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Simultaneous Removal of Cadmium and Copper in Aqueous Solution by Electrocoagulation: Influence of pH and Electric Current Density

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Efficient removal of heavy metals from wastewater is crucial due to their harmful effects on health and the environment. Electrocoagulation is an alternative treatment technique that applies electric current to metallic electrodes, forming coagulants and precipitating contaminants. This study evaluated the efficiency of electrocoagulation in removing copper (Cu) and cadmium (Cd) from aqueous solutions. An experimental study was conducted to assess the simultaneous and independent removal of each metal. Electrodes based on 1050 aluminum alloy were used, and different pH values (2.6, 5, and 7) and electric current densities (1, 2, and 3 mA/cm²) were evaluated. The treatments were carried out for 40 min at room temperature (25 ± 1 °C). Atomic absorption spectroscopy technique was employed for monitoring and quantification of both metals. The results showed the complete removal of Cd in mixture and almost complete removal of Cu (>99 %) when used independently. The removal efficiency increased with pH and electric current density, and it was found that removal was more efficient under neutral or slightly alkaline pH conditions. The findings of this study can be useful for the implementation of this technology in the industry for the treatment of wastewater contaminated with both metals.

1. Introduction

Heavy metal pollution in aquatic ecosystems is a global issue due to their toxic effects and accumulation capacity in water reservoirs (Astatkie et al., 2021). Cadmium (Cd) and Copper (Cu) are two of the most common metals found in industrial and urban wastewater, and their presence at high levels can be detrimental to human health and aquatic life. For example, exposure to Cd can cause kidney, liver, and testicular damage, osteomalacia, cardiovascular diseases, and cancer, as well as interfere with cellular functions such as antioxidant activity and gene regulation (Genchi et al., 2020). Similarly, Cu toxicity in humans can result from various causes, such as genetic mutations, environmental exposure, and liver diseases (Barber et al., 2021). Therefore, the development of efficient methods for the removal of these metals from wastewater is crucial.

Electrocoagulation (EC) is a beneficial electrochemical process for water treatment due to its effective reduction of contaminants, operational advantages such as simplicity, sludge reduction, stable flocs, removal of small colloidal particles, low chemical usage, and low maintenance requirements, making it highly efficient for treating multiple pollutants (Magnisali et al., 2022). The EC produces directly coagulating species in the medium to be treated through the electrochemical oxidation of submerged metal anodes, this advanced technology combines principles of flotation, coagulation, and electrochemistry (Moussa et al., 2017). In particular, the electrocoagulation technique has been used to treat quantities ranging from tens to hundreds of milligrams per liter of heavy metals such as Chromium (Cr), Nickel (Ni), Zinc (Zn), Copper (Cu), and others (Kim et al., 2020).

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Studies have been conducted to improve the efficiency and reduce the cost of the electrocoagulation process in the removal of Cd from industrial wastewater, where an efficient 100 % removal of Cd in 5 min was achieved with low energy consumption and cost, by configuring an electrode distance, monopolar connection mode, stirring speed, a surface-to-volume ratio, and initial temperature (Khaled et al., 2019). Furthermore, it was demonstrated that EC is more efficient than conventional coagulation in the simultaneous removal of Cr and Cd from industrial wastewater (Elkaramany et al., 2020). Likewise, the removal of Cu has been shown to be very effective and its efficiency was dependent on the initial concentration, electrolysis time, and electrolysis voltage (Ano et al., 2023). In another study, CE was used to remove Cu and Pb ions from electroplated wastewater, with removal efficiency increasing with electrocoagulation time and initial metal concentration, and high current density increasing the energy consumption (Prasetyaningrum et al., 2021).

In the scientific literature, there is limited information on research focused on the simultaneous removal of Cu/Cd through the electrocoagulation process, as well as its evaluation under multiple operational parameters (Khan et al., 2023). The objective of this study was to evaluate the efficiency of the Electrocoagulation (EC) process in removing Cd and Cu, both individually and in combination, using aluminum electrodes with a monopolar configuration. The effects of initial pH and electric current density on the rate of removal of the heavy metals present in an aqueous solution were evaluated.

2. Method

2.1 Preparation of Cadmium and Copper Solution

A mother solution for each assay of 1.5 L of 10 ppm of copper and 10 ppm of cadmium was prepared from $Cu(NO_3)_2$ (Sigma aldrich, USA) in HNO_3 0.5 mol/L (1000 mg/L) and $Cd(NO_3)_2$ (Sigma aldrich, USA) in HNO_3 0.5 mol/L (1000 mg/L) standard solutions, respectively. A 2 L precipitation flask was used for its preparation, in which the pH was adjusted with NaOH (0.1 N) and HNO_3 (32 % and 5 %) with constant agitation at 200 rpm.

2.2 Electrocoagulation Cell Configuration

A cell with dimensions of 14.1 cm x 10.5 cm x 18 cm was designed for a volume of 1.5 L (Figure 1). Additionally, a power supply (Hurricane-Power) was used to stabilize the voltage and current of the system (Ilhan et al., 2019). Commercial 1050 aluminum electrodes were used for both anode and cathode, which were cut into plate shapes with dimensions of 6 cm x 9 cm x 3 mm. Before each assay, the electrodes were sanded with paper to remove impurities, then washed with distilled water and rinsed with diluted HNO_3, and finally washed with distilled water. The electrodes were treated in an oven at 110 °C for 30 min to remove any oxidation or passivation layer between experiments. To minimize passivation, the polarity of the electrodes was reversed after each assay (Oliveira et al., 2021).

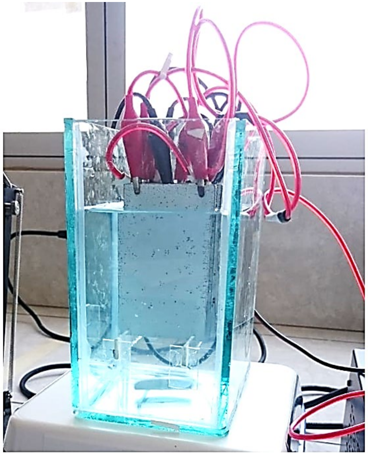

Figure 1. Model of the electrochemical system configuration for the electrocoagulation assays.

2.3 Experimental Assay

A factorial experimental design was used to investigate the percentage of Cu and Cd removal, and energy consumption. The effect of initial pH factors (2.6, 5, and 7) and electric current density (1, 2, and 3 mA/cm^2) was studied (Medina-Collana et al., 2023). Table 1 indicates the matrix of the experimental factors and levels in a total of 9 runs in triplicate, showing a total of 27 assays. The statistical software Design Expert v13 was used to perform the experimental design. Once the necessary pH conditions were adjusted, the solution was transferred to the glass cell that has previously arranged electrodes. At this point, sodium sulfate (1 g of Na_2SO_4) was added to improve electrical conductivity. The treatments were carried out for 40 min at room temperature (25 ± 1 °C).

Table 1: Distribution of independent variables through factorial design.

Run	X1: pH	X2: Electrical current density (mA/cm^2)
1	2.60	1
2	2.60	2
3	2.60	3
4	5.00	1
5	5.00	2
6	5.00	3
7	7.00	1
8	7.00	2
9	7.00	3

2.4 Analytical Method

The atomic absorption spectroscopy technique was used to identify copper and cadmium using the AVANTA GBC 3000 PM spectrophotometer (Australia) (Sahu, 2019). For the calibration curve, a concentration of 0.5, 1, and 2 ppm was used for Cu and 0.25, 0.75, and 1.5 ppm for Cd. The wavelength of 324.7 nm and 228.8 nm was used for copper and cadmium, respectively. The electrical energy consumption ($VAmin/m^3$) was calculated using the following equation (Kuokkanen et al., 2013):

$$EEC=\frac{V.\,I\,.\,t}{v} \tag{1}$$

where V is the applied voltage (V), t is the assay time (min), v is the volume of the treated solution (m^3), and I is the electric current intensity.

2.5 Statistical Analysis

The results obtained under the different experimental conditions were evaluated comparatively using ANOVA tests through the statistical software Design Expert v13. A level of $p < 0.05$ was established to be considered significant (Baldera et al., 2022).

3. Results and discussion

Table 2 shows the results of the efficiency in the removal of Cu and Cd based on the pH and current density in two scenarios: the simultaneous reaction of both contaminants and the individual reaction of each one of them. Under optimal conditions, at pH 7 and a current density of 3 mA/cm^2, complete elimination (100 %) of Cd was achieved in both scenarios, while the elimination of Cu is almost complete (> 99 %). In turn, the lower performance in the elimination of Cu and Cd was observed at pH 2.6 and a current density of 1 mA/cm^2, with a removal rate of Cu and Cd in simultaneous removal of 93.31 ± 0.23 % and 33.31 ± 0.17 %, respectively, and in the individual reactions, the removal of Cu is 98.01 ± 0.02 %, while that of Cd is 35.99 ± 0.23 %. It is important to note that, although the performance in the removal of Cu in experiment 1 is lower compared to other experiments, it is still quite high (above 90 %). The results obtained differ from those obtained by Abd & Hussein (2021), who achieved a maximum removal efficiency of 97 % of copper at a current density of 3 A/cm^2 during 40 min at pH 3. Similarly, high removal yields have been reported such as Oluwabusuyi (2021), who obtained a removal of 98.90 % of copper and 99.78 % of cadmium simultaneously with nickel treated at 25 mA/cm^2 with pH 7 using an iron electrode. In turn, this study data surpasses that obtained by Hawass & AlJaberi (2022) by achieving a removal of Cd and Cu of 64.24 and 89.55 %, respectively, with a monopolar connection for 60 min at pH 7 at 3.88 mA/cm^2 with an aluminum electrode.

The high efficacy achieved in this research is further distinguished by the implementation of electrodes based on the aluminum alloy 1050, which contains traces of iron, these two latter metals are widely used due to their propensity for oxidation and their efficiency as coagulating agents (Mousazadeh et al., 2021).

Likewise, as seen in Table 2, the efficiency in removing Cu and Cd increases as pH increases. At a pH of 2.6, the extraction of Cu and Cd is not ideal, however, at pH values of 5 and 7, the removal of both elements approaches 100 %. This indicates that the electrocoagulation process is more efficient under neutral or slightly alkaline conditions. Similarly, it was found that as the electric current density increases (1, 2 and 3 mA/cm^2), the efficiency of removing Cu and Cd also improves. For example, by comparing the results of run 1, 2, and 3 (pH 2.6), an increase in the removal efficiency of both Cu and Cd can be observed. This indicates that a higher electric current density favors the removal of these elements.

Table 2: Percentage removal of copper (Cu) and cadmium (Cd) based on pH and electric current density in simultaneous and individual removal.

Run	pH	Electrical current density (mA/cm^2)	Simultaneous removal	Cu only	Cd only	Simultaneous removal
			% Cu removal	% Cd removal	% Cu removal	% Cd removal
1	2.60	1	93.31±0.23	33.31±0.17	98.01±0.02	35.99±0.23
2	2.60	2	99.71±0.00	80.88±0.29	99.55±0.03	95.14±0.00
3	2.60	3	99.75±0.00	98.34±0.05	99.41±0.01	99.76±0.00
4	5.00	1	99.65±0.01	88.33±0.12	99.43±0.01	62.95±0.01
5	5.00	2	99.83±0.01	100.00±0.00	99.56±0.03	98.90±0.01
6	5.00	3	99.78±0.01	99.78±0.01	99.48±0.01	100.00±0.01
7	7.00	1	99.71±0.01	97.60±0.15	99.28±0.01	100.00±0.01
8	7.00	2	99.96±0.00	100.00±0.00	99.13±0.04	100.00±0.00
9	7.00	3	99.97±0.00	100.00±0.00	99.55±0.03	100.00±0.00

Table 3 shows the statistical analysis revealing that the general model (R^2=91 %) is significant for the simultaneous removal of Cu and Cd ($p < 0.0001$). The individual factors, pH (A) and electric current density (B), as well as their interaction (AB), significantly influence the efficiency of the electrocoagulation process for removing these elements. These findings underscore the importance of properly adjusting the pH and electric current density to optimize the removal of contaminants in wastewater through electrocoagulation.

Table 3: Analysis of variance (ANOVA) for the simultaneous removal of Cu and Cd by electrocoagulation.

Source	Simultaneous removal							
	Copper				Cadmium			
	Sum of Squares	Mean Square	F-value	p-value	Sum of Squares	Mean Square	F-value	p-value
Model	108.28	13.54	22.94	< 0.0001	11539.33	1442.42	502.18	< 0.0001
A-pH	28.77	14.38	24.38	< 0.0001	4441.65	2220.82	773.18	< 0.0001
B-Electric current density	30.29	15.14	25.67	< 0.0001	3472.82	1736.41	604.53	< 0.0001
AB	49.23	12.31	20.86	< 0.0001	3624.86	906.21	315.5	< 0.0001
Pure Error	10.62	0.5899			51.7	2.87		
Total	118.28				11591.03			

Table 4 shows the ANOVA analysis conducted for the individual removal of cadmium and copper through electrocoagulation. The general model (R^2=99 %) shows high significance for both metals ($p<0.0001$), as well as the significant influence of factors A, B and their interaction on the removal efficiency. Certainly, pH affects the solubility of the electrodes and the generation of ions in the aqueous solution, which impacts the formation of coagulants from hydroxide ions during the electrocoagulation process (Samaka et al., 2019). An additional study showed that, as the pH increases, the efficiency of electrocoagulation in removing contaminants such as copper, manganese and zinc tends to improve, due to the reduction in the dissolution rate at high pH, which can be attributed to the decrease in electrode corrosion in alkaline conditions (Janpoor et al., 2011). Similarly, it has been shown that at higher current density, the dissolution of the anode into Al^{3+} ions increases, resulting in greater sludge production and ion removal by adsorbing into $Al(OH)_3$. Additionally, the increase in hydrogen bubble generation at the cathode optimizes the mixture of hydroxides and aluminum ions, improving flotation and removal efficiency (El-Ashtoukhy et al., 2020).

The simultaneous removal of metals in electrocoagulation can be slightly lower than the individual removal due to competition between metal ions, possibly due to the reduction in the formation of hydroxide cationic complexes, which are responsible for the coagulation process (Zaied et al., 2020). However, under certain conditions, the efficiency of simultaneous removal is similar to individual removal, highlighting the importance of adjusting pH and current density to optimize the process. On the other hand, in Figure 2, a growing trend in energy consumption was observed as the current density increases in all cases, which indicates that the energy efficiency of the process is affected by this parameter. In the case of simultaneous removal, the highest energy consumption (5.43 VAmin/m^3) occurs at pH 2.6 and a current density of 3 mA/cm^2. Similarly, for the exclusive removal of Cd and Cu, the highest energy consumption (3.98 and 4.42 VAmin/m^3, respectively) is recorded under the same conditions of pH and current density. Additionally, the energy consumption in the simultaneous removal of Cu and Cd tends to be slightly higher compared to the individual removal of each metal, although the differences are not too pronounced. This suggests that the competition between metal ions during electrocoagulation can affect the energy efficiency of the process.

Table 4: ANOVA analysis for the single removal of copper and cadmium by electrocoagulation.

Source	Cadmium only				Copper only			
	Sum of Squares	Mean Square	F-value	p-value	Sum of Squares	Mean Square	F-value	p-value
Model	13755.77	1719.47	18795.07	< 0.0001	6.85	0.8566	33.2	< 0.0001
A-pH	2610.68	1305.34	14268.31	< 0.0001	1.42	0.7093	27.49	< 0.0001
B-Electric current density	6970.89	3485.44	38098.46	< 0.0001	2	0.9991	38.72	< 0.0001
AB	4174.2	1043.55	11406.76	< 0.0001	3.44	0.859	33.29	< 0.0001
Pure Error	1.65	0.0915			0.4645	0.0258		
Total	13757.41				7.32			

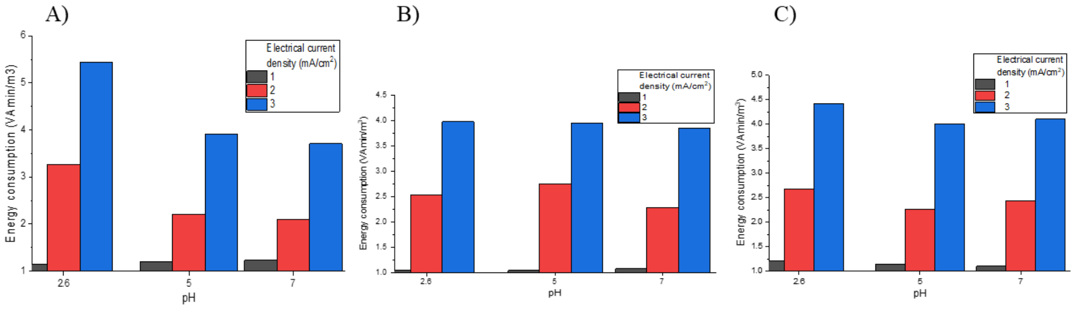

Figure 2. Effect of pH and current density on energy consumption during simultaneous removal (A) and individual removal of cadmium (B) and copper (C).

4. Conclusions

This study showed that electrocoagulation is an effective method for the removal of Cu and Cd in wastewater, with an efficiency greater than 90 % under optimal conditions. It was observed that pH and electrical current density are critical factors in the efficiency of the process, with better results obtained at pH 7 and an electrical current density of 3 mA/cm². Although simultaneous removal of Cu and Cd may be slightly lower than individual removal, by properly adjusting the pH and electrical current density, it is possible to optimize removal efficiency. It is noteworthy that energy consumption increases with electrical current density, which can affect the energy efficiency of the process. Therefore, it is essential to balance the efficiency of metal removal and energy consumption when applying electrocoagulation in wastewater treatments.

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