Study of reducing Chromium (VI) to Chromium (III) ion using reduction and coagulation methods for electroplating industrial waste

M Y Azis1*, N N Amedyan2, Hanefiatni1 and A Suprabawati2

1 Analytical Chemistry Research Division, Chemistry Department, Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung
2 Physical Chemistry Research Group, Chemistry Departement, Faculty of Science and Informatics University of Jendral Achmad Yani

*Email: m.yudhistira.azis@mail.chem.itb.ac.id

Abstract. The electroplating industrial waste is the primary source of environmental pollution due to heavy metal chromium (VI). The method commonly used in treating chromium (VI) metal waste in industry is by reduction and coagulation. Chromium (VI) metal is very toxic because it is very unstable compared to chromium (III). Therefore, chromium (VI) waste must be reduced to chromium (III) before it will be discharged into the environment. The purpose of this study is to find the optimum conditions in reducing levels of chromium (VI). The method used is reduction with sodium metabisulfite, coagulation with Polyaluminium chloride (PAC), and a combination of both. The percentage of reduction obtained in the reduction, coagulation, and combined methods is 96.36%; 20.57%; and 98.57%, with the optimum dose of reducing agents and coagulants of 330 mg/L and 300 mg/L. The best method to reduce the level of chromium (VI) is the combined method at a percentage reduction of 98.57% with a standard deviation of 0.0046 and %RSD of 0.43%. The electroplating waste has reduced percentage until 98.39% at using combination methods.

1. Introduction
Electroplating industrial waste is the main source of environmental pollution; one of the reason cause Chromium (VI) (Cr (VI)) content in the aquatic environment. Waste streams from electroplating may contain up to 2500 mg L⁻¹ Cr (VI), which must be controlled to an acceptable level before being discharged to the environment [1-2]. Chromium plating waste is much contained in automobile parts, process equipment for corrosion resistant [3]. Nowadays, electroplating waste problem contains chromium need to pay attention and trying to solve them as better as possible.

Based on PERMEN LH, 2014, the wastewater electroplating industry Chromium (VI) must contain lower than 0.1 mg.L⁻¹. Chromium (VI) is carcinogenic, skin irritation and harmful to kidney, gastritis and liver. Because of the toxicity level of Chromium (VI) 300 times higher than Cr(III) [4]. In addition, Cr(III) is essential for glucose, lipid and metabolism system so this ion must reduce to Chromium (III) before discharge into the environment [4-5]. Chromium (III) ion can be precipitated as hydroxide salt (Cr(OH)₃) or phosphate or sulphate salt at base condition [5]. Recycle of its waste is an essential aspect for developing electroplating industries contain chromium [6]. Several reductor can used to reduce Cr(VI) content such as ferrosulfate, potassium iodide[7]. Due to the consideration of cost and safety aspects, sodium metabisulfite is an appropriate reducing agent for use on a large scale in the industry.
The method commonly used in treating chromium (VI) ion waste in industry by reduction and coagulation methods [8], but the decreasing percentage to reduce of chromium (VI) still not significant. There are several methods need more cost and time consuming such as electrocoagulation [1,9], precipitation [10], filtration [11], adsorption [12,13] and membrane technique [14]. The decreasing percentage of reducing Cr(VI) to Cr(III) need to evaluate using coagulation or reduction or combination of both methods for industrial scale. This study aims to evaluate the optimum decreasing percentage to reduce chromium (VI) ion level to chromium (III) with three different methods such as reduction, coagulation and combination of both methods using several analytical parameters and applied in electroplating samples.

2. Experimental methods
   2.1. Materials and apparatus
   The experiments were carried out by using chemicals in analytical grades, such as Diphenylcarbazide (DPC) (Merck, Singapore), Chromium hidroxide (Cr(OH)_3) (Merck, Indonesia), sodium metabisulfite (Merck, Indonesia), Sulphuric acid, H_2SO_4 (Sigma-Aldrich, Singapore), Polyaluminiumchloride (PAC) (Sigma-Aldrich, Singapore), NaOH (Merck, Indonesia). All glass equipments and apparatus were prepared from a physical chemistry laboratory of UNJANI.

   2.2. Optimization of reductor and coagulant dose concentration of reducing Cr (VI) to Cr(III)
   The optimization of reductor concentration, we used same concentration of artificial chromium (VI) in several beaker glass then controlled pH 2 with adding H_2SO_4 1 N or NaOH 1 N [14]. Then each beaker glass added Na_2S_2O_3 with variety concentration at 310, 320, 330, 340 mg.L^-1. Each concentration were analyzed by UV-Vis spectrometry.

   100 mL artificial chromium (VI) (CrO_3 powder) dissolved at 75 mg.L^-1 and it was added in each several beaker glasses then controlled pH 9 with adding H_2SO_4 1 N or NaOH 1 N [14]. Then each beaker glass added PAC with variety concentration at 100, 200, 300 mg.L^-1. Each beaker glass was stirred at 125 rpm for 5 minutes. After that, the supernatant filtered and analysis by UV-Vis spectrometry.

   The optimum condition was used for combination methods between coagulation and reduction methods. Chromium (VI) analysis using UV-Vis Spectrometry at 540 nm with added diphenylcarbazide (DPC) as complex solvent [15,16]. The rest of concentration after coagulation/reductor or combination methods determined as Chromium (III).

   2.3. Reduction Cr(VI) to Cr(III) in electroplating waste sample
   Electroplating waste sample was filtered and stored at 4°C before used [14]. It taken from Chitose industry, Cimahi West Java. The characterization of hexavalent chromium showed the violet-blue colour, 4.5 pH, 1020 mg/l Cr (VI), 1732 mg/l COD, 1410 mg/l TDS, 285 mg/l TSS and 89 mg/l Fe ions. The separation of Cr(VI) based on [9]. Batch reduction experiments were performed in 200 mL Erlenmeyer flasks in an incubator maintained at a constant temperature. Sodium metabisulfite solution from optimum condition was added then controlled pH 2 with adding H_2SO_4 1 N or NaOH 1 N. then continue simultaneously for coagulation methods from optimum dose concentration then stirred at 125 rpm for 5 minutes. After that, the supernatant filtered and analysis by UV-Vis spectrometry.

3. Results and discussion
   3.1. Optimization of reductor and coagulant dose concentration of reducing Cr (VI) to Cr(III)
   The reduction reaction between Chromium (VI) ion and sodium metabisulfite are as follows reaction:

   \[
   \text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} (l) \rightarrow \text{NaHSO}_3 (aq) \tag{1}
   \]

   \[
   \text{H}_2\text{CrO}_4 (s) + \text{NaHSO}_3 (s) + \text{H}_2\text{SO}_4 (s) \rightarrow \text{Cr}_2(\text{SO}_4)_3 (s) + 3 \text{NaHSO}_4 (s) + 4\text{H}_2\text{O}(s) \tag{2}
   \]
The theoretical amount of sodium metabisulfite needed to reduce 1 mg.L\(^{-1}\) Chromoiunm (VI) ion is 2.81 mg.L\(^{-1}\) which ratio amount (3:1; NaS\(_2\)O\(_3\):Chromium (VI) ion) However, for the reaction to proceed perfectly, sodium metabisulfite was added in excess of the theoretical dosage requirements. The initial concentration of Cr(VI) ion is 75 mg.L\(^{-1}\) and sodium metabisulfite as reductor required was 210.75 mg.L\(^{-1}\). The results obtained are the largest percentage reduction in the reducing dose of 330 mg.L\(^{-1}\) reached until 96.36%. The optimum ratio amount (4.4:1; NaHSO\(_3\): Chromium (VI) ion) is greater than the theoretical dose. The result obtained is still above the standard quality based on PERMEN LH (0.1 mg.L\(^{-1}\)) or metal concentration level standard (Cr (VI)) is 0.05 mg.L\(^{-1}\) [17]. Percentage of decreased chromium (VI) by PAC coagulant and sodium metabisulfite showed in Figure 1.

The added variation of dose concentration of coagulant is one of the factors to decreasing percentage of Cr(VI) in coagulant process. The optimum dose is needed for coagulation reached until 300 mg.L\(^{-1}\). The advantages using PAC (Polyaluminium Chloride) in coagulation process were to avoid the saturation /precipitation process and color, avoid the disassociation of floc, need a little basic for hydrolysis (avoid using extreme pH). If the dose not enough, floc will not be formed. If excessive doses can also cause floc that is formed imperfectly due to changes in the pH of the solution [17]. The addition of coagulant dose variation gives a lower percentage of Cr(VI) than reduction method.

The percentage of reduction obtained in the reduction, coagulation, and combination methods was 96.36%; 20.57%; and 98.57%, with optimum doses of reducing agents and coagulants of 330 mg.L\(^{-1}\) and 300 mg.L\(^{-1}\).

The Horwitz ratio (HorRat) is performance parameter to identified the acceptability of methods of analysis among-laboratory reproducibility parameter. It is the ratio of the observed relative standard deviation among laboratories calculated from the actual performance data, RSDR (%) [18]. The results obtained coefficient variation Hortwitz optimum at 15.85 and standard deviation at 0.43%. The optimization concentration dose for the combination method adding (reductor and coagulant) to reduce chromium (VI) shown in Table 1.

The combination of coagulation and reduction processes can increase the decreasing percentage of Cr(VI) concentration at electroplating waste. The highest reduction in Cr(VI) concentration was obtained in the combination methods see in Figure 2.
Table 1. Optimization concentration dose for combination method adding (reductor and coagulant) to reduce chromium (VI)

| Validation parameters (n=3) | Cr (VI) concentration dose added in ppm (coagulant:reductor) |
|----------------------------|-------------------------------------------------------------|
| No add coagulant or reductor | (330 : -) | (330 : 100) | (330 : 200) | (330:300) |
| Cr(VI) (ppm)                 | 74.8       | 2.7         | 1.7         | 1.2         | 1.1         |
| SD (%)                      | 0.058      | 0.0058      | 0.0058      | 0.0104      | 0.0046      |
| %RSD (%)                    | 0.08       | 0.21        | 0.33        | 0.83        | 0.43        |
| CV Hortwitz                 | 8.36       | 13.77       | 14.72       | 15.48       | 15.84       |

Figure 2. The decreasing relationship percentage of Chromium (VI) between reduction, coagulation and their combination methods.

The best method for reducing chromium (VI) levels is the combined method at a percentage reduction of 98.57% with an SD value of 0.0046 and % RSD of 0.43%. Application of optimum concentration dose for electroplating waste sample from Cheetose industry, Cimahi, which contain of Cr(VI) can reached 1.8mg/L ± 0.85 decreasing percentage 97.60%. It means the combination method effectively reduce Cr(VI) in electroplating waste sample contain Cr(VI). This decreasing percentage with optimum dose concentration was higher than previously studies using reduction, coagulation or coagulation method in Table 2.

Further validation parameter needs to evaluate to improve analytical performance for the combination method. Also, the analysis method need to improved for quantification using preconcentration to trace of Cr speciation simultaneously using mini-column in FIA-AAS [15].

Table 2. Several decreasing percentages of Cr(VI) with reduction (r) or coagulation (c) method

| Decreasing percentage of Cr(VI) (%) | References |
|------------------------------------|------------|
| 98.57 (r+c)                        | This research |
| 55.5 (c)                           | [19]       |
| 95 (r)                             | [19]       |
| 71.7 (r)                           | [7]        |
| 57.47 (c)                          | [20]       |
4. Conclusion
The percentage reduction of Cr(VI) ion to Cr(III) ion was obtained for reduction, coagulation and combined of them respectively, 96.36%; 20.57% and 98.57% with optimum doses of reducing agents and coagulants, 300 mg.L\(^{-1}\) and 300 mg.L\(^{-1}\). The combination method with coagulation and reduction was the best way to reduce Cr(VI) ion to Cr(III). The best method to reduce the level of Cr(VI) is the combined method at a percentage reduction of 98.57% with a standard deviation of 0.0046 and %RSD of 0.43%. For sample electroplating obtained a decreasing percentage with the combination method 1.8 mg/L\(^{-1}\) ± 0.85 with a decreasing percentage of 97.60%.

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