Reduction of Hexavalent Chromium To Trivalent Chromium Using Green Technology

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***Abstract* – Electroplating industry generate harmful anionic heavy metals which is Hexavalent Chromium (Cr^{6+}) that need to be treated before release it. Exposure of Cr^{6+} through inhalation or dermal contact can lead to cancer disease. These Cr^{6+} need to reduce first using a reducing agent and then undergo precipitation process for complete removal of (Chromium) Cr component. The common reducing agent is using Sodium Metabisulphite (SMBS). This chemical generated harmful gases which are Hydrogen Sulfide (H_2S) and Sulfur dioxide (SO_2). Other inorganic waste of that can be use as reducing agent is Leeden Gas sludge (LG sludge) that are from acetylene production gas. LG sludge contains high in (Calcium) Ca element and (Ferum) Fe ions that are essential for the reduction of Cr^{6+} to (Trivalent Chromium) Cr^{3+}. The analysis of LG sludge characterization was done by XRF and XRD instrument with the result of high Ca and Fe ions with ($Ca(OH)_2$) alkaline properties. The initial concentration of Cr^{6+} is 3.25 mg/L using HACH Method 8023 and the initial total Cr concentration is 1124 mg/L was analyzed by ICP-AES. The result in the effect of pH variation using LG sludge as a reducing agent was at pH 5.51 that shown 1.25 mg/L which is the lowest Cr^{6+} concentration value with 320.2 mV of ORP value. At that pH, the dosage was 1.15 ml with 61.5% reduction that is the highest % reduction. Next, the effect in volume LG sludge variation shown that Cr^{6+} was 100% successful reduce at pH 6.04 with volume LG sludge use at 1.8 ml with 264.9 mV of ORP value.**

Keywords – Hexavalent Chromium, Trivalent Chromium, Reducing agent, Sodium Metabisulphite, Electroplating.

I. INTRODUCTION

Hexavalent Chromium (Cr^{6+}) is carcinogenic to human health and can pollute the environment. Its is an anionic heavy metal contaminant that presence in wastewater from automotive or electroplating industry [1]. A human can be exposed to chromium through dermal contact or inhalation. Research has been done by Singh, S. & Das, A. P in Odisha, India showed more than 200,000 workers and inhabitant resident in Sukinda chromite mine have major chronic diseases such as cancer and many more. The worker and resident have been infected with chromium from the mine and also many animals have died due to the nearby polluted river [2].

In Malaysia, this Cr substance is mainly from the electroplating industry. This industry producing high quality of metals with high corrosion resistance. There are many other substances that can use for corrosion resistance such as zinc, aluminum, copper and steel. Compare to other metals, chromium is highly favored in current electroplating industry due to its properties that have good wear resistance, withstand high temperature and hardness conditions [3].

There is a process called passivation process for coating the metals with layers of chromium oxide to increase its corrosion resistance to the environmental conditions. Example of metals in the electroplating industry is manganese passivation by potassium dichromate ($K_2Cr_2O_7$) solution. The solution has high concentration of Cr^{6+} which is 14000 ppm with the color of orange-red. In the passivation solution, Cr^{6+} ions are in the form of CrO_4^{2-} or $Cr_2O_7^{2-}$ compound [4]. The reaction occur in the passivation process is rapid redox reaction and reduce Cr^{6+} to (Trivalent Chromium) Cr^{3+} with mixed (Manganese (II))Mn^{2+} [5]. The waste solution from the passivation process consists of high concentration of Cr^{6+} and Cr^{3+}. Treating these waste solutions is a must before release it to the drain according to the law of Environmental Quality Act 1974 under section Industrial Effluent Regulation 2009 (IER 2009). This regulation state that the minimum concentration of Cr^{6+} is 0.05mg/L and 1.0 mg/L for Cr^{3+} concentration for Standard B [6].

In treating industrial Cr waste solution, Cr^{6+} need to reduce to Cr^{3+} followed by precipitation method for complete removal of Cr component in the waste solution. The current reducing agent for treating the effluent waste is using Sodium Metabisulphite (SMBS) [7]. The reactions of SMBS with Cr^{6+} to Cr^{3+} followed step by step for the reduction reactions are shown in Eq (1) and (2) [8].

$$Na_2S_2O_5(aq) + H_2O(aq) \rightarrow 2NaHSO_3(aq) \quad \text{Eq (1)}$$

$$2H_2CrO_4(aq) + 3NaHSO_3(aq) + 3H_2SO_4(aq) \rightarrow Cr_2(SO_4)_3(aq) + 3NaHSO_4(aq) + 5H_2O(aq) \quad \text{Eq (2)}$$

There drawback while using this chemical which is the production of Hydrogen Sulfide (H_2S) and Sulfur Dioxide (SO_2). These hazardous gases are harmful and toxic for human health and also corrosive with the contact of metals [9]. These gases can be detected by a pungent odor that generates throughout the treatment process. Furthermore, this chemical is pricey and not environmental friendly with a high volume of sludge production by precipitation of Calcium(III) Hydroxide ($Cr(OH)_3$) [10]. The chemical that is usually used as precipitating agents which is Calcium Hydroxide ($Ca(OH)_2$) or Sodium Hydroxide (NaOH) (Barrera-Díaz, Lugo-Lugo, & Bilyeu, 2012).

Replacement for this chemical is using the waste product from acetylene gas production known as Leeden Gas sludge (LG sludge). LG sludge will act as a reducing agent in treating the industrial Cr waste solution. LG sludge is the by-product of the process which is later then will be disposed as schedule waste SW427. This LG sludge is actually calcium carbonate slurry ($Ca(OH)_2$) from the reaction of calcium carbide (CaC_2) and water (H_2O). The chemical reaction for acetylene gas production is in Eq (3) [12]. This LG sludge is environmentally friendly which does not generate hazardous gases when the reaction of reduction occurs.

$$CaC_2(s)+2H_2O(l)\rightarrow C_2H_2(g)+Ca(OH)_2 \qquad \text{Eq (3)}$$

Hypothetically, ion of Fe^{3+} will exchange an electron with Cr^{6+} to form Cr^{3+}. Then, the Fe^{3+} will oxidize to form Fe^{2+}. These process of oxidation and reduction reaction occur while adding LG sludge to the waste. (Oxidation Reduction Potential) ORP meter is used to detect electron changes that occur and these changes will also affect the pH value of the solution. The reactions of oxidation and reduction of this chemical are in Eq (4) [13]. Further removal of Cr element in the waste solution is by adding alkaline properties that is OH^- so that Cr^{3+} will become precipitate at the bottom and the reaction is Eq (5) (Barrera-Díaz, Lugo-Lugo, & Bilyeu, 2012).

$$CrO_4^{2-}(aq) + 3Fe^{2+}(aq) + 4H_2O(l) \rightarrow 3Fe^{3+}(aq) + Cr^{3+}(aq) + 8OH(aq) \qquad \text{Eq (4)}$$

$$Cr^{3+}(aq) + 3OH^-(aq) \rightarrow Cr(OH)_3(s) \qquad \text{Eq (5)}$$

In this work, LG sludge will act as a reducing agent for the purpose of reduction of Cr^{6+} to Cr^{3+}. First and foremost, the characterization of both LG sludge and the industrial Cr waste solution. Then, the comparison between SMBS and LG sludge performance will determine whether LG sludge can replace SMBS as reducing agent for Cr reduction.

II. METHODOLOGY

2.1. Preparation of sample

2.1.1. Passivation waste containing Cr (Chromium waste)

Chromium waste from electroplating company in Klang is stored in room temperature at 25°C and record all the initial parameters such as pH, temperature and ORP. The wastewater was collected with the amount of 10 L and is stored in an airtight container in the laboratory. This container also needs to avoid direct sunlight to prevent any deterioration of element or compound that may disturb the result of the experiments.

2.1.2 Cr waste preparation

Preparation of Cr waste needs to dilute for five times so that the spectrometer (DR900), Inductively Coupled Plasma Spectrometer Atomic Emission Spectrometry (ICP-AES) and Atomic Absorption Spectrometer (AAS) instrument can detect the concentration within its range. The dilution factor method is used in this preparation and at the end of the experiments, all the value needs to be multiple by the dilute factor to get the actual value (Eq (6)).

$$\text{Dilution Factor} = \frac{\text{Theoretical value}}{\text{Sample value}} \qquad \text{Eq (6)}$$

2.2. Collection of LG sludge

LG sludge was collected from acetylene gas production company at Shah Alam, Selangor. This LG sludge was in the form of cake after the dewatering process by using a filter press. The cake of LG sludge was stored in an airtight container to avoid any contamination that can influence the result of the experiments.

2.2.1. Preparation of LG sludge

Firstly, the caking of LG sludge will be dry in oven to remove any excess water. The oven used is Universal Oven (Model: ULE 600 Memmert). An empty and dry petri dish was weighed before adding 50g of LG sludge. Then, weigh again before drying into the oven. The temperature for the drying process is 105°C for 4 hours so the LG sludge will completely dry. Then, let it cool until it reaches room temperature before grinded using pestle and mortar to become small particle and sieve for even fine powder of LG sludge. The moisture content of LG sludge will be calculated using Eq (7).

$$\text{Moisture Content, \%} = \frac{m_1 - m_2}{m_0 - m_1} \qquad \text{Eq (7)}$$

Where; m_0 = mass of empty petri dish (g), m_1 = mass of petri dish and wet sample (g), m_2 = mass of petri dish and dried sample (g).

2.2.2. Preparation of LG sludge solution

The dried LG sludge is then use equation (8) for preparation LG sludge solution and the concentration is 4%. After calculation, 40g of fine powder LG sludge will mix with 1000 ml of distilled water in a volumetric flask. The volumetric flask will be mixed thoroughly by swirl the flask.

$$\text{weight}/\text{volume}\ \% = \frac{\text{weight of solute (g)}}{\text{volume of solution (ml)}} \times 100 \qquad \text{Eq (8)}$$

2.3. Preparation of chemical

2.3.1. SMBS solution

Preparation SMBS solution from powder with 99.7% purity is using the same as LG sludge preparation in Eq (8). The concentration for SMBS solution is the same as LG sludge which is 4%. This will be easier to compare the performance of both LG sludge and SMBS as reducing agents.

2.4. Characterization of sample

2.4.1. Chromium waste

Equipment used to characterize this Cr waste was Thermo Scientific iCAP 6000 series inductively coupled plasma mass spectrometry (ICP-AES). This equipment was also available in a laboratory at Faculty of Chemical Engineering, UiTM Shah Alam. The wavelength to monitor Cr is 283.563 nm and the temperature is 6000 K. Argon gas and radio frequency (RF) power was at 1150 that is used to generate plasma. The resulting from this analysis will determine the initial concentration of total chromium. Total chromium is a combination of both Cr^{6+} and Cr^{3+} that presence in Cr waste.

2.5. Cr concentration analyze

2.5.1. Detection of Cr^{6+} concentration

To analyze the concentration of Cr^{6+} in the solution, 1,5-Diphenylcarbohydrazide Method (Hach Method 8023) were used. The equipment used was HACH DR900 Multiparameter Portable Spectrometer and the code program was 90. Reagent use in this method was ChromoVer® 3 Chromium Reagent Powder Pillows.

2.5.2. Detection of Total Cr concentration

2.5.2.1. HACH Method 8024

Method use to detect total Cr concentration was Alkaline Hypobromite Oxidation Method (Hach Method 8024). The code program in HACH DR900 was 100 Chromium, Total and the value will get is in mg/L. There were 4 reagents use in this method which were Acid Reagent Powder Pillows, ChromoVer 3 Chromium Reagent Powder Pillows, Chromium 1 Reagent Powder Pillows and Chromium 2 Reagent Powder Pillows. The units detected was in milligrams per liter (mg/l)

2.5.2.2. Atomic Absorption Spectrometer (AAS) Instrument

This instrument determined chemical elements using absorption of optical radiation (lights) by free atoms in the gaseous state. This AAS brand use is Hitachi Z-2000. The wavelength use was 359.3 nm and the gas used was combination of ethylene gas and air. There is standard solution of total Cr in using this instruments that are 0, 0.2, 0.4, 0.6 and 0.8 mg/L concentration. The result of total Cr was also in milligrams per liter (mg/L) units.

2.6.1. LG sludge

2.6.1.1 X-ray Fluorescent (XRF)

Analyze of the component in the fine powder LG sludge was using XRF equipment at Laboratory in Faculty of Chemical Engineering, UiTM Shah Alam. PANanalytical AXIOS Advance was the XRF equipment that available and it from Malvern PANanalytical XRF company. The result from this analysis will determine the percentage of concentration component that maybe presence in LG sludge.

2.6.1.2 X-ray Diffraction (XRD)

Analysis of fine powder LG sludge also was done using XRD instrument that available at laboratory in Faculty of Applied Science UiTM Shah Alam. This PANalytical X'pert Pro equipment uses to determine suspected compound at a specific angle and frequency in the form of a graph with the y-axis (intensity) and the x-axis (2Θ). The minimum and maximum value of the angle used in this characterization is 10° and 90° respectively. Next, the scan rate is 3° per minutes and the step size is 0.05°. The frequency used is Cu type with $\lambda = 1.54079$ Å.

2.7. Jar Test Equipment

All of the experiment in this work were using SW6 flocculator brand Stuart which has 6 agitator propeller that was available in Industrial Effluent Analytical Laboratory, Faculty of Chemical Engineering, UiTM. The speed of agitator was set at 120 rpm. Detector for pH and ORP value were using HI-8424 pH/ORP meter brand HANNA. All of the sample in this experiment were constant with 300 mL of volume.

2.8. SMBS as reducing agent

The effectiveness of comparative performance between SMBS and LG sludge were studied by experimenting with the Cr solution and SMBS solution. Initial pH and ORP value were recorded and dose SMBS solution little by little using micropipette until the ORP value achieve 280 mV [15]. There were also color changes in occur when the value of ORP close to 280 mV [16].

2.9. LG sludge as reducing agent

2.9.1. Effect of pH variation of LG sludge as reducing agent

The desired pH was set with ranging from 3, 4.5, 5, 5.5, 6, 6.5, 7.5, 8, 9 and 10. Adding the LG sludge using micropipette and the volume added will be recorded to achieve the desired pH. All the initial and final value of pH were recorded in tabulated form. The ORP value in the initial and final experiment were also recorded and graph of Cr^{6+} concentration vs pH and ORP value will be plotted.

2.9.2. Effect of volume LG sludge as reducing agent

In this experiment, the manipulated variables were the volume of LG sludge dose in the Cr waste which were 0.7 ml to 2.6 ml (0.7 ml, 0.8 ml, 0.9 ml, 1 ml, 1.1 ml, 1.2 ml, 1.4 ml, 1.6 ml, 2 ml, 2.2 ml, 2.4 ml and 2.6 ml). Then, the final pH and ORP value were recorded in a table form. Based on the result, graph of Cr^{6+} concentration vs pH and ORP value will be plotted.

III. RESULT AND DISCUSSION

3.1 Sample of characterization

3.1.1. Cr waste

Characterization of Cr waste were done by ICP-AES instrument (Table 1). For this purpose of study, only total Cr concentration data was use in this experiment. In this Cr waste, $K_2Cr_2O_7$ reacts with aqueous acid such as sulfuric acid to form Cr^{6+} ions thus, the total Cr result is actually Cr^{6+} ions [17].The initial total Cr concentration in this Cr waste was 1124 mg/L. The value was significant to the standard that have been set by the law under EQA 1974 which is 1.0 mg/L. This company must treat its waste before released to public drain.

Table 1: Composition of Cr solution passivation waste from electroplating company .

Element	Concentration (mg/L)
Aluminum, Al	19.29
Chromium, Cr	1124
Ferum, Fe	58.35
Magnesium, Mg	460.25
Zinc, Zn	239.2

3.1.2. LG sludge

3.1.2.1 XRF characterization

Composition of LG sludge was analyzed by XRF instrument. The result showed that the highest of LG sludge in both element and compound were calcium with 61.11% and 58.56% respectively. The raw material in this Table 2 is material that was used in acetylene gas production which is calcium carbide. This raw carbide material consists of ferum ions element which is 32.86%. Unreacted ferum ions will stay in LG sludge which is then use in the reduction of Cr^{6+} in the Cr solution [18]. The analysis of LG sludge using XRF instrument have also been done by another researcher, R. Saldanha, H. Scheuermann et. al. and the result was different but still CaO is the highest which is the same with result in Table 2 [19]

Table 2: Composition of LG Sludge by XRF

Element	Raw (%)	LG Sludge (%)	Compound	Raw (%)	LG Sludge (%)
C	3.39	3.31	CO_2	10.2	10.22
Mg	0.68	0.77	MgO	0.85	1.02
Si	1.13	0.38	SiO_2	1.91	0.62
Ca	57.9	61.11	CaO	55.6	58.56
Mn	1.02	0.97	MnO	0.82	0.78
Fe	32.9	30.72	Fe_2O_3	28.9	27.18
Ni	2.02	1.89	NiO	1.51	1.43
Cu	0.13	0.12	CuO	0.09	0.09
Zn	0.03	0.022	ZnO	0.02	0.016
Cd	0.08	0.074	CdO	0.06	0.051
Pb	0.06	0.055	PbO	0.04	0.035
O	0.66	0.581			

3.1.2.2 XRD characterization

Figure 1 shown the result of characterization of LG sludge which is P ($Ca(OH)_2$), C (Calcite) and G (Graphite). Each peak represents the high compound that present in LG sludge. This result is the same with research that have been done by Fabio A. et. al [20]. In the research state that the percent of P which is $Ca(OH)_2$ was the highest among C and G that is 92.1%. This result of characterization also had the same dominant compound that have been conducted by Rodrigo Beck Saldanha, et. al [19]. Thus, LG sludge can be classified as carbide lime or calcium carbide.

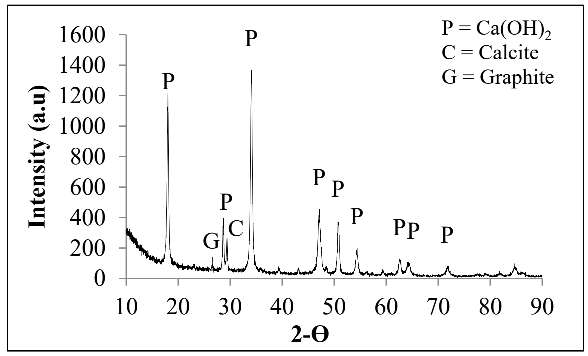

Figure 1 : XRD analysis of LG sludge

3.2. LG sludge as reducing agent

3.2.1. Effect of pH variation

The LG sludge was added to Cr waste until the pH value achieve the desired state. The desired pH value was range between 2 until 10. The initial Cr^{6+} concentration in Cr solution is 3.25 mg/L using HACH Method 8023.

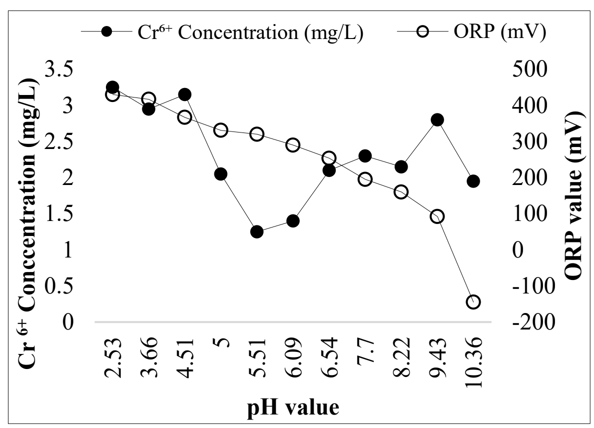

Figure 2(a): Effect of pH varies on Cr^{6+} concentration

In Figure 2(a), the ORP value will decrease as the value of pH keep increasing. The lowest Cr^{6+} concentration is at pH 5.51 with value of 1.25 mg/L. The second lowest of Cr^{6+} concentration is 1.4 mg/L at pH 6.09. The result of pH values is inversely proportional to the ORP values is the same with a comparative study that had been done by J. Duncan, M. Guthrie, K. Lueck et. al. [16]

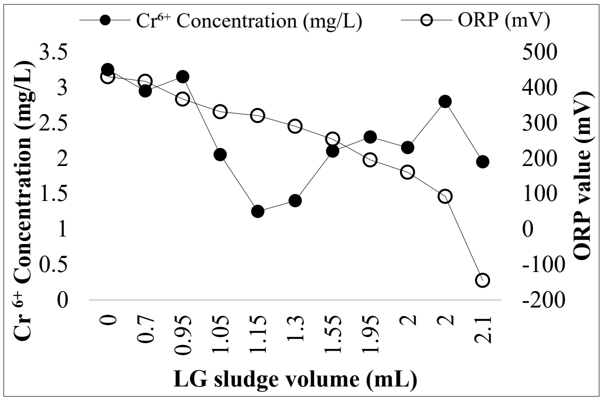

Figure 2(b): Effect of LG sludge volume on Cr^{6+} concentration

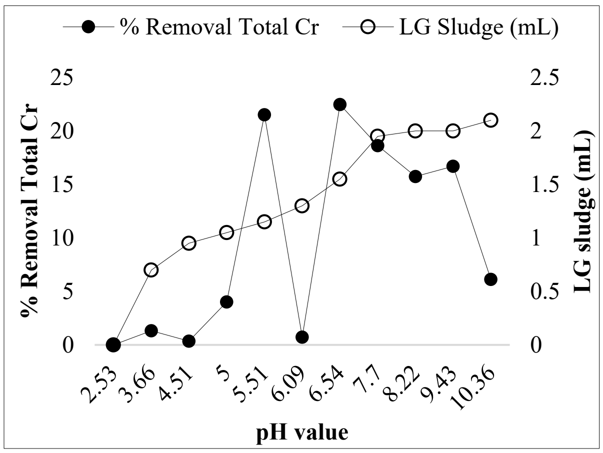

Figure 2(c): Effect of pH value on % removal of Total Cr

LG sludge was calcium-rich which alkaline in one of its properties and this will make the pH of Cr waste increase by the increasing volume used in the experiment. The corresponding of LG sludge volume used as a reducing agent in at pH 5.51 is 1.15 mL in Figure 2(b). Meanwhile, 1.3 mL volume of LG sludge used at pH 6.09. Increasing of pH values result in this experiment were successful by adding LG sludge only without adding any other chemical. Research conducted by R. Ayeche and O. Hamdaoui also states that the higher the LG sludge, the pH will keep increasing [21]. Furthermore, the increasing of LG sludge is inversely proportional to the ORP values. The range of ORP values between pH 5.51 and 6.09 is from 320.2 to 290.1 mV respectively.

In Figure 2(a) also shown that after pH 6.09, the Cr^{6+} keep increasing. In my opinion, Fe ions do not convert Cr^{6+} to Cr^{3+} like it's supposed to be. This means that Fe ions in the LG sludge were overdose by increasing dose of LG sludge in the Cr waste. The ion exchange for the reduction of Cr^{6+} was proven even though Cr^{6+} concentration increase after a certain limit of pH values. This result can be supported by research that already done by D. Jiang, D. Huang et. al from the year 2018 [22].

Table 3: Summary of % Reduction Cr^{6+} for the effect of pH variation experiment.

pH value	LG sludge (mL)	% Reduction
2.53	0	0
3.66	0.7	9.2
4.51	0.95	3.1
5.0	1.05	36.9
5.51	1.15	61.5
6.09	1.3	56.9
6.54	1.55	35.4
7.7	1.95	29.2
8.22	2	33.8
9.43	2	13.8
10.36	2.1	40.0

Result in Table 3 show that the % reduction of Cr^{6+} concentration in this experiment. The highest % reduction was at pH 5.51 with 61.5%. Second highest of % reduction was at pH 6.09 with 56.9 %. At the end of the experiment, there was precipitate at the bottom of the beaker. In Figure 2(c), the graph showed the result of % removal of Total Cr and the highest % removal that is 22.47% at pH 6.54. The removal result can be detected by brownish precipitate and it was belief that the formation of $Cr(OH)_3$ precipitate occur. This finding can be supported by others researcher which is M. A. Mottalib, S. H. Somoal et. al. has conducted study using LG sludge for removal of heavy metal by forming of $Cr(OH)_3$ precipitate [23]. Even though the result of optimum pH from the research study was different compare to the result in Figure 2(c), still the removal of Cr^{3+} ions occurs by the precipitation of $Cr(OH)_3$.

3.2.2. Effect of volume LG sludge variation

Manipulated variables in this experiment was the volume of LG sludge that use in dosing into the Cr solution. The range of LG sludge volume were started from 0.7 ml, 0.8 ml, 0.9 ml, 1.0 ml, 1.1 ml, 1.2 ml, 1.4 ml, 1,6 ml, 1.8 ml and 2.0 ml. The final pH and ORP were recorded and plotted graph data against the Cr^{6+} concentration.

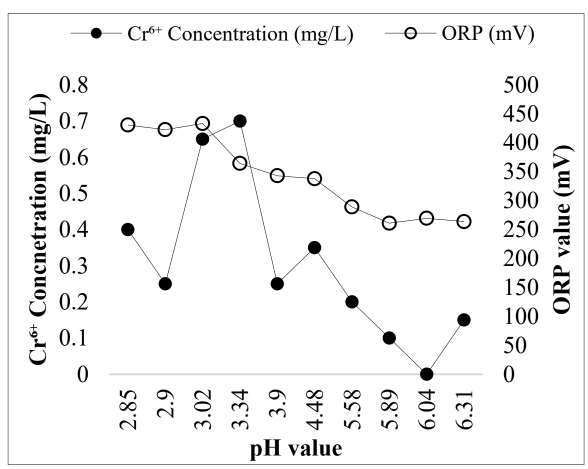

Figure 3(a): Effect of pH on Cr^{6+} concentration

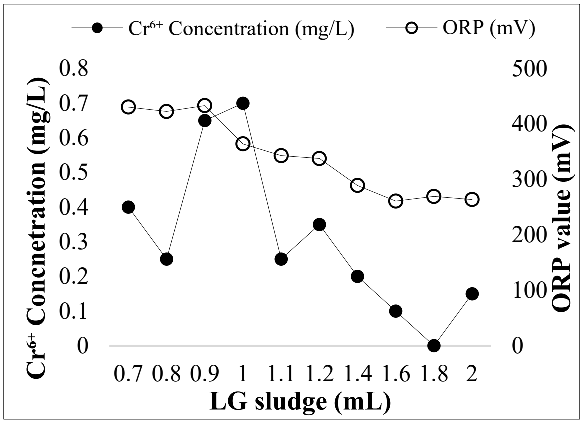

Figure 3(b): Effect of LG sludge on Cr^{6+} concentration

Result state in Figure 3(a) and (b) shown that at pH 6.04 was the lowest Cr^{6+} concentration with 1.8 mL volume of LG sludge used. ORP value at this particular pH was 269.4 mV which is still within the range in first experiment which is the effect of pH variation (320.2 mV-290.1 mV). Compare with the result in the effect of pH variation, the lowest Cr^{6+} concentration is between pH 5.51 and 6.09. Thus, result from both experiments, the optimum pH for the reduction of Cr^{6+} is at pH 6. The ORP value have the same pattern which is decreasing with the increasing of pH value.

Table 4: Summary of % Reduction Cr^{6+} for the effect of LG sludge variation experiment.

pH value	LG sludge (mL)	% Reduction
2.85	0.7	87.7
2.90	0.8	92.3
3.02	0.9	80.0
3.34	1.0	78.5
3.90	1.1	92.3
4.48	1.2	89.2
5.58	1.4	93.8
5.89	1.6	96.9
6.04	1.8	100
6.31	2	95.4

Table 4 shown that the % reduction of Cr^{6+} was 100% successful at pH 6.04. Thus, the result can conclude that all the Cr^{6+} ions were reduce to Cr^{3+} and further undergoes precipitation to become $Cr(OH)_3$ solid. Overall of these results, LG sludge that have the same characteristic as lime can be use in removing Cr in the Cr waste solution. Supporting this fact is according to research that have been study by J. Singh, A. Kalamdhad [24]. Next, another research study about the comparison of grain size for acetylene sludge in the effectiveness of Cr removal process which state that the smaller particles are better than bigger ones [25]. Thus, particles size also one of the factors effecting the result of Cr removal but, in this experiment, the LG sludge is brittle and easily break to smaller pieces. Due to that problems, grinding to become fine powder is the best solution in this experiment.

3.3. SMBS as reducing agent

In this experiment, SMBS was dose using micropipette little by little until the value of ORP is drop to estimated value (250 mV) and record the volume dosage. After that, use Hach Method 8023 to detect the remaining Cr^{6+} concentration. Result shown in Table 3, SMBS dosage use was 10.5 ml and the final ORP value is 245.1 mV which is below the 250 mV. The final Cr^{6+} concentration is 0 mg/L which is 100% reduction reactions occur. The optimum pH for the reduction process occurs was at 2.22 and this result is the same with research done by R. S. Karale, et. al. [26]. Beside that, study by T. Sowmya, P. Mahadevraju, A. Ramesh et. al. also have the same finding which is optimum pH is at 2 and have 100% reduction of Cr^{6+} [27]. Another study also using SMBS as the source of sulfite ions in reducing Cr^{6+} with its optimum pH conditions is between 2<pH<5 [28].

Table 3 : Performance of SMBS as reducing agent

	Concentration (mg/L)
Initial ORP (mV)	580
Initial pH	2.22
Volume of SMBS (ml)	10.5
Final ORP (mV)	245.1
Final pH	3.17
Concentration of Cr^{6+} (mg/L)	0
% Reduction of Cr^{6+}	100

The volume of SMBS used in reduction of Cr^{6+} was higher compare to the volume of LG sludge. Research done by M. Almeida, R. Boaventure also used small volume of acetylene sludge in treating the Cr waste that is $16mg/L^{-1}$ for 97% of removal [29]. Furthermore, this can optimize the cost of chemical purchase cause SMBS is pricey compare to LG sludge which is already waste by-product of acetylene gas production [30]. In addition, LG sludge does not generate hazardous gases during the reduction process.

IV. CONCLUSION

In characterization of LG sludge, XRF result shown that existence of Fe ions and high % in Ca element. XRD result also shown that the LG sludge have the same component as lime which is $P(Ca(OH)_2$, C(Calcite) and G(Graphite) .The initial total Cr concentration that was done by ICP-AES was 1124 mg/L and Cr^{6+} concentration 3.25 mg/L by HACH Method 8023. Result from the effect of pH variation using LG sludge as reducing agent shown that the minimum Cr^{6+} concentration is between pH 5.51 with dosage of 1.15 mL. The highest % reduction in shown in Table 3 was 61.5%. In the effect of volume LG sludge variation, the dose that completely reduce the Cr^{6+} in the Cr waste was 1.8 ml which is lower that using SMBS as reducing agent. The optimum pH for this 100% reduction was at pH 6.04. The ORP value of this successful reduction was 264.9 mV which is between 320.2 mV to 290.1 mV from the first experiment (effect of pH variation).

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