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Degradation of Dichloromethane Containing Laboratory Wastewater Using Photoelectric Fenton Process

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Abstract: Conducting laboratory experiments in educational institutions has been linked with the increased amount of chemical waste disposed in the environment. The excessive usage and disposal of Dichloromethane (DCM) has been attributed to financial and environmental concerns. This present study aimed to treat the DCM containing laboratory wastewater using Photoelectric Fenton (PEF) process. The PEF treatment was done at varying ultraviolet (UV) light intensity (3, 6 and 9 Watts), sacrificial anode (Al, Cu and TiO_2), and oxidizing agent (OA) loading ratio (1.13, 3.76, and 6.39 w/w) under 30°C and 1 atm. Results have shown that the highest degradation (99.82%) of DCM was obtained at 9 Watts of UV light intensity, 3.76 w/w $[H_2O_2]$: $[Fe^{2+}]$ OA loading ratio, and with TiO_2 coated with IrO_2 and RuO_2 as the anode. It was detected that higher UV light intensity favors the degradation efficiency when using the TiO_2 coated with IrO_2 and RuO_2 anode. On the other hand, higher OA loading ratios proved to negatively affect the process as high concentrations of H_2O_2 become ineffectual for the degradation of organics. Finally, analysis of variance (ANOVA) showed the positive correlation between degradation efficiency and UVA light intensity. This confirmed the applicability of the PEF process in degrading of recalcitrant pollutants in wastewater, thus showing potential for mitigating its environmental impact as an eco-friendly and cost-effective approach of wastewater treatment.

Keywords: Advanced oxidation process (AOP), degradation efficiency, laboratory organic waste, photoelectro Fenton process, surface response methodology

1. Introduction

The large generation of waste chemicals from educational chemistry laboratories may greatly contribute to polluting waters and create additional issues for the treatment and subsequent adequate disposal. These laboratory wastes are by-products of analysis, teaching, and testing activities that result in accumulating refractory organics, cytotoxic compounds, and significant metals which offer health risks and greatly impact environmental issues.

Organic compounds used in experiments in the chemistry laboratories are primarily composed of hydrocarbons, carboxylic acids, and oxygen-experimenting compounds. When these organic compounds are exposed to a body of water, oxygen is consumed and measured as the chemical oxygen demand (COD). Some conventional methods of treating mixed waste chemicals include COD removal and reducing heavy metals via chemical action such as precipitation and neutralization. Treating this type of pollutant in wastewater requires high operating costs, including

landfilling and incineration. The development of the most economical methods to treat major pollutants in wastewater with high efficiency of reduction of toxic chemicals is a significant concern in research studies. Conforming to this pursuit, advanced oxidation processes (AOP) were utilized for organic wastewater treatment. AOP generally refers to technologies that employ the use of hydroxyl radicals to oxidize contaminants in wastewater.

To increase the rate of degradation and the production of hydroxyl radicals, ultraviolet rays were introduced to substitute ozone for the decomposition of H_2O_2. It has been shown that UV / H_2O_2 can oxidize several organic and inorganic contaminants including precursors for disinfection of by-products, contagious species, and strong acids [1]. In current researches for water treatment, one of the most reviewed is the development of an electrochemical technique using Fenton's reagents for the dissociation of oxidant due to its low operating cost and effective wastewater degradation cycle [2].

The above technique of advanced oxidation processes is proven to have high energy and cost-intensive processes because of its continuous demand for more reagents for the decomposition of H_2O_2. [3] Moreover, the mechanism of degradation of organic pollutants and inorganic pollutants appears to have a low reaction rate that signifies a longer contact time for the completion of degradation.

Fenton process is effective in treating wastewater, and it is non-selective. However, sludge generation is a disadvantage since a large amount of iron sludge was formed, which will be costly in terms of oxidation requirements. It limits the success of disposing of sludge, and wastewater treatment processes' economic assessment [4]. A high amount of catalyst is required, which is much higher than a minimum requirement for a discharge of wastes to the natural watercourse. The removal of dissolved iron that came from the treated wastewater is a major drawback [5].

Electro-Fenton Process (EF) is an electrochemical technique for wastewater treatment. Electro-Fenton uses hydroxyl radicals to oxidize dangerous pollutants and is particularly useful in the handling of intransigent materials that are not easily destroyed in traditional wastewater plants. In this method, the mounted current densities obtain regeneration from Fe^{3+} to Fe^{2+} [6]. Unlike Fenton Process, Electro-Fenton processes are more efficient due to Fenton's generated reagents which allow high oxidation efficiency. Contaminants are removed throughout the process by reagents of Fenton as well as the anodic oxidation along the surface of the anode. However, the process has a high operational cost which limits its application [7].

The photoelectro-Fenton process (PEF) is applied to increase the production of hydroxyl radicals and lessen the disadvantages of the inventive Electro-Fenton process [8]. A large fraction of iron sludge is decreased. The combination of these techniques has a promising advanced oxidation technology for the maximum degradation of organic pollutants. Organic pollutants are removed effectively from wastewater through this photo-assisted Fenton process. UV irradiation has an important role in this process wherein effectiveness is based on how high the wavelength and irradiance were provided [9].

One particular organic waste of concern is methylene chloride or dichloromethane (DCM), CH_2Cl_2 is polar organochloride chloroform like compound typically used as a solvent in laboratory experiments and with various industrial applications. However, its potential hazard to both humans and the environment has posed a challenge to researchers and scientists. Also, its recalcitrant nature requires a non-conventional approach in the treatment procedure. Currently, not enough study has been conducted dedicated to the removal of common laboratory wastes pollutant like dichloromethane using advance oxidation process are available in the literature. Hence, this study focused on the degradation of DCM in water using the photoelectro-Fenton treatment process as an eco-friendly and cost-effective approach in treating wastewater.

2. Methodology

2.1 Materials

Synthetic dichloromethane solutions were used to examine the effect of different factors in the PEF process. A 1N iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) and 1N hydrogen peroxide (H_2O_2, % purity) were purchased at Thermo Fisher Scientific, Massachusetts, USA. To alter the pH of the solution, perchloric acid ($HClO_4$ 70% purity) and sodium hydroxide (NaOH, 98 % purity) were used; both chemicals can be acquired at Sigma-Aldrich, Missouri, USA.

2.2 Equipment

The PEF tests were carried out on a laboratory size in a 2 L stainless steel cylindrical reactor that was custom fabricated (figure 1). The mass of organic chemical wastes utilized in the manufacture of synthetic wastewater was weighed using a microbalance. To make deionized water for solution preparation, a Mixed Bed Deionizer Standard Model on the Go was employed. A pH meter (Thermo Fisher's Orion Versa Pro) was used to regulate the pH level of the solution. The voltage was regulated using a digital DC power supply (Kala GostaraneFarda, 30 V, 3 A) regulated in galvanostatic mode. The stainless-steel cylindrical reactor served as the cathode. aluminum, copper, and titanium oxide coated with IrO_2 and RuO_2 were obtained from Unilox Ind. Corp, Pasig, Philippines to evaluate the influence of electrode material. An ultraviolet lamp (Sun Bean Tech. Ind. Corp, Taiwan) with a wavelength band range of 100 to 400 nm, 3.2-3.4 V, 350-500 mA where used. A UV-visible spectrophotometer (Lambda 25, Perkin Elmer, Massachusetts, USA) was utilized for determination of standard calibration and analysis of treated wastewater.

2.3 Photoelectro Fenton Process

Each experimental run was based on the experimental matrix design from Box Behnken Design (BBD). The 1 L prepared synthetic wastewater was placed in the cylindrical reactor at atmospheric pressure and at room temperature ($25 \pm 2°C$). The aqueous sample was then mixed with 1M NaOH or 1M HClO$_4$ (based on the measured pH of the sample). The amount of FeSO$_4$ based on the data provided by BBD was added to the sample and was mixed for 15 mins using an electric magnetic stirrer. The voltage was adjusted using a direct current (DC) power source with a set current density of 250 mA/cm^2. The UV lamp was turned on and adjusted to (3, 6, 9 W) to illuminate inside the reactor and ensure the photoionization of the solution. The photoelectro Fenton reaction was initiated by the addition of equal volume of 1 mL of H$_2$O$_2$ at intervals of 10 min. This was done to minimize the quenching of ⁻OH and control the rise in temperature that occurs as the decomposition proceeds. The solution is expected to have a change in color, specifically yellow-orange, because of its reaction with the Fenton reagents. The reaction time of 120 min was applied. The solids in the solution were allowed to settle for one hour after the reaction. Using an ultraviolet-visible spectrophotometer, 5 mL of treated samples were collected for the determination of final percent degradation values.

Fig. 1 - Self-fabricated photoelectron Fenton process composed of steel cylindrical reactor, voltage source, hotplate, anode and cathode terminals and pH meter

2.4 Experimental Design

The parameters that were examined during the single parameter optimization were used to build multiple optimizations using the three-factor Box-Behnken design (BBD). The BBD aided in determining the impact of independent parameters such as UVA Light, Anode, and [H$_2$O$_2$]: [Fe^{2+}] on degradation efficiency. To optimize the parameters, the BBD was applied with a response surface methodology (RSM). The independent variables are UVA Light, Anode, and [H$_2$O$_2$]: [Fe^{2+}] ratio while the degradation efficiency was chosen as the dependent variable. As shown in Table 1, the variables are assigned with coded values of low level (-1), medium level (0), and high level (+1).

Table 1 - Three-factor Box-Behnken design

Standard	Runs	Factor 1 UVA Light	Factor 2 Anode*	Factor 3 [H$_2$O$_2$]:[Fe2+]
1	13	3	-1	3.76
2	2	9	-1	3.76
3	1	3	1	3.76
4	9	9	1	3.76
5	10	3	0	1.13
6	8	9	0	1.13
7	3	3	0	6.39
8	15	9	0	6.39
9	4	6	-1	1.13
10	12	6	1	1.13
11	14	6	-1	6.39
12	6	6	1	6.39
13	11	6	0	3.76
14	7	6	0	3.76
15	5	6	0	3.76

*Type of anode: aluminum (-1), copper (0) and titanium oxide coated with IrO$_2$ and RuO$_2$ (1)

The formula employed for the determination of the degradation efficiency is shown in equation 1:

$$(\%) = \left(\frac{DCM_o - DCM_f}{DCM_o} \right) \times 100\% \qquad (1)$$

Where, DCM_o is the measured concentration in chemistry laboratory organic waste before the PEF treatment and the DCM_f is concentration value in clarified supernatant after the precipitation.

2.5 Sampling Methods

A simulated wastewater solution was prepared by mixing 12 μg of organic chemical waste collected and 1 L of deionized water. The pH of prepared solution was determined and adjusted to pH 4 using either 1 M NaOH or 1M $HClO_4$. The initial DCM concentration of the supernatant was measured as (DCM_o). Under deionized water, Fenton Reagent was dissolved. The concentration of Fenton's reagents was based on the experimental matrix design by Box-Behnken.

To determine the concentration of each treated synthetic wastewater, a standard solution was employed. The concentrations of the standard solution were as follows: 0 ppm (just deionized water); 3, 5, 8, 10, 12, and 15 ppm. The prepared standard solution was tested for percent absorbance using UV-vis spectrophotometer. The standard solution's calibration curve was obtained by plotting the percent absorbance measured against the set concentrations. The linear plot graph describing the relationship between the standard concentration and DCM was used to determine the unknown treated samples.

2.6 Statistical Treatment

The analysis of variance (ANOVA) was utilized to analyze the data gathered based on several runs from Design Expert 12.0 to determine significant relationship for response surface quadratic model. The diagnostic checking tests specified by the ANOVA were used to verify the adequacy of the highest response. The quadratic regression model was obtained to investigate the significant effect of the set parameters in the degradation efficiency.

3. Results and Discussion

3.1 Effect of Parameters On the Degradation of Dichloromethane

Ideal operating conditions determine the degradation reaction during the PEF process. In this study, three experimental factors were considered: $[H_2O_2]$: $[Fe^{2+}]$, w/w, Anode, and UVA light, W. These factors were selected to determine their possible effects on the degradation efficiency of the pollutant dichloromethane, DCM.

Table 2 shows the summary of the dichloromethane degradation efficiency. It was observed that lowest degradation efficiency (75.15%) was obtained with Fenton's reagents equal to 6.39, 6W UVA intensity using an Al anode operating for 120 mins. On the other hand, highest degradation efficiency (99.82%) was obtained with 9 W UVA intensity, w TiO_2 anode and Fenton reagent amounting to 3.76 operating for 120 mins of treatment.

Table 2 - Degradation efficiency of dichloromethane

Standard	Runs	UVA Light	Anode	$[H_2O_2]$:$[Fe2+]$	Degradation Efficiency (%)
1	5	3	-1	3.76	76.32
2	3	9	-1	3.76	85.33
3	14	3	1	3.76	84.55
4	13	9	1	3.76	99.82
5	6	3	0	1.13	86.25
6	12	9	0	1.13	99.69
7	11	3	0	6.39	76.20
8	2	9	0	6.39	89.90
9	4	6	-1	1.13	82.99
10	10	6	1	1.13	99.56
11	9	6	-1	6.39	75.15
12	7	6	1	6.39	84.68
13	8	6	0	3.76	94.47
14	15	6	0	3.76	94.73
15	1	6	0	3.76	95.26

(a) Effect of UVA Light (W) on Dichloromethane Degradation

The effect of UVA light (W) on the degradation of DCM as shown in Table 3 was observed at three different levels of values 3, 6, and 9 W. The maximum DCM degradation percentage of 99.82% was achieved at 9 W, while the minimum DCM degradation percentage of 75.15% was achieved at 6W. The effect of different ultraviolet light intensities on dichloromethane degradation rate was investigated. Consequently, it was observed that DCM degradation was substantially accelerated by increasing ultraviolet intensity, implying that UV light had a major impact on dichloromethane degradation. DCM is destroyed more effectively under the influence of UV radiation due to increased production of OH^- radicals. The positive correlation between UV light intensity and degradation efficiency supported Ono's [10] findings that energy-dissipating components offer certain benefits, such as a faster rate of hydroxyl radical production and hence higher degradation efficiency.

UV oxidation is a destructive method that involves the use of oxidants and UV light, to mineralize or oxidize a range of organic pollutants present in wastewater. The photo-reduction of ferric ions was improved by increasing the UV light intensity, and the interaction between UV light and hydrogen peroxide produced a strong hydroxyl radical (OH^-). During the duration of the 110 minutes' degradation process, it was observed that a lesser amount of sludge was produced which validates the study of Buthiyappan [11]. According to the report, higher UV light intensities are a reliable approach, since almost no sludge is formed at the completion of the reaction, which allows for simpler handling and a faster response time to breakdown pollutants than other AOPs.

Table 3 - Values of dichloromethane percentage degradation based on UVA light (W)

UVA Light (W)	Anode	$[H_2O_2]:[Fe^{2+}]$ (w/w)	Degradation Efficiency (%)
3	-1	3.76	76.32
	0	1.13	86.25
	0	6.39	76.20
	1	3.76	84.55
6	0	3.76	95.26
	-1	1.13	82.99
	1	6.39	84.68
	0	3.76	94.47
	-1	6.39	75.15
	1	1.13	99.56
	0	3.76	94.73
9	0	6.39	89.90
	-1	3.76	85.33
	0	1.13	99.69
	1	3.76	99.82

(b) Effect of Type of Anode on Dichloromethane Degradation

The effect of the type of Anode on the degradation of dichloromethane was shown on Table 4 for Aluminum, Copper, and Titanium Oxide coated with IrO_2 and RuO_2. During the experimental runs, different anode's characteristics have taken consideration to further analyze the influence of the anode material used for PEF Process.

Given a varying amount of supplied voltage for each experimental run, Al anode has decreasing current until 0.104A during the PEF process while TiO_2 and Cu anode have increasing current at 0.14-0.20A. It was identified that the 0.14A was the constant value for all runs as that would give the best amount of current supplied for a given the surface area of the anode material. Based on the study, the decreasing current observed during the process is associated with the formation of Fe^{3+} complexes that are relatively unreactive to hydroxyl radicals, and thus unwantedly collected in the solution. The increasing current during the PEF process promotes enhanced oxidation rates where it is stated in literature, the increase of the applied current density mutually promotes the decay of pollutant concentration. It is also proven in the data gathered in this study, Table 5 shows maximum degradation obtained in both TiO_2 coated with IrO_2 and RuO_2, and Copper material. This distinction is most likely due to the adsorption properties of titanium oxide coated with IrO_2 and RuO_2, as the copper material is more strongly adsorbed to the anode surface than the aluminum anode and cannot be used to oxidize DCM. The increased electrochemical H_2O_2 generation and ferrous ions regeneration result in a greater concentration of homogenous hydroxyl radicals in the solution, leading to an improved DCM oxidation [12-13].

Table 4 - Values of dichloromethane percentage degradation based on type of anode

Anode	UVA Light (W)	$[H_2O_2]:[Fe^{2+}]$ (w/w)	Degradation Efficiency (%)
Aluminum (-1)	3	3.76	76.32
	6	1.13	82.99
	6	6.39	75.15
	9	3.76	85.33
Copper (0)	3	1.13	86.25
	3	6.39	76.20
	6	3.76	95.26
	6	3.76	94.47
	6	3.76	94.73
	9	6.39	89.90
	9	1.13	99.69
TiO$_2$ coated with IrO$_2$ and RuO$_2$ (+1)	3	3.76	84.55
	6	6.39	84.68
	6	1.13	99.56
	9	3.76	99.82

(c) Effect of $[H_2O_2]$: $[Fe^{2+}]$ on Dichloromethane Degradation

Shown in Table 5 is the effect of $[H_2O_2]$: $[Fe_{2+}]$ ratios ranging from 1.13 to 6.39 mM on the PEF treatment while maintaining the FeSO$_4$ dosage, pH, electric current, and reaction duration constant at 1mM. 4, 0.14 A, and 120 minutes, respectively. The peak degradation efficiency of 99.82% was obtained at 3.76 mM H$_2$O$_2$ concentration with UV light intensity of 9W and using Titanium Oxide coated with IrO$_2$ and RuO$_2$ anode. Initial concentration of H$_2$O$_2$ was mainly responsible for the generation of hydroxyl radical (OH$^-$) along with the amount of Fe^{2+} ions. H$_2$O$_2$ is a weak acid with moderately high oxidant potential which alone does not prompt the generation of hydroxyl radicals. The moderate response rates make the process ineffectual while oxidizing more obstinate and unmanageable pollutants. Increasing the concentration of H$_2$O$_2$ increases degradation efficiency. However, excessive H$_2$O$_2$ concentrations promote scavenging reactions with OH$^-$ radicals resulting in a decreased overall degradation efficiency [14-15]. A negative correlation or a reduction of the relative efficiency was observed with the increase of H$_2$O$_2$ concentration beyond the optimal amount. This behavior might be described by the parasitic interaction of H$_2$O$_2$ with OH$^-$, the competitive electrochemical oxidation of H$_2$O$_2$ on the anode surface, that also releases the weaker oxidant HO$_2^-$, and the evolution of oxygen from H$_2$O$_2$ [16-17].

Table 5 - Values of dichloromethane percentage degradation based on $[H_2O_2]$: $[Fe^{2+}]$

$[H_2O_2]:[Fe^{2+}]$ (w/w)	UVA Light (W)	Anode	Degradation Efficiency (%)
1.13	3	0	86.25
	9	0	99.69
	6	-1	82.99
	6	1	99.56
3.76	3	-1	76.32
	9	-1	85.33
	3	1	84.55
	9	1	99.82
	6	0	95.26
	6	0	94.47
	6	0	94.73
6.39	3	0	76.20
	9	0	89.90
	6	-1	75.15
	6	1	84.68

3.2 Statistical Analysis

The RSM experiment in reference to BBD was utilized to determine the end result of the parameters on the degradation of dichloromethane. Fifteen (15) trials were formulated using Design-Expert 12.0 software for this

research, as presented on Table 2. Regression equations based on the statistical testing were checked using the F-test; and for the degradation efficiency using a fitted quadratic polynomial model via ANOVA was given on Table 6. The model's F-value of 152.30 indicated that it was significant.

The correlation value (R^2) of 0.9964 showed that there was a high correlation between the observed and the predicted ones. Using several regression analyses on the collected data, the reaction and test variables were identified using the second-order polynomial equation:

$$\% \text{ Degradation efficiency} = 94.82 + 6.43A + 6.10B - 5.32C + 1.57AB + .065AC - 1.76B - 2.95A2 - 5.36B^2 - 3.86C^2 \quad (2)$$

With A, B, C, as the coded estimation of UVA Light intensity, Anode and $[H_2O_2]$: $[Fe^{2+}]$ respectively.

Table 6 - Analysis of variance for the degradation of DCM

Source	Sum of Squares	df	Mean Square	F-value	p-value	Remarks
Model	1047.05	9	116.34	152.30	<0.0001	significant
A-UVA light	330.62	1	330.62	432.81	<0.0001	significant
B-Anode	297.90	1	297.90	389.99	<0.0001	significant
C-$[H_2O_2]$:$[Fe^{2+}]$	226.34	1	226.34	296.31	<0.0001	significant
AB	9.81	1	9.81	12.85	0.0158	significant
AC	0.017	1	0.017	0.0223	0.8871	significant
BC	12.42	1	12.42	16.26	0.0100	significant
A^2	32.08	1	32.08	42.00	0.0013	significant
B^2	106.18	1	106.18	139.00	<0.0001	significant
C^2	55.06	1	55.06	72.08	0.0004	Significant
Residual	3.82	5	0.7639			
Pure Error	0.318	2	0.1590			
R^2	0.9964					
Adequate Precision	35.1193					

(a) Surface Response Analysis

The model graphs illustrate the interactions of different parameters that affect DCM degradation. The response surface plots were obtained by keeping one factor constant while changing the other two. When the $[H_2O_2]$: $[Fe^{2+}]$ ratio was raised from 1.13 to 3.76, the degradation efficiency increased. On the contrary, when the $[H_2O_2]$: $[Fe^{2+}]$ ratio reached 6.39, the degradation efficiency decreased dramatically. The decrease was attributed to the aforementioned scavenging reactions from excessive concentrations of H_2O_2 in the solution. The influence of the factors on the degradation efficiency is depicted in Fig. 2.
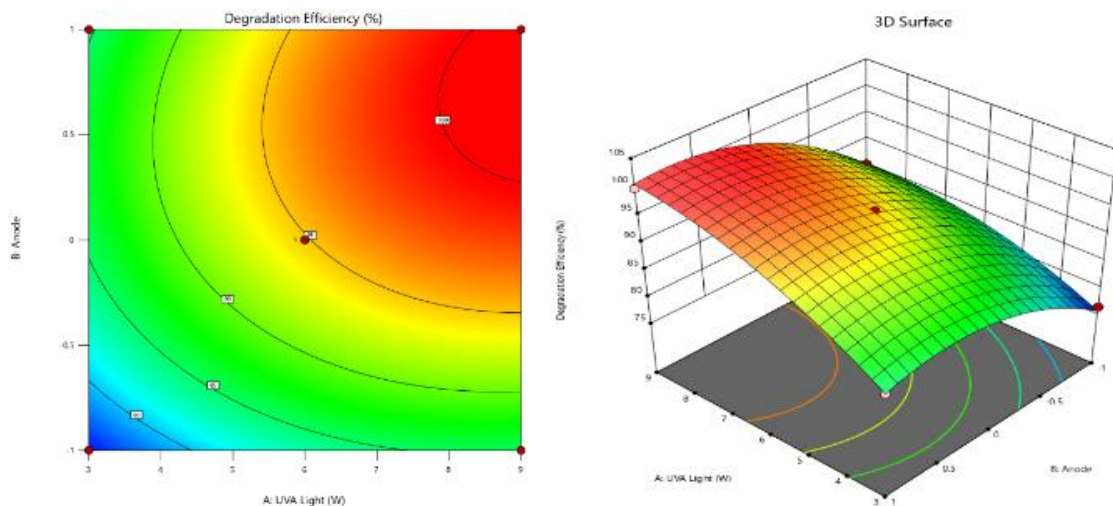

Fig. 2 - Response surface & contour for degradation efficiency of binary interaction of anode and UVA light

Fig. 3 shows the response surface of $[H_2O_2]$: $[Fe^{2+}]$ ratio corresponding to variance of the type of anode used. The coded levels of the anodes are aluminum (-1), copper (0), and titanium oxide coated with IrO_2 and RuO_2. When the coded value of anode was increased, the degradation efficiency also improved.
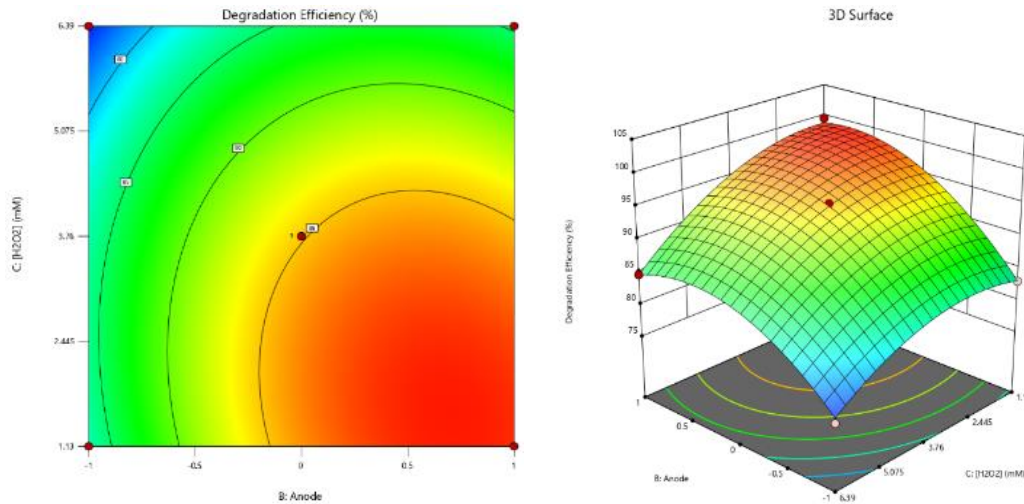
Fig. 3 - Response surface & contour for degradation efficiency of binary interaction of [H₂O₂]: [Fe²⁺] and anode

4. Conclusion

The performance of the PEF process was investigated by determining the percent degradation efficiency of DCM containing laboratory wastewater. The best working parameters for the PEF process, with a percent degradation of 99.82%, was at 9W UVA light, 3.76 w/w [H₂O₂]: [Fe²⁺] ratio, and using TiO₂ coated with IrO₂ and RuO₂ anode. In contrast, generally lower degradation efficiencies were obtained (75.20% min/ 86.25% max) at a supplied 3 W UV irradiation. The degradation of DCM manifested an increasing trend with the intensity of UV light supplied during the process. Also, the best ratio that gives a favorable degradation performance was between 1.13 and 3.76 w/w of H₂O₂]: [Fe²⁺]. On the contrary, using a weight ratio of 6.39 significantly reduces the degradation efficiency of the process.

The type of anode resulting to the highest degradation efficiency was TiO₂ coated with IrO₂ and RuO₂. The promising performance on the use of the novel anode may be attributed to the effective mitigation of recalcitrant pollutants like laboratory wastes.

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