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Correlation Studies and Kinetic Modelling of Electrocoagulation Treatment of Pepper Wastewater

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ABSTRACT

Pepper processing is one of the largest productions that significantly contribute (98%) to Sarawak, Malaysia's economic and agricultural sectors. The prolonged retting process of pepper berries would cause undesirable dark colour and acidic wastewater. This study aims to evaluate the performance of an electrocoagulation treatment using nickel and copper electrodes for the changes in turbidity and pH of pepper wastewater. Some analyses (correlation studies and kinetic modelling) were studied. The electrocoagulation treatment was conducted by having two conditions nickel and copper electrodes immersed in 400 mL of pepper wastewater for 30 minutes. Every 5 minutes, it was monitored, and the sample was taken for further analysis. The results indicated a significant decrease in the turbidity of pepper wastewater for nickel (98.25%) and copper electrodes (86.32%) was noticed with the increase in the electrocoagulation treatment time. At the same time, the pH values for nickel and copper electrodes were increased by 27.43% and 31%, respectively. The results were evaluated by using Principal Component Analysis (PCA). PCA describes the correlation between the wastewater qualities in this study within less time. Among four models (zero, first and second-order) applied in this study, the turbidity for nickel and copper electrodes had the highest R^2 values (0.9457 and 0.9899) in the zero-order model. For pH, the second-order model had the highest R^2 values (0.9508 and 0.9657) for nickel and

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copper electrodes. Electrocoagulation using nickel and process electrodes is a practical method to treat pepper wastewater.

Keywords: Correlation, electrocoagulation, kinetic, pepper, pH, treatment, turbidity, wastewater

INTRODUCTION

Pepper is known as the 'King of Spices', which has a sharp, pungent aroma and flavour and light colour. The pepper processing is one of the largest productions in Sarawak, Malaysia, by 98% (Rosnah & Chan, 2014). According to International Pepper Community and Malaysian Pepper Board, Malaysia was the fifth-largest pepper producer in the world production. The retting process is necessary to soften the pericarp of mature pepper berries to produce the white pepper. The main source of water pollution is bioactive compounds and organic matter leached into the water during the prolonged retting process of pepper berries and pericarp degradation (Aziz et al., 2019). It was caused by the high turbidity of wastewater, which was the presence of suspended particulates in water inhabiting the passage of light that caused the dark colour produced (Mandal, 2014). Meanwhile, the low pH would be produced acidic wastewater. At the same time, the inorganic matter and microorganisms in the water produced low-quality wastewater. The low quality of wastewater produced harms the environment and living things. Pepper wastewater should be treated before discharge to minimise its negative effects on the environment and living things. There are national standards of turbidity and pH for wastewater discharge limit by the Department of Environment (DOE). Therefore, the standard discharge limit for turbidity and pH is 50 NTU and 6-9, respectively.

In order to treat the pepper wastewater, electrocoagulation is used to reduce the turbidity and increase the pH. Electrocoagulation implies simple equipment that can be performed in small and tiny treatment facilities (Dura, 2013). In its most basic form, an electrochemical cell consists of two electrodes, the anode and the cathode. It is immersed in a conducting solution or electrolyte and connected by an electrical circuit with a current source and control device. The reduction occurred at the cathode, while oxidation occurred at the anode. There are three electrocoagulation stages: coagulation, destabilisation of contaminants and particulate suspension, and floatation (Dura, 2013). According to Danial et al. (2017), Liu et al. (2017) and Bakshi et al. (2019), the following are the chemical reactions that occurred at the anode and cathode as shown in Equations 1 to 4.

For cathode:

$$2H^{+}_{(aq)} + 2e^{-} \rightarrow H_{2(g)} \quad (1)$$

For anode:

$$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^{-} \quad (2)$$

$$Cu^{2+}_{(aq)} + H^{+}_{(aq)} + \frac{1}{4}O_{2}{}_{(g)} \rightarrow Cu^{2+}_{(aq)} + \frac{1}{2}H_2O_{(l)} \quad (3)$$

$$Cu^{2+}_{(aq)} + 2H_2O_{(l)} \rightarrow Cu(OH)_{2(s)} + 2H^{+}_{(aq)} \quad (4)$$

Since the turbidity and pH of pepper wastewater were changed during the electrocoagulation treatment, the correlation between wastewater qualities and treatment time was studied. The experimental results were also evaluated using statistical analysis such as Principal Component Analysis (PCA). PCA includes identifying the significant parameters in the experiment and determining the correct relationship between the parameters within less time (Patil & Dwivedi, 2020).

The kinetic orders of reactions, such as the zero, first and second-order models, are used to predict changes in turbidity and pH. The rate equations for zero, first and second-order mathematically express the changes (Li et al., 2022). The orders of reaction are included in the rate equation. There is a lack of studies about the changes in turbidity and pH of pepper wastewater during the electrocoagulation treatment using nickel and copper electrodes. As a result, the objectives of this study were to (1) determine the changes in turbidity and pH of pepper wastewater during the electrocoagulation treatment, (2) perform PCA in determining the clustering turbidity and pH of pepper wastewater within nickel and copper electrodes used during the electrocoagulation treatment and (3) develop kinetic models that express the changes in turbidity and pH of the wastewater.

MATERIALS AND METHODS

Sample Preparation

The wastewater produced from the retting process of pepper berries after 7 days were collected and used as a sample.

Experimental Set-Up

This study conducted the electrocoagulation treatment of wastewater from the retting process of pepper berries using a laboratory scale. The container was made up of transparent plexiglass with dimensions of 12.5 cm (height) × 8 cm (diameter). The experiment of the electrocoagulation treatment of pepper wastewater was set up (Figure 1).

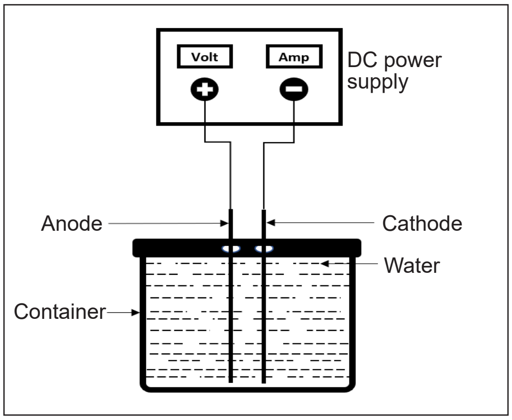

Figure 1. Schematic diagram of the electrocoagulation treatment of pepper wastewater

About 400 mL of wastewater was placed into the container with two vertical electrode plates as an anode and cathode with an interspacing distance of 0.5 cm (Tharmalingam et al., 2017). The electrodes used were made of nickel and copper with the dimensions of 15 cm (length) × 5 cm (width) × 0.1 cm (thickness) (Che et al., 2020). A DC-regulated power supply (MCP M10-SP6005 L) provided current intensities in 0-1A. All runs were done at room temperature. The electrocoagulation treatment was monitored for 30 minutes. The samples were taken at different retention times (0, 5, 10, 15, 20, 25, and 30 minutes) to evaluate the performance of the changes in turbidity and pH of the wastewater using nickel and copper electrodes. After electrocoagulation treatment, the wastewater was allowed to settle for 30 minutes before being collected for analysing turbidity and pH. The electrodes were properly washed with deionised water between runs to remove any solid residue on the surface. Determining turbidity and pH of wastewater were recorded and replicated five times.

Determination of Turbidity

The change in turbidity of wastewater during the electrocoagulation treatment was evaluated using a turbidity meter (2100 Q, HACH, USA). About 10 mL of the wastewater was used to determine turbidity every 5 minutes.

Determination of pH

The change in pH of wastewater during the electrocoagulation treatment was investigated using a pH meter (Spear pH Tester, China). About 30 mL of the wastewater was used to determine pH every 5 minutes.

Turbidity and pH removal efficiencies after each treatment were calculated using Equation 5 (Tharmalingam et al., 2017):

$$\text{Removal efficiency} = \frac{C_0 - C}{C_0} \times 100\% \tag{5}$$

where C_0 and C are turbidity or pH of wastewater before and after treatment.

Kinetic Study

In this study, zero, first, and second-order models described the kinetics of the changes in turbidity and pH determined for wastewater during the electrocoagulation treatment. The coefficient (R^2) was determined to evaluate the best kinetic model-fitting analysis. The zero, first and second-order kinetic models were expressed as Equations 6 to 8 (Azman et al., 2020):

$$Zero\ order = C = -kt + C_0 \tag{6}$$

$$First\ order = C = -kt + lnC_0 \tag{7}$$

$$Second\ order\ = \frac{1}{C} = kt + \frac{1}{C_0} \qquad (8)$$

where C = the measured value for each parameter (turbidity and pH); C_0 = the initial value of the measured turbidity and pH of wastewater; k = rate constant; t = time of electrocoagulation treatment.

Statistical Analysis

A Tukey's test was applied to all data as a function of time by performing a one-way Analysis of Variance (ANOVA) analysis to differentiate and determine the significance of the mean values. Each analysis was analysed for triplicate data, and the mean and standard were reported. The confidence limits were considered as 95% ($p < 0.05$). Correlations between each parameter, including turbidity and pH of wastewater, were assessed by performing the Pearson correlation coefficient ($p < 0.05$). Statistical analyses, including PCA, were performed using Minitab Statistic 16 Edition.

RESULTS AND DISCUSSION

Turbidity and pH of pepper wastewater are the most important factors affecting white pepper quality. Therefore, the pepper wastewater should be monitored and evaluated to ensure that its discharge was followed according to the discharge limit standards by DOE. Table 1 shows the changes in turbidity and pH of wastewater during the electrocoagulation treatment using nickel and copper electrodes.

Determination of Turbidity

The initial turbidity of wastewater for nickel electrodes was 830.67 ± 0.58 NTU. Based on Table 1, the turbidity of wastewater for nickel electrodes had decreased steadily with the value of 558.00 ± 1.00 NTU after 5 minutes of electrocoagulation treatment. It continued to decrease until it reached 14.53 ± 0.58 NTU after 30 minutes of the treatment with a removal efficiency of 98.25%. Next, copper electrodes had the same value of turbidity as nickel electrodes. The wastewater turbidity attained after 5 minutes for copper electrodes was 721.00 ± 1.00 NTU. After 30 minutes of electrocoagulation treatment, it decreased gradually by 86.32% with a value of 113.67 ± 0.58 NTU.

As can be seen in Figure 2(a), the turbidity of wastewater significantly ($p < 0.05$) decreased from 5 minutes until it reached the lowest value after 30 minutes of electrocoagulation treatment using nickel and copper electrodes. The percentage of turbidity removal efficiency for nickel (98.25%) and copper electrodes (86.32%) could be observed with electrocoagulation treatment. The increment in OH^- ions production and hydrogen gas concentration affected this turbidity removal efficiency. The lightweight flocks were forced to float towards the surface, and the large and heavy flocks settled under the gravitational force. From the results (Table 1), electrocoagulation treatment using nickel electrodes proved to be better than copper electrodes in reducing the turbidity of pepper wastewater. Furthermore, the previous work of Tharmalingam et al. (2017) had 90.76% of turbidity removal by using aluminium during the electrocoagulation treatment of pepper wastewater. Therefore, the nickel electrodes had the highest turbidity removal of pepper wastewater compared to the aluminium and copper electrodes.

Table 1
Mean values for turbidity and pH of wastewater during 30 minutes of electrocoagulation treatment

Time (min)	Properties of soaking water			
	Turbidity (NTU)		**pH**	
	Ni	**Cu**	**Ni**	**Cu**
0	830.67 ±0.58[a]	830.67 ±0.58[a]	4.92 ±0.01[g]	4.92 ±0.01[g]
5	558.00 ±1.00[b]	721.00 ±1.00[b]	4.95 ±0.01[f]	5.07 ±0.01[f]
10	457.67 ±0.58[c]	604.67 ±0.58[c]	5.11 ±0.01[e]	5.26 ±0.02[e]
15	334.67 ±0.58[d]	440.33 ±0.58[d]	5.34 ±0.01[d]	5.61 ±0.01[d]
20	89.00 ±0.58[e]	282.67 ±0.58[e]	5.99 ±0.02[c]	6.46 ±0.01[c]
25	43.00 ±0.58[f]	212.33 ±0.58[f]	6.24 ±0.01[b]	6.76 ±0.02[b]
30	14.53 ±0.58[g]	113.67 ±0.58[g]	6.78 ±0.01[a]	7.13 ±0.02[a]

Note. Data are expressed mean ±SD; turbidity (NTU); pH; Ni, nickel electrodes; Cu, copper electrodes. Different letters indicate statistically significant differences exist $p < 0.01$ for each column. The means that do not share a letter is significantly different. Tukey's test was applied with 95% simultaneous confidence intervals.

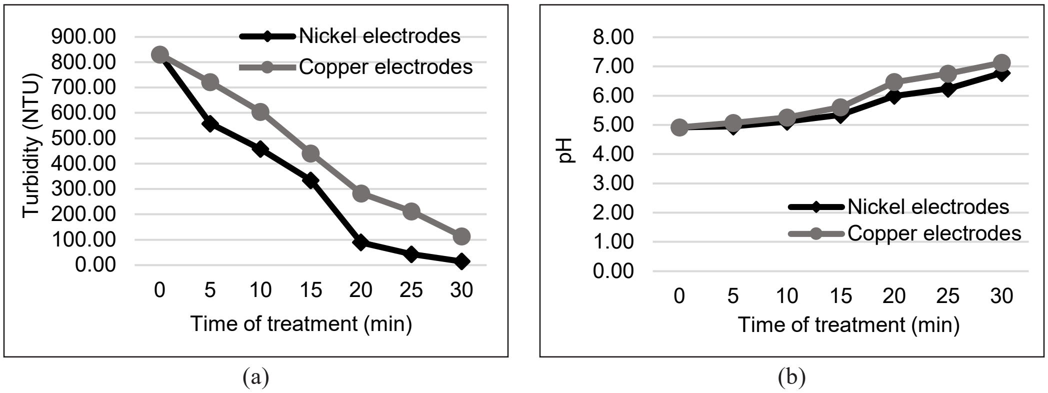

Figure 2. Graph of the effect of electrocoagulation treatment using nickel and copper electrodes on (a) Turbidity; and (b) pH of pepper wastewater

Determination of pH

The initial pH of wastewater for nickel and copper electrodes was acidic, with a value of 4.92 ± 0.01. The pH of wastewater for nickel electrodes had increased gradually with the value of 4.95 ± 0.01 after 5 minutes of electrocoagulation treatment, as shown in Table 1.

It continued to increase until it reached 6.78 ± 0.01 after 30 minutes of the treatment with an increment efficiency of 27.43%. Next, the pH of wastewater attained after 5 minutes for copper electrodes was 5.07 ± 0.01. After 30 minutes of electrocoagulation treatment, it increased steadily by 31% at 7.13 ± 0.02.

As indicated in Figure 2(b), the pH of wastewater was significantly ($p < 0.05$) increased from 5 minutes until it reached the highest value after 30 minutes of electrocoagulation treatment using nickel and copper electrodes. Therefore, the percentage of pH increment efficiency for nickel (27.43%) and copper electrodes (31%) could be observed with electrocoagulation treatment after 30 minutes. Overall, electrocoagulation using copper electrodes proved to be better than nickel electrodes in increasing the pH of pepper wastewater. However, the aluminium electrodes in the previous work had the highest pH increment of pepper wastewater by 37.22% compared to the nickel and copper electrodes (Tharmalingam et al., 2017).

Correlations for Turbidity and pH of Wastewater During the Electrocoagulation Treatment

The correlation analysis showed significant ($p < 0.05$) wastewater qualities for the electrocoagulation treatment using nickel and copper electrodes, as shown in Table 2. For nickel electrodes, the correlation coefficient between turbidity and pH was highly negative, with a value of -0.907 ($p < 0.05$). Also, the turbidity was highly negatively correlated with the pH ($r = -0.977$, $p < 0.01$) for copper electrodes. Therefore, the turbidity decreased proportionally with the increased pH applied for nickel and copper electrodes.

Table 2
Correlations for turbidity and pH of wastewater attribute during the electrocoagulation treatment

Electrode	Ni		Cu	
Parameter	Turbidity (NTU)	pH	Turbidity (NTU)	pH
Turbidity (NTU)	1		1	
pH	−0.907**	1	−0.977***	1

Note. Data are expressed turbidity (NTU); pH; Ni, nickel electrodes; Cu, copper electrodes
*Not significant, **Significant at $p < 0.05$, ***Significant at $p < 0.01$

Principal Component Analysis for Turbidity and pH of Pepper Wastewater During the Electrocoagulation Treatment

PCA was done to determine the clustering turbidity and pH within the electrocoagulation treatment's two different electrodes (nickel and copper). According to Figure 3(a), PC1 explained 92.60% of the total variance of turbidity and pH. Also, PC1 was dominant compared to PC2. Based on the PCA score plot [Figure 3(a)], PC1 and PC2 were used to demonstrate the PCA results. They specified a clear and scattered separation between the two electrodes based on the turbidity and pH during the electrocoagulation treatment of pepper wastewater. Theoretically, the PCA results demonstrated that the turbidity and pH could discriminate the influence of the different electrodes used during the electrocoagulation treatment. Hence, their changes were verified by classifying the two electrodes used during the electrocoagulation treatment.

The PCA loading plot of the turbidity and pH is shown in Figure 3(b). The loading plot delivered information on the correlations among the turbidity and pH during the electrocoagulation treatment using nickel and copper electrodes. Based on Figure 3(b), the pH was loaded positively on PC1, whereas turbidity was loaded negatively on PC1 and PC2, respectively. Figure 3(c) shows the eigenvalues for each PC, which resulted in the scree plot. Figure 3(c) shows that the PC1 has an eigenvalue greater than 1. As a result, a straight line formed in the scree plot, in which only PC1 and PC2 were involved.

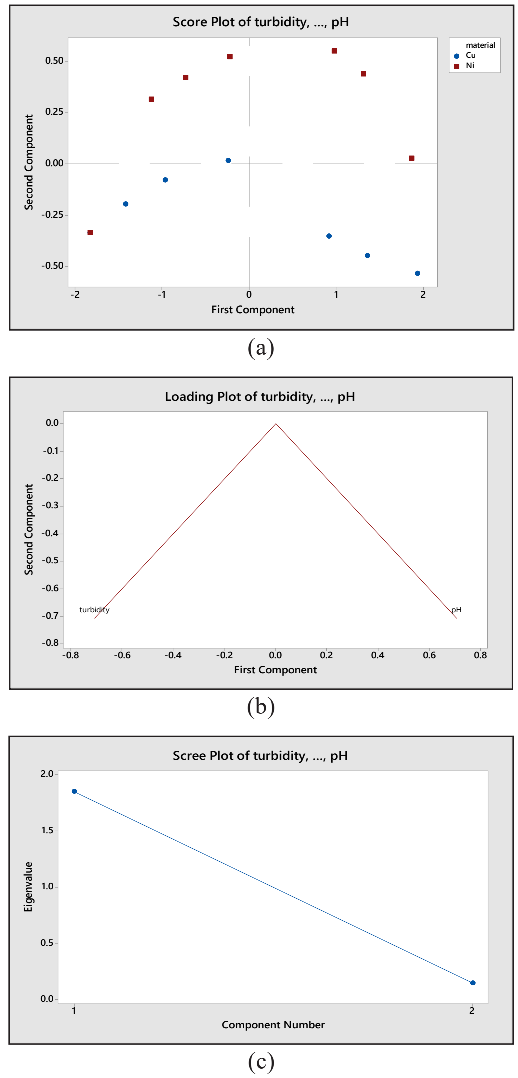

Figure 3. The PCA graph of the turbidity and pH during the electrocoagulation treatment of pepper wastewater. (a) Score plot; (b) Loading plot; and (c) Scree plot

Kinetic Study of Changes in Turbidity and pH of Wastewater

The kinetic parameters for the quality changes in wastewater for nickel and copper electrodes are indicated in Table 3. The turbidity of pepper wastewater agreed with the zero-order model based on the highest R^2 values (0.9457 and 0.9899 for nickel and copper electrodes, respectively) obtained compared to the values of the first and second-order kinetic models. The rate constant (k) value of the zero-order model for turbidity using nickel electrodes was 27.479 NTU min^{-1}, which indicated that the turbidity reduction of pepper wastewater occurred faster than copper electrodes during the electrocoagulation treatment (Table 3). For the pH of pepper wastewater, the second-order model had the highest R^2 values (0.9508 and 0.9657 for nickel and copper electrodes, respectively) obtained compared to the values of the zero and first-order kinetic models. The *k* value of the second-order model for pH using copper electrodes was 0.0023 NTU^{-1} min^{-1}, which indicated that the pH increment of pepper wastewater occurred slightly faster than nickel electrodes during the electrocoagulation treatment.

Table 3
Kinetics of the changes in turbidity and pH of pepper wastewater during the electrocoagulation treatment

Parameter	Type of electrodes	Zero-order model		First-order model		Second-order model	
		k (NTU min^{-1})	R^2	k (min^{-1})	R^2	k (NTU^{-1} min^{-1})	R^2
Turbidity	Ni	27.479	0.9457	0.1350	0.9296	0.0018	0.6361
	Cu	24.931	0.9899	0.0655	0.9563	0.0002	0.7947
Parameter	**Type of electrodes**	**Zero-order model**		**First-order model**		**Second-order model**	
		k (min^{-1})	R^2	k (min^{-1})	R^2	k (min^{-1})	R^2
pH	Ni	0.0646	0.9301	0.0113	0.9417	0.0020	0.9508
	Cu	0.0802	0.9529	0.0678	0.9604	0.0023	0.9657

Note. Data are expressed Ni, nickel electrodes; Cu, copper electrodes; k, rate constant (min^{-1}); R^2, coefficient.

CONCLUSION

The statistical analysis of the changes in turbidity and pH of wastewater showed significant differences ($p < 0.05$). Overall, nickel electrodes were the most affected in turbidity reduction (98.25%) by the treatment time compared to copper electrodes. Meanwhile, copper electrodes had the highest (31%) pH increment after the electrocoagulation treatment compared to nickel electrodes. The correlations indicated that the turbidity was highly negatively correlated with the pH of pepper wastewater for nickel and copper electrodes. PCA very precisely describes the correlation among the wastewater qualities in the study. Also, PCA supports the hypothesis of the study. Furthermore, a kinetic model that expressed the quality changes in wastewater is presented in this study. The wastewater quality changes in turbidity and pH during the electrocoagulation treatment were adequately expressed by zero, first and second-order kinetic models. The changes in turbidity and pH of pepper wastewater using electrocoagulation treatment were evaluated effectively. Electrocoagulation using nickel and copper electrodes is a practical method to treat wastewater from the retting process of pepper berries. The experimental data from this study is estimated to be significant for evaluating wastewater's turbidity and pH changes during the electrocoagulation treatment.

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