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ABSTRACT

STUDIES OF USE HYDROGEN PEROXIDE (H₂O₂) OXIDIZING TO REDUCTION CYANIDE LEVEL IN WASTEWATER

By :

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

Has done conducted research studies the use of oxidizing hydrogen peroxide (H₂O₂) to the reduction of cyanide levels in the wastewater. Parameters measured were the optimum concentration of hydrogen peroxide, pH optimum, optimum contact time between Hydrogen Peroxide with wastewater in reducing the cyanide content. Cyanide obtained from steam distillation of liquid waste and assay using 0.02N silver nitrate. Variations in the concentration used was 100 ppm, 200 ppm, 300 ppm, 400 ppm and 500 ppm; pH variation is (7, 8, 9, 10 and 11) and the variation of contact time are: 30, 60, 90, 120 and 150 minutes. The results showed early treatment of cyanide content of 50.22% w/w and experienced a reduction after the addition of H₂O₂ concentration of 100 ppm, 200 ppm, 300 ppm, 400 ppm and 500 ppm; variations in pH is 7, 8, 9, 10 and 11 and the variation of contact time are: 30, 60, 90, 120 and 150 minutes. The optimum treatment is the optimum concentration of H₂O₂ at 500 ppm with a reduction in levels of 36.40% w/w, pH Optimum pH 8 with reduced levels of 40.91% and an optimum contact time at 60 minutes with a reduction in levels of 37.09% w/w.

Keywords: Cyanide, Hydrogen peroxide, steam distillation. 0:02 N silver nitrate

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INTRODUCTION

Environmental pollution due to the use of cyanide (CN⁻) in the form of sodium cyanide, potassium cyanide and cyanide expanding in line with the increase in the quantity of use of cyanide in an industry that is not matched with the appropriate waste treatment process. Metal plating industries, synthetic fibers, mining and refining of metals generate waste containing cyanide that is harmful to humans (Dasha, R, R., et. All., 2009).

Demand for sodium cyanide and potassium cyanide worldwide is approximately 360,000 tonnes per year of which approximately 120,000 tonnes or one-third is used in the recovery of gold and silver, and about 90% or 450 of the operating gold production significantly around the world currently use cyanide for gold extraction and silver (Mudder, T, I., Botz, M.M 2004). Cyanide is considered among the most toxic compounds and is classified as a hazardous material with the characteristics of acute or chronic toxicity to humans and nature (Deveci, H., et.all. 2006). Used by various industries, especially chemical synthesis plant (nylon, fibers, resins, and herbicides), metallurgical processes (extraction of gold and silver) and plating and surface finishing (Mudder, 2004; Yeddou. AR 2010).

Cyanide (CN) is a constituent chemicals toxic (harmful) commonly contained in B3 waste, including toxic super category. Cyanide and cyanide salts provide rapid toxic effect, in doses of 60-90 mg can cause human death (Manahan, SE, 1989). Limitation of the maximum content of cyanide in the wastewater is allowed dispersed into the environment must be less than 0.05 ppm (PP No. 74 Tahun 2001 dan KLH. 2004). In the gold mining environment, including pollutants CN important because it is used as a key ingredient in the processing of gold so that wasted a lot of waste containing CN and can spread to the surrounding environment through the flow of water and the creatures living in it. (Hidayati, et al., 2009). The gold mining industry, including in Pongkor, compound sodium cyanide (NaCN) is used as a solvent to take the gold metal from rock ore mining results (Sutoto. 2006). Tailings PT Antam Pongkor CN was found to contain up to 0.77 mg kg⁻¹, river water contains 0.14 mg l⁻¹ and stream sediments containing 0.72 mg kg⁻¹ CN. PT Antam Cikotok tailings were found to contain 0.12 mg kg⁻¹ CN. The cyanide pollution does not rule out the possibility of spreading to residential environment and contaminate ground water used by the community. While the danger threshold CN content in drinking water is only 0.005 mg /L (Hidayati, N., et al., 2008).

Research on removal of cyanide from a gold mine tailings has been tested on a laboratory scale with a technique constructed wet land in aerobic and anaerobic by Loredo, 2002; Alvarez et al., 2004 in (Yani. 2012) and requires a long time. Cidu et al. (2011) reported on the processing of tailings with cyanide concentration of approximately 60-400 ppm can be lowered by raising the pH to 8-11, so that the cyanide down to less than 0.5 ppm within a few months. Making gold through leaching with cyanide has a percent gold recovery of over 90% (Smith and Mudder, 1991). Because of the high percent recovery by using cyanide gold miners causing many people began to turn to this method, there is even artisanal miners who use cyanide to process the waste material gold mining with mercury. It turns out this residual material processing give satisfactory results. (Pitoy, M. et al., 2008)

The use of cyanide (CN) in the gold extraction process can cause water pollution, poisoning and death to catch fish resources. Simbolon research results (2010) showed CN content in the liver was higher (6.0 to 18.0 ppm) compared with organ meat (4.2 to 8.5 ppm) (Simbolon. D., 2010). Research free removal of cyanide from an aqueous solution by oxidation with hydrogen peroxide (H_2O_2) is catalyzed by activated carbon-coated copper. Effect of initial molar ratio, copper-coated amount of activated carbon, pH and temperature on the removal of cyanide have been investigated. This process seems to be very interesting because cyanide removal rate is very fast, the reaction using a metal catalyst dissolves and consumes only hydrogen peroxide as chemical products (Yeddou, AR, et.all. 2011). The synergistic combination of hydrogen peroxide and hypochlorite ions in the water to the establishment of transitional high oxidizing species singlet oxygen (1O_2), which is effective in the oxidation of free cyanide (CN-) in water (Teixeira et. All. 2013). Research Sinbuathong states Deletion cyanide (CN-) of wastewater laboratory using sodium hypochlorite (NaOCl) and calcium hypochlorite ($Ca(OCl)_2$) was performed on reaction time of 30 minutes, the optimum dose and chemical costs NaOCl and $Ca(OCl)_2$ vary depending the initial cyanide concentration (Sinbuathong, N. 2000).

Awan. M.A (2004) Research tannery wastes containing high COD (3413 mg / L) is oxidized independently with three oxidant aqueous hydrogen peroxide, sodium hypochlorite and calcium hypochlorite at different temperatures and duration of the reaction. Calcium hypochlorite oxidant potential and reduce COD to 76% and calcium hypochlorite is the most efficient among the three oxidants. Tangkuman (2008), studied the effect of the concentration of cyanide in gold production. The results showed that the concentration of cyanide effects in the production of gold. Cyanide with 100 ppm cyanide significantly different compared with the 200, 400 and 600 ppm in the recovery of gold. Based on statistical analysis, cyanide with a concentration of 400 ppm is the best in the production of gold.

Based Riyanti Research (2010) tapioca starch wastewater treatment using chlorination process with $Ca(OCl)_2$ shows that prior to the chlorination process, the cyanide content was 51.77 mg / L, while after the chlorination process at the optimum condition (weight $Ca(OCl)_2$ 5 mg, pH 8, and the contact time of 1 hour), obtained the cyanide content of 30.08 mg / L with 41.88% decrease effectiveness. Referring to the results of previous studies, in this study will look for a method or an effective way to reduce the levels of cyanide in the waste, so the waste cyanide from mining and processing of gold using cyanide can be minimized and reduce environmental pollution. Required a waste management not only reduces pollutants but also converts pollutants into non-toxic. Materials used to treat waste is expected to easily obtainable and inexpensive material that reaches industries for waste handling costs.

METHODOLOGY

This research is a laboratory experiment, include: distillation cyanide, treatment parameters by testing the optimum treatment concentration, pH and contact time by the addition of oxidizing Hydrogen Peroxide (H_2O_2). Descriptive analyzes were performed in the tabulation of results and graphs the results of each treatment.

A. Equipment and materials Research

Equipment and materials research include: oven (Mettler), analytical balance (Ohaus), a tool of the glass (pyrex), Magnetic Stirrer models 04802-02, pH meter, glass tools, Steam distillation set (pyrex), Elektromantel (Barnstead Electrothermal), burette (Taytec UK), freezer (Panasonic), pH paper (Merck), clamps and the stand, spray bottle, pint flask of 500 mL, 1000 mL of distilled water pumps. NaCN (Merck), NaCl (Merck), NH₃ (Merck), NaOH (Merck), KCN (Merck), K₂CrO₄ (Merck), AgNO₃ (Merck), KI (Merck), H₂O₂ (Merck), Ca (OCL) 2 (Merck), Aquadest, NaOH 2.5%, NaOH 1 N, NH₄OH 10%, KI 5% and AgNO₃ 0:02 N

B. Preparation of standard solution of cyanide;

Cyanide standard solution prepared by dissolving 2.5 g KCN with distilled water in a 1 L flask, then right up to the mark diluted measuring, then shaken. The solution is stored in a brown bottle closed. and assayed once a week;

C. Method Acquisition distillate Cyanide

Samples were prepared by dissolving cyanide KCN as much as 25 mg in 500 mL of distilled water in a flask, then the sample cyanide pH was measured before and after treatment. Furthermore, 500 mL sample of cyanide inserted into the distillate flask, then the steam distillation run for 5 hours at temperatures above 100°C and steam distillation process is carried out to obtain a volume of 100 mL. The distillate is collected in erlenmeyer.

D. Preliminary Determination of Cyanide Content

Results obtained distillate volume of approximately 100 mL accommodated in erlenmeyer and added 7 ml of 2.5% NaOH. Furthermore shaken with the aid of magnetic stirrer and into the distillate is added NH₄OH 10% as much as 8 mL and 5 mL of 5% KI. The solution was titrated using 0.02 N AgNO₃ to form a white precipitate.

E. Determination of Optimum Conditions with Hydrogen Peroxide (H₂O₂)

1) Determination of Optimum Weight H₂O₂

A total of five erlenmeyer containing 100 ml of liquid waste containing cyanide is added to a certain concentration of H₂O₂ (100, 200, 300, 400, and 500 ppm). The mixture was stirred at 120 rpm for 60 minutes with a magnetic stirrer until a homogeneous solution. Solution determined cyanide content of each treatment. Cyanide content indicates the optimum condition.

2) Determination of Optimum pH.

A total of five erlenmeyer containing 100 ml of liquid waste containing cyanide was added H₂O₂ with a particular concentration (optimum concentration) and then the pH was adjusted by the addition of NaOH using the method Jar Test in order to obtain a solution with a specific pH (7, 8, 9, 10, and 11), The mixture was stirred at 120 rpm for 60 minutes with a magnetic stirrer with a magnetic stirrer until a

homogeneous solution. The solution is then determined cyanide content of each treatment. Cyanide content indicates the optimum condition.

3) Determination of Optimum contact time.

A total of five erlenmeyer containing 100 mL of waste containing cyanide is added to a certain concentration of H₂O₂ (optimum concentration). the pH of the solution was adjusted by adding NaOH using Jar Test in order to obtain a certain pH (pH optimum). Each mixture is stirred for a certain time (0 minutes; 30 minutes; 60 minutes; 90 minutes; 120 minutes and 150 minutes) with a magnetic stirrer until a homogeneous solution. The solution is then determined cyanide content of each treatment. Cyanide content indicates the optimum condition.

RESULTS AND DISCUSSION

Optimum concentration of Hydrogen Peroxide (H₂O₂)

The initial content of cyanide effluent is equal to an average of 52.00% w / w. High cyanide content of this potentially large in the pollution of the water environment. The cyanide content also has passed the threshold set by the Ministry of Environment of 0.5 mg / L (Ministry of Environment). Determination of cyanide by administering varying concentrations of H₂O₂ can be seen in Table 1. Each 100 mL of liquid waste is added H₂O₂ with particular concentration gives the percentage decrease in the levels of cyanide.

Table 1 Percentage Reduction CN levels before and after the addition of Hydrogen Peroxide (H₂O₂) with a concentration of 500 ppm (%)

Treatment	Titration	Volume (mL)	Percent concentration (% w/w)	Percentage Reduction CN (% w/w)
CN Without the addition and treatment as early levels	Titration 1	9.7	50.44	50.44
	Titration 2	9.8	50.96	50.96
	Titration 3	10.5	54.60	54.60
	Mean	10	52.00	52.00
Addition of Hydrogen Peroxide (H ₂ O ₂) concentration of 500 ppm	Titration 1	3.0	15.60	34.84
	Titration 2	3.0	15.60	35.36
	Titration 3	3.0	15.60	39.00
	Mean	3	15.60	36.40
Addition of Hydrogen Peroxide (H ₂ O ₂) concentration of 400 ppm	Titration 1	3.4	17.68	32.76
	Titration 2	3.5	18.20	32.76
	Titration 3	3.7	19.24	35.36
	Mean	3.53	18.37	33.63
Addition of Hydrogen Peroxide (H ₂ O ₂) concentration of 300 ppm	Titration 1	3.8	19.76	30.68
	Titration 2	4	20.80	30.16
	Titration 3	3.8	19.76	34.84
	Mean	3.87	20.11	31.89
Addition of Hydrogen Peroxide (H ₂ O ₂) concentration of 200 ppm	Titration 1	4.4	22.88	27.56
	Titration 2	4.0	20.80	30.16
	Titration 3	4.7	24.44	30.16
	Mean	4.37	22.71	29.29
Addition of Hydrogen Peroxide (H ₂ O ₂) concentration of 100 ppm	Titration 1	5.4	28.08	22.36
	Titration 2	5.0	26.00	24.96
	Titration 3	5.2	27.04	27.56
	Mean	5.20	27.04	24.96

In Figure 1 shows the percentage levels of CN with Addition of Hydrogen Peroxide at various concentrations. A reduction in the levels of cyanide by the addition of Hydrogen Peroxide (H_2O_2) can be seen in the Figure 1. Each 100 mL of liquid waste is added Hydrogen Peroxide with particular concentration gives the percentage decrease in the levels of cyanide. The decrease or reduction of cyanide levels with the addition of Hydrogen Peroxide with a concentration of 100 ppm, 200 ppm, 300 ppm, 400 ppm and 500 ppm. Cyanide content is reduced because it has reacted with hydrogen peroxide to form $CNCl$. The more the addition of peroxide, the greater hydrogen cyanide which react to form $CNCl$ so that the content of free cyanide contained in the liquid waste is reduced. Initial cyanide content of hydrogen peroxide without the addition of 52.00 % w/w and the content of the smallest on the addition of hydrogen peroxide with 500 ppm cyanide content of 36.40%. The optimum condition is achieved by the equilibrium between the amount of hydrogen peroxide is added to the cyanide contained in the waste.

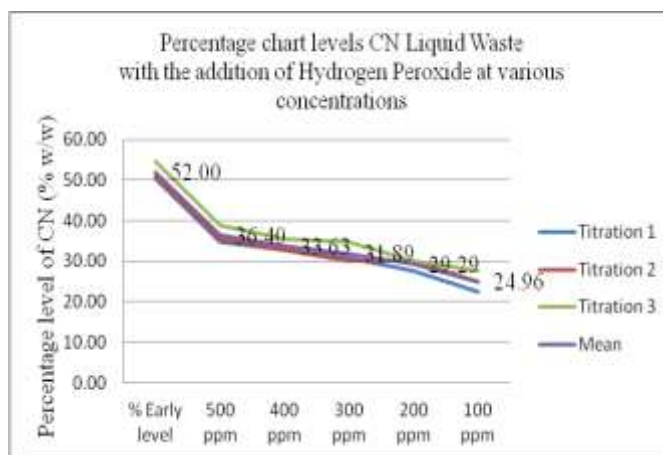


Figure 1. Graph Percentage degree of CN with Addition of Hydrogen Peroxide (H_2O_2) in various concentrations

Optimum pH the Hydrogen Peroxide (H_2O_2)

Next is the determination of cyanide with the pH variation when reacted with Hydrogen Peroxide to reduce the cyanide content in the liquid waste. Hydrogen cyanide oxidation process with peroxide is affected by pH. If the reaction is carried out with an acidic pH, the reaction will be slow but at alkaline pH the reaction will take place rapidly. pH influence on changes in the content of cyanide waste can be seen in Table 2. Each 100 mL of liquid waste is added Hydrogen Peroxide (H_2O_2) with the optimal concentration and a certain pH gives the percentage decrease in the levels of cyanide.

Table 2 Percentage of CN levels before and after the addition of Hydrogen Peroxide (H₂O₂) with a concentration of 500 ppm at pH variation (%)

Treatment	Titration	Volume (mL)	Percent concentration (% w/w)	Percentage Reduction CN (% w/w)
CN Without the addition and treatment as early levels	Titration 1	9.7	50.44	50.44
	Titration 2	9.8	50.96	50.96
	Titration 3	10.5	54.60	54.60
	Mean	10	52.00	52.00
Addition of Hydrogen Peroxide (H ₂ O ₂) concentration of 500 ppm pH 7	Titration 1	2.7	14.04	36.40
	Titration 2	3	15.60	35.36
	Titration 3	2.8	14.56	40.04
	Mean	2.83	14.73	37.27
Addition of Hydrogen Peroxide (H ₂ O ₂) concentration of 500 ppm pH 8	Titration 1	2.2	11.44	39.00
	Titration 2	2.0	10.40	40.56
	Titration 3	2.2	11.44	43.16
	Mean	2.13	11.09	40.91
Addition of Hydrogen Peroxide (H ₂ O ₂) concentration of 500 ppm pH 9	Titration 1	2.0	10.40	40.04
	Titration 2	2.3	11.96	39.00
	Titration 3	2.4	12.48	42.12
	Mean	2.23	11.61	40.39
Addition of Hydrogen Peroxide (H ₂ O ₂) concentration of 500 ppm pH 10	Titration 1	3.2	16.64	33.80
	Titration 2	3.5	18.20	32.76
	Titration 3	3.7	19.24	35.36
	Mean	3.47	18.03	33.97
Addition of Hydrogen Peroxide (H ₂ O ₂) concentration of 500 ppm pH 11	Titration 1	3.7	19.24	31.20
	Titration 2	3.6	18.72	32.24
	Titration 3	3.8	19.76	34.84
	Mean	3.70	19.24	32.76

Subsequent determination of the variation of the pH when reacted with hydrogen peroxide to reduce the cyanide content. The oxidation process is influenced by pH. pH influence on changes in cyanide content of wastewater. A total of 100 ml of liquid waste cyanide by the addition of 500 ppm of hydrogen peroxide at a certain pH obtained the cyanide content as in figure 2. It appears that the decline cyanide content at pH 8 and pH 9. The more alkaline cyanide solution, the reaction between the hydrogen peroxide more quickly. The smallest cyanide content obtained at pH 8 with decreased levels of 40.91% w/w. The optimum condition is achieved because the reaction takes place at a pH of 8 was the maximum. proper pH allows the hydrogen peroxide to react perfectly with cyanide contained in the liquid waste.

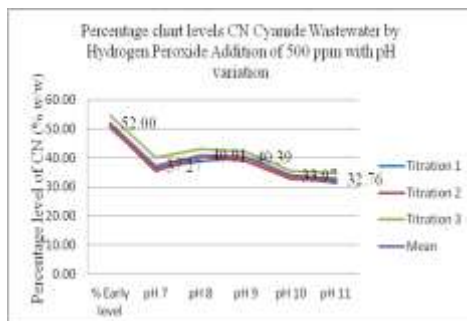


Figure 2. Graph Percentage degree of CN with Addition of Hydrogen Peroxide (H₂O₂) at pH variation

The optimum contact time Hydrogen Peroxide (H₂O₂)

After determination of the optimal concentration of Hydrogen Peroxide and the optimum pH is also determined by administering cyanide assay variation of the contact time between the waste cyanide Hydrogen Peroxide can be seen in Table 3. Each 100 mL of liquid waste is added Hydrogen Peroxide to the concentration optimal, optimal pH and specific contact time gives the percentage decrease in the levels of cyanide.

Table 3. Percentage of CN levels before and after the addition of Hydrogen Peroxide (H₂O₂) with a concentration of 500 ppm, pH 8 and variation of contact time

Treatment	Titration	Volume (mL)	Percent concentration (% w / w)	Percentage Reduction CN (% w/w)
CN Without the addition and treatment as early levels	Titration 1	9.7	50.44	50.44
	Titration 2	9.8	50.96	50.96
	Titration 3	10.5	54.60	54.60
	Mean	10	52.00	52.00
Hydrogen Peroxide (H ₂ O ₂) concentration of 500 ppm pH 8 Contact time 0 minutes	Titration 1	3.6	18.72	31.72
	Titration 2	3.5	18.20	32.76
	Titration 3	3.6	18.72	35.88
	Mean	3.57	18.55	33.45
Hydrogen Peroxide (H ₂ O ₂) concentration of 500 ppm pH 8 Contact time 30 minutes	Titration 1	3.7	19.24	31.20
	Titration 2	3.7	19.24	31.72
	Titration 3	3.9	20.28	34.32
	Mean	3.77	19.59	32.41
Hydrogen Peroxide (H ₂ O ₂) concentration of 500 ppm pH 8 Contact time 60 min	Titration 1	2.9	15.08	35.36
	Titration 2	2.9	15.08	35.88
	Titration 3	2.8	14.56	40.04
	Mean	2.87	14.91	37.09
Hydrogen Peroxide (H ₂ O ₂) concentration of 500 ppm pH 8 Contact time 90 minutes	Titration 1	3.6	18.72	31.72
	Titration 2	3.5	18.20	32.76
	Titration 3	3.5	18.20	36.40
	Mean	3.53	18.37	33.63
Hydrogen Peroxide (H ₂ O ₂) concentration of 500 ppm pH 8 Contact time 120 minutes	Titration 1	4.0	20.80	29.64
	Titration 2	4.1	21.32	29.64
	Titration 3	4	20.80	33.80
	Mean	4.03	20.97	31.03
Hydrogen Peroxide (H ₂ O ₂) concentration of 500 ppm pH 8 Contact time 150 minutes	Titration 1	4.6	23.92	26.52
	Titration 2	4.3	22.36	28.60
	Titration 3	4.4	22.88	31.72
	Mean	4.43	23.05	28.95

The determination of the variation of contact time when reacted with hydrogen peroxide to reduce the cyanide content. A total of 100 ml of liquid waste cyanide by the addition of 500 ppm of hydrogen peroxide at pH 8 with a certain contact time obtained the cyanide content as in Figure 3. It is seen that a decrease in the cyanide content at the optimum concentration, pH optimum and a certain contact time.

In Figure 3 shows the contact time of 0 minutes to 150 minutes. The longer the contact time, the interaction between waste cyanide with optimal concentrations of hydrogen peroxide and an optimum pH the better. Thus correcting lebh perfect. Thus more and more waste water cyanide reacts with hydrogen peroxide will reduce the cyanide content. The cyanide content is obtained with a contact time of 60 minutes with decreased levels of cyanide amounted to 37.09% w / w.

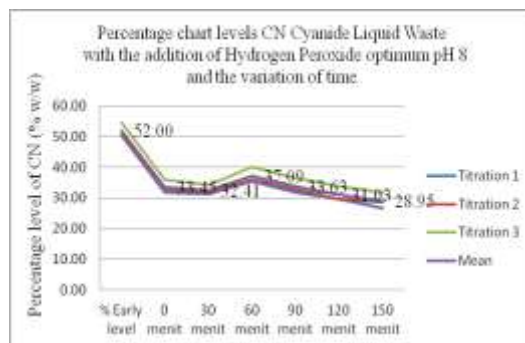


Figure 3. Percentage Graph CN Content with Addition of Hydrogen Peroxide (H_2O_2) in the optimal pH with a certain contact time

CONCLUSION

1. The content of the initial cyanide waste water without the addition of hydrogen peroxide (H_2O_2) of 52% w/w
2. The optimum concentration of hydrogen peroxide in reducing the cyanide content obtained at a concentration of 500 ppm addition of 36.40% w/w
3. pH optimum hydrogen peroxide in reducing the cyanide content obtained at pH 8 amounted to 40.91% w/w
4. The contact time of the hydrogen peroxide in reducing the cyanide content obtained at a contact time of 60 minutes amounted to 37.09% w/w

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Curriculum Vitae

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