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Removal of heavy metals derived from COD analysis wastewater by electrolysis using graphite electrode

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Abstract:

In this study, electrolysis using graphite electrodes was applied to treat wastewater generated from a COD analysis procedure (referred to as COD wastewater). COD wastewater containing high concentrations of H_2SO_4, Hg^{2+}, and $Cr_2O_7^{2-}$ salts were collected and then treated by electrolysis with graphite electrodes in a lab-scale experiment. The results showed that the electrolysis process was not affected by the electrode's distance or area. The most efficient treatment for all three metals was achieved at a current value of 31.58 mA, which corresponds to a current density of 1.974 mA/cm^2 under a voltage of 3 V, 8-h electrolysis time, wastewater pH<1, electrode distance of 4 cm, and electrode area of 16 cm^2. Under these conditions, the concentrations of heavy metals after treatment were 1170.17 mg/l for Hg, 871.20 mg/l for Ag, and 56.3 mg/l for Cr. The treatment efficiencies were 48.15, 66.94, and 50.76%, for Hg, Ag, and Cr, respectively. While this technology is simple, low cost, and achieves a relatively high efficiency, after treatment the COD wastewater still carried a high concentration of heavy metals that exceeded the permissible standards. Therefore, it is necessary to have a further treatment method in place to completely eliminate the heavy metals remaining in wastewater, as well as to recycle and reuse acidic components from wastewater and to treat them up to environmental standards before discharge. In conclusion, electrolysis with graphite electrodes can be applied in practice to treat other sources of wastewater contaminated by heavy metals with low emissions.

Keywords: **COD analysis, COD wastewater, electrolytic, graphite electrode, heavy metal.**

Classification number: **5.3**

Introduction

BOD (biological oxygen demand) and COD (chemical oxygen demand) are two basic parameters that determine the concentration of organic matters that cause pollution of water sources. BOD is the amount of oxygen required by microorganisms to oxidize biodegradable organic substances, while COD is the amount of oxygen required to oxidize all organic compounds, those that are both difficult and easily biodegradable in water. The main advantage of COD analysis is to provide fast results and a simpler, more accurate process when compared to that of BOD. Therefore, COD is often used to assess the organic pollution of water sources and sometimes it can be used as a substitute for BOD. In addition, the COD indicator is also widely used in water quality testing of all wastewater treatment facilities due to its simplicity and quick analysis time.

The COD was determined based on the Standard method 5220B-4b [1]. This procedure involves the use of chemical agents such as sulfuric acid (H_2SO_4), dichromate ($Cr_2O_7^{2-}$), silver (Ag^+), and mercury (Hg^{2+}). H_2SO_4 is used as a catalyst for the oxidation of organic compounds in wastewater along with the powerful oxidant dichromate ($Cr_2O_7^{2-}$). Silver and mercury are used to eliminate agents that interfere with the oxidation reaction. The treated samples continue to heat in a closed reflux at high temperature (150^{o}C) for 2 h. Finally, the obtained samples are used to determine the remaining $Cr_2O_7^{2-}$ by titration with Fe^{2+} (FAS solution) or by the colorimetric method. The $Cr_2O_7^{2-}$ agent in the COD analysis method oxidizes most organic compounds at high temperature in concentrated acid conditions. Some organic matter, especially straight-chain fatty acids, do not oxidize without the Ag^+ ion catalyst. If the chloride concentration is greater than 2000 mg/l, a major obstacle

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in wastewater treatment, the addition of excess Hg^{2+} ions can overcome the high chloride concentration by forming a chloride complex. Although the amount of wastewater generated from COD analysis is not large (about 50-1000 ml/d), due to the use of toxic chemicals COD wastewater often contains high concentrations of H_2SO_4, Hg^{2+}, and $Cr_2O_7^{2-}$ salts. Thus, if COD wastewater is not treated before discharge, it can cause difficulties in storage as well as serious environmental pollution.

COD wastewater from laboratories has been of interest to domestic and foreign researchers for wastewater treatment via various technologies such as physical-chemical treatments, chemical precipitation, ion exchange, and absorption by chitosan; all of which have been shown to be highly effective in removing heavy metals for some time [2-15]. The advantages of these methods include low cost and ease of operation, however, one significant disadvantage is the creation of secondary waste (i.e. sludge). Thus, it is necessary to employ further treatment before discharging the treated water back into the environment [3, 8, 10, 16]. In recent years, several studies on COD wastewater treatment by more modern and less polluting methods have been conducted using electrochemical processes and membrane filters. Electrolysis employed for the treatment of wastewater containing high concentrations of heavy metal is not a new technology. In fact, it has been utilized since its first application in England in 1889 [3]. The combined use of flocculation and oxidizing electrolysis are used to treat wastewater containing heavy metals and to decompose organic compounds due to its low cost. Further, this process does not create secondary pollution because of the complete oxidation of pollutants in the final product. Therefore, it is especially suitable for the treatment of wastewater with high concentrations of heavy metals up to 1000 mg/l [17]. At the electrodes, cations will be reduced and anions will be oxidized causing separate oxidation and reduction reactions to occur.

For example, at the anode there are the anions (OH^-, Cl^-) and the following electrode-metal (Me_1) oxidation reactions occur:

$$Me_1 \text{ (insoluble)} = Me_1^{m+}\text{(soluble)} + me^-$$

$$4OH^- = 2H_2O + O_2 + 4e^-$$

$$2Cl^- = Cl_2 + 2e^-$$

At the cathode, the following reduction reactions occur:

$$Me_1^{m+}\text{(soluble)} + me^- = Me_2 \text{ (insoluble)}$$

$$2H^+ + 2e^- = H_2 \text{ (gas)}$$

Due to the existence of high concentrations of Hg, Ag, and Cr ions in COD wastewater, sulfuric acid was selected as the suitable electrolyte agent for electrolysis. Table 1 shows the studies where electrolysis was used to treat COD wastewater and their effectiveness in removing heavy metals.

Table 1. Results on COD wastewater treatment of researchers.

Technology	Results	References
Electrochemical; using iron electrodes	Ag, Cr, Fe met standards discharge, but Hg levels were still high	Pinisakul and Kritayakornupong (2008) [14]
Electrochemical; using platinum anode and copper cathode	47.19% Ag recovery	Djaenudin and Syafila (2009) [15]
Electrolytic with titanium electrode	88% Hg, 89% Ag, and 81% Cr removal	Diem (2016) [16]

The purpose of this study was to use electrolysis with inert graphite electrodes to remove heavy metal ions and to recover valuable components in COD wastewater with high efficiency that is suitable for the application of additional treatment technologies to reduce treatment cost and achieve discharge at environmental standards.

Materials and methods

Materials

COD wastewater was taken at the environmental laboratory of Ho Chi Minh city, University of Food Industry, with the pollution components shown in Table 2.

Table 2. The components of heavy metals in COD wastewater.

Parameter	Concentration (mg/l)	QCVN 07:2009/BTNMT*
Ag	2635.2	5
Hg	2256.7	0.2
Cr^{6+}	114.4	5
pH	<1	≤2 or ≥12.5

The data in Table 2 shows that COD wastewater has a high acidity with pH<1 and a very high concentration of heavy metals, which exceeds the permitted threshold according to QCVN 07:2009/BTNMT by several times.

The experimental model

The lab-scale experiment model is described as in Fig. 1. The electrolysis for COD wastewater treatment used a graphite electrode consisting of three components: (1) a DC power supply; (2) a graphite electrode with 16

*National Technical Regulation on Hazardous Waste Thresholds.

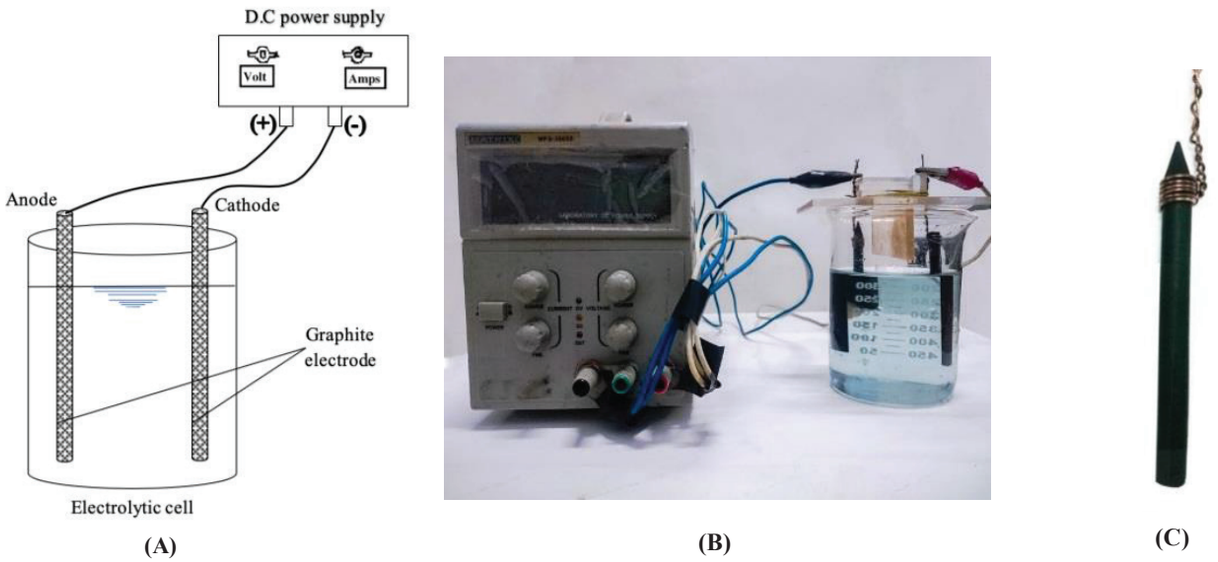

Fig. 1. Electrolytic model of COD wastewater treatment using graphite electrode. (A) drawing, **(B)** actual model, **(C)** graphite electrode.

cm^2 area, diameter (D) and height (h) of 0.7 and 7.5 cm, respectively; and (3) an electrolytic cell (500-ml beaker).

The experiments of COD wastewater treatment using graphite electrodes

Electrolysis for COD wastewater treatment using graphite electrodes was carried out as follows. First, experiments were conducted to evaluate the efficiency of heavy metal removal under various voltages, then the most suitable voltage for electrolysis with the highest removal and the lowest power consumption was chosen. Then, the effect of electrode distance, electrolysis time, and electrode area on the removal of heavy metals of COD wastewater was investigated.

All experiments were conducted in batch-mode in 500-ml beakers. The samples, after treatment, were evaluated to be effective by determining pH and the concentration of heavy metal ion residue in wastewater. The pH was measured with a PHS 550 pH meter and the concentrations of Ag, Hg, and Cr were analysed by titration methods [18-20].

Results and discussion

Effect of voltage on the efficiency of COD wastewater treatment

The experiment was carried out under a fixed distance between the two electrodes (d=4 cm), an electrode area of 16 cm^2, and applied voltage in the range between 1-5 V. A ammeter was used to determine the current density running through the system. The results are shown in Figs. 2 and 3.

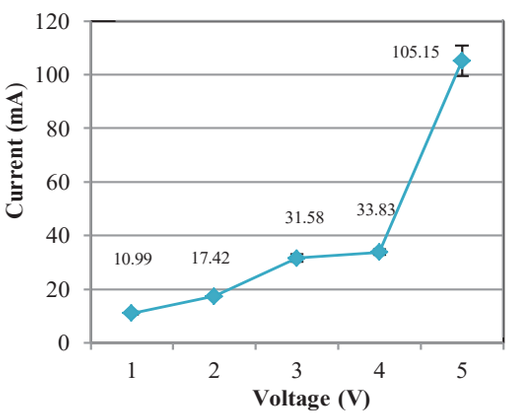

Fig. 2. The correlation between voltage and current.

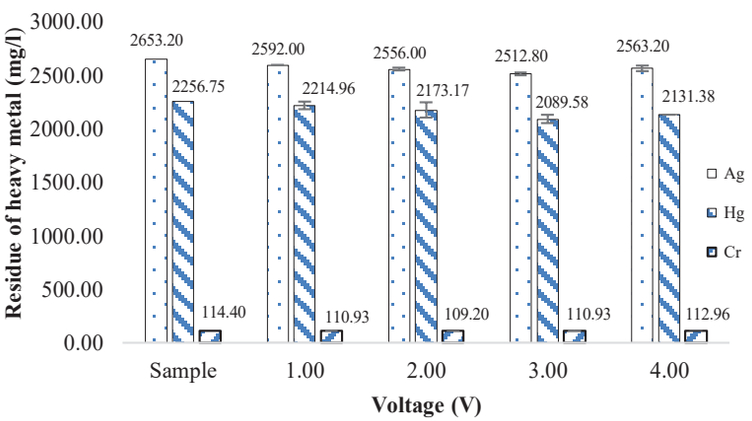

Fig. 3. Effect of voltage on removal of heavy metals.

Figure 2 shows a higher applied voltage induces a larger current. When the voltage was increased from 1 to 3 V, the electrolytic process increased steadily and reached 10.99-31.58 mA. The residual heavy metal concentration is presented in Fig. 3 together with the data from an ANOVA variance analysis, which indicated that the efficiency of heavy metal removal with 1-3 V applied voltage had a significant mean difference at the 0.05 level (α_{Ag}=0.002, α_{Hg}=0.041, α_{Cr}=0.039). These results can be explained with the understanding that the higher the voltage, the greater the current density through the system which caused reduction to occur at the cathode. The amount of metals that attached to the cathode was higher and the colour of solution was lighter than that of the original. However, when the voltage was increased further from 4 to 5 V (the current was 33.83 and 105.15 mA, respectively), electrolysis was strongly affected. However, the results in Fig. 3 show that the heavy metal removal efficiency did not differ significantly from that at 3 V. On the actual image of the setup (Figs. 4 and 5), one can see the unstable and loose electrolyte product attached to the electrodes that easily fell back into the COD wastewater. This excess electrolyte product forms from the intense electrolysis caused by the high voltage, which then released a large amount of H_2 gas at the cathode. The metals, in porous form, begin to attach unevenly to the electrode causing them to fall off and melt back into the solution thereby reducing the efficiency of the treatment. The evaluation of the efficiency of heavy metal removal as a function of applied voltage (Fig. 3) together with the results from the voltage and current correlation (Fig. 2) show that at a voltage of 3 V, electrolysis for all three metals was the most efficient and thus was used for further electrolysis experiments in this study.

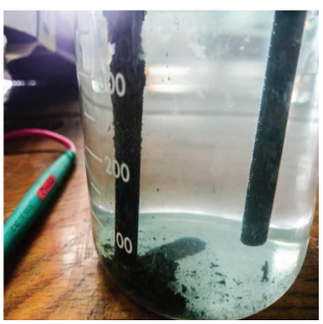

Fig. 4. Electrolyte product falling off the electrode.

Fig. 5. Heavy metals attached to electrode.

Effect of the electrode distance on efficiency of COD wastewater treatment

The electrolysis of COD wastewater was carried out for 1 h, at 3 V, in wastewater with pH<1, and an electrode area of 16 cm^2 while the electrode distance was varied to 2, 4, and 6 cm. An ammeter was used to determine the current density running through the system. The changes in current and the corresponding efficiency of heavy metal removal at different electrode distances are described in Fig. 6.

It can be seen from Figs. 6 A, B that when the electrode distance was changed from 2 to 6 cm, the current decreased from 32.85 to 29.16 mA and there were no statistically significant differences seen in the removal efficiency of heavy metals. When comparing the mean values of heavy metal removal at these different electrode distances, there was no the significant mean difference at the 0.05 level in treatment efficiency of Ag, Hg and Cr (α>0.05). These results prove that the electrode distance

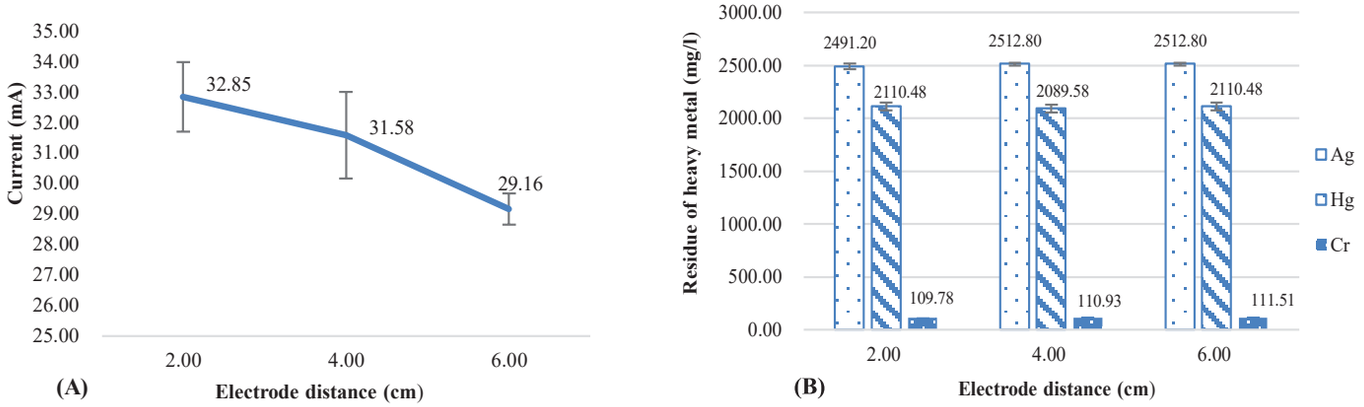

Fig. 6. Effect of the distance between electrodes on (A) the current, (B) the effect of heavy metal removal in COD wastewater treatment.

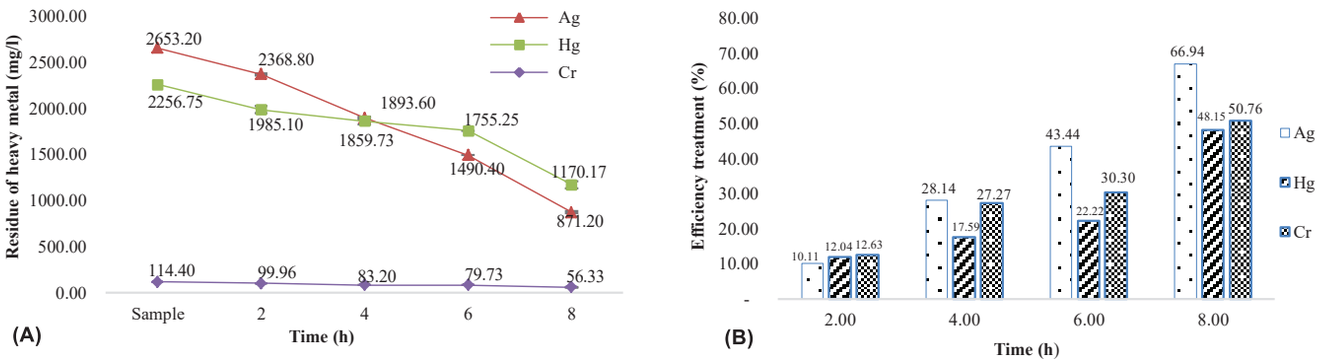

Fig. 7. Effect of electrolysis time on (A) heavy metal concentration and (B) efficiency of removal of heavy metals from COD wastewater.

does not affect the removal of heavy metals in this study. This is because the metals attaching to the electrode cause the ion layer around the cathode to decrease, leading to electrochemical polarization - that is, the discharge rate between the anode and the cathode decreases, which reduces the current [21]. Clearly, the efficiency of the removal of heavy metals was not affected by the change in distance between the two electrodes. Therefore, in this study, it was possible to ignore the effect of the electrode distance and choose an electrode distance fixed at 4 cm for all subsequent experiments.

Effect of electrolysis time on the efficiency of COD wastewater treatment

Electrolysis time is the basis for determining the efficiency of metal ion reduction and the effectiveness of metal recovery [3, 21]. The following experiment was carried out by fixing the electrode distance at 4 cm, the voltage at 3 V, the wastewater at pH<1, and the electrode area at 16 cm^2 while varying the electrolysis time from 2-8 h. Fig. 7 illustrates the effect of electrolysis time on the removal of heavy metals.

As shown in Fig. 7, when the electrolysis time was varied from 2 to 8 h, there was a significant mean difference at the 0.05 level (α=0.027) in the efficiency of heavy metal removal. The general trend was as electrolysis time was increased, the removal efficiency was higher. The highest heavy metal removal efficiency of was achieved at an electrolysis time of 8 h, current density of 1.974 mA/cm^2 where the removal efficiencies were 66.94, 48.15, and 50.76% for Ag, Hg, and Cr, respectively.

Effect of electrode area on the efficiency of COD wastewater treatment

The influence of electrode area was nvestigated by increasing the electrode area to 32 cm^2 (twice the original electrode area of 16 cm^2) and fixing the parameters of distance, voltage, electrolysis time, and pH, to 4 cm, 3 V, 8 h, and 1, respectively. From the results shown in Figs. 8 and 9, it can be seen that the performance trends of the 32-cm^2 electrode area and that of the 16-cm^2 area are quite similar. Specifically, as electrolysis time increased, the removal efficiency also rose higher. The most efficient removal was achieved at an 8-h electrolysis time and a current density of 1.66 mA/cm^2, which yielded removal

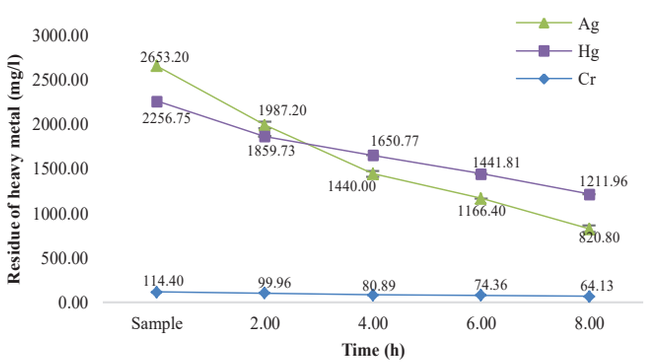

Fig. 8. The change of heavy metal concentration over electrolysis time.

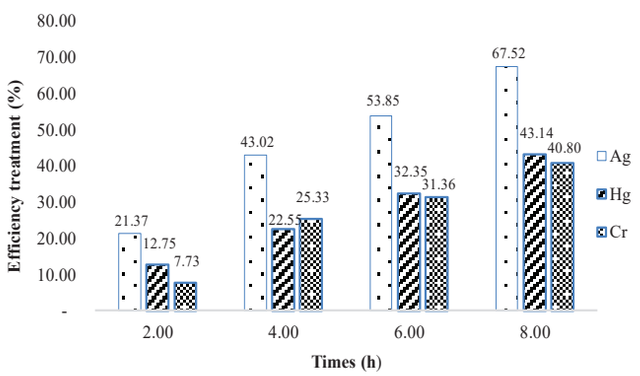

Fig. 9. The removal efficiency of heavy metals over electrolysis time.

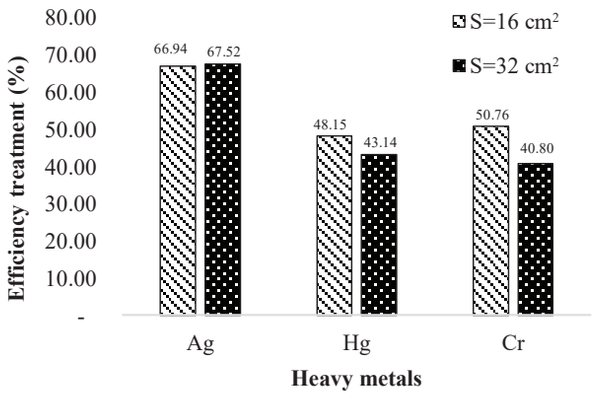

Fig. 10. Comparison of the treatment efficiency of heavy metals between the two electrode areas, 16 and 32 cm², for t=8 h.

Fig. 11. Wastewater and electrode after treatment process.

efficiencies of 67.52, 43.14, and 40.80% for Ag, Hg, and Cr, respectively. The solution colour was observed to fade over time. However, when comparing the heavy metal removal efficiency between the two electrode areas (Fig. 10), these differences were not significant. In other words, increasing the electrode area by a factor of 2 did not increase the efficiency of heavy metal removal and implies that this is not a main factor affecting COD wastewater treatment efficiency in this study (Fig. 11). This result is similar to the research done on a graphite anode, which also achieved a removal efficiency of about 50-70% and current density of 0.03-0.32 A/m² [22].

These results were also compared with other studies using electrolytic methods as presented in Table 3. Table 3 shows electrolysis treatment methods of COD wastewater using graphite electrodes with similar heavy metals removal efficiency to this study [17]. In addition, graphite is an inexpensive and abundant material and, with efficiency treatment more than 50%, they can be considered as a feasible method in wastewater treatment of heavy metals. Although the concentration of heavy metals after treatment was still higher than the Vietnamese standard (QCVN 07:2009/BTNMT), the heavy metals were significantly reduced from the original wastewater and generate favourable conditions for further treatment, which can still reduce cost as well as increase safety during operation. Moreover, one major disadvantage of chemical precipitation and other physical methods of wastewater treatment is oftentimes secondary waste (sludge) is produced, thus creating the need for continued treatment before discharge back into environment. Because secondary waste increases the cost of treatment, this method poses many advantages in addition to feasibility when applied in practice.

Table 3. Comparison of COD wastewater treatment by electrolysis process.

Operating conditions	Electrode type	Removal of heavy metals	References
pH 3.0-3.5, 10 V, electrolysis time 8 h	Fe	Ag, Cr, Fe meet discharge standards but Hg did not	Pinisakul and Kritayakornupong (2008) [14]
6 V, distance 5 cm	Pt (anode, 1x1 cm²), Cu (cathode, 1×3 cm²)	47.19% (for Ag)	Djaenudin and Syafila (2009) [15]
30 V, distance: 5 cm, electrolysis time 8 h, electrode area 50 cm²	Ti	81-89%	Diem (2016) [16]
3 V, distance 4 cm, electrolysis time 8 h, electrode area 50 cm²	Graphite	66.9% (for Ag), 48.15% (for Hg), 50.7% (for Cr).	This study

Conclusions

The electrolysis process using graphite electrodes was successfully employed for COD wastewater treatment with the benefits of low cost, easy operation, and lack of secondary waste. The results showed that the most efficient removal of heavy metals was achieved at a voltage of 3 V, equivalent to a current of 31.58 mA (current density of 1.974 mA/cm²), pH 1 of wastewater, electrolysis time of 8 h, and electrode area of 16 cm². At these optimum conditions, the residual concentration of heavy metals after treatment reached 1170.17 mg/l for Hg, 871.20 mg/l for Ag, and 56.33 mg/l for Cr, which corresponds to treatment efficiencies of 48.15, 66.94, and 50.76% for Hg, Ag, and Cr, respectively. Although the effluent of the treatment process still had a high

concentration of heavy metals and did not reach the Vietnamese standard (QCVN 07:2009/BTNMT), these results make important contributions to the pre-treatment of wastewater contaminated with heavy metals by using a simple technology with low cost and ability to reduce the concentration of pollutants by about 50%, which facilitates further treatment processes and significantly contributes in reducing the cost of an entire treatment process. In addition, the original COD wastewater had high acidity, which is suitable for treatment by electrolysis, and the pH after wastewater treatment remained low so it can be recovered and reused for different destinations.

COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

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