

PAPER 25 – LEACHATE AS A POWERFUL PRECURSOR FOR HYDROGEN SYNTHESIS: PROCESS OPTIMIZATION

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ABSTRACT

Renewable energy is getting more attention due to the depleting of non-renewable fossil fuels and its effects on global warming issues thus trigger the intense research in finding better alternative energy with low emission. The present work aims to study the potential of hydrogen gas production (for renewable energy) by electrocoagulation process from landfill leachate. The central composite design from response surface methodology (RSM) software was implemented to investigate the process variables in the hydrogen production system. The effects of three independent variables; namely pH (4-8) and voltage (3-9V), using different types of electrodes (Al, Fe, and Ni) were studied. At optimal condition of voltage 9V and initial pH 6 at 20 minutes, the Al electrode recorded an upturn maximum H₂ yield of 697 ppm, while 554 and 551 ppm were obtained with Ni and Fe electrode, respectively. More so, a good correlation between the actual and the predicted data was observed as elucidated by the coefficient of determination (R²).

KEYWORDS: H₂ Production, Electrocoagulation, CCD Response Surface Methodology, Electrodes

1. INTRODUCTION

Since hydrogen gas burns quickly, emits no greenhouse gases, has a higher energy density, requires little ignition energy, and has a very high research octane number, it is commonly regarded as a fuel of the future (Nanthagopal et al., 2011). It is important to clarify that the octane number is a measurement of a fuel's resistance to knocking in spark-ignition internal combustion engines, and it is typically used to rate gasoline. Hydrogen's high RON indicates that it has a high resistance to knocking, similar to premium gasoline. However, 95% of the hydrogen produced worldwide now comes from fossil fuels, mostly from the steam reforming of natural gas (Ogden, 1999). Numerous other processes, including electrolysis, thermolysis of water, and the thermocatalytic reformation of hydrocarbons, are also referred to as industrial hydrogen production processes (Demirbas et al., 2010). However, the scope of large-scale hydrogen production using these techniques is undesirable because of the concurrent synthesis mixture with the oxygen (Smolinka et al., 2009). This is especially true for the electrolysis of water.

But electrocoagulation (EC) technology is a method of treatment that uses electrical current to treat pollutants by including coagulant. According to Shammam et al. (2010), in addition to lowering residue for waste production, coagulation has the ability to remove small particles inside pollutants and set them into motion with the applied current. EC can be used to de-fluoridate water and is capable of removing a wide range of contaminants under a variety of circumstances, including suspended particles, metals, petroleum products, colour from dye solutions, and aquatic humus (Holt et al., 1999). This demonstrates that the treatment conditions—such as pH, voltage, electrode types, etc.—have a significant impact on how well the EC process works.

For instance, Shivayogimath et al. (2014) explored the impact of pH values (4, 5.8 and 8) on the elimination of COD throughout the course of a batch run lasting 40 minutes at a 3V applied cell voltage. It was shown that the COD removals increased with a longer reaction time for all three pH values. However, a pH value of 5.8 resulted in the best COD elimination. With 35 minutes of the reaction period and this pH, COD was reduced from 4820 mg/L to 2250 mg/L, yielding a COD removal efficiency of 53.3%. Similar to this, Abdallah et al. (2013) confirmed that pH might considerably affect the generation of both hydrogen and oxygen.

According to the results of the experiments, the synthesis of hydrogen and oxygen is improved the further away from pH 7 there is in the range of pH from 3 to 13. Furthermore, according to Song et al. (2008), it was discovered that an ozone electro-coagulator with an optimal pH of 10, dye concentration of 100 mg/L, a current density of 10 mA/cm², salt concentration of 3,000 mg/L, the temperature of 30 °C, ozone flow rate of 20 mg/L, and electrode distance of 3 cm effectively removed 96% of colour and 80% TOC. Sengil et al. (2009) reported the results of the second investigation, which used electrocoagulation with iron electrodes to remove 98% of Reactive Black 5 from synthetic wastewater.

A dye concentration of 100 mg/L, a pH of 5, a current density of 4.575 mA/cm², a salt concentration of 3,000 mg/L, a temperature of 20 °C, and an inter-electrode spacing of 2.5 cm are the ideal treatment conditions. Additionally, it has been noted that electrocoagulation using Al electrodes has a greater removal effectiveness than electrocoagulation using Fe electrodes (Wang, 2009). According to Ilhan (2008), under the identical treatment settings, Al electrodes provide greater COD and NH₃N elimination of 56% as opposed to 35% for the Fe electrode. According to Shivayogimath et al. (2013), the pH of 6 and a voltage of 9V guarantee the best hydrogen yield when utilising Al electrodes.

It is noteworthy that leachate has the capacity to electrocoagulate hydrogen gas at yields that are close to the theoretical maximum of 4 mol H₂/mol of hexose consumed (Pawar et al., 2013). The EC method for using leachate to produce hydrogen is still only being widely adopted by a small number of companies. Due to the large quantity of garbage that is being accumulated today and how negatively it will damage the environment for decades, there have been few research on the production of hydrogen gas from leachate, despite the fact that it is essential to fixing the leachate problem. The major goal of this work is to investigate the potential for producing hydrogen gas by the EC process utilizing several electrode types (Al, Ni, and Fe), and then to use response surface methodology (RSM) to optimize the operating conditions (pH and voltage).

3 MATERIALS AND METHODS/METHODOLOGY/EXPERIMENTAL PROCEDURE (10 point)

a. *Materials Source*

Leachate samples of about 75 litres were taken from one of the Malaysian treatment facilities in Selangor for the electrocoagulation process. The samples were initially kept in a refrigerator at 4 degrees Celsius. Aluminium, Nickel, and Iron electrodes of three different types, a DC-voltage rectifier with a variable device (BK PRECISION - DC regulated power supply model 1621A), a gas bag and delivery tube (TEDLAR 0.6 LITRES), and acidic buffer solutions (prepared sulphuric solution) were sourced and used in the subsequent experiments.

b. *Physicochemical Characteristics of leachate*

The gathered leachate was sent for laboratory analysis utilising a variety of methodologies, including APHA 2007 and direct measurement with YSI probe (QWI-CH/17-33) to ascertain its properties for comparison with the findings from experiments conducted. According to the ALS Technichem, characteristics like temperature, pH, total suspended solids (TSS), copper, aluminium, and zinc content, as well as biochemical and chemical oxygen demands (BOD and COD), were examined. Using a gas detector (Crowcon), the composition of the biogas that the leachate from each experiment produced was identified.

c. *Experimental Set-up*

The electro-coagulation experimental setup for this study is presented in Figure 1. The experimental set was applied distinctly for the three types of electrodes (Al, Ni and Fe) considered in this study. This shows that electrodes were continuously changed. Initially, 800 ml of the leachate sample was filled into the glass container of 1.3L. The glass container was placed on the hot plate magnetic stirrer (E) while the instalment of electrodes plates (A and B) was connected to the power supply for adjusting different voltage (F) throughout the experiment. After each experiment, the gas collected in the gas bag (D) through the delivery tube (C) was transferred out using a syringe into the Crowcon gas analyser. The volume of gas in ppm was detected and shown in the device for comparing and recording.

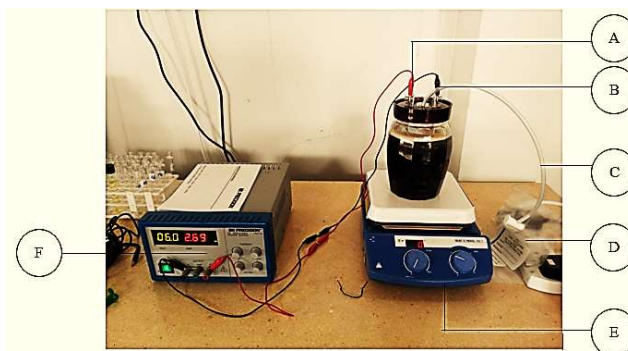


Figure 1. Experiment set-up for the electrocoagulation process for H₂ production from leachate (A-anode wiring, B-cathode wiring, C-tubing of gas flow, D-gas bag 0.6L, E-hot plate magnetic stirrer, F-DC regulated power supply)

d. *Experimental layout and Performance Optimisation*

Design-Expert version 7.0 was used to develop the experimental layout based on the considered two independent factors (voltage and pH). The developed experimental layout was applied independently using the selected electrodes (Al, Ni and Fe). The summary of the experimental layout is presented in Table 1. The experimental factors were varied to different levels which ranged from 4-8 and 3-9V for the pH and voltage, respectively.

Table 1. Summary of the CCD experimental layout for the combined pH-X1 and voltage-X2 factors

Variable	Parameters	Level		
		+1	0	-1
X ₁	pH-A	4	6	8
X ₂	Voltage (V)- B	3	6	9

The central composite design (CCD) component of the response surface methodology (Design-Expert version 10.0) was employed in the optimization of hydrogen gas production from the electrocoagulation process through leachate as a substrate. Based on the experimental layout, a total of 13 runs of experiments were required to perform with 4 replications of the centre point. The regression model was calculated by analysing the analysis of variance (ANOVA), p-and F-value. The adequacy of the model was expressed by the coefficient of determination, R² followed by the predicted- R² and adjusted R² value. The model describes the interaction among the parameters influencing the response by varying them concurrently by 3D surface graph and ANOVA. The value of R² was compared to visualized the modelling abilities towards the experimental data. Hence, readings of predicted values against the experimental values were plotted and investigated for its suitability for optimal conditions. These procedures were applied distinctly for the three types of the electrodes considered in this study, and then the H₂ yield under the varying conditions was compared.

e. *Analytical Methods*

At the end of each experiment using a particular type of the electrode, the collected hydrogen gas in the gas-bag was retrieved with a syringe, H (Model: TERUMO-60ml) and then analysed using Crowcon gas analyser, G (as depicted in Figure 2). Also, the physicochemical characteristics of the leachate were analysed using calorimetric methods in accordance with (APHA Standard Method, 2007).



Figure 2. Setup for gas analysis using the Crowcon Analyser

4 RESULTS AND DISCUSSION

a. Physicochemical characteristics

Table 2 presents the physicochemical properties of the leachate sample alongside the Malaysian discharge limit. Virtually all the examined parameters exceed the standard limits, and this further confirms that releasing of such waste without proper remediation is unhealthy for the environment. It was only the pH that can be considered within the acceptable limit, but as for the other parameters they were far above the Department of Environment Malaysia (DOE) limit (Table 2). It is important to note that the level of contaminants concentrations in leachates depends on several factors such as deposition durations, method of depositions, environmental factors as well as the types of waste (Kabuk *et al.*, 2013; Shivayogimath *et al.*, 2013). Thus, it is crucial to determine the initial physicochemical characteristics of the leachate before treatment to establish the basis for comparison with the DOE standard and level remediation.

Table 2. Physicochemical characteristics of the leachate sample

Parameters	Unit	Leachate	DOE Standards
pH	--	9.7	6-9
Temperature	°C	20.8	20
Total Suspended Solid (TSS)	mg/L	870	50
Biochemical Oxygen Demand (BOD)	mg/L	1610	20
Chemical Oxygen Demand (COD)	mg/L	4340	120
Ammonia-N	mg/L	2440	50
Free Chlorine	mg/L	<0.5	

b. Experimental results

Based on the CCD experimental layout, the treatments were applied and the corresponding hydrogen gas produced using Al; Ni and Fe electrode were recorded into the experimental matrix, as presented in Table 3. Essentially, the three electrodes were subjected to similar treatment conditions.

Table 3. Experimental matrix for treatment factors with respective H₂ values for the electrodes

Run	Factor 1	Factor 2	Hydrogen Gas (ppm)		
	A: pH	B: Voltage	Al-Electrode	Ni-Electrode	Fe-Electrode
1	9	6	510	332	422
2	8	9	696	538	551
3	4	6	463	450	262
4	6	6	697	683	550
5	4	3	153	77	101
6	6	6	697	690	546
7	4	9	697	809	554
8	6	6	697	554	551
9	6	2	151	89	109
10	8	3	156	108	103
11	6	2	173	77	109
12	6	6	695	550	551
13	6	6	600	457	552

The highest volume of 809 ppm of the hydrogen gas was obtained at 9V voltage and pH of 4 with Ni electrode while, 697 and 554 ppm were recorded with Al and Fe electrodes, respectively. At this same voltage magnitude of 9V but pH of 8, the H₂ yield with Ni reduced to 538 ppm, while for AL and Fe electrode remains approximately stable at 696 and 551 ppm, respectively. As the voltage reduced to 2-3V, the H₂ yield using Ni electrode dramatically reduced to 77 ppm and this recorded the least hydrogen gas production in this study. At treatment condition of 6 V and pH of 6, an upturn performance of 697 ppm was obtained with the Al electrode as

against 554 and 551 ppm for the Ni and Fe electrodes, respectively. It can be noticed that higher voltage favours more hydrogen gas production. This remark is in strong agreement with previous studies (Shivayogimath *et al.*, 2013; Bazrafshan. *et al.*, 2007 and Yao Hua Ch. *et al.*, 2008).

c. Analysis of variance (ANOVA) and regression model

The results of the analysis of variance for the H₂ yield data obtained for the three electrodes are as shown in Table 4. The Model F-value of 64.90, 21.42 and 24.34 for the Al, Ni and Fe imply the model is significant at P<0.05 and there is only 0.01-0.04% chance of disturbance due to noise (Table 4). In this analysis, a "Prob > F" value less than 0.0500 indicate model terms are significant. Thus, it is obvious that the regression analysis of the experimental design for the Al-electrode shows that the linear model terms B(Voltage) and the two quadratic model term (A² and B²) are significant at this confidence level (P<0.05) with respective F-values of 146.37, 39.00 and 26.48. It can be noticed that the only significant terms when the Ni electrode was used were B and the quadratic term of A², and the corresponding F-values were 56.24 and 8.75, respectively. The Fe electrodes show a similar response to that of Al. The significant terms were B, A² and B², with corresponding F-values of 57.99, 16.68 and 7.68, respectively. It can be noticed that in all the three regression analysis B-linear term (voltage) is highly significant but its quadratic term only shows some effect with Al and Fe electrode. However, the linear term A (pH) was not significant irrespective of the type electrode. Thus, the regression model for the H₂ production based on the significant terms using Al, Ni and Fe electrodes were as expressed in Eq. 1, 2 and 3, respectively.

$$H_{2-Al\text{ Electrode}} = 691.32 + 257.69 \times B - 131.57 \times A^2 - 115.92 \times B^2 \quad (1)$$

$$H_{2-Ni\text{ Electrode}} = 581.11 + 281.65 \times B - 109.89 \times A^2 \quad (2)$$

$$H_{2-Fe\text{ Electrode}} = 538.06 + 218.35 \times B - 115.82 \times A^2 - 84.04 \times B^2 \quad (3)$$

Table 4. Analysis of variance (ANOVA) of the model for H₂ production using Al, Ni and Fe electrode

Source	Al-Electrode		Ni-Electrode		Fe-Electrode	
	F Value	Prob > F	F Value	Prob > F	F Value	Prob > F
Model	64.90	< 0.0001	21.42	0.0004	24.34	0.0003
A-pH	3.84	0.0843	0.86	0.3837	3.34	0.0758
B-Voltage	146.37	< 0.0001	56.24	0.0001	57.99	0.0001
AB	1.005E-003	0.9756	3.28	0.1132	2.465E-004	0.9879
A ²	39.00	0.0004	8.75	0.0211	16.68	0.0047
B ²	26.48	0.0013	3.70	0.0957	7.68	0.0276
R ²	0.9789		0.9387		0.9251	
Adj-R ²	0.9638		0.8948		0.8165	
Pred-R ²	0.5123		0.6374		0.6021	

The fit of the regression models for the three electrodes was also expressed by the coefficients of determinations R², which were found to be 0.9789, 0.9387 and 0.9251 for Al, Ni and Fe electrodes, respectively. The data were further diagnosed by plotting a linear graph between the actual and predicted values, as presented in Figure 3a, b and c, respectively. It can be observed that the data points were all around the diagonal line, and this implies insignificant deviations. More so, the respective adjustable and predicted R² values were (0.9638; 0.5123), (0.8948; 0.6374) and (0.8165, 0.6021). Thus, the excellent correlation values of R² shows that the regression models are adequate to navigate the design space, and as such, they are suitable for predicting the H₂ yield.

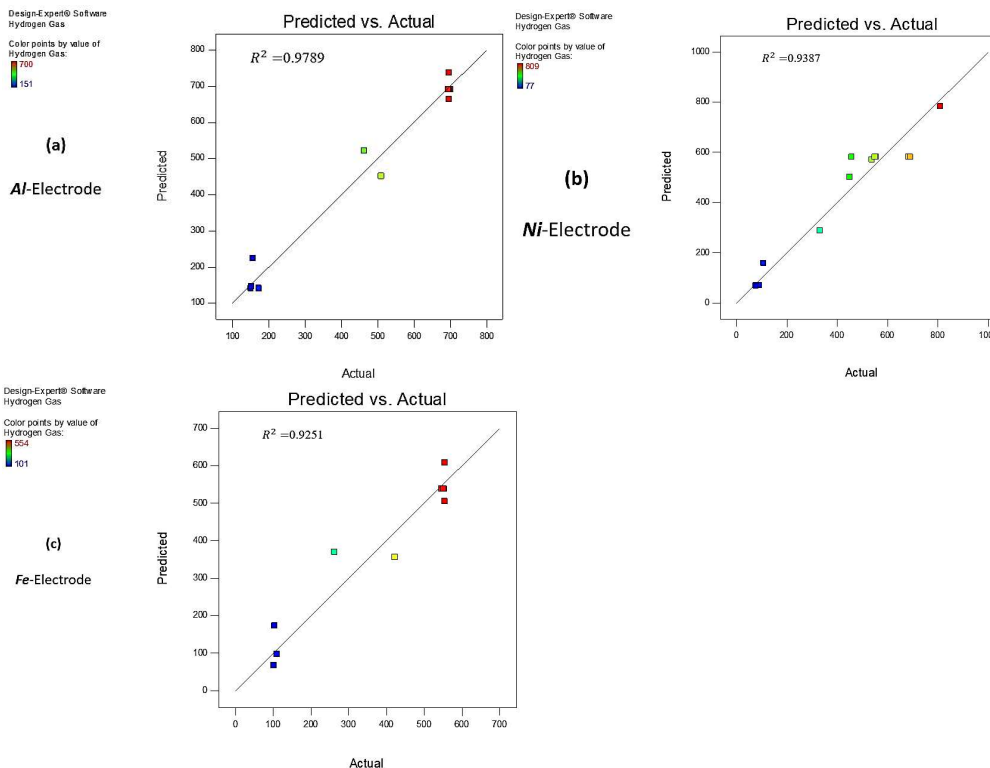


Figure 3. Linear correlation between the actual and predicted H₂ yield using (a) Al-electrode, (b) Ni-electrode, and (c) Fe- electrode

d. Response Surface of the synergistic effect of treatment factors on the optimal hydrogen gas production

As shown in Figure 4a, b and c, hydrogen gas production increases with the voltage but decreases gradually as the voltage decreases to lower ranges. The surface response alongside with contour of Figure 4a, based on the optimization criterion, the optimal hydrogen yield (697 ppm) was obtained at the voltage 9V and pH of 6 with Al electrode, though the corresponding predicted value was 833.091 ppm. Figure 4(b) illustrated the optimized condition for H₂ production using the Ni electrode. Similarly, higher voltage (9V) favours H₂ production with an optimal yield of 554 ppm and the predicted values of 617.391 ppm, but this is considerably lower compared to that of the Al-electrode. This observation is in good agreement with the report of Shivayogimath *et al.*, (2013). Furthermore, Figure 4(c) depicts the surface response of the combined effect of voltage and pH on the optimal hydrogen production using the Fe. An optimal value of 551 ppm with a corresponding predicted value of 672.372 ppm was obtained. Generally, it can be noticed from these figures that the impact of the pH on the H₂ yield was not significant. Bazrafshan. *et al.*, 2007 and Yao Hua Ch. *et al.*, 2008 reported that the increase in pH may be as a result of hydrogen evolution at the cathodes electrode. Chafi *et al.* (2011) contested that the surge in pH was only due to the release of CO₂ from the wastewater, though H₂ bubble were generated as disturbance during the process. They further explained that, at lower pH, the CO₂ is over-saturated in wastewater and as such H₂ is released leading to an increase in the pH value. In this study, the pH did not affect the treatment processes significantly despite the wide range of the variation.

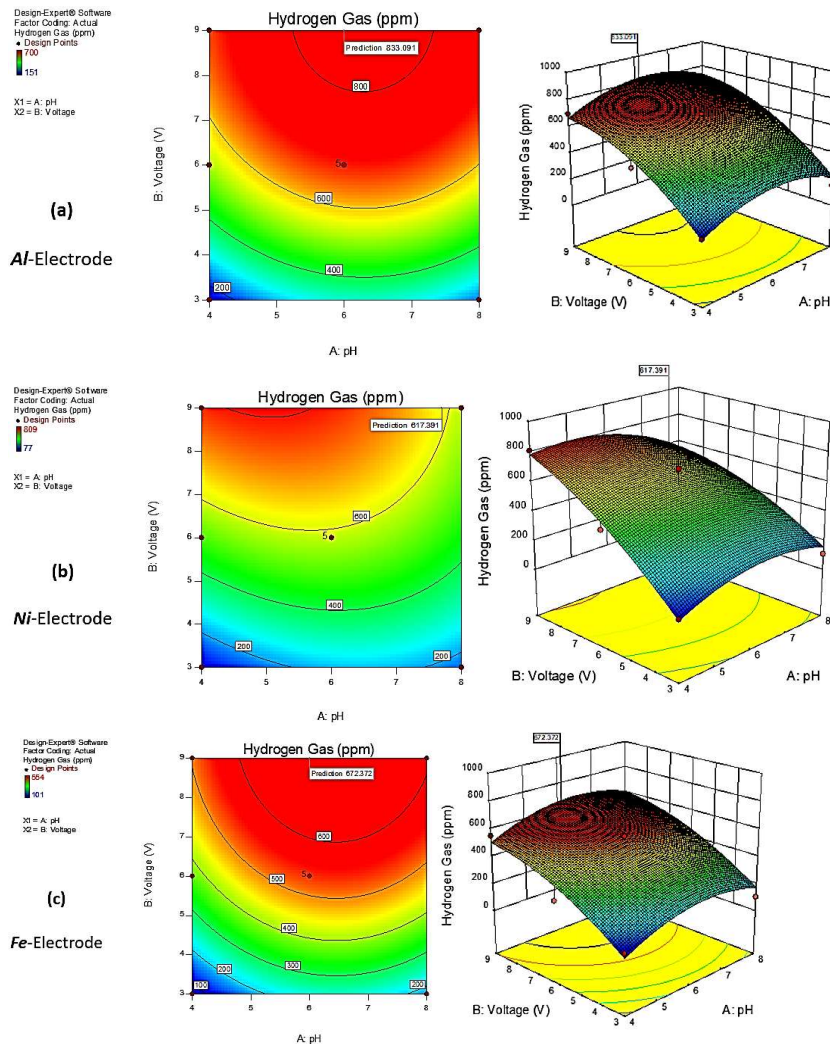


Figure 4. contour plots and response surface of the synergistic effect of combined pH and voltage on optimal hydrogen gas production using (a) Al-electrode, (b) Ni-electrode, and (c) Fe- electrode

4.0. CONCLUSION

The electrocoagulation process based on varying voltage and pH, using different types of electrodes (Al, Ni, Fe) for hydrogen production from leachate was successfully optimized using response surface methodology (RSM). CCD optimization component of RSM was applied in this study and the results show that the Al electrodes give an optimum H_2 yield of 697 ppm at the most suitable treatment parameters of pH 6 with the voltage of 9V for 20 min treatment durations. While, the H_2 yield under these same conditions using Ni and Fe electrodes were 554 and 551 ppm, respectively. The respective model coefficient of correlation (R^2) for the experimental and predicted H_2 value were 0.9789, 0.9387 and 0.9251. This shows the precision of the regression model is adequate to navigate the design space, and as such, it can be efficiently used for the prediction of hydrogen production from leachate under the electrocoagulation process conditions.

5.0. ACKNOWLEDGEMENT

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