Effects Sequential Usage of Coagulations (Ferric Chloride or Alum) and Fenton's Solution or Biochar on Removal Phenolic Compounds and Organic Load from Olive Mill Wastewater

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Abstract

The chemical properties of the wastewater of 17 olive mills in the area between Al-Dafniyah into Qaraboli in the west of Libya were studied and chemical coagulants such as alum, ferric chloride, chemical oxidation, and biochar were used to remove the organic load and phenolic compounds from this water. The results showed that the wastewater of the olive mill is highly acidic with an average pH of 5.15 and its high content of solids reached 192 g/L, while the average of dissolved solids was 63.5 g/L and the organic solids were about 90% of the total solids and the average of chemical oxygen demand is 104.9 g O2/L, and the concentration of phenolic compounds is high and it was 1.86 g /L. In addition, the results showed that the usage of Ferric chloride as a coagulant gave higher removal percentage of phenolic compounds, dissolved solids, and chemical oxygen demand in comparison with Alum in the pH range of 6-9. The removal percentage was higher in alkaline pH, especially for phenolic compounds. Moreover, increasing the amount of the coagulant from 2 to 16 g/L enhanced the removal of phenolic compounds and chemical oxygen demand, while the removal efficiency of dissolved solids was weak, which required the use of chemical oxidation and adsorption on biochar to improve the efficiency of the removal. Although sequential treatments by coagulants and chemical oxidation by Fenton solution or biochar improved the percentage of removal in biochar treatments compared to chemical oxidation, the concentration of pollutants is still high for disposal, especially phenolic compounds. As a result of that, these methods need more studies to improve them. Langmuir and Freundlich’s models gave a good describing the adsorption of phenolic compounds on the surface of biochar. However, the adsorption capacity is low compared to the scientific literature, because this study uses raw olive mill wastewater with a high organic load, which causes competition between these substances on the adsorption sites or inhibits adsorption by depositing them on the surface of the biochar.

Keywords: Alum; Biochar, Olive mill wastewater; Phenolic compounds.

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1. Introduction

The olive trees are considered one of the most abundant and important trees in Libya, whether in terms of area, number and value of the annual output. These trees are an agricultural, strategic and sustainable option for the use of the land in dry and semi-arid zones. Moreover, olive oil production provides a material essential nutrient from the food basket and it is an important economy contribution. For example, Libya is the fifth Arabic country in olive tree agriculture by 7% of total Arabic country production and the total olive tree number is 7 million trees with 157.5 thousand tons in 2001 (Arabic organization for agriculture development, 2003). The olive cultivation and the olive oil extraction industry produce large quantities of solid and liquid wastes (Olive Mill Wastewater) (Khatib et al., 2009; and Shaheen & Abdel Karim, 2007). This liquid waste is produced due to the olive fruits contain water and the use of water for washing the olives fruits and for cleaning the equipment. The olive mill wastewater is a brown liquid, acidic and contains a high concentration of solid and liquid wastes (Olive Mill Wastewatet). It has a high organic content, higher chemical and biological oxygen demand and higher concentration of phenolic compounds as toxic substances for life (USEPA, 1979). These chemical properties with uncontrolled disposal in the environment is...
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considered as one of the serious environmental deterioration (Okasha and Ibrahim, 2010a; Khatib et al., 2009; Mavros et al., 2008; and Shaheen & Abdel Karim, 2007), which has become more serious with the large increases in the area planted with olives in Libya. Moreover, these large quantities of olive mill waste will be disposed of in a short period between October and December (Niaounakis & Halvadakis, 2004), and concentrated in specific geographical areas (Mantzavinos & Kalogerakis, 2005), most of which are located around olive mills, which leads to the occurrence of dangerous environmental problems affecting the chemical and biological properties and soil fertility. Rozzi and Malpei (1996) reported that each 1 m$^3$ of olive mill wastewater have negative effects on the environment equal 200-300 m$^3$ of domestic wastewater.

The negative effects of olive mill wastewater on the environment constituted a major pressure factor on the treatment of these pollutants. Therefore, the development appropriate treatment methods will mitigate its environmental impacts (Khatib et al., 2009). There are many methods and techniques can mitigate the negative effects of olive mill wastewater including physicochemical processes (sedimentation, adsorption, drying and evaporation basins), chemical oxidation processes and biological treatment. However, these techniques are facing many problems such as high cost of treatment, unsatisfactory results due to the high organic load of effluents, the presence of difficult biodegradable organic compounds, presence of phenolic compounds as toxic substances for life (Okasha and Ibrahim, 2010b, Khatib et al., 2009; and Mantzavinos & Kalogerakis, 2005), the short duration of production season and the wide geographical distribution (Mantzavinos & Kalogerakis, 2005).

The treatment of olive mill wastewater has received more attention over the past years and different technologies have been applied. These technologies depended on biological, oxidation and chemical operations which were proposed by various researchers (Okasha et al., 2012; Al-Meshragi et al., 2009; and Mavros et al., 2008). Agalias et al. (2007) and El-Shafey et al. (2005) used membrane separation, filtration, adsorption and coagulation process to remove high organic load and polyphenols in the olive mill wastewater. However, the treated effluent is unlikely to meet regulation of law, that can be attributed to the high organic matter load, COD value and phenolic compounds. Therefore, many of researcher applied a sequence of treatment methods to increase removal percentage (Mavros et al., 2008; and Ginos et al., 2006). The chemical oxygen demand of olive mill wastewater was reduced by 60% when the effluent was coagulated with iron to remove suspended solids and then the effluent was oxidized by Fenton solution (Ginos et al., 2006). In other studies, (Gomec et al., 2007), the olive mill wastewater was treated by flocculation with polyelectrolytes and Fenton oxidation which remove about 90% of the chemical oxygen demand. A similar technique, integrating acid cracking, coagulation with iron and advanced oxidation by ultraviolet (UV) irradiation in the presence hydrogen peroxide led to over 98% reduction in COD (Kestioglu et al., 2005). Due to the lack of appropriate techniques for treatment of the olive mill wastewater, Therefore, this work aims to identify the optimal conditions for removal of higher contamination load from the olive mill wastewater by sequential coagulation and adsorption on biochar or by sequential coagulation and chemical oxidation (Fenton’s reaction) at a laboratory-scale.
2. Materials and Methods

2.1. Material

The olive mill wastewater was collected from (17) olive mills in the area between Al-Dafniyah to Qaraboli in the west of Libya. The biochar used in this study was produced from wood chips in a fixed bed reactor by fast pyrolysis at a high temperature (800°C). The biochar was ground to a particle size <300 μm. Alum (Aluminum sulphate (Al₂(SO₄)₃.12H₂O) used in this study was bought from the local market in Zliten. Ferric chloride (FeCl₃.5H₂O) is obtained from the Environmental laboratory at the Faculty of Marine Resources, Alasmarya Islamic University. Alum solution and Ferric chloride (100 g/L) were prepared and used in the next research steps.

2.2. Analytical methods

Total suspended solids (TSS), total dissolved solids (TDS), total volatile suspended solids (TVSS), and total dissolved volatile Solids (TVDS) were measured by weight methods and volatile material was measured by weight after burning in a muffle furnace at 550 ºC according to standard methods (Clesceri et al., 1999). pH was measured using a pH meter Hanna (type Hi 8014 with glass electrode). Electrical conductivity (EC) was measured using a Conductivity Meter Jenway model 4520. Chemical oxygen demand (COD) was measured by the open reflux method according to Clesceri et al. (1999). Phenolic compounds were measured using 4-Aminoantipyrine reagent’s method according to Clesceri et al. (1999), and the blue colure was measured by Jenway UV-Vis spectrophotometer model 7305. Total phosphorous was measured by Jenway UV-Vis spectrophotometer model 7305 depending on the Ascorbic acid method according to Clesceri et al. (1999). The total nitrogen in the sample was digested by sulfuric acid and converted to ammonia which was measured using Nessler’s method according to Clesceri et al. (1999).

2.3. Effect of coagulants dosage

The effects of coagulants dosages on the removal percentage of phenolic compounds, COD, and TDS were investigated by batch method. Varied the dose of Alum or Ferric chloride from 2 to 16 g/L were added to 800 mL of the olive mills wastewater in beakers of 1.0 L capacity and were agitated at 200 rpm for 2 min then reduced to 30 rpm for 60 min. The sample was then left 30 min and as soon as separation was achieved, the supernatant was collected for analysis.

2.4. Effect of pH value

To investigate of the effects of pH on the removal efficiency of coagulants of phenolic compounds, COD and TDS were investigated by batch method. Varied pH values of 800 ml of the olive mills wastewater ranged from 6 to 9 and the pH of samples were 6, 7, 8, and 9, then 16 g/L of Alum or Ferric chloride was added in beakers of 1.0 L capacity at fixed pH of 7. The beakers were agitated at 200 rpm for 2 min and then reduced to 30 rpm for 60 min
hours. The sample was then left for 30 min and as soon as separation was achieved, the supernatant was collected for analysis to choose the best pH value for removal.

2.5. Biochar adsorption isotherms

To measure the adsorption isotherm, five 100 ml Erlenmeyer flasks were filled out with 50 ml of the treated olive mill wastewater (treated with 16 g/L of Alum or Ferric chloride at pH 8 and 9) and 0.0, 0.1, 0.2, 0.3, 0.4, and 0.5 g of biochar was added to each flask. Then the mixture was agitated at 150 rpm for 24 hours. The samples were centrifuged at 4,000 rpm for 10 min on a centrifuge. The supernatant was collected for analysis of the phenolic compound. The equilibrium phenolic compounds concentration was analyzed for each sample. The adsorption data were treated according to Langmuir and Freundlich models (Eqns. 1 and 2 respectively).

\[
\frac{1}{q_e} = \frac{1}{q_{max} K C_e} + \frac{1}{q_{max}} \quad \text{..... (1)}
\]

\[
q_e = C_f C_e^{n_f} \quad \text{..... (2)}
\]

where, \( C_e \) is the equilibrium phenolic compounds concentration in solution (mg/L), \( q_e \) the adsorbed value phenolic compounds at equilibrium concentration (mg/g), \( q_{max} \) is the maximum adsorption capacity (mg/g), \( K \) is the Langmuir binding constant which is related to the energy of adsorption (L/mg), \( C_f \) is the Freundlich relative constant (mg/g), and \( n_f \) is Freundlich equation constant.

2.6. The olive mill wastewater treatment

2.6.1. Coagulation treatment:

To identify the best removal percentage, two treatment sequences were applied to increase the removal percentage. The first step was coagulation with Alum or Ferric iron to remove suspended solids and then the effluent was oxidized by Fenton solution or treated with different biochar dosages and the scheme of treatment was illustrated in Figure (1).

2.6.2. Chemical oxidation:

To investigate the chemical oxidation, the Fenton solution consisting of 0.54 g of Ferric chloride and 3.0 mL hydrogen peroxide (concentration 12%) was added to 100 mL of the treated olive mill wastewater (treated with 16 g/L of Alum or Ferric chloride at pH 8 and 9). The mixture was agitated at 100 rpm for 1 min and then left for 24 hours. The supernatant was collected for analysis.
2.6.3. Biochar treatment:

To investigate the biochar amendments, 0.8 g of biochar was added to 100 mL of the treated olive mill wastewater (treated with 16 g/L of Alum or Ferric chloride at pH 8 and 9). The mixture was agitated at 100 rpm for 24 hours. The samples were filtered and the supernatant was collected for analysis.

3. Results and Discussions

3.1. The olive mill wastewater properties in study area

The average and range values for the olive mill wastewater samples properties obtained from 17 olive mills in the study area are illustrated in Table 1. The pH values of olive mill wastewater ranged between 4.52 to 5.74 with an average of 5.15. These results agree with the observations of Okasha et al. (2012), Al-Meshragi et al. (2009), Okasha and Ibrahim (2010a), Zouari (1998), Andreozzi (1998), Beccari et al. (1998), Ubay & Oztürk (1997), Borja et al. (1995), and Kissi et al. (2001) agreed that olive mill wastewater is acidic and pH is between 4-6. The acidity of the olive mill wastewater was attributed to the higher organic acids content in olive fruits and during crushing, these acids were released resulting in a low pH value. The electrical conductivity of the olive mill wastewater samples was higher and ranged between 8.90 to 36.70 mS/cm with an average of 14.77 mS/cm. The higher values and differences between the olive mill wastewater samples can be attributed to the higher salts content of groundwater used in the olive mills and the different salts content of groundwater between olive mills locations.

The TS of the olive mill wastewater samples was high with an average of 109.3 g/L organic solid representing about 90% of TS (with an average of 99.1 g/L) and total ash of 10.2 g/L as average (representing 10%), more than 60% of TS were TDS (with average 63.5 g/L) while TSS represents about 40% of TS (with average 45.8 g/L) (Table 1). The TS result of this study is agreed with the observations of Andreozzi (1998), moreover, the TSS of this study also agrees with Kissi et al. (2001) and Ubay & Oztürk’s (1997) observation.

![Figure 1. The sequential treatment scheme of olive mill wastewater](image-url)
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Table 1. Olive mill wastewater properties in the study area

<table>
<thead>
<tr>
<th>Properties</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimum</td>
</tr>
<tr>
<td>pH</td>
<td>4.52</td>
</tr>
<tr>
<td>Electrical conductivity (mS/cm)</td>
<td>8.90</td>
</tr>
<tr>
<td>Total solid (g/L)</td>
<td>43.16</td>
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<tr>
<td>Total dissolved solids (g/L)</td>
<td>24.30</td>
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<tr>
<td>Total suspension solid (g/L)</td>
<td>3.95</td>
</tr>
<tr>
<td>Total organic solid (g/L)</td>
<td>36.07</td>
</tr>
<tr>
<td>Total ash (g/L)</td>
<td>6.31</td>
</tr>
<tr>
<td>Chemical oxygen demand (COD) (g/L)</td>
<td>54.40</td>
</tr>
<tr>
<td>Phenols (mg/L)</td>
<td>480</td>
</tr>
<tr>
<td>Total phosphorus (mg/L)</td>
<td>28</td>
</tr>
<tr>
<td>Total nitrogen (g/L)</td>
<td>100</td>
</tr>
</tbody>
</table>

COD of olive mill wastewater was very high with an average of 104.9 g/L and this content in 17 olive mills ranged between 54.4 to 156.8 g/L. The crushing olive fruit release higher organic materials dissolved in wastewater, these organic materials consume a huge amount of chemical oxygen resulting in higher chemical oxygen demand. These results agree with the observations of Andreozzi (1998), Zouari (1998), and Hamdi (1993) who reported that the COD of olive mill wastewater ranged between 40 to 300 g O2/L.

The toxicity of phenols compound in the olive mill wastewater samples was very higher due to the higher content of phenols which riches 1860 mg/L as average and ranged between 480 to 5,980 mg/L. There were differences between olive mills in phenols compound values which could be attributed to differences in mill technology which used different amounts of water in processing. The old mills use a huge amount of water which diluted the phenols resulting in low values. These results agree with observations of Kissi et al. (2001), Andreozzi (1998), Beccari et al. (1998), and Hamdi (1993) who reported that the phenols compound of olive mill wastewater ranged between 300 to 17,000 mg/L.

The total phosphorus contents of olive mill wastewater ranged between 28 to 148 mg/L with an average of 75 mg/L. Moreover, the total nitrogen contents ranged between 100 to 3,180 mg/L with an average of 1,430 mg/L. The variety in total phosphorus and total nitrogen contents could be attributed to variations in types of olive fruit and land fertilization and services. There is a difference between our total phosphorus result and Zouari's (1998) and Ubay & Oztürk (1997) observation which ranged between 850 to 1,200 mg/L which can be attributed to differences in soil management and fertilization which did not get more attention in Libyan agriculture due to higher cost of fertilizer and use traditional farming methods. Many researchers in the Mediterranean Sea area support our total nitrogen results and their results reported that the total nitrogen concentration was 160 to 2,200 mg/L (Andreozzi, 1998; Zouari, 1998; Beccari et al., 1998; Ubay & Oztürk, 1997; Borja et al., 1995; and Hamdi, 1993), which in same range of our result.
3.2. The olive mill wastewater treatment

Treatment techniques such as coagulation, chemical oxidation and adsorption on biochar were used to investigate the removal percentage of COD, phenolic compounds and TDS in the olive mill wastewater. The characterization of the olive mill wastewater which used in treatments was illustrated in Table (2).

Table 2. The properties of olive mill wastewater before treated by different techniques

<table>
<thead>
<tr>
<th>Properties</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.39</td>
</tr>
<tr>
<td>Electrical conductivity (mS/cm)</td>
<td>0.99</td>
</tr>
<tr>
<td>Total solid (g/L)</td>
<td>151.4</td>
</tr>
<tr>
<td>Total dissolved solids (g/L)</td>
<td>17.1</td>
</tr>
<tr>
<td>Total suspension solid (g/L)</td>
<td>134.3</td>
</tr>
<tr>
<td>Total organic solid (g/L)</td>
<td>138.6</td>
</tr>
<tr>
<td>Total ash (g/L)</td>
<td>12.8</td>
</tr>
<tr>
<td>Chemical oxygen demand (COD) (g/L)</td>
<td>31.7</td>
</tr>
<tr>
<td>Phenol compounds (g/L)</td>
<td>1.73</td>
</tr>
</tbody>
</table>

3.2.1. Coagulation treatment:

3.2.1.1. Effect of coagulant dosage: The influences of varying the dosage of coagulant from 2 to 16 g/L for both Alum and Ferric chloride at fixed pH of 7 were illustrated in Fig. 1. It is evident that coagulant dosage significantly decreased the concentration of COD and phenolic compounds. Initially, the concentrations of these parameters in the olive mill wastewater were 31.7 g O₂/L and 1.73 g/L respectively and the COD concentrations were decreased to 5.1 and 3.9 g O₂/L in Alum and Ferric chloride treatments by 2 g/L respectively and reached the lowest COD concentrations in 16 g/L of Alum or Ferric chloride (Figs. 2 b & c). Moreover, the concentrations of phenolic compounds have similar behavior to COD. The influences of Ferric chloride on the removal of COD and phenolic compounds were higher in comparison with Alum. For example, the concentrations of phenolic compounds were decreased from 0.92 to 0.56 g/L as the dose of Alum increased from 2 to 16 g/L, whereas, in Ferric chloride treatment, the concentration of phenolic compound was decreased from 0.31 to 0.01 g/L as the dose of Ferric chloride increased from 2 to 16 g/L. The concentration of TDS was decreased from 151.7 g/L in the raw olive mill wastewater to 17.3 and 14.1 g/L in the treatment of 2 g/L Alum and Ferric chloride respectively, which agree with the results of Yazdanbakhsh et al. (2015) found that the removal of COD and organic load by Ferric chloride showed better performance in comparison with Alum coagulant. Increasing the coagulant dose from 4 to 16 have little effect on the concentration of TDS as illustrated in Fig. 2a. This could be attributed to the nature of organic compounds which could be difficult to release hydrogen ion and get a negative charger on their surface and/or to change treatment pH to acidity during treatment could inhibit coagulant. This result agrees with the observation of Yazdanbakhsh et al. (2015) reported that the COD and phenolic compounds removal percentages increased when coagulant dosage was increased from 1 to 2 mg/L, and further dosages of coagulant did not influence removal percentages.
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3.2.1.2. Effect of pH value: The influences of olive mill wastewater pH are an important parameter that controls the removed amounts of TDS, COD, and phenolic compounds. The influences of pH on the removal material were investigated by varying the pH of the olive mill wastewater 6 to 9 at a fixed dose of 16 g/L for Alum or Ferric chloride and the results are illustrated in Fig. 3. The concentration of TDS and COD were decreased as the pH increases to 6. The concentrations of TDS and COD were 151.7 g/L and 31.7 g O₂/L respectively in the raw olive mill wastewater which decreased to 17.7 g/L and 4.2 g O₂/L respectively in Alum treatment, whereas in Ferric chloride treatment, this concentration decreased to 22.5 g/L and 2.3 g O₂/L respectively. Moreover, the pH increases from 7 to 9 have slight effects on concentration of TDS and COD in Alum and Ferric chloride treatment.

Figure 2. Influence of coagulant dosage of Alum (■) or Ferric chloride (□) at pH=7 on a) TDS, b) COD, and c) phenolic compound concentration in olive mill wastewater.

Error bars: ± 1 standard deviation (SD, n=3).
This could be attributed to the nature of organic compounds which could be difficult to release hydrogen ions and get a negative charger on their surface and/or to change treatment pH to acidity during treatment could inhibit coagulant. The concentration of phenolic compounds was decreased significantly with an increase in pH value from 6 to 9 in both treatments. However, the decreases in Ferric chloride are bigger than in Alum treatment (Fig. 3c). The higher decreases in phenolic compounds are apparently due to the greater ability of phenolic compounds to release hydrogen ions from the hydroxide group and the negative charge was developed at the molecule. The negative charge serves as an active site and causes strong electrostatic attraction for phenolic compounds to Ferric or aluminum ions with the increase in pH, the negative charge was increased, therefore, the remover of the phenolic compounds increased. These results agree with the observations of Yazdanbakhsh et al.
(2015) who reported increases in the removal efficiency of phenolic compounds and COD with increasing pH value and achieved the highest removal at pH 10 and agree with the results of Dominguesa et al. (2021) who reported enhanced in the COD removal in the higher pH range between 9 and 12, due to the increase of negative charge on organic compounds with the pH increase that enhanced attraction to coagulant’s cations. Moreover, Ferric chloride showed better performance in comparison with Alum (Yazdanbakhsh et al., 2015).

3.2.1.3 Effect biochar dosage: The effect of biochar dosage on the removal percentage of phenolic compounds and TDS was illustrated in Fig. 4 which shows that the removal percentages were increased continuously with the increase of the biochar dosage. Moreover, it can be noted that the increases in the removal percentages of phenolic compounds were higher in comparison with increases in the removal percentages of TDS. For example, the removal percentage of phenolic compounds was enhanced from 34.1% to 67% with increasing of the biochar dosage from 0.1 to 0.4 g in olive mill wastewater treated with Ferric chloride at pH 8, whereas the removal percentages of TDS were slightly increased from 6.6 % to 12.4% with increasing of the biochar dosage from 0.1 to 0.4 g, in olive mill wastewater treated with Ferric chloride at pH 8.

![Graph](image_url)

**Figure 4.** Influence of biochar amendment on removal percentage of a) phenolic compounds and b) TDS for olive mill wastewater treated with 16 g/L Ferric chloride at pH=8 (○) or pH=9 (□), or olive mill wastewater treated with 16 g/L Alum at pH=8 (·) or pH=9 (□·).
The results illustrated in Fig. 4 show that the changing of coagulants types and/or pH value caused differences in the removal efficiency of biochar for both phenolic compounds and TDS solids. For example, the highest removal percentage of phenolic compounds was in the ferric chloride and pH 8. The removal percentage was 34.1% which increased to 67% with increasing the biochar dosage from 0.1 to 0.4 g. in olive mill wastewater treated with Ferric chloride at pH 8, whereas, in olive mill wastewater treated with Ferric chloride at pH 9, this percentage increased from 19.3 % to 50% with an increase in the biochar dosage. However, changing the target material for removal has a different pattern. The removal percentages of TDS were higher in Ferric chloride at pH 9 treatments in comparison with Ferric chloride at pH 8 treatments (Fig. 4b), the removal percentage was 4.9% which increased to 12.8 % with increasing of the biochar dosage from 0.1 to 0.4 g. in olive mill wastewater treated with Ferric chloride at pH 9, whereas in Ferric chloride at pH 8 treatments, this percentage increased from 6.6 to 12.4%. Alum treatments have different patterns in the removal of phenolic compounds and TDS. The removal percentage of phenolic compounds was higher in Alum treatment at pH 9 in comparison with pH 8, whereas the removal of TDS was higher in Alum treatment at pH 8 (Figs. 4 a & b).

Phenolic compounds are adsorbed to the surface of biochar by π-π interactions between the aromatic structure of the graphitic layers and aromatic rings of the phenol structure. Another mechanism was hydrogen bonding (Li et al., 2012), while hydrogen bonding was the main adsorption mechanism for other TDS. Due to the ability of phenolic compounds to interact π-π of the aromatic structure of the biochar and hydrogen bonds, the adsorption capacity of the phenolic compounds was higher than TDS which is only adsorbed by hydrogen bonds. Although the removal percentage of phenolic compounds was higher in comparison with the removal percentage of TDS, these percentages are still low. This seems to be related to competition between water and phenol compounds on adsorption sites. Adsorbed water molecules block the entry of organic molecules to significant parts of the surface; this effect is generally called ‘the solvent effect (Franz et al., 2000). Moreover, the surface oxygen groups, located at the edge of the graphite layers, remove electrons from the π-π electron system which creates positive charges in the graphite layer weakening the interaction between the π-electron of the phenol aromatic ring and π-electron of the graphite layer leading to reduce the phenols uptake (Coughlin and Ezra, 1968). Furthermore, the competition between organic molecules on adsorption sites could be extra reduced removal percentages.

3.2.2 Phenolic compounds Adsorption isotherms:

Phenolic compounds Adsorption isotherms of olive mill wastewater treated by Ferric chloride and Alum at pH 8 and 9 are described in Fig 5. The results show that the maximum adsorption capacity of phenolic compounds was higher in pH 8 treatments than in pH 9 treatments. For example, the maximum adsorption capacity was 0.8 mg/g and increased up to 2.0 mg/g when the initial phenolic compound concentration increased from 0.4 to 1.9 mg/L in olive mill wastewater treated by Alum at pH 8, while in olive mill wastewater treated by Alum at pH 9, this capacity was 0.4 mg/g and increased up to 1.5 mg/g when initial phenolic
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Compound concentration increased from 0.25 to 1.5 mg/L, (Figs. 5 c & d) and this capacity values have same patterns in olive mill wastewater treated by Ferric chloride. This behavior seems to be related to increasing competition between other organic compounds and phenol compounds on adsorption sites in pH 9 treatments due to the increased positive charge on organic compounds with increased pH from 8 to 9. Moreover, the maximum adsorption capacity of phenolic compounds was higher in Ferric chloride treatments in comparison with Alum treatments. The maximum adsorption capacity of phenolic compounds reached up to 3.5 and 1.0 mg/g in Ferric chloride treatments at pH 8 and 9 respectively. Whereas, these capacities were 2.0 and 0.91 mg/g in Alum treatments at pH 8 and 9 respectively. These differences could be attributed to the higher efficiency of Ferric chloride treatment in the removal of dissolved solids from olive mill wastewater that reduced competition between dissolved solids and the phenolic compounds which enhance phenolic compound adsorption.

Figure 5. Absorption isotherms of phenolic compounds on biochar from olive mill wastewater treated with 16 g/L Ferric chloride a) at pH=9 and b) at pH=8; or Alum c) at pH=9, and d) at pH=8. Error bars: ± 1 standard deviation (SD, n=3).
The effects of biochar on the Absorption of phenolic compounds from the olive mill wastewater treated with Alum and Ferric chloride at pH 8 and 9 are shown in Table (3). This result indicates the ability of biochar to absorb phenolic compounds was higher in the olive mill wastewater treated with Ferric chloride compared to that treated with Alum. Moreover, the olive mill wastewater treated with Ferric chloride or Alum at pH 8 was higher than wastewater treated with Ferric chloride or Alum at pH 9. For example, $q_{\text{max}}$ was 9.52 mg/g and the Freundlich relative constant was 5.14 mg/g in the olive mill wastewater treated with Ferric chloride at pH 8 these parameters decreased when pH rose up to 9 and $q_{\text{max}}$ become 3.33 mg/g and the Freundlich relative constant become 1.77 mg/g. The $q_{\text{max}}$ of the olive mill wastewater treated with Alum at pH 8 and 9 were 2.72 and 2.39 mg/g respectively and the Freundlich relative constant were 1.48 and 1.23 mg/g at pH 8 and pH 9 respectively (Table 3). Linear regressions ($R^2$ value) are frequently used to determine the best-fitting absorption parameters. The values of the correlation coefficients ($R^2$) illustrated in table 3 show that the adsorption of phenolic compounds on biochar is well described by the Langmuir and Freundlich models. However, the Freundlich isotherm better described the phenolic compounds adsorption in wastewater treated with Ferric chloride than the Langmuir isotherm, whereas in wastewater treated with Alum the Langmuir isotherm was better fitting the phenolic compounds adsorption in wastewater (Table 3).

Table 3. Langmuir and Freundlich adsorption isotherm parameters of biochar.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Langmuir parameters</th>
<th>Freundlich parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_{\text{max}}$ (mg/g)</td>
<td>$k$ (1/mg)</td>
</tr>
<tr>
<td>Olive mill wastewater treated with 16 g/L Ferric chloride at pH=8</td>
<td>9.52</td>
<td>0.96</td>
</tr>
<tr>
<td>Olive mill wastewater treated with 16 g/L Ferric chloride at pH=9</td>
<td>3.33</td>
<td>0.88</td>
</tr>
<tr>
<td>Olive mill wastewater treated with 16 g/L Alum at pH=8</td>
<td>2.72</td>
<td>1.3</td>
</tr>
<tr>
<td>Olive mill wastewater treated with 16 g/L Alum at pH=9</td>
<td>2.39</td>
<td>1.2</td>
</tr>
</tbody>
</table>

3.2.3. Sequential treatments with coagulants and chemical oxidation:

The sequential treatment with Ferric chloride followed by Fenton solution on removal percentages of TDS, COD, and phenolic compounds was higher in comparison with Alum and Fenton solution treatment, as shown in Fig.6. Removal percentage of TDS were 67.7 and 69.8 % in Ferric chloride and Fenton solution treatment at pH 8 and 9 respectively, while this percentage was 33.4 and 40.3 % % in Alum and Fenton solution treatment at pH 8 and 9 respectively. The removal percentage of COD had the same behavior.
Effects sequential usage of coagulat—ions (Ferric chloride or Alum) 

**Figure 6.** Influence of chemical oxidation (■) or without oxidation (□) on removal percentage of; a) TDS, b) COD, and c) phenolic compound concentration in olive mill wastewater treated with 16 g/L Alum or Ferric chloride at pH=8 or pH=9. Error bars: ± 1 standard deviation (SD, n=3).

However, this percentage increased to 68.9% at pH 9 in Alum and Fenton solution treatment which was less than in Ferric chloride and Fenton solution treatment. Moreover, it can be seen that removal percentages of phenolic compounds were higher which reached 94.9 and 87.3% in Ferric chloride and Fenton solution treatment at pH 8 and 9 respectively, while these percentages were 93.4 and 86.5% in Alum and Fenton solution treatment at pH 8 and 9 respectively, as is shown in Figs. (6 b & c). The removal percentage of COD in this study was higher than Dominguesa et al. (2021) result who reported the combination of coagulation and Fenton's solution were resulting in removing 45% of COD. The contribution of chemical oxidation in the removal percentage of TDS, COD, and phenolic compounds was slightly
lower in comparison with coagulants. For example, the removal percentage of total solids was 67.7 and 69.38 in ferric chloride and Fenton solution treatment at pH 8 and 9 respectively, while these percentages were 65.9 and 65.4 in ferric chloride treatment at pH 8 and 9 respectively. This behavior can be seen in the removal of COD and phenolic compounds as shown in Figs. (6 b & c). These results show that the differences in the removal percentage of phenolic compounds and TDS between chemical oxidation treatment and without chemical oxidation treatments at different pH values in ferric chloride and Fenton solution treatments were insignificant statistically, while in Alum and Fenton solution treatments at pH 8 were higher than the contribution of chemical oxidation in the removal percentage of TDS, COD, and phenolic compounds was slightly lower in comparison with coagulants. For example, the removal percentage of total solids was 67.7 and 69.38 in ferric chloride and Fenton solution treatment at pH 8 and 9 respectively, while these percentages were 65.9 and 65.4 in ferric chloride treatment at pH 8 and 9 respectively. This behavior can be seen in the removal of COD and phenolic compounds as shown in Figs. (6 b & c). These results show that the differences in the removal percentage of phenolic compounds and TDS between chemical oxidation treatment and without chemical oxidation treatments at different pH values in Ferric chloride and Fenton solution treatments were insignificant statistically, while in Alum and Fenton solution treatments at pH 8 were higher than treatments at pH 9, except phenolic compound which was insignificant statistically as it is shown in Fig. 4. These results disagree with the observations of Kallel et al. (2009) and Lucas & Peres (2009) who reported high removal efficiency after Fenton’s oxidation of OMW. The differences between this study and their results could be attributed to Fenton’s reagent being a highly pH sensitive process and the efficiency of Fenton reaction increases with the decreasing of pH and the optimal value of pH is in the range between 2 and 4 (Kallel et al., 2009; and Lucas & Peres, 2009).

3.2.4 Sequential treatments with coagulants and biochar amendment:

The effects of sequential treatments with coagulants followed by biochar amendment on the removal percentage of TDS, COD, and phenolic compounds are illustrated in Fig. 7. It can be seen that the removal percentage of TDS, COD and phenolic compounds in Ferric chloride and biochar treatment were higher in comparison with Alum and biochar treatment. For example, the removal percentages of total solids were 69.5 and 71.25 % in Ferric chloride and biochar amendment at pH 8 and 9 respectively, while these percentages were 44.46 and 44.01% % in Alum and biochar amendment at pH 8 and 9 respectively. Moreover, the removal percentage of COD and phenolic compounds had the same behavior, as shown in Figs (7 b & c). The removal percentage which was obtained in this study was lower than Mavros et al. (2008) results who reported that increasing activated carbon dosage increased COD removal consistently and reached values of 73% at 30 g/L and greater dosage of activated carbon had no effect on removal. These differences could be attributed to differences in the sorption capacity of activated carbon and biochar and the organic load of olive mill wastewater. The coagulants have a massive influence on the removal efficiencies of TDS, COD, and phenolic compounds more than biochar amendments.
Effects sequential usage of coagulants (Ferric chloride or Alum) ............

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Figure 7. Influence of biochar amendments (■) or without biochar amendment (□) on removal percentage of: a) TDS, b) COD, and c) phenolic compound concentration in olive mill wastewater treated with 16 g/l Alum or Ferric chloride at pH=8 or pH=9. Error bars: ±1 standard deviation (SD, n=3).

For example, removal percentages of COD were 77.9 and 78.4 in Ferric chloride and biochar amendment at pH 8 and 9 respectively, while these percentages were 74.5 and 73.2 in Ferric chloride treatment at pH 8 and 9 respectively. This behavior can be seen in the removal of TDS and phenolic compounds as shown in Figs. (7 a & c). Moreover, the results showed that the effect of different pH values (8 or 9) on the removal percentage of TDS, COD, and phenolic compounds is insignificant in all treatments. The removal percentage of COD which was obtained in this study was lower than Mavros et al. (2008) results who reported that Alum reduced COD by 30%. However, the removal percentage increased to 80% when coagulation was coupled with adsorption at 25 g/L activated carbon. These differences could
be attributed to differences in the sorption capacity of activated carbon and biochar, the organic load of olive mill wastewater, and/or pH of treatments.

4. Conclusion

The chemical properties of the olive mill wastewater are highly acidic with an average pH of 5.15 and its high content of solids reached 192 g/L, while the average of TDS was 63.5 g/L and the organic solids were about 90% of the total solids and the average of COD is 104.9 g. O₂/L and the concentration of phenolic compounds is high it was 1.86 g/L. Despite, the use of a Ferric chloride coagulant removing higher amounts of phenolic compounds, TDS, and COD in comparison with Alum, the removal percentages of contaminated compounds do not meet disposal regulations that required more sequential removal treatments. The chemical oxidation by the Fenton solution and adsorption of biochar after coagulation were used to improve the removal efficiency. Biochar treatments remove more contaminated compounds compared to chemical oxidation. However, the concentration of contaminated compounds is still high for safe disposal, especially for phenolic compounds. Moreover, the results of this study are low compared to the scientific literature, because this study uses raw olive mill wastewater with high concentrations and organic load and we need more investigation to improve olive mill wastewater treatments.

References


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