Adsorption of Ammonium Ion from Tofu Industrial Liquid Waste by Coconut Shell-Activated Carbon

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ABSTRACT

Liquid waste from tofu industry will flow or discharge into water. It causes pollution which is characterized by unpleasant odor. If this continues, it can damage the environment and threaten the health of the people who inhale the unpleasant odor. Activated carbon is a carbon that is able to adsorb in the liquid phase or gas phase. Activated carbon is the best adsorbent in the adsorption system. The material for activated carbon comes from animals, plants, and waste or minerals that contain carbon. Coconut shell is an ingredient that can be made into activated carbon. Activated carbon from coconut shell has many benefits one of them can adsorb liquid waste from tofu industry. This study aims to examine the ability of coconut shell to adsorben, that have been activated by K_2CO_3 or HCl activator. In this study given the variation of activated charcoal mass and contact time variations to determine the effect on the ability of activated coconut shell charcoal adsorption on ammonia content in Liquid waste from tofu industry. The results of this study are the greater the mass of activated charcoal and the longer the contact time, the greater the ammonia absorbed by activated charcoal, which indicates that the percent decrease in ammonia concentration is greater.

Keyword: tofu liquid waste, activated coconut shell charcoal, ammonia, mass variation, time variation.

1. INTRODUCTION

1.1 Background

Indonesia as a tropical country has abundant natural resources such as coconuts (cocos nucifera) which can be utilized in various way for further study and human needs. The most utilization of coconut is its shells as a charcoal fuel and water filter. Coconut shell charcoal often processed into briquettes and it became activated carbon. These briquettes are used by the community for household, business, and industrial purposes (Bansal & M, 2005). The coconut shell can be used as an adsorbent, however it must be made into charcoal first. Coconut shell is a good material for charcoal because it has a hard property by silicate content (SiO_2), has a high carbon bound content, and has a low mineral ash content. The components of charcoal consist of bonded carbon, ash, water, nitrogen and sulfur. Most of the pores of charcoal are still covered with hydrocarbons, tar, and other organic compounds (Bansal & M., 2005). Activated carbon produced from coconut shell charcoal has a lot of micopri, a large surface area, and a high adsorption power.

In addition, Indonesia is an industrial country. Industry itself is an activity of processing raw materials or semi-finished goods into finished goods that are needed by the community. The industry process offers a positive impact especially on industrial performance. However it offers a negative impact on the environment in the form of air, water, and soil pollution. Generally, the handling of liquid waste is carried out by biological processes. Because liquid waste contain organic content such as carbohydrates, vitamins, and protein. Therefore, it can be degraded by biological treatment. One of the common industries found in Indonesia is the tofu industry (Bansal & M., 2005).

Tofu is a traditional food that is very popular among Indonesian people. Tofu also contains good nutrition (Yuniarti, 2006). Instead of a good taste and a high nutrition of tofu, the process of making tofu undergo in an easy and simple way, and with relatively small cost. Further, traditional tofu making is still commonly found. Thus, it produces an abundance of tofu production waste. The home producing of tofu just thrown away the waste and rarely people utilize it. Still, the liquid waste of tofu industry containing a high protein content; causing gas in the form of ammonia, nitrogen and sulfur which has a stinky odor; and may interfere human health if continuously inhaled.

According aforementioned discussion, this research is aims to investigate the ability of carbon adsorbents in coconut shell charcoal to absorb ammonia (NH_3) in tofu industry liquid waste. Thus, the tofu waste that cause unpleasant odors as air pollution could be reduce. The following research problems were formulated:

1. How is the ability of activated coconut shell charcoal adsorbent that has been activated by HCl on reducing the concentration of ammonia in tofu industry wastewater?
2. What is the effect of variations in contact time of activated coconut shell charcoal on decreasing ammonia concentration in tofu industry wastewater?

2. RESEARCH METHOD

2.1 Research Sample

The sample used in this research was tofu industrial liquid waste that containing ammonia. The parameter tested was the ability of K_2CO_3 or HCl activated coconut shell charcoal to absorb ammonia in tofu industry liquid waste.

2.2 Tools and Materials

The material used consists of tofu industry liquid waste; coconut shell charcoal; solid K_2CO_3; 0.1 M HCl solution; ammonia solution 0.05 M; ammonia solution 0.002 M; distilled water; sodium hypochlorite (NaClO); sodium nitropruside ($C_5FeN_6Na_2O$) 0.01 M; sodium citrate 0.8 M; phenol (C_6H_5OH) 0.01 M; and filter paper. On the other hand, the tools used are measuring cups, test tubes, measuring flasks, analytical scales, pH meters, stirrers, sizing 100 and 120 mesh sizes, reactors, beaker cups, petri dishes, pipettes, ovens, UV-Visible spectrophotometers.

2.3 Research Procedure

2.3.1 Material Preparation

The sample used in this research came from tofu industry liquid waste at Tejokusuman Tofu Factory.

2.3.2 Carbonization Process

The carbonization process began by heating the raw material of a coconut shell that has been removed through a dehydration process at 400 °C. This carbonization process was carried out until a constant weight was obtained. The carbon obtained from combustion was pulverized to facilitate the sifting process. The process of sifting the coconut shell carbon (charcoal) was carried out using a 100-mesh sized sieve.

2.3.3 Charcoal Activation

In this research, 2 different activation processes were carried out, namely activated charcoal with the K_2CO_3 activator and activated with the HCl activator. Activation with K_2CO_3 is done by mixing solid K_2CO_3 with the raw material (coconut shell charcoal) which has been refined by the ratio of the mass of raw material: mass of K_2CO_3 = 1: 1.5. A total of 10 grams of coconut shell charcoal soaked with 15 grams of K_2CO_3 that has been dissolved with distilled water as much as 100 mL. Whereas activation with HCl is done by mixing HCl solution with coconut shell charcoal with a char mass: HCl mass ratio = 1: 1.5. A total of 10 grams of coconut shell charcoal is soaked with 15 mL HCl solution. Furthermore, the charcoal is let to stand for 1 x 24 hours. After the activation process is complete, activated carbon is drained with filter paper and continued by drying the charcoal using oven at 70°C for 2 hours. The activated carbon from the coconut shell charcoal was weighed, when the mass was constant thus the activated charcoal was ready to use.

***2**.3.4 Making the Calibration Curve*

The analysis of ammonia levels began by optimizing the UV-Vis spectrophotometer. The working solution (ammonia 0,002 M) is put into 5 different test tubes with a volume of 1 mL, 3 mL, 5 mL, 7 mL and 10 mL, respectively. Then each tube was added distilled water to a volume of 10mL. After that several reagents in the form of 0.4 mL phenol solution; 0.4 mL sodium nitropruside solution; 1 mL of oxidizing solution were added on each tube. The oxidizing solution was prepared by mixing and homogenizing a total of 100 mL sodium citrate solution with 25 mL sodium hypochlorite. Leave the mixture of this solution for 1 hour to yield a color. After the color was formed, the solution poured into the cuvette and measured with a spectrophotometer. The absorbance is measured at a wavelength of 640 nm. The calibration curve was prepared from the data in order to achieve straight line equation.

2.3.5 Making Blank Solutions

The blank solution was made by mixing and homogenizing a total of 10 mL of distilled water, 0.4 mL of phenol solution, 0.4 mL of sodium nitroprusid solution, and 1 mL of oxidizing solution. After that, poured the solution into the cuvette and record the absorption on the UV-Vis spectrophotometer at a wavelength of 640 nm.

2.3.6 Mass Variation Adsorption

The procedure began by pouring 50 mL of tofu liquid waste industry sample solution into beaker glass. Then, 0.5 grams of coconut shell activated charcoal; 1 gram; 1.5 gram; and 2 grams in each beaker glass were added. Leave the beaker glasses for 20 minutes, while stirring. After that pick a total of 10 mL of each into a test tube. Add 0.4 mL of phenol solution; 0.4 mL sodium nitropruside; and 1 mL of oxidizing solution into each test tube. Leave for 1 hour for the formation of color. After the color is formed, activated carbon is separated from the sample solution using filter paper. Pour the solution into the cuvette and analyse it using spectrophotometer. Read and record its absorption at a wavelength of 640 nm. Adsorption of mass variations was carried out twice with K_2CO_3 activated charcoal and HCl activated charcoal.

2.3.7 Adsorption Time Variations

Prepared 50 mL of tofu liquid waste industry sample solution into four beaker glass. Add coconut shell activated charcoal as much as 0.5 grams on each glass. Leave for 5 minutes, 10 minutes, 15 minutes, 20 minutes, while stirring. After that, pipette 10 mL of solution in each glass then put it into the test tube. Add 0.4 mL of phenol solution; 0.4 mL sodium nitropruside; 1 mL of oxidizing solution. Leave for 1 hour in order to produce color. After the color is formed, activated carbon is separated from the sample solution using filter paper. Pour into the cuvette on analyse it using spectrophotometer, read, and record its absorption at a wavelength of 640 nm. Adsorption of time variation is conducted two times with K_2CO_3 activated charcoal and HCl activated charcoal.

3. RESULTS AND DISCUSSION

3.1 Preparing Active Carbon

The carbon activation process was done by soaking coconut shell charcoal using HCl and K_2O_3 activator. This activation aims to add some new pores and enlarge the diameter of pores that have been formed in the carbonization process. Activation process could crack the hydrocarbons bonds and the organic compounds in the coconut shell; thus, the charcoal has changed its properties, both the physical and chemical. The surface area is increased and affects the adsorptions strength that brings the charcoal is able to adsorb organic compound in tofu waste, especially ammonia. In addition, the amount of charcoal and activators that used were following the ratio of charcoal mass:

activator mass that is 1: 1,5. The mass of charcoal used as much as 10 grams, thus the mass of K_2CO_3 solid being dissolved is 15 grams and the amount of HCl solution is 15 mL (density of HCl 1.015 g/mL).

The ability of K_2CO_3 activation occurs when K_2CO_3 reacts with carbon at atmosphere pressure. During the reaction process, K_2CO_3 will be reduced inertly according to the following reaction equation:

$$K_2CO_3 + 2C \rightarrow 2K + 3\ CO$$
$$K_2CO_3 \rightarrow K_2O + CO_2$$

Based on the observation, there is no difference color of activated carbon that has been activated by HCl and K_2CO_3. The color of both charcoals were deep black. After the activation process was completed, the activated carbon of coconut shell charcoal is ready to be used to adsorb the tofu waste.

3.2 Making Calibration Curve

Calibration curve is a graph that represent the correlation of concentration solution with its absorbance. It presents in the form of straight line and yielding an equation. The absorbance obtained by measuring the sample using UV-Vis spectrophotometer at wavelength of 640 nm. In making calibration curve, a blank solution (a solution containing all reagents except ammonia samples) and ammonia standard solution is needed. The calibration curve collected in this study seen in Figure 1.

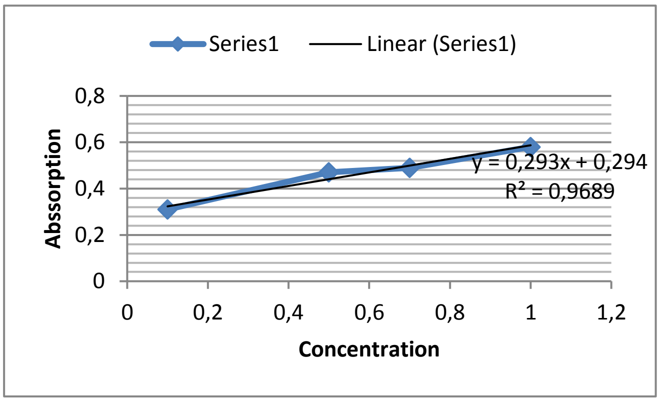

Figure 1. Calibration Curve of Ammonia Standard Solution

Based on Figure 1, it is clearly depicted that the larger amount of ammonia concentration, the larger value of absorbance. The linear equation is $y = 0{,}293x + 0{,}294$. Thus, following those equation, the concentration of ammonia in the tofu waste can be calculated.

3.3 Tofu Waste Adsorption Process

In this research, the measurement of adsorption process of each activiated carbon was varying in the term of the variation and time. This variation aims to determine the concentration of ammonia using phenate method, i.e., the formation of a blue-colored indophenol compound in a range of one hour at room temperature. The phenate method (or phenol) based on Bathelot reaction where ammonia reacts with phenol and hypochlorite in an alkaline conditions. Ammonia is converted to monochloramine at pH 9.7 – 11.5 which reacts with phenol in the presence of hydrochlorine to form the blue-colored indophenol. Sodium nitropusside is used to catalyze indophenol reaction and blue color intensity. The citrate buffer is added to stabilize the pH and prevents the deposition of hydroxide. Furthermore, to know the concentration of ammonia in tofu waste, the titration was perceived and obtained the concentration of ammonia before the absorption process which was 8.085 mg/L.

3.3.1. Mass Variation

Variation of the charcoal mass used were 0.5 grams; 1 gram; 1.5 grams; and 2 grams for tofu samples as much as 50 mL. The mass of the charcoal also varied with the two activators, the HCl and K_2CO_3.

3.3.1.1. Mass Variation with HCl Activator

The adsorption of tofu waste by the charcoal that is activated with HCl obtained the absorbance value after measured using UV-Vis spectrophotometer. From the absorbance data, it can be calculated the concentration of ammonia remaining in the tofu waste and the percentage removal in ammonia concentration can be calculated. The results of adsorption of mass variation with HCl activator presents in Table 1.

Table 1. Adsorption Result of Mass Variation with HCl Activator

Charcoal Mass (gram)	Concentration (mg/L)	Absorbance	Percentage Removal (%)
0.5	1.79	0.821	77.8
1	1.49	0.731	81.5
1.5	1.48	0.728	81.6
2	1.09	0.615	86.5

Based on the Table 1, the more mass of charcoal used, the larger percentage of removal in ammonia concentration in the tofu waste. It means that the more ammonia in tofu waste that is absorbed by charcoal, the more the mass of the charcoal increases.

3.3.1.2. Mass Variation with K_2CO_3 Activator

There is an impact of the mass variation with K_2CO_3 activator to the absorbance of tofu waste. Table 2 shows the findings of adsorption of mass variation with K_2CO_3 activator.

Table 2. Adsorption Result of Mass Variation with K_2CO_3 Activator

Charcoal Mass (gram)	Concentration (mg/L)	Absorbance	Percentage Removal (%)
0.5	2.03	0.890	75
1	1.89	0.850	77
1.5	1.45	0.720	82
2	1.35	0.692	84

Based on the Table 2, the more mass of charcoal used, the less concentration of residual ammonia that is not being held by charcoal and the larger the percent decrease in ammonia concentration in the sample. It means that more ammonia in the tofu waste is absorbed by activated charcoal.

3.3.2. Time Variation

Variation of the time used are 5 minutes, 10 minutes, 15 minutes, and 20 minutes for tofu samples as much as 50 mL for the two activators, the HCl and K_2CO_3.

3.3.2.1. Time Variation with HCl Activator

From the measurement of ammonia concentration after being contact with active carbon signified a decreasing trend. Table 3 presents the adsorption results of time variation with HCl activator.

Table 3. Adsorption Results of Time Variation with HCl Activator

Time (minute)	Concentration (mg/L)	Absorbance	Percentage of Removal (%)
5	1.58	0.731	80.45
10	1.55	0.723	80.83
15	1.48	0.706	81.69
20	1.36	0.673	83.17

The concentration value in the Table 3 shows the remaining concentration of ammonia that isn’t being held by activated carbon. The most effective contact time to reduce the ammonia concentration is a contact time of 20 minutes since it produces greater decrease that is 83.17%. The curve depicts the percentage decreasing trends in ammonia concentration seen in Figure 2.

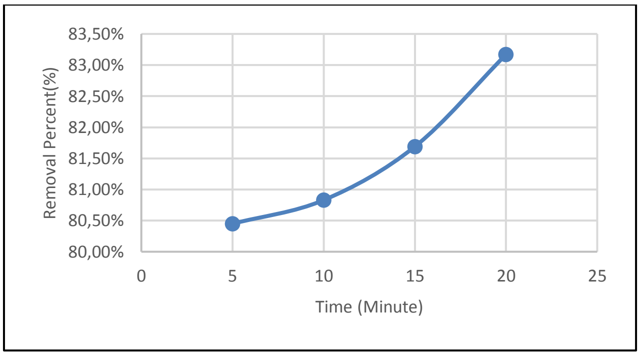

Figure 2. Percentage Decreasing Trends in Ammonia Concentration against Contact Time

The contact time that occurs between sample and adsorbent strongly influenced the absorption process. The longer contact time between sample and adsorbent, the more ammonia can be absorbed by the adsorbent. This is in line with Raghuvanshi et al. (2004) that the capacity will increase the adsorption time at certain point.

3.3.2.2. Time Variation with K_2CO_3 Activator

The contact time that occurs between the sample solution with the adsorbent greatly affects the absorption process. The peak decrease in the concentration of sample occurs within 20 minutes. This is caused by the longer contact time between the sample and the adsorbent, the previously empty pores of the adsorbent will be filled, so that with the increasing contact time, the absorption of the pores will be more maximal. Table 4 showa the adsorption results of time variation with K_2CO_3 activator.

Table 4. Adsorption Result of Time Variation with K_2CO_3 Activator

Time (minute)	Concentration (mg/L)	Absorbance	Percentage of Removal (%)
5	1.70	0.793	78.97
10	1.69	0.788	79.1
15	1.43	0.714	82.31
20	1.11	0.618	86.27

Based on Table 4, the removal percentage increases along with the increasing of the contact time. At the longest contact time (20 minutes), the pore ability of activated carbon to adsorb ammonia is the highest, so the possibility of activated carbon pores closed by ammonia is increasing. Figure 3 presents the relationship of contact time on ammonia concentration in sample.

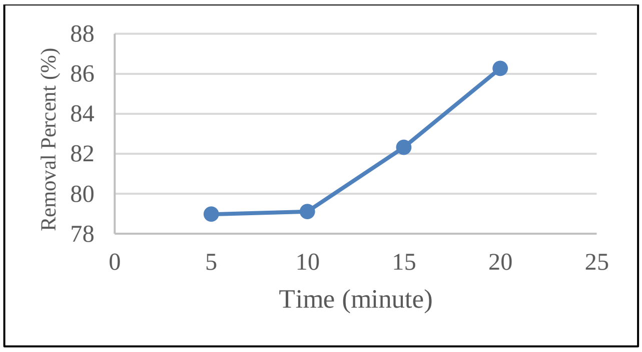

Figure 3. The Realtionship of Contact Time on Ammonia Concentration in Sample.

Based on the data obtained, the percentage of removal is increases along with the increasing contact time. The highest percentage of removal was obtained at 20 minutes by 86.27%. This shows that the pore ability of activated carbon to adsorb ammonia is the highest, thus the possibility of activated carbon pores closed by ammonia is increasing. As seen in Figure 3, it shows that percent removal is directly proportional to the contact time.

4. CONCLUSION

Absorption ability of coconut shell charcoal after activation with HCl is pretty good. HCl is an activator that can produce activated carbon which has a high adsorption power; thus, using HCl as the activator brings much ammonia is absorbed. On the other hand, absorption ability of coconut shell charcoal after activation with K_2CO_3 also signified a good ability to reduce the concentration of ammonia in tofu industry liquid waste. The use of K_2CO_3 activator produced more pores, thus it absorbs ammonia contained in tofu industrial liquid waste.

In addition, the greater the mass of activated coconut shell charcoal that were used, the more the decreasing trends in the concentration of ammonia in tofu liquid waste. It implied that more ammonia is absorbed by activated charcoal. Further, the longer of the contact time of activated coconut shell charcoal, the more of the decreasing of ammonia concentration in tofu liquid waste. It means that more ammonia is absorbed by activated charcoal.

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