Petroleum Sorption by Thermally Treated Rice Husks Derived from Agricultural Byproducts

K.K. Kudaybergenov*, E.K. Ongarbayev, Z.A. Mansurov

Al-Farabi Kazakh National University, The Institute of Combustion Problems, Almaty, Kazakhstan

Abstract

Agricultural byproducts or residues are widely produced in Kazakhstan and their utilization as a sorbent material for petroleum spill can be developed as low cost, high tech environmental technology. Rice husk, an agricultural waste, was used as petroleum sorbent material. The present study examines the sorption capacity of thermally treated rice husk for different petroleum products. Results showed that the petroleum sorption capacity of this material prepared at 700 ºC was 15 g/g for heavy crude petroleum. The material obtained by thermal treatment of rice husk has very good buoyancy characteristics, high petroleum sorption capacity and high hydrophobicity. The effects of heating temperature, contact time and petroleum density on the petroleum sorption capacity of thermally treated rice husks were further studied on the basis of phase composition, microstructure and morphology using X-ray diffraction analysis, FTIR spectrometry, optical digital microscopy and scanning electron microscopy (SEM). The results of the SEM and optical microscopy studies strongly indicate that thermal treatment is a suitable method to improve structure of husk particles regarding porosity compared to virgin samples. The research provides the basis for development of a new environmental material with optimal characteristics, providing efficient sorption of petroleum and petroleum products from aqueous medium.

Introduction

The ever-growing use and transport of crude petroleum and petroleum products has led to an increasing amount of spillages of various scales. Petroleum-spills may contaminate large areas of the sea, as well as the shores where it is eventually washed up. This can cause major environmental problems due to the toxicity of many compounds in petroleum to aquatic organisms, birds and humans [1-3]. It has been estimated that petroleum is annually spilled on the surface of the ocean in amounts between 10,000,000-20,000,000 tons, whereby a ton of it may cover about 12 km^2 of the ocean's surface [4]. Moreover, the toxic volatile constituents of petroleum spills can evaporate and as a consequence, cause atmospheric pollution. Thus, clean-up of petroleum spills from the water surface is an important task.

Different methods can be used for the removal of petroleum from the water surface, for example, thermal, biological, mechanical and physicochemical (using coagulants and adsorbent materials) techniques. So far, removing of petroleum spills by adsorbent materials is the most safety and effective processes. Different types of adsorbents including chrome shavings [2], raw cotton and sand [5], feathers [6], wool and sepiolite [7], peat [8], exfoliated graphite [9], vermiculite [10], silica aerogels, zeolites, organoclays [11] and nonwoven polypropylene [12] have been investigated in this context. Among various reports, most of these petroleum adsorbents were found to have high costs or poor buoyancy after petroleum sorption compared to agricultural waste materials.

In recent years, there has been a growing interest in the production of adsorbents from agricultural wastes for petroleum spills clean-up such as garlic and onion peel [1], barley straw [3], banana trunk fibers [13], kapok [14], walnut shell [15], pith bagasse [16] rice straw [17] and rice husk [4, 18]. The adsorbents on the base of rice husk are widely used in various processes including the purification and recovery of valuable substances from liquid and gaseous media. For example, treated and untreated rice husks were studied as adsorbent materials for the removal of 2,4-dichlorophenol [19], formaldehyde

* Corresponding author. E-mail: kenes_85_85@mail.ru

and acetaldehyde [20], free fatty acids [21, 22], phenol [23], pyridine [24], metal ions [25], ammonium ions [26], methylene blue [27] and humic acids [28] in aqueous systems. Thus, rice husks may be also a suitable source for obtaining valuable adsorbent materials with high specific surface area and large pore volume by thermal treatment.

Rice husks are an agricultural waste that incurs annually at 545 million tons [29]. Typically, rice husks consist of about 75% organic substances (cellulose, lignin, hemicelluloses), 15% amorphous SiO_2, 10% water and microelements [30]. Thus, converting rice husks into petroleum adsorbents can solve two environmental problems: utilization of an agricultural waste and remediation of contaminated aquatic environments. The advantages of petroleum adsorbents obtained from rice husks are their ecological safeness, origin from a broad source of raw materials, floatability after petroleum sorption, high hydrophobicity, low costs and porous structure after thermal treatment that provides a high sorption capacity.

Thermally untreated rice husks have been investigated in several studies [4, 18] for petroleum removal. However, its sorption capacity was relatively low because untreated rice husks are nonporous. On the other hand, the petroleum sorption capacity of rice husks can be increased after thermal treatment due to the enhancement of its surface area and pore volume [31].

The aim of the present study was to investigate the petroleum sorbent efficiency of thermally treated rice husks for the removal of heavy crude petroleum and petroleum products from the water surface and the physicochemical characteristics of the obtained adsorbents. For this, the petroleum adsorbent was prepared by thermal treatment under a CO_2 atmosphere.

Materials and Methods

Sample preparation

The samples were thermally treated according to the procedure developed at R.M. Mansurova Laboratory of Carbon Nanomaterials at the Institute of Combustion Problems [31]. Rice husks were washed with water to remove dirt, then oven-dried at about 110 ºC for 24 h. The dried rice husks were placed in a steel reactor and heated in a muffle furnace under CO_2 flow (200 ml/min) at 300-800 °C for 1 h and the resulting thermally treated rice husks (TRH) were designated as TRH_{300}, TRH_{400}, TRH_{500}, TRH_{600}, TRH_{700} and TRH_{800}, respectively.

Methods

X-ray phase analysis (XPA) of thermally treated samples was performed with DRON-3M diffractometer at an accelerating voltage of 30 kV using tubes with a copper cathode. Recording was performed at a rate of 2 deg/min with an angle range of 5 to 50°. The samples were crushed into powder and placed on glass cuvettes greased with Vaseline.

IR spectra of the samples (tablets pressed with KBr) were recorded with an IR spectrometer (Nicolet-5700) in the wave number range from 4000 to 400 cm^{-1} with Fourier transformation.

The specific surface of the samples was determined by the BET method using a SORBTOMETR-M apparatus.

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 surface appearance of thermally treated rice husk was also observed in Optical Digital Microscopy (Leica DM 6000 M).

The sorption capacities of the samples were evaluated with petroleum products of different density: gasoline AI-80 (ρ = 0.734 g/cm^3); diesel fuel (ρ = 0.818 g/cm^3); industrial petroleum (ρ = 0.886 g/cm^3); heavy crude petroleum (ρ = 0.937 g/cm^3) and light crude petroleum (ρ = 0.792 g/cm^3). The petroleum sorption properties of the samples were determined using the procedure described in [32]. 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 oil 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:

$$PSC = (M_1 - M_2) - 1;$$

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.

The sorption procedure was carried out at different time intervals up to the equilibrium time.

Results and Discussion

Petroleum Sorption of Rice Husks Thermally Treated at Different Temperatures

The effects of heating temperature on the petroleum sorption capacity of the adsorbent materials were studied. Figure 1 shows the relationship between heating temperature and the amount of heavy crude petroleum absorbed by thermally treated rice husk (TRH). One can see in Fig. 1 that the sorption capacity of TRH increased with increasing heating temperature from 300 to 7000 °C and absorbed approximately 15 g/g of petroleum, then at higher temperature, the sorption capacity decreased. This can be explained by the fact that at higher temperature caused a phase transformation of silica from amorphous to crystalline form and hence decreasing the sorption capacity of TRH [27]. Comparing the experimental data shows that TRH had the highest sorption ability, while virgin rice husk (RH) had the lowest one; this is likely to be connected with the high density of thermally untreated rice husk. For further studies, thermally treated rice husk (TRH_{700}) was selected as petroleum adsorbent. The experimental observations show that TRH float on the surface water after petroleum sorption because the TRH has a lower density than virgin rice husk [32].

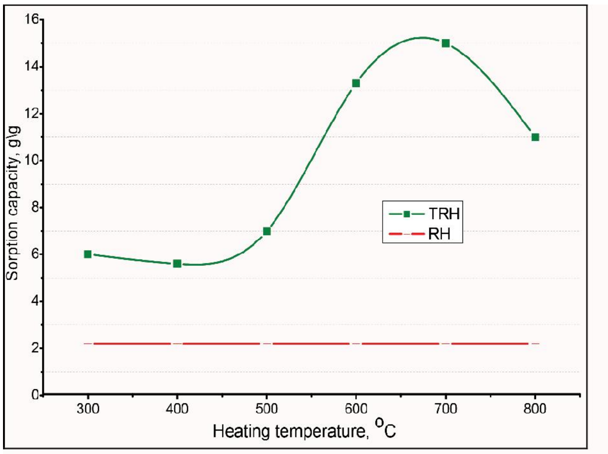


Fig. 1. Effect of heating temperature on heavy crude petroleum sorption properties of TRH_{700} and RH.

The effect of contact time on the sorption capacity of TRH_{700} was studied. Figure 2 shows that the sorption capacity of TRH_{700} increased with the contact time from the first 5 min on, then it reached equilibrium. Also, this curve consists of two phases (rapid phase and slow phase). This effect can be explained as follows: the thermally treated rice husk first absorbed petroleum by macropores and afterwards it penetrated into the micropores until reaching equilibrium time. The equilibrium times for heavy crude petroleum on TRH_{700} and RH were 25 and 10 min, respectively. Summarizing the results, following optimum conditions can be inferred for heavy crude petroleum sorption by TRH_{700}: heating temperature 700 °C and sorption time 25 min (Figs. 1, 2).

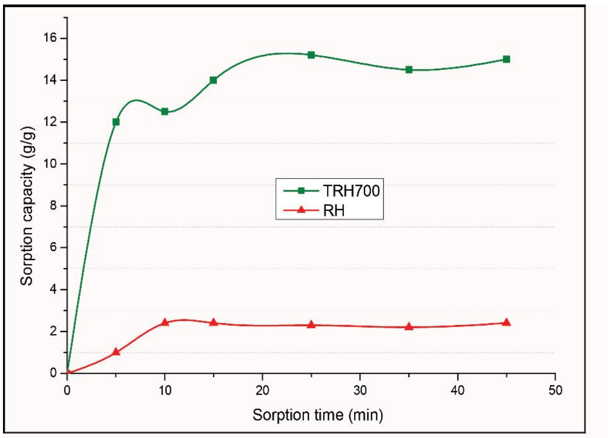


Fig. 2. Effect of contact time on sorption of heavy crude petroleum on TRH_{700} and RH.

The Influence of Petroleum Products Density on the Sorption Capacity of TRH_{700} and RH

The influence of petroleum products density on the sorption capacity of thermally treated rice husks and virgin rice husks are shown in Fig. 3. The sorption capacity of samples increased with the increase of petroleum products' density. Thus the sorption capacity increased three times for TRH_{700} and four times for the RH, whereby the absolute sorption of TRH_{700} was much higher than that of RH. This effect may be due to less retention of petroleum products into the pores of RH. As a result, gasoline (AI-80) with the lowest density (ρ = 0.734 g/cm^3) showed low sorption for the sorbent materials, while the heavy crude petroleum (ρ = 0.937 g/cm^3) indicated a high sorption. The influence of the density of petroleum products on the sorption capacity of the adsorbent materials was also investigated with similar result in earlier study [3]. Our results confirm that petroleum sorption depends both on the adsorbent material and the adsorbate type.

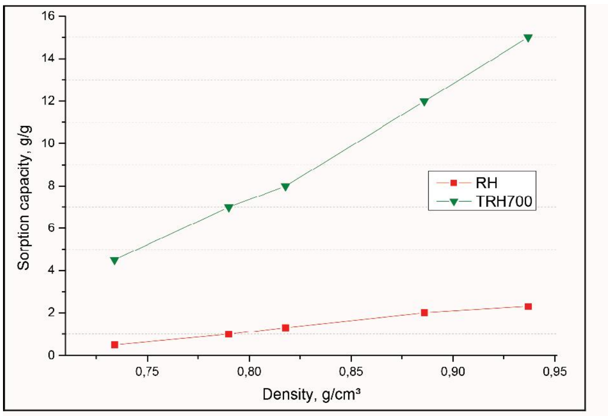


Fig. 3. Influence of adsorbate density on the sorption capacity for TRH_{700} and RH.

Effect of Desorption Time on Holding Capacity of TRH_{700}

The results shown in Fig. 4 indicate that the petroleum retention properties vary for different petroleum viscosities. The heavy crude petroleum with higher viscosity tends to have higher initial sorption ratio. The high viscosity of heavy crude petroleum significantly affects the capillary penetration of petroleum into the small pores of sorbent material. The results show that the retention behavior of all used petroleum follows almost the same trend. As shown, there are three zones in each curve: The first zone is the initial stage of release which occurs over the first min and the rate of release is very high during this period; the second or transition zone occurs from 1 to 5 min over this period which in the rate of release is reduced and the third zone represents the steady state period during this period and additional time will not release any significant amount of petroleum. Light crude petroleum tends to be released from sorbent fast with high release rate compared to the heavy petroleum. Thus, the curve has only two zones.

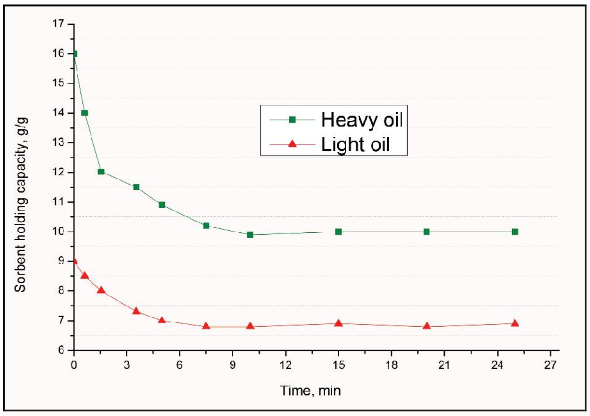


Fig. 4. Effect of desorption time on holding capacity of TRH_{700}.

The Influence of Heating Temperature on the Specific Surface area of TRH

The petroleum sorption by adsorbent materials is dependent on the specific surface area of the latter and hence on the adsorbent preparation process. The effect of the heating temperature on the surface area of rice husks is shown in Fig. 5. The specific surface area increased with increasing heating temperature up to 700 °C, however, the further increase of temperature caused a decrease of the specific surface area. The increasing of the specific surface area can be explained by formation of new micro- and mesopores during the thermal treatment [33].

The decrease of specific surface area after stronger heating of rice husks may be connected with the increase of density due to phase transformation of amorphous SiO_2 into its cristobalite form. A similar result was reported by Sathy Chandrasekhar et al. [34]. The largest surface area of TRH was obtained at 700 ºC and hence the adsorbent obtained that way had the highest sorption capacity for petroleum products.

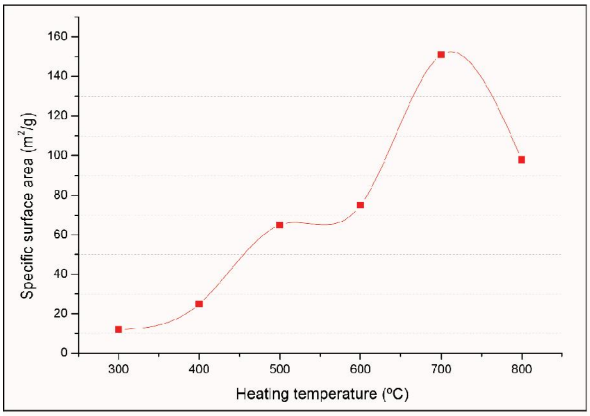


Fig. 5. Effect of heating temperature on the surface area of TRH.

Element Analysis of Rice Husk Samples Thermally Treated at Different Temperatures

Petroleum adsorption by thermally treated rice husks is seemingly dependent on their chemical composition. Figures 6 and 7 summarize the results of microanalyses of TRH_{700} using SEM/EDAX. In Figs. 6 (a) and (b), the variation of weight percent of four elements (Si, C, Al, K) in the heated rice husks is given for different temperatures. While the weight percentage of silicon and potassium increased with increasing heating temperature, the amount of aluminum and carbon decreased. The results of XRD analyses show that thermally treated rice husk consist mainly of amorphous silica (Fig. 8). Thereby, the element silicon in the thermally treated rice husk most probably existing as silica. In detail, the weight percentage of silicon in rice husk increased from 19.4% at 30 ºC to 40.1% at 700 ºC, and the carbon content decreased from 32.6% at 300 ºC to 9.0% at 600 ºC but increased again to 12.3% at 800 ºC. This can be explained by the fact that higher temperatures cause the thermal decomposition of organic substances in the rice husks and hence the relative silica content increases [35]. Increasing weight percent of silica positively influences the petroleum sorption capacity of rice husk due to the good adsorbent properties of silica (SiO_2). Figure 7 show that the principal element in TRH_{700} is silica.

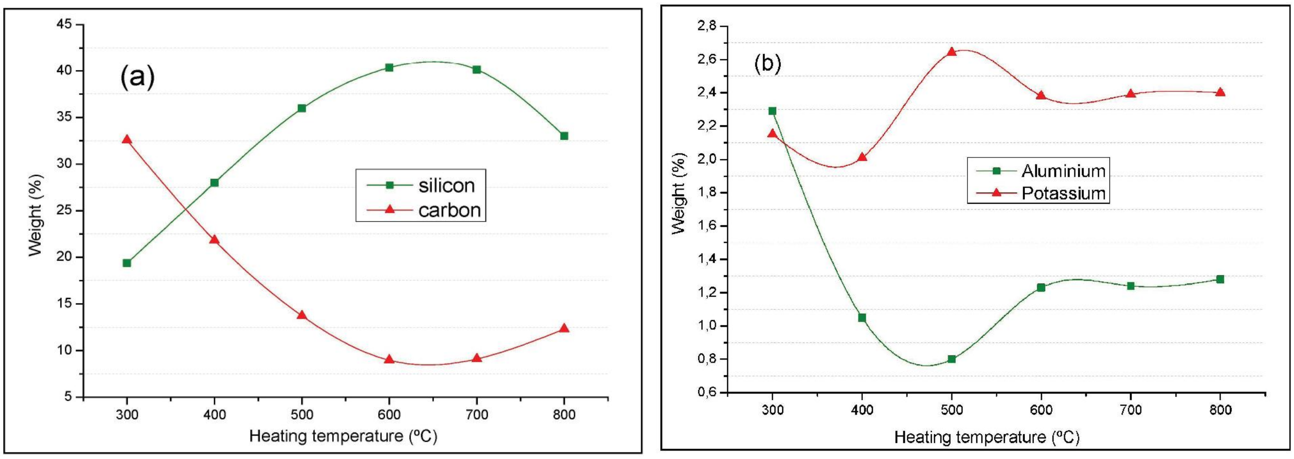


Fig. 6. Variation of weight percentage of silicon, carbon (a) and potassium, aluminum (b) in TRH produced at different temperatures.

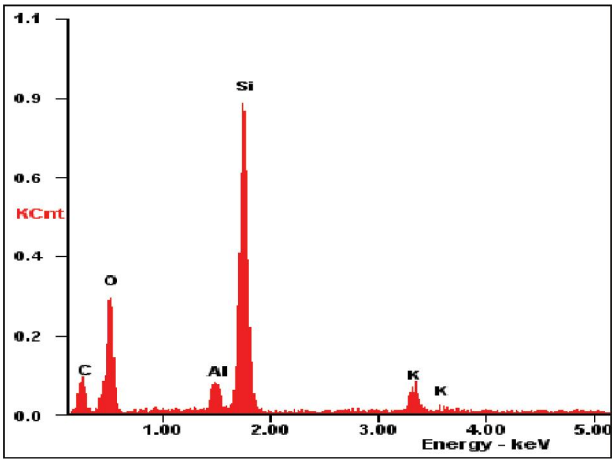


Fig. 7. Microanalysis of TRH_{700} using SEM/EDAX.

X-ray Phase Analysis of Rice Husks Thermally Treated at 400 ºC and 700 ºC

The rice husks thermally treated at 400 ºC and 700 ºC were investigated by X-ray diffraction. No difference was observed between XRD patterns of TRH_{700} and TRH_{400} (Fig. 8). The XRD pattern features two diffused peaks at 2Ɵ 22° and at 2Ɵ 44°, which corresponds to the presence of amorphous silica and graphite structures, respectively [35]. As is seen from Table 1, the full width at half maximum (FWHM 2-Theta) is higher in case of the 400ºC sample, which indicates a smaller size of crystalline carbon. At higher temperatures, the FWHM 2-Theta may decrease due to the destruction of cellulose structures in rice husk. In this sample, probably calcite ($CaCO_3$) was present in small amounts (less than 1.0%). The integral intensity of the amorphous phase (net Area - cps x 2-Theta) was highest in the 700 ºC sample. In summary, it can be concluded from the XRD patterns that thermally treated rice husk mainly consist of amorphous silica.

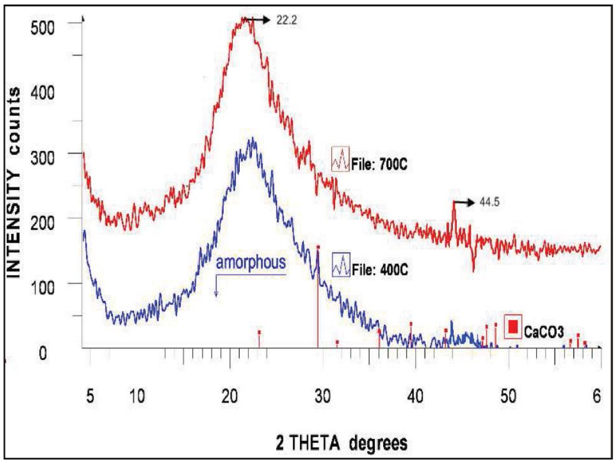


Fig. 8. XRD of the rice husk thermally treated at 400 ºC and 700 ºC.

Table 1.
XRD analysis of thermally treated rice husks

Sample TRH	Obs. Max 2-Theta °	d (Obs. Max) Angstrom	FWHM 2-Theta °	Net Area Cps x 2-Theta °
400 ºC	22.2 44.5	3.9658	8.999	2856.9
700 ºC	22.2 44.5	3.9571	8.161	3195.6

IR-Analysis of Rice Husks Thermally Treated at 400 ºC and 700 ºC

Thermally treated rice husks were also investigated by IR spectroscopy to determine functional groups on the surface of the samples. Figures 9 (a), (b) and (c) show respective IR spectra of rice husks thermally treated at 400 ºC and 700 ºC and after petroleum sorption, respectively. The IR spectrum of TRH_{400} contained intensive absorption bands at 3384, 2922, 2852, 1599, 1453, 1383 and 1089 cm^{-1}. The broad peak at about 3384 cm^{-1} may correspond to the –O–H-stretching vibrations of water molecules. The characteristic absorption bands at 2852 cm^{-1} and 2922 cm^{-1} are related to the –C–H stretching vibrations of methylene groups [36]. The peak at 1599 cm^{-1} can be attributed to the –C=O stretching vibrations of carbonyl groups in aldehydes and ketones. The double peak at 1453 and 1383 cm^{-1} corresponds to the –C–O groups stretching of carboxylates. The pronounced peak at 1089 cm^{-1} with high intensity is attributed to the stretching vibrations of siloxane groups [35]. Figure 9 (b) shows the modified IR spectrum of TRH_{700}. The peaks at 2922 and 2852 cm^{-1} disappeared when the heating temperature was increased from 400 to 700 ºC. This indicates the evolution of CO_2 at higher temperature; i.e. residual methylene group may decompose. Figure 9 (c) shows an IR spectrum of TRH_{700} after petroleum sorption. One can see the emerging of sharp peaks at 2923 and 2853 cm^{-1} indicating that petroleum components were bound to the hydrophobic groups of TRH_{700}.

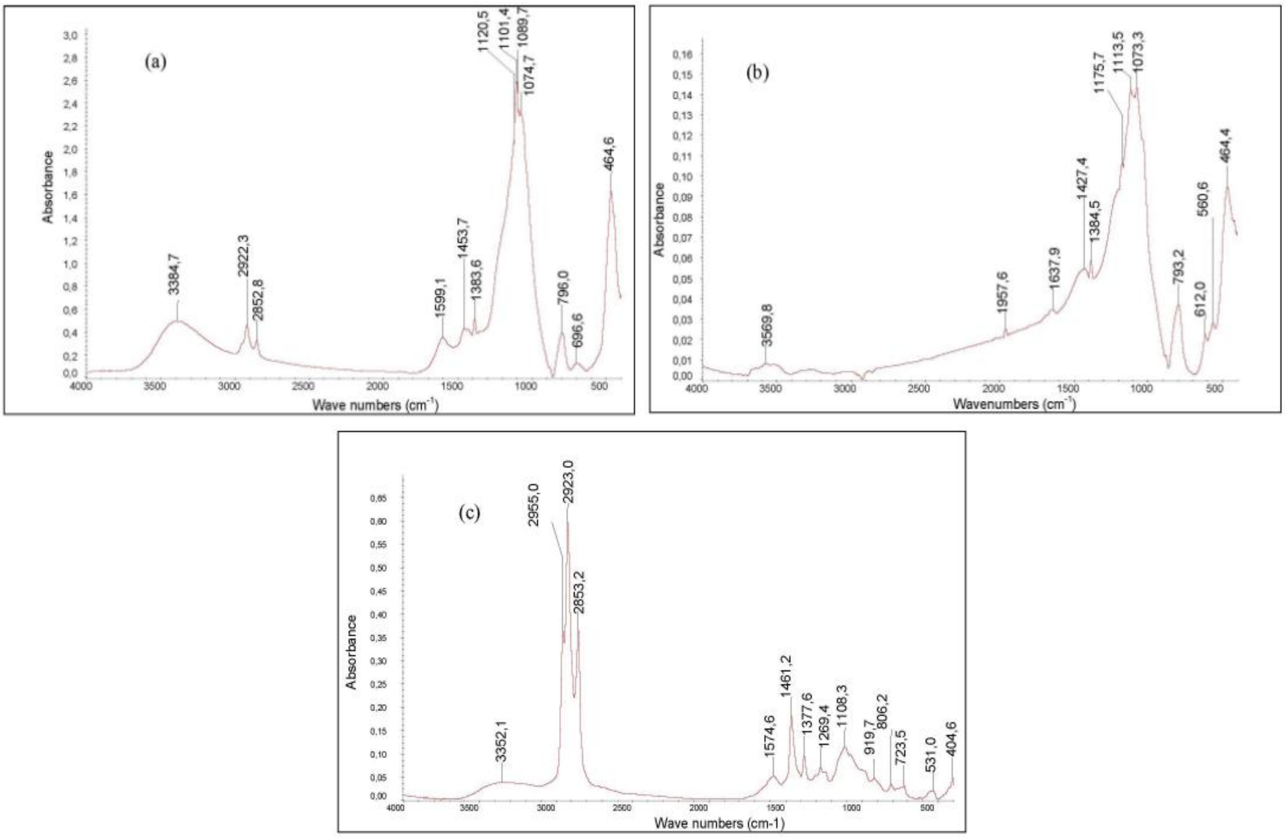


Fig. 9. FTIR spectra of TRH: (a) - TRH_{400}; (b) - TRH_{700} and (c) - TRH_{700} after petroleum sorption.

SEM Study of Virgin and Thermally Treated Samples

The photographs in Fig. 10 depict the microstructure of virgin and thermally treated husk materials. The SEM image of virgin rice husks (Fig. 10 a) shows spherical silica particles of varying form on the organic matrix that consists of cellulose, hemicelluloses and lignin. Furthermore, it is visible that virgin rice husks are compact and do not contain any pore.

The external wall of TRH_{400} shows the occurrence of a large number of button-like structures with small pores, which were not found in the virgin rice husk particles (Fig. 10 b). The emerging of pores and button-like structures may be caused by the fast removal of volatile organic components from the particle [37]. A cross-section of TRH_{400} is shown in Fig. 10 (c) and illustrates the presence of pores and channels in the particles with the diameters of about 5-10 µm. The emerging of channels during combustion of rice husk has been discussed earlier in [29]. The interior structure of TRH_{400} (Fig. 10 d) furthermore indicates the formation of backbone-like structures during combustion [22]. Figure 10 (e) shows again a cross-section (TRH_{700}) that illustrates the distribution of mesopores and macropores in the rice husk particles emerged after treatment at 700 °C. The particles underwent drastic changes in this process of high-temperature treatment. Pores increased both in number and size, new types appeared, two or more smaller pores merged into bigger ones, and the surface and volume of pores changed. Figure 10 (e) is similar to Fig. 10 (c), but the number of pores in TRH_{700} is higher than in TRH_{400} as well as their size are larger. Eventually, the interior structure of TRH_{700} (Fig. 10 f) shows the converting of backbone-like structures into reticulated structures.

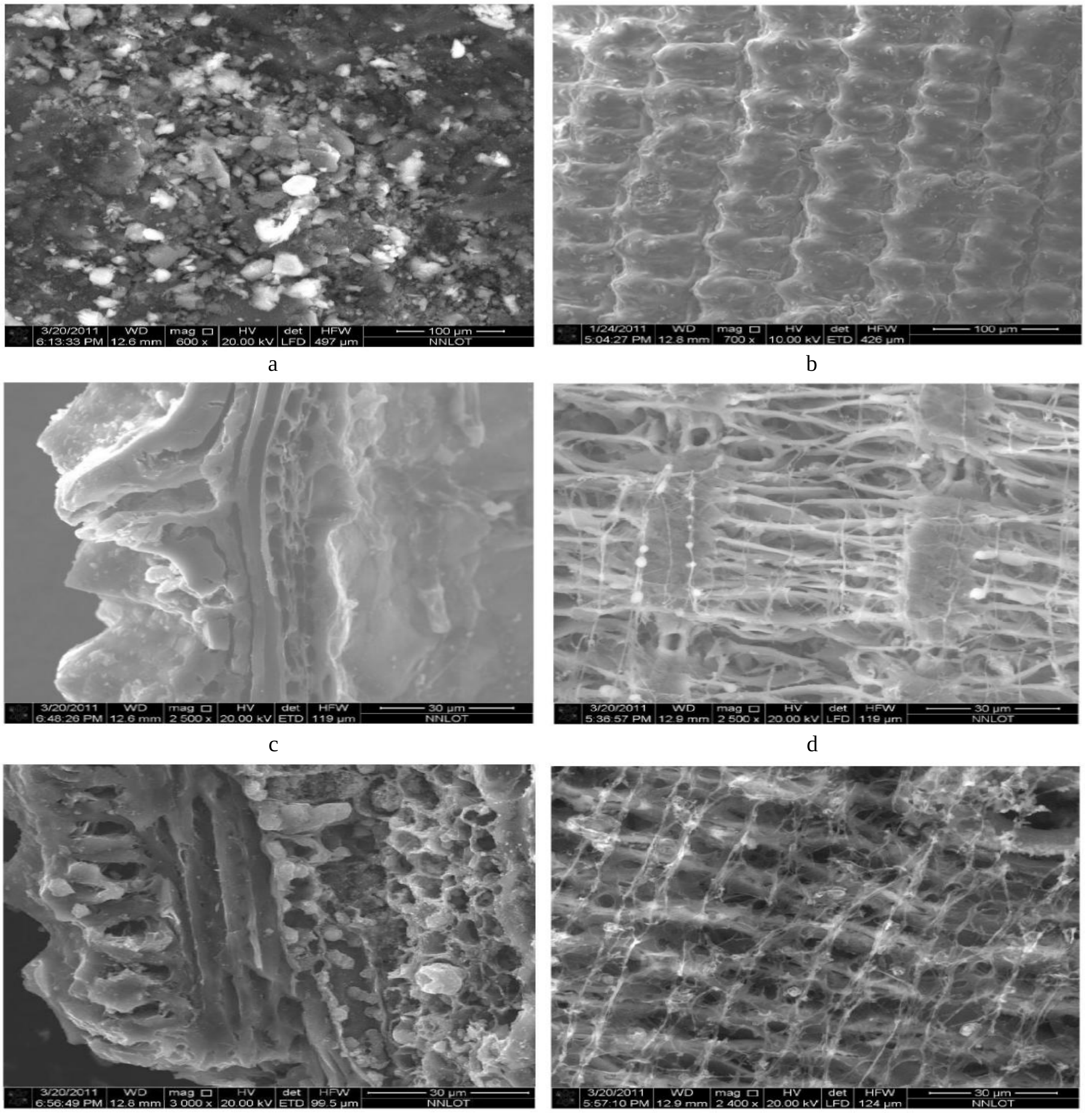
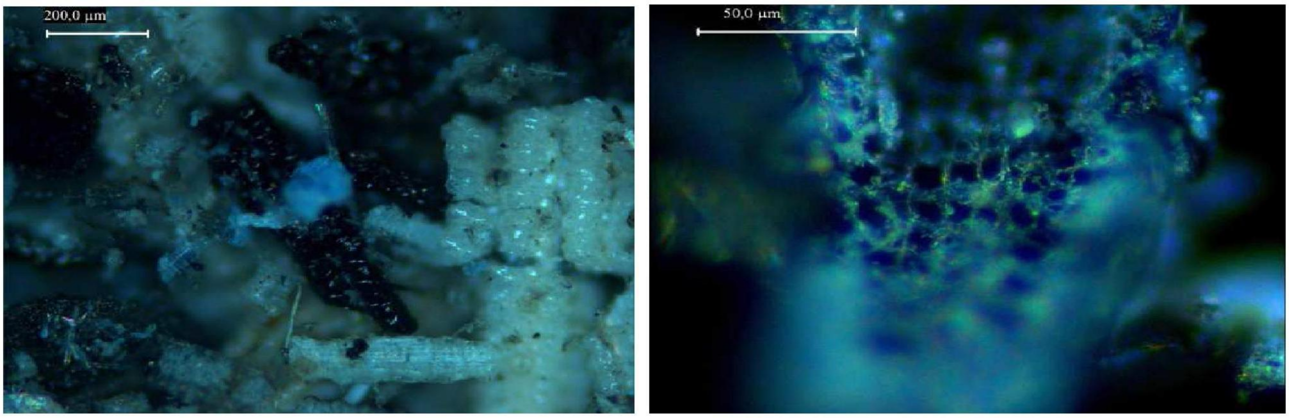


Fig. 10. SEM images of RH and TRH; (a)-RH, (b, c, d)-TRH_{400} and (e, f)-TRH_{700}.

The surface appearance of the TRH_{700} was also observed in optical digital microscopy. Figure 11 shows the optical microscopy images of the TRH_{700}. There are clear differences between the lower (Fig. 11 a) and the higher magnifications (Fig. 11 b). In the lower magnification (Fig. 11 a), some particles of carbon and amorphous silica can be seen. Figure 11 (b) shows the presence of pores with the diameter of 5-15 µm on the surface of the particles.

High petroleum sorption ability is determined by the porous structure of adsorbents, as well as by the physical and chemical interactions of their functional groups with the crude oil components. One can see in SEM and optical microscopy images that thermal treatment allows to obtain a drastically modified structure with higher porosity compared to the virgin husk samples [38].



a b

Fig. 11. Optical microscopy images of the TRH_{700}.

Conclusions

Thermally treated adsorbents based on rice husks are an efficient absorber for heavy crude petroleum and petroleum products, since they possess high porosity and reactive surface functionalities including carboxyl, carbonyl and methylene groups. The results of XRD and SEM/EDAX microanalyses show that thermally treated rice husk consist mainly of amorphous silica (SiO_2). The optimal conditions for the treatment are as follows: heating temperature 700 °C and sorption time 25 min in case of heavy crude petroleum; under these conditions, the maximum sorption capacity of TRH_{700} reached about 15 gram petroleum per gram of husks. In conclusion, this study demonstrates the possibility to obtain effective petroleum adsorbents from rice husks, which are currently considered to be an agricultural waste.

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