Iran. J. Environ. Health. Sci. Eng., 2005, Vol. 2, No. 3, pp. 177-182

DETOXIFICATION OF CYANIDE IN GOLD PROCESSING WASTEWATER BY HYDROGEN PEROXIDE

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Received 1 January 2005; revised 26 February 2005; accepted 28 April 2005

ABSTRACT

Utilizing cyanide compounds in mining and chemical industry is one of the most important environmental issues due to the acute toxic properties of many cyanide compounds to humans and aquatic life. Cyanide tends to react readily with most other chemical elements, producing a wide variety of toxic, cyanide related compounds. This research was aimed at investigating a feasible and economical technique for the detoxification of cyanide from the tailing effluent of Muteh gold mine in Isfahan, Iran. In this research cyanide detoxification was achieved through the oxidation of cyanide by hydrogen peroxide using various hydrogen peroxide solutions at pH levels between 7-13 and temperatures between 12-65 °C using copper sulfate as a catalyst. The optimum pH and dose of hydrogen peroxide for complete cyanide removal in the presence of 30 mg/L copper sulfate as a catalyst were determined as 9.7 and 9.98 g/L, respectively. At high temperatures > 35°C, cyanide was completely removed perfectly at constant pH = 9.7 which was mainly due to cyanide evaporation in the form of HCN.

Key words: Cyanide destruction, hydrogen peroxide, copper sulfate, optimum pH, cyanide

INTRODUCTION

Cyanides are present in effluent waters of several industries especially in chemical and mineral processing industry. Mineral processing industries, especially gold processors, use a great deal of cyanide Ingles and Scott, 1993. Cyanide is used in a similar manner to extract silver from ores. In the extraction of non precious metals such as copper, nickel, cobalt, molybdenum, etc., cyanide is used in the milling and concentration processes to separate the desirable metals from the wastes. Cyanide is also used in a number of chemical synthesis nylon, fibers, resins, and herbicides and metallurgical processes plating and surface fishing and therefore, it is present in their effluent waters Lordi, *et al*., 1980, Patil and Paknikar, 2000. As a class of chemicals, cyanides are highly toxic, short-term exposure can cause the following health effects: rapid breading, tremors and other neurological effects; long term exposure can cause weight loss, thyroid effects and nerve damage. Therefore, cyanide must be destroyed or removed from wastewater prior to discharge. Stricter environmental regulations for the discharge of cyanides make it necessary to develop processes for their removal from wastewater. Several techniques are used for treating cyanide bearing effluents from gold processing. The methods to degrade cyanide solutions can be divided into three major groups: natural, chemical and biological degradation. The chemical treatments include oxidation, ion exchange and adsorption by activated carbon or natural zeolite, (Kurama and Catalsarik, 2000; Parga and Cocke, 2001, Nafaa, and Lotfy 2002).

Oxidation is one of the techniques, which are known for cyanide wastewater treatment Ingles and Scott, 1993. Common oxidants used for the removal of un complexes or weakly bound cyanides include chlorine, peroxide and chlorine dioxide. Research indicates that in the oxidation process,

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cyanide oxidizes and is converted to cyanide CNO^- which is 1000 times less environmentally hazardous than cyanide. Cyanide oxidation results in free cyanide CN^- being converted to cyanate CNO^-, which is a less harmful compound Lordi, 1980; Wild *et al.*, 1994. The maximum allowable cyanide concentration in drinking water is 0.07 mg/L according to EPA , whereas in our case, cyanide concentration in wastewater exceeds 250 mg/L (Anonymous, 1992).

Cyanide concentrations more than 0.07 mg/L, are intensely harmful to aquatics. A common method for the oxidation of cyanide wastewater is chlorination at high pH to form CNO^-, CO_2, N_2 and NH_4^+. However, there are several disadvantages with this type of treatment: 1 it is expensive especially in the case of concentrated solutions; 2 it is not so effective for cyanide complex wastes; and 3 it produces a large quantity of sludge, which contains heavy metal after chemical decomposition and subsequent precipitation processes. Unfortunately, the process effluents contain residual iron complexes cyanides, chlorine, and ammonia, which are toxic and must be removed through further treatment. Excessive chlorine quantities are required when thiocyanate is present, and the efficiency of metals removal is highly pH dependent Chin and Eckert, 1976; Tan, *et al.*, 1985; Hine, *et al.*, 1986; Ho, *et al.*, 1990. Oxidation should be considered when levels of oxidizable cyanide are too high to be processed by a biological treatment system. The most commonly adopted method for cyanide oxidation technique is application of peroxides, peroxymono sulfuric acid and persulfates that all are effective alternatives for cyanide destruction. Copper catalyzed hydrogen peroxide removes free and complexes cyanides including the stable iron complexes cyanides through oxidation. Using hydrogen peroxide systems depends on the reaction time, temperature, pH, the desired products cyanate, CO_2 and NH_3, the types of cyanides being treated and the system economics. While H_2O_2 will oxidize free cyanide, it is common to catalyze the reaction with a transition metal such as soluble copper, vanadium, tungsten or silver in concentrations of 5-50 mg/L Freeman, 1998. The oxidation is described as follows:

$$CN^- + H_2O_2 \rightarrow CNO^- + H_2O \qquad (1)$$

With any hydrogen peroxide system, a pH of 9-10 should be maintained if cyanide is present to avoid release of hydrogen cyanide HCN gas. Reaction rate can be increased by several means: raising the temperature, increasing catalyst dose and/or using excess H_2O_2. The inclusion of 10 mg/L Cu increase the rate 2-3 fold, while a 20% excess of hydrogen peroxide will increase the rate by about 30%. Cyanide oxidation by hydrogen peroxide is also dependant on various parameters such as suspended solids metal and cyanide complexes concentrations (Chapman, 1992), pH and dosage of hydrogen peroxide for cyanide removal.

This research was aimed at investigating the optimum conditions for cyanide wastewater treatment using hydrogen peroxide.

MATERIALS AND METHODS

Wastewater samples were obtained from the tailing dam of Muteh gold processing plant in Isfahan province. Cyanide is used in this plant for gold leaching process. Wastewater at the end of the process line is pumped to the tailings dam without any treatment. The concentration of H_2O_2 and solution density used for this research was 30% and 1.11 kg/L, respectively. Copper sulfate was used as a catalyst with concentrations of 10 to 50 mg/L. Cyanide oxidation was achieved using various hydrogen peroxide solutions at pH levels between 7-13 and temperatures between (12-65) °C. The pH and temperature were monitored by Hanna pH meter. The oxidation and reduction redox reactions result in CNO^- formation as fallows Wild *et al.*, 1994:

$$H_2O_2 + 2H^+ + 2e^- \Leftrightarrow 2H_2O \qquad (2)$$

$$H_2O + CN^- \Leftrightarrow CNO^- + 2H^+ + 2e^- \qquad (3)$$

$$H_2O_2 + CN^- \Leftrightarrow H_2O + CNO^- \qquad (4)$$

As obviously seen from the reactions, the number of electrons transferring, i.e. N is equal to 2. According to stoichiometric balance, one mole of H_2O_2 is sufficient for one mole of CN^-. The fixed minimum volume of H_2O_2 that is essential for cyanide neutralizing must be calculated from the normally-volume equation.

The wastewater samples consist of two main components; 1) the liquid part which is colorless and contains average 270 mg/L cyanide and other heavy metals, 2) The solid part consisting of sewage and solid wastes which are mainly black fines of activated carbon. The filtered liquid portion of the wastewater was used for this research. Cyanide analysis was performed by titration using a rhodanine solution solution prepared by dissolving para-dimethyl amino benzylidine rhodanine in pure acetone solution (Anonymous, 1992) as follows:

Rhodanine solution was prepared by dissolving para dimethyl amino benzylidine rhodanine, which was indicator for cyanide. Dissolving solid rhodanine in 50 mL pure acetone, makes a solution named rhodanine. Silver nitrate preparation for cyanide titration was made by dissolving 163.5 mg of $AgNO_3$ in 50 mL distilled water makes a 1.92 mole/L silver citrate solution. For dilution of wastewater 0.04 mole/L NaOH solution by dissolving 1.6 g NaOH in 1000 mL distilled water was used. The cyanide titration steps are summarized as follows:

1.Taking one mL cyanide wastewater sample original sample and then add 0.04 mole/L NaOH solution to it, until the total volume of mixed solution reach to 100 mL.

2.Taking 10 mL from the recently prepared solution and add 0.5 mL rhodanine indicator solution to it, which changes the solution's color to yellow. Puting the container consisting of diluted solution and rhodanin indicator solution under a micro-burette on a stand containing Ag NO_3. Opening the micro-burette's valve and stiring the container gently, as soon as the solution's color changes from yellow to onion purple color, closing the valve and write down the volume of $AgNO_3$ V which is consumed, by reading from micro-burette. Cyanide concentration in original sample containing cyanide is calculated from the following equation:

Cyanide concentration in diluted solution= Molecular weight of $AgNO_3$ (g). V_a-V_b $\frac{1}{V_a}$ Molecular weight of CN^- (g).

V_a= Volume of diluted sample, taken for titration= 10 mL

V_b= Volume of $AgNO_3$ consumed for blank solution titration.0.04 mole/L NaOH solution is named blank solution.

To determine the volume of $AgNO_3$ consumed for bonding to CN^- (forming Ag CN complex), the blank solution should be titrated by rhodanine indicator solution and silver nitrate. The procedure of blank titration is the same as cyanide titration. The detailed of the sample preparation and titration procedure can be found in Anonymous, 1992.

RESULTS

The concentration of H_2O_2 versus cyanide removal is shown in Fig. 1, which shows that cyanide removal using hydrogen peroxide and copper sulfate as catalyst generally takes place at pH= 9-10, so at the first stage, the experiments were set at pH=9.5 and temperature at 12 °C with a retention time of 60 min.

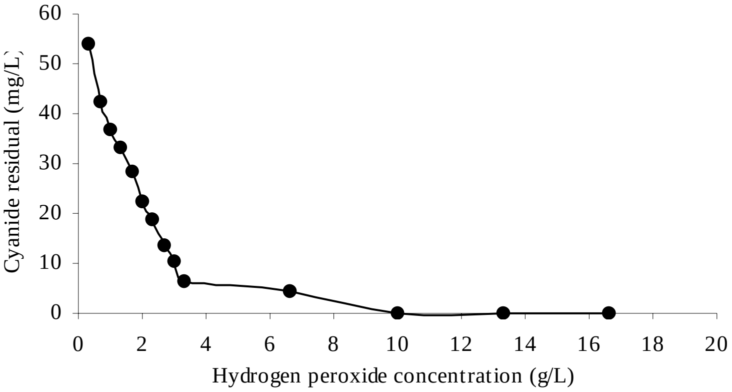

Fig. 1. Cyanide removal results using various hydrogen peroxide concentrations; copper sulfate concentration = 30 mg/L at pH=9.5 and T=12°C

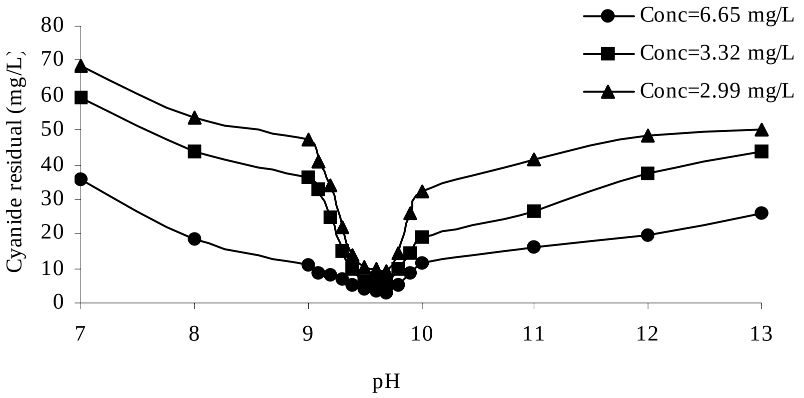

Fig. 2: The effect of hydrogen peroxide concentration on cyanide removal with the presence of 30 mg/L copper sulfate on cyanide removal

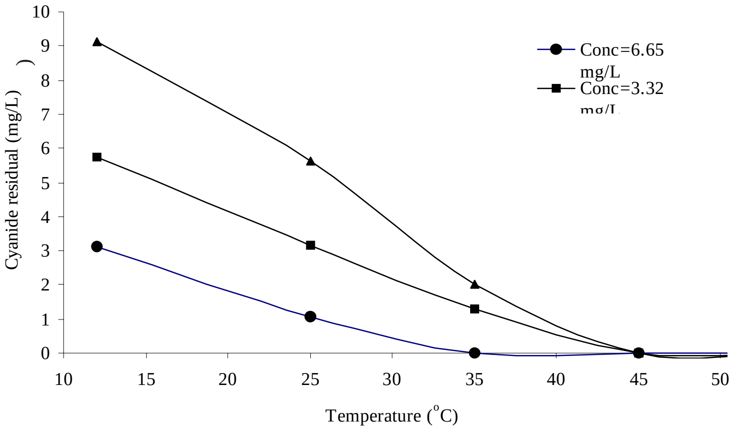

Fig. 3: The effect of temperature on cyanide removal using 6.65, 3.32 and 2.99 g/L of hydrogen peroxide

Table 1: Cyanide removal results using 6.65, 3.32, 2.99 g/L hydrogen peroxide solution and 30 mg/L of copper sulfate at pH=9.7 and temperatures 12-65 °C

Temperature (°C)	Residual cyanide concentration (g/L) 2.99 (mg/L)	 3.32 (mg/L)	 6.65 (mg/L)
12	9.11	5.73	3.1
25	5.62	3.15	1.05
35	2.03	1.29	0
45	0	0	0
55	0	0	0
65	0	0	0

The results of cyanide removal using 6.65, 3.32, 2.99 g/L hydrogen peroxide solutions with 30 mg/L copper sulfate at pH= 7-13 and temperature 12°C are shown in Fig. 2. As it is shown in Fig. 2 pH level of 9.6-9.7 is the optimum one for the maximum removal of cyanides.

The results of cyanide removal using 6.65, 3.32, 2.99 g/L hydrogen peroxide solutions at pH=9.7 and temperatures 12-65 °C are shown in Table 1 and Fig. 3.

The residual of cyanide concentration for all solutions at pH=9.7 and 45-65 °C was reached zero as shown in Fig. 3. Cyanide removal at pH=9.7 and temperatures 12-65 °C is mainly due to HCN formation and its evaporation regarding the very low boiling point of HCN 25.75 °C. Thus removal of cyanide by increasing the temperature above 45 °C is misleading.

DISCUSSION

As demonstrated in Figs.1, 2 and 3, concentrations of hydrogen peroxide, pH of the solution and temperatures are the most important determining factors, the removal of cyanide from wastewater. The color of the treated cyanide wastewater can be used as a guide for recognizing the amount of residual cyanide concentration in the solution. Cyanide solutions that appear to be light green in color, have residual cyanide concentrations of less than approximately 15 mg/L and other treated cyanide wastewaters nearly white in color have exactly the same cyanide concentration as the original wastewater.

Fig. 2 shows that at pH = 9.6 - 9.7, using 6.65 g/L hydrogen peroxide solution, the residual cyanide concentration reaches zero. When the pH increases to 9.8, cyanide removal decreases again and residual cyanide concentration reaches 4.99 mg/L. This is in consistent with the results in the literature obtained from experiments for tailings slurry or low solid containing solution samples from gold mining wastewaters (Knorre and Griffiths, 1984; Botz, 2001; Mudder *et al.,* 2001; Kitis *et al.,* 2005).

The same results were obtained when the concentrations of hydrogen peroxide solutions decreased to 3.32 and 2.99 mg/L, nevertheless the residual cyanide concentrations increased as the concentrations of hydrogen peroxide were reduced. The minimum residual cyanide concentration is at pH= 9.7 for all cases. Thus the optimum pH level was set at pH= 9.7 and cyanide removal was studied at this pH with increasing temperature. Cyanide removal at pH= 9.7 and temperatures of 12-65 °C is mainly due to HCN formation and its evaporation regarding the very low boiling point of HCN 25.75 °C. Thus, removal of cyanide by increasing the temperature above 45°C is misleading. The optimum dose of hydrogen peroxide for complete cyanide removal in the presence of 30 mg/L copper sulfate as catalyst was 9.98 g/L and optimum pH was determined as equal as 9.7. By increasing the temperature at constant pH and concentration of hydrogen peroxide cyanide removal improves, but by temperature increasing, H_2O_2 released O_2 very quickly and the great potential of H_2O_2 for cyanide oxidation decreased, so that prior to cyanate formation, the great amount of cyanide was remained. Thus, cyanide removal at temperature more than 25 is misleading because of O_2 releasing from hydrogen peroxide and on the other hand, due to HCN formation, which temperature increase evaporates rapidly.

ACKNOWLEDGEMENT

The authors gratefully acknowledge support from Mineral Processing Laboratory of Tarbiat Modarres University, Ministry of Industry and Mines (TAVA Projects) and Muteh Complex Company for providing the tailing effluent samples.

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