Characterization of morphological changes on modified sugarcane bagasse with potassium hydroxide

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Abstract. In-depth research is needed to determine the characteristics of sugarcane bagasse as biosorbent. The aims of present work to determine the morphological changes of modified sugarcane bagasse. Modified sugarcane bagasse (MSB) is made by soaking it in a KOH 0.1 N solution overnight, filtered and rinsed with distilled water and neutralized with CH₃COOH 1%. After drying and sieving with a size of 60 mesh, MSB is interacted with Fe solution. The change in MSB morphology was analyzed by comparing IR spectra and SEM images of sugarcane bagasse SB, MSB and MSB samples that have adsorbed Fe. The SEM image and IR spectra of products showed that the addition of KOH and adsorption of Fe on MSB did not cause damage to cellulose and hemicellulose structures. Significant changes in absorption bands occur at 1,725 cm⁻¹ wave number which shows changes in the carboxylic group and is thought to bind Fe. Other changes occurred at wave number 1,247 cm⁻¹, 1,604 cm⁻¹, 1,515 cm⁻¹ and 1,458 cm⁻¹ which are typical for lignin. The SEM image also supports the partial dissolution of lignin.

1. Introduction
The growth of industry and population in developing countries has led to an increase in the use of heavy metals to increase the flux of metal compounds in the aquatic environment. Metal-producing contaminant industries include metal processing and coating, mining, painting, battery, leather tanning and circuit board fabrication as well as agricultural activities that use fertilizers and fungicides intensively. Most of these metals are non-biodegradable, recalcitrant and persistent so they become a serious problem in the environment. Its presence in rivers and lakes has been responsible for several health problems in animals, plants and humans [1,2,3,4].

According to Talokar [5] to control pollution, prevention or processing options can be chosen. Efforts to prevent waste at its source will require much cheaper costs than the method for treating wastewater. Minimizing pollutants can be done by modifying the process, replacing basic materials, product design and fabrication modifications.

Several types of metal removal methods carried out include ion exchange, precipitation, reverse osmosis, vacuum evaporation / evaporation, chemical reduction, membrane technology, solvent extraction and electro dialysis. These methods are less economical because they require a lot of reagents and energy, produce toxic sludge or other waste that must be managed further [3,4,6,7].
The adsorption process is an effective method for removing metal contaminants because many types of adsorbents are available, easy to implement and efficient. The most widely used adsorbent material is activated carbon. But activated carbon is relatively expensive and its use requires a regeneration process that causes part of the carbon to be damaged [4,8].

To overcome this problem, the application of adsorption is directed to produce inexpensive adsorbents. Biomass waste from agriculture activity is one of the attractive alternative adsorbents because it is abundant and inexpensive. Some biomass wastes that have been studied include empty coconut bunches, tamarind seeds, cassava and cassava fiber, coconut peel, peanut shells, tea leaves, cashew nut shells, seaweed or sea algae, biomass slaj, sunflower stalks, Eucalyptus bark, corn husk, tea waste, rice straw, plant leaves, peanut shells and walnuts [3,4,7].

One of the abundant biomass wastes is sugarcane bagasse. The total production of dried bagasse in the world is around 54 million tons per year. This waste has been widely studied as metal adsorbent Cd, Pb, Cr, dyes and oil. Bagasse is one of the most potent biomass. In 2013, the area of sugar cane plantations in Indonesia was 470.94 thousand hectares [9]. In 2014 it increased to 472.68 thousand hectares and in 2015 it declined again to 455.82 thousand hectares. Sugar cane plantations are spread in nine provinces namely North Sumatra, South Sumatra, Lampung, West Java, Central Java, D.I. Yogyakarta, East Java, Gorontalo and South Sulawesi [10]. Of all sugar cane plantations in Indonesia, 50% of them are community plantations, 30% are private plantations, and only 20% are state plantations. In 2002 Indonesian sugar cane production reached ± 2 million tons [11].

Pham [12] examined the adsorption capacity of sugarcane pulp modified with citric acid (CA), NaOH and hydroxide peroxide to adsorb Cd ions from water. Modified bagasse and bagasse were characterized by scanning electron microscopy (SEM) and IR spectroscopy. Surface analysis with SEM shows that the adsorbent pores are relatively large and well developed. The factors that influence the removal of Cd (II) are examined in batches including contact time, pH and adsorption kinetics. The results showed that the adsorption kinetics corresponded to the Langmuir isotherm model and the maximum adsorption capacity was 80.3 mg/g for SHS, 90.9 mg/g for CAS and PHS at pH 6.5 and 60 minutes contact time.

Chand [13] performed batch adsorption of As (III) and As (V) from aqueous solutions on bioadorbent media made from bagasse which was impregnated with Fe (III). The observed variables included the effect of pH, adsorbent dose, adsorbate concentration and contact time. The results showed that maximum adsorption occurred at pH 8 for As (III) and pH 5 for As (V). The optimum contact time is 4 hours for As (III) and 3 hours for As (V), each with an initial concentration of 5 mg/L. The maximum adsorption capacity of As (III) is 25 mg and against As (V) 70 mg/g, for the adsorption of As (III) and As (V), respectively. The adsorption kinetics corresponds to the order of pseudo 2 with the Langmuir isotherm model. This study concluded that sugarcane pulp impregnated with Fe (III) is an efficient, environmentally friendly and economical adsorbent to exclude As (III) and As (V).

Tchoumou [14] studied the adsorption capacity of bagasse which was modified with HCl and NaOH to remove Cu and Ni metals. Research carried out at room temperature includes the influence of pH, contact time, and weight of the adsorbent. The results showed that the increase in pH, contact time and adsorbents, the adsorbed metal also increased. It was also observed that modified bagasse with alkaline was more efficient than HCl; and efficient adsorption of Cu (II)> Ni (II).

Nguyen [15] compared the adsorption capacity of modified bagasse with NaOH, citric acid, tartaric acid and native sugarcane bagasse (unmodified sugarcane bagasse) to cadmium (Cd) metal. The results showed the increasing in adsorption capacity after the chemical modification process. Modification with citric acid produced the highest adsorption capacity, which was 45.45 mg/g. Bagasse modified with tartaric acid had an adsorption capacity of 38.46 mg/g and modified with NaOH of 29.41 mg/g. Unmodified sugarcane bagasse had an adsorption capacity of only 18.8 mg. The results of IR spectra confirmation for modified bagasse showed the addition of carboxyl groups and ester groups at a peak of 1,738 cm\(^{-1}\), thereby it increased the adsorption capacity.
Various studies have been carried out showing changes in the surface of the adsorbent after undergoing the modification process. In this research, it will study modification of sugarcane bagasse with KOH to compare the surface morphology before and after modification and after adsorbing Fe.

2. Research method
Materials used include sugarcane bagasse (from Madukismo sugar factory, Yogyakarta), sulfuric acid solution (H$_2$SO$_4$ 98%), ferric ammonium sulfate analysis grade, potassium hydroxide solution (KOH), acetic acid (CH$_3$COOH), distilled water, and Whatman 42 filter paper. While the equipment were a set of glassware, analytical balance, IR spectrophotometer, SEM micrographs, micro pipette, hot plate, magnetic stirer, desiccator, sieve size 60 mesh, shaker, oven and pH-meter.

The making of Modified Sugar Cane was done by cutting into pieces with a size of about 2 cm, washed thoroughly with distilled water and dried in the sun until completely dry. Dry bagasse was soaked in 0.1 N KOH solution for a night, then filtered and rinsed with aquabides To remove the remaining KOH, bagasse was soaked in 1% CH$_3$COOH solution for 2-3 hours and washed again with aquabides until pH neutral. This material was dried in an oven at 105°C and blended, then sieved with a size of 60 mesh and kept tightly in an airtight container.

The interaction of adsorbent with Fe was carried out by adding 250 µL of 1000 ppm standard Fe solution, diluted to 25 mL, interacted with 125 mg modified bagasse. The solution was shaken with 60 minutes, then allowed to stand for 10 minutes, filtered, and dried at a temperature of ± 105°C until constant weight.

Identification of sugarcane bagasse functional group with modified sugarcane bagasse was carried out by FT-IR spectroscopy. Three sugarcane bagasse samples (which were still original, modified or had adsorbed Fe) weighing 1 mg per sample mixed with 100 mg of dry KBr, then made pellet to be analyzed with FTIR spectrophotometer. The three spectra obtained were compared and analyzed to determine changes in the functional groups on the surface of sugarcane bagasse

Microstructure analysis and surface morphology of the adsorbent were carried out by scanning the sample using an electron microscope (scanning electron microscope: SEM). To increase conductivity and prevent electron loading, dry samples were coated in thin gold in a vacuum, then scanned and recorded the SEM image. The acceleration of the voltage was 10 kV. The results obtained were used to analyze changes in the surface morphology of the adsorbent [16,17].

3. Result and discussion
Milled bagasse can be shaped like particles of needles. The moisture content of the raw material is determined by heating 1,000 g of bagasse in the oven at a temperature of 105 ± 2°C for 3 hours. The results show the moisture content of 4.7 - 8.6% depending on the size of the grain. The smaller size of the grain obtained less water content.

Comparison of Infrared (IR) bagasse with modified bagasse can be seen in Figure 1. IR spectra of original bagasse (before modification with KOH) are pink, after modification with KOH before being used to adsorb in black Fe and after bonding Fe in red.

**Figure 1.** IR spectra of bagasse (a) not yet modified (pink line, in the middle), (b) modified KOH, not yet adsorbing Fe (blue line, bottom), (c) Already bonding Fe (red line, top).
On the three curves, there is a wide band at a wavelength of around 3800 - 3000 cm\(^{-1}\) which shows the vibration of the O-H group, hydrogen bonds in the OH group and intra-molecular and intermolecular hydrogen bonding bands. So this area illustrates the relationship of cellulose crystallinity structure.

The results indicate that the original sugarcane bagasse as well as that modified with KOH and those have been interacted with Fe show that the intensity and width are the same in all three spectra. This indicates that the O-H group in the sugarcane bagasse modified with KOH has not changed crystallinity of cellulose. It is also indicates that functional groups is not an adsorption site for Fe. According to Chandel [18], hydrolysis with strong bases of NaOH causes the breakdown of intra-molecular hydrogen bonds in cellulose and damage to cellulose crystal structures. KOH which is a softer base than NaOH is suspected not to damage intramolecular hydrogen bonds through OH groups or cellulose crystallinity.

The change in the cellulose structure of bagasse was also supported by data that did not change the peak intensity in the area of 2,850 cm\(^{-1}\) due to symmetrical CH and CH\(_2\) stretching characteristic for cellulose.

In the area around 2,994 - 2,895 cm\(^{-1}\), there is a low intensity peak which shows the vibrations of the C-H and O-CH\(_3\) reinforced bands in about 1,600-1,700 cm\(^{-1}\) which shows the presence of C-H bonds in aromatic rings. The peak intensity in the area around 2,994 - 2,895 cm\(^{-1}\) did not show a change in the original bagasse spectra, which was modified with KOH or those that have adsorbed Fe. It is estimated, the modification process with KOH and Fe adsorption does not cause changes in the aromatic ring structure in the matrix of the bagasse. The band is around 1,733 cm\(^{-1}\) characteristic for stretching C = O unconjugated hemicellulose.

Significant changes in peak intensity were observed in the area of 1,725 cm\(^{-1}\) wavelength. This peak was only observed in bagasse which had not been modified and showed the presence of the HO-C=O carboxylic acid group. This peak loss in sugarcane pulp spectra is modified by KOH and bagasse which adsorb Fe is suspected because the OH group of vibration energy decreases dramatically because the H atom is substituted by a much heavier K (of KOH) atom. Likewise, when adsorbing Fe, it is assumed that the OH group in this carboxylic plays a role [19].

Alkaline hydrolysis also affects the peak intensity of 1,247 cm\(^{-1}\) due to the loss of lignin. The 1,604 cm\(^{-1}\) band is a stretch of C = C and C = O lignin aromatic ring, reinforced by a band of about 1,515 cm\(^{-1}\) which shows a stretch of C = C aromatic lignin ring, while the band at about 1,458 cm\(^{-1}\) shows the CH\(_2\) and CH\(_3\) deformation lignin. The bands appear to decrease in intensity after the addition of KOH. Although not as strong as the influence of NaOH, it is thought that KOH has a role in the process of delignification of bagasse components.

The area of the wavelength of around 1,450 to 1,300 cm\(^{-1}\) shows a large molecular coupling which causes the spectra of this area to be very complicated, involving a superposition of several types of vibrations in lignin and carbohydrates.

The area between 1,200 and 1,100 cm\(^{-1}\) is the main contributor of cellulose and hemicellulose. Its highest peak is around 1,035 cm\(^{-1}\) derived from stretching vibrations C-O and 1,164 cm\(^{-1}\) from asymmetrical C-O-C stretches. The tape at 898 cm\(^{-1}\) is characteristic for the glycoside bond β-(1 → 4) in cellulose. The unchanging peaks in this area after the modification process with KOH and adsorption on Fe indicated that the two processes did not affect cellulose and hemicellulose. This is also in line with the observations of Guilherme [17] who concluded that the pre-treatment with bases of bagasse would not change cellulose specific peaks and hemicellulose in IR spectra.

The results of microstructure analysis and surface morphology of the adsorbent are shown in Figure 2.
Figures 2a, b and c show the SEM image of unmodified bagasse. All three show a compact structure, bound together. In Figure 2a shows that the bagasse is composed of fibers which are indicated by parallel lines and core parts arranged on sheets. Both the surface of the fiber and the core show impurity residues (Figure 2b and 2c).

After experiencing the treatment of addition of KOH 0.1 N, SEM image was obtained Figures 2d, e and f. Compared to the addition of KOH, it was seen that the structure of the fiber and nucleus was more clearly separated even though the shape was still relatively the same. Fiber and core surfaces are also cleaner than residues as shown in Figures 2e and 2f which show fibers and nuclei in more detail.

**Figure 2.** Bagasse that has not been modified, has been modified and has already adsorbed Fe.
Allegedly this happened because of the dissolution of some of the lignin components after the addition of the base.

Morphological changes in bagasse which have been modified with KOH and adsorb Fe are seen in Figures 2g and 2h. After adsorbing Fe fiber separation is increasingly apparent. It is suspected that the fiber is separated from each other by inter-molecular hydrogen bonds on the carboxylic group that connects the fibers into a break. This happens because the H atom in the carboxylic group is replaced by the K atom when KOH is added, then this K atom will be replaced by Fe in the adsorption process. This is supported by changing IR spectra which show changes in the intensity of the area around 1,725 cm$^{-1}$ which is suitable for OH carboxylic groups.

4. Conclusion

Based on the comparison of IR spectra of original sugarcane, which is modified by KOH 0.1 N and which has adsorbed Fe, the addition of KOH and adsorption to Fe metal does not damage the cellulose structure in bagasse. The damage to the cellulose structure is beneficial for the adsorption process because it will provide a large enough surface area.

Addition of KOH and adsorption to metal Fe will cause a decrease in the band intensity of the area of 1,725 cm$^{-1}$ originating from the carboxylic group. It is assumed that this group acts to bind K of KOH through ion exchange with H atoms. This exchange will result in reduced inter-hydrogen bonds.

Changes in peak IR spectra were also observed in the area of 1,247 cm$^{-1}$ which is typical for lignin. This is also supported by 1,604 cm$^{-1}$ peaks, 1,515 cm$^{-1}$ and 1,458 cm$^{-1}$ which are typical for lignin. The SEM image also supports the partial dissolution of lignin.

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