International Journal on Advanced Science Engineering Information Technology

Vol.6 (2016) No. 1
ISSN: 2088-5334

Crosslinking of Kapok Cellulose Fiber via Azide Alkyne Click Chemistry as a New Material for Filtering System: A Preliminary Study

Nur Syazwani Abd Rahman[#1], Baharin Azahari[*2], Mohd Firdaus Yhaya[*3], Wan Ruslan Ismail[#4]

[#] *School of Humanities, Universiti Sains Malaysia, 11800, Penang, Malaysia*
E-mail: [1]nursyazwani.rahman@gmail.com; [4]wruslan@usm.my

* *School of Industrial Technology, Universiti Sains Malaysia, 11800, Penang, Malaysia*
E-mail: [2]baharin@usm.my ;[3] firdausya@usm.my

***Abstract*— A new class of green material has been elaborated by grafting the modified kapok fiber, by the means of azidated kapok fiber followed by "click-chemistry" reaction with the terminal alkyne crosslinker. The modified and synthesized product was characterized using Fourier transform infrared spectroscopy (FT-IR), and Scanning electron microscopy (SEM). The study also was undertaken to investigate the effect on the absorption of methylene blue from aqueous solution onto the click fiber prepared. The findings showed that the click kapok absorbed more compared to the untreated kapok. Based on the result, the reaction of click chemistry influenced the properties of the filter made from kapok fiber.**

***Keywords*— kapok fiber; cellulose; click chemistry; adsorption; methylene blue**

I. Introduction

Textile, paper and cosmetic industries used a lot of water in their processes and end up generating a lot of wastewater polluted with different types of dyes [1], [2]. Colour produces by minute amount of organic dyes in water discharged from those industries is considered very important because besides being aesthetically unpleasant from our naked eyes, the content of colour in the water may possibly cause harmful effect [3]. This may cause severe negative impact on organisms and ecological environment as they are considered toxic and have carcinogenic properties which make the water inhibitory to aquatic life [1], [4], [5].

In recent years, several methods including biological and physicochemical technologies have been suggested to remove dyes and other effluent from wastewater [6]. These processes include coagulation, anaerobic treatment, filtration, floatation, adsorption, membrane separation, ion exchange and advance oxidation [6]-[8]. Up to now, sorption technology has gain an interest in academic and industries as one of the most efficient techniques, not only to clean up oil and other effluent but also as a method for the removal of dyes and heavy metal ions [9], [10]. It is now recognized as an economic, efficient and effective method for water decontamination application and for separation analytic purpose [11]. Most of the absorbent used could be in organic, mineral or biological origin such as zeolities, clays, activated carbons, silica beads and agricultural wastes.

Currently, there are growing interests in using cheap and commercially available materials for absorption and filtering process especially absorbents containing natural polymers. The utilization of natural fiber for wastewater treatment is also an attractive and promising option for the environment. The kapok fiber has gained a wide attention as an effective absorbent especially in oil spill cleanup [12] and the other effluents due to its low cost and significant adsorption potential for removal of various pollutants. Kapok fiber or scientifically know as *Ciebapentandra* (L.) Gaertn is a natural plant fiber with silky, yellowish and fluffy characteristic [12], [13]. It is also non-toxic, non allergic, resistant to rot and odourless which make it suitable to be applied as a raw material for water treatment purpose. According to Lim and Huang [17], kapok fiber has a hollow structure with a thin fiber wall and large lumen; which has received increasing attention as an absorbent material in water treatment [12], [14]. Kapok fibers also contain a waxy cutin on the fiber surface that makes them water repellent and oil absorbent [15].

Normally, cellulose fibers tend to agglomerate and unable to disperse uniformly during sheet making process. In order to make this kapok fiber fully functionalize as filtering system in treating wastewater, some modification need to be done. Up to date, the use of modified kapok fiber via azide alkyne has not been widely reported. In this study, the click azide-alkyne click chemistry has been approached. The study will also focus on the formation of filter and finally on the effect of dye absorption.

II. Materials and Methods

A. Materials

The kapok fiber was purchased from Hasrat Bestari Sdn. Bhd. and was cleaned before used. Chemical such as triethylamine, sodium azide, N, N- dimethylformamide (DMF) were purchase from R&M company while for paratoulene sulfonyl chloride (tosyl chloride) and alkyne crosslinker were purchased from Sigma-Aldrich company. All chemicals were used as received unless stated otherwise.

1) FTIR: FTIR spectra were recorded using Perkin Elmer FTIR spectrometer using the potassium bromide (KBr) pellet method.

2) SEM: The morphological study was done using Leo Supra 50 Vp Field Emission Scanning Electron Microscope (Carl-Ziess SMT, Oberkochen, Germany).

B. Methods

The preparation of click azide- alkyne kapok fiber filter was carried out based on method according to Elchinger and co-worker [16], with some slight modification.

1) Pre- treatment of kapok fiber : 300g of kapok fiber was immersed in 2M of sodium hydroxide with ratio 1:7 (fiber: liquor) and undergone chemical pulping using a digester. The cooking time was about 120 minute at 170°C. The treated fiber was washed several times using distilled water and was used in further modification.

2) Tosylation of kapok fiber : Tosylation of fiber was prepared by mixing 6g of pre-treated kapok fiber with 14.16g of tosyl chloride, 17.76ml of triethylamine and 240ml of distilled water. After 24 hours under mechanical stirring, the mixer was filtered and washed with 200ml of hot distilled water and ethanol. Then, the product was dried at 50°C.

3) Azidation of kapok fiber : 3g of tosylated fiber was mixed with 5.78g of sodium azide in 60ml of DMF and undergoes stirring process at 75°C for 48 hours. Then the reaction was cooled down, filtered and washed using distilled water and ethanol. The product was dried at 40°C.

4) Preparation of azide-alkyne kapok fiber : The azidated fiber and alkyne crosslinker was mixed with ratio 1:1 in 75ml of DMF. The mixture reaction was left to react under stirring at 100°C for 24h. Then the product was filtered, washed using distilled water and ethanol, and dried at 40 °C.

5) Absorption studies : In this experiment, a stock of methylene blue solution (1000mg/L) was used. The concentration of methylene blue was determined by using UV-Vis machine. About 0.1g untreated kapok absorbent was added to 50ml dye in a stoppered conical flask and agitated at constant speed (100rpm) on the GFL 3005 orbital shaker in room temperature for 24h. Then the methylene blue solution was filtered through a filter paper. The concentration of methylene blue solution was measured and compared with the blank solution (without absorbent). The same processes were repeated using the pre-treated kapok absorbent and click kapok absorbent.

III. Result and Discussion

A. FTIR Characterization

The FTIR spectra of untreated, pre-treated, tosylated, azidated and click kapok fiber are displayed in Figure 1.

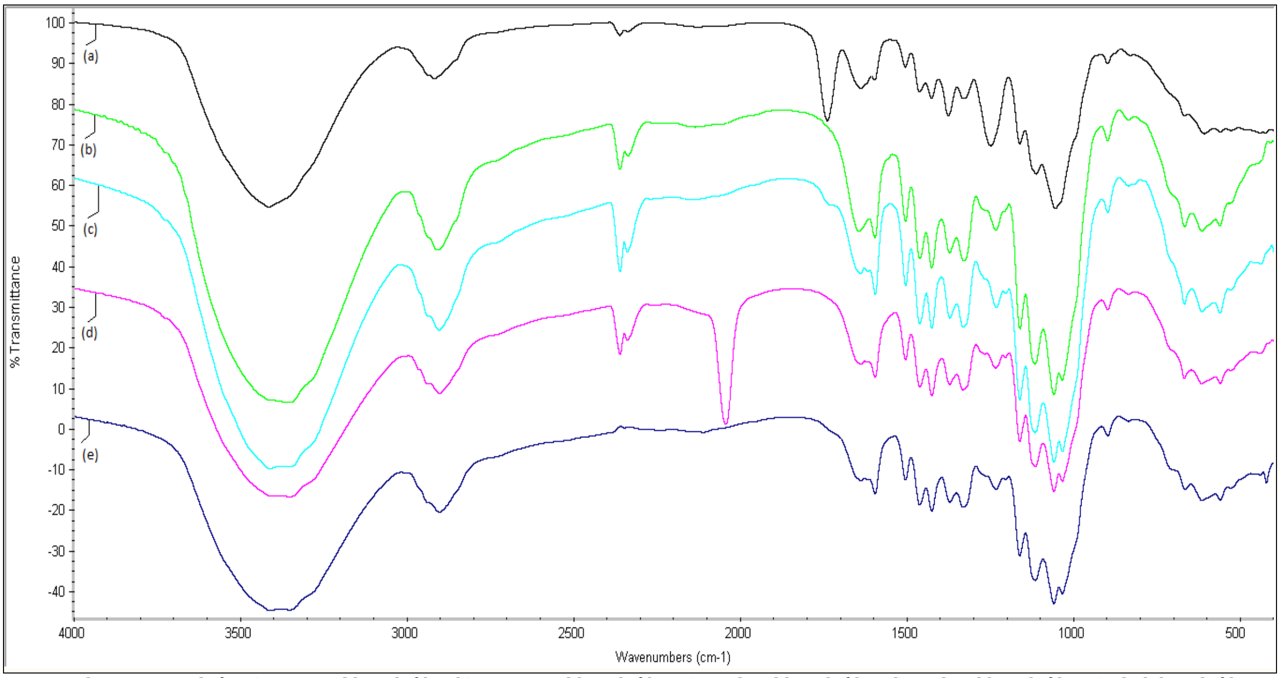
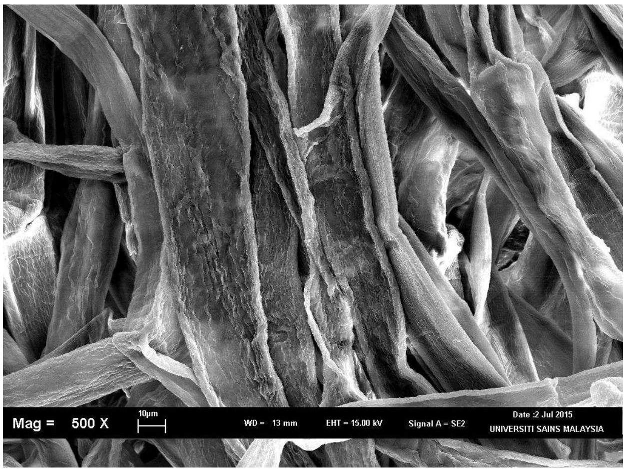


Fig 1 The FTIR result for a) untreated kapok fiber b) pre-treated kapok fiber c) tosylated kapok fiber d) azidated kapok fiber e) click kapok fiber

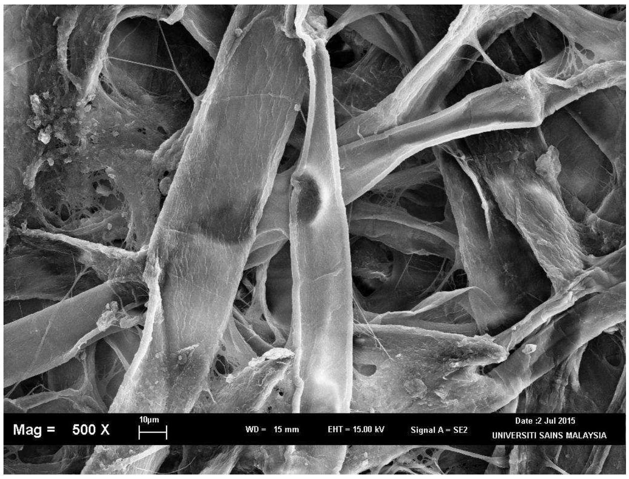
Comparing the entire sample, the major findings are observed at the range of 2900-1600cm-1. For untreated kapok fiber (Figure 1a) and pre-treated kapok fiber (Figure 1b), the difference is observed at absorbance band 1432cm-1 and 1376cm-1 which assigned to $-CH_3$ asymmetric and C-H symmetric deformation of lignin due to alkali treatment. The sharp peak at 1740cm-1 which may attribute to C=O stretching of hemicelluloses and peak at 1250 cm-1 also disappeared after the pre-treatment shows an evidence that the hemicelluloses are removed [18]. The tosylated fiber (Figure 1c) and pre-treated fiber (Figure 1b) do not show obvious changes on the FTIR result. However, for azidated fiber (figure 1d), a strong peak at 2050 cm-1 is observed which corresponding to the azide group. The success of clicking process is clearly seen in Figure 1e where the azide group is disappeared after the crosslink. This indicates that the substantial parts of alkyne and azide groups participated in the click chemistry [17].

B. Morphological analysis

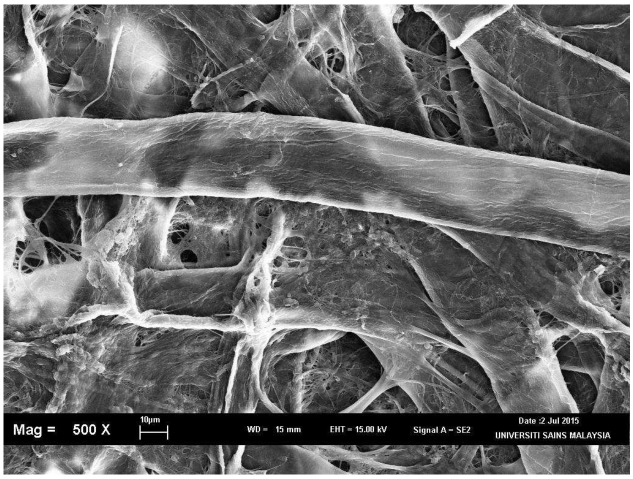
Figure 2 shows the morphology of pre-treated, azide and click fiber. From Figure 2(a), the pre-treatment of the fiber made the fiber surface become rough and forming wrinkled texture which indicates that the waxy coating has been remove from the fiber surface [5], [14]. Different from pre-treated fiber, Figure 2b shows that the surface of the azidated fiber is rougher and some of the fibers are covered by the sodium azide. This is akin to modification of the fibre surface.The observed fibre surface phenomenon is due to the exposition of more cellulose hydroxyl group since the fiber changes from being hydrophilic to hydrophobic after the pre-treatment process. The fiber to fiber bonding is clearly seen on the click fiber (Figure 2c). Less space between the fiber (fiber void) was observed and this is attributed by the success of crosslinking between the croslinker and fiber.



(a)



(b)



(c)

Fig 2 The SEM image for a) pre-treated kapok fiber b) azidated kapok fiber and c) click kapok fiber

C. Absorption studies

Figure 3, shows the concentration of methylene blue dye after treatment with different absorbent. From the result, it is shown that the untreated kapok fiber still can absorb the methylene blue dye even though no modification was done to the fiber. This is maybe due to the presence of hollow lumen [10]. However, the sorption capacity was not as much as pre-treated kapok. The waxy surface of the kapok fiber makes it superhydrophobic, thus decreases the surface energy to absorb more dyes [5]. Comparing the pre-treated kapok fiber with click fiber and untreated kapok fiber, the improvement of dyes absorption in pre-treated kapok fiber is more significant. This is maybe due to the surface roughness of the fiber and more open pore is available since the waxy coating of the fiber was removed. The increased in surface roughness will also lead to better diffusion of dyes through the fiber walls to the hollow lumen [10]. For click kapok fiber, the concentration of dyes after treatment shows a bit higher compared to the pre-treated kapok fiber. This maybe due to some void on the surface of the fiber has been covered up during the crosslinking process. However, the click kapok fiber still shows better performance of dye absorption compared to the pre-treated kapok fiber.

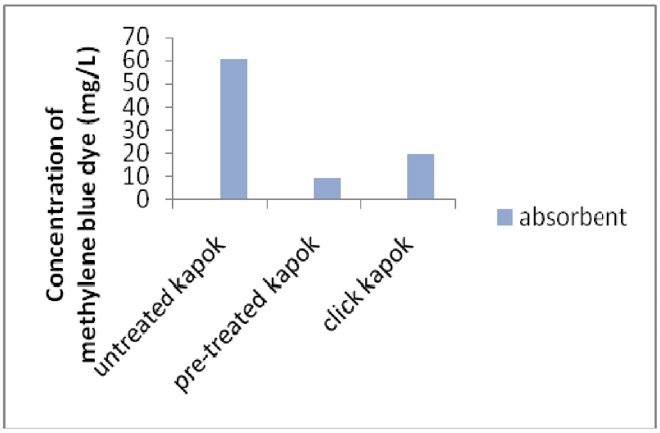


Fig 3 The concentration of methalene blue dye after 24h being immersed with diffrerent absorbent

IV. Conclusions

The present study shows that the click kapok fiber has higher dye absorption capability compared to the pre-treated kapok fiber. The FTIR and SEM analysis also showed that a new method of crosslinking fiber to fiber can be successfully performed by using click technology. Owing to the advantages of clicking technique and high dye absorption capability, the click technology is a new method of modification of fibre for wastewater treatment application.

Acknowledgment

The authors would like to acknowledge the Department of Higher Education of Malaysia for the financial support awarded to Miss Nur Syazwani and Universiti Sains Malaysia (1001.PHUMANITI.816229 and 203.PHUMANITI.6711512).

References

[1] M. Berrios, M. Á. Martín, and A. Martín, “Treatment of pollutants in wastewater: Adsorption of methylene blue onto olive-based activated carbon,” J. Ind. Eng. Chem., vol. 18, no. 2, pp. 780–784, Mar. 2012.

[2] V. K. Garg, M. Amita, R. Kumar, and R. Gupta, “Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a timber industry waste,” Dye. Pigment., vol. 63, no. 3, pp. 243–250, Dec. 2004.

[3] M. T. Uddin, M. A. Islam, S. Mahmud, and M. Rukanuzzaman, “Adsorptive removal of methylene blue by tea waste,” J. Hazard. Mater., vol. 164, no. 1, pp. 53–60, May 2009.

[4] E. N. El Qada, S. J. Allen, and G. M. Walker, “Adsorption of Methylene Blue onto activated carbon produced from steam activated bituminous coal: A study of equilibrium adsorption isotherm,” Chem. Eng. J., vol. 124, no. 1–3, pp. 103–110, Nov. 2006.

[5] J. Wang, Y. Zheng, and A. Wang, “Superhydrophobic kapok fiber oil-absorbent: Preparation and high oil absorbency,” Chem. Eng. J., vol. 213, pp. 1–7, Dec. 2012.

[6] M. Danish, T. Ahmad, R. Hashim, M. R. Hafiz, A. Ghazali, O. Sulaiman, and S. Hiziroglu, “Characterization and adsorption kinetic study of surfactant treated oil palm (Elaeis guineensis) empty fruit bunches,” Desalin. Water Treat., pp. 1–14, Apr. 2015.

[7] H. S. Rai, M. S. Bhattacharyya, J. Singh, T. K. Bansal, P. Vats, and U. C. Banerjee, “Removal of Dyes from the Effluent of Textile and Dyestuff Manufacturing Industry: A Review of Emerging Techniques With Reference to Biological Treatment,” Crit. Rev. Environ. Sci. Technol., vol. 35, no. 3, pp. 219–238, Mar. 2005.

[8] S. Mondal, “Methods of Dye Removal from Dye House Effluent—An Overview,” Environ. Eng. Sci., vol. 25, no. 3, pp. 383–396, Mar. 2008.

[9] W. S. Wan Ngah, L. C. Teong, and M. A. K. M. Hanafiah, “Adsorption of dyes and heavy metal ions by chitosan composites: A review,” Carbohydr. Polym., vol. 83, no. 4, pp. 1446–1456, Feb. 2011.

[10] J. Wang, Y. Zheng, and A. Wang, “Investigation of acetylated kapok fibers on the sorption of oil in water,” J. Environ. Sci., vol. 25, no. 2, pp. 246–253, Feb. 2013.

[11] G. Crini, “Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment,” Prog. Polym. Sci., vol. 30, no. 1, pp. 38–70, Jan. 2005.

[12] T.-T. Lim and X. Huang, “Evaluation of kapok (Ceiba pentandra (L.) Gaertn.) as a natural hollow hydrophobic–oleophilic fibrous sorbent for oil spill cleanup,” Chemosphere, vol. 66, no. 5, pp. 955–963, Jan. 2007.

[13] Y. Y. Tye, K. T. Lee, W. N. Wan Abdullah, and C. P. Leh, “Potential of Ceiba pentandra (L.) Gaertn. (kapok fiber) as a resource for second generation bioethanol: Effect of various simple pretreatment methods on sugar production,” Bioresour. Technol., vol. 116, pp. 536–539, Jul. 2012.

[14] J. Wang, Y. Zheng, and A. Wang, “Effect of kapok fiber treated with various solvents on oil absorbency,” Ind. Crops Prod., vol. 40, pp. 178–184, Nov. 2012.

[15] S. Chaiarrekij, A. Apirakchaiskul, K. Suvarnakich, and S. Kiatkamjornwong, “Kapok I: Characteristcs of kapok fiber as a potential pulp source for papermaking,” Bioresour. Vol 7, No 1, Nov. 2011.

[16] P.-H. Elchinger, H. Awada, C. Zerrouki, D. Montplaisir, and R. Zerrouki, “Kraft Pulp–Starch Covalent Linking: A Promising Route to a New Material,” Ind. Eng. Chem. Res., vol. 53, no. 18, pp. 7604–7610, 2014.

[17] M. S. Robert and X. W. Francis, Spectrometric Identification of Organic Compounds, 7th ed. United States of America: John Wiley & Sons, 2005.

[18] G.B. Nam , J.W. Kim , J.M. Byeon , B.S. Kim , T.K. Kim and J.I. Song “Effect of surface treatment on mechanical behavior of jute fiber-reinforced polyopropylene composite,” in 18th International Conference on Composite Materials, 2009