Electrochemical Treatment for Wastewater Contained Heavy Metal the Removing of the COD and Heavy Metal Ions

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Abstract— *In this work, the goal for an optimum condition of the electrochemical oxidation technique which is used to treat the wastewater from the metal finishing process, was experimentally investigated and obtained. All the experiments were carried out with the effects of operational parameters such as pH value, current density, electrolysis time, chemical oxidation demand (COD), removal efficiency are determined. Because of the property of the wastewater itself which conclude a lot of metal ions, means we don't have to use any of electrolyte solution, Carbon Cloth (5x5 cm) and Platinum wire were proved to be the best cathode and anode materials here respectively. The applied current density are from a solar penal (17 mA), when we don't actually control the pH value, the percentage of COD removal reached 52%, and the removal efficiency of metal ions was 22.5%. Our work focused on decreasing the quantity of heavy metal ions of the wastewater, as long as achieving a high COD removal efficiency by controlling the four key factors which were electrodes, working temperature, pH value and a fixed value of applied current.*

Keywords*— *Metal Finishing Process, Chemical Oxidation Demand, Different Pulse Voltammetry, Electrochemical Processes.

I. INTRODUCTION

Since the 20th Century, our world was improving so fast with the rapid development of industries and technologies, such as power generation facilities, green energies, electronic device manufacturing units, metal industries, the more advance they provided, the more waste they released. During the last two decades, a huge amount of industrial wastewater was discharged into rivers, lakes and other areas. Industrial wastewater is one of the main pollution sources among the pollution of the water environment. Wastewater from metal finishing industries contains heavy metals and other species belongs to the group of persistent toxic substance, which is considered to be hazardous to the environment, human health, irritates plants and animals. Heavy metals are concerned because of their toxicity, which is typically present in metal finishing wastewater with cadmium, chromium, copper, lead, silver, zinc and tin.

TABLE 1
BPT LIMITS FOR METAL FINISHING EFFLUENT

Parameters	Maximum Allowable in one day (ppm)	Daily Average for 30 consecutive days (ppm)
Total Cadmium	0.69	0.26
Total Chromium	2.77	1.71
Total Copper	3.38	2.07
Total Lead	0.69	0.43
Total Nickel	3.98	2.38
Total Silver	0.43	0.24
Total Zinc	2.61	1.48
Total Cyanide	1.20	0.65
pH	6.0-9.5	6.0-9.5

Table 1 shows the EPA (the United States Environmental Protection Agency) best practical control technology, BPT, limits for metal finishing effluent [1]. In the present days, water has become a vital resource which is limited and in many cases, there will be not enough water with appropriate quality to supply for both domestic use and industrial at the same time. According to this situation, there is an urgent need to apply an effective, innovative and reasonable technique for the treatment of wastewater, especially the industrial wastewater.

In literature, there were several technologies can be used to treat those industrial flow streams, but electrochemical treatment seems to be a very promising and suitable technique which requires a minimal additives, high effectiveness, low maintenance cost, rapid achievement of results and less need for labor [2]. Previous researches indicates the relationship between those electrochemical processes which is believed to have three possible mechanism involved: EC (Electrocoagulation), EF (Electro-flotation), and EO (Electro-oxidation) [3].

In this work, we use the EC (Electro-coagulation) to treat the wastewater of the metal industry, in which contains heavy metal ions, without the supports of any electrolyte and additives. Our process is not only different with other conventional processes before, but also proved it's effectively results with further room to improve. According to Chen et al [4], EC has many advantages over the others coagulation process, and has been proven to be one of the best process for wastewater treatment [5], The process is an electrochemical production of destabilization agents which usually is noble metal, the noble metal works as a couple of electrode that bring the neutralization of electric charge for removing pollutants. With the support from the electricity, the metal nano-particles can be charged and act like small magnets to form a mass. During the EC process, the coagulant is generated by the electrolysis oxidation of anode material; the charged ionic particles are removed by reaction among oppositely charged ions, or with flocs of metallic hydroxides [6].

II. EXPERIMENTAL SECTION

Electrolysis is an electrochemical method which is mainly used to treat the wastewater. This process involved in using consumable electrodes to supply ions into the wastewater, the released ions then neutralize the charges of the particles and initiates the coagulation process. These ions remove the undesirable contaminants by means of chemical reaction and precipitation. According to Mollah et al [7], the principle of electrolysis was indicated in figure 2, which has its main process is electrolytic reaction at the surface of each electrode and also occurred the adsorption and removal of soluble and colloidal pollutant.

- At Anode (+): $M \rightarrow M^{n+} + ne$ (1)
- At Cathode (−): $nH_2O + ne \rightarrow nH_2 (\uparrow) + OH^-$ (2)

At Cathode may also happen the reaction by the OH^- ions that were generated together with hydrogen gas at appropriate pH value:

- $M + nH_2O + OH^- \rightarrow M(OH)_n (\downarrow) + nH_2 (\uparrow)$ (3)

The EC (Electro-coagulation) has some advantages over the traditional flotation and coagulation such as better removal rate to the small colloidal particles, along with that, the electricity applied to the system sets the whole process in motion and made out the larger probability of coagulation. We mean to treat the waste water only by control key factors and without the support of chemical additives, but note that the presence of additives such as NaCl would also lead to the decrease of the power consumption because of the increase of the conductivity [8].

- The M^{n+} and OH^- ions are generated by the (1) and (2) reaction at cathode and anode, then react and form up the $M(OH)_n$ as a precipitation.
- The destabilized particles aggregate to form flocs
- Hydrogen bubbles produced at Cathode during the process induce the flotation of most flocs.

With EC technique the electrodes with higher exchange current density were usually used, and Pt was found to be the best electrode [9]. In this work, we used Pt and Carbon Cloth as electrodes, with the purpose to remove the metals ions and COD of the wastewater, formulas that used to calculate the COD Removal, Energy Consumption can be found by the following references [10, 11, 12].

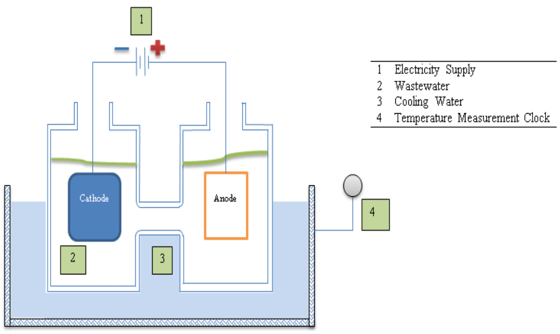


FIGURE 1. ELECTRO COAGULATION EXPERIMENTAL SYSTEM

Figure 1 shows the experiments setup with undivided 100mL capacity electrochemical cell with total of 80mL wastewater. Cathode and Anode materials were selected between many couple of electrodes, such as: carbon cloth, platinum wire, conducting glass. The experiments set up here also by means of producing hydrogen gas from wastewater, so our device is quite different with conventional electrochemical cell. Electrode was connected to a solar panel with a voltage of 17V and current density of 45mA). The electrochemical cell was put in a temperature controlling tank device; the temperature was also carefully managed and keeps at 35 Celsius Degree.

Our work was carried out with a series of experiments that included lots of parameters, such as working temperature, pH value, voltage, electrode types and electrolysis operation time. Table 2 below summarized all the parameters of this research so that all the data can be tracked easily.

TABLE 2
EXPERIMENTAL PARAMETERS SUMMARIZATION

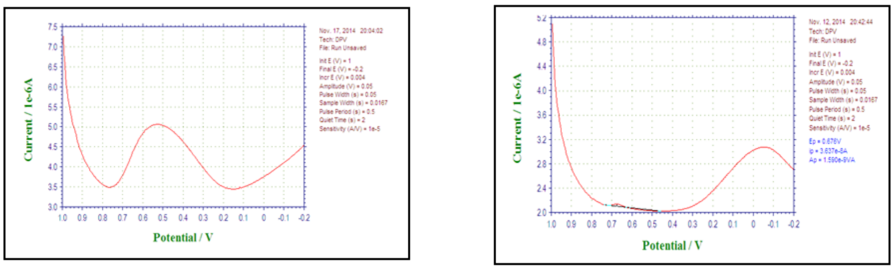
Temperature (^oC)	pH Value	Voltage (V)	Electrolysis Time (mins)	Applied Energy (V)
35	3.5	7.5	15	Solar Panel (17V)
	5	10	30	
	7	15.5	45	
	11	17	60	
	13	20	75	

All the experiments were carried one by one respectively out and compare to each other by COD test and DPV measurement in order to find the optimum working condition of the whole process. Noted that, during the electrolysis process, pH value of the solution was always decrease due to the oxidation reaction, and the creation of the precipitation did not means that all the COD value of the treated wastewater sample will decreased as well. Without the support from the electrolyte solution, some of the treated samples appeared to have a higher COD value than the original sample, due to the appearance of other hydrogel that may was created during the process.

III. RESULTS AND DISCUSSION

3.1. Electrodes Material Selection

The best couple of electrode was selected based on their performance of a high exchange of current density. Nine couples of electrode were used in electrolysis of wastewater from the metal finishing industry, for current density, COD Removal percentage, current efficiency and even hydrogen producing ability. Figure 2 shows the two results of DPV (Different Pulse Volumetric) measurement of an original wastewater sample, and the best treated sample (with carbon cloth was used as cathode and platinum wire as anode) based on the value of COD Removal percentage and current density.



Original Wastewater Sample with COD of 53.26 (mg/mL)

Treated sample (Using Carbon Cloth as cathode and Pt wire as anode) with COD of 25.49 (mg/mL)

FIGURE 2. DIFFERENT PULSE VOLUMERIC (DPV) RESULTS

According to the result listed in Table 3, Pt appears to be the best candidate for anodic material, when carbon cloth was our best shot as cathode. By a sample syringe, we try to take the air close to the cathode inside the electrochemical cell then measure its property and get almost 30% of Hydrogen gas inside that mixture of air. It can be explained by the area surface of the carbon cloth we used in her is much larger than the Pt wire can provide, and thus so when the reduction process happens at cathode, it was provide a higher potential and area to react.

TABLE 3
COD REMOVAL EFFICIENCY OF EACH COUPLE OF ELECTRODE

Electrodes	COD Removal Percentage (%)
Pt Wire (+) and Glass (-)	24.53
Pt Wire (-) and Carbon Cloth (+)	11.32
Pt Wire (+) and Carbon Cloth (-)	52.2
2 Pt Wire	27.63
2 Carbon Cloth a	26.49
2 Glass	13.25

3.2. Effect of Applied Voltage

Electrolysis was conducted using different value of voltage to investigate its effect on the COD Removal percentage of the metal finishing wastewater. Figure 5 shows that the COD Removal was increase proportional to the increase of voltage applied. This result can be explained by the production of oxidant such as hypochlorite ions in the solution [14].

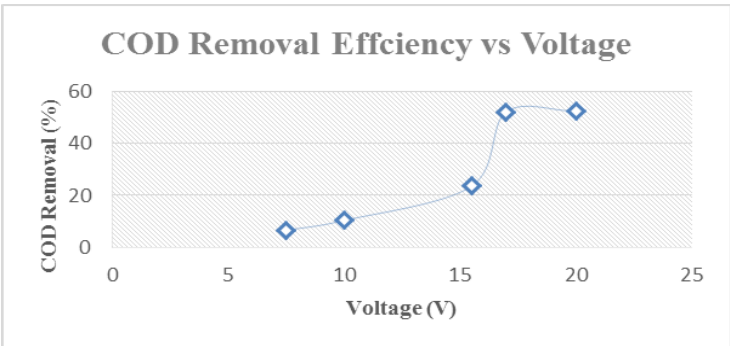


FIGURE 3. EFFECT OF VOLTAGE ON COD REMOVAL EFFICIENCY

The degradation rate of pollutant species is related to the increasing of the current density and voltage which were proportion to the change of the oxidant inside the solution [15] [16]. With the generation of the oxidant increasing, the production of ions was also increase which result to the increasing of the overall reaction rate [17]. However, the significantly increasing of the applied energy may lead to undesirable reactions, which is very hard to control and also waste of energy. According the result obtained, the COD Removal percentage was almost stable at the voltage of 17V and slowly increase until the voltage was recorded at 20V, (significant increase by the voltage of 15V).

3.3. Effect of Electrolysis Time

Figure 4 shows the relationship between COD removal percentages with the electrolysis time. Generally, the organic concentration in wastewater reduces with the increase of the electrolytic time [18]. The COD removal efficiency depends directly on the concentration of the hypochlorite ions which is generated during the electrolysis process.

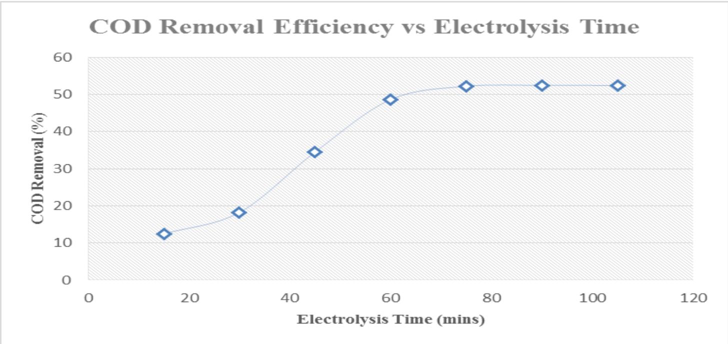


FIGURE 4. EFFECT OF ELECTROLYSIS TIME ON COD REMOVAL EFFICIENCY

The longer operation time, the more of hypochlorite will be generated in the solution (with fixed current density and applied voltage) [19]. As we can observe, the COD removal percentage in Figure 6 rapidly increase along with the increasing of the operation time up to 75 minutes. After 1h of operation, the COD removal percentage was slowly increased until it reaches 52%. The result of COD removal percentage only some slightly differences in comparison between 75, 90 and 105 minutes, so the electrolysis time of 75 minutes can be considered as the optimum operation time.

Our works here was carried out by all means of saving the energy and apply the green energy philosophies to the wastewater treatment, so that we try to avoid any kind of adding more chemical into the wastewater, especially strong alkaline solution such as NaOH and acidic like HNO_3. We measure the pH value of the original wastewater sample and our treated sample (with fixed conditions of electrolysis time and applied energy), and we found that the value was slightly change from 7.2 to 6.1; in this manner, we would like to choose the pH 7 as our optimum pH value, although that the treated pH value always appears to have a higher COD removal efficiency.

Based on the result obtained, the optimum operating conditions selected for treatment of metal finishing wastewater were listed in the table below.

TABLE 4
OPTIMUM CONDITONS OBTAINED

Electrodes	Working Electrode (Anode)	**Platinum Wire**
	Counter Electrode (Cathode)	**Carbon Cloth**
Supporting Electrolyte		**No**
pH Value		**7**
Electrolysis time (mins)		**75**
Voltage Applied (V)		**17**
COD Removal Efficiency (%)		**52.2**

IV. CONCLUSION

The electrolysis has been long used as a very positive and reliable method to treat the wastewater contains heavy metal ions. The process itself was a cost effective process, moreover, electrolysis also has significant advantages such as its simple equipment, convenient operation and non-requirement of chemical substance. Our work focused on decreasing the quantity of heavy metal ions of the wastewater, as long as achieving a high COD removal efficiency by controlling the four key factors which were electrodes, working temperature, pH value and applied current. According to the results that we obtained, the whole process allows the wastewater treatment to reduce the organic contaminants, and also electrochemically oxidized without adding any additives, with the support of a small current density by solar cell, and thus we believe the process was not only saving energy but also a green eco-friendly process, that can be put in use for the advantage of an economic aspects in the near future.

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