

Optimizing Ti/RuO₂-IrO₂ – electro activated persulfate oxidation processes for the degradation of ammonia-nitrogen and color from landfill leachate using Response Surface Methodology

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Abstract. Landfilling disposal method has raised many environmental concerns especially water pollution from the discharge of landfill leachate. This study is aimed at investigating degradation of ammonia and removal of color of landfill leachate by electro-persulfate activation using ruthenium-iridium coated titanium (Ti-RuO₂/IrO₂) electrode. Process variables such as reaction time, current density and persulfate dosage were optimized using central composite design via response surface methodology (RSM). RSM models show high coefficient of determination, R² of 0.9182 and 0.9249 for ammonia-nitrogen (NH₃-N) and color respectively. The maximum removal efficiency for NH₃-N and color were recorded as 83.7% and 65.8% respectively. Persulfate can be used in oxidation processes as an activating agent to remove NH₃-N and color from landfill leachate.

1 Introduction

Landfill leachate represents a significant pollutant source due to its complex and toxic composition which brings adverse effects to the environment [1-2]. Pertaining to these issues, treatment has been developed as in (i) biological treatment method; (ii) physical and chemical treatment method; (iii) biological, physical, and chemical treatment method [3]. However, due to the complexity of landfill leachate composition, physicochemical treatment solely is not sufficient to degrade organic matter. Hence, adaptation and wide development of electrochemical technology has been implemented. Electrochemical treatments have high efficiency, small physical footprints, and are easier to manage effective removal of organic matter [4 – 5]. Pirsahab et al. (2015), reported that the aforesaid treatment is effective in removing COD, ammonia-nitrogen (NH₃-N), heavy metal pollutants, and chroma [6]. Not just that, electrochemical treatments using persulfate oxidation technology have been widely used in landfill leachate treatment. Sulfate radical (SO₄•-) has strong oxidizing capability,

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longer half-life and higher resistant to destruct in water compared to hydroxyl radical ($\bullet\text{OH}$) [7].

Electrodes include BDD, Ti/RhO₂ – TiO₂, Pt, Ti/PbO₂, graphite, Ti/Pt as well as Al are the examples of materials used in this processes which has excellent electrocatalytic activity [8]. Song et al. (2023), achieved 100% of COD removal and 92.2% NH₃-N removal from composting leachate biochemical effluent (CLBE) in under 100 minutes of treatment [9]. Okur et al. (2022), perform the same treatment in degrading organic contaminant from real textile wastewater achieved 88% color removal using Ti/RuO₂-IrO₂ electrode [8].

Based on the information above, none of the studies investigated the efficiency of Ti/RuO₂-IrO₂ – electro activation by persulfate for NH₃-N and color removal. Therefore, the removal efficiency of NH₃-N and color by Ti/RuO₂-IrO₂ . electro activated persulfate will be optimized using central composite design (CCD) via response surface methodology (RSM). The effect of persulfate dosage, reaction time as well as current density towards the removal efficiency will be elucidated.

2 Materials and methods

2.1 Leachate sample collection

30 L of samples were collected and characterized within 24 hours from the time of sampling collection from a landfill that receives solid waste annually since 2000 in about 660,000 metric tons and grouped as improved anerobic sanitary landfill leachate (class III). The initial pH was recorded 8.9, NH₃-N and color was 1448 mg/L and 14700 Pt Co respectively.

2.2 Experimental set-up and procedure

A simple electrolysis set up was designed using a power supply (GWINSTEK GPS-3303) connected to anode and cathode cable to the Ti-RuO₂/IrO₂ electrode using retort stands. The distance between the electrode is fixed to 3 cm and 200 ml of leachate sample was used per treatment. The rotational speed was fixed at 250 rpm. pH was altered using 0.1N hydrochloric acid (HCL) as well as 0.1N sodium hydroxide (NaOH).

2.3 Removal efficiency

NH₃-N and color were evaluated using DR/2800 HACH spectrophotometer [10]. The removal efficiency of NH₃-N and color were calculated using the following Eq.1:

$$\% \text{ Removal Efficiency} = \frac{X_i - X_f}{X_i} \times 100 \quad (1)$$

where X_i and X_f refer to the initial and final concentration of NH₃-N and color respectively.

2.4 Experimental design and statistical analysis

The software used for the design of the laboratory experimental parameters is version 6.0.7 design expert (STAT-EASE Inc., Minneapolis, USA). 20 sets of experiments were designed at five levels of CCD (-2,-1,0,+1,+2) with three independent variables (current density, persulfate dosage, and reaction time). Preliminary study has been used as a baseline for the independent variables. Analysis of Variance (ANOVA) is used to analyze the model. Table 1 summarized the parameter ranges and levels of the variables used in the experimental works.

Table 1. Experimental range and levels of the independent variables.

Factors	Factor Code	Levels and Ranges				
		-2	-1	0	1	+2
Current density (mA/cm ²)	A	10	30	50	70	90
Dosage (g/L)	B	0	2	4	6	8
Reaction time (min)	C	5	20	35	50	65

3 Result and discussion

3.1 ANOVA analysis for parameters

The responses to the experimental design are NH₃-N and color removal efficiency and analyzed by ANOVA. According to Sohrabi et al. [11], the positive sign indicates the increment of the responses and vice-versa. The empirical relationship between the independent variable in the Ti/RuO₂-IrO₂ – electro activated persulfate coded factors for NH₃-N and color removal efficiencies (%) as a function of current density, persulfate dosage, and reaction time are shown in Eq. 2 - Eq. 3.

$$\begin{aligned} \text{NH}_3\text{-N removal efficiency (\%),} \\ = 46.7205 + 9.69059 * A + 6.05529 * B - 0.401176 * C - 0.87625 * AB + 2.17125 \\ * AC - 6.02625 * BC + 34.1051 * A^2 + 28.6651 * B^2 - 43.4549 * C^2 \end{aligned} \tag{2}$$

$$\begin{aligned} \text{Color removal efficiency (\%),} \\ = 64.8301 - 1.17412 * A - 1.29235 * B + 0.369412 * C - 1.1325 * AB - 1.9175 * AC \\ - 0.0375 * BC + 1.51518 * A^2 - 2.78482 * B^2 - 2.68482 * C^2 \end{aligned} \tag{3}$$

NH₃-N removal shows that linear coefficient and quadratic coefficient of current density and persulfate dosage, coefficient of interaction between current density and time has positive effects and rest have a negative effect on the removal. Color removal shows that linear coefficient of time and quadratic coefficient of current density has positive effects on the removal and other has negative effect. The applied model of ANOVA results is shown in Table 2. The significance of the terms is defined as higher *F* values and lower *P* value [12]. The model is at its best fit when *R*² values approaches 1 [13]. Guvenç (2019), stated that, the proposed quadratic model is a good fit when value of *R*² is at least 80% [14]. Table 2 shows that NH₃-N and color removal model imply *R*² value of >90% respectively indicating a good model fit. Lack of Fit *F* value for NH₃-N is 0.7938 implies insignificant relative to pure error and 59.69% is a possibility it occurs due to noise. Same as color, indicating 6.03% possibility of occurrence 4.58 Lack of Fit *F*-value due to noise. ANOVA analysis concluded that model is a good fit as NH₃-N and colors present insignificant lack of fit.

3.2 Effect of independent variables

Figure 1 shows the three-dimensional (3D) response surface plot for the effects of the variables on the removal efficiency of NH₃-N and color. Figure 1(a) shows that by increasing the persulfate dosage the degradation of NH₃-N raised from 34.6% to 83.7%. This is due to the increment of SO₄²⁻ concentration which allows more reaction-active adsorption sites to occupy on the electrode surface and resulting enhanced direct electrolysis capacity [15]. Yu et al. (2021), reported that the persulfate generation is enhanced by persulfate synthesis compliment to the electrolytic equilibrium due to the increment of SO₄²⁻ concentration [16]. In terms of reaction time, from 5 to 35 min of reaction, the oxidant concentration is the highest and the reaction rate is naturally the fastest resulting to most pollutants removed and degraded at the early stage [17]. Whereas for color removal as shown in Figure 1(b), the removal is not directly proportional to the increment of the persulfate dosage as the degradation starts to deteriorate after the optimum condition is achieved. This is the state where the scavenging

phenomenon occurs due to the excess of $S_2O_8^{2-}$ anions in the solution acting as radical scavenger that inhibit the removal efficiency and simultaneously annihilate themselves [18]. This also happened because of the reaction between $SO_4^{\cdot-}$ and its maternal persulfate molecule Eq. 4 where the applied persulfate dosage is greater than the optimal concentration, causing in the declining of the removal efficiency [19].

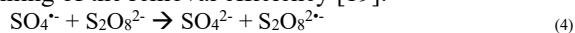


Table 2. ANOVA results for NH_3-N and color.

Source	Sum of Squares	DF	Mean Square	F Value	P Value
NH_3-N					
Model	3566.68	9	396.30	12.46	0.0002
A	798.2100	1	798.2100	25.1000	0.0005
B	311.6700	1	311.6700	9.8000	0.0107
C	1.3700	1	1.3700	0.0430	0.8398
A ²	217.07	1	217.07	6.83	0.0259
B ²	153.35	1	153.35	4.82	0.0528
C ²	352.4	1	352.4	11.08	0.0076
AB	6.14	1	6.14	0.1932	0.6696
AC	37.71	1	37.71	1.19	0.3017
BC	290.53	1	290.53	9.14	0.0128
Lack of Fit	140.7	5	28.14	0.7938	0.5969
R ²	91.82%				
Adj. R ²	84.45%				
Color					
Model	137.53	9	15.28	13.67	0.0002
A	11.72	1	11.72	10.49	0.0089
B	14.20	1	14.20	12.70	0.0051
C	1.16	1	1.16	1.04	0.3323
A ²	0.4284	1	0.4284	0.3834	0.5496
B ²	1.45	1	1.45	1.30	0.2816
C ²	1.35	1	1.35	1.20	0.2983
AB	10.2605	1	10.2605	9.1822	0.01267
AC	29.4145	1	29.4145	26.3233	0.0004
BC	0.01125	1	0.0112	0.0100	0.9220
Lack of Fit	9.17	5	1.83	4.58	0.0603
R ²	92.49%				
Adj. R ²	85.72%				

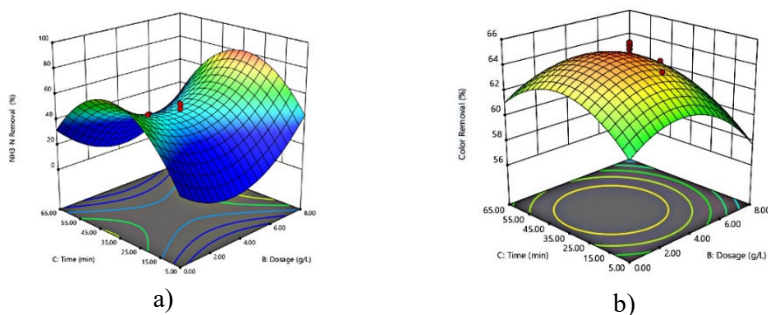


Fig. 1. Three-dimensional response plot on the effects of time versus persulfate dosage for (a) NH_3-N removal and (b) color removal.

Figure 2(a) and (b) shows the influence of current density on NH_3-N and color removal. The increment of the current density and the persulfate dosage increases the NH_3-N removal (Figure 2(a)). The high current density promotes the anodic oxidation of water thus enhanced

the production of hydroxyl radicals which that provide indirect electrochemical oxidation of organic molecules [8]. However, Figure 2(b), shows that increasing the current density does not improve the color removal. Abdulhadi et al. (2019) reported that minimal current density can result in satisfactory removal after achieving 88% of color removal with only 4 mA/cm² of current density [20]. Therefore, a lower current density should be tested for the color removal in future. It is to be noted that, in this study current density contributed more for NH₃-N removal.

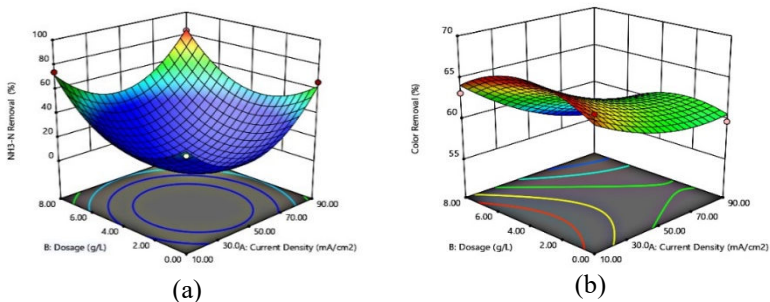


Fig. 2. Three-dimensional response plot on effect of persulfate dosage versus current density for (a) NH₃-N removal and (b) color removal.

The highest removal efficiency of NH₃-N (83.7%) was obtained at the following optimum conditions: current density: 90 mA/cm², persulfate dosage: 8 g/L, and reaction time: 5 min whereas for color (65.8%) were attained at current density: 50 mA/cm², persulfate dosage: 4 g/L and reaction time: 35 min. Similar results for NH₃-N (86%) removal was reported using titanium dioxide anode electro-oxidation in treated municipal landfill leachate [21]. Comparatively, our work performed better as it uses pure leachate. Whereas another report showed only 11% and 14% of NH₃-N removal from leachate via electrocoagulation using aluminum and iron electrodes respectively [6]. This proves that activation using persulfate could remove NH₃-N better than other types of activation. The final NH₃-N and color value of treated leachate from this study were recorded as 236.46 mg/L and 2400 Pt Co respectively.

3.3 Effect of Ti/RuO₂-IrO₂ electrode to persulfate activation

The removal performance of the electrode depends on the capabilities to produce radicals which have an important responsibility in the mineralization of organic compounds. Electrode has two classifications; active electrode that undergoes chemisorbed •OH which oxidizes the organic matter selectively and non-active electrode that undergoes physisorbed •OH which oxidizes organic species directly [8]. Active electrodes such as Pt, Ir and Ru-based oxides have low oxidation potential (RuO₂-TiO₂ = 1.4-1.7V, IrO₂-Ta₂O₅ = 1.5-1.8V, Pt = 1.7-1.9V) whereas non-active electrode having high potential oxidation such as boron doped diamond (BDD = 2.2-2.6V) [22]. The activation of persulfate by Ti/RuO₂-IrO₂ electrode produce radicals and active species to degrade the organic compounds by direct oxidizing the adsorbed water to produce HO• or indirect oxidizing process as persulfate cannot decomposition itself [8, 23, 24].

4 Conclusion

Ti/RuO₂-IrO₂ – electro activated persulfate process capable in degrading NH₃-N and color with the removal efficiency of 83.7% and 65.8% respectively. The optimum operating condition for NH₃-N are current density: 90 mA/cm²; reaction time: 5 min and persulfate

dosage: 8 g/L, whereas for color the optimum conditions are current density: 50 mA/cm²; persulfate dosage: 4 g/L and reaction time: 35 min. RSM model R^2 values were more than 90% indicating a good fit of the model developed and data optimization. Normally, Ti/RuO₂-IrO₂ have low oxidation potential in degrading contaminants in leachate. However, with the aid of persulfate the removal efficiency is enhanced. As a conclusion, this treatment method is feasible and has a potential for removal of NH₃-N and color from landfill leachate. However, the performance could achieve the Malaysian standards. Hence, for future studies it is suggested to test the removal efficiency by changing the distance between the electrode and using different types of electrolytes.

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