CHARACTERIZATION AND BEHAVIOUR OF PALM OIL MILL EFFLUENT AND POLYALUMINIUM CHLORIDE: INFLUENCE OF PH

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ABSTRACT

A preliminary study was conducted to characterize the nano-sized suspended solids in palm oil mill effluent (POME) as a function of pH. A similar analysis was carried out on polyaluminium chloride (PACl) as well. In both experiments, the zeta potential and the corresponding particles size were measured at each pH value within a pH range from 3 to 12. At an initial pH of 7.9, POME exhibited a strong negative charge of -14.8 mV with an average particle size of 659 d.nm. The zeta potential for POME remained negative throughout the pH adjustment but it reached the lowest value of -32.9 mV at pH 12. On the contrary, the results obtained for PACl were different where its initial pH was recorded at 4.4 with zeta potential and particle size of 43.5 mV and 171.3 d.nm respectively. PACl indicated both positive and negative charges within the experimented pH range. The point of zero charge (PZC) for PACl was measured in between pH 11 and 12 where the charge was dominantly positive preceding the region and oppositely thereafter. Both samples rose in terms of particle size growth but the range for POME was found to be smaller than PACl at 15269 d.nm and 56962 d.nm respectively. It can be concluded by availing the optimum conditions obtained from this research and pairing POME and PACl of contradicting charge will help to improve coagulation performance.

Keywords: Coagulation, palm oil mill effluent, particle size, polyaluminium chloride, zeta potential.

INTRODUCTION

The humid tropical climate of Southeast Asia particularly in Malaysia and Indonesia is considered the best environment for oil palm trees cultivation. Originally brought from the West Africa, the oil palm species of *Elaeis guineensis* has been extensively grown in this region [1] stemming from its high productivity, lucrative financial returns and increasing demand on palm oil globally [2]. In 2003, more than 13 million tonnes annual production of crude palm oil (CPO) was recorded; consuming 11% of the total Malaysian land area. The total oil palm plantations coverage further expanded to 4.98 Mha, occupying almost 73% of the agricultural land [3]. Hitherto, the extensive amount of land dedicated for palm oil plantations has made it apparent of the industry's contribution towards Malaysia's export earnings and the improvement of the population's living standard [4]. Looking forward, demand for CPO is anticipated to rise remarkably as it gains the global recognition as an important food source and feedstock for chemical and biofuel industries [5]. However, despite the considerable development the business brings, the processing of palm oil involves many tradeoffs. One of the important issues is regarding the multitude forms of waste that are produced including palm oil mill effluent (POME), empty fruit bunches (EFB), mesocarp fibre and pressed shells. From the aforementioned list, POME constitutes the largest portion of by-products of around 60% [6].

In a conventional palm oil mill processing, sources of POME may accrue from sterilizer condensate, separator sludge, hydro cyclone drain-off, reject fruit washing water, boiler blow down, tank and decanter flushes [7]. Raw POME is a mixture of colloidal suspension with 95 – 96% water, 0.6 – 0.7% oil and 4 – 5% total solids including 2 – 4% suspended solids [8]. Due to the high organic content present in POME, indiscriminate discharge of the effluent either partially or untreated into the nearby waterways can be very concerning.

The natural biological degradation of the organic matter will eventually deplete dissolved oxygen (DO) level in the rivers; outcompeting the aquatic organisms' need for oxygen. The seemingly increase of the demand for palm oil will definitely produce voluminous POME discharge. Hence, there is a dire need to develop a systematic waste management for its utilization, treatment and disposal [9]. As part of the effort to counter the negative environmental implications, the Malaysian Department of Environment (DOE) has enacted the Environmental Quality (Prescribed Premises) (Crude Palm Oil) Regulations 1977 that strictly outlines the discharge limits for POME. There are many available treatments for POME but the Malaysian status quo is dominated by the biological system of aerobic and anaerobic ponds with more than 85% of local palm oil mills adopting such system. Despite the technique being relatively stable, requires low operation and maintenance costs [10, 11], many mills are still struggling to comply with the established discharge regulations [12]. The use of anaerobic treatment alone does not give certainty to produce on-spec effluent but rather, it needs complementary post-treatments to help achieve the target [13]. In this sense, physicochemical treatment of coagulation and flocculation has been widely used in industrial scale to eliminate suspended solids and colloidal particles from wastewater by using relatively inexpensive and readily available inorganic coagulants [14].

Coagulation is primarily induced by inorganic metal salts or mineral additives like alum, PACl, ferric chloride, ferrous sulphate, calcium chloride and magnesium chloride [15] where the benefits of using PACl as a coagulant strike the most. PACl is a pre-polymerized Al (III) chemical that gives out large-sized hydrolysis and polymeric species carrying high cationic charge [16, 17]. Besides, it requires minimal pH adjustment prior to usage, needing only low dosage [18], provides quick aggregation rate and able to form heavier and larger flocs for faster settling [16]. Previous literatures have reported positive results for the coagulation of POME with PACl [19–23] but the conventional method of trial and error without constructive evidence is still the common practice for determination of the optimum coagulant dosage. The influence of pH is only investigated at a later stage in their experiments.

To date, many studies have employed zeta potential-pH plots as the main criteria to elucidate the electrostatic interaction between pollutants and coagulating agents apart from the proven ability to economize coagulant dosages when the optimal operating window is found. Implementing the strategy has resulted in more effective coagulation-flocculation treatments of semiconductor industrial wastewater using polyelectrolytes [24], *nejayote* using chitosan [25], municipal wastewater using dicarboxyl acid cellulose (DCC) [26], brewery wastewater using carbon nanotubes [27] and humic acid-kaolin synthetic water using composite coagulant polymeric ferric aluminum chloride-polydimethyl diallylammonium chloride [28]. Ergo, the novelty of this research centers on the fundamental study of pH variation on the change of zeta potential and particle size of POME and coagulant PACl. The plots will then be used to determine the optimum pH range before proceeding to seek the optimum coagulant dosage range. The outcome of this research is expected to provide a key significance to guide PACl applications in the industrial sector.

MATERIALS AND METHODS

Experimental materials

POME was collected from the final discharge tank following a series of anaerobic and aerobic pond treatments of a local palm oil mill, MALPOM Industries Sdn. Bhd., located at Nibong Tebal, Penang. The collected sample was later stored in plastic carboys. To preempt further biological activity, the sample was kept in a cold storage room set at a temperature of 4℃. PACl solution (Darco Industrial Wastewater, Malaysia) with a concentration of 18% was utilized in this study. A PACl stock solution of 100 mg/L was prepared to carry out characterization tests as a function of pH. Analytical grade aqueous hydrochloric acid (HCl) and pelletised sodium hydroxide (NaOH) were respectively used for pH adjustment. The acid and the alkali solutions were prepared with concentration of 0.25 M each by using deionized water.

Experimental procedure

Characterization of POME suspensions

Tests for Chemical Oxygen Demand (COD) and Total Suspended Solids (TSS) were done using colorimetric technique with HACH 2800 DR Spectrophotometer. The fresh POME sample was tested for COD and TSS according to HACH Method 8000 and 8006 respectively. Triplicate COD and TSS readings were taken to compute the average value. For COD test, the POME sample was filtered and the filtrate was diluted to a ratio of 1:10 using deionized water. 2 mL of the filtrate was mixed in a COD vial with 1.5 mL of $K_2Cr_2O_7$ and 3.5 mL acid reagent solutions totaling up to 7 mL. Meanwhile, for TSS, the sample was tested directly without any dilution.

Zeta potential and particle size measurements as a function of pH on POME

The POME suspensions were analyzed at room temperature based on the experimental method which was adapted and modified from Mohd Omar *et.al* [29]. The POME sample was filtered with a Standard 2 filter paper to remove the macro-size particles prior to conducting zeta potential and particle size measurements. The filtrate was collected in a conical flask until it reached the 100 mL mark. The sample was then transferred into a plastic beaker and stirred continuously at 150 rpm to ensure suspension homogeneity. The initial pH of the sample was measured and recorded using pH meter (Seven Compact) before analyzed for zeta potential and particle size using Malvern Zetasizer Nano ZS. 1 mL aliquot was extracted from the suspension using a syringe and filled into a capillary cell. At least ten zeta potential and five particle size measurements were recorded for each analysis and the readings were averaged. Next, the suspension pH was adjusted accordingly using 0.25 M HCl and 0.25 M NaOH to cover a pH range from 3 to 12. The zeta potential and particle size measurements were done separately at each pH value. Before filling in the next aliquot, the content of the capillary cell was emptied and rinsed briefly with deionized water. After the cell had been filled with the aliquot from the pH-adjusted sample, the exterior of the cell was cleaned briefly with a paper towel before placing it back in the Zetasizer for subsequent analysis. This is crucial to increase reading accuracy since the measurements are based on dynamic light scattering (DLS) technique. \

Zeta potential and particle size measurements as a function of pH on PACl

The procedures were replicated from the previous experiment for POME in Section 2.2.2. Since the stock solution concentration was considered too high, it was diluted to a lower concentration of 100 mg/L. To avoid cross contamination that may affect the data, a different syringe and capillary cell were used to extract and fill aliquots from the PACl solution.

RESULTS

Characteristics of POME suspensions

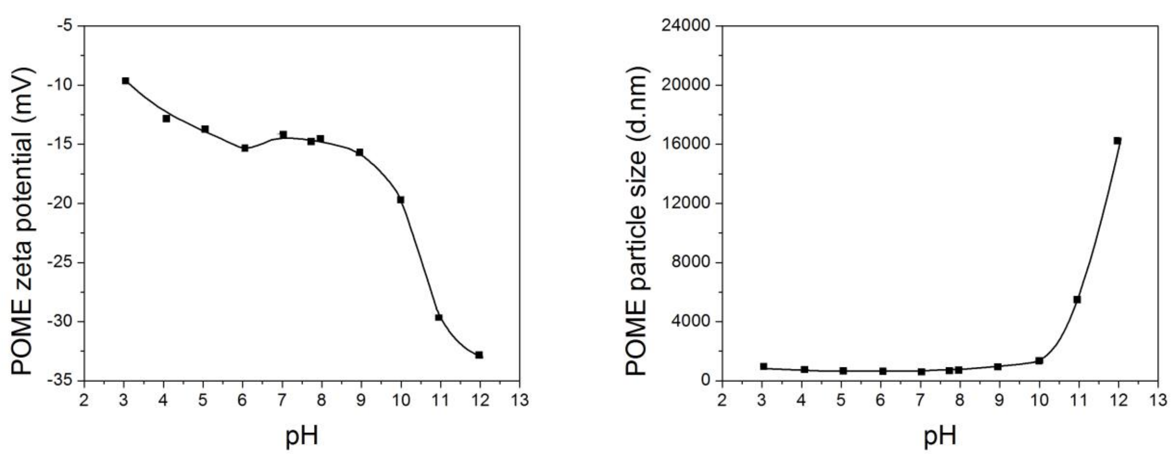
The preliminary analysis results for the freshly collected POME sample are displayed in Table 1.

Table 1: Initial readings for a freshly collected POME sample from a local palm oil mill

Parameter	Average value	Unit
pH	7.9	-
COD	1040	mg/L
TSS	332	mg/L
Zeta potential	-4.8	mV
Particle size	659	d.nm

Zeta potential and particle size measurements as a function of pH on POME

Figure 1 (a) and (b) are plots showing the change of POME's zeta potential and particle size when pH of the suspension was adjusted from 3 to 12.

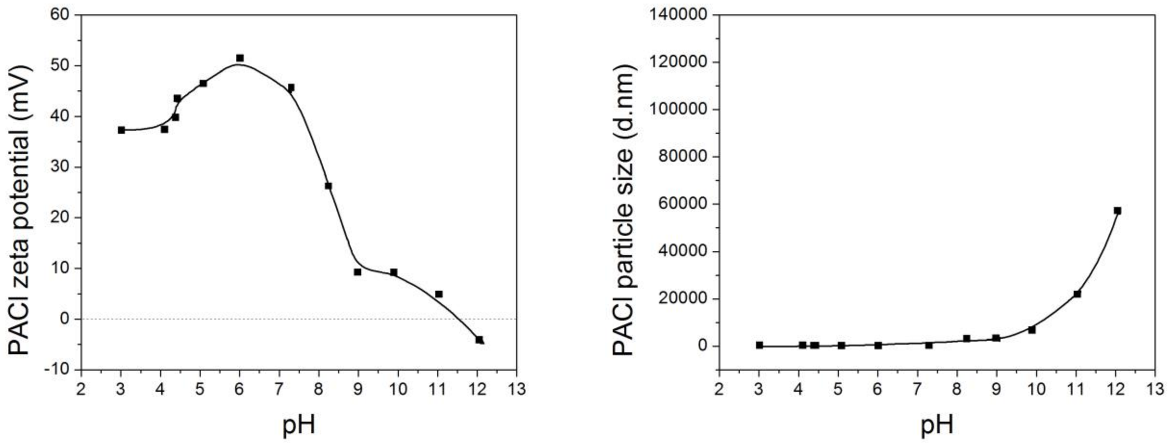


Left: Figure. 1 (a) shows the change in zeta potential of POME in response to pH adjustment on the suspension from 3 to 12

Right: Figure. 1 (b) shows the change in particle size of POME in response to pH adjustment on the suspension from 3 to 12

Zeta potential and particle size measurements as a function of pH on PACl

Figure 2 (a) and (b) show the zeta potential and particle size change for PACl across a pH range from 3 to 12.



Left: Figure. 2 (a) shows the zeta potential profile of PACl as a function of pH within pH range from 3 to 12

Right: Figure. 2 (b) shows the particle size profile of PACl as a function of pH within pH range from 3 to 12

DISCUSSION

Characteristics of POME suspensions

COD and TSS tests conducted on the freshly collected POME sample seem to show the company's good standing. Vis-à-vis the Malaysian DOE's specified TSS limit of 400 mg/L, the TSS content for the analyzed effluent has an average value of 332 mg/L, which sits below the limit. Meanwhile, for COD in particular, there has been no delineated limit after 1/1/1984. From the analysis, the sample gave an average reading of 1040 mg/L. However, with standards potentially becoming more stringent in the future, the industries should constantly seek for avenues to improve their wastewater discharge quality. The sample was found to be slightly alkaline, as it has gone through a series of aerobic treatments before reaching the final discharge tank.

Zeta potential and particle size measurements as a function of pH on POME

Based on Figure 1 (a) and (b), initial pH of the POME sample was measured at around pH 7.7 to 8.0, with a negative zeta potential of –14.8 mV and particle size of 659 d.nm. As the pH was adjusted from pH 7.7 to 3 towards the acidic region, the addition of H^+ ions has increased the zeta potential slowly becoming less negative until – 9.7 mV at the lowest pH of 3. The particle size recorded at the same pH was 946.4 d.nm. In the alkaline region, when the pH was adjusted from pH 8 to 12, the zeta potential gradually declined from -14.6 mV to -32.9 mV with a corresponding particle size change from 706.8 d.nm to 16215 d.nm. The large particle size of POME at pH 12 indicates an increase in aggregation and formation of larger aggregates. The lowering of the zeta potential may also attribute from the addition of OH^- ions to increase the suspension alkalinity. A significant difference in the zeta potential measurements is observed between pH 10 and 11 where the corresponding particle size increased from 1336 d.nm to 5472 d.nm. Overall, the POME suspension clearly displays a strong negative charge, which remains unaffected by the pH alteration. This could be due to the reason that the main components of POME are natural organic matter (NOM), which majorly comprises of humic substances. The range between the minimum and the maximum particle size is 15269 d.nm.

Zeta potential and particle size measurements as a function of pH on PACl

Referring to Figure 2 (a) and (b), PACl was found to be slightly acidic at an initial pH of 4.4 with zeta potential and particle size of 43.5 mV and 171.3 d.nm respectively. When pH adjustments were made towards the acidic region until pH 3, the zeta potential and particle size slightly dropped to 37.3 mV and 263 d.nm respectively. By further addition of 0.25 M NaOH, the zeta potential continued to decline monotonically but as it passed by pH 12, it reached a negative zeta potential of - 4.13 mV. The

PZC for PACl was observed between pH 11 and 12, which is in sound agreement with the growth of particle size ending up as 57225 d.nm at pH 12. By and large, the range for the particle size growth from pH 3 to 12 is 56962 d.nm. The peak of the zeta potential is observed in between pH 5 and 6, with a recorded value of 51.5 mV at the latter pH. Between pH 7.3 and 8.3, there was a notable rise of particle size from 180.4 d.nm to 3005 d.nm while the respective zeta potential reduced from 46 mV to 26 mV. The entire zeta potential profile for PACl proves the high cationic charge the coagulant has even at its initial pH. Thus, PACl makes a good complement with POME suspension that is negatively charged in order to achieve charge neutralization and formation of flocs that can settle under gravity.

CONCLUSION

The data collated proves that POME suspension has a negative charge throughout pH 3 until 12. This is closely linked to the presence of NOM, made up largely of humic substances known of carrying negative charges with them. Therefore, no pH adjustment is necessary prior to any POME treatment. The extent of particle size growth across the pH range from 3 to 12 for POME is found to be smaller than PACl at 15269 d.nm and 56962 d.nm respectively. In terms of coagulant analysis, PACl qualifies as a highly recommended coagulant to treat POME because it has a high positive charge even at its initial condition, which will work well with POME to reach charge neutralization.

For future work, further optimization may be done by altering the pH of PACl solution between pH 11 and 12, where PZC was observed before being dosed into the POME suspension. A systematic interaction between POME and PACl should also be studied to determine the optimum coagulant dosage range at the optimum conditions.

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