Oily wastewater treatment by hybrid ultrasound and electrocoagulation batch process

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Abstract

Chemical coagulants are often added to destabilize secondary oil in water emulsions. However, numerous studies showed that electrocoagulation is an adequate alternative for the chemical coagulation process in wastewater treatment. Therefore, the effect of a hybrid system with ultrasound and electrocoagulation batch processes on the treatment of oily wastewater is analyzed in this paper. Totally, six experiments, with three different setups, were performed on a laboratory scale. For removal of mineral oil, the combination where electrocoagulation was used prior to ultrasound, with the addition of NaCl, showed to be the most efficient as the mineral oil concentration decreased by 70% after 40 min of the treatment. This combination also showed to be the most efficient for chemical oxygen demand (COD) removal (35% removal efficiency). The addition of electrolyte also positively affected the COD removal efficiency in the other two setups, that is, in parallel (simultaneous) operation and when electrocoagulation was used after the ultrasound. The parallel operation with the addition of electrolyte showed to be the most successful for Cr (99.12%), Ni (98.15%) and Pb (99.79%) removal. Regardless of the electrolyte addition, electric conductivity decreased during the electrocoagulation process due to the oxidation of chloride and metal ions.

Keywords: Chemical oxygen demand removal; Electrocoagulation; Heavy metals removal; Mineral oil removal; Oily wastewater; Ultrasound; Wastewater treatment

1. Introduction

Petrochemical, metallurgical and oil industries generate large quantities of oily wastewater [1]. These effluents contain high concentrations of hydrocarbons, cyanide, oil, phenols, benzene, sulfide, etc. and are rich in biological oxygen demand and chemical oxygen demand (COD) [2]. Different national regulations apply to these industries so oils and grease are removed or reduced by a wastewater pretreatment prior to its discharge into the municipal sewerage system. Further, inadequate treatment and uncontrolled discharge of oily wastewater can lead to irreversible environmental pollution and contamination of water bodies [1]. Oil in water can occur in several manners, but secondary oil-in-water emulsions are usually a problem in wastewater treatment. These emulsions are very stable due to the formation of interfacial films encapsulating the oil droplets, which makes them very difficult to separate by conventional methods. These oil droplets are very small and, from the macroscopic point of view, it may appear that the emulsion of oil and water is a homogeneous liquid, although it is a mixture, that is, a heterogeneous system. To destabilize this emulsion and break the electrostatic repulsive forces between oil and water, chemical coagulants are usually added to the wastewater [1,3].

Recently, several studies showed a successful application of electrochemical technologies for oil removal [1,2,4]. Electrocoagulation (EC) is a technology that combines...
electrochemistry, coagulation and flotation (or settling) [5]. More specifically, this technology consists of four main steps: electrolytic reaction at the electrode surface, formation of metal hydroxides (coagulants), adsorption of soluble (colloidal) particles onto coagulants, and finally removal by sedimentation or flotation [6]. Direct current is commonly used, and the electrode material and its setup depend on the wastewater pollution and the required effluent quality [7]. Aluminum (Al) and iron (Fe) electrodes are mostly used because these materials are cheap and readily available [6,8]. Electrocoagulation is usually easy to operate, has high removal efficiency, can handle multiple pollutants, no addition of chemicals is required and encompasses moderate to short operating time. However, like any treatment process, electrocoagulation has some disadvantages such as electrode passivation, electrode dissolution and power consumption.

Due to the low electrical conductivity of most wastewaters, the electrolyte is usually added. Also, electrocoagulation is not effective in removing light organic materials or inorganic contaminants that do not form precipitates and sludge [6,7]. To overcome these drawbacks electrocoagulation is often combined with other technologies, usually advanced oxidation processes [6,7,9-11].

Ultrasound (US) belongs to the group of homogeneous advanced oxidation processes and its main mechanism is related to ultrasonic cavitation, in which the sound waves generate pressure fluctuations under extreme temperature and pressure conditions, causing the formation, growth and implosion of microbubbles and the production of hydroxyl radicals [10,12,13]. These generated hydroxyl radicals are highly reactive due to their high oxidation-reduction potential (1.8–2.70 V, depending on the pH of the solution/water) and therefore they enhance oxidation reactions more than conventional oxidants [14]. Ultrasound is simple and versatile technology with generally low investment costs, but it is usually not very effective as a stand-alone water treatment, so it is often combined with other technologies, such as advanced oxidation or electrochemical processes [9,13,15]. The combination of electrocoagulation and ultrasound, as a hybrid process, is based on the dissolution of the positively charged metal ions at the electrodes, which neutralize the repulsive forces between the particles attracting each other and forming flocs that can be easily removed by flotation or sedimentation, with the parallel production of highly reactive and non-selective radicals from ultrasonic cavitation, resulting in additional contaminant degradation.

The reactions at the cathode are associated with the formation of hydroxyl radicals and hydrogen gas [Eqs. (1) and (2)], that is, the production of hydrogen peroxide at the cathode and oxygen decomposition are accelerated, leading to the increase in hydroxyl radical production in the presence of ultrasound [16].

$$\text{M}^{n+} (\text{aq}) + n\text{OH}^- (\text{aq}) \rightarrow \text{M(OH)}_n (s) \quad (1)$$

$$2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad (2)$$

Therefore, the aim of this study is to investigate the application of electrocoagulation, as well as its combination with ultrasound, for the removal of COD, heavy metal and mineral oil, which are the main contaminants monitored in oily wastewater.

2. Methodology

2.1. Materials

The oily wastewater samples used in this study were obtained from oil and grease traffic-rated separators provided by a company specialized in handling oily wastewater (Kemis-Termoclean Ltd., Croatia). The experiments were performed in a batch mode reactor by using a 2,000 mL plastic container. For each experiment, 1,500 mL of oily wastewater was used. Two sets of experiments were considered. In the first set of experiments (experiments M1, M2 and M3), electrocoagulation and ultrasound were used without the addition of electrolytes. Since several previous researchers [17,18] showed that the addition of sodium chloride (NaCl) can positively affect the removal efficiency, in the second set of experiments (experiments M4, M5 and M6), 1 g of NaCl, in the form of common table salt, was manually added to the wastewater samples to increase the electrical conductivity and thus to increase the efficiency of the electrocoagulation process.

In experiments M1 and M4, electrocoagulation is used prior to ultrasound, while experiments M2 and M5 were performed in the reverse order, thus ultrasound prior to electrocoagulation. In experiments M1, M2, M4 and M5, both (iron and aluminum) electrodes run for 10 min, while ultrasound runs for 20 min. Experiments M3 and M6 refer to the combined electrocoagulation and ultrasonic process (parallel operation). The total duration of experiments M2 and M6 was 20 min, the first 10 min for iron electrodes and ultrasound, and the last 10 min for the aluminum and ultrasound process.

The physical characteristics and initial concentrations of both sets of experiments are shown in Table 1. The initial characteristics of each sample differ slightly because the samples were taken from a larger container whose content needs to be premixed to obtain a homogeneous solution. pH, conductivity, total dissolved solids, NaCl, dissolved oxygen (DO), temperature and electrical resistivity were measured continuously using a CyberScan PCD 650 multi-meter (from Eutech Instruments, The Netherlands). Mineral oil concentrations were measured using NEXIS GC-2030 (from Shimadzu, Japan), while COD concentrations were measured by an external collaborating laboratory using the standard permanganate method. Heavy metal concentrations were also measured by the external laboratory using the inductively coupled plasma (ICP) mass spectrometry method. COD, mineral oil and heavy metal concentrations were measured at the beginning and at the end of the experiments, while mineral oil concentrations were additionally measured after each process step (iron electrodes; aluminum electrodes; ultrasound). Therefore, mineral oil concentrations were measured four times for experiments M1, M2, M4 and M5, and three times for experiments M3 and M6. Finally, all samples, except the initial one, were allowed to settle for 60 min before measuring.
2.2. Experimental procedures

In the electrocoagulation part of each experiment, four iron electrodes were always used firstly, followed by six aluminum electrodes to remove the color remaining from the Fe(III) salts. The electrodes were placed in a monopolar parallel arrangement, 10 mm apart. All electrodes were immersed 20 mm into the wastewater, giving a total effective area of 44.03 cm² for the iron electrodes and 24 cm² for the aluminum electrodes. Power supply DF 1730 LCD (from Goobay, Germany/China) was used for voltage and current control. The voltage of 30 V was used in all experiments. In the first set of experiments, the average electric current was 0.4 A, thus giving the current density of 90.85 A/m² for iron electrodes, and 166.67 A/m² for aluminum electrodes. In the second set of experiments, with electrolyte addition, the average electric current was 1.6 A, resulting in the current density of 363.39 A/m² for iron electrodes, and 666.67 A/m² for aluminum electrodes. The applied current densities were within the usual suggested range of 10–1,000 A/m² [19].

The ultrasonic homogenizer SONOPULS HD 2200.2 (from Bandelin, Germany) was used in the ultrasonic part of the experiments. An ultrasonic transducer with titanium flat tip TT 13 (Ø13 mm) was immersed 15 mm into the sample. The ultrasonic frequency used was 20 kHz, 200 W with 50% amplitude.

During the experiments, the batch reactor was placed on a magnetic stirrer RCT basic PT1000 (from IKA, Germany) and samples were continuously mixed at 150 rpm.

The setup of the electrocoagulation and the ultrasonic unit, as well as their parallel operation, are shown in Fig. 1.

3. Results and discussion

3.1. Mineral oil removal

The final physical characteristics and concentrations obtained for all six experiments are shown in Table 2. The change in mineral oil concentrations for all experiments is shown in Fig. 2. In the first 20 min, when electrocoagulation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>M4</th>
<th>M5</th>
<th>M6</th>
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<tr>
<td>pH</td>
<td>7.4</td>
<td>7.25</td>
<td>7.08</td>
<td>7.12</td>
<td>7.07</td>
<td>7.16</td>
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<tr>
<td>Conductivity (µS)</td>
<td>542.4</td>
<td>528.1</td>
<td>577.3</td>
<td>1,819.0</td>
<td>1,850.0</td>
<td>1,828</td>
</tr>
<tr>
<td>Total dissolved solids (mg/L)</td>
<td>400.8</td>
<td>408.1</td>
<td>422.3</td>
<td>1,390</td>
<td>1,413</td>
<td>1,403.0</td>
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<tr>
<td>NaCl (mg/L)</td>
<td>398.6</td>
<td>407.2</td>
<td>422.4</td>
<td>1,462</td>
<td>1,488</td>
<td>1,474</td>
</tr>
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<td>DO (mg/L)</td>
<td>3.93</td>
<td>2.01</td>
<td>1.64</td>
<td>2.21</td>
<td>1.68</td>
<td>2.04</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>18.9</td>
<td>21.8</td>
<td>18.7</td>
<td>19.8</td>
<td>19.6</td>
<td>19.8</td>
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<tr>
<td>Electrical resistance (Ω)</td>
<td>1,249</td>
<td>1,228</td>
<td>1,186</td>
<td>359.8</td>
<td>353.9</td>
<td>357.2</td>
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<tr>
<td>Mineral oil (mg/L)</td>
<td>6.89</td>
<td>4.00</td>
<td>2.22</td>
<td>2.28</td>
<td>2.67</td>
<td>2.17</td>
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<tr>
<td>COD (mg O₂/L)</td>
<td>288</td>
<td>288</td>
<td>288</td>
<td>310</td>
<td>310</td>
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<td>Chrome (µg/L)</td>
<td>64</td>
<td>64</td>
<td>64</td>
<td>78</td>
<td>78</td>
<td>78</td>
</tr>
<tr>
<td>Nickel (µg/L)</td>
<td>81</td>
<td>81</td>
<td>81</td>
<td>91</td>
<td>91</td>
<td>91</td>
</tr>
<tr>
<td>Lead (µg/L)</td>
<td>110</td>
<td>110</td>
<td>110</td>
<td>125</td>
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Fig. 1. The experimental setup: (a) electrocoagulation (iron electrodes), (b) ultrasound and (c) electrocoagulation (aluminium electrodes) and ultrasound in parallel mode.
and ultrasound were used separately, electrocoagulation alone (experiments M1 and M4) had almost 20% higher mineral oil removal efficiency than ultrasound (experiments M2 and M5). The NaCl addition (experiments M4, M5 and M6) had a positive effect on the mineral oil removal efficiency in all cases. When the parallel operation was considered (experiments M3 and M6), it was found that electrocoagulation and ultrasound combined had some positive effects. The results showed that parallel operation was 5% better than ultrasound alone in mineral oil removal, but worse than stand-alone electrocoagulation. Moreover, the combination of aluminum electrodes and ultrasound (the next 10 min) showed higher removal efficiency than the combination of iron and ultrasound (the first 10 min).

3.2. COD removal

It is known that the ultrasonic process generates •OH free radicals, which are strong oxidants and can remove organic pollutants such as COD. Some authors like Chu et al. [20] reported that •OH radicals are the reason for the higher removal COD efficiency. In addition, other authors such as Al-Rubaey and Al-Barazanjy [4] stated that ultrasound can eliminate electrode passivation, which leads to increased formation of metal hydroxides that adsorb pollutants. Therefore, ultrasound should enhance COD removal without adding the electrolyte.

During the experiments, the initial and final concentrations of COD were measured and the results are shown in
• OH radicals were generated by ultrasound application, but the results related to the parallel operation (experiments M3 and M6) and when ultrasound was used after electrocoagulation (M1 and M4), have a higher removal rate than experiments when ultrasound was used prior to electrocoagulation (M2 and M5). Thus, the highest COD removal efficiencies were achieved in experiments M1 (27.27%) and M4 (35.48%). This higher efficiency can be explained by the fact that the ultrasound caused the removal of the electrode passivation layer, which lead to more efficient production of metal hydroxides and thus to a higher removal efficiency. Also, the additional ultrasonic mixing apart of the cavitation area could also accelerate the flocculation as it happened in the study of Al-Rubaiey and Al-Barazanjy [4]. However, it should be noted that in this study flocs were generated during the ultrasonic run and that these experiments (M3 and M6) were basically 20 min shorter than the others.

The addition of electrolyte resulted in about 3% higher removal efficiency only in experiment M4 when electrocoagulation was used prior to the ultrasound. Therefore, the best removal efficiency for the given operating conditions is achieved in this experiment and is shown in Table 3.

Furthermore, if the addition of electrolytes for COD removal is considered, it generally has a positive effect on the removal efficiency. This was particularly noticeable when ultrasound was used after electrocoagulation and in the parallel mode (experiments M4 and M6). These results are in agreement with previous studies by Safari et al. [3], Al-Rubaiey and Al-Barazanjy [4] and Maha Lakshmi and Sivashanmugam [17] which showed a decrease in the concentrations of COD in experiments with electrolyte assistance.

3.3. Heavy metal removal

The final heavy metal concentrations of chromium (Cr), nickel (Ni) and lead (Pb) are shown in Table 2 and Fig. 4. Removal efficiencies greater than 90% were achieved in all experiments for each analyzed element. The combination of electrocoagulation and ultrasound was particularly efficient in removing Lead with removal efficiencies greater than 98% in all experiments. It can be concluded that the parallel operation of electrocoagulation and ultrasound, with the addition of electrolyte (experiment M6), is better than any other used set-up configuration, resulting in removal efficiencies of 99.12% (Cr), 98.15% (Ni) and 99.79% (Pb). The reason for this is most likely due to the observed effect in which ultrasound removes the passivation layer that normally forms on the electrode surface during electrocoagulation and that the addition of electrolyte increases the electrical conductivity of the effluent, which intensifies the flocculation and contributes to the overall removal efficiency [4]. Further, Al-Rubaiey and Al-Barazanjy [4] are some of the few authors with a similar study on oily wastewater. Their research showed a positive effect of ultrasound on electrocoagulation for the removal of heavy metals, as the removal of zinc was 10% higher when ultrasound was used.

Regarding the addition of electrolytes, the treatment efficiency was significant only for nickel removal. When NaCl was used, nickel removal efficiencies were 3% to 5% higher, depending on the experiment.

3.4. Electrical conductivity

Regardless of the electrolyte addition, electrocoagulation and ultrasound alone were found to affect electrical conductivity. In all experiments (Figs. 5 and 6), electrical conductivity decreased compared to initial values during the electrocoagulation due to the oxidation of chloride ions already present in the wastewater, but also because metal...
ions from metal hydroxides [3,18,21,22]. Considering the electrode type, when aluminum electrodes were used, the electrical conductivity decreased up to 4% compared to the electrical conductivity when iron electrodes were used. The reason is due to Faraday's second law and the fact that iron has a higher relative atomic mass. Considering the valence of iron and aluminum, it was concluded that iron releases more cations to the wastewater solution. Therefore, the total number of free ions was reduced. A similar effect of conductivity decrease due to the use of aluminum electrodes was reported by Ahmed et al. [23] in a study of dye removal. Moreover, several authors have found a decrease in electrical conductivity from the initial to the final value in their electrocoagulation experiments regardless of the wastewater source and electrode type [18,23,24]. Further, this need for additional electrolytes may affect the operating cost but moreover can lead to secondary contamination by excess Cl anions, which are difficult and costly to remove [23]. The electrical conductivity could be increased by applying a higher voltage, but this results in increased energy consumption. In addition, an increase in conductivity has been observed at high pH values due to anode dissolution and consequent release of ‘OH ions [18].

When ultrasound was used prior to electrocoagulation (experiments M2 and M5), electrical conductivity decreased slightly (less than 1% compared to the initial value). However, electrical conductivity started to increase when ultrasound was applied after electrocoagulation (experiments M1 and M4), but never reached initial levels. In parallel mode (experiments M3 and M6), electrical conductivity also decreased, but at a slower rate than electrocoagulation alone. The ultrasonic waves cause the flocs to break up and release ions near the ultrasonic probe. In addition, ultrasound generates more free ions and consequently higher electrical conductivity due to the breaking of chemical bonds within the contaminants. This can be observed especially in experiment M4 (Fig. 6).

These results could also be related to the additional mixing process that occurs during the ultrasound. This increases the electrical conductivity and proportionally the flocculation away from the probe due to the additional mixing, resulting in overall removal efficiency. This effect was
particularly evident in the removal of heavy metals when ultrasound was used after electrocoagulation (experiments M1 and M4), as the additional mixing of already formed flocs enhanced their further flocculation and accelerated the sedimentation process. This is also in agreement with the work of Al-Rubaiey and Al-Barazanjy [4], who found that the efficiency of turbidity removal was reduced by 50% without additional mixing with the magnetic stirrer.

In the second set of experiments, M4, M5 and M6, NaCl addition increased the conductivity of the effluent and thus the potential to overcome the stability of the oil droplet emulsion. As a result, the potential associated with the electrochemical coagulation is increased, leading to higher removal efficiency [25], Fig. 2. In addition, it must be emphasized that uncontrolled electrolyte addition involves a high concentration of chloride ions, which can also act as secondary pollutants [25].

Electrolyte addition also increases the amount of sludge produced since more flocs are formed, Fig. 7.

Electrical energy consumption of magnetic stirrer and US homogenizer is measured in kWh by Emos P5821 power meter. 20 min of ultrasound consumed 0.022 kWh and 20 min of stirring consumed 0.004 kWh. The consumption of the electrodes is calculated according to the following expression [Eq. (3)] [6]:

\[
C_{\text{electricity}} = U \cdot I \cdot \frac{t}{m}
\]  

(3)

where \( U \) is the power supply voltage (V), \( I \) is the power supply current (A), \( t \) is the duration of the electrocoagulation process (h) and \( m \) is the mass of the removed COD (kg).

At best performance conditions, in Table 3 (experiment M4), the energy consumption was 254.55 kWh/kg COD.

4. Conclusions

Due to their high stability, secondary oil-in-water emulsions have proven difficult to separate by conventional treatments. However, chemical coagulants are often added to destabilize secondary oil in water emulsions. To avoid the addition of chemical coagulants, the combination of electrocoagulation and ultrasound was investigated to reduce mineral oil, COD and heavy metal concentrations.

The study showed that the experimental setup using electrocoagulation prior to ultrasound with the addition of electrolyte was the most successful for both mineral oil and COD removal, reducing the concentrations by 70% and 35%, respectively. The addition of electrolytes also had a positive effect on the removal of COD in the other two setups.

Fig. 6. The change of electric conductivity during the experiments with NaCl: M4 (EC prior to US), M5 (US prior to EC), M6 (parallel mode); EC 10 min Fe, 10 min Al, 30 V; US 20 min, 20 kHz.

Fig. 7. A comparison between (a) initial wastewater sample, (b) sedimentation process after experiment M5, (c) the amount of generated sludge with the electrolyte addition (experiment M6) and (d) the amount of generated sludge without the electrolyte addition (experiment M2).
that is, in parallel mode and when electrocoagulation was used after the ultrasound. In order to achieve higher COD removal efficiencies and to meet the standards related to the maximum allowed discharge of COD concentrations (e.g., European standard: 125 mg O$_2$/L) into the natural water bodies, it is necessary to extend the treatment time or to increase the current density.

In terms of heavy metal removal and comparison of the different setups, parallel operation with the addition of electrolyte proved to be the most efficient [Cr (99.12%), Ni (98.15%) and Pb (99.79%)].

This study also showed that the additional mixing by ultrasound positively affected the removal efficiencies. When ultrasound was used after electrocoagulation, this additional ultrasonic mixing of the already formed flocs enhanced their further flocculation and accelerated the settling process. Since settling is one of the most important steps in the electrocoagulation process, this could lead to a general reduction in sedimentation time by introducing the ultrasonic process as the final step in wastewater treatment by electrocoagulation.

Future research should focus on the optimization of process parameters for higher removal efficiency, scale-up of electrocoagulation and ultrasonic processes and the improvements in settling time at a pilot-scale wastewater treatment plant.

Acknowledgment

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Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>$I$</td>
<td>Current density, A/m$^2$</td>
</tr>
<tr>
<td>$I_p$</td>
<td>Power supply current, A</td>
</tr>
<tr>
<td>$m$</td>
<td>Mass of COD removed, kg</td>
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<tr>
<td>$t$</td>
<td>Duration of the electrocoagulation process, h</td>
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<tr>
<td>$U$</td>
<td>Power supply voltage, V</td>
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References


