the state of aggregation of suspension-either aggregation (flocculation) or desegregation (dispersion, de-flocculation). Floc formation and breakage of flocs can be monitored by PDA as shown in Fig. 1. Similar dynamic systems have been employed using PDA to show and indicate the comparison of floc size index (FSI) [14–16]. The optical technique used in this work is based on the measurement of fluctuation in the intensity of narrow light transmitted through the flowing suspension at 820 nm wavelength. Transmitted light intensity as direct current (D.C.) is measured along with the root mean square value of the fluctuating component known as root mean square (RMS). In practice, the RMS value is divided by the steady D.C. to give a term ratio = RMS/D.C. The ratio (RMS/D.C.) provides a sensitive measure of particle aggregation [17]. The ratio value is called the floc size index (FSI). A liter of sample was used to investigate the dynamics of flocculation using a PDA. A sample was pumped from a rectangular reactor (10 cm × 10 cm × 20.5 cm) at 20 mL/min through the tubing at 3 mm size. Frequency for the RMS and transmitted light intensity was measured at every 10 s intervals. The steady state of samples was prepared before the addition of flocculants. Supernatant samples were withdrawn for the measurement of turbidity, COD, NH_3-N and TP.

2.2. Preparation of flocculant and piggery wastewater

In this study, aluminium sulphate [alum ($Al_2(SO_4)_3.14H_2O$)], ferric sulphate ($Fe_2(SO_4)_3.nH_2O$) and ferric chloride ($FeCl_3.6H_2O$) were used as flocculants. Omitting the non-reacting species, these reactions can be written as shown in Eq. (1) and Eq. (2).

$$Al_3^+ + 3HCO_3^- \rightarrow Al(OH)_3 + 3CO_2 \quad (1)$$

$$Fe_3^+ + 3HCO_3^- \rightarrow Fe(OH)_3 + 3CO_2 \quad (2)$$

In stoichiometric terms, each 1 mg/L of alum, $Fe_2(SO_4)_3$ and $FeCl_3$ removes 0.45 mg/L, 0.75 mg/L and 0.92 mg/L of alkalinity (as $CaCO_3$) respectively. The presence of alkalinity acts as a buffer against the excessive lowering of pH, the value of which has an important influence on flocculation [10]. Alum, $Fe_2(SO_4)_3$ and $FeCl_3$,with a reported purity of 99 %, 98% and 98%, were prepared by dissolving analytical reagents in distilled water to a concentration of 50 g/L with pH adjustment during the flocculation process by the addition of lime.

Piggery wastewater was obtained from a pig farm located in Gumi city, Korea. Piggery wastewater was

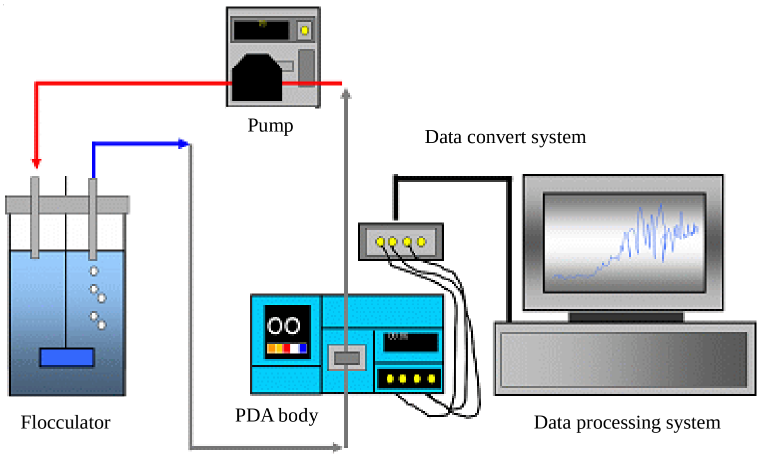


Fig. 1. Experimental set-up of PDA.

Table 1
Chemical characteristics of piggery wastewater (all units are in mg/L except pH)

COD	5,134
BOD	3,375
TKN	230
NH_3-N	205
TP	146
SS	2,125
pH	7.7

sieved through 1 mm diameter mesh and allowed to settle for 1 h to remove suspended solids. Chemical characteristics of piggery wastewater before using flocculation process were measured according to the standard method for the examination of water and wastewater as shown in Table 1 [18]. Chemical composition of supernatant in terms of NH_3-N and TP were measured by using a HS-2300 Series, Humas Co., Ltd. Turbidity residual was measured by using an Orion Aquafast II, Thermo Electron Corporation and COD was measured by using a closed reflux-titration method.

3. Results and discussion

3.1. Effect of flocculant types and their dosages

A series of experiments were conducted to investigate the optimum flocculant dosage for the treatment of piggery wastewater. The three types of flocculants used were, alum, $Fe_2(SO_4)_3$ and $FeCl_3$. Charge neutralization has been found to be one of the dominant mechanisms in the flocculation process. Without this neutralization of the ionic charges, the particles will repel with each other and that prevents agglomeration to form larger floc size [19]. In this experiment, at flocculants dosage of 500 mg/L, particles could not achieve complete neutralization as shown in Table 2. At 83 NTU for alum, 53 NTU for $Fe_2(SO_4)_3$ and 54 NTU for $FeCl_3$ residual turbidity could not be removed by gravity settling. With the increase of flocculant dosage, the negative electric charges on the particle are reduced due to high positive charges of alum or iron rapidly move toward colloids and adsorbed on the negative charged surface of particles [2]. The suspension is now considered to be destabilized and the particles can be brought together among other forces such as Brownian movement and Van der Waals forces. These compounds become large enough to settle on their own and tend to trap turbidity particles as they settle [20]. Hence, the most suitable amount of flocculants should be added to destabilize suspended colloids and to create a good settling flocs. The optimum coagulant dose was determined by comparing the effectiveness of alum, $Fe_2(SO_4)_3$ and $FeCl_3$ in terms of turbidity removal. In this study, optimum dosage for each flocculant was found to be 2,000 mg/L for alum, 1,500 mg/L for $Fe_2(SO_4)_3$ and 1,500 mg/L for $FeCl_3$ with the residual turbidity of 1.9 NTU, 1.7 NTU and 2.0 NTU respectively as shown in Table 2. As the excess amount of flocculant dosage was added, residual turbidity increased with the increase of floc-culant dosage. In this case, flocculants overdosing can cause charge reversal and restabilization of particles [21].

On-line monitoring of floc size was conducted at various operating conditions and their results were evaluated based on the FSI value. Increase of the FSI value was strongly correlated with floc size as it grows larger during the rapid mixing process. The FSI value increased drastically with the addition of flocculants. Average floc size and floc growth velocity of $FeCl_3$ were larger than those of $Fe_2(SO_4)_3$ and alum. Peak FSI value was 12.1 in $FeCl_3$, 11.7 in $Fe_2(SO_4)_3$ and 10.2 in alum at the optimum dosage. When alum and ferric salts (sulphate or chloride) are added to water in the presence of alkalinity the ion species remaining in solution for aluminum are con-

Table 2
Residual turbidity of supernatant at various flocculants dosage (Rapid mixing 200 rpm – 1 min, slow mixing 30 rpm – 20 min, settling – 30 min, temperature 25°C±1°C)

Flocculant dosage (mg/L)	Residual turbidity (NTU)					
	500	1,000	1,500	2,000	2,500	3,000
Alum	83	3.4	2.0	1.9	2.8	4.5
$Fe_2(SO_4)_3$	53	9.0	1.7	1.9	2.8	6.2
$FeCl_3$	54	7.7	2.0	2.2	2.4	3.3

sidered to be : Al^{3+}, $Al(OH)^{2+}$, $Al_7(OH)_{17}^{4+}$, $Al_{13}(OH)_{34}^{5+}$, $Al(OH)^{4-}$, $Al_2(OH)^{24+}$ and for iron : Fe^{3+}, $FeOH^{2+}$, $Fe(OH)^{2+}$, $Fe_2(OH)_2^{4+}$, $Fe(OH)^{4-}$. It was reported that iron hydroxide is much less soluble than aluminum hydroxide [21]. Furthermore, the total available surface in $FeCl_3$ was more than alum [22,23]. This is the main reason why $FeCl_3$ and $Fe_2(SO_4)_3$ had higher active ions than alum in terms of particle removal and floc formation. A high FSI value indicated the high degree of floc settlement as a result of high density flocs. Variation of the FSI value with time at various types of flocculants is summarized in Fig. 2. The FSI value of $FeCl_3$ decreased immediately after the system changed to settling process and then became stabilized. Flocs in $Fe_2(SO_4)_3$ and alum were settled slowly, due to the formation of low density flocs. Complete floc settlement was observed from the stable value of FSI during settling process. It took 7.5, 18.5 and 22.0 min in $FeCl_3$, $Fe_2(SO_4)_3$ and alum respectively. $FeCl_3$ formed easily settled flocs compared to $Fe_2(SO_4)_3$ and alum.

Physico-chemical treatment processes of coagulation-flocculation with alum or iron salts are the most commonly used for removal of phosphorus compounds in wastewater [24]. The addition of metal salts reacts with soluble phosphate to form solid precipitates that are removed by solids separation processes. A typical reaction between alum or iron salts with phosphorus is shown in Eq. (3) and Eq. (4) [25].

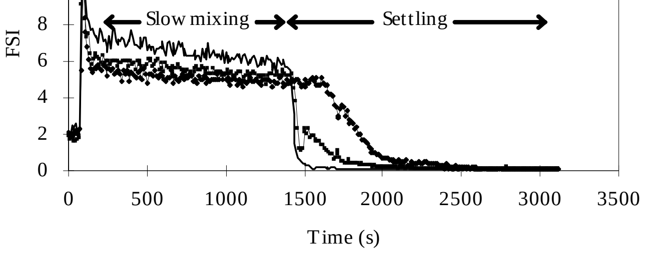


Fig. 2 On-line monitoring of floc size index at various types of flocculants (Rapid mixing 200 rpm – 1 min, slow mixing 30 rpm – 20 min, settling – 30 min, temperature 25°C±1°C).

Phosphate precipitation with alum:

$$Al_2(SO_4)_3 \cdot 14H_2O + 2PO_4^{3-} \rightarrow 2Al(PO_4) + 3SO_4^{2-} + 14H_2O \quad (3)$$

Phosphate precipitation with iron:

$$FeCl_3 \cdot 6H_2O + PO_4^{3-} \rightarrow Fe(PO_4) + 3Cl^- + 6H_2O \quad (4)$$

Alum or iron flocculants precipitate phosphorus by combining with the metal ions as shown in molar ratio of 1:1. Coagulation studies have shown that greater than this dosage is necessary to precipitate phosphorus from wastewater [26–28]. One of the competing reactions with natural alkalinity is shown in Eq. (5) and Eq. (6) [25].

$$Al_2(SO_4)_3 \cdot 14H_2O + 6HCO_3^- \rightarrow 2Al(OH)_3 + 3SO_4^- + 6CO_2 + 14H_2O \quad (5)$$

$$FeCl_3 \cdot 6H_2O + 3HCO_3^- \rightarrow Fe(OH)_3 + 3CO_2 + 3Cl^- + 6H_2O \quad (6)$$

In this experiment at optimum flocculant dosage, the molar ratio of Al:P, Fe:P as $Fe_2(SO_4)_3$ and Fe:P as $FeCl_3$ were 1.25, 2.88 and 2.13 with effluent phosphorus concentration of 0.48, 0.43 and 0.38 mg/L respectively. The molar ratio of metal salts:P was higher than the theory. Similar study investigated the effect of metal salts on phosphorus removal using piggery wastewater [26]. It was found that molar ratio of Al:P, Fe:P as $Fe_2(SO_4)_3$ and Fe:P as $FeCl_3$ were 1.46, 3.60 and 2.66 with effluent phosphorus concentration of 20.12, 15.34 and 9.97 mg/L respectively. Effluent phosphorus concentration remained high in subsequent experiment even it was operated at higher molar ratio of metal salts:P. A comparison of two experiments indicated that higher molar ratio of metals salts:P was not the only factor affecting efficiency of phosphorus removal. There are many factors affecting the phosphorus removal performance such as pH, alkalinity, coagulant dose, mixing intensity and other interfering substances [28]. Currently, phosphorus precipitation using metal salts are applied in the various alternatives for phosphorus removal with different types of wastewater treatment systems as shown in Table 3.

Table 3
Phosphorus precipitation using metal salts in various wastewater treatment systems

Treatment system	Types of wastewater	Flocculant	Molar metal salts:P ratio	Influent TP (mg/L)	Effluent TP (mg/L)	% TP removal	References
CP	Piggery wastewater	Alum	1.25:1	145.5	0.48	99.7	This study
		$Fe_2(SO_4)_3$	2.88:1	145.5	0.43	99.7	
		$FeCl_3$	2.13:1	145.5	0.38	99.7	
CP	Piggery wastewater	Alum	1.46:1	155.1	20.12	87.0	[26]
		$Fe_2(SO_4)_3$	3.60:1	155.1	15.34	90.1	
		$FeCl_3$	2.66:1	155.1	9.97	93.6	
Biological process + CP	Biologically treated wastewater	$FeCl_3$	2.50:1	5.30	0.37	93.0	[27]
Biological process + CP	Biologically treated wastewater	Alum	4.13:1	2.73	0.12	95.6	[28]
		PAC	4.37:1	2.66	0.16	94.0	
		$FeCl_3$	2.95:1	2.75	0.35	87.3	
BAF + CP	Primary settled sewage	$FeCl_3$	1.00:1	7.66	1.23	83.9	[29]
		$FeCl_3$	1.25:1	7.46	0.86	88.5	
		$FeCl_3$	1.50:1	8.11	0.83	89.8	
UASB + CP	Synthetic wastewater	$FeCl_3$	2.23:1	18.50	2.90	84.3	[30]

Note: CP — chemical precipitation; BAF — biological aerated filter; UASB — up-flow anaerobic sludge blanket

The settling process was suitable for particle removal, however, remaining soluble organic substance and nutrients can not be effectively removed by CP process only [31]. Combined processes such as biological treatment are necessary to further remove remaining pollutants into public water ways. Average removal efficiency for turbidity, COD, NH_3-N and TP for each optimum flocculant dosage is summarized in Table 4.

3.2. *Effect of mixing intensity*

Another series of experiments was conducted to investigate the effect of mixing intensity. Optimum flocculant dosage was maintained throughout the experiment. An increase in shear force is suspected to cause the breakage of aggregated flocs which leads to a lower FSI value. Table 5 shows that an increase in mixing intensity results in a decrease of the FSI value. Its value reduction rate was 50% in alum, 21% in $Fe_2(SO_4)_3$ and 10% in $FeCl_3$ when the mixing intensity increased from 200 to 400 rpm. Aggregated flocs should be kept away from high shear force to prevent them from disaggregation into smaller particles [8]. This is an important process, since smaller particle formations lead to lower particle removal efficiency. The FSI value provides a degree of floc growth and allows a comparison among flocculants under different shear conditions [16]. In this experiment $FeCl_3$ flocs had lower degrees of floc disaggregation and produce stronger flocs compared to alum and $Fe_2(SO_4)_3$ flocs at the same mixing intensity.

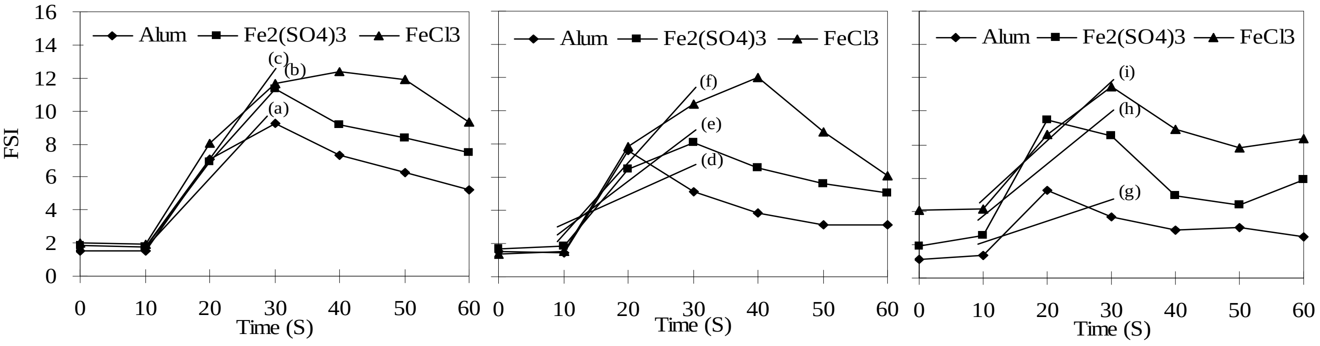
Mixing time also had a significant effect on floc formation [9]. The change of the FSI value with time at various mixing intensities is shown in Fig. 3. The FSI value increased immediately after the addition of flocculant as it is proportional to aggregated floc size. After 30 s of mixing, the FSI value started to decrease. It was found

Table 4
Removal efficiency of turbidity, COD, NH_3-N and TP at various types of flocculants (Rapid mixing 200 rpm – 1 min, slow mixing 30 rpm – 20 min, settling – 30 min, temperature 25°C±1°C)

Flocculant type	Optimum dosage (mg/L)	Settling time (min)	Removal efficiency (%)			
			Turbidity	TP	COD	NH_3-N
Alum	2,000	22.0	99.8	99.7	68.7	40.2
$Fe_2(SO_4)_3$	1,500	18.5	99.8	99.7	68.2	31.5
$FeCl_3$	1,500	7.5	99.8	99.7	67.7	32.4

Table 5
Effect of mixing intensity on floc formation (Rapid mixing – 1 min, slow mixing – 20 min, settling – 30 min, temperature 25°C±1°C)

Flocculant type	Optimum dosage (mg/L)	Average FSI value		
		Mixing 200 rpm	Mixing 300 rpm	Mixing 400 rpm
Alum	2,000	6.12	4.04	3.11
$Fe_2(SO_4)_3$	1,500	7.52	5.60	5.97
$FeCl_3$	1,500	9.21	7.76	8.20



a) 200 rpm b) 300 rpm c) 400 rpm

Fig. 3. Floc aggregated during rapid mixing process (Rapid mixing – 1 min, slow mixing – 20 min, settling – 30 min, temperature 25°C±1°C).

that 30 s of mixing was sufficient to disperse the flocculants and the formation of aggregated flocs. Increase of mixing time after that created high shear force which leads to floc breakage.

Linear equation can be used to explain the rate of flocculation process as it was plotted within 30 s during the flocculation process. y represents the FSI value while x the operational time. Linear equations for $FeCl_3$, $Fe_2(SO_4)_3$ and alum at 200 rpm were $y = 0.4865x - 2.5200$, $y = 0.4800x - 2.9167$ and $y = 0.3845x - 1.7400$ respectively. The degree of flocculation in $FeCl_3$ is higher than those of $Fe_2(SO_4)_3$ and alum. These phenomena are suspected due to the physical characteristic of flocculant as described previously. Besides, iron solubility is much less than Al one at the normal pH of water [32]. The flocculation degree for the mixing intensity of 300 and 400 rpm can be predicted from the linear equation as shown in Table 6.

3.3. Effect of temperature

Temperature is one of the important parameters for controlling the flocculation process. In this experiment, temperature varied within the range of 5–35°C, while optimum flocculant dosage was maintained throughout the experiment. Temperature variation did not significantly affect on the particle destabilization of $FeCl_3$ compared to alum and $Fe_2(SO_4)_3$ as shown in Table 7. This result is similar to the previous study on the effect of temperature in floc formation [33]. Temperature did not have a measurable effect on floc formation.

Table 6
Linear equation of floc aggregation at various rapid mixing intensity (Rapid mixing – 1 min, slow mixing – 20 min, settling – 30 min, temperature 25°C±1°C)

Flocculant type	Linear equations		
	Rapid mixing 200 rpm	Rapid mixing 300 rpm	Rapid mixing 400 rpm
Alum	$y = 0.3845x - 1.7400$ (a)	$y = 0.1845x + 1.0233$ (d)	$y = 0.1150x + 1.1400$ (g)
$Fe_2(SO_4)_3$	$y = 0.4800x - 2.9167$ (b)	$y = 0.3085x - 0.6967$ (e)	$y = 0.2985x + 0.9000$ (h)
$FeCl_3$	$y = 0.4865x - 2.5200$ (c)	$y = 0.4440x - 2.3133$ (f)	$y = 0.3665x + 0.7200$ (i)

Table 7
Effect of temperature on floc formation at various types of flocculants (Rapid mixing 200 rpm – 1 min, slow mixing 30 rpm – 20 min, settling – 30 min)

Flocculant type	Optimum dosage (mg/L)	Average FSI_c value during coagulation process					
		5°C	10°C	15°C	20°C	25°C	35°C
Alum	2,000	7.03	6.25	5.83	5.66	5.57	5.27
$Fe_2(SO_4)_3$	1,500	7.71	7.11	6.95	6.94	5.95	7.13
$FeCl_3$	1,500	8.58	9.19	8.77	8.93	9.37	9.14

Percentage of decreased FSI value was compared to the efficiency of floc settlement in each flocculant type and temperature. It was calculated by using Eq. (7).

Percentage of decreased FSI value (%)

$$= \frac{\left(FSI_c - FSI_s\right)}{FSI_c} \times 100 \qquad (7)$$

where FSI_c is an average FSI value during coagulation process as shown in Table 7; FSI_s is an average FSI value during settling process as shown in Table 8.

High percentage of decreased FSI value was correlated with high degree of floc settlement. From the results, temperature played an important role in the floc settling capacity especially for alum. At the temperature of 5°C most of alum flocs was suspended after the settling time. Only 92.4% of decreased FSI value after thirty minutes as shown in Table 8. At low temperature, it can be more difficult to disperse the flocculants into the sample due to the increased water viscosity and the decreased rate of floc settling [33]. As a result, the flocculant becomes less efficient and higher flocculant dosages are required to compensate for these effects. Previous studies have shown that the flocculation efficiency at the temperature of 20°C is not sensitive to shear rate, but at a temperature of 5°C impeller geometry is much more important. Alum flocs was significantly weaker than iron one at every condition tested [11]. A sharp decrease in the turbidity removal efficiency was also reported in the low temperature of Kaolin synthetic water [12]. However, with the increase of temperature particles tended to settle down rapidly. At the highest temperature of

Table 8
Effect of temperature on floc settling capacity at various types of flocculants (Rapid mixing 200 rpm – 1 min, slow mixing 30 rpm – 20 min, settling –30 min)

Settling time (min)		Average FSI_s value during settling process						Percentage of decreased FSI value					
		5°C	10°C	15°C	20°C	25°C	35°C	5°C	10°C	15°C	20°C	25°C	35°C
Alum	5	4.83	4.25	4.31	3.70	4.00	2.04	31.3	32.1	26.0	34.5	28.2	61.3
	10	3.46	2.72	3.04	1.39	1.01	0.18	50.7	56.5	47.9	75.4	81.8	96.5
	15	2.59	1.91	2.01	0.67	0.88	0.17	63.2	69.5	65.4	88.1	84.3	96.8
	20	2.32	1.53	1.37	0.78	0.52	0.12	67.1	75.5	76.5	86.3	90.6	97.7
	25	1.18	1.00	0.67	0.79	0.25	0.10	83.2	84.0	88.5	86.0	95.5	98.2
	30	0.54	0.75	0.47	0.46	0.19	0.08	92.4	88.0	92.0	91.8	96.6	98.5
$Fe_2(SO_4)_3$	5	4.96	4.78	4.27	4.36	2.91	2.17	35.7	32.7	38.6	37.1	51.1	69.6
	10	2.43	1.84	1.90	1.72	1.28	0.10	68.4	74.1	72.7	75.2	78.4	98.6
	15	2.30	1.94	1.95	1.50	0.62	0.06	70.1	72.7	71.9	78.4	89.6	99.2
	20	1.43	0.84	0.89	0.55	0.36	0.04	81.5	88.1	87.3	92.0	94.0	99.4
	25	0.67	0.53	0.41	0.38	0.24	0.03	91.3	92.5	94.1	94.5	96.0	99.6
	30	0.44	0.38	0.31	0.28	0.17	0.03	94.3	94.7	95.5	96.0	97.1	99.6
$FeCl_3$	5	3.60	4.25	2.99	2.96	2.46	1.49	58.1	53.7	65.9	66.8	73.8	83.7
	10	0.82	0.85	0.58	0.57	0.38	0.22	90.5	90.7	93.4	93.6	95.9	97.6
	15	0.47	0.39	0.37	0.28	0.22	0.15	94.5	95.8	95.8	96.8	97.6	98.4
	20	0.29	0.26	0.27	0.20	0.16	0.11	96.6	97.1	96.9	97.8	98.3	98.8
	25	0.22	0.20	0.23	0.14	0.12	0.08	97.4	97.8	97.4	98.5	98.7	99.1
	30	0.17	0.18	0.17	0.14	0.10	0.07	98.0	98.0	98.1	98.5	98.9	99.3

35°C, alum flocs immediately settled down as shown in the changes of the FSI value during settling process with time. Due to the increase of temperature, the water viscosity decreased [34]. It promoted the particles movement faster and enhanced the opportunity of particles to collide with each other. Aggregated flocs became larger in floc size and settled easily. Hence, the rate of floc settlement was more rapid than its rate at low temperature. Similar pattern was observed in $Fe_2(SO_4)_3$ flocs. The floc settling capacity increased with the increase of temperature. Floc settling rate of $Fe_2(SO_4)_3$ was higher than that of alum at the same temperature. In case of $FeCl_3$, less variation of floc settling with temperature was shown. A floc settling rate of $FeCl_3$ did not depend on temperature. It was more rapid than those of $Fe_2(SO_4)_3$ flocs and alum flocs at temperature ranging from 5°C to 25°C. Nevertheless, the floc settling rate had similar trends in all the flocculants at the highest temperature (35°C). These results were due to the characteristics of water viscosity change at high temperature. At the temperature of 35°C, percentage of decreased FSI value for alum, $Fe_2(SO_4)_3$ and $FeCl_3$ were 98.5%, 99.6% and 99.3% respectively.

A linear equation was used to explain the particles settling rate as shown in Fig. 4. Y represents the FSI value while x the operational temperature. Decrease of the FSI value in alum and $Fe_2(SO_4)_3$ flocs was strongly related to the increase of temperature. However, there were no relationships between a decreased FSI values in $FeCl_3$ flocs with temperature. Characteristics of turbulent flocculation, fluid dynamics and solubility of $FeCl_3$ may not change with temperature. $FeCl_3$ may appear in non-dissolved forms at broad temperature range which made $FeCl_3$ the good flocculant especially in the winter season.

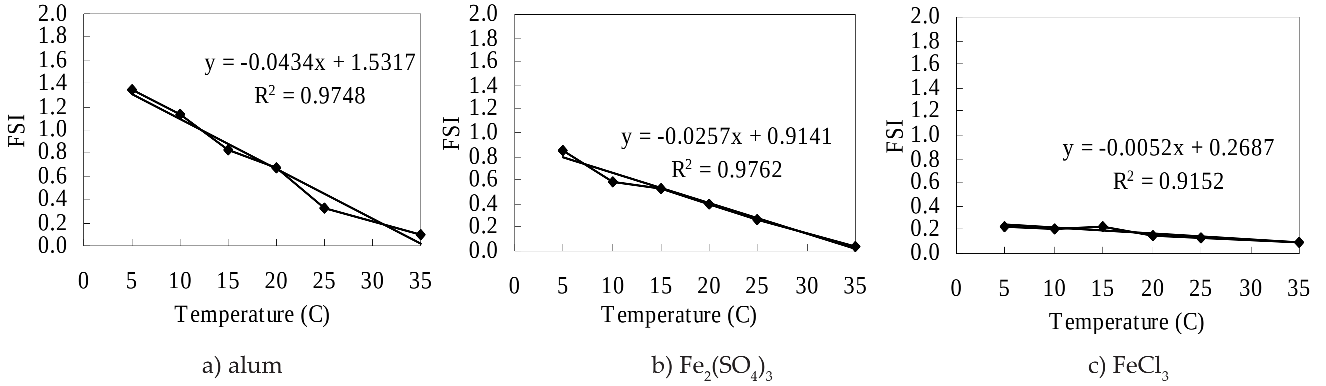
3.4. Supernatant characteristics

The effect of rapid mixing intensity on particle removal was investigated. The FSI value was found to be inversely related to turbidity and TP removal. Turbidity and TP removal efficiency decreased with the increase of FSI value. The relationships of the FSI value with turbidity and TP removal efficiencies are shown in Fig. 5. $FeCl_3$ has shown the highest turbidity and TP removal efficiencies at the mixing intensities of 200 rpm and 300 rpm. With an increase of rapid mixing intensity, turbidity removal efficiencies decreased drastically. TP removal followed the same pattern with turbidity. However, the mixing intensity had little effect on COD and NH_3-N removals as shown in Fig. 6. Removal efficiencies of COD and NH_3-N were in the range of 69.3–75.5% and 22.5–29.5% respectively.

Another series of experiment were conducted to study the effect of temperature on the performance of particle removal. Fig. 7 shows that the particle removal efficiency of piggery wastewater in alum and $Fe_2(SO_4)_3$ decreased with the decrease of temperature. During the decrease of temperature from 35°C to 5°C, the turbidity removal efficiency decreased from 99.6% to 96.5 % in alum and 99.7% to 98.6 % in $Fe_2(SO_4)_3$. TP removal efficiency decreased from 99.6% to 98.7% in alum and 99.7% to 99.2% in $Fe_2(SO_4)_3$. There was no significant effect on turbidity and TP removals by $FeCl_3$. Removal efficiencies of piggery wastewater using these flocculants were more than 99.5% and 99.6% in turbidity and TP respectively. COD and NH_3-N removals were much less than turbidity and TP as shown in Fig. 8. As COD and NH_3-N concentration in the supernatant is in the soluble form, it can not be eliminated by chemical precipitation.

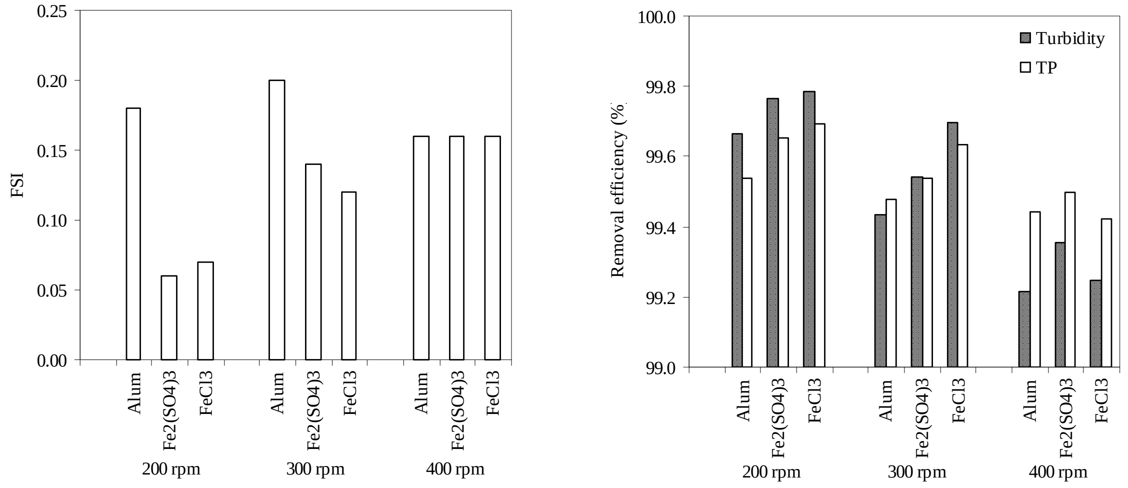
4. Conclusions

In this study, an optical monitoring technique was applied to investigate the dynamics of floc formation in the flocculation process using piggery wastewater. The following conclusions were made based on the several series experiments conducted.



a) alum b) $Fe_2(SO_4)_3$ c) $FeCl_3$

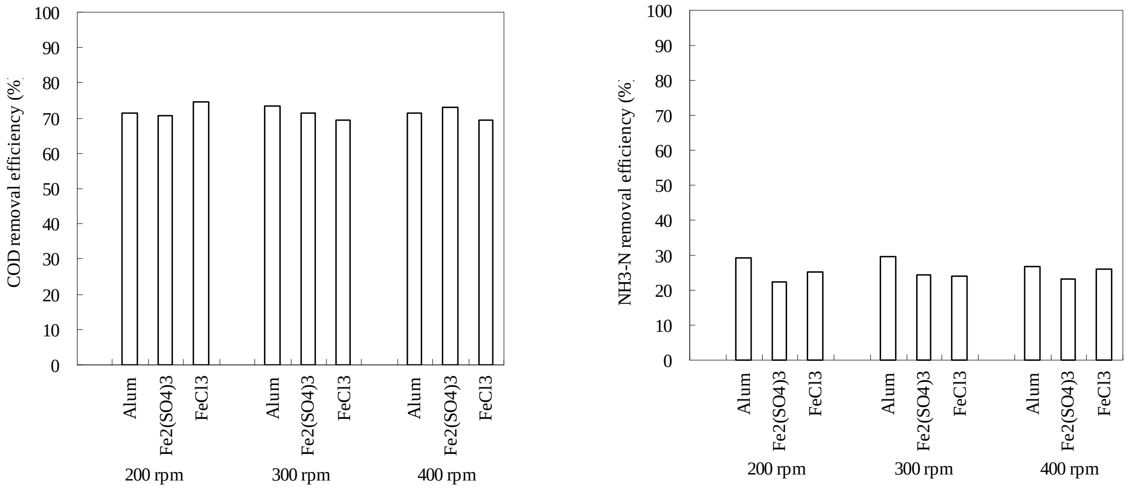
Fig. 4. Linear equation of floc settled after precipitation (Rapid mixing 200 rpm – 1 min, slow mixing 30 rpm – 20 min, settling – 30 min).



a) Average FSI value

b) Turbidity and TP removal

Fig. 5. Comparison of average FSI value in turbidity and TP removal (Rapid mixing – 1 min, slow mixing – 20 min, settling – 30 min, temperature 25°C±1°C).



a) COD removal

b) NH_3-N removal

Fig. 6. Removal efficiencies of water quality parameters at various mixing intensity (Rapid mixing – 1 min, slow mixing – 20 min, settling – 30 min, temperature 25°C±1°C).

1. Optimum flocculants dosage was found to be 2,000 mg/L for alum, 1,500 mg/L for $Fe_2(SO_4)_3$ and 1,500 mg/L for $FeCl_3$ within the range of concentration. During the rapid mixing process, $FeCl_3$ showed the highest FSI value followed by $Fe_2(SO_4)_3$ and alum. The peak FSI values of $FeCl_3$, $Fe_2(SO_4)_3$ and alum were 12.1, 11.7 and 10.2 respectively. As well, $FeCl_3$ formed the larger floc size than those of $Fe_2(SO_4)_3$ and alum. The FSI value was proportional to the degree of settlement. It took 7.5 min in $FeCl_3$, 18.5 min in $Fe_2(SO_4)_3$ and 22.0 min in alum for complete floc settlement. $FeCl_3$ produced the most easily settled flocs compared to $Fe_2(SO_4)_3$ and alum.

2. Applications of higher shear rate resulted in floc breakage and thus produced smaller sizes of flocs. The FSI value reduction rate was 50% in alum, 21% in $Fe_2(SO_4)_3$ and 10% in $FeCl_3$, when the mixing intensity increased from 200 to 400 rpm. The degree of flocculation in $FeCl_3$ was higher than those of $Fe_2(SO_4)_3$ and alum. An increase in mixing intensity has led to lower turbidity and TP removals, while mixing intensity had little effect on COD and NH_3-N removals.

3. Low temperature played an important role in the floc settling rate especially for alum and $Fe_2(SO_4)_3$, while $FeCl_3$ had no significant effect. These results were due to

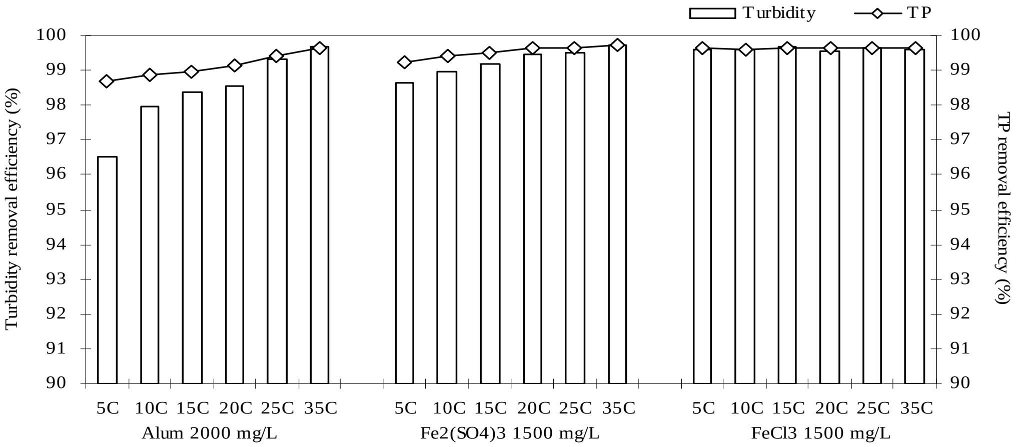


Fig. 7. Comparison of removal efficiency in turbidity and TP at various types of flocculants (Rapid mixing 200 rpm – 1 min, slow mixing 30 rpm – 20 min, settling – 30 min).

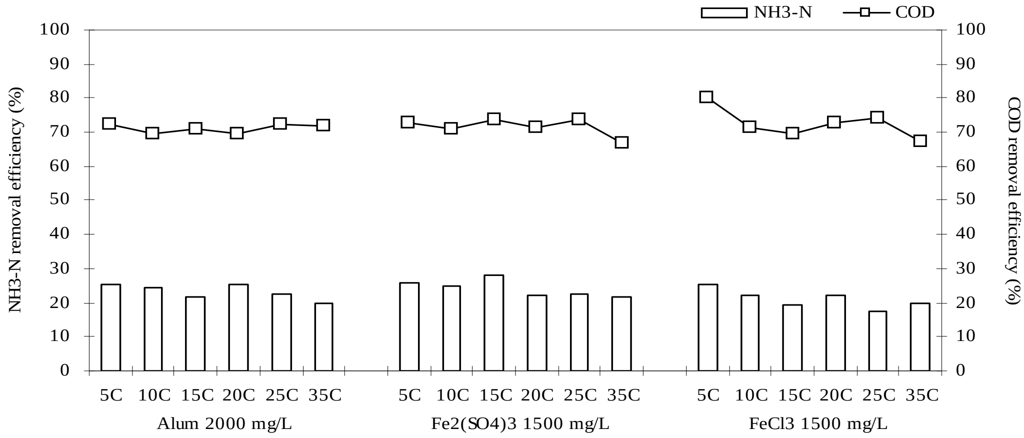


Fig. 8. Comparison of removal efficiency in NH_3-N and COD at various types of flocculants (Rapid mixing 200 rpm – 1 min, slow mixing 30 rpm – 20 min, settling – 30 min).

the increase of water viscosity at low temperature. Degree of floc settlement was indicated by the percentage of decreased FSI value. It was only 92.4% for alum flocs and 94.3% for $Fe_2(SO_4)_3$ flocs at the temperature of 5°C. At the high temperature of 35°C, the floc settling rate had similar trends for all the flocculants. With the increase of temperature, the reaction rate increased as the particles moved faster and collided more frequently. The degree of particle settling in $FeCl_3$ was higher than those of $Fe_2(SO_4)_3$ and alum. $FeCl_3$ gave a higher removal efficiency for turbidity and TP removals than those of $Fe_2(SO_4)_3$ and alum. Characteristic of turbulent flocculation, fluid dynamics and solubility of $FeCl_3$ did not change with the temperature.

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