Performance Evaluation of Fenton Based Processes in Reducing COD of the Petroleum Effluents Using the Waste of Steel Slag

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Performance evaluation of Fenton based processes in reducing COD of the petroleum effluents using the waste of steel slag

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Abstract

Petroleum effluents pollution is an important challenge for many countries. The aim of this study was to investigate the efficiency of Fenton, Photo-Fenton (PF), Electro-Fenton (EF) and Photo-Electro-Fenton (PEF) processes in reducing chemical oxygen demand (COD) of desalination unit effluent using steel slag as catalyst, cathode and anode. For achieving this goal the experimental design by Taguchi method using Mintab18 software was used. The desired variables include pH (3, 5 and 7), hydrogen peroxide (5, 10 and 15 mmol/l), contact time (30, 60 and 90 minutes), catalyst (5, 7.5 and 10 g/l), radiant intensity (16, 24 and 32 watts) and voltage (5, 15 and 30 volts). In order to perform the experiments, the pilot was made using UV-C lamps (wavelengths of 200-280 nm) each with a power of 8 watts and an AC power supply of 0-30 volts in the range of 0-2 amps. According to the results, PEF process under pH = 7, 10 mmol/l hydrogen peroxide, catalyst content of 5 g/l, radiant intensity of 24 watts and voltage of 5 volts for 90 minutes, provides the highest COD removal rate (98.7%). The present study showed that following the combined process of PEF, EF, PF and Fenton processes have a high potential in reducing COD using steel slag.

Keywords: EF, PF, PEF, COD, Taguchi, Steel slag, Petroleum effluent

1. Introduction

Treatment of industrial wastewater containing toxic and hazardous substances is one of the world's environmental challenges. Various methods are used to treat industrial wastewater, including physical, chemical and biological processes. Technologies such as adsorption or coagulation, transfer the contaminators from one phase to another and the contaminant is not completely eliminated (Padmanabhan *et al.*, 2006). In recent years, among all chemical treatment processes, advanced oxidation process (AOP) methods have been widely studied due to their effective efficiency in removing various contaminators, especially stable organic contaminators (Wang *et al.*, 2016). In these methods, contaminants are degraded with the contribution of oxidant agents such as catalyzers and peroxides and transformed to inorganic matter such as carbon dioxide and water.

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Advanced oxidation was first used for water treatment in 1980 (Glaze, 1987; Glaze, Kang and Chapin, 1987). AOP processes are based on processes that produce an appropriate amount of active radicals such as hydroxyl radical (OH^o), radical (SO_4^{o-}) and oxygen radical (O^o) (Cho *et al.*, 2005; Ikai *et al.*, 2010; Deng and Zhao, 2015).

Since hydroxyl radicals have high oxidizing power (E° = 2.8 V), they remove most contaminators (especially organic contaminators). These methods are more capable of treating toxic contaminators, usually do not have the problem of surplus disposition and waste, are performed at room temperature and atmospheric pressure and are relatively inexpensive, and also the reaction speed is fast (Gaya and Abdullah, 2008). Advanced oxidation such as photochemical oxidation, wet catalytic oxidation, sonochemical oxidation, O_3 oxidation, electrochemical oxidation and Fenton oxidation are widely used for direct mineralization of organic contaminators or to improve the degradability of organic contaminators (Bokare and Choi, 2014; Sharma, Ahmad and Flora, 2018). Compared to other advanced oxidation processes, Fenton processes are the most popular due to some significant advantages such as wide application range, strong anti-interference ability, simple operation, fast degradation and mineralization (Chen *et al.*, 2011; Wang *et al.*, 2016).

Various factors such as temperature, pH, H_2O_2 concentration, iron ion content, contact time, etc. affect the efficiency of Fenton-based processes (Stepnowski *et al.*, 2002; Meriç, Kaptan and Ölmez, 2004; Mousavi *et al.*, 2010; Jaafarzadeh, Ghanbari and Moradi, 2015; Lopez-Saavedra *et al.*, 2018). Performance of Fenton-based processes are differen; Comparison between Fenton, EF, Sono-Electro-Fenton (SEF) and PEF processes for phenol removal showed that the degradation efficiency of the processes is as follows: PEF < SEF < EF < Fenton (Babuponnusami and Muthukumar, 2012a). In the Photo Catalysis / PEF hybrid system 85% of TOC and 96% of COD were removed from effluent containing Polyaniline (Ou *et al.*, 2019).

Testing all the parameters for different Fenton process requires a lot of time and cost, but in such cases, the experiment design method can be used. The Taguchi method is one of the experiment design that compared to factor methods provides advantages such as less number of experiments and therefore less cost and time of testing, the ability to evaluate the interaction effects and conducting experiments in parallel and ultimately predicting the optimal response. In general, this method reduces the number of experiments required for optimization and increases the accuracy of the results. The most important and effective factor can be determined with this method (Yonar and Kurt, 2017; Suraj *et al.*, 2019) One of the important issues in electrochemical processes is selecting the right electrode (especially anode). The anodes such as BDD[5], Pt, and DSA[6] due to produce more powerful (OH^o) have shown their high potential in removing various contaminants (Villanueva-Rodríguez *et al.*, 2014; Brillas and Martínez-Huitle, 2015; Flores *et al.*, 2016; Steter, Brillas and Sirés, 2016; Komtchou *et al.*, 2017; Moreira *et al.*, 2017; Aveiro *et al.*, 2018; Guelfi *et al.*, 2019; Thiam and Salazar, 2019; Ye *et al.*, 2019). Some studies have investigated the effect of the similar cathode and anode electrode (such as identical electrodes of Na_2SO_4 (Babuponnusami and Muthukumar, 2012b); graphite electrodes (Nidheesh and Gandhimathi, 2014) and identical BBD electrodes (Villanueva-Rodríguez *et al.*, 2014) in the Fenton based processes and achieved good results.

[5] Boron-doped diamond
[6] Dimensionally stable anodes

Khuzestan province in southwestern Iran has large industries such as petroleum and steel industries. High pollution of the effluents of petroleum industry desalination units and the presence of high slag in the steel industry are among the environmental problems of this region.

Since, in novel research, the use of solid iron catalysts or iron-modified cathodes with it has shown good performance (Brillas, 2020), therefore steel slag (containing iron compounds) was used as catalysts and electrodes. The present study aimed to compare different Fenton-based processes in reducing pollution of petroleum industry effluents by using waste materials (steel industry slag). Also, the most effective parameters for reducing COD were identified in each of the processes using the Taguchi method.

2. Materials and methods

This study was designed and implemented to evaluate the efficiency of Fenton, PF, EF and PEF processes in reducing COD from effluents of petroleum desalination unit and, the effect of factors such as pH, contact time, catalyst content, hydrogen peroxide content, radiant intensity and current on the reduction efficiency of COD was investigated. The measured parameters of the effluent of one of the desalination units, by the petroleum-rich areas of the south have been presented Table (1). The catalysts for all four processes of F, EF, PF and PEF were selected from fine particle slag; also cupal slag because of its nature was used as the cathode and anode for EF and PEF processes. According the XRF analysis (Table 2), the compounds of iron oxide and calcium oxide have the highest amount. The experiments were designed using Taguchi orthogonal array and Minitab 18 software. The results of the experiments were analyzed using Microsoft Office Excel and Minitab 18 software using two types of signal analysis to noise and variance.

2.1. Experiment design

The Taguchi method minimizes the number of experiments required using orthogonal arrays. Array L_9 (3^4) was used to determine the appropriate conditions based on this statistical model; this means that 4 effective parameters were selected as arrays and examined at three levels, as shown in Tables (3).

Achieving optimal conditions for a specific objective in Taguchi method is based on the signal to noise index S/N. S/N is the transformed value of the loss function used to measure the deviation of the performance characteristic from the ideal value. The higher S/N indicate the better performance of the system (Gönder *et al.*, 2010). The calculation method of S/N is selected according to the intended optimization type. Here, according to the goal of achieving the maximum range, S/N of "larger is better" type was used (Milkey *et al.*, 2014).

2.2. Required solutions

Solutions of sulfuric acid (98.08%), nitric acid (63.01%), sodium hydroxide (98%) for pH adjustment according to Taguchi orthogonal arrays design and H_2O_2 concentration (29-31%) were prepared from Merck Germany for experiments.

2.3. Reactor used

All experiments related to Fenton were performed on a 1250-cc beaker with a diameter of 90 mm and a height of 150 mm. To perform the PF test, a black box designed from wood was used to prevent the radiation from penetrating into the medium and to have a higher efficiency. In order to produce radiation from 4 UV-C lamps with a wavelength of 200 to 280 nm each with a power of 8 watts and a total of 32 watts, were installed vertically on all four sides of the box and a glass beaker with a volume of 1250 ml was placed exactly in the middle of the box so that of radiation should be uniformly reflected on the sample from each side. To perform an EF test, a Pyrex beaker with a volume of 1250 ml was used as the reaction medium, and the cathode and anode, both made of Cupal slag, were placed in unknown shapes at a distance of 3 cm from each other. The power supply in this experiment was a variable voltage device of DAZHENG model PS-302 D with variable current characteristics of 0 to 2 amps and variable voltage of 0 to 30 volts. The required catalyst content and the required hydrogen peroxide (according to the required level) were added to each sample. In the combined state of PEF, two small holes (with the size of a wire) are made in the upper part of the black box, and the power cords of the cathode and anode are passed through them and connected to the AC power supply.

Table 1. Chemical properties of petroleum effluent used

parameters	Amounts	the unit	parameters	Amounts	the unit	parameters	Amounts	the unit

SO_4	410	ppm	PO_4	1.3	ppm	pH	5.33	_
F	4.5	ppm	NO_3	1.55	ppm	TDS	181000	ppm
CO_3	less than0.1	ppm	NO_2	0.15	ppm	EC	362000	µS/cm
HCO_3	9	ppm	Cl	102930	ppm	COD	More than 10000	ppm
Bi	less than0.1	ppm	Ba	less than0.1	ppm	Ag	less than0.1	ppm
Ca	60804	ppm	Be	Less than 0.2	ppm	Al	less than100	ppm
Co	less than1	ppm	Ce	less than1	ppm	Cd	less than0.1	ppm
Mg	6243	ppm	Fe	342	ppm	Cr	4	ppm
Li	41	ppm	Mo	less than0.3	ppm	Cs	Less than 0.5	ppm
K	4993	ppm	Mn	6	ppm	Cu	less than3	ppm
P	10	ppm	Zn	5	ppm	Na	less than10	ppm
Pb	3	ppm	Ni	2	ppm	V	5	ppm
						S	972	ppm

Table 2. XRF analysis related to Khuzestan steel slag

Sample slag	SiO_2	Al_2O_3	Fe_2O_3	**CaO**	Na_2O	**MgO**	K_2O	**TiO_2**	**MnO**	P_2O_5
%	12.48	2.16	32.433	23.368	0.339	4.647	0.083	1.2	0.355	0.307

Table 3. Variables and levels

		Level 1	**Level 2**	**Level 3**
Fenton	**pH**	3	5	7

	H_2O_2(mmol/l)	5	10	15
	Catalyst (gr/l)	5	7.5	10
	Time (min)	30	60	90
Photo-Fenton	**pH**	3	5	7
	H_2O_2(mmol/l)	5	10	15
	Catalyst (gr/l)	5	7.5	10
	UV(W)	16	24	32
Electro-Fenton	**pH**	3	5	7
	H_2O_2(mmol/l)	5	10	15
	Catalyst (gr/l)	5	7.5	10
	Voltag (V)	5	15	30
Photo-Electro-Fenton	**pH**	3	5	7
	H_2O_2(mmol/l)	5	10	15
	Catalyst (gr/l)	5	7.5	10
	UV(W)	16	24	32
	Voltag (V)	5	15	30
	Time (min)	30	60	90

2.4. Test Method

For Fenton-based processes, the required amount of slag as catalyst, cathode and anode was washed and then dried in an oven at 105 °C for 2 hours. Hydrogen peroxide and 0.1 N sodium hydroxide solutions were prepared. Then the pH value was adjusted using sulfuric acid and 0.1 N sodium hydroxide (portable pH meter model 330 I - WTW Germany). Certain catalyst content (weighed with a Japanese GF300 scale with an accuracy of 0.001 g) and hydrogen peroxide were added to the samples and the retention times according to the intended levels were applied using a stopwatch. After performing experiments related to Fenton process and complementary experiments, the time parameter of 60 minutes was considered as the optimal parameter for PF and EF processes.

To perform the PF test, the cathode and anode were both made of slag in unknown shapes placed at the distance of 3 cm. The required catalyst content and required hydrogen peroxide (Table 3) was added to each test sample and, the required retention time was applied.

Before and after the experiments, a certain volume of sample was taken and the COD content was measured using a spectrophotometer (Hach 5000) by closed reverse digestion (600 nm wavelength). Then the percentage of COD removal was calculated according to Equation (1).

(1) $\text{Removal percentage} = 100 \times \frac{C_0 - C_1}{C_1}$

Where C_0 and C_1 present the initial and final concentrations of COD, respectively.

2.5. Statistical analysis of data

After the experiments, signal-to-noise analysis and analysis of variance were performed on the removal percentages obtained using Mintab18 software. The following equation was used for S/N analysis (Oh *et al.*, 2005):

(2) $$\frac{S}{N} = -10 \log \frac{\sum_{i=1}^{r} \frac{1}{y_i^2}}{r}$$

Where y_i represents the response value for each experiment and r denotes the number of repetitions of each experiment.

3. Results and discussion

The Taguchi method provided 9 experiments for each of the Fenton, PF and EF methods and 27 experiments for the combined PEF method. The experiments were performed and the results were analyzed using MINTAB 18 software.

3.1. Fenton

Table (4) shows the average COD removal rate at different levels of each factor and Figure (1-a) displays the main effects for the signal-to-noise ratio in Fenton experiments. The highest and lowest removal percentages in the 9 experiments were 73.99% and 26.81%, respectively. Considering the range of slope variation, it can be said that the hydrogen-oxygen parameter has been the most effective factor on the Fenton process. The appropriate levels for each of the factors influencing the process are at the highest point, or the so-called highest signal-to-noise ratio, which, will result in the highest COD removal rate when applied. Therefore, the appropriate conditions to achieve the maximum response value are when pH = 7, H_2O_2 = 10mmol/l, catalyst = 10gr/l and time is 60 minutes. Experimental factors in terms of maximum impact can be ranked according to the delta value (difference between the highest and lowest signal-to-noise values). Therefore, after hydrogen peroxide factor, pH, catalyst and time factors had the greatest effect on COD removal percentage, respectively (Figure (1-a) and Table 4).

Basically, the optimal contact time is a very important parameter in chemical reactions and if it exceeds the optimal limit, the process will no longer be economic (Coelho *et al.*, 2006). The optical contact time of 60 min obtained in some other research (Byrappa *et al.*, 2008).The highest COD removal percentage occurs at pH 7 for the Fenton

process. However, some previous studies have shown that the Fenton process in the acidic state shows better performance (Wang *et al.*, 2016).The contaminant adsorption rate on the catalyst surface increases with increasing the number of catalyst particles and the available surface area, which leads to the production of more hydroxyl radicals (Tony *et al.*, 2009). By increasing the concentration of hydrogen peroxide from 5 to 10 mmol/L, the COD removal percentage increases and then decreases with increasing H_2O_2 to 15 mmol/L. Excess concentration of H_2O_2 can act as a hydroxyl radical scavenger. It acts instead of a hydroxyl radical, $HO_2\bullet$, which has less oxidizing ability and longer life compared to OH● (Xing, Sun and Yu, 2010).

Table 4. The average response value at different levels of each factor

		Level 1	Level 2	Level 3	Delta	grade
Fenton	**pH**	51.75	40.72	65.63	24.91	2
	H_2O_2(mmol/l)	37.21	69.5	51.39	32.28	1
	Catalyst (gr/l)	44.9	48.48	64.73	19.83	3
	Time (min)	51.05	54.99	52.07	3.94	4
Photo-Fenton	**pH**	72.35	62.54	29.45	42.9	1
	H_2O_2(mmol/l)	65.92	52.66	45.76	20.15	3
	Catalyst (gr/l)	46.04	55.48	62.82	16.78	4
	UV(W)	45.95	51.6	66.8	20.85	2
Electro-Fenton	**pH**	56.51	63.55	66.19	9.68	4
	H_2O_2(mmol/l)	86.13	35.03	65.09	51.11	1
	Catalyst (gr/l)	69.81	60.29	56.15	13.66	3
	Voltag (V)	57.34	71.2	57.71	13.85	2
Photo-Electro-Fenton	**pH**	73.04	74.38	71.15	3.23	6
	H_2O_2(mmol/l)	65.09	82.17	71.31	17.08	3
	Catalyst (gr/l)	79.63	63.84	75.09	15.79	4
	UV(W)	64.06	79.38	75.12	15.32	5
	Voltag (V)	61.81	80.19	76.57	18.39	2
	Time (min)	54.3	84.68	79.6	30.38	1

3.2. Photo-Fenton

The maximum and minimum chemical oxygen demand in 9 experiments were 86.39 and 12.30%, respectively. The average COD removal rate at each level and for each factor has been shown in Table (4) and the main effects for the signal-to-noise ratio have been shown in Figure (1-b).

According to Figure (1-b), the most effective factor in the PF process was pH. Delta values in Table (4) also show that after pH, the most important factors are radiant intensity, hydrogen peroxide and catalyst, respectively. The

appropriate levels for each of the factors influencing the process are at the highest point or so-called maximum signal-to-noise ratio. Therefore, the best conditions for PF test are pH = 3, H_2O_2 = 5mmol/l, catalyst = 10gr/l and radiant intensity is 32 watts.

As the radiant intensity increases, the potential for hydroxyl radical generation increases, resulting in higher COD removal rate. According to the diagram, it can be said that the optimal radiant intensity is equal to 32 watts. This finding is consistent with a study by Chinese researchers (using a 30-watt lamp) for the PF process. (Tambosi *et al.*, 2006). The most effective factor in this experiment was pH, which obtained the best conditions at an acidic value of pH = 3 unlike Fenton. The effect of this parameter on the PF process has been expressed differently in previous research. Some have preferred acidic pH (Dehghani *et al.*, 2014) and some alkaline pH (Xing, Sun and Yu, 2010). Therefore, after pH, factor radiant intensity, hydrogen peroxide and catalyst factors had the greatest effect on COD removal percentage, respectively (Figure (1-b) and Table 4). The hydrogen peroxide content at the lowest experimental value has given the best result which is consistent with other research (Dehghani *et al.*, 2014). The amount of $HO_2\bullet$ (which has less oxidizing ability) increase at high level of H_2O_2 (Xing, Sun and Yu, 2010). As with the Fenton process, the highest COD removal rate is associated with the highest catalyst content.

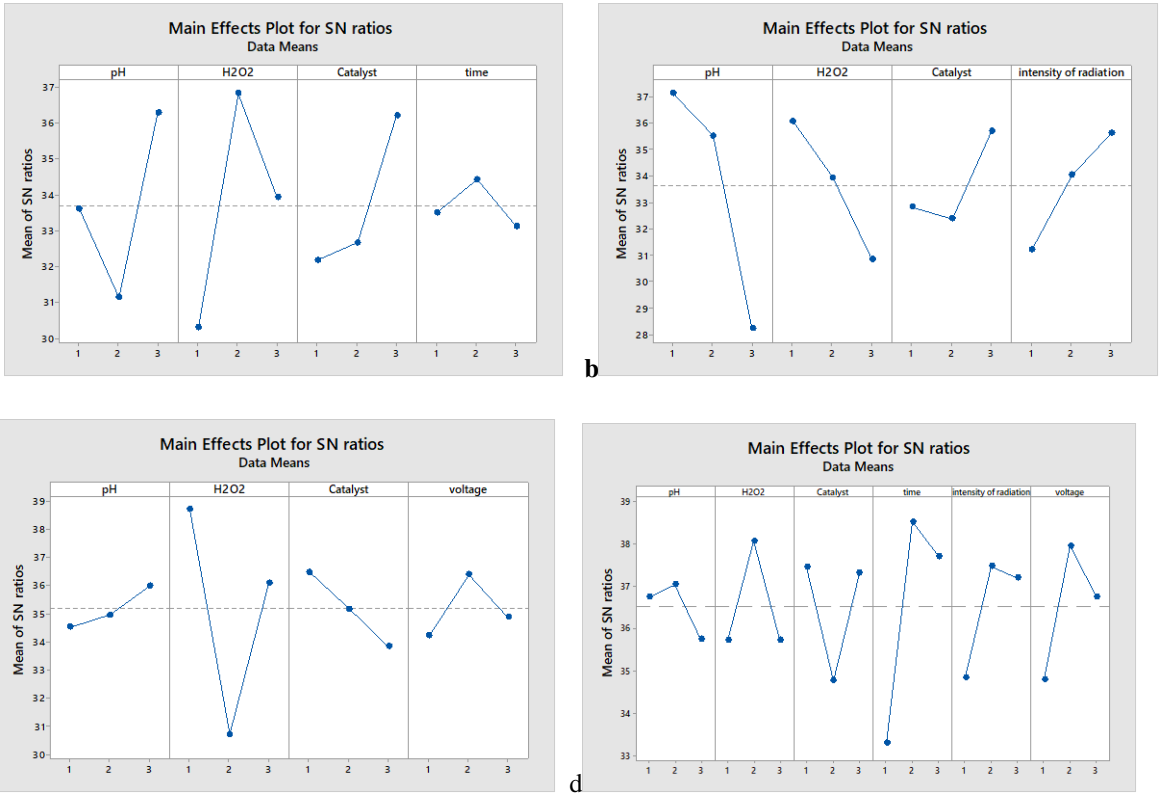

Fig. 1. Diagram of the main effects for the signal-to-noise ratio related to the COD removal percentage. a) Fenton process, b) PF process c) EF process, d) PEF process

3.3. Electro-Fenton

9 experiments were performed for the EF process, the highest and lowest COD removal rates were 93.42% and 25.82%, respectively. Table (4) and Figure (1-c) show the average COD removal rate at each level for each factor and the main effects for the S/N ratio. Given the signal-to-noise for each level of factors (Figure 1-c), the appropriate conditions for achieving the maximum response value are when the pH factors are at the third level (pH = 7), the voltage is at the second level (15 volts), and the hydrogen peroxide and the catalyst contents are in the first level (5 mmol/l and 5 g/l, respectively).

The most effective factor is hydrogen peroxide and after that catalyst, voltage and pH, respectively, were effective on the EF process in the COD removal percentage (Figure 1-c). As with Fenton and PF conditions, the lowest hydrogen peroxide content has had the best response. But in the case of the catalyst in this process, these two reversal processes of Fenton and PF, lower catalyst content has provided more appropriate results. The pH, similar to the Fenton process, has performed better under neutral conditions.

3.4. Photo-Electro-Fenton

According to Taguchi design for this process, 27 experiments were performed. The highest COD removal rate was 98.78% and the lowest was 14.59%. Table (4) shows the average COD removal rate at different levels of each factor and Figure (1-d) shows the main effects for the signal-to-noise ratio in PEF experiments.

According to the slope of variations in Figure (1-d), it can be said that the most effective factors are time, voltage, catalyst, radiant intensity, hydrogen peroxide and pH, respectively. In this experiment, the highest COD removal rate will occur when the optimal conditions for achieving the maximum response value include pH = 5, H_2O_2 = 10 mmol/l, catalyst = 5gr/l, 24 watt radiant intensity, 15 voltage and 60 minutes time.

Statistical analysis was performed to confirm the results of Taguchi method. Given the number of experiments performed on different processes, this study was feasible for the PEF process. Analysis of linear model of variance was performed for signal-to-noise ratio values and mean COD (Table 5). The results of multivariate analysis of variance showed that the time factor is significant at the level of one percent and the other parameters do not have a significant effect on the output variable. The study of the main effects of S/N ratio also showed a large effect of the time parameter. The R2 value of the linear model was 61.65% and the S value was 10.7354. The parameter S is used instead of R^2 to compare the suitability of models without any constant. The value of S is measured in response variable units and indicates how much the data values fall from the corresponding values. The lower the S value, the better the model describes the response. However, a low value of S or a high value of the coefficient of determination do not in themselves indicate that the model conforms to the assumptions of the model; The residual diagrams should be examined to validate the hypotheses (Figure 2). According to Figure (2), the residual values have been placed around the zero line, indicating the accuracy of the model. As observed in the NPP diagram, the points are almost on a straight line, indicating that the data is approximately normal. The residual versus order diagram is plotted for the independence of the observations. Given that the data are located around the horizontal axis, it can be said that our observations are completely independent and there is no correlation between them. According to the versus Fits diagram, it can be said that the assumption that the variances are constant is accepted.

The shape of the histogram has a positive or straight skew. This means that the data have dissymmetry relative to the mean, and the larger data lead to the lower frequency.

Table 5. Analysis of variance for signal to noise ratio and COD values

Source	S/N			COD		
	DF	Seq SS	P	DF	Seq SS	P
pH	2	8.332	0.682	2	47.3	0.931
H2O2	2	33.093	0.245	2	1344.7	0.167
Catalyst	2	40.981	0.182	2	1189.1	0.201
time	2	142.693	0.009	2	4765.7	0.007
UV	2	37.218	0.209	2	1125.4	0.217
Voltage	2	45.613	0.153	2	1707.2	0.111
Residual error	14	148.541		14	4616.3	
Total	26	456.471		26	14795.9	

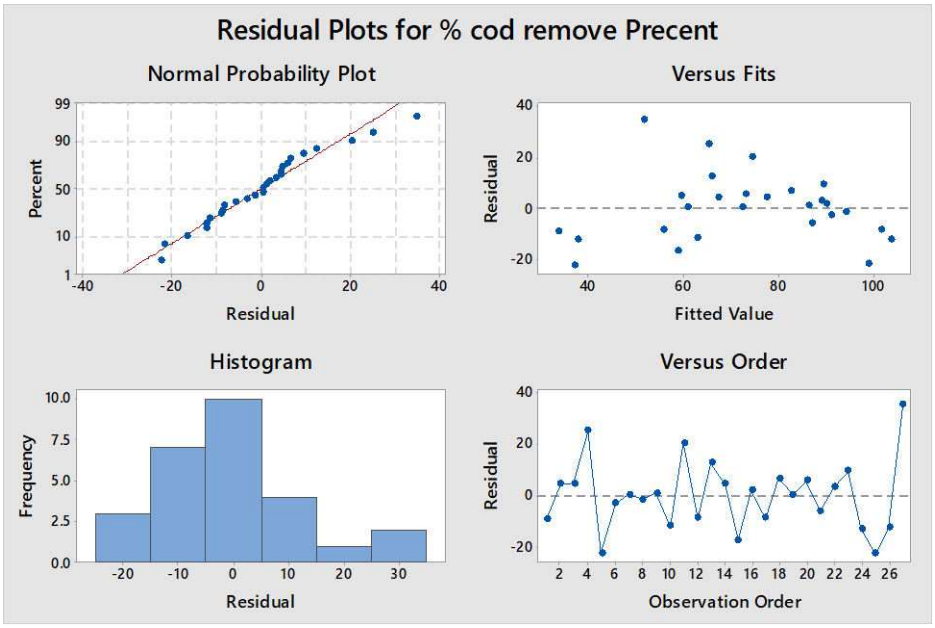

Fig. 2. Residual diagrams for COD removal percentage

Then, Tukey test was used to find the factor or factors that have a significant difference with other factors.

Table (6) shows a Tukey pairwise comparison at the 95% confidence level. The results of Tukey test also showed that the factor of time has a significant difference with other factors for COD removal in the PEF process.

3.4.1. Effect of experimental variables (PEF)

3.4.1.1 Effect of pH

Considering previous researches, little information is available on the performance of the heterogeneous PEF process. On the other hand, in these studies, most experiments have been performed on acidic pH (where catalysts can be partially dissolved) (Khataee, Zarei and Asl, 2010; Khataee and Zarei, 2011; Mousset *et al.*, 2017; Flores *et al.*, 2018; Oriol *et al.*, 2019; Ou *et al.*, 2019; Ye *et al.*, 2019). Thus, the efficiency of this process in neutral pH was also investigated. Experiments demonstrated that Fenton and EF processes performed best in neutral conditions and PF and EPF processes in acidic conditions. In PEF process, the rate of COD removal (due to reduced hydroxyl radical production) decreases near neutral. However, a decrease in system performance is observed at very low pH due to dissolution. This matter has been confirmed in previous research (Zhang *et al.*, 2009; Coronado *et al.*, 2013).

3.4.1.2 Effect of voltage

In the hybrid mode of the PEF process, the voltage level of 15 volts is optimal which is also economical in terms of energy consumption. Therefore, it can be said that in the PEF process, compared to the EF process, the COD removal efficiency has increased due to the use of radiation by applying a suitable voltage.

Table 6. Tukey pairwise comparison at 95% confidence level (COD removal in PEF process)

Parameter	level	N	Avarage	Group
pH	2	9	74.3771	A
	1	9	73.0413	A
	3	9	71.1509	A
H2O2	2	9	82.17	A
	3	9	71.3064	A
	1	9	65.0929	A
Catalyst	1	9	79.6327	A
	3	9	75.092	A
	2	9	63.8446	A
Time	2	9	84.6752	A
	3	9	79.5962	A
	1	9	54.2979	B
UV	2	9	79.3821	A
	3	9	75.1239	A
	1	9	64.0633	A
Voltage	2	9	80.194	A
	3	9	75.5676	A
	1	9	61.8077	A

* Averages with different letters are significantly different from the others

3.4.1.3 Effect of catalyst

The experiments showed that the optimum amount of catalyst in this process is equal to 5 g/l. The COD removal decreased for the catalyst amount of 7.5 g/l, and it increased again for the amount of 10 g/l. This final result being not consistent with the published data by Byrappa et al. (Byrappa *et al.*, 2008). Because of the amount of contaminants absorbed on the catalyst surface decreased with the increasing number of catalyst particles. It can be said that in general, when the amount of catalyst exceeds the optimum value, due to the turbidity of the environment, UV rays do not effectively reach the surface of the catalyst, and thus the removal efficiency decreases. The conditions of our study are consistent with Bayat et al. (BAYAT, EBRAHIMI and KEYVANI, 2013) in terms of process and acidic environment.

3.4.1.3 Effect of H_2O_2

According to Figure (1-b), the rate of 10 mmol/l is optimal for hydrogen peroxide which is consistent with the research by Felebuegu and Ezenwa (Ifelebuegu and Ezenwa, 2011). They were able to perform wastewater treatment operations during the Fenton-like oxidation process with this amount of hydrogen peroxide and other optimal conditions. Since the concentration of $HO_2\bullet$ is higher than OH● in solution, the ability of any reactions of

$HO_2\bullet$ is prevalent. It should be noted $HO_2\bullet$ has lower oxidizing ability and a longer lifetime than OH● (Tony *et al.*, 2009).

3.4.1.4 Effect of radiation intensity

Obviously, with increasing radiation intensity, the potential for hydroxyl radical production increases, and thus it causes for increasing the removal efficiency of COD. However, by increasing the radiation from 24 watts to 32 watts, due to the high concentration of organic matter, contaminants settle on the catalytic surface and prevent light from reaching the catalyst, ultimately reducing the photocatalytic removal (Takeuchi, Hidaka and Anpo, 2012). As a result, according to Figure (1-d), it can be said that the optimal radiation intensity is equal to 24 watts, which is consistent with the research of Xing and Sun (Xing, Sun and Yu, 2010).

3.4.2.5 Effect of contact time

The COD removal rate increases with increasing contact time. This increased time cause for more photon absorption by the catalyst surface and stimulate the photocatalyst, resulting in more free radical generation of OH● and higher removal efficiency. As shown in Figure (1-d), the S/N value increases significantly with increasing time to level 2 (60 minutes) and then decreases.

The optimal contact time in the PEF process for COD removal is 60 minutes. The contact time is a very important parameter in chemical reactions, and if it exceeds the optimal limit, it will not be an economic process (Oh *et al.*, 2005). However, it should be noted that with increasing time, the pores of the cathode surface fill with contaminate, which reduces the production of H_2O_2 and ultimately reduces the removal efficiency.Babuponnusami and Muthukumar (Babuponnusami and Muthukumar, 2012a), compared different Fenton processes, and found that the amount of pollutant degradation in the PEF process is higher which is consistent with our study.

3.5. Comparison of the efficiency of different processes for COD removal

In order to evaluate the efficiency of PEF process, the role of Fenton, PF, EF processes on the COD removal was investigated under the conditions of the highest removal percentage obtained. The effect of different processes on COD removal efficiency has been shown in Figure (3). According to Figure (3), it can be seen that PEF, EF, PF and Fenton, respectively, have high efficiency of removing COD from the desalination unit effluent samples. On average, they have between 70 and 100 percent COD removal capability. It seems that dissolved iron in the studied effluent has helped to increase the production of H_2O_2 (especially in electrochemical processes) (Ganiyu, Zhou and Martínez-Huitle, 2018; Nidheesh, Zhou and Oturan, 2018).

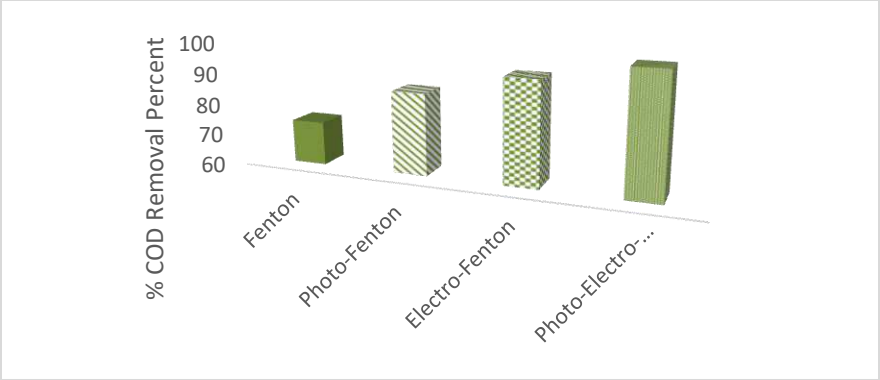

Fig. 3. The COD removal rate in various processes

4. Conclusion

Among the numerous advanced oxidation processes to reduce the chemical oxygen demand of petroleum effluents, Fenton-based methods are prominent. The chemical oxygen demand (COD) in the petroleum contaminated effluent during Fenton, PF, EF and PEF processes under the conditions of maximum removal is 74%, 86.39%, 93.42% and 98.781%, respectively, which shows that the combined PEF process with the highest rate of COD removal has a greater ability to mineralize the contaminated oil effluent; after that, EF, PF and Fenton processes have a good ability to reduce organic contaminators, respectively.

Considering the removal percentages obtained during these processes, it can be said that the slag fine particle catalyst of Khuzestan Steel Industries can be a suitable alternative to iron ions in Fenton-based processes as a catalyst. Also, cupal slag of steel industries of Khuzestan province, with suitable electrical resistance and current establishment, can be used as a cathode and anode in Fenton-based electrochemical process. Slag catalyst as a waste of Khuzestan steel industry has a very good potential for the treatment of petroleum industry effluents with very high organic pollution and resistant to biodegradation.

The results show that although Fenton-based processes can be used to reduce chemical oxygen demand pollution from petroleum industry desalination effluents; but the combined PEF process has a higher potential than other processes in removing chemical oxygen demand contamination from the effluent. The implementation of this system for the treatment of industrial effluents such as oil is recommended due to its high efficiency in reducing pollution, cost-effectiveness in industry, simplicity of work and ultimately less toxicity.

Declarations

-Ethics approval and consent to participate: 'Not applicable'

-Consent for publication: 'Not applicable'

-Availability of data and materials: The datasets used and analysed during the current study are available from the corresponding author on reasonable request.

-Competing interests: The authors declare that they have no competing interests.

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-Authors' contributions: All authors (F.E; P.T; SM.K and N.JH) conceived and designed the study. F.E carried out the experiments. Both F.E and P.T analyzed the data, wrote the manuscript, and discussed the results. F.E, P.T, SM.K and N.JH contributed to manuscript revision and approve it.

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