The International Journal of Integrated Engineering

Reduction of Hexavalent Chromium to Trivalent Chromium using Sludge from Acetylene Gas Production

Nur Ain Mohd Zainuddin[1], Nursyahzani Mohamad Sarwani[1], Siti Wahidah Puasa[1*], Kamariah Noor Ismail[1]

[1]Integrated Separation Technology Research Group, School of Chemical Engineering, College of Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, MALAYSIA

*Corresponding Author

Abstract: Electroplating industry generates harmful anionic heavy metal which is Hexavalent Chromium (Cr^{6+}) that need to be treated before it can be discharged into the environment following accordance to the Environmental Industry (Effluent Regulation) 2009. These Cr^{6+} ions must be reduced to chromium trivalent (Cr^{3+}) using a reducing agent before undergoing precipitation process for complete removal of (Chromium) Cr component. The common reducing agent is using Sodium Metabisulphite (SMBS). This chemical generates harmful gases which are Hydrogen Sulphide (H_2S) and Sulphur Dioxide (SO_2). Circular economy practices encouraged by the Department of Environment (DOE) includes repurposing industrial waste, where the undesired by product is seen as a potential resource for other purposes. In this study, sludge from Acetylene gas production is used as a reducing agent. Acetylene production sludge (APS) contains high (Calcium) Ca element and (Ferum) Fe ions that are essential for the reduction of Cr^{6+} to Cr^{3+}. The analysis of APS characterization is 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 and total Cr concentration is 1124 mg/L. The highest percentage reduction is 61.5% found at pH 5.51 with the APS dosage of 1.15 ml. For the effect of APS dosing, 100% reduction of Cr^{6+} is achieved at pH 6.04 with volume of APS used at 1.8 ml.

Keywords: Hexavalent chromium; trivalent chromium; reducing agent; acetylene production sludge, electroplating wastewater

1. Introduction

Hexavalent Chromium (Cr^{6+}) is carcinogenic to human health and can pollute the environment. It is an anionic heavy metal contaminant that is present in wastewater from automotive or electroplating industry [1]. Humans can be exposed to chromium through dermal contact or inhalation. Research done by Das et al. [2] in Odisha, India showed more than 200, 000 workers and inhabitant resident in Sukinda chromite mine have major chronic diseases such as cancer. The workers and residents were poisoned with chromium from the mine and many animals died due to the nearby polluted river [2].

In Malaysia, the main source of Chromium (Cr) substance is from the electroplating industry. This industry producing high quality of metals with high corrosion resistance. There are many other substances that can be used for corrosion resistance such as zinc, aluminium, copper, and steel. Compare to other metals, chromium is highly favoured 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
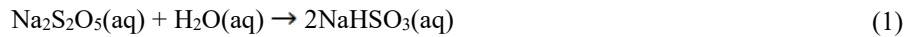
passivation by potassium dichromate ($K_2Cr_2O_7$) solution. The solution has high concentration of Cr^{6+} which is 14000 ppm with the colour of orange red. In the passivation solution, Cr^{6+} ions are in the form of CrO_4^{2-} or $Cr_2O_7^{2-}$ compound [4]. The reaction occur in the passivation process 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 necessary before releasing 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 in Environmental Quality Act 1974 (Act 127) [6].

In treating industrial Cr waste solution, Cr^{6+} needs to be reduced 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 Eq. (2).
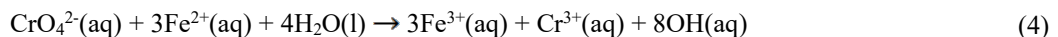
$$Na_2S_2O_5(aq) + H_2O(aq) \rightarrow 2NaHSO_3(aq) \tag{1}$$

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

The drawback while using this chemical which is the production of Hydrogen Sulphide (H_2S) and Sulphur Dioxide (SO_2). These hazardous gases are harmful and toxic for human health and also corrosive with the contact of metals [8]. These gases can be detected by a pungent odour 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 ($Cr(OH)_3$) [9]. The chemical that is usually used as precipitating agents which is Calcium Hydroxide ($Ca(OH)_2$) or Sodium Hydroxide (NaOH) [10].

Replacement for this chemical is using the waste product from acetylene gas production known as Acetylene gas production sludge (APS). APS will act as a reducing agent in treating the industrial Cr waste solution. It is the by-product of the process which will be disposed as scheduled waste SW204. APS is 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) [11]. APS is environmentally friendly as it does not generate hazardous gases when the reaction of reduction occurs.

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

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 APS 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 oxidation and reduction reaction of this chemical is shown in Eq. (4) [12]. Further removal of Cr element in the waste solution is carried out by adding alkaline properties that is OH^- so that Cr^{3+} will precipitate at the bottom as shown in Eq. (5) [10].

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

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

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

2. Method

2.1. Passivation Wastewater Preparation

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

Preparation of Cr waste needed to be diluted 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 was used in this preparation and at the end of the experiments, all values were multipled by the dilution factor to get the actual values using Eq. (6).

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

2.2. Preparation of APS

APS was collected from acetylene gas production company at Shah Alam, Selangor. It was in the form of cake after the dewatering process using a filter press. The cake of APS was stored in an airtight container to avoid any contamination that can influence the result of the experiments. Firstly, the caking of APS was dried in an oven to remove any excess water. The oven used was Universal Oven (Model: ULE 600 Memmert). An empty and dry petri dish was weighed before adding 50g of APS. Then, the petri dish was weighed again before drying in the oven. The temperature for the drying process was 105°C for 4 hours to ensure complete drying of the APS. Then, the APS was cooled until it reached room temperature before it was grinded using pestle and mortar into small particle and sieved for even finer powder of APS. The moisture content of APS will be calculated using Eq. (7).

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

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).

The dried APS was then calculated using Eq. (8) for preparation of APS solution at 4% concentration. After calculation, 40g of fine powder APS was mixed with 1000 ml of distilled water in a volumetric flask. The volumetric flask was mixed thoroughly by swirling the flask.

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

2.3. Preparation of SMBS Solution

Preparation SMBS solution from powder with 99.7% purity followed the same method as APS preparation in Eq. (8). The concentration for SMBS solution was the same as APS which was 4%. This enabled easier comparison of the performance of both APS and SMBS as reducing agents.

2.4. Chromium Waste

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

2.4.1. Detection of Chromium Hexavalent Concentration

To analyse the concentration of Cr^{6+} in the solution, 1,5-Diphenylcarbohydrazide Method (Hach Method 8023) was 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.

2.4.2. Detection of Total Cr Concentration
2.4.2.1. Hach Method 8024

Method used 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 obtained was in mg/L. There were 4 reagents used 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 litre (mg/L).

2.4.2.2. Atomic Absorption Spectrometer (AAS) Instrument

This instrument determined chemical elements using absorption of optical radiation (lights) by free atoms in the gaseous state. The AAS brand used was Hitachi Z-2000. The wavelength used was 359.3 nm and the gas used was a

combination of ethylene gas and air. There was standard solution of total Cr used for this instrument which were 0, 0.2, 0.4, 0.6 and 0.8 mg/L concentration. The result of total Cr was also in milligrams per litre (mg/L) units.

2.5. APS Analysis

2.5.1. X-Ray Fluorescent (XRF)

Analysis of the component in the fine powder APS was done using XRF equipment at Laboratory in School of Chemical Engineering, UiTM Shah Alam. PAN analytical AXIOS Advance was the available XRF equipment from Malvern PANanalytical XRF company. The result from this analysis determined the percentage of concentration component that may be present in APS.

2.5.2. X-Ray Diffraction (XRD)

Analysis of fine powder APS was done using XRD instrument available at laboratory in School of Applied Science UiTM Shah Alam. This PANalytical X'pert Pro equipment determined 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 were 10° and 90° respectively. The scan rate was 3° per minutes and the step size was 0.05°. The frequency used was Cu type with $\lambda = 1.54079$ Å.

2.6. Jar Test

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

2.7. SMBS as Reducing Agent

The effectiveness of comparative performance between SMBS and APS were studied by experimenting with the Cr solution and SMBS solution. Initial pH and ORP value were recorded and SMBS solution was dosed in little increments using a micropipette until the ORP value achieved 280 mV [13]. Colour changes were observed when the value of ORP close to 280 mV [14].

2.8. APS as Reducing Agent

2.8.1. Effect of pH Variation of APS as Reducing Agent

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

2.8.2. Effect of Volume APS as Reducing Agent

In this experiment, the manipulated variables were the volume of APS 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 values were recorded in a table form. Based on the result, graph of Cr^{6+} concentration vs pH and ORP values was plotted.

3. Results and Discussion

3.1. Sample Characterization

3.1.1. Sample Cr Waste

Characterization of Cr waste was done using ICP-AES instrument and results are shown in Table 1. For this purpose of study, only total Cr concentration data was used 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 [15].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 it may be released to public drain.

Table 1 - Composition of Cr solution passivation waste from electroplating company

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

3.1.2. APS Characterization

3.1.2.1. XRF Characterization

Composition of APS was analysed by XRF instrument. The result showed that the highest of APS 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 was calcium carbide. This raw carbide material consisted of 32.86% ferum ions element. Unreacted ferum ions in APS is used in the reduction of Cr^{6+} in the Cr solution [16]. The analysis of APS using XRF instrument was also done by another researcher, Saldanha et al. [17]. The result was different but CaO was still the highest similar to the result in Table 2 [17].

Table 2 - Composition of APS by XRF.et

Element	Raw (%)	APS (%)	Compound	Raw (%)	APS (%)
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

Fig. 1 shows the result of characterization of APS which is P ($Ca(OH)_2$), C (Calcite) and G (Graphite). Each peak represents the high compound present in APS. This result is the same with research that have been done by [18]. 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 characterization results also had the same dominant compound that have been conducted by Saldanha et al. [17]. Thus, APS can be classified as carbide lime or calcium carbide.
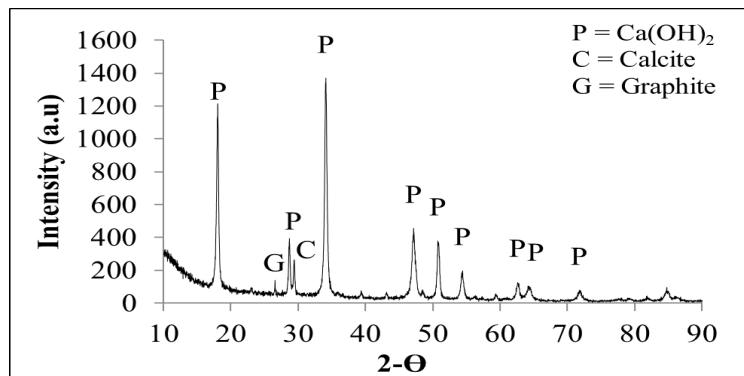
Fig. 1- XRD analysis of APS

3.2. APS as Reducing Agent

3.2.1. Effect of pH Variation

APS was added to Cr waste until the pH value achieved the desired state. The desired pH value ranged between 2 until 10. The initial Cr^{6+} concentration in Cr solution was 3.25 mg/L using HACH Method 8023. In Fig. 2, the ORP value decreased as the value of pH increased. The lowest Cr^{6+} concentration was at pH 5.51 with value of 1.25 mg/L. The second lowest of Cr^{6+} concentration was 1.4 mg/L at pH 6.09. The result of pH values was inversely proportional to the ORP values which is the same with a comparative study done by Duncan et al. [14].
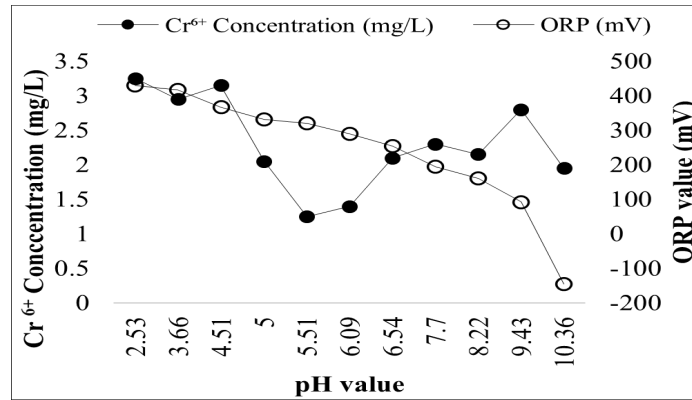

Fig. 2 - Effect of pH varies on Cr^{6+} concentration

APS was calcium-rich which alkaline. This will make the pH of Cr waste increase by the increasing volume used in the experiment. The corresponding APS volume used as a reducing agent at pH 5.51 was 1.15 mL in Fig. 3. Meanwhile, 1.3 mL volume of APS was used at pH 6.09. Increasing of pH values result in this experiment were successful by adding APS without any other chemicals. Research conducted by Ayeche et al. [19] also stated that the higher the APS, the higher the pH [19]. Furthermore, the increase of APS was inversely proportional to the ORP values. The range of ORP values between pH 5.51 and 6.09 were from 320.2 to 290.1 mV, respectively.
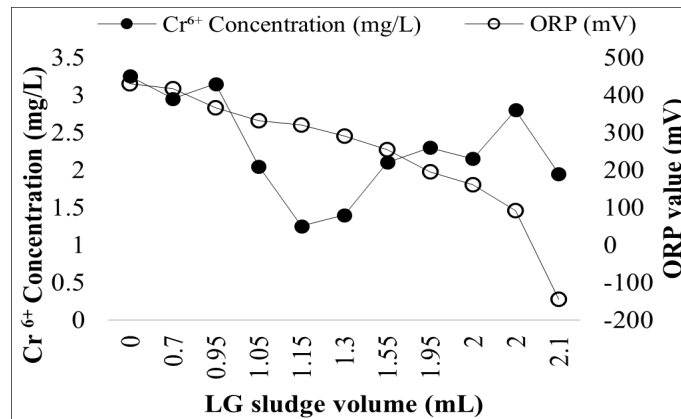

Fig. 3 - Effect of APS volume on Cr^{6+} concentration

Fig. 4 also shows that after pH 6.09, the Cr^{6+} kept increasing. In our opinion, Fe ions do not convert Cr^{6+} to Cr^{3+} accordingly. This means that Fe ions in the APS were overdosed by increasing dose of APS in the Cr waste. The ion exchange for the reduction of Cr^{6+} was proven even though Cr^{6+} concentration increased after a certain limit of pH values. This result is supported by research done by Jiang et al. [20] in the year 2018.
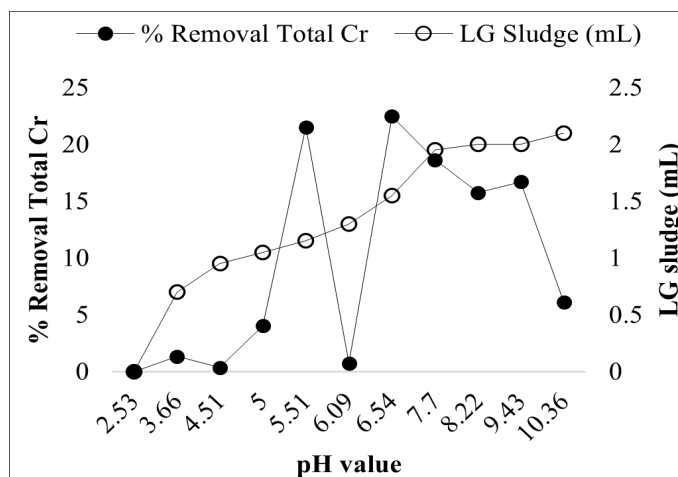
Fig. 4 - Effect of pH value on percentage removal of Total Cr

Result in Table 3 shows the percentage reduction of Cr^{6+} concentration in this experiment. The highest percentage reduction was at pH 5.51 with 61.5%. Second highest percentage 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 Fig. 4, the graph showed the result of percentage removal of Total Cr and the highest percentage removal was 22.47% at pH 6.54. The removal result can be detected by brownish precipitate, and it was believed that the formation of $Cr(OH)_3$ precipitate occurred. This finding is supported by other researcher which are Mottalib et al. [21] who have conducted study using APS for removal of heavy metal by forming of $Cr(OH)_3$ precipitate [21]. Even though the result of optimum pH from the research study was different compared to the result in Fig. 4, still the removal of Cr^{3+} ions occurred by the precipitation of $Cr(OH)_3$.

Table 3 - Summary of percentage Reduction Cr^{6+} for the effect of pH variation experiment

pH value	APS (mL)	Percentage 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

3.2.2. Effect of volume APS variation

Manipulated variables in this experiment was the volume of APS dosed into the Cr solution. The range of APS volume were incremented 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 in a graph against the Cr^{6+} concentration.

Result stated in Fig. 5 and Fig. 6 and Table 4 shows that at pH 6.04, the lowest Cr^{6+} concentration was achieved with 1.8 mL volume of APS used. ORP value at this particular pH was 269.4 mV which was still within the range in first experiment which was the effect of pH variation (320.2 mV-290.1 mV). Compared with the result in the effect of pH variation, the lowest Cr^{6+} concentration was between pH 5.51 and 6.09. Thus, result from both experiments concluded that the optimum pH for the reduction of Cr^{6+} was at pH 6. The ORP value had the same decreasing pattern with the increasing pH value.

3.3. SMBS As Reducing Agent

In this experiment, SMBS was dosed using micropipette little by little until the value of ORP dropped to estimated value (250 mV) then the volume of dosage was recorded. After that, Hach Method 8023 was used to detect the remaining Cr^{6+} concentration. Result shown in Table 5 found that SMBS dosage used was 10.5 ml and the final ORP value was 245.1 mV which was below the 250 mV. The final Cr^{6+} concentration was 0 mg/L which meant 100% reduction reaction occurred. The optimum pH for the reduction process occurred at 2.22 and this result is the same with

research done by Karale, et al. [22]. Besides that, study by Sowmya et al. [23] also have the same finding which was optimum pH was at 2 and 100% reduction of Cr^{6+} [23]. Another study also using SMBS as the source of sulphite ions in reducing Cr^{6+} with its optimum pH conditions was between 2<pH<5 [24].

The volume of SMBS used in reduction of Cr^{6+} was higher compared to the volume of APS. Research done by Almeida et al. [25] also used small volume of acetylene sludge in treating 16mg/L^{-1} of Cr waste for 97% of removal [25]. Furthermore, this can optimize the cost of chemical purchase because SMBS is pricey as compared to APS which is a waste by-product of acetylene gas production [26]. In addition, APS does not generate hazardous gases during the reduction process.
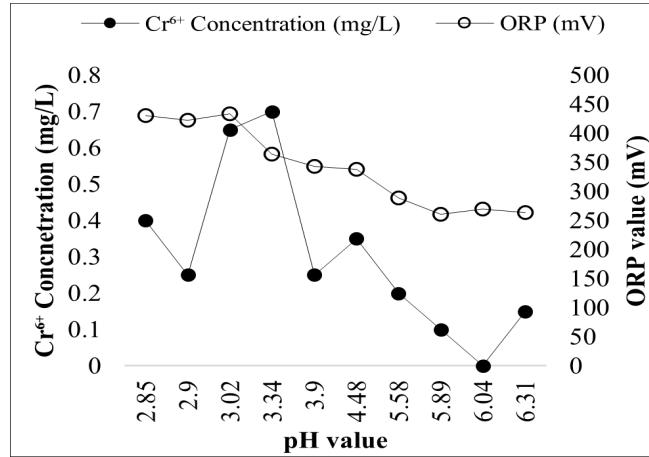

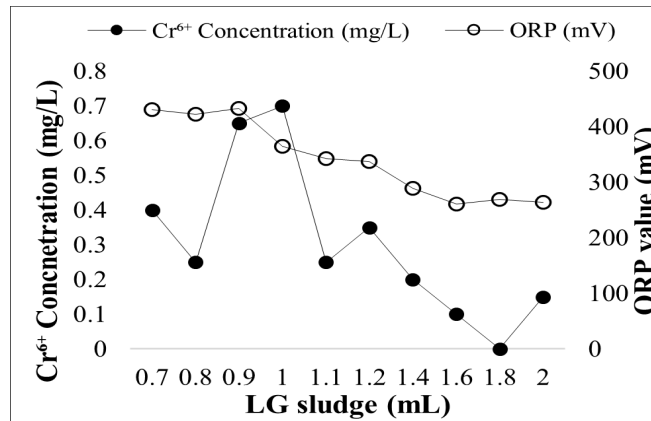**Fig. 5 - Effect of pH on Cr^{6+} concentration**

Fig. 6 - Effect of APS on Cr^{6+} concentration

Table 4 - Summary of Percentage Reduction Cr^{6+} for the effect of APS variation experiment

pH value	APS (mL)	Percentage 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

Table 5 - 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

4. Conclusion

In characterization of APS, XRF result showed existence of Fe ions and high percentage of Ca element. XRD result also showed that APS had the same component as lime which was P(Ca(OH)2, C(Calcite) and G(Graphite). The initial total Cr concentration done by ICP-AES was 1124 mg/L and Cr6+ concentration was 3.25 mg/L by HACH Method 8023. Result from the effect of pH variation using APS as reducing agent showed that the minimum Cr6+ concentration was between pH 5.51 with dosage of 1.15 mL. The highest percentage reduction shown in Table 3 was 61.5%. In the effect of APS volume variation, the dose that completely reduce the Cr6+ in the Cr waste was 1.8 ml which is lower that using SMBS as reducing agent. The optimum pH for 100% reduction was at pH 6.04. The ORP value of this successful reduction was 264.9 mV which was between 320.2 mV to 290.1 mV from the first experiment (effect of pH variation).

Acknowledgement

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