Abstract: A method and apparatus for the treatment of waste water, said method comprises the steps of (a) pre-treatment of the wastewater with ozone; and (b) biological treatment of the water from step (a).
"Treatment of Wastewater"

Field of the Invention

The invention relates to a method and apparatus for removing waste materials from wastewater using ozone gas. More specifically, the invention relates to the pre-treatment of Palm Oil Milling Effluent with ozone gas.

Background Art

Palm oil is a type of oil used in a wide variety of products, such as pharmaceuticals, food, cosmetics, and chemicals. Palm oil is grown in plantations in many South East Asia and African countries and processed in mills. Production of palm oil provides a great benefit to the economy of these countries. However, there are many disadvantages associated with the by-products generated from the extraction of palm oil. Disadvantages of the milling process include a large land requirement for the treatment of the waste products of the oil production, and the generation of milling residues, such as empty fruit bunches, shell and fibre, and Palm Oil Mill Effluent (POME).

Various countries are in the process of designing systems to generate energy (biomass) from the fruit bunches, shell and fibre. Alternative uses for these wastes have been proposed, including using fibre from the empty fruit bunches in paper and pulp, using oil palm fronds to produce furniture and as a planting medium.

In contrast, disposal of the POME is considered less environmentally friendly. POME is generated from the sterilization and clarification processes involved in palm oil production. It is made up of about 95% water, about 1% oil and about 4% total suspended solids—such as debris from the palm mesocarp.

More specifically, POME is a highly concentrated industrial wastewater, defined by the following characteristics: pH of between 3.4-5.2, a Biological Oxygen Demand (BOD) between 10,250 - 43,750 mg/L, a Chemical Oxygen Demand
(COD) of between 16,000-100,000mg/L, total solid content of between 11,500-75,000 mg/L and suspended solids of about 5,000-54,000 mg/L. Since the BOD may reach up to over 40,000 mg/L it is considered to have the potential to cause serious pollution problems.

Much interest has been recently expressed in the development of methods to use the POME to generate usable by-products, thus maximising the profit of the mills and reducing the effects on the environment. One such method is the generation of acetone-butanol-ethanol (ABE) using Clostridium bacteria (Kalil et al., 2003). This study showed that POME was suitable for ABE production by fermenting Clostridia. However, the concept of using POME as a profitable asset is yet to be realised in any sizable scale in palm oil plantations.

The majority of plantation mills treat POME for discharging back into the environment. Known treatment systems include anaerobic ponds, aerobic ponds, and facultative processes. However, the process of anaerobic/aerobic ponds is prone to silting such that the quality of the water is not sufficient to be discharged into the water courses. Improvements to the pond system include introducing enclosed anaerobic digestion systems which reduce the BOD and the COD of the effluent and also captures methane gas.

The above processes generally require POME to the collected in a sludge pit. The POME is retained in the pits for one or more days, which allows the residue oil to separate to the top and then the oil is collected by scraping.

The ponding system is one of the most popular forms of treatment used in the palm oil industry, as it is cheap to construct. It generally produces a reasonable quality wastewater with an acceptable BOD to be discharged into the water courses. However, this system requires a large amount of land, and is difficult to control and monitor. In addition, the ponds are difficult to maintain given the oil accumulates with the solids, forming an oily and sticky scum, which is difficult to remove.
The pond system involves a mixing step which requires gas to be bubbled up through the POME. As a result, suspended solids form dead spots, causing ineffective digestion of the POME and delays in the process of treatment. In addition, the ponds require frequent removal of the sludge - a time consuming and costly procedure. Addition of coagulants or solidifiers may aid in the prevention of the above problems by creating a semi-solid mass. However, these compounds do not sufficiently alleviate the problem.

Thus, one of the most difficult parameters to address in the treatment of wastewater, such as POME, is the reduction in BOD to acceptable levels. In POME, the authorities limit the amount of BOD in wastewater to 50 mg/l. However, as mentioned, the raw POME has an extremely high BOD and due to the very low biodegradability of the oil and polyphenol compounds, is very difficult to treat with known treatment systems.

Further, an important percentage of the oil from the milling process is lost in the wastewater. Present wastewater treatment processes do not provide satisfactory means for extracting oil from the wastewater.

In addition, present wastewater treatment systems require large amounts of space to store the water during treatment. In general, there is very little space available and use of the space often has significant environmental and social impact on the area.

Thus, there exists a need to provide an alternative method and apparatus for the treatment of wastewater and in particular wastewater generated from the process of palm oil extraction.

**Summary of the Invention**

The subject invention relates to a unique method for rapid, efficient and simple treatment of wastewater. It also relates to an apparatus suitable for use in the method. Use of the described apparatus while not essential for practising the method of the invention has been found to significantly improve the pre-treatment of wastewater.
According to a first aspect of the invention there is provided a method for the treatment of wastewater which method comprises the steps of (a) pre-treatment of wastewater with ozone; and (b) biological treatment of the water from step (a).

The method of the present invention may further comprise the step of treating wastewater using Dissolved Air Flotation (DAF) prior to the ozone gas pre-treatment step.

In accordance with a second aspect of the invention there is provided an apparatus for the treatment of wastewater, said apparatus comprising: a reaction tank, an ozone generating means and a belt filter system for use with a biological treatment unit. Optionally, the apparatus may further comprise a DAF unit. The apparatus may also comprise a scraper system for removal of oil scum. Optionally, the apparatus may further comprise a recycling mechanism for recycling treated wastewater back into the reaction tank for further treatment.

**Brief Description of the Drawings**

**Figure 1**
A pictorial diagram of the process.

**Figure 2**
A flow diagram showing the optimal treatment process.

**Figure 3**
Illustrates the amount of BOD and COD measured in POME during treatment steps.

**Figure 4**
Illustrates the amount of suspended solids and total solids in POME during treatment steps.

**Figure 5**
Illustrates the amount of fat/oil in POME during treatment steps.

**Figure 6**
Illustrates the amount of fat/oil in POME and sludge during treatment steps.
Detailed Description of the Invention

General

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variation and modifications. The invention also includes all of the steps, features, compositions and compounds referred to or indicated in the specification, individually or collectively and any and all combinations or any two or more of the steps or features.

The present invention is not to be limited in scope by the specific embodiments described herein, which are intended for the purpose of exemplification only. Functionally equivalent products, compositions and where appropriate methods are clearly within the scope of the invention as described herein.

The term "wastewater" as used herein is intended to include water that has been used in, for example a manufacturing process, such as palm oil extraction, and therefore contains waste products. The term also includes effluent from biological treatment ponds and raw wastewater, such as POME.

The term "biological treatment" is intended to include the treatment of wastewater via either enzymatic or biological methods.

Throughout this specification and the claims that follow, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

Description of Preferred Embodiments

This invention relates to the separation and removal of impurities from wastewater. More specifically, it relates to the removal of impurities such as BOD and COD, from POME using ozone gas. Oxidation by ozone gas is a selective process and can be used to remove impurities. Surprisingly, the inventors found
that a pre-treatment step of the POME with ozone provided a more suitable wastewater for the biological treatment step using known aerobic or anaerobic ponding systems. In addition, the inventors also found that treating wastewater using Dissolved Air Flotation (DAF) prior to ozone pre-treatment also significantly reduced BOD.

The resulting biological treatment step may be significantly reduced by the ozone pre-treatment step(s). Although ozone has been used in the past to treat wastewater, the combination of an ozone pre-treatment step followed by biological treatment has the unexpected result of reducing the BOD and COD of wastewater. In addition, the significant reduction in biological treatment time as a direct result of the ozone pre-treatment step is surprising.

In one embodiment of the invention, there is provided a method for the treatment of wastewater which method comprises the steps of:

(a) pre-treatment of the wastewater with ozone; and

(b) biological treatment of the water from step (a).

Pre-treatment of the wastewater with ozone may take place in a tank, such as a reaction tank. The ozone treatment comprises ozone dissolution and an oxidation reaction. In a highly preferred embodiment, the ozone-gas is generated from a high-voltage ozone-generator with oxygen as feed gas into the tank. The output gas is a mixture of oxygen and ozone. Preferably the mixture is 90% oxygen and 10% ozone. This mixture is transferred to the water-phase by systems known to those skilled in the art. An example of the transfer system is the venturi system.

The ozone step may be carried out at a temperature between about 25 °C and about 80 °C. Preferably the ozone step is carried out at about 50 °C.

The ozone is applied for a period of between about 1 hour to about 6 hours. Preferably the ozone pre-treatment step is for between about 2 hours to about 4 hours.
The method of the present invention may further comprise the optional step of using Dissolved Air Flotation (DAF) in the treatment of wastewater prior to pre-treatment with ozone.

In one embodiment of the invention, wastewater is cooled to about 50 °C and then pure air is applied to the wastewater for between about 1 hour and about 5 hours. During this time, the wastewater is recirculated.

The use of DAF allows oil recovery from the wastewater. After DAF treatment, the oil-sludge mixture may be sent back to the mill for further oil separation. The wastewater after DAF treatment is then further treated using the method of the present invention. The wastewater treated in step (a) of the method of the present invention may be raw wastewater - such as POME, effluent collected in holding ponds, effluent stored in biological treatment ponds - prior to the biological treatment step, or effluent which has been already undergone some biological treatment step.

The biological system used to treat the pre-treated wastewater may be any biological system known to a person skilled in the art. Biological systems include, but are not limited to enzymatic or biological methods. Biological treatment methods include the use of anaerobic and aerobic treatment methods.

According to a highly preferred embodiment of the invention, there is provided a method for removing organic compounds from wastewater, which comprises the following steps:

(a) introducing wastewater into a reaction tank to perform an ozone dissolution and oxidation reaction for a period of time between 1 to 6 hours;

(b) allowing the resulting ozone-treated water from said reaction tank to flow through into holding ponds;

(c) treating the water from step (a) using a biological system; and
(d) discharging the water from step (c) or recirculating the water to repeat step (a) above.

In another preferred embodiment of the invention, wastewater is collected in holding tank(s). The wastewater in the holding tank(s) is pre-treated using the ozone pre-treatment step of the present invention. Following pre-treatment, the wastewater is transferred to ponding systems, known in the art, where the wastewater is further treated by biological treatment methods, such as anaerobic or aerobic systems.

In a further aspect of the invention, the wastewater is retained in the existing treatment ponds and treatment of the wastewater is carried out using standard techniques. During treatment, the existing ponds are connected to the apparatus of the present invention and the wastewater treated in accordance with the method of the present invention.

In another embodiment of the invention, the method further includes the step of adding a salt to wastewater after the ozone pre-treatment step. Preferably, the salt is selected from magnesium, sodium, calcium, potassium, aluminium, iron, chromium, titanium or niobium. More preferably the salt is selected from calcium hydroxide, calcium carbonate, calcium oxide, magnesium carbonate, magnesium hydroxide, magnesium oxide, iron salts or aluminium salts, such as aluminium hydroxide. However, a person skilled in the art would realise any salt that resulted in the sedimentation of impurities could also be used. It may also be necessary to adjust the pH if salt is to be added to the wastewater. In addition, polymers may be used in the present invention. The wastewater may then be recirculated back to the biological treatment system or discharged.

There are many advantages as a result of the method of the present invention, including: improved odour during processing of the wastewater; improved quality of discharge water; reduction in the BOD and colour of the discharge water; reduced time for treatment from 6-12 months to several days and as such a greater turn around of wastewater; less space required for pond systems; where the amount of rainfall influences the capacity of the ponds, there is a reduction in
requirement for the size of the ponds due to the shortness of time the wastewater is required to be treated; new mills will not require so much land; less reliance on availability of water source; treatment ponds may be located closer to the plant operations, reducing transport costs and time; and cheaper running costs due to reduction in treatment size and time.

According to a second aspect of the invention, there is provides an apparatus for the removal of impurities from wastewater, said apparatus comprising a reaction tank, an ozone generating system and a belt filter system. The apparatus may be utilised with any biological treatment system. For example, the biological treatment system may be a biological fixed film reactor.

In a further embodiment of the invention, the apparatus comprises a recycling mechanism for recycling the wastewater after biological treatment to the reaction tank for further ozone treatment. The recycling mechanism may be a pipe system that transfers the treated wastewater back into the reaction tank for further ozone treatment.

In a preferred embodiment, the apparatus of the present invention also comprises a dissolve air flotation (DAF) system. The DAF system assists in the further recovery of oil from the wastewater. The wastewater may be treated using DAF prior to the pre-treatment of wastewater with ozone. This step has the effect of further increasing the efficiency of the ozone pre-treatment step.

The apparatus of the present invention may be utilised with existing ponding systems. Alternatively, the apparatus of the present invention may be incorporated into newly developed treatment plants.

**Best Mode(s) for Carrying Out the Invention**

Further features of the present invention are more fully described in the following non-limiting Examples. It is to be understood, however, that this detailed description is included solely for the purposes of exemplifying the present invention. It should not be understood in any way as a restriction on the broad description of the invention as set out above.
Examples

A mill operation in Sarawak, Malaysia was utilised in the testing of the following wastewater treatment method.

Current operating system

The mill currently operates 7 days a week and processes, on average 1200 ton of fruit branches per day, producing about 230 tons of oil on a daily basis. The daily water requirements for this production is about 846 m³ and generates about 30 m³ of wastewater per hour.

The current mill comprises one small receival pond, four anaerobic ponds (volume \(= 58300 \text{ m}^3\)), three facultative ponds (23800 m³) and five algae ponds (15120 m³), giving a total capacity of 97220 m³. In theory, the ponds should retain the wastewater for one year. However, due to dilution from the seasonal rains, the retention time in practice is closer to six months. The current system requires three employees to work on the wastewater treatment and eight employees to distribute the sludge.

Test operation system

The test unit consisted of a reaction tank divided into compartments. The test unit was a self made prototype. It was found that the test unit could be used on either batch or flow through systems.

A 500 micron belt filter was used to filter, aerate and/or ozonise, and recirculate the wastewater. An automatic scraper system was situated on top of the reaction tank, which ensured that the sludge produced was skimmed off the top. The temperature, pressure, flow and timing of each operation could be monitored throughout the process.
Ozone was produced by an ozone-generator (Ozonia CFS-1) with bottled oxygen as the feed gas. The floatation gas mixture used in the tests was 10% ozone and 90% oxygen. The process was carried out at a temperature of 50 °C.

The system test unit utilised a mini biological fixed film reactor based on Expo-Net BIO-BLOK elements, having a total volume of 800 litres, for the biological treatment step. The process time could be gradually set on the pump control unit.

In one set up of the apparatus, peristaltic dosing pumps, pumped wastewater, such as pre-treated POME into eight compartments in series, containing BIO-BLOK elements (surface for bacteria) and continuous aeration. The end chamber acted as a lamellar-separator for sedimentation, before treated water leaves the system by an overflow. The temperature for this process was between 28 to 32 °C.

After treatment, the water was collected in barrels. The water could be re-treated by ozone/oxygen and Ca(OH)₂ until flocks were seen, generally to a pH above 10.

The above test unit was used in five different protocols:

(1) ozone treatment of effluents in existing pond systems utilising biological treatment of POME,

(2) dissolved air flotation (DAF) of raw POME for recovery of oil,

(3) ozone flotation treatment of POME for reducing BOD,

(4) biological treatment of ozonated POME in an intensive biological system; and

(5) testing of different chemical techniques to improve results.

1. Ozone Treatment of Effluents from Existing Pond Systems used for Biological Treatment of POME
Effluent from a pond system was collected in barrels (1000 litres) by employees at the mill and taken to the test-site.

Test tube sized samples of the effluent were treated with ozone in order to find the relevant treatment period. That is, small samples of effluent were treated directly by ozone for different time periods. Simply by observing the samples, the progress of the process could be seen. In order to optimise the treatment time to be used on 1000 litres, a mini-scale experiment on 0.5 litres was made.

The test unit was filled with effluent and started. Samples were continuously taken for the visual control of the process. That is, to identify the changes in suspended particles/colour of the treated effluent. Several lab-size tests were also performed along with the test unit.

After about 23 minutes, the test was finished, as it appeared on visual inspection that the samples fulfilled the criteria for treatment of wastewater to reduce BOD. The test was repeated and further samples taken. The result of the amount of BOD (mg/L) in the treated water is shown below in Table 1.

<table>
<thead>
<tr>
<th>BOD (mg/L) Before</th>
<th>BOD (mg/L) After</th>
<th>Relative (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>96.2</td>
<td>14.0</td>
<td>85.4</td>
</tr>
</tbody>
</table>

Table 1

2. Treatment of raw POME using Dissolved Air Flotation (DAF)

1000 litres of raw POME was taken directly from the outlet-channel of the mill and was pumped into barrels. The POME was left to stand overnight to cool from about 75 °C to about 50 °C.

The POME was placed into the test unit described above. Testing commenced at t=0 by applying pure air into the POME while recirculating the sample. On the first day, the air-injection was continued until no more oily sludge was created. Oil content was measured after 1 hour (t=1), 3 hours (t=3) and 5 hours (t=5). The result are shown in Table 2 below.
3. Treatment of POME using Ozone Flotation

The same procedure of ozone flotation, as outlined above for treatment of effluent (see 1 above), was carried out on raw POME, and continued for 6 hours. The economical optimal time for treatment of the POME with ozone was determined during this test.

The treatment of POME was repeated the next day by varying the treatment parameters, including the amount of air, ozone, pressure and time.

The optimal treatment of POME was determined to be:

Step 1: 1 hour DAF treatment;

Step 2: 4 hours ozone treatment.

Water samples were taken at the start ($t=0$), after 1 hour ($t=1$), 3 hours ($t=3$) and after 5 hours ($t=5$) of treatment. The sludge fractions were also collected during testing. The POME water samples and samples of sludge were then analysed.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Raw POME ($t=0$)</th>
<th>Sludge ($t=1$)</th>
<th>Sludge ($t=3$)</th>
<th>Sludge ($t=5$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil loss dry basis</td>
<td>13.5</td>
<td>54.33</td>
<td>34.23</td>
<td>29.66</td>
</tr>
<tr>
<td>Oil loss wet basis</td>
<td>0.59</td>
<td>7.55</td>
<td>2.27</td>
<td>1.40</td>
</tr>
<tr>
<td>Non-oil solids</td>
<td>3.79</td>
<td>6.35</td>
<td>4.36</td>
<td>3.32</td>
</tr>
<tr>
<td>Oil after extraction</td>
<td>15.61</td>
<td>118.96</td>
<td>52.04</td>
<td>42.18</td>
</tr>
<tr>
<td>Relative Oil loss wet basis</td>
<td></td>
<td>12.8</td>
<td>3.8</td>
<td>2.40</td>
</tr>
</tbody>
</table>

Table 2
4. Biological Treatment of Ozonated POME in an Intensive Biological System

The biological system was started up by treating a mixture of raw POME and pond effluents, mixed with aerobic sludge from the existing pond system. The outside temperature was between 28 °C and 33 °C, which was considered optimal biological conditions for biological treatment.

The pre-treated effluent from the DAF tests and the POME from the ozone flotation system tests was collected in barrels and placed in the biological systems. The flow through system was set for a process period of 24 hours. Air was continuously blown into the system for oxygenation and to created turbulence. The pH of the system was adjusted to neutral. Water samples were collected from the outlet of the system at 0 hours (t=0), 1 hour (t=1), 3 hours (t=3) and 5 hours (t=5).

5. Test of Different Chemical Techniques to Improve Results

Different chemical techniques were applied during the treatment of POME to determine whether they would improve the results.

Additional chemicals included Fe$^{3+}$ and Al$^{3+}$ salts (for flocculation); polymers; and precipitation chemicals. In addition, Ca(OH)2 and ashes from burned fruit branches (waste product form energy production at the mill) were tested. All tests were carried out on an experimental laboratory scale.

The results suggested that most flotation chemicals used in municipal wastewater treatment systems would be too expensive to be used in commercial full scale plants, due to the requirement of large amounts of the chemicals to treat the high BOD. Therefore experimental tests focused on the use of Ca(OH)$_2$ and ashes.

The results also indicated the use of Fe$^{3+}$ and Al$^{3+}$ salts reduced the possibility of using the sludge for other purposes than deposition. In contrast, the use of Calcium improved the value of the sludge as a fertiliser.
The optimal treatment process is shown in Figure 2. Referring to the Figure, the diagram begins with the oil-mill plant, shown in the top left hand corner. Fruit branches are received at the mill for extraction of the oil. The resulting POME proceeds to Step 1. Step 1 is the oil recovery process which consists of a DAF unit. The resulting oil-sludge mixture is then sent back to the mill for oil separation. This step has been shown to increase the amount of oil produced from the fruit branches.

After step 1 (DAF treatment), the POME is treated in an Ozone-flotation unit (step 2), which has two functions; (i) flotation of the sludge to lower the BOD, oil content etc; and (ii) oxidation of non-biodegradable substances in POME. The sludge derived from this process is sterile and can be used for other purposes, such as fertiliser.

Step 3 shows the biological treatment of the pre-treated POME in a concentrated fixed film reactor. Further sludge is produced at this step and can also be utilised for other purposes.

Steps 4 and 5 consists of further oxidation by ozone of the effluents from biological treatment. Step 5 includes a Ca(OH)2 precipitation step and recirculation of the wastewater back to the biological treatment. The pH of the waste water is adjusted if needed, or may be reused in mill technical purposes, such as washing. Tests were preformed on each of the above steps and the final analysis was carried out in Kuching Laboratory.

Results

Even though Sarawak Plantation has its own laboratories, samples were analysed by a third party laboratory, because of lack of capacity at Sarawak Plantation. The laboratory was Chemisain Consultant SDN BHD, Kuching, Sarawak. Analyses of the samples were made according to international standards.

The POME, according to protocol 4 above, was analysed for pH, BOD, COD, suspended solids (mg/l), total solids content (mg/l), fat/oil content (mg/l), total
Nitrogen (mg/l) and NH$_3$N (mg/l). The results of analysis of the POME are shown in Table 3 below.

<table>
<thead>
<tr>
<th>Component measured</th>
<th>t=0</th>
<th>t=1</th>
<th>t=3</th>
<th>t=5</th>
<th>biology</th>
<th>Biology+Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>4.2</td>
<td>4.2</td>
<td>4.0</td>
<td>4.0</td>
<td>7.3</td>
<td>12.2</td>
</tr>
<tr>
<td>BOD (mg/l)</td>
<td>23,500</td>
<td>23,900</td>
<td>17,800</td>
<td>17,500</td>
<td>1,030</td>
<td>441</td>
</tr>
<tr>
<td>COD (mg/l)</td>
<td>47,300</td>
<td>46,500</td>
<td>44,200</td>
<td>41,100</td>
<td>1,670</td>
<td>736</td>
</tr>
<tr>
<td>Suspended solids (mg/l)</td>
<td>23,100</td>
<td>19,200</td>
<td>15,200</td>
<td>18,600</td>
<td>346</td>
<td>696</td>
</tr>
<tr>
<td>Total solids (mg/l)</td>
<td>39,000</td>
<td>35,500</td>
<td>29,100</td>
<td>29,800</td>
<td>7,980</td>
<td>3,450</td>
</tr>
<tr>
<td>Fat/oil (mg/l)</td>
<td>2,170</td>
<td>1,220</td>
<td>706</td>
<td>963</td>
<td>39</td>
<td>20</td>
</tr>
<tr>
<td>Total N (mg/l)</td>
<td>300</td>
<td>274</td>
<td>286</td>
<td>262</td>
<td>25.7</td>
<td>9.5</td>
</tr>
<tr>
<td>NH$_3$N</td>
<td>198</td>
<td>184</td>
<td>191</td>
<td>153</td>
<td>12.4</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Table 3

As can be seen from the results in Table 3, the pre-treatment of POME was able to reduce the BOD from 23,500 mg/l at T=0 to 17,500 mg/l at T=5. However, the most significant drop in BOD occurred during the biological treatment of the POME after pre-treatment with ozone. As can be seen in Table 3, the BOD fell to 1,030 mg/l and 441 mg/l in the BIOLOGY test group and BIOLOGY+Ca group, respectively.

The decrease in COD is also shown in Table 3. At t=0 the COD was measured at 47,300 mg/l, which fell to 41,100 mg/l at T=5. A significant decrease in COD was then observed in the BIOLOGY test group and BIOLOGY+Ca group, were COD dropped to 1,670 mg/l and 736 mg/l, respectively.

A graphical representation of these results is shown in Figure 3. Figure 3 shows that BOD and COD in the POME fell during the ozone flotation step. However, it was surprising to see that the biggest and most important fall in BOD was during the following biological treatment of the POME. The amount of time required for the removal of BOD to an environmentally acceptable level was significantly less than the biological treatment of POME without the ozone pre-treatment step.
Table 3 and Figure 4 further show that the amount of solids in the POME also fell as a result of pre-treatment of POME with ozone gas. At t=0, the total solid content was 39,000 mg/l and the suspended solids (SS) was 23,100 mg/l. At t=5, the total solid content and SS had dropped to 18600 mg/l and 29800 mg/l, respectively. However, the most significant drop in total solid content was seen in test groups BIOLOGY and BIOLOGY+Ca, where the total solid content dropped to 7980 mg/l and 3450 mg/l, respectively. In addition, SS dropped to 345 mg/l and 696 mg/l in test groups BIOLOGY AND BIOLOGY+Ca, respectively. This drop in solid content on the POME may be a result of the solids becoming suspended during ozone treatment.

Table 2 and Figure 5 show the results of fat/oil in the POME during treatment in the five test groups. At t=0, the amount of fat/oil was 2170 mg/l. At t=5, the fat/oil content had dropped to 963 mg/l. However, the most significant reduction in fat/oil content resulted after biological treatment of the POME, with the amount of fat/oil dropping to 39 mg/l and 20 mg/l in the BIOLOGY and BIOLOGY+Ca groups, respectively. Thus, the recovery of fat/oil just using air is evident and continues during the ozone treatment. Approximately 43% of the fat/oil is recovered during the air floatation and a further 10-20% during the ozone pre-treatment step. However, approximately 50% of the fat/oil content is still present after ozone treatment, as can be seen from a comparison of fat/oil content at t=0 and t=5 in Table 3.

The method of the present invention does not appear to affect the total nitrogen content, NH3N, and pH of the POME. However, these factors are affected by the biological treatment of the POME after ozone pre-treatment (see Table 3).

The pH, BOD, COD, suspended solids, total solid content, fat/oil content and nitrogen content of the sludge was also measured as shown in Table 4 below.
Apart from a decrease in the fat/oil content of the sludge, the use of ozone in the pre-treatment of POME does not seem to affect pH, BOD, COD, suspended solids, total solid content, and nitrogen content the above content of sludge. The fat/oil content of the sludge decreases as a direct result of the fat/oil removal from the POME. This result is illustrated in Figure 6.

In summary, the use of ozone in a pre-treatment step for treating effluent produced from palm oil extraction, reduces BOD, COD, total solids form extremely high and thus potentially dangerous levels to more acceptable levels for waste water within a 24 hour period.

<table>
<thead>
<tr>
<th>Component measured</th>
<th>t=1</th>
<th>t=5</th>
</tr>
</thead>
<tbody>
<tr>
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**Table 4**


The Claims Defining the Invention are as Follows

1. A method for the treatment of wastewater which method comprises the steps of (a) pre-treatment of the wastewater with ozone; and (b) biological treatment of the water from step (a).

2. The method according to claim 1 further comprising the step of treating the wastewater using Dissolved Air Flotation (DAF) prior to step (a).

3. The method according to claim 1 or 2 wherein the ozone pre-treatment step uses gas which is a mixture of oxygen and ozone.

4. The method according to claim 3 wherein the mixture of gas is 90% oxygen and 10% ozone.

5. The method according to any one of the preceding claims wherein step (a) is carried out at a temperature of between about 25 °C and about 80 °C.

6. The method according to claim 5 wherein the temperature is about 50 °C.

7. The method according to anyone of the preceding claims wherein step (a) is carried out for a period of between about 1 hour and about 6 hours.

8. The method according to claim 7 wherein step (a) is carried out for about 2 hours to about 4 hours.

9. The method according to any one of the preceding claims wherein step (b) includes enzymatic or biological methods of treatment.

10. The method according to claim 9 wherein the biological method of treatment is the use of anaerobic and/or aerobic treatment methods.

11. A method for removing organic compounds from wastewater, comprising the steps of:
(a) introducing wastewater into a reaction tank to perform an ozone dissolution and oxidation reaction for a period of time between 1 to 6 hours;

(b) allowing the resulting ozone-treated water from said reaction tank to flow through into holding ponds;

(c) treating the water from step (a) using a biological system; and

(d) discharging the water from step (c) or recirculating the water to repeat step (a) above.

12. The method according to any one of the preceding claims further comprising adding a metal salt after the ozone pre-treatment step.

13. The method according to claim 12 wherein the salt is selected from magnesium, sodium, calcium, potassium, aluminium, iron, chromium, titanium or niobium.

14. The method according to claim 13 wherein the salt is selected from calcium hydroxide, calcium carbonate, calcium oxide, magnesium carbonate, magnesium hydroxide, magnesium oxide, iron salts or aluminium salts, such as aluminium hydroxide.

15. The method according to any one of the preceding claims wherein polymers may be added during the biological treatment step.

16. The method according to any one of the preceding claims wherein the wastewater is raw wastewater, POME, effluent from biological treatment ponds, effluent before biological treatment ponds, recirculated wastewater.

17. An apparatus for the treatment of wastewater, said apparatus comprising: a reaction tank, an ozone generating means, and a belt filter system.
18. The apparatus according to claim 17 wherein the reaction tank of the apparatus further comprises a Dissolved Air Flotation unit.

19. The apparatus according to claim 17 or 18 wherein the reaction tank may also comprise a scraper system for removal of oil scum.

20. The apparatus according to any one of claims 17 to 19 further comprising a recycling mechanism for recycling wastewater after the biological treatment step back to the reaction tank for further ozone treatment.

21. The apparatus according to any one of claims 17 to 20 for use with an existing ponding systems.
FIGURE 1
FIGURE 2
FIGURE 4
FIGURE 5
FIGURE 6
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.
C02F1/78 (2006.01) C02F3/00 (2006.01) C02F 9/14 (2006.01)

Action Date: 19 December 2005

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DWPI: C02F 1/78, 9/14, 3/00 and keyword ozon+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C

See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search: 19 December 2005

Date of mailing of the international search report: 1 January 2006

Name and mailing address of the ISA/AU

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Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX