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Oil removal from an oil-in-water emulsion by electrochemical process using Taguchi method

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ABSTRACT

In this study an electrochemical treatment process of an oil-in-water emulsion was investigated using an anode composed of carbon-polytetrafluoroethylene and manganese oxide as an electrocatalyst. The effects of operating parameters including initial chemical oxygen demand (COD), NaCl concentration, pH, voltage and time on decreasing COD of the emulsion were studied. The Taguchi method was used in the design of experiments, and to analyze data. $L_{16}(4^5)$ orthogonal array was selected for experimental designing. Analysis of variance was applied to determine optimum conditions and the most significant parameters affecting the response of the process. According to the results of analysis, time is the most effective parameter, with percentage contribution of 65.6% followed by NaCl concentration of 17.49%, voltage of 7.29%, and initial COD concentration of 7.09%. Also it was found that pH has an insignificant effect on COD removal percentage. The optimum conditions were found as follows: the fourth level of initial COD (1,200 mg/L) and NaCl concentration (1,500 mg/L), third level of voltage (5 V) and fourth level of time (180 min). Finally the confirmation test was performed under optimum conditions. Observed value of this experiment (70.11%) was within the range of confidence limit of predicted performance (73.19 ± 5%).

Keywords: Oil-in-water emulsion; Electrocatalyst; Electrochemical treatment; Taguchi method

1. Introduction

Fats, oil, and grease (FOG) exist in various forms in waste water, floating oil, in an emulsion, or bound with solids. Free floating oil would be separated by gravity. Emulsified oil is the stable oil in aqueous mixtures that cannot be separated by gravity alone. Emulsions are physical or chemical. Physical emulsions are produced mechanically and are less stable than chemical emulsions. Chemical emulsions are usually found in metalworking fluids. They are mixtures of two immiscible liquids stabilized by an emulsifying agent. The sources of FOG consist of food processing, metalworking and petroleum industries and other industries. Lubricants, coolant, and cutting oils are used as metalworking fluids. Petroleum refinery wastes also include free and emulsified oil that may contain crude oil, light and heavy hydrocarbon fuels, tars, and waxy emulsions [1]. This kind of pollutants would be separated by many processes consisting chemical, physical, biological, and electrical methods. This phase of treatment requires breaking emulsion. In chemical method, coagulants mostly iron and aluminum salts are used to break emulsion [2,3]. Then, separation with settling or flotation would be done as the next step. This process is costly and creates excessive chemical sludge. Physical methods consist of heating, centrifugation, ultra-filtration, carbon adsorption, and membrane process. These methods

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have some problems such as high cost, regeneration requirement, low rate, and membrane fouling. Application of electrochemical technology such as electro-oxidation, electrocoagulation and electroflotation for treatment of various wastewaters has been reviewed by Chen [4]. Electroflotation provides an excellent alternative for the treatment of oil-in-water emulsions [5]. In an electrocoagulation process, coagulants are generated from a sacrificial anode mostly iron or aluminum. It involves three main processes: electrolytic reaction at electrode surface, formation of coagulants by electrolytic oxidation in aqueous phase and adsorption of colloidal particles on coagulant, and removal by sedimentation or flotation [6]. Electrochemical oxidation is performed in situ electro-generation of strong oxidants that shows better efficiency in comparison with chemical destruction [7]. Electrochemical oxidation is divided into direct oxidation and indirect-oxidation. In direct oxidation, pollutants are oxidized by hydroxyl radicals produced at the electrode surface but in indirect-oxidation, oxidants which are produced from destruction of radicals continue the oxidation process [8]. These reactions are in competition with oxygen-evolution reaction. Nature of anodic material influences both the selectivity and the efficiency of process [7]. During the last two decades, many studies have been done on anode material as the most important part of electrochemical cell. Graphite, Pt, PbO_2, IrO_2, SnO_2, and conductive diamond films have been widely employed as the anode [4]. Some advantages of electrochemical methods are versatility, energy efficiency, and amenability to automation, environmental compatibility and cost efficiency [7]. In this work; treatment of an oil-in-water emulsion was investigated by studying the parameters, such as initial COD concentration, conductivity, voltage and time, on electrochemical oxidation process in a laboratory scale. Anode was composed of carbon-polytetrafluoroethylene (PTFE) and manganese oxide as an electrocatalyst and cathode was stainless steel. The design of experiments and the analysis of results were done based on the Taguchi method.

2. Experimental

2.1. Wastewater samples

Oil-in-water emulsions were prepared from tap water and 80 wt.% heavy diesel from Oil refinery (Company of Shazand in IRAN) and 20 wt.% from a non-ionic surfactant (Tween®80 from Acros organics Co.) as an emulsifier. The solution was constantly stirred at 200 rpm with a magnetic stirrer for 20 min in order to maintain uniform concentration of the solution. This mixture was diluted to desirable oil concentrations and exhibited chemical stability. Some specifications of diesel are available such as: SP gravity 15.5/15.5(℃) = 0.8265, IBP = 239℃, FBP = 380℃, flash point = 111℃, total sulfur = free.

2.2. Experimental devices and methods

The electrochemical cell consists of a glass vessel with two electrodes positioned vertically and parallel to each other with an inner gap of 15 mm. The superficial surface of the working electrode was approximately 20 cm^2. The electric power was supplied with a DC power supply. The current and voltage could be adjusted between 0–2.5 A and 0–35 V respectively. The initial pH of the solution was measured using a digital WTW pH meter (Model 740i, Germany). H_2SO_4 and NaOH were used to adjust pH at desirable value. All experiments were performed at ambient temperature (20–25℃). Temperature increased with time, although it did not exceed 45℃ in the longest test (180 min). The treated samples were taken from the bottom of vessel.

Chemical oxygen demand (COD) was chosen as criteria to evaluate performance of the process and was measured according to the Standard Methods [9].

2.3. Electrode preparation

The anode was a very thin conductive porous sheet comprising 70% carbon (721 $m^2 g^{-1}$ surface area supplied by Iranian Co., Iran), 30% PTFE powder (Aldrich Co.), and 8% (in proportion to weight of carbon and PTFE) manganese oxide (II) (Merck Co.). The conductive porous sheet was prepared by thorough mixing of carbon, PTFE, and powder of manganese oxide (II). The uniform mixture was extruded into a sheet and expanded on a silver-plated nickel mesh (5 cm × 4 cm × 4 mm) as a current collector.

2.4. Design of experiments

Taguchi method is a statistical method used to design and analyze experiments. For the Taguchi designing and analyzing, the software Qualitek-4 was applied. Orthogonal arrays are used to reduce and design experiments. The appropriate orthogonal array is selected based on the number of parameters and their levels. Table 1 shows parameters and their levels that were considered in this study. $L_{16}(4^5)$ orthogonal array involving 16 experiments for five

Table 1
Parameters and value of experiments

Parameter	Level			
	1	2	3	4
COD (mg/L)	500	700	900	1,200
NaCl concentration (mg/L)	500	750	1,000	1,500
pH	2	3	4	5
Voltage (V)	3	4	5	6
Time (min)	45	90	135	180

parameters with four levels was selected. In this work, COD removal percentage was defined as the response of the process (Eq. (1)). COD_0 and COD_t are COD at initial time and after passing time t respectively.

$$\text{COD removal percentage} = \frac{COD_0 - COD_t}{COD_0} \times 100 \tag{1}$$

2.5. Analysis of variance (ANOVA)

ANOVA and the F-test (standard analysis) are utilized to investigate influence and relative importance of the parameters. ANOVA is a technique for optimization of observed values based on Taguchi method. F-test is used to determine which factors significantly affect on response of process. These analyses are performed as follows [10]:

$$CF = \frac{T^2}{n} \tag{2}$$

$$SS_T = \sum_{i=1}^{16} Y_i^2 - CF \tag{3}$$

$$SS_A = \left(\sum_{i=1}^{k_A} \frac{Ai^2}{n_{Ai}}\right) - CF \tag{4}$$

$$f_A = (\text{number of levels of parameter A}) - 1 \tag{5}$$

$$f_T = (\text{total number of experiments}) - 1 \tag{6}$$

$$f_e = f_T - \sum f_A \tag{7}$$

$$V_A = SS_A / f_A \tag{8}$$

$$SS_e = SS_T - \sum SS_A \tag{9}$$

$$V_e = SS_e / f_e \tag{10}$$

$$F_A = V_A / V_e \tag{11}$$

$$SS'_A = SS_A - (V_e \times f_A) \tag{12}$$

$$P_A = \frac{SS'_A}{SS_T} \times 100\% \tag{13}$$

$$P_e = \left(1 - \sum P_A\right) \times 100\% \tag{14}$$

where CF is correction factor, T is total of all results, n is total number of experiments, SS_T is total sum of squares to total variation, Y_i is value of results of each experiment ($i = 1$–16), SS_A is sum of squares of parameter A, K_A is number of the levels of factor A, n_{Ai} is number of all experiments at level i of factor A, A_i is sum of all experiments of level i of factor A, f_A is degree of freedom (DOF) of parameter A, f_T is total degree of freedom, f_e is DOF of error term, V_A is variance of parameter A, SS_e is sum of squares of error term, V_e is variance of error term, F_A is F ratios of parameter A, SS'_A is pure sum of square, P_A is percentage contribution of parameter A, P_e is percentage contribution of error term.

3. Result and discussion

3.1. Data analysis

All the analyses were performed based on Taguchi method and by Taguchi software (Qualitek-4). Results of ANOVA analysis are listed in Table 2. The main effects of each parameter are calculated by averaging responses at each level of each factor. These values indicate the trend of effects of each factor as shown in Figs. 1–4. According to results of ANOVA, time with the largest variance is the most important parameter. The importance of the parameters decreases in order from NaCl concentration to voltage and initial COD concentration. Error DOF is calculated by Eq. (7). This quantity was zero in this work. Therefore, the variance of error and F-ratio cannot be calculated. Due to ignorable variance of pH, this parameter could be considered insignificant. After pooling pH, values of F-ratio were calculated as given in Table 3. If the calculated F-ratio exceeds F_{cr}-critical value, it indicates that the statistical test

Table 2
ANOVA analysis and *F*-test

Factor	DOF	Sum of sqrs (*S*)	Variance (*V*)	Percent *p*%
COD (mg/L)	3	77.981	25.993	7.593
NaCl concentration (mg/L)	3	184.817	61.605	17.995
pH	3	5.175	1.725	0.503
Voltage (V)	3	80.063	26.687	7.795
Time (min)	3	678.962	226.32	66.111
Total	15	1,027.002		100.00

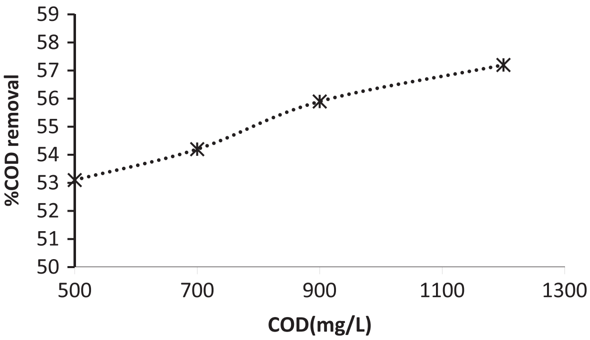

Fig. 1. The effect of initial COD concentration on pollutant removal.

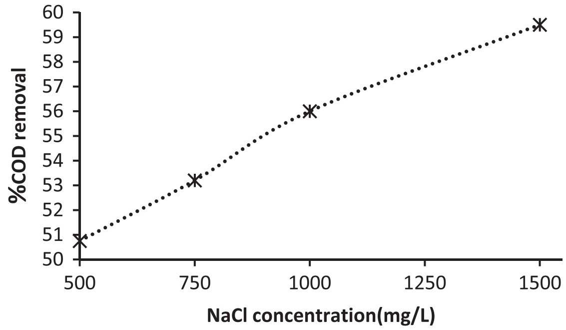

Fig. 2. The effect of NaCl concentration on pollutant removal.

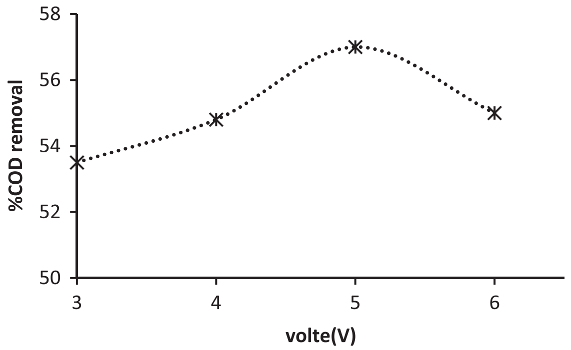

Fig. 3. The effect of voltage on pollutant removal.

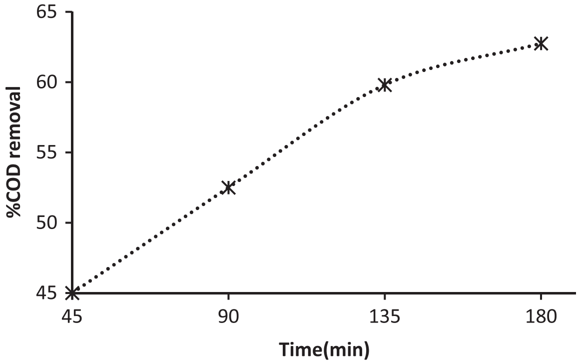

Fig. 4. The effect of time on pollutant removal.

Table 3
Pooled ANOVA analysis and *F*-test

Factor	DOF	Sum of sqrs (*S*)	Variance (*V*)	*F*-ratio (*F*)	Pure sum (*S*′)	Percent *p*%
COD (mg/L)	3	77.981	25.993	15.067	72.806	7.089
NaCl concentration (mg/L)	3	184.817	61.605	35.711	179.641	17.491
pH	(3)	(5.175)	1.725	POOLED	(CL = *NC*)	
Voltage (V)	3	80.063	26.687	15.47	74.887	7.291
Time (min)	3	678.962	226.332	131.191	673.787	65.607
Error	3	5.177	1.725			2.522
Total	15	1,027.002				100

Note: Tabulated *F*-ratio at 95% confidence level: F0.05; 3; 3 = 9.2766.

is significant at the selected confidence level. In this study DOF of error was 3. The F_{cr}-critical value of all parameters for DOF of 3 at a confidence level of 95% is 9.2566 [10]. *F*-ratios are used only for qualitative evaluation. For quantitative evaluation, percentage contribution (%*P*) is used. According to the results in Table 3, time is the most important parameter with percent contribution of 65.61%. Effect of NaCl concentration with percent contribution of 17.49% is also noticeable. Initial COD concentration and applied voltage have the same effects of 7.089% and 7.291% respectively.

3.2. Response graphs

The main effects of each parameter are calculated by averaging responses at each level of each factor. Figs. 1–4 show the effect of each parameter on the response of the process when they vary from one level to another.

3.2.1. Effect of COD concentration

Effect of COD concentration on removal efficiency is shown in Fig. 1. Increasing initial COD concentration results in enhancement of removal percentage. This may be due to produced oxidants have much chance of reacting with organics. In addition, by increasing the oil concentration, collisions between oil droplets increase and larger droplets are formed. Therefore, removal of pollutants will increase by electroflotation [5].

3.2.2. Effect of NaCl concentration

According to Fig. 2, COD removal has a rising trend by increasing NaCl concentration. Under enough concentration of NaCl, electroxidation of pollutants can occurr through indirect oxidation. With anodical generation of chlorine, hypochlorite, and hypochlorous acid, complete conversion of organics to CO_2, H_2O, and other inorganic components would happe [7]. Thus, it is clear that at higher NaCl concentration, higher COD removal has been obtained. Also with enhancing conductivity and then decreasing resistivity, current passing through the cell and rate of production of oxidants increase.

3.2.3. Effect of pH

According to obtained results of ANOVA analysis, initial pH of samples does not have a noticeable effect on removal efficiency. In acidic conditions, pH was stable during the process. Therefore, it is not necessary to adjust initial pH.

3.2.4. Effect of voltage

Fig. 3 shows that increasing the voltage from 3 to 5 V causes the increasing removal percentage and then by more enhancement of voltage, the percentage of removal of COD declines. Effect of voltage can be described according to reactions that occur during the process. Mechanism of reactions and behavior of oxide anodes (MO_x) was proposed by Comninellis [11]. At the first step, discharge of water occurs to produce hydroxyl radicals. There are two states of active oxygen; physically adsorbed active oxygen (adsorbed hydroxyl radicals $MO_x(OH)$) and chemisorbed active oxygen (oxygen in the oxide lattice MO_{x+1}) [12]. In the presence of oxidizable organics, combustion and conversion reactions may take place (Eqs. (15) and (16)). These oxidation reactions compete with side reactions of oxygen evolution (Eqs. (17) and (18));

$$MO_x(HO^\bullet) + RH \rightarrow MO_x + mCO_2 + nH_2O + H^+ + e^- \tag{15}$$

$$MO_{x+1} + RH \rightarrow MO_x + ROH \tag{16}$$

$$MO_x(HO^\bullet) \rightarrow MO_x + \frac{1}{2}O_2 + H^+ + e^- \tag{17}$$

$$MO_{x+1} \rightarrow MO_x + \frac{1}{2}O_2 \tag{18}$$

Electrochemical oxidation of organics occurs theoretically before oxygen evolution [11]. By applying higher voltage concomitant oxygen evolution takes place that results in decreasing efficiency of organic oxidation. On the other hand, performing the process at higher voltages causes oxidation of poisoning products formed at the anode surface.

3.2.5. Effect of time

Figure 4 indicates that variations of COD removal with time are noticeable. Rate of oxidation is faster at initial intervals of time. By passing the time results in decreasing pollution concentration, thus the rate of COD removal decreases.

3.3. Prediction of optimum performance

Table 4 shows the optimum conditions for this study predicted by ANOVA analysis. At these conditions, best response predicted by the Qualitek-4 software is 73.19%. Next step is performing confirmation test to verify obtained results.

3.4. Confirmation test

The confirmation experiment is the final step to verify experimental conclusions in Taguchi method. The confirmation test is performed to compare the obtained response of process with predicted one. This experiment was done under optimum conditions listed in Table 4. In order to compare response of the experiment, it is necessary to calculate confidence interval as following equation [13].

$$\text{C.I} = \sqrt{F_\alpha(1, f_e)V_e\left[\frac{1}{n_{\text{eff}}} + \frac{1}{R}\right]} \tag{19}$$

where:

$F_\alpha(1, f_e) = F$ ratio required for $\alpha = $ risk; $f_e = $ error DOF; $V_e = $ error variance
$n_{\text{eff}} = $ effective number of replications

Table 4
Optimal settings of process conditions

Parameter	Level	Value
COD (mg/L)	4	1,200
NaCl concentration (mg/L)	4	1,500
Voltage (V)	3	3
Time (min)	4	180
Predicted COD removal percentage %	–	73.19%

$$n_{\text{eff}} = \frac{N}{1 + \text{total DOF associated in the estimate of mean}}$$

$R = $ number of repetitions for confirmation experiment;
$N = $ total number of experiments.
The calculated C.I is: C.I = ±5.23.
The predicted COD removal percentage: Y_{opt}.

So, predicted optimal range is obtained as;
$73.19 - 5.23 < Y_{\text{opt}} < 73.19 + 5.23$, which is;
$67.96 < Y_{\text{opt}} < 78.42$

The result obtained from confirmation experiment was 70.11/%. So it is within predicted optimal range.

3.5. Electrode assessment

The electrode used in this study was composed of carbon as the base material, manganese oxide as electrocatalyst and PTFE as a stabilizing agent. PTFE was used to bind carbon and oxide manganese particles to form the sheet electrode material. In addition, PTFE/carbon composition make electrode hydrophobic. This characteristic prevents concomitant oxygen evolution. Hydrophobicity of the electrode was assessed by water contact angle measurements. Fig. 5 shows water contact angle is larger than 90°. Hydrophobicity of the electrode was improved by increasing composition percentage of PTFE. Appropriate performance of the electrode was approved by high COD removal.

4. Conclusions

Oxidation of oil in oil-in-water emulsion was studied with carbon-PTFE/MnO_2 anode. Performance of electrode was evaluated by investigation effects of four factors such as COD concentration, NaCl concentration, pH, voltage, and time on the COD removal efficiency. Taguchi method was used to determine the

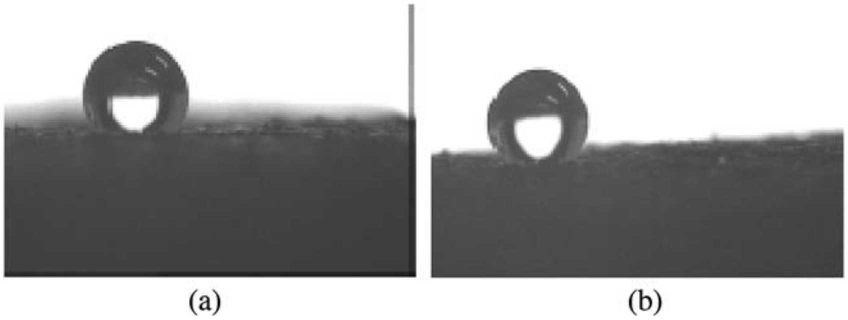

Fig. 5. Water contact angle > 90°, PTFE/carbon electrode composition of: (a) 30/70 and (b) 35/65.

main effects, significant factors and the optimum operating conditions to increase COD removal percentage. Results of ANOVA indicated that time, NaCl concentration, initial pollutant concentration, and voltage were the important parameters respectively. pH was found to be an insignificant parameter. The optimum conditions were found as follows: the fourth level of initial COD (1,200 mg/L) and NaCl concentration (1,500 mg/L), third level of voltage (5 V), and fourth level of time (180 min). The confirmation experiment was carried out to obtain maximum COD removal percentage under optimum conditions. The observed value of the confirmation test was 70.11% that was within the range of confidence limit of predicted performance (73.19%).

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