Oil and grease removal from vegetable oil polluted wastewater; advanced oxidation process approach (Fenton Process)

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ABSTRACT
Oil and grease removal process, through the use of fenton oxidation reaction on an oil polluted wastewater from a vegetable oil plant has been studied. The study was designed to assess the effectiveness of fenton oxidation reaction process in eliminating oil and grease contaminant in the wastewater. The raw wastewater was subjected to analysis through standard methods to determine BOD, Oil and grease, phenol, salinity and sodium batch oxidation process was adopted to remove the oil and grease in which four input parameters; pH, Fe2+, temperature and hydrogen peroxide(H2O2) were considered. Four runs of experiment were performed where each parameter was varied while the other three remained constant. In each run, oil and grease removal was determined at ten minutes interval for 60 minutes through analysis. The results showed that the highest oil and grease removal efficiencies of 96.28%, 98.74%, 99.02% and 93.03% were achieved at the optimum conditions of pH=3, Fe2+ = 3.2 g/l, temp=45°C and H2O2=4.5mole respectively and the oil and grease removal was progressive with time until at the point of inflection at 50 minutes where the removal appeared steady. Oil and grease removal efficiency was highly sensitive to the operating conditions. At excess values of the operating conditions, that is, at values beyond the optimum values, the rate of formation of the hydroxyl radical (OH•) became sluggish, impairing removal process. This also explained why the removal efficiency progressed to the plateau at the optimum condition values, and then declined as the values of the operating conditions increased.

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Introduction
Waste discharges from production processes have always pose enormous threat to the environment. Often, liquid waste changes adversely the physiochemical properties of the receiving medium[1] in most cases oil contaminant wastewater channeled in water bodies affects the water quality, beaches and mangrove[2]. Waste water from diary and palm oil processing plants has been reported to have high values of BOD, COD and oil and grease component of the waste water was targeted for removal [3]. Waste water from petrol chemical plants has similar characteristics in addition to some traces of toxic pollutants[4]. Conventional treatment processes have partially remediated the pollution problem with 1,4 dioxane 2B carcinogen component of the COD pollutant been resistant to both aerobic and anaerobic biodegradation[5]. Fenton process has offered a more holistic remediation technique with appreciable cost effectiveness. Fenton ((H2O2/Fe2+) is a solution of hydrogen peroxide and an iron catalyst that is used to oxidize contaminants mainly of organic origin[6]. As advance oxidation process (AOP), fenton shows its effectiveness through oxidation by hydroxyl radical released after a reaction between the iron salt and hydrogen peroxide[7]. The radical mechanism in acidic medium is described by the following equations as presented by prabir and samanta 2010[5]

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^- \quad (1)
\]

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{OOG}^- + \text{H}^+ \quad (2)
\]

Ferrous Iron (ii) is oxidized by the hydrogen peroxide to ferric iron(iii), hydroxyl radical and a hydroxyl anion. In equation 2, the iron(iii) formed in turn is oxidized by the hydrogen peroxide to produce iron (ii), peroxide radical and a proton. In recent times many researchers have focus mainly on the investigation of COD removal from diverse pollutants. Shafieiyoun et al 2011[8] examined COD removal from Organic load removal of landfill leachate. Dincer et al 2007[9] studied COD removal from crude oil recovery wastewater. This study will therefore explore Oil and grease removal from vegetable oil processing wastewater and the influence of initial operating conditions such as pH, time, temperature, concentrations of Fe2+ and H2O2 on the removal process.

Materials and Methods
The raw wastewater from the vegetable oil manufacturing company was collected and analyzed for; BOD, Oil and grease, phenol, salinity and sodium. All the parameters were analyzed using standard methods provided in APHA, AWWA, WPCF 1992 Version[10]. For the fenton oxidation process, oil and grease component of the waste water was targeted for removal due to its heavy presence in the wastewater. The batch oxidation process was carried out in four runs with respect to the following variables; pH, Fe2+, temp. and H2O2. In each run, one variable was varied while others were kept constant. In the first run, 250ml of the waste water was introduced into each 500ml
capacity round bottom flask replicated into five places and the content of each flask adjusted to pH values of 1, 2, 3, 4 and 5 respectively. 1.6mg/l and 1.9 moles of ferrous sulphate solution and hydrogen peroxide respectively were also introduced in the flask and the temperature of the set-up controlled at ambient temperature of 25°C before it was agitated at 300rpm to ensure proper mixture of the components. In order to monitor the progress of the oxidation process, 35ml of the aliquot of the mixture was taken from each pH flask at various periods of 10, 20, 30, 40, 50 and 60mins to analyze for oil and grease using standard methods. The second run was conducted with the iron sulphate solution (Fe²⁺) varied at the concentrations of 1.6, 3.2, 5.0 and 6.0 mg/l and at the optimum pH of 3 and 1.9 moles of H₂O₂ observed in the first run. The second run was replicated into four places according to the numbers of varied Fe²⁺. After the agitation, the oil and grease analysis was carried out with 35ml quantity of aliquot taken from each Fe²⁺ flasks at various oxidation periods. In the third run, temperature variations of 25°C, 35°C, 45°C and 60°C were used at the optimum pH values of 3 and Fe²⁺ of 3.2. In the same vein, analysis of oil and grease was carried on the 35ml quantity of aliquot taken from flasks at various temperature values after agitations. Finally, hydrogen peroxide was varied at different values of 1.9, 3.0, 4.5, 6.0, 7.5 and 9.0 moles while pH, temp., and Fe²⁺ were kept constant at their optimum values of 3, 45°C and 3.2 respectively in the fourth run. After the usual agitation and the aliquot withdrawn from flask of various H₂O₂ values at different oxidation periods, oil and grease analysis was done on all withdrawn samples.

Results

Characteristics of the Vegetable Oil Wastewater

Table 1 shows the characteristics of wastewater from vegetable oil processing plant. Although the results show that the wastewater effluent contains high value of oil and grease, values for other parameters slightly exceeded the wastewater standard[11].

<table>
<thead>
<tr>
<th>parameters</th>
<th>Values (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD</td>
<td>37.3</td>
</tr>
<tr>
<td>Oil and grease</td>
<td>73.0</td>
</tr>
<tr>
<td>Phenol</td>
<td>0.55</td>
</tr>
<tr>
<td>Salinity</td>
<td>3.5</td>
</tr>
<tr>
<td>Sodium</td>
<td>12.3</td>
</tr>
</tbody>
</table>

Effects of Ph Variation on Oil and Grease Removal

The Oil and grease removal effect was studied through fenton process with the pH medium varied between 1 – 5 range. The trend of variation is represented in fig 1. The figure shows the graph of the amount of oil and grease removed with time of removal.

Effects of Fe²⁺ Dosage

At the optimum pH of 3 and at room temperature of 25°C with the initial H₂O₂ value of 1.9 mole, Fe²⁺ was varied as follows; 1.6, 3.2, 5.0 and 6.4 to study its variation effects on Oil and grease removal.

Effects of Temperature

Figure 3 presents the effects of varying temperature range between 25°C – 60°C on the oil and grease removal efficiency.

Effects of Hydrogen Peroxide (H₂O₂)

Figure 4 expresses the relationship between oil and grease removal and reaction time at various values of H₂O₂.

Removal Efficiency

Figure 5 shows various efficiency levels corresponding to changes in pH values.
Discussions

Results in table 1 shows that wastewater from the vegetable oil processing plant contains high value of oil and grease and the values of other parameters are slightly below the wastewater standard stipulated for discharge in the environment[11]. Without adequate treatment, the high Oil and grease value alters the physiochemical properties of the wastewater receiving body leading to death of most marine lives, the zoo and phytoplankton[12]. In most case the oil film blocks the trachea of the zooplanktons and that of the fishes bringing impairment of breathing to those organisms and consequently their death[13]. In this regard, there is need to avert this situation through advance treatment process and indeed fenton process.

Effects of Ph variation On Oil and Grease Removal

It was observed in figure 1 that removal process increased with time up to the point of inflection. The point of inflection which appeared at the processing time of 50 minutes showed the maximum oil and grease removal values for various ph processing media. The maximum removal values for ph values of 1,2,3,4 and 5 were 65.7, 67.04, 68.9, 54.64 and 38.68mg/l respectively. looking at the ph values and the amount of Oil and grease removed, it is believed that the amount of oil and grease removal is highly ph sensitive. The removal process was more with low ph medium . It was also observed that oil and grease removal increased as the ph value increased but got to the plateau at the ph of 3 and began to reduce gradually from ph of 3 to 5 through 4 . This could be attributed to the impairment of total regeneration of Fe$^{2+}$ during the reaction of Fe$^{3+}$ and H$_2$O$_2$ and also stabilization of H$_3$O$_2$ at the point of low ph, (less than 3 ) and higher ph (more than 3) as equally observed by[22]. On the contrary, Shafieiyoun et al 2011[8] reported optimum ph of 2 for COD removal from the organic load of land fill leachate . The variation form the present study could be due to differences in operating conditions such as temperature, H$_2$O$_2$/Fe molar ratio etc. Fe$^{2+}$ catalyzes the decomposition of H$_2$O$_2$ to produce a strong radical(hydroxyl radical HO•) which is capable of remediating any contaminated site by oxidation[14]. Although with different pollutants, several researchers have concurred with the trend of pH variation with Oil and grease removal as observed in this study. Jonathan et al 2011[15] observed low production of Fe$^{2+}$ at pH lower than 2.5 during the degradation of a model azo dye via photo-fenton process. They further observed that H+ reacts with the OH• radical which act as a radical scavenging agent. At pH value higher than 4, Gogate and Pandit 2004[16] equally observed low production of free Fe$^{2+}$ due to slow reaction of ferrous and ferricoxy hydroxide with H$_2$O$_2$.

Effects of Fe$^{2+}$ Dosage

From figure 2, oil and grease removal varied linearly with time as different values of Fe$^{2+}$ was dosed during the oxidation process of fenton. As presented in figure 2 the Fe$^{2+}$ value was varied between 1.6-6.4g/l, the removal increased progressively on addition of various Fe$^{2+}$ values until at the point of inflection when the oil and grease removal seemed to remain constant with time. The points of inflection at 50mins removal period was observed at the points of maximum oil and grease removal for various Fe$^{2+}$ values(1.6, 3.2, 5.0, 6.4) and these were shown in figure 2 as 61.45, 71.3, 32.98 and 31.78 respectively. As shown in figure 2, the oil and grease removal increased with increased amount of Fe$^{2+}$ dosed but decreased progressively as Fe increased beyond 3.2 up to 6.0 concentration. The gradual reduction of oil and grease removal observed from 3.2 to 6.4 through 5.0 concentration was due to low production of OH
radical occasioned by excessive dosage of Fe\textsuperscript{2+}. The excessive Fe\textsuperscript{2+} produces scavenging effects in the solution which inhibits further reduction effect as equally observed by Martins et al 2010 could also be factor. Anna et al 2010 made similar observations on the evaluation, biodegradability and toxicity of landfill treatment using fenton process, although the decline in the landfill treatment process was observed at the dosage point of 30mg/l as against that of the present study which is between 3.2-6.4g/l. The glaring disparity could be attributed to differences in the contaminants of the wastewater to be treatment and other environmental conditions such as temperature, pH etc[17]

**Effects of Temperature**

As an important factor in most chemical reaction rates, effects of temperature was studied on the fenton reaction process of oil and grease removal. To do this, the wastewater sample was prepared according to the experimental procedure, and temperatures of various replicates of the third run were adjusted to their desired values of 25\textdegree C, 35\textdegree C, 45\textdegree C and 60\textdegree C before the initial hydrogen peroxide value of 1.9moles was added. Subsequently, the entire experiment was adjusted to the optimum pH and Fe\textsuperscript{2+} values of 3 and 3.2 respectively before observation showed in figure 3 commenced. It was observed that reduction of oil and grease was progressive until at the point of inflection which occurred at the removal period of 50mins. This can be assumed as the point of saturation when the oil and grease removal value remained constant. The figure equally showed that the rate of oil and grease removal is temperature sensitive as it responded to varying temperature values. The removal procedure increased linearly with temperature up to the optimum temperature of 45\textdegree C before a decline was observed beyond the optimum. This is probably the inefficient decomposition of H\textsubscript{2}O\textsubscript{2} with its consequent insufficient production of HO\textsuperscript{•}. This implies that at the temperature of 45\textdegree C a considerable amount of free hydroxyl radicals (HO\textsuperscript{•})was sufficiently available to effect the oxidation reaction with oil and grease and consequently, its effective removal process. On the other hand, there was insufficient availability of the free hydroxyl radical and slow removal of oil and grease at temperatures between 50 and 60\textdegree C. In comparison, optimum temperature values of previous studies vary with the present study. For instance, Jonathan et al 2011 recorded 40\textdegree C , Shafieiyoun et al 2011[8] reported 50\textdegree C and Djedjess et al 2010[18] observed that Oxidation of Sodium Dodecylsulphate by Fenton’s Reagent took at the optimum temperature of 60\textdegree C. The variation was perhaps due to differences in contaminant type and other environmental factors.

**Effects of Hydrogen Peroxide (H\textsubscript{2}O\textsubscript{2})**

Hydrogen peroxide, provides the radical hydroxyl substance responsible for the oxidation of the oxidizable contaminants. This study, therefore examined the effects of hydrogen peroxide on oil and grease removal by changing its concentrations in the values of 1.9, 3.0, 4.5, 6.0, 7.5 and 10moles during the experiment. Also, the values of pH, Fe\textsuperscript{2+} and temperature were maintained at their optimal values of 3.0, 3.2 and 45\textdegree C respectively as determined in the previous runs. Like in the other runs the removal process increased progressively with time until the point of inflection where it witnessed steady state. At this point of 55mins, the removal process was constant. With respect to various dosage of H\textsubscript{2}O\textsubscript{2}, oil and grease removal also increased with increase concentrations dose of H\textsubscript{2}O\textsubscript{2}. The figure showed the increase in oil and grease removal with increase H\textsubscript{2}O\textsubscript{2} concentration of 1.9, 3.0 and to its peak at 4.5moles then the removal decline from H\textsubscript{2}O\textsubscript{2} dosage of 6.0 to10moles through 7.5 moles. At the lower dosage of 1.9, 3.0 up to 4.5moles the radical hydroxyl group, OH\textsuperscript{•} was produced progressively with its maximum at H\textsubscript{2}O\textsubscript{2} of 4.5mole. This implies that sufficient OH\textsuperscript{•} was on hand to oxidize the oil and grease contaminant of the wastewater. Although at different ranges of concentrations several researchers corroborated with the trend of removal process observed in this study. Anna et al 2010[19] observed the progressive dye removal with H\textsubscript{2}O\textsubscript{2} dosage range of 5-30moles. The increase on H\textsubscript{2}O\textsubscript{2} concentration from 22.28 to 66.84 g l\textsuperscript{-1} improved the removal of COD in a crude oil recovery wastewater but could not remove any further beyond 66.84g/l of H\textsubscript{2}O\textsubscript{2}[9]. Shafieiyoun et al 2011[8] reported 39 mole dosage of H\textsubscript{2}O\textsubscript{2} for the removal of Organic load removal of landfill leachate using Nano Sized Zero Valant Iron particles. On the other hand, excess H\textsubscript{2}O\textsubscript{2} in the system reacts with the radical hydroxyl OH\textsuperscript{•} producing a scavenging effect with a consequent reduction in oil and grease[20].

**Removal Efficiency**

This study also tested the Efficiency of removal of oil and grease from the wastewater. The test was based on the four factors: pH of the medium, amount of added Fe\textsuperscript{2+} temperature of the medium and concentration of the hydrogen peroxide. In run 1 where ph of the medium was varied between 1 and 5 and other factors kept constant, varying removal efficiency was observed as the pH was adjusted to their various values. Removal efficiency increased as pH values increased but got to its peak at pH of 3 and began to decrease beyond pH of 4. Highest removal efficiency of 96.28% was observed at the ph of 3. Other removal efficiencies observed at pH values of 1, 2, and 4 were 86.9%, 91.23% and 70.05% respectively. This implies that low pH range favors sufficient availability of the oxidizing agent i.e radical hydroxyl (OH\textsuperscript{•}) with its highest production observed at pH of 3. At pH greater than 3 efficiency of oil and grease removal began to reduce suggesting that further increase in pH cannot effect any tangible removal due to low production of HO\textsuperscript{•} at pH values slightly above that of the present study in their COD removal study of Optimizing the treatment of landfill leachate by conventional Fenton and photo-Fenton processes. The variation could probably be due to differences in the type of contaminants between theirs and the present study and also varying experimental conditions. An appreciable oil and grease removal efficiency was equally observed when Fe\textsuperscript{2+} was varied between 1.6-6.4g/l. The highest removal efficiency of 98.74% was observed at 3.2g/l Fe\textsuperscript{2+} dosage, followed by Fe\textsuperscript{2+} dosages of 1.6, 5.0, and 6.4g/l with their removal efficiencies of 58.1, 55.1and 40.05% respectively. Removal efficiency decreased progressively beyond 3.2g/l dosage due to scavenging effects of excess Fe\textsuperscript{2+} in the solution meaning that further dosage of Fe\textsuperscript{2+} may not produce tangible removal efficiency. This observation is in line with the study of Mehrdad and Hashemzadeh 2010[21]. Oil and grease removal efficiency was also studied at varying temperature ranges. Fig 7 shows that oil and grease removal efficiency was at its peak of 99.02% at 35\textdegree C process temperature. Efficiency reduced to 79.49 at temperature value of 45\textdegree C and further reduced to 57.63% at 60\textdegree C. This pattern of efficiency variation with temperature suggested that negligible oil and grease removal will take place with further increase in temperature due to inefficient H\textsubscript{2}O\textsubscript{2} decomposition at high temperature to produce the radical hydroxide. Oil and grease removal efficiency was
also enhanced with increase H₂O₂ dosage until it got to optimum before a decline was observed. Fig 8 shows that removal efficiency increased from 73.78-93.03% with increase H₂O₂ dosage between 1.9-3.0 moles.

Beyond 3.0mole a decrease in efficiency removal was observed between 88.71-50.58% with increase dosage of between 4.5-9.0 moles. This shows that high H₂O₂ dosage caused an increase concentration of oil and grease in the solution due to lack of potential to decompose H₂O₂ thereby producing insufficient availability of OH⁻.

Conclusions
Oil and grease removal studied under the following factors; ph, temperature, amount of Fe²⁺ and concentrations of H₂O₂ showed that removal progressed until at a point of inflection where it remained steady and gradually reduced. the maximum removal was achieved at ph=3, Fe²⁺=3.2 g/l, temp= 45°C and H₂O₂=4.5moles all at the processing period of 50minutes, meaning that beyond the maximum points . In the presence of large quantity of the varying factors, the removal process became sluggish and unable to removal appreciable amount. Removal efficiency also increased with increased values of the varying factors up to the maximum before it reduced progressively. At the impute factor values of ph=3, fe⁺⁺=3.2 g/l, temp=45°C and H₂O₂=4.5moles the maximum efficiency of 96.28% 98.74%, 99.02 and 93.03% respectively were achieved.

References