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Polyacrylamide-induced coagulation process removing suspended solids from palm oil mill effluent
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**ABSTRACT**

Palm oil mill effluent (POME) is a colloidal suspension with 2\textendash}4\% suspended solids. About 50\% of the suspended solids are cellulosic compounds, which are not degraded in the typical biological treatment systems. Chemical (polymer-induced coagulation) and physical (settling) pretreatment methods were examined to remove the suspended solids in this study. A novel physicochemical treatment with high water recovery and sludge compressibility including three cationic polyacrylamides (C-PAM; as coagulant) and three anionic polyacrylamides (A-PAM; as floculant) with different molecular weights and charge densities was used. The coagulants used were biodegradable. The combination of a C-PAM (Chemfloc1515C) with medium molecular weight and charge density and an A-PAM (Chemfloc 430A) with high molecular weight and charge density at doses of 300 and 50 mg/dm\textsuperscript{3} showed the best total suspended solids (TSS) and chemical oxygen demand (COD) removal (96.4 and 70.9\%, respectively). The optimal condition was found at pH 5, rapid mixing at 150 rpm for 1 min, and slow mixing at 40 rpm for 30 s. As a conclusion, the physicochemical pretreatment using biodegradable coagulants was a promising alternative to effectively separate TSS (96.4\%) with high water recovery (76\%).

**Introduction**

Palm oil is one of the world’s most important vegetable oils. It is used mainly for edible purposes and has become an important raw material for many applications since the past few decades. A typical palm oil mill releases liquid effluent, known as palm oil mill effluent (POME).\textsuperscript{[1]} This effluent, if not disposed properly, will have a great adverse impact on the surrounding environment.\textsuperscript{[2,3]} POME is highly polluting due to its organic nature, and its discharge to a relatively small river can be devastating to its ecosystem, which is caused by oxygen depletion owing to its high chemical (COD) and biochemical (BOD) oxygen demands.\textsuperscript{[4\textendash}6] POME is a thick, brownish, viscous liquid waste discharged from the palm oil mills during the extraction of palm oil from the fruits and is nontoxic but has an unpleasant odor. POME is a colloidal suspension of 95\textendash}96\% water, 0.6\textendash}0.7\% oil, and 4\textendash}5\% total solids, including 2\textendash}4\% suspended solids with a BOD higher than 20 g/dm\textsuperscript{3} originating from a mixture of sterilizer condensate, separator sludge, and hydro cyclone wastewater.\textsuperscript{[2,3,7,8]}

Complete anaerobic digestion of the raw POME without pretreatment demands high hydraulic retention time (HRT), which is not easily achieved due to the high volume of POME produced by most palm oil mills. Coagulation\textendash}flocculation is widely used for industrial wastewater pretreatment, as it is efficient and simple to operate and many factors can influence its efficiency, such as the type and dosage of coagulant/floculant, pH, mixing speed and time, temperature and retention time.\textsuperscript{[9]} Recently, natural coagulants/floculants such as rice starch\textsuperscript{[10]} and Cassia obtusifolia seed gum\textsuperscript{[11]} were attempted successfully in the treatment of POME. Shak and Wu (2015) found that the combination between alum and C. Obtusifolia seed gum treated POME adequately at natural pH with lesser alum dosage and shorter settling time, reflecting the importance of using both coagulant and floculant in the treatment of POME efficiently.\textsuperscript{[12]} As typical floculants, polyelectrolytes are widely used to decrease colloidal stability and thus initiate flocculation. During polyelectrolyte-induced flocculation, polymer
adsorption onto colloid surfaces is vital. High molecular weight water-soluble polymers are widely used to induce the aggregation of aqueous colloids. In most cases, the flocculants are slightly cationic, to encourage adsorption, and are linear with molecular weights in the millions. Cationic copolymers of polyacrylamide (PAM) are typical examples. In one study, four different types of coagulant combinations, aluminum sulfate, ferric chloride, ferric sulfate, and ammonium sulfate, with a commercial polymer SR316 as flocculant were investigated as a pretreatment of POME. The coagulation and flocculation processes could reduce turbidity by about 97% and COD removal by 64% by the combination of coagulants (10% of ferric sulfate, 1% of alum, and 1% w/w of ammonium sulfate with commercial polymer SR316). In another study, a modified industrial-grade alum (Envifloc-40L) as a coagulant and Profloc 4190 as a flocculant were examined. Statistically designed experiments were used to optimize three variables in the coagulation–flocculation process, including the coagulant dosage, the flocculant dosage, and pH. The optimum values of the tested variables were determined as 15000 mg/dm³, 300 mg/dm³, and 6 for coagulant dose, flocculant dose, and pH, respectively. Turbidity of 19 nephelometric turbidity unit (NTU) and water recovery of 76% were obtained at the optimum condition. Moringaoleifera, as an environmental-friendly and natural coagulant, was tested for the pretreatment of POME. In that study, 95% suspended solids removal and 52.2% COD removal were reported. Sludge produced in the process had a high sludge volume index (SVI) (210 cm³/g), indicating low water recovery (50.25%).

Due to high suspended solids concentration in raw POME and its adverse effect on microbial flocs, a pre-treatment process is necessary before this effluent can be anaerobically treated by a high-rate anaerobic digester. A fraction of total suspended solids (TSS) that is not digestible gradually accumulated in the bioreactors by attaching to the sludge flocs, causing degradation in process efficiency. From a practical point of view and in order to have a reliable, stable, and efficient high-rate anaerobic process, the oil-bearing suspended solids need to be removed (partially or completely) before the anaerobic treatment. About 50% of the suspended solids are cellulosic compounds, which are not degraded in the typical biological treatment systems. With regard to POME characteristics, alternative/complementary combinations of physical-chemical-biological processes are needed for the adequate treatment of this wastewater. Thus, the combination of coagulation–flocculation and anaerobic/aerobic biotreatment processes might substantially reduce the HRT operating conditions using six different biodegradable cationic polyacrylamides (C-PAM) and anionic polyacrylamides (A-PAM), which have not been reported to date. Therefore, the present work is focused on investigating the efficiency of a pretreatment coagulation–flocculation stage under different operating conditions using six different biodegradable C-PAM and A-PAM.

### Experimental

#### Wastewater characteristics

POME samples were weekly taken from a nearby palm oil mill in Nibong Tebal, Penang, Malaysia. The samples were stored in a cold room (4°C) before use. This storage step had no observable effect on its composition. The characteristics of the POME sample used in this study are as shown in Table 1.

#### Settling characteristics of POME’s suspended solids

In order to study the settling ability of suspended solids’ content of POME, the zone settling test was carried out. A transparent cylinder with 1 m height and 5 cm diameter was used as the settling vessel (Fig. 1). The column was equipped with six sampling ports at various heights to analyze the water composition at each height. By using a thin rod, the suspension near the vessel wall over the entire depth of suspension was gently stirred at a low peripheral speed. Raw POME was maintained in a container under a uniformly mixed condition. A well-mixed sample was taken from the container and the settling vessel was filled to its height (100 cm). The height of the solid–liquid interface was recorded at intervals of 30 min for 3 h and samples were then taken from each sampling port to measure TSS to represent the suspended solids’ concentration in the sample. At the end of the experiment, a suitable settling time was obtained and applied for the pre-settled POME biological digestion.

#### Physicochemical pretreatment (coagulation and flocculation)

A standard jar test unit (SW1, Stuart scientific, UK) was applied as the flocculator in this study. It is equipped

### Table 1. Characteristics of POME sample used in the chemical pretreatment study.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/dm³)</td>
<td>49200</td>
</tr>
<tr>
<td>Soluble COD (mg/dm³)</td>
<td>22800</td>
</tr>
<tr>
<td>SS (mg/dm³)</td>
<td>19800</td>
</tr>
<tr>
<td>Oil and grease (mg/dm³)</td>
<td>5100</td>
</tr>
<tr>
<td>pH</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Values are averages of three measurements. The differences between the measurements for each parameter were less than 1%.
with six paddles, diameter $6.4 \times 10^{-2}$ m (6.4 cm) and the speed ranging from 0 to 227 rpm. Six C-PAMs and A-PAMs of commercial grade in a wide range of molecular weights and charge densities were used. Organopol 5415 was supplied by Ciba Speciality Chemicals. Chemfloc 1515C and Chemfloc 430A were supplied by Chemkimia. AN 913 and AN 913SH, manufactured by SNF Floerger, were provided by Kempro. The properties of the PAMs used are as shown in Table 2.

In order to determine the optimum dosage of the PAMs, a range of dosage was examined for selected C-PAM and A-PAM as 100–600 and 10–110 mg/dm$^3$, respectively. In every test, 500 cm$^3$ of raw POME sample was used. After C-PAM (as the coagulant) was added with a certain dosage, the sample was mixed rapidly at 150 rpm for 1 min. A-PAM was then added as a flocculant and the sample was mixed slowly at 40 rpm for 30 s. The flocs formed were allowed to settle for 30 min. After settling, TSS, COD, and oil and grease of the supernatant were determined. The experiments were conducted in duplicate.

### Analytical methods

The concentrations of COD, TSS, and oil and grease were determined by using standard methods.$^{[19]}$ For COD, a colorimetric method with the closed reflux method was developed. A spectrophotometer (DR 5000, Hach, Jenway, USA) at 600 nm was used to measure the absorbance of the COD samples. Oil and grease was measured by the partition gravimetric method. In this method, oil and grease content of the sample was initially extracted by n-hexane as the solvent. n-hexane was then evaporated in a rotary evaporator. The residual is reported as oil and grease.$^{[19]}$ Scanning electron microscopy (SEM) was used to examine the physical features of the suspended particles. The sample was examined using a Leo Supra 50 VP Field emission SEM (UK) equipped with Oxford INCA 400 energy-dispersive X-ray microanalysis system.

### Results and discussion

#### Zone settling

Primary sedimentation was used as a method to remove suspended solids and oil and grease as is currently done in the ponding system in most palm oil mills. Poor settlability of the suspended solids makes the separation difficult. As POME contains a high concentration of oil-bearing suspended solids, both hindered or zone settling and compression settling usually occur in addition to discrete (free) and flocculant settling. The settling phenomenon is illustrated in Fig. 2. Because of the high concentration of fine particles, the liquid tended to move up through interstices of the contacting particles. As a result, the contacting particles tended to settle as a zone or blanket.$^{[20]}$ A recognizable interface developed between the upper region and the zone-settling region, as represented in Fig. 2. As settling continued, a compressed layer of particles began to be formed at the bottom of the settling column in the compression-settling region.

As the compression layer formed, regions containing lower concentrations of solids than those in the compression region extended upward in the settling column. Thus, the zone settling region contained a gradation in solids concentration from that found at the interface of the settling region to that found in the compression-settling region. From Fig. 2, the height of the interface maintained almost constant after 3 h. Figure 3 depicts a 3-D graph for TSS removal at different heights of settling column and settling time. It shows that 86.8–62.5% TSS removals (corresponding to TSS concentrations of 2580 and 7340 mg/dm$^3$, respectively) were obtained from sampling ports 1 and 4, respectively, after 3 h, whereas

### Table 2. The properties of the polyacrylamides used.

<table>
<thead>
<tr>
<th>Polyacrylamides</th>
<th>Molecular weight</th>
<th>Charge</th>
<th>Charge density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organopol 5415</td>
<td>Very high</td>
<td>Cationic</td>
<td>Low</td>
</tr>
<tr>
<td>Chemfloc 3876</td>
<td>Medium</td>
<td>Cationic</td>
<td>High</td>
</tr>
<tr>
<td>Chemfloc 1515C</td>
<td>Medium</td>
<td>Cationic</td>
<td>Medium</td>
</tr>
<tr>
<td>Chemfloc 430A</td>
<td>High</td>
<td>Anionic</td>
<td>High</td>
</tr>
<tr>
<td>AN 913</td>
<td>High</td>
<td>Anionic</td>
<td>Low</td>
</tr>
<tr>
<td>AN 913 SH</td>
<td>Very high</td>
<td>Anionic</td>
<td>Low</td>
</tr>
</tbody>
</table>

Figure 1. 1-m column for the settling test.
about 50% water recovery was obtained. The results showed that the fiber suspended particles are light and bulky. SEM of the fiber-shaped particles is shown in Fig. 4.

Physicochemical pretreatment

Initially, the effect of various C-PAMs and A-PAMs was examined separately. Figure 5 shows the effect of C-PAMs on the TSS removal at various dosages (100–600 mg/dm³). From Fig. 5, Organopol 5415 and Chemfloc1515C showed a better performance compared with Chemfloc 3876. Despite the relatively high molecular weight of Organopol 5415, more compacted sludge was obtained with Chemfloc1515C (with medium molecular weight and charge density). The sludge volume obtained with Chemfloc1515C was 860 cm³/dm³ after 30 min of settling, whereas it was 940 cm³/dm³ for Organopol 4515. This result was due to the lower charge density of Organopol 5415 to sufficiently neutralize a large number of negatively charged particles present in POME. Another contributing factor was based on the fact that polyelectrolytes with very high molecular weights do not readily dissolve in water but tend to form gel lumps.[21]

As can be seen in Fig. 5, only 10% of TSS removal was obtained without the addition of C-PAM, which was attributed to gravity settling. Around 92.4 and 91.7% TSS removals were achieved at 200 mg/dm³ of both Organopol 4515 and Chemfloc1515C. No further improvement in TSS removal was observed at dosages higher than 200 mg/dm³ for all C-PAMs. The same experiments were carried out with A-PAMs at various dosages (10–100 mg/dm³), but no positive improvement in the removal of TSS and COD was achieved for the three A-PAMs. This result was associated with the intensification of repulsion forces between negatively charged particles in POME and the A-PAM molecules.

Due to poor compressibility of the sludge (high sludge volume) obtained with C-PAMs and in order to improve the effectiveness in the removal by C-PAMs, two selected C-PAMs (Organopol 5415 and Chemfloc1515C) were tested with subsequent addition of the various A-PAMs. The experimental results in the first part showed that better sludge characteristics were found at the dosage of C-PAM and A-PAM of 250 and 100 mg/dm³, respectively. Therefore, the obtained amounts were considered as doses of the chemicals used in the following test to explore the best combination of the selected C-PAMs and A-PAMs. Figure 6a and b shows the performance of the pretreatment process in terms of TSS and COD removals for Organopol 5415 and Chemfloc1515C, respectively, in combination with various A-PAMs. As can be seen, the combination of Chemfloc1515C and Chemfloc 430A showed the best result.
with 95 and 70.8% TSS and COD removal, respectively, with better sludge settling characteristics.

The aggregation of the particles occurred through two mechanisms, i.e. charge neutralization and a sweep-floc mechanism. Apart from lowering the surface charge on the particles (mostly by C-PAM), these polymers formed bridges between particles and polymer. Subsequently, the bridged particles become intertwined with other bridged particles during the flocculation process. Finally, Chemfloc 430A as an A-PAM enhanced the flocculation process through bridging the intertwined flocs.

To determine the optimum dosage of the combined PAMs, different combinations of Chemfloc1515C (as C-PAM) and Chemfloc 430A (as A-PAM) at different dosages were then examined. The ranges of exploration for the C-PAM and A-PAM were 100–600 and 10–110 mg/dm$^3$, respectively. Figure 7a and b, respectively, shows TSS and COD removal by combinations of various dosages of PAMs. It is noted in the figures that at 300 mg/dm$^3$ of Chemfloc1515C and 50 mg/dm$^3$ of Chemfloc 430A, the highest TSS and COD removal (96.4 and 70.9%, respectively) were achieved. At the optimum condition, sludge volume after 30 min of settling was 660 cm$^3$/dm$^3$. Oil and grease was measured throughout the experiments and higher than 95% oil and grease removals were achieved in all experimental conditions studied.

The sludge produced at the optimum condition is shown in Fig. 8. This figure confirms the high compressibility of the sludge. It must be noted that the sludge compressibility is one of the important factors to improve sludge dewatering. In the sludge dewatering, the filtrate flow becomes independent of the pressure applied for such an extremely compressible solid. As seen in the figure, residual turbidity of the supernatant is very less due to high integrity in the sludge produced. Ariffin et al. reported lower dosages of their synthesized PAMs compared with the optimum dosages obtained in this study. This may be due to the different compositions of the PAM used in this study during the manufacturing processes. The optimum conditions obtained from this study can be used for the chemical pretreatment of POME prior to its post-treatment in an anaerobic treatment process.
Figure 6. TSS and COD removal by combinations of C-PAM and A-PAM; (a) a C-PAM (Organopol 5415) at a dosage of 350 mg/dm$^3$ with various A-PAM at 100 mg/dm$^3$, (b) Chemfloc 1510C at a dosage of 350 mg/dm$^3$ with various A-PAM at 100 mg/dm$^3$.

Figure 7. (a) TSS removal and (b) COD removal by combinations of a C-PAM (Chemfloc 1510C) and an A-PAM (Chemfloc 430A) at various dosages.

Figure 8. Sludge produced at the optimum condition.
Conclusions

Removal of the suspended solids from raw POME using a novel physicochemical treatment with high water recovery and sludge compressibility was successfully performed using three C-PAMs (as the coagulant) and three A-PAMs (as the flocculant) with different molecular weights and charge densities. The combination of a C-PAM (Chemfloc1515C) with medium molecular weight and charge density and an A-PAM (Chemfloc 430A) with high molecular weight and charge density at dosages of 300 and 50 mg/dm³, respectively, showed the best effectiveness in removing TSS and COD (96.4 and 70.9%, respectively). Oil and grease removal was higher than 95% in all experimental conditions studied. The chemical pretreatment approach seemed more suitable with higher TSS and COD removal efficiency and more compressible sludge. As a conclusion, the chemical pretreatment using the biodegradable coagulants is a promising alternative to effectively separate TSS with high water recovery (76%).

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