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Abstract. The study of Fe, Ca, and Mg removal from wastewater using the electrocoagulation method in the Center for Accelerator Research and Technology (CART) has been carried out. Electrocoagulation is one of the effective wastewater treatment methods, especially for metal removal. The main purpose of this study was to evaluate the effectiveness of the electrocoagulation method in CART wastewater treatment, especially Fe, Ca, and Mg removal, before being released into the environment. The electrocoagulation reactor operates continuously using aluminium electrodes. Several parameters were used to obtain the optimal condition for Fe, Ca, and Mg removal: operational time, flow rate, and electrode distance. The result showed that the optimum condition is on the operational flow rate 1 mL/s, the processing time 2 minutes, and the distance between electrodes is 1 cm. The optimum efficiency for Mg, Fe, and Ca removal was 96.0%, 95.2%, and 79.15%, respectively; meanwhile, Total Suspended Solid (TSS) decreased by 87.5%. In addition, the kinetic model in this study was carried out by determining the reaction rate constant (k) as a function of time for three variations of flow rate. The k value for Ca and Fe removal followed the second-order kinetic model, while the Mg removal fitted the first-order kinetic model.

Keywords: Electrocoagulation; kinetic model; wastewater

1. Introduction

The Centre for Accelerator Research and Technology (CART) is one of the research and development (R&D) institutions for nuclear technology in Indonesia. These research and development activities will produce liquid waste, both radioactive and hazardous waste. The CART applied a policy of zero release system for hazardous and radioactive waste, where both wastes are not disposed into the environment directly. To facilitate environmental safety monitoring, wastewater from the CART laboratory is discharged into a wastewater integrated canal treated using a sedimentation and delay system. The contaminant and hazardous material are analysed before releasing the wastewater into the environment [1]. It was carried out to ensure that the wastewater released into the environment complies with the quality standards and regulations.

Based on several studies, the wastewater released into the environment can affect the composition of the water [2,3]. There are various types of pollutants in wastewater, including iron (Fe), calcium (Ca),

and magnesium (Mg). These elements negatively impacted the environment, such as the appearance of brown colour in water [4]. Waste disposal containing metal compounds is not only toxic to plants but also animals and humans. The characteristic of heavy metals is difficult to degrade, so it is difficult to be removed naturally. It can easily accumulate in aquatic and sedimentary environments, including aquatic biotas, such as fish and shellfish. On the other hand, heavy metals have a high half-life in the body of aquatic biota and have a large concentration value in the organism's body [5].

Based on previous studies, the TSS and hazardous materials amount in the CART wastewater affected by the rainfall, and the results are still above the environmental quality standard [1]. The concentration of TSS and hazardous materials during the rainy season fluctuates and has a lower tendency than in the dry season. The higher content in the dry season is probably due to the oxidation of Fe and Mn, which causes the water to become turbid [6]. Several processes to reduce or eliminate heavy metal content in wastewater can be carried out through chemical treatment such as precipitation, adsorption, filtration, and coagulation [7,8]. The chemical processing is usually carried out by precipitation through a flocculation coagulation process with various coagulants [9]. However, the chemical wastewater treatment process requires high cost and a difficult processing technique [10]. Therefore, it is necessary to study other methods that are more effective to remove a metal and TSS concentration in the wastewater integrated canal in the CART.

Recently, alternative methods of wastewater treatment using the electrocoagulation process have been developed. Reddhithota, *et al*. (2007) stated that the electrocoagulation method is an inexpensive and effective industrial waste treatment method. The simplicity of the electrocoagulation tool and operation, no added chemicals, low sludge formation, high removal efficiency, and effectiveness for removing suspended solids in waste made electrocoagulation a desirable treatment method [11]. Electrocoagulation is an electrochemical method for water treatment. Basically, wastewater solution is subjected to a direct electrical current (DC) through electrodes (cathodes and anodes) that are generally made of iron or aluminium. The anode will release active coagulant metal ions, while at the cathode occurs an electrolysis reaction that produces hydrogen gas. The main objective of this study is to evaluate the effectiveness of the electrocoagulation method in the treatment of wastewater in the CART integrated canal, especially Fe, Ca, and Mg removal, before being released into the environment.

2. Method

In this paper, the study of Fe, Ca, and Mg removal from the wastewater was carried out using an electrocoagulation reactor shown in Figure 1. Several parameters were evaluated, such as the efficiency of Fe, Ca, and Mg removal as a function of time, flow rate, and electrode distance. The evaluation of the TSS decrease as a function of the electrode distance was carried out, wherein the optimum current was measured in this process. In addition, the kinetic study to determine the reaction rate constant for Ca, Mg, and Fe removal was also observed.

The step of this study is shown in Figure 2. The samples were collected from the wastewater integrated canal. The wastewater has an initial concentration of Fe, Ca, Mg, and TSS 13.33 mg/L, 128.11 mg/L, 47.01 mg/L, and 160 mg/L, respectively. The electrode used was an aluminium plate with dimensions 9 cm × 8.5 cm which was arranged parallelly in an electrocoagulation reactor. The electrodes were connected to a direct electrical current (DC) power supply providing voltage 5 V, then the optimum time, flow rate, and electrode distance were observed. The operating time was ranged from 0 to 60 minutes. Furthermore, the obtained optimum time was used to determine the optimum electrode distance (1, 2, and 3 cm). The optimum time and electrode distance were used to determine the optimum flow rate with variations of 1, 3, and 5 mL/second. The residual metal concentration at wastewater samples from the electrocoagulation process was analysed using the Atomic Absorption Spectrophotometry (AAS) method.

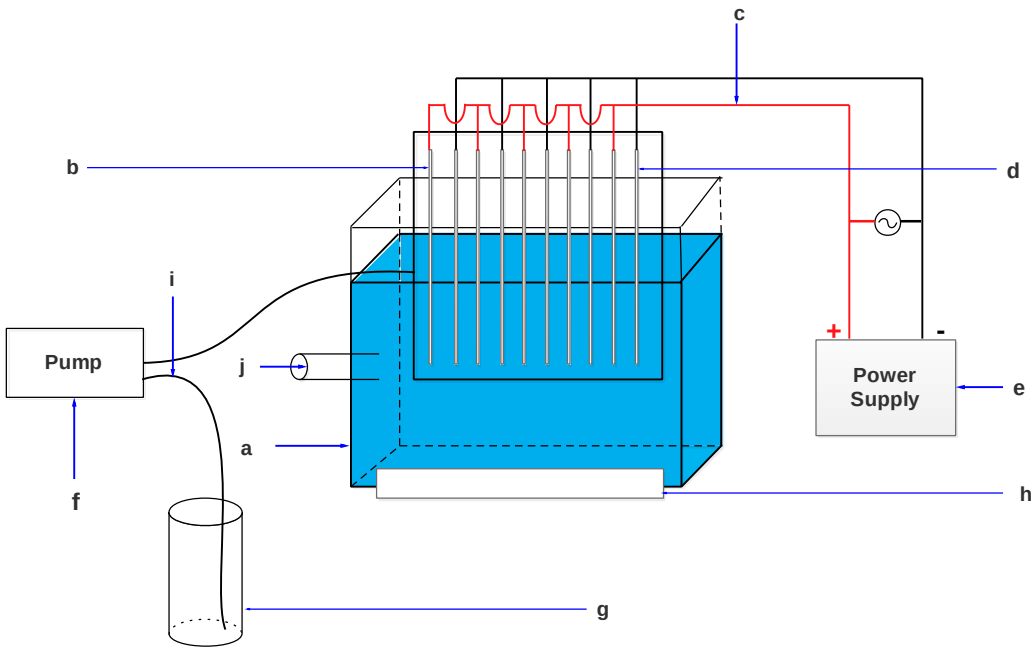

Figure 1. Schematic diagram of electrocoagulation system: a. Electrocoagulation Reactor; b. Cathode; c. Connecting cable; d. Anode; e. Power supply; f. Pump; g. Sample container, h. hot plate, i. Pump hose; j. Effluent valve.

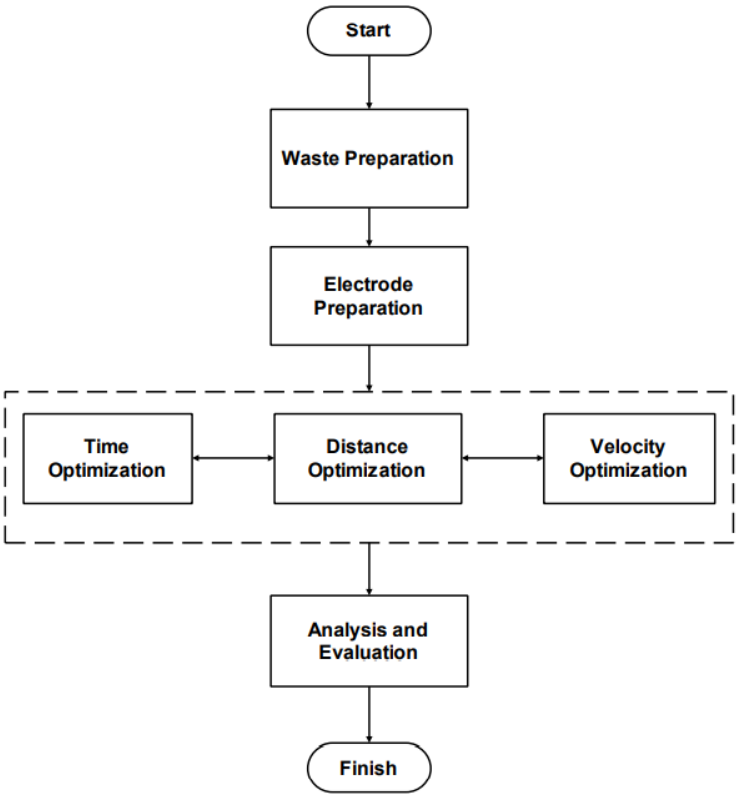

Figure 2. Flowchart of Fe, Ca, and Mg removal analysis using electrocoagulation process.

In this work, the kinetic study refers to the decrease of Fe, Ca, and Mg concentration from wastewater in a continuous reactor. Based on the previous studies, the electrocoagulation process to remove contaminants follows the first-order or second-order reaction rate. The reaction rate constant (k) is calculated using equation (1) for first-order and equation (2) for second-order. To estimate the reaction order, it is considered from the squared-correlation coefficient (R^2), which is used to measure the kinetic model's goodness [12], where C_A is the final concentration, C_{A0} is the initial concentration, and τ is residence time.

$$C_A = \frac{C_{A0}}{1+\tau k} \quad (1)$$

$$k = \frac{C_{A0}-C_A}{C_A^2.\tau} \quad (2)$$

3. Results and Discussion

In general, the dominant waste product from CART research activities is radioactive waste whose processing is carried out by the Center for Radioactive Waste Technology – BATAN. In addition, hazardous waste containing metals also existed. Based on the Ministry of Environment Regulation No. 05/2014, the quality standards of wastewater were already determined before it was released to the environment, including limits on metal elements such as Fe and TSS parameters. One of the methods used to reduce the concentration of metal elements in wastewater is the electrocoagulation method. This method has several advantages compared to other methods such as chemical processes. One of the advantages of using the electrocoagulation method is less sludge generation.

Table 1. Comparison of the electrode (anode & cathode) weight before and after the electrocoagulation process.

No	Electrode plate	Before (g)	After (g)	Difference (g)
1	Anode-1	19.820	19.790	-0.030
2	Anode-2	19.693	19.650	-0.043
3	Anode-3	19.774	19.730	-0.044
4	Anode-4	19.363	19.310	-0.053
5	Anode-5	19.550	19.519	-0.031
6	Cathode-1	19.661	19.749	0.088
7	Cathode-2	19.667	19.693	0.026
8	Cathode-3	19.850	19.897	0.047
9	Cathode-4	19.458	19.491	0.033
10	Cathode-5	19.589	19.642	0.053

The main objective of this study is to evaluate the effectiveness of the electrocoagulation method for wastewater treatment at an integrated canal in the CART. The effectiveness is determined based on the efficiency value and the constant rate of the Fe, Ca, Mg, and TSS removal. The electrode used was an aluminium plate, and the liquid waste containing metals Fe, Ca, and Mg was utilised as an electrolyte solution. The cathode is negatively charged; thus, metal ions in the electrolyte solution will be attracted to the cathode [13]. The comparison of the electrode weight before and after the electrocoagulation process is presented in Table 1. This study also evaluated the effect of several variables on the efficiency of the electrocoagulation process, including operating time, the distance between electrodes, and flow rate variables.

3.1. The effect of flow rate and time on electrocoagulation process

The variations of flow rate (1, 3, and 5 mL/second) and operating time (2, 4, 6, 8, 10, 20, 30, 40, 50, and 60 minutes) were employed in this study. The effect of operating time on the removal efficiency for Fe, Ca, and Mg is presented in Figure 3. It shows that the efficiency of metal removal increase as a function of operating time. Moreover, the flow rate also affects the continuous system electrocoagulation process since the slower flow rate causes longer electrolyte contact time so that the ion reaction increases [14]. The results show optimum waste removal efficiency occurs at a 1 mL/second flow rate. Less waste floc was produced at flow rates of 3 and 5 ml/sec because of lower contact time. Furthermore, the presence of gas prevents the waste floc bonded to the cathode.

The highest efficiency for Mg, Fe, and Ca were 96.0%, 95.2%, and 79.15%, respectively. Accordingly, the concentration reduction of magnesium and iron in the wastewater was faster than calcium. This is considered because the solubility constant (K_{sp}) of Ca is greater than that of Fe and Mg, where K_{sp} for Ca, Mg, and Fe are 4.7×10^{-6}, 5.6×10^{-12}, and 4.9×10^{-17}, respectively. A low K_{sp} value indicates that the compound is easily precipitated and otherwise [15]. Thus, it can be inferred that Ca ions would be removed slower than Mg and Fe ions under the same conditions.

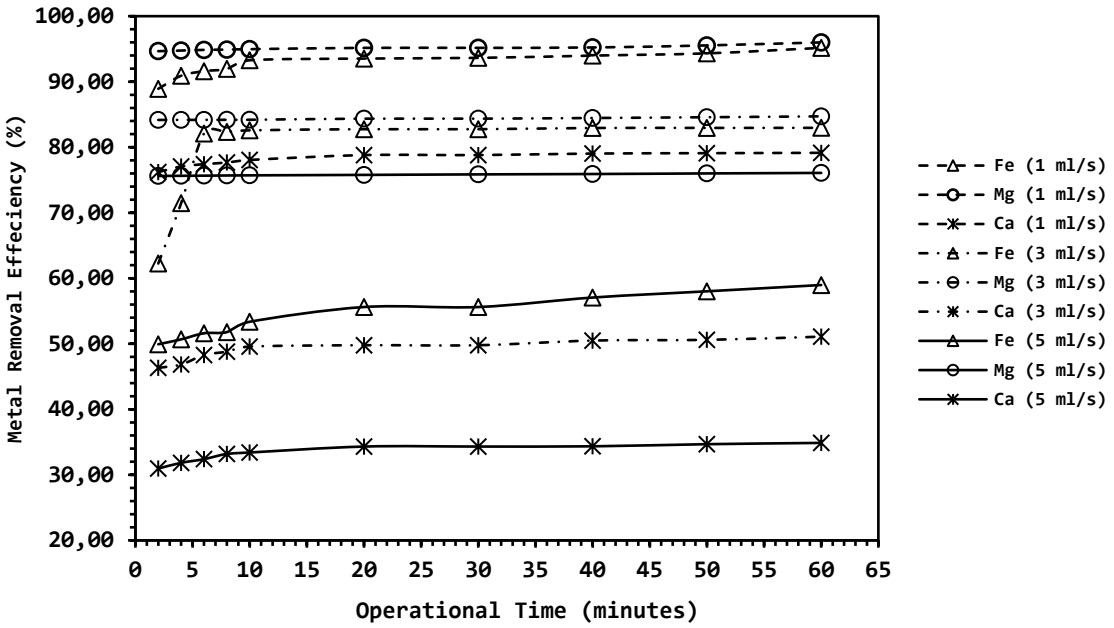

Figure 3. The effect of time on Fe, Ca, and Mg removal efficiency.

3.2. The effect of electrode distance on the electrocoagulation process

The effect of various electrode distances was evaluated by placing the electrodes at different distances of 1, 2, and 3 cm. The result of removal efficiency as a function of electrodes distance is presented in Figure 4. The results reveal that the highest removal efficiency of Fe, Ca, and Mg were obtained at the electrode distance of 1 cm. The removal efficiency decreased as the distance between the electrodes increased because the short distance between the electrodes reduces the resistance to the ion movement resulting in higher ion collisions that enhance the coagulation [16].

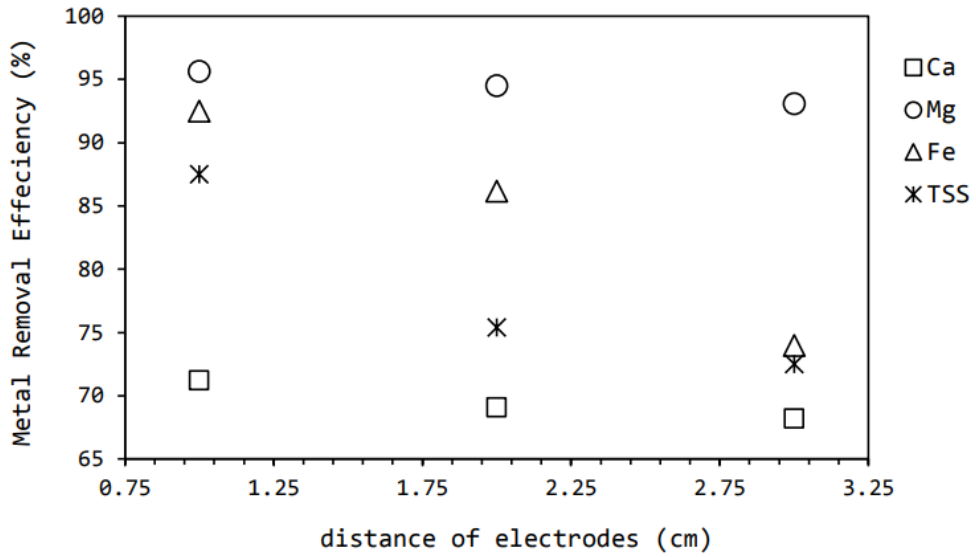

Figure 4. The effect of electrode distance on metal removal efficiency.

The effect of electrode distance on TSS removal was also evaluated. The TSS removal during the electrocoagulation process occurs when the coagulant or air bubbles absorb the solid material of the suspended solids. The adsorption results in a suspension in wastewater and reduces TSS concentration, both organic and inorganic pollutants [17]. Figure 4 shows the highest TSS removal efficiency of 87.5% obtained at an electrode distance of 1 cm, with an optimum current of 3.2 mA. The small resistance between two adjacent electrodes increases the voltage on the electrodes. As the distance between the electrodes becomes shorter, the number of gas bubbles generated increases, leading to high mass transfer and a high reaction rate between coagulants and pollutants. Otherwise, increasing the electrode distance, leading to higher resistance and smaller current, less contaminant reduction efficiency is expected [11,18].

3.3. Kinetic study

Several studies [19–21] stated that the rate of contaminants removal in the electrocoagulation reactor followed the first-order reaction, but other studies [16] stated that the removal rate followed the second-order. Based on the previous research, the removal rate of Fe, Ca, and Mg in wastewater using the electrocoagulation method is assumed to be first-order or second-order. If the reaction rate follows the first-order, the calculation is carried out using equation (1), whereas if the reaction rate follows the second-order, the analysis uses equation (2). The results of the predicted reaction rate constants are presented in Table 2.

Table 2 presents the reaction rate constant (k) value for Ca, Mg, and Fe at a flow rate of 1, 3, and 5 mL/second, including the correlation coefficients (R^2). The reaction rate constant for Ca and Fe were considered following the kinetic model of second-order, where the R^2 obtained is relatively higher than the first-order kinetic model. The kinetic model of Mg tends to fit into the first-order kinetic model. The result shows that the R^2 for the first-order kinetic model was higher than the second-order. The k-value obtained is a constant that can be used to predict the rate of Ca, Mg, and Fe removal as a function of operating time in the electrocoagulation reactor.

Table 2. The predicted reaction rate constant.

Metal	Flow rate (mL/second)	First-order model $-dc/dt=k_1C$ k_1 (min^{-1})	R^2 (-)	Second-order model $-dc/dt=k_2C^2$ k_2 ($ppm^{-1}min^{-1}$)	R^2 (-)
Ca	1	0.0018	0.7351	0.00006	0.7496
	3	0.0012	0.6834	0.00002	0.6944
	5	0.0008	0.6876	0.000009	0.6941
Mg	1	0.0039	0.9010	0.0018	0.8838
	3	0.0006	0.9802	0.00008	0.9790
	5	0.0003	0.9949	0.00003	0.9951
Fe	1	0.0104	0.7612	0.0114	0.8359
	3	0.0116	0.8165	0.0040	0.9083
	5	0.0033	0.9634	0.0005	0.9717

4. Conclusion

This study evaluates Ca, Mg, and Fe removal from wastewater by the electrocoagulation method with several variables such as contact time, flow rate, and electrode distance. The result shows that the electrocoagulation method effectively decreased the metal concentration and TSS from wastewater of the integrated canal in the CART. The optimum condition for Mg, Fe, and Ca removal is on the operational flow rate of 1 mL/second, operating time of 2 minutes, and electrode distance of 1 cm. The highest efficiency for Mg, Fe, and Ca removal were 96.0%, 95.2%, and 79.15%, respectively. Meanwhile, the highest efficiency of TSS removal was 87.5%. The kinetics study shows that the reaction rate constant (k) for Ca and Fe follows the second-order kinetic model, while Mg is fitted to the first-order kinetic model. Furthermore, it is recommended to compare this electrocoagulation method with another method to get an optimum metal removal from the wastewater for future work.

Acknowledgment

The authors would like to thank the Director of the Center for Accelerator Research and Technology, for the permission given to conduct research at the wastewater canal facility. Furthermore, the author also would like to thank the Head of Safety Division and his staff for the support provided so that the data can be obtained for this study.

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