A graphite cathode modified by an industrial grade of carbon black for assisting electro-Fenton technique: A pesticide wastewater treatment

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Abstract

In this study, Electro-Fenton (EF) reaction was employed to treat a hazardous and resistant wastewater from a pesticide factory using graphite cathode modified with industrial carbon black (N330). Carbon black nanoparticles (N330) could increase the porosity of cathode surface and hydrogen peroxide production during the electro-Fenton reaction. In order to examine the quality of the porous surface of modified cathode, Atomic Force Microscopy (AFM) and Field Emission Scanning Electron Microscopy (FESEM) tests were successfully applied. Moreover, the performance of the modified cathode was assessed by the Cyclic Voltammetry (CV) test. The experiments were designed using the Central Composite Designs (CCD) technique under the Response Surface Methodology (RSM). The Analysis of Variance (ANOVA) showed that the model was accurately able to predict the process. 78.15% of COD removal was optimally found a current intensity of 253 mA, air flow rate of 1.56 L/min, Fe^{2+} catalyst dosage of 0.63 g, pH of 3, and reaction time of 126 min, while 33.78% of COD removal (with 15 mmol/l of hydrogen peroxide production) was obtained at pH of 6 (close to the original pH of wastewater) on the modified cathode.

Keywords: Advanced Oxidation Process, Effluent, Neutral pH, Optimization

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Introduction

Pesticides are substances or chemical compounds used to kill, repel, and eradicate pests or stop their growth [1] . These chemicals are one of the most powerful things in managing agricultural pests and have a wide range of effects and applications in the greater yields of crop production [1, 2]. Pesticides have been used in the public health, as well. They were as savior of human during the widespread diseases outbreak [3, 4]. The effluents of pesticide production units have recently become a serious problem for the solution. Therefore, some studies on this effluent treatment have been encouraged [5, 6]. The advanced oxidations are classified as photochemical and non-photochemical reactions. There are included various technologies such as wet air oxidation, photocatalytic oxidation, ozonation, electrochemical oxidation, and Fenton [7, 8]. Among these, Fenton process as a standard approach has been proposed to treat several wastewaters containing pesticides and insecticides. Some researchers used the Fenton and photo-Fenton process to degrade diazinon (DZN) [9]. Gonçalves et al. employed photo-Fentonto treat a synthetic wastewater containing imidacloprid, atrazine, ametrine and tebuthiuron [10]. Vasseghian et al. compared three processes, sono-photo Fenton, photo-Fenton and Fenton, for treating a synthetic wastewater containing malathion [11]. Fenton process was accidentally recognized first in 1894 when Henry John Horstman Fenton was researching the oxidation of tartaric acid by a mixture of hydrogen peroxide (H_2O_2) and iron salts (Fe^{2+}) [as shown in Eq. (1)] [12, 13]. This process was later introduced by Haber and Weiss in 1939 when they found that hydroxyl radical ($°OH$) was an effective agent for decomposition during the Fenton process [14]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^· + OH^- \tag{1}$$

One of the main challenges of the Fenton reaction is hydrogen peroxide cost [15-17]. This can be assisted by electrical current which is called electro-Fenton process. Hydrogen peroxide is generated on the cathode surface [as shown in Eq. (2)] [17, 18]:

$$2e^- + O_2 + 2H^+ \rightarrow H_2O_2 \tag{2}$$

There also is the possibility of reducing the ferrous ions on the cathode surface during the electro-Fenton reaction [as shown in Eq. (3)] however, ferrous ions are regenerated according to Eq. (4) [17, 19, 20].

$$e^- + Fe^{3+} \rightarrow Fe^{2+} \tag{3}$$

$$H_2O_2 + Fe^{3+} \rightarrow HO_2^· + Fe^{2+} + H^+ \tag{4}$$

Furthermore, the amount of H_2O_2 produced in the electro-Fenton process directly affects the treatment process [15, 17] .To make hydrogen peroxide through Eq. (2), oxygen and electricity should be supplied in the reaction medium [21]. Moreover, dissolution of pure oxygen in water at the ambient temperature of 25 ± 2 °C and atmospheric pressure is about 40 mg/l. Since the ambient air is used to supply the required oxygen where air dissolution at the ambient temperature and atmospheric pressure is significantly reduced about 7 mg/l, more electricity should be consumed to compensate this shortage of oxygen during the hydrogen peroxide production. So, the process costs would be escalated [17, 19]. Several researches have focused on this issue to improve cathode material with increasing its porosity and electrical conductivity. According to a study, the electro-Fenton process was assisted by a surface-reconstructed graphite felt cathode to degrade norfloxacin [22]. According to another

research, the other researchers designed ordered mesoporous carbon (OMC) as a bifunctional catalyst to produce hydrogen peroxide and hydroxyl radical in the electro-Fenton reaction [23]. Hongkai et al. used a graphite cathode modified by acetylene black/polytetrafluoroethylene to treat Norfloxacin [24]. Gao et al. employed a carbon felt cathode modified by free anthraquinone /polyaniline for selective hydrogen peroxide production and pollutant removal in the electro-Fenton reaction [25]. The porosity and electrical conductivity increment of cathode leads to more effective contact of dissolved oxygen in the solution with the surface of cathode. This would limit the electrical energy consumption [21, 26-28].

In this study, a graphite cathode modified by carbon black nanoparticles (N330) was utilized to treat a real resistant and hazardous effluent from a pesticide factory through the electro-Fenton process. Modification of the cathode surface will increase hydrogen peroxide production from injected air. This industrial-grade carbon black is usually applied to improve the characteristics of pipes, belts, hoses, and cable sheathing. The porosity of the modified electrode surface was examined using FESEM and AFM images, although its performance was evaluated using the Cyclic Voltammetry (CV) test .Then, the amounts of hydrogen peroxide produced at various stages were carefully measured using the iodometric method. Then, the effects of multiple parameters such as Fe^{2+} catalyst dosage, current intensity, air flow rate and reaction time on the amounts of H_2O_2 production at a fixed concentration of electrolyte (0.05 M Na_2SO_4) were also investigated through the electro-Fenton process with unmodified (graphite) and a modified cathode [coated by carbon black nanoparticles (N330)] under two pHs of 3 (as the best pH for electro-Fenton process) and 6 (as original pH of wastewater) for treating a wastewater obtained from a pesticide factory. CCD under RSM was applied to design, analyze and optimize the operating conditions.

Experimental and methods

Wastewater

A wastewater sample from Arman Sabz Adineh Co. (Saveh, Iran), a pesticide factory, was provided. The properties of the sample are shown in Table 1.

Table 1: Properties of the applied pesticide wastewater

Parameter	Unit	Range	Average
COD	mg/l	1098-1148	1123
BOD	mg/l	593-631	612
TOC	mg/l	967-1003	985
pH	-	5.8-6.2	6

Materials

The pure graphite sheets were purchased from Parse Graphite Co. (Iran). They were carefully cleaned with distilled water and acetone. Figure 1 shows a chemical analysis of a pure graphite sheet .Industrial carbon black (grade N330) was purchased from Pars Saveh Industrial Carbon Black Co. Its uniform distribution with particle size of 150 µm was considered by an ideal sieve. Table 2 lists the specifications of this industrial-grade carbon black although Figure 2 shows its FESEM images in two scales.
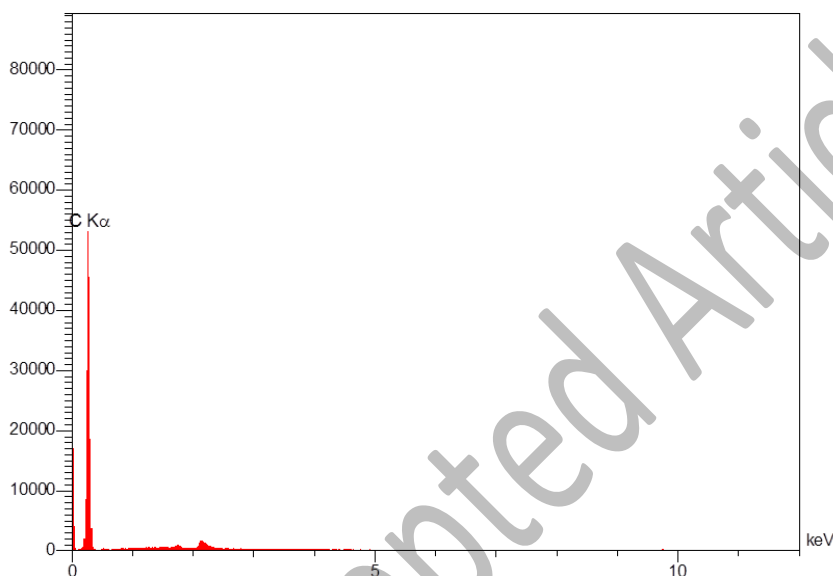

Figure 1: EDAX spectrum of graphite

Table 2: Properties of the carbon black (N330)

Parameter	Value
Purity	*>99.3 (wt %)*
pH	*8.7*
Bulk density	*0.375 (g/cm^3)*
Blackness	*285*
Surface area	*250 (m^2/g)*
Ash content at 650 °C	*0.8 (wt %)*
Electrical conductivity	*≤150 (µs/cm)*
Oil absorption number	*52 (ml/ 100g)*
Average primary particle size	*45(nm)*
Volatile matter content at 950 °C	*1*

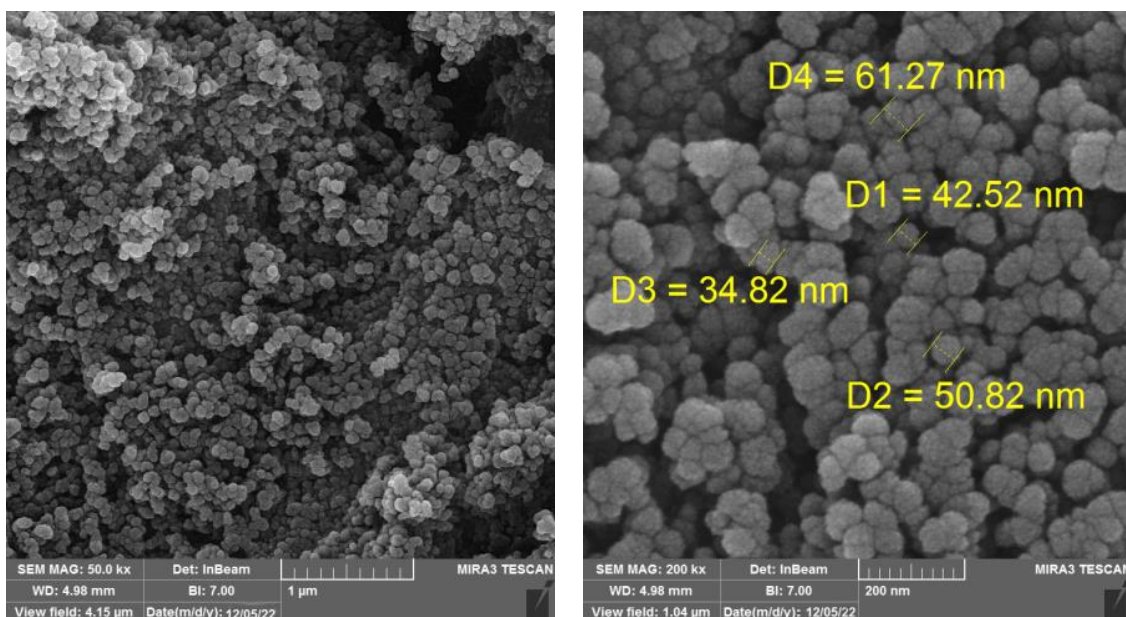a)   b)

Figure 2: FESEM images of carbon black (N330) nanoparticles in two scales: 1µm (a) & 200 nm (b)

Polytetrafluoroethylene (PTFE) powder was purchased from Nano Bonyan Asia Trading Co. (Iran). N-butanol, sodium sulfate, hydrogen peroxide, potassium hydrogen phthalate, potassium iodide, sodium hydroxide ammonium, molybdatetetrahydrate, sulfuric acid and iron (II) sulfate were supplied by Merck Co.

Facilities

The CV was done by a potentiostat-galvanostat (VIE MP2C, IVIUM Vertex). The morphology of the modified electrode was considered by an Atomic Force Microscope [(AFM) ARA-AFM Full Plus, Iran]. FESEM was carried out by a TESCAN MIRA3 device (Czech). A COD-meter (HANNA HI83214, US) and BOD-meter (OXITOP IS6, German) were used to measure the wastewater COD and BOD. The pH was adjusted using a pH-meter (PRT-79, Iran). A DC power supply (Iran, Micro PW-4053S) prepare the required electric current. An air pump (China, SB-2800) was applied to inject air into the wastewater.

Methods

Cathode preparation

0.5 g of industrial carbon black nanoparticles with 2 g of polytetrafluoroethylene were initially mixed and then dissolved in 150 ml of 3% n-butanol solution in an ultrasonic bath for 30 minutes .The blend was then warmed up to 80 °C to form a paste .Finally, pure graphite sheet was coated by this paste and then calcined for 30 min at 350 °C under N_2 purge .350 °C was chosen for the calcining process because carbon black would be more stable after the calcining process [27-29].

Electrochemical system

250 ml of sodium sulfate solution (0.05 M) was used at ambient temperature (25 ± 2 °C) in the electrolytic cell where hydrogen peroxide would also be measured .The anode electrode (stainless steel 316) and graphite cathode were positioned at 5 cm distance. Both rectangular cathode and anode electrodes had the exact size of 2 mm (thickness)× 2 cm (width) × 4 cm (height). A magnetic stirrer with the angular velocity of 400 rpm (without vortex) was employed to homogenize the reaction medium. The pH of the solution was adjusted using sodium hydroxide (0.05 M) and sulfuric acid (0.05 M) solutions. Air was continuously fed into the reaction cell (before starting each experiment and preparing electricity voltage) for 10 min to saturate it with oxygen. The same electrolytic cell was used for the electro-Fenton process [volume of 250 ml, temperature of (25 ± 2 °C), angular velocity of 400 rpm for stirrer and M 0.05 Na_2SO_4]. Figure 3 shows a schematic of the applied electrochemical cell for hydrogen peroxide production and the electro-Fenton process.
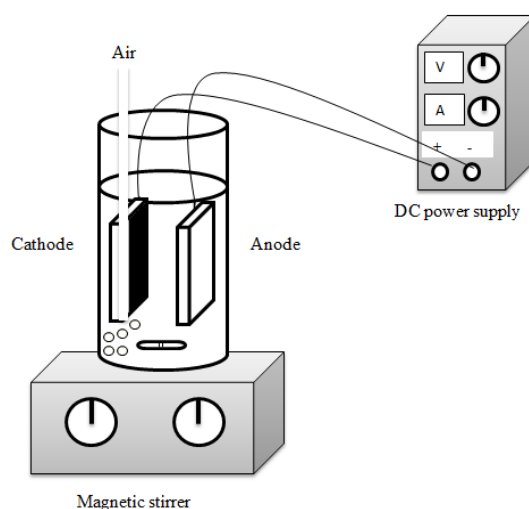

Figure 3: Schematic of the electrolytic cell

Analytical methods

The electrochemical behavior of the modified cathode was investigated using the CV test [21,30, 31] .The employed electrolytic cell had three auxiliary electrodes [a platinum auxiliary electrode, a calomel standard electrode (as a controller), and a graphite electrode (in its unmodified and modified forms) as the working electrode]. The iodometric method was also employed to measure the H_2O_2 produced on the cathode surface .A spectrophotometer (US,UV-Vis HACH) was used to measure the concentration of I_3^- ions produced from the reaction between H_2O_2 and a concentrated solution of I^- at a wavelength of 351 nm [21, 28, 32].

Experiments design

Design Expert software [(DoE) version 7.0.0] was used with a full factorial design and $=\alpha 1$ to design and minimize the number of experiments. The independent variables such as time (A), current intensity (B), air flow rate (C), and catalyst dosage (D) were introduced to the software. They were coded as shown in Table 3:

Table 3: Independent variables and their low and high levels

	full factorial	*∝=1*			
		Coded levels of variables			
symbol	*Factor*	*-1*	*+1*	*-alpha*	*+alpha*
A	*Reaction time (min)*	*10*	*150*	*10*	*150*
B	*Current intensity (mA)*	*100*	*500*	*100*	*500*
C	*Air flow rate (l/min)*	*0.5*	*2*	*0.5*	*2*
D	*Fe^{2+} catalyst dosage (g)*	*0.1*	*1*	*0.1*	*1*

The COD removal (Y) as a response was calculated by Eq. (5):

$$Y\ (\%) = \frac{X_i - X_o}{X_i} \times 100 \tag{5}$$

Where, X_i and X_0 are initial and final CODs.

The energy utilization (Wh/m^3) was calculated by the Eq. (6) [33, 34]:

$$\text{Energy consumption} = \frac{U \times I \times T}{V} \tag{6}$$

Where, T, U, V, and I are the treatment time (h), voltage (v), solution volume (m^3) and current intensity (A).

Results and discussion

Cathode characteristics

The cathode surface porosity increment can significantly improve hydrogen peroxide production [27, 28]. Figures 4 (a & b) show FESEM images of graphite and modified cathode, respectively.

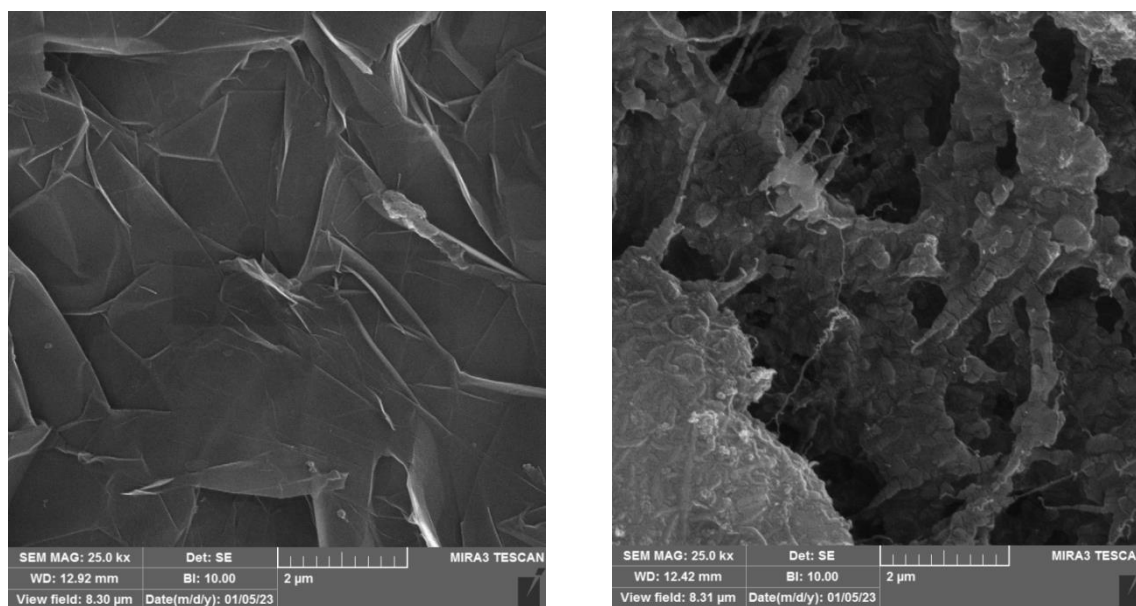a)   b)

Figure 4: FESEM images of graphite cathode before (a) and after modification (b)

This would increase the specific surface area of graphite, allowing more oxygen regeneration. Oxygen regeneration widely increases with increasing specific surface area of cathode. This leads to more H_2O_2 production [21, 26-28]. Figures 5 (a & b) confirm the above issue through three-dimensional images of AFM for carbon black (N330) nanoparticles (in scale of 2 µm) on the graphite cathode before (a) and after modification (b), respectively.
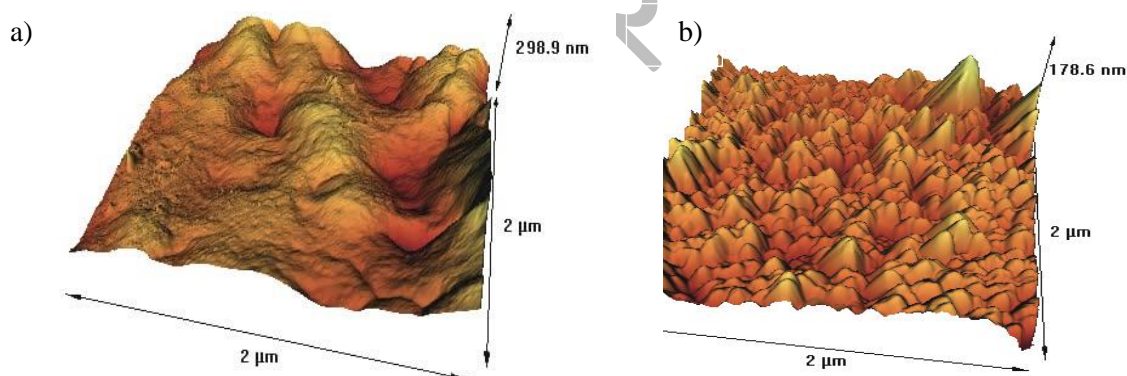

Figure 5: AFM images of graphite cathode before (a) and after modification (b)

Electrochemical performance

The electrochemical performance of the graphite cathode before and after modification was assessed by the CV test .The voltage range arising from the oxygen reduction, hydrogen peroxide production and accumulation on the cathode surface (compared with the calomel electrode) was around -1 to -0.3 v [21, 27, 30, 31] .Figure 6 (a) shows a weak peak for the voltage range. This is due to producing minimum hydrogen peroxide on the unmodified cathode surface with few pores. At the same time Figure 6 (b) shows that the voltage range is unaffected for the modified electrode used without air injection.
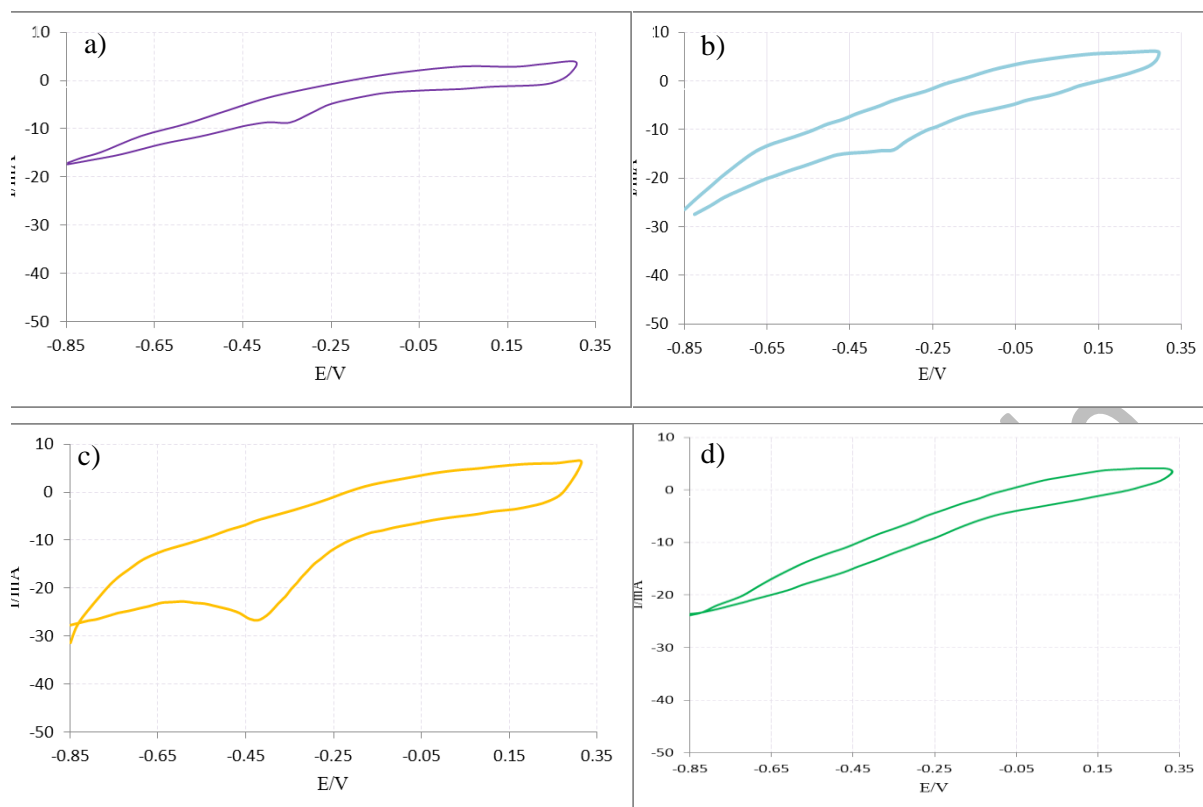
Figure 6: Cyclic voltammeter (CV) diagrams at pH of 6, M 0.05 Na₂SO₄, scanning speed of 10 mv/s: Graphite cathode with air flow 2.0 L /minutes (a), modified graphite cathode without air flow rate (b), modified graphite cathode with flow 2.0 L /minutes (c), modified graphite cathode with nitrogen purge (d)

This is resulted from presence of low amount of dissolved oxygen in the reaction medium .Figure 6 (c) shows a much stronger peak for voltage range on the modified cathode under air injection due to the presence of more oxygen (and producing more hydrogen peroxide) in the reaction medium. The CV test was then studied under a new condition where the electrolyte was under nitrogen purge, and the solution was discharged from extra oxygen. This confirms that the voltage changes only are due to reducing oxygen although Figure 6 (d) shows lack of a clear peak. This reveals that no hydrogen peroxide was produced due to the absence of oxygen in the electrolyte.

Effect of various parameters on H₂O₂ production

Effect of current intensity

Electricity consumption plays animportant role in the reaction development and costs [17, 19, 35]. In order to determine the maximum amount of H₂O₂ production on the modified cathode, current intensities of 100-500 mA (with intervals of 100) were used under air flow of 2 l/min at various times of 10, 30, 60, 90, 120 and 150 min at pH of 3. Figure 7 shows that more hydrogen peroxide was produced when the current intensity increased from 100 to 300 mA.
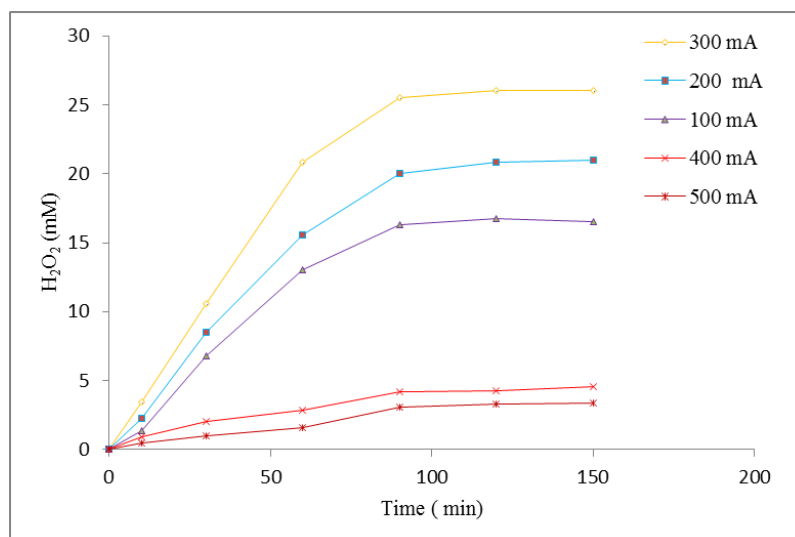
Figure 7: Effect of current intensity on the rate of H₂O₂ generation (modified cathode at a pH of 3 and air flow rate of 2 L/minutes)

Furthermore, less hydrogen peroxide is produced in high current intensities. According to Eq. (7), oxygen undergoes a four-electron reduction rather than a two-electron reduction at high current intensities or voltages. This leads to water synthesis rather than hydrogen peroxide production [21, 36]:

$$4e^- + 4H^+ + O_2 \rightarrow 2H_2O \qquad\qquad E^0 = 1.230V/SHE \qquad (7)$$

Effect of air flow rate

In order to reduce the process costs and risks, the required oxygen was provided through the ambient air. Therefore, effect of various air flow (0.50, 1.0, 1.5 and 2.0 L/min) at differenttime steps of 10, 30, 60, 90, 120 and 150 min and current intensity of 300 mA at pH of 3 was studied. According to Figure 8, the produced H_2O_2 increased with the air flow rate increment. This is due to the presence of more oxygen in the reaction environment [27, 28]. According to the volume of electrochemical cell, maximum possible air flow rate (2.0 L/min) was chosen.
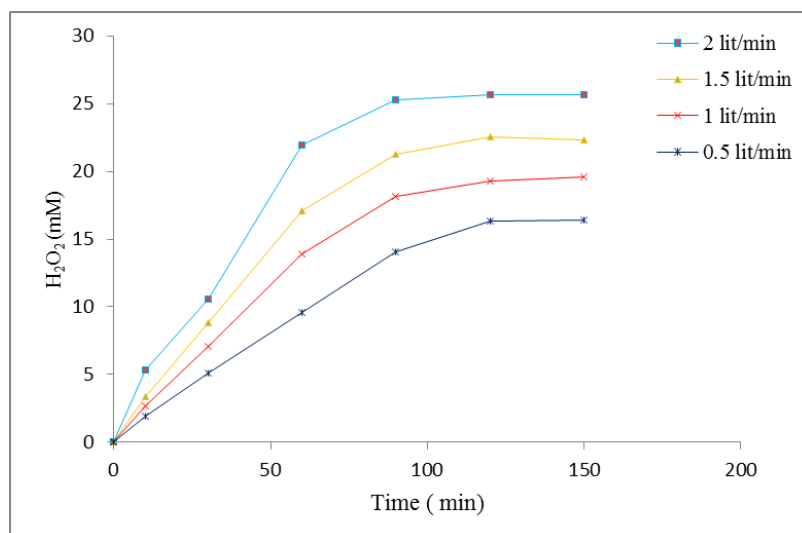
Figure 8: Effect of air flow rate on the rate of H_2O_2 generation (modified cathode at a pH of 3 and current intensity of 300 mA)

Effect of pH

Effect of various medium pHs (3-7) on the hydrogen peroxide production was investigated at current intensity of 300 mA under air flow rate of 2.0 L/min at various times of 10, 30, 60, 90, 120 and 150 min. Figure 9 shows that the maximum hydrogen peroxide would be produced at pH of 3 (acidic pH) where electro-Fenton functions excellently. In addition, the rate of hydrogen peroxide production would be reduced with time at various pHs. This is due to decreasing H^+ ions in the reaction medium [14, 17].
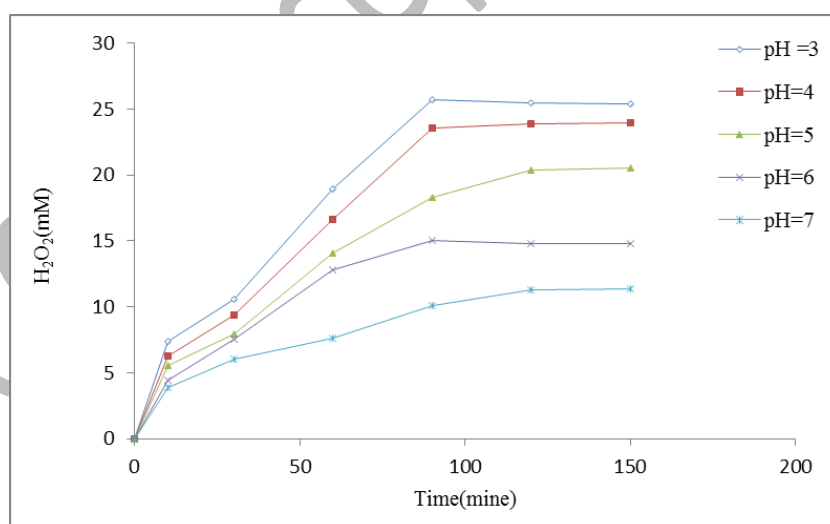

Figure 9: Rate of H_2O_2 formation (modified cathode at an air flow rate of 2.0 L/min and current intensity of 300 mA)

Hydrogen peroxide generation on cathode

Hydrogen peroxide production rate at both pHs 3 and 6 (original pH of wastewater) was investigated on the cathode before and after modification. According to Figure 10, the graphite cathode produced 3.23 mmol/l of

hydrogen peroxide when the operating conditions were fixed at pH of 3, air flow 2.0 L/ min, current intensity of 300 mA and time of 90 min while 25.68 mmol/l of hydrogen peroxide was produced when a modified graphite cathode was used.
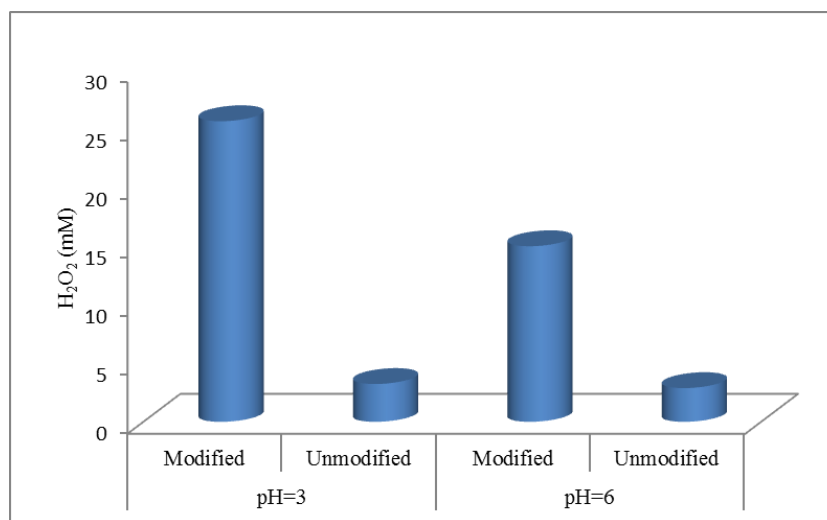

Figure 10: Hydrogen peroxide generation rate under reaction time of 90 minutes, current intensity of 300 mA, air flow of 2.0 L/min, and (graphite cathodes before and after modification at pH of 3 and pH of 6)

It seems that the modification on cathode would increase hydrogen peroxide production around 8 times. Also, the graphite cathode would produce hydrogen peroxide around 2.88 mmol/l at pH of 6 (the other conditions remained constant) while it would rise to 15 mmol/l (around 5 times) for a modified cathode.

Electrochemical stability

The stability of the modified cathode was studied at both pHs of 3 and 6. As shown in Figure 11, the amount of H_2O_2 produced at pH of 3 decreased by 12.96% (from 25.68 to 22.35 mM) while it decreased around 9.33% (from 15 to 13.60 mM) at pH of 6 after five steps.
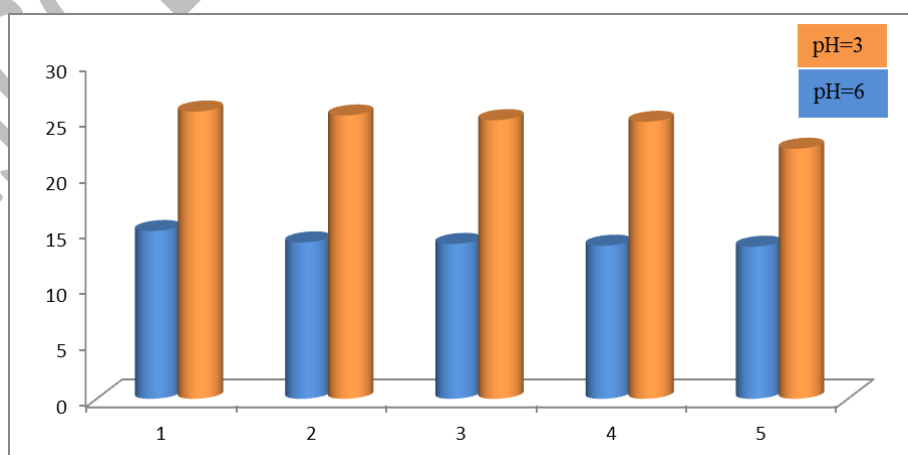

Figure 11: Hydrogen peroxide generation during 5 experiments [modified cathode at a reaction time of 90 minutes, the current intensity of 300 mA, an air flow rate of 2.0 L/min, and under two pHs of 3 and 6

This is perhaps due to proper and stable layering the carbon particles on the surface of modified cathode. This confirms that a modified cathode will produce higher amounts of H_2O_2 during the electro-Fenton reaction at a pH of 3.

Electro-Fenton reaction

The Electro-Fenton reaction with a modified cathode treated a toxic and resistant effluent from a pesticide factory. The treatment process was performed at initial pH of 3 for each run. To find the optimal conditions, the RSM under the CCD was statistically applied. Thirty runs with four independent parameters such as reaction time [A (min)], current intensity [B (mA)], air flow rate [C (l/min)], and Fe^{2+} catalyst dosage [D (g)] were designed (Table 4).

Table 4: CCD matrix based on four independent variables and response

Run	Reaction time (min)	Current intensity (mA)	Air flow rate (L/min)	Fe²⁺ catalyst dosage (g)	COD removal (%)	
					Actual	Predicted
1	150	500	2	0.1	47.51	46.83
2	80	300	0.5	0.55	53.15	54.22
3	10	100	2	1.0	38.58	37.63
4	10	100	0.5	0.1	21.14	19.91
5	150	100	0.5	0.1	32.21	33.84
6	150	500	0.5	1.0	42.58	43.20
7	10	100	2	0.1	31.03	31.43
8	150	500	2	1.0	52.98	52.55
9	80	300	2	0.55	63.23	64.65
10	80	500	1.25	0.55	58.98	62.43
11	10	500	0.5	0.1	17.36	16.82
12	80	100	1.25	0.55	69.60	68.64
13	80	300	1.25	0.1	52.35	54.28
14	150	100	0.5	1.0	49.31	46.43
15	10	500	0.5	1.0	26.56	25.57
16	150	300	1.25	0.55	76.67	79.57
17	80	300	1.25	0.55	73.85	73.28
18	80	300	1.25	0.55	73.98	73.39
19	80	300	1.25	0.55	74.05	73.95
20	150	100	2	0.1	53.98	53.30
21	80	300	1.25	0.55	73.48	72.35
22	10	500	2.0	0.1	21.03	22.51
23	80	300	1.25	0.55	73.15	73.29
24	150	100	2	1.0	60.31	61.87
25	80	300	1.25	0.55	73.15	73.10

26	80	300	1.25	1.0	62.37	62.94
27	10	500	2.0	1.0	27.58	26.97
28	150	500	0.5	0.1	32.87	31.12
29	10	300	1.25	0.55	60.23	59.82
30	10	100	0.5	1.0	27.15	30.18

Also, a quadratic polynomial regression model was found to predict the response [Eq. (8)]. Table 4 also shows a good agreement among the observed and predicted data.

$$\text{COD removal (\%)} = 72.36 + 9.88A - 3.10B + 5.22C + 4.33D + 0.34AB + 1.99\,AC + 0.58AD - 1.52BC - 0.38BD - 2.65A^2 - 6.81B^2 - 12.91C^2 - 13.74D^2 \tag{8}$$

In order to evaluate the significant effects of independent parameters on the response, the Analysis of Variance (ANOVA) was carefully investigated (Table 5).

Table 5: Analysis of Variance results for the model

Source	Sum of squares	df	Mean Square	F-Value	p-value Prob > F	Remark
Model	10487.66	14	749.12	154.37	<0.0001	significant
A-Reaction time	1755.48	1	1755.48	361.75	<0.0001	
B-Curren intensity	173.35	1	173.35	35.72	<0.0001	
C-Air flow rate	489.84	1	4849.84	100.94	<0.0001	
D-Fe^{2+} catalyst dosage	337.48	1	337.48	69.54	<0.0001	
AB	1.89	1	1.89	0.39	0.5419	
AC	63.20	1	63.20	13.02	0.0026	
AD	5.41	1	5.41	1.11	0.3079	
BC	37.09	1	37.09	7.64	0.0145	
BD	2.30	1	2.30	0.47	0.5021	
CD	16.24	1	16.24	3.35	0.0873	
A^2	18.25	1	18.25	3.76	0.0715	
B^2	120.31	1	120.31	24.79	0.0002	
C^2	432.12	1	432.12	89.05	<0.0001	
D^2	489.44	1	489.44	100.86	<0.0001	
Residual	72.79	15	4.85			
Lack of Fit	71.96	10	7.20	43.45	0.0003	Significant
Pure Error	0.83	5	0.17			
Cor Total	10560.45	29				

Coefficient of Variance (CV %)	*4.35*	*Mean*	*5068*
Standard Deviation	*2.20*	*R^2*	*0.9931*
Adequate Precision	*40.288*	*R^2 Adjusted*	*0.9867*
Press	*411.04*	*R^2 Predicted*	*0.6911*

The significance of fit test guarantees that the points were well located around the model. R^2 is an important parameter for expressing the significance of the fit test. In fact, a closer value of R^2 to the unity will properly model the response data [33, 34].

Three dimensional plots

Three dimensional diagrams can show simultaneous effect of two parameters on the COD removal .The optimal value of an operating parameter under the influence of another operating parameter can be found through a diagram [33, 34, 37].

Figures 12 (a-f) show the effect of reaction time and current intensity (a), reaction time and air flow rate (b), reaction time and Fe^{2+} catalyst dosage (c), current intensity and air flow rate (d), current intensity and Fe^{2+} catalyst dosage (e), and air flow rate and Fe^{2+} catalyst dosage (f). As shown in Figure 12 (a), the current intensity has an optimum impact on the COD removal while the reaction time increment continuously increases it. It may be due to undesired reactions on the cathode surface during the current intensity enhancement. Four-electron reduction of oxygen at the porous surface of the cathode would generate water rather than hydrogen peroxide [Eq. (7)] [21, 36]. Moreover, water production by hydroxyl radical [Eq. (9)] and hydrogen peroxide [Eq. (10)] plays an important role in reducing the COD removal. Furthermore, a large amount of H_2O_2 in the reaction solution can reduce the efficiency of COD removal by consuming hydroxyl radicals and producing hydroperoxyl radicals [Eq. (11)], which have a lower oxidizing power than $OH^.$ [38-40]:

$$e^- + OH^. + H^+ \rightarrow H_2O \tag{9}$$
$$2e^- + H^+ + H_2O_2 \rightarrow H_2O \tag{10}$$
$$H_2O_2 + OH^. \rightarrow OOH^. + H_2O \tag{11}$$

Figure 12 (b) shows the interaction between reaction time and air flow. As shown in this figure, the air flow has an optimum impact on the COD removal while the reaction time increment continuously increases it. According to the literature, reaction time would dramatically affect the Fenton process [33, 34] .However air flow rate increment may assist the COD removal but, Fe^{2+} catalyst dosage (and hydrogen peroxide) reduction (with passing the reaction time) in the reaction medium would decrease the COD removal [36, 41, 42].

Figure 12 (c) shows interaction between reaction time and Fe^{2+} catalyst dosage. As shown in this figure, the Fe^{2+} catalyst dosage has an optimum impact on the COD removal while the reaction time increment continuously increases. High amounts of Fe^{2+} ions in the reaction medium leads to some unwanted reactions such as Eq. (12) which hydroxyl radicals are consumed however ferrous ions are not also regenerated according to Eq. (13) [43-45]:

$$OH \cdot + Fe^{2+} \rightarrow Fe^{3+} + OH^- \tag{12}$$

$$H_2O_2 + Fe^{3+} \rightarrow H^+ + OOH \cdot + Fe^{2+} \tag{13}$$

Figure 12 (d) shows the interaction between current intensity and air flow rate. The amounts of oxygen in the reaction wastewater and on the cathode surface as well as the current intensity would affect hydrogen peroxide production amount [26, 27] .As shown in this figure, air flow rate and current intensity have optimum impacts on the COD removal.

Figure 12 (e) shows interaction between current intensity and Fe^{2+} catalyst dosage. In fact, current intensity plays an important role in the H_2O_2 production and the ferric ions reduction. As shown in this figure, both current intensity and Fe^{2+} catalyst dosage have optimum impacts on the COD removal.

Figure 12 (f) shows the interaction between air flow rate and Fe^{2+} catalyst dosage. However, hydrogen peroxide and Fe^{2+} ions together have significant effect on the process [33, 34] but, both air flow rate and Fe^{2+} catalyst dosage have optimum impacts on the COD removal.
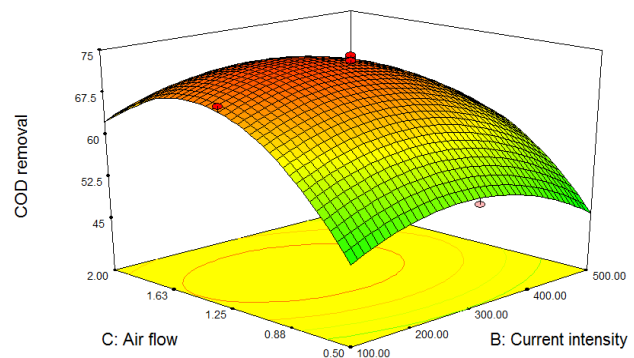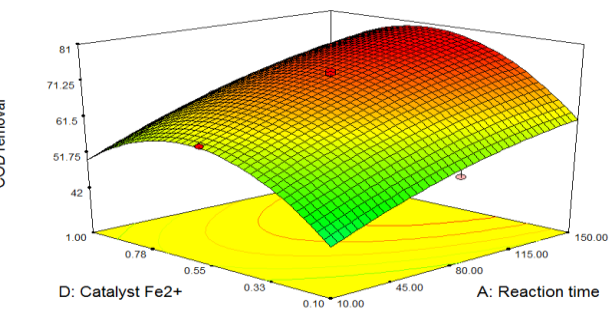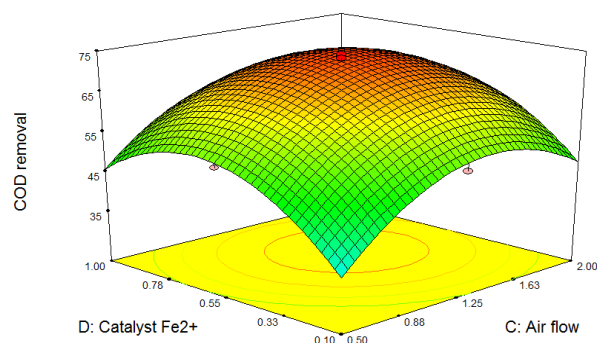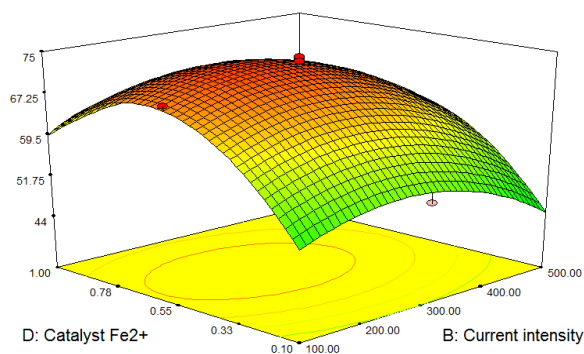
a)

b)
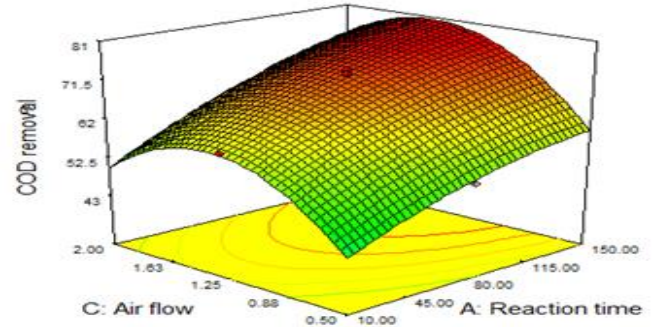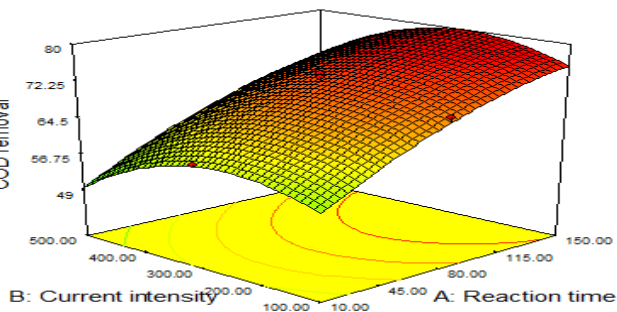
c)

d)

e)

f)

Figure 12: Effects of various variables on the COD removal: Reaction time and current intensity (a), reaction time and air flow rate (b), reaction time and Fe²⁺ catalyst dosage (c), current intensity and air flow rate (d), current intensity and Fe²⁺ catalyst dosage (e), air flow rate and Fe²⁺ catalyst dosage (f)

Optimization and validation

The operating conditions optimization with maximizing COD removal is a goal of experiment design. The optimum conditions were obtained from the experiment design. Then, the same conditions were experimentally prepared and validated with comparing the COD removal data from the software and experiment. Therefore, the optimum conditions were experimentally obtained at air flow of 1.56 L /min, reaction time of 126 minutes, Fe^{2+} catalyst dosage of 0.63 g and current intensity of 253 mA under pH of 3 for the COD removal of 78.15% while this was statistically found at 78.98% (Table 6).

Table 6: Optimum conditions obtained from the software and experiment at pH of 3

Reaction time (min)	Current intensity (mA)	Air flow rate (L/min)	Fe^{2+} catalyst dosage (g)	COD removal (%)	
				Actual	Predicted
126	253	1.56	0.63	78.15	78.98

The optimum conditions were experimentally repeated at the wastewater sample original pH of 6. As shown in Table 7, the COD removal was obtained at 33.78%. An increase in pH (pH>5) would provide more hydroxide ions (OH⁻). So, Fe^{2+} ions would widely be converted to Fe (OH)$_2$ [40, 46].

Table 7: COD removal from the pesticide effluent (modified cathode under the optimum conditions at pHs of 3 and 6)

Reaction time (min)	Current intensity (mA)	Air flow rate (L/min)	Fe^{2+} catalyst dosage (g)	COD removal (%)	
				pH=3	pH=6
126	253	1.56	0.63	78.15	33.78

Since the metal hydroxides (in comparison with ferrous ions) do not generally tend to react so, their presence in the reaction medium would decrease the treatment efficiency [43, 44, 47].

Feasibility study

Feasibility analysis is often recognized as one of the key factors for a treatment process consideration [48]. In this research, cost of electric energy consumption, cathode surface modification and catalyst supply can economically evaluate the electro-Fenton reaction .The graphite cathode surface was modified using an industrial type of carbon black nanoparticles to reduce the treatment costs. Carbon black nanoparticles would increase the porosity of cathode surface which would increase the amount of H_2O_2 production in the reaction solution under a constant current intensity. Therefore, a quick treatment process with maximizing the COD removal under the optimum conditions (minimum consumption of the catalyst and electricity) would provide an economic process.

According to Table 7, the electro-Fenton process would consume 25.83 KWh/m^3 [based on Eq. (6)] in both pHs. In fact, a treatment process under an acidic pH would be more efficient than that under a near neutral one. However, electro-Fenton process works at an acidic pH but, a heterogeneous catalyst may modify the operating pH [39, 46].

Conclusions

In this study, a porous structure [based on an economic, industrial carbon black nanoparticles (N330)] on the graphite surface was provided. Then, this novel cathode was tested in the electro-Fenton reaction to improve the quantity of hydrogen peroxide generation. The electro-Fenton process was designed by DoE software to minimize the number of runs and optimize the operating conditions for treating pesticide industrial wastewater. A model was also proposed by the software. It was properly able to predict the COD removal as a response. Furthermore, the modified cathode could efficiently (even economically) modify the electro-Fenton process under an acidic pH due to more production of °OH in the reaction solution. The low efficiency of electro-Fenton reaction under original pH (near neutral pH) of wastewater may be due to the Fe^{2+} catalyst precipitation and its transformation into $Fe(OH)_2$ molecules in the reaction medium.

Nomenclature

AFM	Atomic Force Microscopy
ANOVA	Analysis of Variance
BOD	Biological Oxygen Demand
CCD	Central Composite Design
COD	Chemical Oxygen Demand
CV	Cyclic Voltammetry
DOE	Design of Experiments
FESEM	Field Emission Scanning Electron Microscopy
RSM	Response Surface Methodology
TOC	Total Organic Carbon

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