Journal of Engineering and Applied Sciences 13 (Special Issue 13): 10664-10670, 2018
ISSN: 1816-949X

COD Removal Form Oilfield Produced Water by Electro-Feton and Photoelectro-Fenton Processes

Rand Q. Al-Khafaji and Abdul Halim A.K. Mohammed
Department of Chemical Engineering, College of Engineering, University of Baghdad, Baghdad, Iraq

Abstract: Considerable amounts of Produced Water (PW) is usually accompanied with the production of oil. Most countries with oilfields are generally water stressed countries. This study proposed Electro-Fenton (EF) as alternative for the degradation of organic pollutants in PW. Treatment was carried out in a batch EF reactor with T_i-RuO_2/IrO_2 anode and activated carbon fiber felt cathode. Response Surface Methodology (RSM) was employed to achieve energy efficient removal of Chemical Oxygen Demand (COD). The effect of crucial process variables, namely, initial ferrous ions concentration (0.1-0.5 mM), current intensity (100-500 mA) and reaction time (30-90 min) on the removal efficiency of COD was studied using contour and response surface plots. The experimental results were analyzed by Analysis of Variance (ANOVA). It was found that under optimum conditions, the COD removal percentage was 82.88%. This percentage was increased to 89.71% and 93.06 by assisting EF process with UVA irradiation of 3 and 6 W, respectively. It is concluded that EF is an effective process for treating produced water and further improvement can be achieved by photo assisting the process.

Key words: Electro-fenton, photoelectron-fenton, produced water, response surface methodology, COD removal, pollutants, degradation

INTRODUCTION

Oil is produced with large volume of wastewater, it is estimated that three barrels of water are produced for every barrel of crude oil (Gomes *et al*., 2009). Many countries have implemented more strict regulations for discharging PW.

Produced Water (PW) is a complex mixture of dissolved and particulate organic and inorganic chemicals in water (mostly oils, salts and minerals) (Nasiri and Jafari, 2016). Some factors such as geological location of the field, lifetime of its reservoirs affect the physical and chemical properties of produced water.

The oil content in produced water is frequently classified into four groups according to its nature of physical phase which are: free oil (larger than 150 μm) dispersed oil (20-150 μm), emulsified oil (<20 μm) and dissolved oil.

Treatment methods of produced water can be classified into three main categories namely, primary to separate free oil such as gravity separators, secondary to removal dispersed oil such as coagulation and flotation processes and tertiary treatment to eliminate emulsified and soluble oil such as Advanced Oxidation Processes (AOPs).

AOPs defined as the oxidation methods of aqueous solutions in the presence of highly active materials which can destroy the pollutants. Hydroxyl radical is a powerful oxidant which is able to non-selectively destroy most organic contaminants until their complete mineralization into CO_2, water and inorganic ions (Sires *et al*., 2014).

The conventional Fenton method which achieved by the addition of Fe(II) salt to Hydrogen peroxide (H_2O_2) in aqueous media has been found, since, the end of the 19th century. This Fenton reaction generates Hydroxyl radicals (OH) under acidic conditions that can oxidize organics and convert it to non-toxic products. However, this Fenton process produces large amounts of Fe(III) oxyhydroxide solid byproduct that inhibiting the catalytic role of Fe(II) in generating OH (Qiu *et al*., 2015). Electro-Fenton (EF) is one approach to resolve this issues in conventional Fenton. In EF the Fe(III) reduced to Fe(II) at the cathode. Also, hydrogen peroxide *in-situ* generated at the cathode (Qiu *et al*., 2015).

New AOPs based on the electrochemical technology have been investigated in recent years, i.e., the so-called Electrochemical Advanced Oxidation Processes (EAOPs), have been developed. The EAOPs provide several advantages for the prevention and remediation of pollution problems because electron is a clean reagent. Other advantages include high energy efficiency, amenability to automation, easy handling because of the simple equipment required and safety because they operate under mild conditions (room temperature and pressure) (Sires *et al*., 2014).

Corresponding Author: Rand Q. Al-Khafaji, Department of Chemical Engineering, College of Engineering, University of Baghdad, Baghdad, Iraq

In the EF process, hydroxyl radicals are produced by the reaction between hydrogen peroxide and ferrous ions, which can destroy organic compounds. The reduction of ferric ion to ferrous ion which can reduce iron sludge production is one advantage of the EF process over the conventional fenton process (Mirshahghassemi *et al*., 2016).

Electro-Fenton mainly relies on *in situ* and catalytic electro generation of Fenton's reagent a mixture of Fe(II) ions and Hydrogen peroxide (H_2O_2) to produce hydroxyl radicals (OH) and react with organic pollutants in aqueous media, leading to their destruction (Eq. 1-4) (Zhang *et al*., 2014):

$$H_2O_2+Fe^{2+} \rightarrow Fe^{3+}+OH\bullet+OH \quad (1)$$

$$RH+\bullet OH \rightarrow R\bullet+H_2O \quad (2)$$

$$R\bullet+\bullet O_2 \rightarrow \text{products} \quad (3)$$

$$R+OH \rightarrow \text{products} \quad (4)$$

The optimum pH for COD removal is 3. A pH >3 lower the COD removal efficiency. At a higher pH, the oxidation efficiency of EF process decreases due to the formation of low active $Fe(OH)_3$ which has a lower tendency to react with hydrogen peroxide (Mirshahghassemi *et al*., 2016). pH lower than optimum affects the pollutant removal by producing less hydroxyl radicals increased scavenging effects of H^+ and hydroxyl radicals (Umar *et al*., 2010).

Electro-Fenton method has been applied successfully for the treatment of various wastewater such as paper mill wastewater (Guvenc *et al*., 2017), fertilizer manufacturing wastewater, diary industry wastewater (Yavuz *et al*., 2011, synthetic dye wastewater (Sennaoui *et al*., 2015), photographic processing wastewater (Bensalah *et al*., 2013) and petroleum refinery wastewater (Saber *et al*., 2014).

The efficiency of electro-Fenton process can be further improved in the presence of UV irradiation by a process called Photoelectro-Fenton (PEF). The catalytic effect of Fe^{2+} can be enhanced by assisting electro-Fenton process with UV irradiation. The photoelectro-Fenton process can increase the regeneration rate of Fe^{2+} in the presence of UV. An increased concentration of OH increases the oxidative capability of the process. In addition, H_2O_2 produces two OH by photocatalytic effect of UV irradiation (Eq. 5) (Umar *et al*., 2010):

$$H_2O_2+hv \rightarrow 2\bullet OH \quad (5)$$

The PEF process involves the solution irradiation with UVA light whose action is quite complex. Photons can prevent the large accumulation of Fe(III) species, responsible for a gradual deceleration of decontamination, thanks to the reductive photolysis of $[Fe\ (OH)]^{2+}$ via. Eq. 8. Moreover, this enhances the Fe^{2+} regeneration and the production of additional amounts of OH. UVA photons can also photolyze organic intermediates like Fe (III)-carboxylate complexes, originated from the destruction of aromatic pollutants via. the general (Eq. 6-9) (Tirado *et al*., 2018):

$$O_2+2H^++2e^- \rightarrow H_2O_2 \quad (6)$$

$$Fe^{2+}+H_2O_2+H^+ \rightarrow Fe^{3+}+OH+H_2O \quad (7)$$

$$[Fe(OH)]^{2+}+hv \rightarrow Fe^{2+}+OH \quad (8)$$

$$[Fe(OOCR)]^{2+}+hv \rightarrow CO_2+R \quad (9)$$

The traditional technique of experimental design in which one process variable is changed while the other variables are settled dose not demonstrate the interaction between the process variables. Response Surface Methodology (RSM) is able to assess this interaction (Mirshahghassemi *et al*., 2016). Response surface methodology finds the optimum values of process variables for a desirable response by using a statistical-based technique to evaluate the simultaneous effects between these variables (Thiruganasambandham *et al*., 2014; Hakizimana *et al*., 2017).

The aim of this research is to examine the effectiveness of electro-Fenton process for treating Iraqi oilfield produced water. The response surface methodology has been employed to optimize the process conditions for EF for maximizing COD removal efficiency while minimizing electrical energy consumption. Moreover, this study aimed to further improve EF efficiency by UVA irradiation (photo-EF).

MATERIALS AND METHODS

Produced water sample: The produced water sample was collected from oilfield, Midland Oil company, Iraq. First, the sample treated by electrocoagulation unit, filtered and analyzed for COD. The COD content of the sample used in this study is 457 mg/L.

Electrochemical reactor: Treatment of PW by the electro-Fenton process was performed at room temperature (25±2°C) in a cylindrical glass electrochemical

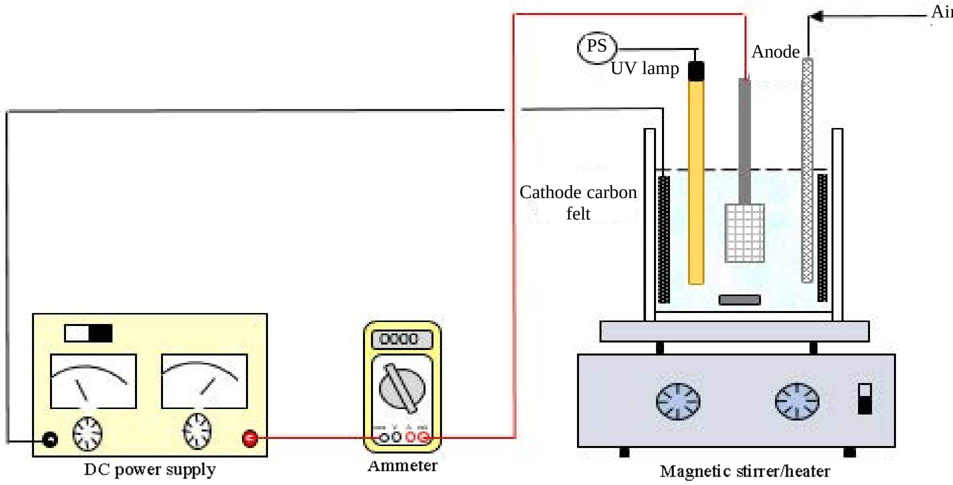

Fig. 1: Schematic diagram of batch photoelectron-fenton system

Fig. 2: Photograph of the experimental system used for batch photoelectron-fenton

cell of 1 L equipped with two electrodes. The cathode was cylindrical Activated Carbon Fiber Felt (ACFF). The anode was T_i/RuO_2-IrO_2 mesh placed in the center of the cell. The solution was rigorously stirred with a magnetic stirrer (Jenway 1000, UK) at 500 rpm. A laboratory model DC power supply (Yaogong 1052DD, China) was used maintain constant DC current and to measure voltage and current. The pH was measured by pH-meter (Hanna Instruments pH 211). Schematic diagram and photograph of the experimental system was shown in Fig. 1 and 2, respectively.

Analytical procedure: All samples were filtered through Whatman filter paper with a pore size of 11 μm. COD was analyzed using a COD thermoreactor (RD125, Lovibond) and a direct reading spectrophotometer (MD200, Lovibond) The equation used to calculate the percentage of COD Removal (R%) was:

$$R\% = \frac{COD_o\text{-}COD}{COD_o}\times 100 \tag{10}$$

where, COD_o and COD are the initial and final chemical oxygen demand, respectively.

Experimental design: A total of 20 experiments were performed to optimize and determine the relationship between the removal efficiency of COD with respect to crucial operating parameters, i.e., initial Fe(II) ions concentration (0.1-0.5 mM), current intensity (100-500 mA) and reaction time (30-90 min). Response Surface Methodology (RSM), the Central Composite Design (CCD) was performed using Minitab Software (Version 17). Experimental data were fitted to a quadratic Eq. 11:

$$Y_i = b_o+\sum b_i x_i+\sum b_{ii} x_i^2+\sum b_{ij} x_i x_j \tag{11}$$

where, b_o, b_i and b_{ij} are the regression coefficients for the equation terms. Y_i is the percentage Removal of COD (R%) and Electrical Energy Consumption (EEC). The regression coefficients were analyzed by the F-test and p-value. The statistical significance of the model was tested by the Analysis of the Variance (ANOVA). The relationship between the response and the variables was used to construct a three dimensional surface plots to study the effect of variables on the response. Multiple response optimization of the EF process was done to determine the optimum parameters for maximum COD removal efficiency and for minimum power consumptions.

Experimental procedure: All electro-Fenton experiments were conducted in a batch mode under galvanostatic conditions. Before starting-up the process, compressed air was fed to the cathode by an air pump with 2.5 L/min for 15 min to saturate the solution with oxygen and was maintained during the process of electrolysis. In each run, 800 mL of produced water was placed into the reactor and all runs were performed under stirring at 500 rpm. Initial pH values was adjusted to 3 with 0.1 M solution of H_2SO_4. The average of voltage from the start to the end of experiment was used for the determination of energy consumption.

One of most important parameters that affect the application of any method of wastewater treatment is the cost. The operation cost in EF process includes material, consuming of energy cost, labor, maintenance and disposal and fixed cost. Consuming of energy cost is the major cost in EF process. The Electrical Energy Consumption (EEC) for EF treatment was calculated using the following Eq. 12 (Tirado *et al*., 2018):

$$EEC = \frac{U.I.t1000}{(COD_O\text{-}COD)V} \quad (12)$$

Where:

EEC = Electrical Energy Consumed (kWh/kg COD)
U = Voltage (V)
I = Current intensity (A)
t = Time (h)
V = Water Volume (L) COD_0 and COD = Initial and final COD (mg/L)

RESULTS AND DISCUSSION

Experimental design analysis: The results of the total number of 20 experiments with six center points based on the Response Surface Methodology (RSM) with Central Composite Design (CCD) are shown in Table 1.

The relationship between COD removal efficiency (R%), Electrical Energy Consumption (EEC) and the three process variables were fitted to a second order polynomial (Eq. 13):

$$COD(R\%) = 11.5+131.1C+183.0I+0.479t-206.3C*C-293.7I*I-0.00288t*t+3.9C*I-0.000C*t+0.013I*t \quad (13)$$

Table 2 shows the ANOVA for the removal efficiency of COD (R %) response and variables selected to fit the model. The F-value of 14.41 for the model implying that the model is significant. A p-value lower than 0.05 indicates that the model is statistically high significant. Terms with p-values less 0.05 indicates that these terms are significant. The model was also tested using the determination coefficient (R^2). The closer R^2 values to 1, the stronger the model and better predict of response. The determination coefficient value of 0.9284 for COD removal efficiency illustrate that the data prediction ability of the response surface model was satisfactory.

Effect of process variables on COD removal: Three factors at three levels CCD were used in this study to investigate the effect of process variables COD removal efficiency. Figure 3-5 represents 3 Dimensional (3D) response surface and 2 Dimensional (2D) contour plots of COD removal efficiency as a function of initial Fe(II) ions Concentration (C), current Intensity (I) and reaction time (t).

It was found that the removal efficiency of COD increased rapidly with current intensity up to 250 mA. This can be explained to the fact that the hydroxyl free radical formation rate is controlled by the applied I and hence increasing I improve the COD removal. However, above 250 mA, lower COD removal efficiency was noticed which might be attributed to the increase of the ratio of (mol H_2O_2/moL Fe^{2+}) above the optimum value which increase the reaction that scavenged hydroxyl radical leading to decrease the COD removal efficiency.

It has been found that initial Fe^{2+} concentration is an important parameter affecting the performance of EF process. It was observed that COD removal efficiency increased with increasing initial Fe^{2+} concentration from 0.1-0.32 mM. This increase because of the increase of the reactive material in the reaction media due to the catalytic effect of Fe^{2+}. Beyond 0.32 mM lower COD removal efficiency was noticed which might be due the increase of Fe^{3+} concentration which lead to the formation of yellow precipitate of $Fe(OH)_3$ which deposited on the electrode surface.

The COD removal efficiency increase with increasing reaction time up to 60 min. Initial rapid degradation is largely due to the easily degradation organics leading to higher COD removal. Thereafter, 60 min, the removal efficiency had slight effect on the removal of COD. This can be attributed to the presence of large molecular and complex compounds in oil which are difficult to oxidize with electro-Fenton. These molecules were degraded to simpler products and then further decomposed to simpler and lower molecules.

Optimization and validation: Multiple response optimization was performed for maximizing COD removal efficiency (R%) while minimizing Electrical Energy Consumption (EEC). The optimization gave initial Fe^{2+}

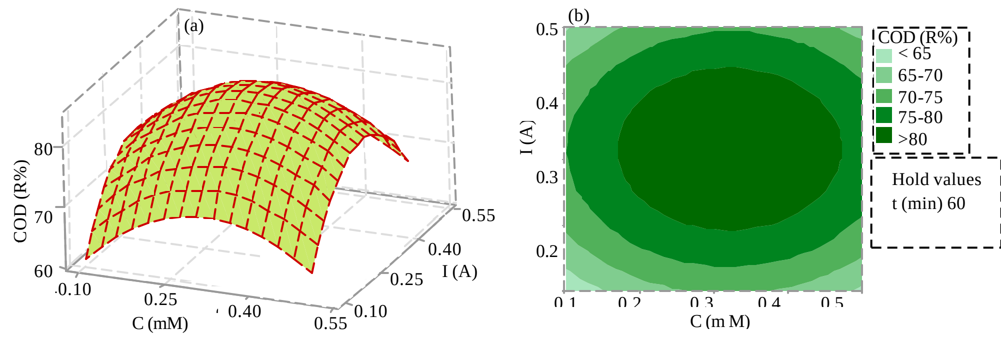

Fig. 3: Surface plot and contour plot for COD removal efficiency (R%) vs. C, I, at t = 60 min

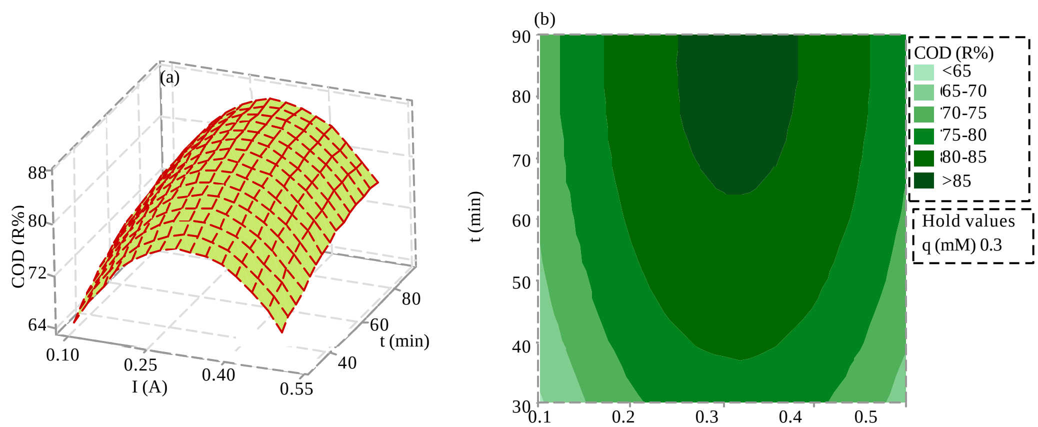

Fig. 4: Surface plot and contour plot for COD removal efficiency (R%) vs. t, I, at C = 0.3 mM

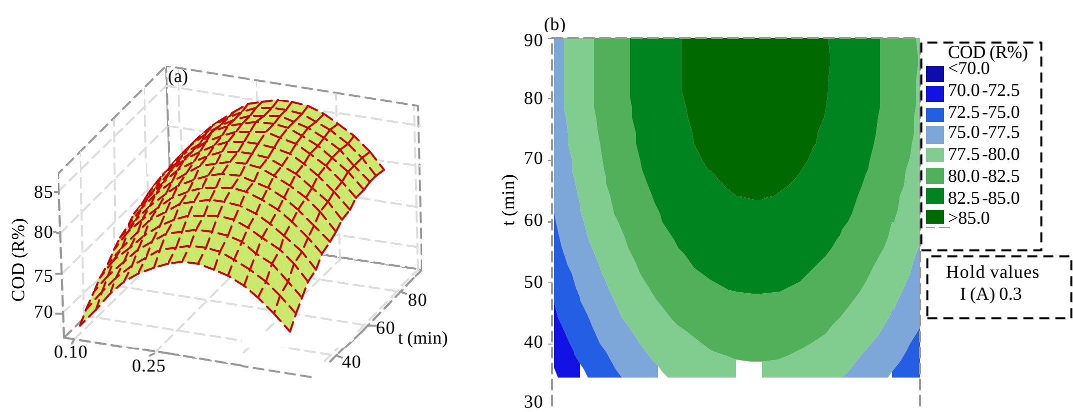

Fig. 5: Surface plot and contour plot for COD removal efficiency (R%), vs. t, C at I = 300 mA

concentration of 0.322 mM, current intensity of 249.5 mA and reaction time of 60.91 min as optimal points. The optimization predicts removal efficiency of 83.42% and energy consumption of 1.163 kWh/kg COD at these optimal points. Figure 6 illustrate the response optimization of COD removal efficiency and electrical energy consumption.

Validation experiment conducted under the optimal parameters gave 82.88% COD removal efficiency and 1.170 kWh/kg COD electrical energy consumption which in agreement with the predicted values.

Photoelectro-Fenton: To investigate the effect of UVA irradiation on the COD removal efficiency, one and two

Table 1: Experimental design and the obtained responses

Run	Fe(II) concentration C (mM)	Current intensity I (mA)	Time (min)	COD removal efficiency (R%)	Electrical energy consumption EC (kWh/kg COD)
1	0.5	0.5	30	62.35	2.0838
2	0.3	0.1	60	67.33	0.4062
3	0.3	0.3	60	84.78	1.5486
4	0.5	0.3	60	79.77	1.6459
5	0.3	0.3	60	85.90	1.5284
6	0.5	0.1	90	64.11	0.6400
7	0.5	0.5	90	67.33	5.7890
8	0.3	0.3	30	69.87	0.9395
9	0.1	0.3	60	70.66	1.8581
10	0.3	0.3	60	86.06	1.5256
11	0.3	0.5	60	75.11	3.4596
12	0.3	0.3	60	86.91	1.5107
13	0.1	0.1	30	57.83	0.2365
14	0.3	0.3	60	83.10	1.5799
15	0.5	0.1	30	59.56	0.2296
16	0.3	0.3	60	84.81	1.5481
17	0.1	0.5	90	64.99	5.9974
18	0.1	0.1	90	62.50	0.6565
19	0.3	0.3	90	91.88	2.1434
20	0.1	0.5	30	60.11	2.1614

Table 2: ANOVA for COD removal efficiency (R%)

Source	Sum of squares	df	Mean square	F-values	p-values	Remark*
Model	2185.28	9	242.808	14.41	0.000	S
C	29.00	1	29.002	1.72	0.219	NS
I	30.84	1	30.835	1.83	0.206	NS
t	168.84	1	168.839	10.02	0.010	S
C*C	187.23	1	187.234	11.11	0.008	S
I*I	379.44	1	379.437	22.52	0.001	S
t*t	18.47	1	18.467	1.10	0.320	NS
C*I	0.19	1	0.192	0.01	0.917	NS
C*t	0.00	1	0.00	0.00	0.999	NS
I*t	0.05	1	0.051	0.00	0.957	NS
Residual	168.47	10	16.847			
Lack-of-fit	158.58	5	31.717	16.04	0.004	
Pure error	9.88	5	1.977			
Cor total	2353.74	19				

*S = Significant, NS = Not Significant

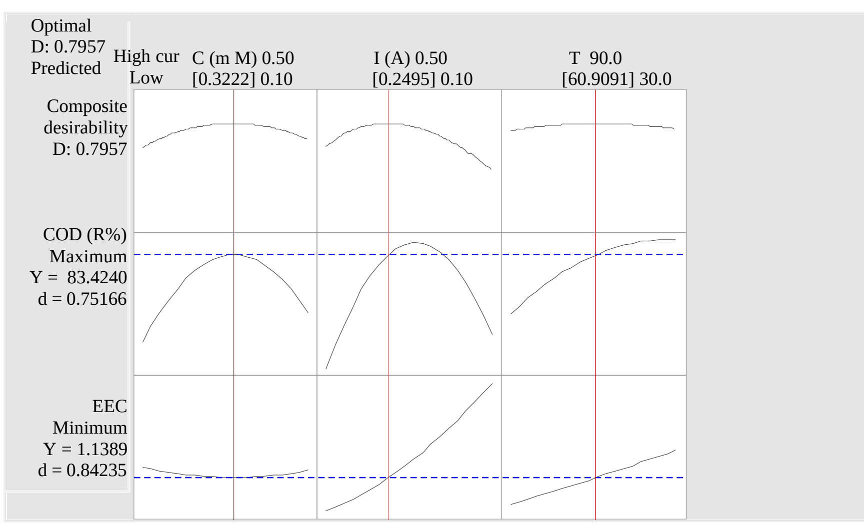

Fig. 6: Multiple response optimization of COD Removal efficiency (R%) and Electrical Energy Consumption (EEC)

UVA lamps (3 W each) was applied to the reaction media at optimum operating conditions (initial Fe^{2+} concentration of 0.322 mM, current intensity of 249.5 mA and reaction time of 60.91 min). It was found that COD removal efficiency was increased from 82.88-89.71 and 93.06% using one and two UVA lamps, respectively.

This improvement in the COD removal efficiency has a drawback which is the sharply increase in the electrical energy consumption from 1.170 -9.422 and 18.945 kWh/kg COD when using one and two UVA lamps, respectively.

CONCLUSION

Electro-Fenton process has been successfully employed for treating of oilfield produced water using Response Surface Methodology (RSM). Multiple response optimization for maximizing COD removal efficiency while minimizing electrical energy consumption revealed that the optimum initial Fe^{2+} concentration, current intensity and reaction time are 0.322 mM, 249.5 mA and 60.91 min, respectively. It was found that under these conditions, the COD removal efficiency was 82.88%. This removal efficiency was increased to 89.71 and 93.06% when the reaction media irradiate by one and two UVA lamps (3 W each), respectively. It was found that electrical energy consumption increased sharply when using UVA lamps, so, it was suggested to use a cheaper source of light such as solar energy to obtain a cost-effective photoelectron-Fenton process.

REFERENCES

Bensalah, N., A. Bedoui, S. Chellam and A. Abdel-Wahab, 2013. Electro-Fenton treatment of photographic processing wastewater. Clean-Soil Air Water, 41: 635-644.

Gomes, J., D. Cocke, K. Das, M. Guttula and D. Tran *et al*., 2009. Treatment of produced water by electrocoagulation. Proceedings of the EDP Congress 2009 Symposia on Minerals, Metals & Materials Society (TMS), February 15-19, 2009, San Francisco, California, pp: 15-19.

Guvenc, S.Y., H.S. Erkan, G. Varank, M.S. Bilgili and G.O. Engin, 2017. Optimization of paper mill industry wastewater treatment by electrocoagulation and electro-fenton processes using response surface methodology. Water Sci. Technol., 76: 2015-2031.

Hakizimana, J.N., B. Gourich, M. Chafi, Y. Stiriba and C. Vial *et al*., 2017. Electrocoagulation process in water treatment: A review of electrocoagulation modeling approaches. Desalin., 404: 1-21.

Mirshahghassemi, S., B. Aminzadeh, A. Torabian and K. Afshinnia, 2016. Optimizing electrocoagulation and electro-fenton process for treating car wash wastewater. Environ. Health Eng. Manage. J., 4: 37-43.

Nasiri, M. and I. Jafari, 2016. Produced water from oil-gas plants: A short review on challenges and opportunities. Period. Polytech. Chem. Eng., 61: 73-81.

Ogedey, A. and M. Tanyol, 2017. Optimizing electrocoagulation process using experimental design for COD removal from unsanitary landfill leachate. Water Sci. Technol., 76: 2907-2917.

Qiu, S., D. He, J. Ma, T. Liu and T.D. Waite, 2015. Kinetic modeling of the electro-fenton process: Quantification of reactive oxygen species generation. Electrochim. Acta, 176: 51-58.

Saber, A., H. Hasheminejad, A. Taebi and G. Ghaffari, 2014. Optimization of fenton-based treatment of petroleum refinery wastewater with scrap iron using response surface methodology. Appl. Water Sci., 4: 283-290.

Sennaoui, A., F. Sakr, S. Alahiane, A. Assabbane and E.H.A. Addi, 2015. Response surface methodology analysis of electrochemical oxidation of a reactive yellow 17 dye by electro-fenton/BDD Process. Int. J. Mater. Chem. Phys., 1: 67-73.

Sires, I., E. Brillas, M.A. Oturan, M.A. Rodrigo and M. Panizza, 2014. Electrochemical advanced oxidation processes: Today and tomorrow a review. Environ. Sci. Pollut. Res., 21: 8336-8367.

Thirugnanasambandham, K., V. Sivakumar and M.J. Prakash, 2014. Optimization of electrocoagulation process to treat biologically pretreated bagasse effluent. J. Serbian Chem. Soc., 79: 613-626.

Tirado, L., O. Gokkus, E. Brillas and I. Sires, 2018. Treatment of cheese whey wastewater by combined electrochemical processes. J. Appl. Electrochem., 48: 1307-1319.

Umar, M., H.A. Aziz and M.S. Yusoff, 2010. Trends in the use of Fenton, electro-Fenton and photo-Fenton for the treatment of landfill leachate. Waste Manage., 30: 2113-2121.

Yavuz, Y., E. Ocal, A.S. Koparal and U.B. Ogutveren, 2011. Treatment of dairy industry wastewater by EC and EF processes using hybrid Fe? Al plate electrodes. J. Chem. Technol. Biotechnol., 86: 964-969.

Zhang, J., M.H. Shao and H. Dong, 2014. Degradation of oil pollution in seawater by bipolar electro-fenton process. Pol. J. Environ. Stud., 23: 933-941.