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Cyanide Removal from Laboratory Wastewater Using Sodium Hypochlorite and Calcium Hypochlorite

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ABSTRACT

Removal of cyanide (CN^-) from laboratory wastewater using sodium hypochlorite (NaOCl) and calcium hypochlorite ($Ca(OCl)_2$) were performed at the reaction time of 30 minutes. The product of chlorination at an alkaline pH of 12.3 was CNO^- which could be oxidized further to N_2. Colorimetric method was used to determine the amount of CN^- before and after chemical treatments. The optimum doses of chemicals used were determined. It was found that 100% removal of this contaminant could be achieved. The optimum doses and chemical costs of NaOCl and $Ca(OCl)_2$ varied depending on the initial cyanide concentration. The optimum doses of NaOCl and $Ca(OCl)_2$ for 100% CN^- removal were Y = 17.3X and Y = 3.32 X, respectively (where X = initial CN^- concentration in mg/l, and Y = chemical dose in mg/l). The chemical costs of NaOCl and $Ca(OCl)_2$ were Y = 0.69 X and Y = 0.50X, respectively (where X = initial CN^- concentration in mg/l, and Y = cost, baht/m^3 of wastewater). $Ca(OCl)_2$ is more effective than NaOCl considering the cost and dosage used.

Key words: cyanide removal , laboratory wastewater, chlorination

INTRODUCTION

The high toxicity of cyanide to life is well defined. Seventy mg KCN has a 50% chance of killing a 70 kg person within 15 minutes (Lygre, 1994). Standard regulation for the maximum contaminant level (MCL) of cyanide in wastewater, set by the Ministry of Science Technology and Environment, is 0.2 mg/l as HCN, *i.e.*, 0.182 mg/l as CN^-. Cyanide concentrations up to 30 mg/l have been successfully treated in biological process (Eckenfelder, 1966). Cyanide concentration was reduced from 75,000 mg/l to 0.2 mg/l after 18 days of treatment using electrolytic oxidation under optimum operating condition (Easton, 1967). Electrolytic oxidation is economical and efficient for use with concentrated waste. However, treating dilute solution has some restriction because low conductivity results in poor current efficiency (Larry *et al.*, 1982). Alkali chlorination is another technique used for cyanide treatment. The first reaction product is cyanogen chloride(CNCl), a highly toxic gas. At an alkali pH, CNCl hydrolyzes to cyanate ion (CNO^-), which has low toxicity. The CNO^- can be

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oxidized further by chlorine at a nearly neutral pH to CO_2 and N_2 (APHA and AWWA, 1992).

Cyanide generated from most laboratory wastewater is usually in CN^- form as used in calibration curve for determination of cyanide. These standards must be freshly prepared because they gradually lose strength. Moreover, the dissolved KCN salt used as standards are in alkali solutions. Thus, pH of standard solutions are above 12 which is an optimum condition for cyanide removal. In the case of concentration and volume of cyanide from laboratory wastewater is not high, chlorination may be the appropriate technique to use. In this study, chlorine compounds were used instead of chlorine gas (Cl_2). The method was focused on the chemical optimum doses and costs of chlorine compounds for removal at various cyanide concentrations.

MATERIALS AND METHODS

The wastewater with CN^- concentrations ranging from 1-100 mg/l were prepared in NaOH solutions. The pH of these solutions were already at 12.3 which needed not be adjusted further. Different amount of NaOCl or $Ca(OCl)_2$ was added to each cyanide concentration. The reaction time was set at 30 minutes. The residual CN^- left at any dose was determined by colorimetric method at maximum absorption of 587 nm (APHA and AWWA, 1992). The graphs were plotted to show the relationship of residual cyanide and the amount of NaOCl and $Ca(OCl)_2$ added to determine the optimum doses for each initial CN^-concentration. The chemical costs were calculated from the optimum doses. After that, the relationships showing the different initial cyanide concentrations and the optimum doses of chemical for CN^- removal and costs were expressed in the form of graphs and equations. The calculated doses were also tested with the laboratory wastewater containing high CN^- concentration.

RESULTS AND DISCUSSION

The optimum doses of chemical were defined as the amount of NaOCl or $Ca(OCl)_2$ used to achieve MCL and 100% removal. At 10 mg/l cyanide removal, the optimum doses of NaOCl were 86.8 mg/l and 90 mg/l to get MCL and 100 % CN^-removal, respectively (Figure 1). At this initial cyanide concentration, the optimum doses of $Ca(OCl)_2$ were 20 mg/l and 22 mg/l to achieve MCL and 100% CN^- removal, respectively (Figure 2). The optimum doses of chemical varied depending on the initial cyanide concentrations. These results were determined and summarized in Table1 and 2 and the graphs were plotted accordingly as shown in Figure 3 and 4.

Chemicals used in CN^- removal varied depending on the initial cyanide concentrations of 0-100 mg/l (Figure 3 and 4). In case of using NaOCl, the relationships were:-

$Y = 17.3 X$ (for 100%CN^- removal) (1)

$Y = 15.2 X$ (for MCL) (2)

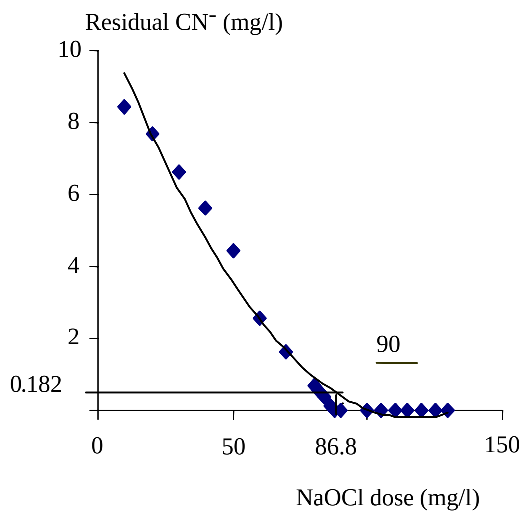

Figure 1 The optimum doses of NaOCl for 10 mg/l initial CN^- removal.

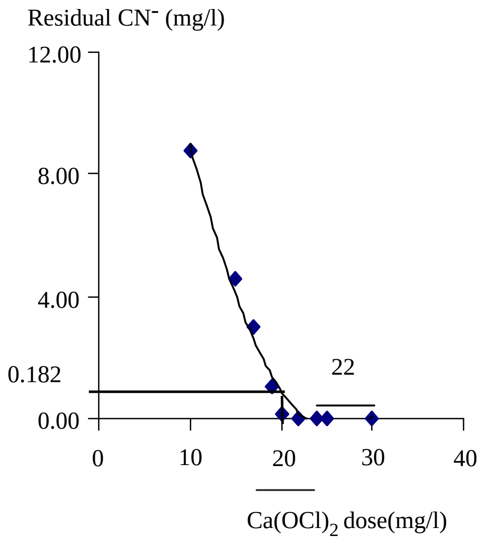

Figure 2 The optimum doses of $Ca(OCl)_2$ for 10 mg/l initial CN^- removal.

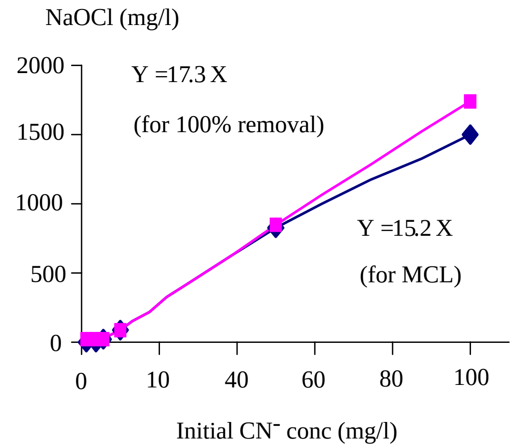

Figure 3 The optimum doses of NaOCl for cyanide removal at various initial concentrations.

As for $Ca(OCl)_2$, the relationships were:-

Y = 3.32 X (for 100% CN^-removal) (3)

Y = 2.93 X (for MCL) (4)

where

X = initial CN^- concentration (mg/l)

Y = chemical dose (mg/l)

In chlorination using chlorine gas, 2.7 mg/l of Cl_2 was required for 1 mg/l of CN^- (Larry et al., 1982). Compare to this study, 17.3 mg/l of NaOCl or 3.32 mg/l of $Ca(OCl)_2$ was required for 1 mg/l of CN^-.

The 0.67 mg/l CN^- laboratory wastewater

Table 1 The optimum doses of NaOCl for cyanide removal at various initial concentrations.

Initial CN^- concentration (mg/l)	NaOCl dose (mg/l) for MCL	NaOCl dose (mg/l) for 100% removal
0.20	n.a.	5
1.00	8.7	13
3.75	6.3	20
5.90	25.8	30
10.00	86.8	90
50.00	823.1	850
100.00	1502.6	1750

n.a. = not analyzed

Table 2 The optimum doses of $Ca(OCl)_2$ for cyanide removal at various initial concentrations.

Initial CN^- concentration (mg/l)	$Ca(OCl)_2$ dose (mg/l) for MCL	$Ca(OCl)_2$ dose (mg/l) for 100 % removal
0.20	n.a.	2.2
1.00	2.68	3.0
3.75	9.13	15.0
5.90	13.85	30.0
10.00	20.00	22.0
50.00	126.49	130.0
100.00	303.85	350.0

n.a. = not analyzed

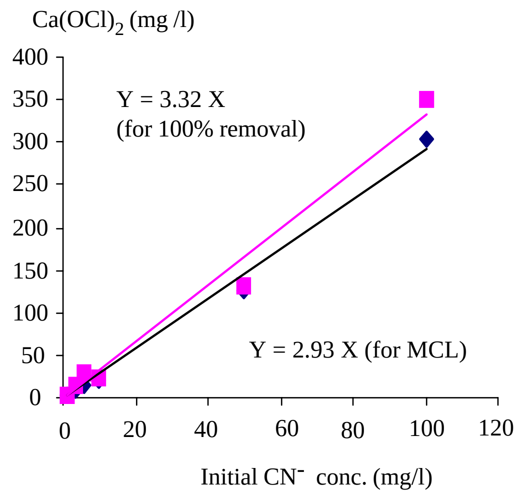

Figure 4 The optimum doses of $Ca(OCl)_2$ for cyanide removal at various initial concentrations.

was treated with NaOCl and $Ca(OCl)_2$ at the doses obtained from equations (1) and (3), respectively. The experiments were also done with the 88.0 mg/l CN^- laboratory wastewater. There was no cyanide detected after treatment.

Moreover, test was also done on high CN^- concentration of laboratory wastewater (270 mg/l) using $Ca(OCl)_2$ at the dose calculated from equation (3). It was found that 98.89 % of CN^- was removed. The remaining cyanide of 2.99 mg/l was gradually removed and meet the standard regulation of 0.182 mg/l as CN^- (MCL) after 47 hours .

Considering the oxidation reaction of chlorine compound which has been changing from CN^- to CNO^-, hypochlorite ion (OCl^-) is the active chlorine group in the oxidation process. The $Ca(OCl)_2$ has 2 groups of OCl^- presenting more effective in oxidation than NaOCl. Therefore, the lower dosage of $Ca(OCl)_2$ was used in cyanide removal.

The chemical cost was calculated from the optimum dose of NaOCl and $Ca(OCl)_2$ (commercial grade NaOCl costs 40 baht/kg and $Ca(OCl)_2$ costs 150 baht/kg). The chemical costs depended on the initial cyanide concentrations were summarized in Table 3.

For 100% CN^- removal, the relationships were:-

Y = 0.69 X (for NaOCl) (5)

Y = 0.50 X (for $Ca(OCl)_2$) (6)

where

X = initial CN^- concentration (mg/l)

Y = chemical cost (baht/m^3)

0.08 baht was required to remove 1 cubic metre of 1 mg/l CN^- wastewater using chlorine gas (Cl_2 costs 30 baht/kg) whereas 0.69 , 0.50 baht was required to remove 1 cubic metre of 1 mg/l CN^- using NaOCl and $Ca(OCl)_2$, respectively.

Although the costs of using chlorine compounds are higher than using chlorine gas in removing the same amount of CN^- and wastewater volume, but chlorine compounds are recommended as the practical alternative for CN^- removal from laboratory wastewater which contains less volume than industrial wastewater. The chlorine compounds are readily available and not dangerous to use while the handling process is much more convenient

Table 3 Chemical costs for 100% CN^- removal at various initial cyanide concentrations.

Initial CN^- conc. (mg/l)	NaOCl cost (baht/m^3)	$Ca(OCl)_2$ cost (baht/m^3)
0.20	0.2	0.33
1.00	0.5	0.45
3.75	0.8	2.25
5.90	1.2	4.50
10.00	3.6	3.30
50.00	34.0	19.50
100.00	70.0	52.50

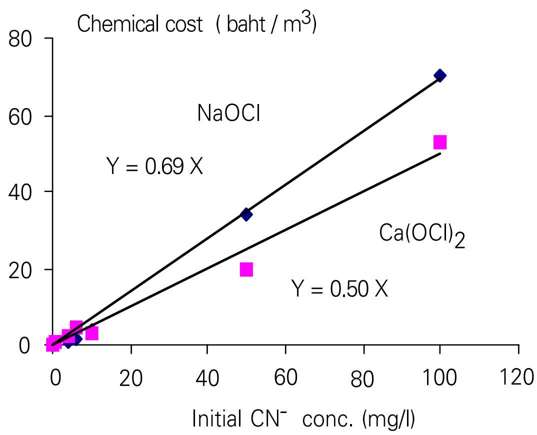

Figure 5 The chemical costs for 100% CN^- removal at various initial cyanide concentrations.

compared to chlorine gas. Using equations (1), (3), (5) and (6), to remove an equal amount of CN^-, $Ca(OCl)_2$ was 5.2 and 1.4 times more effective than NaOCl considering the dosage and cost.

CONCLUSION

The removal of CN^- from laboratory wastewater using either NaOCl or $Ca(OCl)_2$ could be achieved. The optimum dose and cost of each chemical have been reported. $Ca(OCl)_2$ was more effective than NaOCl considering the cost and dosage. We, therefore, have an alternative of using these 2 chemicals instead of chlorine gas.

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