

Int'l Conference Proceedings

5th International Conference on Research in Chemical, Agricultural and
Biological Sciences (RCABS-2017)

International Conference on Studies in Architecture, Civil, Construction and
Environmental Engineering (SACCEE-2017)

International Conference on "Advances in Engineering and Technology" (BICAET-17)

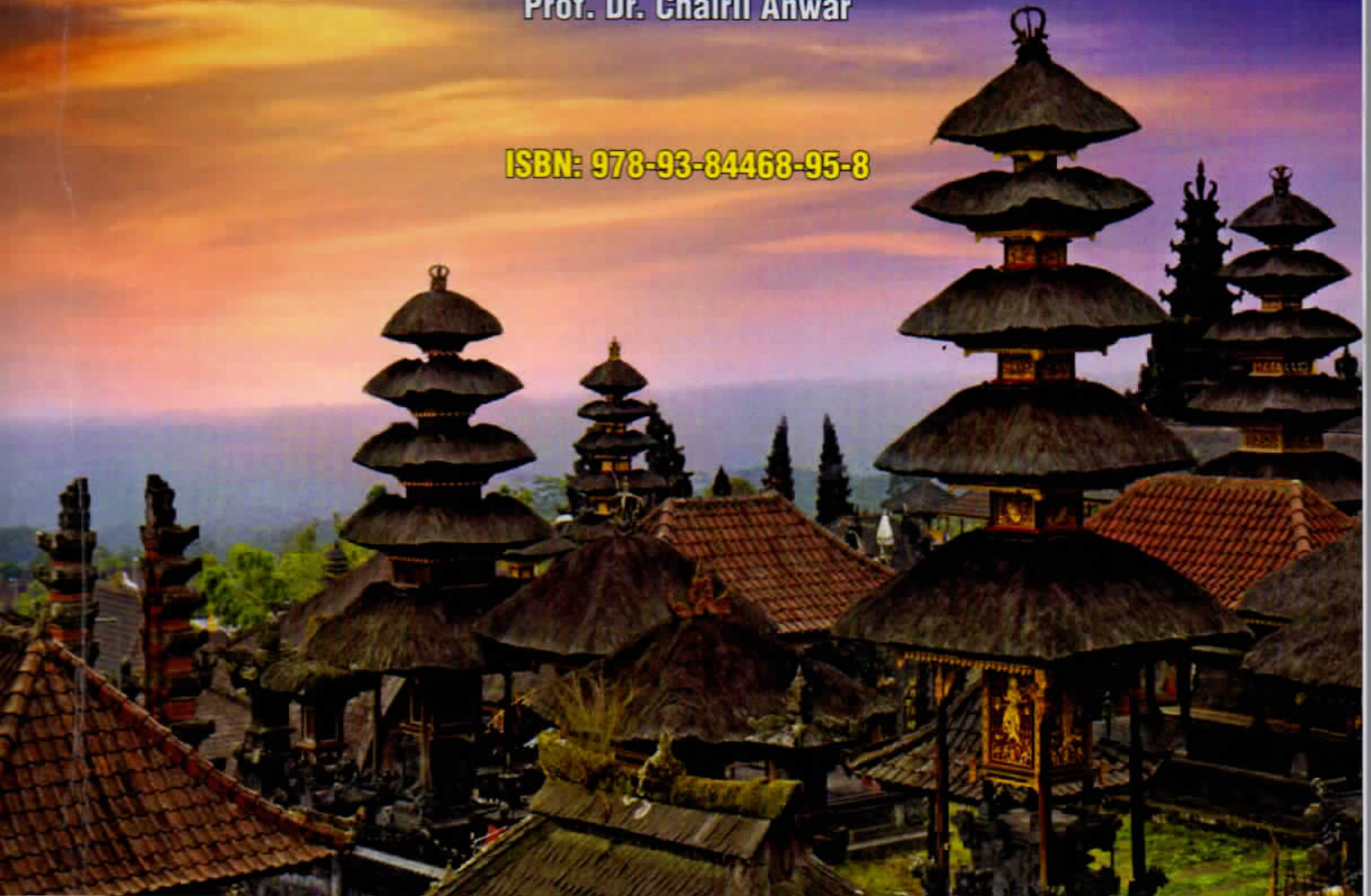
Jan. 10-11, 2017 Bali (Indonesia)

Editors:

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ISBN: 978-93-84468-95-8



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PREFACE

Dear Distinguished Delegates, Colleagues and Guests,

The URUAE, EAP Organizing Committee warmly welcomes our distinguished delegates and guests at Universal Researchers (UAE), BICAET-17, Eminent Association of Pioneers in Research, RCABS-2017, and SACCEE-2017. Int'l Conferences scheduled on *Jan. 10-11, 2017 Bali (Indonesia)*. The main themes and tracks are Chemical, Agricultural and Biological Sciences, Architecture, Civil, Construction and Environmental Engineering, Advances in Engineering and Technology.

These conferences are managed and sponsored by Universal Researchers (UAE), Eminent Association of Pioneers and assisted by University of Johannesburg and University of Quebec. URUAE, and EAP are striving hard to compile the research efforts of scientists, researchers and academicians across the broad spectrum of Science, Engineering and Technology. These conferences are aimed at discussing the wide range of problems encountered in present and future high technologies among the research fraternity.

The conferences are organized to bring together the members of our international community at a common platform, so that, the researchers from around the world can present their leading-edge work. This will help in expansion of our community's knowledge and provide an insight into the significant challenges currently being addressed in that research. The conference Program Committee is itself quite diverse and truly international, with membership from the America, Australia, Europe, Asia and Africa.

The conferences has solicited and gathered technical research submissions related to all aspects of major conference themes and tracks. This proceeding records the fully refereed papers presented at the conference.

All the submitted papers in the proceeding have been peer reviewed by the reviewers drawn from the scientific committee, external reviewers and editorial board depending on the subject matter of the paper. Reviewing and initial selection were undertaken electronically. After the rigorous peer-review process, the submitted papers were selected on the basis of originality, significance, and clarity for the purpose of the conference. The main goal of these events is to provide international scientific forums for exchange of new ideas in a number of fields that interact in-depth through discussions with their peers from around the world.

The program has been structured to favor interactions among attendees coming from many diverse horizons, scientifically, geographically, from academia and from industry. We would like to thank the program chairs, organization staff, and the members of the program committee for their work. We like to thank and show gratitude to Editors from URUAE, and EAP. We are grateful to all those who have contributed to the success of URUAE, and EAP Bali (Indonesia) Jan. 10-11, 2017 Conferences. We hope that all participants and other interested readers benefit

scientifically from the proceedings and also find it stimulating in the Process in their quest of achieving greater heights. Finally, we would like to wish you success in your technical presentations and social networking.

We hope you have a unique, rewarding and enjoyable week at URUAE, and EAP Conferences at vibrant Bali (Indonesia).

With our warmest regards,

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Jan. 10-11, 2017

Bali (Indonesia)

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Effectiveness of Electroplating Wastewater Treatment by Electrocoagulation

Siti Marwati and Regina Tutik Padmaningrum

Abstract. Electroplating wastewater can cause environmental damage. Research was conducted to determine the effectiveness of electroplating wastewater treatment by electrocoagulation (EC). The sample was taken from silver industrial center, Kotagede Yogyakarta Indonesia. The electrolytic cell used to conduct the experiment consists of 500 mL of sample in glass beaker. The electrodes were aluminum plate (7.50 cm x 4.00 cm x 0.05 cm) as a cathode and iron plate (7.50 cm x 4.00 cm x 0.10 cm) as an anode. The effective area of each electrode used was 16 cm² (4.0 cm x 4.0 cm). The anode/cathode gap was kept constant at 1 cm. A gentle agitation was made using a magnetic stirrer. The applied electrical potential was 1 Volt. The pH of the solution was 8. Effectiveness was reviewed based on analysis of wastewater parameters before and after EC process with clean water quality standard in Health Minister of Indonesian No. 416 / PERMENKES / PER / IX / 1990 and according to the effluent standard for the metal coating industry regulations Governor of Yogyakarta Indonesia No. 7 Year 2010. In conclusion, EC process is an effective method for reducing metal ions and increase the pH but less effective in reducing some of the anions. All of the parameters which analyzed after EC process were below the quality standard parameters except SO₄²⁻ ion and conductivity.

Keywords-- electrocoagulation, electroplating, wastewater

I. INTRODUCTION

Electroplating industry is one of the industries which grow rapidly in particular at Yogyakarta Indonesia. This development can provide positive and negative effects. The positive effects may be varied products electroplating such as craft and metal decoration. On the other hand, there are some negative effects like increasing amount of waste particularly liquid waste containing harmful substances.

The industrial wastewater contains various types of harmful heavy metals and toxic substances such as cadmium, chromium, lead, copper, zinc, cyanide and greasing solvent [1]. Lead has been the main concern in wastewater treatment because it is the disruption of the growth process in children and interfere the metabolism in the body. The excessive Cu²⁺ consumption leads to its deposition in liver and subsequent vomiting, headache, nausea, respiratory problems, abdominal pain, liver and kidney failure and finally gastrointestinal bleeding [2]. Cadmium and chromium are the probable human carcinogen [3]. The harmful effects of cadmium include number acute and chronic disorders, such as "itai-itai" disease, renal damage, emphysema, hypertension and testicular atrophy [4,5]. Some of the anions contained in the electroplating wastewater are CN⁻, SO₄²⁻, NO₃⁻ and NO₂⁻. Anions have caused environmental pollution, especially SO₄²⁻ and CN⁻.

Several methods for electroplating wastewater treatment has been carried out by industry practitioners, but has not managed optimally. Many industry practitioners do not treat wastewater and the waste is directly throw away into the environment. As a result, the concentration of these metals exceeded the environmental quality standards.

Various treatments are employed to treat wastewater containing small or large concentration of heavy metals. The treatment methods such as adsorption [6], biosorption [7], ion exchange [8], zeolite [9], and chemical coagulation [10] are used for the efficient removal of heavy metals. Each treatment method has advantages and disadvantages. Ion exchange, for example, while highly effective in removal of certain charged contaminants, requires resin regeneration or replacement at a high cost. While chemical precipitation is a simple process, it does generate a high volume of sludge. Alternatively, EC process was found to be an effective technique for precipitating industrial wastewater pollutants [11,12]. The simplicity of EC operation, low energy consumption, high quality effluent, low sludge formation and low dissolved solids made EC a desirable treatment method [11,13,14].

According Kobya, et al [15], EC is a metal hydroxide floc formation process in wastewater with electrodisolution by aluminum or iron as an electrode. The main reaction that occurs in the electrocoagulation is the formation of Al³⁺ ions at the anode and OH⁻ ions and H₂ gas at the cathode. Aluminum hydroxide floc acts as adsorbent of heavy metal ions in the wastewater. Furthermore, metal ions combine with OH⁻ ions at the cathode and precipitation. It can be used to remove heavy metal pollutants in wastewater.

The EC technology is essentially electrolytic processes that involve the destabilization of suspended, emulsified or dissolved pollutants in an aqueous medium, by the application of an electric current. In EC process, there is a reduction of the net surface charge to a point where the colloidal particles can approach closely enough for Van der Waal's forces to hold them together and allow aggregation to take place [16]. EC has shown effective results on textile wastewater [17], pulp and paper wastewater [18], tannery wastewater [19], slaughterhouse wastewater [20], and dairy wastewater [17].

This research studied the effectiveness of the EC method. Effectiveness was reviewed based on analysis of wastewater parameters before and after EC with clean water quality standard in Health Minister of Indonesian No. 416 / PERMENKES / PER / IX / 1990 and according to the effluent standard for the metal coating industry regulations Governor of Yogyakarta Indonesia No. 7 Year 2010

II. MATERIAL AND METHODS

Wastewater sample was taken from silver industrial center, Kotagede Yogyakarta, Indonesia. Different concentrations were prepared by dissolving appropriate amount of salts of Cd^{2+} , Cr^{3+} , Cu^{2+} , Pb^{2+} , Zn^{2+} , Mn^{2+} , and Fe^{2+} in distilled water. The pH of the solution was arranged using 1 M $\text{NH}_4(\text{OH})$ and 1 M HNO_3 , and buffer solution.

The electrolytic cell used to conduct the experiment consists of a 1 L glass beaker which contain 500 mL of sample. The electrodes were aluminum plate (7.50 cm x 4.00 cm x 0.05 cm) as a cathode and iron plate (7.50 cm x 4.00 cm x 0.10 cm). The effective area of each electrode used was 16 cm^2 (4.0 cm x 4.0 cm). The anode/cathode gap was kept constant at 1 cm. A gentle agitation was made using a magnetic stirrer. The applied electrical potential at 1 Volt regulated direct current (DC) Hitachi 0-300 V, 0-1,2 A power supply, and the voltage cell was continuously recorded. The pH of the solution was 8 which measured using pH meter GLP-21.

A schematic diagram of electrochemical cell is shown in Fig 1.

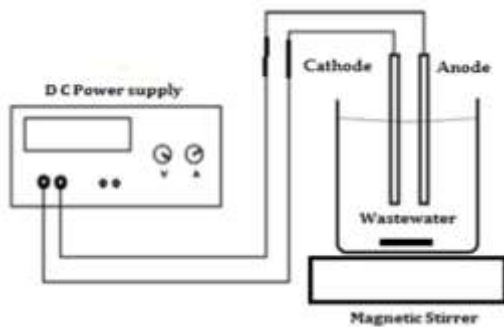


Fig. 1. Schematic Diagram of Experimental setup

Effectiveness of this method was reviewed based on analysis of wastewater parameters before and after EC. Specification analysis methods and wastewater parameters are shown in Table 1.

TABLE 1. SPECIFICATION ANALYSIS METHODS AND WASTEWATER PARAMETERS

Parameter	Methods
pH	SNI 06-6989.11-2004
Odor	IKM/5.4.24/BLK-Y
Temperature	IKM/5.4.127/BLK-Y
Colour	IKM/5.4.27/BLK-Y
Turbidity	IKM/5.4.29/BLK-Y
Total Dissolved Suspension (TDS)	IKM/5.4.30/BLK-Y
Cl^-	APHA, 4500-Cl-B, 2005
Hardness	APHA, 2340-C, 2005
SO_4^{2-}	APHA, 4500-sulfate E, 2005
F ⁻	SNI 06-6989, 29-2005
NO_2^-	APHA, 4500-nitrite B, 2005
NO_3^-	IKM/5.4.12/BLK-Y
Fe	APHA, 3500-Fe-B, 2005
Cd	IKM/5.4.11/BLK-Y
Cr^{6+}	APHA, 3500 Cr-B, 2005
Mn	IKM/5.4.48/BLK-Y
Pb	APHA, 3111 B, 2005
CN^-	IKM/5.4.49/BLK-Y
Zn	IKM/5.4.50/BLK-Y
Detergent	IKM/5.4.53/BLK-Y
Total Solid Suspended (TSS)	APHA 2540-D, 2005
Cu	APHA 3111 B, 2005
Conductivity	SNI 06-6989.1-2004

III. RESULT AND DISCUSSION

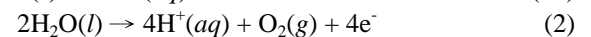
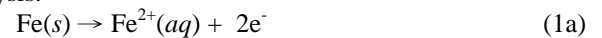
EC process is quite complex because it is influenced by several operational parameters such as a combination electrode, time, temperature, electrical potential and effective area of electrodes. This research only discuss several parameters in wastewater according in Table 1.

After a preliminary analysis of wastewater and then EC process. The first stage in electrocoagulation process can be seen at Fig 2.

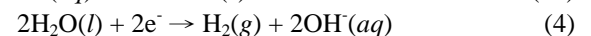


Fig 2. The First Stage in EC

According to Mollah et al [21], there are three main stages in EC process. The first stage is the formation of coagulant for electrolytic oxidation of the electrodes. Fig 2 shows the initial process of EC. The main reactions occurring at the anode are dissolution of iron or aluminum (oxidation) and water electrolysis:



It is generally assumed that iron is dissolved as Fe^{2+} [22, 23, 24]. The main reactions occurring at the cathode are water electrolysis and direct electrochemical metal reduction:



Anodic metal ions and hydroxide ions generated at the electrode surfaces undergo immediately further spontaneous reactions in the bulk wastewater solution to form hydroxides, $\text{Fe}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, and polymeric hydroxyl-complexes, namely: $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$, $[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]^+$, $[\text{Fe}_2(\text{H}_2\text{O})_8(\text{OH})_2]^{4+}$, $[\text{Fe}_2(\text{H}_2\text{O})_6(\text{OH})_4]^{4+}$ and $[\text{Al}(\text{OH})]^{2+}$, $[\text{Al}(\text{OH})_2]^+$, $[\text{Al}_2(\text{OH})_2]^{4+}$, $[\text{Al}(\text{OH})_4]^-$, $[\text{Al}_6(\text{OH})_{15}]^{3+}$, $[\text{Al}_7(\text{OH})_{17}]^{4+}$, $[\text{Al}_8(\text{OH})_{20}]^{4+}$, $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}]^{7+}$, $[\text{Al}_{13}(\text{OH})_{34}]^{5+}$ for Fe and Al electrodes respectively, depending on the pH of the aqueous medium. The suspended aluminum or iron hydroxides can remove pollutants from the solution by sorption, precipitation or electrostatic attraction, followed by coagulation [21].

The second stage in EC process was flocculation process for their bubbles of H_2 and O_2 gas produced by the electrolysis of water. Flocculation process can be seen in Fig 3.



Fig 3. Flocculation Process

The gas bubbles produced in the electrolysis process. This process causes the pollutant that was formed will be lifted to the surface of the wastewater. These pollutants called floc because of the relatively small particle size. The more pollutants that rise to the surface of wastewater then became larger and finally deposited at the bottom of the reactor. The deposition process until the solution was clear and all the flock has been settled in the bottom of the reactor. In this second phase occurs destabilization of contaminants, suspended particles and emulsion breaking.

The third stage in EC process was destabilization aggregation phase to form floc. It can be seen in Fig 4. The floc was then separated by filtration using Whatman 42. The filtrate obtained was analyzed as effluent characteristics after the EC process.



Fig 4. The Formation of Floc

The effectiveness of EC method can be determined by comparing several parameters in Table 1 between the result of the analysis before and after EC process. The effluent characteristics can be seen at Table 2.

TABLE II EFFLUENT CHARACTERISTICS

Parameters	Unit	Result		Standard Reference
		Before	After	
Odor	-	Odorless	odorless	odorless
pH	-	2.3	7.8	6.8-9
Temperature	°C	28.4	28.4	28.2±3.0
Colour	TCU scale	100	10	50
Turbidity	NTU scale	1.820	0.540	25
TDS	mg/L	1694	1491	1500
Cl ⁻	mg/L	37.48	45.00	600
Hardness	mg/L	<3.27	148.74	500
SO ₄ ²⁻	mg/L	1695.000	741.475	400
F ⁻	mg/L	0.630	0.644	1.5
NO ₂ ⁻	mg/L	<0.001	0.506	1.0
NO ₃ ⁻	mg/L	9.003	7.923	10
Fe	mg/L	0.065	0.137	1.0
Cd	mg/L	0.086	<0.0008	0.005
Cr ⁶⁺	mg/L	0.024	<0.0005	0.05
Mn	mg/L	0.162	0.096	0.5
Pb	mg/L	0.295	<0.0007	0.05
CN ⁻	mg/L	<0.006	0.006	0.1
Zn	mg/L	1.965	0.0083	1.0
Detergent	mg/L	0.297	0.316	0.5
TSS	mg/L	5.000	3.000	20
Cu	mg/L	11.455	0.0062	0.5
Conductivity	µmhos/cm	2590.0	1863.0	1562.5

According to Table 2, no changes in odor and temperature of sample between before and after EC process. Both of these parameters in accordance with the quality standards. EC process do not change these parameters significantly. This method is more effective to reduce chemical pollution.

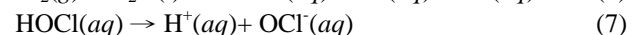
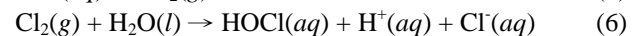
pH is an important factor in EC process. This process is highly dependent on the pH of solution. It has a significant

effect on forming metal hydroxide species and removal mechanism of ions and pollutants [15,25,26,27]. Generally, pH changes during EC process depend on the type of used electrode and the initial pH [25,26]. The pH increase is attributed to the formation of H₂ in cathode electrode and aggregation of hydroxide ions in the solution [15,27,28]. Therefore, EC process could act as a pH regulator [15,29]. In this research, initial pH was 2.3 and final pH was 7.8. Hence, EC process is effective to increase pH till enter the range specified quality standards.

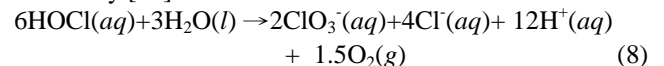
Presence of colour and its causative compounds has always been undesirable in water used for either industrial or domestic needs. Colour is a visible pollutant [30]. After EC process, the effluent in this research almost colourless and the efficient removal of colour reached 90 %. The colour parameter (TCU scale) below the quality standards.

Turbidity, TDS, and TSS can be removed by EC method. Physically able to distinguish between before and after EC process. After EC process the effluent was clearer than before. The turbidity removal occurs as the result of destabilization of colloids due to the effect of the electric field generated between the electrodes and the reactions with coagulating compounds formed in situ during anode oxidation, followed by a subsequent flotation of agglomerates of the particles. Turbidity removal by faster producing hydrolyze products [31]. Some type of sorption mechanism occurs during turbidity removal by EC process. After the colloidal suspension has been destabilized, effective aggregation requires adequate contact between the coagulant and pollutant particles. Consequently, the transport mechanism is important transportation of including collisions between particles coagulant and bubbles [31]. The removal efficiency of turbidity, TDS, and TSS, respectively for 70.33%, 11.98% and 40.00 %. Despite reduction of TDS was insignificantly but this parameter below the quality standards.

The concentration of chloride increase after EC process because the formation of hypochlorite through indirect oxidation of chloride ions [32]. Chlorine is easily produced in wastewater containing chloride and a very important role in the electrolysis of many actual wastes. Chlorine is produced on the anode surface and it suffers disproportionation to hypochlorous acid, and hydrolysis to hypochlorite. Chlorine reacts with water to produce hypochlorous acid and chloride [32].



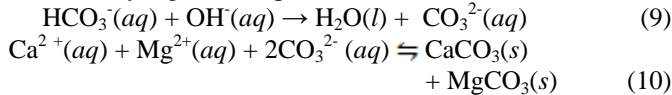
Production of chlorates may occur either electrochemically or chemically [32]



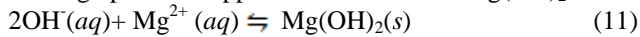
Based on the equation (6) and (8) shows the contribution of Cl⁻ in the final reaction. Despite concentration of Cl⁻ increased but it below the quality standards.

Not only Cl⁻ but also hardness increased after EC process. Based on the method of determining hardness (APHA 2340-C, 2005) showed that the hardness expressed total hardness of CaCO₃ and MgCO₃. The increase in hardness is due to the formation of Al(OH)₃ and the influence of pH. According to K.

Brahmi et al [33], $\text{Al}(\text{OH})_3$ is not an efficient coagulant for EC at extremely high or low pH values.



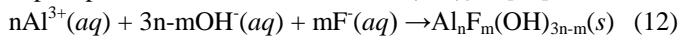
The high pH also support the formation of $\text{Mg}(\text{OH})_2$.



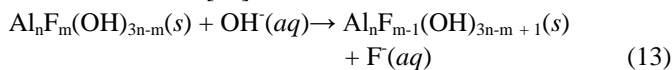
At alkaline pH (8), the formation of $\text{MgCO}_3(s)$ and $\text{CaCO}_3(s)$ films on the active surface of the electrode. This film reduced the active surface of the anode, which prevented the anodic dissolution of the Al plate. In addition to the factors of pH, the presence of other anions such as SO_4^{2-} and Cl^- cause hardness increase after EC process. Although there was an increase 97.80% of hardness but it below the quality standards.

Unlike the previous parameter, concentration of SO_4^{2-} decreased significantly, 56.26%. EC process has not been able to reduce it to below the quality standard due to the initial concentration of SO_4^{2-} was so high.

The concentration of F^- increase slightly, 2.17%. This increase can be observed from reactions that occur during the electrocoagulation process. F^- reduction mechanism is by adsorption chemicals namely the replacement of the F^- position to OH^- group of floc $\text{Al}_n(\text{OH})_{3n}$. F^- ions and OH^- ions can form coprecipitation with Al^{3+} form $\text{Al}_n\text{F}_m(\text{OH})_{3n-m}$ [34].

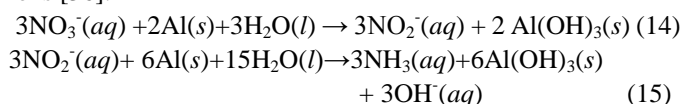


However, the fluoride ions in the precipitate are very easy to substitute for OH^- [35].

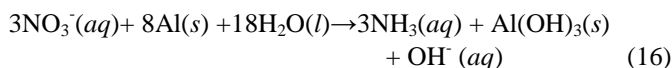


Although the concentration of F^- increase but still below the quality standards.

The concentration of NO_2^- ions increase dramatically (99.82 %) after the EC process while NO_3^- ions concentration decreased slightly (11.99 %). It can be influenced by pH of the system. At high pH, nitrate ions to be reduced to form nitrite ions [36].



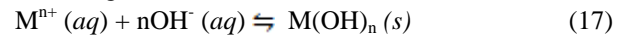
The overall reaction



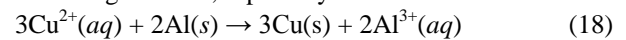
Based on the reactions (14) and (16) indicate that the presence of nitrate ions turn into nitrite ions therefore concentration of nitrite ion increase. In addition, the concentration of OH^- also increase.

In general, electrocoagulation effective to reduce metal ions in wastewater except iron. Concentration of iron increased dramatically, 62.86 %. This condition due to the addition of Fe^{2+} ions from iron plate as the anode electrode. Despite concentration of Fe increased but this parameter still below the quality standards. Concentration of other metals such as Cd, Cr^{6+} , Mn, Zn, Pb and Cu decreased significantly after EC process. The efficient removal reached 99.07%, 97.91%, 40.74%, 99.57% and 99.76% respectively for Cd, Cr^{6+} , Mn, Zn, Pb and Cu. All of metals concentration in the sample below the quality standard after EC process. The mechanism of metal

removal in EC process are the coagulant material such as $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ produced at the anode and cathode during EC process. The presence of the coagulant act as adsorbent and can trap the metals electroionic therefore floc will have a tendency to stable. Moreover, the existence of the coagulant donates OH^- ions and it reacts with the metals form a precipitate hydroxides. Furthermore floc had tied the contaminant metals settle to the bottom of the reactor. In general, the precipitation reaction of these metals can be written the following reaction [37]:



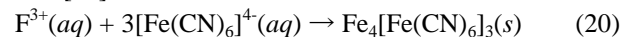
According to the reaction (17), the deposition of these metals are affected by pH. The aluminum hydroxide floc acts as adsorbent for heavy metal ions. Furthermore, heavy metal ions combine with the electrogenerated OH^- ions at the cathode and precipitate in form of their insoluble hydroxides [15] based on the following reaction, especially for Cu:



Other parameters such as concentration of cyanide almost the same between before and after EC process. According to the released ferrous ions from the anode surface reacts directly with free cyanide form metal complex cyanides. Ferrous ions are released from the reaction (1a) occurred at the anode surface. Depending upon the pH of the bulk solution, ferrous ions react with free cyanide in accordance with the reaction presented below [38]:



The produced hexacyanoferrate(II), $[\text{Fe}(\text{CN})_6]^{4-}$, thereafter, reacts with ferrous ions in accordance with the following reaction[20]:



The end product is called "Prussian Blue", the insoluble form, which turns the bulk solution to blue color. Cyanide can be removed at pH 8–8.5. Precipitate ferrous hydroxide which can be resulted in encapsulating the prussian blue particles through the bulk solution [38]. Hence, it is needed to use an alkaline substance such as sodium hydroxide to make that happen in order to increase the removal efficiency.

Unlike another parameters, concentration of detergent increased slightly after EC process. Detergent is one of the organic compounds. Detergent contains of surfactants, builders, fillers and additives. Surfactant can be reduce by EC process because the surfactant adsorption at surface of particles therefore surface hydrophobic formed [39]. According to Riyanto and A. Hidayatillah [40], the ability of the aluminium electrode in detergent wastewater is limited despite prolonged contact time. The effect of the formation of $\text{Al}(\text{OH})_3$ at the anode surface will be covered electrode surface. In addition, the reaction at the anode is also inhibited so that the oxygen binding of alkyl benzene surfactant is also reduced. Finally, in this research, concentration of detergent increased 6.01 % after EC process but it still below the quality standards.

The conductivity of sample decreased after EC process. Conductivity is number of the liquid solution ability to conduct electricity. This ability depends on the presence of ion types, the total concentration of ions, ion valence relative concentration, and the current temperature measurement. After EC process,

conductivity decreased 28.07% because almost of all ions can be removed by sorption, precipitation or electrostatic attraction, followed by coagulation. Although conductivity decreased slightly but it was above the quality standards because this sample was the real wastewater sample which contained many kinds of ion.

IV. CONCLUSION

The result of this research showed that EC process could be removed heavy metals in electroplating wastewater such as Cd, Cr⁶⁺, Pb, Mn, Zn and Cu. The efficient removal reached 99.07%, 97.91%, 40.74%, 99.57% and 99.76% respectively for Cd, Cr⁶⁺, Mn, Zn, Pb and Cu. Another parameters like turbidity, colour, TDS, SO₄²⁻, NO₃⁻, conductivity also could be removed by EC process. In contrast, concentration of Cl⁻, F⁻, NO₂⁻, and Fe increased after EC process although all of them below the quality standards. After EC process, the pH increased significantly till enter the range specified quality standards. In conclusion, EC process is an effective method for reducing metal ions and increase the pH but less effective in reducing some of the anions. All of the parameters after EC process were below the quality standards except SO₄²⁻ ion and conductivity.

ACKNOWLEDGEMENT

This research was supported by the Research and Higher Education Ministry, Indonesia through “Hibah Bersaing” Research Grant 2016 for financial support.

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