Fuel Processing Technology 171 (2018) 140–147

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Research article

Micro- and mesoporous-enriched carbon materials prepared from a mixture of petroleum-derived oily sludge and biomass

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ARTICLE INFO

Keywords:
Active carbon
Rice husk
Oily sludge
High specific surface area
Adsorption isotherm

ABSTRACT

An innovative way of producing micro-mesoporous enriched active carbon (AC) materials from mixtures of petroleum industrial waste (oily sludge) and agricultural residue (rice husk) is presented. The quality of the products was evaluated by N_2 adsorption–desorption isotherms and methylene blue (MB) adsorption tests. The asphaltene content of the oily sludge significantly affected the AC's specific surface area. The higher asphaltene content led to a higher specific surface area (2575 m^2/g) than that observed for the mixture with a lower asphaltene content (1849 m^2/g). Moreover, the ACs derived from mixtures of raw materials exhibited lower microporosity levels than those prepared with only oily sludge or rick husk. This may have been caused by the asphaltenes contained in oily sludge forming a carbon skeleton with the ash from the rice husk wrapped inside, generating more mesopores. The products prepared from the mixture also possessed far more oxygen-containing functional groups than AC produced from oily sludge alone. Meanwhile, the cellulose in the rice husk appeared to increase the amount of oxygen-functional groups in the AC products. The highest MB adsorption capabilities for the two AC samples were 588.24 and 757.58 mg/g for AC-S1-3 and AC-S2-3, respectively. The Langmuir model fitted the experimental data better than the Freundlich model, suggesting the process can be described as homogeneous monolayer adsorption. X-ray diffraction and X-ray photoelectron spectroscopy data revealed the amorphous nature of the carbon in the AC products. Overall, mixtures of oily sludge and rice husk offer a promising option for preparing porous AC.

1. Introduction

As a result of rapidly increasing demand for petroleum and the development of petroleum industry, dealing with oily sludge has become a widespread problem [1]. In China, over 3 million tons of oily sludge were generated from the storage, transportation and refinery of petroleum [2]. Owing to its toxicity, oily sludge has been classified as a hazardous waste in Europe and China [3] (*No. HW08, National Catalogue of Hazardous Wastes, 2007, Ministry of Environmental Protection of the People's Republic of China*). Oily sludge is a complicated mixture of hydrocarbons and other hazardous components including bacteria, benzenes, heavy metals and chemical additives. It can be roughly divided into three parts: water (20%–40%), oil (30%–60%) and solids. The oil component consists of saturates, aromatics, asphaltenes and resins [4,5]. The combination of asphaltenes and resins is responsible for the notably high viscosity of the oily sludge. Moreover, it is difficult to make use of or deal with the asphaltenes and resins individually. One example that has been published focused on preparing asphalt-based activated carbons (ACs) from oily sludge on account of its high asphaltene content [6]. Although the specific surface area of the AC products reached 3292 m^2/g, the asphaltene concentration procedure made the overall process expensive.

Porous carbons have been widely studied and developed in various fields. Owing to their large specific surface area, high stability and good electrical conductivity, [7] they have uses in water treatment [8], as a catalyst carrier [9], in industrial purification processes [10], as electrode materials for batteries and capacitors [11] and in hydrogen storage [12,13]. The traditional precursors used to produce active carbons are coal, pitch and petroleum [7], which are expensive and non-renewable. In recent years, biomass resources (such as shells, wood, cork powder straw and rice husk) have been considered as the raw material for active carbons preparation. Among them, rice husk has drawn extensive attention owing to the low price and wide sources. Globally, the annual production of rice husk is approximately 1440 million tons [14]. However, researchers [15–17] have found that the ACs derived from rice husk possessed low specific surface areas and narrow pore size distributions. Besides, the AC yield from rice husk tended to be low because of the high ash content of the raw materials [10,18]. Some

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https://doi.org/10.1016/j.fuproc.2017.11.013
Received 31 July 2017; Received in revised form 17 November 2017; Accepted 17 November 2017

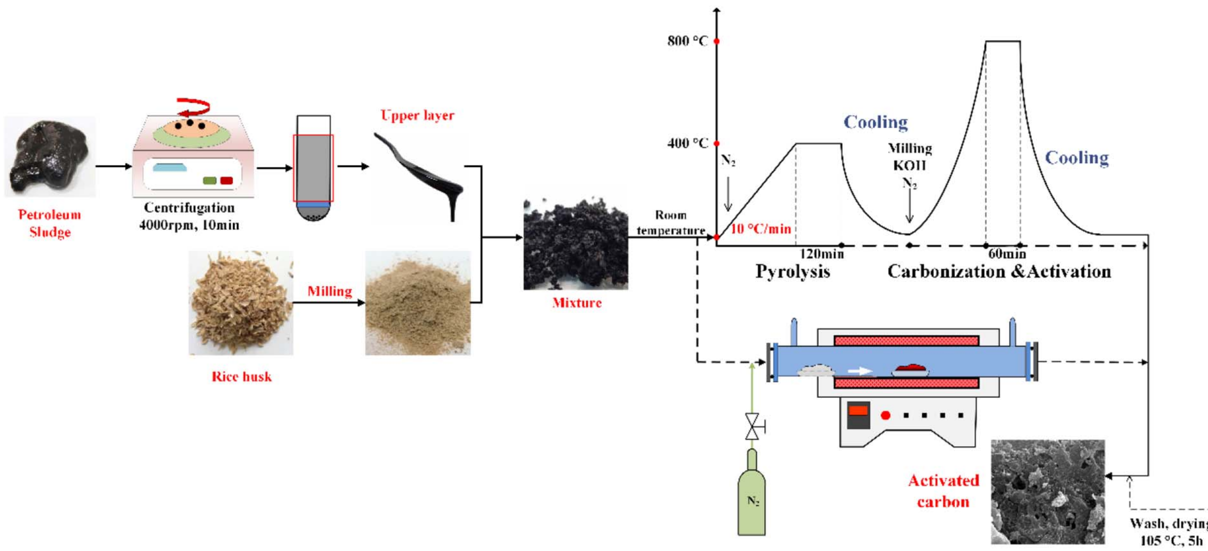

Fig. 1. The procedure for preparing porous carbon materials from mixture of oily sludge and rice husk.

researchers have studied ACs generated from a mixture of fossil fuel-derived materials and biomass to attempt to combine their advantages. For example, Meng et al. [19] prepared ACs with high surface areas by the co-carbonization of coal-tar pitch and biomass with KOH activation. The ACs possessed both the tubular morphology of the biomass and a hierarchical porous structure resulting from the coal-tar pitch. The specific surface area reached 2224 m^2/g with abundant oxygen-containing species on the surface. Elsewhere, Stoycheva et al. [20] prepared ACs by the hydro-carbonization of a mixture of coal-tar pitch and biomass materials. The derived ACs exhibited a high adsorption of mercury ions (149 mg/g), demonstrating the high quality of the products. Moreover, Plaza et al. [21] added coal-tar pitch to pine sawdust to prepare ACs and this addition promoted the carbon yield up to 35%, which is an extraordinarily high yield for a wood-based AC.

In this work, a mixture of oily sludge and rice husk is proposed as the precursor for AC production. The asphaltenes contained in oily sludge were hoped to boost the AC's quality, but have a low oxygen content. Oxidation usually plays a crucial role in AC generation from oily sludge by introducing oxygen into the carbonized intermediates. Thus plenty of active sites for the activation process that follows can be generated. However, because of the rice husk's high oxygen content, ACs produced using rice husk possess abundant oxygen-containing functional groups, negating the need for the oxidation step. Thus, the combination of these two raw materials was supposed to enhance the porosity and the amount of functional groups of ACs, generating products that simultaneously possess a high specific surface area and abundant oxygen-containing functional groups.

2. Materials and methods

2.1. Materials

Samples of oily sludge (OS) were obtained from Zhoushan, Zhejiang Province, China. The first sample, S1 (Xingzhong oily sludge), was collected from the bottom of crude oil tanks at Sinochem Xingzhong Oil Staging Co., Ltd (Zhoushan, China). The second sample, S2 (Zhoushan oily sludge), was collected from the Nahai Solid Waste Disposition Co., Ltd (Zhoushan, China).

Rice husk (RH) was collected from Zhejiang Province, China. Analytical-grade, pure solid KOH was provided by Sinopharm Chemical Reagent Co., Ltd.

The saturates, aromatics, resins and asphaltenes (SARA) content of the oily components was obtained according to the ASTM method D2007-02. The water content was determined by the procedure defined in SATM-D95-05, and the total hydrocarbon content was derived using a Soxhlet extraction.

2.2. AC production

The procedure used to produce porous carbon is illustrated in Fig. 1. The oily sludge was first centrifuged at 4000 rpm for 10 min to remove the solid particles and free water. After centrifugation, the oily sludge was approximately divided into oil, water and solids components. The oil (the upper layer) was collected and used to prepare the porous carbon. The rice husk was ground in a ball mill to less than 0.5 mm. Then it was mixed with oily sludge with a mass ratio of *x* (oily sludge:rice husk = *x*). The mixture was pyrolyzed in a N_2 atmosphere. The temperature was increased at 10 °C/min from room temperature to 400 °C and then held there for 120 min to obtain char. The char was milled to less than 2 mm and mixed with four times its mass of solid KOH. Activation was then carried out by 60 min of flowing N_2 at 800 °C. After cooling, the product was washed with deionized water to remove the residual KOH. The final AC products were obtained after drying at 105 °C. The AC samples were named AC-S1-*x* and AC-S2-*x* depending on the oily sludge:rice husk mass ratio.

2.3. Methylene-blue-adsorption test

The adsorption experiments were conducted in batch mode. Standard solutions (0.1, 0.2, 1.0, 2.0, 5.0 mg/L) for the concentration–absorbance curve were prepared by dissolving methylene blue (MB) in deionized water. The concentration of the solutions was determined by a UV spectrometer (UV 752 N, Yoke Co., China) at 665 nm. The MB concentration can be calculated according to absorbance.

To determine a sample's MB adsorption capability, 0.10 g of the AC product and a certain amount of standard MB solution (1.5 g/L) were mixed in a conical flask. The mixture was then shaken for 30 min at 200 rpm. The AC's absorptive capacity was calculated according to the concentration of the solution after adsorption.

In adsorption-isotherm studies, solutions with different initial MB concentrations (50, 100, 250, 500, 800, 1000, 1500 and 2000 mg/L) were used with an equilibrium time of 24 h. In each set, a mixture of 0.10 g AC and 30 mL of the MB solution was added to a flask and then shaken at 200 rpm. The samples were separated by centrifugation and the MB concentrations were analyzed. Each experiment was repeated