COD Removal of Edible Oil Content in Wastewater by Advanced Oxidation Process

Aola Hussein Flamarz Tahir¹, Nagham Obeid Kareim¹ & Shatha Abduljabbar Ibrahim¹

¹ Faculty of Engineering, Al Mustansiriayah University, Baghdad, Iraq

Correspondence: Aola Hussein Flamarz Tahir, Faculty of Engineering, Al Mustansiriayah University, Baghdad, Iraq. E-mail: aola90@gmail.com

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Abstract

Different Advanced Oxidation Processes (Photo Fenton process, Fenton process and H₂O₂/UV) were studied in order to reduce COD from oily compounds aqueous solution using batch system. To get the optimum condition, different variables were studied for each of these processes; such as pH, time, concentration of H₂O₂, concentration of oil, concentration of FeSO₄·7H₂O and temperature as parameters. It was found that the optimal pH value for the three processes was 3 and the optimal temperature was 30°C for Photo-Fenton and UV/H₂O₂ system and 20°C for Fenton process. Photo-Fenton process gave a maximum COD reduction of 80.59% (COD from 2684 to 521 mg/l), Fenton gave 53.22% (COD from 2587-1130) and the combination of UV/H₂O₂ gave a COD reduction of 22.69% (COD from 2450 to 1894). The percentage of removal found was after the total reaction time (180 min.). The optimum chemical reagents for Photo-Fenton, Fenton and UV/H₂O₂ were as the following H₂O₂ = 800 mg/l, 1500 mg/l and 2000 mg/l, Fe₂SO₄·7H₂O = 60 mg/l, 100 mg/l.

Keywords: advanced oxidation process, edible oil, sunflower oil, photo-fenton, fenton, hydrogen peroxide

1. Introduction

Edible refined oil processing industry is a major issue of environmental concern due to the increase in production and demand in developing countries in the past three decades. The waste stream effluents create serious environmental problem such as great threat to aquatic life due to its high organic content. Hence its treatment is essential prior to its disposal. The choice of effluent treatment methods depends on the organic content present in the effluent and its discharge conditions (Sharma et al., 2014). The oil seeds are usually processed to obtain the oil contents which are subsequently processed for human consumption and industrial applications. Thus the vegetable oil industries are, equally, associated with oil extraction, refining, transportation, uses and reuses. However, these industries have been linked with environmental pollutions resulting from oil spill, oily effluent discharge into water bodies and oily sludge discharge into the environment indiscriminately, untreated or in conditions below the standard discharge limits (Alade et al., 2011).

Crude vegetable oils are mainly triacylglycerols (around 95%) along with some free acids, monoacylglycerols, and diacylglycerols. They also contain variable amounts of other components such as phospholipids, free and esterified sterols, triterpene alcohols, tocopherols and tocotrienols, carotenes, chlorophylls and other coloring matters, and hydrocarbons as well as traces of metals, oxidation products and some undesirable flavors (Gunstone, 2005). Vegetable oil wastewater (VOWW) has been treated in different ways. Its characteristics depend largely on the type of oil processed and on the process implemented that are high in COD, oil and grease, sulphate and phosphate content, resulting in both high inorganic as well as organic loading of the relevant wastewater treatment works. The wastewater varies both in quantity and characteristics from one oil industry to another. The composition of wastewater from the same industry also varies widely from day to day (Chin & Wong, 1981). Also the oil type processed may be a reason for these fluctuations.

Wastewaters containing oil can be treated either in chemical or biological units. The efficiency of treatment depends on the ratio of free oil to emulsified oil. The free oil can be easily removed from wastewater by physical processes but in order to remove emulsified oil from wastewater, de-emulsification should be done. The conventional treatment of vegetable oil industry wastewater consists of mechanical dewatering of sludge produced with physical, chemical and biological processes. In general, biological treatments that are applied in the industry to treat the VOWW. It will start with oil removal and dissolved air flotation (DAF) with alum as
coagulant before entering into biological treatments. Variation in wastewater flow and composition has led to the inefficiency of bioprocess resulting the treated effluent could not meet the discharge limits (Ng, 2006).

Advanced oxidation processes (AOPs) belong to the chemical treatment category and are used to oxidise organic compounds found in wastewater which are difficult to handle biologically into simpler end products. Advanced oxidation processes (AOPS) are technologies based on the generation of hydroxyl radicals, especially the hydroxyl radical (OH), which is highly reactive substance used to degrade toxic organic compound in a medium. The main reason why AOPs was chosen in this study is due to its reputation in treating highly recalcitrant pollutant and removal wide range of (Wols & Hofman-Cal, 2012).

Depending upon the nature of the organic species, four types of initial attach are possible: Radical addition Equation (2.1), hydrogen abstraction Equation (2.2), electron transfer Equation (2.3) and radical combination Equation (2.4). In the following equations, $R$ is used to describe the reacting organic compound (Heponiemi & Lassi, 2012):

Radical addition: Reaction of the hydroxyl radical and unsaturated or aliphatic organic compound produces organic radical which can further oxidize by oxygen or ferrous iron to form stable oxidized end products.

$$ R + HO \cdot \rightarrow ROH \; (1.1) $$

Hydrogen abstraction: Generated hydroxyl radical can be used to remove hydrogen from an organic compound forming an organic radical and initiating a chain reaction where the organic radical reacts with oxygen. This produces a peroxyl radical, which can react with another organic compound, and so on.

$$ R + HO \cdot \rightarrow R \cdot + H_2O \; (1.2) $$

Electron transfer: Electron transfer results in the formation of ions with a higher valence. Oxidation of a monoatomic negative ion will result in the formation of an atom or a free radical.

$$ R^a + HO \cdot \rightarrow R^{a-1} + HO^- \; (1.3) $$

A radical combination: Two radicals form a stable product.

$$ HO \cdot + HO \cdot \rightarrow H_2O_2 \; (1.4) $$

Generally, the reaction of hydroxyl radicals and organic compounds will produce water, carbon dioxide and salts (SES, 1994).

Three processes are investigated in this study:

**Fenton process** ($H_2O_2/UV$): The conventional ‘dark’ Fenton process was reported first by Fenton (1894) over a century ago for the oxidation of maleic acid. The process involves the reaction between dissolved Fe$^{2+}$ and hydrogen peroxide in acidic aqueous solution, leading to the formation of hydroxyl radicals.

**Photo-Fenton process** ($H_2O_2/Fe^{2+}/UV$): This process involves the hydroxyl radical (‘OH) formation in the reaction mixture through photolysis of hydrogen peroxide ($H_2O_2/UV$) and Fenton reaction ($H_2O_2/Fe^{2+}$).

**Hydrogen peroxide/UV light process**: This process includes $H_2O_2$ injection and mixing followed by a reactor that is equipped with UV light (200 to 280 nm). During this process, ultraviolet radiation is used to cleave the O-O bond in hydrogen peroxide and generate the hydroxyl radical.

### 2. Method

Commercial sunflower oil was been used as the model pollutant and to prepare an artificial sample. The commercial sunflower oil used was from Bil Bak, double refined sunflower oil and imported for Iraqi ministry of trade/ state company for foodstuff trading, for the purpose of ration card. It was analyzed at the Iraqi vegetable oil company laboratories (Table 1). Artificial sunflower oil-water emulsion was prepared as it is the critical level of oil wastewater. The emulsion was prepared by using 2.5 ml of 100 ppm sodium dodecyl sulphate (Biltrec, Spain) for every 100 ml of oil in 1 liter distilled water (Ebrahim et al., 2013).

All experiments are conducted in a 2 Liter thermostatic batch glass reactor mounted at magnetic stirrer with hot plate (LMS-1003, DAIHAN LAB TECH, KOREA). UV radiation (254 nm) is produced from UV lamps (UVM 9311 G, 6 watt 4P-SE, SO SAFE WATER TECHNOLOGIES, UAE), which is set vertically at the top of the reactor. The lamp is totally immersed in the cylindrical reactor. UV lamp is covered in a quartz sleeve for protection and has the characteristics shown in Table (3.5). The distance between the lamp and the reactor wall is fixed to be 5 cm to ensure maximum light irradiation as shown in Figure (2.1).
Table 1. Physical properties of sunflower oil sample

<table>
<thead>
<tr>
<th>Test</th>
<th>Result</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Density</td>
<td>0.920</td>
<td>0.918-0.923</td>
</tr>
<tr>
<td>Refractive index (40 °C)</td>
<td>1.468</td>
<td>1.467 – 1.469</td>
</tr>
<tr>
<td>Cloud point</td>
<td>2</td>
<td>+ 6°C</td>
</tr>
<tr>
<td>Peroxide value</td>
<td>1.6</td>
<td>Max. 2</td>
</tr>
<tr>
<td>F.F.A</td>
<td>0.05</td>
<td>0.18 – 0.20</td>
</tr>
<tr>
<td>Fe</td>
<td>5</td>
<td>Max. 15 ppm</td>
</tr>
<tr>
<td>Colour</td>
<td>0.9R 4.8Y</td>
<td>3R 30Y</td>
</tr>
<tr>
<td>Odor</td>
<td>Acceptable</td>
<td>Acceptable</td>
</tr>
</tbody>
</table>

Figure 1. Laboratory unit – scale batch reactor

2.1 Reagents

All the reagents used in the experiments was research grade reagents without further purification whereby H2O2 (50%, w/w) from Solvochem, FeSO4·7H2O from Hopkin and Williams (England) and Na2S2O3, NaOH and H2SO4 from Central Drug House (India).

2.2 Analytical Method

Chemical oxygen demand of samples was analyzed by using Lovibond Checkitdirect COD Photometer (Germany). The COD ranges used were from 0-15000 mg/l and 0-1500 mg/l.

3. Results and Discussion

Different important factor were studied in this study to discuss its different effects on the AOP’s. The performance of single Fenton’s reagent, Photo-Fenton and combination of UV radiation with hydrogen peroxide for COD removal from oily compounds aqueous solution using batch system were investigated. The following topics were also studied: wastewater characterization, pH value, temperature, effect of H2O2 concentration, effect of FeSO4·7H2O concentration and irradiation time.

3.1 The Effect of Irradiation Time

The effect of time required for the Photo-Fenton process and UV/H2O2 in order to get best removal efficiency was studied. For both processes fixed initial amount of H2O2, FeSO4·7H2O pH, and temperature was set. Initial oil concentration (1000) mg/l (COD = 2500 ± 500) was used in the experiments. The results for Photo-Fenton and UV/H2O2 process plotted in Figure (1).

The optimum time that gave best removal efficiency was found after 180 min. for both processes. It gave a total 67.07 % and 16.34 % COD reduction for Photo-Fenton and UV/H2O2 process respectively. It also found that the oil degradation rate did not increase after 180 min. process time. The removal efficiency was decrease slightly or no change. The total degradation of organic compounds undergoes this reaction sequence (Nasr et al., 2004):

\[ \text{Organic compound} \rightarrow \text{Intermediate A} \rightarrow \text{Intermediate B} \rightarrow \text{CO}_2 \]

Some intermediates are non volatiles compounds, causing the lowness of COD reduction increase. Such intermediates (quinines, acetic acid etc.) require sufficient time to push reaction beyond CO2 (Nasr et al., 2004).
3.2 The Effect of H$_2$O$_2$ Concentration

The effect of initial concentration of H$_2$O$_2$ on Photo-Fenton, Fenton and UV/H$_2$O$_2$ process was tested to optimize the amount of H$_2$O$_2$ required to reduce the COD. The H$_2$O$_2$ concentration range for Photo-Fenton was (200, 400, 600, 800 and 1000) mg/l, whereas for Fenton and UV/H$_2$O$_2$ the range was (500, 1000, 1500, 2000 and 2500 mg/l). Fixed initial oil concentration, Fe$_2$SO$_4$·7H$_2$O concentration, pH and temperature was used in all experiments. The results were plotted in Figure (2).

![Figure 2](image1.png)

Figure 2. Effect of irradiation time on the COD removal by Photo-Fenton and UV/H$_2$O$_2$ system at H$_2$O$_2$ = 1000 mg/l, pH = 7, oil conc. = 1000 mg/l, temp. = 20°C and Fe$_2$SO$_4$·7H$_2$O = 100 mg/l (for Photo-Fenton process only)

From this figure it can be noticed that the COD removal increased as the concentration of H$_2$O$_2$ increased with the increasing of its dosage, reaching a maximum removal efficiency of 69.02 %, 35.68 % and 18.44 % for Photo-Fenton, Fenton and UV/H$_2$O$_2$, respectively. At higher H$_2$O$_2$ dosage than the optimum found there was an increase or no change in COD removal efficiency, the following point is a brief explanation about the H$_2$O$_2$ effect:

Hydrogen peroxide was the main responsible species of the degradation process by the generating of hydroxyl radicals from the direct photolysis. It can be observed that the degradation rate increased considerably when H$_2$O$_2$ was used (Esplugas et al., 2002).

After optimum H$_2$O$_2$ conc. it was found that further increase of H$_2$O$_2$ concentration retarded effluents COD. This inhibition of mineralization is probably due to both auto decomposition of H$_2$O$_2$ into oxygen and water and the scavenging of hydroxyl radicals by the excess of H$_2$O$_2$ according to the following reactions (Chatzisymeon et al., 2008):

$$2H_2O_2 + 2H_2O + O_2$$  \hspace{1cm} (3.1)

$$\cdot OH + H_2O_2 \rightarrow H_2O + HO_2$$  \hspace{1cm} (3.2)

Hydroxyl radical may recombine and participate in radical-radical reactions to form H$_2$O$_2$. 

![Figure 3](image2.png)

Figure 3. Effect of initial H$_2$O$_2$ concentration on the COD removal by Photo-Fenton, Fenton and UV/H$_2$O$_2$ system at pH = 7, oil conc. = 1000 mg/l and temp. = 20°C and Fe$_2$SO$_4$·7H$_2$O = 100 mg/l (for Photo-Fenton and Fenton process only)
At higher H$_2$O$_2$ concentrations lower light intensity available for oil degradation, since H$_2$O$_2$ also absorb lights in the system (Ebrahim et al., 2013).

3.3 The Effect of Fe$_2$SO$_4$\cdot$7$H$_2$O Concentration

The effects of initial Fe$_2$SO$_4$\cdot$7$H$_2$O on Photo-Fenton and Fenton process were tested by carrying out experiments with different concentration of Fe$_2$SO$_4$\cdot$7$H$_2$O (20, 40, 60, 80 and 100 mg/l) for Photo-Fenton process and (50, 100, 150, 200 and 250 mg/l) for Fenton process. Fixed initial oil concentration, pH and temperature was used in all experiments. The results were plotted in Figure (3). By these figures it can be noticed that the degradation rate of oil increased with the increasing amounts of iron salt. It reached its maximum value (72.35 %) at 60 mg/l for Photo-Fenton process and (35.68 %) at 100 mg/l for Fenton process after about 180 min. of irradiation time. The addition of the iron salt above these values this did not affect the degradation; it decreased and or remained unchanged.

Adding ferrous ions increases wastewater brown turbidity during the photo-treatment, which hinders the absorption of the UV light, required for the Photo-Fenton process (Dincer et al., 2008). Also excessive formation of Fe$^{+2}$ which can compete with the organic carbon for OH radical may be a reason for the decrease. High Fe ions disposal will require another process to remove the iron residual so for an economical point of view, in this condition, it is not necessary to have high concentration of Fe ion (Galvão et al., 2006). Fixed H$_2$O$_2$ concentration can be the limiting factor (Rodriguez et al., 2002).

3.4 The Effect of pH Value

The pH plays an important role in the AOP’s and has a considerable effect on the reactions, because of the big influence to the oxidation potential of OH radical according to the reciprocal relation of the oxidation potential to the pH value ($E_0=2.8$ V and $E_{14}=1.95$ V) (Alalm & Tawfik, 2013). Different values of pH were examined in this study (3,7 and 11) keeping the other parameters and dosage constant. The results are plotted in Figure (4).

Optimum pH was found equal to 3 for Photo-Fenton, Fenton and UV/H$_2$O$_2$ system which gave a removal efficiency of (79.4 %, 40.3 % and 21.31 %).

The optimum pH found (3) can be explained by:

The operational pH must be low (pH $<$ 4) to nullify the effect of sequestering radical species, specifically ionic species such as carbonate and bicarbonate ions, leading to a better degradation rate (Mota et al., 2008). At lower pH ($<$ 2.5), the formation of [Fe(H$_2$O)$_6$]$^{2+}$ complex occurs. These reacts more slowly with H$_2$O$_2$ than does [Fe(OH)(H$_2$O)$_5$]$^+$ complex therefore produces less amount of reactive hydroxyl radicals thereby reducing the COD removal efficiency as mentioned by (De Laat and Gallard, 1999). At high pH, iron reacts with the hydroxide ions (HO$-$), precipitating the iron hydroxide (Fe(OH)$_3$) or Fe(OH)$_2$, which does not react with H$_2$O$_2$, which will decrease the degradation rate (Mota et al., 2008). The removal efficiency of COD was improved at
the acidic conditions, raising the pH from 3 to 7 decreased the COD removal efficiency. Similar findings was reported by (Li et al., 2009) who found that the decomposition rate of H₂O₂ is low at pH exceeding 4 resulting a drop in the hydroxyl radicals production. In high pH condition, the reaction between Fe³⁺ and OH⁻ will leads to the formation of Fe(OH)₃. This species will start to precipitate after pH 4.8 based on the calculation from its solubility constant value; K_{sp} (Fe(OH)₃ is 2.79 E⁻⁹ This precipitate will then act as coagulant. Therefore, it is expected that no dominance oxidation and OH radicals generation will occur at this stage (Fadzil et al., 2013).

An adjustment in pH may be required in the wastewater to be treated before adding the Fenton reagents.

Figure 5. Effect of pH value initial concentration on the COD removal by Photo-Fenton, Fenton and UV/H₂O₂ system at oil conc. = 1000 mg/l and temp. = 20°C, H₂O₂ = 800 mg/l, 1500 mg/l, H₂O₂ = 2000 and Fe₂SO₄.7H₂O = 60 mg/l, 100 mg/l for Photo-Fenton, Fenton process and UV/H₂O₂ system, respectively.

3.5 The Effect of Oil Concentration

Different concentrations of vegetable oil (1000, 2000 and 3000) mg/l were used at fixed pH, temperature, H₂O₂ and Fe₂SO₄.7H₂O dosage for all experiments. The results were plotted in Figure(5).

Figure 6. Effect of oil concentration on the COD removal at pH = 3, temp. = 20°C, H₂O₂ = 800 mg/l, 1500 mg/l, 2000 and Fe₂SO₄.7H₂O = 60 mg/l, 100 mg/l for Photo-Fenton, Fenton and UV/H₂O₂ system, respectively.

By these figures it can be observed that the removal efficiency decreases linearly in Photo-Fenton from 79.4 % to 28.05 % as the concentration of oil increases from 1000 to 3000 mg/l respectively. Similarly, in UV/H₂O₂ process the maximum removal efficiency at 1000 mg/l was 21.31 % and decrease down to (18.17) % at 3000 mg/l. In Fenton process the removal efficiency increased at the oil concentration increased up to 2000 mg/l, from (53.22 %) to (24.62 %).

This can be attributed to the increase in COD which leads to high turbidity of the solution. In Photo-Fenton the COD for 3000 mg/L oil solution was measured to be 5861, whereas for 1000 mg/L oil solution the COD was 2587 only. As turbidity in the solutions during the photo treatment hinders the absorption of the UV light for the
photo Fenton process (Rodriguez et al., 2002). (Dincer et al., 2008) diluted wastewater with 21000 ppm COD (80%) in order to treat it with Photo-Fenton. On the other, more COD was removed at higher oil conc. (COD strength) than lower COD in Fenton process and this may due to the absence of UV irradiation and turbidity effect, also because it enhances the attack on the organic matter due to its high content.

3.6 The Effect of Temperature

Reaction temperature is another important process parameter that affects the degradation process. Different temperatures (20, 30 and 40)°C were used. The dosage of the reagents and other parameters were remained constant as obtained from previous sections.

The results were plotted in Figure (6). These figures shows that the COD removal efficiency increases at 30°C and then decreased at 40°C for Photo-Fenton process. For Photo-Fenton and UV/H2O2 system the maximum removal efficiency were 80.59 and 22.69%, respectively. For Fenton process the removal efficiency is 53.22% at 20°C.

The increase in temperature accelerated the decomposition of H2O2 thus increasing the generation of OH radicals which enhances the degradation process slightly. There is no significant COD removal different with different temperatures; the range of the COD removal on predetermined time for these three different temperatures is less than 10%. This finding is in agreement with the previous observation of (Leong & Bashah, 2012). The optimal temperature is in the range of 20-40°C and this result is similar to other researches findings (Leong & Bashah, 2012; Lucas & Peres, 2009; Nieto et al., 2011).

![Figure 7. Effect of temperature on the COD removal at pH = 3, oil concentration = 1000 mg/l, 2000 mg/l, 1000 mg/l, H2O2 = 800 mg/l, 1500 mg/l, 2000 and Fe2SO4.7H2O = 60 mg/l, 100 mg/l for Photo-Fenton, Fenton and UV/H2O2 system, respectively](image)

5. Conclusions

The COD removal from synthetic vegetable oil wastewater was investigated by the Photo-Fenton, Fenton and UV/H2O2 processes. The COD removal efficiency was strongly affected by many factors such as the concentration of H2O2, Fe2SO4.7H2O, pH, temperature and the oily content amount.

It was found that the Photo-Fenton, Fenton and combination of UV and H2O2 processes have the potential to partially reduce the COD of oily wastewater in different removal percentage. The overall results of this study indicate that the application of Photo-Fenton process is a feasible method to treat vegetable oily content wastewaters achieving a significant decrease of COD. Optimum initial pH was found 3 for all three processes studied, temperature of 30°C was found optimum for Photo-Fenton and UV/H2O2 system and 20°C for Fenton system. Optimum chemical reagents dosage for Photo-Fenton at H2O2 = 800 mg/l and Fe2SO4.7H2O = 60 mg/l, leads to a COD reduction of 80.59%. Fenton’s reagent at H2O2 = 1000 mg/l and Fe2SO4.7H2O = 1500 mg/l, leads to a COD reduction of 53.22%. UV/H2O2 combination process a low COD removal efficiency 22.69% was found.

References


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