UDC 541.16, 546.344, 541.183

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The study of microstructures of the rice husk and apricot stone for wastewater treatment

The microstructures of carbonized rice husk (CRH) and apricot stone (CAS) were studied to understand its adsorption of oil from refinery wastewater. Carbonization temperature affects the pore development of adsorbent materials resulting in elongated large pores as well as appearance of micropores, as evident from the SEM data. The results of chromatographic analysis of refinery wastewater showed that almost 86.2 and 92.4 % of oil product can be removed from the solution using CRH and CAS, respectively.

Keywords: Carbonized rice husk, carbonized apricot stone, refinery wastewater, adsorption.

Introduction

The modern technological processes related to oil production, oil refining, oil product storing and transportation are often the main reason of the scale pollution of the basins. This can become the major environmental problem due to the toxicity of many compounds in oil to aquatic organisms, birds and humans [1-3]. There are various techniques to remove these pollutants from soils or water, but adsorption of oil products by adsorbent materials is the most safety and effective process [4-6].

The oil adsorption properties of carbonized rice husks and apricot stone are an interesting research subject in industrial and environmental context. The production of oil adsorbent materials on the base of the rice husk and apricot stone can solve two environmental problems: utilization of agricultural wastes and remediation of contaminated aquatic environments. The advantages of oil adsorbents obtained from agricultural wastes are their ecological safety, origin from a broad source of raw materials, high hydrophobicity, low costs and porous structure after thermal treatment that provides a high sorption capacity. The objective of this study is to investigate the oil adsorption performance and microstructure of carbonized rice husk and apricot stone. In the previous study, rice husk and apricot stone carbonized at 700 °C and tested for crude oil achieved the greatest oil adsorption in our experiments [7].

Materials and methods

Sample preparation

The samples were carbonized according to the procedure developed at the Laboratory of Oxidation of Hydrocarbon raw material at the Institute of Combustion Problems [7]. Rice husks and apricot stone were washed with water to remove dirt and other contaminants and then oven-dried at about 110ºC for 24 h. The dried materials were placed in a crucible, burned in a muffle furnace under CO_2 flow of 200 ml/min at 700 °C for 1 h and the resulting carbonized rice husk and apricot stone are designated as CRH_{700} and CAS_{700}.

Methods

Oil sorption was investigated in the continuous tubular contractor. We used real oily wastewater, which was supplied by oil-field Karazhanbas of Kazakhstan (initial oil concentration is 1745 mg/dm^3). Sorption in continuous tubular contractor was carried out with 10 g of adsorbents. Two sorption columns (15 mm in diameter and column depth was

500 mm) were formed for experiments. Flow rate of oily wastewater was 2.5 cm^3/min, effluent volume was 200-2000 cm^3 and contact time between adsorbent and water was 30 min [8]. The experiments were conducted at room temperature.

The total oil concentration of oily wastewater was determined by Gas Chromatography-Mass Spectrometry (Agilent 6890N/Agilent 5973N). The adsorption behaviors of the samples were studied by evaluating the percentage removal efficiency of oil, using the equation:

$$\text{Removal efficiency (\%) Re} = [(C_0 - C) / C_0] \cdot 100,$$

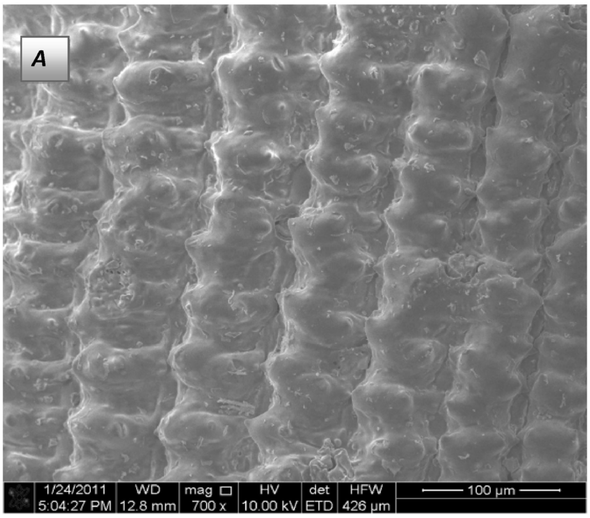
where C_0 is the initial concentration of oily wastewater, C is the oily wastewater concentration after adsorption by adsorbents.

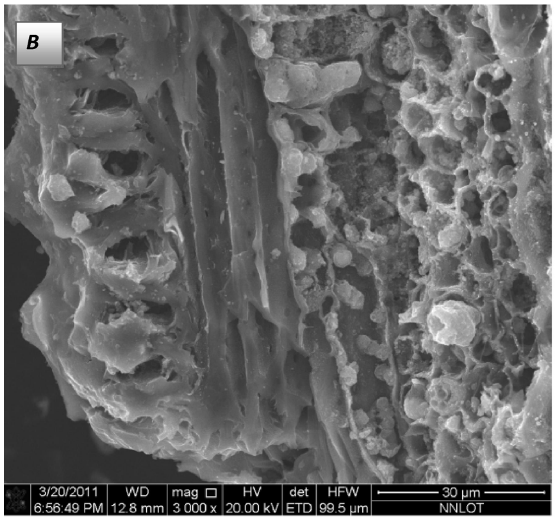
The microstructures of adsorbents were investigated with SEM (Quanta 3D 200i, USA) at an accelerated voltage of 20 kV and pressure of 0.003 Pa (performed by National Nanotechnological Laboratory of Open Type of Kazakh National University). The surface appearance of carbonized rice husk was also observed in Optical Digital Microscope (Leica DM 6000 M).

Results and discussion

Results of SEM and optical microscopic images of the carbonized materials

Figure 1 shows the SEM images of the rice husk and apricot stone carbonized at 700°C. The SEM image of CRH at 700°C (Fig. 1 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 [7]. The presence of pores and bumps can be explained due to fast removal of volatile components from the particle surface at high temperature. The cross-sections of CRH at 700°C are shown in Fig. 1 (B). The SEM image (B) of CRH at 700°C clearly shows the presence of macro- and mesopores. The microstructures of CAS at 700 °C (C, D) are different from those of CRH. Heating at 700 °C resulted in appearance of numerous micropores on the surface of carbonized apricot stone. Thus, the adsorbent has higher oil sorption capacity than CRH (Fig. 3). This can be explained by the good retention of oil products into the micropores of the apricot stone.





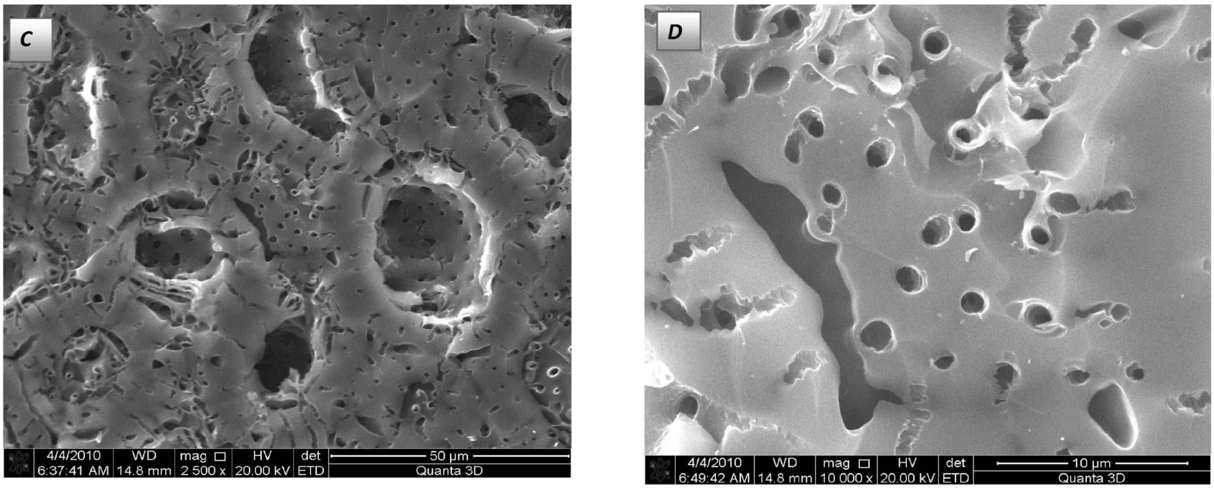


Figure 1 – SEM images of carbonized rice husk (A, B) and apricote stone (C, D).

The surface appearance of the CRH_{700} was also observed in optical digital microscope. Figure 2 shows the optical microscopic images of the CRH_{700}. There are clear differences between the lower (Fig. 2A) and the higher magnifications (Fig. 2B). In the lower magnification (Fig. 2A), some particles of carbon and amorphous silica can be seen. Fig. 2B shows the presence of pores with the diameter of 5–15 μm on the surface of the particles. High oil sorption ability is determined by porous structure of adsorbents (the presence of a large number of macro-, meso- and micropores), as well as by chemical interaction with the surface functional groups present in carbonized samples [9, 10].

One can see in SEM and optical microscopic images that carbonization allows to obtain a drastically modified structure with higher porosity compared to the virgin samples.

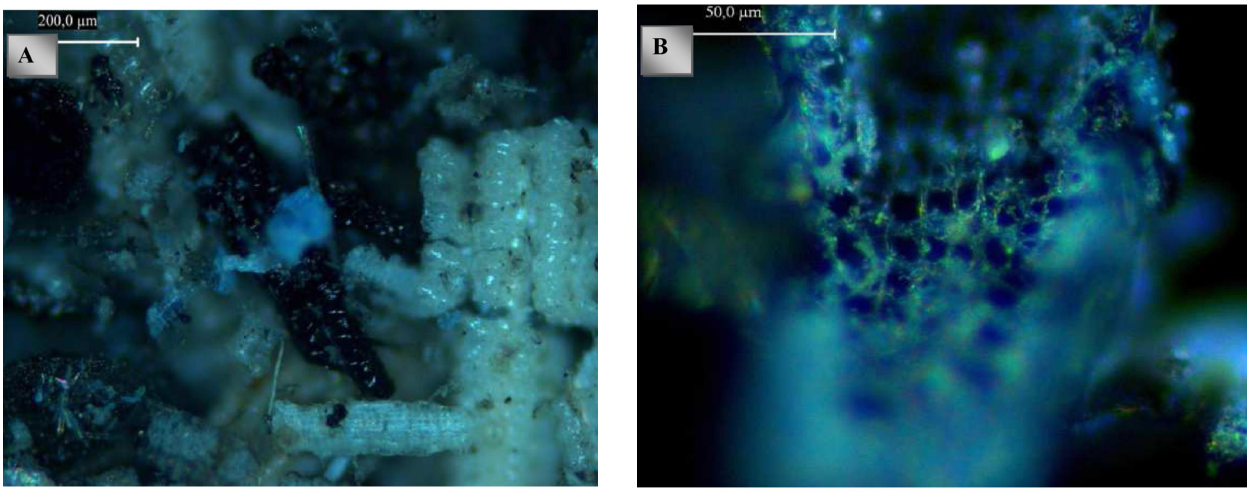


Figure 2 – Optical microscopic images of the CRH_{700}

Using of CRH_{700} and CAS_{700} for oil removal from real wastewater

We have investigated the efficiency of CRH_{700} and CAS_{700} for oil removal from real wastewater. The percentage of oil removal for two adsorbents in continuous tubular contractor is presented in Table 1. From this results the oil concentration was reduced from 1745 mg/dm^3 to 240 and 150 mg/dm^3 which is almost 86.2 and 92.4 % of oil product can be removed from the solution using CRH_{700}, CAS_{700}, respectively.

The chromatographs of oil extracts of real oily wastewater (1) and after the sorption on CRH_{700} (2) and CAS_{700} (3) in continuous tubular contractor are shown in Fig. 3. Apparently, CAS_{700} adsorbent showed higher sorption capacity compared to CRH_{700}. The sorption ability of CAS_{700} is mainly ascribed to its high surface area and having micropores [6].

The dependence of removal efficiency of CAS_{700} and CRH_{700} on the effluent volume is shown in Fig. 4. The increase in effluent volume of wastewater up to 2000 cm^3, led to the decrease in removal efficiency. The efficiency decreased for 20% and 29% in case of CAS_{700} and CRH_{700}, respectively.

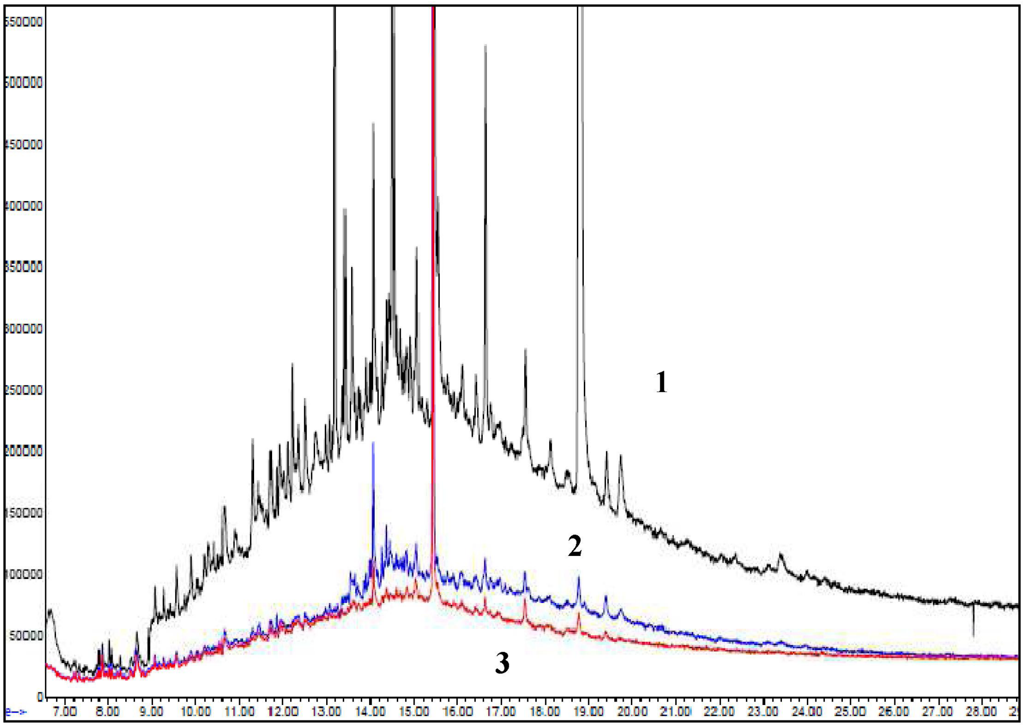


Figure 3 – Chromatograph of real oily wastewater (1) and after the sorption on CRH_{700} (2) and CAS_{700} (3) in continuous tubular contractor

Table 1 – The percentage of oil removal for two adsorbents in continuous tubular contractor.

Adsorbent	C_{oil}, mg/dm^3	Removal efficiency (%)
CRH_{700}	240	86,2
CAS_{700}	150	92,4

(wastewater flow rate: 2,5 cm^3/min, effluent volume: 200 cm^3 t: 20°C, and $\tau_{contact}$: 30 min, pH=2; initial oil concentration: 1745 mg/dm^3)

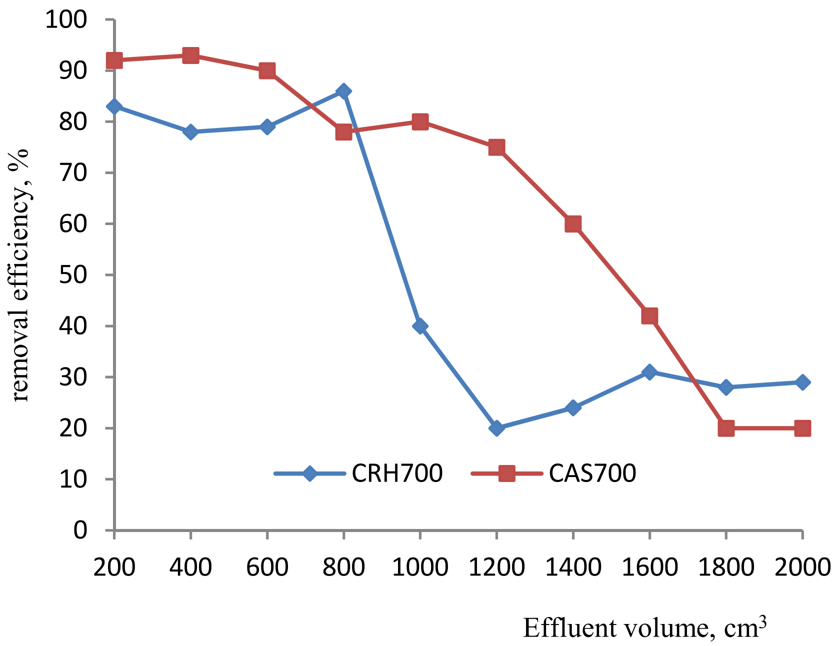


Figure 4 – The effect of effluent volume on removal efficiency of CAS_{700} and CRH_{700} (wastewater flow rate: 2,5 cm^3/min, T: 20◦C, $\tau_{contact}$: 30 min, and C_{oil} = 1745 mg/dm^3).

Conclusions

In this paper, the adsorption performance of CRH and CAS for the removal of oil from wastewater is determined in relation to their pore structure. Thermally treated adsorbent based on apricot stone is an efficient absorber for oil products since it possesses high porosity and has reactive surface groups. Thus, the investigations confirm the possibility to obtain efficient oil adsorbent from rice husk and apricot stone considered to be agricultural wastes.

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