Reduction and Adsorption Mechanism of Chromium Hexavalent in Electroplating Industry Passivation Tank Effluent Using New Linz-Donawits Slag Waste Material.

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Abstract. Hexavalent chromium Cr(IV) is widely used as electroplating agent to produce a hard, durable coating to a metal with excellent wear and corrosion resistance properties. Yet the effluent of this process needs to be carefully treated as Cr(IV) has been recognized as hazardous, a known carcinogen and mutagen to the human body. Current treatment of Cr(IV) in electroplating industry is by using sodium metabisulfite (SMBS) with a maximum reduction of 100% in a solution of pH 2. Nevertheless, despite the remarkable performance, the application of SMBS as reducing agent generates a massive amount of sludge which eventually will be disposed to the landfill. It also poses detrimental health effects due to the release of hydrogen sulfide (H₂S) and sulfur dioxide (SO₂) gas. Thus, a less harmful reducing agent was studied to replace SMBS in Cr(IV) reduction process. Linz-Donawitz (LD) slag has been discovered to be a good reducing agent due to the presence of Iron in the form of Fe²⁺. The characterization of electroplating industrial effluent using ICP-MS shows a highest composition of Chromium which is 1614.6mg/L. Meanwhile, characterization of LD slag shows that the major component is Ferrous (II) Oxide, (FeO) which constitutes 37.2% of the total mass. By using SMBS as reducing agent, 8 ml of 4% v/v SMBS concentration is required to reduce 40% of Cr(IV) in the sample solution. The optimum treatment duration of Cr(IV) using LD slag is found to be 5 minutes and the best pH of the sample solution for optimal reduction rate is 2. In addition, smaller particle size of the LD slag is more advantageous as smaller amount of LD slag is required to completely reduce Cr(IV) concentration in the solution. However, the best particle size is 0.425mm because the reduction rate is more controllable. ORP value at zero Cr(IV) concentration is found to be ±488 mV.

1. INTRODUCTION
As human needs increase and advanced technology, we are witnessing the upsurge in industrial and technological sector. This increases metals and non-metals consumption, [1]. Yet, these materials have a limited lifespan due to internal factors, external factors, and its operating environment that attacks the surface of the material. There are numerous coating processes that are available and are capable to protect the functionality of the materials which is vacuum evaporation, weld-surfacing; Molten Metal Coating Processes, Organic Coating (painting), Thermal Spraying, and Metallizing or also known as Electroplating, [2].

One of the widely held surface treatment method that is currently used by most company is the electroplating technique, [3]. Surface treatment or plating industries in Malaysia itself has grown up to about 40 companies in operation including leading companies such as AKN Technology, Dipsol Chemical, Ueda Plating, Metek Kitamura, Ampmas, and Metal Polishing Industries, [4]. With this rate of growth of electroplating industries, the effluent treatment must be continuously improved to make sure it would not leave an effect neither environmentally nor the well-being of mankind.

Chromium has an extensive use in electroplating industry and consequently produce Cr(IV) in the industrial effluent, [5]. Cr(IV) has been recognized as hazardous and a known carcinogen and...
mutagen to the human body. Structurally, chromate is similar to phosphate and sulfate thus it readily enters all cells by means of the general anion channel protein [6]. Once Cr(IV) enters a cell, it will be reduced to Cr(III) by body mechanism. As the result of the reduction process, unstable and reactive intermediates such as chromium pentavalent, Cr(V), hydroxide, thiy and organic radicals and active oxygen radicals are produced [6]. It is believed that these moieties are at fault chromium carcinogenicity.

Due to the above health and environmental concerns, it is pertinent that the remediation method should be such that brings chromium within tolerable limits before the effluent is released. Effluent standard in Malaysia is regulated by the Environmental Quality Regulations, 1979. By referring to Table 1: Acceptable Conditions for Discharge of Industrial Effluent or Mixed Effluent of Standard B, (Environmental Quality Act, 1974), it is clearly stated that the allowable amount of Cr(IV) in effluent of standard B is 0.05 mg/L.

Table 1: Acceptable Conditions for Discharge of Industrial Effluent or Mixed Effluent of Standard B, (Environmental Quality Act, 1974)

| Parameters                   | Unit   | Standard B |
|------------------------------|--------|------------|
| 1 Temperature                | °C     | 40         |
| 2 pH value                   | -      | 5.5-9.0    |
| 3 COD                        | mg/L   | 200        |
| 4 BOD at 20°C                | mg/L   | 50         |
| 5 Suspended Solids           | mg/L   | 100        |
| 6 Chromium, Hexavalent       | mg/L   | 0.05       |
| 7 Chromium, Trivalent        | mg/L   | 1.0        |

Cr(IV) can be treated using multiple reaction and mechanism such as reduction followed by chemical precipitation, electrochemical precipitation, reduction, ion-exchange, solvent extraction, evaporation and membrane separation [7]. At the present, the process of converting Cr(IV) to Cr(III) by reduction method. There are several reducing agent including Sodium Metabisulfite or also known as SMBS (Na$_2$S$_2$O$_5$) [8][9][10][11], glucose [9], ascorbic acid [9], steel wool [12], and sawdust [13]. However, SMBS is commonly used as the reducing agent since it is beneficial economically due to its inexpensive price [11]. Nevertheless, the odour released during the process poses a detrimental effect on the environment and the industrial health problems associated with SO$_2$ gas and H$_2$S gas [14]. The process is then followed by precipitation of chromium hydroxide by addition of alkali. The product of the precipitation is a massive amount of sludge. The increment in the production of sludge is concerning as most of the treated sludge from the sludge treatment plant in Malaysia were dried and disposed of by landfill [15].

As an effort to support The Sustainable Development Goals, the objective of this study is to investigate the performance of LD slag as a new economical and more environmental substitute to SMBS as a reducing agent for Cr(IV) into Cr(III)

2. METHODOLOGY

2.1 Preparation of sample

2.1.1. Cr(IV) Sample Solution Preparation. Sample used was an untreated effluent collected from electroplating industry in Klang, Malaysia. 10 liters of the waste water sample was obtained and stored in a compatible container. The temperature and pH of the sample will be taken on site to avoid any changes by using pH and temperature indicator. Then, it was transported immediately to the laboratory and stored at around 4 °C in a refrigerator to maintain the components in the sample. The sample
collected was kept away from direct sunlight to avoid deterioration or reaction between the components in the sample. The sample was used within one week as after that the components will degrade and affect the results.

2.1.2. LD Slag Preparation. Raw LD slag was obtained from a steel making industry was grinded using a jaw crusher by Pascal Engineering Jaw Crusher model type 1397_00_C that is available in Concrete Laboratory, Faculty of Civil Engineering, UITM Shah Alam. The jaw crusher was first cleaned up and dusted using an air compressor. LD slag was grinded into particle sizes of 1.18mm, 0.425mm, 0.15mm, 0.063mm and less than 0.063mm (powder). Processed LD slag was then stored according to their respective sizes in an air tight container to preserve the property and quality of the slag. Along with that, it was stored away from heat and humidity. then stored according to their respective sizes in an air tight container to preserve the property and quality of the slag.

2.2 Sample Characterization

2.2.1. Characterization of Cr(IV) Sample Solution. Thermo Scientific iCAP 6000 series inductively coupled plasma mass spectrometry (ICP-MS) which is available in Instrumental Laboratory II, Faculty of Chemical Engineering, UITM Shah Alam was used to characterize the waste water sample. Argon gas was used to produce a plasma. Radio frequency (RF) power of 1150 was supplied to create a plasma with a temperature of 6000 K. Chromium was monitored at a wavelength of 283.563 nm. Sample was introduced at a nebulizer gas flowrate of 0.7 L/min and at atmospheric temperature and pressure.

2.2.2. Characterization of LD Slag. JSM-7600F by Jeol that is available at FESEM Lab (OM 110) in Faculty of Applied Science, UITM Shah Alam was used to study the topographical information of LD slag at magnification range of 10X to 300 000X. Axios FAST by Malvern Panalytical XRF that is available in the X-Ray laboratory in Faculty of Chemical Engineering, UITM Shah Alam was used to determine the elemental composition of LD slag.

2.3. SMBS as a reducing agent

To study the effectiveness of SMBS as a reducing agent, SMBS was added gradually until the ORP reading reaches approximately 250mV. NaOH was added to the solution until the pH value of the solution is 8. The solution was then filtered and tested for Cr(IV) concentration. The agitating process of the sample and SMBS was done using Stuart SW6 flocculator which is available at Pilot Plant, Faculty of Chemical Engineering, UITM Shah Alam and was agitated at a speed of 120 rpm.

2.4. LD Slag as a Reducing Agen

The main equipment used was the Stuart SW6 flocculator which is accessible at Pilot Plant, Faculty of Chemical Engineering, UITM Shah Alam to uniformly agitate the solution mixture. The rotational speed of the propeller was 120 rpm. Meanwhile HANNA instrument, HI-8424 was used to measure pH and ORP value of the solution.

2.4.1. Effect of Treatment Duration on LD slag reducing performance. To study the effect of time, one gram of 0.425mm LD slag particle size was used to treat the Cr(IV) in the sample solution. The length of time which the LD slag will be in contact with the sample solution was varied from 5 minutes to 20 minutes with an increment of 5 minute for each run. Before the addition of LG slag, the initial ORP value and concentration of Cr(IV) was taken. After treatment, the solution was filtered to remove traces of LD slag particle and the solution was tested for the concentration of Cr(IV). The ORP reading was also taken right after each run.
2.4.2. Effect of particle size on LD slag reducing performance. To study the effect of LD slag particle size on the removal of Cr(IV), one gram of the 1.18 mm particle size of LD slag was introduced to the Cr(IV) sample of known volume and concentration. Initial ORP reading of the solution before adding LD slag was be taken. LD slag was added to the sample solution and agitated using a magnetic stirrer for five minutes. After five minutes, the solution was filtered and the final ORP reading was taken and the sample was tested for Cr(IV) concentration. This method was repeated for 0.425mm, 0.15mm, and 0.063mm LD slag particle size.

2.4.3. Effect of pH on LD Slag Reducing Performance. The pH of Cr(IV) solution was altered from 2-8 using Sodium Hydroxide (NaOH). The initial ORP and Cr(IV) reading was taken prior to treatment. The sample solution was the treated with one gram of 0.425 mm particle size LD slag for 5 minutes for each pH value. After 5 minutes, the solution was filtered and tested for Cr(IV) concentration. The final ORP value was also taken.

2.4.4. Effect of LD slag doses on LD slag reducing performance. For each particle size, different dosing of LD slag was introduced to the sample solution of known volume and Cr(IV) concentration. The initial ORP value and Cr(IV) concentration of the solution was recorded before adding LD slag. The mixture was then agitated using a magnetic stirrer for 5 minutes and the ORP reading was taken after five minutes. The solution was filtered before tested for the concentration of Cr(IV). For every dose, a new sample solution was prepared to make sure the only manipulating data is the dose of LD slag.

2.5. Cr(IV) Concentration Analysis

The concentration of Cr(IV) in the solution was determined using the HACH DR900 Multiparameter Portable Colorimeter, Method 8023, USEPA 5,5-Diphenylcarbohydrazide Method and program code 90 was selected from all program. Calorimetric determination of Cr(IV) was aided by ChromaVer® 3 Chromium Reagent Powder Pillows.

3. RESULTS AND DISCUSSION

3.1. Sample Characterization

3.1.1. Characterization of Cr(IV) Sample Solution. The Chromium sample from the electroplating industry effluent was analyzed using ICP-MS. Though there was a lot of element present in the solution, to serve the purpose of this study, only Chromium is considered. From Table 2, elemental component present in electroplating industrial effluent is shown and the amount of total chromium in the sample is 1614.6 mg/L. This amount constitutes of total chromium which is the combination of Cr(III) and Cr(IV).

For both Cr(III) and Cr(IV), the amount of chromium is beyond the tolerable amount specified by EQA 1974 as stated in Table 1: Acceptable Conditions for Discharge of Industrial Effluent or Mixed Effluent of Standard B, (Environmental Quality Act, 1974) which is 0.1 mg/L for Cr(III) and 0.05 mg/L for Cr(IV). If this electroplating industrial effluent is irresponsibly discharged to the river, it would cause a detrimental effect to humankind and the environment.
Table 2: Elemental Component Present in Electroplating Industrial Effluent

| Component      | Concentration (mg/L) |
|----------------|----------------------|
| Silver, Ag     | 34.290               |
| Aluminum, Al   | 49.461               |
| Boron, B       | 624.39               |
| Calcium, Ca    | 23.207               |
| Chromium, Cr   | 1614.6               |
| Iron, Fe       | 0.930                |
| Indium, In     | 10.765               |
| Potassium, K   | 30.403               |
| Magnesium, Mg  | 7.346                |
| Nickel, Ni     | 350.001              |
| Lead, Pb       | 9.725                |
| Thallium, Tl   | 0.883                |
| Zinc, Zn       | 55.050               |

3.1.2. Characterization of LD Slag. Since the adsorption from liquid phase to the solid phase is highly influenced by the surface morphology of the adsorbent, the surface structure for LD slag was investigated. A Field Emission Scanning Electron Microscope (FESEM) of the surface of LD slag was done using JSM-7600F by Jeol that is available at FESEM Lab (OM 110) in Faculty of Applied Science, UITM Shah Alam and the result is illustrated in Figure 1: FESEM of LD Slag Surface. The image was captured at 3000 times magnification and as shown in the photo, LD slag has a rough surface texture with porous structure, which is verified by study by Sarkar, Basu, et al. [16] and Singh, Gorai, et al. [17]. The cellular structure is the results of gas entrapped in the hot slag during cooling and solidification process. Therefore, owing to the high mechanical strength, high basicity and its unique porous structure, LD slag has a high potential as an adsorbent.

![Figure 1: FESEM of LD Slag Surface](image)

The composition of grinded LD slag was then analyzed, and the LD slag composition is shown in Table 3: LD Slag Composition. From the result, we can see that Ferrous Oxide (Fe(II)) has the highest amount followed by Calcium oxide. This result verified Sinha, Shinde, et al. [12] statement that LD slag contains high amount of iron which is 23.17–24.13%.

In a previous study by Qin, McGuire, et al. [19], Fe(II) was able to reduce Cr(IV) to Cr(III) of concentration of 100 mg/L to below detection level with a dose of 10 to 50 times the Cr(IV)
concentration. In another study by Mon, Novotný, et al. [20], shows that when 70% w/w of ferrous sulphate heptahydrate is added, the concentration of Cr(IV) 0.27ppm to 0.05 ppm. Therefore, it is safe to say that Iron has the ability to reduce Cr(IV) to Cr(III).

Proposed chemical equation for the redox reaction is as follows, [21]:

\[
\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O} \quad \text{Eq. (1)}
\]

| Component | Percentage (%) |
|------------|----------------|
| MgO        | 5.057          |
| Al₂O₃      | 7.406          |
| SiO₂       | 13.931         |
| P₂O₅       | 0.114          |
| SO₃        | 0.101          |
| CaO        | 24.761         |
| MnO        | 11.446         |
| FeO        | 37.184         |

3.2. SMBS as Reducing Agent
The reducing performance of SMBS was studied to compare with the LD slag reducing performance. The summary of the study is listed in Table 4: SMBS Performance as a Reducing Agent. Total amount of SMBS added to the sample solution was 8 ml for the solution ORP reading to reached 250mV. This is because according to J. B. Duncan, et. al. [22], SMBS successfully reduce Cr(IV) at the lower pH ranges and at an oxidation reduction potential (ORP) of approximately +250 mV. After coagulation the concentration of Cr(IV) in the solution is 0.45 mg/L which is still high and did not pass the tolerable amount by standard B which is 0.05mg/L. Furthermore, the reduction percentage is only 40% which is low.
Table 4: SMBS Performance as a Reducing Agent

| Parameter                              | Value      |
|----------------------------------------|------------|
| Initial ORP (mV)                       | 433.4      |
| Initial pH                             | 2.67       |
| Initial concentration of Cr(IV) (mg/L) | 0.75       |
| Volume SMBS Added (ml)                 | 8          |
| Final ORP (mV)                         | 248        |
| Volume NaOH Added (ml)                 | 1.1        |
| Final pH                               | 8          |
| Final concentration of Cr(IV) (mg/L)   | 0.45       |
| Percent Reduction (%)                  | 40         |

3.3. LD Slag as Reducing Agent

3.3.1. Effect of Treatment Duration on LD slag reducing performance. Sample solutions was treated with LD slag at a various duration ranging from 5, 10, 15 and 20 minutes and the result is shown in Figure 2: Effect of Treatment Duration Against Concentration of Cr(IV). As seen from the graph, the lowest concentration of Cr(IV) recorded was at 5 minutes which is 0.1 mg/L. After that, the concentration of Cr(IV) increases and decreases again at 15 min but the concentration was 0.15 mg/L which is not as low as at 5 minutes. Therefore, the optimum treatment duration of the solution sample using LD slag was considered as 5 minutes.

![Figure 2: Effect of Treatment Duration Against Concentration of Cr(IV)](image)

3.3.2. Effect of pH on LD Slag Reducing Performance. The pH of the solution was varied from pH 2 to 8 by adding NaOH 5% concentration. The highest reduction of Cr(IV) concentration bt LD slag was at pH 2 and 6 which is 0.1 mg/L and this is illustrated in Figure 3: Effect of pH of Sample Solution against Concentration of Cr(IV). In an acidic solution, the concentration of hydrogen ions, H\(^+\) is higher than hydroxide ions, OH\(^-\). Therefore, acidic solution has a higher potential to reduce Cr(IV) to Cr(III) by donating electrons.

ORP reading decreases as the pH value increases. This is consistent with James, Copeland, et al. [23] statement which stated that ORP decreased with increasing pH, regardless of the oxidant type or concentration.
Basicity and acidity of a solution is governed by the ratio of $H^+$ and $OH^-$. In a basic solution, ratio of $OH^-$ ions are higher than of $H^+$. Since oxidizing agent is said to be species that accepts electron and reduced to a lower oxidation number, $OH^-$ ions is an oxidizing agent. ORP value decreases as the reducing potential increases. Therefore, ORP decreases when pH increases as the reducing potential of the solution increases.

![Figure 3: Effect of pH of Sample Solution against Concentration of Cr(IV)](image)

3.3.3. Effect of particle size on LD slag reducing performance. From Figure 4: Effect of Different LD Slag Particle Size Against Concentration of Cr(IV) is illustrated. It is shown that the highest removal of Cr(IV) is by using 0.425mm particle size. The concentration of Cr(IV) reduced from 0.75 mg/L to 0.15 mg/L which is 80% removal. Meanwhile the least removal rate is from the 1.18mm and 0.063 mm with only 26.7% removal rate.

![Figure 4: Effect of Different LD Slag Particle Size Against Concentration of Cr(IV)](image)
3.3.4. Effect of LD slag doses on LD slag reducing performance

Figure 5: Effect of Mass of LD Slag Against Concentration of Cr(IV) for 1.18 mm Particle Size

Figure 6: Effect of Mass of LD Slag Against Concentration of Cr(IV) for 0.425 mm Particle Size

Figure 7: Effect of Mass of LD Slag Against Concentration of Cr(IV) for 0.15 mm Particle Size
From Figure 5 until Figure 8, it is obvious that as the particle size becomes smaller, the amount of LD slag required is significantly reduced. For an instance, for the particle size of 0.063 mm, the amount of LD slag required to reduce Cr(IV) initial concentration from 0.65 to 0.05 mg/L is 0.1 g. This is 92.3% of Cr(IV) reduction from its initial concentration. But for 1.18 mm particle size, the amount to reduce Cr(IV) concentration from 0.75 mg/L to 0 mg/L is 1.8 g.

As the particle size becomes smaller, the surface area ratio to volume increases [25]. Greater surface area means more contact area between the Cr(IV) in the solution and reducing agent Fe(II) on the LD slag surface and thus, higher amount of Cr(IV) can be reduced to Cr(III). Moreover, this result is supported by Grandison & Lewis, [26] in their writing that surface area exposed has a big influence on physical properties for instance wettability, dispersion, dissolution and chemical reactions such as oxidation. The ORP reading does not shows any pattern regarding the Cr(IV) removal and size of LD slag particle.

From Figure 4 to Figure 7, after Cr(IV) concentration was reduced to the lowest amount, further addition of LD slag will increase the concentration of Cr(IV). For example, in Figure 5: Effect of Mass of LD Slag Against Concentration of Cr(IV) for 1.18 mm Particle Size, complete reduction of Cr(IV) is achieved by using 1.8 g of LD slag. But when 2 g of LD slag is used, the concentration of Cr(IV) increases back.

Since reduction-oxidation reaction of chemical compound occurs constantly in order to achieve stability or equilibrium, Cr(IV) species that has been reduced to Cr(III) has reversed the role as an oxidizing agent to reducing agent and accepts electron. This will make Cr(III) oxidized into Cr(IV). This statement is supported by Xin, Xian, et al. [27], in their study stated that oxidant–reductant pair, over multiple redox cycles was constant and fully reversible.
Therefore, from the pattern shown in the graphs, we can deduce that reduction of Cr(IV) using LD slag happens at a certain amount. This is because insufficient amount of LD slag leads to partial reduction of Cr(IV). In the other hand, excessive amount of LD slag will reverse the reaction in where LD slag will be the oxidizing agent with more electrons and oxidize Cr(III) to Cr(IV).

3.4. Relationship Between ORP value and Cr(IV).

Even though the ORP reading does not shows any pattern toward all the parameter studied, except for pH of the solution, the ORP reading at zero concentration of Cr(IV) is fairly constant which is at ±488 mV. This is comparable with SMBS as reducing agent where the ORP reading that indicated complete reduction of Cr(IV) at ±250mV.

Thus, with the same sample solution volume, a minimal amount of LD slag is required to reduce the initial ORP value of the solution which is approximately 500 mV to obtain a complete reduction of Cr(IV) which is at ±488mV. In contrary, more amount of SMBS is required to reduce Cr(IV) as complete reduction of Cr(IV) using SMBS as reducing agent occurs at ±250mV.

Table 6: ORP reading mV at Zero Concentration of Cr(IV)

| Particle Size (mm) | Cr(IV) Concentration (mg/L) | ORP reading (mV) |
|-------------------|-----------------------------|------------------|
| 1.18              | 0                           | 493.8            |
| 0.425             | 0                           | 482.3            |
| Average           |                             | 488.05           |

4. CONCLUSION

The characterization of electroplating industrial effluent shows a highest composition of Chromium which is 1614.6. FESEM imaging of LD slag shows that LD slag possess a unique porous surface and has high potential as an adsorbent. Characterization of LD slag shows that the major component is FeO which constitutes 37.184% of the total mass. By using SMBS as reducing agent, 8 ml of 4% v/v concentration SMBS is required to reduce 40% of Cr(IV) in the sample solution. The optimum treatment duration of Cr(IV) using LD slag is found to be 5 minutes and the best pH of the sample solution for optimal reduction rate is 2. In addition, smaller particle size of the LD slag is more advantageous as smaller amount of LD slag is required to completely reduce Cr(IV) concentration in the solution. However, the best particle size is 0.425mm because the reduction reaction is more controllable. Particle size that is smaller than this tends to be more sensitive. ORP value at zero Cr(IV) concentration is found to be ±488 mV.

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