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Original scientific paper

Phenol removal by electro-Fenton process using a 3D electrode with iron foam as particles and carbon fibre modified with graphene

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Abstract

The 3D electro-Fenton technique is, due to its high efficiency, one of the technologies suggested to eliminate organic pollutants in wastewater. The type of particle electrode used in the 3D electro-Fenton process is one of the most crucial variables because of its effect on the formation of reactive species and the source of iron ions. The electrolytic cell in the current study consisted of graphite as an anode, carbon fiber (CF) modified with graphene as a cathode, and iron foam particles as a third electrode. A response surface methodology (RSM) approach was used to optimize the 3D electro-Fenton process. The RSM results revealed that the quadratic model has a high R^2 of 99.05 %. At 4 g L^{-1} iron foam particles, time of 5 h, and 1 g of graphene, the maximum efficiency of phenol removal of 92.58 % and chemical oxygen demand (COD) of 89.33 % were achieved with 32.976 kWh kg^{-1} phenol of consumed power. Based on the analysis of variance (ANOVA) results, the time has the highest impact on phenol removal efficiency, followed by iron foam and graphene dosage. In the present study, the 3D electro-Fenton technique with iron foam partials and carbon fiber modified with graphene was detected as a great choice for removing phenol from aqueous solutions due to its high efficiency, formation of highly reactive species, with excellent iron ions source electrode.

Keywords

Wastewater treatment; organic pollutants; removal efficiency; 3D-electrode system; iron foam; response surface methodology; analysis of variance

Introduction

Phenol is one of the most significant bio-recalcitrant pollutants found in numerous chemical and biochemical industries. It is created during the operation of manufacturing facilities for resins, coke, pharmaceuticals, olive groves, and other food-related businesses [1,2]. Pesticides, herbicides, dye molecules, phenolic compounds, antibiotics, medicines, and surfactants are a few examples of organic pollutants that are typically exceedingly difficult to break down [3]. Phenolic compounds are

among the substances that should be the most concerned due to their tendency to persist in the environment for long periods and their potentially dangerous effects [4]. The presence of phenol in drinking water and irrigation poses substantial health hazards to people as a possible carcinogen, even at low dosages [5]. The health of people and all other living things are highly impacted by water quality. Therefore, surface and groundwater contamination by harmful or persistent contaminants became a significant issue [6,7].

Several aromatic and aliphatic intermediates that are more toxic than phenol are produced during the electrochemical oxidation of phenol [8]. Since it is a clean process that produces high concentrations of hydroxyl radicals ($OH^{\bullet}$) which can be used to oxidize, degrade, and mineralize a variety of organic compounds, the electro-Fenton process has been identified as a particularly attractive technology. It is a promising and emerging advanced oxidation process (AOPs) [9,10]. The use of transition metals as heterogeneous catalysts will prevent the production of iron sludge and increase the range of potential catalysts that may be employed in AOPs [11]. The proposed heterogeneous electro-Fenton system exhibited high efficiency, stability and economy [12]. The electro-Fenton method has many advantages; it is an appealing technology for wastewater treatment because it does not create secondary pollutants. The power used is clean and pollution-free, it uses no hazardous chemicals, which make this method to be an environmentally benign procedure [13,14]. Electro-Fenton's fundamental idea is summarized in equation (1), where the oxidation of Fe^{2+} to Fe^{3+} makes it easier for H_2O_2 to become the highly oxidizing $OH^{\bullet}$. The $OH^{\bullet}$ radical is a strong, non-selective oxidant that takes part in the degradation of organic contaminants [15]. Fe^{2+} and H_2O_2 are necessary for OH• to be continuously produced [16]. If Fe^{3+} ions do not form hydroxide precipitates in the solution phase, the Fe^{2+} ions can be created by reducing the Fe^{3+} at the cathode (equation (2)), providing a nearly constant supply of Fe^{2+}. The H_2O_2 is produced by the two-electron reduction of dissolved oxygen, as shown in equation (3) [17]. The rate constant (k) for each reaction is illustrated as follows [18]:

$$Fe^{2+} + H_2O_2 + H^+ \longrightarrow Fe^{3+} + OH^{\bullet} + H_2O;\ k = 55.0\ M^{-1}\ s^{-1} \quad (1)$$

$$Fe^{3+} + e^- \longrightarrow Fe^{2+};\ k = 0.1\ s^{-1} \quad (2)$$

$$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2;\ k = 5.9\ nM\ s^{-1} \quad (3)$$

Due to the comparatively easy handling of the reagents needed for this process and the efficient performance that can be obtained at a low cost, the electro-Fenton process has been widely used in wastewater treatment [19]. Furthermore, no hazards are associated with the handling, storage, or transportation of H_2O_2 [20]. The electro-Fenton process is affected by several factors, including the initial contaminant concentration, pH, current intensity, and reagent dosage [21].

Carbonaceous electrodes are often employed as anodes in wastewater treatment due to their large surface area per volume [22]. To enhance the efficiency of electrochemical processes for eliminating organic pollutants, the selection of cathode material is considered an essential factor. The good characteristics of carbon fiber (CF), like high specific surface and low cost, make it a good choice as a cathode for H_2O_2 generation. The modification of carbon electrodes with graphene was confirmed to exhibit better performance in producing H_2O_2 [23]. The modified electrode demonstrated higher electron-transfer ability than the raw carbon felt electrode since the redox current and charge-transfer resistance are increased [24].

Among sophisticated oxidation methods, the three-dimensional (3D) electrode reactor has received attention for efficiently degrading organic pollutants due to its high efficiency, ease of operation, and environmental compatibility, among other factors [25]. In comparison to standard two-dimensional (2D) electrode technology, the electrocatalytic property of 3D particle electrodes

is the core technology of the 3D electrode reactor [26]. In terms of current efficiency, energy consumption (EC), and pollutant removal efficiency, the 3D electrode technology outperforms the 2D electrode technology. The overall 3D electrode system offers a large effective contact area as well as a large number of micro-electrolysis cells, and the electrochemical reaction takes place not only on the surface of the main electrode but also on the surface of each particle electrode [27,28]. On the other hand, using iron foam has two benefits. Iron foam functions as a 3D particle to offer active sites and increase reaction efficiency and supplies the reaction with Fe^{2+}, which reacts with H_2O_2 to create $OH^{\bullet}$ that oxidizes phenol [29].

The goal of the current study is to detect the enhancement of phenol removal efficiency by utilizing CF modified with graphene as cathode and iron foam as the third electrode in a 3D electro-Fenton system and optimizing results using Box-Behnken design.

Experimental

Materials

All aqueous solutions were prepared using distilled water. All reagents were of analytical grade and no additional purification was needed. The chemicals were: phenol crystals (C_6H_5OH, 99.5 % purity, Alpha Chemical Reagent Company, India), SDFCL or ferrous sulfate heptahydrate $FeSO_4.7H_2O$ (CDH Company, India), sodium sulfates (Na_2SO_4, purity ≥99.0 %, SDFCL), and sulfuric acid (H_2SO_4, with a concentration of 98 %, Sigma-Aldrich). CF (99.5 % Carbon content, China) was used as a cathode that has a 0.111 mm thickness and a 12K yarn size purchased from Jiaxing ACG composites Co. Ltd. (China) and iron foam was purchased from Xiamen Top new energy Technology (China) with porosity of 110 (pores per cm)

Experimental methods

The electro-Fenton reaction was conducted in 1 L cylindrical beaker. The batch reactor contained 150 mg L^{-1} of a phenol solution and three electrodes that were fully submerged in the solution. A cathode was made of carbon fiber felt modified with graphene (18×6 cm), and the anode was a graphite plate (18×6×0.5 cm). Iron foam particles (1×1×1 cm) served as a third electrode and the distance between anode and cathode was 3 cm. The iron foam was washed with 0.1 M H_2SO_4 and deionized water in sequence to remove the oxide layer on its surface. To enhance the amount of dissolved oxygen, the solution was aerated with (ACO-001 electromagnetic, China) for 20 minutes before the reaction and continued until the completion of the experiment at a rate of 10 L h^{-1}. Before each experiment, a pH value of 3 was achieved by adding 0.1 M H_2SO_4 acid to the solution, and the pH value was measured with a pH meter of HANNA (Romania). To achieve the desired concentration of iron ions, they were released in a specific amount from iron foam particles into the solution. To keep the ionic strength constant and increase the medium conductivity, 0.05 M of Na_2SO_4 was added to the solution. Electrolytes improve the effectiveness of electrodes and processes, such as increasing the conversion of oxygen to hydrogen peroxide at the cathode surface due to an acceleration in the speed of ion exchange and the electrostatic resistance between electrodes and ions [30]. The electrodes were connected to a DC power supply type (UNI-T, UTP3315PE) which operated at a constant current density of 4 mA cm^{-2}. A digital voltmeter (FLOWTECH, China) was used to detect voltage and current values. Before the pH correction, a first sample of 10 ml of aqueous solution with phenol was obtained. Before analysis, periodic samples of treated solution were filtered through 0.45 µm filter papers to eliminate any suspended contaminants. The temperature throughout the 3D electro-Fenton process was kept constant at 27 ±1 °C. Samples

were taken and analyzed to determine COD and phenol concentration by the RD125, Lovibond, and UV-9200 spectrometers, respectively. A schematic drawing of the 3D electro-Fenton system is shown in Figure 1. The efficiency of phenol removal was evaluated using equation (4) [31].

$$RE_{phenol} = [(C_1-C_2)/C_1]100 \quad (4)$$

where RE_{phenol} / % is phenol removal efficiency, C_1 and C_2 / mg L^{-1} represent the original and final phenol concentrations, respectively**.**

The energy consumption (EC / kWh kg^{-1} phenol) that defines the amount of energy required to digest one kilogram of phenol was estimated by equation (5) [31]:

$$EC = 1000IUt/\Delta C_{phenol}V \quad (5)$$

where I / A is the operating current intensity, U is voltage, V / L is the volume of the solution, t / h is the electrolysis time, and ΔC_{phenol} / mg L^{-1} is the difference in experimental phenol concentrations.

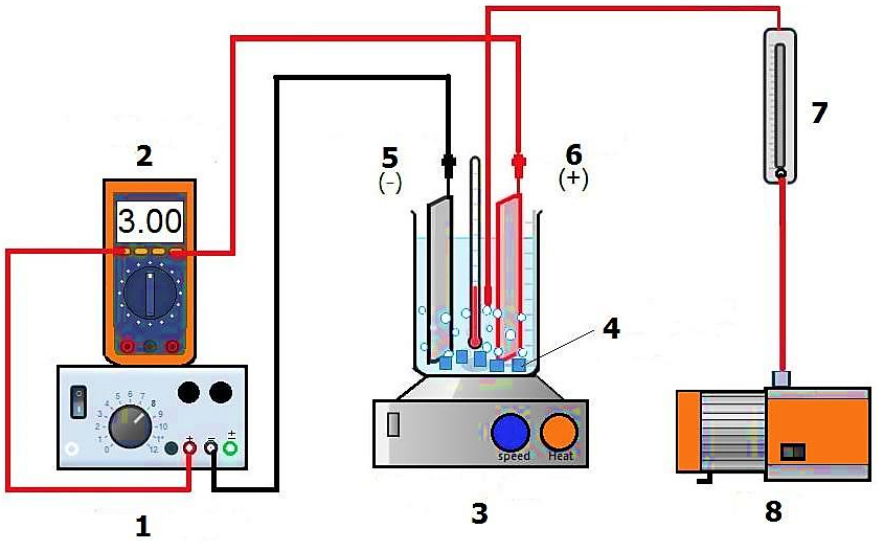

Figure 1. *Schematic drawing of the electro-Fenton system: 1) power supply, 2) multimeter, 3) magnetic stirrer, 4) iron particles, 5) cathode, 6) anode, 7) flow meter and 8) pump*

Carbon fiber modification

Before each process, the commercial CF used as one of the working electrodes (cathode) was cut into an 18×6 cm^2 rectangle piece. This CF piece was activated for 30 minutes at 80 °C with 5 % HNO_3, cleaned, and stored in distilled water. The CF cathode was then modified using a certain amount of graphene. The slurry was created by combining 0.14 ml of polytetrafluoroethylene (PTFE), 3 ml of ethanol, and 2 ml of deionized water. Using a brush, this mixture was applied to the two sides of the CF. The CF was then allowed to dry at ambient temperature before being calcined for 30 minutes at 360 °C [32,33]**.**

Characterization of electrodes

Graphite and CF modified with graphene were used as the anode and cathode, respectively. The crystallographic characterization of the graphite, graphene, pure CF, and modified CF was examined by X-ray diffraction (XRD) as shown in Figure 2. The XRD device characteristics were Model, XRD 6000, and Shimadzu, Japan. A scan speed of 5 degrees per minute was used with a 40 kV voltage and 30 mA current for the X-ray tube. A scanning electron microscope (SEM) was employed to investigate the electrodes surfaces as shown in Figure 3. Energy dispersive X-ray spectroscopy (EDX)

data was also measured at a voltage of 25 kV for iron foam before and after the reaction, as shown in Figure 4.

Figure 2 demonstrates that CF modified with graphene structure can be identified as the source of the sharp diffraction peak visible at 2θ of 26.99°, corresponding to the diffraction line C (002). There is a weaker abrupt peak at 2 θ of 18.81° related to the PTFE as it is used in the modification process. The pure graphite shows a sharp and tight peak at 26.5°, corresponding to the diffraction line C (002) [34].

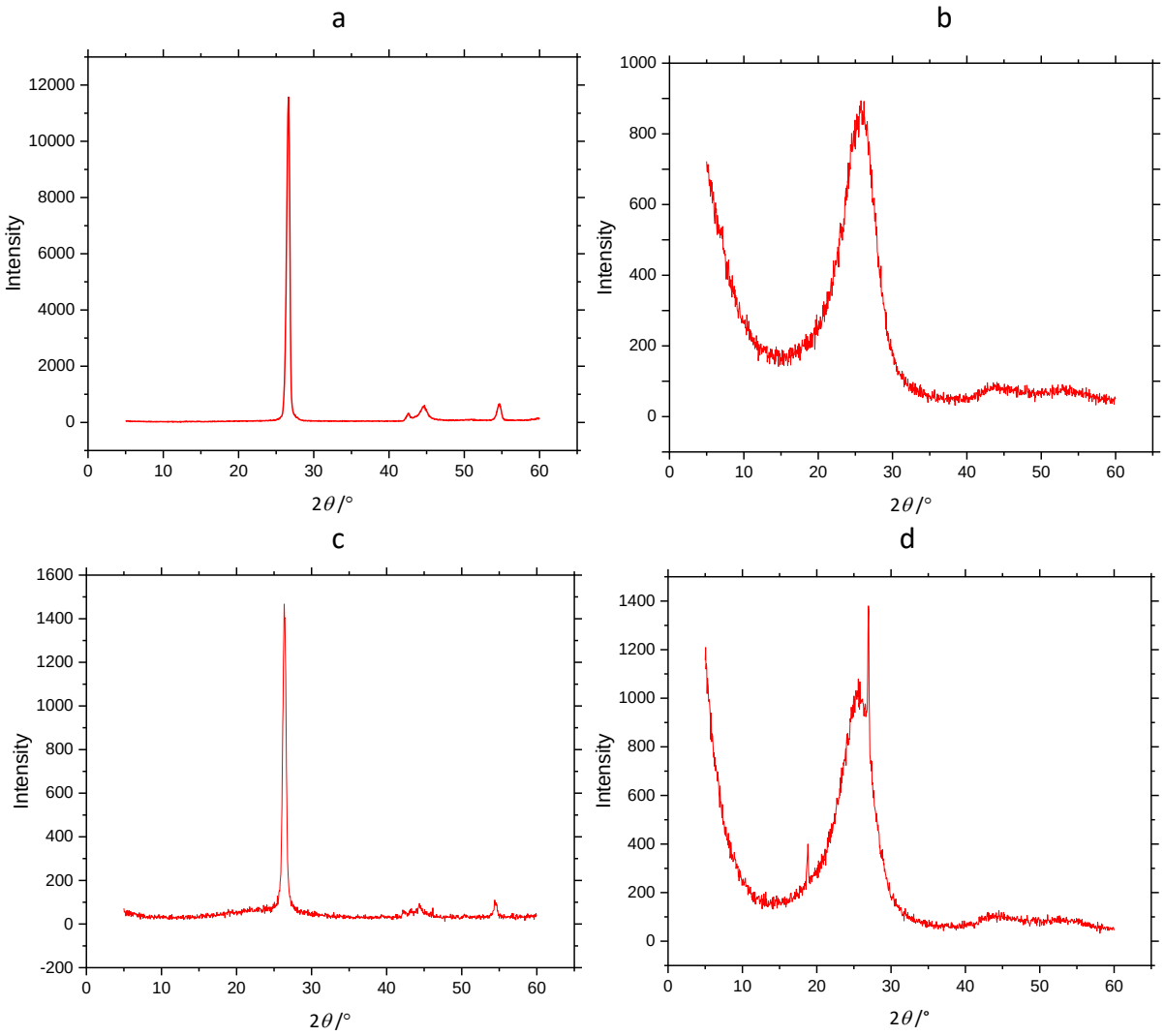

Figure 2. *XRD patterns of a - graphite, b - pure CF, c - graphene and d - CF modified with graphene*

By utilizing SEM, the morphology of graphene on the CF was revealed. Figure 3 displays the SEM images of the pure and modified cathode. The graphene flakes were thin sheets, and they were all aligned on the CF surface. Figure 3a illustrates the CF without modification, while Figure 3b shows the transparent layer of graphene developed on the CF. A definite penetration of graphene between the CF threads can be detected in Figures (3a and b) which indicates an increase in the probability of solution mixture penetration between the CF threads. This penetration of graphene between the CF threads increases the surface area, enhances electrode performance, and produces more H_2O_2. Figures 3c and d show the structure of the third electrode (the iron foam).

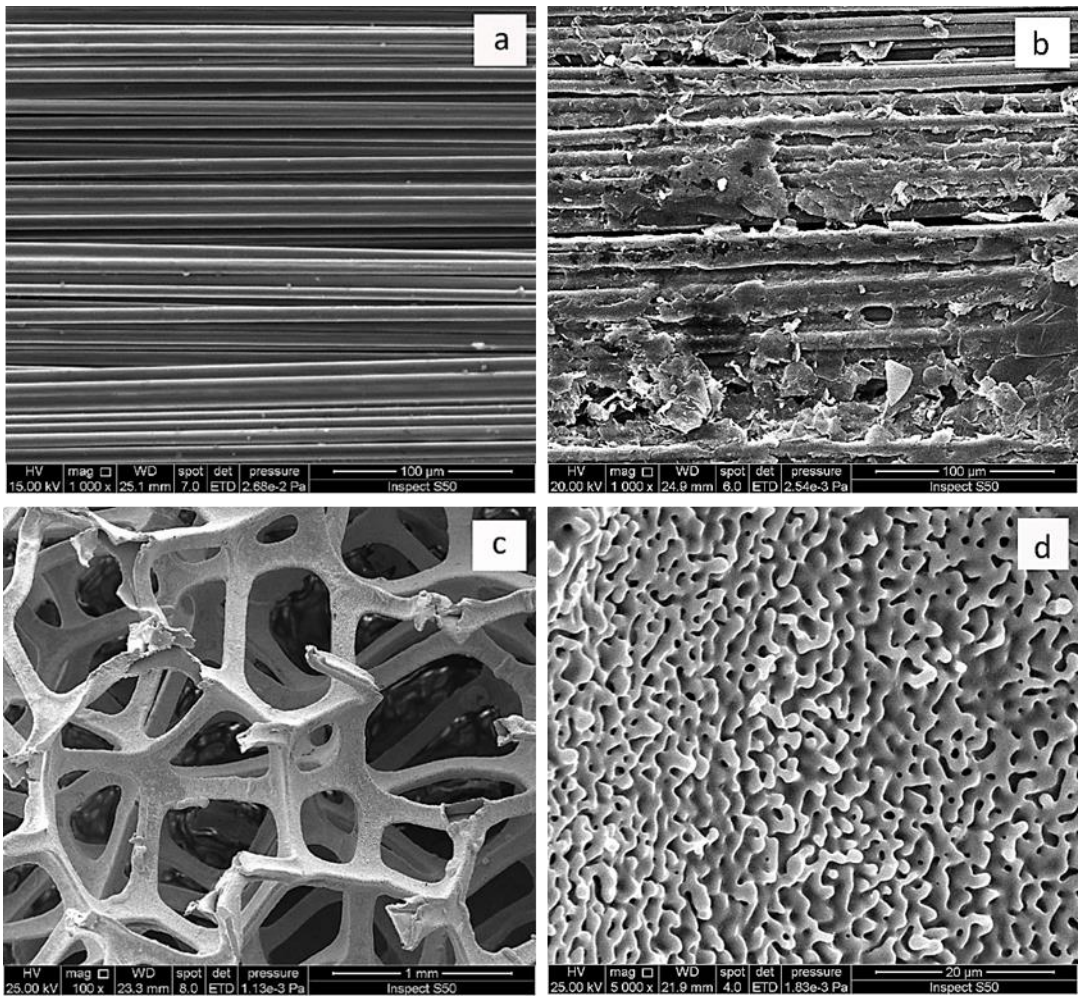

Figure 3. *SEM images of: a - CF before modification, b to d - CF after modification with graphene and iron foam before the electro-Fenton process*

Design of experiment

With the aid of mathematical and statistical data collection techniques, including response surface methodology (RSM), it is feasible to ascertain the relationship between a process response and its contributing elements [35]. In order to detect the best conditions for higher phenol removal efficiency in the 3D E-Fenton process, a Box-Behnken design (BBD) was employed. Using preliminary data, this study used three main independent variables and three levels. Iron particles, graphene dosage, and electrolysis time were selected as variables in the performed experiments. Table 1 displays the experimental range and levels of independent variables. Table 2 displays the Box-Behnken design**.**

Table 1. *Variables and different levels of experimental design*

Independent variable	levels		
	-1	0	1
X_1 - mass of iron particles, g	2	3	4
X_2 - mass of graphene, g	0.5	0.75	1
X_3 - time, h	3	4	5

The empirical quadratic polynomial model depicted by equation (6) can represent the mathematical relationship between independent factors and response [36,37].

$$Y = a_0 + \Sigma a_i x_i + \Sigma\, a_{ii}\, x_i^2 + \Sigma\, a_{ij}\, x_i x_j \quad (6)$$

Table 2. *Design of experiments with the level of each factor using Box-Behnken designs, Bk. = 1*

Run	Coded values			Real values		
	x_1	x_2	x_3	Mass of iron particles, g X_1	Mass of graphene, g X_2	Time, h X_3
1	-1	1	0	2	1.00	4
2	1	0	-1	4	0.75	3
3	0	-1	-1	3	0.50	3
4	-1	0	1	2	0.75	5
5	0	-1	1	3	0.50	5
6	0	1	1	3	1.00	5
7	1	1	0	4	1.00	4
8	-1	0	-1	2	0.75	3
9	0	0	0	3	0.75	4
10	0	1	-1	3	1.00	3
11	0	0	0	3	0.75	4
12	1	0	1	4	0.75	5
13	0	0	0	3	0.75	4
14	1	-1	0	4	0.50	4
15	-1	-1	0	2	0.50	4

Where Y represents the response (RE_{phenol}), i and j are the index numbers for independent variables, a_0 is the intercept term, x_1, x_2 … x_k are the process variables (independent variables) in coded form. a_i is the first-order (linear) main effect, a_{ii} is the second-order main effect, and a_{ij} is the interaction effect [36,37]. The Minitab-18 software was used to examine the results of phenol removal efficiency.

Iron foam characterization

Figure 4a and b shows the surface compositions of the iron before and after the reaction which were analyzed by EDX. The results showed that the highest elemental peak is for the Fe element with a content of 72.32% before the reaction, and there are other peaks for other elements with (Co of 24.67 wt.% and C of 4.01 wt.%). The results show a reduction in the Fe element to 69.32 wt.% after the reaction due to the release of iron ions needed for the reaction.

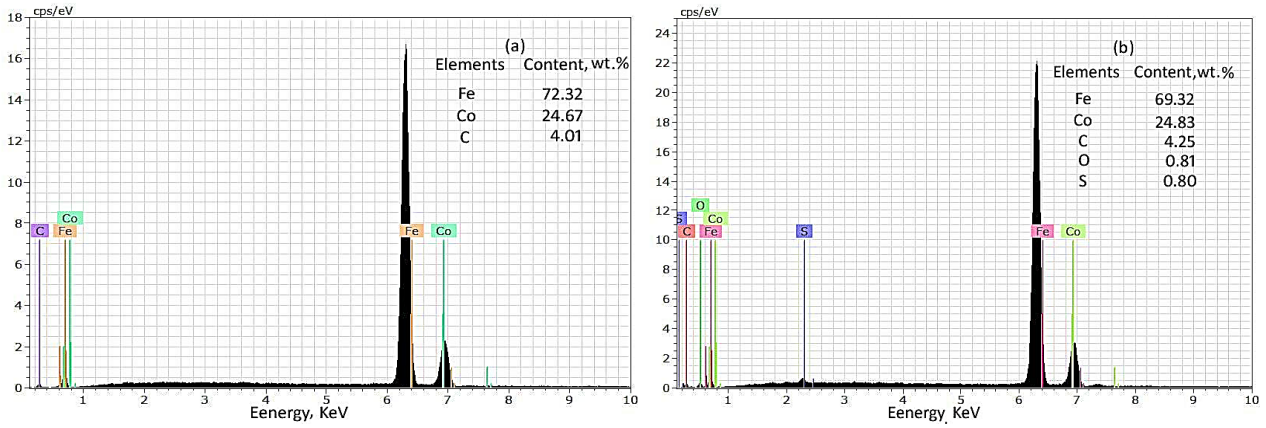

Figure 4. *EDX results for iron foam: (a) before reaction, (b) after reaction*

Iron foam is characterized by high surface porosity, where fluid can move easily through the connections between porous structures, and it plays a vital role in the 3D electro-Fenton system as a source of iron ions [29]. Based on the images of SEM for iron foam after the reaction, as illustrated in Figures 5a and 5b, the structure was varied due to the iron ions releasing.

Figure 5. *SEM images of iron foam after reaction*

Results and discussion

Statistical analysis

The following quadratic model of the phenol removal efficiency in terms of real values of process parameters was obtained by evaluating the phenol removal effectiveness by the Minitab-18 program.

$$RE_{phenol} = -39.3 + 8.10X_1 + 18.0X_2 + 27.19X_3 - 0.960(X_1)^2 + 20.1(X_2)^2 - 2.940(X_3)^2 - 9.90X_1X_2 + 2.794X_1X_3 - 0.40X_2X_3 \quad (7)$$

Table 3 displays the experimental phenol removal efficiency (RE_{phenol}) and energy consumption.

Table 3. *Experimental results for phenol removal efficiency and power consumed obtained using the Box-Behnken design, Bk. = 1*

Run	Mass, g		Time, h	RE_{phenol} / %		Voltage, V	*EC* / kWh kg^{-1} phenol
	Iron particles	Graphene		Actual	Predicted		
1	2	1.00	4	75.460	73.8532	3.98	31.012
2	4	0.75	3	62.290	60.5942	4.07	28.813
3	3	0.50	3	55.110	55.1990	4.25	34.009
4	2	0.75	5	70.216	71.9117	3.98	41.661
5	3	0.50	5	79.820	78.8905	4.25	39.134
6	3	1.00	5	87.220	87.1310	4.06	34.911
7	4	1.00	4	80.312	81.0782	4.09	29.944
8	2	0.75	3	53.330	54.0072	3.95	32.682
9	3	0.75	4	72.310	72.9467	4.25	43.559
10	3	1.00	3	62.910	63.8395	4.00	28.040
11	3	0.75	4	72.820	72.9467	4.25	34.317
12	4	0.75	5	90.350	89.6727	4.11	33.344
13	3	0.75	4	73.710	72.9467	4.23	33.743
14	4	0.50	4	75.980	77.5867	4.05	31.342
15	2	0.50	4	61.230	60.4637	3.94	37.845

The results show that the efficiency of phenol removal is in the range of 53.33 to 90.35 % and the specific energy consumption is in the range of 28.040 to 41.661 kWh kg^{-1} phenol. The impact of time on phenol removal was superior, as shown by the comparison of runs 2 and 12. Thus, at the constant graphene dosage of 0.75 g and iron particles of 4 g, phenol removal increased from 62.29 to 90.35 %, making a difference of 28.06 % as time increased from 3 to 5h. Also, based on this comparison, it is

clear that increasing the electrolysis time from 3 to 5 h led to an increase in *EC* from 28.813 to 33.344 kWh kg^{-1} phenol. Phenol removal efficiency increased from 70.216 to 90.35 % with a difference of 20.134 %, as shown in runs 4 and 12 results by increasing the iron particles dosage from 2 to 4 g. This indicates that increasing the dosage of iron particles has the second influence on phenol removal. Also, by comparing the values of EC, it is obvious that by increasing the iron particles dosage from 2 to 4 g, the *EC* decreased from 41.661 to 33.344 kWh kg^{-1} phenol due to an increase in the removal of phenol by increasing the iron particles dosage. Additionally, when the graphene dosage increased from 0.5 to 1 g as shown in runs 15 and 1, an increase in phenol removal from 61.23 to 75.46 % with a 14.23% difference was attained. Also, based on this comparison, it is clear that increasing the graphene from 0.5 to 1g led to an increase in EC from 31.012 to 37.845 kWh kg^{-1} phenol due to a decrease in phenol removal.

Analysis of variance (ANOVA)

The influence of three variables (electrolysis time, graphene dosage, and amount of iron particles) and their interactions can be examined comprehensively by the ANOVA analysis. ANOVA was used to examine the model's significance. The results of ANOVA are presented in Table 4. The terms "sum of the square" (Seq. SS), "adjusted sum of the square" (Adj. SS), and "adjusted mean of the square" (Adj. MS) are used to represent statistical terms. Contr. denotes the contribution of each variable, and *DF* represents the degree of freedom of the model and its parameters [38]. Table 4 displays the low probability value (*P* value = 0.0001) and high *F* model value (57.87), these two values denote the significance of the obtained model [39]. The P-values lower than 0.05 specify that the terms of the model are significant [40]. The multiple regression models can be used to predict the effectiveness of phenol removal in the 3D electro-Fenton reactor, as evidenced by the high value of R^2 (0.9905). High values of adjusted R^2 and predicted R^2 confirmed that the model fit is sufficient for the regression of experimental data. Electrolysis time had the highest significant effect on the phenol efficiency with a high *F*-value = 350.29 and Contr. of 66.6 %, the iron particles had lower Contr. = 17.89 %, and finally the graphene dosage had the lowest effect on the phenol removal efficiency with Contr. of 8.60 %.

Table 4. *ANOVA tests in removing phenol by electro-Fenton process*

Source	DF	Seq. SS	Contr., %	Adj. SS	Adj. MS	***F*-value**	***P*-value**
Model	9	1641.09	99.05	1641.09	182.34	57.87	0.0001
Linear	3	1542.60	93.10	1542.60	514.20	163.20	0.000
X_1	1	296.41	17.89	296.41	296.41	94.08	0.000
X_2	1	142.48	8.60	142.48	142.48	45.22	0.001
X_3	1	1103.70	66.61	1103.70	1103.70	350.29	0.000
Square	3	42.74	2.58	42.74	14.25	4.52	0.069
X_1X_2	1	2.63	0.16	3.40	3.40	1.08	0.346
X_2X_2	1	8.19	0.49	5.85	5.85	1.86	0.231
X_3X_2	1	31.92	1.93	31.92	31.92	10.13	0.024
2-Way interaction	3	55.75	3.36	55.75	18.58	5.90	0.043
X_1X_2	1	24.49	1.48	24.49	24.49	7.77	0.039
X_1X_3	1	31.21	1.88	31.21	31.21	9.91	0.025
X_2X_3	1	0.04	0.00	0.04	0.04	0.01	0.915
Error	5	15.75	0.95	15.75	3.15	-	-
Lack-of-fit	3	14.75	0.89	14.75	4.92	9.79	0.094
Pure error	2	1.00	0.06	1.00	0.50	-	-
Total	14	1656.84	100.00			-	-
Model summary			S	R^2 / %	R^2 (adj.) / %	Press	R^2 (pred.) / %
			1.77504	99.05	97.34	238.256	85.62

Effect of studied factors

RSM makes it feasible to identify the best available selection for the examined parameters and provides fundamental data on actual interactions between them. The contour and its related 3D surface plots can be investigated in order to more extensively understand the interaction between studied parameters on phenol reduction [41]. The effectiveness of phenol elimination was investigated by changing electrolysis time (3, 4 and 5 h) and amount of iron particles (2, 3 and 4 g) under constant graphene dosage, as shown in Figure 6. The contour plot in Figure 6a shows that high RE_{phenol} > 85 % is obtained over a narrow range of iron particles (3.5- 4 g). According to the 3D surface Figure 6b, when iron particulates increased from 2-4 g, the effectiveness of phenol removal increased progressively before essentially remaining constant as time increased to 5 h. The surface plot makes it obvious that at the time of 3 h, the efficiency of phenol removal dramatically dropped as the amount of iron particles dropped from 4 to 2 g. The effectiveness of phenol elimination increased linearly as the amount of iron particles raised to 4 g at a longer electrolysis time (5 h). So, the results showed that increasing the reaction time would improve the phenol removal efficiency. These results are in agreement with Zhang *et al.* [42], who also demonstrated that an increase in the reaction time improves COD removal from the landfill leachate by the EF process, and also-Umar *et al*. [10], who described how the removal of landfill leachate is mostly dependent on H_2O_2 dose. The generation of OH• increased by increasing H_2O_2 in the electrolytic solution and the ferrous ions, which led to an increase in phenol removal efficiency [43].

Figure 7 shows the contour and 3D surface plots obtained by changing the graphene dosage over a range of electrolysis times (3, 4 and 5 h). The highest phenol removal efficiency (85 %) was attained at an electrolysis time of 5 h and 1 g of graphene. Graphene has a high surface area and strong conductivity, which boosts the electron transfer rate and enhances the formation of H_2O_2 from the oxygen reduction reaction that takes place on the cathode electrode (equation (3)) [44,45]. At modified cathodes, the effectiveness of phenol removal is increased. The rate of the Fenton reaction and, consequently, the rate of homogenous OH• production in the medium are controlled by the yield of H_2O_2 generation [46,47]. So, the results approved that increasing graphene dosage leads to an increase in phenol removal efficiency.

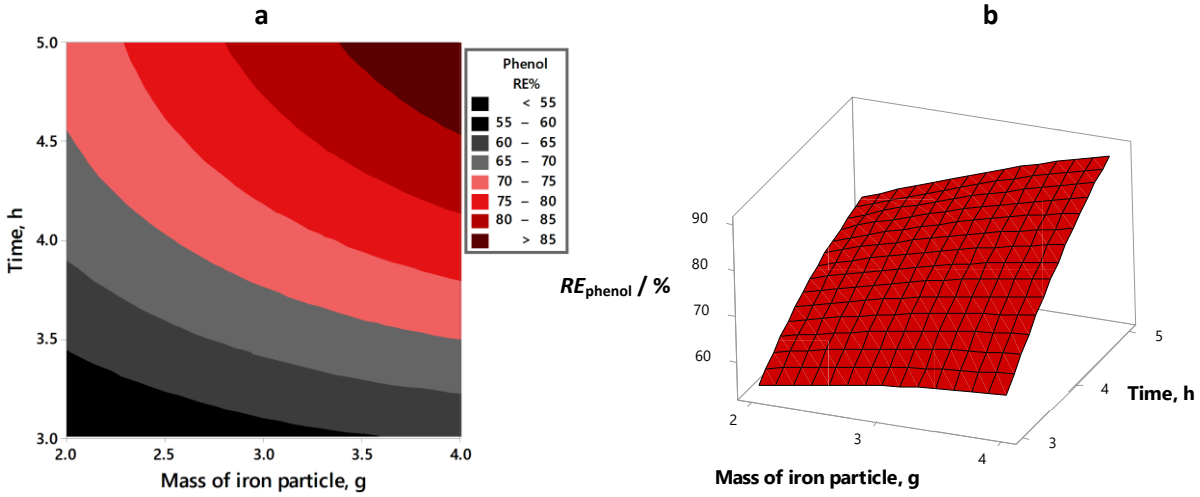

Figure 6. *Effect of time and amount of iron particles on RE_{phenol} at hold value of graphene 0.75 g: (a) contour plot and (b) 3D surface plot*

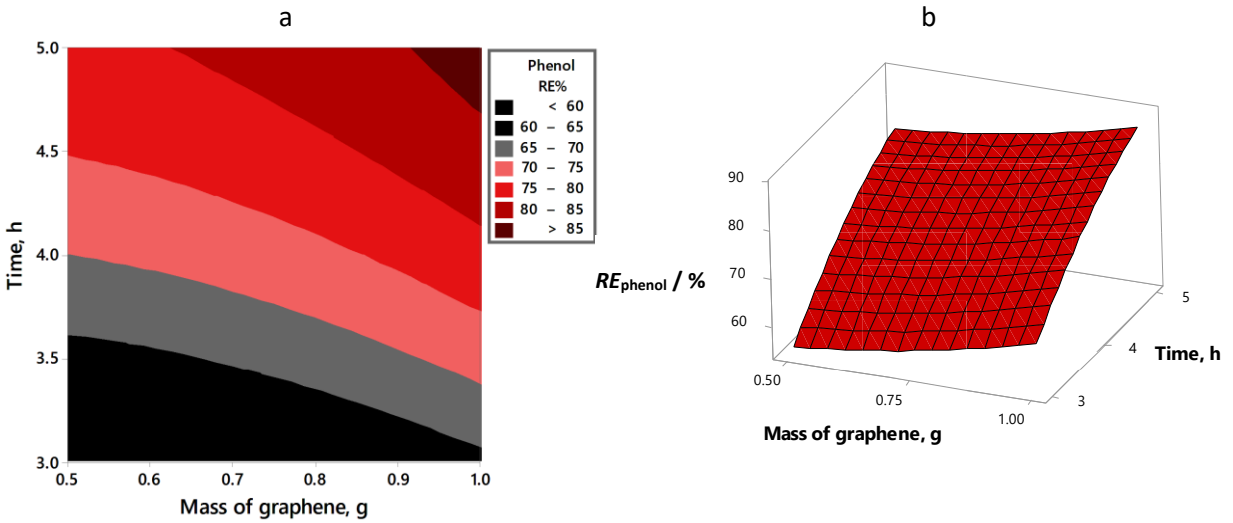

Figure 7. *Effect of time and graphene dosage on RE_{phenol} at hold value of iron particles of 3 g: (a) contour plot and (b) 3D surface plot*

Figure 8 shows the contour and 3D surface plots by changing iron particles (2, 3, and 4 g) over a range of graphene dosages (0.5, 0.75, and 1 g) at a constant electrolysis time of 4 h. The highest phenol removal efficiency (>85 %) was attained at iron dosage of 4 g, and 1 g of graphene. Graphene is very appropriate for electrochemical methods, such as its application in the electro-Fenton systems to generate H_2O_2 by the reduction of dissolved oxygen. Using carbon or graphite felt coated with graphene as a support for cathodes is one of the most common approaches due to low cost, high surface area, excellent conductivity, and high porosity [32].

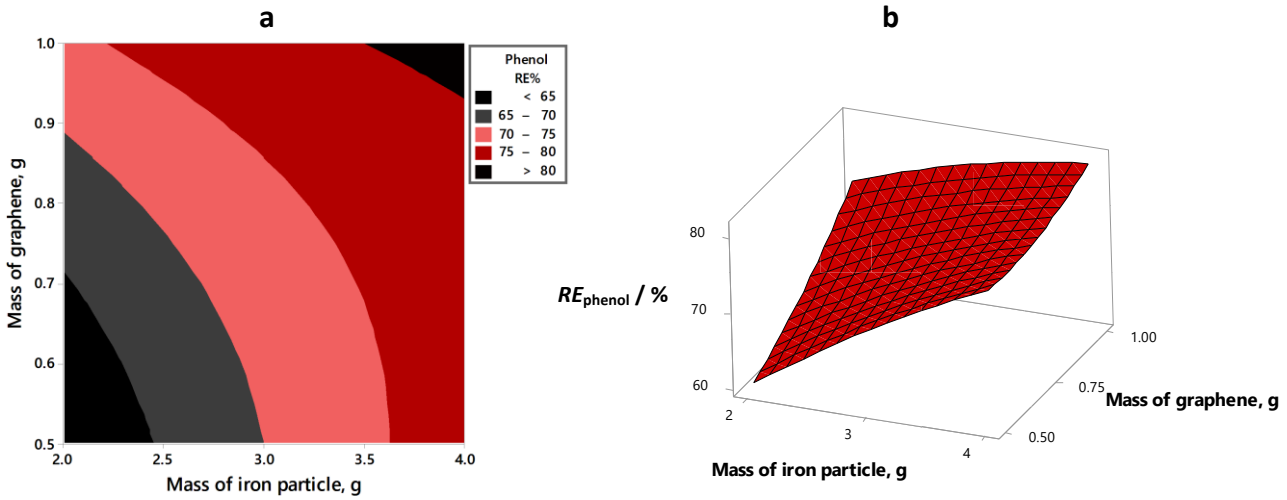

Figure 8. *Effect of graphene dosage and amount of iron particles on RE_{phenol} at hold value of time 4h: (a) contour plot, and (b) 3D surface plot*

Optimization of 3D electro-Fenton process

Outlining the optimal values of parameters to maximize phenol removal efficiency is the primary objective of the optimization. There are five options for the target field of the variables: maximize, objective, minimize, within the range, and none. The maximum removal of phenol with a corresponding weight of 1.0 was chosen as the goal. The results of the optimal values are presented in Table 5. Two confirmation experiments were conducted under optimal values of operating variables to obtain the highest value of phenol removal efficiency and the corresponding value of COD. The average phenol removal efficiency attained at optimum conditions was 92.83 %, as shown

in Table 6, and the COD value at these conditions was 89.33 % with consumed energy of 32.976 kWh kg^{-1} phenol. Previous study by Zheng *et al*. [29], who utilized the 3D electrode with iron foam particles, gave 70.4 % of folic acid removal efficiency in 6 h, while in the present study, the modification of the cathode electrode increased the efficiency of the 3D electro-Fenton process in removing 92.58 % of phenol in 5 h, what which signifies the enhancement obtained in the present electrolytic cell.

Table 5. *Optimal results of system parameters for the maximum elimination of phenol*

Response	Goal	Lower	Target		Upper	Weight	Importance
RE_{phenol} / %	Maximum	53.33	90.35			1	1
Solution of parameters			Multiple response prediction				
Mass of iron particles, g	Mass of graphene, g	Time, h	RE_{phenol} / % fit	Standard error fit	Confidence interval 95 %	Prediction Interval 95 %	Composite desirability
4	1	5	92.58	2.10	(87.19; 97.97)	(85.51; 99.64)	1

Table 6. *Confirmation tests for phenol removal efficiency and consumed energy*

Run	Mass, g		Time, h	Voltage, V	*EC* / kWh kg^{-1} phenol	RE_{phenol}, %	
	Iron particles	Graphene				Actual	Average
1	4	1	5	4.15	33.076	92.66	92.835
2	4	1	5	4.16	32.876	93.01	

Conclusion

3D electro-Fenton reactor for phenol elimination with the carbon fibers (CF) modified by graphene cathode and graphite anode was assessed in the presence of iron foam particle electrode. The response surface methodology (RSM) was employed to ascertain the impact of electrolysis time, graphene dosage, and iron foam dosage on the phenol removal efficiency and how these factors interact. The predicted multiple regression correlation showed a high value of R^2 (0.9905), which confirmed that the model sufficiently fits the regression of experimental data. High F-values and low P-values indicated that all variables influence phenol removal efficiency. The highest phenol removal efficiency of 92.835 % was achieved at 5 h, iron foam dosage of 4 g, and graphene of 1 g. CF approved its effectiveness in the present study as one of the most favored cathodes for H_2O_2 generation. This is due to the high specific surface and low cost of CF, which modification with graphene-enhanced its performance in producing H_2O_2. Iron foam functions were a good choice since 3D particles offer active sites, serve as iron ions source, and increase removal efficiency. Finally, the results of the experiments clarified that the 3D electrodes technology approved its high efficiency in the degradation of phenolic compounds as an innovative option.

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