Biochar produced from cotton husks and its application for the adsorption of oil products

Mouyuan Yang1*, Jiaqi Wang1, Yan Chen2, Junkai Gao2

1Naval Architecture and Mechanical-electrical engineering, Zhejiang Ocean University, Zhoushan, 316022, China
2School of Port and Transportation Engineering, Zhejiang Ocean University, Zhoushan, 316022, China
E-mail: 1642422723@qq.com

Abstract. Due to their low-cost, light weight, environmental protection, biological carbon as the oil adsorbent has aroused widespread attention. The discovery and research of novel biological carbon for the separation of oil from water is still required urgently. In this work, the cotton husks were prepared through high-temperature pyrolysis and they are utilized to adsorb different oils. The adsorption process and reusability were also investigated, it founded that the carbonized cotton husks (CNH) exhibit fast adsorption capacity and excellent sorption capacity and reusability, which can be the great candidate for oil spill cleanup application.

1. Introduction
There is an increasing demand for petroleum with the rapid development of industrialization[1]. However, oil spill events have frequently occurred in the progress of exploration, transportation, storage and usage, which have caused vast concern because it not only influences the health of coastal residents, but also leads to the great destruction of marine ecosystems and negative economic impacts[2]. To deal with the oily wastewater, several common methods have been put forward by scientists including bioremediation, physical methods (sorbents, skimmers, etc.), chemical methods (in situ burning and solidifiers, etc.)[3]. Nevertheless, bioremediation has the drawback of low efficiency, which has become one of the most greatest obstacles in scientific research and practical applications[4]. And chemical methods could reduce the interfacial tension between oil spill and water, which is conduitive to the emulsification and dispersion of oil spill, so that the oil could be easy to be biodegraded by water and purified by water. However, it can produce harmful substances, then further reduce water quality and damage lots of marine life[5]. Among these methods, adsorption is one of the most preferred technique for dealing with oil pollution due to the simple operation, low energy consumption, environmentally friendly[6].

To date, various adsorbing materials have investigated for oil spill recovery, including traditional absorbent materials such as activated carbon[7], zeolites[8], bentonite[9], etc and modern absorbent materials like graphene oxide[10], sponge[11], biomass[12], etc. However, traditional absorbent materials showed the drawbacks of low absorption capacity, poor recyclability in treatment for oil spill events[13]. Recently, some new adsorbents from the food-processing industry and agricultural wastes attract extensive attention of scientists, which is attribute to the advantages of low cost, good reusability, with low water pickup, etc[14].

In this work, the CNH were used for oil remove, which possessed excellent hydrophobic and
lipophilic. And then, four kinds of oils (pump oil, diesel oil, peanut oil, and lubricating oil) were used to investigate the adsorption capacity. In addition, the recyclability of carbonized cotton husk for the adsorption of lubricating oils was tested for five times. The results showed that the carbonized cotton husk possessed the better adsorption capacity and recyclability characteristic.

2. Experimental Methods

2.1. Preparation and Treatment samples
The cotton husks were taken from local farm. Then they were cleaned with water to remove undesired materials, after that the cotton husks were exposed to the sun for seven days and crushed. The dried products were put into a tube furnace and heated to 800 °C for 2 h at a heating rate of 4 °C min⁻¹ to obtain the CNH.

2.2. Oil adsorption capacity test
Four kinds of oil with different densities were tested at room temperature. We place 0.5 g sorbent in a glass beaker filled with 30 mL of oil. After 2 h of sorption, the oil sorbent were taken out for weight measurement. The oil adsorption capacity calculated according to the following equations [15]:

\[ Q = \frac{(M_0 - M_1)}{M_1} \]

Where Q is the oil adsorption capacity (g/g), M₀ is the total weight including water and sorbent, M₁ is the initial sorbent weight. The recyclability of sMS was evaluated by repeated pyrolysis processes under the nitrogen flow at the maximum temperature of 600 °C. The recovered sorbent were retest for 6 cycles.

3. Results and Discussion
To further demonstrate the oil adsorption process, the lubricating oil was dyed red by Sudan III firstly. As shown in figure 1 a, the lubricating oil (red liquid) floated on the surface of water because the oil have the lower density. Figure 1 b display the oil adsorption process at the beginning stage, it can be see that the red liquid started to close to the adsorbent, and red area was getting less. The adsorption progress were so quickly that the oil was absorbed within 60 seconds, which showed the CNH possess excellent adsorption rate.

![Figure 1. Digital photographs showing the adsorption process of oil.](image)

To quantitatively study the adsorption capacity of different oil, four kinds of oil that represent the common pollutants in Industries and daily life were used to test, and the capacity was defined as the weight of absorbed oils per unit weight of the CNH. In figure 2, the adsorption capacity of CNH for pump oil, diesel oil, peanut oil, and lubricating oil were 5.5 g/g, 3.1 g/g, 3.2 g/g, 5.1 g/g, respectively. However, the decreased order of adsorption capacity was pump oil > lubricating oil > peanut oil > diesel oil. In fact, the influence factors of adsorption capacity are related to the porosity of adsorbent and the viscosity of oil. Generally, the adsorbent which possess the higher porosity have the more adsorption capacity. The viscosity of different oil were shown in Table 1, it’s clearly that the increased adsorption capacity of CNH were consistent with rising trend of viscosity of oil. However, the
viscosity of oil is greatly influenced by the temperature. With the temperature increased, the viscosity will decreased, which can cause the lower adsorption capacity.

Table 1. Characteristics of different oil samples and organic solvents at 25 ℃

|          | Viscosity (cst) | Adsorption capacity (g/g) |
|----------|----------------|--------------------------|
| diesel oil | 5              | 3.1                      |
| peanut oil | 60             | 3.2                      |
| lubricating oil | 242      | 5.1                      |
| pump oil   | 243            | 5.5                      |

Figure 2. The adsorption capacity of CNH with different oils

To investigate the reusability of CNH, the adsorbent was pyrolyzed in the tube furnace at the tempertaure of 600 ℃ under a nitrogen atmosphere. In this work, The repeated recycling tests were carried out for 6 cycles (pump oil as an example) at room temperature. As showed in figure 3, it is clearly that the adsorption capacity had significant reduction compare with the first cycle result, which may related to destruction of the molecular structure of the adsorbent. However, after 6 cycles, the sorption capacity showed a negligible change.

Figure 3. The recyclability of CNH for the adsorption of pump oils.
4. Conclusion
In summary, the CNH was successfully prepared by simple pyrolysis. Taking advantages of the excellent hydrophobicity and porosity of carbon base materials, the CNH possess an adsorption capacity of 3.1-5.5 times their own weight. Furthermore, the CNH exhibit great reusability through 6 cycles. Therefore, the CNH had the characteristic of low-cost, facile preparation, favorable adsorption capacity and reusability, which had great potential for practical applications.

Acknowledgments
This work was supported by the Fundamental Research Funds for Zhejiang Provincial Universities and Research Institutes (No. 2019J00018) and the Science and Technology Planning Project of Zhoushan of China (No. 2019C21007, 2018C21017).

Reference
[1] Kang H, B Zhao, L Li, J Zhang. 2019. Durable superhydrophobic glass wool@polydopamine@PDMS for highly efficient oil/water separation. J Colloid Interf Sci. 544 257-65.
[2] Li Z T, H T Wu, W Y Chen, F A He, D H Li. 2019. Preparation of magnetic superhydrophobic melamine sponges for effective oil-water separation. Sep Purif Technol. 212 40-50.
[3] Chen L, Z Guo. 2018. A facile method to mussel-inspired superhydrophobic thiol-textiles@polydopamine for oil/water separation. Colloid Surface A. 554 253-60.
[4] Fard A K, G Mckay, Y Manawi, Z Malabari, M A. Hussien. 2016. Outstanding adsorption performance of high aspect ratio and super-hydrophobic carbon nanotubes for oil removal. Chemosphere. 164 142-55.
[5] Song B, J Zhu, H Fan. 2017. Magnetic fibrous sorbent for remote and efficient oil adsorption. Mar Pollut Bull. 120 159-64.
[6] Qiu L, W Wan, Z Tong, R Zhang, L Li, Y Zhou. 2013. Controllable and green synthesis of robust graphene aerogels with tunable surface properties for oil and dyes adsorption. New J Chem. 00 1-3.
[7] Okiel K, M El-Sayed, M Y. El-Kady. 2011. Treatment of oil–water emulsions by adsorption onto activated carbon, bentonite and deposited carbon. Egyptian Journal of Petroleum. 20 9-15.
[8] Samadi S, S S Yazd, H Abdoli, P Jafari, M Aliabadi. 2017. Fabrication of novel chitosan/PAN/magnetic ZSM-5 zeolite coated sponges for absorption of oil from water surfaces, Int. J. Biol. Macromol. 105 370-76.
[9] Salem S, A Salem, A. AghaBabaei. 2015. Preparation and characterization of nanoporous bentonite for regeneration of semi-treated waste engine oil: Applied aspects for enhanced recovery. Chem. Eng. J. 260 368-76.
[10] Huang T, J Dai, J H Yang, N Zhang, Y Wang, Z W Zhou. 2018. Polydopamine coated graphene oxide aerogels and their ultrahigh adsorption ability. Diam Relat Mater. 86 117-27.
[11] Xu Z, J Wang, H Li, Y Wang. 2019. Coating sponge with multifunctional and porous metal-organic framework for oil spill remediation. Chem Eng J. 370 1181-87.
[12] Angelova D, I Uzunov, S Uzunova, A Gigova, L Minchev. 2011. Kinetics of oil and oil products adsorption by carbonized rice husks. Chem Eng J. 172 306-11.
[13] Chen B, Q Ma, C Tan, T T Lim, L Huang, H Zhang. 2015. Carbon-Based Sorbents with Three-Dimensional Architectures for Water Remediation. CARBON. 11 3319-36.
[14] Zhang T, Z Li, Y Lv, Y Liu, D Yang, Q Li, F Qiu. 2019. Recent progress and future prospects of oil-absorbing materials. Chinese J Chem Eng. 27 1282-95.
[15] Yue X, T Zhang, D Yang, F Qiu, Z Li. 2018. Hybrid aerogels derived from banana peel and waste paper for efficient oil adsorption and emulsion separation. J Clean Prod. 199 411-19.
[16] Gu X, K Zhou, Y Li and J Yao. 2016. Millimeter-sized carbon/TiO 2 beads fabricated by phase inversion method for oil and dye adsorption. RSC Adv. 6 16314-18.