

## TREATMENT OF TRADITIONAL ETHANOL FERMENTATION WASTE WITH ELECTROLYSIS METHOD FOR DECREASING COD AND SULFIDE

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### Abstract

*Ethanol is produced from molasses by a fermentation process. In Bekonang, ethanol manufacturing by a home-scale industry so the waste just thrown away in free water then pollution occurs both in rivers and in paddy fields. Ethanol waste has very high chemical oxygen demand (COD) and contain high sulfide. Electrolysis that use for reduce levels COD dan Sulfide with electricity as main source for direct current flowing electricity (dc) to the anode and cathode. Electrolysis time 10, 15, 20, 25 and 30 minutes and voltage variation 5, 10 and 15 volt. Based on data obtained in the test COD obtained optimum levels of 284.5 mg/L from the initial content of 586 mg/L, at a time variation of 30 minutes and voltage 15 volt. The sulfide test obtained optimum levels of 0.0661 mg/L from the initial content of 0.305 mg/L, at time variation of 25 minutes and a voltage of 15 volt.*

**Keywords:** ethanol, chemical oxygen demand, sulfide, electrolysis

### 1. PRELIMINARY

The ethanol industry or commonly in their call as *ciu*, located in Sentul, Bekonang Village, Mojolaban Subdistrict, Sukoharjo Regency, is an industry that has to much effluents. Understanding ethanol according to (de Vasconcelos, 2015) Ethanol is commonly determined to be the chemical component ethanol or ethyl alcohol (de Vasconcelos, 2015). Whereas according to (Dalena *et al.*, 2019) is an alcohol mainly produced from agricultural residues and it can be derived from fermentation of sucrose or simple sugars, coming from the biomass treatment (Dalena *et al.*, 2019). In bekonang, ethanol is produced from molasses by a fermentation process. Molasses from sugarcane industry is it common raw material used in ethanol production due to its easy availability and low cost (Patel and Durgavati Vishwavidyalaya, 2018).

The ethanol manufacturing industry is a home-scale industry so that the processing of the waste has not been properly processed. The waste is thrown away in free water and only a little is processed in the WWTP (Waste Water Treatment Plant) which does not function properly so that the smell of waste disturbs the surrounding environment. Not only smells, ethanol waste or the usual local residents call it *badek* also give effects in agricultural products whose commodities are rice in the surrounding environment can not grow optimally even up to crop failure.

Distillery effluent has very high biological oxygen demand (BOD), chemical oxygen demand (COD) and high BOD/COD ratio. The amount of inorganic substances such as nitrogen, potassium, phosphates, calcium, sulphates is also very high. These compounds have antioxidant properties which render them toxic to many microorganisms such as those typically present in wastewater treatment processes. Ethanol waste are acidic, have a brown colour, have a high content of organic substances and contain large amount of dark brown coloured molasses wastewater (MWW). The highly colored components of the effluent can block out sunlight from in rivers, lakes or lagoons which in turn decrease both photosynthetic activity and dissolved oxygen concentration affecting aquatic life (Patel and Durgavati Vishwavidyalaya, 2018).

To treat both organic and inorganic waste in this study we agreed to use the electrolysis method. Electrochemical technologies such as electrolysis have been successfully employed for the treatment of many wastewaters on an industrial scale. The electrical conductivity as well as salinity was decreased through the electrolysis procedure, because of the loss of electrolyte ions in the wastewater through the formation of compounds and its sedimentation. Most electrochemical processes use a couple of metallic electrodes, usually a relatively stable anode such as titanium and a relatively active cathode such as aluminum and iron (Chopra, Kumar Sharma and Kumar, 2011).

## 2. METHODOLOGY

This research was conducted with the aim to determine the reduction of COD and Sulfide levels from ethanol liquid waste by using the electrolysis method. By using these methods, in this study there are two factors that are varied. The first factor is the variation of voltage (5, 10 and 15 volts) and the second factor is the variation of electrolysis time (10, 15, 20, 25 and 30 minutes).

### 2.1. Time and place of sampling

This research was conducted in October-December 2019 at the Chemical Engineering Laboratory, Muhammadiyah University, Surakarta. Ethanol waste sample was taken from one of the home industries in Bekonang Village, Mojolaban District, Sukoharjo Regency, Central Java Province.

### 2.2. Research tools

The tools used in this study include; weigh bottle, burette, erlenmeyer, beaker, measuring cup, hotplate, measuring flask, suction rubber, watch glass, magnetic stirrer, glass stirrer, dropper pipette, measuring pipette, volume pipette, power supply, stopwatch, UV-Vis spectrophotometer, scales analytic, cuvette, goblet, digestion vessel, heating block.

### 2.3. Research materials

Materials used in this study include;  $\text{Ag}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{HPO}_4$ ,  $\text{HgSO}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{NaOH}$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ , distilled water, N,N dimetil-p-fenilendiamin oxalic,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{KI}$ ,  $\text{I}_2$ ,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , kanji, salicylic acid, zinc acetate,  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$

### 2.4. Work Procedures

#### 2.4.1. Dilution of liquid waste

Ethanol waste taken before treatment is diluted using water in a ratio of 1: 500

#### 2.4.2. Testing of initial waste levels

Ethanol waste that has been taken is tested by COD and Sulfide parameter levels as comparison levels after treatment

#### 2.4.3. Electrolysis

After conducting the initial testing, as much as 1000 ml of waste is put into the beaker. Then the aluminum electrode is installed as the anode on the pole (-) and the copper electrode as the cathode is mounted on the pole (+). The two electrodes were inserted into a beaker containing a waste sample with a distance of 5 cm, the power supply was turned on with a voltage variation of 5, 10, 15 volts and with a variation of treatment time of 10, 15, 20, 25 and 30 minutes in each sample. Then each sample with a

different voltage and treatment time is carried out the COD and sulfide analysis process.

#### 2.4.4. COD analysis

##### 2.4.4.1. Making digestion solution

Mix 1.022 g of  $\text{K}_2\text{Cr}_2\text{O}_7$  that has been dried at  $150^\circ\text{C}$  for 2 hours then add 500 ml of distilled water, add 167 mL of concentrated  $\text{H}_2\text{SO}_4$  and 33.3 g of  $\text{HgSO}_4$  and cool at room temperature then dilute to 1000 mL.

##### 2.4.4.2. Manufacture of sulfideic acid reagents

Dissolve 10.12 g of  $\text{Ag}_2\text{SO}_4$  crystal into 1000 mL concentrated  $\text{H}_2\text{SO}_4$  then stir until dissolved.

##### 2.4.4.3. Analysis of COD levels

Measurement of COD levels using the closed reflux method, where the sample was added with a digestion solution and sulfuric acid reagent solution which was first refluxed at a temperature of  $150^\circ\text{C}$  for 2 hours.

#### 2.4.5. Sulfide analysis

##### 2.4.5.1. Test preparation

Mix 1.022 g of  $\text{K}_2\text{Cr}_2\text{O}_7$  that has been dried at  $150^\circ\text{C}$  for 2 hours then add 500 ml of distilled water, add 167 mL of concentrated  $\text{H}_2\text{SO}_4$  and 33.3 g of  $\text{HgSO}_4$  and cool at room temperature then dilute to 1000 mL.

##### 2.4.5.1.1. Standardization of sodium thiosulfate solution with potassium bi-odate

Dissolve 2 g of  $\text{KI}$  in 300 ml size erlenmeyer ash with 100 ml of sulfide free water. Add 1 mL of 6 N sulfideic acid and add 20 mL of a standard solution of potassium bi-odate to an erlenmeyer containing  $\text{KI}$ . Place for 5 minutes in a dark room and dilute to 300 mL then titrate with sodium thiosulfate to light yellow color. Add 1 ml of the starch indicator and titrate to the end point marked by the loss of blue.

##### 2.4.5.1.2. Manufacture of main liquor

Weigh 3.75 g of sodium sulfide ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ) in a weighing bottle. Transfer quantitatively into a 500 mL volumetric flask and place it until the marking mark with sulfide free water. (1 mL = 1.00 mg  $\text{S}^{2-}$ ). Standardize the solution with iodometric titration

##### 2.4.5.1.3. Preparation of 100 mg sulfide standard solution $\text{S}^{2-} / \text{L}$

Dilute 10 mL of 1000 mg sulfide master solution  $\text{S}^{2-} / \text{L}$  with sulfide free water into 100 mL measuring flask until the

##### 2.4.5.1.4. Manufacture of sulfide working solutions

Make a working solution series from the standard 10 mg  $\text{S}^{2-} / \text{L}$  sulfide solution with 1 blank

and at least 3 different levels in a 50 mL volumetric flask.

#### 2.4.5.2. Making calibration curves and measuring test samples

##### 2.4.5.2.1. Making a calibration curve

As much as 50 mL of sulfide-free water is put into a measuring flask then add 0.5 mL H<sub>2</sub>SO<sub>4</sub> and 3 drops of FeCl<sub>3</sub> and mix, then wait for 5 minutes. Add 1.6 mL of diammonium hydrogen phosphate solution. This solution is used as a zero instrument. To the working solution series and blank add 0.5 mL of sulfideic-amine acid reagent and 3 drops of FeCl<sub>3</sub> solution. The mixture is immediately converted slowly and wait for minutes. Add 1.6 mL of HPO<sub>4</sub>(NH<sub>4</sub>) solution, let stand until it forms a blue color.

##### 2.4.5.2.1. Test for sulfide content

Put the test sample into a 50 mL volumetric flask and then dilute with sulfide free water to the pitch mark, add 0.5 mL of amine sulfideic acid reagent and 0.15 mL of FeCl<sub>3</sub> solution. The mixture is immediately converted slowly. Add 1.6 mL of 2HPO<sub>4</sub>(NH<sub>4</sub>) solution then let stand for 10-15 minutes read and record the absorption of the test sample.

### 3. RESULT AND DISCUSSION

Wastewater can contain substances that are highly toxic to aquatic life and human populations. The pollutants may be dissolved or suspended in the water. Toxic contaminants, both organic and inorganic are carried by suspended particles and dissolved in the water, increasing the organic load and transporting hazardous chemical compounds (Burroughs and Burroughs, 2011).

Chemical Oxygen Demand (COD) is the chemical oxygen demand test (COD) determines, the oxygen required for chemical oxidation of organic matter with the help of strong chemical oxidant. The COD is a test which is used to measure pollution of domestic and industrial waste. The waste is measure in terms of required for oxidation of organic matter to produce CO<sub>2</sub> and water (Candia-Onfray et al., 2018).

Hydrogen Sulfide (H<sub>2</sub>S) is a colorless, very poisonous gas flammable. This gas can cause bad effects for health. At low concentrations it can cause eye, nose or irritation esophagus, and for a long time can cause permanent effects like respiratory disorders, headache, and chronic cough. Even exposure to hydrogen sulfide in concentrations higher than 500 ppm can result in loss of consciousness and maybe death (Pakpahan, et al. 2015).

**Tabel 1. the initial levels of COD and Sulfide**

Parameter	Highest Level (mg / L)	Pollution load (kg / ton)
BOD <sub>5</sub>	100	1.5
COD	300	4.5
TSS	100	1.5
Sulfide (as S)	0.5	0.0075
pH	6.0-9.0	
Highest waste discharge	15 m <sup>3</sup> per tonne of tapioca products	

To find out the effect of the treatment, two parameters of waste are used namely COD and sulfide. The following table shows the results of initial levels of ethanol liquid waste

**Tabel 2. the initial levels of COD and Sulfide**

Sample	Unit	COD	Sulfide
Initial	mg/L	586	0.305
Electrolysis	mg/L	284.5	0.0661

At first the COD level was 586 mg / L. After treatment, the waste COD level becomes 284.5 mg / L, so the effect given from this treatment is 51.45%. For the initial comparison, the sulfide content of the ethanol waste is 0.305 mg / L. After treatment using electrolysis the level changed to 0.0661 mg / L, meaning that the effect given from this stage on sulfide levels was 78.32%.

**Tabel 3. the results of the analysis of the influence of voltage variations**

Parameter	unit	Voltage ( volt)		
		5	10	15
COD	mg/L	466.5	488	426.5
Sulfide	mg/L	0.029	0.033	0.017

Table 3 is the result of electrolysis treatment with voltage variations with a testing time of 10 minutes. The COD and sulfide parameters occur irregularly from their initial levels. From this it is known that stress has a very significant effect on COD treatment. Among these variations (5 volts, 10 volts, 15 volts) the 10 volt voltage gives a less significant effect because the COD level becomes 488 mg / L which means the level of decrease is 16.72%. Whereas for 5 volt voltage there was a significant decrease to 466.5 mg / L which means that the level of reduction was 20.39%. For the voltage of 15 volts,

the greatest decrease occurred compared to 5 and 10 volts, which is 426.5 mg / L, which means the rate of decrease is 27.21%. As for the sulfide content, the greatest effect also occurs at a voltage of 15 volts until the sulfide level becomes 0.017 mg / L, which means that the reduction level is 94.42%. The 10 volt voltage has a significant effect because the sulfide level becomes 0.033 mg / L which means that the reduction level is 89.18%. The 5 volt voltage has a significant effect also because the COD level becomes 0.029 mg / L which means that the reduction level is 90.49%. When viewed from the percentage decrease for both sulfida parameters voltage of 5v, 10v, and 15v the difference is not too significant compared to COD where the percentage decrease is quite large.

**Tabel 4. The results of the analysis of the influence of time variations**

Parameter	Units	Time ( minutes )				
		10	15	20	25	30
COD	mg/L	344.5	319.5	324.5	317	284.5
Sulfide	mg/L	0.0901	0.0803	0.0829	0.0661	0.0859

Table 4 is the result of electrolysis treatment with a time variation with a test voltage of 15 volts, a selection of 15 volt voltage due to tests that have been carried out before carrying out the time variation test and have been described above. Test results on the COD and sulfide parameters occur irregularity. From this it is known that time has a significant effect on COD treatment. Among these time variations (10 minutes, 15 minutes, 20 minutes, 25 minutes and 30 minutes) the 10 minute time gave a decrease in COD level to 344.5 mg / L which means the level of reduction was 41.21%. Whereas for 15 minutes there was a decrease to 319.5 mg / L which means that the level of reduction was 45.47%. For a period of 20 minutes there was a decrease to 324.5 mg / L which means that the level of reduction was 44.62%. Whereas for 25 minutes there was a decrease to 317 mg / L which means that the level of reduction was 45.90%. For 30 minutes there was a decrease to 284.5 mg / L which means that the level of reduction was 51.45%. From the above results it is known that the greatest decrease in COD parameters occurred in the 30th minute which was 51.45%. As for sulfide levels, for a period of 10 minutes there was a decrease to 0.0901 mg / L which means that the levels decreased by 70.45%. for 15 minutes there was a decrease to 0.0803 mg / L which means that the level of reduction was 73.67%. for a period of 20 minutes there was a

decrease to 0.0829 mg / L which means that the level of reduction was 72.81%. for a period of 25 minutes there was a decrease to 0.0661 mg / L which means that the level of reduction was 78.32%. And for 30 minutes there was a decrease to 0.0859 mg / L, which means the level of decline was 71.83%. It is known that the biggest decrease occurred in the 25th minute with a decrease in percentage of 78.32%.



**Figure 1. Process of electrolysis**

Figure 1 is a process when the waste is processed using the electrolysis method to reduce the parameters of cod and sulfide as well as other parameters by using aluminum as an anode and copper as a cathode with the help of an electric current. This process aims to reduce levels of waste that exist in the ethanol waste.

The electrochemical process is a very attractive method to extirpate just about any pollutant in water and wastewater involving extremely small particles or toxic organic compounds, and it can dissolve even water itself because of the electrochemical characteristic softthese substances. A number of electrochemical processes have been derived to remove deleterious or dispensable constituents in water, for example, electro-oxidation, electro-degradation, electro-coagulation, electro-flocculation, electro-Fenton process , and so on (Kim et al., 2013). The process occurs in an electrolyte, a watery or a salt melting solution that gives a possibility to transfer the ions between two electrodes. When an electrical current is applied, the positive ions move to the cathode while the negative ions move to the anode. At the electrodes, the cations are reduced and the anions will be oxidized (Chopra, Kumar Sharma and Kumar, 2011).

Before the electrolysis process is carried out, the waste is given a pretreatment by diluting pure waste with water so that it can be analyzed because pure waste is so concentrated that it hinders the analysis process. dilution is done with a ratio of 1: 500.



**Figure 2. The comparison of pure ethanol waste with ethanol waste after diluting**

The picture above illustrates that it is so concentrated in pure waste that it takes time to dilute it with a ratio of 1: 500 until the waste is ready to be tested to determine the content of cod and sulfide. Table 1 is the standard quality of ethanol wastewater issued by the Minister of Environment in the Republic of Indonesia Minister of Environment Regulation number 5 of 2014 concerning the quality standard of wastewater.

#### 4. CONCLUSION

From the research and the results of the discussion, the following conclusions are obtained:

First one, The greater the voltage, the more effective it is to reduce COD and sulfide levels, this is evidenced by the results of the 15 volt voltage test which is greater in reducing COD and sulfide levels than the 10 and 5 volt voltages with decreases in COD and sulfide respectively by 27.21% and 94.42 %.

Second one, The longer the treatment time, the more effective it is to reduce COD levels, this is evidenced by the results of the most effective 30 minute time variation test with a decrease of 51.45%

The longer the treatment time does not affect the effectiveness of the decrease in sulfide parameters, this is evidenced by the results of the test that states that the 25 minute time variation is more effective than the 30 minute time variation with a decrease of 78.32%.

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