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Effective coagulation-flocculation treatment of highly polluted palm oil mill biogas plant wastewater using dual coagulants: Decolourisation, kinetics and phytotoxicity studies

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Abstract

The performance of several chemical coagulants including ferric chloride, calcium lactate, magnesium hydroxide, aluminium chlorohydrate, and polydiallyldimethylammonium chloride (polyDADMAC) were investigated in removing colour of palm oil mill biogas plant wastewater (POMBPW). The results show that ferric chloride as a sole coagulant can achieve high colour removal of more than 80% without needed for pH adjustment, which indicates the effectiveness of the coagulant to treat palm oil mill biogas plant wastewater

(POMBPW).However, dual coagulants i.e. ferric chloride-anionic polyacrylamide (APAM) shows better performance than ferric chloride-polyDADMAC in terms of colour removal, pH, with shorter sedimentation time. The addition of polymer to system not only reduces the ferric chloride dosage, but also increases the colour removal of more than 20%. Comparison between APAM and polyDADMAC as flocculant aids shows that APAM can achieve stable removal at wider pH range and lowest sedimentation time at 20 minutes while polyDADMAC was at one hour. Both dual coagulants were followed second order kinetic and APAM shows the highest rate over polyDADMAC i.e. 3×10^{-5}/PtCo.min and 2×10^{-5}/PtCo.min respectively. Addition of polymers reduced phytotoxicity of generated sludge and the sludge has potential to be reused for land application.

Keywords: Biogas; decolourisation; palm oil mill; dual coagulants; physico-chemical treatment.

1. Introduction

Most of palm oil mills have to deal with their highly polluting wastewater that is known as palm oil mill effluent (POME). This has led to the emergence of a new treatment technology with environmental friendly approach. Palm oil mill has adopted anaerobic digestion system technology known as biogas plant where it can convert the organic carbon i.e. chemical oxygen demand (COD) and biochemical oxygen demand (BOD) to biogas with the help of anaerobic bacteria. This renewable energy generated from this plant can be used to generate electricity and can save tones of fossil fuel. However, the performance of biogas plant is primarily depending on the bacteria that readily exist in the wastewater. This bacteria can be sensitive to their environment, namely pH and temperature. It has been reported that biogas plant can remove up to 80% of COD from the POME after being anaerobically digested (Tong and Jaafar, 2006).Nevertheless, the treated wastewater from this plant has high level of polluting contents, which do not comply with the discharge requirement limit set by Department of Environment (DOE). Moreover, the wastewater colour turned from brownish (POME) to blackish after POME was digested. This colour transformation might be due to Maillard reaction of natural condensation between carbonyl groups and free amino groups in POME that produce melanoidin, which is an anaerobic fermentation by product (Yaser et al., 2013). As a result, this highly coloured wastewater can create aesthetic problem and affect the photosynthesis activity by reducing the sunlight penetration if it is discharged into the watercourse (Neoh et al., 2013, Grainger et al., 2010, VukoviĆ et al., 2008, Mohan and Karthikeyan, 1997). Bunrung et al. (2014 and 2011) have studied the decolourisation of palm oil mill biogas plant wastewater (POMBPW) by using physical method and also combined with biological method. They found out that the decolourisation of more than 80% can be achieved when using palm ash as adsorbent and after pre-treated with biological method of mixed cultures(Bunrung et al., 2014, Bunrung et al., 2011). However, the characteristics of POMBPW in their studies were lower as compared in this study; especially the colour and COD. In addition, the proposed treatments involve longer contact time in adsorption where the decolourisation increased with increase in agitation time, as well as in mixed cultures cultivation.

Typically, coagulation-flocculation process is regarded as one of the most important treatment processes of industrial wastewater (Teh et al., 2016) and raw water (Teh and Wu, 2014) due to its simplicity, effectiveness, and low energy consumption. Coagulation-flocculation process is widely used in industry in the past few decades. In addition, this process usually used is used as a pre-treatment to other integrated treatment process such as membrane filtration

(Zahrim et al., 2011, Citulski et al., 2009, Harrelkas et al., 2009), biological treatment (El-Gohary and Tawfik, 2009, Sklyar et al., 2003) and advanced oxidation processes (Garcia-Morales et al., 2012, Durán et al., 2009, Ma and Xia, 2009). The attribute of wastewater plays an important factor in choosing the most suitable coagulant for the process treatment. Inorganic coagulants such as aluminum and iron salts are commonly used in water treatment. However, they can alter the pH of the treated water, increase toxicity level and sometimes can increase the wastewater colour, which can make secondary contamination (Mageshkumar and Karthikeyan, 2016, Teh et al., 2016).Synthetic organic polymers such as polyacrylamide (PAM) and poly(diallyldimethylammonium chloride) (PolyDADMAC) have been widely used not only as flocculant aids but also as direct flocculation in most industries(Lee et al., 2014, Zhu et al., 2009).Generally, polymers will bind the flocs via bridging mechanism and produce larger, denser, stronger, and rapid-settling flocs. The formation of larger and denser flocs is mainly due to the higher molecular weight of polymer coagulants which improve interparticle bridging and provide more adsorption sites (Shak and Wu, 2015, Subramonian et al., 2015, Teh et al., 2014).

Ferric salt was used to further studied due to problems associated with aluminium salt. High concentration of aluminium species in water may lead to Alzheimer's disease upon consumption (Teh et al., 2016, Bhatti et al., 2009). Therefore, the residue of Al^{3+} content in the discharge should be below 10 – 15 mg/L according to Malaysian standard (DOE, 2016). Furthermore, several researchers agreed that the usage of alum-based coagulants is not preferable due to limitation by its concentration (Amuda and Alade, 2006, Ahmad et al., 2006, Bhatia et al., 2006, Zahrim et al., 2011, Teh et al., 2016) hence, it is not suitable to treat POMBPW.

Over the years, the usage of dual coagulants (inorganic coagulant and polymer based coagulant) has benefits over the sole use of inorganic or polymer coagulants. These benefits are mostly related to the reduction of the inorganic coagulant dosage while producing larger, denser, and stronger flocs (Lee et al., 2014). Several studies have reported the effectiveness of dual coagulants application when dealing with various types of wastewater where it can reduce up to 90% of COD, total suspended solids (TSS), turbidity, and colour. Furthermore, it can reduce the consumption of coagulant demand, thus reduce the overall cost of the coagulation-flocculation process (Lee et al., 2014, Zahrim et al., 2014, Irfan et al., 2013, Sher et al., 2013, Martín et al., 2011, Amuda and Amoo, 2007, Amuda and Alade, 2006, Ahmad et al., 2005a).

The concern in accumulation of large amount of sludge from this process has led to finding the best way to manage the sludge in economically and environmentally approach. To the best of our knowledge, there were small amount of work in the literature concerning studies of phytotoxicity from sludge generated through the coagulation-flocculation process alone. Most researchers combine the coagulation-flocculation with another treatment process in which to further degrade the organic compound to lower level. Bedekar et al. (2016) reported that the coagulated dye sludge was fermented by using consortium-BBA and found that the phytotoxicity was decreased after coagulation and degradation mechanism (Bedekar et al., 2016). In another study, combination of coagulation, acid cracking, and Fenton-like process could result the phytotoxicity of final olive oil mill wastewater to decrease (Yazdanbakhsh et al., 2015). Another combination was reported by Turki et al. (2015), where they found high toxicity removal up to 90% in their phytotoxicity test of landfill leachates. The combination was coagulation-flocculation-Fenton and powder zeolite adsorption (Turki et al., 2015).

Lee et al. (2011) has used a ferric chloride–polyacrylamide inorganic–organic hybrid polymer which was synthesized using a ferric chloride/polyacrylamide ratio of 1:1 via free radical solution polymerization. The hybrid polymer was then tested on kaolin suspension flocculating activities and Terasil Red R dye wastewater and the results showed it is capable to decolourise up to 99% of colour (Lee et al., 2011). Another study reported by Yang et al. (2014) used polyferric chloride (PFC) and poly(epichlorohydrin-dimethylamine) [P(ECH-DAM)] to test for the coagulation treatment of reactive dye suspensions and found that composite PFC-P(ECH-DAM) can improved characteristics, such as increased efficient polymeric speciation concentration, improved zeta potential, and enhanced flocculation performance (Yang et al., 2014). In summary, both of these studies were using hybrid polymer and focusing on dye wastewater. The hybrid polymer synthesizing is time consuming due to the complicated preparation (Lin et al., 2013). To the best of our knowledge, there is no publication in the literature dealt with dual coagulants before in POMBPW decolourisation.

In this study, the ability of various coagulants in removing colour of POMBPW was investigated by various metal coagulants such as ferric chloride, calcium lactate, magnesium hydroxide, and aluminium chlorohydrate. Then, the addition of polymers i.e. polyDADMAC and PAMs as flocculant aids was studied. Last but not least, the coagulation kinetic order was predicted and phytotoxicity test of the filtered sludge was carried out.

1.1 Coagulation kinetics

The kinetics of coagulation process can be described as (Mageshkumar and Karthikeyan, 2016, Nnaji et al., 2014);

$$\frac{dC}{dt} = -kC^{n} \quad (1)$$

where "C" is the total mass of particle per litre, "t" is the coagulation time, "k" is the nth order coagulation rate constant, and "n" is the order of the coagulation process. The turbidity concentration decrease as a function of increasing time (t), is represented as a negative sign in Eq. (1).

During the coagulation process, the rate of removal of colour is proportional to the initial colour concentration and amount of coagulant used. For a first order (n = 1) coagulation process, the rate equation is shown as;

$$\frac{-dC}{dt} = k_1 C \quad (2)$$

and the integral form is written as follows;

$$\ln\left(\frac{C_o}{C}\right) = k_1 t \quad (3)$$

where "C_o" is initial colour of the POMBPW in PtCo, "C" is final colour of the POMBPW at time "t" and "k_1" is the first order rate constant in (1/min). Eq. (3) shows that the plot of $\ln(C_o/C)$ against time (t) should be a straight line passing through the origin and the slope is k_1. However, if the line does not pass through the origin but intercepts along the Y-axis line, it follows second order coagulation process (n = 2) which is shown as;

$$\frac{-dC}{dt} = k_2 C^2 \quad (4)$$

and the integral form is written as follows;

$$\frac{1}{C} = k_2 t + \frac{1}{C_o} \quad (5)$$

where "k_2" is the second order rate constant in (1/PtCo.min).

2. Methodology

2.1 Materials

The biogas plant wastewater was collected from the Lahad Datu, Sabah. In this mill, the palm oil mill effluent (POME) from the cooling pond is fed into three anaerobic digester tanks which are located in the biogas plant area. The hydraulic retention time (HRT) for the three tanks is ~18 days. The wastewater is appeared to be blackish in colour (Dexter et al., 2016). The characteristics of the palm oil mill biogas plant wastewater (POMBPW)taken was measured and summarized in Table 1.

Table 1. Summary of Biogas Plant Wastewater Characteristics

Characteristic	Value
pH	7.2 – 8.4
Conductivity (μS/cm)	12500 – 24000
Chemical Oxygen Demand (mg/L)	8100 – 21000
Suspended Solid (mg/L)	290 – 12750
Zeta Potential (mV)	(-15.0) – (-12.0)
Colour (PtCo)	31407 – 198792

Five types of metal coagulants; calcium lactate, magnesium hydroxide, ferric chloride hexahydrate, and aluminium chlorohydrate (two types) are used. Calcium lactate (Molecular mass 308.32 g/mol) (Merck, Germany), magnesium hydroxide (Molecular mass 58.32 g/mol) (Sigma-Aldrich, USA), and ferric chloride hexahydrate (Molecular mass 270.30 g/mol) (Techno Pharmchem, India) were prepared by dissolving their solid form in distilled water. Two flocculants in liquid form were supplied by Chemkimia Sdn. Bhd. Both flocculants are aluminium chlorohydrate; Chemchlor CK-800 and Chemchlor CK-1000 are in 45% wt, also prepared by dissolving in distilled water. Polymers used in this study include polyDADMAC and cationic/anionic polyacrylamide. The polyDADMAC (Tramfloc® 724, 40% wt) and anionic polyacrylamide i.e. Tramfloc® 141 (anionic) were supplied by Tramfloc, Inc., Houston, Texas. Another polymers: AN 1500 (anionic), AN 1800 (anionic), QF 25610 (cationic), QF 23912 (cationic), and QF 24807 (cationic) were used. Details of solid and liquid coagulant are shown in Table 2 and 3 respectively.

Table 2. Physical and chemical properties of solid coagulant.

	Calcium lactate	Magnesium hydroxide	Ferric chloride
Physical state, colour, odour	white to almost white crystalline or granular powder	White in powder form	Yellow brown deliquescent crystals
pH	6.0 – 8.0	9.5 – 10.5	1.8 – 2.0
Boiling point/ range (^oC)	NA	NA	NA
Water solubility	50 g/L (20^{o}C)	0.0064g/L (25^{o}C)	92 g/L (20^{o}C)
Melting point/ range (^oC)	240	350	37
Flash point (^oC)	NA	NA	NA
Freeze point (^oC)	NA	NA	NA
Vapour pressure, mm @ 25 ^oC	Low	NA	1.1 (194^{o}C)
Density, kg/m^3	*300 – 500	2.360	2.90
Octanol/water partition coefficient	log Pow:-0.62	NA	NA
Viscosity, cps	NA	NA	NA
VOC content, % volatile	NA	NA	0 (21^{o}C)

*Bulk density

Table 3. Physical and chemical properties of liquid coagulant.

	Chemchlor CK-800	Chemchlor CK-1000	PolyDADMAC
Physical state, colour, odour	Clear to hazy liquid with odourless	Clear liquid with odourless	Straw coloured, viscous liquid with amine odour
pH	3.5 – 5.0	3.5 – 5.0	5.0 – 8.0
Boiling point/ range (^{o}C)	~ 100	~ 100	> 100
Water solubility	Soluble	Soluble	Soluble
Melting point/ range (^{o}C)	NA	NA	-2.8 – 0
Flash point (^{o}C)	NA	NA	> 100
Freeze point (^{o}C)	NA	NA	NA
Vapour pressure, mm @ 25 ^{o}C	NA	NA	20 – 30
Specific gravity	1.32	1.32 – 1.38	1.08 – 1.09
Octanol/water partition coefficient	NA	NA	Kow< 10
Viscosity, cps	NA	NA	~ 1,000
VOC content, % volatile	NA	NA	NA

NA = not available

2.2 Experimental set-up

The coagulation process with various concentrations of metal coagulants solution ranging from 500 – 10,000 mg/L was conducted using a standard jar test equipment (Phipps & Birds™)(Zahrim et al., 2014). The solution pH was adjusted using 1.0M of hydrochloric acid or 1.0M of sodium hydroxide in order to observe the effect of pH during coagulation-flocculation process. The effect of various polymers as flocculant aids was carried out after the best coagulant and dosage was determined, *2.3 Physico-chemical analysis*

The colour was analysed using V-650 UV/Vis Spectrophotometer (Jasco). The absorbance at 455 nm was used to analyse the apparent colour by using APHA 8025 Method(APHA Platinum-Cobalt Standard Method). The pH and conductivity were determined using HI 9611-5 Meter (Hanna Instrument).

2.4 Zeta potential

After sedimentation, the supernatant was filled in the capillary cell and inserted into the zeta potential equipment's compartment with the weld line facing in front of the instrument. Zeta potential was measured using a Malvern-Zetasizer Nano Series model ZS. Each sample measurement was taken at least three times in order to obtain the best result. Finally, results are obtained and the zeta potential ranges are evaluated based on different samples. Supporting measurement of zeta potential permitted a more detailed study on the relation between coagulants properties and treatment effectiveness (Shak and Wu, 2017).

2.5 Germination index

The settled solids were filtered using a vacuum pump and dried using an oven. The dry solids were tested their phytotoxicity based on germination index (GI). Cabbage seeds were used in this GI test with a mixture of 50% dry solids and 50% commercial soil (Troy et al., 2013, Prasad et al., 2010).The commercial soil was supplied by Jaya Pot Enterprise, Malaysia, consists of 0.15% sodium, 0.50% phosphorus, 0.30% potassium, and 0.15% magnesium oxide. The mixture was added to 25 mL of distilled water and mixed thoroughly together to make a water-soluble extract. The extract was then analysed for its pH and conductivity. Fifteen seeds were sown in a 5 mL of water-soluble extract in a petri dish. As a control, 5 mL of distilled water was added in a petri dish along with the cabbage seeds. Each test was undertaken in triplicate and the dishes were put in a dark room at room temperature. After three days (72 hours), the germinated seeds were counted and measured the root length. The result of GI test was calculated as follows (Tiquia and Tam, 1998):

$$\text{Relative seed germination (RSG\%)} = \frac{\text{number of seed germinated in sample extract}}{\text{number of seed germinated in control}} \times 100 \quad (6)$$

$$\text{Relative root growth (RRG\%)} = \frac{\text{root length in sample extract}}{\text{root length in control}} \times 100 \quad (7)$$

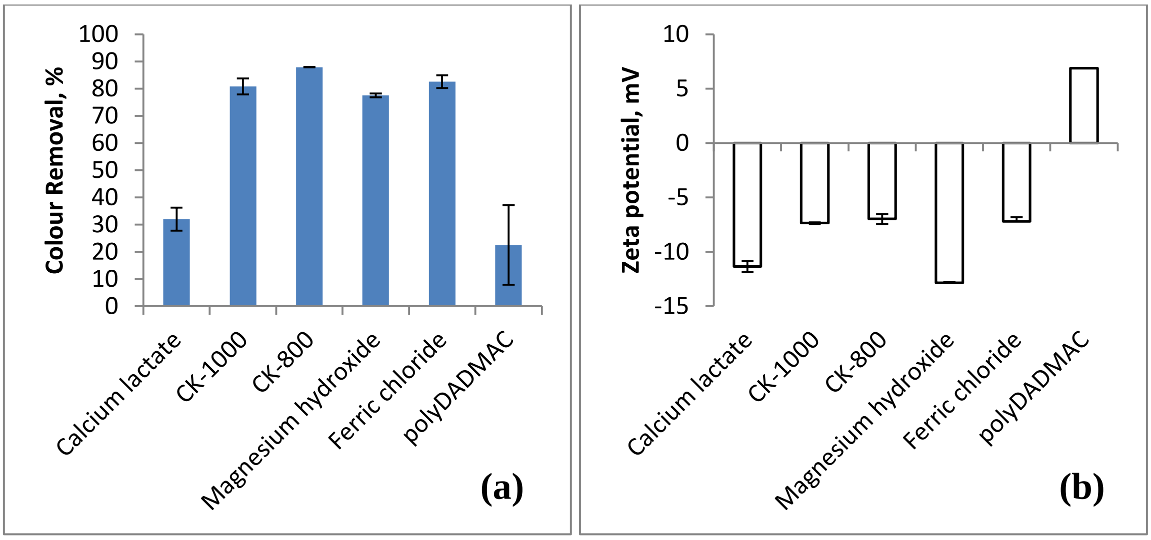
$$\text{Germination Index (GI\%)} = \frac{\text{RSG\%} \times \text{RRG\%}}{100} \quad (8)$$

3. Results and discussion

3.1 Flocculation using metal coagulant

3.1.1 Effect of metal coagulant type

Fig. 1a shows the effect of coagulant on the colour removal of POMBPW at the dosage of 8000 mg/L. CK-800 gives the highest removal i.e. 87.9%, followed by ferric chloride (82.6%), CK-1000 (80.7%), magnesium hydroxide (77.5%), calcium lactate (32.0%), and polyDADMAC (22.5%). It was observed that during CK-800, CK-1000, and rejection of ferric chloride into the wastewater, there was an instant formation of flocs occurred. It is believed due to charge neutralization mechanism. According to (Saukkoriipi, 2010), the charge neutralization occurs in between 0.01–1 second while another mechanism, i.e. sweep coagulation, occurs in the range of 1–7 seconds (Lu et al., 2005). The most probable reason for this is that wastewater particles are normally negatively charged, cationic coagulants can neutralize or reduce the negative charge on the particles. As a result, the electrical repulsion force is decreased between particles, and van der Waals force of attraction is formed to promote initial aggregation of colloidal and fine suspended materials to form microfloc (Lee et al., 2014, Bolto and Gregory, 2007, James et al., 2003). Contrary with magnesium hydroxide and calcium lactate, where there was no instant formation of flocs after adding them into the wastewater. Instead, precipitation was formed during the process. One of the main reasons is the solubility that may affect the behaviour of the coagulant. Low solubility of magnesium hydroxide (0.009 g/L) forms precipitates, where precipitates adsorb to and enmesh particles as the flocs settle (FCH, 2011, Duan and Gregory, 2003). The precipitates have large adsorptive surface area and positive electrostatic surface charge that can attract the negatively charged particles in the solution (Zahrim and Dexter, 2016, Zhang et al., 2011, Gao et al., 2007, Semerjian and Ayoub, 2003). This is the most probable reason why the amount of settled solids was higher due to mixing with white precipitate at the bottom of the beaker. Similar phenomena occur with the calcium lactate, however calcium (1.0) is lesser electronegative than the magnesium (1.2), thus particles in the solution is less attracted to calcium compared to magnesium. PolyDADMAC might make the flocs undergo charge neutralization and bridging mechanisms (Zahrim and Dexter, 2016, Pearse, 2005). However, the colour removal was the lowest compared to others due to an excess of polyDADMAC molecules that cause charge reversal occurs on the particle surfaces (Zahrim et al., 2014, Ariffin et al., 2012). In addition, polyDADMAC alone can achieve up to 40% of colour removal at dosage of 1000 mg/L as shown elsewhere (Zahrim and Dexter, 2016).



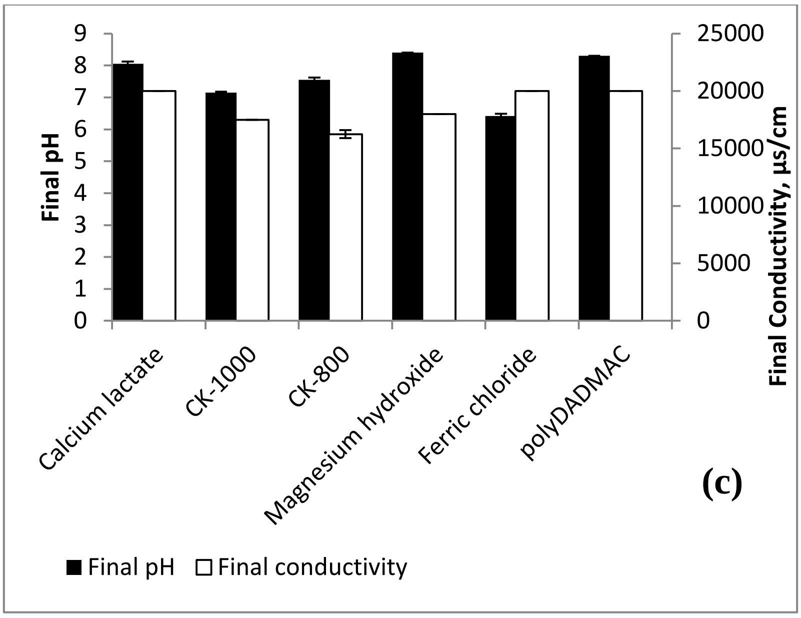


Fig. 1. The coagulation of biogas plant wastewater by various types of metal flocculant (a) colour removal (b) zeta potential measurement (c) pH and conductivity (Flocculant dosage = 8000 mg/L; pH = 7.95; conductivity = 17297 µS/cm; initial zeta potential = -13.35 mV).

Fig.1b shows the zeta potential value after the coagulation-flocculation process at the dosage of 8000 mg/L. Initially, the zeta potential value for the wastewater was -13.35 mV, showing the presence of negatively charged particles in the wastewater. The presence of positively charged coagulant adsorbs onto the particle surface thus alters the zeta potential value to lower negative value (Tripathy and De, 2006). PolyDADMAC gives a very drastic change due to high solubility at the given pH and completion of charge neutralization mechanism. Electrostatic interactions are the main factor for the particles to transfer from the water to the polymer chain during flocculation (Zemaitaitiene et al., 2003). Positive value indicates the presence of high residual polyDADMAC molecules (cationic) during the coagulation-flocculation process, i.e N^+ attached or are adsorbed by the neutralized particles (Zahrim et al., 2015, Ariffin et al., 2012). Less increments were observed in calcium lactate and magnesium hydroxide,which might be due to a weak ionization behaviour of both flocculants (Zahrim et al., 2015). This might be the cause for insignificant change in zeta potential value.

Fig. 1c shows the effect of metal flocculants on treated water pH and conductivity. The wastewater pH was increased from the initial pH of 7.95 to 8.05, 8.40, and 8.30 in calcium lactate, magnesium hydroxide and polyDADMAC respectively. The increment of pH for the first two flocculants are due to the presence of hydroxide ion (OH^-) when dissociated and dissolved in water and the presence of OH^- ions indicating that the properties of the solution is basic (Bruice, 2007).In the polyDADMAC case, it is due to a wide range pH that has lifted up the value. Hydrolysis phenomenon might occur during the process which is at pH higher than 5.5 (SNF-FLOERGER, 2015, Zahrim et al., 2015). Contrary with the other flocculants, they tend to decrease the final pH to 7.15, 7.55, and 6.42 for CK-1000, CK-800, and ferric chloride respectively. This is due to the characteristic of Fe^{3+} and Al^{3+} that behaves as Lewis acid, reacts with OH^- ions (Lewis base) of wastewater precipitate in the form of $Fe(OH)_3$ or $Al(OH)_3$ (Song et al., 2004, Amokrane et al., 1997). Thus, by adding Lewis acid into a solution, it should decrease the pH by changing the balance between H^+ and OH^- ions. Normally, inorganic coagulants such as iron and aluminum salts may lower the alkalinity and pH of the solution into acidic condition (Zahrim et al., 2010). Therefore, the treated wastewater cannot be directly discharged into the watercourse, hence it needs to be neutralized (Zahrim et al., 2015). The conductivity of raw POMBPW indicates the total of ionized constituent of water related to the total sum of inorganic cations or anions that present in water (Fondriest, 2015, Emerson, 2010). This means that high conductivity indicates the water contains a large amount of inorganic salt and other ions. High conductivity in the receiving water may result in undesirable ecological effects on aquatic organisms (Morrison et al., 2001, Zahrim and Mariani, 2014). Nevertheless, the aim of this paper is to investigate the coagulation-flocculation process as a membrane pre-treatment. Overall, the conductivities of treated water have increased from around 1% to 13.5% for calcium lactate, CK-1000, magnesium hydroxide, ferric chloride, and polyDADMAC. This is due to the presence of excess unreacted chemical ions (Zahrim et al., 2015, Solberg and Wagberg, 2003). However, the conductivity for treated water using CK-800 reduced around 6%. The dissolved organics were removed by adsorption and precipitation along with the settlement of flocs (Van Benschoten and Edzwald, 1990). These findings indicate that the coagulation-flocculation process might release a minimum amount of residual flocculant in the treated water.

3.1.2 Effect of ferric chloride dosage

Fig.2a shows the colour removal at different dosage ranging from 500 – 10000 mg/L. From this figure, the colour removal increased with increasing dosage of ferric chloride up to 9000 mg/L, with a maximum of 82.8% colour removal achieved. High dosage was needed due to deal with high recalcitrant organic matter content and initial appearance of the raw POMBPW, which is blackish in colour. However, the colour removal was seen to be consistent at 7000 to 9000 mg/L dosage, i.e. the particles are further away from each other (Zahrim et al., 2015, Ariffin et al., 2012).Ahead of the optimal dosage of ferric chloride, the particles are re-stabilized and charge reversal takes place on the particle surface due to an excess of ferric chloride molecules (Zahrim et al., 2015, Ariffin et al., 2012).Furthermore, the appearance of the pretreated POMBPW was changed into dark orange hence, the colour removal was drop to 36% .

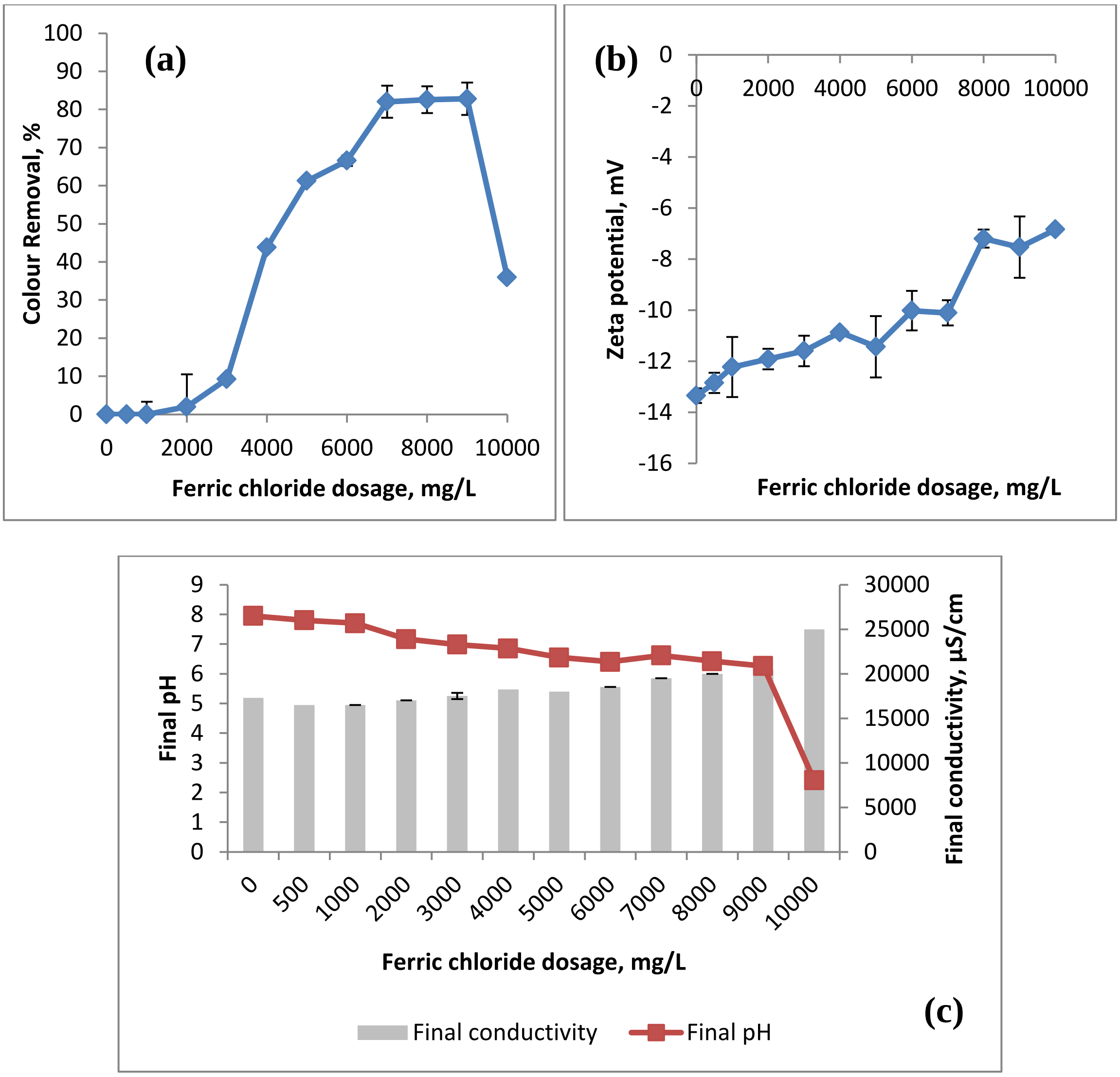


Fig. 2. The coagulation of biogas plant wastewater by ferric chloride at the dosage of 500 – 10000 mg/L (a) colour removal (b) zeta potential measurement (c) pH and conductivity (pH = 7.95; conductivity = 17297 µS/cm; initial zeta potential = -13.35 mV).

Fig. 2b shows the zeta potential at different dosage of ferric chloride. It clearly shows that the zeta potential value increases as the ferric chloride dosage. Cationic inorganic salt is capable to reduce the negative charge of particles by charge neutralization (Zahrim et al., 2015, Lee and Westerhoff, 2006). Electrical repulsion between particles is reduced, which results the formation of flocs and surface charge reduction (Bolto and Gregory, 2007, James et al., 2003).Fig. 2c shows the treated pH and conductivity at different dosages by ferric chloride. As the dosage increases, the treated solution pH decrease indicates that ferric chloride lower the pH of the solution which turn treated water pH into acidic solution (Zahrim et al., 2010). Inorganic salts in solution form react with alkalinity in the water to form insoluble hydrous oxide that coagulate by sweep flocculation and charge neutralization (Zeta-Meter, 1988).The conductivity shows increment of value as the dosage increase. This is due to the presence of unreacted ferric chloride as residues in the wastewater (Solberg and Wagberg, 2003).

3.1.3 Effect of pH

Fig. 3a shows the colour removal and zeta potential value of POMBPW after treatment by ferric chloride at various pH values. From this figure, we can see that the pH of POMBPW has an influence on coagulation-flocculation through using ferric chloride. Furthermore, the figure shows an optimum colour removal was at pH 10.0 giving 93.0% removal. This high removal may be due to the presence of most of the ferric chloride hydrolysates, such as $Fe(OH)^{2+}$ and $Fe(OH)_2^+$ in the solution. These are then neutralized by abundance of OH^- ions and anionic particles in the POMBPW (Boulestreau and Miehe, 2010, Duan and Gregory, 2003). However, at pH below 10.0, the colour removal was in the range of 83.0-87.0%, which indicates the abundance of H^+ ions in acidic solution over anionic particles, hence restricted the charge neutralization to take place. It can be elucidated in the zeta potential profile, where the value was beyond zero at pH 3.0 and 6.0 indicating that the solution contains more cationic ions after neutralization take place. The initial zeta potential value at pH 3.0 and 6.0 was -5.95 mV and -9.53 mV respectively. Same case with at pH 7.0 and 10.0, where the zeta potential value was increased from -15.00 mV and -16.28 mV respectively after the addition of ferric chloride, however the dosage was not enough to neutralize completely the anionic particles in the solution.

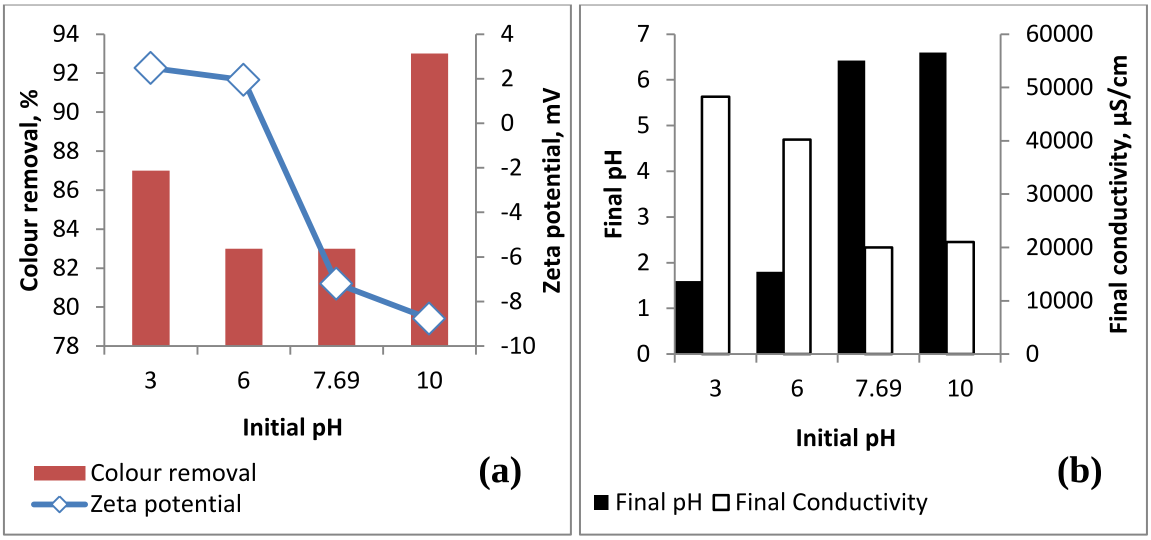


Fig. 3. The coagulation of biogas plant wastewater by ferric chloride at different pH (a) colour removal and zeta potential measurement (b) pH and conductivity (Ferric chloride dosage = 8000 mg/L).

Fig. 3b shows the pH and conductivity after coagulation-flocculation process by ferric chloride at various pH values. It clearly shows that inorganic metal salts tend to decrease the pH solution regardless the pH. At pH 3.0and 6.0, the solution is too acidic and cannot be directly discharged into the watercourse hence it needs to be re-neutralized and thiscan increase the capital cost. Beyond those values, i.e. 7.0and 10.0, the solution showed nearly neutral pH and therefore can be directly discharged into the watercourse as they meet the discharge requirement standard (5.0−9.0) by the Malaysian Department of Environment (Liew et al., 2015). However, it seems impracticable to adjust the pH up to 10.0 just to achieve nearly neutral pH after treatment as it involves more cost. The conductivities result show very high value at pH 3.0 and 6.0 due to an excess of unreacted ferric chloride and also hydrochloric acid in the solution which has the same charge. Slightly high removal was observed at pH 3.0 due to self-aggregation of POMBPW particles at acidic conditions. However, at pH 7.0 and 10.0, the conductivities were much lesser due to improvement of flocculation.

3.2 Flocculation using ferric chloride-polymer

In this preliminary study, polyDADMAC was added as a flocculation aid to ferric chloride in order to reduce the dosage of ferric chloride. PolyDADMAC dosage was fixed at 8 mg/L and was added into the solution during slow mixing time. Based on the Fig. 4, the colour removal was increasing as the dosage of ferric chloride increased. The optimum dosage of ferric chloride was found to be at 5800 mg/L, i.e. 83.4% removal. Beyond this optimum dosage, the removal was observed to be consistent. The zeta potential profile also shows increment of value towards zero as the dosage of ferric chloride was increased. Cationic ions that are presence in ferric chloride and polyDADMAC were affected the behaviour of particles surface charge measurement in the solution during charge neutralization mechanism.

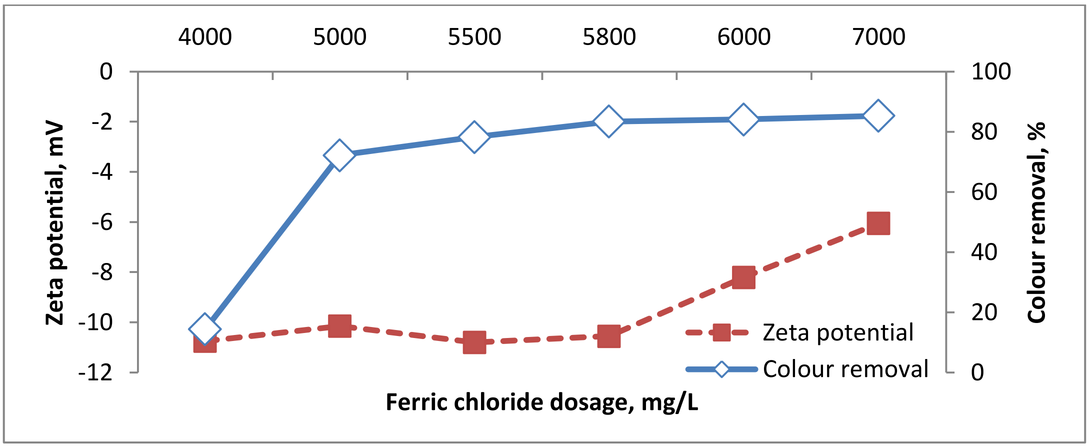


Fig. 4. The colour removal and zeta potential of biogas plant wastewater by ferric chloride at different dosage coupled with fixed polyDADMAC concentration (polyDADMAC dosage = 8 mg/L; pH =8.22; conductivity = 15645 µS/cm).

3.2.1 Effect of polymer type

Six types of polyacrylamide (PAM) with different charge and molecular weight were tested and compared the performance in treating POMBPW as a flocculation aid. Fig. 5ashows that Tramfloc 141 (anionic polyacrylamide a.k.a. APAM) gave the highest colour removal at

91.5%, followed by Tramfloc 724 (polyDADMAC). Based on this figure, the usage of dual coagulants could enhances the coagulation-flocculation process compared to the use of sole coagulant application which gave only at 60.1% removal. However, not all dual coagulants combination show good colour removal. The lowest removal was recorded at 46.2% by QF23912 followed by QF25610 and QF24807 at 58.8%and 63.1% removal respectively. The reason behind this isthat PAMs are cationic. The availability of cationic ions from this dual coagulants exceeded the requirement of charge neutralization occurrence, hence it deteriorates the performance, resulting restabilization of flocs due to charge reversal(Lee et al., 2014, Bolto and Gregory, 2007, Duan and Gregory, 2003). Another two flocculants, i.e AN1500 and AN1800 were observed which could slightly enhance the removal at 73.1% and 71.4% respectively. Inorganic metal salts are often combined with anionic or non-ionic polymeric flocculants in the coagulation-flocculation process to enhance the overall performance (Lee et al., 2014, Chong, 2012).After charge neutralization by ferric chloride, APAM molecules extend into solution and produce loops and tails to promote bridging of flocs (Lee et al., 2014, Bolto and Gregory, 2007). However, the APAM dosage was not sufficient to form bridging contact. Fig. 5b shows the pH and conductivity of treated POMBPW by ferric chloride coupled with various types of polymers. Based on the figure, the pH was consistent despite the type of polymer used, which clearly indicates that the solution was not affected by the polymer due to the dosage was small. Contrary with conductivity, lowest value was observed at 13000 µS/cm by ferric chloride-polyDADMAC and ferric chloride-APAM. This indicates that the dissolved organics have also been removed during the coagulation-flocculation process.

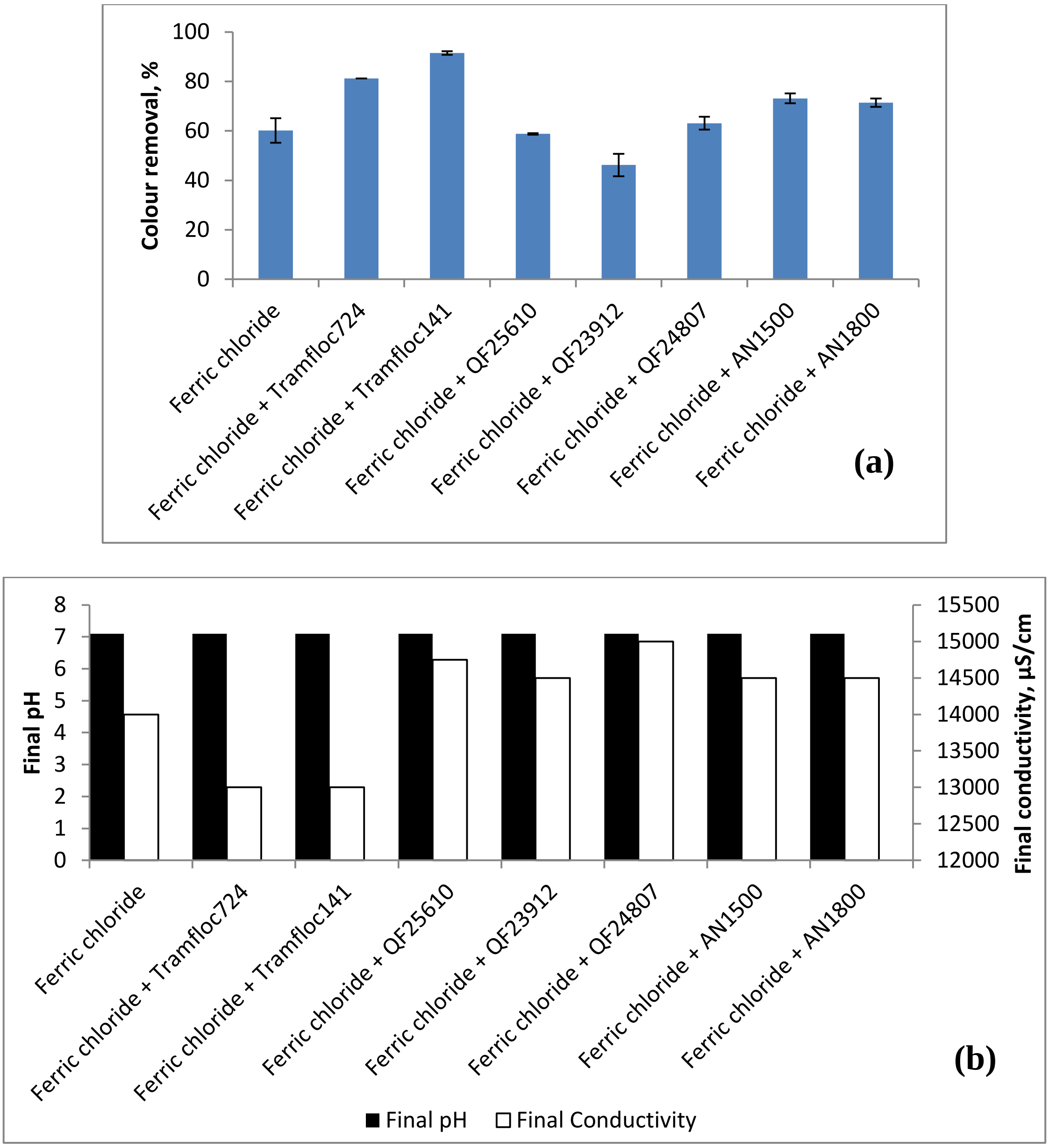


Fig. 5. The coagulation of biogas plant wastewater by ferric chloride coupled with various type of polymer (a) colour removal (b) pH and conductivity (Ferric chloride dosage = 5800 mg/L; polymer dosage = 8 mg/L; pH = 7.95; conductivity = 14250 µS/cm).

3.2.2 Effect of flocculant aids dosage

The study was extended by varying the polymer dosage from 0 to 10 mg/L for polyDADMAC and APAM as the best dual coagulants combination. This study was conducted in two different sets namely for ferric chloride-APAM and ferric chloride-polyDADMAC respectively with both sets have three trial runs. Based on Fig. 6, ferric chloride-APAM combination shows increase in colour removal as the dosage of APAM was increased, whereas for ferric chloride-polyDADMAC combination, the removal was consistent regardless the polyDADMAC dosage. It shows that polyDADMAC slightly affect the decolourisation whereas ferric chloride was primarily affect the overall performance. The highly viscous properties of APAM solution was suitable to be used as a flocculation aid since the POMBPW was rich in suspended solids content. Therefore, it bridges most of the microflocs into macroflocs during the process. However, it was reported that the presence of multivalent metal ions such as ferric ions (Fe^{3+}) could severely affect the flocculation by APAM, due to complexation of the metal with carboxylate groups on the polymer chain and thus effective reduction in charge density(Bolto and Gregory, 2007, Henderson and Wheatley, 1987). Even so, ferric chloride-APAM combination did not show any bad result, in fact it can still gives over 90% of colour removal at dosage of 8 mg/L and 10 mg/L. Such a finding implies that the concentration of APAM was sufficient enough to use as a flocculation aid with the specific concentration of ferric chloride used in this study.

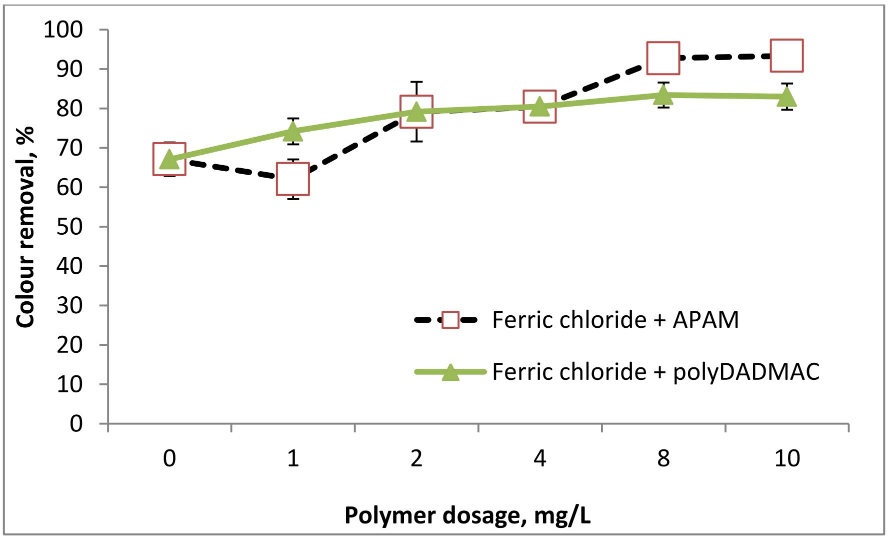


Fig. 6. The colour removal of biogas plant wastewater by ferric chloride coupled with various polymer dosages (Ferric chloride dosage = 5800 mg/L; pH = 8.0; conductivity = 12625 µS/cm).

3.2.3 Effect of pH

The performances of dual coagulants were then tested at various pH as shown in Fig. 7. Based on the figure, it was found the colour removal by using ferric chloride-APAM doesn’t show significant changes from pH 6.0 to 10.0. As mentioned before, APAM acts as a "bridger" and attaches the particles altogether during the flocculation process despite the changes of pH. The destabilized particles aggregate into a large mass and settle fast. Similar finding was reported by(Ariffin et al., 2012). Hence, it can be deduced that the solution properties also have significant effects on the colour removal as has been explained earlier. For ferric chloride-polyDADMAC case, the colour removal dropped drastically at pH 10.0. It can be elucidated with high availability of OH^-ions in the solution which cause stronger mutual repulsion between the particles. Thus, the concentration of ferric chloride-polyDADMAC was not sufficient enough to suppress the charged surface layer of the particles and to produce flocs.

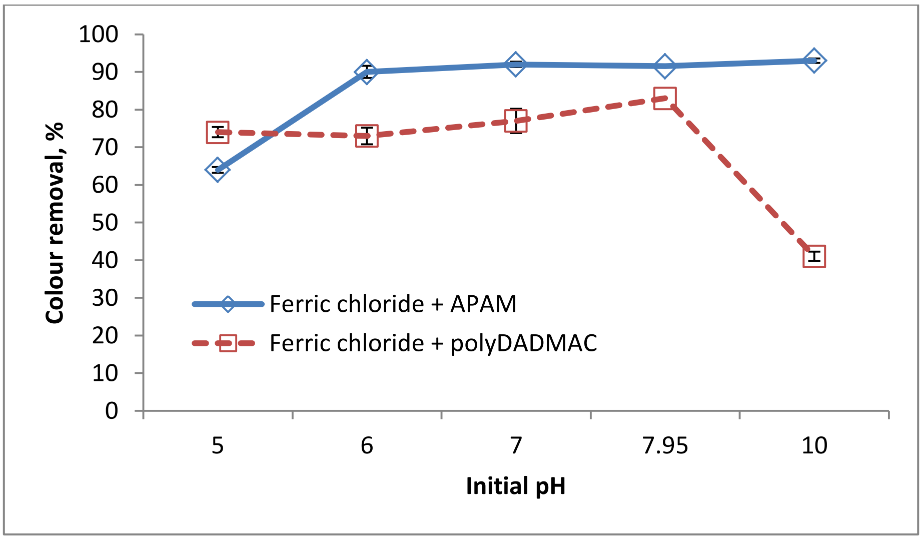


Fig. 7. The colour removal of biogas plant wastewater by ferric chloride coupled with polymer at different pH (Ferric chloride dosage = 5800 mg/L, polymer dosage = 8 mg/L).

3.2.4 Effect of sedimentation time

During the coagulation-flocculation process, the settling speed of flocs determines the efficiency of the whole process. Sedimentation time of the flocs in the POMBPW was investigated at 20, 30, 60, 120, and 180 minutes as shown in Fig. 8. Based on the figure, it was observed that the sedimentation of flocs from ferric chloride-APAM combination was faster than the ferric chloride-polyDADMAC combination during the first 20 minutes. It doubles the removal after another 10 minutes, however still no change was observed in ferric chloride-polyDADMAC combination until 60 minutes of sedimentation. Both dual coagulants were recorded to achieve over 90% of colour removal at 180 minutes. However, for ferric chloride-APAM combination, the removal was recorded with no significant change from 120 to 180 minutes since most of the flocs were already settled. The ferric chloride-APAM was efficient in producing high density of flocs in this kind of wastewater which can settle fast. Therefore, it can be concluded that the optimum sedimentation time for this process was at 120 minutes as per recorded in this study.

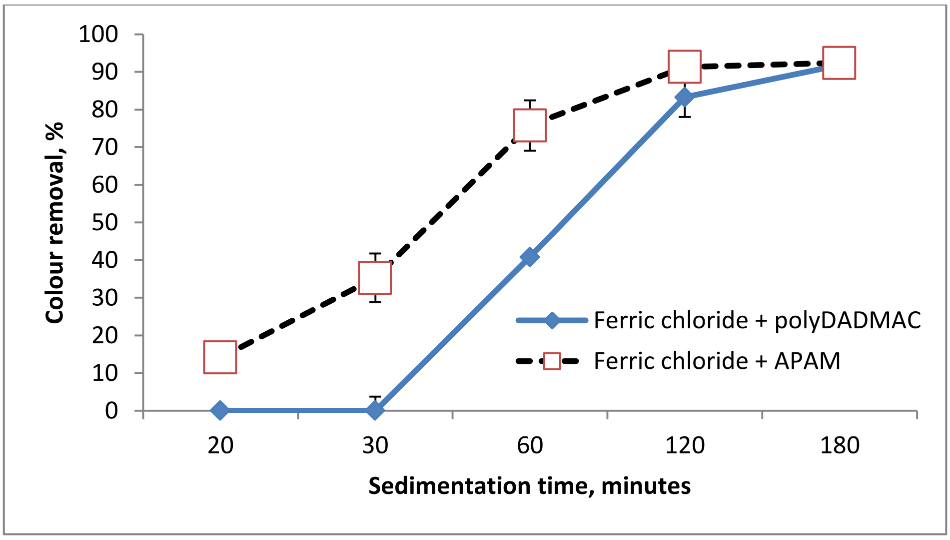


Fig. 8. The effect of sedimentation time on colour removal of biogas plant wastewater by ferric chloride coupled with polymer (Ferric chloride dosage = 5800 mg/L, polymer dosage = 8 mg/L; pH = 8.08; conductivity = 13625 µS/cm).

3.3 Flocculationkinetics

The plot for second order kinetic to the experimental data of the coagulation-flocculation process carried out on the POMBPW using ferric chloride coupled with polymers i.e. polyDADMAC and APAM is shown in Fig. 9. Based on the figure, it was observed that there is a linear relationship between 1/C versus reaction time, t. The plot in this graph obeys second order kinetic equation as it shows the Y-axis intercept. Similar finding of second order kinetic result were reported by several researchers(Mageshkumar and Karthikeyan, 2016, Vijayaraghavan and Shanthakumar, 2015, Nnaji et al., 2014). The kinetic constant for ferric chloride-polyDADMAC and ferric chloride-APAM were 2×10^{-5}/PtCo.min and 3×10^{-5}/PtCo.min respectively. Based on these rate constant values, ferric chloride-APAM was higher than ferric chloride-polyDADMAC, which indicates that the rate of reduction in colouris faster for ferric chloride-APAM than ferric chloride-polyDADMAC. APAM enhances the flocculation by creating larger floc size from microflocs to macroflocs which yields to a rapid settling (Teh et al., 2016, Aguilar et al., 2005). Table 4 shows the relationship between half-life period ($t_{1/2}$) with initial colour of POMBPW for both dual coagulants. It should be noted that the half-life value was small due to the type of colour measurement used in this study. However, it still shows the ferric chloride-APAM was faster in terms of reduction to one-half the original colour.

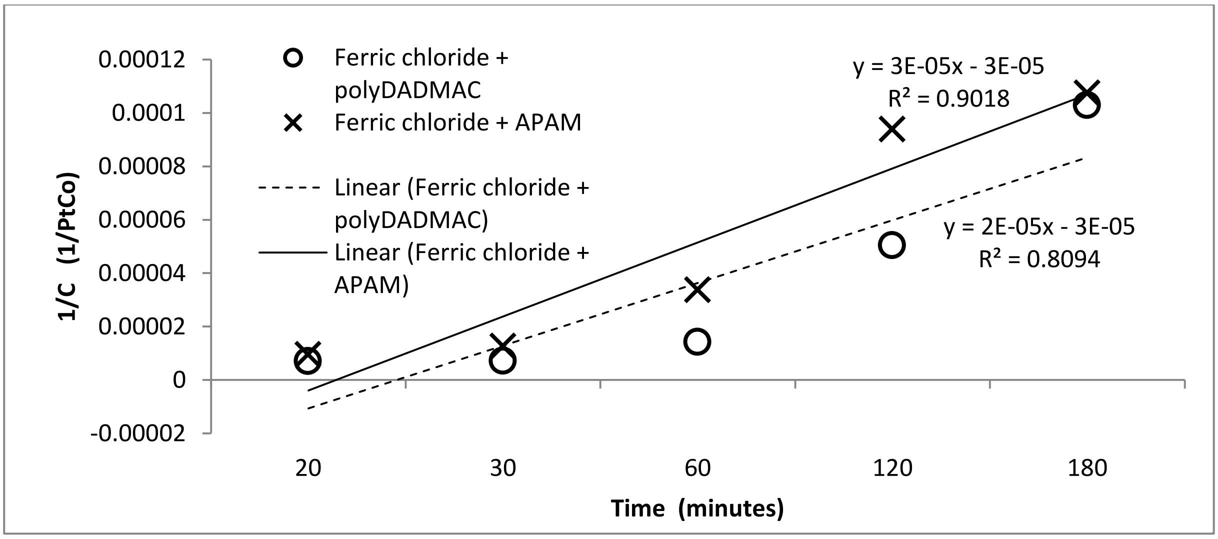


Fig. 9. Kinetic plot for ferric chloride-polymer for second order process (Ferric chloride dosage = 5800 mg/L, polymer dosage = 8 mg/L; pH = 8.08; conductivity = 13625 μS/cm, initial colour = 120382 PtCo).

Table 4. Kinetic parameters for second order dual coagulants

Parameter	Ferric chloride-APAM	Ferric chloride-polyDADMAC
R^2	0.901	0.809
k_2 (1/PtCo.min)	3×10^{-5}	2×10^{-5}
$t_{1/2}$ (min)	0.277	0.415

A simple cost evaluation of using sole coagulant, dual coagulants, and other treatment methods has been compared and the results are shown in Table 5. The cost of chemical used in all studies are roughly calculated and compared to this study. The calculations are based on the respective optimum dosage for the treatment of one m^3 of wastewater feed.

From the table, studies from Ahmad et al. (2006 and 2005b) possess the cheapest cost, however the studies only mentioned about removal of residual oil and suspended solid i.e. more than 95% removal. Dual coagulants showed a very reasonable cost in treating POMBPW that is still consists of high COD value. The total cost for both dual coagulants are US $5.80/$m^3$ of POMBPW feed and can be considered as economical in treating POMBPW. In addition, the cost is reduced to 27% from the sole ferric chloride used and yet achieved higher decolourisation.

Table 5. Estimated costs to treat one m^3 of wastewater feed at the optimum dosages.

Chemical	Optimum dosage (mg/L)	Cost/MT	Cost/m^3 of wastewater	Colour removal (%)	Reference

Ferric chloride	8000	US $500	US $8.00	82.6	This study
Ferric chloride-APAM	5800-8		US $5.82	> 90.0	This study
Ferric chloride-polyDADMAC	5800-8		US $5.82	> 80.0	This study
PolyDADMAC	1000	US $1500	US $3.00	48	(Zahrim and Dexter, 2016)
Granular activated carbon	200000	US $1000	US $2275.22	50.0	(Zahrim et al., 2009)
Hydrogen peroxide	250	US $600	US $2.37	61.3	(Abdullah, 2008)
Ferric sulphate-hydrogen peroxide	400-1150		US $7.47	95.1	(Aris et al., 2008)
Chitosan	500	US $30000	US $4.37	NA	(Ahmad et al., 2005b)
Bentonite	10000	US $200	US $0.58	NA	(Ahmad et al., 2005b)
Activated carbon	8000	US $1000	US $2.33	NA	(Ahmad et al., 2005b)
Polyaluminium chloride	6000	US $300	US $0.52	NA	(Ahmad et al., 2006)
Alum	8000	US $200	US $0.47	NA	(Ahmad et al., 2006)

*Cost/MT of APAM =US $1500

*Cost/MT of polyDADMAC = US $1500

*Cost/MT of ferric sulphate = US $200

*All cost for chemicals were derived from www.alibaba.com (accessed on 12th December 2016)

3.4 Germination Index

Cabbage seed was used in germination tests due to it is one of the main highland vegetable that is mostly planted here in Sabah, Malaysia (Jipanin et al., 2001). The tests were performed to access the phytotoxicity of the settled solids from the coagulation-flocculation process and the results are shown in Fig. 10. The test was a continuation to previous experiment (subsection 3.2.1), where the sludge was collected after the coagulation-flocculation process. Therefore, the extracts have equivalent amount of ferric chloride dosage (5800 mg/L) and polymer (8 mg/L) i.e. APAM and polyDADMAC. Based on Figure 10, all extracts show GI value above 80% which indicated phytotoxins free (Troy et al., 2013, Tiquia and Tam, 1998). It was reported that GI% values below 50% indicated the presence of phytotoxic compounds in the water-soluble extracts (Troy et al., 2013). Studies in agricultural field by using APAM showed that the application of APAM to the soil may improve the soil permeability, stabilizing the soil structure, minimizing dispersion, and encourage aggregate formation to enhance pore continuity (Kumar and Saha, 2011, Jiang et al., 2010, Busscher et al., 2007, Entry et al., 2002, Sojka and Entry, 2000). Furthermore, APAM had a significant effect on the reduction of surface runoff and nutrient loss from the soil (Sojka et al., 2007, Flanagan and Canady, 2006, Lentz et al., 2001). In another study, (Skene et al., 1995) reported that alum/polyDADMAC sludge could be used as plant growth medium when it is mixed with fertiliser. While in water, hydrophobic groups of polymer travelled inside the aggregates and created hydration of hydrophilic groups and water molecules by hydrogen bonding. This bond produces a water molecule monolayer on the surface of aggregates. Osmotic pressure gradient was formed due to the ion concentration gradient between the inner and outer of the monolayer, which prevents some water molecules inside the layer from moving freely, thus limiting soil nutrient losses (Jiang et al., 2010, Yuan et al., 2005).

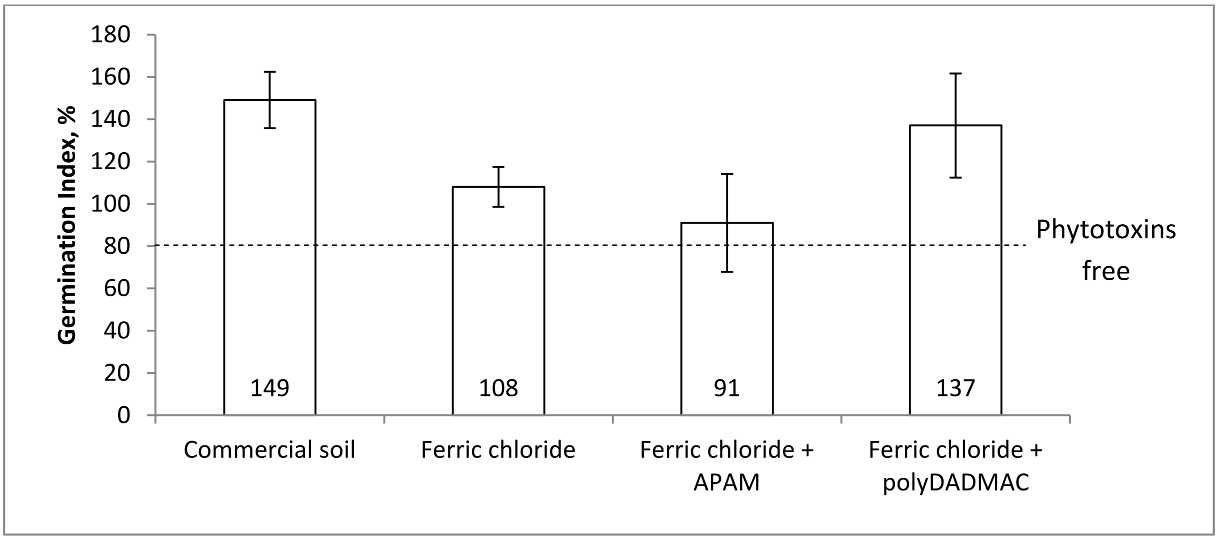


Fig. 10. The germination index (GI%) of cabbage seeds in the water-soluble extracts at different types of dry solids sample (50% commercial soil + 50% dry solids).

4. Conclusion

Decolourisation of POMBPW using various metal flocculants including calcium lactate, ferric chloride, magnesium hydroxide, aluminum chlorohydrate (CK-1000 and CK-800), and polyDADMAC; was investigated. The optimum colour removal was found at coagulant dosage 8000 mg/L for ferric chloride. At pH 10.0, ferric chloride showed a good performance in removing colour up to 90%.

Dual coagulants shows better performance than the sole ferric chloride, not only in terms of colour removal but also reduces the amount of ferric chloride used in the treatment. The dual coagulants of ferric chloride-APAM was found to be the best combination compared to ferric chloride-polyDADMAC, where it can achieve up to 90% of colour removal, and was not affected by the changes in POMBPW pH at higher value. Furthermore, it can produce high density flocs which can settle fast at early of 20 minutes of sedimentation.

The coagulation-flocculation process followed second order kinetic equation for both dual coagulants. The kinetic rate constant for ferric chloride-APAM was found to be more than the ferric chloride-polyDADMAC, which indicates rapid settling of flocs. The germination index results show both dual coagulants were phytotoxin free i.e. 91% and 137% for ferric chloride-APAM and ferric chloride-polyDADMAC respectively, thus they have the potential to be reused for land application in the future.

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