

Scanning Electron Microscopic Studies of Carbonized Rice Husk And Apricot Stone

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Keywords: rice husks, apricot stone, carbonization, petroleum spills, adsorption.

Abstract. The microstructures of carbonized rice husk (CRH) and apricot stone (CAS) were studied to understand its adsorption of crude petroleum from water. Carbonize temperature affects the pore development of CRH, resulting in elongated large pores, as evident from the SEM data. The sorption capacities of CRH and CAS were compared in relation to different petroleum products. It was evaluated their possible practical use for water clean up from petroleum spills.

Introduction

Large-scale petroleum spills in aquatic environments commonly occur during the production, transportation, refining and storage of crude petroleum. This can cause major environmental problems due to the toxicity of many compounds in petroleum to aquatic organisms, birds and humans [1-4]. Thus, clean-up of petroleum spills from the water surface is an important task.

In recent years, there has been a growing interest in the production of adsorbents from agricultural wastes for petroleum spills clean-up such [2-6]. The adsorbents on the base of agricultural wastes are widely used in various processes including the purification and recovery of valuable substances from liquid and gaseous media [7-16]. Thus, rice husk and apricot stone may be also a suitable source for obtaining valuable adsorbent materials with high specific surface area and large pore volume by thermal treatment [17].

The aim of the present study was to investigate the adsorption performance and microstructure of CRH and CAS.

Materials and methods

The samples were carbonized according to the procedure developed at the Laboratory of Oxidation Hydrocarbon raw material in the Institute of Combustion Problems (Almaty). Rice husk and apricot stone were washed with water to remove dirt, then oven-dried at about 110 °C for 24 h. The dried samples were placed in a steel reactor and heated in a muffle furnace at 300-700 °C for 1 h

The microstructures and microanalysis of adsorbents were investigated with an SEM (Quanta 3D 200i, USA) at an accelerated voltage of 20 kV and a pressure of 0.003 Pa (performed by National Nanotechnological Laboratory of Open Type of Kazakh National University).

The sorption capacities of the samples were evaluated with petroleum products of different density: gasoline AI-80 ($\rho=0.734 \text{ g/cm}^3$); diesel fuel ($\rho=0.818 \text{ g/cm}^3$); industrial petroleum ($\rho=0.886 \text{ g/cm}^3$); heavy crude petroleum ($\rho=0.937 \text{ g/cm}^3$) and light crude petroleum ($\rho=0.792 \text{ g/cm}^3$). The petroleum sorption properties of the samples were determined using the procedure described in [17]. For that purpose 1 g adsorbent material was placed in an unwoven fabric pack then immersed into the petroleum (200 ml) or petroleum products. The sample was left in the petroleum for 30 min

without any agitation. The unwoven fabric pack with adsorbent material was taken out of petroleum and drained of excess petroleum for 10 min then weighed. The experiment is conducted at room temperature.

The petroleum sorption capacity (PSC) of the sample was calculated according to the equation:

$$\text{PSC} = (M_1 - M_2) - 1;$$

where M_1 is the mass of the petroleum adsorbed by the unwoven fabric pack with adsorbent material and M_2 is the mass of the petroleum adsorbed by the unwoven fabric pack without adsorbent material.

Results and discussion

Figures 1 and 2 represents the microstructure of virgin and carbonized materials. Figure 1 shows the SEM images of the virgin rice husk (A) and apricot stone (B). The SEM image of virgin rice husk structure resembles that of a composite material with globular particles regularly interspaced in the matrix. In this case, the globular particle is silica and the matrix consists largely of cellulose, hemicellulose and lignin. As is clear from SEM images of virgin rice husk and apricot stone are very compact and does not contain pores on the surfaces.

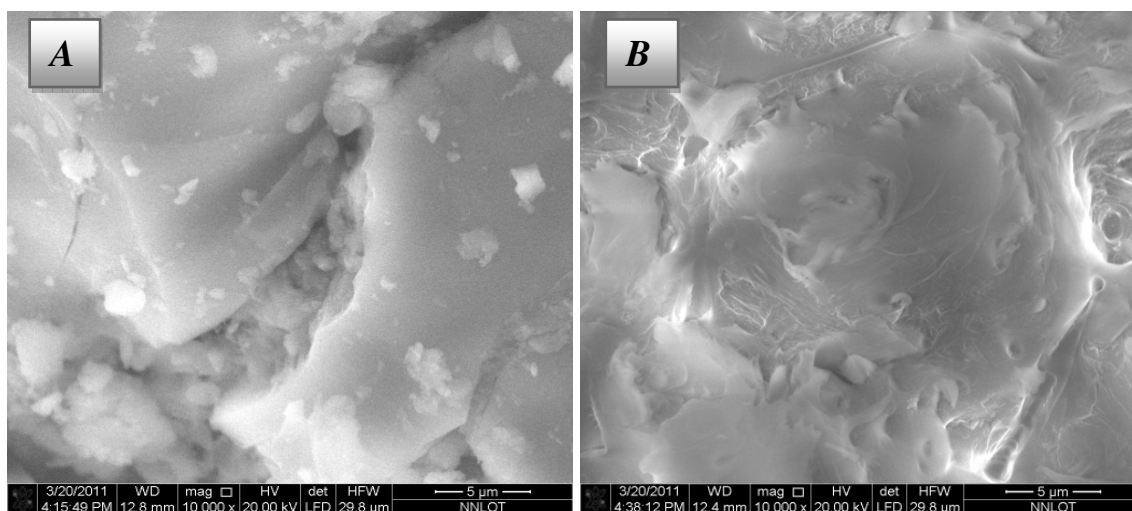


Figure 1. SEM images of the surface of virgin rice husk (A) and apricot stone (B)

The SEM image of CRH at 400°C (Fig. 2 A) shows the presence of a large number of button-like structures or bumps interspaced with small pores. These were not present initially on the virgin particles. The presence of bumps and pores can probably be explained by the volatiles escaping from the surface as a result of rapid thermal degradation between 200 and 400°C. The cross-sections of CRH at 400°C are shown in Fig. 2 (B) and (C). The SEM image (B) of CRH at 400°C clearly shows the presence of pores. Carbonize of the cellulosic material has selectively consumed the matrix leaving the silica particles behind. Cell walls around pores are fractured and elongated on heating and somewhat ordered reticulated backbones are exposed due to burning off of less dense materials (Fig. 2 C). Figure 2 (D) shows the cross-section of the CRH at 700°C. The surface of the particle shows a large number of pores and bumps. This is similar to Figure 2 (B), except that the number of pores is more and their size larger. The image of CRH at 700°C (E) showed less fractured internal structure and thicker cell walls, giving fewer pores than CRH at 400°C (C). The microstructure of CAS at 700 °C (F) is different from those of CRH. Heating at 700 °C results in a somewhat "dense" appearance with smooth very small pores are scattered on the heterogeneous surface. Thus, the sorbent having low sorption capacity toward petroleum products (Fig. 3). This can be explained by the less retention of these products into the capillaries and pores of the apricot stone.

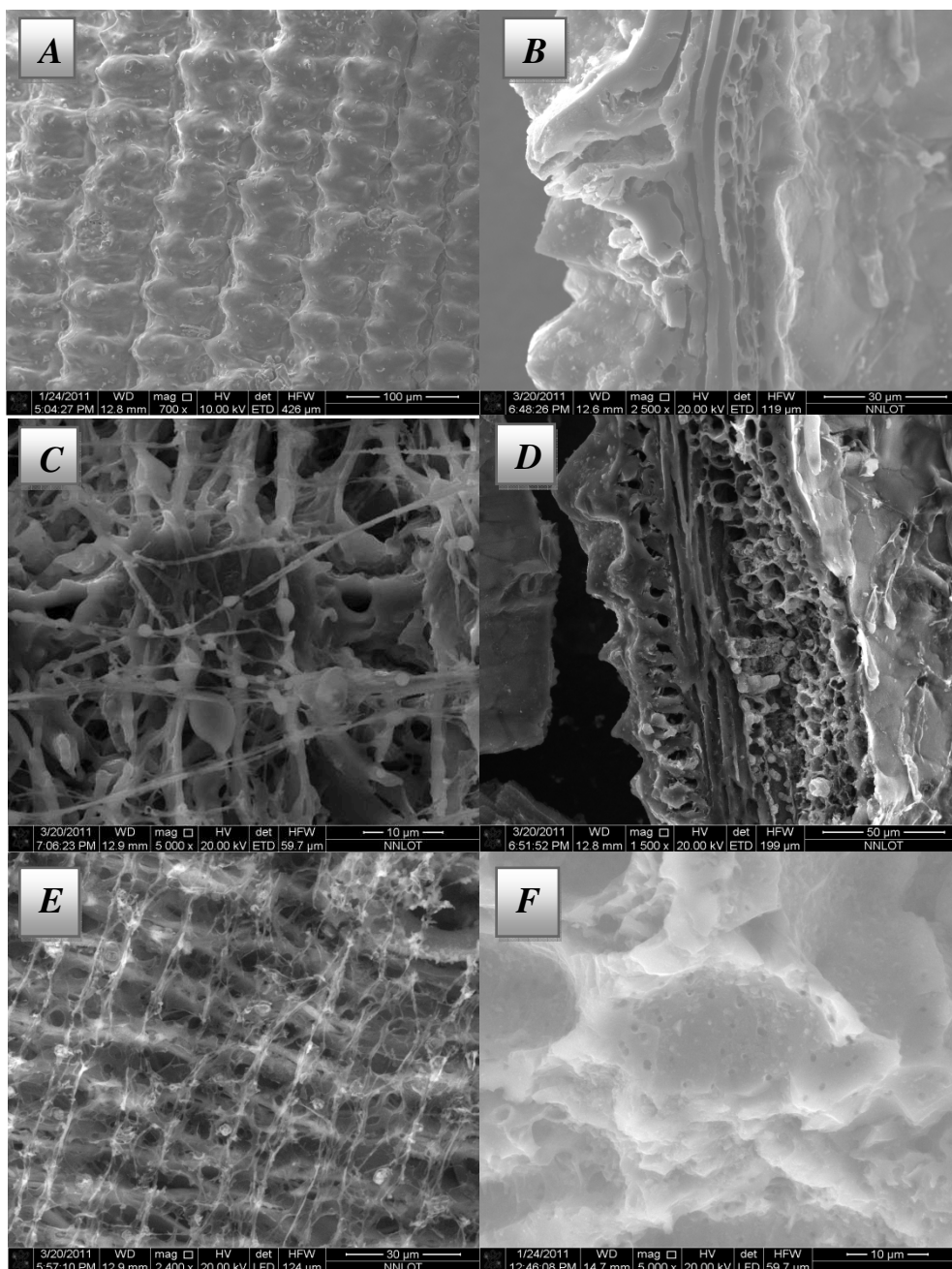


Figure 2. SEM images of CRH and CAS; CRH at 400°C (A, B, C), CRH at 700°C (D, E) and CAS at 700 °C (F)

The influence of petroleum products density on the sorption capacity of rice husks and apricot stone obtained by carbonization of them is presented on Fig. 3. With increase of petroleum products density, the sorption capacity increases linearly throughout the entire density range. For the case of apricot stone this increase is expressed more weakly for petroleum products with low density. For the investigated range of densities the sorption capacity of CRH increases 3 times, while for the CAS the increase is 6 times. This is related to the fact that with increase of the petroleum product density the size and the number of capillaries formed between the particles of the two materials will exert greater influence upon the sorption capacity than their physicochemical properties [18].

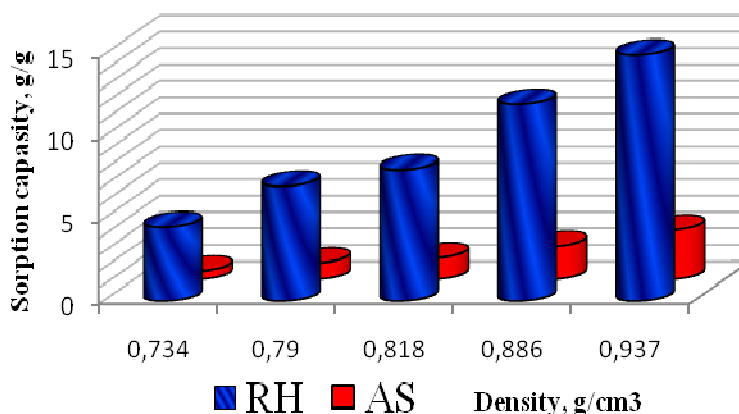


Figure 3. Dependence between adsorbate density and sorption capacity for carbonized rice husks (RH) and apricot stone (AS) carbonized at 700 °C

Summary

In this paper, the adsorption performance of CRH and CAS for the removal of petroleum spills is determined in relation to their pore structure. The adsorbent obtained by carbonizing rice husks displays high efficiency and opens up possibilities for its practical application for removal of spills of crude petroleum and petroleum products.

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