Phenol reducing of petroleum refinery wastewater using electrocoagulation / electrooxidation technique

Dhulfoqaar Amer Salman [1], Shaker Salih Bahar[2]

Department of Chemical Engineering, Faculty of Engineering, University of Babylon, 51001 Babil, Iraq

eng489.dhulfoqaar.amer@student.uobabylon.edu.iq, eng.shakir.salih@uobabylon.edu.iq

https://orcid.org/0009-0006-1709-6055,

A B S T R A C T

Water pollution from industrial waste, toxic biological waste, and crude oil refining water: All of these pollutants are released into the environment and have become a major problem today due to their toxic organic and inorganic contaminants. The study found that two electrical methods, electrocoagulation(EC) followed by electro-oxidation(EO) and electro-oxidation alone, effectively reduced organic phenol(C_6H_5OH) levels in oil refining water of Najaf refineries in Iraq. Both methods achieved remarkable success, with some differences in the factors affecting the removal of dissolved phenol. The work was done using aluminum and graphite electrodes as the cover of the electric cell and steel (SS) electrodes as the cathode of the cell made of resistant plastic in the first method and graphite electrodes as the anode of the cell with steel (SS) electrodes in the other method. The initial concentration of phenol in the treated water was 50 ppm under the following conditions for both methods: electric current density (10, 15, 20) mA/cm², sodium chloride (NaCl) concentration (0, 1.5and 3) g/L, and acidity (pH) (3, 7and 10) with a fixed time of 1 hour for the (EC) process and 2.5 hours for the (EO) process for the first method, while in the other method the time was varied from (2-4) hours. The results showed that the removal rate was directly proportional to the high current density and NaCl concentration under mild acidic conditions for the first method, where the optimum conditions for the removal process were (CD = 20mA/cm^2), (PH = 7), and (NaCl = 3g/L). A removal rate of 95.05% was achieved under the mentioned conditions for the first method. While the results for the removal rate in the second method were under the following conditions (CD = 15mA/cm^2), (PH = 3), (NaCl = 3g/L) and (Time=3h). A removal rate of 96.3% was achieved under the mentioned conditions.

Optimization tests were performed using the response surface methodology with Box-Behnken design to identify key operational factors influencing phenol removal from wastewater.

Keywords: phenol, wastewater, electrocoagulation, electrooxidation, treatment

١. INTRODECTION

The aquatic ecosystem is severely contaminated, causing significant damage to natural waterways and posing a significant threat to Earth's life[1]. Oil refinery wastewater is a significant source of pollution, containing harmful chemicals like oxygen demand, phenol, BTEX, and fats, oils, and grease[2]. Oil refineries produce large amounts of wastewater that contains many organic contaminants and is very toxic and doesn't break down easily. This wastewater is an important part of the world's energy supply[3] . Consequently, it is essential to devise efficient and cost-effective techniques for the treatment of petroleum refinery effluent. Diverse methodologies, such as ion exchange, have been used in this domain [4]. biosorption [5], membrane filtration [6] coagulation flocculation[7].Electrochemical procedures like electrocoagulation and electrooxidation are more effective due to their fewer chemicals and ease of control[8][٤٣].

(EC) coagulants are made by Electrolyzing anodic electrodes, typically iron or aluminum, releases ions and forms hydrogen gas at the cathode, forming metal ions that encapsulate contaminants[8] .

Phenol and its derivatives are among the most common organic contaminants present in effluent from the oil refining sector. These substances are very harmful due to their poor biodegradability, high toxicity, and environmental consequences[9] .

Electrochemical treatment technologies like electrooxidation, electrocoagulation, and electro-flotation(EF) have gained popularity for remediating various types of wastewater[10]. The EO procedure is a prevalent main treatment method within electrochemical treatment techniques [11][٤٤]. A multitude of investigations on the electro-oxidation of phenol have been conducted on a modest scale using various electrode materials[12].

A study on using Fe–Co–O–$_4$ thin film electrodes to electrolyze phenol in an alkaline environment found that 100% breakdown was achieved after 54 hours of electrolysis[13]. Many methods can conduct electrooxidation in wastewater treatment. For instance, when chloride ions are present in the solution, an indirect electrochemical oxidation (EO) process transpires, whereby organic pollutants such as phenol, colors, glucose, and aniline may be degraded by chlorine and hypochlorite produced anodically during the EO process [14]. via various replies [15] .

At anode:

$$٢Cl^{-}\rightarrow Cl_{٢}+٢e^{-} \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\;(1)$$

At cathode:

$$٢H_{٢}O+٢e^{-}\rightarrow 2OH^{-}+H_{٢} \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(٢)$$

At bulk solution:

$$Cl_{٢} + H_{٢}O\rightarrow HOCl + H^{+} + Cl^{-} \leftrightarrow OCl^{-} + Cl^{-} + 2H^{+}\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(3)$$

Pollutants on anodes are broken down by "active oxygen" that sticks to them physically during direct anodic oxidation.

Anodic oxidation requires neither the incorporation of chemicals or oxygen nor does it produce secondary pollutants, and it does not need intricate equipment. In the anodic oxidation process, the anode material is the principal component. The main types of anodes used in anodic oxidation are graphite, glassy carbon, carbon fiber, stainless steel, Ti/Pt–Ir, Ti/RuO$_2$, and boron-doped conductive diamond (BDD)[16]. Despite its considerable expense, BDD has shown superior overpotentials for oxygen and hydrogen evolution, along with stability and efficiency throughout the electrooxidation process [8].

These features enable their effective use in the oxidation of organic contaminants [17]. Electrosynthesis [16]. decolorization of solutions [18]. surfactant degradation [19]. and oxidation of benzoic and carboxylic acids [20]. In the presence of chloride ions, graphite is favored for active chlorine formation owing to its elevated overpotential for chlorine release compared to other anodes [8].

The EO technique offers benefits like easy equipment, organic pollutants breakdown, low maintenance costs, and antimicrobial agent production, but faces issues like suspended particle removal and resistive film buildup[21].

Researchers frequently utilize EO due to its simplicity, clean reagents, and flexibility in eliminating various pollutants without the need for additional chemicals[22].

(EC) for potable water was first implemented in 1946 by Fred E. Stuart [23]. A multitude of research studies were undertaken in the latter part of the 20th century owing to the increasing interest [24].

Electrocoagulation (EC) is a cost-effective, eco-friendly method for treating industrial wastewater, offering expedited treatment, reduced sludge, and improved effluent transparency[25].

Electrolysis of electrodes makes metal ions at the anode and hydrogen gas at the cathode, which is where the coagulants come from. The metal ions generated at the anode neutralize the charged particles in the wastewater, resulting in the formation of neutral particles [26][27] .

The primary reactions in the electrocoagulation process utilizing aluminum electrodes are as follows [28] [29][30]:

Anodic reaction

$$Al \rightarrow Al^{٣+} + ٣e^{-} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

$$٢H_{٢}٠ \rightarrow ٤H^{+} + O_{٢} + ٤e^{-} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

$$x\,Al^{+٣} + y\,OH^{-} \rightarrow Al_{x} + \left(OH_{y}^{z+}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

cathode reaction

$$٢H_{٢}O + ٢e^{-} \rightarrow H_{٢\ (g)} + ٢□H^{-} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

The present research aims to evaluate the practical application of using EC, EO and EO techniques to treat actual wastewater obtained from Najaf refinery by reducing the phenol value using the mentioned methods and to study the effect of factors (NaCl concentration, CD, pH and time) on the effectiveness of performing both methods.

2.Experimental Work for two methods EC-EO and EO:

80 liters of effluent from the crude oil refining process were extracted from the Najaf refinery and preserved in a laboratory refrigerator to maintain its characteristics. shown in Table 1.

Table 1: Qualities of Wastewater

Properties	Values
$COD\ (ppm)$	1340
$TDS\ (ppm)$	3400
$Turbidity(NTU)$	40.4
$POD\ (ppm)$	122.6
$Phenol\ (ppm)$	50
$Oil\ (ppm)$	30.6
$Cl^{-}(ppm)$	2340
$PO_{٤}(ppm)$	0.15

٢,١ Chemicals used

- HCl, conc. (36%), Thomas Indian Bakers in brands, has been used to create a (1M) solution for the purpose of modifying the initial pH of wastewater and also prepare 5% (v/v) for the purpose of cleaning and reactivating the electrodes.
- NaOH, purity ≥97.0 %, pellets, Thomas Indian Bakers in brands, , has been used to create a (5M) solution for the purpose of modifying the initial pH of wastewater .
- NaCl, that has purity (99.9%), Barcelona, Spain, has been employed for the preparation of concentrated solutions with appropriate electrical conductivities.
- Distilled water for cleaning, Chemical Engineering Department Laboratories, University of Babylon.

2.2 Tools and Equipment:

As shown in Fig.1 We conducted the experiments in a single-electrode electrochemical cell for electrochemical (EC) and electrooxidation (EO) in batch mode at ambient temperature. The cell was made from a plastic container with dimensions of 20 cm in length, 6 cm in width, and 15 cm in height. The cell was then placed on a magnetic stirrer functioning at 200 rpm (DAIHAN LABTECH CO, 0-450 rpm). The cathode electrodes in the electrochemical process included three sheets of 316-AISI stainless steel, whereas the anode electrodes consisted of two aluminum plates. In the electrochemical oxidation process, the anode electrodes were two graphite plates, and the cathode electrodes were three identical stainless-steel sheets. The electrodes measured uniformly at 18×5×0.3 cm. The submerged dimensions of each side of the anode were 8×5 cm, yielding an effective surface area of 160 cm^2. Each anode is positioned between two cathodes, with a separation of 2 cm, and the effective area of the aluminum and graphite electrodes has been calculated. The anode electrode, potentially composed of aluminum in the process or graphite in the electrolysis procedure, is connected to the positive terminal of a DC power supply (MCH-305 D-II, 0–30V, 0–5A dual output), while the stainless-steel cathodes are attached to the negative terminal. An RMS multimeter (UNI-T, UT803) is then connected in series with the anode. We conducted a number of exploratory tests to evaluate the range of objects under examination and to gain a comprehensive understanding of the proposed method. The investigations revealed that the EC procedure lasted around 1 hour, but the EO process required 2.5 hours. During the first hour of each run in the EC and EO tests, aluminum electrodes function as anodes in the electrochemical process. Subsequently, we substitute the aluminum electrodes with graphite electrodes and use the electrooxidation procedure for the remainder of the period. Samples were collected and filtered using Whatman filter paper and thereafter evaluated to establish therapeutic effectiveness concerning phenol.

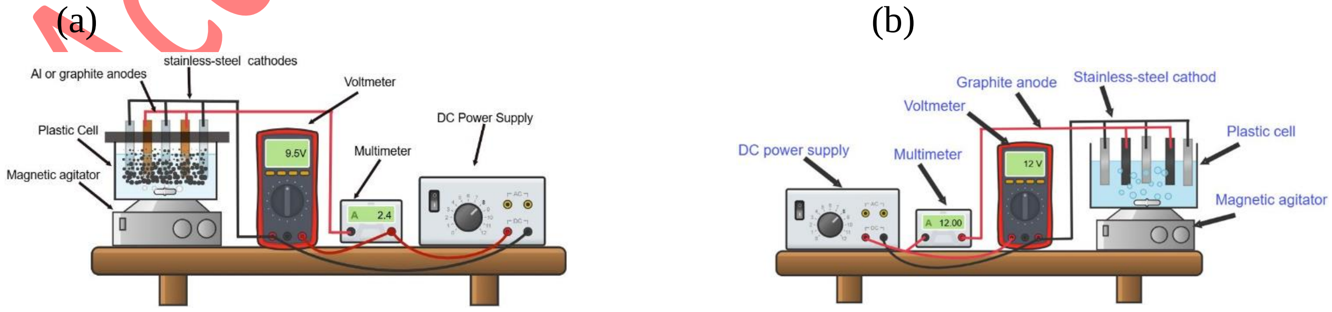
(a) (b)

Figure 1: (a) Diagram of the sequential EC &EO process, (b) Diagram of the sequential EO process

2.3 Measurement and analysis method

A phenol solution with a known concentration of 100 ppm was prepared. The material was examined using an ultraviolet (UV) light spectrometer to determine the wavelength of phenol. The results were then compared with those of a previous reference solution. Phenol was detected in a wastewater sample from the Najaf refinery. Several measurements of known concentrations were performed to establish a calibration curve for both processes, as shown in Figures 2 and 3, using Equations 8 and 9 for the phenol measurement. Three tests on the samples showed an S value of less than 0.05.

For (EC-EO):

$Y = 0.01\,x - 0.079$ ………………………….. (8)

$R^2 = 99.35\ \%$

For (EO):

$Y = 0.01\,x - 0.079$ …………………………..(9)

R2 =98.83%

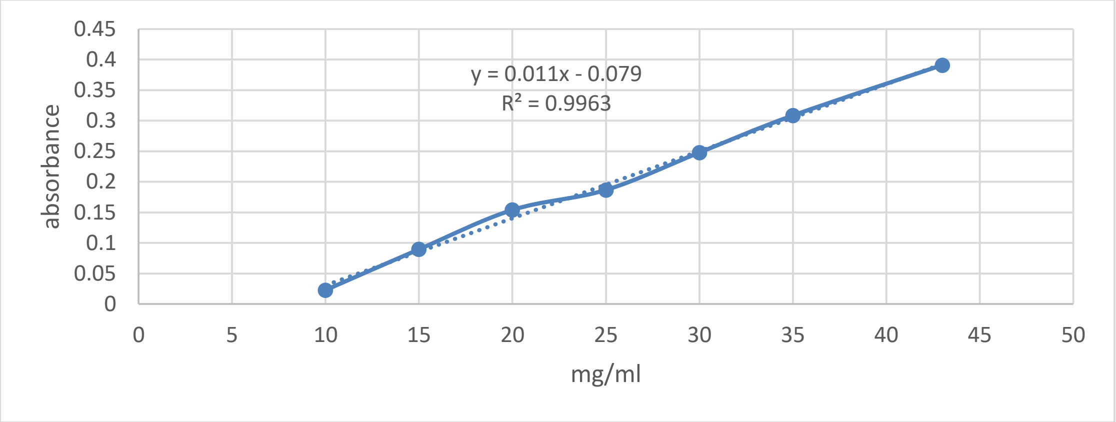

Figure ٢: Calibration curve for absorbance of phenol for(EC-EO)

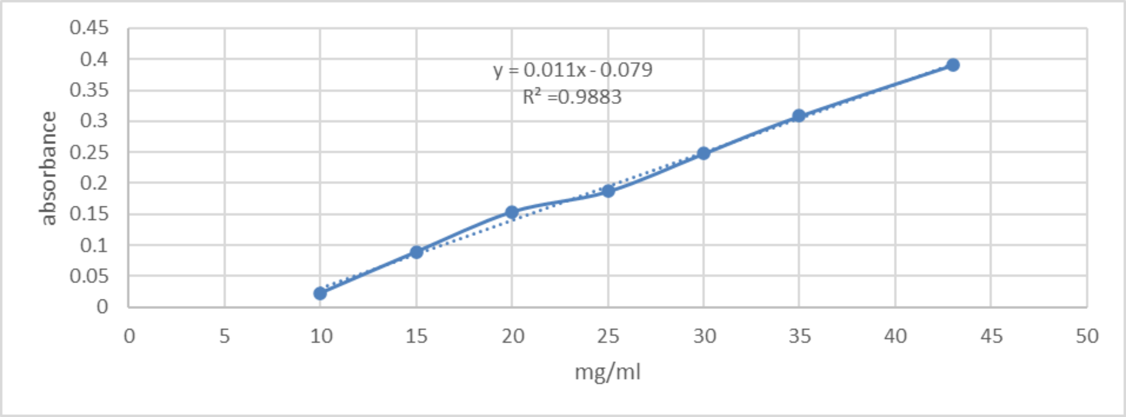

Figure3: Calibration curve for absorbance of phenol for (EO)

3.Results and Discussion

3.1 For EC-EO method:

This study examines three controllable variables: Sodium chloride(NaCl)content g/L, current density (CD) (mA/cm²), and solution pH, maintaining a consistent duration of 3.5 hours, including 1 hour for the EC process and 2.5 hours for the EO process. Table 2 illustrates three tiers of these characteristics. NaCl was used to enhance wastewater treatment. These criteria were selected due to their significance in influencing wastewater treatment.

Table 2: Customized levels for the experimental parameter levels

parameters	Symbols	Level 1	Level 2	Level 3
$CD\ mA/cm^{2}$	B	**10**	**15**	**20**
PH	A	**3**	**7**	**10**
$NaCl$content g/l	C	**0**	**1.5**	**3**

As shown in table 3, optimization experiments are carried out using response surface methodology (RSM) with Box-Behnken design (BBD) to identify the statistically significant operational factors that affect the removal of phenol from wastewater [31]. The results were fitting to second order polynomial equation as follows [32]:

$$Y = \beta o + \beta_1 A + \beta_2 B + \beta_3 C + \beta_4 AB + \beta_5 AC + \beta_6 BC + \beta_7 A^2 + \beta_8 B^2 + \beta_9 C^2$$

where (Y) is predicated value for phenol concentration, (β_0) is the y-axis intercept parameter, (β_1 ,β_2 , and β_3) are the linear part of input variable xi, (β4 , β_5 ,and β_6) is interaction impact of two input variables xi, and (β_7,β_8 , and β_9) is quadratic effect.

Table ٣: Box-Behnken design experiment with operational parameters and effectiveness of removal for the EC-EO system

Run No.	pH	CD$mA/cm^{٢}$	NaCl g/L	Phenol ppm	Econs KWh/m^3
1	3	10	1.5	59.94	39.2
2	10	10	1.5	35.47	38.08
3	3	20	1.5	73.63	94.08
4	10	20	1.5	85.52	89.6
5	3	15	0	64.16	77.28
6	10	15	0	59.08	58.8
7	3	15	3	76.96	80.4
8	10	15	3	63.14	63
9	7	10	0	47.06	33.6
10	7	20	0	74.93	89.9
11	7	10	3	52.5	36.4
12	7	20	3	95.05	137.76
13	7	15	1.5	67.85	64.68
14	7	15	1.5	67.85	64.68

3.1.1 Multivariate regression model for (EC-EO)

Final Equation Expressed in Coded Factors

$$Phenol = 68.296875 - 2.813125\ A + 15.63375\ B + 5.575625\ C + 7.95375\ AB - 1.911875\ AC + 3.67\ BC - 2.205\ A^2 - 1.33\ B^2 + 0.865\ C^2 \ldots\ldots\ldots.(10)$$

The equation expressed in coded factors may facilitate predictions on the response at specified values of each element. Typically, the elevated values of the components are designated as +1, while the diminished levels are designated as -

1. The encoded equation is important in determining the relative influence of the variables by analyzing the factor coefficients.

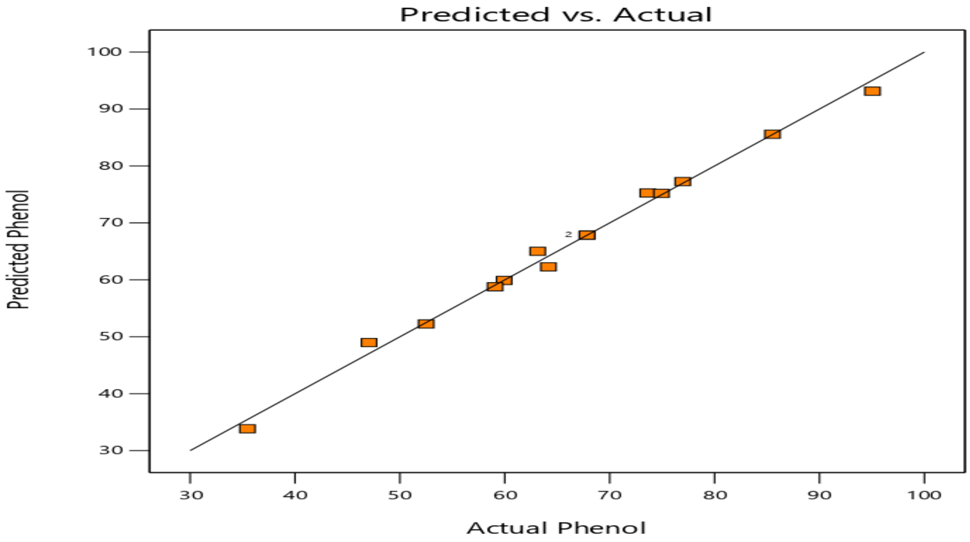

Figure ٤ : Phenol behavior against Phenol actual

3.1.2 Analysis of (ANOVA) Optimization

We perform the ANOVA analysis to evaluate the impact of each controllable element on the process response, specifically the efficiency of phenol removal. The ANOVA evaluation facilitates a deeper comprehension of the acceptability of the results and the extent to which the experiments are conducted under controlled settings [33].

The data indicates that a substantial proportion of writers hail from the United States, India, and China. Additionally, several writers are associated with esteemed higher education institutions, like Universidad de São Paulo, Universidad Est dual Paulita "Júlio de Mesquita Filho," and Tehran University of Medical Sciences. This report offers a summary of the volume and allocation of contributors to the progress of ANOVA research [34]. As seen in Table 4

The model F-value of 67.43 indicates that the model is statistically significant [38]. The probability of an F-value of this magnitude arising from random noise is about 0.05%.

P-values below 0.0500 indicate that model terms are statistically significant. A, B, C, AB, and BC are pertinent model words in this instance. Values beyond 0.1000 indicate that the model terms lack significance. Model reduction may enhance your model if several inconsequential terms exist, except those necessary for hierarchy support.

Table 4: ANOVA Analysis data

Source	Sum of squares	df	Mean of Square	F-value	P-value	
Model	3039.01	9	337.67	67.43	0.0005	significant
A-PH	71.52	1	71.52	14.28	0.0195	
B-CD	1896.06	1	1896.06	378.61	<0.0001	
C-NaCl	241.16	1	241.16	48.16	0.0023	
AB	330.51	1	330.51	66.00	0.0012	
AC	19.10	1	19.10	3.81	0.1226	
BC	53.88	1	53.88	10.76	0.0305	
A^2	26.54	1	26.54	5.30	0.0827	
B^2	5.66	1	5.66	1.13	3476	
C^2	2.39	1	2.39	0.4781	0.5273	
Residual	20.03	4	5.01			
Lack of Fit	20.03	3	6.68			
Pure Error	0.0000	1	0.0000			
Cor Total	3059.04	13				

3.2 For (EO) method:

Four adjustable factors—sodium chloride (NaCl) concentration (g/L), current density (CD) (mA/cm²), solution pH, and time—are investigated in this paper. The four tiers of these qualities are shown in Table 5. Wastewater treatment was improved by NaCl. These criteria were chosen for their relevance in affecting wastewater treatment.

Table 5: levels that are specific to the experimental parameter levels

parameters	Symbols	Level 1	Level 2	Level 3
CD mA/cm^{٢}	A	10	15	20
PH	B	3	7	10
Time / hour	C	2	3	4
NaClcontent g/l	D	0	1.5	3

According to table 6 Six optimization tests are conducted using response surface methodology (RSM) with Box-Behnken design (BBD) to find the important operational factors that influence phenol removal from wastewater[31].

Run no.	pH	CDmA/ cm^{٢}	NaCl g/L	Time /hour	Phenol ppm	Econs KWh/m^3
1	3	10	1.5	3	76.48	26.4
2	3	20	1.5	3	83.6	78.72
3	10	10	1.5	3	52.22	31.68
4	10	20	1.5	3	44.8	97.92
5	7	15	0	2	39.8	45.2
6	7	15	0	4	50.76	90.24
7	7	15	3	2	82.52	33.6
8	7	15	3	4	78.9	68.16
9	7	10	0	3	52.53	37.44
10	7	20	0	3	36.45	96.96
11	7	10	3	3	76.44	29.28
12	7	20	3	3	83.62	78.72
13	3	15	1.5	2	71.55	33.6
14	10	15	1.5	2	56.34	33.6

15	3	15	1.5	4	90.49	70.08
16	10	15	1.5	4	55.34	79.68
17	7	10	1.5	2	77.23	20.48
18	7	20	1.5	2	60.34	58.24
19	7	10	1.5	4	70.32	41.6
20	7	20	1.5	4	75.92	112.64
21	3	15	0	3	47.44	59.04
22	10	15	0	3	39.24	47.52
23	3	15	3	3	96.3	46.08
24	10	10	3	3	56.73	41.76

3.2.1 Multivariate regression analysis

Conclusive Equation Represented in Coded Variables

$$\text{Phenol}=57.45-\ 1.34*13.43*B+3.23*C+18.08*D3.82*AB+5.62*AC+5.82*AD-5.15*BC-7.63*BD3.65*CD+6.15*A^{2}+1.84*B^{2}+8.60*C^{2}+0.0000*D^{2}\ldots\ldots..(11)$$

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

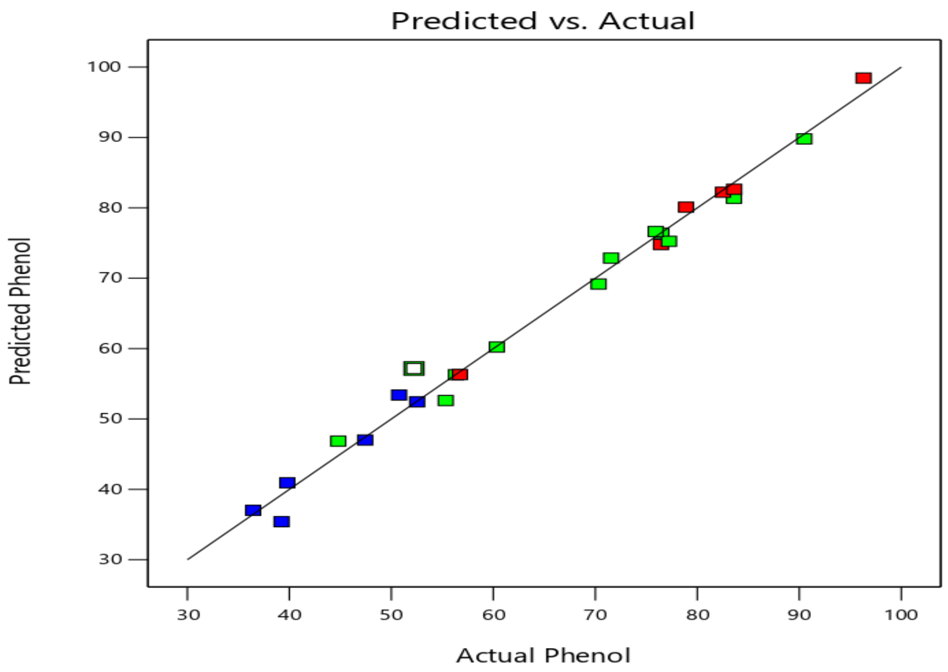

Figure ٥ : Phenol behavior against Phenol actual

3.2.2 Optimization Analysis of (ANOVA)

To evaluate how acceptable the results are and how well the tests worked in controlled conditions, we use ANOVA analysis to look at how each controllable factor affects the process response, specifically the success of phenol removal[34].

The data indicates that a substantial proportion of writers hail from the United States, India, and China. Furthermore, several writers are associated with esteemed higher education institutions, like the University of São Paulo, São Paulo State University "Júlio de Mesquita Filho," and Tehran University of Medical Sciences. This report offers a comprehensive analysis of the quantity and distribution of contributions to the progression of ANOVA research[35]. As seen in Table 7

The model's F-value of 64.73 indicates statistical significance. The likelihood of an F-value of this size resulting from random noise is around 0.01%.

P-values less than 0.0500 indicate that model terms are statistically significant. In this case, B, C, D, AB, AC, AD, BC, BD, CD, A^2, and C^2 are relevant model terms. Values beyond 0.1000 indicate that the model terms are insignificant. Model reduction may improve your model if several insignificant terms are present, except those essential for hierarchical support.

Table 7: ANOVA Analysis data

Source	Sum of squares	df	Mean of Square	F-value	P-value	
Model	6951.58	13	534.74	64.73	<0.0001	significant
A-CD	21.11	1	21.11	2.56	0.1410	
B-PH	2165.18	1	2165.18	262.11	<0.0001	
C-Time	128.79	1	128.79	15.59	0.0027	
D-Salt	3821.79	1	3821.79	462.66	<0.0001	
AB	59..05	1	59.05	7.15	0.0233	
AC	126.45	1	126.45	15.31	0.0029	
AD	135.26	1	135.26	16.37	0.0023	
BC	107.59	1	107.59	13.03	0.0048	
BD	235.96	1	235.96	28.56	0.0003	
CD	53.14	1	53.14	6.43	0.0295	
A2	151.41	1	151.41	18.33	0.0016	
B2	12.96	1	12.96	1.57	0.2389	
C2	295.67	1	295.67	35.79	0.0001	
D2	0.0000	0				
Residual	82.60	8.26				

Cor Total	7034.19	23				

3.3 Effect of operational parameters on Phenol removal

3.3.1 Impact of PH

For (EC-EO):

The findings indicated that the optimal and most expensive phenol elimination rate occurs at pH 7, as seen in Figure 6 and7. Experiments conducted under these circumstances demonstrated the generation of sodium hydroxide radicals and active chlorine species, including Cl_2, HOCl, and ClO^-, as detailed in the preceding paper [35]. In this media, $Al(OH)_3$ is not very soluble and settles as thick "flocs," which are powerful and big. The surfaces of these precipitates contain positive charges that absorb and neutralize the phenol molecules' charge. At pH 7, the phenol molecules are not bonded to anything, so they may be absorbed more easily.

After coagulation, some of the phenol is still dissolved, but not as much. This makes it simpler for free radicals (•OH) and oxidizing species generated at the anode to finish oxidizing the rest of the phenol. A neutral medium (pH≈7) strikes a beneficial compromise between generating free radicals and keeping them stable, as they don't break down as quickly as they do in a very alkaline medium. as demonstrated in the previous study[٤٥]. The findings indicated that the phenol removal process in this approach (EC, EO) is more effective in acidic or neutral environments, contingent upon the operational factors.

For (EO):

While The results demonstrated that pH 3 yielded the greatest and most cost-effective phenol removal rate, as seen in Figure 8 and 9. Experiments conducted under these conditions demonstrated the formation of sodium hydroxide radicals and active chlorine compounds, such as Cl_2, HOCl, and ClO□, which are potent oxidizers that efficiently decompose phenol, while simultaneously augmenting the concentration of (H+), thereby facilitating oxidation reactions on the electrode surface. However, several researches have stated that the optimal acidity level for the highest clearance rate is pH 7, as noted in the preceding publication[35][45]

We conclude from both methods that the first method EC.EO requires a neutral acidic medium, while the second method EO requires an acidic medium.

3.3.2 Impact of CD

For (EC-EO):

Electric current is a crucial element in the processes of electrocoagulation (EC) and electrooxidation (EO) for the removal of phenol from wastewater, influenced by other parameters like temperature, pollutant concentrations, and electrode type. Experiments were performed using several current densities (10, 15, and 20 mA/cm²), revealing that optimal phenol elimination occurred at a current density of 20 mA/cm². This finding aligns with prior investigations[15] [36].

In the electrooxidation (EO) process, elevating the current results in a heightened production of HCLO, while in the electrochemical (EC) process, raising the current leads to an augmentation in mass due to the substantial release of Al ions by anodic dissolution, as dictated by Faraday's law in Equation 12 [38] .

$$C_{Al} = \frac{M.I.t}{n.F.V} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(12)$$

Where C_{Al}= Theoretical concentration of Al (g/l)

M= The molecular weight of Al (g/mol)

I=The applied current (A)

n= Number of electrons (n=3 for Al)

F= Faraday constant (96500 C/mol)

V= Volume of liquid in the reactor (l)

It is clear that high currents cause an increase in the decomposition of the electrodes (Al), which leads to an increase in consumption costs. To reduce these costs, we resort to increasing the process time with lower currents, as shown in Figure 10,11,7.

For (EO):

While experiments conducted with this method at different current levels (10, 15, and 20 mA/cm²), the best phenol removal occurred at a current level of 15 mA/cm². Other factors, such as time and sodium chloride concentration, depend on the current. This result is consistent with previous studies[39].

In electrolysis, increasing the current boosts the production of hypochlorous acid (HOCl) or sodium hypochlorite (NaClO) when chloride ions (Cl^-) are in the solution, which speeds up the reactions at the electrodes (anode and cathode)[40].

The clearance rate is superior at a high current of 20 mA/cm² for 4 hours. The increased current produces a large amount of reactive free radicals, enhancing the speed and efficiency of removal. However, at the same time, the increased current leads to the depletion of some oxidizing agents due to side reactions or the generation of unwanted byproducts. Therefore, due to these side reactions, a longer duration is required to achieve sufficient phenol removal, as shown in Figure ٨.

Also, a low current of 10 mA/cm² and a short duration of 2 hours were shown to provide optimal removal results. The low current produces a sufficient amount of free radicals for effective removal. This is attributed to the inability of the low current to induce the loss of oxidizing agents, due to the absence of side reactions common at high currents. Consequently, the response time of the removal process is reduced, as shown in Figure 12,13. We find that effective removal efficiencies can be achieved in both scenarios; however, the difference lies in the consumption of the oxidizing agents and their reaction with phenol.

To achieve maximum efficiency, an appropriate balance between current and time must be found to avoid unwanted side reactions, as described previously[٤٦][٤٧].

It was found that the current density in both methods is directly proportional to the rate of phenol removal depending on other influencing factors.

3.3.3 Impact of NaCl

For (EC-EO):

The addition of sodium chloride significantly influences the phenol removal process. Experiments indicate that the addition of NaCl positively influences both processes (EC, EO) by enhancing conductivity and reducing voltage. During this process, several forms of chlorine, including hypochlorous acid, are generated at the anode electrodes. These facilitate the decomposition of organic molecules by a mechanism known as indirect oxidation, as shown in equations (10) and (11)[15].

$$\boldsymbol{2Cl^- + 2e^- \rightarrow Cl_2} \text{ .... (13)}$$

$$\boldsymbol{Cl_2 + H_2O \rightarrow HCl + HClO^{\cdot}} \text{ .... (14)}$$

Figure 14,11 shows the effect of adding NaCl on the phenol removal process. Laboratory experiments were conducted without adding salt and with adding salt in quantities of 0, 0.15 and 3 g/l. It was found that the effect of salt has a positive effect on the removal process at all current densities, as stated in previous studies [35,36] .

For (EO):

The incorporation of sodium chloride substantially influences the phenol elimination process. Experiments demonstrate that the incorporation of sodium chloride favorably influences the electrooxidation process by improving conductivity and reducing the potential. The anode electrodes produce many chlorine species, including hypochlorous acid, throughout this process. These forms promote the breakdown of organic molecules by a process termed indirect oxidation.

Figure 15 ,13This study illustrates the impact of NaCl supplementation on the process of phenol removal. We performed laboratory experiments with and without the incorporation of salt, particularly at concentrations of 0, 1.5, and 3 g/l. Research demonstrates that salt enhances the removal process at all current densities, as supported by previous studies[41].

We conclude from this that sodium chloride is directly proportional to the current density and the removal rate in both methods.

3.3.4 Impact of Time

For EC-EO:

The duration was established at three and a half hours, with the electrocoagulation process requiring one hour and the electrooxidation procedure necessitating two and a half hours for all tests.

For EO:

The results showed that how long the electrooxidation process takes greatly affects how quickly phenol is removed, depending on other factors like current density and sodium chloride concentration. The optimal removal rate was achieved in three hours with a current density of 15 mA/cm², a sodium chloride concentration of 3 g, and a pH of 3. The values fluctuate during the duration of the procedure. The study results indicate that time significantly influences CD density and the efficacy of phenol removal. This is evident in Figure 16,17.

The likelihood of phenol decomposing into less dangerous chemicals or carbon dioxide and water increases with time. Excessive processing time may result in heightened energy consumption without substantial gains in efficiency and the generation of unwanted oxidation byproducts, as shown in a previous study[42].

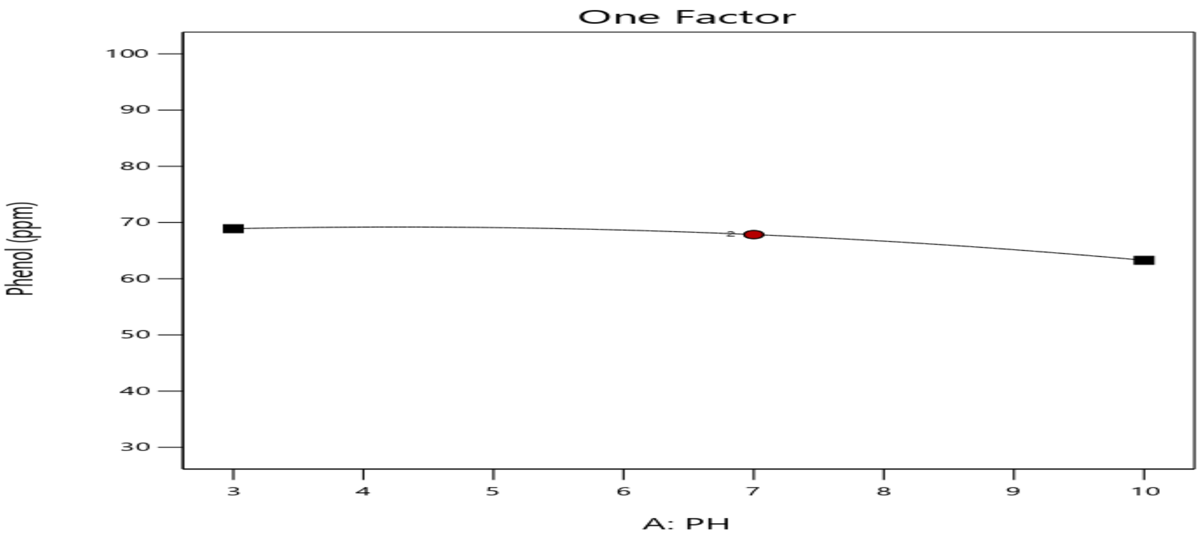

Figure 6: Effect of PH on Phenol removal efficiencies at Ph=7,CD=15(mA/cm2),Salt=1.5(g/L)

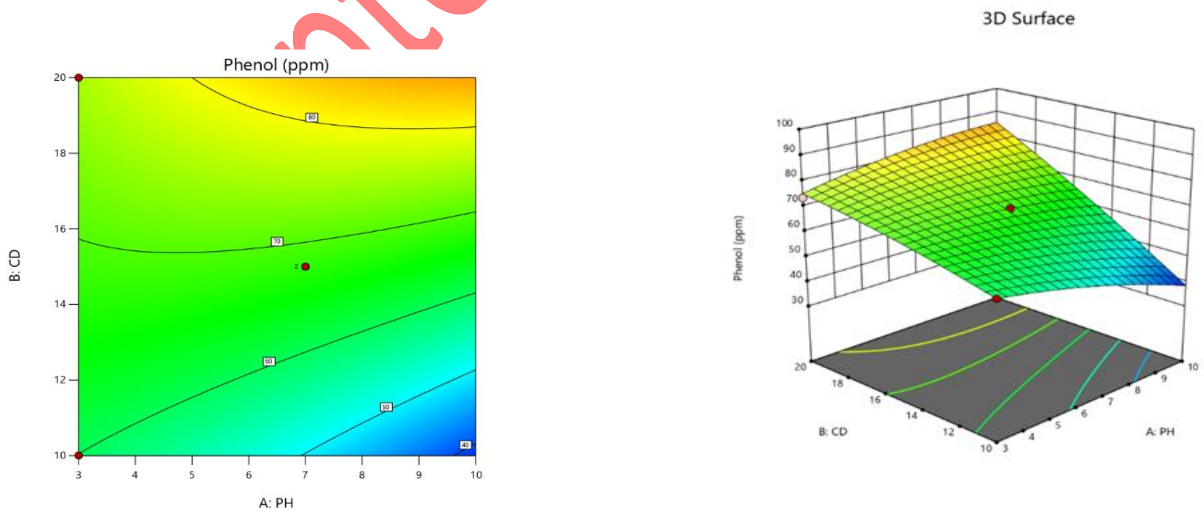

Figure 7: contour and 3D for Phenol % vs PH and CD

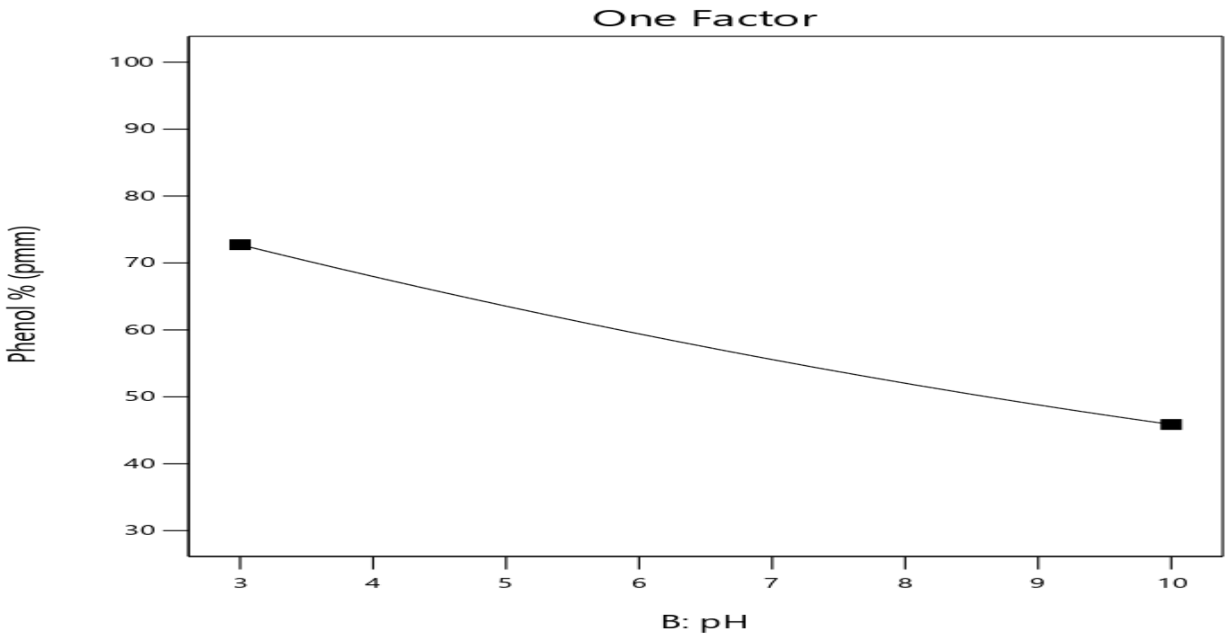

Figure 8: Effect of pH on Phenol removal efficiencies at Time=3h,CD=15(mA/cm2),Salt=1.5(g/L).

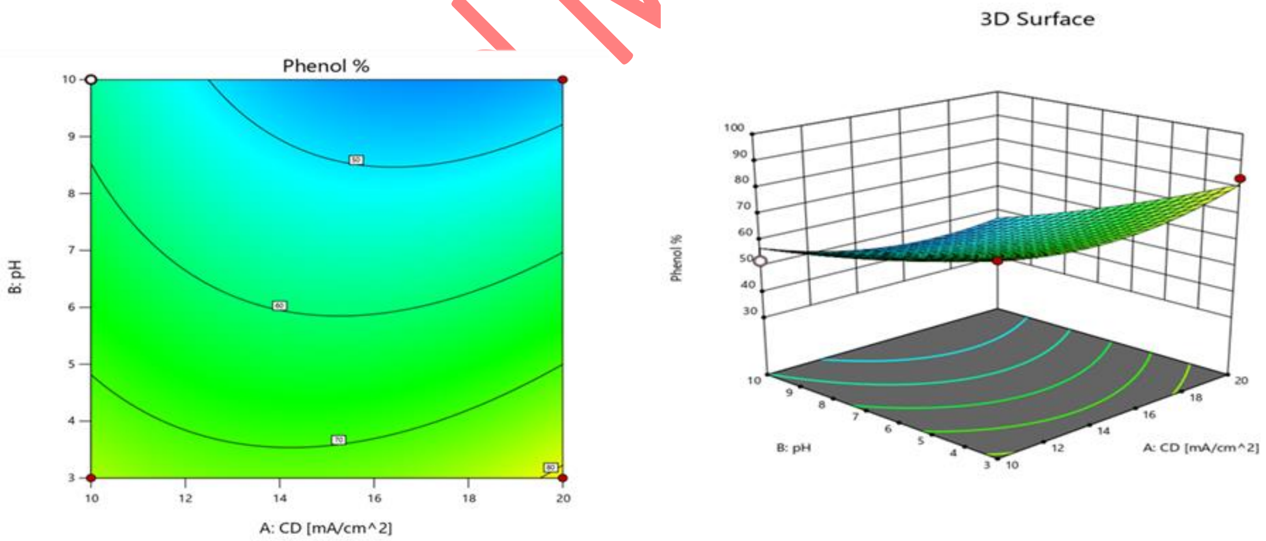

Figure 9**:** contour and 3D for PH and CD vs Phenol %

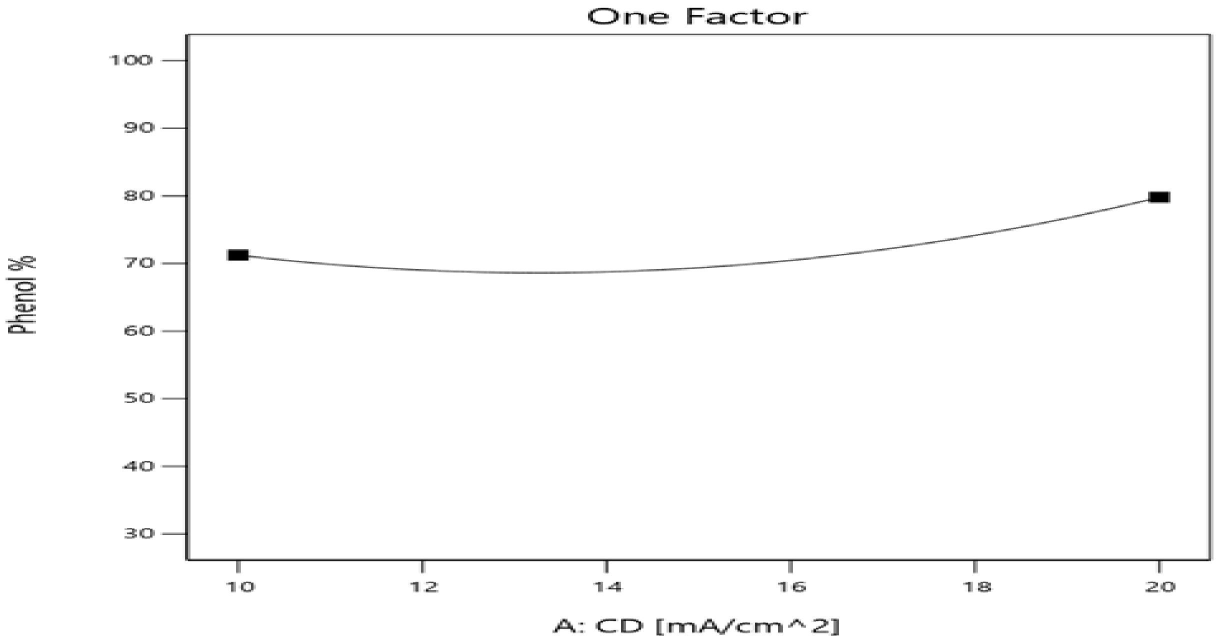

Figure 10: Effect of CD on Phenol removal efficiencies.at CD =20(mA/cm2),time= 4hour,NaCl=1.5 (g/l),PH=6.5

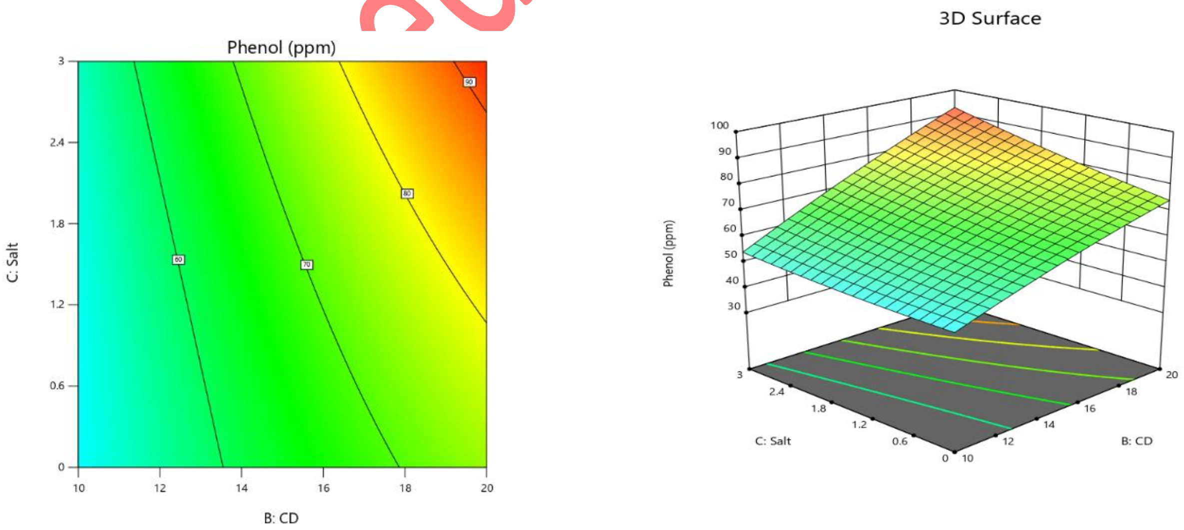

Figure 11: contour and 3D for Phenol % vs CD and Nacl

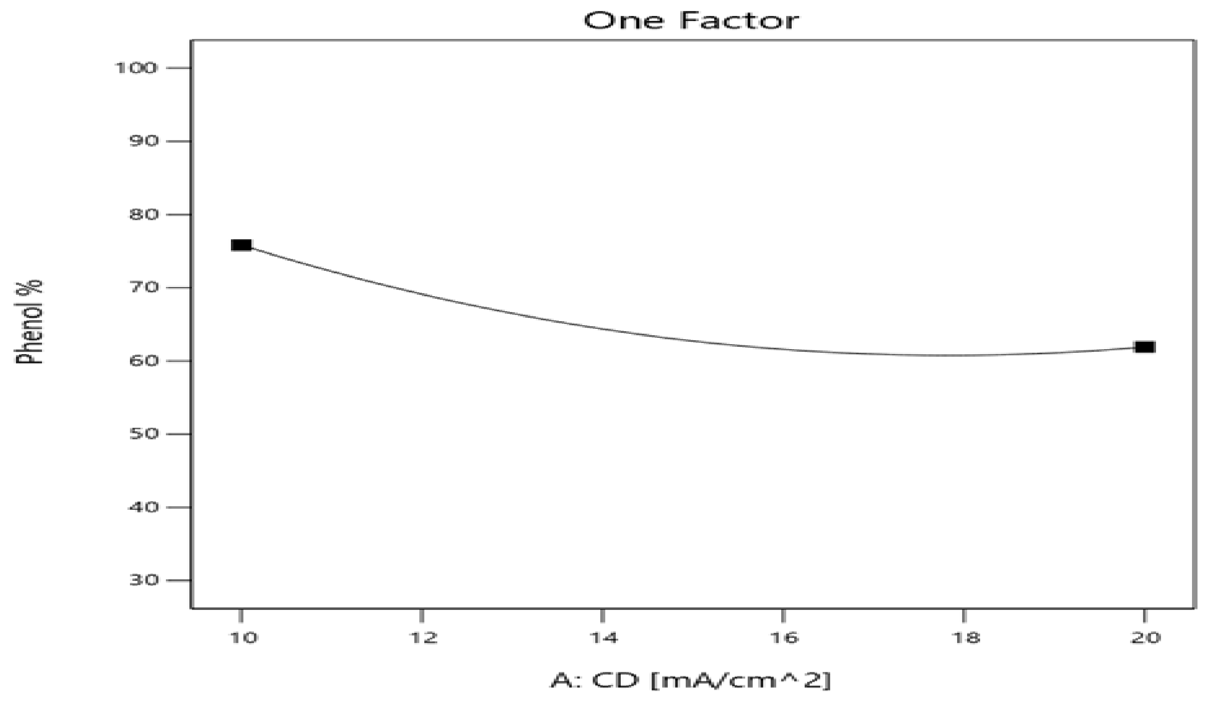

Figure 12: Effect of CD on Phenol removal efficiencies.at CD= 10(mA/cm2),time=2hour,NaCl=1.5(g/l),PH=6.5

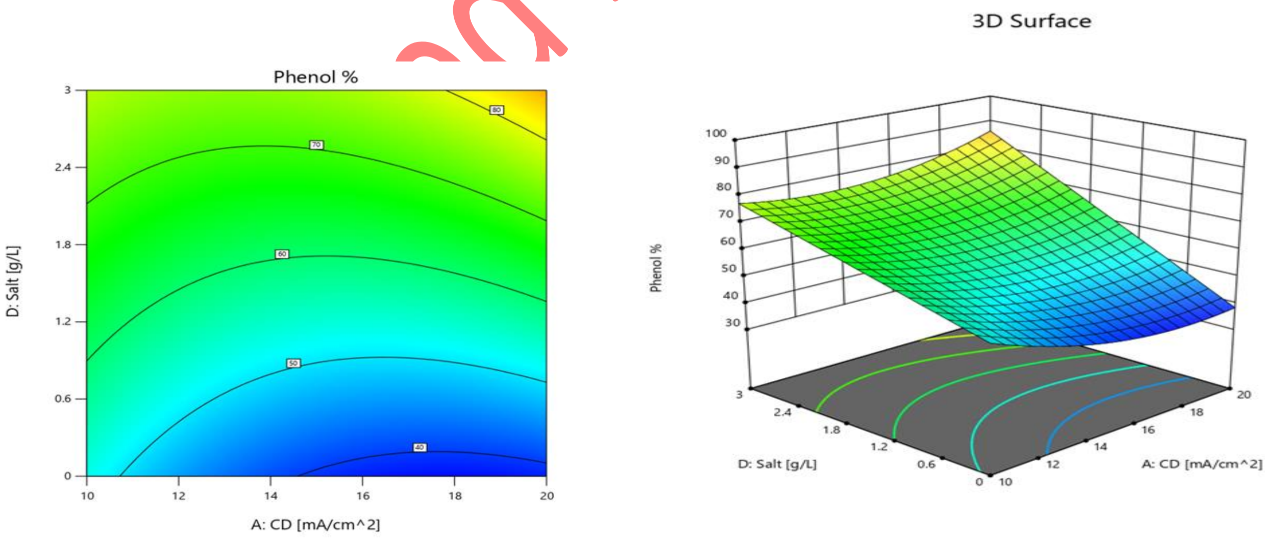

Figure 13: contour and 3D for Salt and CD vs Phenol %

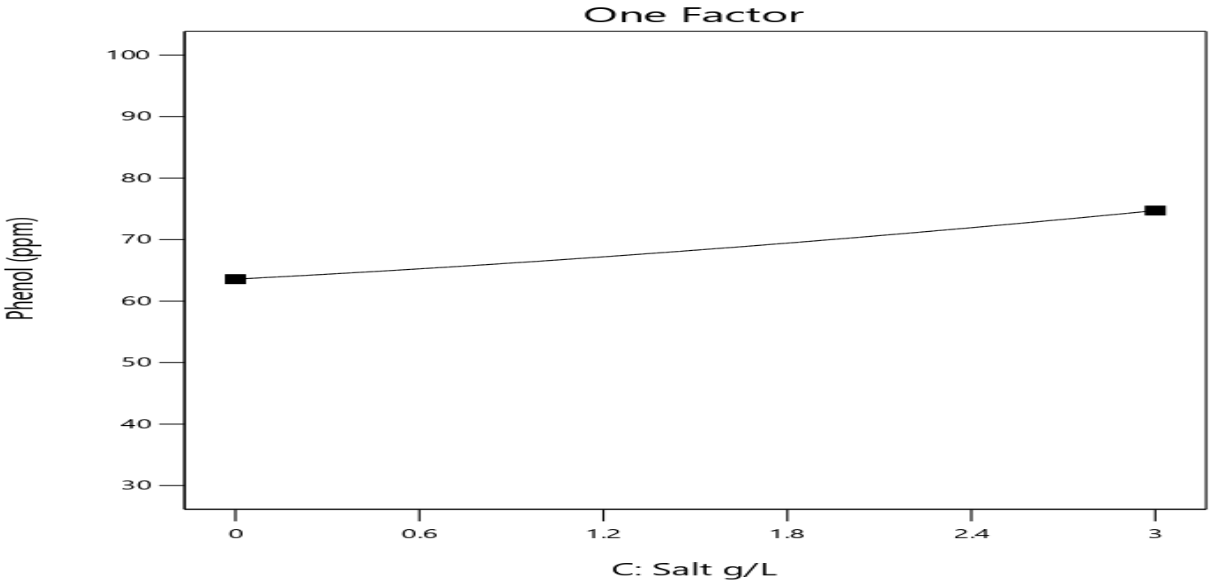

Figure 14**:** Effect of NaCl on Phenol removal efficiencies at PH =7,NaCl=3 (g/L) ,CD= 15(mA/cm2).

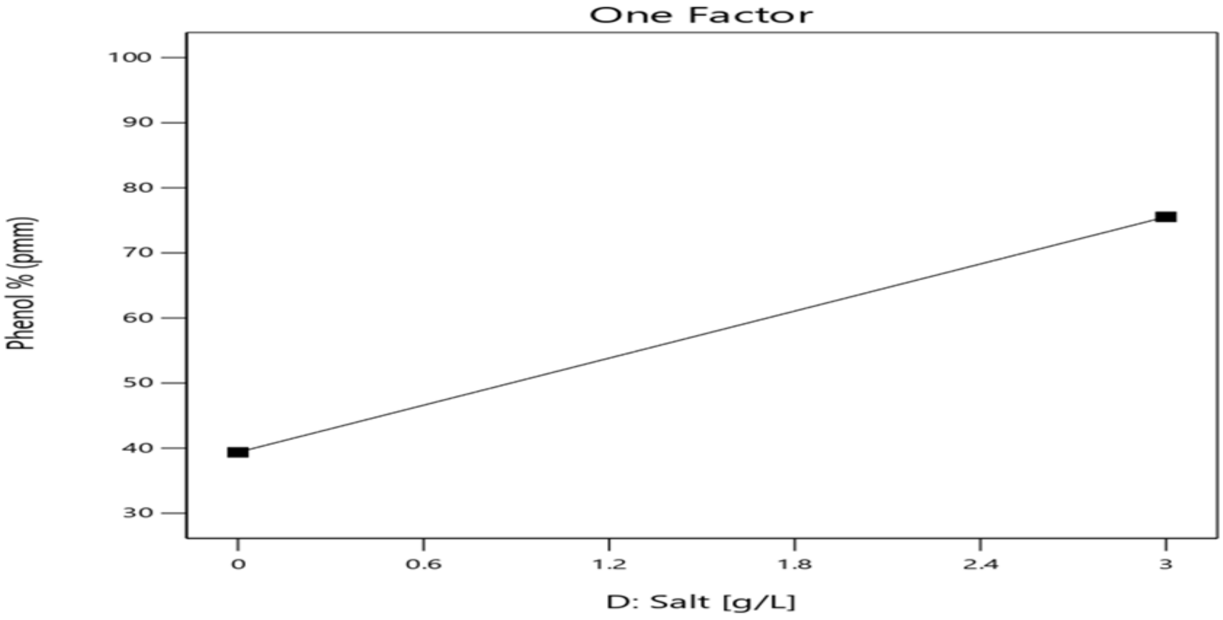

Figure 15: Effect of NaCl on Phenol removal efficiencies at Ph=7,CD=15(mA/cm2),Time=3h .

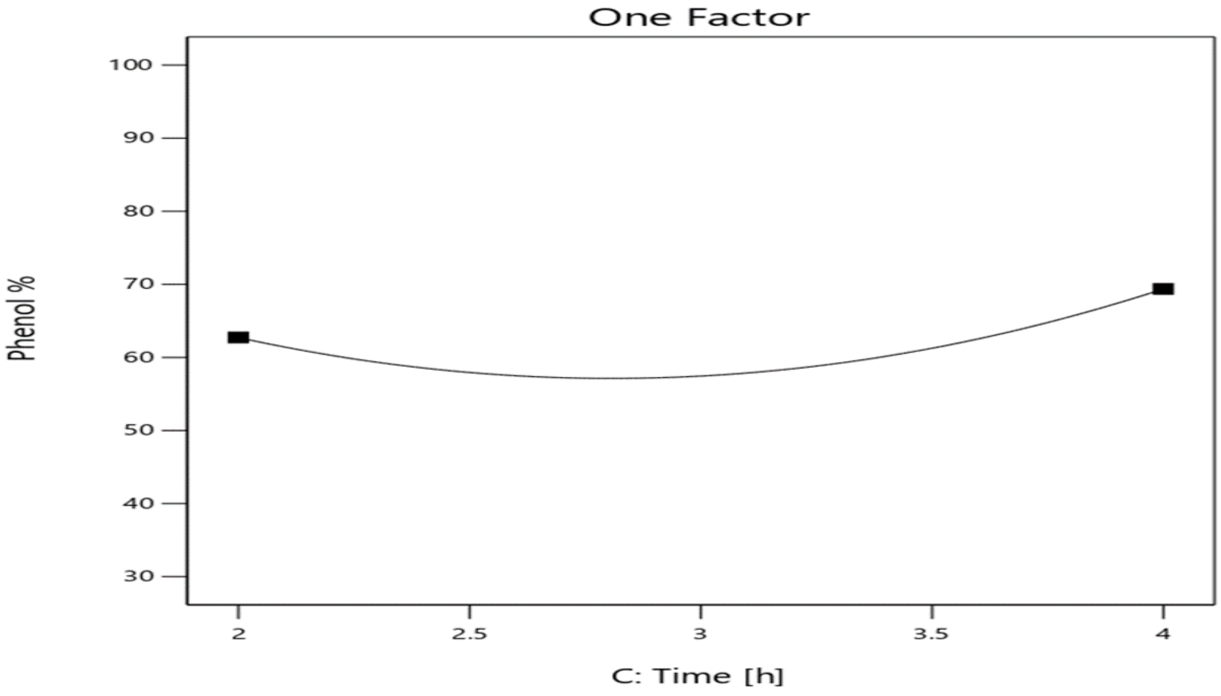

Figure16: Effect of Time on Phenol removal efficiencies at Ph=7,CD=15(mA/cm2),Salt=1.5(g/L).

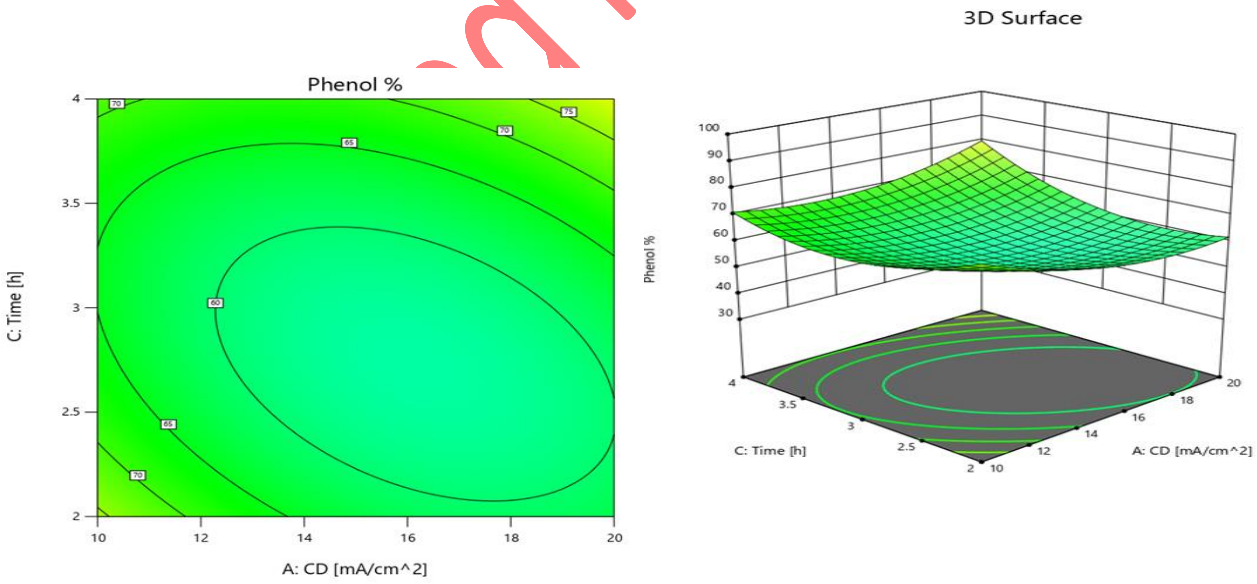

Figure 17: contour and 3D for Time and CD vs Phenol %

The results showed that the removal rate was directly proportional to the high current density and sodium chloride concentration under mild acidic conditions for the first method. The optimum conditions for the removal process were (CD = 20 mA/cm2), (PH = 7), and (NaCl = 3 g/L). A removal rate of 95.05% was achieved under the mentioned conditions for the first method. The results of the removal rate for the second method were (CD = 15 mA/cm2), (PH = 3), (NaCl = 3 g/L), and (Time = 3 h). A removal rate of 96.3% was achieved under the mentioned conditions. Compared to previous studies, as shown in Table 8.

Table 8: Comparison table with previous studies comparing the results of the manuscript

Wastewater source	**The technology used**	**Anode /Cathode**	**Initial phenol mg/l**	**Operating condition**	**Removal efficiency**	**Best condition**	**Year**	**References**
wastewater from an olive millin Extremadura, Spain.	EC	Zn/S.S	٧٤٠	pH=3-9 CD=120-500A/m^2 NaCl=0-1.5g/l space=0.5-2cm	84.2%	pH=3.2 CD=250A/m^2 NaCl=1.5g/l t=180min space=1cm	٢٠١٥	Fajardo et al. (2015)
Diwaniyah refinery	EC-EO	Al/S.S Graphite/S.t	0.17	CD=5-15mA/cm^2 pH=7 NaCl=2g/l	96.2%	CD=12mA/cm^2 NaCl=2g/l t=60min	2021	(Abbar and Alkurdi 2021)
Synthetic	EC	Al/S.S	120	CD=4,6,8mA/cm^2 t=1-120min	60%	CD=6mA/cm^2 t=120min	2021	(Kadhim and Abdulredha 2021)
Synthetic	EO	BDD S.S	100	CD=50-200A/m^2 t=30-240 min pH=3.6-9.6 NaCl=2-6g/l	92%	t=50 min pH=7.6 CD=200A/m^2 NaCl=4g/l	2025	(Akhtar and Kobya 2025)

4.Energy Consumption

The wastewater treatment procedure needs electrical energy. Consequently, Econs must be articulated and analyzed to circumvent costly endeavors.

The Econs value was calculated using equation 15

All calculations were conducted at a capacity of one liter. The EO process duration was established at 2-4 hour.

$$E_{cons} = \frac{E\times I\times t}{\text{١٠٠٠}\square} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(15)}$$

Econs : Energy consumed

E: Cell potential

I: The current

t: time

v: volume

5. Conclusion

As mentioned, industrial water, such as oil refining water, contains many toxic organic and inorganic substances that are harmful to the environment and life. One of the most important of these toxic and carcinogenic organic substances is phenol dissolved in oil refining water taken from the Najaf Refinery. The amount of this substance was reduced using effective electrical methods, as in the first method (EC, EO) and the other (EO), and was effectively removed using operating conditions such as CD, pH, and NaCl. Both processes took 3.5 hours for the first method, while in the second method, an additional variable was added, which is the time factor (2-4) hours. Design-Expert software was used to calculate the time for each of the 13 laboratory experiments for the first method and 24 experiments for the other method. Experiments in the first method showed that high CD with medium to strong acidity removed phenol more effectively when the amount of NaCl increased (PH = 7, CD = 20, NaCl = 3), while the optimum removal conditions in the second method were (CD = 15), (PH = 3), (NaCl = 3), and (Time = 3). The results of the analysis of variance (ANOVA) showed that the P and F values in this study indicate that all process variables affect the phenol removal process, either directly or in relation to one of the process variables. We hope that this study has achieved at least some reduction in the phenomenon of environmental pollution.

Table 9: Symbols used in the manuscript

chemical symbol	**chemical Term**
Y	absorbance of phenol
X	Concentration of phenol
A	CD (Current Density)
B	PH
C	NaCl Concentration
D	Time
$COD\ (ppm)$	Chemical Oxygen Demand
$TDS\ (ppm)$	Total Dissolved Solids
$BOD\ (ppm)$	Biological Oxygen Demand
CD	Current Density

6. References:

[1] P. V Nidheesh, J. Scaria, D. S. Babu, and M. S. Kumar, "An overview on combined electrocoagulation-degradation processes for the effective treatment of water and wastewater," *Chemosphere*, vol. 263, p. 127907, 2021. https://doi.org/10.1016/j.chemosphere.2020.127907

[2] H. A. Gasim, S. R. M. Kutty, M. H. Isa, and M. P. M. Isa, "Treatment of petroleum refinery wastewater by using UASB reactors," *International Journal of Chemical and Biological Engineering*, vol. 6, no. 1, pp. 174–177, 2012. https://doi.org/10.1016/j.watres.2011.05.049

[3] L. Wei, S. Guo, G. Yan, C. Chen, and X. Jiang, "Electrochemical pretreatment of heavy oil refinery wastewater using a three-dimensional electrode reactor," *Electrochim Acta*, vol. 55, no. 28, pp. 8615–8620, 2010. https://doi.org/10.1016/j.electacta.2010.08.011

[4] Z. Fang, C. He, Y. Li, K. H. Chung, C. Xu, and Q. Shi, "Fractionation and characterization of dissolved organic matter (DOM) in refinery wastewater by revised phase retention and ion-exchange adsorption solid phase extraction followed by ESI FT-ICR MS," *Talanta*, vol. 162, pp. 466–473, 2017. https://doi.org/10.1016/j.talanta.2016.10.064

[5] S. A. Younis, N. S. El-Gendy, W. I. El-Azab, and Y. M. Moustafa, "Kinetic, isotherm, and thermodynamic studies of polycyclic aromatic hydrocarbons biosorption from petroleum refinery wastewater using spent waste biomass. Desalin Water Treat 56: 3013–3023," 2015. https://doi.org/10.1080/19443994.2014.964331

[6] B. Santos, J. G. Crespo, M. A. Santos, and S. Velizarov, "Oil refinery hazardous effluents minimization by membrane filtration: An on-site pilot plant study," *J Environ Manage*, vol. 181, pp. 762–769, 2016. https://doi.org/10.1016/j.jenvman.2016.07.027Get rights and content

[7] B. Singh and P. Kumar, "Pre-treatment of petroleum refinery wastewater by coagulation and flocculation using mixed coagulant: Optimization of process parameters using response surface methodology (RSM)," *Journal of water process engineering*, vol. 36, p. 101317, 2020. https://doi.org/10.1016/j.jwpe.2020.101317

[8] A. H. Abbar and S. S. Alkurdi, "Performance evaluation of a combined electrocoagulation–electrooxidation process for the treatment of petroleum refinery wastewater," in *IOP Conference Series: Materials Science and Engineering*, IOP Publishing, 2021, p. 12027. **DOI** 10.1088/1757899X/1076/1/012027

[9] S. Vasudevan, "An efficient removal of phenol from water by peroxi-electrocoagulation processes," *Journal of Water Process Engineering*, vol. 2, pp. 53–57, 2014. https://doi.org/10.1016/j.jwpe.2014.05.002

[10] F. Ozyonar and B. Karagozoglu, "Treatment of pretreated coke wastewater by electrocoagulation and electrochemical peroxidation processes," *Sep Purif Technol*, vol. 150, pp. 268–277, 2015. https://doi.org/10.1016/j.seppur.2015.07.011

[11] F. Ozyonar, "Treatment of train industry oily wastewater by electrocoagulation with hybrid electrode pairs and different electrode connection modes," *Int J Electrochem Sci*, vol. 11, no. 2, pp. 1456–1471, 2016. https://doi.org/10.1016/S1452-3981(23)15933-5

[12] O. E. Abdel-Salam, E. M. Abou Taleb, and A. A. Afify, "Electrochemical treatment of chemical oxygen demand in produced water using flow-by porous graphite electrode," *Water and Environment Journal*, vol. 32, no. 3, pp. 404–411, 2018. **https://doi.org/10.1111/wej.12336**

[13] C.-H. Lee, E.-S. Lee, Y.-K. Lim, K.-H. Park, H.-D. Park, and D.-S. Lim, "Enhanced electrochemical oxidation of phenol by boron-doped diamond nanowire electrode," *RSC Adv*, vol. 7, no. 11, pp. 6229–6235, 2017. DOI: 10.1039/C6RA26287B

[14] Z. Isik, E. B. Arikan, Y. Ozay, H. D. Bouras, and N. Dizge, "Electrocoagulation and electrooxidation pre-treatment effect on fungal treatment of pistachio processing wastewater," *Chemosphere*, vol. 244, p. 125383, 2020. https://doi.org/10.1016/j.chemosphere.2019.125383

[15] H. M. Ibrahim and R. H. Salman, "Real wastewater treatment by electrocoagulation-electro-oxidation combined system: optimization using Taguchi approach," *Egypt J Chem*, vol. 65, no. 3, pp. 135–145, 2022. DOI: 10.21608/ejchem.2021.88245.4247

[16] R. H. Salman and A. H. Abbar, "Optimization of a combined electrocoagulation-electro-oxidation process for the treatment of Al-Basra Majnoon Oil field wastewater: Adopting a new strategy," *Chemical Engineering and Processing-Process Intensification*, vol. 183, p. 109227, 2023. https://doi.org/10.1016/j.cep.2022.109227

[17] M. A. Oturan and J.-J. Aaron, "Advanced oxidation processes in water/wastewater treatment: principles and applications. A review," *Crit Rev Environ Sci Technol*, vol. 44, no. 23, pp. 2577–2641, 2014. https://doi.org/10.1080/10643389.2013.829765

[18] P. Bhatt, B. A. Engel, K. B. Shivaram, R. F. Turco, Z. Zhou, and H. Simsek, "Treatment and optimization of high-strength egg-wash wastewater effluent using electrocoagulation and electrooxidation methods," *Chemosphere*, vol. 347, p. 140632, 2024. https://doi.org/10.1016/j.chemosphere.2023.140632

[19] F. Sopaj, M. A. Rodrigo, N. Oturan, F. I. Podvorica, J. Pinson, and M. A. Oturan, "Influence of the anode materials on the electrochemical oxidation efficiency. Application to oxidative degradation of the pharmaceutical amoxicillin," *Chemical Engineering Journal*, vol. 262, pp. 286–294, 2015. https://doi.org/10.1016/j.cej.2014.09.100

[20] M. A. Alkhadra *et al.*, "Electrochemical methods for water purification, ion separations, and energy conversion," *Chem Rev*, vol. 122, no. 16, pp. 13547–13635, 2022. https://doi.org/10.1021/acs.chemrev.1c00396

[21] I. Sirés, E. Brillas, M. A. Oturan, M. A. Rodrigo, and M. Panizza, "Electrochemical advanced oxidation processes: today and tomorrow. A review," *Environmental Science and Pollution Research*, vol. 21, pp. 8336–8367, 2014. DOI 10.1007/s11356-014-2783-1

[22] M. S. Ahmad, M. H. Ab Rahim, T. M. Alqahtani, T. Witoon, J.-W. Lim, and C. K. Cheng, "A review on advances in green treatment of glycerol waste with a focus on electro-oxidation pathway," *Chemosphere*, vol. 276, p. 130128, 2021. https://doi.org/10.1016/j.chemosphere.2021.130128

[23] F. E. Stuart, "Electronic water purification progress report on the electronic coagulator– a new device which gives promise of unusually speedy effective results," *Water sewage*, vol. 84, pp. 24–26, 1946.

[24] G. Chen, "Electrochemical technologies in wastewater treatment," *Sep Purif Technol*, vol. 38, no. 1, pp. 11–41, 2004. https://doi.org/10.1016/j.seppur.2003.10.006

[25] T. Shahriari, A. R. Karbassi, and M. Reyhani, "Treatment of oil refinery wastewater by electrocoagulation–flocculation (Case Study: Shazand Oil Refinery of Arak)," *International Journal of Environmental Science and Technology*, vol. 16, pp. 4159–4166, 2019. https://doi.org/10.1007/s13762-018-1810-z

[26] J. N. Hakizimana *et al.*, "Electrocoagulation process in water treatment: A review of electrocoagulation modeling approaches," *Desalination*, vol. 404, pp. 1–21, 2017. https://doi.org/10.1016/j.desal.2016.10.011

[27] I. Kabdaşlı, I. Arslan-Alaton, T. Ölmez-Hancı, and O. Tünay, "Electrocoagulation applications for industrial wastewaters: a critical review," *Environmental Technology Reviews*, vol. 1, no. 1, pp. 2–45, 2012. https://doi.org/10.1080/21622515.2012.715390

[28] S. K. Ajjam, B. H. Hlih, and H. H. Alwan, "Enhancing lead ion removal from simulated wastewater through continuous electrocoagulation process: investigating operating parameters and adsorption behavior," *Chemical Papers*, 2024, doi: 10.1007/s11696-024-03771-1. https://doi.org/10.21203/rs.3.rs-3477742/v1

[29] A. M. Al-Yaqoobi, M. N. Al-Rikabey, and K. H. R. Algharrawi, "Treatment of dairy wastewater by electrocoagulation and ultrasonic-assisted electrocoagulation methods.," *Environmental Engineering & Management Journal (EEMJ)*, vol. 20, no. 6, 2021. http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

[30] A. M. Al-Yaqoobi, M. N. Al-Rikabey, and M. K. H. Al-Mashhadani, "Electrochemical harvesting of microalgae: Parametric and cost-effectivity comparative investigation," *Chemical Industry and Chemical Engineering Quarterly*, vol. 27, no. 2, pp. 121–130, 2021. https://doi.org/10.2298/CICEQ191213031A

[31] A. N. Kassob and A. H. Abbar, "Treatment of petroleum refinery wastewater by graphite–graphite electro fenton system using batch recirculation electrochemical reactor," *Journal of Ecological Engineering*, vol. 23, no. 10, pp. 291–303, 2022.

https://doi.org/10.12911/22998993/152524

[32] M. A. Aljaleel and H. H. Alwan, "Modeling the Effect of Operation Variables on Copper Ions Removal by Electrocoagulation," in *2022 2nd International Conference on Advances in Engineering Science and Technology (AEST)*, 2022, pp. 111–115. doi: 10.1109/AEST55805.2022.10413162.
DOI: 10.1109/AEST55805.2022.10413162

[33] S. R. Korake and P. D. Jadhao, "Investigation of Taguchi optimization, equilibrium isotherms, and kinetic modeling for cadmium adsorption onto deposited silt," *Heliyon*, vol. 7, no. 1, 2021. https://doi.org/10.1016/j.heliyon.2020.e05755

[34] U. Sutrisno, Y. Wulandari, S. Arifin, M. M. Manurung, and M. Faisal, "Trends, Contributions and Prospects: Bibliometric Analysis of ANOVA Research in 2022-2023," *Indonesian Journal of Applied Mathematics and Statistics*, vol. 1, no. 1, pp. 27–38, 2024.

https://doi.org/10.71385/idjams.v1i1.7

[35] E. GilPavas, I. Dobrosz-Gómez, and M.-Á. Gómez-García, "Efficient treatment for textile wastewater through sequential electrocoagulation, electrochemical oxidation and adsorption processes: Optimization and toxicity assessment," *Journal of Electroanalytical Chemistry*, vol. 878, p. 114578, 2020. https://doi.org/10.1016/j.jelechem.2020.114578

[36] H. M. Ibrahim, "Study the optimization of petroleum refinery wastewater treatment by successive electrocoagulation and electro-oxidation systems," *Iraqi Journal of Chemical and Petroleum Engineering*, vol. 23, no. 1, pp. 31–41, 2022. https://doi.org/10.31699/IJCPE.2022.1.5

[37] Alwan, H. H., Abd, A. A., Makki, H. F., & Othman, M. R. (2024). Optimizing hydrodesulfurization of naphtha using NiMo/graphene catalyst. Journal of Industrial and Engineering Chemistry, 135, 539-551.https://doi.org/10.1016/j.jiec.2024.01.066

[38] R. H. Salman, "Removal of manganese ions (Mn2+) from a simulated wastewater by electrocoagulation/electroflotation technologies with stainless steel mesh electrodes: process optimization based on Taguchi approach," *Iraqi Journal of Chemical and Petroleum Engineering*, vol. 20, no. 1, pp. 39–48, 2019. https://doi.org/10.31699/IJCPE.2019.1.6

[39] S. Salvestrini, A. Fenti, S. Chianese, P. Iovino, and D. Musmarra, "Electro-oxidation of humic acids using platinum electrodes: an experimental approach and kinetic modelling. Water 12, 2250," 2020. **https://doi.org/10.3390/w12082250**

[40] Q. Li, G. Liu, L. Qi, H. Wang, and G. Xian, "Chlorine-mediated electrochemical advanced oxidation process for ammonia removal: Mechanisms, characteristics and expectation," *Science of The Total Environment*, vol. 896, p. 165169, 2023. https://doi.org/10.1016/j.scitotenv.2023.165169

[41] H. Rubí-Juárez, C. Barrera-Díaz, I. Linares-Hernández, C. Fall, and B. Bilyeu, "A combined electrocoagulation-electrooxidation process for carwash wastewater reclamation," *Int J Electrochem Sci*, vol. 10, no. 8, pp. 6754–6767, 2015. https://doi.org/10.1016/S1452-3981(23)06759-7

[42] A. S. Fajardo *et al.*, "Electrochemical oxidation of phenolic wastewaters using a batch-stirred reactor with NaCl electrolyte and Ti/RuO2 anodes," *Journal of Electroanalytical Chemistry*, vol. 785, pp. 180–189, 2017. https://doi.org/10.1016/j.jelechem.2016.12.033

[٤٣] A. Habl, A. Amooey, M. Mustafa, and H. A. Alalwan, “Electro oxidation process for wastewater treatment in petroleum refineries,” *Pollution*, vol. 10, no. 2, pp. 819–832, 2024. DOI: https://doi.org/10.22059/poll.2024.371677.2236

[٤٤] S. M. Safwat, N. Y. Mohamed, M. N. A. Meshref, and A. Elawwad, “Adsorption of phenol onto aluminum oxide nanoparticles: performance evaluation, mechanism exploration, and principal component analysis (PCA) of thermodynamics,” *Adsorpt. Sci. Technol.*, vol. 2022, p. 1924117, 2022. https://doi.org/10.1155/2022/1924117

[٤٥] N. A. Akhtar and M. Kobya, “Efficient degradation of phenol by electrooxidation process at boron-doped diamond anode system,” *MANAS J. Eng.*, vol. 13, no. 1, pp. 52–63, 2025. https://doi.org/10.51354/mjen.1656854

[٤٦] E. M. Abou-Taleb, M. S. Hellal, and K. H. Kamal, “Electro-oxidation of phenol in petroleum wastewater using a novel pilot-scale electrochemical cell with graphite and stainless-steel electrodes,” *Water Environ. J.*, vol. 35, no. 1, pp. 259–268, 2021. doi:10.1111/wej.12624

[٤٧] Y. Zhu, K. Wen, B. Li, Y. Hao, and J. Zhou, “Electrocatalytic Degradation of Phenolic Wastewater Using a Zero-Gap Flow-Through Reactor Coupled with a 3D Ti/RuO2-TiO2@ Pt Electrode,” *Molecules*, vol. 29, no. 5, p. 1182, 2024. **https://doi.org/10.3390/molecules29051182**