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Version of record first published: 18 Nov 2011

To cite this article: Tamer Coskun, Fatih İlhan, Neslihan Manav Demir, Eyup Debik & Uğur Kurt (2012): Optimization of energy costs in the pretreatment of olive mill wastewaters by electrocoagulation, Environmental Technology, 33:7, 801-807

To link to this article: http://dx.doi.org/10.1080/09593330.2011.595829

Environmental Technology

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tent20

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Optimization of energy costs in the pretreatment of olive mill wastewaters by electrocoagulation

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(Received 8 February 2011; final version received 6 June 2011)

In this study, the electrocoagulation process was evaluated as a pretreatment process for olive mill wastewaters. Aluminium (Al) and iron (Fe) electrodes, several contact times and 0.5, 1 and 2 A currents were used to compare chemical oxygen demand (COD) removal efficiencies for each case. The optimum contact time and current were 45 minutes and 1 A, respectively, which resulted in a COD removal of 58.7% with an Al electrode. Experimental data from distinct operational conditions were used to fit a model for COD removal efficiencies. Energy consumption was also predicted. Under optimum operational conditions, the treatment cost was approximately £0.13 kg$^{-1}$ COD$_{\text{removed}}$ and £4.41 m$^{-3}$. The results showed that the electrocoagulation process was a cost-effective method for the pretreatment of olive mill wastewaters.

Keywords: chemical oxygen demand removal; electrocoagulation; modelling; olive mill wastewaters; pretreatment

Introduction

Today, the production of olives and olive oil is increasing along the coasts of the Mediterranean Sea. Turkey is one of the countries with the highest production capacity. Turkey’s total production between 1994 and 2004 was 1,250,000 tons, and its global market share was 8.41% [1].

Olive mill wastewater is generated during two- and three-phase olive oil production processes. Over 30 million m$^3$ of olive mill wastewater are produced along the Mediterranean coast yearly [2].

Olive mill wastewater has a very high organic content. In addition, high phenol, fatty acid and suspended solid concentrations make this wastewater extremely difficult to treat. Previous studies have shown that the biochemical oxygen demand (BOD) of olive mill wastewater ranges from 15,000 to 135,000 mg l$^{-1}$. The ranges in the chemical oxygen demand (COD), total suspended solids (TSS) and pH of this wastewater are 37,000–318,000 mg l$^{-1}$, 6000–69,000 mg l$^{-1}$ and 4.6–5.8, respectively [3–7]. The variation in the character of olive mill wastewater depends on whether the production process is continuous or batch.

Wastewater from batch processing is stronger due to the lower consumption of water during the production. Due to the above-mentioned characteristics, olive mill wastewater has adverse effects on receiving water bodies and therefore needs to be treated prior to discharge. In addition, producers suffer from handling the wastewater because final treatment is very difficult and expensive. Previous studies related to the treatment of olive mill wastewater investigated the use of advanced oxidation processes [8–11], anaerobic treatment [12,13], chemical precipitation [9,14,15] and electrocoagulation [16–19]. However, it seems that none of the treatment methods alone are sufficient. Moreover, there are no widely accepted full-scale treatment techniques.

In recent years, electrochemical treatment has gained attention as a promising method for olive mill wastewater treatment because it is relatively cheap and efficient. Electrocoagulation is one of the simplest and most efficient electrochemical methods. It can be used to purify many types of water and wastewater [17]. Characterized by its lower equipment costs, sludge volume reduction and easy operation, electrocoagulation employs a metal electrode, which acts as an anode, to produce the coagulant via electrolytic oxidation. At an appropriate pH level, the coagulant, in turn, precipitates as metal hydroxides, resulting in high COD removal efficiencies [20]. In addition to the removal by precipitation, partial oxidation around the anode also increases COD removal rates [21].

Previous studies have focused on the treatment of various types of wastewater, including metal processing wastewater [22], olive mill wastewater [16,20], textile dyeing wastewater [23–26], semiconductor production wastewater [27,28], tannery wastewater [29–33] and urban wastewater [34] and organics removal from poultry slaughterhouse wastewater [35,36]. Electrocoagulation is highly efficient, especially in the treatment of particulate organic pollution [37]. In addition to the precipitation process, electrocoagulation is also effective in the removal of soluble species as oxidation processes also take place.

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 ISSN 0959-3330 print / ISSN 1479-487X online
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 http://dx.doi.org/10.1080/09593330.2011.595829
 http://www.tandfonline.com
The chemistry of the aqueous medium, especially its conductivity, has a very strong effect on the mechanism of electrocoagulation. The precipitation mechanism in the electrocoagulation process can be explained with the dissolution of sacrificial electrodes pair and the generation of metal hydroxide. In an electrolytic system, iron produces ferric hydroxide. Two mechanisms have been proposed for the production of metal hydroxide in the cases of iron (Fe) and aluminium (Al) electrodes [38–40]. The reactions are shown in Equations (1)–(7) [40]. The reaction at the cathode is shown in Equation (8).

For the Al anode:

\[ \text{Al} + 3\text{e}^- \rightarrow \text{Al}^{3+}, \]  

under alkaline conditions:

\[ \text{Al}^{3+} + 3\text{OH}^- \rightarrow \text{Al(OH)}_3 \]  

and under acidic conditions:

\[ \text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3\text{H}^+. \]  

For the Fe anode:

\[ \text{Fe} + 2\text{e}^- \rightarrow \text{Fe}^{2+}, \]  

under alkaline conditions:

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

and under acidic conditions:

\[ 4\text{Fe}^{2+} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Fe}^{3+} + 4\text{OH}^-. \]  

In addition, there is the following oxygen evolution reaction:

\[ 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow \text{O}_2 + 4\text{H}^+. \]  

The reaction at the cathode is

\[ 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- . \]  

The aim of this study is the following: to investigate the feasibility of the electrocoagulation process as a primary treatment method for olive mill wastewaters prior to final treatment; to develop a model for predicting COD removal efficiencies as a function of operational conditions and to compare the COD removal efficiencies and treatment costs with other treatment methods presented in previous studies.

Materials and methods

Characterization of the olive mill wastewater

The wastewater was obtained from an olive oil production plant in Milas, Turkey, that uses the continuous three-phase system. This raw wastewater was used directly without a primary preparation process, such as dilution or precipitation. The characteristics of the raw wastewater are given in Table 1.

Electrocoagulation process parameters

The electrocoagulation process was performed in a lab-scale Plexiglas reactor with dimensions of 6 cm × 6 cm × 17 cm (W × L × H). The active volume of the batch reactor was 250 ml. Al and Fe electrodes were used in the experimental studies. The distance between the electrode plates was 5.5 cm. The widths of the Al plates and Fe electrodes were 4.9 and 5.8 cm, respectively. The surface area that was in contact with the wastewater was 34.3 cm² for Al plates and 40.6 cm² for Fe electrodes.

The current was kept constant at 0.5, 1 and 2 A, and the change in voltage was monitored during experiments. The current density was 14.6–58.4 mA cm⁻² for the Al electrode and 12.3–49.2 mA cm⁻² for the Fe electrode. Six different contact times (15, 30, 45, 60, 90 and 120 minutes) were used. The wastewater was allowed to precipitate, and the treated wastewater was drawn from the top of the reactor.

Analyses

Volatile suspended solids (VSS), TSS and COD were analysed according to standard methods [41]. COD analyses were performed using the open reflux method. Merck analytical quality chemicals were used in the preparation of reagents. All of the experiments were performed at room temperature.

A digital direct current (DC) power supply (GW Instek, GPS 3030 DD, 0–30.0 V, 0.0–3.0 A) was used to regulate the electrical current in the electrochemical cell.

Statistical analysis

The final section of this paper addresses optimization. With this aim, models that predict treatment efficiency depending on the operational conditions and the type of electrode were designed. The reliability of these models was evaluated based on the values of the coefficient of determination (R²) and other statistical parameters, shown in Table 2. The process was optimized using models to determine the optimum operational conditions that maximize the treatment efficiency. Statgraphics Centurion XV software was used for curve fitting and for all other statistical analyses.
Table 2. Descriptive statistics of the fitted model.

<table>
<thead>
<tr>
<th>Statistics</th>
<th>Fe electrode</th>
<th>Al electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R^2$</td>
<td>90.2362</td>
<td>92.5294</td>
</tr>
<tr>
<td>$R^2$ (adjusted for degrees of freedom)</td>
<td>86.9816</td>
<td>90.0392</td>
</tr>
<tr>
<td>Standard error of estimate</td>
<td>7.2636</td>
<td>7.1683</td>
</tr>
<tr>
<td>Mean absolute error</td>
<td>5.2226</td>
<td>5.1798</td>
</tr>
<tr>
<td>Durbin Watson statistic</td>
<td>2.5503</td>
<td>2.5278</td>
</tr>
<tr>
<td>Lag 1 residual autocorrelation</td>
<td>−0.2948</td>
<td>−0.2706</td>
</tr>
</tbody>
</table>

Results and discussion

Electrocoagulation process

In previous studies, dilution and pH adjustment were employed as preparation processes, whereas wastewater was used directly without dilution or pH adjustment in this study. The pH of the wastewater was 4.3 to begin with, but it gradually increased during the electrocoagulation process due to the generation of $\text{OH}^-$ as a result of electrolytic reactions at the cathode. Thus, by the end of the contact time, the precipitation rate had increased, and the pH of the treated wastewater had increased to near neutral [20]. Aysar et al. [42] stated that this outcome was one advantage of electrocoagulation applied to wastewaters of acidic character.

The COD removal efficiencies from low-pH wastewater in experiments conducted using Al and Fe electrodes are shown in Figure 1 [43].

Contact time is an important performance parameter in the electrocoagulation process. As increasing the contact time results in additional treatment costs, such as larger reactor volume requirements and higher energy and maintenance costs, optimization of the electrocoagulation process was required. Figure 1 clearly depicts that the rate of change in the COD removal efficiency decreases significantly with respect to the increasing contact time after the first 45 minutes. The COD removal efficiency increased from the 30th to the 45th minutes by 11.3% for the Fe electrode and by 14.3% for the Al electrode. In contrast, the increase in the COD removal efficiencies when the contact time was raised from 45 to 60 minutes was 1.5% and 1.4% for the Fe and Al electrodes, respectively. Therefore, the contact time did not significantly affect the COD removal efficiency after 45 minutes, although it did increase energy consumption. In fact, Feng et al. [44] also suggested that contact time was one of the most important operational parameters of electrocoagulation and must be optimized for a cost-effective treatment.

As is obvious from Figure 1, the COD removal efficiencies for Al electrodes were higher than those for Fe electrodes. Furthermore, at the current of 1 A, the COD removal efficiencies for the Fe electrode at 120 minutes of contact time were achieved within 60 minutes for the Al electrode. For 45 minutes as the optimum contact time, the COD removal efficiencies were 47.5%, 53.4% and 56.3% for the Fe electrode at currents of 0.5, 1.0 and 2.0 A, respectively, and were 48.7%, 58.7% and 64.4% for the Al electrode, respectively. The differences in the COD removal efficiencies were 10.0% and 5.7% between 0.5 and 1 A and 1 and 2 A for the Al electrode.

Economical analysis of electrocoagulation

Energy consumption (as kWh) during the electrocoagulation process was calculated as a function of the current density (A), voltage (V) and contact time (h). Figure 2 shows the energy consumption per cubic meter of wastewater treated by the process for both the Fe and Al electrodes.

The rate of the increase in the treatment costs was constant for both the Al and Fe electrodes until the contact time reached 45 minutes. However, for longer periods of contact time, costs started to increase (especially for 0.5 and 1 A) exponentially because of an increase in the voltage for both electrodes after 45 minutes of contact time. Increasing the contact time from 45 to 120 minutes raised the treatment cost by 3.7 times. Energy consumption was higher with the Al electrodes than with the Fe electrodes. The rate of change in energy consumption with respect to increasing the COD removal efficiency and contact time showed a decreasing trend for the Fe electrode. The energy consumptions with the Fe electrode per kg of the COD removed with a 1 A current density were 1.45, 2.28 and 4.51 kWh at 30, 60 and 120 minutes, respectively. This trend occurs because the voltage...
for the Fe electrode does not increase as much as it does for the Al electrode with increasing contact time. The values of energy consumption per kg of the COD\_removed with a 1 A current density for the Al electrode were 1.87, 2.79 and 6.43 kWh at 30, 45 and 60 minutes, respectively. Treatment costs per cubic meter wastewater are shown in Figure 3.

As seen in Figure 3, the rate of increase of the treatment costs was increased with contact time. For 45 minutes, the treatment costs per cubic meter wastewater in current of 0.5, 1 and 2 A were €1.50, €3.55 and €8.93 for the Fe electrode, respectively. They were €1.59, €4.37 and €10.54 for the Al electrode. The best operational conditions were the Fe electrode and 0.5 A in terms of treatment costs. On the other hand, the best operational conditions in terms of the COD removal efficiency were for the Al electrode and 2 A. However, the Al electrode obtained better COD removal efficiencies than the Fe electrode with the same treatment costs. Moreover, for the Al electrode, the increase of treatment costs was €2.78 and €6.17 between 0.5 and 1 A and 1 and 2 A, respectively. The increase of the COD removal efficiency was 10.0% and 5.7%, respectively. The increase of 10% in the COD removal efficiency is significant for high-strength wastewater, such as that from olive mills. Therefore, the optimum operational conditions seem to be 45 minutes of contact time at 1 A.

**Model results for electrocoagulation**

A model was also fit to the experimental data. The model calculates the COD removal efficiencies as a function of operational conditions (current density and time). The experimental data obtained from this study were used to fit the model. The results are shown in Figures 4 and 5. The fitted equations for Fe and Al electrodes are shown in Equation (9). Furthermore, descriptive statistics of the model fit are presented in Table 2.

The model equation for the Fe electrode and the Al electrode is as follows:

$$E_{COD} = a + bL + ct + dL^2 + eLt + fL^2.$$

Here, $E_{COD}$ is the percent of COD removal efficiency, $L$ is the current density in amperes, $t$ is the contact time in minutes and $a$, $b$, $c$, $d$, $e$ and $f$ are regression coefficients. Values of these coefficients for Fe and Al electrodes are given in Table 3.

Statistical analyses were performed on the experimental and model data. Firstly, the performances of the Al and Fe electrodes were compared by an independent $t$-test for differences in their variances. Twenty-one batches of experimental results from both electrode types were used in the analysis. The average COD removal efficiencies were calculated to be 46.83% for the Al electrode and 43.26% for the Fe electrode, with variances of 515.9 and 405.3, respectively. The 95% confidence interval for the difference between averages was calculated as $3.57 \pm 21.37$ ($t_{0.025, 40} = 2.32$). This interval shifted towards the positive side, although it included zero. Thus, although there was no persuasive evidence that the performances significantly differ, the Al electrode performed better than the Fe electrode for the COD removal efficiency.

Performing an $F$-test on experimental and model results tested the reliability of each model. Two batches were examined as the experimental and model results for both the Al electrode (AlEM) and the Fe electrode (FeEM). The variances in model results were 962.3 and 470.8 for the Al and Fe electrodes, respectively. For both batches, the null hypothesis was established as follows: ‘the experimental
and model results do not statistically differ from each other. The calculated $f$ values for the AlEM and FeEM batches were 1.87 and 1.16, respectively. At a 5% significance level with 20 degrees of freedom for both the numerator and denominator, the limit value was calculated to be 2.12. It was concluded that the alternative hypotheses were unlikely to be true, because the calculated values of $f$ were less than the limit values of $f$ in both batches. Therefore, it was proven that there was no significant difference between experimental and model results in both batches.

Comparison of the study results with previous studies

The current study proved that electrocoagulation is a cost-effective and less time-consuming process for the pretreatment of olive mill wastewater. For olive mill wastewater treatment, results of previous studies using the electrocoagulation process and other processes are given Tables 4 and 5, respectively.

A limited number of research studies are available in the literature. Most of the previous studies focused on the use of one type of electrode, whereas both the Fe and Al electrodes were used and evaluated for their performance in this study (Table 4). The COD removal efficiencies obtained in this study were considered satisfactory compared to the results from previous studies. As seen in Table 5, the results in this study were considered satisfactory compared to the results from previous studies with other treatment processes. Most previously published research unfortunately did not include cost optimization, and if it did, it was not detailed. In this study, the most detailed cost optimization analyses possible were included, which allowed the cheapest treatment option to be suggested. Moreover, none of the previous studies have focused on the development of a model to estimate the treatment efficiency for any given set of operational conditions, whereas this study offers a model to predict treatment efficiency for a given set of two independent variables, namely current and contact time.

Conclusions

This study focused on the pretreatment of olive mill wastewater by the electrocoagulation process. The results from the experimental study showed that optimum COD removals of 58.7% and 53.4% were achievable with a current density of 1 A and a contact time of 45 minutes using the Al and

Table 4. Different operational conditions and obtained results from the literature.

<table>
<thead>
<tr>
<th>Reaction time, min</th>
<th>Current, mA cm$^{-2}$</th>
<th>Electrode type</th>
<th>Pollutants, g l$^{-1}$</th>
<th>Removal efficiency</th>
<th>Economical analysis</th>
<th>Statistical analysis</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>30–180</td>
<td>20–75</td>
<td>Al and Fe</td>
<td>COD: 45.0</td>
<td>62.0%–86.0%</td>
<td>€0.18–6.75 kg$^{-1}$ COD 13.0–188.0 kWh m$^{-3}$</td>
<td>-</td>
<td>[17]</td>
</tr>
<tr>
<td>120</td>
<td>25</td>
<td>Fe</td>
<td>sCOD*: 36.9</td>
<td>33.6%</td>
<td>-</td>
<td>-</td>
<td>- [19]</td>
</tr>
<tr>
<td>5–60</td>
<td>15–120</td>
<td>Al</td>
<td>COD: 75.1</td>
<td>76.0%</td>
<td>-</td>
<td>-</td>
<td>- [20]</td>
</tr>
<tr>
<td>15</td>
<td>5–40</td>
<td>Al</td>
<td>COD: 20.0</td>
<td>42.0%–83.5%</td>
<td>€0.12–4.04 kWh kg$^{-1}$ COD €0.03–0.38 kg$^{-1}$ COD €4.41 m$^{-3}$</td>
<td>-</td>
<td>- [45]</td>
</tr>
<tr>
<td>15–120</td>
<td>12–58</td>
<td>Al and Fe</td>
<td>COD: 56.9</td>
<td>54.2%–71.5%</td>
<td>€0.13 kg$^{-1}$ COD 1.8–2.0 kWh kg$^{-1}$ COD €3.57 m$^{-3}$</td>
<td>It is done by Statgraphics® This study</td>
<td></td>
</tr>
</tbody>
</table>

*sCOD: soluble COD.

Table 5. Results of other pretreatment processes from the literature.

<table>
<thead>
<tr>
<th>Method</th>
<th>Pollutants, g l$^{-1}$</th>
<th>Removal efficiency</th>
<th>Economical analysis</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electro-Fenton</td>
<td>COD: 113</td>
<td>68%</td>
<td>-</td>
<td>[8]</td>
</tr>
<tr>
<td>Lime treatment</td>
<td>COD: 103</td>
<td>46.3%</td>
<td>-</td>
<td>[14]</td>
</tr>
<tr>
<td>Electrochemical oxidation</td>
<td>COD: 42</td>
<td>43%</td>
<td>-</td>
<td>[46]</td>
</tr>
<tr>
<td>Acid cracking</td>
<td>COD: 115</td>
<td>46.0%</td>
<td>€1.60 m$^{-3}$</td>
<td>[47]</td>
</tr>
<tr>
<td>Acid cracking + chemical</td>
<td>COD: 115</td>
<td>67%</td>
<td>€3.57 m$^{-3}$</td>
<td>[47]</td>
</tr>
<tr>
<td>coagulation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electro-coagulation</td>
<td>COD: 57</td>
<td>58.7%</td>
<td>€0.13 kg$^{-1}$ COD €4.41 m$^{-3}$</td>
<td>This study</td>
</tr>
</tbody>
</table>
Fe electrodes, respectively. Increasing the contact time led to very low increases in the COD removal efficiencies for both the Al and Fe electrodes.

Energy costs calculated in this study also suggest that current density and contact time are of great importance to process optimization. For optimum operational conditions (45 minutes at 1 A), energy costs per cubic meter of wastewater for the Fe and Al electrodes were 54.3 and 66.9 kWh, respectively. Under the same operational conditions, the energy costs per kg of COD removal were calculated to be 2.0 and 1.79 kWh for the Fe and Al electrodes, respectively. Moreover, under optimum operational conditions, the treatment cost was approximately €0.13 kg⁻¹ COD removed and €4.41 m⁻³.

In conclusion, current density and contact time must be optimized in the electrocoagulation process for a cost-effective operation. The electrocoagulation process used in this study is essentially a primary treatment method, because the organic content of the effluent from the electrocoagulation process is not low enough to meet discharge standards for receiving bodies. In fact, none of the physicochemical treatment methods alone can achieve the discharge standards. Thus, further research to investigate the usability of wastewater pretreated by electrocoagulation in the final treatment processes is warranted.

The fitted model proved to be a useful and accurate tool to predict the COD removal efficiency as a function of operational parameters. Input parameters for the model were current density (A) and contact time (hours). The model was used along with other experimental data to assess its validity. R² values exceeding 90% and adjusted R² values over 87% prove the reliability of the model. As another performance criterion, the standard error for the estimation from the use of Fe and Al electrodes was approximately 7%, which means that the actual COD removal efficiency for a given set of operational parameters would be ±7% at a confidence level of approximately 70%.

References


