Performance and Kinetic Study on Oil Removal Via Electrocoagulation Treatment

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Abstract. Electrocoagulation (EC) is a reliable technology for wastewater treatment. It has been applied in treating various source of wastewater from tannery, electroplating, dairy, textile processing, oil and oil-in-emulsion. It is crucial to strengthen the fundamental of the EC treatment on oily water sample for further studies. However, in depth studies on the performance of EC treatment on oily water sample is still requires in depth studies. In this research, a series of experiment has been conducted on the performance of EC treatment including effect of the amount of sodium chloride (NaCl), applied voltage and pH to determine the efficiency in oil removal. The EC treatment took placed in room temperature and constantly agitated for 30 minutes meanwhile samples were collected for every 5 minutes for UV–Vis analysis. Then, the efficiency of the treatment was determined followed by simulating the results in kinetic models. The highest efficiency of EC treatment was achieved with 89.26% of oil removal with the addition of 7.5g of NaCl, 4V of applied voltage and at pH 6. In addition, the results have better fitness towards pseudo second order (PSO) which indicates the mechanism of EC treatment is chemisorption.

1. Introduction

Alternative green treatment system has gained researchers’ attentions like electrocoagulation (EC) technology. EC is well known by its superior properties such as energy efficiency, cost effective, simple operation and minimal chemical usage \cite{1-2}. EC treatment is highly recommended in treating oily wastewater. This is due to EC treatment is capable of destabilizing and neutralising emulsified oil droplets in wastewater via redox reaction and separate/remove them through adsorption by the coagulant produced. In fact, EC technology has tackled on the residual oil issue (emulsified oil, dissolved oil and oil droplets) which cannot be done by conventional treatment such as skimming and gravitational separation. EC treatment takes place by supplying DC voltage to the electrodes (commonly is iron or aluminium metal). There are several mechanisms involved in EC treatment which make it efficient as pre-treatment system. As the electrical charge passes through the anode, the anodic electrode will undergo dissolution and produce positively charged metal ions. Equation (1) shows the reaction take place at the anode.
Then, the metal ion will be hydrolysed into metal hydroxide (Equation (2)) which will destabilise the colloidal particles in the solution.

\[
M^{n+}(aq) + nH_2O(l) \rightarrow M(OH)_n(s) + 3H^+(aq)
\]  

(2)

The metal hydroxides also act as coagulants where the destabilised colloidal particles will agglomerate with the coagulants and precipitate out. Precipitated colloidal particles that sink at the bottom of the vessel are known as sludge however with the help of the effervescences produce at the cathode (Hydrogen, H\(_2\)) (Equation (3)), some of the precipitated particles will float at the surface of the water as flocs. Both the sludge and flocs can be easily removed by gravitational separation or filtration.

\[
2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)
\]  

(3)

However, to our best knowledge there are limited studies conducted on the oil removal of oily water sample by EC technology. Plus, the mechanism of this technology still requires in depth investigations. Thus, this paper aims to study the performance of EC treatment in oil removal under different conditions such as the amount sodium chloride (NaCl), applied voltage and pH. Correspondingly, the results obtained will be simulated with kinetic models such as Pseudo first order (PFO) and Pseudo second order (PSO) to determine the mechanism of the EC treatment.

2. Methodology

2.1. Preparation of synthetic oily water sample

1L of synthetic oily water sample was prepared by mixing 0.1% w/w of store bought cooking palm oil, 0.01% w/w of non-ionic surfactant (Tween 80) and salinized with sodium chloride (NaCl) as supporting electrolyte. The mixture was homogenised with a homogeniser at 10,000 rpm for 10 minutes.

2.2. EC system

Laboratory scale EC cell was set up as illustrated in figure 1. 1L beaker was used as the vessel for the treatment process and aluminium plates as electrodes (both anode and cathode). The working surface area of the electrodes was 10cm × 7cm and placed in a monopolar arrangement with 2cm gap in between. The electrodes were connected to a DC supply meter which output voltage can be controlled [3].
2.3. Performance studies of EC treatment

The efficiency of the EC treatment was investigated in terms of the removal capacity of oil. The EC treatment was carried out with different amounts of NaCl (2.5g, 5.0g, 7.5g and 10.0g), applied voltage (1V, 2V, 3V and 4V) and pH (3, 5, 6, 7 and 8). Every batch was run for 30 minutes and samples were collected every 5 minutes. The samples were then filtered with filter paper prior to UV-Vis analysis at 231nm wavelength. The percentage of oil removal was calculated with Equation (4).

\[
% \text{Oil removal} = \left( \frac{C_i - C_f}{C_i} \right) \times 100%
\]  

(4)

where \(C_i\) is the initial concentration of the oil and \(C_f\) is the final concentration of oil.

2.4. Kinetics studies

Kinetic studies were investigated in order to understand the rate degradation of the EC treatment. Results obtained from the performance tests were simulated with Pseudo First Order (PFO) (Equation (5)) and Pseudo Second Order (PSO) (Equation (6)). The parameter estimation of the kinetic model was obtained from nonlinear least-square regression using the Levenberg-Marquardt method Polymath R Version 6.2 (CACHE Corp., USA) software. The software was applied in order to estimate the value of parameters within the non-linear equations from the experimental results by minimizing the sum of square error [4].

\[
C = C_e - \exp(-k_{1}t) \left(C_e - C_0 \right)
\]  

(5)

\[
C = C_e + \frac{1}{\left(k_{2}t \right)} - \frac{1}{\left(C_e - C_0 \right)}
\]  

(6)

where \(C_e\) and \(C_0\) are the concentration of O&G at equilibrium and initial, respectively; \(k_n\) is the rate constant of the pseudo-n-th order kinetic model per minute; \(t\) is the interval time.

3. Results and discussion

3.1. Effect of NaCl

NaCl is a good supporting electrolyte which able to enhance the ionic conductivity of the electrolyte and correspondingly boost the current efficiency of the EC treatment process. Cl ions also aid in breaking down the passive films of the aluminium electrodes and triggering corrosion pitting.
phenomena [5-6]. This will increase the rate of dissolution of the anode electrode thus more metal ions are produced and hydrolysed to form coagulant for the removal of oil droplets. Figure 2 shows the effect of NaCl on the percentage of oil removal.

From the figure 2, it shows that the percentage of oil removal increased with the addition of NaCl from 2.5g to 7.5g with the percentage of oil removal of 74.55%, 77.29% and 77.76% but decreased to 70.54% with the addition of 10.0g of NaCl. Similar results were also reported in other EC studies [7]. High amount of NaCl will be able to induce the conductivity of the electrolyte. Moreover, with the present of high concentration of Cl\textsuperscript{-} ions the rate of anode passivation will decrease while increase the current efficiency of the Al anode dissolution. Hence, the efficiency of the system is increased with better performance in oil removal. However, to an extent, the abundance NaCl in the electrolyte causes a strong interionic attraction between the NaCl and Al\textsuperscript{3+} ions that reduces the activity and diffusivity of the metal ions. Therefore, the coagulant produced is drawn towards NaCl and less effective in oil removal [7].

3.2. Effect of applied voltage

Voltage is also one of the important factors in determining the efficiency of the EC treatment. The applied voltage has direct effect towards the amount of coagulant, the rate and size of the effervescence as well as the growth of the flocs [8]. The effect of the applied voltage on the percentage removal of oil can be observed in figure 3.

**Figure 2.** shows the effect of different amount of dissolved NaCl towards the percentage of oil removal.

**Figure 3.** shows the effect of applied voltage on percentage of oil removal.
As the applied voltage increased from 1V, 2V, 3V and 4V, the percentage of oil removal increased accordingly, 65.23%, 70.11%, 74.94% and 75.15%. From this result, it can be determined that 4V has the highest removal rate of oil. In fact, at higher voltage, the rate of dissolution of anode electrode increases with a consequent increase of Al$^{3+}$ ions. High concentration of Al$^{3+}$ ions will result in neutralising more anionic oil droplets and coagulation takes place to form sludge or flocs with the aid of the catholically evolved hydrogen gas, H$_2$. Thus, the efficiency of the treatment system is improved at higher voltage. Contrariwise, at low applied voltage the rate of dissolution of metal ions is low as well as the rate of the formation of sludge and flocs. Plus, less amount of hydrogen produced at the cathode results in low efficiency treatment system. So, to achieve the same efficiency as 4V, longer treatment period is required with lower applied voltage.

3.3. Effect of initial pH

The performance of the treatment system is also significantly affected by initial pH. Efficiency of the treatment changes with different initial pH. This is because at different initial pH various type of hydrolysed aluminium ions and flocculants will be produced plus the stability of the samples will also be affected [3]. The results obtained from the experiment were plotted in graph as shown in Figure 4.

![Figure 4. shows the effect of pH on percentage of oil removal.](image)

As plotted in figure 4, the percentage of oil removal was increasing at acidic environment from pH 3 (13.15%) to pH 5 (77.21%) and the highest percentage of oil removal was achieved at pH 6 with 89.26% of oil removal. Instead of increasing, the efficiency of the system decline slightly at neutral condition with 86.73% of oil removal and downward trend was shown when the sample was in alkaline condition. At pH 8, only 78.28% of oil was removed from the oil sample. The result obtained is similar with study conducted by Priya, M. and Jeyanthi, J on the removal of oil and grease from automobile wash water effluent where the highest efficiency of the treatment occurs at pH 6 with 92.5% [9]. EC treatment mainly involves the oxidation-reduction mechanisms where the reactions transformed the dissolved organic molecules into organometallic compounds [9]. In fact, at very low pH (pH < 4), the coagulants produced are dominated by positively charged compound which are actively neutralising the negatively charged oil droplets. The coagulants produced are highly positive such as Al(H$_2$O)$_6^{3+}$ and [Al(H$_2$O)(OH)]$^{12+}$ that is capable for destabilising emulsified oil droplets, yet the tendency to form agglomerates are low. As the pH approaches neutrality, more polynuclear aluminium complex ions are formed and these complexes has higher tendency for polymerization with less positively charged ions which favours the adsorption of the emulsified oil droplets [3]. Thus, the percentage of oil removal is high. At alkaline pH, more negative charged coagulants are formed like
Al(OH)$_3$ and Al(OH)$_4^{2-}$ which are soluble in water and electrostatically repelled by the negatively charged emulsified oil droplets, hence reduces the efficiency of the system [3].

3.4. Kinetic study

EC treatment involves complex mechanism. In order to describe the nature and mechanism of EC technology, kinetic modelling was studied. Kinetic models are able to describe the interaction between the absorbate and the absorbent such as physisorption or chemisorption. The mechanism is determined by using curve fitting method based on the data obtained from the experiment. Table 1 shows the tabulated data on the estimated parameter and $R^2$ values of PFO and PSO models fitting curve for each parameters (amount of NaCl, applied voltage and pH). whereas figure 5 (a), (b) and (c) illustrate the curve fitting for the experimental and simulated value of PSO for each parameters. From table 1, the EC treatment has better fitting towards PSO with higher $R^2$ values compared to PFO. This indicates that the EC treatment taken place via chemisorption where the process involves the oxidation and reduction between the metal ions and emulsified oil to form sludge and flocs.

Table 1. Estimated parameter values of the PSO models by the numerical calculations for the EC process with different amount of NaCl, applied voltage and initial pH.

| Parameter | Pseudo first order (PFO) | Pseudo second order (PSO) |
|-----------|--------------------------|---------------------------|
|           | $C_e$ $k_1$ $C_0$ $R^2$ | $C_e$ $k_1$ $C_0$ $R^2$ |
| 2.5g NaCl | 276.0385 0.6879 995.8137 0.9966 | 260.7770 0.0039 998.8226 0.9981 |
| 5.0g NaCl | 246.2074 0.5324 1001.2680 0.9982 | 222.7920 0.0023 1001.3500 0.9997 |
| 7.5g NaCl | 243.0128 0.5141 997.3326 0.9974 | 216.6864 0.0021 997.4423 0.9993 |
| 10.0g NaCl| 311.5622 0.5201 999.4851 0.9979 | 288.8637 0.0024 999.5590 0.9994 |
| 1V        | 357.8494 0.4706 995.9353 0.9984 | 332.8759 0.0021 996.0932 0.9999 |
| 2V        | 309.2180 0.5580 996.9444 0.9989 | 291.0363 0.0030 996.9927 0.9998 |
| 3V        | 266.9016 0.4986 997.1863 0.9984 | 241.3243 0.0021 997.3000 0.9998 |
| 4V        | 270.8735 0.4774 998.0576 0.9983 | 243.7425 0.0019 998.1527 0.9993 |
| pH 3      | 853.9224 0.1227 1004.2480 0.8909 | 788.6454 0.0004 1002.0460 0.9267 |
| pH 5      | 239.9252 0.5061 1001.6910 0.9994 | 216.1981 0.0022 1001.6890 0.9999 |
| pH 6      | 113.5074 0.6350 998.7670 0.9997 | 98.3871 0.0037 998.7891 1.0000 |
| pH 7      | 141.1103 0.4547 999.8617 0.9984 | 106.0024 0.0015 1000.1620 0.9997 |
| pH 8      | 230.4735 0.5527 998.9937 0.9987 | 209.3615 0.0026 999.0423 0.9997 |

Figure 5(a). Model fitting of the experimental data to the PSO model describing EC process over time with the effect different amount of NaCl.
Figure 5(b). Model fitting of the experimental data to the PSO model describing EC process over time with the effect of different supply voltage.

Figure 5(c). Model fitting of the experimental data to the PSO model describing EC process over time with the effect of different initial pH.

5. Conclusion
The efficiency of the EC treatment is dependent on the studied parameters. The amount of NaCl will determine the conductivity of the system while applied voltage will enhance the activity and diffusivity of the metal ions to produce more metal hydroxide for the coagulation purpose whereas pH will determine the type of metal hydroxide and flocculent produced and the stability of the emulsified oil samples. From this study, it was identified that the EC treatment has the best efficiency with the addition of 7.5g of NaCl, applied voltage of 4V and in pH 6 environment which achieved the percentage of oil removal of 89.26%. EC treatment mainly undergoes oxidation and reduction reaction of metal ions and negatively charged emulsified oil droplets to form sludge and flocs so its mechanisms naturally inclined towards PSO, chemisorption.
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