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Utilization of Activated Carbon Prepared from Aceh Coffee Grounds as Bio-sorbent for Treatment of Fertilizer Industrial Waste Water

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Abstract. The people of Aceh are well known as coffee drinkers. Therefore, a lot of coffee shops have been established in Aceh in the past decade. The growing of coffee shops resulting to large amounts of coffee waste produced in Aceh Province that will become solid waste if not wisely utilized. The high carbon content in coffee underlined as background of this research to be utilized those used coffee grounds as bio-sorbent. The preparation of activated carbon from coffee grounds by using carbonization method that was initially activated with HCl was expected to increase the absorption capacity. The prepared activated carbon with high reactivity was applied to adsorb nitrite, nitrate and ammonia in wastewater outlet of PT. PIM wastewater pond. Morphological structure of coffee waste was analyzed by using Scanning Electron Microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The result showed that the adsorption capacity of iodine was equal to 856.578 mg/g. From the characterization results, it was concluded that the activated carbon from coffee waste complied to the permitted quality standards in accordance with the quality requirements of activated carbon SNI No. 06-3730-1995. Observed from the adsorption efficiency, the bio-sorbent showed a tendency of adsorbing more ammonia than nitrite and nitrate of PT. PIM wastewater with ammonia absorption efficiency of 56%.

1. Introduction

Used coffee grounds are inexpensive and widely available materials that can be utilized to reduce the levels of nitrite, nitrate and ammonia in wastewater. Coffee grounds are organic materials that can be converted to activated carbon to be used as adsorbent [1,2]. Activated carbon is a porous solid that produced from carbonaceous material by heating at high temperatures. The previous study mentioned that the activated carbon from coffee grounds could adsorb iron and mercury up to 99.43 and 99%, respectively [3]. In this study, the coffee grounds were used as raw material to be prepared as activated carbon. Furthermore, activated carbon was used to reduce the content of ammonia, nitrite and nitrate in the fertilizer industry wastewater effluent.

Activated carbon is an amorphous carbon material consisting mostly of free carbon and has excellent adsorption ability. Activated carbon has been generally used as an ingredient for dye relievers as well as in the application of gas adsorbent, metal adsorbent and so on [4,5]. Used coffee grounds are inexpensive and widely available materials that can be utilized to reduce the content of



ammonia, nitrite and nitrate in wastewater. Activated carbon is a porous solid that can be produced by heating up carbonaceous material at high temperatures. The larger surface area of the activated carbon caused the higher of adsorption capability [6]. Even though the content of ammonia, nitrite and nitrate in the wastewater pond of outlet wastewater treatment unit of PT. PIM are still under the allowed quality standards, but with continuous discharge the levels of those wastes will accumulate and exceed the quality standards especially on the near location of this wastewater treatment unit before it is expanding. The presence of urea in certain concentrations can cause increased growth of algae. In addition to urea, excess content of nitrites and nitrates in the effluent can also cause death to the aquatic organisms. Therefore, proper treatment is required to reduce the negative impacts caused by industrial waste, particularly the urea fertilizer industry.

2. Method

Experiment was conducted as follows: (1) preparation of activated carbon bio-sorbent from coffee waste; and (2) the process of adsorption of ammonia, nitrite and nitrate using a batch process.

2.1. Preparation of activated carbon

Coffee waste was dried under the sun and then soaked in a solution of 0.1 M HCl for 48 hours. Next drained and washed with distilled water to pH neutral. Coffee waste that have been activated chemically then put in oven to reduce the moisture content, finally those materials were inserted into muffle furnace at a temperature of 350°C for 3.5 hours. The produced activated carbon was sieved using a sieve of +80-100 mesh and later activated carbon was stored in a desiccator.

2.1.1. Yield

The yield of activated carbon was calculated by comparing the weight of raw material to the weight of produced activated carbon after carbonization:

$$\text{Yield (\%)} = \frac{b}{a} \times 100\% \quad (1)$$

where: a = initial weight of the carbon (g)
 b = weight of dried carbon (g)

2.1.2. Water content

The water content was determined by comparing the initial weight of the carbon with the weight of dried carbon. 2 grams of activated carbon was put in a porcelain cup that had been weighed beforehand. Afterwards, the cup was placed in an oven at a temperature of 105°C for 3 hours then cooled down in a desiccator and weighed.

$$\text{Water content (\%)} = \frac{(a - b)}{a} \times 100\% \quad (2)$$

where: a = initial weight of the carbon (g)
 b = weight of dried carbon (g)

2.1.3. Ash content

The ash content was calculated by comparing the initial weight of dried carbon with the weight of the ash. 2 grams of activated carbon was put in a porcelain cup that had been weighed previously. Subsequently, the cup was placed in a muffle furnace at a temperature of 600°C for 3 hours then cooled down in a desiccator and weighed.

$$\text{Ash content (\%)} = \frac{a}{b} \times 100\% \quad (3)$$

where: a = weight of the ash (g)
 b = initial weight of dried carbon (g)

2.1.4. Iodine adsorption

A total of 2 grams activated carbon was put into a dark and sealed container. 50 mL of 0.1N iodine solution was added into the container then shaken for 15 minutes and filtered. As much as 10 mL of filtrate was titrated with sodium thiosulfate solution 0.1N. Once the yellow solution about to be disappeared, 1% of starch indicator was added. The titration was then continued right until the blue color disappeared.

$$\text{Iodine Adsorption} \left(\frac{\text{mg}}{\text{g}} \right) = \frac{\left\{ 10 - \left(\frac{N \times V}{0.1} \right) \right\}}{S} \times 12.69 \times 5 \quad (4)$$

where: V = total sodium thiosulfate required
 N = concentration of sodium thiosulfate solution
 S = mass of activated carbon (g)
 12.69 = amount of iodine in accordance with 1 ml of sodium thiosulfate solution 0.1

2.2. Absorption of nitrate and nitrite using batch process

Liquid waste of fertilizer industry as much as 100 mL was contacted with activated carbon as much as 0.2 grams with size of 80-100 mesh at various stirring time. The wastewater before and after contacted with adsorbents was measured the ammonia, nitrite and nitrate concentrations by using spectrophotometry.

3. Result and discussion

Characteristics of activated carbon from Aceh coffee grounds are shown in table 1.

Table 1. Characteristics of activated carbon from Aceh coffee grounds

Parameter	Analysis Results	Quality requirements for activated carbon according to SNI 06-3730-1995
Yield	18.7	-
Water content	6.38	Maximum 15 %
Ash content	1.05	Maximum 2,5 %
Absorption of iodine	856.575	Maximum 750 mg/g

Table 1 shows the analysis results of prepared activated carbon. The result of parameter was the yield value of 18.7, the water content of 6.38%, the ash content of 1.05%, and the adsorption capacity of iodine of 856.575 mg / g. From those characteristics of prepared activated carbon as shown in Table 1 it can be concluded that the prepared activated carbon meet the quality standards in accordance with the quality requirements of activated carbon refer to SNI No. 06-3730-1995.

3.1. Analysis of the functional groups and morphology of prepared activated carbon

Chemical functional groups of samples were identified by using Fourier transformation infrared spectroscopy (FTIR) with a range of 500 to 4000 cm^{-1} . Graph of infrared spectra of samples was shown in figure 1. Figure 1 shows that the results of FTIR analysis on prepared activated carbon before and after adsorption have a bit similar spectra, but there is a change and a shift in the absorption band in each region after adsorption process with the sample waste of nitrite and nitrate, in which the occurrence of absorption band shift was predicted due to the process of interaction that occurs is physically caused by the force of van der Waals or hydrogen bonds. This suggests that the interaction between waste of nitrite and nitrate with functional groups that existing on the surface of the adsorbent can occur through interaction of the van der Waals, hydrogen bonding, ion exchange or complex formation and this usually occurs on the surface of a solid-rich functional group [7,8].

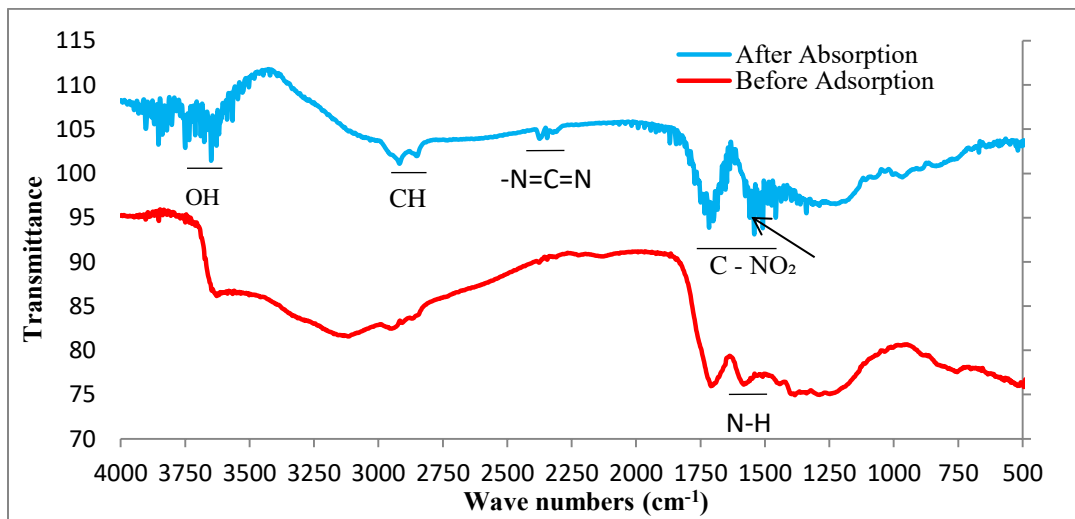


Figure 1. Spectra of prepared activated carbon.

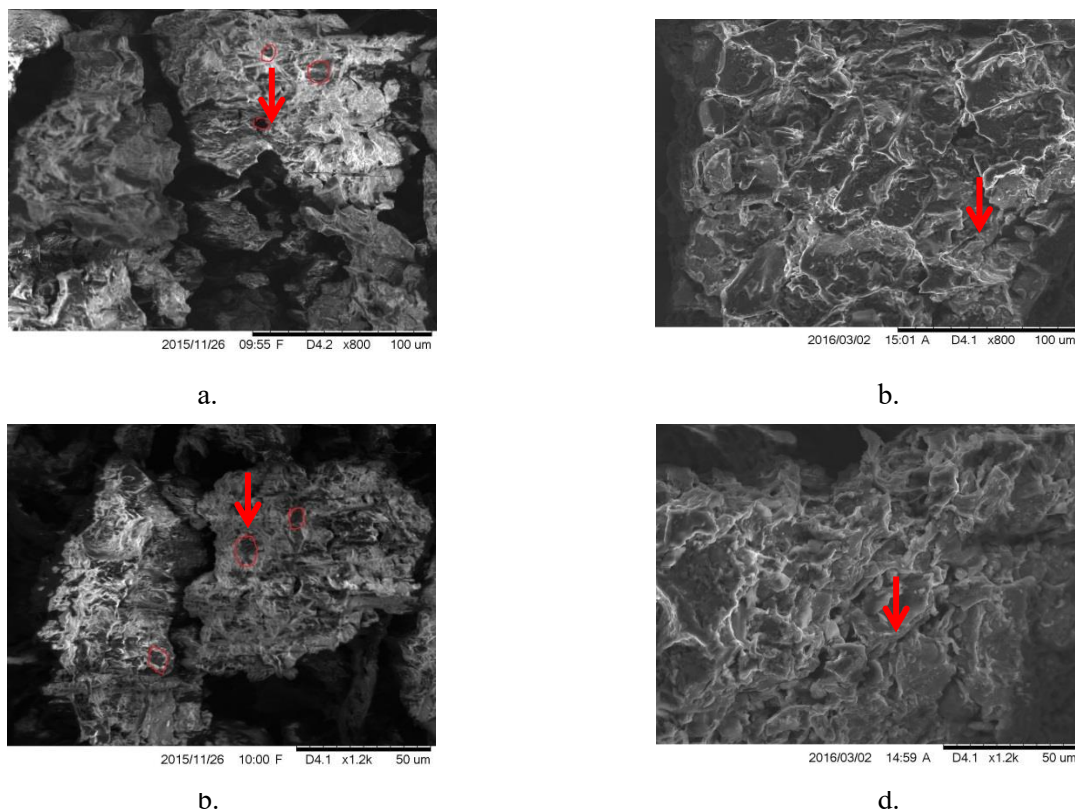


Figure 2. SEM pictures of prepared activated carbon: a. prior to adsorption process with a magnification of 800X, b. After adsorption process with 800X, c. prior to adsorption with a magnification of 1200X, and d. after adsorption with a magnification of 1200X.

The functional group obtained after analysis by FTIR is an OH group (alcohol) with a length of absorption bands (3580-3650) cm^{-1} , CH with a length of absorption bands (2900-3300) cm^{-1} , group -N=C=N (Isocyanides) with a length of absorption bands (2240-2275) cm^{-1} , group NH (amine) with a length of absorption bands (1575-1650) cm^{-1} and group NO_2 with a length of absorption bands (1550-1570) cm^{-1} . Deeply it can be seen from arrow sign inside the figure the distinguishing of the absorption bands before and after absorption that refer to the existence of nitrite and nitrate components in the liquid waste. Morphological structure of the prepared activated carbon was

characterized by using Scanning Electron Microscope (SEM). SEM characterization results can be seen in figure 2 that shows the surface shape of each sample before and after the adsorption of nitrite nitrate.

Even though the results of SEM analysis are not so focus but the figure shows clearly some differences on each figure. On activated carbon sample before contacting with the adsorbate, it can be seen many visible and empty pores as shown by the arrow in figure 2. However, on sample of activated carbon after contacting with the adsorbate it seem that some visible pores were filled by a substance but not yet fully charged (as shown by the arrow). Pores contained in prepared activated carbon may enhance the ability to adsorb adsorbate concentration. In this study, it is predicted that adsorption process of the nitrites and nitrate occurs on the pores surface of the prepared activated carbon.

3.2. The adsorption efficiency of nitrite and nitrate in liquid waste of PT PIM

The adsorption efficiency stated the percentage of adsorbate adsorption on the surface of adsorbent. This adsorption efficiency is influenced by the concentration of adsorbate, where the increase of concentration of adsorbate will also increase the adsorption efficiency. The adsorption efficiency of nitrite and nitrate in liquid waste of PT PIM can be seen in figure 3.

SEM pictures of prepared activated carbon

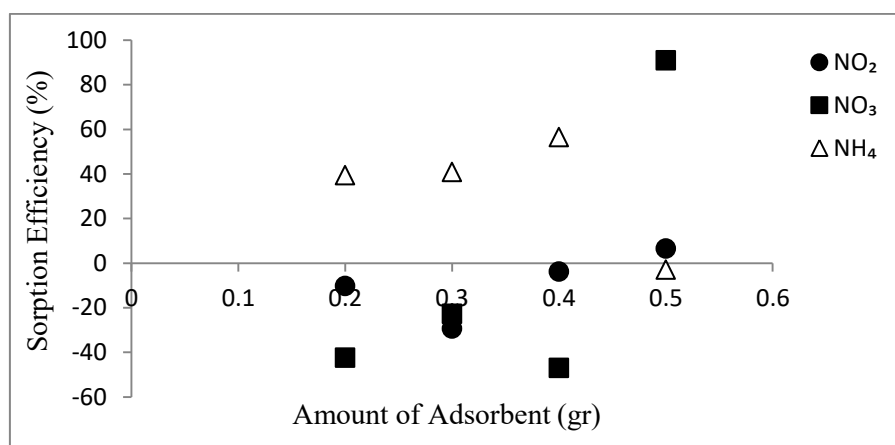
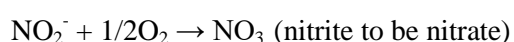
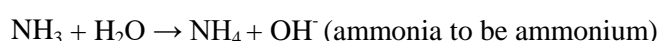


Figure 3. The adsorption efficiency of nitrite and nitrate in liquid waste of PT PIM at contact time of 40 minutes.

With increasing the used adsorbent amount, therefore the adsorption efficiency would also increase. The increasing of adsorbent weight is proportional to the increase the number of particles and the surface area of activated carbon, causing a number of binding levels of nitrite, nitrate and ammonia also increases and as a result the adsorption efficiency also increases [9]. From the above figure we can see that the adsorbent cannot adsorb all of the three components in the waste at the same time of adsorption process, but adsorbent would tend to absorb more ammonia component compare to nitrate nitrite components. Most ammonia in nature and in the wastewater is oxidized to form nitrite and nitrate that are carried out by two kinds of autotroph bacteria during nitrification process following reaction:



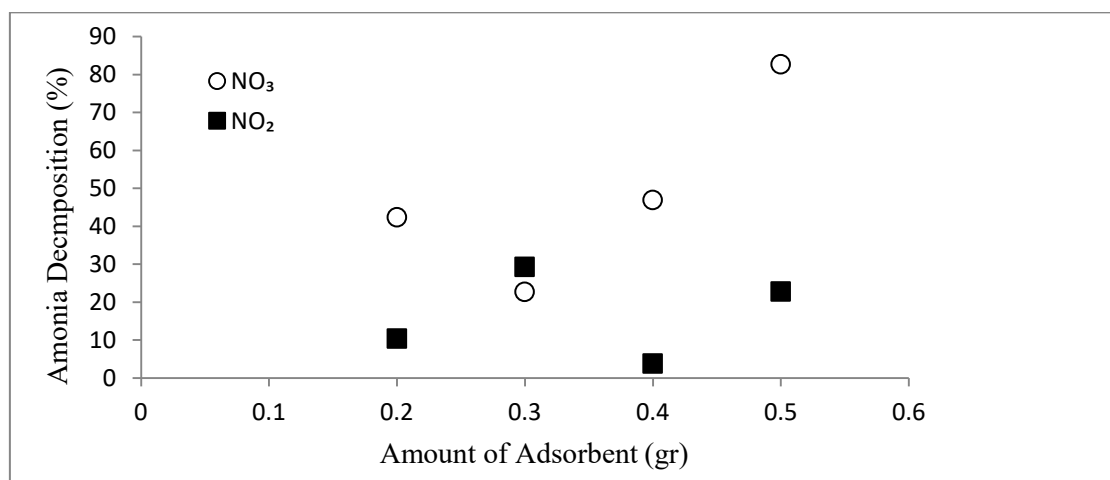


Figure 4. Percentage of ammonia decomposition after adsorption process for 40 minutes

Activated carbon from waste coffee grounds prefer absorbed components of ammonia, and ammonia remaining in the waste reacted quickly to form nitrite and nitrate and as a result the components of nitrites and nitrates in the effluent increased. From the above figure we can see that is likely to occur due to the interaction between the components in the waste cause decomposition ammonia into nitrite reached 30% and finally decompose again to be nitrate as much as 80%.

4. Conclusion

The analysis results of prepared activated carbon meet quality standards that are permitted by SNI No. 06-3730-1995. The prepared activated carbon has the capacity to absorb nitrites, nitrate and ammonia, however the adsorbent tend to adsorb more ammonia compare to sorb nitrite and nitrate. The highest ammonia adsorption efficiency was 56%. The results showed that the remaining ammonia decomposes into nitric reached 30% and breaks down into nitrates by 80%.

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