Treatment of Oily Wastewater From Port Waste Reception Facilities by Electrocoagulation

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ABSTRACT: The present study investigated oil/water demulsification and treatment of oily wastewater originated from port waste reception facilities by electro coagulation using aluminum electrodes in a batch reactor. The efficiency of Al electrodes in removing SS, COD, and oil & grease from wastewater with different current densities and operational times were investigated. The characteristics of the wastewater vary in a wide range e.g. SS 13.3–660 mg/L, COD 240–2783 mg/L, and oil & grease 6.5–736 mg/L. The results of the study indicated that the SS, COD, and oil & grease can be removed effectively by EC process using Al electrodes. The optimum EC time and current density for SS removal (98.8%) was determined as 5 min and 16 mA/cm², respectively. The first 5 min of the EC process give a considerable removal of COD for all current intensities (61-90%). The optimal current density for COD removal was determined as 12 mA/cm² with the EC time of 20 min. Results indicated that oil & grease removal reached to a rate higher than 80% after EC time of 10 min for all current densities. The results demonstrated the applicability of electrocoagulation as a possible and reliable technique for the treatment of wastewater of port waste reception facilities.

Key words: Electrocoagulation, Waste reception facility, Oily wastewater, Al electrode

INTRODUCTION

The protection of the marine environment against the impact of the discharge of various types of ship-generated waste is overall regulated by specific legislations. Among many contaminants, a particular contaminant of concern is petroleum hydrocarbon present in shipyard wastewater, including the oily wastewater resulting from cleaning of ship bilges and fuel tanks (Asselin et al., 2008). Oily wastewaters from onshore and offshore industry and from engine rooms of ships (bilge waters) are one of the major pollutants of the aquatic environment (Grita et al., 2001; Karakulski et al., 1998; Yang et al., 2000). Wastewater generated from these sources generally consists of water, oils, fuels, surfactants, salts, cleaners, trace metals, glycols, and other contaminants (Penny and Yeah, 2006). Usually, the oil present in these kinds of waters is found as emulsion because of the presence of chemical emulsifiers such as cleaning agents and solvents (Penny and Yeah, 2006). Conventional oil/water separation technology consists of a chemical treatment and heating to break oil emulsions followed by a gravity separation (Benito et al., 2007; Körbahti and Arakut, 2010; Peng and Trembalay, 2008). However, a second step treatment is necessary to fulfill the current legislations (Sun et al., 2009). Currently available treatment technologies for oily wastewaters originating from ships consists of a series of physical and chemical steps, namely, free oil removal, suspended solids removal, chemical emulsion break, dissolved air floatation, clarification, and filtration. But some soluble organic components (e.g., surfactants) go untreated in these treatment steps, resulting in increased levels of BOD and COD in the plant effluent. Thus, it is very common to conduct a biological treatment, such as the activated sludge process (Chang et al., 2001). However, there is no single technology that can meet all requirements according to the variable nature of the wastewater. Electro coagulation process is playing a more prominent role in the treatment of oily wastewaters (Asselin et al., 2008), because of its several advantages including simple equipment, easy operation, low capital and operating cost and decreased amount of sludge (Tir and Mostefa, 2008). Tir and Mostefa (2008), investigated to separate oil from oily wastewater emulsion with sacrificial aluminum anode. The experimental results of their study indicated that electro coagulation was very efficient and able to achieve 99% turbidity and 90% chemical oxygen demand (COD) in less than 22 min
and current density of 25 mA/cm². Dimoglo et al. (2004), indicated that EC removes the turbidity, COD, phenol, hydrocarbon, and grease from petrochemical wastewater effectively. Asselin et al. (2008) investigated the treatment of oily bilge water using an electro coagulation technique. Under the optimal conditions they obtained removal yields higher than 90% for BOD, Oil and Grease, hydrocarbons, TSS, and turbidity. Also the removal rates for soluble and total COD were determined as 61.3 and 78.1%, respectively. El-Naas et al. (2009) evaluated the removal of sulfate and COD from petroleum refinery wastewater using aluminum, stainless steel, and iron electrodes. Their study indicated that the utilization of aluminum, as anode and cathode, was the most efficient arrangement in the reduction of both the contaminants.

The present study investigated the characteristics of wastewater samples collected after physical separation of oil/water from Haydarpasa Port (Istanbul/ Turkey) Waste Reception Plant. In this context, suspended solids (SS), total phosphorus (TP), pH, chemical oxygen demand (COD), oil & grease, chloride (Cl⁻), total Kjeldahl nitrogen (TKN), cyanide (CN⁻), fluoride (F⁻), potassium (K), iron (Fe), copper (Cu), zinc (Zn) and lead (Pb) analyses were carried out for characterization study. Additionally, treatability of wastewater by electro coagulation process as a second treatment is investigated. Oil/water demulsification and treatment of oily wastewater originated from port waste reception facilities were investigated by electro coagulation using aluminum electrodes in a batch reactor. The efficiency of Al electrodes in removing SS, COD, and oil & grease from wastewater with different current densities and operational times are investigated. Additionally, the amount of the sludge produced after each run is determined in order to observe the sludge production.

**MATERIALS & METHODS**

Haydarpasa port waste reception plant is treating wastes in the scope of Marpol 73/78 Appendix I including oil and its derivatives (bilge water, slob, sludge, contaminated ballast water, and waste oil). Wastes received by waste collecting ships are being stored in storage tanks according to their origin. The storage tanks are being heated in order to obtain a better separation of oil and water. After this separation, the emulsified water is being treated in two separators with a capacity of 12 m³/h. Wastewater generated after this separation step is being treated chemically in the treatment plant. In this study, we collected wastewater samples from the separator unit. Samples were collected weekly between February and May 2010. The schematic diagram of the experimental set-up is shown in Figure 1. Electro coagulation treatments were carried out in an 80 mm x 80 mm x 125 mm Plexiglas reactor. Electrode sets (two anodes and two cathodes) comprised four monopolar (MP) parallel aluminum plates (70 mm width x 120 mm height), each had 63 cm² effective areas and situated 1.6 cm apart. For each test, 500 mL wastewater sample was used. Electrolyte solution was not used because of high salinity of the wastewater samples. Between two tests, surfaces of electrodes were cleaned with acetone and then kept in a cleaning solution (35% 100 mL HCl and 2.8% 200 mL (CH₂)₆N₄) for at least 10 min and finally rubbed with a sponge and rinsed with tap water. Electrodes connected to positive and negative outlets of a digital DC power supply (Good Will GPC-3060D).

Fig. 1. Schematic diagram of the experimental set-up
The parameters were analyzed according to the Standard Methods for the Examination of Water and Wastewater (APHA, 2005). SS, TP (vanadomolybdophosphoric acid colorimetric method), pH, COD (open reflux-titremetric method), oil & grease (soxhlet extraction method), chloride (argentometric method), TKN (macro-Kjeldahl method), CN⁻ (Merck Spectroquant Nova 60 Photometer), F⁻ (Merck Spectroquant Nova 60 Photometer) were analyzed during the characterization studies. Additionally, metals such as K and Fe and heavy metals such as Cu and Zn were analyzed by atomic absorption spectrophotometer (Perkin-Elmer, Simaa 6000 model) during the characterization studies of wastewaters from port waste reception facilities. All chemicals used in this study were supplied from Merck (Germany) and distilled water was used in the experiments. Different time (5, 10, 20, and 30 min) and current intensity (8, 12, 16 and 24 mA/cm²) arrangements were studied in order to determine optimum conditions for oily wastewater originated from port waste reception facilities. The efficiency of the EC process for the treatment of port waste reception plant wastewater samples was measured by the removal of SS, COD, and oil & grease. Also, the amount of sludge produced at the end of EC process as dry (dried for 24 h) weight was determined.

RESULTS & DISCUSSION

Wastewater samples were collected for characterization studies after physical separation of oil and water from petroleum wastes and its derivatives generated by ships collected in Haydarpasa Port Waste Reception Plant. In this concept, pH, SS, TP, COD, oil & grease, Cl⁻, TKN, CN⁻, F⁻, Ca, K, Fe, Cu, Zn, and Pb analysis were carried out and the results are presented in Table 1.

As mentioned in the literature, petroleum wastes and its derivatives generated by ships have variable nature and characterization (Peng and Tremblay, 2008). As can be seen from Table 1, wastewater characteristics vary in a wide range. SS concentration varies between 13.3 – 660 mg/L, COD concentration varies between 240 – 2783 mg/L, and oil & grease varies between 6.5 – 736 mg/L. Exhaustively variable characteristic of oily wastewater effects treatment efficiency negatively. For this reason, alternative technologies which are not affected by variations in characteristics of influent should be investigated.

Table 1. Wastewater characterization of Haydarpasa Port waste reception plant

<table>
<thead>
<tr>
<th>Parameters</th>
<th>22.02.2010</th>
<th>01.03.2010</th>
<th>09.03.2010</th>
<th>17.03.2010</th>
<th>23.03.2010</th>
<th>25.03.2010</th>
<th>29.04.2010</th>
<th>03.05.2010</th>
<th>18.05.2010</th>
<th>24.05.2010</th>
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<tr>
<td>pH</td>
<td>7.25</td>
<td>8.06</td>
<td>6.77</td>
<td>6.83</td>
<td>6.36</td>
<td>6.98</td>
<td>7.33</td>
<td>6.34</td>
<td>6.50</td>
<td>6.68</td>
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<tr>
<td>SS (mg/L)</td>
<td>327</td>
<td>660</td>
<td>123.8</td>
<td>139</td>
<td>143.8</td>
<td>182.3</td>
<td>245</td>
<td>13.3</td>
<td>177</td>
<td>500</td>
</tr>
<tr>
<td>Cl⁻ (mg/L)</td>
<td>21527</td>
<td>8257</td>
<td>9297</td>
<td>10346</td>
<td>23727</td>
<td>7817</td>
<td>9796</td>
<td>10566</td>
<td>7890</td>
<td>13206</td>
</tr>
<tr>
<td>O&amp;G (mg/L)</td>
<td>125</td>
<td>200</td>
<td>56</td>
<td>6.5</td>
<td>110</td>
<td>440</td>
<td>39</td>
<td>50</td>
<td>736</td>
<td>230</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>587</td>
<td>2783</td>
<td>240</td>
<td>661.5</td>
<td>497.5</td>
<td>674</td>
<td>1145</td>
<td>256</td>
<td>590.6</td>
<td>1445</td>
</tr>
<tr>
<td>TP (mg/L)</td>
<td>0.42</td>
<td>0.61</td>
<td>0.536</td>
<td>0.587</td>
<td>0.192</td>
<td>0.674</td>
<td>0.434</td>
<td>0.33</td>
<td>0.814</td>
<td>0.276</td>
</tr>
<tr>
<td>CN⁻ (mg/L)</td>
<td>0.053</td>
<td>0.15</td>
<td>0.143</td>
<td>0.102</td>
<td>0.080</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
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<tr>
<td>F⁻ (mg/L)</td>
<td>0.2</td>
<td>1.63</td>
<td>0.91</td>
<td>0.13</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
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<tr>
<td>TKN (mg/L)</td>
<td>19.6</td>
<td>32.2</td>
<td>32.2</td>
<td>30.7</td>
<td>21.7</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>K (mg/L)</td>
<td>941</td>
<td>590</td>
<td>497</td>
<td>484</td>
<td>1528</td>
<td>448</td>
<td>ND</td>
<td>ND</td>
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<tr>
<td>Ca (mg/L)</td>
<td>514</td>
<td>626</td>
<td>790</td>
<td>274</td>
<td>568</td>
<td>679</td>
<td>ND</td>
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<td>Fe (mg/L)</td>
<td>0.755</td>
<td>1.039</td>
<td>1.188</td>
<td>1.143</td>
<td>0.388</td>
<td>0.305</td>
<td>ND</td>
<td>ND</td>
<td>4.05</td>
<td>ND</td>
</tr>
<tr>
<td>Cu (mg/L)</td>
<td>0.088</td>
<td>0.063</td>
<td>0.055</td>
<td>0.030</td>
<td>0.053</td>
<td>0.060</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Zn (mg/L)</td>
<td>0.506</td>
<td>0.472</td>
<td>0.581</td>
<td>0.496</td>
<td>0.502</td>
<td>0.221</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Pb (mg/L)</td>
<td>0.862</td>
<td>0.712</td>
<td>0.610</td>
<td>0.668</td>
<td>0.836</td>
<td>0.608</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>
Treatment studies were conducted with 8, 12, 16, and 24 mA/cm² current intensities in order to investigate treatability of petroleum wastes and its derivatives generated by ships. Kobya et al. (2003) suggested that current intensity and operating time could influence the treatment efficiency of electro coagulation process. In this concept, treatment studies were conducted in 5, 10, 20, and 30 minutes for each current intensity. After treatment and settling processes, samples were collected from aqueous phase and SS, COD, and oil & grease analysis were conducted. Additionally, the amount of the sludge produced after each run is determined in order to observe the sludge production.

The variations of pH during the electro coagulation studies are shown in Fig. 2. From previous studies (Hu et al., 2005; Modishahla et al., 2007; Yilmaz et al., 2005) the treatment process can be described by Equations (1)–(3) when Al is used as electrode material. The electrochemical reactions (1, 2) are followed by the chemical one (3) (Kobya et al., 2003).

\[ 3H_2O + 3e^- \rightarrow \frac{3}{2}H_2 (g) + 3OH^- \]  

(1)

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

(2)

\[ Al^{3+} (aq) + 3H_2O \rightarrow Al(OH)_3 + 3H^+ (aq) \]  

(3)

According to Fig. 3, SS concentrations were measured below 200 mg/L in first 5 min for all current intensity and then no significant change observed. The maximum SS removal rates were observed as 77.6 and 73.6% for the current densities of 8 and 12 mA/cm², respectively. On the other hand, SS removal rate was determined as 98.8% for 16 and 24 mA/cm² current densities after the treatment times of 5 and 10 min, respectively. Thus, it can be concluded that the optimum current density and treatment time for suspended solids removal (98.8%) was 16 mA/cm² and
5 min. Longer treatment times then 10 min results with the increase in SS concentrations for 16 and 24 mA/cm². Asselin et al. (2008), indicated that during electro coagulation treatment, some fine particles of hydroxides re-enter the suspension, which can slightly affect the TS and TSS concentrations (e.g. increase in turbidity).

Chemical oxygen demand (COD) is a measure of the amount of the oxygen used in the chemical oxidation of inorganic and organic matter present in wastewater. Although COD is not a specific compound, it is considered a conventional pollutant, and it has been widely used by regulatory agencies worldwide to gauge overall treatment plant efficiencies. It is also an indicator of the degree of pollution in the effluent and of the potential environmental impact of the discharge of wastewater in bodies of water (Moreno et al., 2007).

The characterization studies show that COD concentrations varies between 240 and 2783 mg/L in wastewater samples collected from Haydarpasa Port waste reception facility, while the average COD concentration is 900 mg/L. COD of the sample used in the electro coagulation treatment studies was 1445 mg/L. The change of the COD concentrations during electro coagulation treatment for different current densities is given in Fig. 4. As seen in the fig. the removal efficiencies of COD increase according to time. The first 5 min of the EC process give a considerable removal of COD for all current densities (61-90%). The increase in the EC time to 20 min results in removal efficiency to reach 93% for current densities except for 8 mA/cm². Therefore, the optimal time for the COD removal by EC treatment of Haydarpasa Port waste reception facility is around 20 min. Otherwise, from an energetic point of view the optimal current density for the COD removal is determined as 12 mA/cm². These results are in agreement with the results obtained by Tir and Mostefa (2008) who obtained 90% COD removal after 20 min treatment time with 20 mA/cm² current density.

Moreno et al. (2007) indicated that when COD is highly removed, compounds that react with metals to form insoluble compounds such as suspended solids, fecal coliforms, turbidity, fats oil and grease, and suspension such as milk and TSS will be completely removed. This is due to the in situ generated coagulants. The portion of the remaining COD will be the soluble portion of parameters that does not react with Al to form insoluble compounds (Moreno et al., 2007).

Oil & grease in wastewater can exist in several forms: free, dispersed or emulsified (Cheryan and Rajagopalan, 1998). Presence of detergents, surfactants and/or high suspended solids in wastewaters from waste receiving facility causes chemical emulsification of oil (Körbahti and Artut, 2010) and it is extremely hard to remove small droplet sized and emulsified oil & grease by gravity based classical methods. Electro coagulation directly addresses three main factors that lead to a stable suspension of suspended solids and emulsified oils: ionic charge, droplet or particle size, and droplet or particle density (Asselin et al., 2008).

Oil and grease concentrations varied between 6.5 and 736 mg/L and the average concentration was 200 mg/L in the analyzed samples from Haydarpasa Port waste reception facility. Oil and grease concentration of the wastewater sample used in the EC treatment studies was 590.6 mg/L.

Fig. 5 presents oil and grease variations during EC treatment of oily wastewater for 8, 12, 16 and 24 mA/cm² current intensities. As seen in the figure, the removal of oil and grease has the same trend as for the COD removal was. For the first 10 min, oil and grease removal reached to a rate higher than 80% for all current intensities. Increasing EC time did not affect the removal rate significantly. The maximum removal rate (93.2%) observed for 8 mA/cm² and 30 min EC time. The removal rates for 12, 16, and 24 mA/cm² for 30 min EC time were determined as 73.2, 89.5, and 79.7%, respectively.

The amount of coagulant generated at fixed time during the EC treatment is related to the current flow. The presence of coagulant in solution contributes to an increase of oil removal efficiency by flotation. This phenomenon can be attributed to (i) flocculation of the oil droplets, (ii) reduction of electrostatic repulsion
between the air bubble and oil droplets, and (iii) an increase of oil droplets hydrophobicity (Tir and Mostefa, 2008). Experimental results indicated that increasing the EC time and current intensity results by the fine oil emulsions to re-enter to the solution and thus, increase slightly the oil concentration in the treated water.

EC forms less sludge which is readily settable and easy to dewater as it is primarily composed of metallic oxides and hydroxides. Flocs formed by EC are similar to chemical flocs except that EC flocs are larger, contain less bound water and are more stable. Hence, they can be separated faster by settling and filtration (Kumar and Goel, 2010). Kobya et al. (2007) stated that sludge amount increases with increasing current density for all connection modes and electrode material types. Also, EC sludge production is proportional to characteristics of raw wastewater, settable solids and matter destabilized by coagulation and concentration flocculent (Kobya et al., 2006).

Fig. 6 gives the amount of produced sludge after the treatment times for the studied current densities. The amount of the produced sludge was 12,000 mg/L for 8 mA/cm², while it is increased to 24,000 mg/L for 16 mA/cm². The sludge production was increased when current density was increased from 8 to 16 mA/cm². Correspondingly, the water quantity was decreased. Also it is indicated that the amount of the produced sludge increased with the increasing removal rate of SS, COD, and oil & grease.

![Fig. 5. Effect of operating time and current intensity on oil & grease removal](image1)

![Fig. 6. Effect of current intensity on sludge production](image2)
CONCLUSION

This study investigated the applicability of electro coagulation method in the treatment of wastewater from a port waste reception facility. After a detailed characterization of the wastewater, the influence of variables such as electrolysis time, current density, type of electrode material on the removal of SS, COD, and oil & grease has been determined.

Wastewater samples were collected after the physical separation of oil and water in Haydarpasa Port waste reception facility. The average concentrations of SS, COD, and oil & grease were determined as 250, 900, and 200 mg/L, respectively. Also, wastewater samples can be characterized with almost neutral pH, high chloride content, and low metal concentrations. However, the characterization studies showed the characteristics of wastewater from port waste reception facilities contain pollutants in wide range. The experimental studies were conducted in a batch electro coagulation cell using Al electrodes. The results of the study showed that SS, COD, and oil & grease can be removed effectively by this method in a short reaction period. The optimal EC time for the removal of these pollutants was determined to be 20 min, while the optimum current intensity was 16 mA/cm². Removal efficiencies for SS, COD, and oil & grease under these conditions were determined as 98.8, 93, and 81%, respectively. The results indicate that the application of electro coagulation process in the treatment of oily wastewater from a port waste reception plant reached quite high removal efficiencies in a short time. The study demonstrated that electro coagulation may prove to be a practical approach for the treatment of oily wastewater generated after physical oil/water separation unit of port waste reception facilities.

REFERENCES


