

BREADFRUIT LEAVES WASTE AS AN ECO-FRIENDLY AND EFFECTIVE BIOSORBENT IN REMOVING OIL WASTE

*M. Abdullah^{1,a}, M. H. Alias¹, S. N. Razali¹, W. N. F. A. Jani^{1,b}, M. H. Mustafa^{1,c} and M. Z. Sukor^{1,d}

¹ College of Engineering, UiTM Cawangan Johor, Kampus Pasir Gudang, 81750 Masai, Johor, Malaysia.

*Corresponding author's
email:
moham3767@uitm.edu.my

^amoham3767@uitm.edu.my, ^bwanfazlina@uitm.edu.my,
^cmohdh233@uitm.edu.my, ^ddmdzaki@uitm.edu.my

Abstract

The breadfruit leaves (*Artocarpus altilis*) can be easily found in Malaysia and natural adsorbents in removing oil waste. This study focused on determining the performance of untreated breadfruit leaves and chemically modified breadfruit leaves with hydrochloric acid (HCl) and sodium hydroxide (NaOH). Vegetable oil, diesel, petrol and lubricant has been used to examine the performance of breadfruit leaves. At the highest packing density of 0.09 g/cm³, the oil dripped out from the breadfruit leaves was 3.8% for treated breadfruit leaves with NaOH, 4.8% for breadfruit leaves treated with HCl and 5.8% for untreated breadfruit leaves. The percentage of oil removal data showed that chemically modified breadfruit leaves are more efficient as it has undergone further treatment that enhances breadfruit leaves characteristic as natural sorbents. In the adsorbent reusability testing, the reusability of breadfruit leaves can be observed as the chemically modified breadfruit leaves achieved a constant value sooner than untreated breadfruit leaves at the 4th and 5th cycle while the untreated breadfruit leaves only achieved the constant value at 6th and 7th cycle. This condition shows that chemically modified breadfruit leaves can retain the adsorbed oil without losing it than the untreated breadfruit leaves. It is proved that chemically modified breadfruit leaves can perform better in each testing compared to untreated breadfruit leaves.

Keywords: Breadfruit leaves; oil sorption; organic absorbent

1.0 INTRODUCTION

Nowadays, our earth was exposed to many kinds of water pollution that could harm our human being and other creatures [1]. One of the pollutions that the researchers are now focusing on is water pollution, which usually comes from petroleum industry, food production, and petroleum mining [2]. Water pollution contains chemical and biological substances which will produce more toxic by-products that are harmful to animals and humans' health [3]. Oil spillage is one of the factors resulting in water pollution. Most of the oil producing companies usually discharged their production waste to the water bodies without proper treatment resulting in water pollution in the area [4]. Besides, the oil spillage can affect the environment because some of the chemicals in the oil waste can be volatile and oxidized to the air [5]. Later on, the toxins

accumulated by humans, animals, and the environment will probably result in acute or chronic diseases. For instance, it may cause lung irritation, dizziness, chest pain and sore eyes [6].

Moreover, the oil spillage may produce specific odor which could disturb people in the residential areas. In addition, oil spills can affect marine life too. For example, marine birds are especially diving birds and fishes in the ocean, cannot live longer due to the oil spillage [7]. Therefore, it is necessary to use an efficient method in removing oil from the contaminated area so that many lives can be saved.

A previous study stated that the natural sorbents were quite effective and eco-friendly sorbent for oil spill clean-up [8]. Other than that, the advantages of using natural sorbents instead of synthetic sorbent are that natural sorbents are highly biodegradable and can be decomposed [9]. In addition, natural adsorbent such as kapok, eggshell, wheat straw and

vegetable fibres are easy to obtain and can be found in local areas. Hence, the source can get quickly because of its availability. Natural adsorbents also have an excellent sorption capacity, free from chemical [10]. Thus, the adsorption of oil waste using natural adsorbents can be done in such an economical and effective technique.

In this study, breadfruit leaves waste can also be natural adsorbents in removing oil waste. Breadfruit (*Artocarpus altissilis*) is a tropical tree that belongs to the plant family of Moraceae that can be easily found in Malaysia. This is because the breadfruit trees approximately contain 60 species in Australasia, the Indian subcontinent and Southeast Asian, including Malaysia [11]. It can reach a height of 15-20 m. The leaves are alternate, dark green and smooth on their upper side and the leaves. Its lengths are about 45cm long. The sample of breadfruit leaves can be easily collected because the breadfruit trees are easy to grow and only needs minimal attention to take care of and it can grow easily under a wide range of ecological conditions [12].

Besides, the leaves from the breadfruit trees are produced all year. It is usually come in a big size, making it easy to be collected as a sample [13]. Even though there is another effective way to reduce oil spillage, such as using activated carbon, it is found to be quite expensive because it needs further procedures in producing them [14]. This is because using the breadfruit leaves, a natural adsorbent of oil can be easily made because it does not need any further procedures. This will work when the breadfruit leaves wastes are treated using solvents such as NaOH and HCl. As a result, breadfruit leaves can overcome the oil spillage problem in the ocean with their ability to absorb oil. The types of oil that have been used to test the ability of breadfruit leaves to be a natural sorbent of oil are diesel, petrol, lubricants and vegetable oil. Therefore, the objective of using breadfruit leaves as a natural adsorbent in removing oil waste can be achieved as it can overcome the oil spillage problem with its ability to absorb oil.

2.0 EXPERIMENTAL

Preparation of biosorbent samples

Samples used in this study were untreated breadfruit leaves and chemically modified breadfruit leaves; dissolve with HCl and NaOH [15, 16]. First, the breadfruit leaves were rinsed with tap water and sun-dried for a day, as shown in Fig. 1.



Fig. 1: Sun-dried breadfruit leaves

Then, for chemically modified breadfruit leaves with NaOH, One litre of water and 40 grams of NaOH pellets were used to produce 1 mol of concentrated NaOH. Next, mixed 100mL of concentrated NaOH with 900mL of ultra-pure water to form diluted NaOH and soaked the breadfruit leaves for a day. After one day, the breadfruit leaves were rinsed with ultra-pure water and neutralised with 0.5 mol of HCl. To prepare breadfruit leaves with HCl, A 100mL of HCl was prepared and mixed with 500mL of ultra-pure water to produce 0.5 mol of HCl. Then, 100mL of mixed HCl and 900mL of ultra-pure water were taken to form diluted HCl and soaked the breadfruit leaves for a day. After one day, 1 mol of concentrated NaOH was prepared to neutralise the breadfruit leaves and left it for 30 minutes. These treated breadfruit leaves (with HCl and NaOH) were dried in an oven at 60°C. Finally, breadfruit leaves were grinded and sieved using a grinding machine and sieve-shaking with siever size of 45mm, 120mm and 250mm.

Types of Oil

Different type of oils was used for the oil evaluation test. This is because every oil has different viscosity [10]. Therefore, the types of oil used for this experiment are vegetable oil, diesel, petrol and lubricant.

Characterization of Breadfruit Leaves

A Thermogravimetric Analysis (TGA)

TGA (Perkin Elmer Simultaneous Thermal Analyzer, TGA 8000) is an instrument of thermal analysis in which the mass of a sample is measured over time as the temperature changes. The condition for this evaluation is 30°C to 950°C at 10°C/min under a nitrogen atmosphere.

B Water and Swelling Test

In order to determine the relative rate of adsorption of water by specimens, a water and methanol swelling test was carried out with 24-hours immersion of specimens, as shown in Fig. 2. Teabags were used to fill up the specimens. This test was carried out for 5 days and every 24-hours, the specimens were taken out from distilled water and dried at room temperature. The average weight of specimens was calculated using the eq. 1:

$$\text{Swelling Test} = W_a - W_i \times 100 \quad (1)$$

Where w_a = Weight of Specimens after immersed,
 w_i = Weight of specimens before immersed



Fig. 2: Water and swelling test

C Reusability

In this method, 1g of breadfruit leaves were weighted and filled in the teabag. The teabag filled with breadfruit leaves were soaked into different type of oils in a certain of time. Next, dripped the tea bag and weighed it. The step was repeated until a constant weight difference is achieved. Use this formula to calculate the reusability (Eq. 2):

$$\text{Reusability} = \text{Final Weight} - \text{Initial Weight} \quad (2)$$

3.0 RESULTS AND DISCUSSION

Characteristic of Breadfruit Leaves as an oil absorbent

A Thermogravimetric Analysis (TGA)

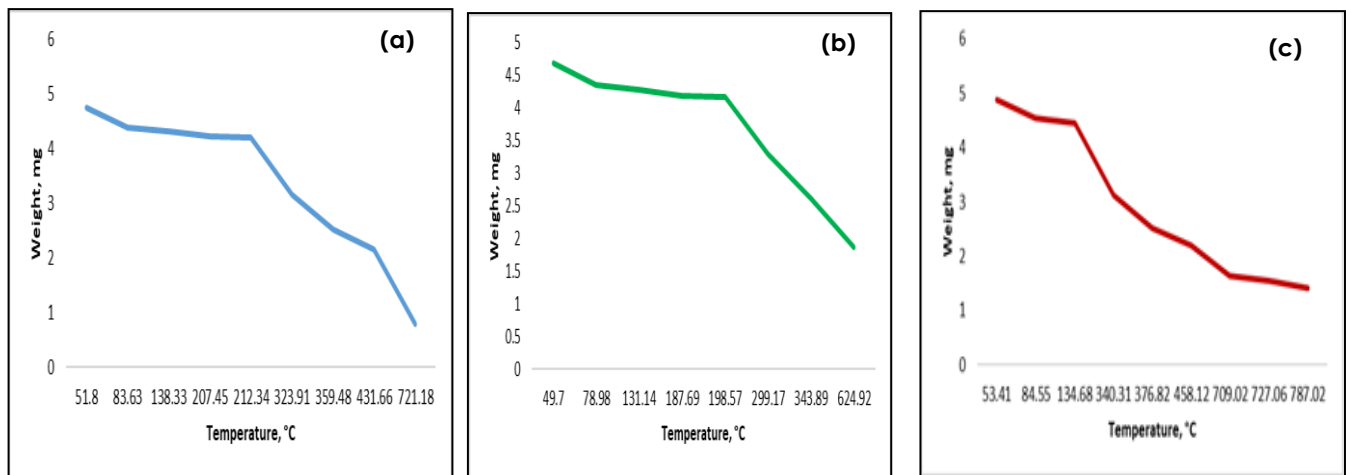


Fig 3: TGA analysis on treated breadfruit leaves with; (a) NaOH, (b) HCl, and (c) untreated breadfruit leaves

B Water and Methanol Swelling Test

The absorption test can be observed using water and methanol swelling test. In this test, water and methanol are used as a solvent because water is a polar solvent while methanol is a non-polar solvent. Based on Fig. 4, the graph showed that the thickness

of swelling between breadfruit leaves treated with NaOH, HCl and untreated sample of breadfruit leaves depends on the two solvents: water and methanol. Based on Fig. 3, overall, the weight of the samples decreased as the temperature increased. All samples experienced initial weight loss at an early stage, ranging from 49°C to 85°C. This is due to the evaporation of moisture content within the samples [17]. Besides, a slight decrease occurs at ranging temperature from 78°C to 300°C for breadfruit leaves treated with NaOH and HCl while untreated breadfruit leaves experienced a sudden decrease which attributes to dehydration, dissociation of lignin cellulose and residual of breadfruit leaves [18].

In the second region ranging from 300°C to 730°C, treated breadfruit with leaves with HCl showed a steadily decrease due to the slow degradation of cellulose and lignin content. However, the untreated breadfruit leaves experienced the unstable loss of mass caused by hemicellulose molecule, which has low thermal resistance [19].

The result of TGA shows that chemical modification of breadfruit leaves with NaOH and HCl does not change the structure and thermally stable compared to untreated breadfruit. Furthermore, a previous study by the Department of Polymer Science and Technology [19] has proved that acid and alkali treated can increase cellulose crystalline, which has been found to increase the thermal properties. Thus, the treated breadfruit leaves can give high efficiency in absorbing oils and being constant in their structure.

Based on the swelling test using methanol as a solvent, the highest thickness achieved by untreated breadfruit leaves with around 82.48% increment, while the breadfruit leaves treated by NaOH have

the lowest swelling thickness with only 76.07% increment. Thus, it also shows that the thickness of untreated breadfruit leaves is higher than the treated sample. Besides, the swelling thickness using water as a solvent at NaOH treated sample is the highest with 89.53% compared to HCl and untreated breadfruit leaves by a slight difference of 0.94% and 1.1%, respectively. This can be concluded that untreated breadfruit leaves were more attracted to absorb methanol rather than both treated breadfruit leaves

while the NaOH treated breadfruit leaves tends to absorb more water molecule than the other.

To be concluded, the porosity lead increase due to the absorption as the water filled the void space in the composites structure due to the lumen's geometry, structure and the breadfruit leaves void space. Hence, the swelling thickness values increase with water and methanol absorption time which is every 24 hours.

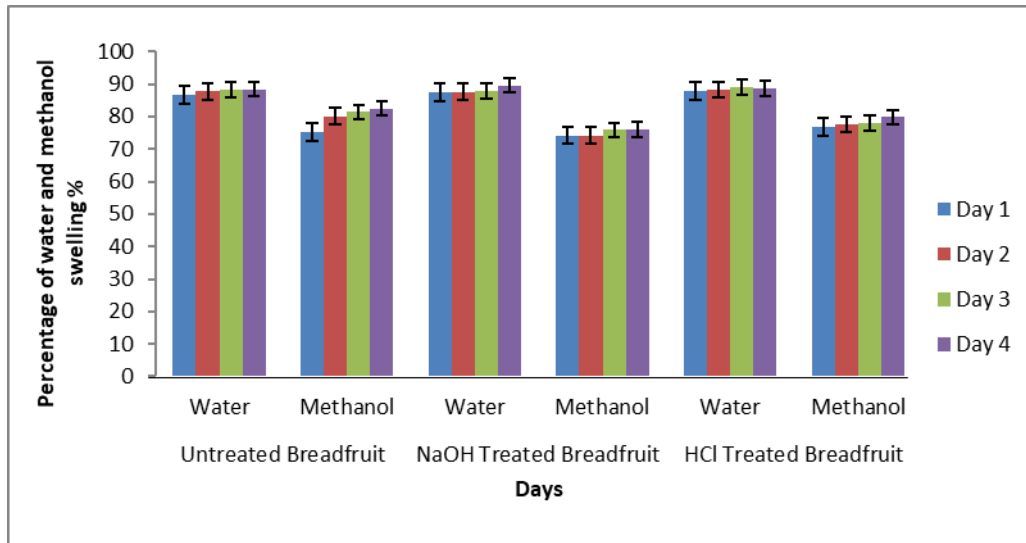


Fig 4: Percentage of water and methanol swelling on treated NaOH Breadfruit Leaves, treated HCl Breadfruit Leaves and untreated Breadfruit Leaves

Adsorbent Reusability

Adsorbent reusability tests are being used to determine the treated and untreated breadfruit leaves based on eight sorption cycles until it achieves constant value. The purpose of this test is to check whether the ability of the breadfruit leaves in retaining the adsorbed oil without losing it while handling the sorbents [20]. The figure below shows the reusability of untreated, HCl and NaOH treated breadfruit leaves dipped in four types of oil: petrol, lubricant, used vegetable oil (UVO), and diesel.

The reusability of breadfruit leaves in adsorbing petrol did not show a positive result. Some errors may occur because petrol oil can be easily volatile in room temperature, affecting the weight difference. This can be seen in the weight difference of NaOH treated breadfruit leaves in which it constantly decreased and achieved constant value at the 4th to 6th cycle; then, the weight difference value constantly decreases again until the 8th cycle.

Meanwhile, in Fig. 5(b), the reusability of breadfruit leaves in adsorbing oil in diesel shows a better result compared to the adsorption of breadfruit leaves in petrol because diesel is not easily volatile needs a higher temperature than petrol does. The reusability of treated HCl and NaOH in

adsorbing diesel can be seen when the weight difference becomes constant at the 5th to the 8th cycle while the untreated breadfruit leaves achieve a constant value of weight difference at 6th cycle until the last cycle.

Based on Fig. 5(c), the reusability of the treated HCl and NaOH breadfruit leaves in adsorbing the lubricant oil shows a positive result as it can be seen at the 5th to 8th cycle, where the weight difference between the cycles becomes constant. This is followed by untreated breadfruit leaves where the weight difference achieves constant value at the 6th to 8th cycle.

The last graph in Fig. 5(d) shows the reusability of breadfruit leaves in used vegetable oil. The weight difference of the treated breadfruit leaves in UVO shows significant value, just like oil adsorption in lubricant and diesel oil. This is because it achieves constant value at the 5th cycle until the last cycle. This followed by the untreated breadfruit leaves, which shows the reusability at the 7th to 8th cycle. The same finding also reported by [21] and [22] in their previous study about the oil removal using Kapok fibre. While, the researcher also reported about the usage of lemon peel waste in removing oil and the same observation about the reusability also reported similar with this study [23].

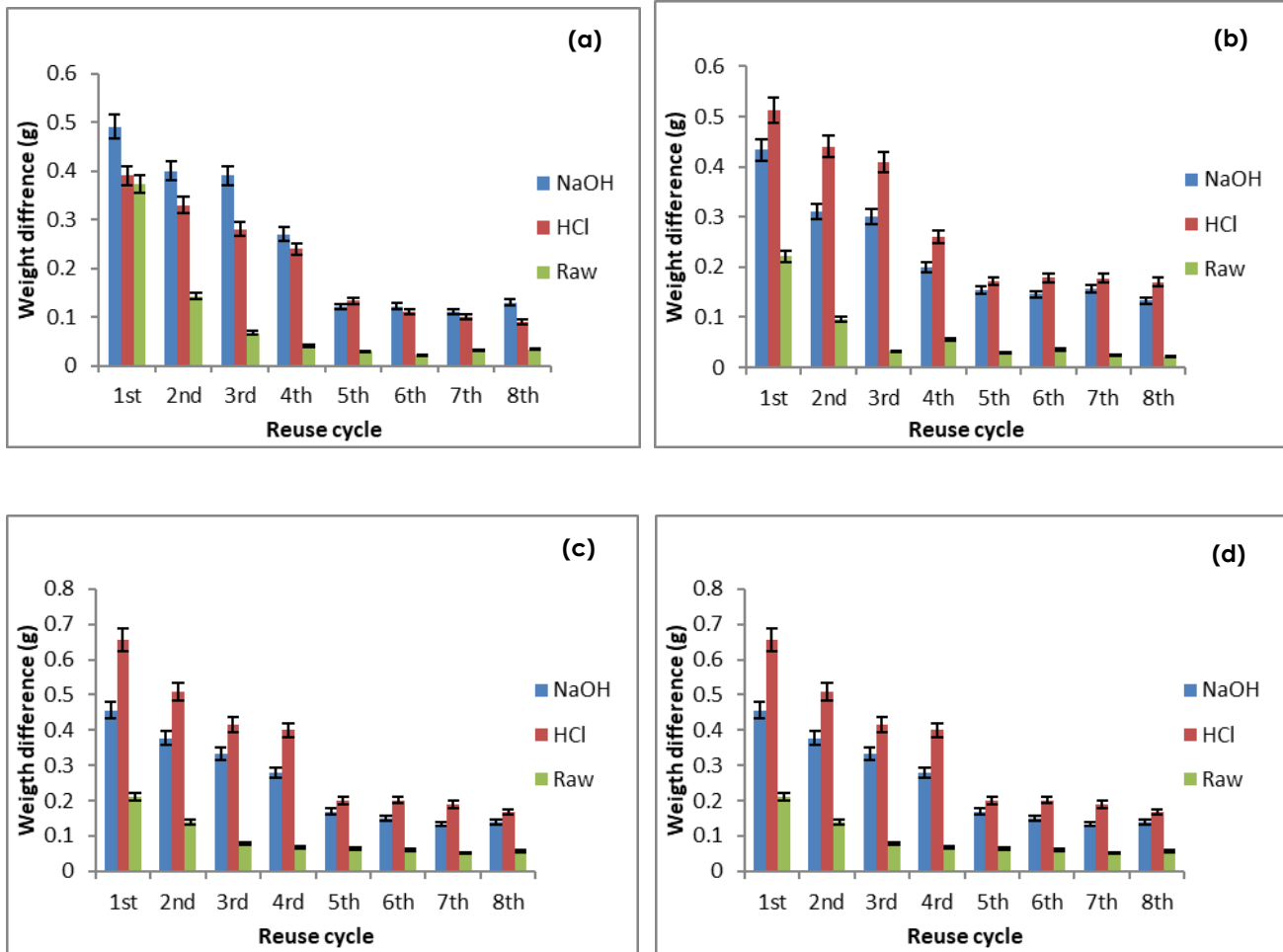


Fig 5: The reusability of breadfruit leaves in; (a) petrol, (b) diesel oil, (c) lubricant oil and (d) vegetable oil (UVO)

4.0 CONCLUSION

The study of untreated breadfruit leaves and chemically modified breadfruit leaves with HCl and NaOH has achieved its purpose. Breadfruit leaves have proved to be a low percentage of oil removal and high reusability. The breadfruit leaves act as organic sorbents are a possibility of sorbent and easy to dispose of compared to other sorbents. Despite their advantages, the breadfruit leaves have their disadvantage in terms of high-water uptake, which results in low hydrophobicity or water repelling ability of the sorbent. However, acid and alkali treatment, which can increase the waxy coating on the surface of breadfruit leaves, can contribute to high hydrophobicity and oil absorption capacity. The same finding also supported by [24] researcher. In conclusion, breadfruit leaves can be an alternative for oil removal from wastewater than synthetic sorbent such as microcrystalline cellulose. In term of economic, breadfruit leaves is environmental friendly as it is biodegradable and cost effective.

Acknowledgement

This research was supported by Faculty of Chemical Engineering, UiTM Pasir Gudang. A big thanks to UiTM Pasir Gudang for this opportunity and a lot of guidance from Sir Mohammad Abdullah. The contribution of other teammates is much appreciated.

References

- [1] M. Abdullah, M.Z. Sukor, A. Roslan, M. Tumar, Preliminary Study of Adsorption Copper (II) Ions from Aqueous Solution Using Aromatic Green Dwarf Waste as an Biosorbent. *Journal of Applied Environmental and Biological*. (2016) 6(7S)58-62. ISSN: 2090-4274
- [2] J. Wang, y. Zheng, A. Wang, Coated kapok fiber for removal of spilled oil. *Marine Pollution Bulletin*, 69(1-2), (2013) 91-96.

- [3] C. Fan, C.J. Hsu, J.Y. Lin, Y.K. Kuan, C.C. Yang, J.H. Liu, J.H. Yeh, Taiwan's legal framework for marine pollution control and responses to marine oil spills and its implementation on T.S. Taipei cargo shipwreck salvage. *Marine Pollution Bulletin*, 136(September), (2018) 84–91.
- [4] M. Bagheri, R. Roshandel, & J. Shayegan. Optimal selection of an integrated produced water treatment system in the upstream of oil industry. *Process Safety and Environmental Protection*, 117, (2018) 67–81.
- [5] M. Santander, R. T. Rodrigues & J. Rubio. Modified jet flotation in oil (petroleum) emulsion/water separations. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 375(1–3), (2011) 237–244.
- [6] C. J. Karr, G. M. Solomon & A. C. Brock-Utne. Health Effects of Common Home, Lawn, and Garden Pesticides. *Pediatric Clinics of North America*, 54(1), (2007) 63–80. <https://doi.org/10.1016/j.pcl.2006.11.005>
- [7] A. A. Al-Majed, A. R. Adebayo & M. E. Hossain. A novel technology for sustainable oil spills control. *Environmental Engineering and Management Journal*, 13(2), (2014) 265–274. <https://doi.org/10.1016/j.jenvman.2012.07.034>
- [8] M. O. Adebajo & R. L. Frost. Acetylation of raw cotton for oil spill cleanup application: An FTIR and ¹³C MAS NMR spectroscopic investigation. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, 60(10), (2014) 2315–2321. <https://doi.org/10.1016/j.saa.2003.12.005>
- [9] R. Pagnucco & M. L. Phillips. Comparative effectiveness of natural by-products and synthetic sorbents in oil spill booms. *Journal of Environmental Management*, 225, (2018) 10–16.
- [10] T. R. Annunciado, T. H. D. Sydenstricker & S. C. Amico. Experimental investigation of various vegetable fibers as sorbent materials for oil spills. *Marine Pollution Bulletin*, 50(11), (2005) 1340–1346. <https://doi.org/10.1016/j.marpolbul.2005.04.043>
- [11] J. C., N. Zerega, D. Ragone & J. T. C Motley (a ,m): o. *American Journal of Botany*, 91(5), (2004) 760–766.
- [12] D. Wu, L. Fang, Y. Qin, W. Wu, C. Mao & H. Zhu. Oil sorbents with high sorption capacity, oil/water selectivity and reusability for oil spill cleanup. *Marine Pollution Bulletin*, 84(1–2), (2014) 263–267. <https://doi.org/10.1016/j.marpolbul.2014.05.005>
- [13] L. B. L. Lim, N. Priyantha, D. T. B. Tennakoon, H. I. Chieng, M. K. Dahri & M. Suklueng. Breadnut peel as a highly effective low-cost biosorbent for methylene blue: Equilibrium, thermodynamic and kinetic studies. *Arabian Journal of Chemistry*, 10, (2017) S3216–S3228.
- [14] M. M. Rao, A. Ramesh, G. P. Chandra & K. Seshiah. Removal of copper and cadmium from the aqueous solutions by activated carbon derived from *Ceiba pentandra* hulls, 129, (2006) 123–129. <https://doi.org/10.1016/j.jhazmat.2005.08.018>
- [15] T. T. Lim & X. Huang. Evaluation of kapok (*Ceiba pentandra* (L.) Gaertn.) as a natural hollow hydrophobic-oleophilic fibrous sorbent for oil spill cleanup. *Chemosphere*, 66(5), (2007b) 955–963. <https://doi.org/10.1016/j.chemosphere.2006.05.062>
- [16] J. Wang, Y. Zheng & A. Wang. Effect of kapok fiber treated with various solvents on oil absorbency. *Industrial Crops and Products*, 40(1), (2012a) 178–184.
- [17] V. A. Alvarez & A. Va. Thermal degradation of cellulose derivatives / starch blends and sisal fibre biocomposites, 84, (2004) 13–21.
- [18] S. D. S Fauziah, R. Daik, F. A. Latif & S. M. El-sheikh. Com Characterization and Thermal Decomposition Kinetics of Kapok (*Ceiba pentandra* L.) – Based Cellulose, 9, (2014) 8–23.
- [19] A. Pradesh & A. Pradesh. Impact Properties of Kapok Based Unsaturated Polyester Hybrid Composites, 27(16) (2015).
- [20] D. Wu, L. Fang, Y. Qin, W. Wu, C. Mao & H. Zhu. Oil sorbents with high sorption capacity, oil/water selectivity and reusability for oil spill cleanup. *Marine Pollution Bulletin*, 84(1–2), (2014) 263–267. <https://doi.org/10.1016/j.marpolbul.2014.05.005>
- [21] M. Abdullah, N. A. F. N. Mohd Azlin Shah, M. A. A. Mohamed Saadun, K. A. Kadiran, S. N. 'A. Zaiton, H. A. Azman, Z. S. Othman & M. S. Osman. Comparative study of acid-treated and alkali-treated carbonised Kapok-fibres for oil/water absorption system. *J. Phys.: Conf. Ser.* (2019) 1349: 012104.
- [22] N. A. F. N. Mohd Azlin Shah, M. Abdullah, M. A. A. Mohamed Saadun, S. N. A. Zaiton, H. A. Azman, D. Che Lat, A. K. Khalid & N. Hambari. A Comparison Study of Carbonized Kapok Fibres Treated by Sodium Hydroxide Solution and Hydrochloric Acid Solution as an Absorbent in Removing IOP Conf. Ser.: Mater. Sci. Eng. (2019) 551 012004.
- [23] N. S. A. Mohd Jopery, M. Abdullah, S. Kum Yoke & A. R. Mustaffa. The preliminary study of oil removal using lemon peel waste. *Malaysian Journal*

of Chemical Engineering and Technology (MJCET), 3
(1). (2020) 56-61. ISSN 2682-8588.

[24] M. Abdullah, A. N. F. Azmi, M. Z. M. Muzakhar Azahar, F. N. Mohd Amri, K. A. Kadiran, D. Che Lat, H. Abu Kasim, & A. H. Khalid. Application of Casuarina Equisetifolia needle for the removal of heavy and light oil waste. AIP Conference Proceedings 2339, 020156 (2021); <https://doi.org/10.1063/5.0044212>.