Removal of Hg, Fe and Cr from Chemical Oxygen Demand (COD) analysis waste by hydroxide precipitation method

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Abstract. Wastewater from Chemical Oxygen Demand (COD) analysis is one of laboratory liquid wastes that is dangerous and potentially polluting the environment due to it contains dissolved heavy toxic metals such as silver (Ag), mercury (Hg), iron (Fe) and chromium (Cr). One of the treatment methods for removing heavy metals on a laboratory scale is precipitation method. The purpose of this research was to determine the most optimum condition for Hg, Fe and Cr removal. Hydroxide precipitation method was used with NaOH as the precipitant. The varied parameter was pH (3,7,9 and 11). Based on the results, the most optimum efficiency of metal Hg, Fe and Cr removal was observed at pH 11, reaching 99% removal efficiency for all metals.

1. Introduction
Chemical analysis laboratories generate liquid waste with a high content of hazardous materials that should be treated before being discharged into the environment [1]. Liquid waste produced by a laboratory generally has a relatively small volume but continuously produced. One type of chemical analysis that generates hazardous liquid waste is the Chemical Oxygen Demand (COD) analysis. The COD analysis uses silver sulfate (Ag₂SO₄) as a catalyst, mercury sulfate (Hg₂SO₄) to eliminate chloride interference, ferric ammonium sulfate [(NH₄)₂Fe(SO₄).6H₂O] for titration, potassium dichromate (K₂Cr₂O₇) as an oxidizing agent; the reaction occurs at acidic pH with the addition of concentrated sulfuric acid (H₂SO₄) [2]. Therefore, wastewater from COD analysis is dangerous and potentially polluting the environment because it contains dissolved heavy toxic metals namely silver (Ag), mercury (Hg), iron (Fe) and chromium (Cr) [3]. Until now, COD analysis wastewater has not received adequate attention for the wastewater treatment.

There are many treatments or methods that can be used to remove heavy metals such as precipitation method (chloride, hydroxide, sulfide), electrodeposition, electrocoagulation, electrolysis etc. However, the one method that has been proven to effectively remove heavy metals is the precipitation method. Precipitation method (sedimentation) is one of the processing methods that is normally used to remove heavy metals from liquid waste due it has a simple working principle among other methods for laboratory scale. This method works by adding certain chemicals to convert easily dissolved compounds into insoluble solids [4]. Chemicals commonly used for precipitation processes are hydroxide, carbonate, sulfide and chloride compounds [5]. Heavy or toxic metals can be deposited by adding lime or sodium hydroxide to a pH value where minimum solubility occurs [6].
The treatment of COD analysis wastewater aims to remove the dissolved metals Ag, Hg, Fe, and Cr. Silver (Ag) can be removed from the wastewater by chloride precipitation, and recovered as silver chloride (AgCl) that has a high economic value [7]. Hydroxide precipitation method can be used for Hg, Fe, and Cr removal. The purpose of this research was to determine the most optimum condition to remove Hg, Fe, and Cr from COD analysis wastewater using hydroxide precipitation method. Sodium hydroxide (NaOH) was used as a precipitating agent because, during the process of precipitation, the metals were usually deposited in the form of hydroxide [8]. The observed parameters focused on changes in the concentrations of Hg, Fe, and Cr and type of chemical compounds produced as deposits. The concentration of all metals was tested with Atomic Absorption Spectroscopy (AAS) and deposits analysis was tested by X-Ray Diffraction (X-RD).

2. Methods

2.1. Hydroxide precipitation method

Before hydroxide precipitation, COD analysis wastewater (henceforth referred to as COD wastewater) was treated with chloride precipitation. The purpose of the chloride precipitation process was to remove Ag from the wastewater by recovering Ag as AgCl. The initial concentration of Ag in COD wastewater was 1289 ppm. At the optimum condition of chloride precipitation, the final Ag concentration was 0.04 ppm, corresponded with a removal efficiency of 99.998% [9].

COD wastewater that had been treated with chloride precipitation under optimum conditions was further processed with hydroxide precipitation, which aimed to remove the other metals (Hg, Fe, and Cr). In this research, sodium hydroxide (NaOH) was used as a precipitant and the process was carried out under pH 3, 7, 9, or 11.

A schematic of the hydroxide precipitation process is shown in Figure 1. We transferred 250 ml of COD wastewater from optimum chloride precipitation into a beaker glass with a volume of 500 ml. Then, we added NaOH (flakes from Pudak) at a certain weight while stirring using a magnetic stirrer at 60 rpm. During the addition of NaOH, pH measurement was also carried out by using a pH meter (AMT20) to achieve the desired pH condition. After reaching the desired pH condition, the last step was separating the two fractions by using filter paper. There were two fractions produced from the hydroxide precipitation process, namely solid fraction and liquid fraction. The liquid fraction was measured with Atomic Absorption Spectroscopy (AAS) and the solid fraction was collected for analysis with the X-Ray Diffraction (XRD).

2.2. Analysis

Parameters being analyzed from hydroxide precipitation process were Hg, Fe, and Cr concentrations, pH, color (visual), solid fraction mass and type of chemical compounds contained. The pH of the mixture was measured during the experiment using a lab bench pH meter AMT20. Concentrations of Hg, Fe, and Cr in the wastewater and the liquid fraction were measured with AAS according to Indonesian
National Standard for each metal [10-12]. Solid fraction mass was measured using the gravimetric method [13]. Solid fraction mass analysis aimed to ensure that all metals had been converted from soluble substances into insoluble substances. The type of chemical compounds in the solid was determined using X-RD by comparing with the ICDD database.

3. Result and discussion

3.1. Initial characterization of COD wastewater

The initial characterization of COD wastewater included parameters of pH, color, and concentrations of Hg, Fe, Cr as shown in Table 1.

Table 1. Initial characterization of COD analysis wastewater.

| Parameters      | Unit | Test result | Quality Standarda | Description |
|-----------------|------|-------------|-------------------|-------------|
| pH              |      | 0.75        | 6.9               | X           |
| Color           |      | Clear blue  | -                 | -           |
| Hg concentration| ppm  | 745         | 0.002             | X           |
| Fe concentration| ppm  | 490         | 5                 | X           |
| Cr concentration| ppm  | 162         | 0.5               | X           |

a Quality standard refers to Minister of Environment Decree 51 of 1995

X = exceeding (fail to meet) quality standard

According to the initial characterization of COD wastewater, the concentrations of Hg, Fe, and Cr were highly exceeding the wastewater quality standard [14], so the wastewater had to be processed before being discharged into the environment. COD wastewater also had a very low pH (0.75) due to the COD analysis is done in acidic condition by adding sulfuric acid (H₂SO₄).

3.2. Color

Figure 2 shows COD wastewater color before treatment, after treated with chloride precipitation, and after treated with hydroxide precipitation at pH 3, 7, 9, and 11. After the process, the color changes occurred for all pH variations. The changes were due to each metal had different optimum pHs for the precipitation process, which was the pH where the metal had minimum solubility. The smaller the solubility of a metal, the easier it was to settle. The different colors produced at different pHs depended on the metal that was removed at that pH.

![Figure 2. The color of untreated COD wastewater, an optimum condition from chloride precipitation, and after hydroxide precipitation at different pHs.](image-url)
Figure 2 shows that at pH 3, the resulting color was green, which indicated the presence of dissolved chromium (Cr). The color formed at pH 7 was brown, which came from Fe(OH)₃ deposits. At pH 9, the color almost became clear white, which indicated that almost all metals were removed. While at pH 11, the color of the solution becomes a clear white color, which indicated that all metals had been removed or changed into insoluble substances. This is supported by the measurements of metal concentrations with AAS, which also show that Hg, Fe and Cr concentrations significantly decreased at pH 11.

3.3. Removal of Hg
Figure 3 shows the Hg concentration and removal efficiency at different pHs. At pH 3, the concentration of Hg decreased from 745 to 610 ppm. At pH 7, the concentration of Hg decreased to 13 ppm. While at pH 11, the concentration of Hg decreased until 8 ppm. Optimum condition with the highest removal efficiency of Hg was pH 11, with 99.732% removal efficiency and the final concentration of 8 ppm. This research shows that the hydroxide precipitation method could remove Hg from COD wastewater, but the final concentration still exceeded the wastewater quality standard.

![Figure 3. Hg concentration and removal efficiency at different pHs.](image)

3.4. Removal of Fe
Figure 4 shows Fe concentration and removal efficiency at different pHs. Hydroxide precipitation method also could remove Fe. At pH 3, the concentration of Fe began to decrease to 453 ppm. Similar to Hg, the concentration of Fe also decreased significantly until reaching 0.36 ppm at pH 11. Optimum
condition with the highest removal efficiency of Fe was pH 11, with 99.927% removal efficiency. The final concentration of Fe in the optimum condition was 0.36 ppm, which already met the wastewater quality standard.

3.5. Removal of Cr
Figure 5 shows Cr concentration and removal efficiency at different pHs. Cr also could be removed by hydroxide precipitation method. The initial concentration of metal Cr was 162 ppm. At pH 3, the concentration of Cr had not decreased significantly, with concentration was 155 ppm. Similar to Hg and Fe, the concentration of Cr also decreased significantly until 0.41 ppm at pH 11. Optimum condition with the highest removal efficiency of Cr was pH 11, with 99.772% removal efficiency. The final concentration of Cr in optimum condition was 0.41 ppm and this concentration did not exceed the wastewater quality standard.

![Figure 5. Cr concentration and removal efficiency at different pHs.](image)

3.6. Solid fraction (deposit)
Deposit or solid fraction was formed during the hydroxide precipitation process, which contained all metals that had been transformed into insoluble compounds. Figure 6 shows that the highest deposit mass was formed at pH 11, reaching 57.563 gram. The pH 11 was the optimum condition, at which all tested metals (Hg, Fe, and Cr) had the highest percentage of removal efficiency. This is due to the metals became less soluble at higher pH value.

![Figure 6. Solid fraction mass at different pHs.](image)
3.7. X-Ray Diffraction (X-RD)

Figure 7 shows the deposits produced from all pH variations, in the form of powder for X-RD analysis. The deposits formed at pH 3, pH 7, and pH 9 had a reddish-brown color due to the presence of Fe, which was precipitated from the wastewater and changed into iron (III) oxide Fe(OH)$_3$. The deposit formed at pH 11 had a green color and the highest mass compared with pH 3, 7, and 9. The deposit’s color at pH 11 was the result of a combination of Hg, Fe, and Cr, which were precipitated almost completely from the wastewater, so that the deposit was complex.

![Figure 7. Deposits/solid fraction produced at different pHs.](image)

In this study, X-RD analysis aimed to determine the content of the deposits. A diffractogram of X-RD analysis of the deposits is presented in Figure 8. The horizontal and vertical axis show 2theta (the reflected angle) and intensity, respectively. Figure 8 shows that many chemical components were contained in deposits, including Na$_2$SO$_4$, Fe(OH)$_3$, AgCl, Hg, Ag, and HgO, which were formed through the following reactions:

\[ \text{Cr}^{3+} + 3\text{NaCl} \rightarrow \text{CrCl}_3 + 3\text{Na}^+ \]  \hspace{1cm} (1)
\[ \text{Fe}^{3+} + 3\text{NaCl} \rightarrow \text{FeCl}_3 + 3\text{Na}^+ \]  \hspace{1cm} (2)
\[ \text{CrCl}_3 + 3\text{NaOH} \rightarrow \text{Cr(OH)}_3 + 3\text{NaCl} \]  \hspace{1cm} (3)
\[ FeCl_3 + 3NaOH \rightarrow Fe(OH)_3 + 3NaCl \]  
\[ 4AgCl + NaOH \rightarrow 4Ag + 2H_2O + 4NaCl + O_2 \]  
\[ Hg_2Cl_2 + 2NaOH \rightarrow Hg + HgO + 2NaCl + H_2O \]  
\[ 2Na^+ + SO_4^{2-} \rightarrow Na_2SO_4 \]

3.8. Final characterization of COD wastewater

Table 2 shows the final characteristics of COD wastewater after being processed by hydroxide precipitation method at pH 11, which was selected as the optimum condition.

| Parameters       | Unit | Test Result | Quality Standard | Description |
|------------------|------|-------------|------------------|-------------|
| pH               | -    | 11          | 6-9              | X           |
| Color            | ppm  | Clear White | -                | -           |
| Hg concentration | ppm  | 8           | 0.002            | X           |
| Fe concentration | ppm  | 0.36        | 5                | ✓           |
| Cr concentration | ppm  | 0.41        | 0.5              | ✓           |

* Quality standard refers to Minister of Environment Decree 51 of 1995  
  X = exceeding (fail to meet) quality standard  
  ✓ = lower than quality standard

Table 2 shows that the final concentration of Fe and Cr did not exceed the wastewater quality standard. On the other hand, the pH and final concentration of Hg still exceeded the wastewater quality standard, so the treated COD wastewater still could not be discharged into the environment and needed some further processing.

4. Conclusions and recommendations

Hydroxide precipitation method was able to remove metal Hg, Fe, and Cr with optimum condition chosen at pH 11. At the optimum pH, the highest removal efficiency for Hg was 99.732\%, for Fe was 99.927\%, and for Cr was 99.772\%. The final concentration of Fe and Cr did not exceed the wastewater quality standard, while the pH and final concentration of Hg still exceeded the wastewater quality standard. For the next research, it is recommended to add pH variation (pH > 11) to further remove Hg.

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