Effect of Different Chemical Treatments on the Settleability of Palm Oil Mill Effluent

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ABSTRACT

The effect of alum and ferric chloride on the settleability of suspended solids in raw palm oil mill effluent (POME) was compared with that of natural zeolite and calcium carbonate. This work forms part of our overall research on minimal discharge technology in the overall management of POME. The results showed that all the flocculants could effectively reduce more than 80% of the suspended solids but only 40-50% of the COD. The settled volume after 3-7 hours was generally within 35-50% of the original mixture. The best settleability in increasing order were at 3 g/L ferric chloride, 11 g/L alum, 10 g/L zeolite and 20 g/L calcium carbonate. The fastest settling rate was obtained with 20 g/L calcium carbonate, where settling was almost completed within 2 hours as compared to more than 20 hours for raw POME. The dosage of zeolite was comparable to the traditional coagulants. As for calcium carbonate, although the dosage was higher, subsequent disposal or utilisation of the metal-free sludge solids fits well with our minimal discharge system for POME.

INTRODUCTION

Palm oil mill effluent (POME) is one of the most highly polluting organic wastewater in Malaysia. It is a combined effluent made up mainly of the steriliser condensate, centrifuge sludge and the discharge from the hydrocyclone. The essential characteristics of this effluent can be summarised as being of high organic strength (25000-30000 mg/L BOD and 40000-50000 mg/L COD), hot during discharge (60-70°C), acidic (pH 3.5-4.5) and highly turbid (20000-30000 mg/L suspended solids with 45000-60000 mg/L total solids). The solids which contribute to the BOD comprise mainly fine lignocellulosic materials and a small amount of residual oil. There are currently about 300 palm oil mills operating in Malaysia. A typical mill processes about 60
tons of fresh fruit bunch per day (Ma et al. 1993), producing more than twice the amount of POME. The POME is normally collected in a pit where part of the residual oil which floats upon cooling is recovered. The effluent is then pumped into either large digester tanks or more commonly to a series of anaerobic and aerobic lagoons for a combined treatment prior to discharge. Typical residence times in these lagoons exceeds 30 days (Ma et al. 1993). Mixed microbial action on the organic matter resulted in the formation of biogas which is rarely utilised and normally released to the atmosphere. The final treated effluent must meet the BOD and COD discharge standards of 100 mg/L, set by the Department of Environment for the palm oil industry, before discharge to watercourses. This represents a 300-fold reduction of the organic strength. This fact, coupled with the large daily volumetric throughput involved, means that the treatment system has to cope with a very high organic loading rate, putting a severe strain on the treatment facility.

Traditional wastewater treatment from food and agro-based industries employs primary treatment systems consisting basically of sedimentation tanks or primary clarifiers aimed at removing settleable solids prior to the secondary treatment which is essentially biological in nature. With this strategy, usually about one-third of the initial BOD present will be removed with the solids, hence reducing the load on the subsequent secondary treatment. Thus, with POME, it would seem logical to remove the bulk of the suspended solids prior to biological treatment. Unfortunately, most of the suspended solids in POME are very fine and are difficult to remove by gravity settling (Ho and Tan 1989). Flocculants and coagulants such as alum (aluminium sulphate) and ferric chloride have been used to remove suspended particulate matter from water and wastewater worldwide (Sawyer et al. 1994; Rossini et al. 1999). There have been several reports on the use of such agents on POME (Abdul Karim and Lau 1987; Ng et al. 1987). Although the effluent solids could be removed by these methods, the use of heavy metals such as aluminium and iron and their presence in the settled sludge means that the disposal of such sludges would be problematic.

Our research group has been concerned with the utilisation of POME incorporating a minimal discharge strategy towards a zero-discharge system in the management of POME (Hassan et al. 1997; Nor Aini et al. 1999). Thus we propose the use of other flocculants such that the eventual sludge could be more easily disposed or put to beneficial use. The use of natural zeolite and calcium carbonate would produce a concentrated biological solid from POME which could be used for the production of value-added products such as biodegradable plastics (Hassan et al. 1997). The objective of this work is to evaluate the effect of appropriate chemical precipitants such as zeolite and calcium carbonate on the settleability of POME in comparison to the use of conventional agents such as alum and ferric chloride. In consonant with our overall strategy, the characteristics of the residual clarified effluent will also be assessed in order to determine subsequent treatment methods.

MATERIALS AND METHODS

Materials

Raw POME, obtained fresh from Bukit Raja Palm Oil Mill (Sime Darby Group), Klang was kept in the cold room at 4°C prior to use. The characteristics of raw POME is shown in Table 1. Laboratory grade alum (aluminium sulphate, \( \text{Al}_2(\text{SO}_4)\cdot18\text{H}_2\text{O} \)) was obtained from BDH, ferric chloride (\( \text{FeCl}_3 \)) from Merck and calcium carbonate (\( \text{CaCO}_3 \)) from Fluka. Natural zeolite-mordenite was obtained from Harta Semarak Sdn. Bhd., Batu Pahat, Johor, Malaysia in a rock-like form. The zeolite was dried, pulverised, sieved, washed several times with distilled water and dried prior to use.

Experimental Procedure

The settleability experiments were performed using several 100 milliliters measuring cylinders onto which 10 mm x 100 mm strips cut from standard graph paper were attached. POME which was thoroughly mixed with different dosages of the chemical flocculants in separate beakers was then poured into the measuring cylinders, and left to sediment. Raw untreated POME was used as control for each treatment. All the treatments were carried out at 30°C. The settling velocity was determined by measuring the change in height of the sludge zone with time (Ng et al. 1987). From the plot of this data, the constant maximum settling velocity was obtained.
Analyses
BOD, COD, total solids and suspended solids were determined as in the Standard Methods (APHA 1985).

RESULTS

Effect of Alum
Fig. 1 shows the rate of sedimentation of POME with 0-20 g/L alum. The settling rate is measured by the drop in the level of the clarified liquid interface with time. It is evident that most of the settling occurred within the first 5-7 hours. In the first 3-4 hours, settling was fastest and the rates were constant. The best settling was at 11 g/L of alum, whereby the lowest solids volume of 30% of the original volume was obtained. Table 1 gives the constant settling velocity as well as the residual suspended solids and COD of the supernatant. The settling rate at 11 g/L alum was nearly 3 times faster than raw POME, with the lowest suspended solids and COD in the clarified liquor. It is evident that alum could effectively reduce the suspended solids in POME but not its COD or BOD (Table 1).

Effect of Ferric Chloride
Fig. 2 showed that the same pattern was obtained with ferric chloride as with alum. The concentrations of Ferric chloride required were lower, and the final solids volume was quite similar. From Table 1, the best settleability was with 3 g/L ferric chloride. Increasing the flocculant level resulted in slower settling, as was also observed by Ng et al. (1989), probably due to restabilisation instead of flocculation. The reduction in suspended solids and BOD (Table 1) were significant, but not the COD.

Effect of Zeolite
From Fig. 3, zeolite treatment on POME resulted in good settling of the solids, with 50% settled volume achieved with only 10g/L zeolite after only 3 hours. As shown in Table 1, the settling rates were even better than alum and...
Fig. 2. Effect of Ferric chloride (FeCl₃) on settleability of POME. Symbols represent: control (●); 1g/L (○); 2g/L (▲); 3g/L (■); 4g/L (△); 5g/L (◇); 6g/L (●); 10g/L (○).

Fig. 3. Effect of Zeolite on settleability of POME. Symbols represent: control (●); 5g/L (○); 10g/L (◇); 30g/L (△); 60g/L (▲); 100g/L (◇)
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Fig. 4. Effect of Calcium carbonate (CaCO3) on settleability of POME. Symbols represent:
control (○); 5g/L (□); 10g/L (▲); 20g/L (△); 40g/L (◇); 60g/L (◆); 80g/L (●); 100g/L (□)

TABLE 1
Characteristics of raw POME before and after chemical treatment

<table>
<thead>
<tr>
<th>Flocculant</th>
<th>Concentration (g/L)</th>
<th>BOD (mg/L)</th>
<th>COD (mg/L)</th>
<th>Suspended solid (mg/L)</th>
<th>Constant settling rate (mm/h)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Raw POME)</td>
<td>–</td>
<td>23200</td>
<td>45000</td>
<td>17500</td>
<td>–</td>
<td>4.20</td>
</tr>
<tr>
<td>Alum</td>
<td>11</td>
<td>23000</td>
<td>20000</td>
<td>1940</td>
<td>52</td>
<td>3.35</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>3</td>
<td>16000</td>
<td>30000</td>
<td>3420</td>
<td>28</td>
<td>3.44</td>
</tr>
<tr>
<td>Zeolite</td>
<td>10</td>
<td>15000</td>
<td>40000</td>
<td>4140</td>
<td>76</td>
<td>4.30</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>20</td>
<td>21000</td>
<td>31000</td>
<td>4100</td>
<td>96</td>
<td>5.20</td>
</tr>
</tbody>
</table>

ferric chloride. Again, as with the other flocculants, suspended solids removal was good. However, the COD reduction was increased.

Effect of Calcium Carbonate

The effect of Calcium carbonate is given in Fig. 4. Settling was quite fast and almost completed within 2-3 hours at concentrations above 10 g/L, with about 40% compacted solids volume. From Table 1, the best settling rate approaches 100 mm/h at 20 g/L Calcium carbonate – by far the most superior amongst all the flocculants tested. There was a big reduction in suspended solids. Although the COD was reduced by about 30%, however the BOD was essentially unchanged.
DISCUSSION

Generally, the effect of the chemical flocculants used in this study on the settleability of POME was quite similar, resulting in higher settling rates with higher clarified volume obtained. The suspended solids removal were also better, but the reductions in COD and BOD were not as good. Overall, the best concentrations for alum, ferric chloride, zeolite and calcium carbonate in weight/volume are 1.1%, 0.3%, 1% and 2% respectively. In terms of ratio of coagulant used to suspended solids present in raw POME, the values are 0.63, 0.17, 0.57 and 1.15 respectively. Apart from calcium carbonate, these figures are comparable to earlier reports (Abdul Karim and Lau 1987; Ng et al. 1987) for alum, lime and ferric chloride. Essentially the action of these flocculants can be ascribed to ionic interactions between the positively-charged $\text{Al}^3+$, $\text{Fe}^{3+}$, zeolite and $\text{Ca}^{2+}$ and the biological particulate matter in POME being mainly negatively charged. Flocs could be formed by bridging between different particles, thus increasing in size as well as density which aided the settling (Sawyer et al. 1994; Ho and Tan 1989). Since alum and ferric chloride have more charges per unit mass, hence it is expected that the quantities of these flocculants required were less than Calcium carbonate. With zeolite however, there is an additional mechanism – binding within the pores (Ouki et al. 1994), thus the quantity required is comparable to alum. Although the highest concentration required was for Calcium carbonate, the settling was the fastest. This would be beneficial in sizing-up for the sedimentation tanks, since a smaller retention time would be sufficient. The effect of chemical addition on pH as shown in Table 1 varies by only within 1 pH unit. Based on our observation, within pH 2-10 (adjusted by NaOH), there is no effect on the settleability of raw POME. Thus the settling behaviour of POME in this study was not due to pH. In relation to our objectives, it is seen that zeolite and calcium carbonate would be equally suitable in comparison to the traditional flocculants (alum and ferric chloride), if not better. Settled solids associated with zeolite or Calcium carbonate would be more amenable to subsequent utilisation or disposal. In industrial application, the Calcium carbonate could be replaced with lime. We will look into that in our future work. As for the high residual BOD in the clarified effluent – probably due to dissolved organics – subsequent biological treatment would obviously be necessary. However, the added advantage of using calcium carbonate is that the pH of the POME became higher (Table 1) which would facilitate its utilization such as bioconversion to value added products.

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