

Decolourisation of palm oil mill biogas plant wastewater using Poly-Diallyldimethyl Ammonium Chloride (polyDADMAC) and other chemical coagulants

A Y Zahrim^{1, 2, 3, 4*} and Z DDexter¹

¹Chemical Engineering Programme, Faculty of Engineering, *Universiti Malaysia Sabah*, Jalan UMS 88400 Kota Kinabalu, Sabah, Malaysia

²Water Research Unit, *Universiti Malaysia Sabah*, Jalan UMS 88400 Kota Kinabalu, Sabah, Malaysia

³Sustainable Palm Oil Research Unit, *Universiti Malaysia Sabah*, Jalan UMS, 88400 Kota Kinabalu, Sabah, Malaysia

⁴Energy Research Unit, *Universiti Malaysia Sabah*, Jalan UMS 88400 Kota Kinabalu, Sabah, Malaysia

E-mail: ¹zahrim@ums.edu.my

Abstract. Palm oil mill effluent was expected as a future source of renewable biogas. Nevertheless, colours in palm oil mill biogas plant wastewater (POMBPW) causes negative perception among the public and the wastewater is difficult to be treated biologically. In this study, the performance of various chemical coagulants i.e., calcium lactate, magnesium hydroxide, ferric chloride, aluminium chlorohydrate i.e. CK-800, CK-1000, and polyDADMAC, for POMBPW colour removal were investigated. PolyDADMAC (1,000 mg/L) shows best colour removal (~48%). The main coagulation process with polyDADMAC could be due to charge neutralization-bridging mechanism. The zeta potential analysis supports the finding where the value became positive as the dosage increases. The addition of polyDADMAC has increased the conductivity of the treated wastewater up to 9.22%; however, the final pH is maintained (8.0-8.3). It can be deduced that polyDADMAC has potential to treat POMBPW at low dosage.

1. Introduction

Biogas plant is adapting the anaerobic digestion technology system where it uses anaerobic bacteria to convert the organic carbon i.e. chemical oxygen demand (COD) and biochemical oxygen demand (BOD) to biogas [1]. Nevertheless, the liquid wastewater from this plant i.e. palm oil mill biogas plant wastewater (POMBPW) still has high level of polluting contents, thus cannot be discharged into the watercourse. Nowadays, polymers such as poly-diallyldimethylammonium chloride (PolyDADMAC) and polyacrylamide (PAM) are used widely in coagulation process as a sole coagulant or in combination with inorganic metals. PolyDADMAC is a synthetic, high molecular weight, and highly positively charged (cationic) polymer [2]. In this study, the colour removal of POMBPW was

¹ To whom any correspondence should be addressed.



investigated by a coagulation/flocculation process using a polyDADMAC as a sole coagulant. In addition, the effect of various coagulants was also investigated i.e. calcium lactate, magnesium hydroxide, ferric chloride, and aluminium chlorohydrate.

2. Materials and methods

The POMBPW was collected from the overflow of anaerobic digester tanks in Lahad Datu, Sabah. Six types of coagulant were used in this study and prepared for their stock solution such as 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 coagulants in liquid form were supplied by Chemkimia Sdn. Bhd. Both coagulants are aluminium chlorohydrate; Chemchlor CK-800 and Chemchlor CK-1000 are in 45% wt. Polymer i.e. polyDADMAC (Tramfloc® 724, 40% wt) was supplied by Tramfloc, Inc., Houston, Texas. Details on coagulation/flocculation experiments as well as physico-chemical analysis were described in previous publications [3, 4]

3. Results and discussions

3.1 Effect of various coagulants

Figure 1 shows the effect of coagulant types on the colour removal of POMBPW at the dosage of 1,000 mg/L. PolyDADMAC gives the highest removal i.e. 47.9%, followed by CK-800 (37.4%), magnesium hydroxide (21.9%), and calcium lactate (9.2%). However, both CK-1000 and ferric chloride did not show any removal. PolyDADMAC might make the flocs undergo charge neutralization and bridging mechanisms [5]. Despite the same chemical (ACH), both CK-1000 and CK-800 have different specific gravity. This specific gravity is the measurement of the chemical strength and has a strong relationship with the basicity and molecular weight of the chemical [6]. Higher specific gravity indicates higher molecular weight. Molecular weight of chemical may affect its dissolution in water where the dissolution rate decreases as the molecular weight increased [7]. Therefore in this case, CK-800 is easily soluble in compared to the CK-1000 which is has high molecular weight. Contrary with magnesium hydroxide and calcium lactate, where there was no rapid formation of flocs after been added into the wastewater. Magnesium hydroxide form precipitates, which have large adsorptive surface area and positive electrostatic surface charge, that can attract the negatively charged particle in the solution through charge neutralization and adsorption [8-10]. Same case with calcium lactate, adsorption and charge neutralization mechanisms are occur during the process, however electronegative behaviour of calcium is lesser than the magnesium, thus it affect the attraction of particle of the solution with the metal.

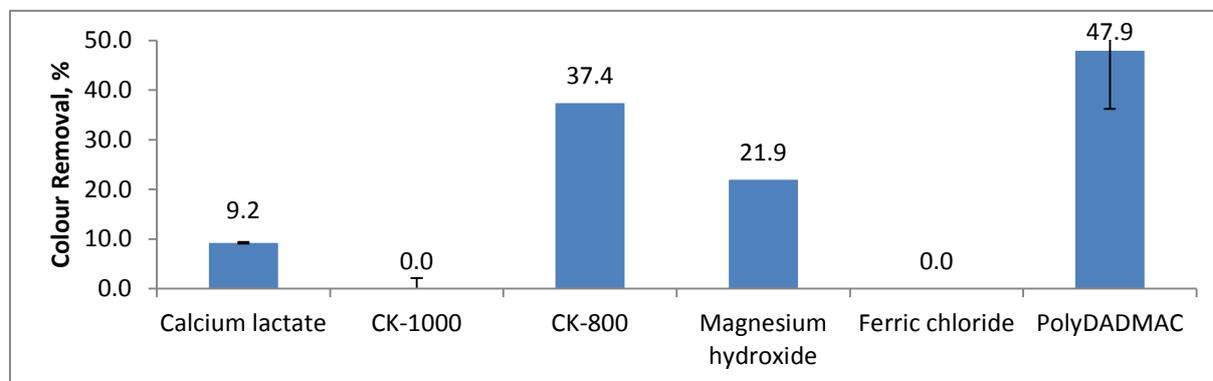


Figure 1. The colour removal of POMBPW by various coagulants at the dosage of 1,000 mg/L, pH = 7.95, Conductivity = 17297 $\mu\text{s}/\text{cm}$

Figure. 2 shows the zeta potential value after the coagulation process at the dosage of 1,000 mg/L. Initially, the zeta potential value for the wastewater is -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 alter the zeta potential value towards less negative value [11]. However, at low dosage, they did not give a big effect in the wastewater. PolyDADMAC gives a very significant change i.e. -8.01 mV due to high solubility at the given pH. Electrostatic interactions are the main factor for the particles to transfer from the water to the polymer chain during flocculation [12].

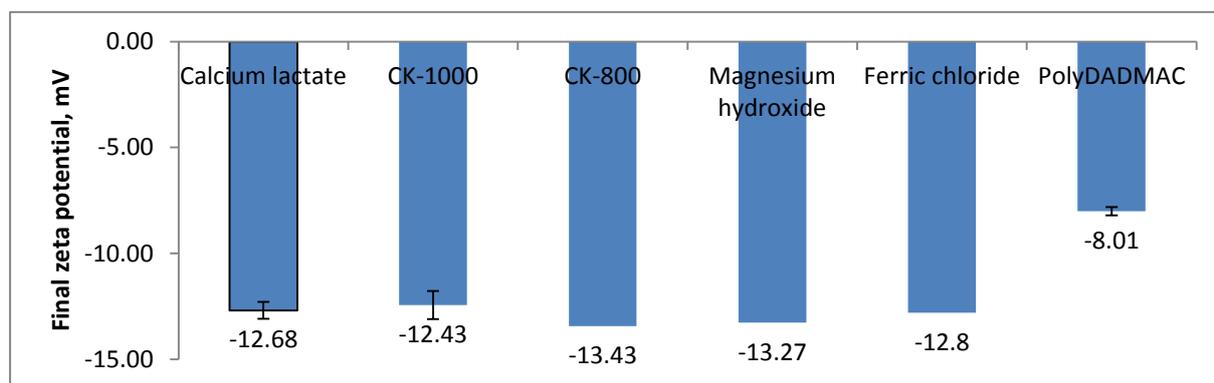


Figure.2. Final zeta potential of POMBPW by various coagulants at the dosage of 1,000 mg/L, pH = 7.95, Conductivity = 17297 $\mu\text{s}/\text{cm}$

Figure. 3 shows the effect of coagulant on treated water pH and conductivity. The pH of the wastewater is increase from the initial pH of 7.95 to 8.45, 8.50, 8.35, and 7.97 in calcium lactate, magnesium hydroxide, polyDADMAC, and CK-800 respectively. The first two coagulants are due to the presence of hydroxide ion (OH^-) when dissociated and dissolved in water and the presence of OH^- ion indicates the properties of the solution to be basic [13]. In polyDADMAC case, it is due to wide range pH that has lift up the value a little. Hydrolysis phenomenon might occur during the process which is at pH higher than 5.5 [3, 14]. CK-800 only shows very small increment. Contrary with the other coagulants, they tend to decrease the final pH to 7.78 and 7.70 for CK-1000 and ferric chloride respectively. This is due to the characteristic of Fe^{3+} and Al^{3+} that behave as Lewis acids, react with OH^- ions (Lewis base) of wastewater precipitate in the form of $\text{Fe}(\text{OH})_3$ or $\text{Al}(\text{OH})_3$ [15, 16]. 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 [17]. Therefore, the treated wastewater cannot be directly discharge into the watercourse hence it needs to be re-neutralized [3].

The conductivity for raw POMBPW is 17297 $\mu\text{s}/\text{cm}$, yet, this value is still within the range of 6500 - 35900 $\mu\text{s}/\text{cm}$ [4, 18]. This parameter indicates of total ionized constituent of water and related to the total sum of inorganic cations or anions that presence in water [19, 20]. Means that, high conductivity indicates the water still contains a large amount of inorganic salt and other ions. The conductivity of treated water using calcium lactate as coagulant has increased by 2.62%. This is due to the excess presence of unreacted calcium lactate [3, 21]. However, the conductivities for treated water using CK-1000, CK-800, magnesium hydroxide, ferric chloride, and polyDADMAC were decreased around 7.50%, 10.39%, 1.72%, 4.61%, and 0.27% respectively. The dissolved organics were removed by adsorption and precipitation along with the settlement of flocs [22]. These findings indicate that the coagulation process might release minimum amount of residual coagulant in the treated water.

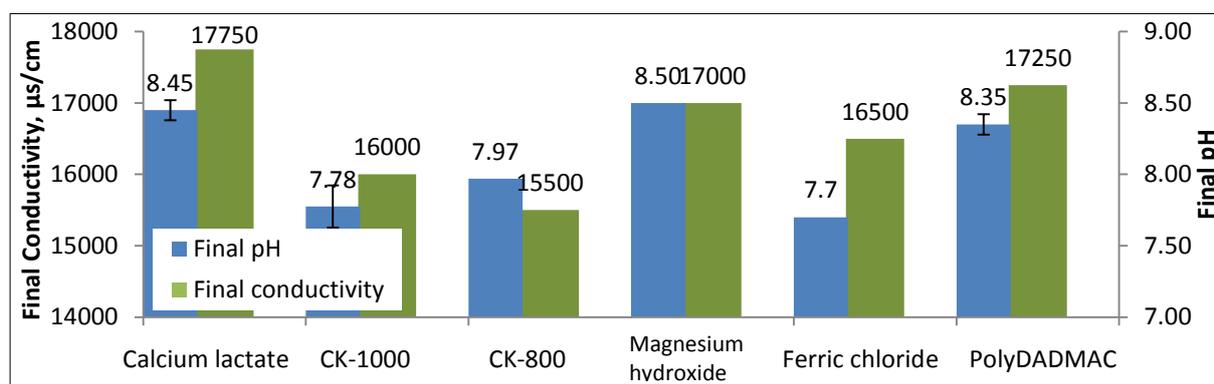


Figure.3. Final pH and conductivity of POMBPW by various coagulants at the dosage of 1,000 mg/L, pH = 7.95, Conductivity = 17297 µs/cm

3.2 Effect of polyDADMAC dosage

Figure. 4 shows the colour removal at different dosage ranging from 500 – 10,000 mg/L. From this figure, polyDADMAC is indeed capable to treat wastewater as a sole coagulant at higher than 1,000 mg/L. The removal is between 40 – 56%; indicates that the characteristic of raw water was varied and polyDADMAC is sensitive to the small change in wastewater characteristics. Similarly, the performance is inconsistent as the dosage increase where it tends to decrease. Ahead of the optimal dosage of polyDADMAC, the particles are re-stabilized and charge reversal take place on the particle surfaces due to an excess of polyDADMAC molecules [3, 23].

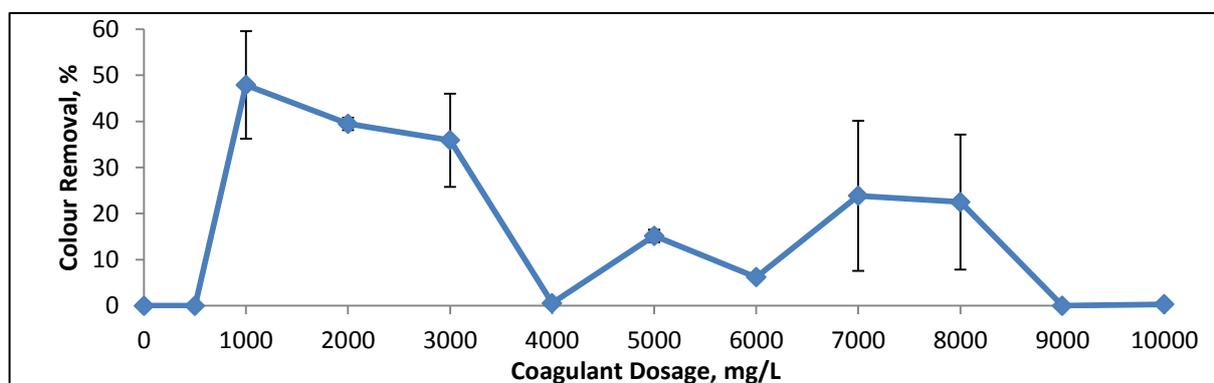


Figure.4. The colour removal of POMBPW by polyDADMAC at different dosages, pH = 7.99, Conductivity = 18,156 µs/cm

Figure. 5 shows the zeta potential at different dosages of polyDADMAC. It clearly shows the zeta potential value is increases as the polyDADMAC dosage increased. Cationic polymer is capable to reduce the negative charge of particles by charge neutralization [3, 24]. Electrical repulsion between particles is reduced, which results the formation of flocs and surface charge reduction [25, 26]. As the polyDADMAC dosage increases, the zeta potential value become greater than zero indicating after complete neutralization mechanism [3] which can be explained by the presence of excess polyDADMAC during the process. The chains of polyDADMAC carry N^+ are attached or adsorbed by the neutralized particles [3, 23].

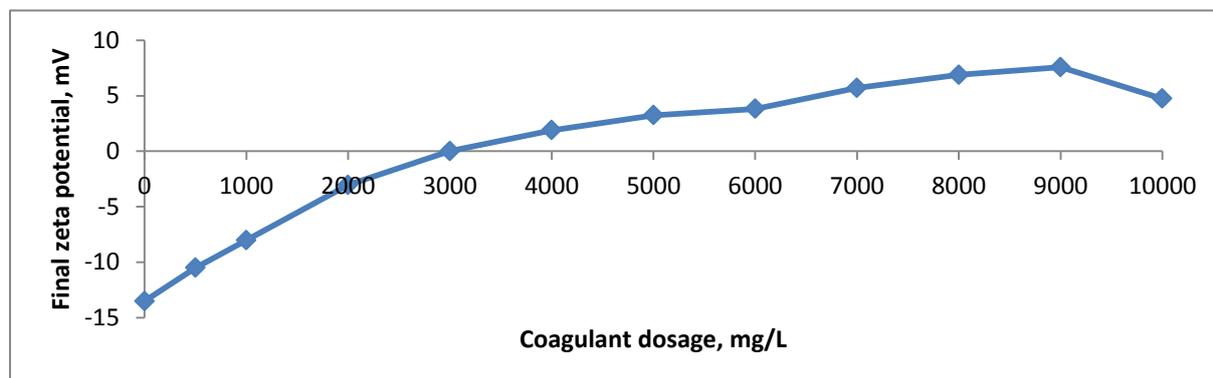


Figure.5. Final zeta potential of POMBPW by polyDADMAC at different dosages, pH = 7.99, Conductivity = 18,156 $\mu\text{s}/\text{cm}$

Figure. 6 shows the pH and conductivity at different dosages by polyDADMAC. The pH shows stable reading between 8.0-8.3 as the dosage increased indicates that it does not consume alkalinity unlike the inorganic coagulant [17]. Inorganic salts in solution form react with alkalinity in the water to form insoluble hydrous oxide that coagulate by sweep flocculation and charge neutralization [27]. The conductivity shows increment of value as the dosage increase. This is due to the presence of unreacted polymer as residues in the wastewater [21]. At optimum dosage of 1,000 mg/L, the conductivity is lesser than the initial value. It was reported that at optimum dosage the conductivity may show zero or minimum increment [3].

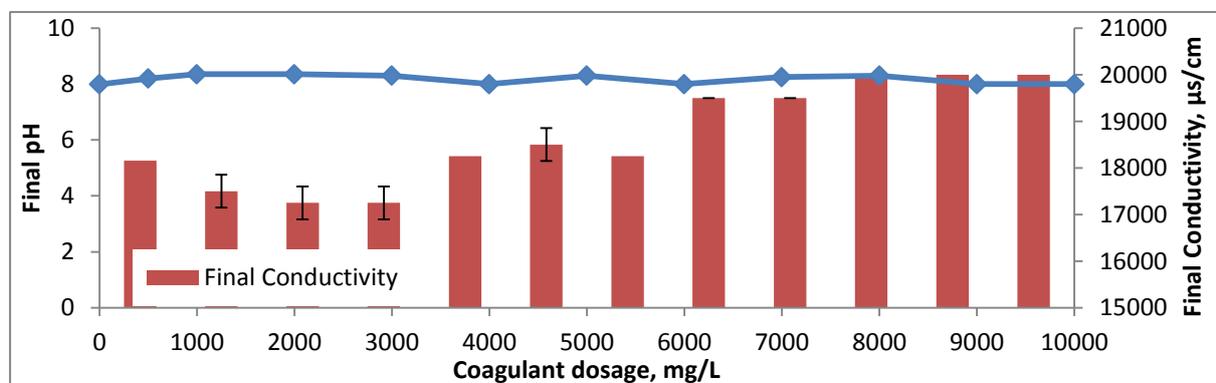


Figure.6. Final pH and conductivity of POMBPW by polyDADMAC at different dosages, pH = 7.99, Conductivity = 18156 $\mu\text{s}/\text{cm}$

4. Conclusions

In this study, at low dosage of 1,000 mg/L, polyDADMAC shows the best removal which is between 40 – 56%. The coagulation process with polyDADMAC may undergo a charge neutralization-bridging mechanism. The zeta potential also shows the value has increase significantly when the dosage was increased. Unreacted polyDADMAC presence in the treated water increase the treated water conductivity. At optimum dosage (1,000 mg/L), the conductivity was lesser than the initial value. The pH was however to be unchanging along the experiment at any dosage. It can be deduced that polyDADMAC has potential to remove the colour of POMBPW at the dosage of 1,000 mg/L. However, the treated water is cannot be discharged into the watercourse yet and a post treatment is highly recommended.

5. References

- [1] Chin M J, Poh P E, Tey B T, Chan E S, and Chin K L 2013 *Renewable and Sustainable Energy Reviews*, **26** pp 717-726
- [2] Zahrim A Y, Tizaoui C, and Hilal N 2011 *Desalination*, **266** pp 1-16
- [3] Zahrim A Y, Nasimah A, and Hilal N 2015 *Journal of Environmental Chemical Engineering*, **3** pp 2145-2154
- [4] Zahrim A Y, Nasimah A, and Hilal N 2014 *Journal of Water Process Engineering*, **4** pp 159-165
- [5] Pearse M J 2005 *Minerals Engineering*, **18** pp 139-149
- [6] Gebbie P 2006 University Central Queensland Campus, Rockhampton
- [7] Miller-Chou B A and Koenig J L 2003 *Progress in Polymer Science*, **28** pp 1223-1270
- [8] Gao B-Y, Yue Q-Y, Wang Y, and Zhou W-Z 2007 *Journal of Environmental Management*, **82** pp 167-172
- [9] Semerjian L and Ayoub G M 2003 *Advances in Environmental Research*, **7** pp 389-403
- [10] Zhang G, Li X, Li Y, Wu T, Sun D, and Lu F 2011 *Desalination*, **274** pp 255-261
- [11] Tripathy T and De B R 2006 *Journal of Physical Science*, **10** pp 93-127
- [12] Zemaitaitiene R J, Zliobaite E, Klimaviciute R, and Zemaitaitis A 2003 *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **214** pp 37-47
- [13] Bruice P Y 2007 Upper Saddle River, NJ: Pearson/Prentice Hall
- [14] SNF-FLOERGER (2015, 3 December). Available: snf.com.au/downloads/Preparation_of_Organic_Polymers_E.pdf
- [15] Amokrane A, Comel C, and Veron J 1997 *Water Research*, **31** pp 2775-2782
- [16] Song Z, Williams C J, and Edyvean R G J 2004 *Desalination*, **164** pp 249-259
- [17] Zahrim A Y, Tizaoui C, and Hilal N 2010 *Journal of Hazardous Materials*, **182** pp 624-630
- [18] Poh P E, Ong W Y J, Lau E V, and Chong M N 2014 *Journal of Environmental Chemical Engineering*, **2** pp 1174-1181
- [19] Fondriest (2015, 7 December). Available: <http://www.fondriest.com/news/what-is-conductivity.htm>
- [20] Emerson (2015, 7 December). Available: www2.emersonprocess.com/siteadmincenter/.../Liq_ADS_43-018.pdf
- [21] Solberg D and Wagberg L 2003 *Colloids Surf. A*, **219** pp 161-172
- [22] Van Benschoten J E and Edzwald J K 1990 *Water Res.*, **24** pp 1519-1526
- [23] Ariffin A, Razali M A A, and Ahmad Z 2012 *Chemical Engineering Journal*, **179** pp 107-111
- [24] Lee W and Westerhoff P 2006 *Water Research*, **40** pp 3767-3774
- [25] James M, Ebelinga, Kata L, Risbela, Philip L, and Sibrellb 2003 *Aquacultural Engineering*, **29(1)** pp 23-42
- [26] Bolto B and Gregory J 2007 *Water Res.*, **41(11)** pp 2301-2324
- [27] Zeta-Meter I 1988: Zeta-Meter

Acknowledgement

Authors would like to thank the Universiti Malaysia Sabah (SGI0013) and the Ministry of Higher Education, Malaysia (FRGS/2/2013/TK05/UMS/02/1) for funding this work.