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Sorption Efficiency in Dye Removal and Thermal Stability of Sorghum Stem Aerogel

Eka Lutfi Septiani[1,a*], Okky Putri Prastuti[1], Yuni Kurniati[1], Mar'atul Fauziyah[2], Widiyastuti[2,b], Heru Setyawan[2], Wahyudiono[3], Hideki Kanda[3], and Motonobu Goto[3]

[1]Department of Chemical Engineering, Universitas Internasional Semen Indonesia, Kompleks PT. Semen Indonesia (Persero) Tbk, Jl. Veteran, Gresik 61122, Indonesia

[2]Department of Chemical Engineering, Institut Teknologi Sepuluh Nopember, Kampus ITS Sukolilo, Surabaya 60111, Indonesia

[3]Department of Material Process Engineering, Nagoya University, Furo-Cho, Chikusa-Ku, Nagoya 464-8603, Japan

[a*]eka.septiani@uisi.ac.id, [b]widi@chem-eng.its.ac.id

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Abstract. Agroindustry waste containing cellulose compound, Sorghum stem, was utilized to become cellulose aerogel which was then used as dye absorbent in textile dye wastewater. Cellulose was prepared by sorghum stem powder delignification using 6%w of NaOH solution. The ratio of powder and NaOH was varied in 1:12, 1:15, and 1:20. After this process, the powder was synthesized with NaOH/Urea to produce an aerogel by the freeze-drying method. The result shows that a higher amount of NaOH in the delignification process could increase aerogel density and decrease the porosity. Thermal stability and sorption efficiency of the aerogel was analyzed in this study. Higher porosity of aerogel tends to raise % removal in methylene blue absorption. This study reveals that aerogel three times more effective than activated carbon in dye removal.

Introduction

Since UNESCO avows batik as one of the cultural heritage of Indonesia in Abu Dhabi, 2009, Batik industry has been significantly increasing. This development also raises economic development in many segments [1]. However, most of the dye waste from Batik industry is directly released to the environment without any specific treatment, as it is with many big batik factory [2]. Continuity of this condition may contribute interference of human health and environment due to acute toxicity and genotoxicity [3,4]. Adsorption method using commonly adsorbent, activated carbon, was considered by researchers gives the best performance compared to others method because it is cheap, simple and easy to handle [5,6].

Nevertheless, applying activated carbon in a large amount of wastewater still needs a high cost, that an alternative adsorbent is needed. Cellulose aerogel is a mesoporous synthetic solid material that obtained from freeze-dried gel with high porosity [7]. Its properties make aerogel has been used as an insulator, catalyst, thickening agent, supercapacitor, drug delivery, and super absorbent. Jian Li e. al studied superabsorbent production based on a wheat straw can absorb methyl orange color [8]. Cellulose aerogel is a green material which can absorb water 99 times of its weight. The simple process to produce this material make the production in industrial scale can be conducted [9]. Hydrophobic cellulose aerogel can be obtained from recycling paper with a cross-linking agent and trimethylchlorosilane give 12-22 times oil and dye absorbed per gram aerogel [10]. These researches have not reported the use of cellulose aerogel in a textile dye waste. This paper analyzed the performance of cellulose aerogel in dye removal in batik wastewater. As Indonesia is an agrarian country, agricultural waste with rich of cellulose compound can be easily found. One of the agricultural products is sweet sorghum, in which the whole parts of the plant can be utilized. The seed is collected to eat and its stem was pressed to be a sweetener. Then the residual stem becomes an agricultural waste that can be used as superabsorbent by several steps in this study. Sorption efficiency was calculated through the different amount of sodium hydroxide solution in delignification process.

Material and Method

Material

The Sorghum stem waste was collected from Sorghum field in Universitas Internasional Semen Indonesia, Gresik city, East Java, Indonesia, in May 2018. Sodium hydroxide pellet and ethanol, methylene blue (Merck, Darmstad, Germany), and demineralized water were used without further purification were purchased from UD SUP, a local market in Surabaya city, East Java. Urea was purchased from PT Petrokimia (Persero) Tbk, Gresik, Indonesia. Dye wastewater from batik industry was obtained from local industry in Tuban city, East Java.

Method

Preparation. Sorghum stem waste was dried under sunlight about 24 hours then followed by oven at 80ºC for 24 h. The dried Sorghum stem was then ground into 100 mesh powder. Plant stem normally contains cellulose, hemicellulose, and lignin. In purpose to remove lignin content, the powder was delignified by 6%w sodium hydroxide (NaOH) solution in the flask with ratio of powder to NaOH was varied as 1:12, 1:15, and 1:20. The lignin was extracted at 100ºC for 4 hours. Then the residue was separated and washed using demineralized water until a clear color of filtrate was obtained.

Synthesis. Hydrogel synthesis is the first step in this study, one gram of each residue of delignification process was mixed with $NaOH_{(s)}$ and urea with ratio 1:1:4 in 5 ml demineralized water. This mixture was sonicated in 60 minutes then frozen into a refrigerator at -5ºC in 24 h. Due to the coagulation process to get a hydrogel, the mixture was contacted by ethanol 99% for 24 h. Thereafter, ethanol in the hydrogel should be changed by demineralized water. After a solvent exchange, the hydrogel was chilled at -5ºC for 24 h and dried using freeze-drying method at vacuum pressure five mtorr, -40ºC, for 24 h (Ilshin, Kryptonstraat, Netherlands).

Characterization. The morphology of aerogel was characterized by Scanning Electron Microscopy (SEM), JEOL,JSM-6390LV, operating at 10 kV and 10 μA. The density of the sample was measured through its weight by using analytical balance (METTLER TOLEDO, Japan) and its volume by measuring aerogel diameter and thickness in 9 different positions. And the porosity of the aerogel is also calculated following

$$P = (1 - (d_p/d_b)) \times 100\% \quad (1)$$

Where P is for porosity, d_p is the density of aerogel, and d_b means bulk cellulose with a value of 1.59 [11,12]. Chemical composition was analyzed by Fourier Transform InfraRed (FT-IR) Microscopy, Two Spectrum (PerkinElmer, England).

Sorption effectivity of Sorghum-based aerogel was compared to commercially activated carbon with the same amount of adsorbent. Then the different composition aerogel also applied in dye removal of Methylene Blue and Batik wastewater. Absorption effectivity was conducted by isothermal absorption. In order to compare absorbent performance, 30 mg of each absorbent was contacted to 50 ml of 10 ppm Methylene Blue. The absorbance of the solution was measured by Genesys 10S UV-Vis Spectrophotometry, Thermo Scientific. Absorption effectivity was calculated by % removal from Eq. 2

$$\%Removal = (Ci - Ce)/Ci \quad (2)$$

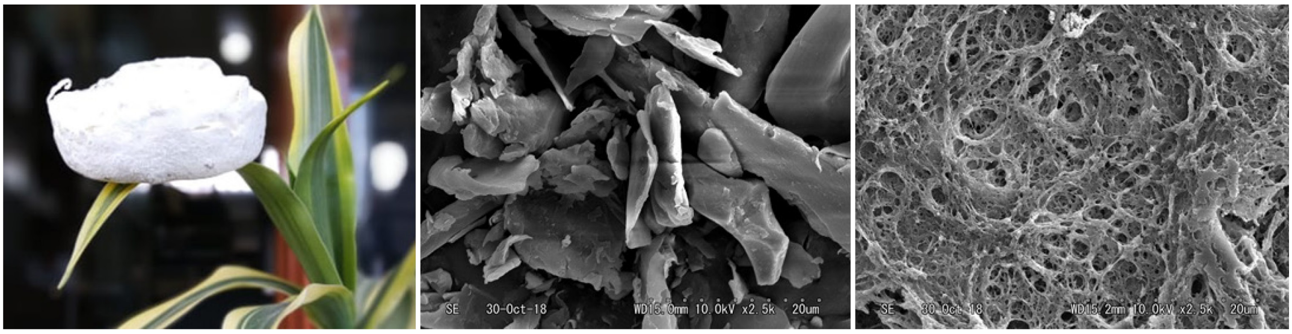
Ci is initial concentration and Ce is equilibrium concentration (mg/l). Amount of dye (mg) per g absorbent, q_e, was calculated following

$$q_e = (Ci - Ce)*(V/M) \quad (3)$$

V is the volume of solution and M is mass of absorbent [13]. Absorption performance of Batik dye wastewater also done with the same method. Batik dye wastewater was diluted ten times before it is contacted the absorbent. Calculation method in % removal used an analogy of concentration to the absorbance of waste solution.

Result and Discussion

Ultralight Sorghum stem aerogel as in Fig. 1(a) was obtained with density 0.146 g/cm^3, 0.156 g/m^3, 0.167 g/m^3 consecutively for different ratio sorghum powder to NaOH in delignification process 1:12, 1:15, 1:20. Based on Eq.1 each sorghum stem aerogel has porosity 90.8%, 90.2%, and 89.5% respectively. SEM result, with a magnification of 2500, shows that Sorghum stem powder has particles form (Fig. 1(b)). Whereas Sorghum stem aerogel composed by fibers because there is crosslinking of the hydrogen bond between cellulose and NaOH [14]. The presence of urea provides accessibility of it for forming a complex fiber. As it can be seen in Fig. 1(c) Sorghum stem aerogel has a form of fibrillar network structure. It has a large pore in the body with mean pore diameter 1.66 um. This aerogel is a macroporous aerogel since its pore diameter > 50 nm [5].



(a) (b) (c)

Fig. 1 (a) Ultralight sorghum stem aerogel, (b) Sorghum stem powder, (c) Sorghum stem aerogel.

FT-IR analysis in Fig. 2 shows that there is an O-H stretch polymer between 3400 cm^{-1} and 3230 cm^{-1}. It indicates the O-H bond in the water content of Sorghum stem powder. In the aerogel, this bond represents water and NaOH. Higher NaOH which used in the delignification process makes the O-H peak deeper. 2915 cm^{-1} or 2916 cm^{-1} is a -CH_2 Stretch asymmetry. 1605 cm^{-1} peak in the Sorghum stem powder is C=C bond of an alkene from cellulose, hemicellulose, and lignin.

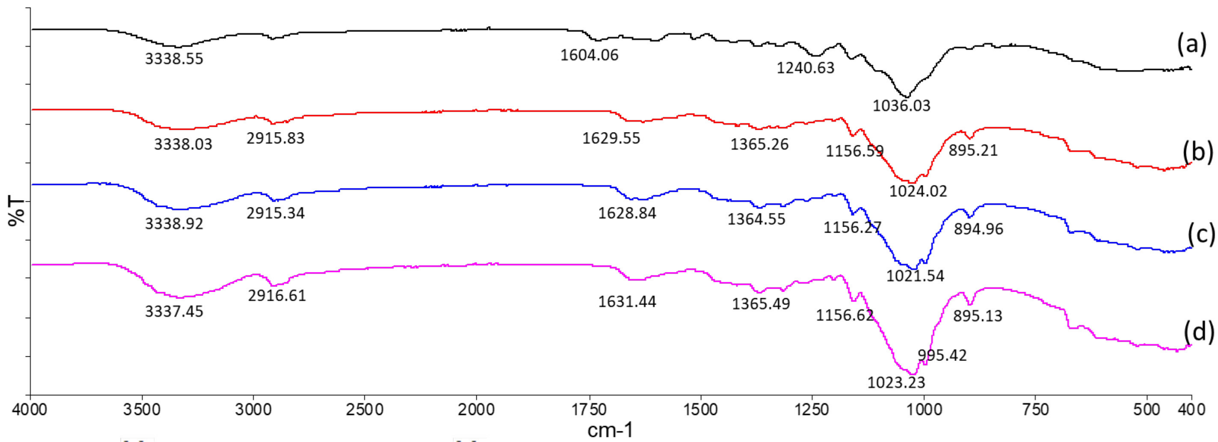


Fig. 2. FT-IR result of (a) Sorghum stem powder, Sorghum stem aerogel (c) 1:12, (b) 1:15, (c) 1:20.

While peak between (1650 -1620) cm^{-1} and (1690 – 1620) cm^{-1} shows NH stretch and/or C=N stretch from the presence of urea and cellulose bond. 1628 cm^{-1} peak is O-H vibration of water present in cellulose. 1365 cm^{-1} peak is C-H deformation of hemicellulose, it still composed by hemicellulose with a negligible amount. C-O stretching at C6 was occurred in about 1033 cm^{-1}. 1156 cm^{-1} peak shows C-O-C asymmetric stretching vibration of the glycosidic ring in cellulose [15]. About 895 – 905 cm^{-1} denote C-H bond deformation of cellulose become amorphous cellulose [16].

Fig. 3(a) represents concentration change in methylene blue solution contacted with absorbent step by step in 150 minutes. The solution was analyzed by UV-Vis Spectrophotometry every 20 minutes. The decline of Methylene Blue concentration not only determined by absorbance recorded but also from solution color. As shown in Fig. 4(a), rising a contact time made the solution brighter. Absorption performance from few aerogels represents in Fig. 3(b). % removal of Batik dye waste was obtained from the change of the absorbance in UV Vis Spectrophotometry since the absorbance decreases proportionally to the concentration. The result shows the removal percentage of 30.94%, 38.79%, 19.64% respectively to Aerogel 1:12, 1:15, 1:20. The result has different behavior with Methylene Blue absorption because of the complexity of batik textile wastes [17].

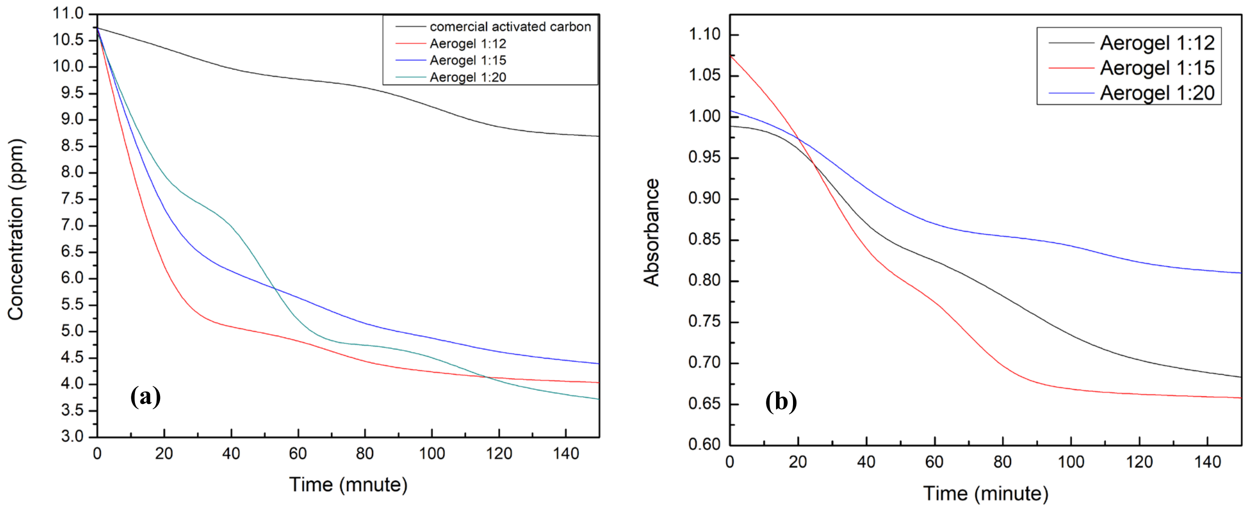


Fig. 3. (a) Concentration change in sorption process of Methylene Blue, (b) Absorbance Change in sorption process of Batik dye waste.

Percentage of removal was obtained about 19.08%, 65.08%, 62.42%, and 59.10% respectively for commercially activated carbon, aerogel 1:12, aerogel 1:15, and aerogel 1:20. This figure indicates that sorption using sorghum stem aerogel is better than activated carbon because of %removal using sorghum stem aerogel is three times greater than activated carbon. q_e value also has been evaluated with the result 3.42, 11.55, 11.18, and 10.58 mg amount of dye/g absorbent. The best performance in methylene blue removal was found in sorghum aerogel with delignification composition 1:12 because it has the biggest porosity [18].

One cycle was determined by 150-second contacting time for a new absorbent to the solution. After the first 150 s, new absorbent was added to the solution, and the older was taken. % removal was calculated in the term one cycle. Fig. 4(b) shows the isothermal absorption method with certain stirring. To remove 10 ppm methylene blue using sorghum stem aerogel 1:12, it needs twice cycle to make the solution clear as can be seen at Fig. 4(c). Whereas Fig. 4(d) provide calculation result, by performance comparison in two cycles was obtained that application of sorghum stem aerogel 1:12 in 10 ppm methylene blue removal reveals the brightest result.

Investigation of thermal stability of Sorghum stem aerogel was conducted by Thermo Gravimetry Analysis method as shown in Fig. 5. Initial weight loss due to water content evaporation at 100ºC is about 8%. The rapid weight loss occurred at temperature 250ºC; there is 53% mass reduction until 350ºC. Then it continues to decrease until 10.7% remaining mass at 800ºC. Based on this analysis, sorghum stem aerogel cannot be used as a good insulator without any modification of composition.

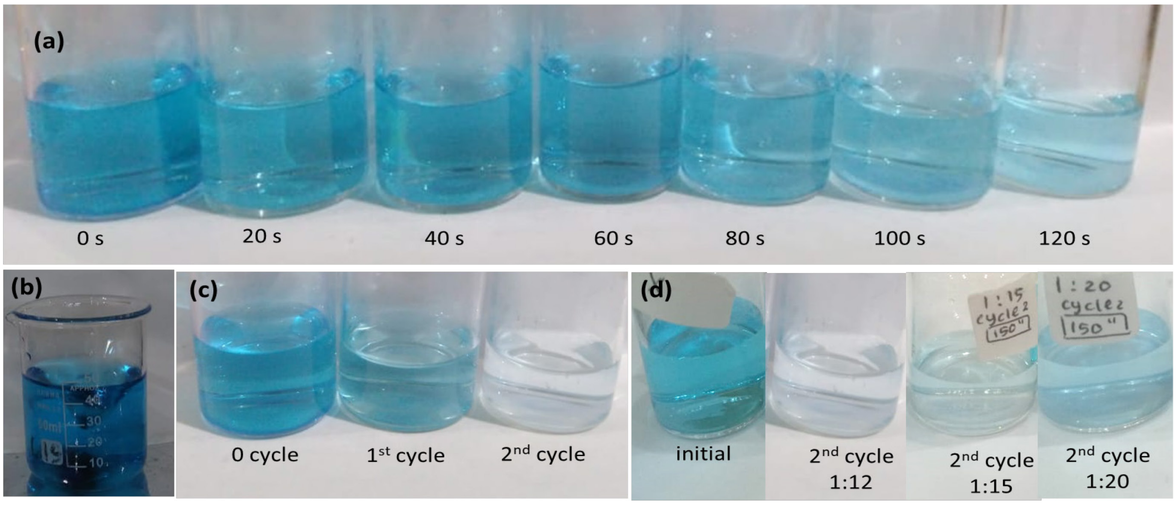


Fig. 4. Visualization Methylene Blue Absorption (a) 10 ppm Methylene Blue with 1:12 aerogel in 1 cycle, (b) isothermal absorption process, (c) cycle comparison of 10 ppm Methylene Blue with 1:12 aerogel, (d) performance comparison in a number of aerogels.

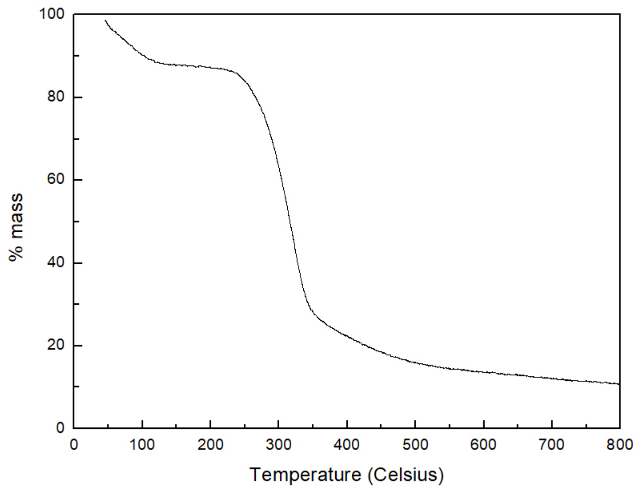


Fig. 5. Thermal Gravimetry of sorghum aerogel.

Conclusion

Sorghum stem as an agroindustry waste can be used to produce ultralight aerogel which has a density of less than 0.2 g/m^3 with high porosity. Three types of aerogel have been analyzed by their performance to remove methylene blue and textile dye in the wastewater. Aerogel gives %removal three times greater than the most commonly adsorbent, activated carbon. Because of the complexity of Batik dye wastewater content, %removal of dye content decreased to almost half of methylene blue removal using the same aerogel. The thermal stability of aerogel has also been investigated by thermogravimetry analysis. The result indicates that the aerogel cannot be used as a good insulator without further modification by adding another material.

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