

Carbonaceous Composites from Agricultural Wastes for Adsorption of Hydrocarbon Contamination in Water

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Abstract

Mechanical recovery of oil by oil sorbents is one of the most important countermeasures in marine oil-spill response. The preparation of oil-sorbents from agricultural waste increases economic return and reduces pollution. The sorption capacities of the carbonized rice husks and the apricot stone compared in relation to different petroleum products. Sorption capacity showed strong dependence on the particle size of sorbent and oil film thickness. The phase composition, microstructure and morphology of the composite material C/SiO₂, prepared by carbonize of rice husks were investigated by X-ray diffraction analysis, FTIR spectrometry and scanning electron microscope (SEM).

Introduction

Spills of oil on land and waters (marine, rivers, lakes and groundwater) as a result of oil transportation and storage cause serious environmental pollution and consequently call for prompt action to be taken. The spilled oil conducts to an undesirable taste and odor of drinking water and causes serious environmental damage. Contaminated oily waters cannot be used for municipal water supply, for industry, nor for irrigation. Increasing environmental concerns, especially after several hazardous accidental oil spills in the past decades renewed the interest for investigation of cleanup methods. Physical, chemical and biological processes can be used to remove oil spill from water surface or to decompose it in situ. In case of marine oil spills pollution, dispersants, booms and skimmers [1] can be used as clean-up methods to remove oil slicks from water surface. Likewise, the application of sorbent materials is an attractive method for combating of oil spill pollution mainly due to the lower costs and high effectiveness. In this respect, using of low-cost materials is very important. The low-cost sorbents are defined as materials which

are abundant in nature or as by-products or waste materials from another industry that require usually little processing [2]. Different types of sorbents such as organic, inorganic and synthetic materials have been successfully used for oil spill sorption [3, 4]. However, only natural organic sorbents such as: kapok, peat moss, straw, hay, rice husk, sawdust, ground corncobs, feathers, and other readily available carbon-based products are considered as efficient low-cost materials for oil spill clean-up. The major factors promoting application of organic products are: biodegradability, using of renewable resources, waste recycling of life cycle extension, lower cost per unit, lower impact on ecosystem if released or lost during clean-up operations, and public perception that the products are environmental friendly [5]. To address different local environmental issues, the regional available rice husk was prepared correspondingly as a low-cost sorbent for oil spill and heavy metals sorption. The application of rice husk based sorbents for the removal of heavy metals ions from wastewater were investigated [6].

Production of sorbent on base of the rice husk is quite economical and settles the ecological problems connected with purification of the water surfaces and industrial waste water and utilization of agricultural.

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The aim of the present paper is obtaining and characterization of rice husks adsorbent material as well as the investigation of its efficiency for removal of crude oil and petroleum products from aqueous medium.

Experimental part

Sample preparation

The investigations were carrying out with rice husks obtained by rice threshing of Kazakhstan variety rice grown in Kyzylorda region. Rice husks were placed in a crucible, carbonized in air in a muffle furnace (furnace 1000, Russia) at 300, 400, 500, 600, 700 and 800 °C for 1-5 h and cooled to room temperature in a desiccator. Also carbonized apricot stone was obtained with this method.

The furnace temperature was increased linearly from room temperature to the desired carbonize temperature over 1 h and then was maintained at the desired temperature for 1–5 h. The hold time is defined as the carbonize time. Samples were placed in glass screw-cap bottles and stored at room temperature until evaluation.

Methods for determination of the adsorbent's sorption capacity

The sorption capacity of the prepared materials were evaluated in case of typical oil products possess different density: gasoline Ai-80 ($\rho=0.734$ g/cm³); diesel fuel ($\rho=0.818$ g/cm³); industrial oil ($\rho=0.886$ g/cm³); heavy crude oil ($\rho=0.937$ g/cm³) and light crude oil ($\rho=0.792$ g/cm³).

The oil adsorption properties of the samples were evaluated using a simple, easily reproduced, and easily applied procedure. 1 g of sample enclosed in a pack made of unwoven polypropylene fabric of thickness 0.1 mm was dipped into the heavy oil for 5 min without stirring. The size of the pack was 70 mm x 80 mm. The bulk density of the fabric was 0.20 g/cm³, and the diameter of the polypropylene fiber was 20 mm. The oil-adsorbed sample was then suspended for 5 min to allow the excess of oil to drip away. The dipping and dripping stages were conducted at 22-24 °C and a relative humidity of 45-55%. The weight of the oil adsorbed by the unwoven fabric with and without samples was measured; the difference between the two weights was taken to indicate the oil adsorption capacity.

Analyses

The phase composition was determined by a Russian Dron 3 diffractometer using CuK_a radiation. The voltage of diffractometer's generator is 30 kV and diffraction angle 10°-60° 2 θ angle. The infrared spectra were recorded on a Nicolet-5700 FTIR spectrometer in a tablet of KBr.

The measurement of the specific surface area by the BET method was carried out on an analyzer to specific surface SORBTOMETR apparatus.

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

Results and Discussion

Effect of particle size and oil film thickness on the sorption capacity of carbonized materials

Figure 1 shows that decreasing of the average particle size increases its oil sorption capacity, where optimum are obtained at average particle size of 1 mm for rice husk and 0.5 mm for apricot stone, but the oil sorption decreases back again.

Adsorption is a surface phenomenon that is directly related to specific surface area. So increasing the specific surface area, the adsorption will increase. Also specific surface area affects the absorption of the material to a certain extent.

The oil sorption capacity and specific surface area of the rice husks carbonized at 300-800 °C for 1 h are shown in table 1. Specific surface area and oil sorption capacity increase with growth of the carbonize temperature, but weight yield decreases. As the specific surface area increases, it increases the capillaries that are being formed and hence enhance the absorption.

Depending on the kind of absorbent, the holding areas can be divided into two zones:

a) Area between the particles/fibers: The oil held between the particles is due to the formation of capillaries, this kind of absorption (most commonly found) is called Capillary absorption.

b) Area within the particles/fibers: some materials have a very unique structure with tiny micro-pores and they serve as a trap zones for fluids [7]. This kind of absorption mechanism is called Micro-porous absorption. Rice husk absorbs oil both through capillaries and the micro-pores presenting in its structure Fig. 6.

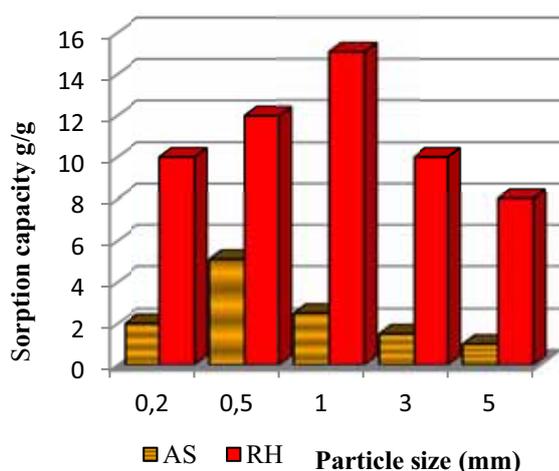


Fig. 1. Effect of particle size of carbonized rice husk and apricot stone on the sorption capacity (carbonized at 700°C for 1 h)

Table 1

Specific surface area of rice husks carbonized at different temperatures

Carbonize temperature, °C	Specific surface area, m ² /g	Oil sorption capacity, g/g	Weight yield, %
300	12	6.2	83.1
400	25	7.1	79.2
500	54	10.3	71.1
600	73	11.2	62.4
700	151	15.3	56.3
800	160	14.5	51.2

Figure 2 shows that the sorption capacity increases by increasing the oil film thickness. The figure also shows that the heavy crude oil has the highest sorption capacity until it reaches a maximum value of 16 g/g at oil film thickness of 5 mm. Light crude oil has the second highest sorption capacity of 7.03 g/g at film thickness of 5 mm; finally the lowest sorption capacity of 5.8 g/g at oil film thickness of 5 mm. The result indicates that the sorption capacity of carbonized rice husk is enhanced by increase the oil film thickness. The oil film contact sorbent surface to oil is the maximum and inhibits sorbent contact with water to minimum value i.e., the oil sorption capacity improves as the amount of oil increases. These results are in agreement [7, 8] as they have studied the effect of thickness of the oil layer.

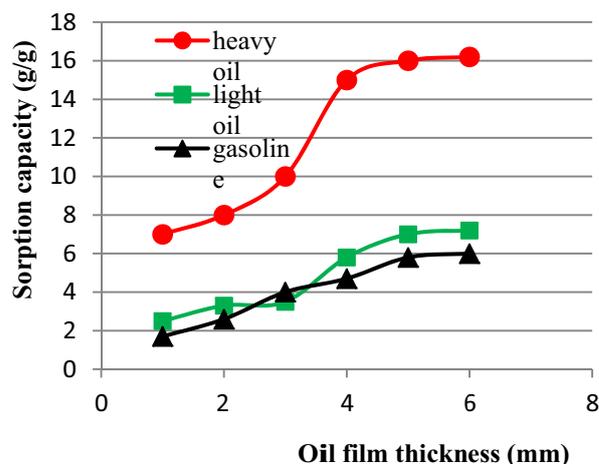


Fig.2. Effect of oil film thickness on the sorption capacity of rice husk (carbonized at 700°C for 1 h)

Investigation of the sorption capacity of carbonized rice husks and apricot stone for different petroleum products

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 enhances linearly throughout the entire density range. In case of apricot stone that growth is expressed more weakly for petroleum products with low density. This can be explained by the less retention of these products into the capillaries and pores of the apricot stone. For investigated range of densities the adsorbent sorption capacity increases 3 times, while for the apricot stones it is 6 times. This is related to the fact that with growth 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. The adsorbent obtained by carbonizing of rice husks displays higher efficiency at the adsorption of various petroleum products compared to similar adsorbents [9]. The achieved predominant mezoporous structure provides a good retention of the petroleum product into the pores of the sorbent.

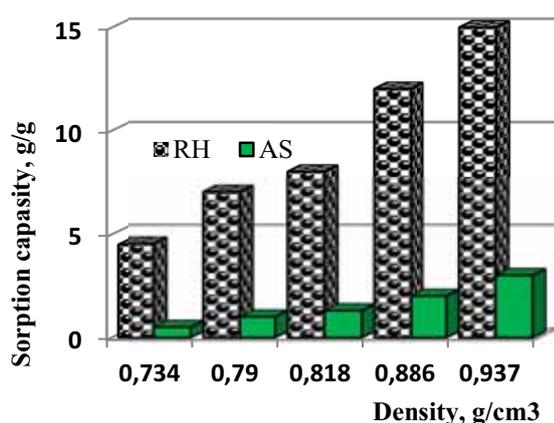


Fig. 3. Dependence between adsorbate density and sorption capacity for carbonized rice husks (RH) and apricot stone (AS) (carbonized at 700°C for 1 h)

Physicochemical properties of the carbonized rice husks

The broad smooth hump between 15° 2θ and 35° 2θ diffraction in Fig. 4 is a characteristic feature of amorphous material, indicating that carbonization converted the crystalline cellulose structure to amorphous, random, disordered structure, potentially capable to adsorb. The X-ray diffraction of the sample contains a mixture of amorphous silica and carbon. The possible bonding of silicon with monosaccharide's in rice husks has already been presented by Patel et al. [10]. The carbonization causes the decomposition of organic material and breaking of the bonds between silicon and the organic matrix. The Si – O groups become

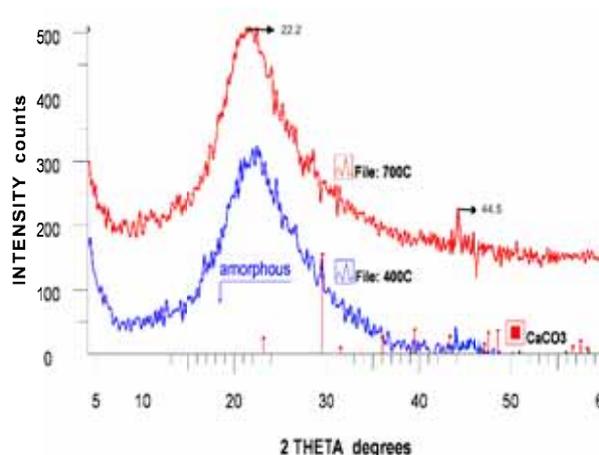


Fig. 4. XRD of the carbonized rice husk materials (400, 700°C)

attached to each other to produce a low form of cristobalite and tridimite. The resulting amorphous silica and carbon in the material show an XRD pattern with two diffused peaks. The sharp halo observed at 2θ 22° corresponds to the presence of amorphous SiO₂ [11]. The halo at 2θ 44° is typical for carbonized cellulose and reflects the initial formation of (002) and (100/101) planes related to the graphite structure [12].

As it is seen from tab. 2 the full width at half maximum (FWHM 2-Theta) is bigger for sample "400°C" that indicates the smaller size of crystallite carbon. Perhaps the calcite - CaCO₃ presents in this sample in very small amounts (less then 1.0 %). The integral intensity of the amorphous phase (net Area - cps x 2-Theta) is more for sample "700°C".

Table 2

XRD analysis of the rice husks carbonized at the temperature 400-700 °C.

Sample	Obs. Max 2-Theta °	d (Obs. Max) Angstrom	FWHM 2-Theta °	Net Area Cps x 2-Theta °
400°C	22.2 44.5	3,9658	8,499	2856,9
700°C	22.2 44.5	3,9571	8,161	3195,6

Figure 5 shows FTIR spectra of carbonized rice husks. The bands of the silicon dioxide as well as carbonaceous material in the carbonized rice husks are dominating in the IR spectrum. Our data show that the biogenic silica, comprised in the composition of the rice husks, presents in two forms: α-cristobalite and tridymite. The basic absorption band at 1095 cm⁻¹ is a singlet with weakly expressed shoulders. It is typical for

spectrum of the tridymite. The singlet band at 802 cm⁻¹, the ones at 666 cm⁻¹ and at 463 cm⁻¹ are typical for the crystal lattice of cristobalite. The broad band around 3400 cm⁻¹ is attributable to the existence of surface hydroxyl groups and chemisorbed water. The band at 1641 cm⁻¹ is due to hydrogen bonded C=O bands. The peaks at 2849 and 2921 cm⁻¹ are assigned to the C – H symmetric and asymmetric stretches of residual methylene

groups on the surface. The double peak around 1370 cm^{-1} is assigned to C – O stretching vibrations of the carboxylate groups. The band with a maximum at 1095 cm^{-1} relates to the vibrations of C – OH bond and also this wave number is characteristic of the stretching vibrations of the siloxane groups [13, 14].

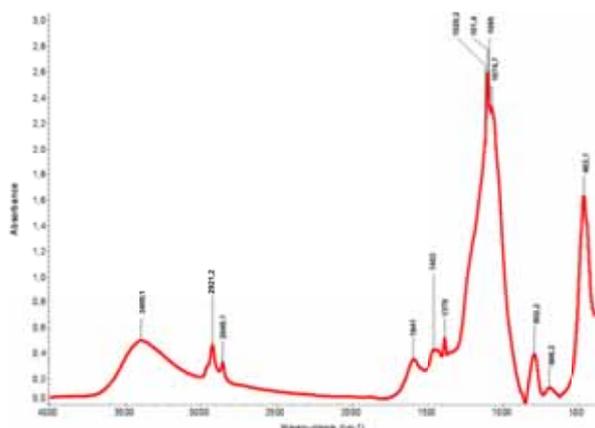


Fig. 5. FTIR spectrum of carbonized rice husk (700°C)

Figure 6 represents the microstructure of original and carbonized materials (RH-rice husk, AS-apricot stone). The SEM photographs show progressive changes of the particles surface. It is seen from Fig. 6 (A, C) that sample on the original form is very compact and does not contain pores on the surfaces. In the course of carbonization occurs change the structure of the sorbent. The SEM structures of AS700 and RH700 are shown in Fig. 6 (B) and (D), correspondingly. Heating at 700 °C (RH700) results in a somewhat "glassy" appearance with smooth very small pores (Fig. 6(D)) scattered on the heterogeneous surface [15]. The microstructure of AS700 (Fig. 6(B)) is different from the RH700. The Fig. 6(B) shows that the surface of apricot stone possesses the bigger pores than RH once and that the AS is very dense material. Thus the sorbent has low sorption capacity. This can be explained by the less retention of these products into the capillaries and pores of the apricot stone.

The SEM studies of original and carbonized samples have shown that more developed structure can be obtained by carbonization.

Table 3

Microanalysis of carbonized rice husk and apricot stone: RH500 (A), RH700 (B) and AS (C)

A			B			C		
Element	Wt %	At%	Element	Wt %	At%	Element	Wt %	At%
CK	17.98	22.48	CK	30.73	41.75	CK	94.49	95.81
OK	52.27	61.39	OK	31.68	32.52	OK	5.51	4.19
SiK	27.26	14.93	SiK	35.73	24.95	Matrix	Correction	ZAF
KK	2.50	1.20	KK	1.86	0.78			
Matrix	Correction	ZAF	Matrix	Correction	ZAF			

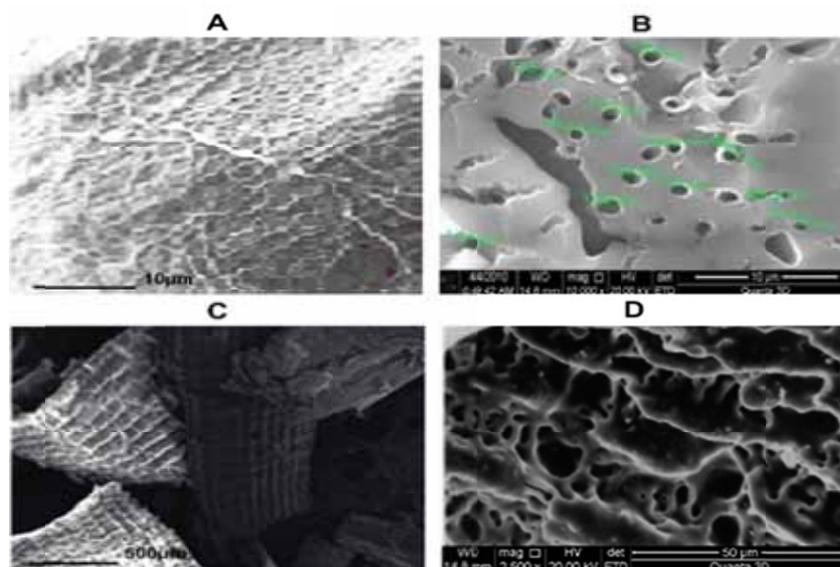


Fig. 6. SEM micrographs of original and carbonized materials: original AS (A), AS700 (B) and original RH (C), RH700 (D)

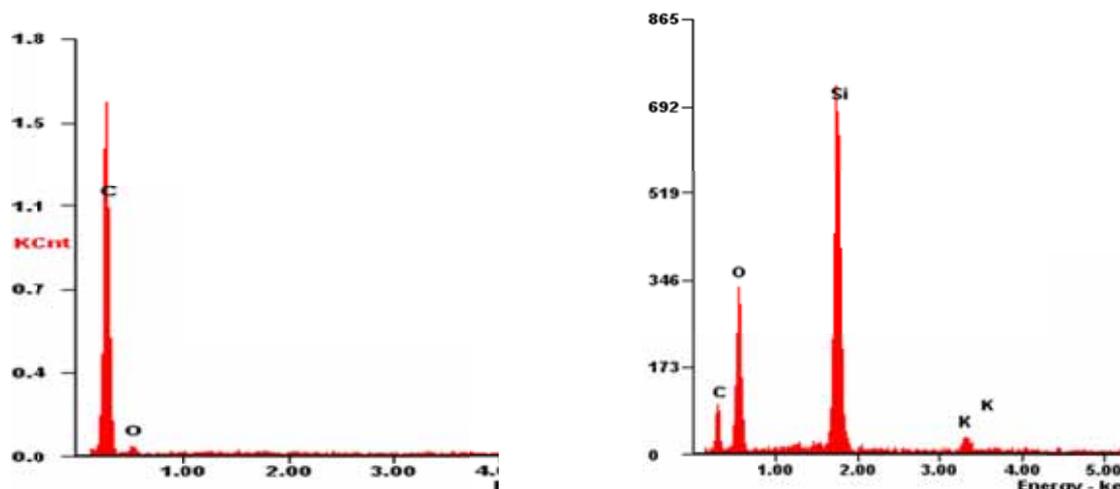


Fig. 7. Microanalysis of apricot stones and rice husk carbonized at the temperature 700 °C

The microanalysis of apricot stones and rice husks which were carbonized at the temperature 500, 700 °C were performed with SEM as well. Quantitative and qualitative analysis of carbonized sorbents are shown on fig. 7 and in tab. 3. The amount of carbon in apricot stone reaches 95% and contains only organic elements (tab. 3). The rice husk was carbonized at the temperature 500, 700 °C and contains organic and inorganic elements (27-35% of silicon and less potassium). With increase of carbonize temperature the amount of silicon and carbon increased. The higher SiO₂ content determines higher sorption capacity bearing in mind that SiO₂ itself is a good adsorbent material.

Conclusions

In this study, the oil adsorption and related properties of carbonized rice husks were evaluated. It was found that sorption capacity strongly depends on the particle size: it enhances with decreasing the particle size of sorbent and with increasing the oil film thickness. These results indicate that thermal treatment of rice husks leads to obtaining of an adsorbent material with 2-3,5 times higher sorption capacity for the whole range of petroleum products - industrial oil; gasoline Ai-80; diesel fuel; light and heavy crude oil.

The adsorbent obtained by carbonizing rice husks displays high efficiency and gives possibilities for its practical application for removal of spills of crude oil and petroleum products.

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