Optimation of Cyanide Adsorption from Tapioca Industry Liquid Waste Using Activated Sludge

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Abstract — **Optimation of cyanide adsorption has been done from tapioca industry liquid waste using activated sludge. This study was aimed to know the optimum condition of the adsorption process and to determine the adsorption efficiency of active sludge to cyanide contents of tapioca industry liquid waste. The roommate's sludge was dried, and activated using 3M HCl and calcinated at temperatures of 800oC. The optimum condition was determined using adsorption time variations at 7, 8, 9 and 10 hours and adsorbent weight variation of 150 mg, 200 mg, 250 mg, and 300 mg. This optimum condition determination was done to 50 mL of simulated waste. The optimum condition results of adsorption time were 8 hours, adsorbent weight was 250 mg, and adsorption efficiency was 85.36%. The optimum condition refers to tapioca industry liquid waste. Cyanide content before adsorption was 8.32 ppm and after adsorption was 1.22 ppm, its adsorption efficiency was 85.30%. This result has not fulfilled the requirement according to KEP-51 / MENLH / 10/1995 yet, about "Liquid Waste Quality Standards For Tapioca Industry" which states that the maximum cyanide content is 0.5 ppm.**
Keywords: *activated sludge, cyanide, tapioca liquid industrial waste*

I. INTRODUCTION

Cassava starch as raw material contains cyanogenic glycosides (Soemirat, 2009). Cyanogenic glycosides (glycosides Cyanophere) is widely spread as amygdalin when hydrolyzed would produce *mandelonitrile glucoside* and one molecule of *glucose*. *Mandelonitrile glucoside* will return to hydrolysis produces *benzaldehyde* and *hydrogen cyanide* (Varro et al, 1977). Therefore, cyanide compound 8.08 ppm can be found in the liquid waste in the tapioca industry based on research conducted by Nur Aji (2011), while according to KEP-51/MENLH/10/1995 the standards for the tapioca Industry cyanide maximum levels content was 0.5 ppm.

Most cyanides in industrial wastewater are hydrogen cyanide (HCN) or in the form of cyanide ion (CN-) (Ahmad, 2004). In humans, cyanide will cause cytochrome oxidase (cellular respiration enzyme) to stop its activity and will decrease the amount of hemoglobin (Hadiwiyoto, 2014). Therefore, wastewater treatment is urgently needed.

Activated sludge contains microbial decomposers, serves to accelerate the stabilization process of wastewater (Sugiharto, 2008). Certain microbial cells in activated sludge either alive or dead, has been found to accumulate in the cell surface of the metal in its ionic form, namely magnesium (Mg^{2+}) and calcium (Ca^{2+}) (Urban et al, 1993). The use of acid activation and calcined in the activated sludge process are known to increase the surface area and pore diameter of activated sludge (Mustopa et al, 2013). The presence of H+ ions on the surface can absorb adsorbent in the form of the anion (Salmariza et al, 2016).

Several methods have been used to reduce the levels of cyanide in the liquid waste of tapioca flour industry among others, by the method of adsorption-photodegradation with zeolite as a photocatalyst (Fatimah and Karna, 2005), adsorption methods using activated carbon (Rumidatul, 2006) and ground rice husks (Kusaeri, 2014). Simple liquid water treatment with low cost and efficiently is needed by the starch industry.

Based on the above background, this study will be conducted in the cyanide adsorption process of tapioca industry liquid waste using activated sludge that has been activated by acid and calcined process, also with the determination of the adsorption process optimum conditions.

II. RESEARCH TOOLS, MATERIALS, AND METHODOLOGY

A. Tools

The tools used in this study was laboratory glassware, sieve mesh 100, UV-Vis spectrophotometer (GENESYS 10s), strips pH indicator (Merck), pH meter (Mettler Toledo), a set of distillation equipment, filter paper, Centrifugator (HC-12), analytical scales (Mettler Toledo), vacuum pump (Fj.115 Fuji), magnetic stirrer, incinerator, oven (Memmert), desiccator.

B. Materials

Materials used in this study is pyridine p.a, NaOH p.a, KCN p.a, distilled water, KI p.a, Acid barbiturates p.a, NaCl p.a, chloramine T p.a., Ca(OCL)2, AgNO3, NH4OH, K_2CrO_4, H_2SO_4, NaH_2PO_4, sodium citrate, citric acid, $FeCl_3$, Na_2S, KSCN, HCl, Pb Acetate, amylum, Picric acid

C. Methods
Sample Preparation
Sample Simulation

Sample were prepared by dissolving KCN 0.25 ppm in 0.16% NaOH, then added Na_2S 1ppm, KSCN 10 ppm and 100 mg $FeCl_3$ (Aji, 2011).

Waste
Tapioca liquid waste pH, sulfide and oxidation were checked. After that, wastewater added to a bottle containing 5 mL of 5N NaOH and add until 1 liter, check the final pH (HACH, 2012).

Sludge Preparation
Obtained sludge washed using distilled water and dried at temperature 80°C. Further, a crushed sample and sieved with 100 mesh sieve to obtain dried sludge powder to be activated. Activation was done by mixing the solution of 3M HCl for 15 minutes at temperature 80°C. After that, sludge calcined at temperature 800oC using an incinerator.

Standard Determination
Standardization of AgNO3
Added 5 mL NaCl 0.1M to 250 ml Erlenmeyer and add 3 drops of K_2CrO_4 1%, titrated with $AgNO_3$ solution until the change first brick-red precipitate.

Standardization of KCN
50 mg KCN added to 250 ml Erlenmeyer. Then added 10 ml NH_4OH 0,24M, aqua DM 10 ml, 2 ml of 0.01 M KI indicator, titrated with $AgNO_3$ solution until a yellow precipitate was formed.

Cyanide Calibration Curve Preparation
A standard solution made by dissolving the KCN standard in NaOH. Then made a serial dilution of the standard solution with varying concentrations of 0.15 ppm; 0.20 ppm; 0.25 ppm; 0.30 ppm; 0.35 ppm and 0.40 ppm. Added to each concentration 1 ml Na_2S 1 ppm and 5 ml KSCN 10 ppm. After that enter into the distillation flask, neutralize with 3M H_2SO_4 then add $FeCl_3$ 100 mg, add the citrate buffer pH 4. Distillation was done under vacuum conditions. Collect distillate with 2.5% NaOH. The distillate was neutralized with 3M H_2SO_4 then added 10ml phosphate buffer pH 8. After that add chloramine T 1% 2ml, 2ml pyridine-barbituric acid and add 50 ml phosphate buffer pH 8, leave for 17 minutes. Measure absorbance at 580 nm wavelength.

Optimum Conditions Determination Adsorption Time and Adsorbent Weight
Created 50 ml of simulated waste with a concentration of 0.25 ppm cyanide, further distilled and collected in 2.5% NaOH. Distillate and adsorbent were mixed and shaken at sometimes. Adsorption was done on time variation of 7 hours, 8 hours, 9 hours, 10 hours using adsorbent weight variation of 150 mg, 200 mg, 250 mg, and 300 mg. The mixture was centrifuged and the filtrate was separated. Measured absorbance of the filtrate after derivatized with

chloramine T 1% and pyridine-barbituric acid using a UV-Vis spectrophotometer at 580 nm. % Absorption efficiency can be calculated by the equation :

$$E = \frac{Co - Ca}{Co} \times 100\%$$

Information :
E   = Absorption efficiency (%)
Co   = Solution initial concentration (ppm)
Ca   = Solution final concentration (ppm)

Waste Content Analysis and Cyanide Adsorption
After the optimum conditions determination, the optimal amount of adsorbent and adsorption contact time was found out. Furthermore applied to tapioca industrial waste, the solution was adsorbed to the activated sludge waste in optimal conditions and absorption efficiency was calculated.

III. RESULTS AND DISCUSSION

Sample Preparation
Sample Simulation
In the simulation sample, KCN dissolved in 0.16% NaOH then added KSCN, Na_2S, and $FeCl_3$. The selection of NaOH as a solvent for KCN was to stabilize under alkaline conditions, at pH below 7, overall cyanide form volatile HCN. Na_2S and KCN were added as an intruder on analysis and $FeCl_3$ were added as a masking agent.

Sample Waste
Tapioca liquid waste was collected in a bottle filled with NaOH so that cyanide will remain stable. Qualitative sulfides and oxidator tests must be done in less than 24 hours if the sample contains sulfide and the oxidator. Sulfide test was done using lead acetate paper, while the chlorine as an oxidator testing done using starch iodide paper. The absence of color changes in each test indicates that the sample did not contain sulfide and an oxidator.

Preparation of Activated Sludge
Sludge has been washed and dried crushed sieved, this was done to reduce the particle size of the sludge, because the smaller the particle size the greater the surface area of the adsorbent, it will have high adsorption capacity. Activation using acid performed to remove compound impurity that still attached to the pores of the sludge that would hinder the adsorption process and adding a more active side of the adsorbent. Then, the calcination process that aims to eliminate the CO_2 content of the adsorbent through the decomposition of the calcium carbonate ($CaCO_3$) compound was done.

Cyanide Standard Determination
Standardization of $AgNO_3$
Standardization of $AgNO_3$ uses argentometri Mohr titration method in which the chromate ion was used as an

indicator. Silver chromate (Ag_2CrO_4) is more soluble (about 8.4 x 10-5 mol/liter) than silver chloride (AgCl) (approximately 1x10-5 mol/ liter). If silver ions are added to the solution containing chloride ions with great concentration and chromate ions with small concentration, silver chloride (AgCl) will precipitate first (Underwood, 2001). Early emerged precipitate silver chromate (Ag_2CrO_4) reddish color taken as the endpoint. The process was based on the results obtained $AgNO_3$ levels were 0.0978 M.

Standardization of KCN

Standardization of KCN conducted by the Liebig titration method. The basis of this method is the formation of stable complex ions $(AgCN)_2$. At first, endpoint based on the appearance of turbidity due to the deposition of silver cyanide. However, it decomposes back precipitated when the solution was stirred. Therefore in this study conducted Deniges modification wherein iodide ions were added as an indicator. The precipitated silver iodide was easier to see and less soluble than silver cyanide. But this final point appeared too early so that the ammonia was added to set up a soluble compound $Ag(NH_3)^{2+}$, which slows the deposition of silver iodide until the right time. Ammonia did not prevent the formation of $Ag(CN)^{2-}$ so did not disturb titration reactions (Underwood, 2001).

**Calibration Curve Cyanide Preparation**

At this stage, the waste created simulations to 6 variation cyanide concentration 0.15 ppm, 0.20 ppm, 0.25 ppm, 0.30 ppm, 0.35 ppm, and 0.40 ppm, using vacuum distillation method. Each simulated waste added citrate buffer pH 4. Under these conditions the overall cyanide form HCN that volatile and distilled. If the distillation carried out at pH below 4, Na_2S will turn into H_2S which then will join distilled and interfere with the measurement process. $FeCl_3$ was added as a masking agent in which SCN- and $FeCl_3$ complex will form $Fe(SCN)_3$ stable so it did not interfere with the analysis. Distillation was done at 60°C-70°C with an airflow rate of 1-2 bubbles per second and show the pump pressure 25 mmHg. The distillate was collected in 2.5% NaOH solution, the condition of the analyte was stable under alkaline conditions.

Cyanide is colorless, a one-way analysis of cyanide is cyanide reacting with chloramine-T and pyridine-barbituric acid. At the analysis stage, the results of the first distillate were neutralized by using H_2SO_4. Then added to phosphate buffer pH 8 according to the pH stability of complex formation. The process formation of the complex is divided into two phases, as were described by Pohling (2014). The first was the creation of sianoklorin (CNCl) from the addition of chloramine T were dissolved in water with the following reaction:
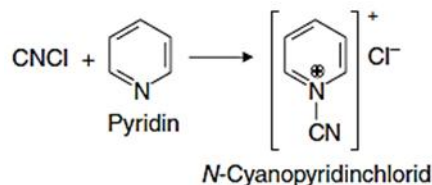
Cyanide reaction formed sianoklorin:

$$CN^- + OCl^- + 2H^+ \longrightarrow CNCl + H_2O$$
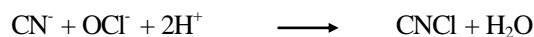
At pH 8 sianoklorin compound will be stable, while at pH>10 will be changed to cyanate oxide, the neutralization stages of distillation were done.

$$CNCl + OH^- \longrightarrow OCN^- + Cl$$
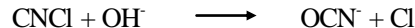
At a later stage, sianoklorin formed to be reacted with pyridine to form *N-Cyanopyridinchlorids*

N-Cyanopyridinchlorid

N-Cyanopyridinchlorids hydrolyzed to form *Glutacondialdehyd*. *Glutacondialdehyd* formed will react with barbiturates and form complex compounds following reaction:
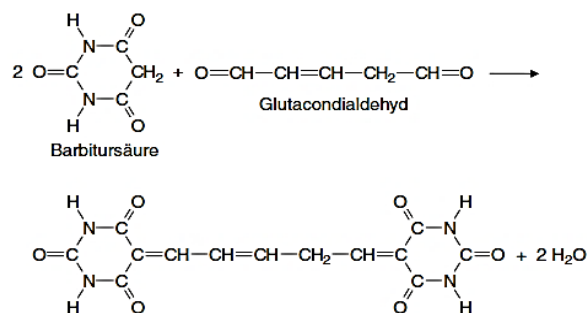
The intensity of the purple color is proportional to the cyanide content in the sample. Based on absorbance measurements using UV-Vis spectrophotometry at each concentration and the calibration curve obtained as follows:

y = 2,0337x - 0,0278
r = 0,9987
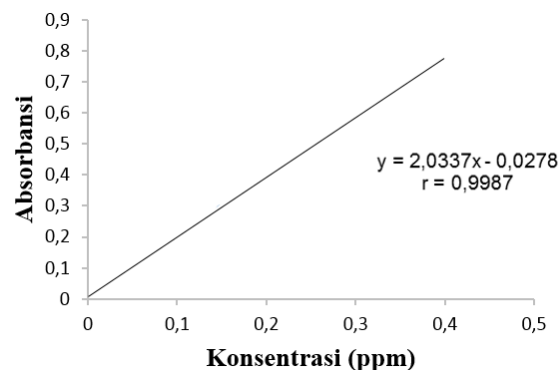
Picture 1. Cyanide calibration curve

The regression equation obtained was y = 2,0337x - 0.0278 with a correlation coefficient (r) of 0.9987. A correlation coefficient close to 1 means good linearity.

Optimum Conditions Determination of Weight Adsorbent and Adsorption Time

Optimum adsorption conditions determination performed on simulated waste with an initial concentration of 0.25 ppm cyanide which then distilled and the distillate was collected in 2.5% NaOH as much as 25ml. Effect of contact time between adsorbent and adsorbate were done by the time variation of adsorption was 7 hours, 8 hours, 9 hours and 10 hours and the weight of adsorbent used in each variation of the concentration was 200 mg. From the research that has been done contact time of 7 hours to 8 hours results in adsorption efficiency increasing from 81.20% to 83.32%. This increase occurred because the adsorbent was not a monolayer, so it takes time for adsorption. Decrease in absorption efficiency at the time of 9 hours and 10 hours, from 68.36% to 62.48%. This occurred because the contact time was too long causing adsorbate desorption event. Along the desorption process, their competitive anions (with different affinities that OH-) adsorbed on the active sites of the adsorbent and decreasing the cyanide ion adsorption process. Thus obtained optimum adsorption time is 8 hours with 200 mg adsorbent. Figure 2 shows the effect of adsorption time on adsorption efficiency.
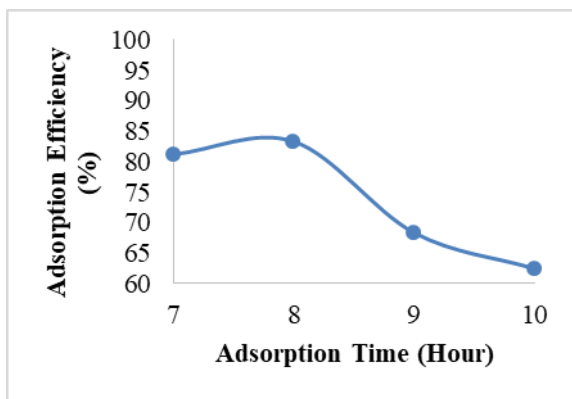

Figure 2. Adsorption efficiency vs adsorption time graph

Optimum time determination was done with adsorbent variation weight 150 mg, 200 mg, 250 mg and 300 mg with each 8 hours adsorption time. Efficiency adsorption of heavy conditions adsorbent 150 mg, 200 mg, and 250 mg, increasing from 79.96%, 82.96%, and 86.88%. This was due to the increase in weight of the adsorbent, the more active the adsorbent, the more it will be adsorbed and increase the adsorption efficiency. Adsorption efficiency deterioration occurred in severe conditions where adsorbent was 300 mg and adsorption efficiency was 61.68%. This happens because at 300 mg adsorbent occurred clots so the surface of the adsorbent was not entirely open, causing a reduction in the active surface area of the adsorbent thus decreasing the absorption efficiency. Optimum adsorbent weight for adsorption was 250 mg with 8 hours adsorption time. Figure 3 shows the heavy influence of the adsorbent on adsorption efficiency.
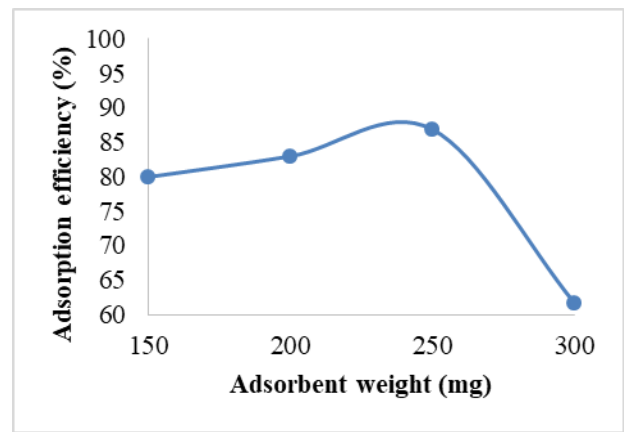

Figure 3. Adsorbent weight vs adsorption efficiency graph

Duplication of tests on the two optimum conditions on the weight of the adsorbent 200 mg with adsorption time of 8 hours and weighs 250 mg adsorbent with adsorption time of 8 hours to ensure the absence of a significant difference in both adsorption efficiency. Statistical tests result obtained sig (2-tail) on T-test Independent test of 0.0002 and it can be concluded that there were significant differences between the adsorption conditions with an average efficiency value of 200 mg (82.31%) and 250 mg (85.36%). Therefore, 250 mg adsorbent with 8 hours adsorption time was optimum adsorption condition.

Cyanide Levels and Adsorption Analysis on Waste

Optimum adsorption conditions applied to cyanide adsorption in tapioca industry liquid waste. Measurement results obtained an initial concentration of cyanide in tapioca industry liquid waste was 8.32 ppm. The result comes from 250 mg adsorbent which was carried out 8 hours adsorption time. Cyanide concentration was measured after the end of the adsorption process which was equal to 1.22 ppm and obtained 85.3% adsorption efficiency. Adsorption efficiency did not reach 100% due to the competitive anions on the adsorption process and due to a lack of active sites on the adsorbent.

IV. CONCLUSION

The optimum conditions obtained from the cyanide adsorption process in tapioca industry liquid waste by using activated sludge with 250 mg adsorbent and adsorption time of 8 hours resulted in 85.35% absorption efficiency. The cyanide level in tapioca liquid waste was 8.32 ppm which was then carried out following adsorption process optimum conditions, the final levels of cyanide obtained after adsorbed were 1.22 ppm resulting in 85.03% adsorption efficiency. These results did not fulfill the requirements according to KEP51/MENLH/10/1995 about "Liquid Waste Quality Standards For the Tapioca Industry" cyanide content maximum levels which are 0.5 ppm.

V. SUGGESTION

There will be necessary to optimize the acid concentration for the activation process, along with adsorbent morphological analysis and optimization adding NaOH as distillate container so that no excess OH- cause competitive process bonding to the active site of the adsorbent, so the adsorption efficiency will be improved.

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