CHEMICAL ENGINEERING TRANSACTIONS
VOL. 78, 2020
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Jeng Shiun Lim, Nor Alafiza Yunus, Jiří Jaromír Klemeš

ISBN 978-88-95608-76-1; **ISSN** 2283-9216
DOI: 10.3303/CET2078046

Esterified Durian Peel Adsorbents with Stearic Acid for Spill Removal

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The treatment of oil spill using natural adsorbents is considered as an eco-friendly and cost-effective way. Agriculture waste is preferred as an oil cleanup technology due to its biodegradation and buoyancy. The goal of this study is to examine the diesel oil adsorption efficiency, the capacity of raw peels and stearic acid esterified peels for three durian types: Ri6, CB, and 6H, which are the most popular in Vietnam. The oil adsorption capacity in artificial oil-polluted water depends on the oil content, particle size, and adsorption time. Analytical techniques of durian peel, such as microstructure and morphology using FTIR spectrometry and scanning electron microscopy are also studied. The result shows that Ri6 raw powder has the highest oil adsorption capacity. The oil adsorption capacity of raw and esterified durian peels are 0.2340 g/g and 0.3780 g/g. The results explain that the best conditions were established at 0.15 – 0.3 mm particle size of modified absorbents and pH ranging from 6.5 – 9.3 for 20 min. Adsorption capacity of esterified durian peel absorbent confirms to a Langmuir isotherm adsorption line with maximum adsorption capacity of 453.9 mg/g.

1. Introduction

In recent years, there have been many oil spills, oil-polluted wastewater causing serious impacts on the environment and ecosystems (Chuong, 2008). According to the statistics of Vietnam Environment Department, more than 90 oil spills from 1987 to 2007 in estuarine and coastal areas had caused great economic losses as well as serious environmental pollution for a long time (Thang, 2016). Oil-polluted wastewater affects fisheries, aquaculture, and tourism (Thung et al., 2007) and kills fish, especially causing serious consequences to health (Wardley-Smith, 1983).

In addition, pollution of mineral oil at some seaports in Vietnam is also a concern. Oil concentration in surface water of all 91 ports exceeded the allowable Vietnam standard of 0.1 mg/L, i.e., 0.42 mg/L in Hai Phong port and 0.6 mg/L in Cai Lan port (VASI, 2018). Therefore, it is necessary to take effective measures to recover oil quickly on a large surface area of water, without affecting to aquatic organisms.

The methods used to remove oil in the water can be divided into three groups: chemical methods (solidification, dispersion), biological methods and mechanical methods (skimmers, oil seals, adsorption) (El-Din et al., 2018). Chemical methods cause secondary pollution due to the addition of chemicals to the environment, affecting the aquatic organism, high cost and inefficient in trace level (El-Din et al., 2018). Biological methods have not yet met the requirements of the emergency response because they take so much time. The adsorption methods are still the most preferred techniques for oil clean-up because it is the most rapid (Gheorghiu et al., 2014), a simple method, friendly to the environment (El-Nafaty et al., 2013), and low cost (Nurul et al., 2011). Although organic polymer products such as polypropylene, polyethylene polyurethane have been widely used to adsorb oil in surface water, there are major disadvantages due to the difficulty to biodegrade (Gerald et al., 2003). In recent years, many researchers have focused on the use of agricultural residues natural adsorbents for oil clean-up such as banana peel (El-Din et al., 2018), duckweed, corn cob, peanut shell, bagasse (Lan, 2016), rice husk (Nui and Thuy, 2012), or greasy raw wool as natural adsorbent materials (Periolatto and Gozzelino, 2015).

To improve oil capacity adsorption, making the material surface hydrophobic is necessary (Bannerjee et al., 2006). Hence, there are many methods to increase the hydrophobic, oil-loving of adsorbents such as

Paper Received: 15/04/2019; Revised: 07/09/2019; Accepted: 30/10/2019
Please cite this article as: Nam T.V., Nguyen T.T., Dung D.N., Phuong P.T.H., 2020, Esterified Durian Peel Adsorbents with Stearic Acid for Spill Removal, Chemical Engineering Transactions, 78, 271-276 DOI:10.3303/CET2078046

pulverization to increase the contact area of the material (El-Din et al., 2018), treating with fatty acid (Sayed et al., 2006) or base (Tham et al., 2010), and esterification (Bannerjee et al., 2006).
In this study, the oil adsorbent used is durian peel (DP). It has high porosity, contains composition of cellulose being suitable to adsorb many organic pollutants (Uyen, 2012). DP waste has a volume about 115,816 to 117,992 tons/year in the southern provinces of Vietnam, showing great potential to producing natural adsorbents for oil clean-up. However, DP contains many hydroxyl groups (-OH) which are hydrophilic groups that need to convert into oil-loving tails through an esterification reaction (Bannerjee et al., 2006). Esterified DP adsorbent is easier to float on surface water so it is convenient for oil collection to recycle, and recover. This paper demonstrates the efficacy of surface modification of DP by stearic acid, which is the most common saturated fatty acid in nature, for oil adsorption.

2. Experimental

2.1 Materials

Durian has many types in Vietnam, but there are three popular types: Ri6, 6 Huu (6H) and Chuong Bo (CB). This three types of (DP) were collected from the market in Ho Chi Minh City, washed several times with tap water to clean up mud and soil. Then, the exterior thorn was removed and cut into small pieces, 1-2 cm, oven-dried to constant mass at 80 °C. Samples after drying were crushed and sieved to particles with different sizes. Dried powders in different sizes were stored and preserved in plastic containers at room temperature. Adsorbents were denoted by DP-Ri6, DP-6H, and DP-CB.
Diesel oil (DO) 0.05S was purchased at a gas station in Ho Chi Minh City used as an oil-contaminant in water (d = 0.84 g/mL). The chemicals used were of analytical grade (E. Meck).
The oil-polluted water was created by adding the appropriate amount of diesel oil into glass beakers (volume 250 mL) containing 100 mL distilled water. Tested mineral oil concentrations were based on actual oil levels at Vietnam seaports (Vietnam Administration of Seas and Islands, 2018).
Through analysis of DP with the highest oil adsorption capacity, DP-Ri6 was selected, then grafted with stearic acid according to the research of Banerjee et al. (2006). The sample of DP-Ri6 dried powder (1.00 g) was treated with 0.1 - 0.6 g of stearic acid in 100 mL of n-hexane containing one drop of concentrated H_2SO_4 as a catalyst. The mixture was refluxed in a Dean - Stark apparatus at 65 ± 2 °C for 6 h. After the reaction, the esterified DP-Ri6, named as DP-Ri6AS, was washed repeatedly with n-hexane. The material is dried in an oven at 80 °C for 24 h and stored in a plastic container.

2.2 Research methods

On the surface of untreated DP, many groups -OH (of alcohol and phenol) make materials that tend to be hydrophilic resulting in oil absorption capacity reduction. When the oil-loving tails of stearic acid were grafted to the material, they help to attract the oil molecules in the water towards the material to increase the oil absorption capacity in the water. The esterification reaction scheme is shown in Eq(1).

$$DP - OH + C_{17}H_{35} - COOH \overset{H^+}{\leftrightarrow} Cell - OCOC_{17}H_{35} + H_2O \quad (1)$$

Surface morphology of adsorbents before and after modification with stearic acid was investigated by scanning electron microscopy (SEM), JEOL JSM-5300. The oscillation frequency of molecules is analyzed by Fourier transform infrared spectroscopy (FTIR) using FTIR spectrometry, JASCO-4700.
The oil content in the water is determined by the extraction method with n-hexane solvent (Bien, 2011). The emulsion is completely dehydrated by passing anhydrous sodium sulfate, and finally, n-hexane in the mixture was removed by drying at 85 °C. The remaining oil is determined by the weighing method.
The amount of oil adsorbed on adsorbents is determined by taking the amount of initial oil minus the amount of remaining oil in water after the adsorption (g oil/g material).
To determine the highest oil adsorption potential of DP waste, SEM and FTIR were used. Also, the mineral oil adsorption capacity of three types of DP waste was also investigated by adding 1.00 g each of raw DPs to a beaker (volume 250 mL) containing 100 mL of distilled water polluted with 0.42 g of oil for 30 min (Bien and Thoi, 2011). Then, the oil absorption capacity of DPs was calculated and compared.
DP-Ri6 with suitable particle size (0.15 to 0.3 mm) was selected because of the highest oil adsorption potential to conduct the esterification reaction with stearic acid. The oil adsorption capacity and the amounts of sunk adsorbents were compared to determine the best ratio of acid and DP-Ri6. Experimental conditions: poured 0.42 g of oil into 100 mL of distilled water, at pH 6.5, and adsorption time of 30 min (Nam and Nguyen, 2016). FTIR spectrometry was used to verify the ester bond formation of DP-Ri6AS.
In this study, factors were investigated by the single-factor method. Specifically, factors independently surveyed were the oil content in the water, particle size, contact time, and maximum adsorption capacity.

When a factor was surveyed, the remaining factors were fixed at selected levels. Evaluation criteria are the mineral oil adsorption and capacity of adsorbents. Through these experiments the best value of each factor affecting the oil adsorption capacity was determined.

3. Results and discussion

3.1 Determination of drying time and moisture of DP waste

The moisture of the three DP types has little change after 8 h, from 76.31 % to 83.40 %, the highest is in DP-Ri6. Therefore, the selected drying time for the next experiment is 8 h.

3.2 Determination of the highest oil adsorption potential of DP waste

DP-Ri6, DP-6H and DP-CB with suitable particle size (0.15 to 0.3 mm) were recorded by FTIR. Figure 1 shows that the three types of DPs have the bands in the region 3,400 cm^{-1} indicating the presence of stretching of strong hydroxyl groups. In addition, the stretching C – O can be seen at 1,205 cm^{-1}, while the bands at 1,715 cm^{-1} correspond to the stretching of a carbonyl group, C=O (hemicellulose) (Bannerjee et al., 2006). DP-Ri6 has stronger and broader peaks of -OH and -C=O, so they have higher moisture and the ability to form an esterification reaction is also better. Table 1 indicates that the oil adsorption efficiency of DP-Ri6 was significantly higher than that of DP-CB and DP-6H at 1.67 and 1.73 times. Because this efficiency is still low, DP-Ri6 was chosen to graft with stearic acid through esterification.

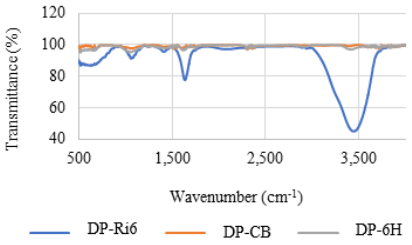

Figure 1: FTIR spectra of the three DP types

Table 1: The amount of oil adsorption of the three DPs waste

DP types	g oil/100 mL	Amount adsorbed (g oil/g adsorbent)*	Efficiency (%)
6H	0.42	0.1541 ± 0.0107[b]	36.69
CB	0.42	0.1679 ± 0.007[b]	37.99
Ri6	0.42	0.2670 ± 0.089[a]	63.57

* Oil adsorption capacity with different superscripts (a, b) are significantly ($p < 0.05$) different.

3.3 Comparison of oil adsorption capacity of DP-Ri6 and DP-Ri6AS

The levels of adsorbed oil increased from 0.234 to 0.3780 g/g when the dose of stearic acid mixed up to 0.4 g stearic/1g DP-Ri6, and the weights of adsorbents sunk decreased from 0.6068 g (DP-Ri6) to 0.0227 g (0.4 g stearic acid) (Figure 2). Thus, the ratio of acid and adsorbent (w/w) at 0.4 is the highest oil adsorption capacity and the floating ability is the best.

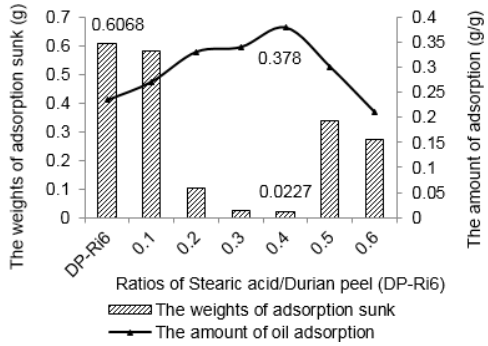

Figure 2: Effect of stearic acid dose to oil adsorption capacity and floating capacity of adsorbents

This result explained the fact that raw DP-Ri6 contains a lot of hydroxyls (-OH) groups on the surface, causing hydrophilic capacity, and easily settle-down; hence, the oil adsorption capacity is poor. When stearic acid levels increase, many bonds of DP-$OCOC_{17}H_{35}$ formed lead to improve the capacity of the oil adsorption and material buoyancy (Bannerjee et al., 2006) (Eq(1)). However, higher levels of stearic acid would cover the surface of DPs so that the oil molecules could not be adsorbed. In addition, the alkane strings ($C_{17}H_{35}$-) may limit each other because they could roll instead of forming tentacles in the water environment, thereby reducing the oil adsorption capacity of DP-Ri6AS. To verify this identification, the SEM image and the FTIR spectrum of DP-Ri6 and DP-Ri6AS were analyzed. It was found that both adsorbents have porous surfaces to allow oil and water to penetrate into the internal parts of the materials easily. After grafting with stearic acid, the material surface appears yarns of the $C_{17}H_{35}$ strings without covering pores.

Figure 3a shows a broad and strong peak at ~3,300 cm^{-1} corresponding to O-H group (alpha – cellulose). The intensity of O-H groups of DP-Ri6AS declines due to forming of carboxyl bonds (-COO-) in esterification. Some new bonds created provide evidence that the esterification occurred. The band at 2,930 cm^{-1} corresponds to C–H asymmetric stretching of $–CH_2$- groups (from stearic acid). Stronger peak intensity at 1,730 – 1,740 cm^{-1} of DP-Ri6AS indicates that the number of C=O groups increased. In addition, the presence of C–O stretching shows that stearic acid has been esterified with –OH groups of DP to form DP-$OCOC_{17}H_{35}$ (Figure 3b). This result is similar with the analysis of infrared spectrometry of DP cellulose that converts cellulose to carbon methyl cellulose (CMC) (Uyen, 2012).

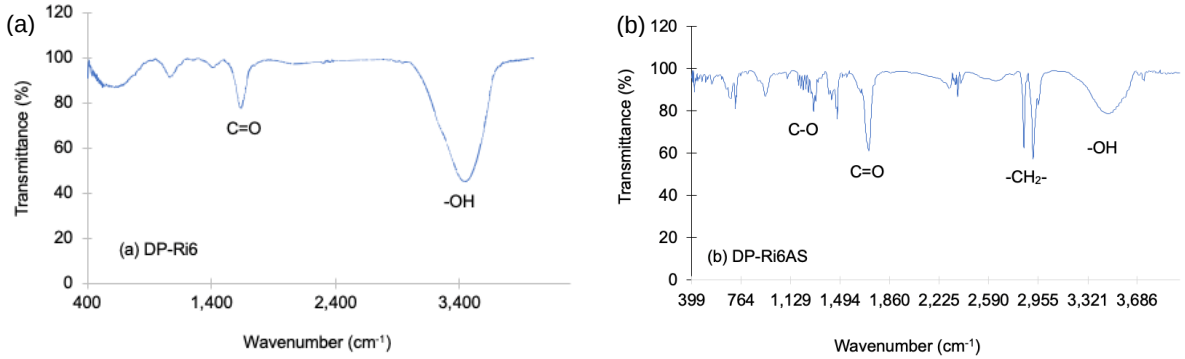

Figure 3: FTIR spectra of (a) DP-Ri6 and (b) DP-Ri6AS

3.4 Factors affecting oil adsorption capacity of DP-Ri6AS

3.4.1. Effect of oil content in water

The amount of oil adsorption increased from 0.2486 to 0.4474 g/g when the volume of oil increased from 0.3 to 0.9 mL (corresponding from 0.252 g to 0.756 g), and the oil adsorption efficiency decreased from 99.86 % to 59.18 % (Figure 4). When the volume of oil increased and proceeded to saturation state, oil in water cannot well adsorb to DP-Ri6AS; hence oil adsorption efficiency would decrease. This rule is similar to previous results (Duong et al., 2010) about the oil adsorption capacity.

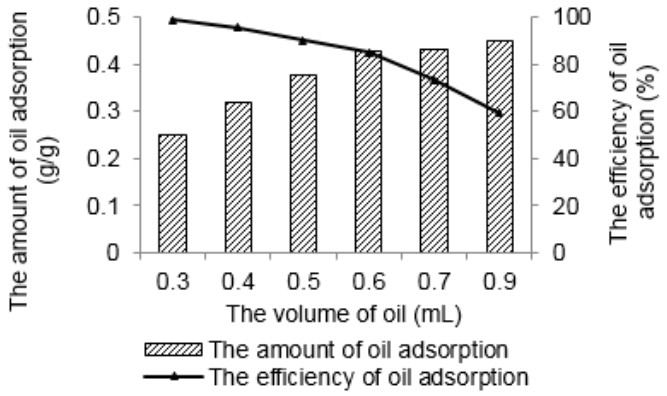

Figure 4: The effect of oil content to adsorption capacity of DP-Ri6AS

If compared with the Vietnam standard of oil content in coastal seawater, 0.1 mg/L is an allowable limit. When the oil content ranges from 0.254 g to 0.42 g (0.3 mL - 0.5 mL), oil-polluted water after adsorption is below the standard in the most suitable conditions. With a higher oil volume, the water quality after treatment is not guaranteed. Adsorption efficiency of oil content at 0.42 g (0.5 mL) is about 90 % and oil content in water is below the allowable limit after treatment.

3.4.2. Effect of particle size

With the oil content of 0.42 g in 100 mL of distilled water and 1.00 g of DP-Ri6AS material, the oil adsorption efficiency descends according to the particle size of the material, 99.5 % - 81.67 % corresponding to the amount of oil adsorbed 0.418 g/g - 0.343 g/g. This result is completely consistent with the study of Nui and Thuy (2012), which shows that the oil adsorption capacity increases as the size of the material decreases. There were no significant differences ($p < 0.05$) between < 0.15 mm and 0.15 - 0.3 mm. If the particle size is small, it would be affected by wind in practical application. Therefore, the best particle size from 0.15 to 0.3 mm is selected, smaller than the particle size of banana peel adsorbent, 0.3625 mm (El-Din et al., 2018).

3.4.3. Effect of adsorption time

The oil adsorption capacity reached 0.3193 g/g within 10 min and 0.3987 g/g (94.93 %) after 20 min, showing that oil is trapped so fast. It is highly potential for oil spill removal and interruption of oil getting away farther into the sea (Bannerjee et al., 2006). After 20 min, the oil adsorption efficiency was nearly constant and the material reached a saturation state. As a result, the most suitable adsorption time is 20 min for the next experiments.

3.4.4. Maximum adsorption capacity of DP-Ri6AS

The data obtained in this experiment, i.e., C_e and C_e/q_e, were analyzed using a Langmuir isotherm model to identify q_m. Figure 5 shows the Langmuir equation with the correlation coefficient, $R^2 = 0.9996$. The adsorption data of DP-Ri6AS could be best fitted by the Langmuir model. Therefore, the adsorption could be described as monolayer coverage and the maximum adsorption capacity of DP-Ri6AS was found, $q_m = 453.9$ mg/g.

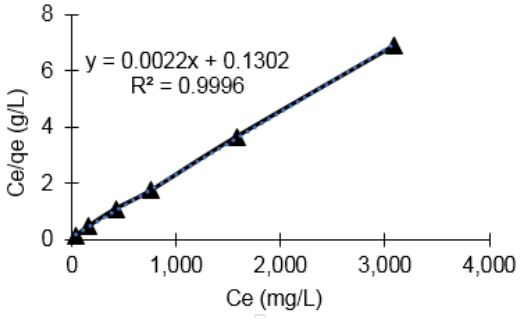

Figure 5: Langmuir isotherm of DP-Ri6AS

Compared with some research results on the oil adsorption capacity of natural adsorbents in previous studies (Duong et al., 2010; Sayed and Zayedb, 2006), the oil absorption capacity of DP – Ri6AS is higher, but still lower than that of the results of Bannerjee et al. (2006), and El-Din (2018) (Table 2). The difference is that those authors gave the adsorbent materials directly contacting with crude oil. In addition to assessing the oil adsorption capacity, this research also assessed adsorption efficiency of oil content after treatment.

Table 2: Comparison between DP-Ri6AS and other organic sorbents

Sorbents	Adsorption capacity (g/g)	Oil type	Reference
Banana Peel	5 – 7	Crude oil	EL-Din et al. (2018)
Stearic Grafted Saw Dust	5.23	Crude oil	Benerjee et al. (2006)
Untreated Saw Dust	3.77	Crude oil	Benerjee et al. (2006)
Onion Peel	0.455	Crude oil	Sayed and Zayedb (2006)
DP-Ri6AS	0.454	Oil in water	This study
Garlic Peel	0.385	Crude oil	Sayed and Zayedb (2006)
Duckweed	0.29	Oil in water	Duong et al. (2010)
Coconut Fiber	0.21	Oil in water	Duong et al. (2010)
Corn Cob	0.178	Oil in water	Duong et al. (2010)

4. Conclusion

Study on the oil adsorption capacity of the three DP types showed that DP-Ri6 has the highest potential in adsorption of mineral oil. The best mixing ratio between DP and stearic acid is 0.4 g acid/1g of DP-Ri6 to create the product of esterification process, DP-Ri6AS, having the highest oil adsorption capacity. Oil adsorption capacity of DP-Ri6AS is higher than that of DP-Ri6 1.61 times. Experimental results of oil adsorption capacity of 1.00 g of VSR-Ri6AS showed the maximum contaminant oil content in water that the adsorbent may treat to meet the standard is 0.42 g in 100 mL distilled water, with an optimal particle size of 0.15 - 0.3 mm, optimal adsorption time of 20 min. The maximum oil adsorption capacity of VSR-Ri6AS is 453.9 mg/g and the oil adsorption process of VSR-Ri6AS follows the isothermal Langmuir equation.

References

Banerjee S.S., Joshi M. V., Jayaram R.V., 2006, Treatment of oil spill by sorption technique using fatty acid grafted sawdust, Chemosphere, 64, 1026 - 1031.

Bien N.H., 2011, Research and investigate the ability to handle spill oil with Water Mimosa, Master's Thesis, Ba Ria-Vung Tau University, Vung Tau City, Vietnam.

Chuong N.V., 2008, Oil spills pollution in the Central Sea<doc.edu.vn/tai-lieu/de-tai-o-nhiem-dau-tran-o-bo-bien-mien-trung-49268/> accessed 15.06.2016 (in Vietnamese).

Duong P.T., Hoan B.Đ., Tam N.V., 2010, Study on the oil adsorption capacity in wastewater with natural materials such as duckweed, corn cob, straw, and coconut fiber, Journal of Marine Science and Technology, 24, 67 - 71.

El-Din G.A., Amer A.A., Malsh G., Hussein M., 2018, Study on the use of banana peels for oil spill removal, Alexandria Engineering Journal, 57, 2061 - 2068.

El-Nafaty U.A., Muhammad I.M., Abdulsalam S., 2013, Biosorption and kinetics studies on oil removal from produced water using banana peel, Civil and Environmental Research, 3 (7), 125 - 136.

Gerald D., Herve C., Marie-Elisabeth B., Christophe B., Christian V., 2003, Oil removal from water by selective sorption on hydrophobic cotton fibers, Study of sorption properties and comparison with other cotton fiber-based sorbents, Environmental Science and Technology, 37, 1013 - 1015.

Gheorghiu A.D., Torok Z., Ozunu A., Antonioni G., Cozzani V., 2014, Natech risk analysis in the context of land use planning. Case study: Petroleum products storage tank farm next to a residential area, Chemical Engineering Transactions, 36, 439 - 444.

Ha V.T.T., 2012, Research on manufacturing new selectively absorbs oil in mixture of oil and water that can be applied in the process of separating and treating oil spills, Report, Vietnam Institute of Industrial Chemistry, 26 - 27.

Lan P.T.N., 2016, Survey and evaluate the ability to handle spill oil with natural adsorbent, Journal of Water Resources & Environmental Engineering, 5, 69 - 76.

Nam T.V., Nguyen T.T., 2016, Study on mineral oil absorption capacity of durian peel modified with fatty acid, The 2016 international conference on advanced technology & sustainable development, 21st – 23rd August, Ho Chi Minh City, Vietnam, 1364 - 1369.

Nui P.X., Thuy N.V., 2012, Study on the use of modified rice husk in the process of treating oil-polluted wastewater, Project Report, Hanoi University of Mining and Geology, Ha Noi City, Vietnam.

Nurul I.H., Nor A.A.W., Norain I., Rozan B., 2011, Sorption equilibrium and kinetics of oil from aqueous solution using Banana Pseudostem Fibers, International Conference on Environment and Industrial Innovation, 12, 177 - 181.

Periolatto M., Gozzelino G., 2015, Greasy raw wool for clean-up process of marine oil spill: From laboratory test to scaled prototype, Chemical Engineering Transactions, 43, 2269 - 2274.

Sayed S.A., Zayed A.M., 2006, Investigation of the effectiveness of some adsorbent materials in oil spill clean-ups, Desalination,194 (1-3), 90 - 99.

Tham Y.J., Shamala D.A., Nur H.A.L., Ahmad M.A., Puziah A.L., 2010, Effect of activation temperature and heating duration on physical characteristic of activated carbon prepared from agricultural waste, Environment Asia, 3, 143 - 148.

Thung D.C., Thanh C.D., 2007, Assessing the impact of oil pollution on marine ecosystems in Vietnam, Institute of Marine Environment and Resources, Vietnam Academy of Science & Technology, 2 - 5.

Uyen P.H., 2012, The study transfer cellulose from durian peel into carboxyl methyl cellulose, Master's Thesis, Danang University, Da Nang City, Vietnam.

Vietnam Administration of Seas and Islands (VASI), 2018, Five consequences of marine pollution due to oil spill, Vietnam Administration of Seas and Islands <www.vasi.gov.vn/712/-05-hau-qua-moi-truong-cua-su-co-tran-dau/t708/c249/i1273> accessed 05.02.2019 (in Vietnamese).

Wardley-Smith J., 1983, The Control of Oil Pollution, Graham and Trotman Publication, London, UK.