The combination of coagulation, acid cracking and Fenton-like processes for olive oil mill wastewater treatment: phytotoxicity reduction and biodegradability augmentation

Ahmadreza Yazdanbakhsh, Fayyaz Mehdipour, Akbar Eslami, Hajar Sharifi Maleksari and Farshid Ghanbari

ABSTRACT

Olive oil mill wastewater (OOMW) is one of the most important industrial wastewaters in the world due to high organic load and phenolic compounds. In this study, an integration of three processes including coagulation, acid cracking and Fenton-like was evaluated to treat OOMW. The performance of alum, ferric chloride and polyaluminum chloride was studied as coagulants. Among coagulants, ferric chloride showed the best results in comparison with the others. Coagulation process with FeCl₃ removed 91.2% chemical oxygen demand (COD), 91.3% phenol, 98.9% total suspended solids and 99.2% turbidity at condition of pH = 6 and 3,000 mg/L coagulant dosage. Acid cracking process following the coagulation process with ferric chloride could slightly degrade organic compounds and provided suitable condition for the next process. Fenton-like process with zero valent iron (ZVI) was applied after coagulation and acid cracking. The optimal removal efficiency was achieved by Fenton-like process which was accomplished in condition of 7 g/L ZVI, 1,000 mg/L H₂O₂ and 180 min reaction time. The biodegradability of final effluent of this integration was improved significantly and biochemical oxygen demand₅/COD value increased from 0.14 to 0.83. The results of germination tests revealed that phytotoxicity of the final effluent decreased.

Key words | biodegradability augmentation, integrated chemical processes, olive oil mill wastewater, phenol, phytotoxicity

INTRODUCTION

One of the biggest problems among environmental issues is discharge of untreated wastewater to water bodies. This problem is increasingly hazardous where sources of wastewater are from industries with huge productions. Among industries, olive oil industry is environmentally important since its produced wastewater is very toxic with high organic load. The olive oil mill wastewater (OOMW) volume is around 1 cubic meter per one ton of olives (Ahmadi et al. 2005; Barbera et al. 2013). OOMW is characterized by high chemical oxygen demand (COD), high total suspended solids (TSS), turbidity, dark color and high concentration of various phenolic compounds (Michael et al. 2014; Oz & Uzun 2015). Owing to the presence of phenolic compounds, OOMW is too non-biodegradable to be treated through the biological processes (Hanafi et al. 2011). Thus, increase of interest toward chemical processes for destruction of toxic compounds to harmless ones is justified. Integrated treatment processes have usually been used for high-strength wastewaters such as landfill leachate (Moradi & Ghanbari 2014), OOMW (Kyriacou et al. 2005; Kiril Mert et al. 2010), etc. Coagulation process is an effective conventional method for the removal of TSS and organic pollutants of wastewater which can be used as a pretreatment for further processes. In coagulation process, solid particles and some organic compounds are agglomerated by coagulants and then are flocculated and finally settled. Coagulation process alone cannot sufficiently remove all organic compounds and its efficiency is not high in removing soluble organic compounds. Accordingly,
coagulation process can be a pretreatment for high-strength wastewater with high TSS (Moradi & Ghanbari 2014).

Advanced oxidation processes (AOPs) are promising techniques which are used for degradation of various soluble organic pollutants. These processes are based on in situ generation of hydroxyl radical (OH) as a powerful oxidant (Pignatello et al. 2006). Hydroxyl radicals with E° = 2.8 V/NHE (natural hydrogen electrode) are inordinately reactive species attacking most organic compounds converting them to smaller molecules or mineral compounds (Eslami et al. 2013; Babuponnusami & Muthukumar 2014). Fenton oxidation is the most common process in AOPs in which hydrogen peroxide is decomposed by transitional metals (Fe, Cu, Co, etc.) thereby producing hydroxyl radicals (Equation (1)) (Bokare & Choi 2014; Syafalni et al. 2014).

\[
H_2O_2 + M^{n+} \rightarrow HO^* + M^{(n+1)+} + OH^- \tag{1}
\]

Iron is an environmentally benign metal which has been used in form of ferrous ion for catalytic decomposition of hydrogen peroxide to produce hydroxyl radical. Zero valent iron (ZVI) has been alternatively used as a source of ferrous ion in Fenton's reagent. The use of ZVI in Fenton-like reagent has a particular advantage in comparison with iron salts which is no need of adding counter anion (Cl-, SO4^2-, etc.) to the effluent (Lücking et al. 1998). Moreover, ZVI is a cost-effective catalyst for activation of hydrogen peroxide that has been successfully applied in Fenton-based processes. ZVI usually produces ferrous ions through Equations (2)–(4) (Özdemir et al. 2010; Ghanbari et al. 2014; Yin et al. 2014).

\[
Fe^0 \rightarrow H^+ + Fe^{2+} + 2e^- \tag{2}
\]

\[
Fe^0 + H_2O_2 + 2H^+ \rightarrow Fe^{2+} + 2H_2O \tag{3}
\]

\[
Fe^0 + 2Fe^{3+} \rightarrow 3Fe^{2+} \tag{4}
\]

Combinations of coagulation and AOPs have been frequently studied to treat high-strength wastewater such as landfill leachate and olive oil wastewater. Kestioglu et al. (2005) and Kiril Mert et al. (2010) have studied physicochemical processes along with AOPs for OOMW treatment. They have used sequential processes of acid cracking, coagulation and AOPs for OOMW treatment (Kestioglu et al. 2005; Kiril Mert et al. 2010). According to their study, we decided to use coagulation process first, to remove suspended solids and then use acid cracking process for destroying some organic compounds and also acidifying the solution for the next process which is the Fenton process. The latter process has the highest efficiency in acidic condition. In this study, effect of each process on removal efficiencies of phenol and COD was evaluated and biodegradability improvement was also assessed by means of 5-day biochemical oxygen demand (BOD5/COD ratio as a conventional biodegradability index. Finally, phytotoxicity of the effluents was assessed using germination index (GI).

### MATERIALS AND METHODS

#### Wastewater sampling

The OOMW used in this study was collected from Gilvan Zeyton Company which is located in Zanjan province (Tehran, Iran). The collected samples were kept in a polyethylene container in refrigerator at 4°C. Total volume of collected OOMW was 60 L. Some characteristics of OOMW are given in Table 1.

#### Materials and reagents

Ferric chloride (FeCl₃), aluminum sulfate (Al₂(SO₄)₃.18H₂O), sodium hydroxide, ZVI, sulfuric acid (98%), hydrogen peroxide (30%) were purchased from Merck Company. All reagents used in COD test were from Sigma-Aldrich Company. Polyaluminum chloride (PAC) was commercially purchased from Taha Chemical Company (Tehran, Iran) with purity of 25%. Potassium ferricyanide and 4-aminoantipyrine were purchased from Fisher Chemical and ACROS Organic, respectively.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unit</th>
<th>Values</th>
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</thead>
<tbody>
<tr>
<td>COD</td>
<td>mg/L</td>
<td>58,800</td>
</tr>
<tr>
<td>Phenol</td>
<td>mg/L</td>
<td>444</td>
</tr>
<tr>
<td>BOD₅</td>
<td>mg/L</td>
<td>8,250</td>
</tr>
<tr>
<td>TSS</td>
<td>mg/L</td>
<td>28,477</td>
</tr>
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<td>Turbidity</td>
<td>NTU</td>
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<tr>
<td>Chloride</td>
<td>mg/L</td>
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</tr>
<tr>
<td>pH</td>
<td>–</td>
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<tr>
<td>EC</td>
<td>mS/cm</td>
<td>10.23</td>
</tr>
<tr>
<td>Total dissolved solids</td>
<td>mg/L</td>
<td>5,100</td>
</tr>
</tbody>
</table>

Table 1 | Characteristics of the raw OOMW. EC – electrical conductivity
Experimental procedures

Coagulation experiments

Three conventional coagulants were used in this study including ferric chloride, alum and PAC. The coagulation process was carried out by a standard Jar test (Phipps and Bird) with impellers equipped with 2.5 × 6 cm rectangular blades inserting into six beakers (800 mL). 400 mL of raw OOMW was poured in each jar. After adjusting pH, specific amounts of coagulant (FeCl₃, Al₂(SO₄)₃·18H₂O and PAC) were added to sample. The OOMW was mixed for 60 s in rapid mix stage at 120 rpm, 20 min in slow mix stage at 40 rpm and it was allowed to settle for 1 h in sedimentation stage. A 20 mL supernatant was carefully taken from 2 cm below the top of the liquid level for analysis of parameters. The best coagulant was selected based on its performance in removing COD, phenol, TSS and turbidity. The pH range of each coagulant in Jar test was chosen on the basis of previous studies and literatures while ranges of their dosages were determined based on the primary experiments.

Acid cracking experiments

Acid cracking was performed on effluent of coagulation process. Acid cracking process was also carried out by Jar test in 6 beakers. The concentrate sulfuric acid was used to adjust pH in range of 1.5–4. After adjustment of pH, samples were mixed for 2 h at 200 rpm to crack some organic compounds. 30 min sedimentation was considered after mixing stage.

Fenton-like experiments

The effluent obtained from coagulation and acid cracking stages entered the Fenton-like reactor. Fenton-like process was conducted by different ZVI dosage and H₂O₂ concentrations in 500 mL beakers under Jar test instrument. First, a specified ZVI dosage in range of 1–11 g/L was added. The Fenton process was started by adding H₂O₂ solution to beaker for generation of hydroxyl radical. At the same time, the impellers were turned on at 200 rpm in the first 5 min and then 80 rpm for the rest of the reactions. At end of reaction time, solution pH was increased to 9 by 6 N NaOH for precipitation of ferric hydroxide and then the supernatant was withdrawn for analyses. To remove hydrogen peroxide residuals, sodium thiosulfate was used.

Phytotoxicity test

GI was used as a phytotoxicity test for toxicity evaluation of effluents obtained in each stage. Four species of plants were selected for GI including tomato (Lycopersicum esculentum), radish (Raphanus sativus), lettuce (Lactuca sativa) and cress (Lepidium sativum). The tests were carried out with 30 seeds placed in a Petri dish containing a Whatman filter paper. In each Petri dish, 10 mL sample was poured from each stage of treatment and then incubated for 72 h at 26 °C. Control tests were conducted by distilled water. The GI was determined by Equation (5). All tests were repeated three times and mean values are reported as results. Root length was measured by a simple ruler (Tiquia et al. 1996).

\[
GI(\%) = \frac{G_s \times L_s}{G_c \times L_c} \times 100
\]

where \(G_s\) is the number of germinated seeds in effluent, \(G_c\) is the number of germinated seeds in control test, \(L_s\) is root length in sample and \(L_c\) is root length in control test.

Analytical methods

All measurements of pH were carried out using pH meter (WTW 720) which was calibrated with pH 4.0 and pH 7.0 standard buffers. TSS and settleable solids were analyzed based on Standard Methods (APHA 1999). Electrical conductivity (EC) was measured by EC meter (Hach-Company). COD values were determined by open reflux method with potassium dichromate as oxidant. Phenol was measured by a spectrophotometer (Hach DR5000) based on colorimetric method at 500 nm according to reaction of phenol compounds with 4-aminoantipyrine. Chloride and sulfate ions were measured by Mohr and turbidimetric methods, respectively. BOD₅ values were assessed by determining oxygen consumption (respirometric method) using a WTW InoLab after 5 days of incubation of a micro-organism culture obtained from activated sludge (APHA 1999). Turbidimeter (Hach, 2100N) was used to measure turbidity of OOMW.

RESULTS AND DISCUSSION

The performance of three coagulants

Selection of coagulant in coagulation process is the most important factor. Three coagulants (alum, FeCl₃ and PAC)
were studied on OOMW treatment. Effects of pH and dose of each coagulant on COD, phenol, turbidity and TSS removals were evaluated. Figure 1(a) shows effect of pH on alum performance in OOMW treatment at constant dose of 2,000 mg/L. As can be seen, with increasing pH, gradual increase was observed in removal of phenol, COD and turbidity. At pH of 10, COD, phenol, TSS and turbidity removals were at the highest levels. Effects of alum dosages on treatment of OOMW at initial pH of 10 are shown in Figure 1(b). As shown in this figure, TSS and turbidity were almost completely removed in all doses of alum. The COD and phenol removal efficiencies increased when coagulant dose was increased from 1,000 to 2,000 mg/L. In alum concentrations exceeding 2,000 mg/L, COD and phenol removal trends reached a plateau depicting that further addition of coagulant did not influence removal of organic compounds. At pH 10 and 2,000 mg/L alum as the best conditions, COD, phenol, TSS and turbidity removal efficiencies were 88, 88.7, 98.3 and 99%, respectively.

Figure 1(c) shows effect of pH on removal efficiencies of various pollutants at fixed dose of 2,000 mg/L. As displayed in Figure 1(c), the highest efficiency occurred at pH = 6. It can be observed that the trend of TSS removal efficiency is similar to that of the turbidity, presenting that these
parameters are significantly correlative. Figure 1(d) displays effect of FeCl₃ dose on OOMW treatment at fixed pH of 6. As illustrated in Figure 1(d), increase in coagulant dose from 1,000 to 3,000 mg/L enhances performance of coagulation especially in case of phenol removal while further addition of coagulant dose between 4,000 and 6,000 mg/L does not markedly influence organic pollutants and TSS removals. Therefore, 3,000 mg/L FeCl₃ is selected as the optimum dose. Under optimum condition (pH = 6 and 3,000 mg/L FeCl₃), COD, phenol, TSS and turbidity removal efficiencies were 91.2, 91.3, 98.9 and 99.2%, respectively.

Figure 1(e) and 1(f) show effects of pH and PAC dose on OOMW treatment, respectively. As can be clearly seen, pH = 7 has the best efficiency in phenol and COD removals. A wide range of pH (7 ≤) was the optimal pH for PAC. In Figure 1(f), increase in PAC dose slightly improves COD and phenol removal efficiencies in a way that in 1,500 mg/L PAC, enhancement of removal efficiency is not observed. Hence, PAC dose of 1,250 mg/L is the optimum condition for treatment of OOMW. In conditions of pH = 7 and dose of 1,250 mg/L, COD, phenol, TSS and turbidity removal efficiencies were 87.3, 89, 99.1 and 99.4%, respectively.

Regarding the obtained results for the three coagulants, FeCl₃ showed better performance in comparison with the other two coagulants. It should be noted that the cost of FeCl₃ in Iran’s market is 5 and 10 times less than the costs of alum and PAC, respectively. Therefore, not only FeCl₃ is more effective for agglomeration of suspended solids, but also it is economically superior. Besides, ferric chloride has less human health risks than the aluminum-based coagulants in an overdose condition (Liu et al. 2012; Moradi & Ghanbari 2014). Furthermore, results of settleable solids test showed that FeCl₃ had the lowest value (516 mL/L) compared to alum (583 mL/L) and PAC (523 mL/L), which justifies selection of FeCl₃ as the superior coagulant. Subsequent experiments were carried out on the effluent coagulated by FeCl₃.

**Acid cracking**

Acid cracking was carried out on coagulation effluent (coagulated by FeCl₃) using concentrate sulfuric acid under 2 h reaction time while pH of coagulated effluent was 4.6. The results of COD reduction are illustrated in Figure 2. As can be seen, with reduction of pH, COD removal increased. In this way, a small difference was there between COD removals (%) within pH values of 1.5–3 whereas after pH of 3, COD removal decreased. Moreover, the volume of acid consumption was considered to select the optimum condition. Regarding the volume of acid consumption and COD removal (%), pH = 3 was selected as the optimum condition. The solution pH after acid cracking with initial pH = 3 reached pH = 3.2. Hence, the next process (Fenton-like) was set up with initial pH of around 3.2. This pH value is very close to the ideal pH (2.8–3) of the Fenton process that is advantageous from pH adjustment point of view (Pignatello et al. 2006; Nidheesh et al. 2013).

**Fenton-like**

**Effect of hydrogen peroxide dosage**

In Fenton-based processes, determination of optimum H₂O₂ concentration is of principal importance in practical applications. The effect of H₂O₂ concentration on COD and phenol removals was evaluated at constant ZVI dosage of 5 g/L after 2 h reaction time and the results are given in Figure 3(a). As shown in Figure 3(a), phenol removal percentages were 54, 63.8, 76, 76.8, 79 and 80% for initial H₂O₂ concentrations of 250, 500, 1,000, 1,500, 2,000 and 3,000 mg/L, respectively. It is apparent that higher H₂O₂ concentration can produce more hydroxyl radical to destruct phenolic compounds of OOMW. Nevertheless, consecutive increase of H₂O₂ concentration led to slight increase of phenol removal percentages. This behavior is supposed to be due to consumption of ·OH by additional H₂O₂ and production of less reactive ·OOH consequently (Equation (6)) (Nidheesh et al. 2013). In this way, 1,000 mg/L H₂O₂ concentration was chosen as the optimal condition.

\[
\text{H}_2\text{O}_2 + \text{HO}^* \rightarrow \text{HO}_2^* + \text{H}_2\text{O}
\]
Effect of ZVI dosages

ZVI dosage is another essential factor in Fenton-like process that is the main source of ferrous ion for decomposition of hydrogen peroxide. The effects of ZVI dosage on COD and phenol removal percentages are depicted in Figure 3(b). The corresponding results are gained in experimental condition of 1,000 mg/L H₂O₂ concentration and 2 h reaction time. It was observed that phenol and COD removals were markedly influenced by ZVI dosages. Removal efficiency increased significantly with an increase in ZVI from 1 to 7 g/L. Supposedly, an increase in the amount of available iron species reacting with H₂O₂ leads to an increase in production of reactive radicals. A little difference was observed when ZVI dosage increased from 7 to 9 g/L that was related to overdose of ZVI and its dissolution producing more ferrous ions scavenging hydroxyl radicals (Equation (7)) (Babuponnusami & Muthukumar 2014). Therefore, the optimal conditions are 7 g/L ZVI dosage and 1,000 mg/L H₂O₂ concentration.

\[
\text{Fe}^{2+} + \text{OH}^* \rightarrow \text{Fe}^{3+} + \text{OH}^-
\]  

Effect of reaction time

The effect of reaction time on treatment of OOMW at optimum condition (7 g/L ZVI dosage and 1,000 mg/L H₂O₂ concentration) is demonstrated in Figure 3(c). It is displayed that removal efficiency reaches its maximum levels at 180 min in a way that COD and phenol removal efficiencies are 94 and 98%, respectively. After 180 min reaction time, removal efficiency trend did not remarkably change until 360 min. It is concluded that produced hydroxyl radicals are consumed by organic compounds during 180 min reaction time. Appearance of the final effluent was clear and relatively colorless. As a result, with regard to high efficiency of phenol removal, phenol compounds can be removed based on mechanisms of coagulation and oxidation in this study. Hydroxyl radical is well known for efficient degradation of phenolic compounds in Fenton-based processes. In this way, hydroxyl radical is added to the aromatic rings of phenolic compounds thereby producing organic radical species (phenyl or hydroxyl cyclohexadienyl radicals). In excess of HO’, these radical species can be converted to organic acids, ring opening products and even mineral compounds as the end products.

Biodegradability improvement

To evaluate biodegradability, BOD₅/COD ratio was used as index. Herein, BOD₅ and COD were measured before and after each process. BOD₅/COD ratio of higher than 0.4 is suitable for biological treatment processes (Saidi et al. 2015; Moradi & Ghanbari 2014). BOD₅/COD ratios in various conditions are shown in Figure 4. As shown in
Figure 4, low biodegradability of raw OOMW is defined by BOD$_5$/COD of 0.14. Coagulation process could remarkably increase BOD$_5$/COD value to more than 0.4 for all three coagulants indicating biodegradability improvement. Moreover, it can be stated that non-biodegradable compounds in the OOMW were in form of suspended and colloidal solids that were removed by coagulation process. After coagulation (using FeCl$_3$), acid cracking and Fenton-like processes, BOD$_5$/COD value increased to 0.84 which represented high biodegradability of the obtained effluent from integrated processes. This increase in BOD$_5$/COD value is attributed to production of smaller organic compounds resulting from oxidation of refractory organics by high concentration of hydroxyl radicals (Ghanbari & Moradi 2015). As a conclusion, combination of these processes significantly improved biodegradability of OOMW and provided condition for discharge of OOMW to municipal sewer.

**Phytotoxicity evaluation**

The results of GI (%) after each treatment in various dilutions are reported in Table 2. As can be seen, coagulated effluent by FeCl$_3$ coagulant is severely phytotoxic. Regarding the results, the phytotoxicity for lettuce was very high since at dilution ratio of 1:10, no seed was grown. This inhibitory effect of coagulated effluent on growth of seeds can be attributed to presence of dissolved phenolic compounds that are toxic for plants. Among seeds, radish was resistant to toxicity of coagulated effluent in ratios of 1:6, 1:8 and 1:10.

The final effluent of integrated processes including coagulation, acid cracking and Fenton-like processes revealed low toxicity for the plant species in a way that values of GI (%) were 40 ± 5.6, 44 ± 10.2, 89 ± 5.6 and 53 ± 9.9% for lettuce, cress, radish and tomato, respectively. These results revealed that application of Fenton-like process after coagulation and acid cracking processes considerably reduced the phytotoxicity. Therefore, final effluent can be considered in water reuse for the purpose of plant irrigation.

### CONCLUSION

The treatment and toxicity reduction of OOMW is an environmental concern being considered in many countries. In this study, an integrated process including coagulation, acid cracking and Fenton-like was evaluated. These processes performed effectively for the removal of dissolved and non-dissolved organic compounds. Among the studied
coagulants, ferric chloride was more efficient in comparison with alum and PAC. The combination of coagulation, acid cracking and Fenton-like processes brought about very efficient removal of phenol and COD. Moreover, these processes significantly improved biodegradability regarding BOD5/COD values which increased from 0.14 to 0.83 for processes significantly removal of phenol and COD. Furthermore, phytotoxicity with GI test was not reduced by coagulation process while the combination of coagulation, acid cracking and Fenton-like processes reduced phytotoxicity markedly. In spite of the fact that the integrated processes are effective in removals of COD, TSS and phenol, disposal and treatment of sludge produced in coagulation and Fenton-like processes must be considered as an environmental challenge. As a conclusion, the application of sequential chemical processes substantially decreased organic load and phytotoxicity and increased biodegradability of final effluent.

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