Corn Husk as Anionic Surfactant Biosorbent in Detergent Waste

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Abstract

Corn Husk contains cellulose which has potential to become a biosorbent of anionic surfactant. This research aimed to know the optimum mass of corn husk biosorbent to reduce the amount of anionic surfactant in detergent waste and knew the characteristic of the biosorbent pores by using *Scanning Electron Microscope* (SEM). This research used activation method by using NaOH 5 % for 90 minutes, and used mass variation 28 gr, 32 gr, 36 gr. The amount of anionic surfactant was determined with MBAS method. The result of SEM showed that the diameter of the biosorbent pores got larger after being activated from 2.12 nm to 3.41 nm. This experiment showed that activation had removed lignin which was bound to cellulose. The optimum mass of biosorbent was 32 gr which had reduced the amount of anionic surfactant from 92.8 mg/l to 77.9 mg/l with maximum adsorption capacity 0.1862 mg/g.

INTRODUCTION

Water is an important natural resource for human. The average water requirement is 60 liters/person/day in meeting their daily needs (Utomo et al., 2018). Clean water which meets health requirements must be free from pollution and meet standards so it will not interfere organism's health. However, along with the increasing use and production of chemicals in household industries, the types and amounts of pollutants in water are also increasing.

Detergent is one of the chemicals that is often used in households and represents one of the pollutants found in water. The main compounds contained in detergents is surfactants which can reduce the surface tension of water (Sugiharto, 2014). One of the surfactants found in detergents is anionic surfactant, which is a surfactant whose it's tail is attached to an anion group. Anionic surfactants are the most widely used surfactants, which is 50%, non-ionic 45%, cationic 4% and amphoteric only 1% (Wardah, 2012).

The use of detergents from domestic waste that continues to increase will cause environmental pollution because some detergent ingredients cannot be degraded by microorganisms in water. Maqfirah's research (Maqfirah, 2015) stated that the effect of anionic surfactants on tilapia was to inhibit growth and cause gill damage in fish. In addition, anionic surfactants in detergents can inhibit the growth of marine micro algae, inhibit plant metabolism, and cause unpleasant smell in the waters (Astuti, 2018). This pollution does not only have an impact on the waters but also has an impact on the health of the people who live around waters (Prasetryo, 2013).

The methods which can be used to overcome water pollution are coagulation-flocculation, phytoremediation and adsorption (Sari, 2018). Phytoremediation has the disadvantage that it takes a long time, about 10 to 15 days to remove pollutants in an area (Sholeh & Griyanitasari, 2016) while coagulation-flocculation has the disadvantage that it takes a long time to obtain concentration of microalgae and this method uses a lot of chemicals (Sasmita et al., 2004).

Adsorption is the entry of materials and collects in an adsorbent. The advantage of adsorption is that it only takes 60-90 minutes. At the contact time of 90 minutes the adsorption process decreased, it is because the functional group of the adsorbent had reached a saturated and constant state (Puspitasari, 2006).

One of adsorbent which is commonly used for adsorption is biosorbent. Biosorbents or natural adsorbents are adsorbents derived from natural materials that have many pores, where the pores are the place where adsorption takes place. Natural adsorbents are used because the costs are not too expensive and the materials used come from nature, so it is good for environment and do not produce new pollutant substances (Saptati, 2018). Corn husk is a natural material that has the potential to be used as an adsorbent because it has a fairly high cellulose content. Corn husk contains 36, 81% cellulose, 15,7% lignin, 27.01% hemicellulose and 6.04% ash. Dea's research (Apriliani D Elok., Triastuti, 2017) showed that corn husk biosorbent activated with 3% NaOH was able to absorb phosphate in wastewater with a percentage reduction of 93.7% and restu's research (Larasati, 2017) stated that using corn husk biosorbent was able to reduce COD and BOD 74%. . Furthermore, Aliyatul's research (Farida, 2019) proved that corn husk biosorbent was able to reduce cd metal content with an adsorption efficiency of 88.31%.

METHOD

Research equipment includes analytical balance, cuvette, 250 mL separating funnel, glassware, 100 mL volumetric flask, 50 mL volumetric flask, and 25 mL volumetric flask, volumetric pipette, drip pipette, heating oven, magnetic stirrer, blender and mesh sieve. , while the instruments used in this study include UV-VIS spectrophotometry, and SEM.

The materials used in this study were Soklin Softergen detergent wastewater, corn husk waste from the Jakabaring Central Market Palembang, phenolphthalein indicator, 1 N NaOH, 1 M HCL, H_2SO_4, 5% NaOH, filter paper, glass wool, washing solution, and chloroform.

Production of Corn Skin Biosorbent (Apriliani D Elok., Triastuti, 2017)

Corn husks that had been washed thoroughly were cut to a size of 2 cm to facilitate the grinding process and it was put into the oven at 105°C for 2 hours. Then milled using a blender and sieved with a size of 80 mesh. The next step is delignification and activation of corn husk biosorbent. Corn husk biosorbent was immersed in 5% NaOH solution. Then it was dried in the oven at 70ºC. Corn husk morphology analysis was determined using a Scanning Electron Microscope (SEM).

Adsorption of detergent waste

The detergent waste adsorption procedure referred to the research of Dhea (Apriliani D Elok., Triastuti, 2017). At this stage, 4 samples were prepared in the form of detergent waste. A total of 400 ml of detergent waste was added with corn husk biosorbent with variations of 28 g, 32 g and 36 g and then stirred. This variation referred to Dhea's research which stated that the greater the weight of the adsorbent, the greater the reduction in waste. Then let stand for 90 minutes. The detergent waste was then re-measured the surfactant content to determine the level of surfactant decrease after the addition of corn husk biosorbent.

Determination of Anionic Surfactant Levels Using the MBAS Method

Determination of anionic surfactant content was determined by using the MBAS method based on SNI 06-6989.51-2005 (*SNI 06-6989.51-2005. Air Dan Air Limbah – Bagian 51 : Cara Uji Kadar Surfaktan Anionik Dengan*

Spektrofotometer Secara Biru Metilen. Badan Standarisasi Nasional, n.d.). In determining the anionic surfactant content, 100 mL of sample solution was taken and put in a 250 mL separating funnel. The sample was dripped with 3 to 5 drops of phenolphthalein indicator and 1 N NaOH solution until the sample was pink and then 1 N H_2SO_4 solution wa added until the pink color disappeared. The next step was to add 25 mL of blue methylen solution and 10 mL of croroform, shook for 30 seconds and occasionally the separatory funnel cover was opened to release excess vapor pressure. The mixture was left until phase separation occurred and if an emulsion was formed, isopropyl alcohol could be added until the emulsion was lost.

The bottom layer was separated by opening the separatory funnel and accommodated in a 100 mL volumetric flask through glass wool. Extraction in a separatory funnel was repeated twice and collected in the same volumetric flask. The mixture was added as much as 50 mL of wash solution into the chloroform phase and then shaken for 30 seconds and left until phase separation occurred. The bottom layer was removed and collected back in the volumetric flask through glass wool, extracted again twice. The collected results were calibrated using chloroform and measured with a UV-Vis spectrophotometer at a wavelength 652 nm and the absorption was recorded.

RESULT AND DISCUSSION

Production of Corn Skin Biosorbent
a. Corn Skin Preparation

In this study, the corn husk cellulose was separated using 5% NaOH. At first, the corn husks were washed to remove the adhering dirt. Then the clean corn husks were cut into small pieces to facilitate the milling process and baked at 105ºC for 2 hours. The drying process aimed to evaporate the water contained in the corn husk so it increased the ability of the corn husk as a biosorbent. The cleaned corn husks were ground using a blender and sieved with an 80 mesh sieve to obtain a same size of corn husk powder.

b. Corn Skin Powder Activation

Corn husk powder was activated in 5% NaOH solution in a ratio 1:15. The purpose of the activation was that NaOH would dissolve the hemicellulose and lignin that binds to the cellulose. NaOH would damage the lignin structure in the amorphous and crystalline parts and extract hemicellulose (Putera, 2012). NaOH was used because Yulius' research (Ngapa, 2017) stated that the use of alkaline activator to activate pineapple crown cellulose was better than acid activator. The activated corn husks were dried again in the oven at 70º C.

In Dhea's research (Apriliani D Elok., Triastuti, 2017) succeeded in reducing phosphate levels with an adsorbent activated using 3% NaOH so that in this study the NaOH concentration was increased to 5% to get more optimal results. Activator with a high concentration has a better ability to activate because it can produce adsorbents with a large surface area so that the pores are getting bigger. The larger the pore surface area of the adsorbent, the higher the absorption capacity (Pitulima, 2018). The delignification reaction can be seen in Figure 1.
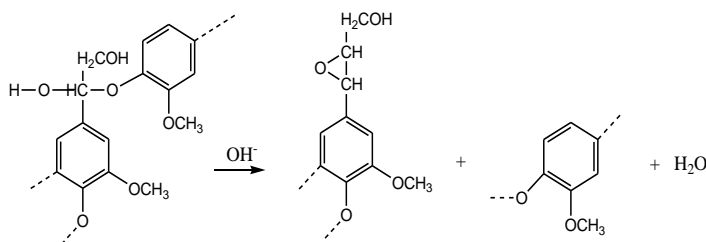
Figure 1. Delignification reaction

The delignification reaction is a reaction to sever lignin in cellulose. In Figure 1, along with the addition of NaOH concentration the lignin content would decrease. This was because the addition of an activator NaOH would facilitate the breaking of the bonds of lignin compounds. NaOH particles would enter the material and break down the lignin structure so that lignin was more soluble which results the decrease of lignin.

NaOH solution reacted with lignin which dissociated into Na^+ and OH^- ions. The OH^- ion reacted with the H group on the lignin, then formed H_2O. This caused the O group form free radicals and reacted with C to form an epoxy ring (C-O-C) and a series of groups unbonding to the O group (Pradana et al., 2017). This reaction produced two separate benzene rings, each of ring had a reactive O group. This reactive O group reacted with Na^+ and dissolved in alkaline solution so that lignin was lost when it was rinsed (Prasetryo, 2013). The properties of cellulose were optimized then carried out by an alkalization process using NaOH solution which aimed to remove lignin.

NaOH solution can break hydrogen bonds, especially intermolecular bonds of cellulose. Temperature, pressure, and concentration are factors that affect the rate of dissolution reaction of lignin, cellulose and hemicellulose. Cellulose will not be damaged in the lignin dissolution process if the solution concentration is low and the temperature used is appropriate. The use of temperatures above 180ºC will cause higher cellulose degradation (Putera, 2012).

Scanning Electron Microscope (SEM) Analysis

Scanning Electron Microscope (SEM) analysis was used to determine the pore morphology and pore size of a sample. The results of the SEM analysis of biosorbents before and after delignification can be seen in Figure 2 and Figure 3.
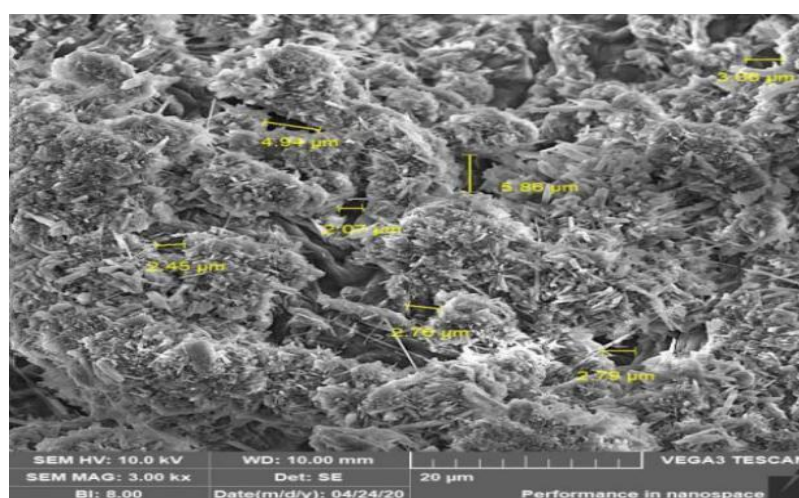

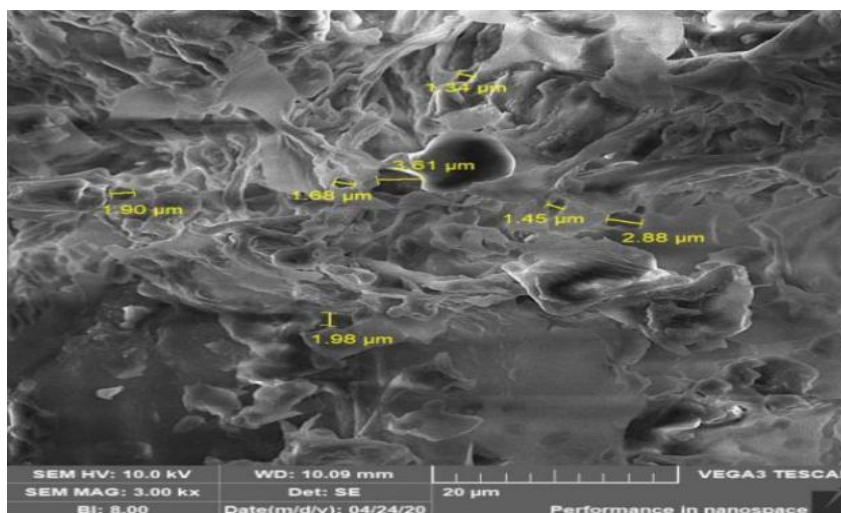Figure 2. Biosorbent before delignification (BBD)

Figure 3. Biosorben after delignification (BAD)

The BBD and BAD in that figures showed a difference in the pores. In activated biosorbent, it could be seen that the size of the pore diameter was enlarged. This indicated that the activation of the biosorbent had removed the lignin bound to the cellulose and removed impurities in the pores. The figure also showed that the average diameter before and after activation is 2.12 nm and 3.41 nm. The results of the analysis using SEM showed that the majority of pores were in the mesoporous range. The mesoporous size has a larger surface and pore area than the unmodified biosorbent which has a size of 2-50 nm. This change was expected to increase the ability of biosorbents to adsorb surfactants in detergent waste.

Determination of Anionic Surfactant Levels Using the MBAS Method

a. Reaction to MBAS Method

The levels of anionic surfactants before and after the adsorption process were determined by the MBAS (blue methylene Active Surfactant) method. At this stage, it was begun with the addition of NaOH, H_2SO_4 and phenolphthalein to the sample solution. This aimed to make the solution neutral. Then blue methylene and cloroform were added so that the reaction between the anionic surfactant and blue methylene formed an ion pair complex in the chloroform phase. In addition of chloroform, chloroform was in the lower layer because the density of water was smaller than the density of chloroform. The reaction of anionic surfactant and blue methylene can be seen in Figure 4.
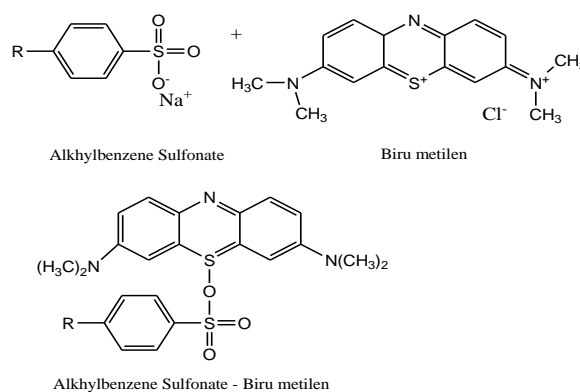

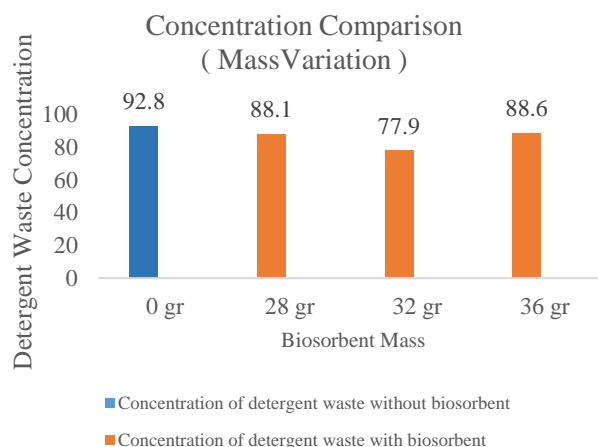Figure 4. Reaction of anionic surfactants and methylene blue

Figure 5. Graph of Effect of Biosorbent Mass on Concentration of Detergent Waste

The reaction in Figure 4 showed that the side of blue methylene that would bind to alkyl benzene sulfonate was in the part of the ring containing positively charged S so that the O which initially binds to Na^+ will become O^-. Alkyl benzene sulfonate must first release Na ions so it could bind to blue methylene. Then Na^+ ions from blue methylene bind with Cl^- ions in the aqueous phase so that the anions in alkyl benzene sulfonate and cations in blue methylene formed complex compounds (Utomo et al., 2018). The amount of anionic surfactant would be proportional to the solution extracted into the organic solvent.

The purpose of the extraction was to concentrate the surfactant. The addition of washing solution in the extraction process aimed to remove the emulsion during filtering. The intensity of the blue color formed from the reaction was then analyzed with a UV-Vis spectrophotometer at a wavelength of 652 nm.

b. Surfactant Level in Detergent Waste Before and After Adsorption

The graph of the concentration test results before and after being adsorbed can be seen in Figure 5.

The mass of the biosorbent had a big effect on the adsorption process. Based on the graph in Figure 5 where the initial concentration is 92.8 mg/l, the largest decrease in concentration in waste adsorbed with 32 gr biosorbent is 77.9 mg/l but at 36 gr biosorbent the decrease was not greater than detergent waste with 32 gr biosorbent, which was 88.6 mg/l. This indicated that it had experienced a saturation state where the concentration did not experience a large decrease but experienced desorption. Desorption was the re-release of substances that have been adsorbed (Fuadah \, 2019). Desorption occurred because the surface of the biosorbent was saturated. The ability of corn husk biosorbent in adsorption decreased as the corn husk biosorbent mass increased. So the adsorption is strongly influenced by the mass of the biosorbent and the optimum mass is 32 g. After reaching the maximum reduction level, there was no significant increase in the surfactant reduction percentage because equilibrium was reached.

Adsorption capacity stated the ability of the biosorbent to accumulate adsorbate on its surface. The adsorption capacity of the biosorbent can be seen in Figure 6.
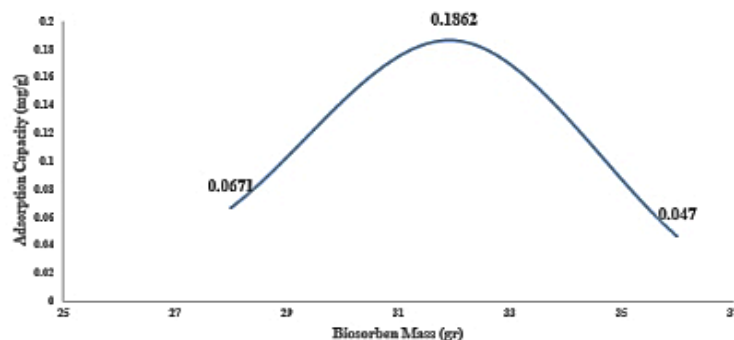
Figure 6. Graph of adsorption capacity

The optimum mass of corn husk biosorbent in this study was 32 g with an absorption capacity of 0.1862 mg/g. After the adsorption reached the optimum point or what was called the adsorption equilibrium, a decomposition process would occur. After passing the equilibrium point, the adsorbed surfactant undergoes a desorption process.

In graph 4.6, it can be seen that at 36 g of biosorbent, the ability of biosorbent to adsorb decreased by 0.047 mg/g. This showed that the addition of 32 g of biosorbent gave the best results for absorbing surfactants in detergent waste at a concentration of 92.8 mg/l.

CONCLUSION

Based on the results of the research that had been done, it could be concluded that the results of the Scanning Electron Microscope (SEM) analysis showed that there was a change in the average pore diameter before and after activation, from 2.12 nm to 3.41 nm.

Corn husk activated with 5% NaOH was able to reduce surfactant levels. The optimum mass of biosorbent occurred at a mass of 32 g where it was able to reduce surfactant levels from 92.8 mg/l to 77.8 mg/l with a maximum adsorption capacity of 0.1862 mg/g.

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