

Research on Green Remediation Technology of Oil Spill By Biosorbent

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Abstract. Oil spillage is a serious problem all over the world. Usage of agricultural by-products for raw materials in biosorbents applications is a promising way to solve this problem. In this paper, a green biotechnological procedure has been developed using *Phanerochaete chrysosporium* to produce an oil-sorbent from corn stalk and corn cob. Without fungal modification, the maximum sorption of oil by raw corn stalk and corn cob was 6.95 g/g and 4.14 g/g, whereas the treatment with *Phanerochaete chrysosporium* increased up to 9.03 g/g and 7.69 g/g, respectively. SEM and XRD were applied to characterization of treated and untreated materials, which showed the changes in the surface morphology and crystallinity of all biosorbents. The agricultural by-products can be utilized as biosorbent for efficient oil removal, and fungal treatment can serve as a mild and green method to increase the sorption capacity.

1. Introduction

Oil is the major source of energy for human life and production, and so many oil spillages are occurred during oil exploration, exploitation, refining, transportation, storage and usage[1]. According to NASA's report, there are more than 700 million gallons of oil end up into the oceans through these ways every year, such as the Arabian Gulf spill during the Gulf War in 1991 and the Gulf of Mexico spill of 2010. Rivers, oceans and coasts are polluted by spilled oil, which endangers human health[2, 3]. The growing number of oil accident is beginning to arise the concern and research of many scholars, so efficient and immediate technologies to remove spilled oil have been developed by various methods[4]. Conventional methods exist on removal of oil, including *in situ* burning, dispersion, skimmers, boomers, sorbents and bioremediation, among those removal techniques, usage of oil sorbents is a promising way because of its effectiveness, economical, and environment-friendly[5]. biosorbents derived from agricultural residues are made of cellulose, hemicellulose and lignin, with rough surfaces, pores, and active functional groups, which are in favour of sorption. Cellulose-based raw materials or their modified forms have been explored as biosorbents for removal of spilled oil from oil/water surface by capillary forces and van de Waals forces, such as sawdust, kapok, sisal, cotton and sugarcane bagasse as oil-sorbents. They have the advantages of selective removal of oil over water, biodegradability, relatively low cost, and limited impact on the environment[6].



Corn is one of the major economical crops all over the world, and it produces abundant of byproducts such as corncob, corn leave and corn stalk, so the importance of utilization the abundantly available and inexpensive resource has been realized[7]. The usage of corn stalk as an oil-sorbent in recovery of spilled oils has received attention recently. Considering oil sorption capacity of raw corn stalk is relatively low, some modification methods, mainly physical and chemical, should be taken in order to produce high-efficiency oil-sorbent. Compared to physical and chemical modification, biological modifications, such as fungal cultivation and enzyme treatment, are promising methods that have been used for biosorbent modification, as biological process can avoid use of toxic reagents, and will not cause secondary pollution. White-rot fungi have abundant extracellular enzymes and mycelia which can penetrate into plant cell walls and degrade lignocellulose[8].

In our previous studies, cellulase is utilized as a modifier to improve oil sorption of corn stalk[9]. The conditions of cellulase-modification are mild, and the equipment is simple, and the oil sorption of modified corn stalk is significantly increased about 6 times. This work aims to evaluate the potential of *Phanerochaete chrysosporium* as a modifier to produce a novel biosorbent for oil spill. To our knowledge, this is the first report on the use of white-rot fungal cultivation as a treatment approach to enhance the oil sorption capacity of biomass.

2. Materials and Methods

2.1. Materials

Two raw materials, namely corn straw (RCS) and corn cobs (RCC), were collected from Pennsylvania state university (USA). RCS and RCC were washed by distilled water to remove dusts and impurities, and then crushed to particles after air dried. The fraction between 0.25 to 0.85 mm was selected by sieving. The typical white-rot fungus, namely *Phanerochaete chrysosporium* (PC), was taken from Dr. Tien's lab in Pennsylvania state university (USA). The fungus was maintained on potato dextrose agar (PDA) Petri dish at 4 °C and activated before use. Machine oil (density at 20°C=0.87 g/cm, viscosity=0.021 Pa/s) from Shell was used in the experiment.

2.2. Methods

2.2.1. Culture condition. The solid medium containing raw materials, millet and wheat bran, with 10% distilled water was autoclaved at 121 °C for 20 min prior to fungus inoculation. *Phanerochaete chrysosporium* was inoculated in Unicorn culture bags, and each bag with 255 g RCS or RCC was inoculated with ten PDA disks (diameter of 2 mm) cut from the margins of actively growing fungal colony. Culture bags were put in an incubator at 37 °C, and culture materials were stirred every week[10].

2.2.2. Material characterization. The morphology and structure of cultivated and uncultivated materials were inspected by SEM (Model S-3700N, HITACHI). The X-ray diffraction properties were measured by a Rigaku D/max-III A Diffractometer, and crystallinity index (CrI) was calculated by Segal's equation[11]:

$$CrI = \frac{I_{002} - I_{am}}{I_{002}} \times 100$$

Where I_{002} is the maximum intensity of the 002 peak at $2\theta=22.5^\circ$, and I_{am} is the lowest intensity of the amorphous area at $2\theta=18.7^\circ$.

2.2.3. Sorption studies. Based on previous studies, the gravimetric method was used to determine the sorption capacity of oil. All tests were performed at 25°C. To evaluate the oil sorption properties of samples, a 0.2g sample was put on a steel wire mesh, and then placed into a 500 ml beaker containing 150 ml of deionized water with initial oil quality of 20 g. After 60 min, the sample was lifted up and drained for 5 min. The weight of the sample before and after adsorption was measured; the difference between the two weights was oil sorption capacity[9].

2.2.4. Evaluation of capillary rise. The wicking method was used for evaluation the relative wettability of corn stalk and corn cob[12]. Modified and unmodified biomass were packed into a glass column (diameter of 20 mm, height of 200 mm) at room temperature. At the bottom of the column, a glass filter with a pore diameter of 120 mm and a thickness of 2 mm was soldered to keep the sample. The glass tube was immersed in the oil. When the oil surface in the glass tube is consistent with the oil in the beaker, start the timer to continuously measure the height of oil in the tube during the sorption process by ruler[13].

3. Results

3.1. Effect of Modification Time

Effect of inoculation time on the modification of corn stalk and corn cob for oil sorption capacity (OSC) was investigated under the condition of temperature 37 °C during 1 to 4 weeks. As can be observed in Fig. 1, the OSC was increased as the inoculation time rises. After 3 weeks, *Phanerochaete chrysosporium* modified corn stalk (PCCS) and corn cob (PCCC) obtained the highest OSC, which was 9.03, 7.69 g/g. The solid fermentation of corn stalk and corn cob by *Phanerochaete chrysosporium* can improve their oil sorption. Compared with RCS and RCC, the OSC of PCCS and PCCC performed up to 75.3% and 85.7% better, respectively. Corn cob shows a slight advantage in improvement.

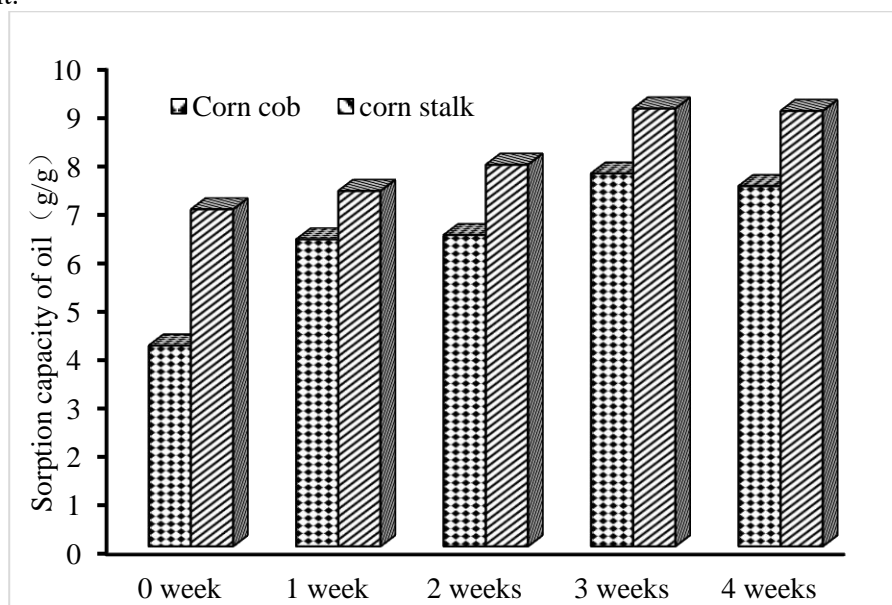


Figure 1. Effect of modification time on the sorption of oil

3.2. Material Characterization

Figure 2 presents the SEM of fungus treated and untreated materials. The surface of RCS is compact and smooth, while the surface of PCCS has formed a lot of grooves. The inner surface of RCS consists of spongy region that compact tightly, after PC treatment, the inner spongy region with a layer structure was expanded, so that PCCS provides more sites for the sorption of oil molecules[14]. As can be seen from Figure 2, the structure of PCCC has a significant change, the inner region showed a porous structure, which also formed a hollow tubular structure, and the compact layer structure was enlarged, which is conducive to accommodate more oil molecules.

Depending on XRD analysis (table 1), the crystallinity of PCCC is the smallest among all materials, and after PC modification, the CrI of PCCS and PCCC decreased by 6.6% and 26.3%, respectively. The decrease of CrI is directly proportional to the increase in the capacity of oil sorption, indicating that the smaller the crystallinity of the biosorbents, the easier the oil molecules to be sorbed. The fungal modification really enlarged the sorption area with spilled oil. Based on all characterization

results, the enhanced sorptive capacity of PCCS and PCCC should be mainly attributed to fungal modification.

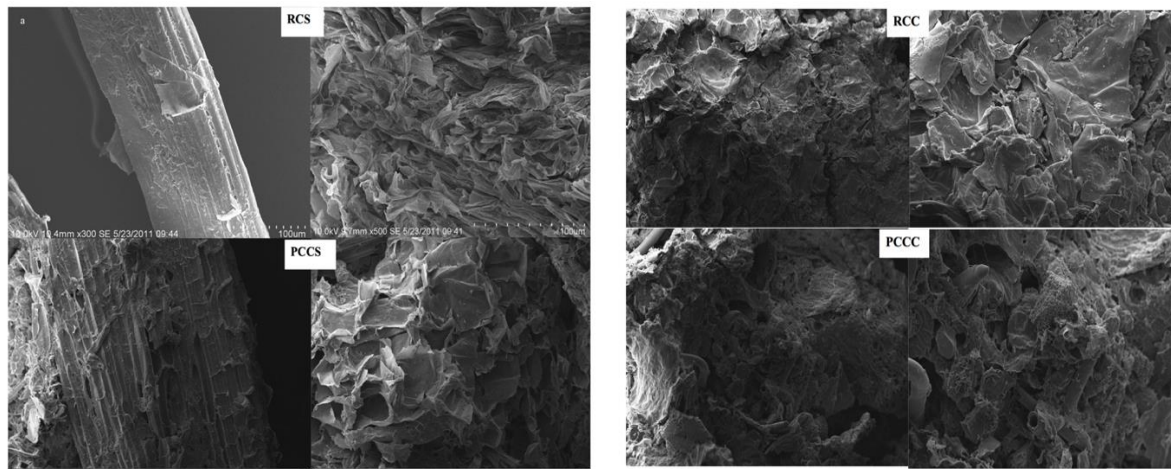


Figure 2. The SEM observation of untreated and treated corn stalk and corn cob

Table 1. Characteristics of untreated and treated corn stalk and corn cob

Biosorbent	CrI (%)
RCS	46.8
PCCS	43.7
RCC	33.5
PCCC	24.7

3.3. Evaluation of Capillary Rise

Capillary rise is one of the main driving forces for oil sorption into biosorbent, which can measure the wettability of biomass. Ribeiro reported that different materials have different capillary forces, and even the different tissues in the same biomass have significant differences in the capillary force[15]. According to this research, Fig. 3 exhibits the relationship between the heights of sorbed oil by capillary rise and the sorption time. The wettability of the materials was proportional to the rate of oil-level rise. It can be seen from fig.3 that the hydrophobicity of PCCC is improved, and the hydrophobicity of PCCS is not significantly changed. The higher capillary rise was observed for PCCC.

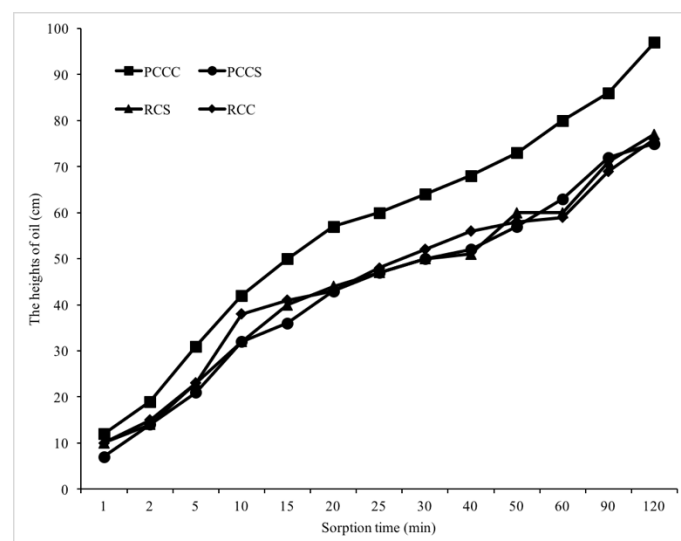


Figure 3. Capillary rises of all biosorbents

4. Conclusions

This study suggests that fungal modification is a green and effective way to produce biosorbent for recovering spilled oil from polluted water. The main mechanism governing the oil sorption is changes in chemical composition, and physical properties in PCCC and PCCS. The maximum sorption of PCCC and PCCS was 7.69 and 9.03 g/g, which increased by 85.7% and 75.3%. The experiment shows that the modification of agricultural wastes by PC has an obvious effect on improvement of oil sorption with no harm to the environment, and also can solve the disposal problem especially for agricultural by-products.

5. References

- [1] J.K. Nduka, L.O. Ezenweke, E.T. Ezenwa, Comparison of the mopping ability of chemically modified and unmodified biological wastes on crude oil and its lower fractions, *Bioresource Technology*, 99 (2008) 7902-7905.
- [2] A.A. Al-Majed, A.R. Adebayo, M.E. Hossain, A sustainable approach to controlling oil spills, *J Environ Manage*, 113C (2012) 213-227.
- [3] W. Duan, G. Chen, Q. Ye, Q. Chen, The situation of hazardous chemical accidents in China between 2000 and 2006, *J Hazard Mater*, 186 (2011) 1489-1494.
- [4] G. Hu, J. Li, G. Zeng, Recent development in the treatment of oily sludge from petroleum industry: A review, *J Hazard Mater*, 261C (2013) 470-490.
- [5] S. Sabir, Approach of Cost-Effective Adsorbents for Oil Removal from Oily Water, *Critical Reviews in Environmental Science and Technology*, 45 (2015) 1916-1945.
- [6] H. Liu, B. Geng, Y. Chen, H. Wang, Review on the Aerogel-Type Oil Sorbents Derived from Nanocellulose, *ACS Sustainable Chem. Eng.*, 5 (2017) 49-66.
- [7] S. Yang, W. Ding, H. Chen, Enzymatic hydrolysis of corn stalk in a hollow fiber ultrafiltration membrane reactor, *Biomass and Bioenergy*, 33 (2009) 332-336.
- [8] J. Liu, E. Li, X. You, C. Hu, Q. Huang, Adsorption of methylene blue on an agro-waste oiltea shell with and without fungal treatment, *Sci Rep*, 6 (2016) 38450.
- [9] D. Peng, Z. Lan, C. Guo, C. Yang, Z. Dang, Application of cellulase for the modification of corn stalk: Leading to oil sorption, *Bioresource technology*, 137 (2013) 414-418.
- [10] S. Sato, F. Liu, H. Koc, M. Tien, Expression analysis of extracellular proteins from *Phanerochaete chrysosporium* grown on different liquid and solid substrates, *Microbiology*, 153 (2007) 3023-3033.
- [11] L. Segal, J.J. Creely, A.E. Martin, C.M. Conrad, An Empirical Method for Estimating the Degree of Crystallinity of Native Cellulose Using the X-Ray Diffractometer, *Textile Research Journal*, 29 (1959) 786-794.
- [12] E.V. Lebedeva, A. Fogden, Wettability alteration of kaolinite exposed to crude oil in salt solutions, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 377 (2011) 115-122.
- [13] T. Suzuki, E. Takahashi, S. Oishi, M. Endo, M. Inagaki, Evaluation of inter-particle space network of carbon material using capillary rise of liquid, *Carbon*, 42 (2004) 2771-2773.
- [14] S. Kim, M.T. Holtzaple, Effect of structural features on enzyme digestibility of corn stover, *Bioresource Technology*, 97 (2006) 583-591.
- [15] T.H. Ribeiro, R.W. Smith, J. Rubio, Sorption of Oils by the Nonliving Biomass of a *Salvinia* sp., *Environmental Science & Technology*, 34 (2000) 5201-5205.

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