Fuel Processing Technology 162 (2017) 13–19

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Research article

Production and characterization of high quality activated carbon from oily sludge

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ARTICLE INFO

Article history:
Received 13 November 2016
Received in revised form 15 March 2017
Accepted 15 March 2017

Keywords:
Activated carbon
Oily sludge
High specific surface area
Adsorption capability

ABSTRACT

To convert the hazardous oily sludge into high quality activated carbon for water pollutant adsorption, a new preparing procedure has been proposed in current study by adding a de-oiling step before activation. The pore structure and surface chemistry of produced active carbons (ACs) were characterized by scanning electron microscopy, N_2 adsorption-desorption, XRD, FTIR and XPS. Due to the high content of asphaltene, oily sludge is a promising material for activated carbon production. The surface area of the activated carbon prepared with the proposed de-oiling step was 3292 m^2/g which was two times higher than that of normally prepared AC. Moreover, by applying the de-oiling step, the methylene blue adsorption capacities significantly increased from 17.8 mL/0.1 g to 64.6 mL/0.1 g reaching that of ACs generated from commercial asphalt. Moreover, the heavy metal leaching values of the ACs prepared were far below that of hazardous materials. Therefore, the oily sludge could be promising raw material for activated carbon production and the de-oiling procedure could improve the quality of ACs significantly.

1. Introduction

As a result of rapid economic development in recent years, massive crude oil has been exploited and consumed worldwide [1]. In 2015, around 500 million tons of crude oil have been consumed in China and over 3 million tons of oily sludge were generated [2] during the storage, transportation and refining. Oily sludge is a complex mixture of water, oil and solid particles with extremely high viscosity. Generally, approximately 30% to 60% of the oily sludge is oil, 20% to 40% is water, and the remainder is solid particles. These components are strongly mixed and sometimes stabilized as emulsion [3]. The oil phase primarily consists of saturates, aromatics, asphaltenes, and resins [4,5]. In addition to valuable hydrocarbons, many hazardous and toxic substances are also presented in oily sludge, including chemical additives, benzene derivatives, heavy metals, and pathogens [6]. Consequently, oily sludge is classified as hazardous waste in European and China [7] (No. HW08, National Catalogue of Hazardous Wastes, 2007, Ministry of Environmental Protection of the People's Republic of China).

In order to reduce sludge disposal costs and to conserve limited natural resources, the conversion of sludge into valuable materials has attracted extensive attention. Porous or activated carbon is widely used for waste water purification due to its high surface area and adsorption capability. Over the past several years, many researches have been devoted to producing adsorption carbon material from various sludge feedstock [8,9]. Jindarom et al. [10], Agrafioti et al. [11] and Tan et al. [12] have produced activated carbon from municipal sewage sludge by pyrolysis. However, the specific surface area of the carbon particles which they produced ranged from 60 to 90 m^2/g which was relatively low. To improve the adsorption surface, Li et al. [13] mixed sewage and agricultural sludge (from corn stalks) to prepare AC through chemical methods and they found that the surface area of the produced AC could reach 769.0 m^2/g at a corn stalk adding ratio of 25.0 wt%. Niasar et al. [14] used petroleum coke as material to prepare AC with KOH as activator. They reported that due to the high carbon content of the coke, the products had very high surface area and showed excellent adsorption performance. Mohammadi et al. [15] studied the possibility of producing porous carbons from oily sludge by thermochemical treatment and found that the addition of activator could increase the surface area and the pore volume of the product. Anom Guritno [16] has synthesized porous carbon from oily sludge using mesoporous silica as template. The elemental analysis results showed the sludge he used contained 47.10% carbon and the produced porous carbon was rich in mesopore structure (61% of total pore volume).

Previous research indicated that due to its high carbon content, oily sludge was potential material for producing AC. However, the reported adsorption capability of the AC derived from oily sludge was still not good enough for industrial application. Moreover, the environmental risks of using oily sludge derived AC in water treatment must be assessed.

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http://dx.doi.org/10.1016/j.fuproc.2017.03.017
0378-3820/

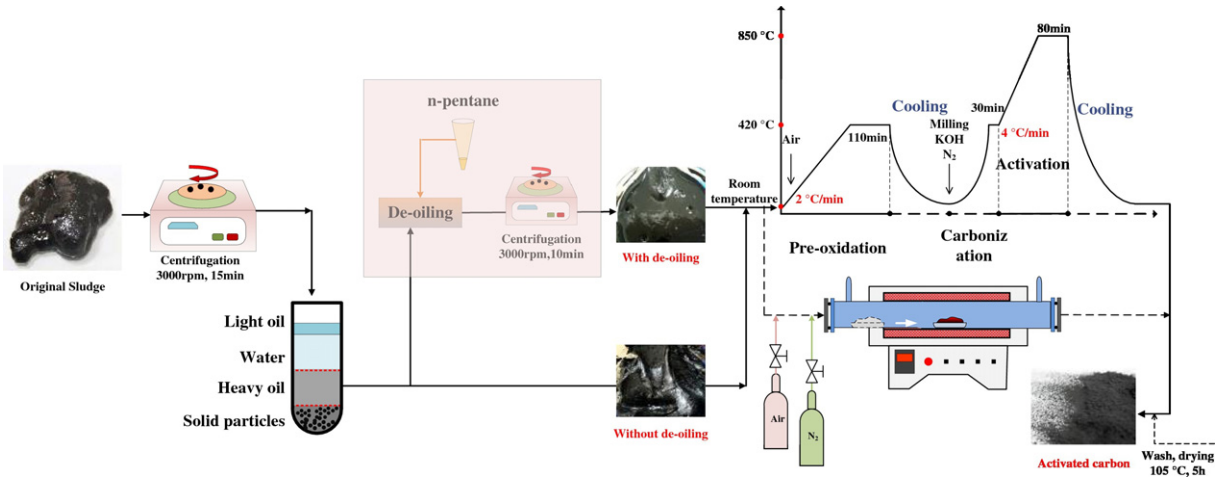

Fig. 1. The new procedure for preparing activated carbon from oily sludge.

2. Materials and methods

2.1. Materials

Sludge samples were obtained at Zhoushan national crude oil storage base located at east of China. Over 50 crude oil tanks are built there and each tank has a capacity of more than 100,000 m^3. Each of these tanks will be cleaned every 2 to 3 years to remove bottom sludge. The oily sludge used in this paper was collected from two different spots during tank cleaning and mixed before test to make it more representative. The SARA (saturates, aromatics, resins, asphaltenes) content of the oily components were obtained according to the ASTM method D2007-02. The water content was determined by ASTM-D95-05 procedure, and the total hydrocarbon content was derived according to Soxhlet extraction. The total contents of heavy metals were determined by ICP-AAS. For comparing purpose, commercial asphalt purchased from China Petrochemical Corporation was also used as material for AC preparing.

2.2. Modified AC producing procedure

The AC producing procedure is illustrated in Fig. 1 along with activation setups. To remove large solid particles and free moisture, the raw oily sludge samples were centrifuged at 3000 rpm for 15 min. After centrifugation, the oily sludge was separated into four layers (light oil, water, heavy oil and solid particles) and the heavy oil layer was subjected to AC preparation. In current work, the traditional procedure was modified by adding a new de-oiling step, which was used to remove light fraction of the oil and enhance the purity of heavy asphalt before pyrolysis treatment. The de-oiling procedure was based on the different solubility of heavy asphaltene and other light oil in the solvent. The asphaltene contained can be concentrated after the procedure. Other relatively light oil fraction such as saturates, aromatic species was dissolved into n-pentane with a mass ratio of 1:1 at room temperature and removed at a centrifugation speed of 3000 rpm for 10 min. The effect of this step was evaluated by comparing the properties of AC with or without de-oiling treatment. During the oxidation procedure, the separated product was heated at a heating rate of 2 °C/min and maintained at 420 °C for 110 min in the air, and then the product was cooled to room temperature. Then the intermediate product was milled to a particle size of less than 2 mm and mixed with solid KOH. The mixture was carbonized at 400 °C for 30 min under nitrogen atmosphere. The product was heated directly from 400 °C to 850 °C at 4 °C/min and held for 80 min for the activation treatment. The products were then washed with deionized water to remove residual alkali and dried at 105 °C for 5 h to obtain the final AC. The activated carbons prepared with and without de-oiling treatment were respectively $AC_{de\text{-}oil}$ and AC_{oil}.

All chemical agents used for the AC production, including *n*-pentane and KOH, were analytical grade and purchased from the Sinopharm Group Co., Ltd.

Table 1
Composition of oily sludge.

Composition		Sludge sample
Water, solid, oil fraction (wt%)	Water by distillation	23.25 ± 0.93
	Solid residues	34.67 ± 4.33
	Oil by solvent extraction	41.93 ± 3.25
SARA fraction of oil/(wt%)	Saturates	27.58 ± 2.66
	Aromatics	29.44 ± 3.53
	Resins	18.23 ± 2.37
	Asphaltenes	24.76 ± 3.81
Heavy metal (mg/kg)	Cd	16.20 ± 0.30
	Cu	999.95 ± 476.65
	Pb	51.75 ± 6.05
	Zn	1706.4 ± 548.8
	Cr	69.85 ± 2.25

2.3. Active carbon characterization

The morphologies of the produced active carbon were assessed by scanning electron microscopy (SEM, SIRON, FEI Co., Netherlands). The specific surface area and pore structure were determined via nitrogen adsorption at −196 °C by the surface area analyzer (Quantachrome, Autosorb-IQ2-MP, USA). Before test, the sample was degassed at 300 °C for 20 h. The surface area (S_{BET}) was estimated by the Brunauer-Emmett-Teller (BET) method, while the t-plot method and Barret-Joymer-Hanlenda (BJH) method were used to calculate the micropore (S_{mic}) and mesopore (S_{mec}) surface area. The total pore volume (V_{total}) was obtained based on nitrogen adsorption at a relative pressure (p/p_0) of approximately 0.99. Density functional theory (DFT) were employed to retrieve the pore size distribution [17].

X-ray diffraction (XRD) analysis of the AC samples was carried out using an X' Pert Pro diffractometer (PANalytical B.V., Netherlands) with a Cu $K\alpha$ radiation source. Fourier Transform Infrared Spectroscopy (FTIR) of all samples were obtained with a Nicolet 5700 (ThermoFisher Co., USA) over the range of 400 to 4000 cm^{-1}. X-ray photoelectron spectroscopy (XPS) was acquired with an X-ray photoelectron spectrometer (VG ESCALAB MARK II, UK) to analyze the surface characteristics of the AC samples. The binding energies of all core levels were referenced to the C 1s C—C bond at 284.6 eV [18].