

Elimination Cyanide with Hydrogen Peroxide (H_2O_2) and Calcium Hypochlorite ($\text{Ca}(\text{OCl})_2$) on Gold Mine Waste from North Luwu, South Sulawesi

Muntasir*, M. Sjahrul, Muhammad Zakir, Indah Raya

Department of Chemistry, Graduate School of Science, Hasanuddin University, Makassar, South Sulawesi, Indonesia

Email address:

munbasrypps@yahoo.com (Muntasir)

*Corresponding author

To cite this article:

Muntasir, M. Sjahrul, Muhammad Zakir, Indah Raya. Elimination Cyanide with Hydrogen Peroxide (H_2O_2) and Calcium Hypochlorite ($\text{Ca}(\text{OCl})_2$) on Gold Mine Waste from North Luwu, South Sulawesi. *American Journal of Environmental Protection*. Vol. 5, No. 4, 2016, pp. 97-102. doi: 10.11648/j.ajep.20160504.14

Received: June 15, 2016; Accepted: June 27, 2016; Published: July 13, 2016

Abstract: In this study, the elimination of cyanide by the addition of hydrogen peroxide and calcium hypochlorite was investigated. This study was conducted to determine the optimum conditions of H_2O_2 and $\text{Ca}(\text{OCl})_2$: concentration, pH and contact time, and the combined ratio of concentration H_2O_2 with $\text{Ca}(\text{OCl})_2$ to remove cyanide in gold mining wastewater. Cyanide obtained by steam distillation of wastewater by steam distillation and Barnstead electromantel and assay using 0.02N silver nitrate. The results showed that the cyanide level was 50.22% w/v. The optimum conditions were obtained when the concentration of H_2O_2 at 500 ppm, pH 8 within 60 minutes contact time and $\text{Ca}(\text{OCl})_2$ concentration was at 500 ppm, pH 8 within 60 minutes contact time. The best cyanide removal was obtained at the concentration ratio of 5:5 amounting to 45.76% w/v.

Keywords: Cyanide, Hydrogen Peroxide, Calcium Hypochlorite, Steam Distillation, Silver Nitrate

1. Introduction

The quality of wastewater has become a serious problem for the environment and human health [1], one of the waste is cyanide, is a toxic substance that is found in industrial waste generated by various processes [2], discarded by various industries, especially plants synthetic chemical, metallurgical processes, plating and surface finishing [3], a compound that is most toxic to humans and nature [4]. About 90% of the gold operations produce significant worldwide currently utilize cyanide for the extraction of gold and silver [5].

Many industrial applications such as plastics, electroplating, organic chemicals production, photographic development, and drugs are important sources of cyanide wastes. In gold and silver mines, cyanide is used to recover the precious metal through the washing process [6]. Cyanide is the most preferred solvent in the extraction of gold and silver ore over a century because of strong complexing ability, availability of existing, relatively low cost and famous chemical [7]. Cyanide is widely used in electroplating, pesticide manufacturing industry. Cyanide is

highly toxic. The lethal dose of potassium or sodium cyanide is 200-300 mg whereas prussic acid (HCN) is 50 mg [8]. Cyanide is a highly toxic ion [9], is easily absorbed by the organism by inhalation, oral and dermal exposure to live, lethal levels of cyanide in the blood assumed to be 11.5 mM [10]. All cyanide are classified as hazardous to the characteristics of acute and chronic toxicity [11].

Industrial waste generally contains between 0.01 and 10 mg/L total cyanide, even no waste containing 1% to 3% (from 10.000 to 30.000 mg/L) cyanide. Some electroplating industrial waste has been found to contain cyanide levels even higher than 100,000 mg/L. the concentration of cyanide waste is found to be very high compared to the requirements of cyanide level of about 0.001 to 0.05 mg/L [12]. Cyanide into the environment very existence contain ingredients harmful to health [13]. Cyanide inhibits cytochrome oxidase of the mitochondrial respiratory chain for short-term exposure can cause rapid breathing, tremors, and other neurological effects and long-term exposure can cause weight loss, thyroid effects and neurological damage and death [14].

Elimination of cyanide from the solution needed when human health and the protection of ecosystems considered [15]. Many countries have imposed strict regulations to prevent contamination of surface and ground water caused by cyanide [16]. Many conventional processing methods, such as alkaline chlorination, hydrogen peroxide, ozonation, air condition, ion exchange, the basic technology of sulfur and biological processes, have been used in the treatment process of wastewater containing cyanide [16]. In some cases, cyanide contamination process solutions must be treated with strict standards and are released into the environment [17].

Processing of tailings cyanide concentration of approximately 60-400 ppm can be lowered by raising pH to 8-11 so that the cyanide down to less than 0.5 ppm within a few months [18]. Study the synergistic combination of hydrogen peroxide and hypochlorite ions in the water on the formation of the transition of high-oxidizing species singlet oxygen ($^1\text{O}_2$), which is effective in the oxidation of free cyanide (CN^-) in water [19]. elimination of cyanide (CN^-) of wastewater laboratory using sodium hypochlorite (NaOCl) and calcium hypochlorite $\text{Ca}(\text{OCl})_2$ carried out for 30 minutes. The optimum dose and cost of chemicals NaOCl and $\text{Ca}(\text{OCl})_2$ varies depending on the initial concentration of cyanide [20]. a tannery wastewater is oxidized independently with three oxidants aqueous hydrogen peroxide, sodium hypochlorite and calcium hypochlorite at different temperatures and reaction time. Calcium hypochlorite oxidant and potentially the most efficient among the three oxidants [21].

This work is dedicated to the elimination of cyanide to study the use of a combination of oxidizing hydrogen peroxide (H_2O_2) and calcium hypochlorite $\text{Ca}(\text{OCl})_2$ to the reduction of cyanide levels in the wastewater. Parameters measured were the optimum concentration of H_2O_2 and $\text{Ca}(\text{OCl})_2$, and the combined ratio H_2O_2 concentration with $\text{Ca}(\text{OCl})_2$ at the wastewater in reducing the cyanide content.

2. Methodology

2.1. Preparation of Sample and Assay of Cyanide

Samples obtained from the cyanide waste effluent gold mine north Luwu regency of South Sulawesi. A total of 1000 mL of liquid waste cyanide inserted into the distillate flask, then do the steam distillation for 5 hours at temperatures above 100°C and to obtain a distillate of 100 mL. Determination of cyanide content with the standard silver nitrate titration [22]. Furthermore distillate obtained accommodated approximately 100 mL Erlenmeyer and added 7 ml of 2.5% NaOH . Furthermore shaken with the aid of magnetic stirrer and then into the distillate was added 8 ml of 10% NH_4OH and 5 mL of 5% KI . Then the solution is titrated using 0.02 N AgNO_3 to form a white precipitate [23].

2.2. Determination of Cyanide by the Addition of H_2O_2 Optimum Conditions

A total of five Erlenmeyer flask containing 100 mL of

distillate cyanide waste with an optimum concentration of H_2O_2 was added. pH of the solution set with the addition of NaOH 1 N solution to obtain a pH of 8. Each mixture was stirred at the optimum time with a magnetic stirrer until a homogeneous solution. The solution was then determined the cyanide content of each treatment. Cyanide content indicates the optimum condition. The execution is done triple [24].

2.3. Determination of Cyanide by the Addition of Optimum Conditions $\text{Ca}(\text{OCl})_2$

A total of five 100 mL Erlenmeyer flask containing cyanide waste distillate calcium hypochlorite is added to the optimum concentration of 500 ppm. Furthermore, the pH is set by addition of NaOH 1 N solution to obtain a pH of 8. Each mixture was stirred at the optimum time with a magnetic stirrer until a homogeneous solution. The solution was then determined the cyanide content of each treatment. Cyanide content indicates the optimum condition. The execution is done the triple.

2.4. Determination of Cyanide Level with $\text{H}_2\text{O}_2 + \text{Ca}(\text{OCl})_2$ Variation (1:1, 1:2, 1:3, 1:4 and 1:5)

A total of five Erlenmeyer containing 100 mL of distillate liquid waste cyanide was added $\text{H}_2\text{O}_2 + \text{Ca}(\text{OCl})_2$ with the optimum concentration ratio (1:1, 1:2, 1:3, 1:4 and 1:5), at pH 8 and the optimum contact time. The mixture is stirred using a magnetic stirrer at 120 rpm for 60 minutes and then allowed to stand until the solution is completely mixed. The solution was then determined the cyanide content of each treatment, the cyanide content indicates the optimum condition. The execution is done the triple.

2.5. Determination of Cyanide Level with $\text{H}_2\text{O}_2 + \text{Ca}(\text{OCl})_2$ Variation (1:1, 2:1, 3:1, 4:1 and 5:1)

A total of five Erlenmeyer containing 100 mL of distillate waste cyanide was added $\text{H}_2\text{O}_2 + \text{Ca}(\text{OCl})_2$ (1:1, 2:1, 3:1, 4:1 and 5:1) at pH 8 and the optimum contact time. The mixture is stirred using a magnetic stirrer with a speed of 120 rpm for 60 minutes and then allowed to stand until the solution is completely mixed. The solution was then determined the cyanide content of each treatment, the cyanide content indicates the optimum condition. The execution is done the triple.

2.6. Determination of Cyanide Level with $\text{H}_2\text{O}_2 + \text{Ca}(\text{OCl})_2$ Variation (1:1, 2:2, 3:3, 4:4 and 5:5)

A total of five Erlenmeyer containing 100 mL of distillate liquid waste cyanide was added $\text{H}_2\text{O}_2 + \text{Ca}(\text{OCl})_2$ with the optimum concentration ratio (1:1, 2:2, 3:3, 4:4 and 5:5) at pH 8 and the optimum contact time. the mixture is stirred using a magnetic stirrer at 120 rpm for 60 minutes and then allowed to stand until the solution is completely mixed. The solution was then determined the cyanide content of each treatment, the cyanide content indicates the optimum condition. The execution is done the triple.

3. Results and Discussions

Cyanide waste obtained from the areas of the districts Rampi Tedeboe Masamba North Luwu regency of South Sulawesi province. A total of 1000 mL of liquid waste cyanide inserted into the distillate flask, then do the steam distillation for 5 hours at temperatures above 100°C and to obtain a distillate of 100 mL. Determination of cyanide content with the standard silver nitrate titration [22]. Distillate obtained accommodated approximately 100 mL Erlenmeyer and added 7 ml of 2.5% NaOH. Furthermore shaken with the aid of magnetic stirrer and then into the distillate added NH₄OH 10% as much as 8 mL and 5 mL of 5% KI. Then samples were titrated using 0.02 N AgNO₃ to form a white precipitate [23].

3.1. Optimum Condition of Hydrogen Peroxide (H₂O₂)

Hydrogen peroxide reacts with cyanide to produce cyanate with equation [25]

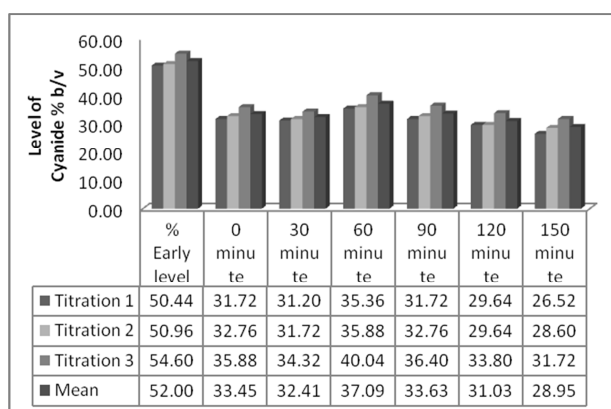
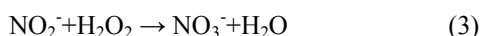
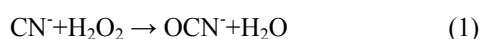


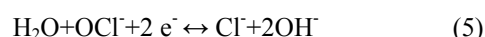
Figure 1. Diagram of CN levels with the addition of hydrogen peroxide (H₂O₂) to 500 ppm, pH 8 and contact time (minutes).

Elimination of cyanide can be done with the addition of hydrogen peroxide. In Figure 1 shows the percentage of CN levels with the addition of hydrogen peroxide (H₂O₂) at a concentration of 500 ppm, pH 8 with a contact time of 60 minutes a reduction in the levels of cyanide, cyanide content of the initial 52.00% w/v was reduced to 37.09% w/v. Each 100 mL of liquid waste cyanide was added H₂O₂ with optimum conditions a concentration of 500 ppm, pH 8 and a contact time of 60 minutes gives the percentage decrease in the levels of cyanide. Cyanide content is reduced because it has reacted with hydrogen peroxide to produce cyanate and when added in excess amount will form nitrite and nitrate carbonate and finally. The more the addition of H₂O₂, the greater the cyanide react to form cyanate so the content of free cyanide contained in the liquid waste is reduced. The optimum condition is achieved by the equilibrium between the amount of H₂O₂ is added to the cyanide contained in the

waste. This study is in line with research the use of hydrogen peroxide at reduced levels of free cyanide (CN⁻) [26], which describes cyanide processing methods with the use of hydrogen peroxide and the addition of hydrogen peroxide [27, 28]. The optimum condition is achieved because the reaction takes place at pH 8 was the maximum. proper pH allows for H₂O₂ to react perfectly with cyanide contained in wastewater. This is in line with research [18] reported a cyanide concentration of approximately 60-400 ppm can be lowered by raising pH to 8-11 so that the cyanide levels dropped to less than 0.5 ppm within a few months.

3.2. Optimum Conditions Calcium Hypochlorite

Oxidation and reduction reactions involving cyanide and hypochlorite followed the reaction equation [29]



Chlorination with alkali is another technique for the treatment of cyanide. The first reaction produces cyanogen chloride (CNCl), toxic gas is great, the atmosphere is alkaline, CNCl hydrolyzed to cyanate ion (CNO⁻) which has low toxicity, can CNO⁻ with chlorine dioxide at a pH near neutral to CO₂ and NO₂ [30].

Figure 2. shows the percentage of CN levels with the addition of calcium hypochlorite at a concentration of 500 ppm, pH 8 with a contact time of 60 minutes, initial cyanide content 52.00% w/v was reduced to 41.60% w/v. Each 100 mL of liquid waste hydrogen is added calcium hypochlorite with optimum conditions, the concentration of 500 ppm, pH 8 and a contact time of 60 minutes gives the percentage decrease in the levels of cyanide.

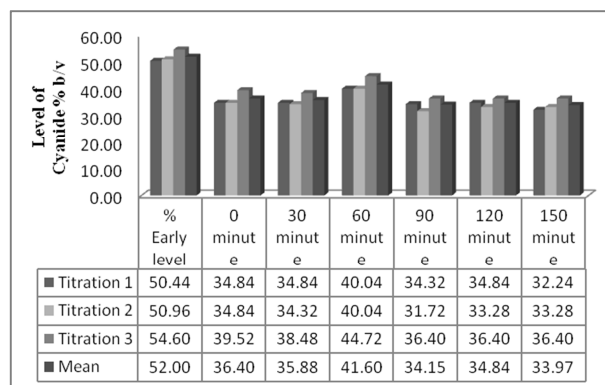
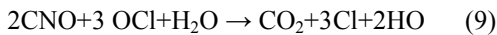
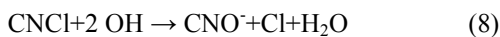
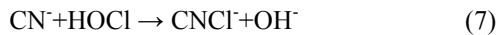


Figure 2. Diagram of CN levels with the addition of Calcium hypochlorite 500 ppm, pH 8 and contact time (minutes).

Cyanide content is reduced because it has been reacting with Ca(OCl)₂ by forming CNCl. The more the addition of Ca(OCl)₂, the greater the cyanide reacts to form CNCl so the content of free cyanide contained in the liquid waste is reduced. Cyanide is oxidized into cyano CNO and finally into CO₂ and N₂. Treatment with active chlorine is done by

raising the pH of the solution with the addition of NaOH, then given Ca(OCl)₂. The reaction occurs as follows:



Reactions (7) runs fast, whereas the reaction (8) slow pH of about 9.0 unless there is an excess of chlorine. If the pH is adjusted to about 8-10 while the oxidation of cyanide to be CNO finished about 5 minutes. When in solution their cations Na⁺, the reaction will be slow about 30 minutes to 2 hours [31].

The optimum condition is achieved by the equilibrium between the amount of calcium hypochlorite is added to the cyanide contained in the waste. This study is in line with research synergistic combination of hydrogen peroxide and hypochlorite ions in the water on the formation of the transition of high-oxidizing species singlet oxygen (¹O₂) are effective in the oxidation of free cyanide (CN⁻) in water [19].

3.3. Optimum Conditions H₂O₂+Ca(OCl)₂ Variation (1:1, 1:2, 1:3, 1:4 and 1:5)

Figure 3 shows the percentage of CN levels with the addition of a combination of H₂O₂+Ca(OCl)₂ at a concentration of 500 ppm, pH 8 with a contact time of 60 minutes a reduction in the levels of cyanide, cyanide content of the initial 52.00% w/v experienced a reduction of 43.16% w/v on the variation of the combination of 5:1. Each 100 mL of liquid waste hydrogen is added the combination of H₂O₂+Ca(OCl)₂ with optimum conditions, the concentration of 500 ppm, pH 8 and time contact 60 minutes gives the percentage decrease in the levels of cyanide.

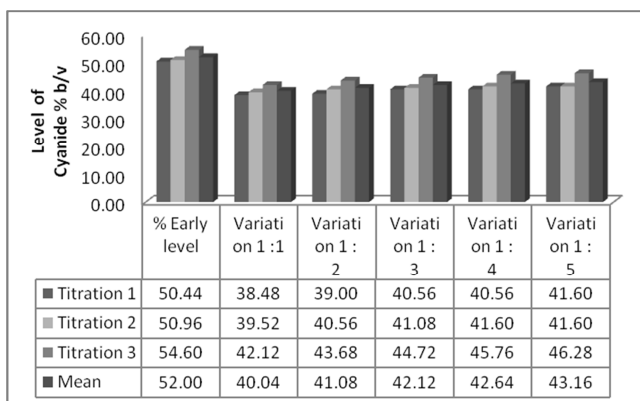


Figure 3. Diagram of CN levels with the addition of H₂O₂+Ca(OCl)₂ variation (1:1, 1:2, 1:3, 1:4 and 1:5).

3.4. Optimum Condition of H₂O₂+Ca(OCl)₂ variation (1:1, 2:1, 3:1, 4:1 and 5:1)

Figure 4 shows the percentage of CN levels with the addition of a combination of H₂O₂+Ca(OCl)₂ at a concentration of 500 ppm, pH 8 with a contact time of 60 minutes a reduction in the levels of cyanide, cyanide content

of the initial 52.00% w/v experienced a reduction of 43.16% w/v on the variation of the combination of 5:1. Each 100 mL of liquid waste hydrogen is added the combination of H₂O₂ and Ca(OCl)₂ with optimum conditions, the concentration of 500 ppm, pH 8 and contact time of 60 minutes gives the percentage decrease in the level of cyanide.

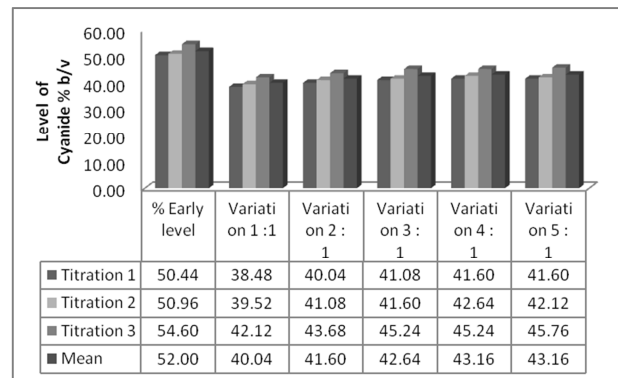


Figure 4. Diagram of CN levels with the addition of H₂O₂+Ca(OCl)₂ variation (1:1, 2:1, 3:1, 4:1 and 5:1).

3.5. Optimum Condition of H₂O₂+Ca(OCl)₂ Variation (1:1, 2:2, 3:3, 4:4 and 5:5)

Figure 5 shows the percentage of CN level with the addition of a combination of H₂O₂+Ca(OCl)₂ at a concentration of 500 ppm, pH 8 with a contact time of 60 minutes a reduction in the levels of cyanide.

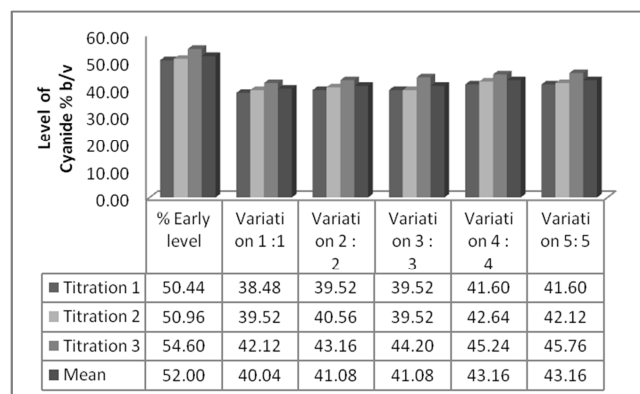


Figure 5. Diagram of CN levels with the addition of H₂O₂+Ca(OCl)₂ variation (1:1, 2:2, 3:3, 4:4 and 5:5).

Initial cyanide content 52.00% w/v experienced a reduction of 45.76% w/v on the variation of the combination of 5:5. Each 100 mL of liquid waste hydrogen is added the combination of H₂O₂+Ca(OCl)₂ with conditions The optimum concentration of 500 ppm, pH 8 and a contact time of 60 minutes gives the percentage decrease in the levels of cyanide. This is in line with research [32] on the measurement of pH and concentration for the removal of cyanide levels. Using calcium hypochlorite and sodium hypochlorite, in terms of lower cost by using chlorine compounds instead of chlorine gas. This research is a new one by doing variations of the addition of hydrogen peroxide and calcium hypochlorite that has never been done by

previous research. With cyanide effluent concentration of 52.00% w/v can be reduced by 45.76% w/v indicates the use of a combination of (H_2O_2) and $\text{Ca}(\text{OCl})_2$ with optimum conditions, the concentration of 500 ppm, pH 8 and contact time of 60 minutes gives the potential removal of cyanide greater.

4. Conclusion

The use of hydrogen peroxide (H_2O_2) and calcium hypochlorite ($\text{Ca}(\text{OCl})_2$) with optimum conditions, namely concentration, pH and contact time to the decreased levels of cyanide in waste water can be applied. The combination of $\text{H}_2\text{O}_2 + \text{Ca}(\text{OCl})_2$ in reducing the cyanide content was obtained by the addition of a concentration of 500 ppm, pH 8 and a contact time of 60 minutes gives a decrease in cyanide levels at most. The combination of H_2O_2 and $\text{Ca}(\text{OCl})_2$ at a concentration ratio variation variations of 5:5 provides decreased levels of cyanide most with a reduction of 45.76% w/v. The analysis showed variation of (H_2O_2) and $\text{Ca}(\text{OCl})_2$ can be considered for removal of cyanide levels effectively.

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