Application of waste water treatment technology from exhaust electroplating and anodizing process using electro-coagulation method

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Abstract. Production process in vehicle exhaust small industry releases waste water from exhaust tube electroplating and anodizing without any pre-treatment. It contains plating and coloring from Chroom hexavalent as much as 65,586 mg/l and lead 86,576 mg/l, which is more that the electroplated and anodized waste water quality limit of 0.3 mg/l and 0.1 mg/l for Lead concentration. In addition Chroom and Lead is categorized as toxic and dangerous waste substances. This research is aimed at studying the fundamental characteristics of Chroom and Lead separated from electroplated waste water in exhaust tube by means of electro-Coagulation. To get a comprehensive understanding of process characteristics, two intrinsic parameters are the focus of this research. This include electro-chemistry (installed voltage and current gain) and psycho-chemistry-fluid (process time and contaminant concentration). The research method involved designing assembly and fabrication of an electro-coagulation unit in the laboratory scale. It also a characteristic study of separation process by varying both electro-chemistry and psycho-chemistry-fluid parameters, whilst developing a characteristic model of Chroom and lead separation. Those research stages provided measured contributions that resulted in a prototype of a compact and modular electrocoagulation device. This was designed with 5 pairs of aluminum electrodes that capable of separating chroom and lead with a gain of 88.76% and 87.54%.

1. Introduction
Technological advancement requires the use of heavy metal in improving production processes. One of the industries using heavy metal is the vehicle exhaust production, especially in the process of exhaust tube coloring by means of anodizing. The method is aimed at improving metal resistance against corrosion, increasing the adhesive property of colorants, and giving appealing look. Anodizing involves the use of colorants that contain lead. Colored exhausts are used as accessories in motor vehicles [1].

Among the colorant (paint) used in the vehicle exhaust industry is yellow brown containing lead. The results of tests on waste of colorant washings from aluminum painting in the industry zone show lead content of 83.916 mg/l. The waste water is dumped indirectly into the ditch since the industry lack any necessary treatment facility. This certainly contributes to environmental pollution, something that comes with side effects [2].
Brubahan village and Purbulingga regency processing plants produce waste above the Waste Water Quality Standard of local regulation in Central of Java No. 10 year 2004. The standard stipulates that the maximum lead content in the waste of metal polishing industry should be 0.1 mg/l. The regulation citing lead as a dangerous substance is The Republic of Indonesia Government Regulation No. 85 year 1999 on Treatment of Dangerous and Toxic Waste. It perceives that lead from the washing of anodizing and galvanizing processes as dangerous and toxic, assigning the code Waste D 215. Other than that, lead is also categorized as a chronic pollutant with the coded D 526 [3].

This research focuses on methods of separating lead from wastes. In addition, the use of electro-coagulation will also be elaborated in the course of the study, a criteria of lead separation through accumulating it on the aluminum surface as the electrode, or precipitation it from waste water [4]. Lead separation technology using electro-coagulation can be an alternative of treating wastes from anodizing industries. The resulting separated lead is of economic value and can be recycled to make accumulator plates, fish hooks, or even electrodes for anodizing [5]. The study of waste water treatment in exhaust anodizing industry involves two approach, theoretical modelling and numerical simulation of the effects of intrinsic parameters on the characteristics of lead (Pb) separation. Therefore, there is the need for a reliable and environment friendly technology to achieve it. Lead separation process is unique and it is facilitated by two factors. First, the aluminum plate that serves as coagulants to control separation selectivity collect Pb and allow it to float. Second, an electric field is created between the anode and the cathode.

Oxidation in the electro-coagulation cells takes place at the (+) electrode, the anode, while reduction happens at the (-) electrode, the cathode. This allows continuous separation without calling for chemical precursors, and therefore it is environmentally friendly [6]. Other than that, the electro-coagulation unit used is in the form of modulates is easy to scale-up according to the number of inputs processed. The most costly component of this continuous electro-coagulation technique for lead separation is electricity (power) and installation. These two parameters depend on lead transfer rate along with current efficiency, which in turn, determine the size of both installation and electrical power [7].

Feasibility in terms of technology, economy, and engineering for the continuous electro-coagulation method depend on both design and operational parameters. This high cost of installation and energy requires process optimization. This is especially true for the case when current density is no longer linear with installed power strain, as some of the energy available is allocated for water electrolysis during hydrolysis [8]. An optimum condition can only be reach via laboratory scale investigation, pilot scale system stability test, and simulation for process characteristics. One of the ways of producing strong protective oxide is anodizing, a process carried out through passing of direct current through an electrode as to make the anode converted into a protective and decorative layer. Anodizing is meant to improve resistance against corrosion, the adhesive property, and also the appearance of metal [9].

| Treatment | Material Used | Required Condition |
|-----------|---------------|--------------------|
| Cleaner   | Detergent     | 3 minutes          |
| Etch      | NaOH 5 %      | 1-10 minutes, 55º-70º C |
| DE smut   | Nitric acid 5-25% | 1 minutes, 20º-35º C |
| Anodizing | Sulphate acid 150-250 g/l | 30-60 minutes, 1.6 A/dm², 21º C, 17-19 V |
| Dye       | Nitric lead 50-100 g/l | 5-10 minutes, 50º C |
|           | Potassium permanganate 50-100 g/l |                       |
| Seal      | Silica 10 mg/l  | 2 hours, 96º-100º C   |
The maximum condition for anodizing includes sulphate nitric electrolyte concentration of 12-15%, immersion temperature of 18-20º C, current density of 1.4-2.8 A/dm², voltage of 13 volts, and immersion duration of 30-45 minutes. A layer of Al₂O₃ will form during anodizing. It consists of two layers of porous layer and inhibiting layer. The outermost porous layer (anodic layer) is thick, porous, and hard, whereas underneath it is a thin inhibiting layer (barrier layer). Anodized aluminum surface is porous, and onto this, a layer of aluminum can be added as to make it appealing. During aluminum coloring, the colorant is deposited into the molecule structure and galvanized. The porous layer serves to retain the color and stabilizes the surface [10]. The electrolyte used for anodizing can be of sulphuric acid or chromatic acid, thought it is more commonly used because it is cheaper and is easier to obtain. Specifications of both substances are given in Table 2.

| Specification | Sulphate Acid | Chromatic Acid |
|---------------|--------------|---------------|
| Resulting colour | Metallic bright | Non-metallic soft |
| Abrasion resistance | Good and can be modified to make the layer harder | Good but can’t be modified |
| Corrosion resistance | Good | Good |
| Cracking resistance | No cracks | Sometimes results in cracks or scratches |

Inorganic yellow brown is the colorant used to paint exhaust tube through anodizing. This colorant comes in powder that requires distilled water to dissolve it prior to usage. Specifications of this colorant are given in Table 3.

| Parameter | Condition |
|-----------|-----------|
| Content | 50 -100 g/l nitric lead |
| | 50-100 g/l potassium |
| Process temperature | permanganate |
| pH | 50º C |
| Process time | 4.5 ± 0.5 |
| | 5-10 minutes |

Exhaust industry waste water comes from washings of exhaust tubes after anodizing, as this process uses chemical substances. The chemical substances used are toxic and detrimental to living organisms. Sources of waste water from anodizing in vehicle exhaust industry include: Electro-coagulation is a destabilization process of suspension, emulsion, and solution containing contaminants by passing electric current through water to form coagulates. It can also be through electric energy via electrolysis to reduce or lower the content of metal ions and particles in a solution [11].

The condition required for electro-coagulation is DC current with water as conductor, and aluminum electrodes as the coagulant agent. Aluminum electrodes can either be in the shape of a plate, ball, wire, bar, or pipe. The container should be a rectangular with the aluminum electrodes are arranged parallel with certain spacing. Electric current cause electrolyte to disperse into new compounds. Oxidation takes place at the (+) electrode, the anode, while reduction is at the (-) electrode, the cathode [12].

The pollutants in the electrolyte can be separated in a number of ways including: (1) electro-phoresis that makes pollutant metals attach themselves to aluminum. As electric current passes, Pb²⁺ ions around the cathode are released as a layer forms on the cathode. The Pb²⁺ ions concentration is transferred to the cathode, (2) formation of precipitates from pollutant metals and OH⁻ ions, (3)
coagulation by Al (OH)$_3$ on Pb, that makes that Pb floats, and (4) electro-flotation bubbling that enhances separation efficiency [13].

During electrolysis, the cathode produces hydrogen and hydroxide, whereas in the anode there is oxidation of aluminum ions. Al$^{3+}$ ions from anode solution react with OH$^-$ ions to form aluminum hydroxide (Al (OH)$_3$) [14]. The product create flocks that separates unstable particles. Al (OH)$_3$ coagulates suspended solids and makes the water clear, while bubbles of O$_2$ and H$_2$ that form during the process help to push coagulants to float to the surface [15].

Electro-coagulation is capable of separating all kinds of pollutants in the water, including suspended particles, heavy metals, oil products, colorants, and humus solution. Moreover, electro-coagulation can be employed as the initial technology of filtering membranes such as reverse osmosis [16]. The Coagulation reactor consists of one anode and one cathode arranged parallel and connected
to a power supply, a multi-meter that measures current, and electrolyte of waste water. The bigger the electrodes area, the more efficient pollutant separation is. Pollutant separation is done via precipitation, electrolysis and electro-flotation. More reactive conditions allow pollutants to be released from water [17]. Electro-coagulation does not require the use of chemicals and therefore neutralization is not necessary. In this regard, no further wastes will be caused by high concentration of chemical agents. In addition, air bubbles that form during the process bring pollutants to the surface for easy collection and separation. The use of an electro-coagulation instrument is very flexible [18].

2. Method
In general, this research consists of three examinations; (i) laboratory experiment, both in small scale and pilot scale, (ii) development of empirical model on the correlation of process performance and operational parameters, and (iii) preliminary design and evaluation of technological and economic aspects.

Sixteen (16) electrodes are installed in the reactor and connected to a DC current power supply. For each couple of electrodes, one is connected to the anode and the other connected to the cathode. Afterwards, 8 couples of electrodes are connected in parallel to a volt-meter, an ampere-meter and a power source. The positive pole of volt-meter is connected to the positive pole of power supply and then to the anode. Similarly, the negative pole of volt-meter is connected to the negative pole of ampere-meter and then to the cathode. The scheme of an electro-coagulation instrument in this research is given in Figure 2.

The start-up begins by checking the reactor and measuring instruments, there are clear of issues. The following stage is observation of current distribution and stability. For a start-up, Pb (NO₃)₂ solutions are used as baits and concentrates. The waste water for simulation is varied between 2 – 20 litter/hour and put into the reactor. The power source is then turned on and set at 0.1 – 4 A, with varied voltage of 1 – 50 volts. The use of this ampere is based on the research that established that ampere is the optimum amount for laboratory scale for aluminium electrode area of 375 cm² consisting of 8-16 couples of electrodes spaced 0.5 inches from each other and are arranged in parallel. Sample taking was carried out on the 15th minute and the 30th minute collection results in 90 % lead separation; hence, 30 minutes separation efficiency is the goal to observe. The research was carried out for 150 minutes, in line with a previous work that established that 120 minutes processing is capable of separating 99 % lead. Time was varied for 10 times repetition and it was conducted every 15 minutes. Each time variation is taken twice as to ensure stronger justification.

10 of water effluent after electro-coagulation was taken. The amount of lead in this sample was then analysed using an Atom Absorption Spectrometer to figure out the amount of separated lead. This sample should be kept in a refrigerator if it was not to be tested directly. Prior to testing, the sample must first be filtered. This allows remaining flocks not to be measured by the spectrometer.

An Atom Absorption Spectrometer is a device used to determine concentration of heavy metal of a substance based on the absorption of light passing through its atoms. The working principle of this instrument is measuring atom absorption released by the substance. It comes with an accuracy of 0.0001 mg/l and is capable of reading absorption waves from 0 nm to 880 nm, a range that lead (with 283.3 nm wavelength) accommodates. Atom Absorption Spectrometer analysis begins with making curve for calibration. It is made with a solution of 1000 ppm Pb²⁺ concentration, before being diluted into varied concentrations of 2 mg/l, 5 mg/l, 10 mg/l, 15 mg/l, and 20 mg/l. This solution is then put into a flame of air and acetylene for its absorption to be measured. Readings of absorbance are then used as input data automatically calculated by the computer of an Atom Absorption Spectrometer.
3. Result and Discussion

Inorganic yellow brown is a colorant used to paint exhaust tubes with anodizing. It comes in form of a powder that it has to be made into solution using distilled water prior to usage. Specification of this colorant is given in Table 4. Meanwhile, optimum condition for electro-coagulation is given in Table 5.

**Table 4. Specification of inorganic yellow brown colorant.**

| Parameter          | Condition                        |
|--------------------|----------------------------------|
| Content            | 50 -100 g/l nitric lead          |
|                    | 50-100 g/l permanganate potassium|
| Process temperature| 50º C                            |
| pH                 | 4.5 ± 0.5                        |
| Process time       | 5-10 minutes                     |

**Table 5. Optimum condition for co-agulation on a laboratory scale.**

| Parameter            | Result                                      |
|----------------------|---------------------------------------------|
| Waste water debit    | 4 gpm                                       |
| Current              | 4 A                                         |
| Electrode space      | 0.5 inches                                  |
| Aluminum electrode   | Length: 24 inches                           |
|                      | Width: 2.5 inches                           |
|                      | 8 – 16 plates                               |
| Repetition time      | Parallel fully immersed for                 |
Heavy metals separated as electrodes pass allows the flow of electric current. The motion force generated by the electrodes, according to the metal concentration is also reduced with the formation of Al(OH)$_3$ flocks. A comparative test of electro-coagulation shows a result of 76.5813 mg/l initial concentration between the first and second repetition. This is aimed at ensuring the significance of average differences between the two. The calculated statistics is in the acceptance region of 0.2506 < 2.086. for this reason, $H_0$ is accepted. Hence, it can be said that there is no significant difference in average concentration of lead between the first and second repetitions, for an initial lead concentration of 76.5813 mg/l.

A graph showing the relationship of lead separation time and its concentration for an initially at 76.5813 mg/l shows an exponential line as depicted in Figure 3.

![Graph showing lead separation time and concentration](image)

**Figure 3.** Relationship of separation time and concentration for a 76.5813 mg/l initial lead concentration.

Calculated F statistics is greater than the table F (69.3568 > 5.32), therefore, $H_0$ is rejected. Hence, it can be stated that there is no relationship between separation time and final lead concentration, as shown in Figure 4.

![Graph showing final concentration and separation time](image)

**Figure 4.** Relationship of final concentration and separation time for a 24.4931 mg/l lead concentration.

The model formula is:

$$\ln Y_{(t)} = 3.5195 - 0.021 t$$

$$Y_{(t)} = 33.7659e^{-0.021t}$$
where \( Y(t) \) is lead separation concentration (mg/l), and \( t \) is separation time (minutes).

Initial statistics analysis starts with comparing lead concentration after electro-coagulation between the first and second treatment. This is aimed at determining whether there are significant differences in its average or not. For this reason, a t-test was conducted. Results show that there are no significant average differences between the first and second repetition. Therefore, equation model for the relationship of separation time and final concentration after electro-coagulation can be drawn from data of final lead concentration from either the first or second repetition.

This equation is then used to make a graph of relationship between the two parameters, which in turn show an exponential line. Thus, an exponential equation model for separation time and final concentration can be formulated. An initial lead concentration of 76.5813 mg/l has \( R^2 \) of 0.8966, means 89.66 % of final lead concentration is linear with separation time, if other factors are not taken into account. Meanwhile, an initial lead concentration of 24.4931 mg/l has \( R^2 \) of 0.9848. Implying that 98.48 % of final lead concentration is linear with separation time, and that other factors are not taken into account.

This model equation is then tested to ensure if there is a relationship between separation time and lead concentration. It involved F and t-tests. Results of both tests for an initial lead concentration of 76.5813 mg/l showed a relationship between separation time and final lead concentration. This means that longer separation time results in more effective lead separation. Results of both F and t-test for an initial lead concentration of 24.4931 mg/l also showed the same outcome.

Therefore, it is proven that the model developed in this research can be accepted and that it can be used to determine the time it takes to separate a certain amount of lead. The model provides the most \( R^2 \) value. This model can be applied for the treatment of waste water from exhaust tube coloring process in the industry concerned in order to figure out how much time is required to treat the waste water. Further experiments then show that the time required to treat waste water treatment from vehicle exhaust industry processes to meet the standard waste water quality of 0.1 mg/l lead concentration is 4 hours.

Results of Anova tests reveal that there is a difference in treatment for both 76.5813 mg/l and 24.4931 mg/l initial lead concentrations, and that the time set for treatment does affect final lead concentration. Hence, different treatment durations for each concentration results in different final concentration as well.

4. Conclusion

Electro-coagulation is proven to have the ability to separate lead from waste water in the vehicle exhaust small industry. Lead separation for waste water from exhaust tube coloring process was able to reduce an initial lead concentration of 57.4913 mg/l to 2.2189 mg/l, with 96.14 % efficiency. Meanwhile for an initial lead concentration of 24.4931 mg/l, the reduction is down to 1.4078 mg/l, with 94.25 % efficiency. The time it takes for electro-coagulation of lead separation follows a formula that relates separation time and final lead concentration:

\[
Y(t) = 33,7659e^{-0.02t}
\]

where \( Y(t) \) is final lead concentration (mg/l), and \( t \) is separation time (minutes).

Reuse of separated lead from electro-coagulation of vehicle exhaust industry waste water treatment makes it an environmental friendly industry.

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References
[1] Zalnezhad, E., Ahmed A.D. Sarhanand M. Hamdi 2013 The International Journal of Advanced Manufacturing Technology vol 68 (1-4) pp 453-464.

[2] Saiedikhani, M., M. Javidi, A. Yazdani 2013 Anodizing of 2024-T3 aluminum alloy in sulfuric–boric–phosphoric acids and its corrosion behavior Department of Materials science and Engineering, School of Engineering, Shiraz University, Shiraz 7134851154, Iran

[3] Yunxia G, Jijia R, Fuyuan F 2010 Aluminum Surface Treatment Metallurgical Industry Press; 286.

[4] Dizhen W 2008 Research and application on aluminum exchange hard anodizing technology Paint Electrop;23-6

[5] Mani V, Govindasamy M, Chen S.M, Subramani B, Sathiyan A, and Merlin JP Int. J.Electrochem. Sci., 12 (2017) 258-267.

[6] Mani V, Umamaheswari R, Chen SM, Govindasamy M, Su C, Sathiyan A, Merlin JP and Keerthi M, Int. J. Electrochem. Sci., 12 (2017) 475-484.

[7] Guisbiers, G 2010 Nanoscale Research Letters 5: 1132-1136.

[8] Ge M, Cao C, Huang J, Li S, Chen Z Zhang K, et al. 2016 Journal of Materials Chemistry A 4: 6772-6801.

[9] Rao B, Torabi A, Varghese O 2016 MRS Communications 6: 375-396.

[10] Lamberti A, Virga A, Chiadò A, Chiodoni A, Bejtka K 2015 Journal of Materials Chemistry C 3: 6868-6875.

[11] Sun Z, Liao T, Kou L 2016 Strategies for designing metal oxide nanostructures Science China Materials 60: 1-24.

[12] Yang W, Yu Y, Starr MB, Yin X, Li Z 2015 Nano Letters 15: 7574-7580.

[13] Yajun J 2014 RSC Advances 4: 4047440481.

[14] Popat K, Leoni L, Grimes C, Desai T 2009 Influence of engineered titania nanotubular surfaces on bone cells Biomaterials 28: 3188-3197.

[15] Fadlallah M 2017 Magnetic, electronic, optical, and photocatalytic properties of nonmetal and halogen-doped anatase TiO2 nanotubes Physica E: Low dimensional Systems and Nanostructures 89: 50-56.

[16] Gong D, Grimes C, Varghese O, Hu W, Singh R 2001 Journal of Materials Research 16: 3331-3334.

[17] Jin R, Liao M, Lin T, Zhang S, Shen X 2017 Materials Research Express 4: 6.

[18] Chernozem R, Surmeneva M, Surmenev R 2016 IOP Conference Series: Materials Science and Engineering 116: 012025.