Chemosphere 170 (2017) 68–74

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Facile and fast removal of oil through porous carbon spheres derived from the fruit of *Liquidambar formosana*

Yi Feng, Shichang Liu, Guozhen Liu, Jianfeng Yao*

College of Chemical Engineering, Nanjing Forestry University, Nanjing 210037, China

HIGHLIGHTS

- Porous carbon spheres were synthesized via direct carbonization of fruit of *Liquidambar formosana*.
- Fast oil absorption was achieved by using natural centimeter-sized biochar.
- Excellent recycling ability and high mechanical properties of the carbon spheres.

ARTICLE INFO

Article history:
Received 23 May 2016
Received in revised form
18 November 2016
Accepted 26 November 2016
Available online 8 December 2016

Handling Editor: X. Cao

Keywords:
Liquidambar formosana
Biochar
Carbon sphere
Oil removal

ABSTRACT

Porous carbon spheres with a diameter of 1–2 cm were prepared via a simple carbonization of the fruit of *Liquidambar formosana*. After carbonization, the spherical structure and inner finger-like pores were maintained with high resistance to impact. Due to the porous structure and the hydrophobic nature, the carbonized fruit of *Liquidambar formosana* can float on the water surface and show a super-fast oil or organic solvent sorption ability (sorption saturation can be achieved within 1–2 min). Moreover, about 99% of adsorbed oil can be easily removed from spheres via organic solvent such as ethanol or hexane, which shows good recyclability of samples. In general, considering the low-cost and abundance of raw material collected from nature and the facile synthetic process (only by carbonization), the centimeter-sized porous spheres via the carbonization of fruit of *Liquidambar formosana* are very promising to be used for the application of oil or organic solvent spill cleanup.

1. Introduction

The effective removal of organic pollutants from contaminated water is of great importance because of the rapidly growing exploitation, transport and use of oils which have led to an increasing risk of oil spillages (Gui et al., 2010; Jung et al., 2011; Wang et al., 2015; Wu et al., 2014). Water pollution caused by oil spillages not only poses a great threat to the marine ecosystem, but also represents a great loss of energy resources. Among the existing techniques used for cleaning up spilled oil, sorption is a popular choice due to its simplicity and high efficiency (Nardecchia et al., 2013; Tandjaoui et al., 2016; Wang et al., 2014; Yang et al., 2011).

The sorbent materials used for oil spill clean-up can be classified into three typical groups: inorganic materials (Gui et al., 2011; Iqbal and Abdala, 2013), synthetic organic materials (Khosravi and Azizian, 2015; Li et al., 2012; Zhou et al., 2015) and natural organic materials (Singh et al., 2014; Wang et al., 2013; Zang et al., 2015; Zhao et al., 2011). Inorganic adsorbents (i.e., graphene, fly ash, diatomite, etc.) usually have high synthesis costs, complicated fabrication procedures and low adsorption capacities. For synthetic organic absorbents such as polypropylene, polyurethane, polystyrene and polydimethylsoloxane, though they possess high affinity to oil, one of the main drawback is the slow degradation that would result in a waste problem. Besides, such materials usually have tedious fabrication procedures and are not cost-effective. Natural organic materials from plants and animal residues, such as cotton wool, chitosan and coconut husk, have been examined for oil adsorption (Likon et al., 2013; Teas et al., 2001; Venkatanarasimhan and Raghavachari, 2013). Due to the fact that natural organic materials are abundant, renewable, biodegradable and low in cost, much attention has been paid to the use of such materials for oil adsorption. Therefore, natural organic materials are very promising to be used for the removal of oils from water in terms of large-scale production and practical applications.

Liquidambar formosana, commonly known as the *Chinese sweet*

* Corresponding author.
E-mail address: jfyao@njfu.edu.cn (J. Yao).

http://dx.doi.org/10.1016/j.chemosphere.2016.11.166

gum or *formosan gum*, is a species of tree in the family Altingiaceae native to East Asia (Chen et al., 2013; Dat et al., 2004; Konno et al., 1988; Wang et al., 2010). The fruit of *Liquidambar formosana* under the name of *Lu Lu Tong* (LLT) has been used as a traditional Chinese medicine in China for thousands of years. The fruit has the diameter of 2–3 cm, and comprises a dense spherical cluster of achenes with numerous stiff hairs. The inside of fruit is highly porous with finger-like structure radiating from the center to the external surface. Due to the wooden and the porous structure, such spherical fruit is a very promising candidate to obtain porous carbon spheres for oil adsorption via a simple carbonization process. In this study, the fruit of *Liquidambar formosana* are used to prepare porous carbon spheres via a simple carbonization process without any other treatments. After carbonization, the spherical structure and the inner pores can be maintained that would facilitate the fast adsorption and desorption of oils. Moreover, due to hydrophobic nature of carbon, the carbon spheres can float on the surface of water, which facilitates the removal of oils from water and the recycling of adsorbed oils. Considering the abundance of the fruit of *Liquidambar formosana* and simple fabrication procedure (only by carbonization), such *Liquidambar formosana* fruit derived carbon spheres are very promising to be used for the removal of organic pollutants from water.

2. Methods

2.1. Chemicals

The fruit of *Liquidambar formosana* were collected from the campus of Nanjing Forestry University (Nanjing, China). The chemicals were used as received. They included Turpentine oil (AR, Aladdin industrial corporation, China), Paraffin oil (CP, Shanghai Lingfeng chemical reagent Co., Ltd., China), Soybean (CP, Shanghai Titanchem Co. Ltd., China), N-Methyl-2-pyrrolidone (NMP) (AR, Sinopham chemical reagent Co. Ltd., China), Methylsilicone oil (Jiangxi beyond silicone Co. Ltd., China), Hexane (AR, Sinopham chemical reagent Co. Ltd., China) and Anhydrous ethanol (≥99.7%, Sinopham chemical reagent Co. Ltd., China).

2.2. Sample preparation and characterization

In this study, a series of carbon spheres were prepared via the carbonization of fruit of *Liquidambar formosana* in a nitrogen atmosphere at 300 °C for 1 h and then at 400, 600, 800 °C respectively for 2.5 h at a heating rate of 10 °C/min. Before and after carbonization, samples were washed by deionized water (DI) water for several times and then dried in oven at 80 °C overnight.

Scanning electron microscopy (SEM) images were taken with a JSM-7600F microscope operated at an accelerating voltage of 5.0 kV.

2.3. Density, porosity and shrinkage ratio

The true density of carbon spheres derived from the fruit of *Liquidambar formosana* was calculated via the mass of sample divided by Archimedes volume whereas bulk density was calculated via the mass of sample divided by the whole volume of the sphere. The pore volume of sphere was roughly calculated via the whole volume minus the Archimedes volume whereas the porosity was the ratio of pore volume and the whole volume of one sphere.

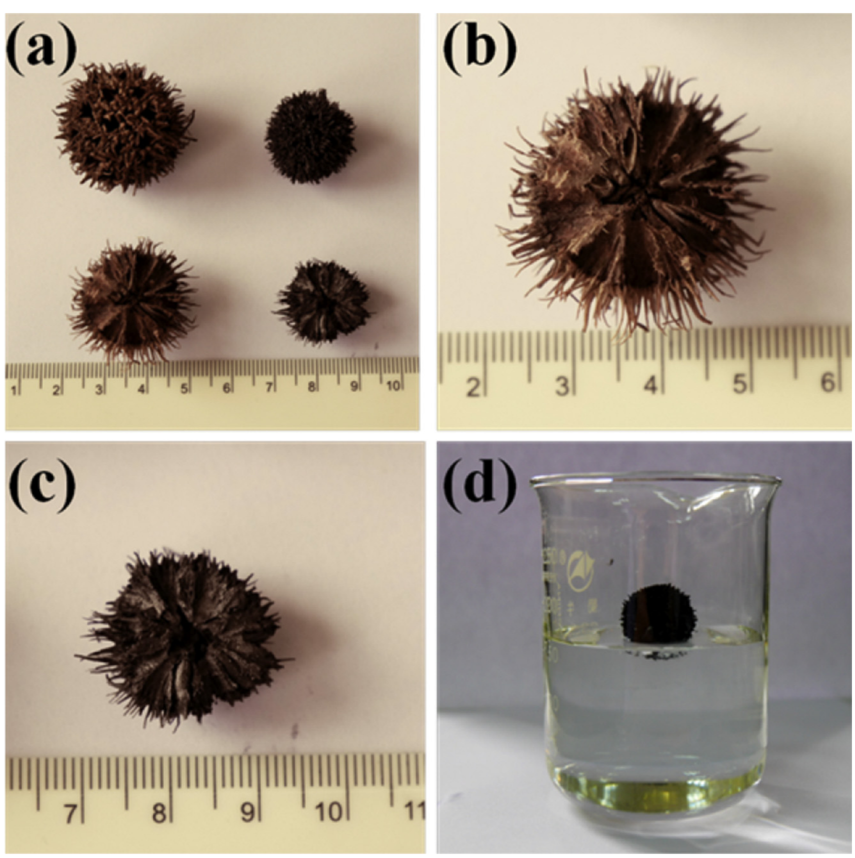

Fig. 1. Photos of (a–c) the appearance and the cross-section of fruit of *Liquidambar formosana* before and after carbonization: (b) is before carbonization and (c) is after carbonization; (d) a carbon sphere float on the surface of water, showing high hydrophobicity.