



Development of a Digitally Baffled Electro-Photocatalytic Oxidation Batch Reactor for High-Efficiency Treatment of Refinery Wastewater

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Abstract

This study presents the growth and optimization of a new design of an electro/photocatalytic organic compounds oxidation batch reactor with a digital baffle for refinery wastewater (RWW). The system combined electro and photo oxidation with zinc oxide as a photo catalyst by using a stainless steel anode and an iron cathode. The combined design was operated under varying oxidation times (5–25 min), pH solution (3–9), agitation speed (100–300), and catalyst (10–50 mg/L) to assess treatment competence and enhance working parameters by Box-Behnken design under response surface design. The digital baffled configuration was used to enhance mixing and irritation distribution, confirming the activation of the catalyst and mass transfer throughout the batch electrooxidation reactor. Results established important organic degradation, with electro-oxidation alone attaining a maximum removal efficiency of 91.2%, while the combined photo-electrochemical process reached up to 99.5% competence under optimal conditions of 25 min, 300 RPM, 50 ppm catalyst concentration, and 9 pH. The reactor's presentation was credited to the synergistic effects of free radical production, the activity of photocatalytic, and enhanced hydrodynamics eased by the digital baffling design for organic compounds in refinery wastewater.

Keywords: wastewater; organic compounds; wastewater treatment; Advanced Oxidation Processes; Electro-catalytic; optimization.

1. Introduction

Crude oil aids as a main source of many derivative byproducts found through advanced refining and purification processes. Though, petroleum production also produces considerable quantities of wastewater, necessitating complete treatment and organization to alleviate adverse ecological influences [1]. About 0.4 to 1.6 times more than the crude oil production in the oilfields refinery, which can contain a wide range of hydrocarbons with different concentrations such as aromatic, phenol and dissolved organic compounds are all of specific ecological anxiety. The composition of wastewater is very complex and changeable that effect on the environment if the wastewater is discharge [2]. Earlier being removed, the method is vital since oilfield wastes contaminate the atmosphere. Taking the treatment on these wilds could lead to better water reusing, crude recovery, and environmental license obedience [3]. So, one of the greatest vital aspects of the contamination regulator in oilfield refineries at the instant is the elimination of these organic compounds from oily wastewater that complies with ecological rules and is recycled and castoff as quickly as likely is a subject raised by many authors that studies for organic removal from wastewater such as adsorption [4], filtration [5], biological processes [6] and membrane [7]. Though, these methods do have certain limits and difficulties. For instance, the adsorption of organic compounds can alter the phase of organic without removing them, subsequent in further contamination issues [8]. The chemical oxidation



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treatment are important component processes targeted at refinery wastewater dispensation, according to empirical evidence [9]. By employing irradiation light by using UV light as a cost-effective alternative to classical treatment such as ozone, fenton oxidation and granular-activated carbon processes, the advanced oxidation processes (AOPs) used for organic compounds and converted to CO_2 , H_2O , and metal oxides [10]. In this work, organic compounds in wastewater is removed by combined treatment of UV light and electro-catalytic oxidation (ECO), using a newly created, used computerized baffle electro photo catalytic oxidation batch reactor (DBEBR). The DBEBR was said to have a bigger effect than a batch oxidation reactor. In this experimentation, we used the new design to oxidize organic compounds in wastewater with the aid of catalyst agent concentration and UV light. Finally, the optimization method using software program was applied to find the finest employed for the electro photo catalytic oxidation (EPCO) organic oxidation treatment—the stage at which the removal of pollutants compounds was maximized

1. The paper should have the following structure

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2. Experimental

2.1 Wastewater and Organic Measurement

The wastewater discharge from the oilfields refinery of the Midland Oil Company in southern Iraq, and the specification is listed in Table 1. After the organic treatment, the amount of sodium salt was added to 40 mL of refinery wastewater in the separating funnel and mixed with 4 mL of CCl_4 by shaking for 2 minutes, and waited to separate the two layers of water and organic pollutant in the solvent, and from the calibration curve, the organic pollutants were obtained [11].

Table 1. Wastewater properties.

Parameters	Values	Parameters	Values
Organic compounds	152.3 (ppm)	Density	0.9992(gm/cm ³)
Turbidity	117.8 NTU	TSS	62345.262 (ppm)
TDS	17.9(ppm)	Viscosity	1.042 m Pa/S

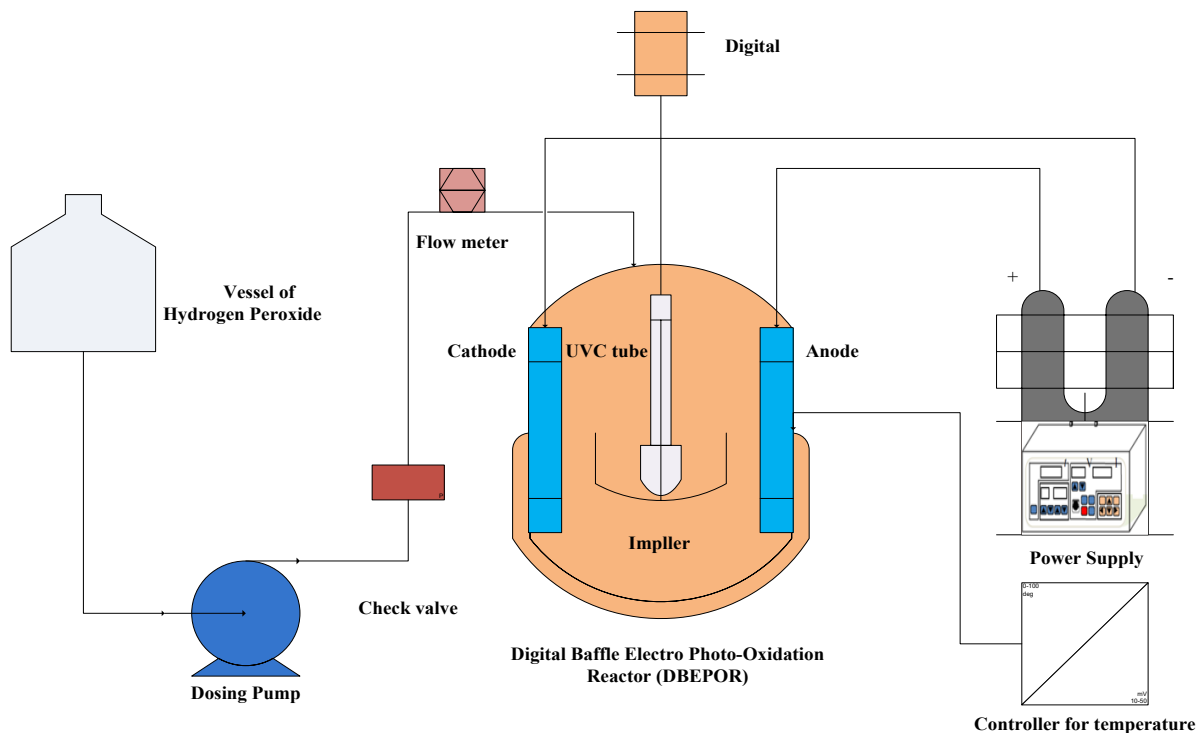
2.2. The Electro photo-catalytic oxidation reactor

The photo-electro-catalytic oxidation treatment, the DBEPCB, is locally built to provide mass transfer at room temperature. The University of Al Muthanna-Iraq's Chemical Department of Engineering, has built a new design. Table 2 displays the new reactor characterization. Integrated the electro-photo-catalytic oxidation reactor, there are three baffle accessories with the reactor wall: a digital mixer controller, a 15 cm shift of the impeller, and an impeller design (three flat-blade turbine) with a shift diameter of 0.7 cm. The entire untested system consisted of the power device and photo-catalytic reactor. The shape of the electro /photo system is shown in Figure 1. The power supply (RXN-305D,) for electro oxidation reactor with which diameter of 1.2 cm and a length of 20 cm. It was designed to minimize these destructive items while maintaining the light's 12 W devastating disinfecting possible with one amp current for organic removal in wastewater. The iron cathode size was $9 \times 2 \times 0.15 \text{ cm}^3$ and the steel anode electrode size was $11 \times 3 \times 0.2 \text{ cm}^3$. In the DPEBR reactor, the internal electrode space was kept at 4 cm, and the real electrode area was kept at 25 cm^2 . The ratio of the initial organic compounds (C_o) to the residual pollutant compounds (C_t) after treatment was used to illustrate the discount for organic compounds. Equation (1) could be used to design the organic removal (OR) with change the experimental variables of oxidation time, pH, catalyst and agitation speed:

$$\%OR = \frac{C_o - C_t}{C_o} \quad (1)$$

Table 2: Characterization of the electro photo-catalytic Technology

No.	Description	Requirement
1.	DBEPCB reactor	200 ml
2.	Reactor Diameter (Pyrex)	6 cm
3.	Preheater	Electrical heater
4.	Shift the length and diameter of the shaft	25 cm and 0.8 cm
5.	Insulated reactor	Glass wool
6.	Baffle (design from Pyrex)	Three distributions on the wall of the batch
7.	Depth of reactor	8 cm
8.	Baffle design	High 5 cm, width 0.3 cm, and thickness 2 mm

**Fig. 1:** Design of Electro/photo-catalytic oxidation reactor

2.3. Statistical analysis

In this work, the untried circumstances for organic oxidation treatment by the digital baffle batch reactor were enhanced by changing the independent variables. The Minitab software was used for data analysis and to plot the experimental design of the employed variables of oxidation time (X_1), catalyst agent concentration (X_2), pH (X_3), and agitation speed (X_4) as listed in Table 3.

Table 3: Working parameters

Parameters	Ranges	Parameters	Ranges
X_1 : Oxidation time	5-25	X_3 : pH	3-9
X_2 : catalyst (ppm)	10-50	X_4 : Agitation speed (RPM)	100-300

2.4. AOPs effectiveness and kinetic model

Using a UV spectrophotometer, the change in the pollutants compound in RWW during the electro photo-catalytic treatment was determined by equation (1). The kinetic oxidation model for organic oxidation in wastewater by the Langmuir-Hinshelwood mathematical model, the kinetics of the photo-catalytic degradation rate of organic elimination in wastewater were strongly influenced by (Eq. (2)): $k_1(\text{min}^{-1})$, the pseudo-first-order rate coefficient. For every experiment, a plot of concentration ratio versus time leads to a straight line with a slope of the first-order coefficient [12].

$$\ln \left[\frac{C_0}{C_A} \right] = K_1 t \quad (2)$$

3. Results and discussion

3.1 Statically analysis of the electro photo-catalytic system

The parameters, variable values, the removal to the ultimate organic oxidation treatment, and removal competence for each run are shown in Table 4. The data analysis by Minitab software was obtained through trials using the combined electro and photo-catalytic oxidation process, with four replicates at the central point. A Design Expert by a second-order model then used the least-squares approach for ECO and ECPO treatment, as indicated in equations (2) and (3), to examine the findings.

$$\text{ECO organic removal} = -12.5 + 4.29 X_1 + 1.009 X_2 + 5.06 X_3 + 0.117 X_4 - 0.0646 X_1^2 - 0.0072 X_2^2 - 0.005 X_3^2 + 0.000032 X_4^2 - 0.0184 X_1 X_2 - 0.0975 X_1 X_3 - 0.00265 X_1 X_4 + 0.0125 X_2 X_3 - 0.00052 X_2 X_4 - 0.00933 X_3 X_4 \quad (3)$$

$$\text{ECPO organic removal} = 20.7 + 3.37 X_1 + 0.833 X_2 + 0.82 X_3 + 0.048 X_4 - 0.0484 X_1^2 - 0.00216 X_2^2 + 0.232 X_3^2 + 0.000204 X_4^2 - 0.0167 X_1 X_2 - 0.0583 X_1 X_3 - 0.00215 X_1 X_4 + 0.0138 X_2 X_3 - 0.00141 X_2 X_4 - 0.00658 X_3 X_4 \quad (4)$$

Where X_1 , X_2 , X_3 and X_4 are time, catalyst, pH and agitation speed respectively that effect on the organic removal in the wastewater treatment.

Table 4. The parameter variables used for organic elimination

Run no.	Time (min) X_1	Catalyst (ppm) X_2	pH X_3	RPM X_4	Organic elimination by ECO	Organic elimination by EPCO
1	5	10	6	200	55.4	61.4
2	25	10	6	200	74.2	79.6
3	5	50	6	200	77.4	82.8
4	25	50	6	200	81.5	87.6
5	15	30	3	100	68.4	76.8
6	15	30	9	100	86.5	90.7
7	15	30	3	300	82.6	88.6
8	15	30	9	300	89.5	94.6
9	5	30	6	100	59.2	66.9
10	25	30	6	100	74.7	80.5
11	5	30	6	300	68.9	75.6
12	25	30	6	300	73.8	80.6
13	15	10	3	200	65.7	72.8
14	15	50	3	200	72.8	80.6
15	15	10	9	200	70.4	77.6
16	15	50	9	200	80.5	88.7
17	5	30	3	200	51.4	60.6
18	25	30	3	200	76.7	81.7
19	5	30	9	200	75.3	80.6
20	25	30	9	200	88.9	94.7
21	15	10	6	100	72.5	78.8
22	15	50	6	100	83.6	90.6
23	15	10	6	300	72.5	81.7
24	15	50	6	300	79.4	82.2
25	15	30	6	200	78.4	81.9
26	15	30	6	200	78.55	80.9
27	15	30	6	200	79.4	81.6

The ANOVA analysis by the Minitab software program is listed in Tables 5 and 6 for organic compounds by ECO and ECPO, respectively, and was based on the F and P analysis. The Minitab equation will demonstrate supplementary variations in organic removal if the Fisher value remains higher. The BBD competency documentation was finished, with the use of change components and the fulfillment of certain change sources.

Table 5. ANOVA analysis of ECO Organic Elimination

Foundation	DOF	Seq. SS	Adj. MS	Fisher Value	P-test Value
1-Model	14	1845.48	131.82	4.36	0.007
Linear	4	1399.55	349.887	11.57	0
X₁	1	563.07	563.07	18.61	0.001
X₂	1	346.69	346.688	11.46	0.005
X₃	1	450.19	450.187	14.88	0.002
X₄	1	39.6	39.603	1.31	0.275
Square	4	291.58	72.894	2.41	0.107
X₁²	1	222.45	222.454	7.35	0.019
X₂²	1	44.72	44.725	1.48	0.247
X₃²	1	0.01	0.011	0	0.985
X₄²	1	0.53	0.535	0.02	0.896
2-Way Interaction	6	154.35	25.726	0.85	0.556
X₁*X₂	1	54.02	54.023	1.79	0.206
X₁*X₃	1	34.22	34.222	1.13	0.308
X₁*X₄	1	28.09	28.09	0.93	0.354
X₂*X₃	1	2.25	2.25	0.07	0.79
X₂*X₄	1	4.41	4.41	0.15	0.709
X₃*X₄	1	31.36	31.36	1.04	0.329
Error	12	363.02	30.252	-	-
Lack-of-Fit	10	362.44	36.244	124.62	0.008
Pure Error	2	0.58	0.291	-	-
Total	26	2208.5	-	-	-

Table 6. ANOVA analysis of ECPO for Organic Elimination

Foundation	DOF	Seq. SS	Adj. MS	Fisher Value	P-test Value
1-Model	14	1845.48	131.82	4.36	0.007
Linear	4	1399.55	349.887	11.57	0
X₁	1	563.07	563.07	18.61	0.001
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Figure 2a and b show that the high organic elimination occurs along the oxidation time of oxidation for all values of the organic removal by electrocatalytic and electrophoto-catalytic oxidation. This is because there were not enough locations on the electro-photo catalytic oxidation, and free radicals from the catalyst agent and iron that were produced from the cathode to attain a relatively high removal ratio. The combined effects of catalyst agent, pH, agitation speed, and oxidation time had a strong relation directed towards organic elimination (OR), where increasing the pH increased organic removal [13].

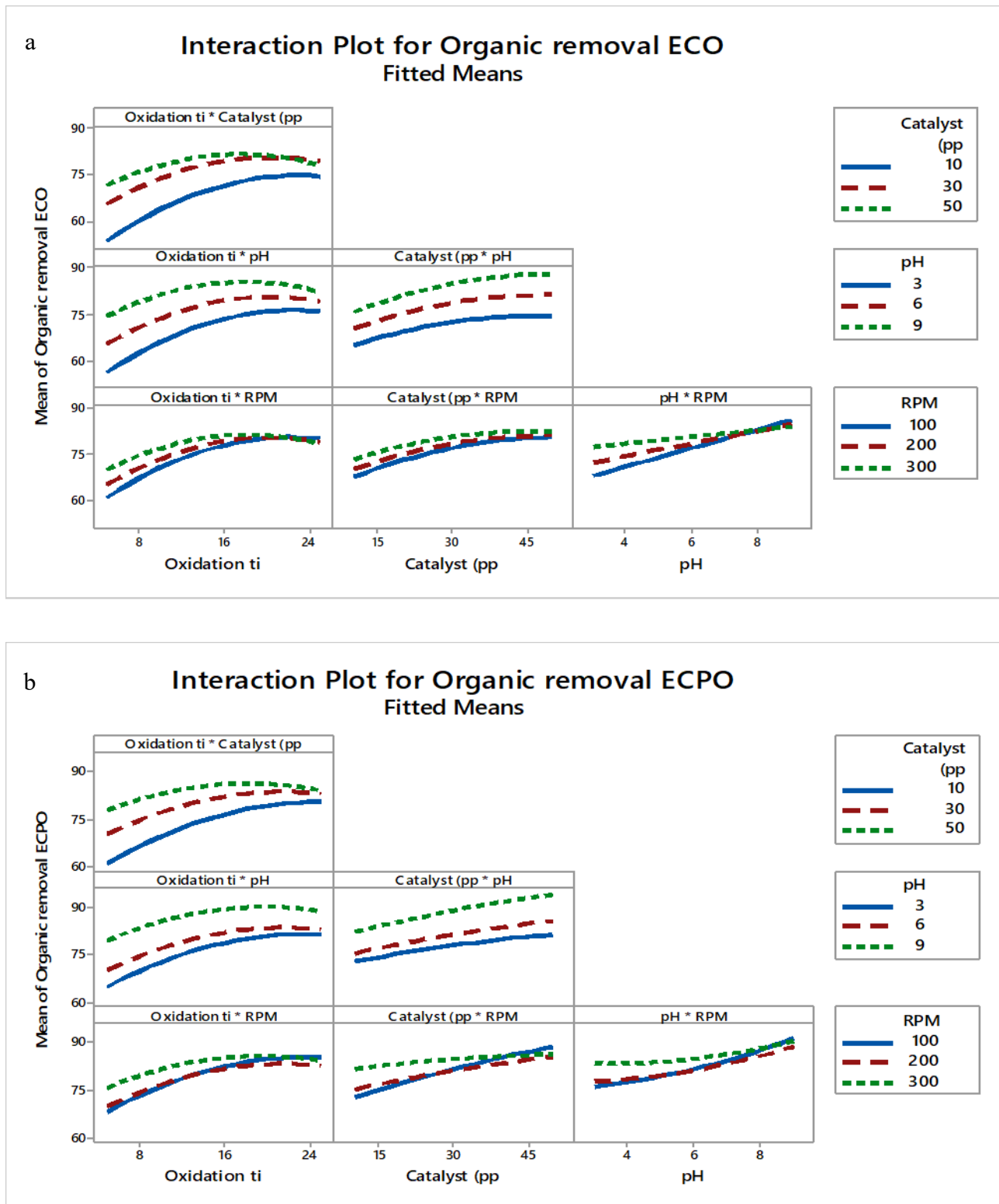
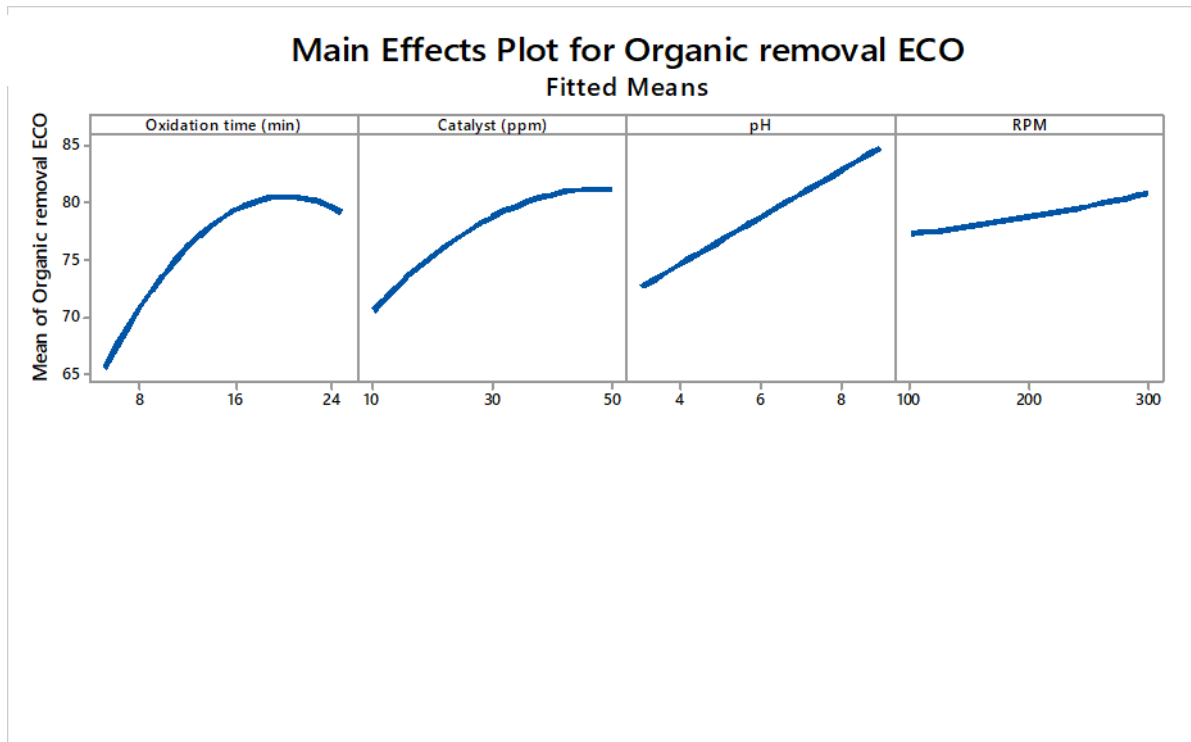


Fig. 2: Represent the interaction plot of (a) ECO and(b) ECPO treatment

The data analysis with the box behnken design, and the main assumptions concerning the issues were dependable. The variation in organic removal resulting from a variation in the level of an issue still determines its consequence [14]. This is usually denoted as the main result because it challenges the main issues of attention in the investigation, where the principal contents of each OR limit for ECO-ECPO organic compounds in refinery wastewater are shown in Figures 3a and b, respectively. The concentration of zinc oxide under UV light, pH, agitation speed, and oxidation time were the most important variables affecting the elimination of organic compounds in wastewater. This positive-sign constant shows how increasing the independent variables within the range being studied would increase OR and, on the other hand, how raising rpm would have little effect on the organic removal due to the high production of free radicals by electro and photo-catalytic oxidation [15].

a



b

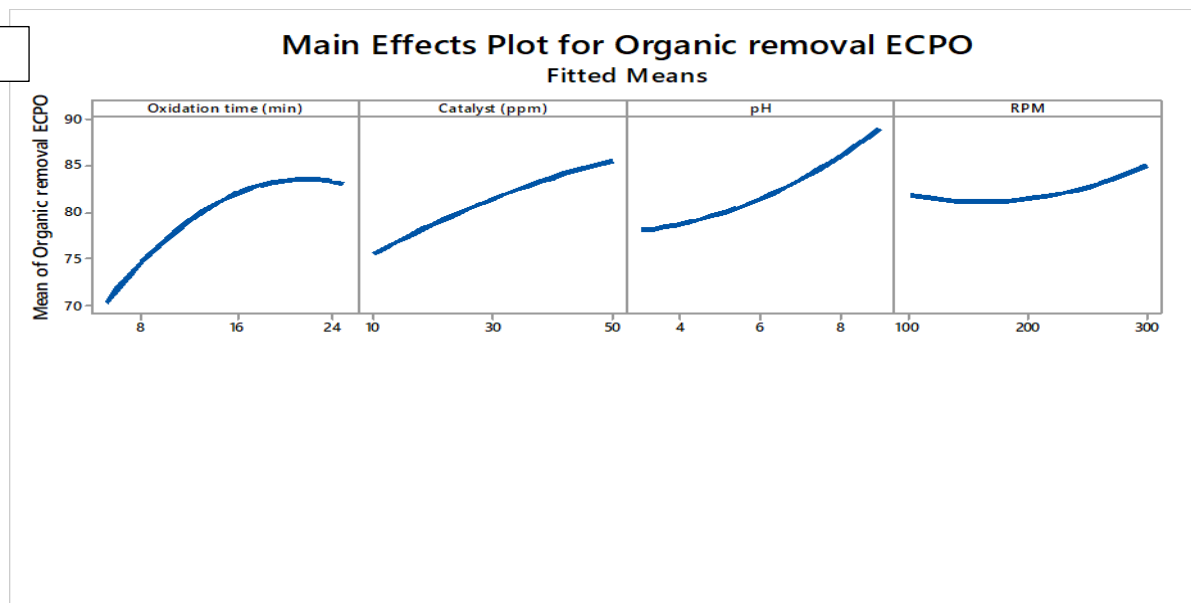


Fig. 3: Impact of organic elimination of (a) ECO and (b) ECPO

It is still necessary to find the best values for active variables, including pH, zinc oxide, agitation speed, and oxidation time. Figure 4 displays the measurement effects of the D-optimization for hybrid electro-catalytic oxidation and electro photo-catalytic oxidation, which eliminate organic compounds from refinery effluent with a high efficiency of 99.8% for combined electro photo-catalytic oxidation treatment [16].

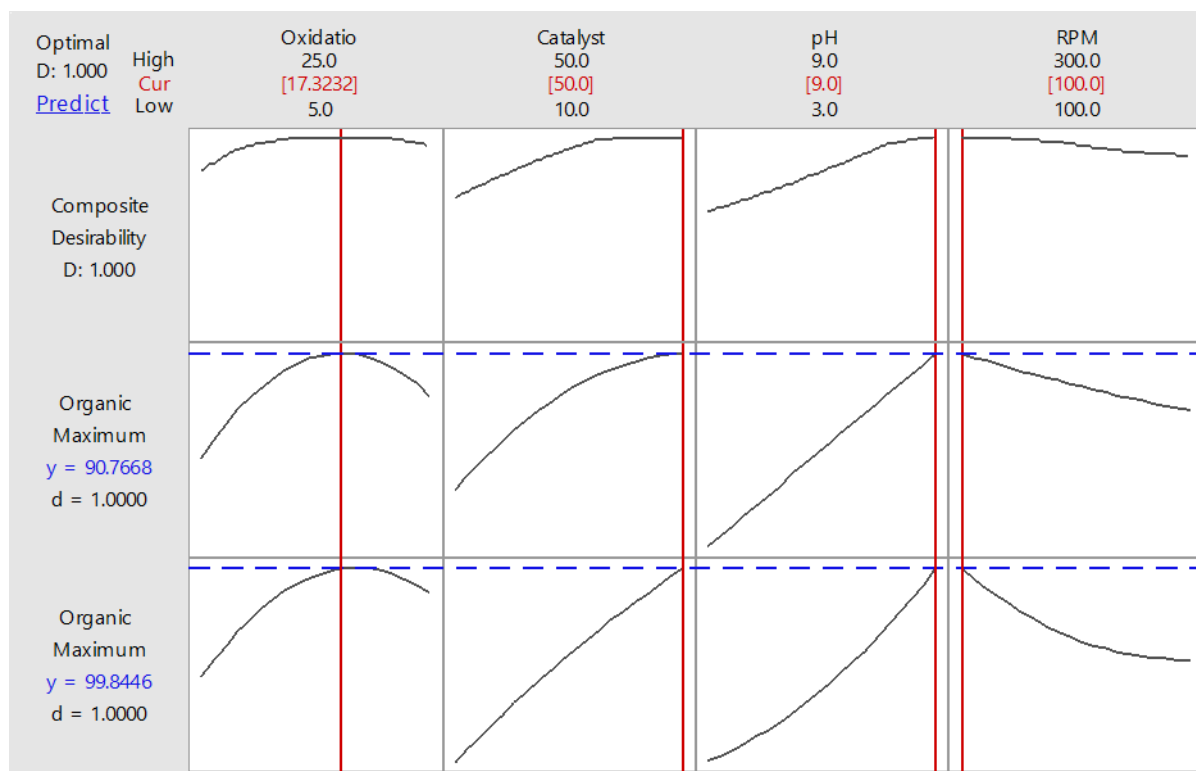


Fig. 4: Optimization of ECO-ECPO for organic removal

3.2 Effect of pH

The effect of pH solution was examined while both anode and cathode electrodes oxidized for 25 minutes at a steady current and pH values between 3 and 9. Figure 5 illustrates how the proportion of organic elimination for both anode and cathode electrodes is impacted by the starting pH. The results demonstrate that organic elimination effectiveness was higher at basic pH values [17]. A substantial decrease in treatment efficiency as pH levels rise has been demonstrated by earlier research that also displayed the temporal patterns of the percentage of total organic compounds eliminated in response to pH values. Therefore, it may be concluded that the electrophoto-catalytic procedure works better in alkaline environments than in acidic ones. These results suggest that, in order to minimize organic compounds in wastewater, basic solutions produce more radicals than acidic solutions due to the zinc oxide agent concentration that relates to free radicals [18].

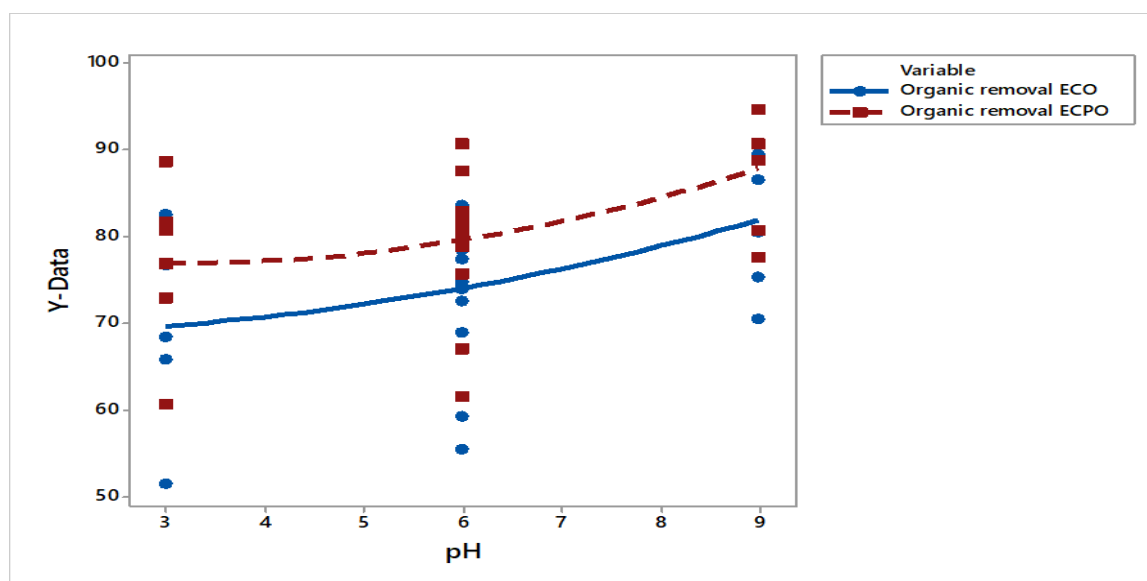


Fig. 5: The pH effect on organic elimination

3.3 The effect of agent concentration

The catalyst agent plays a significant role in the degradation of organic compounds in wastewater by free radicals ($\bullet\text{OH}$) by electrophoto-catalytic oxidation treatment, which is essential for electro-catalytic oxidation [19]. Figure 6 illustrates how wastewater is affected by amounts varying from 10 to 50 ppm. The effectiveness of the agent concentration as an electro-photo-catalytic. Also, during the electro-photo-catalytic treatment, remaining zinc oxide with the ability to decrease can consume organic compound oxidant, causing an overestimation of organic compounds in wastewater by free radicals. The content of the catalyst agent directly correlates with the degree of inaccuracy of organic compounds in wastewater. The additional catalyst will therefore probably result in an organic compound. Additionally, many organisms are poisoned by the excess zinc oxide concentration [20].

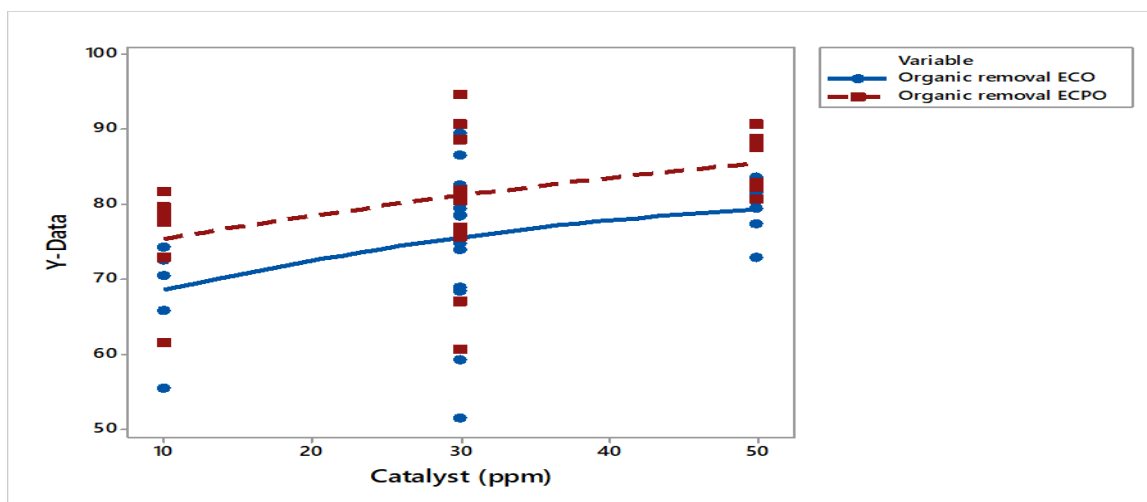


Fig. 6: The effect of catalyst concentration on organic removal

3.4 The rpm effect

The organic compounds in refinery wastewater that removed electro-photo catalytic oxidation as a result of the deliberate application of changing degrees of mixing as shown in the Figure 7 for the percentage of organic removal increased little with increasing mixing speed due to the high free radical production from combined electro and photo catalytic oxidation compared to the production from classical from zinc oxide under UV light that need agitation for free radical production that led to a greater mass transfer in the electro photo catalytic oxidation treatment after careful measures were performed to remove the tanning and organic contaminants from wastewater [21]. Although increasing the mixing agitation speed led to a slight development in organic elimination, the overall presentation gain was comparatively limited, signifying that the system's radical generation was previously optimized under moderate mixing circumstances. The treatment proved effective in degrading of organic pollutants and more complex compound.

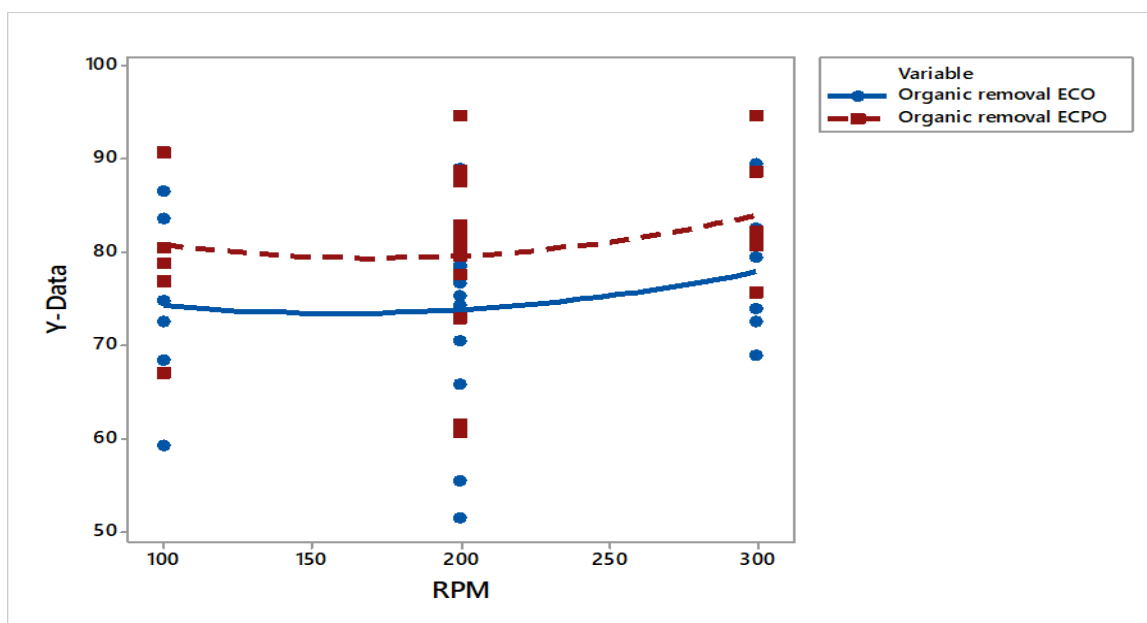


Fig. 7: The RPM effect on the organic elimination

3.5 Oxidation time effect:

To evaluate the influence of oxidation duration, experiments were conducted under constant operating circumstances by electro photo-catalytic oxidation, as illustrated in Figure 8, the percentage of organic elimination increased sharply with oxidation time up to 25 minutes, reaching a to 87.5%. However, after this, there was no discernible development in the proportion of organic elimination. The trend in the percentage of organic elimination that has been noted may be because of changes in the concentration of organic compounds in the refinery wastewater that is undergoing electrophoto-catalytic treatment [22]. The longer the oxidation period, the more effectively organic compounds are removed from the wastewater. This is mostly because, as the oxidation time increases, the adsorption process becomes more active throughout the electrooxidation reactor

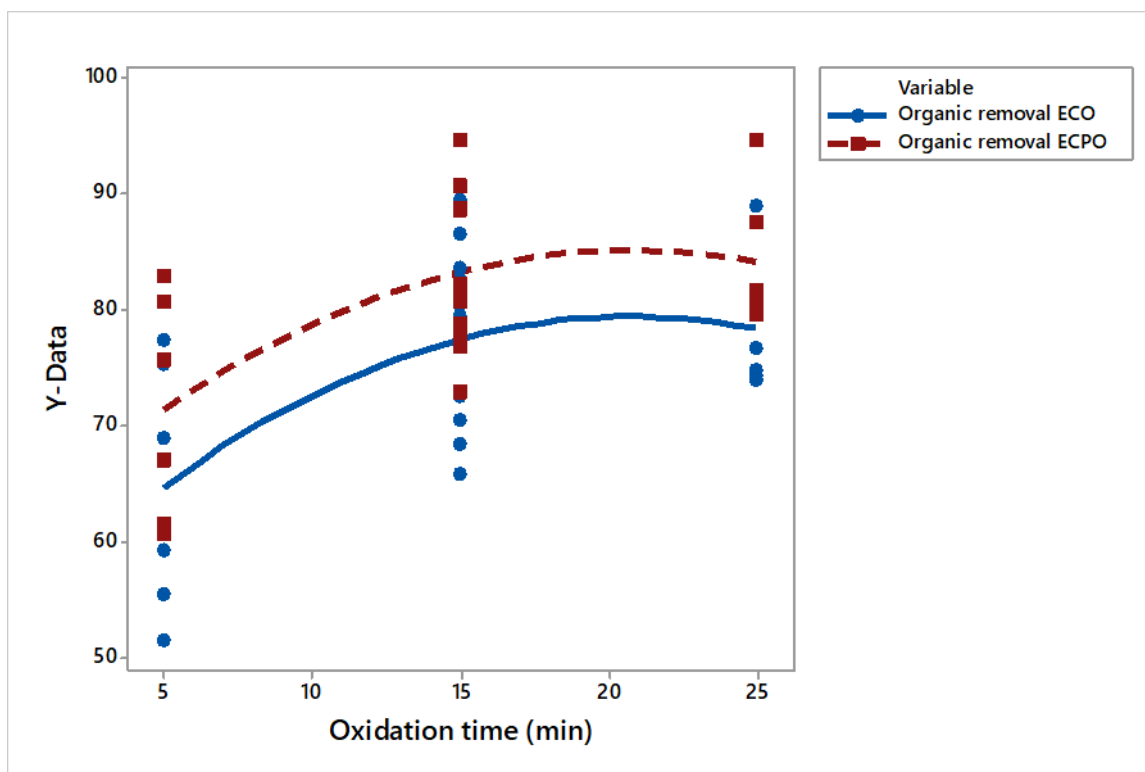


Fig. 8: The effect of electrolysis time on oil elimination

3.6 Kinetic study

Figure 9 illustrates the use of the kinetic model pseudo-first order models in electrocatalytic amount experiments by changing the catalyst concentration from 10 to 50 ppm with constant other parameters at the best conditions of pH and agitation speed, and real wastewater was used to ascertain the impact of catalyst concentration on the kinetic constants of organic elimination. Fitting the experimental data using Eq. (2) yielded the parameter value k_1 (min^{-1}). Figure 9 displays the values of concentration ratio as a function of normalized oxidation time, that related to the free radical production by the combined treatment of electrocatalytic and photocatalytic oxidation addition to the mixing solution that leading to high free radical production that oxidizes organic compounds in refinery wastewater [24].

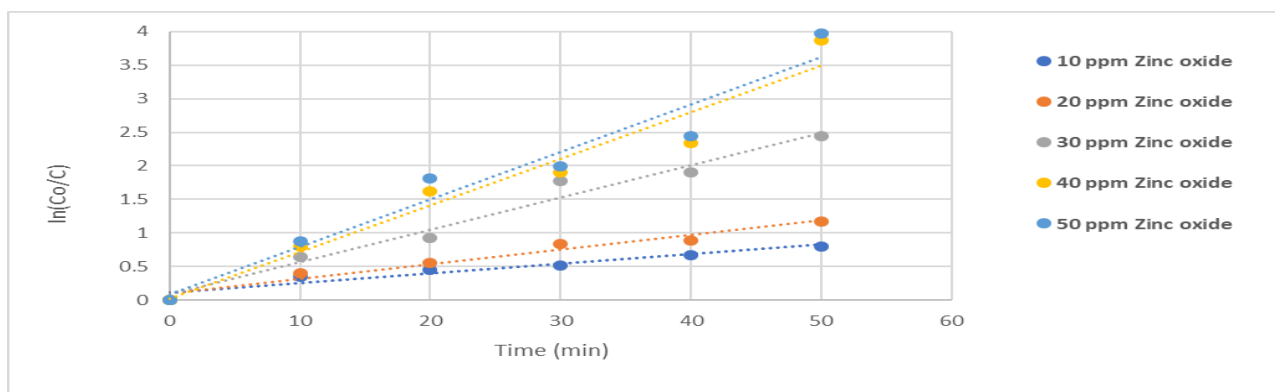


Fig. 9: Pseudo-first-order mathematical model at 300 rpm, 9 pH solution, and room temperature

3.7 The Mechanism of Photo-Fenton Oxidation Reaction

The photo-catalytic mechanism was related to the production of free radicals from zinc oxide in solution, and the enhanced by iron production from the cathode that reacted with organic compounds in refinery wastewater and converted to carbon dioxide and water, as shown in Figure 10 [25]. Through sophisticated oxidation mechanisms, these radicals subsequently break down organic compounds in wastewater. The light energy increases the catalyst's efficiency, which in turn accelerates the breakdown of organic compounds according to the equations. The equations (5–8) expand on the important oxidation treatment of the photocatalytic process[26].



On the other hand, free radicals can react with organic compounds in wastewater in equation 9 [27];

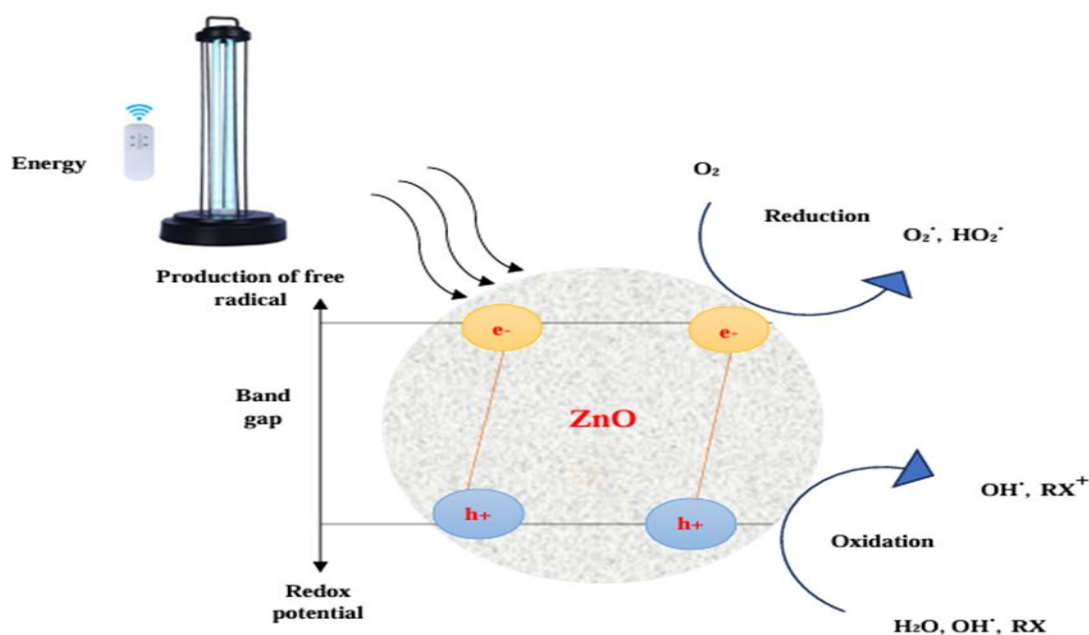
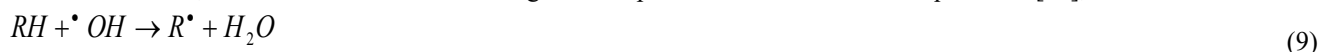


Fig. 10: Mechanism Recommended for Photo-catalytic Organic Oxidation

4. Conclusion

The presence of a digital baffled electro-photocatalytic oxidation batch reactor has established a highly real and flexible method for treating wastewater. Using stainless steel and iron as the anode and the cathode respectively, in combination with zinc oxide as a photo catalyst, the oxidation reactor achieved excellent elimination efficiencies—up to 99.5% for electro-photo catalytic oxidation compared to 91% for electro catalytic oxidation. With the following ideal parameters of 9 pH solution, 300 RPM agitation speed, 25 oxidation time and 50 ppm catalyst agent concentration, when combined with electro oxidation, zinc oxide a key factor in ultimately encouraging the production of free radicals that oxide all organic compounds in wastewater. This method has the potential to be an effective water treatment method, given the remarkable performance of ECPO operation.

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