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Study of Chlorination Application in Tapioca Wastewater for Cyanide Removal

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Abstract - *Tapioca wastewater contains a high concentration of organic matter and cyanide. Chlorination has known as one of alternative cyanide removal methods. The fact that must be an attention is carcinogenic compound such as Tri Halo Methane could be produced as byproduct chlorination of organic waste. This research aimed to determinecondition of chlorination application in tapioca wastewater cyanide removal especially calcium hypochlorite dosage and pH thus meeting the criteria of the quality standard of waste and Tri Halo Methane identification. Effluent of chlorination using calcium hypochlorite dosage based on stoichiometry reaction between chlor and cyanide (mole ratio chlor : cyanide = 1:1) which carried out at pH operation 8for 60 minutes has observed for cyanide content and Tri Halo Methane identification. Other variation of calcium hypochlorite dosage applied until meet the standart quality or lower cyanide content of effluent with no Tri Halo Methane detected. pH optimum determined from comparation of quality effluent of chlorination using calcium hypochlorite optimum dosage with variation pH operation 6, 7, 8. The results showed that the optimum condition for chlorination application in tapioca wastewater removal was 5,986 mg/L for calcium hypochlorite dosage (1,75 stoichiometry reaction) and 8 for pH operation. This chlorination condition able to reduce cyanide of 192 mg/L to 0,272 mg/L with no Tri Halo Methane detected in the effluent.*
Keywords - *Tapioca wastewater; chlorination; cyanide; Tri Halo Methane; calcium hypochlorite dosage; pH*

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Introduction

Tapioca wastewater are highly organic. In order to produce 1 ton of starch, a tapioca processing factory discharges about 12 m^3 of wastewater containing 11.000-13.500 mg/LO_2 in terms of COD (Mai, 2006). Cyanide concentrationin cassava mill wastewater also has been reported to contain as highas 200mg/L (Kaewkannetra et al., 2009).

Biological treatment could be used for handling wastewater containing high COD. But, highly cyanide could be inhibitor for biological treatment. Cyanide is a well-known metabolic inhibitor (Mai, 2006). The study about cyanide removal in tapioca wastewater has done by many researcher. Riyanti et al. (2010) said that chlorination for each 100 ml tapioca wastewater which taken at pH operation 8 for 1 hour will needs 5 mg calcium hypochlorite in order to remove 89,02% COD and 41,88% cyanide. Calcium hypochlorite addition in tapioca wastewater based on stoichiometry reaction between chlor and cyanide (mole ratio chlor:cyanide 1:1) at the same operation condition also noted could decrease 83,35% COD.

The case that must become a big attention is that highly organic waste chlorination also could produce carcinogenic compound Tri Halo Methane (THM) as byproduct. THM concentration will increase along with the increase of chlorin dosage and operation pH (Hua and Yeats, 2010). It is important to determine chlorination optimum condition especially calcium hypochlorite dosage and operation pH thus meeting both the criteria of the quality standard of waste and no Tri Halo Methane existence.

Experimental Methods

The research stage divided assix steps.They arewastewater sampling and handling, characteristic analysis of wastewater, calculation of reagent needs, chlorination, characteristic analysis of chlorination effluent, and data analysis.

Tapioca wastewater which used in this research was taken fromfrom tapioca starch industry in Margoyoso, Pati, Central Java, Indonesia. In order to avoid significant change in quality, wastewater was stored in cool box at 4°C.

Characteristic analysis of wastewater was taken to assess the pH and cyanide. The formula to calculate calcium hypochlorite amount which must be added for chlorination based on stoichiometry reaction are:

$$the\ amount\ of\ calcium\ hypochlorite\ 0{,}1\%(ml) =$$

$$\frac{\frac{mg}{L} CN^{-}\ x\ ml\ limbah\ x\ \frac{BMCl_2}{BMCN^{-}}}{\frac{mg}{L} Cl_2\ dalam\ larutan\ kaporit\ 0{,}1\%} \quad (1)$$

Titration of mixture of tapioca wastewater and calcium hypochlorite with calcium hypochlorite 1% until reach desirable pH was become a method to determine the amount of calcium hydroxide required.

Chlorination in this research divided as three steps. They are chlorination using calcium hypochlorite dosage based on rasio mole chlor:cyanide 1:1 (stoichiometry reaction), determination of optimum calcium hypochlorite dosage, anddetermination of optimum pH.All of chlorination was taken for 60 minutes at operation pH 8.

Effluent samples of chlorination based on stoichiometry reaction were taken to assess cyanide content and THM identification. Because cyanide content does not fulfill the criteria standard (above 0,3 mg/L) and no THM detected, optimum calcium hypochlorite dosage determined by chlorination with increasing calcium hypochlorite dosage until the cyanide content effluent meet the standard criteria with no THM detected. Determination of optimum pH was determined by chlorination using optimum dosage with variation pH 6,7, and 8 in order to gain effluent with lowest cyanide and no THM detected.

Results and Discussions

Table 1 showscomparation between tapioca wastewater characteristics and quality standard Peraturan Daerah ProvinsiJawa Tengah No.10 Tahun 2004.

Table1. Comparation betweentapioca wastewater characteristicand quality standard

Parameter	Content	Quality standard
CN^-	192	0,3 mg/L
pH	5,8	6-9

Highly cyanide content in tapioca wastewater shows that cyanide decrease still needed beforewaste could discharged into receiving body water.CN^-toxic effect could cause death in short time. Effluent data of chlorination for determining optimum calcium hypochlorite dosage was presented in Table 2.

Table 2. Effluent quality of chlorination for determination of optimum calcium hypochlorite dosage

Calcium hypochlorite dosage (g/L)	CN^- (mg/L)	THM detection
3,421	17,142	N.D
4,276	9,6	N.D
5,131	2,571	N.D
5,986	0,286	N.D

Table 2 shows that no THM detected in all of variation calcium hypochlorite dosage. This case probably caused by content of carbohydrate and fat in tapioca wastewater. Each of 100 gram tapioca wastewatercontains 25-37 gram ofcarbohydrateand 0,19 gram offat (Setyawati et al., 2011).Reaction betweenchlor and double bound in organic matter such as carbohydrate, aceton, fat, and fatty acid was taken place slowly (Snoeyinks and Jenkins, 1979).

Table 2also shows that calcium hypochlorite addition could decrease cyanide contentin tapioca wastewater.The decrease was occurred based on this reaction.

$$Cl_2 + CN^- \rightarrow 2Cl^- + 2\ H^+ + OH^- + HCO_3^- + NH_4^+ \quad (3)$$

(Botz, 2002)

Chlorination using calcium hypochlorite dosage based on stoichiometry reaction (3,421 g/L) still results effluent with high cyanide content. The increased dosage exceed theoretical dosage was indicated because of existence of N in tapioca wastewater which could reach 65-74 mg/L (Mai, 2006). Cl_2 could oxidize NH_4^+based on this reaction.

$$Cl_2+2NH_4^+ \rightarrow N_2+6HCl+2H^+ \quad (4)$$

(Botz, 2002)

pH optimum was determined by chlorination using optimum calcium hypochlorite dosage 5,986 mg/L (1,75 stoichiometry reaction) with operation pH variation 6, 7, and 8. The results of research shows that pH optimum is 8 according to data presented in Table 3.

Table 3. Effluent quality of chlorination for determination of optimum operation pH

pH	CN^- (mg/L)	THM detection
6	3,6	N.D
7	0,9	N.D
8	0,286	N.D

Conclusion

Effluent chlorination using calcium hypochlorite based on stoichiometry reaction (mole ratio chlor:cyanide = 1:1) still contains high content of cyanide which exceeds quality standard. Optimum condition of chlorination application in tapioca wastewater cyanide removal is 5,986 mg/L calcium hypochlorite (mole ratio chlor:cyanide = 1,75:1) and operation pH 8.

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