Chemical Treatment and Enhancement of Bioavailability of Olive Mill Wastewater

Bassim Eid Abbassi

Al-Balqa’ Applied University, 19117 Al-Salt – Jordan

In this research, the potential of chemical treatment of olive mill wastewater (OMW) using different compounds such as lime, potassium permanganate, hypochlorite, and Fenton’s reagent has been investigated. The capability of these compounds to breakdown the carbonaceous content of OMW was tested at different concentration ratios and contact times using a batch system. Chemical oxygen demand (COD) was used as an indicator for the organic content of the OMW. The results showed that chemical treatment is an effective means of treating highly concentrated wastewater such as OMW. A COD removal of about 90% was obtained at permanganate:COD ratio of 1:25 and contact time of 25 minutes. Using Fenton’s reaction, more than 93% COD removal was observed at COD:Fe ratio of 50:1, H₂O₂:Fe ratio of 10:1, and contact time of 10 minutes. The lowest COD removal was observed using sodium hypochlorite. It was possible to reduce the bioavailability indicator, COD/BOD ratio, by 40 and 50% by treating the OMW with permanganate and Fenton’s reagent, respectively. These results along with the short contact time required indicate that chemical treatment is an effective alternative to conventional biological treatment of highly concentrated OMW.

Key words: olive mill, wastewater, chemical treatment, oxidation, Fenton’s reagent, bioavailability

Introduction

Olive oil is an important cash crop that constitutes a source of income for almost all Mediterranean economies. The production of olive oil generates two major types of waste (i.e., pomace, a solid residue, and olive mill wastewater [OMW]), both of which might differ in composition according to the extraction process used. Improper management of these wastes, especially OMW, causes a negative environmental impact and pollution of natural resources.

Olive-oil mills generate dark coloured, foul-smelling, and turbid aqueous wastes. These wastewaters consist of mildly acidic effluents with high conductivity, especially those coming from traditional mills (El Hadrami et al. 2004). Typically, OMW is rich in inorganic ions (sodium, chloride, and phosphorus), organic matter, and suspended solids. El Hadrami et al. (2004) reported that OMW is characterized by a great variety of pollutants including aromatics (such as cathecol, p-coumaric acid, 4-methylcathecol, benzenacetaldehyde, phenyl ethyl alcohol, benzofuran, and tyrosol) and aliphatic compounds (such as hexane, octane, nonanol nonanoic acid, decanoic acid, dichloropropene, pentadecene, and hexadecane). Its organic load is usually around 80 to 200 grams of chemical oxygen demand (COD) per litre, although it depends on the type of extraction process used. Fresh OMW is particularly phytotoxic, mainly due to the presence of phenolic compounds. In addition, these phenolic compounds possess antimicrobial activity, which is an obstacle to the use of biological processes during treatment of OMW. The treatment and safe disposal of organic waste material contained in the OMW in an environmentally acceptable manner and at a reasonable cost is a topic of great importance. It is generally accepted that an ecological and economic solution for the treatment of OMW does not exist. As a result, in Jordan as in other olive-oil-producing countries, nearly all olive oil mills discharge OMW with minimal treatment or without any treatment into the surrounding environment causing acute ecological problems.

Common technologies used in the treatment of this kind of aqueous waste are anaerobic digestion and advanced oxidation processes (Beccari et al. 1996; Benitez et al. 1999; Ahmadi et al. 2005). Gomes et al. (2007) and Capasso et al. (1992) reported that high amounts of biorefractory and oxidation-refractory organics still remain at the end of both of these treatments, especially for those involving anaerobic digestion.

There is little doubt that biological processes will continue to be employed as a baseline treatment process of OMW (Mantzavinos and Psillakis 2004). However, biological processes do not always result in satisfactory removal of all organic substances produced by the olive industry, in particular substances that are inhibitory, toxic, or resistant to biological treatment. Therefore, advanced technologies based on chemical treatment may be the only viable option for decontamination of biologically recalcitrant wastewater.

Chemical treatment technologies constitute the use of specific chemicals (e.g., oxidizing agents used to break down organic material in wastewater). However, some chemicals exhibit lower rates of degradation than others. For example, ozone and hydrogen peroxide exhibit lower rates of degradation when compared with processes that
use free radicals (Zwiener and Frimmel 2000; Arslan and Balcioglu 2001). Moreover, additional mass transfer resistance between the pollutant and oxidizing agents used generally hamper the overall efficiency of the process, especially when an ozonation process is used. Free radicals are generated when ozone is used in combination with hydrogen peroxide, or the action of ozone or hydrogen peroxide is supplemented by other energy dissipating components such as use of ultraviolet light from sunlight or ultrasound. These hybrid techniques have been found to result in lower treatment times as compared with any of the individual techniques used (Khoufi et al. 2006), although cost and energy efficiency of these processes will be dependent on the operating conditions and the type of effluent.

Treatment of organic materials found in OMW with iron catalyzed hydrogen peroxide (Fenton’s reaction) has been suggested to increase the noninhibitory material available for use in biodegradation processes (Vlyssides et al. 2003). This approach has potential to increase the oxidation mean of the waste, making the biodegradation process more efficient. Fenton’s oxidation is a complicated system that involves a large number of reactions, including redox reactions, complexation, and precipitation equilibrium. In Fenton’s reaction, the ferrous and/or ferric cation catalyzes use of hydrogen peroxide as an oxidizing agent capable of degrading many organic and inorganic substances. However, there is uncertainty in the nature of oxidizing species generated during this process (formation of radical species or generation of aquo- or organo-complexes of high valence iron) (Rivas et al. 2003). Use of Fenton’s oxidation for the detoxification of OMW has been tested by Vlyssides et al. (2003). They showed that when Fenton’s reaction was applied to the degradation of OMW, it resulted in a significant reduction in total phenolic compounds. They reported that this method seems to be feasible when it is followed by conventional biological treatment of the Fenton reaction products.

Generally, chemical treatment and oxidation technologies may be used either for a complete mineralization of all pollutants to carbon dioxide, water, and mineral salts, or for partial removal of certain target pollutants and their conversion to intermediate degradation products. In general, a chemical oxidation method aimed at complete mineralization could be extremely costly (Mantzavinos and Psillakis 2004). A potentially attractive alternative to complete oxidation through chemical means is the use of a chemical oxidation pretreatment step to convert initially biorecalcitrant organics to more readily biodegradable intermediates, followed by biological oxidation of these intermediates to biogas, biomass, and water (Rizzo et al. 2008). The standard five-day biochemical oxygen demand (BOD₅) test has been commonly employed as a measure of aerobic biodegradability. Changes in biodegradability are assessed by measuring COD/BOD₅ ratios through comparison of the values of the treated samples with those of the original effluents (Khoufi et al. 2006). Vlyssides et al. (2003) identified the COD/BOD₅ ratio as a toxicity indicator, where a COD/BOD₅ ratio in OMW greater than 3.1 indicated a strong inhibition for biological treatment.

Although chemical oxidation has, indeed, received some attention for OMW treatment, it is notable that there is a lack of information concerning the use of cost effective and locally available chemical treatment for OMW pretreatment. In Jordan, the use of chemical oxidation of OMW has been traced over the last ten years in an attempt to show some degree of wastewater treatment before disposal. These methods lack the scientific and theoretical proof needed for proper implementation of the method. Therefore the aim of this work was to assess the potential for use of chemical treatment/oxidation of OMW using different chemicals: i.e., permanganate, lime, hypochlorite, and Fenton’s reagent. This investigation aimed at identifying the chemical concentrations and contact times needed to optimize treatment of OMW. The work also aimed to investigate the bioavailability of OMW subjected to chemical oxidation based on the measured COD/BOD₅ ratios. This research also will help to identify a suitable biological treatment system for use in the chemical pretreatment unit processes.

Methodology

Olive Mill Wastewater (OMW)

The OMW used in this study was taken from a three-phase olive mill processing plant located at Al-Sat city in Jordan during the harvesting season of 2007/2008. Effluent samples were stored in 1,000-mL glass bottles in a refrigerator at 4ºC until tested. Raw OMW samples were analyzed for major constituents according to the Standard Methods for the Examination of Water and Wastewater (APHA et al. 2005). The main characteristics of the OMW used in these studies are given in Table 1. The water quality parameters in Table 1 indicate clearly that the OMW used in this investigation is a moderately strong OMW compared with other similar wastewaters (Benitez et al. 1999; Gomes et al. 2007).

Treatment of OMW with Permanganate, Lime, and Hypochlorite

Chemical treatment/oxidation tests were carried out in a batch system using glass beakers with a working volume of 200 mL. Tests were done at room temperature with a mixing speed of 100 rpm to ensure similar conditions in all runs. In addition, all tests were performed without any pH adjustment: i.e., at pH 4 to 5. Because the addition of chemical agents to the mixture produced a change in the solution pH, the use of additional chemicals for pH adjustment would not be representative of field conditions. For tests using permanganate, lime, and hypochlorite, concentrations of the applied chemicals
Treatment of Olive Mill Wastewater

TABLE 1. Average characteristics of OMW

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Average value</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>SU</td>
<td>4–5</td>
<td>0.2</td>
</tr>
<tr>
<td>Chemical oxygen demand, COD</td>
<td>mg/L</td>
<td>89,250</td>
<td>5,355</td>
</tr>
<tr>
<td>Biochemical oxygen demand, BOD₃</td>
<td>mg/L</td>
<td>23,200</td>
<td>1,166</td>
</tr>
<tr>
<td>Fat, oil, and grease, FOG</td>
<td>mg/L</td>
<td>5,720</td>
<td>360</td>
</tr>
<tr>
<td>Total dissolved solids, TDS</td>
<td>mg/L</td>
<td>11,395</td>
<td>433</td>
</tr>
<tr>
<td>Total suspended solids, TSS</td>
<td>mg/L</td>
<td>9,460</td>
<td>274</td>
</tr>
<tr>
<td>Total volatile suspended solids, TVSS</td>
<td>mg/L</td>
<td>4,810</td>
<td>168</td>
</tr>
<tr>
<td>Total fixed suspended solids, TFSS</td>
<td>mg/L</td>
<td>980</td>
<td>67</td>
</tr>
<tr>
<td>Total kjeldahl nitrogen, TKJ-N</td>
<td>mg/L</td>
<td>680</td>
<td>56</td>
</tr>
<tr>
<td>Total phosphorous, T-P</td>
<td>mg/L</td>
<td>230</td>
<td>14</td>
</tr>
<tr>
<td>Turbidity</td>
<td>NTU</td>
<td>1,840</td>
<td>158</td>
</tr>
<tr>
<td>Phenol</td>
<td>mg/L</td>
<td>2,645</td>
<td>204</td>
</tr>
</tbody>
</table>

were calculated based on the COD:chemical (wt/wt) ratio. For each chemical treatment, tests were carried out in two parts. In the first part, different concentration ratios were tested using a 10 minute contact time. An optimum concentration ratio was then determined, and in the second set of experiments different contact times for the optimum concentration ratio were used (Table 2). At the end of each experiment, COD and BOD₃ tests were performed according to the Standard Methods for the Examination of Water and Wastewater (APHA et al. 2005). Each experiment was repeated five times with the results presented as mean values for five trials.

Treatement of OMW with Fenton’s Reagent

Oxidation of OMW was tested using Fenton’s reaction, where iron (Fe²⁺) in the form of FeSO₄·7H₂O (GR for Analysis, MERCK) plus 30% (vol/vol) extra pure stabilized hydrogen peroxide (H₂O₂) solution (Riedel-de Haen) were added to each sample. Three different ratios of H₂O₂ and Fe²⁺ were tested: i.e., 5:1, 10:1, and 15:1. Chemical oxidation tests were carried out at different COD:Fe ratios (wt/wt) as shown in Table 3. All tests were carried out at room temperature with a 10 minute contact time. At the end of each experiment, COD and BOD₃ tests were performed according to Standard Methods for the Examination of Water and Wastewater (APHA et al. 2005). Each experiment was repeated five times with the results presented as the mean of five trials.

Bioavailability Test

As previously mentioned, the COD/BOD₃ ratios provided a bioavailability index for the wastewater in question (Vlyssides et al. 2003). COD/BOD₃ ratios, for a raw OMW sample as well as for chemically treated samples, were calculated. The lower the ratio, the more enhanced bioavailability is achieved, indicating less inhibition for further biological treatment.

Results

An optimum COD:chemical (wt/vol) concentration for each of the chemical oxidizing agents (i.e., permanganate, lime, and hypochlorite) was identified using a 10 minute contact time (Fig. 1, 2, 3). The error bars indicate the corresponding standard deviations. OMW samples oxidized with permanganate at different concentration ratios with a 10 minute contact time did not exhibit an optimum concentration ratio (COD: permanganate) (Fig. 1). Although the amount of permanganate added by a concentration ratio of 10:1 went far beyond twice the permanganate amount added by a concentration ratio of 25:1, the difference in COD removal was found not to exceed 5%. Therefore, a concentration ratio of 25:1 was taken as the optimum concentration ratio where 78% of the COD had been oxidized and removed from the sample. This concentration ratio was kept fixed during the second part of the experiment where the oxidation tests were carried out at different contact times (Fig. 4). The optimum contact time achieved occurred in 25 minutes where 90% of the COD was oxidized and removed. The standard deviations indicated by the error bars in Fig. 1 and Fig. 4 show clearly the significant effect of concentration ratio and contact time on OMW treatment. These results agreed to a greater extent with those achieved by studying the oxidation effect of permanganate on some other highly contaminated wastewater (Costin et al. 2003).
The optimum concentration ratio for lime was found to be 7:1 at a 10 minute contact time (Fig. 2). At this optimum contact time, 87% of the COD was removed. There was no detected optimum contact time in the second part of the test (Fig. 5). COD removal was found to remain unchanged over all contact times tested. However, the lowest contact time in this run was 5 minutes, which can be practically used as an optimum contact time in the field. The results show relatively high standard deviations as indicated by the error bars. This can be attributed to the vacillating potential of lime in chemical treatment of OMW and production of precipitate, which is greatly dependent on mixing intensity and filtration processes (Aktas et al. 2001).

The optimum concentration ratio for sodium hypochlorite was 200:1, where 66% of the COD was removed (Fig. 3). A decrease in COD removal at higher concentration ratios can be attributed to the formation of chloramines as a result of high concentrations of nitrate in the OMW. The second part of the test showed that the optimum contact time was 30 minutes with 80% COD removal (Fig. 6). This rate of hypochlorite oxidation was found to be much higher than the oxidation rate reported by Tezcan et al. (2008), who reported that 80% of COD removal was achieved at a contact time of 120 minutes.

Oxidation tests using Fenton’s reagent were conducted at different concentration ratios (COD:Fe) using a 10 minute contact time. All tests were carried out at the normal pH level for the OMW (4 to 5) which has been reported to be the optimum pH value for Fenton’s reagent (Khoufi et al. 2006). The concentration ratio was a determining factor in Fenton’s oxidation (Fig. 7). The lower the concentration ratio was observed to be, the higher the oxidation power and COD removal efficiency. It was also noted that a \( \text{H}_2\text{O}_2:\text{Fe}^{2+} \) ratio of 10:1 produced a maximum oxidation potential at all COD concentrations examined. Maximum COD removal was achieved at a concentration ratio of 50:1 and an \( \text{H}_2\text{O}_2:\text{Fe}^{2+} \) ratio of 10:1. At this optimum point, 93.3% removal of COD was achieved. The standard deviations indicated by the error bars show the significant effect of chemical concentration ratios on OMW treatment. The high COD removal efficiency using Fenton’s reagent over relatively short contact times suggests that this method has significant potential for decontamination of agro-industrial wastewater.

Calculated COD/BOD\textsubscript{5} ratios of treated and untreated OMW samples were used to assess the bioavailability of the end products for use in further biological treatments following chemical treatment with permanganate, lime, and hypochlorite (Fig. 8). The results show that addition of permanganate resulted in a decrease in the COD/BOD\textsubscript{5} ratio from 3.65 to 2.15. This implies an increase in bioavailability by more than 40%. The other tests produced a lesser effect of the chemical treatment on bioavailability of OMW, where the COD/BOD\textsubscript{5} ratios decreased from 3.7 to 3.6 and from 3.7 to 3.2 using lime and hypochlorite, respectively. These
results indicate that chemical treatment can be used as an efficient means for detoxification of OMW. In addition, conventional biological treatment of OMW could be significantly enhanced by implementing a chemical pretreatment process.

Enhanced bioavailability of readily oxidized OMW with Fenton’s reaction was also tested. The calculated COD/BOD$_5$ ratios for Fenton’s reaction increased the bioavailability of OMW for all H$_2$O$_2$ concentrations at the different applied COD:Fe$^{2+}$ ratio of 10:1 exhibited the highest effect on bioavailability enhancement at all concentration ratios. The lowest COD/BOD$_5$ ratio of 1.85 was achieved at a H$_2$O$_2$:Fe$^{2+}$ ratio of 10:1 and a concentration ratio of 50:1, which resulted in a total COD/BOD$_5$ ratio reduction of more than 50%. At lower iron concentrations, no significant differences in COD/BOD$_5$ ratios at different H$_2$O$_2$ concentrations were noticed. The low values of COD/BOD$_5$ ratios achieved in this investigation show high potential for use of chemical treatments, especially Fenton’s reaction, in solving the intricate and acute problem of wastewater discharges from agro-industrial olive mill processing plants.

Based on the current market prices of the chemicals used in this investigation and the amount of each chemical required to achieve about 80% COD removal, permanganate was found to be the cheapest among all chemicals used. Fenton reagent exhibits the highest cost due to the use of the relatively expensive oxidizing agent of hydrogen peroxide.

**Conclusion**

Chemical treatment has been proven to be an effective means of reducing the carbonaceous content of OMW. The high oxidation potential of permanganate and Fenton’s reagent resulted in enhancement of the bioavailability of readily oxidized OMW, so that chemical treatment/oxidation is highly recommended as a pretreatment unit process before use of conventional biological treatment.
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References


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