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Removal of chemical oxygen demand (COD) from hospital wastewater by electro fenton process using graphite–graphite electrochemical system

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ABSTRACT

Removal of COD from hospital wastewater generated from Al- Diwaniyah hospital located in Iraq was achieved using graphite–graphite electro-Fenton (EF) system. The effect of various operational parameters on the COD removal efficiency was investigated based on response surface methodology (RSM). Optimal conditions were current density of $20 mA/cm^2$, $FeSO_4$ concentration of 0.697 mM and time of 48.687 min. At these conditions COD elimination efficiency of 97.964 % was achieved at a specific energy consumption of 10.78 kWh/kg. The results indicated that time had the least effect on the COD removal efficiency, while the impact of current density had the greatest effect, followed by the $FeSO_4$ concentration. The adequacy of the model equation was confirmed by its high R^2 value (99.62%). The present study shows that graphite–graphite EF system was an efficient tool for removing of COD from hospital wastewaters.

1. Introduction

Medical wastewater contains a large number of macro and micro-pollutants with a wide range of concentrations such as microorganisms, toxic chemicals, antibiotics, and radioactive elements coming from laboratories, research units, operating rooms, and polyclinics [1]. Recently, the issue of wastewater containing drug residues and their derivatives has taken on a new importance. Numerous studies have been conducted and revealed the detrimental effects of pharmaceutical pollutants on various components of the environment. [2]. Appropriately, scientists are attempting to develop a method of disinfecting wastewater that is successful and meets the standards for practically total removal of contaminants. The latter is because even a trace amount of a medical pollutant has a detrimental effect on the environment's elements [3]. Many conventional techniques of hospital wastewaters (HWWs) treatment are used such as biological and physiochemical processes [4, 5]. Nevertheless, these methods have not the ability to treatment HWWs perfectly because of the composition and nature of these effluents. It was found that the biological treatment process suffered from many problems in the treatment of HWWs due to the adverse effects of the contaminants on the community of organisms used in the biological treatment [6]. Among advanced techniques, advanced oxidation processes (AOPs), as identified for the first time by Glaze et al. 1987[7], represent potential technology. These techniques are generated by means of strong oxidants in place, primarily radicals' hydroxyl (HO°), the second most potent oxidizing species ($E° = 2.80\ V/SHE$), capable of oxidizing any organic pollutant non-selectively up to the point of mineralization (conversion to Carbon dioxide and H_2O) (reactions 1α and 1β). HO° might well be created using a variety of activation mechanisms, including chemical (Fenton reaction), Photochemical reactions (Photolysis by ultraviolet light, photocatalysis on

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a heterogeneous scale, and photo-Fenton), sonochemistry, and electro-Fenton-reaction. [8-10].

$$HO^{\circ} + Organic\ pollutant \rightarrow Primary\ intermediates \qquad (1\alpha)$$

$$Primary\ intermediates + HO^{\circ} \rightarrow CO_2 + H_2O + inorganic\ ions \qquad (1\beta)$$

The most modern AOPs are electrochemical advanced oxidation processes (EAOPs). They have been created as a non-toxic, environmentally friendly, and cost-effective method of destroying organic compounds in water. [11-13]. The electrochemical oxidation (or anodic oxidation) and electro-Fenton (EF) processes are the most widely used EAOPs [8, 14, 15]. The chemical synthesis of OH° is commonly accomplished using the Fenton reaction (2), which utilizes a combination of H_2O_2 and a soluble ferrous iron salt, dubbed "Fenton's reagent." [8,9]:

$$H_2O_2 + Fe^{+2} \rightarrow Fe^{+3} + OH^{-} + HO^{\circ} \qquad (2)$$

Actually, H.J.H. Fenton discovered an increase in the oxidation power of hydrogen peroxide in the presence of (Fe^{+2}) at the end of the nineteenth century.[16]. After 4 decades, wise and Haber [17] established the reaction's dynamics and mechanism, establishing the explanation for the increase in oxidation efficiency caused by the production of HO° from Fenton's reagent via processes (1α) and (1β). The Fenton reaction is an easy method of producing HO°. Furthermore, the method requires a large volume of reagent to generate sufficient OH°. This has economic implications additionally to the production of sludge ferric that requires additional processing. Additionally, increased agent concentrations increase sludge processes (3) and (4), resulting in decreased effectiveness:

$$HO^{\circ} + H_2O_2 \rightarrow H_2O + HO_2^{\circ} \qquad (3)$$

$$HO^{\circ} + Fe^{+2} \rightarrow Fe^{+3} + OH^{-} \qquad (4)$$

These reactions are extremely damaging because they consume reagents and deplete HO°. As a result, the decrease in mineralization efficiency results in the development of potentially hazardous oxidation reaction intermediates. [18]. To eliminate these interactions, it is necessary to carefully manage the amount of Fenton's reagent .The optimum pH for EF is taken as 3. pH value higher than 3 leads to decrease EF oxidation efficiency due to the formation of low active $Fe\ (OH)_3$which has a lower tendency to react with H_2O_2 while a pH value lower than 3 generates less hydroxyl radicals and increases scavenging effect of H^+ and hydroxyl radicals [19]. Few works have been published which confirmed suggested graphite can be utilized as both electrodes in the EF process. [20]. Nidheesh et al [21] reported that graphite–graphite EF system has been demonstrated to be an effective electrolytic system for the dyes removal [22-24] and salicylic acid [25] from aqueous solution. The advantage of application graphite–graphite EF process as reported by Nidheesh et al [22] is that using graphite–graphite EF system would enhance the efficiency of the system as a result of forming graphite layer on the cathode from anode particles with no effecting on the homogeneity of the system.

The aim of present work is to treat hospital wastewater generated from Al-Diwaniyah hospital in Iraq using an electrochemical cell composed of porous graphite plates as cathode and anode materials. No such research had been conducted in the literatures. On the other hand, this work investigates the feasibility of EF technology in removal of COD from hospital wastewater where hydrogen peroxide is generated in-situ at porous graphite cathode and Fe^{+2} is added externally. The efficiency of COD removal was evaluated using constant-current mode of operation which is the most preferable mode for industrial scale-up. The impacts of three operating parameters namely applied current density, Fe^{+2}concentration, and time on the removal of COD from hospital effluent were investigated and optimized using Box-Behnken design (BBD) base on the response surface methodology (RSM).

2. Experimental work

As a case study, 30L of hospital wastewater was collected from sewage system of the General Diwaniyah hospital (located at Al- Diwaniyah city in Iraq) before mixing with the domestic wastewater of the city. **Table 1** shows the properties of the hospital wastewater. This hospital sewage was kept at 4 ºC during the period of the experimental program and the required sample (0.25 L) for each experiment was taken from this vessel before the operation.

Table 1. Characteristics of wastewater from the sewage system at Al-Diwaniyah Hospital

Variable	**value**
COD	780 (mg/l)
pH	7 (mg/l)
T.D.S	1130 (ppm)
Cl^-	1.6 (g/l)
SO_4^{-2}	0.4 (g/l)
Turbidity	11.2 (NTU)
Conductivity	2.29 (mS/cm)

Any chemicals utilized in this experiment were of analytical degree. $Na_2SO_4.10H_2O$ (purity 99.0%, Pellets, Sigma-Aldrich), $FeSO_4.7H_2O$(purity 99.5%, Pellets, Sigma-Aldrich), H_2SO_4(98% w/w, Sigma-Aldrich), and NaOH (purity 99%, Pellets, Sigma-Aldrich) were used in the Electro-Fenton reaction. Every experiment was performed in a batch manner with the aid of a cylindrical Perspex reactor provided with a cover. It has an internal diameter of 89 mm, a length of 80 mm, and a thickness of 5 mm (Fig. 1). The working volume of the reactor was approximately 0.25 L. The reactor cover was a square plate with 160 mm on the outside length and 10 mm on the thickness. Three holes with inside diameter of 15mm were made in the cover of reactor for inserting probes of conductivity meter, pH-meter, and sampling taking out. A further hole of 10mm for air distribution tube was made on the cover as well as two slots for inserting the electrodes. The anode and cathode were made of porous graphite. Each one of two electrodes has dimensions of 53 mm wide, thickness of 4 mm, and length of 85 mm. The distance between anode and cathode was fixed at 2.0 cm. porous graphite was provided from Tokai Carbon Co., Ltd. as ARC furnace. It has a surface area of approximately 0.892 m^2/g measured based on ISO-9277-2010 method at petroleum R &D center, ministry of oil in Iraq using BET surface area analyzer model No. Qsurf9600, Thermo Finnegan Co. USA. An air flow meter (0-5l/min, China) combined with air pump (model-ACO-208,45W, China) were used to supply the air to the reactor. The reactor and its cover were covered by aluminum foil to prevent the effect of light penetration hence dark conditions for the Fenton reaction was maintained.

Each experiment was carried out at a temperature of 25 ∓ 2 °C using a hot plate magnetic stirrer (model number MR HEI-Standard, HEIDOLPH) at a rotation speed of 250 rpm. The electrolyte pH was measured using a smart pH meter “HNNA Equipment Inc.PH211, Romania”, pH was changed using 0.1 M sodium Hydroxide or 0.1M sulfuric acid solutions. Constant current was supplied via a DC power supply type (UNI-T, UTP3315TFL-II, China). At the beginning of each run, 0.25L of wastewater was put into the reactor, then its pH was adjusted to 4 to make iron species soluble. The required amount of $FeSO_4.7H_2O$ was added with continuous stirring for 20 minutes before adjusting the pH to the required value. 0.05M of Na_2SO_4 was added as a supporting electrolyte to increase the conductivity to the suitable level.

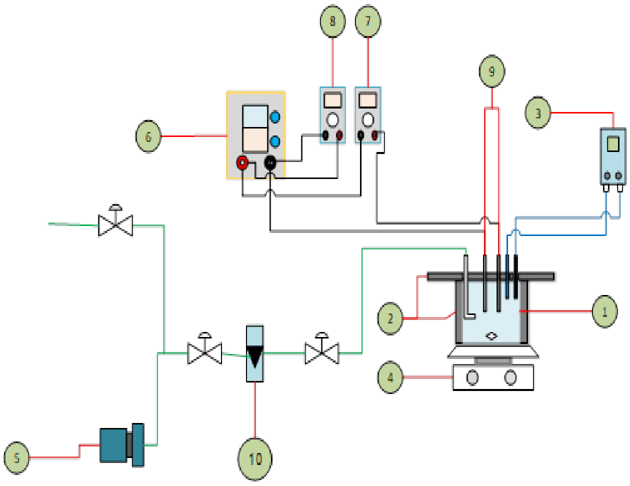


Figure 1. The Electro-Fenton System: 1) Reactor, 2) Aluminum Foil, 3) Conductivity and pH-Meter, 4) Hot Plate Magnetic Stirrer ,5) air pump, 6) power supply ,7) Ammeter ,8) Volt meter,9) Anode and cathode (porous graphite),10) Air flow meter.

The cell was provided with air for 15 minutes at a flow rate of 0.5 l/min then the power supply was switched on to provide the cell with the required current and started to record the time of experiment At the end of each run and before carrying out COD tests, solution pH was adjusted to 8.0 for removing residual Fe^{+2} (Fe^{+3}) then filtrated and tested its COD value. Conductivity and total dissolved solids (TDS) were determined by utilizing “Version COM-100, HM Digital Inc., Korea”. At the end of electrolysis, samples were collected and analyzed to check the COD and phenol concentrations. Solution turbidity was measured by (Jenway-6035, Germany). SO_4^{-2} and Cl^{-1} was analyzed by using Photo Flex. Series, (WTW model no 14541, Germany).

To determine the COD, a sample of effluent (2ml) was digested with $K_2Cr_2O_7$ for a period 120 min using COD thermos-reactor (RD125, Lovibond) at a temperature of 150 °C, the sample was then cooled to room temperature before COD determining by a spectrophotometer (MD200, Lovibond). Eq. 5 was used to compute the COD elimination efficiency, [26]:

$$RE\% = \frac{C_I - C_F}{C_I} \times 100 \qquad (5)$$

where C_F represents the final COD (mg/l) while C_I reflects the initial COD in milligrams per liter (mg/l).

The specific energy consumption (SEC) value represents the quantity of energy consumed during the process of digesting a kilogram of chemical oxygen demand. SEC in (kWh/kg) can be calculated using eq. 6. [27]:

$$SEC = \frac{E \times I \times t \times 1000}{(C_I - C_F) \times V} \qquad (6)$$

Where SEC refers for specific energy consumption per kilogram of chemical oxygen demand (kwh/kg COD), E denotes the applied cell voltage (Volt), t denotes the electrolysis period (h), I denotes the current (A), V denotes the effluent volume (L).

2.1. Design of experiments

Response surface methodology (RSM) summarized as a collection of mathematical and statistical tools for determining a regression model equation that correlate an objective function with its independent variables [28]. The present study used a three-level, three-factor Box–Behnken design (BBD) to investigate the effects of process variables on COD elimination. "Current density (X1)", "time (X2)", and "concentration of $FeSO_4$(X3)" were considered as process factors, while the COD removal efficiency (RE %) will be used as a responding. Process factor scales were classified into three levels namely (-1), (0), (+1) for low, intermediate and high value, respectively [29]. Table 2 depicts the process variables at their selected levels, while Table 3 depicts the experiments array recommended by BBD for this work using Minitab-17 software.

Table 2. Variables in the process of hospital wastewater treatment along with their level.

Variables of the process	**Box– Behnken level**		
Levels that are coded	Low(-1)	Middle (0)	High (+1)
X1-current.density (mA/cm^2)	10	15	20
X2- Time(min)	20	40	60
X3-Fe SO_4(mM)	0.2	0.5	0.8

Correlation between the response and its independent variables was determined in this study using the following second-order model and least-squares approach [30]:

$$Y = a_0 + \sum a_i x_i + \sum a_{ii} x_i^2 + \sum a_{ij} x_i x_j \qquad (7)$$

Where Y is the response (Removal %), i and j denote the index numbers for the pattern, a_0 denotes the intercept term, and x_1, x_2,... x_k denote the parameters used in the operation in coded form. The primary influence of the first order (linear) is denoted by a_i. the second-order main effect is denoted by a_{ii}, and the interaction effect is denoted by a_{ij}. After doing an analysis of variance, For the purpose of demonstrating the model's suitability, the regression coefficient (R^2) was computed.

3. Results and Discussion

3.1. Results of experimental design

According to BBD design, fifteen runs were performed to investigate the optimum conditions for COD removal. The experimental results for Removal efficiencies (RE percent) and specific energy consumption (SEC) are summarized in Table 4.

Results showed that efficiency of COD removal was in the range of 81.38-97.3% while the specific energy consumption ranged between (1.970-14.294) (kwh/kg. COD). As a preliminary inspection, a comparison between run (6) and run (7) demonstrated that the concentration of $FeSO_4$ has a significant effect on COD removal efficiency where RE% increased from 81.38 to 92.465 % making a difference of 11.085 % as $FeSO_4$ concentration increased from 0.2to 0.8 mM at constant current density of 10mA/cm^2 and time of 40 min. While the comparison between running (7) and (12) demonstrated that the density of current followed the concentration of $FeSO_4$ in its impact on the COD removal efficiency where the RE% increased from 92.465 to 97.3% which made a difference of 4.835% as the current density increased from 10 to 20 mA/cm^2 at constant $FeSO_4$ concentration of 0.8 mM and time of 40 minutes.

Table 3. Experimentation with the Box-Behnken style

Run	Blk	Coded levels			Real value		
		x_1	x_2	x_3	Current density (mA/cm^2), X1	Time (min), X2	FeSO$_4$(mM), X3
1	1	1	-1	0	20	20	0.5
2	1	0	1	1	15	60	0.8
3	1	0	0	0	15	40	0.5
4	1	-1	1	0	10	60	0.5
5	1	0	-1	-1	15	20	0.2
6	1	-1	0	-1	10	40	0.2
7	1	-1	0	1	10	40	0.8
8	1	1	0	-1	20	40	0.2
9	1	1	1	0	20	60	0.5
10	1	-1	-1	0	10	20	0.5
11	1	0	1	-1	15	60	0.2
12	1	1	0	1	20	40	0.8
13	1	0	0	0	15	40	0.5
14	1	0	0	0	15	40	0.5
15	1	0	-1	1	15	20	0.8

Table 4. Box–Behnken design (BBD)for COD elimination experimental results

Run Order	Blocks	Parameters			E (volt)	RE%		SEC
		X1	X2	X3		Actual	Predicted	$\frac{KWh}{kg\ COD}$
1	1	20	20	0.5	6.52	94.17	94.05738	5.065
2	1	15	60	0.8	5.565	95.125	95.51863	9.804
3	1	15	40	0.5	5.305	94.192	93.938	6.0333
4	1	10	60	0.5	4.525	90.065	90.17763	5.569
5	1	15	20	0.2	6.43	84.031	83.63738	4.242
6	1	10	40	0.2	4.53	81.38	81.4595	4.0996
7	1	10	40	0.8	4.885	92.465	91.95875	3.816
8	1	20	40	0.2	6.49	88.026	88.53225	10.974
9	1	20	60	0.5	6.22	96.093	95.77888	14.294
10	1	10	20	0.5	4.625	87.01	87.32413	1.970
11	1	15	60	0.2	5.265	85.02	84.82788	10.351
12	1	20	40	0.8	6.05	97.3	97.2205	9.053
13	1	15	40	0.5	5.32	93.856	93.938	6.252
14	1	15	40	0.5	5.305	93.766	93.938	6.269
15	1	15	20	0.8	5.335	91.942	92.13413	3.247

However, the precise effect of these parameters and their interactions can be observed via ANOVA results.

The findings of the Removal effectiveness were evaluated using the Minitab-17 program, and a quadratic model of the Removal efficiencies (RE percent) in terms of real units of process parameters was developed as follows:

$$RE\% = 50.85 + 1.685\,X1 + 0.3406\,X2 + 55.47\,X3 - 0.0268\,(X1)^2 - 0.003583\,(X2)^2 - 38.61(X3)^2 - 0.00283\,X1X2 - 0.302\,X1X3 + 0.0914\,X2X3 \quad (8)$$

In which X1X2, X1X2, and X2X3 denote the model parameters' interaction effects. $X1^2$, $X2^2$, and $X3^2$each constitute a parameter's principal influence. Using equation 8, the predicted values of the COD removal efficiency was estimated and tabulated in Table 4.

In eq.8, the positive coefficient in front of any parameter reveals that RE% increases with its increasing and vice versa. Analysis of variance (ANOVA) was used to determine the acceptability of BBD. It really is an analytical technique that utilizes Fisher's F-test and P-test to estimate the model's and its parameters' significance [31]. In principle, bigger F-values and lower p-values indicate that the coefficient terms are more important [32]. Table 5 illustrates an ANOVA using the response surface model. In this table, Contr.% denotes percentage of contribution of each variable, DF represents degree of freedom of the model and their parameters, and the statistical terms are represented by sum of the square (Seq. SS), adjusted sum of the square (Adj. SS), and adjusted mean of the square (Adj. MS) respectively. P-value of (0.0001) and F-value of (145.59) were obtained which elucidate that regression model is highly significance. The model's multiple correlation coefficient (R^2) was 0.9962, indicating that the regression is statistically significant and only (0.0038) of the overall variation is not confirm by the model. The adjusted multiple correlation coefficient (adj. R^2) =0.9894 and the predicted multiple correlation coefficient (pred. R^2) =0.9435 in this model were well-matched since the difference between them less than 0.2 [33].

Results of Table 5 showed that $FeSO_4$ concentration has the major effect followed by current density with contributions of 56.78% and 23.46% respectively. While time has a lower effect with contribution of 3.23%. The high contributions of current density and $FeSO_4$ concentration confirm that EF governed by these two variables. This result is expected since EF process is governed by Eq.2 where Fe^{+2} is furnished externally and H_2O_2 is generated internally based $FeSO_4$ and current density. The squared interactions are significant with a contribution of 15.43% in which squared interaction of $FeSO_4$ concentration has the most effect. The 2-way interactions among the variables are non-significant. The P-value for lack of fit ($0.120 > 0.05$) indicates that the lack of model fit was not statistically significant in comparison to the pure error in this investigation [34].

As a result, the model can generate an adequate prediction that corresponds to the response values.

Table 5. Analysis of variance for chemical oxygen demanded reduction

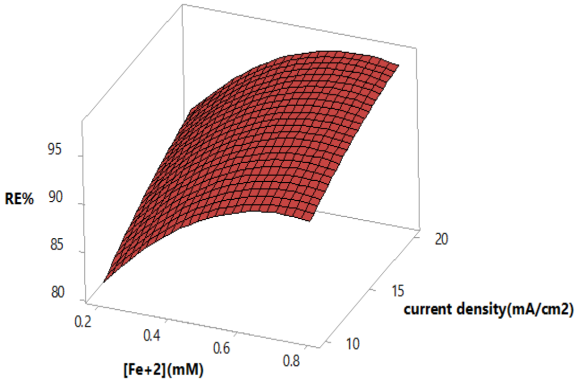
Source	DF	Seq. ss	Contr. %	Adj. ss	Adj. Ms	F-value	P-value
Model	9	322.981	99.62	322.981	35.887	145.59	0.001
Linear	3	270.615	83.47	270.615	90.205	365.95	0.001
(X1)	1	76.070	23.46	76.070	76.070	308.61	0.001
(X2)	1	10.465	3.23	10.465	10.465	42.46	0.001
(X3)	1	184.080	56.78	184.080	184.080	746.80	0.001
Square	3	50.022	15.43	50.022	16.674	67.64	0.001
"X1 ∗ X1"	1	0.381	0.12	1.658	1.658	6.73	0.049
"X2 ∗ X2"	1	5.050	1.56	7.586	7.586	30.78	0.003
"X3 ∗ X3"	1	44.590	13.75	44.590	44.590	180.90	0.001
2-Way Inter.	3	2.344	0.72	2.344	0.781	3.17	0.123
X1 ∗ X2	1	0.320	0.10	0.320	0.320	1.30	0.306
X1 ∗ X3	1	0.820	0.25	0.820	0.820	3.33	0.138
X2 ∗ X3	1	1.203	0.37	1.203	1.203	4.88	0.078
Error	5	1.232	0.38	1.232	0.246		
Lack of Fit	3	1.132	0.35	1.132	0.377	7.48	0.120
"Pure-Error"	2	0.101	0.03	0.101	0.050		
Total	14	324.213	100.00				
Model-summary		S.	R^2	R^2(adj.)	PRESS	R^2(pred.)	
		0.496481	99.62%	98.94%	18.3331	94.35%	

3.2. The Influence of process factors on the efficiency of COD removal

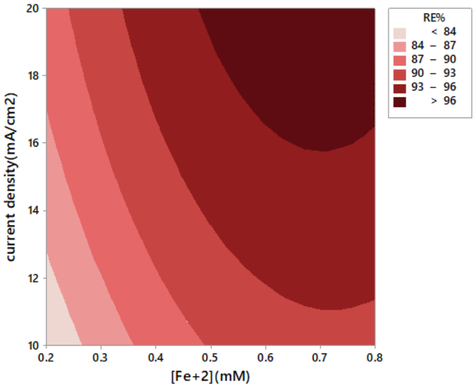
Graphical representations of RSM can be used to demonstrate the influences of specified variables on the response. The Figs. (2-i and 2-j) illustrate the effect of FeSO$_4$ concentration on the RE percent at different current densities (10-20 mA/cm^2) during a constant time period (40 min.). Fig. 2-i depicts the surface response plot, while Fig 2-j depicts the contour plot. The surface plot revealed that, at the same current density (10 mA/cm^2), an increase in COD removal efficiency occurs as the Fe^{+2} intensity rises from 0.2 to 0.8 mM. The increasing in RE% occurs rapidly at the first stage then tends to be sluggish at final stage. Similar observation was identified at higher current density (20mA/cm^2). This behavior can be interpreted as increasing Fe^{+2} concentration improved the hydrogen peroxide's oxidizing ability to degrade big molecules, therefor increasing concentration of Fe^{+2} leads to more degradation of organic compounds in wastewater [29]. Previous studies showed that Fe^{+2} has the ability to destroyed big molecule in wastewater such as dyestuffs, in real dyeing wastewater [35].

At any concentration of FeSO$_4$, RE% increases linearly with increasing of current density from 10 to 20 mA/cm^2. This behavior of the effect of current density on RE% is in agreement with previous work [36, 37] and could be explained as the current considers as the driving force for the reduction of oxygen on the cathode surface leading to generate H$_2$O$_2$ hence, by increasing the current density, more generation of $^\bullet$OH would be happened due to reaction of H$_2$O$_2$ with ferrous ions.

The corresponding contour plot indicates that the ≥96 percent COD removal efficiency value is contained inside a limited area with a current density of (16-20 mA/cm^2) and FeSO$_4$ concentration of (0.5-0.8 mM). The shape of control plot indicates the nature and extent of the interaction. The Figs. (3-i and 3-j) explain the impact of time on the RE percent at varied current densities (10-20 mA/cm^2) and constant FeSO$_4$ concentration (0.5mM).



(i) Contour plot

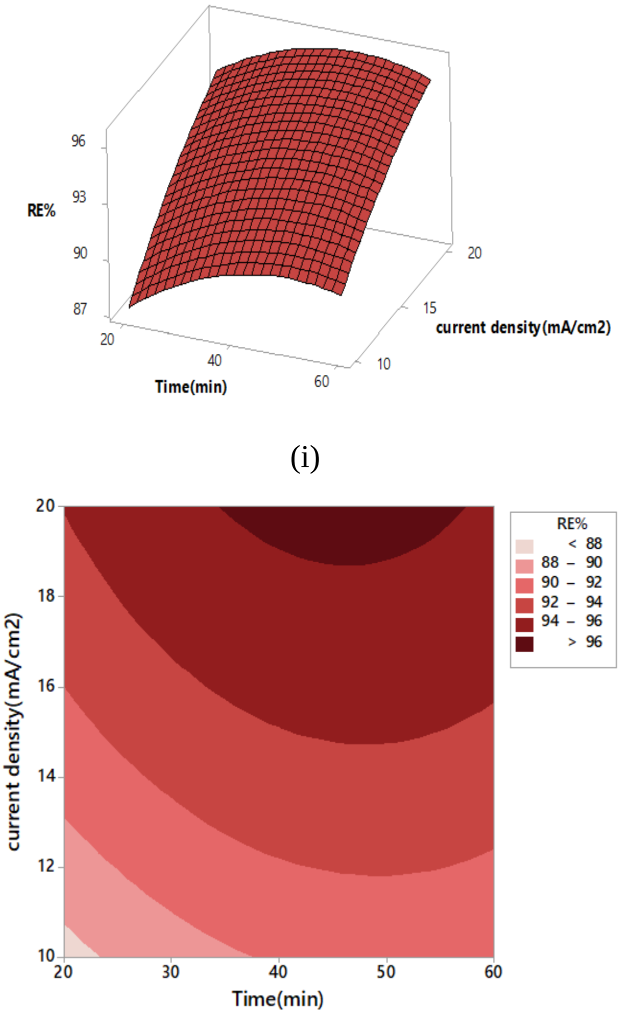


(j)

Values maintained for a period of 40 minutes

Figure 2. Display of the impact of FeSO4 concentration and current density on the percent of RE in a three-dimensional surface plot

As illustrated in Fig. 3-i, the effectiveness of COD elimination is exponentially grown in proportion to the growth of time then started to be approximately constant beyond 40 min for any values of current density. These findings agree those seen in the previous studies [38-41]. The findings indicate that the reaction time has a positive impact on the progress of the EF process for a limited period. The corresponding contour plot (3-j) indicates that the ≥96 percent COD elimination efficiency occurs in a limited area with a current density of (19-20 mA/cm^2) and a time range of 35-55 minutes.

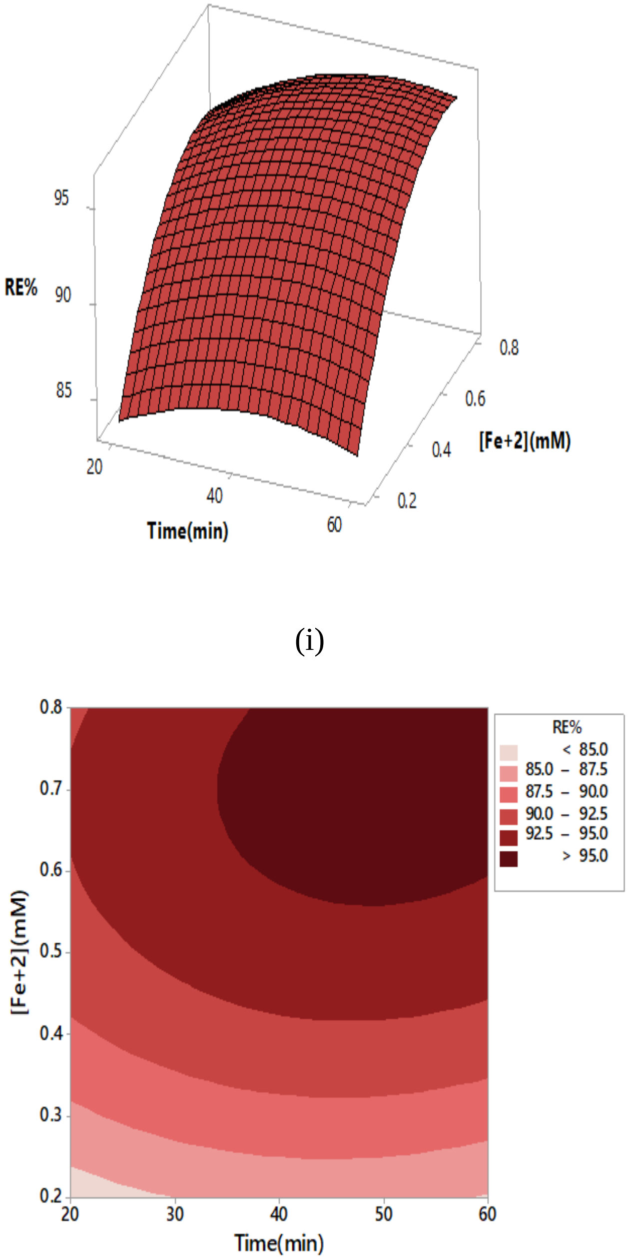


(i)

(j)

Figure 3. Shows the effect of time and current density on the RE percent using a 3d surface plot (i) and a contour plot (j). (Maintain value: FeSO4 concentration =0.5mM).

The figs. (4-i and 4-j) illustrate the impact of time on the RE percent for varied $FeSO_4$ concentrations (0.2-0.8 mM) and a constant current density of 15mA/cm^2. At any $FeSO_4$ concentration, Fig. (4-i) demonstrates that the COD removal efficiency increases exponentially with increasing time. The reaction time has a positive effect on the progress of electro- Fenton process up to 40min then start to sluggish. At any time, the results show that the increasing in RE% occurs rapidly at the first stage then tends to be sluggish at the final stage when concentration of $FeSO_4$ increased from 0.2 to 0.8mM. The corresponding contour Fig. (4-j) demonstrates that the ≥95 percent COD removal efficiency value is contained within a limited area with $FeSO_4$ concentrations ranging from (0.6-0.8 mM) and times ranging from (35-60 min). As a result, the application of RSM enabled the identification of feasible optimum values for the researched parameters, as well as its function in providing valuable information about the interactions among variables.



(i)

(j)

Figure 4. shows the impact of time and concentration of Fe^{+2} on the RE percent using a 3d surface plot (i) and a contour plot (j). (Hold value: current density =15 $\frac{mA}{cm^2}$)

Table 6. Process parameter optimization for optimal COD removal efficiency (RE %).

Response	**Goal**	**Lower**	**Target**	**Upper**	**Weight**	**Importance**	
RE (%)	*maximum*	81.38	Maximum	97.3	1	1	
Solution:							
Parameters			**Results**				
Current density (mA/cm^2)	FeSO$_4$ (mM)	Time (min)	R E (%) Fit	D$_F$	SE Fit	95% CI	95% PI
20	0.697	48.687	97.97	1	0.362	(97.035, 98.896)	(96.386, 99.545)

Table 7. Confirmative value of the optimum COD removal efficiency

Run	**Current density (mA/cm^2)**	**FeSO$_4$ (mM)**	**Time (min)**	**E (Volt)**	**COD (ppm)**		**R E (%)**		**EC (Kwh /kg COD)**
					Initial	**Final**	**Actual**	**Average**	
1	20	0.697	48.687	6.03	786	16	97.964	97.831	10.78
2	20	0.697	48.687	6.045	782	18	97.698		10.89

Table 8. Comparison between untreated and treated sewage

Parameter Effluent	**COD (ppm)**	**Phenol (ppm)**	**Turbidity (NTU)**	**SO$_4^{-2}$ (ppm)**	**Cl$^-$ (g/l)**
Raw effluent	786	0.38	11.2	400	1.6
Treated effluent	16**(97.964%)**	0.013**(96.58%)**	0.37**(96.70%)**	810	0.95

Improving of an electrochemical system is essential to reduce energy losses. Numerous criteria should be considered when optimizing the system in order to achieve the desired target via maximization of the desirability function (D$_F$) [28]. The target function choices could be "maximized", "objective", "minimize", inside the limit, and neither one. The target of COD removal was designated as the ‘maximum’ with D$_F$=1.0. The process factors studied in the present work were recognized within current at range of (10-20 mA/cm^2), FeSO$_4$ concentration at range of (0.2-0.8mM), and time at range of (20-60 min). A COD elimination effectiveness of 81.38 percent was chosen as the lower limit value, while the upper limit value was allocated at 97.3%. Under these boundaries and settings, optimization was carried out and the results are shown in Table 6. Two confirmative runs were conducted under the optimized settings to verify them; the results are shown in Table 7. After electrolysis of approximately 49 min, COD removal efficiency of 97.83% as average value was achieved at pH=3 that is consistent with optimization analysis limiting range of the optimal value (Table 6). As a result, BBD is effective and useful at optimizing Removal efficiencies via the porous graphite–graphite EF system.

Table 8 shows a comparison between untreated and treated sewage based on the results of this study. As can be seen, treated wastewater has improved characteristics and conforms to the standard limits for effluent discharge (100ppm) [26]. Chemical oxygen demanded removal efficiency of 97.96%, phenol removal efficiency of 96.58%, and turbidity removal efficiency of 96.70% based on the raw effluent properties were achieved in the present work approving the activity of EF process in treatment wastewater generated from Al- Diwaniyah hospital in removal both of COD and turbidity. The increase in sulfate ions in the treated effluent is due to the using of ferrous sulphate while the decreasing in Cl$^-$ ions is due to the generation of some chlorine on the anode which has another benefit for decreasing COD due to indirect oxidation of pollutant by ClO$^-$ [27].

The present work demonstrates that the graphite–graphite EF system may be effectively utilized to the treatment of Al- Diwaniyah hospital wastewater. Starting from an initial COD of 786 ppm, it could be achieved a COD removal efficiency of 97.964% at operating time of approximately 49min with an energy consumption not exceeded 10.78 kWh/kg COD. In comparison with our previous work [27]. using the same source of wastewater and applying an electrocoagulation method, the present system is more efficient in term of time and energy consumption where in our previous work by beginning with an initial chemical oxygen demand (745 ppm), The effectiveness of COD elimination of 99.3% was achieved at electrolysis time of 90 min with energy consumption of 26.079 kWh/kg COD , while in present work, approximately the same removal efficiency of COD was obtained at 49min and 10.78 kWh/kg COD. This an indication that EF process oxidizes the refractory natural or organic compounds that existing in hospital wastewater in a more proficient way. Moreover, the present system could be considered as an economic one since it used electrodes made from cheap materials and its specific energy consumption is approximately lower and suitable in comparison with previous studies [27].

4. Conclusions

The present work examined the reduction of chemical oxygen demand from hospital sewage by electro- Fenton process using an electrochemical cell having cathode and anode made from porous graphite. Impacts of Current density, $FeSO_4$ concentration on the chemical oxygen demand reduction from the hospital wastewater generated at Al- Diwaniyah hospital located in Iraq were investigated using RSM. Based on RSM, the optimal conditions were current density of 20mA/cm^2, $FeSO_4$ concentration of 0.697 mM and time of 48.7 min, in which COD removal and specific energy consumption were 97.964% and 10.78 kWh/kg. COD respectively. The high value of R^2, adj.R^2 and pred. R^2 value indicate that the model fitted very well to the experiment data and RSM was successfully applied to analyze the impact of various operating factors at lower number of runs and lower cost of chemicals. The efficiency of graphite–graphite EF system was found to be influenced by two main parameters current density and $FeSO_4$ concentration in which $FeSO_4$ concentration has the main effect followed by current density. The present system gave better performance and lower energy consumption in comparison with previous works due to the powerful oxidation mechanism adopted in the present system. Graphite–Graphite EF technique for the removal of COD from sewage water was shown to be an environmentally beneficial procedure, according to the findings of current study.

Authors' contribution

All authors contributed equally to the preparation of this article.

Declaration of competing interest

The authors declare no conflicts of interest.

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