

Reduction of Chromium and Manganese Heavy Metal Concentration in Leachate by Electrocoagulation

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Landfill leachate is a notorious problem. It possesses high toxicity levels of heavy metals that can cause severe danger and threat to human health. Electrocoagulation is used in this work to treat landfill leachate at Payatas dumpsite in Quezon City, Philippines. The electrocoagulation process is an electrochemical method that treats wastewater, which can potentially remove heavy metal pollutants from the leachate. The concentrations of Cr and Mn in the samples are reduced, resulting in an acceptable removal rate of 71.25 % for Cr and 74.95 % for Mn. Results also indicate that increasing the voltage supply and electrocoagulation time increases the removal rate of the heavy metals. The highest removal rate for both Cr and Mn heavy metal concentration is achieved at pH 5, 8 V applied potential, and 90 min electrolysis time. These optimized values of the parameters result in the high removal efficiency of heavy metals found in the leachate. The results of this work could be used in the management of leachate at the Payatas dumpsite before it reaches surrounding bodies of water. It could also be replicated in other landfill facilities in the country for the sustainable treatment of other heavy metals through the integration of an electrocoagulation setup with renewable energy sources.

1. Introduction

The production of waste has increased over the years due to continuous industrialization and urbanization, growth in the economy and the population, and technical development. Huge amounts of waste materials are being discharged into the environment daily. Landfilling is the most used method for waste control (Siddiqua et al., 2022). There are still major issues concerning the use of landfills. One is the generation of leachate which must be maintained properly to avoid problems in the environment. Leachate brings harm to the environment since it contains pollutants like heavy metals and organic pollutants. Leachate, if not treated properly, may cause water pollution that poses harm to aquatic ecosystems and affects the sources of freshwater (Iravani and Ravari, 2020). The heavy metals found in leachates are not only harmful to the environment but also to humans exposed to excessively high concentrations of heavy metals.

Landfill leachate is a notorious problem. It possesses high toxicity levels of heavy metal that can cause severe danger and threat to human health, especially to those people living near landfills and dumpsites (Rookesh et al., 2022). Heavy metal contamination of water streams is a result of human activities, usually by vehicle emissions, mining, and the metals-containing compounds used in industries (Li et al., 2011). Industrial activities such as metal smelting, chemical industries, manufacturing processes, and electroplating are a few sources of anthropogenic heavy metals in water (Sewvandi et al., 2011). Leachate-containing wastewater is the most difficult to treat as it consists of complex and widely variable content generated within a landfill. Many pretreatment and combined treatment methods have been used to treat leachate. Some of these methods are advanced oxidation techniques, biological treatment methods, coagulation-flocculation methods, membrane processes, and lagoon, and wetland applications that have been studied in the literature (Ortenero et al., 2022).

Because its characteristics change with the advancing years of the landfill, these test methods have troubles, such as decreasing treatment efficiencies and increasing costs. The implementation of a joint treatment comprising a few treatment steps has been used to solve the problem (Castro et al., 2023).

Payatas is the largest open dumpsite in the Philippines located in Quezon City, the largest component city of Metro Manila. Today, despite its lack of liners and piping systems required for sanitary landfills, it receives around 1,200 t/d of trash. The landfill produces leachate that is perceived to contain heavy metals that are deliberately discharged into surrounding bodies of water. A typical wastewater treatment plant consists of a combination of physical, chemical, and biological unit operations to target the removal of different constituents/pollutants. Relatively new technologies that utilize the concepts of electrochemistry are also available, such as electrocoagulation (EC), electrooxidation (EO), and electro-flotation (EF). In the past two decades, electrochemical wastewater treatment technologies started to regain importance as an environmentally friendly option that generates minimal sludge, requires no chemical additives, and has minimal footprint without compromising the quality of the treated water (Moussa et al., 2017). Electrocoagulation has been successfully applied to treat numerous varieties of wastewater of either industrial or urban origin (Valdiviezo-Gonzales et al., 2023). It is an effective electrochemical approach in treating different types of contaminated water and has received considerable attention in recent years due to its high efficiency in dealing with numerous stubborn pollutants (Khandegar et al., 2013). Electrocoagulation involves many chemical and physical phenomena that make use of consumable electrodes to supply ions into the pollutant system (Butler et al., 2011).

Since there is no proper treatment done prior to the discharge of leachate to any body of water in the Philippines, this study addresses this problem through the treatment of leachate by using electrocoagulation. It is done to prevent the potentially harmful effects of leachate pollutants on the health and environment in the surrounding communities. Specifically, two heavy metals were investigated in this work: manganese and chromium. Parameters such as applied potential, pH, and electrolysis time were varied to determine the effect on the removal rate of manganese and chromium.

2. Materials and Methods

The leachate samples were taken from the Payatas dumpsite following standard procedure. All samples obtained were treated for preservation prior to the electrocoagulation process.

2.1 Materials and Experimental Setup

Figure 1 shows the location of the sampling point in Payatas dumpsite. The samples were collected in 2 L plastic bottles and acidified with concentrated nitric acid to 1 L leachate for preservation. The properties of leachate, such as pH and temperature, were analyzed in situ. The aluminum electrodes used were purchased from local suppliers. All the chemicals used were reagent grade.

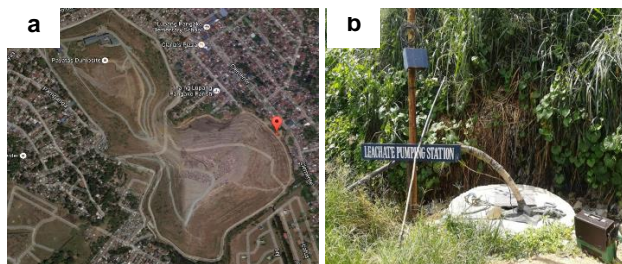


Figure 1: (a) Location of the sampling point at Payatas dumpsite, and (b) sampling point

The experimental equipment consisted of nine 50 mL beakers. Each beaker contained two aluminum electrodes (anode and cathode) with dimensions of 1.5 cm x 7 cm x 0.04 cm that were fully immersed in leachate samples. Two sheets of aluminum with dimensions of 1.5 cm x 56 cm were used as hangers to hold the electrodes. The two hangers were clamped together using C-clamps with rubbers between them to set the inter-electrode distance. A DC power supply was used to supply the voltage with copper wires connecting it to the hangers. Iron stands and yarn were used to suspend the hangers.

2.2 Experimental Procedure

Each beaker was filled with 50 mL leachate sample. Effect of different parameters was tested by varying one parameter at a time: (i) initial pH: 5, 8, and 11 (Un et al., 2015) (ii) voltage: 4 V, 6 V, and 8 V, (iii) electrolysis

time: 30 min, 60 min, and 90 min (Zailani et al., 2018). A sample of 200 mL of untreated sample was filtered into a 400 mL beaker. Then, 10 mL of HNO_3 was added, and the sample was stirred and heated over a hot plate. After that, it was simmered without boiling, and once the volume was reduced to 50 mL, another 10 mL of HNO_3 was added. It was then covered with a watch glass, and it was heated again for 10 min. The sample was then diluted to 250 mL with distilled water, and the pH was measured. It was transferred to sample tubes for inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis to determine the initial concentration. After electrocoagulation, treated samples were filtered using 12.5 cm filter paper. Filtered treated samples were acid digested using concentrated HNO_3 . The heavy metal concentration was then determined again using ICP-OES.

3. Results and Discussion

Physico-chemical properties of the leachate samples were evaluated to provide insight into the chemical composition prior to electrocoagulation.

3.1 Physical Properties of Leachate Sample

A conventional leachate has a pH of 4.5 to 9. A pH of less than 6.5 is considered young, while a pH of more than 7.5 is considered old. The leachate samples taken had an average pH of 8.62 taken at 33 °C and is considered an old landfill leachate. The leachate sample before electrocoagulation appears to have a dark brownish, almost black color. Electrical conductivity (EC), pH, turbidity, and salinity of the leachate were measured in-situ using HORIBA U-10 water quality meter. COD was measured using COD analyzer, Br- using Ion Chromatography, and Cr and Ni using Atomic Absorption Spectrometry (AAS). Table 1 shows the result of the analysis of the leachate sample.

Table 1: Selected properties and composition of the Payatas leachate

Parameters	Value/Concentration
pH	8.4
Salinity (%)	1.3
Conductivity ($\mu\text{S}/\text{cm}$)	21.2
Turbidity (NTU)	641
COD (mg/L)	4510
Nitrate (mg/L)	0.05
Phosphate (mg/L)	32
Chromium (mg/L)	6.2
Nickel (mg/L)	21.7
Bromide (mg/L)	3.8

As the electrocoagulation process continued, flocs form that gathered impurities from the sample such as heavy metals. Figure 2 shows the leachate sample before and after the electrocoagulation experiment.



Figure 2: Leachate samples (a) before and (b) after the electrocoagulation experiment

The concentrations of Cr and Mn before electrocoagulation are 3.35 mg/L and 4.02 mg/L. It clearly indicates that the initial concentration of Cr and Mn found in the sample taken exceeds the Department of Environment and Natural Resources (DENR) Administrative Order DAO-34 Class C limit of 0.02 mg/L and 2 mg/L.

3.2 Removal of Chromium and Manganese

Figure 3a and Figure 3b show the removal rate of Cr and Mn with respect to time. The highest removal rate for Cr is 71.25 % and at 74.95 % for Mn.

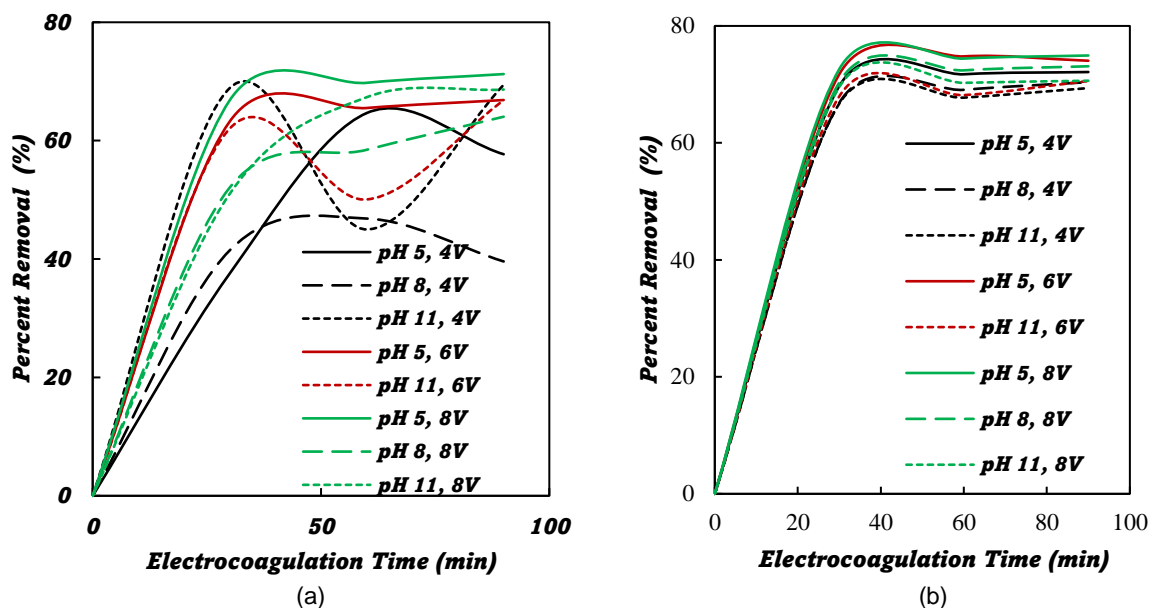


Figure 3: Removal rate of heavy metals as a function of time for various applied potentials for (a) chromium and (b) manganese

Also indicated in the figures are the removal rates of Cr and Mn across different pH values. No significant trend is evident for the Cr heavy metal. The removal rate is observed to be highest at pH 5, followed by pH 11, and lowest at pH 8. A maximum removal rate of 71.25 % was achieved at pH 5 (90 min, 8 V). This is because of the generation of hydrogen and OH^- ions at the cathode (Eq.1). The generated OH^- ions react with generated Al^{3+} at the anode, forming the $\text{Al}(\text{OH})_3$ flocs (Eq.2). The generated OH^- ions also react with Cr^{3+} ions to form $\text{Cr}(\text{OH})_3$ precipitate which has lower solubility at acidic solutions (Eq.3) (Dermentzis et al., 2018). A pH within the range of 3 – 5 facilitates maximum removal. The best pH obtained in this study is closer to the pH that was reported by Khandegar et al. (2013). They reported that the maximum removal efficiency of Cr was obtained at pH 4.

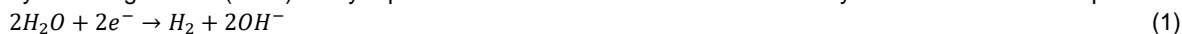


Figure 3b indicates that as the pH increases the percentage of Mn metal removed from the sample decreases. This study contradicts the result obtained by Elabbas et al. (2016). The study reported that the maximum removal efficiency of Mn was obtained at high pH, specifically at pH 9. The maximum removal rate of 74.95 % was achieved at pH 5 (90 min, 8 V) for the Mn metal.

An increasing trend can be observed for Cr metal, as shown in Figure 3a. As the applied voltage increases, the removal rate of Cr metal also increases. This increasing trend is also apparent for the Mn metal at times 30 min and 90 min, while at 60 min, 6 V is slightly higher than 8 V. A study performed by Rekha et al. (2014) also observed that the removal efficiency increases with increasing voltage. In their study, it was reported that the reaction is maximum at 8 V compared to 4 V. This is because more bubbles are generated when the applied voltage is high. Increasing the supply of voltage also increases the formation rate of coagulants.

A sharp increase of Cr removed is apparent in the first 30 min of the electrocoagulation run, and it slightly increases until 60 min, as shown in Figure 3a. It continues to increase gradually until 90 min. This increase in the removal rate as the set-up runs is also observable in Mn heavy metal given in Figure 3b. The highest removal rate achieved at 90 min is 71.25 % for Cr and 74.95 % for Mn.

3.3 Energy Consumption

The relationship between energy consumption and voltage is shown in Figure 4. It can be observed that as the voltage increases, the energy consumption also increases. This is also true with energy consumption and time. This is due to the direct proportionality relationship between these parameters. In the relationship of energy consumption with voltage, the average energy consumption at 4 V is 0.00172 kWh, at 6 V is 0.00288 kWh and at 8 V is 0.00424 kWh. The average energy consumption at 30 min is 0.001473 kWh, at 60 min is 0.002947 kWh, and at 90 min is 0.00444 kWh. It can be observed that the increase of energy consumption at a 2 V interval is almost the same as the increase at a 30 min interval of time. Time at 30-minute intervals has a little more

influence on energy consumption than voltage. There is a significant difference among the energy consumption at different voltages as well as various electrolysis times ($P < 0.05$).

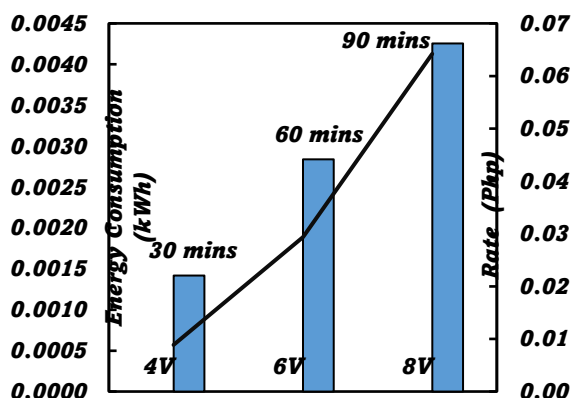


Figure 4: Energy consumption versus voltage and time

From the data that was gathered, it can be implied that the lowest energy consumption, which is 0.00086 kWh, is at 4 V and 30 min. While the highest energy consumption, which is 0.00636 kWh, is given by 8 V under the time of 90 min.

The electricity rate that was used in the calculation of cost was based on the prevailing local electricity rate in the Philippines in 2023. From Table 2, the lowest energy consumption, which is at 4 V and at 30 min, the amount that is to be paid is Php 0.0075. The highest energy consumption given by 8 V under 90 min will have a rate of Php 0.055. From that computation, it can be concluded that the highest energy consumption has 7 times higher costs. If the amount of leachate to be treated is increased to 1,000 L, the amount to be paid is Php 16.667 and Php 122.22 for 4 V and 30 min and for 8 V and 90 min.

Table 2: Energy consumption and rate of various voltages with their respective electrocoagulation time

Voltage (V)	Current (A)	Time (h)	Energy (kWh)
4	0.43	0.5	0.00086
4	0.43	1	0.00172
4	0.43	1.5	0.00258
6	0.48	0.5	0.00144
6	0.48	1	0.00288
6	0.48	1.5	0.00432
8	0.53	0.5	0.00212
8	0.53	1	0.00424
8	0.53	1.5	0.00636

Multiple reactions usually take place simultaneously in the electrocoagulation process. On the surface of the anode, the aluminum metal ion is driven into the leachate. On the surface of the cathode, water is hydrolyzed into hydrogen gas and hydroxyl groups. These hydroxyl ions bond with the heavy metals present in the contaminant and form an insoluble hydroxide precipitate, which removes the heavy metals from the solution.

In ionic bonding, the electronegativity difference is 1.8 or greater. Hydroxide forms ionic bonds with metals. If an atom is more electronegative, the electron/s of the bond has more tendency to be attracted to that atom. In the periodic table, to distinguish its electronegativity, as the elements go down, the electronegativity decreases, and the elements from left to right, electronegativity increases. It can be observed that manganese is more electronegative than chromium. No competition between the two heavy metals was observed since hydroxide ions are equally attracted to the two metals.

In the removal rate of manganese and chromium, it can be observed that manganese has a higher removal rate. This is partly because of the effect of aluminum as the electrode, and through this, it can be concluded that aluminum is selective of manganese. Manganese is removed by hydroxide precipitation and absorption on the $\text{Al}(\text{OH})_3$ flocs.

4. Conclusions

The concentrations of Cr and Mn in the sample were reduced to an acceptable removal rate of 71.25 % for Cr and 74.95 % for Mn. This indicates that electrocoagulation is effective in removing the heavy metal contaminants from Payatas leachate. Variations in the initial pH, voltage, and electrocoagulation time during the experiment affect the removal of Cr and Mn from the samples. Results indicate that increasing the applied voltage and electrocoagulation time increases the removal rate of the heavy metals. Increasing the initial pH of the sample decreases the removal rate of the heavy metals. The parameters that achieved the highest removal rate for both Cr and Mn are at pH 5, 8 V applied potential, and 90 min electrocoagulation time. Using these parameters resulted in high removal efficiency of heavy metals found in the leachate.

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