

Influence of voltage input to heavy metal removal from electroplating wastewater using electrocoagulation process

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Abstract. In medium capacity, electroplating industry usually treats wastewater until 5 m³ per day. Heavy metal content becomes concern that should be reduced. Previous studies performed electrocoagulation method on laboratory scale, either batch or continuous. This study was aimed to compare the influence of voltage input variation into heavy metal removal in electroplating wastewater treatment using electrocoagulation process on laboratory-scale in order to determine the optimum condition for scaling up the reactor into pilot-scale. The laboratory study was performed in 1.5 L glass reactor in batch system using wastewater from electroplating industry, the voltage input varied at 20, 30 and 40 volt. The electrode consisted of aluminium 32 cm² as sacrifice anode and copper 32 cm² as cathode. During 120 min electrocoagulation process, the pH value was measured using pH meter, whereas the heavy metal of chromium, copper, iron, and zinc concentration were analysed using Atomic Absorption Spectrophotometer (AAS). Result showed that removal of heavy metals from wastewater increased due to the increasing of voltage input. Different initial concentration of heavy metals on wastewater, resulted the different detention time. At pilot-scale reactor with 30 V voltage input, chromium, iron, and zinc reached removal efficiency until 89-98%, when copper reached 79% efficiency. At 40V, removal efficiencies increased on same detention time, i.e. chromium, iron, and zinc reached 89-99%, whereas copper reached 85%. These removal efficiencies have complied the government standard except for copper that had higher initial concentration in wastewater. Kinetic rate also calculated in this study as the basic factor for scaling up the process.

1. Introduction

Electroplating is an electro-deposition process for producing a dense, uniform, and adherent coating, usually of metal or alloys, upon a surface by the act of electric current deposits metal coating onto metal or plastic by electrolytic process [1]. On their process, electroplating industries need raw water that usually comes from groundwater which later result wastewater with high heavy metals concentration, i.e. copper, nickel, chrome, and zinc diluted in cyanide, acid, alkaline and phosphate. They must install wastewater treatment plant to comply government standard before they discharge the wastewater into water body. In medium capacity, each industry could discharges wastewater until 5 m³ per day. From environmental prospective, this condition results not only waste water with high heavy metals concentration, i.e. copper, iron, chrome, and zinc, but later also facing the lack of ground water.

Heavy metal in wastewater could be reduced by electrochemical, hydroxide precipitation and extraction [2]. Previous researches applied hydroxide precipitation process for metal wastewater treatment that usually requires different optimum pH. This precipitation might cause some problems



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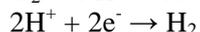
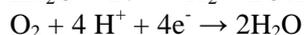
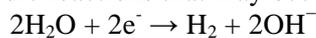
of bulky low-density-sludge and different optimum pH that probably dilute the other metals present in wastewater [2]. Electrochemical is applicable for heavy metal removal with high concentration, as well as wastewater from electroplating industry, and more selective compare to hydroxide precipitation.

Electrocoagulation, as one of the electrochemical processes, could minimize sludge that usually exists as the end product from any conventional hydroxide precipitation process [3]. Electrocoagulation produces less sludge than conventional precipitation process for removing chromium [4].

Electrocoagulation combines electrochemical and coagulation-flocculation process that apply cell with metal anode (usually steel and aluminium), and requires electric supply to produce chemical reaction. Anode in this system would function as “sacrificial electrode ion”. Ion Al^{3+} and OH^- resulted on electrode surface would react with metals in wastewater and later forms aluminium hydroxide. Main chemical reactions on electrocoagulation process are:

Anodic reaction [3]: $\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$

Cathodic reactions that may occur might be expressed as [3,5] :



Further, Al^{3+} and OH^- ions generated at electrode surfaces react in the bulk wastewater to form aluminium hydroxide:



Base on Faraday law, the amount of sacrifice anode dissolved depend on electricity pass through electrolytic solution, so the heavy metal removal by electrocoagulation is influenced by direct voltage input. The optimum voltage input could produce less sludge production on maximum removal efficiency [6]. Previous studies performed electrocoagulation process on heavy metal or organic removal from synthetic or industrial wastewater on laboratory-scale, either batch [3,6,7,8,9] or continuous [7]. This study present work would determine studied the optimum voltage input base on removal efficiency on batch laboratory-scale to determine kinetical rate for scaling-up into pilot-scale reactor.

2. Experimental

2.1. Materials

This study was conducted in 1,5 L batch-reactor with aluminium-plate anode and copper-plate cathode with 2 cm width x 8 cm length x 1 mm thickness respectively. Wastewater sample was taken from rinsing wastewater of degreasing and metal plating process in electroplating industry PT.DSB near Bandung, West Java.

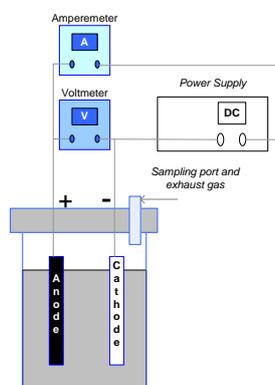


Figure 1. Scheme of electrocoagulation process.

2.2. Experimental setup

The laboratory-scale experiment was performed, as shown in Figure 1., on room temperature ($\pm 25^\circ\text{C}$), and pressure 1 atm. The electroplating wastewater was placed in the chamber. Previous studies showed optimum reactor performance on 12V [3] and 30V voltage input [6], or current density of 3 A dm^{-2} [8] and 4.8 A dm^{-2} [9], depend on initial concentration. Considering the initial concentration of wastewater, in this study the direct voltage from power supply was varied at 15, 20, 30 and 40 volt during 120min. Optical density and pH were measured overtime and every 10 min sample was taken for metal concentration measurement. Using parameters from laboratory-scale experiment, pilot-scale reactor would be constructed and tested using further detention time calculation.

2.3. Analysis

The soluble metal concentration of Cr(VI), Cu(II), Fe(II), Zn(II) was analysed using Flame Atomic Absorption Spectrophotometer Varian GBC 903, the pH was measured using pHmeter Lutron PH-208, and Optical Density/OD was measured using Spectrophotometer LW Scientific V325XS on 464nm. OD measurement was performed to describe the turbidity fluctuation on reactor which was assumed to be correlated with metal concentration.

2.4. Calculation

Electrocoagulation process performance is described by the different of initial anode and cathode mass (m_0 , g) with the mass of each electrode at time t (m_t , g):

$$\text{Electrode mass} = m_0 - m_t \quad (1)$$

To calculate kinetic rate from batch experiment, the equation below was used [10]

$$y = kx + a \quad (2)$$

where k is the slope of metal ion concentration, y , during reaction time, x .

The reaction rate would help the calculation of the laboratory-batch scale into scaling-up continuous reactor. Using continuous equation on continuous stirred tank reactor (CSTR)

$$V \cdot \frac{dC_i}{dt} = F \cdot (C_i - C_0) + R_A \cdot V \quad (3)$$

where V = reactor volume (liter), C_i = wastewater concentration (mg.L^{-1}); C_o = outlet concentration (mg.L^{-1}); F = debit ($\text{L} \cdot \text{second}^{-1}$), $R_A = -k \cdot C_o$, and k is the value from batch reaction. In steady state condition,

$$V \cdot \frac{dC_i}{dt} = -k \cdot C_i = 0 \quad (4)$$

So that:

$$k \cdot C_o \cdot V = F \cdot (C_i - C_o) \text{ or } V = \frac{F(C_i - C_o)}{k \cdot C_o} \quad (5)$$

Heavy metal removal (%) was calculated based on initial metal concentration (C_o , mg.L^{-1}) and metal concentration at time t (C_t , mg.L^{-1}):

$$\text{Removal} = \frac{C_o - C_t}{C_o} \times 100\% \quad (6)$$

3. Result and discussion

3.1 Electrode mass and removal

Electrocoagulation process occurred including reaction on anode and cathode. Al^0 from sacrifice anode is oxidized into Al^{3+} ion, reacts with ion hydroxide in cathode, tend to flock in $\text{Al}(\text{OH})_3$ form and sweep the other metal in electroplating wastewater. Base on equation (1), during 120 min for each voltage input, anode and cathode mass change occurred, as shown in Figure 2.

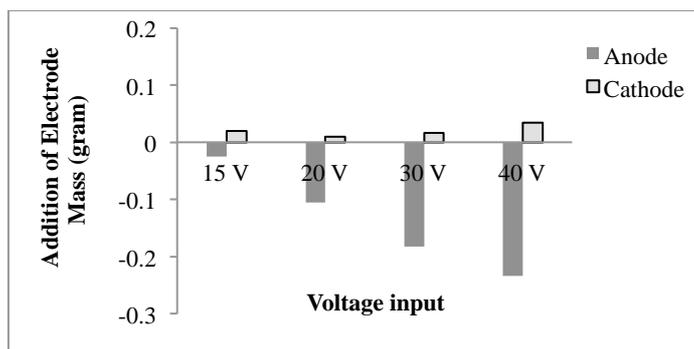


Figure 2. Mass change on anode and cathode.

Positive mass change on cathode means an addition on surface area, whereas negative change on anode means a mass reduction on anode or anode has sacrificed its metal to dilute in electrolyte solution. Base on Figure 2, electrocoagulation process occurred as expected. Higher voltage input gives higher anode mass reduction rate compare to cathode mass addition. On electrolysis cell (as electrocoagulation process), cathode has negative charge and anode has positive charge. It means oxidation rate of Al^0 anode into Al^{3+} was dominant that allows other ion metals in wastewater (positive charge) swept by $Al(OH)_3$ precipitate before attract to cathode surface (negative charge).

The metals in wastewater could present as colloid. Although initial pH of wastewater is around 5.2 until 7.5, at the end of the process it tends to increase for every voltage input variation, as shown in Figure 3. This condition allows the metals that present in colloid are swept by $Al(OH)_3$ precipitate, since aluminium hydroxide species from sacrifice anode are transformed into insoluble as the pH increase [11] and provide advantage for metal removal by hydroxide precipitation. This condition could be described by optical density as shown in Figure 4.

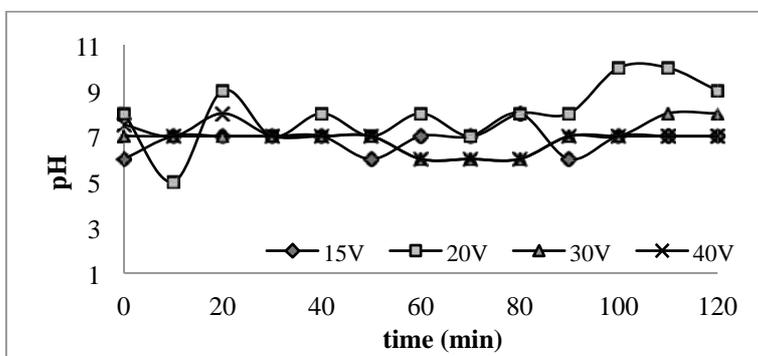


Figure 3. pH during reaction time.

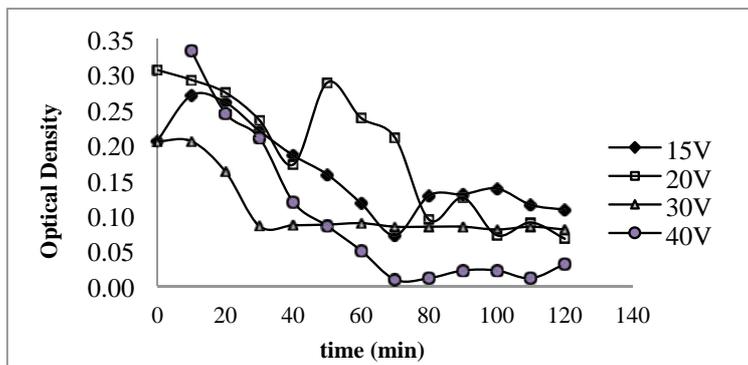


Figure 4. Optical density during reaction time.

Base on Figure 4, OD decreased during electrocoagulation and higher voltage input give faster OD decreasing. On 30V, at $t = 30\text{min}$ the process has reach its lowest OD value, whereas on 40V it needs 70 min to reach its lowest OD value and afterward the value relatively constant. The OD decreasing on 30V and 40V give better result than 15 and 20V voltage input. However, even OD decreasing also occurred on 40V, but there was no significant difference between 30V input voltage. Further detail for every heavy metal removal would be analysed on 30V and 40V.

3.2 Kinetic rate

To determine the reaction kinetic rate, regression with polynomial approach was made on first order 30V and 40V input [11, 13]. Initial copper concentration was quite high compare to other metals concentration, so that copper concentration plotted in second axis. Using 30V input, iron, zinc and copper concentration drastically decreased at first 10 min. Chromium required 40 min until reach constant concentration. It means no significant metal removal after $t = 40\text{ min}$. As shown in Figure 5., based on the equation (2), the slope during electrocoagulation process is 0,035/min until 0,067/min, with $k_{average}$ is 0,051/min.

Using 40V input, all metals decrease significantly at $t = 10\text{min}$. After that, the removal showed insignificant decreasing. Based on equation (2), the decreasing results slope between 0.003/min until 0.032/min, with $k_{average}$ is 0,018/min.

Due to equation (5) k value affects to volume dimension of the reactor where higher k gives less volume of reactor when debit and concentration are constant.

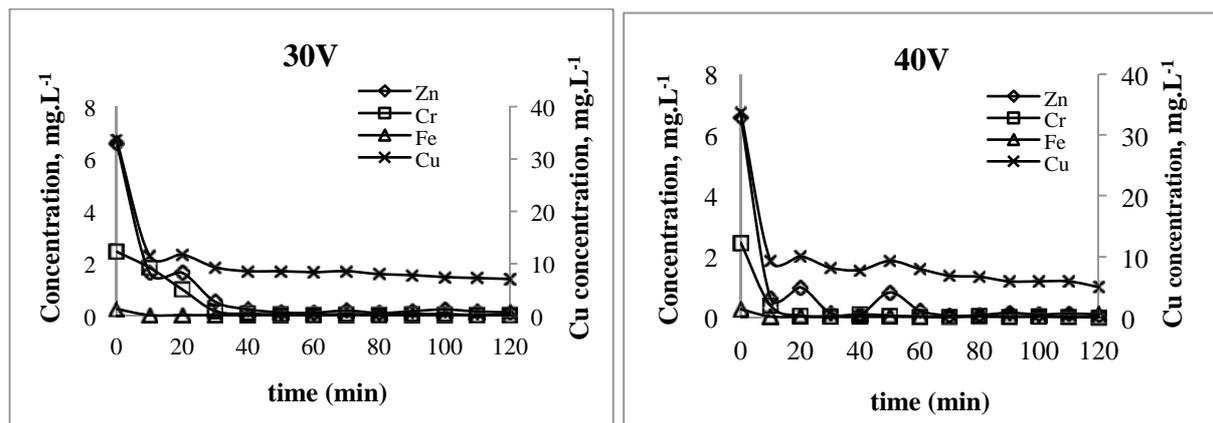


Figure 5. Heavy metal concentration at voltage input variation.

3.3 Pilot-scale

Electrocoagulation process on laboratory-scale of 1.5 L on batch system results kinetic rate as the basic factor for pilot scale calculation. Base on equation (5), it assumed that wastewater debit (F) 3 m^3 on 6 hours working period or equal with $500\text{ L}\cdot\text{hour}^{-1}$, and the metal concentration in the effluent fulfilled to standard regulation, so the pilot-scale reactor volume is 915 L. Detention time on the reactor, t , is calculated by dividing reactor volume by debit [13]. It results 100 min detention time.

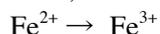
Pilot-scale was constructed and tested using 30 and 40V input, due to the optimum OD removal efficiency on laboratory-scale, then the removal efficiency was calculated using Equation (6). The removal of metal concentration during 100 min detention time that shown in Table 1, compared with regulation standard, met the requirement except for copper. It might be caused by copper initial concentration that higher than other metals, which impact into longer reaction time to remove all concentration. Value of pH may influence copper removal since copper removal using hydroxide precipitation occurs on high basic condition, around pH 10 [14].

In electrocoagulation process, heavy metals may react in some different ways, as [3]:

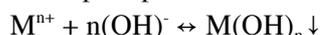
- a reduction at the cathode, as in the case of chromium (VI):



- or oxidation, as in the case of iron:



- or hydroxide precipitation of heavy metals as the reaction below:



The reduction of chromium (VI) occur in cathode into Cr (III) then precipitate as hydroxide.

Table 1. Removal efficiency.

Heavy Metal	Influent Conc. (mg.L ⁻¹)	Standard* (mg.L ⁻¹)	30 V		40 V	
			Effluent Conc. (mg.L ⁻¹)	η (%)	Effluent Conc. (mg.L ⁻¹)	η (%)
Cr	2.450	0.5	0.054	98	0.063	97
Cu	33.670	0.5	7.052	79	5.000	85
Fe	0.265	5.0**	0.030	89	0.030	89
Zn	6.600	1.0	0.108	98	0.077	99

*Regulation of Ministry of Environmental no. 5 year 2014

**Decree of Governor of West Java no. 6 year 1999

Based on Table 1, voltage input between 30 and 40V does not give significant differences. Since operation cost also being a consideration factor when deciding the optimum condition [15], so 30V should be the optimum voltage input that suggested to fulfil the regulation standard.

4. Conclusion

Electrocoagulation using aluminium anode and copper cathode on electroplating industry wastewater on laboratory and pilot-scale has been studied. Voltage input influence the removal efficiencies. Due to efficiency, the optimum voltage input to remove chrome, copper, iron, and zinc from electroplating wastewater in this study was 30V. On this optimum voltage, OD removal efficiency on laboratory-scale is 60% in 30min while on pilot-scale removal efficiency ranges between 79-98%, depend on initial heavy metal concentration. Series installation of electrocoagulation might be an alternative to overcome high concentration of copper in the effluent.

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