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Thermally treated rice husks for petroleum adsorption

Abstract

Rice husks, an agricultural waste, were thermally treated and evaluated as an adsorbent for petroleum with the goal of being used as a remediation strategy for petroleum spills of petroleum based products. The petroleum sorption capacity was examined of thermally-treated, carbonized rice husks which are mainly composed of silicates. Results showed that the petroleum sorption capacities of the carbonized rice husks prepared at 700ºC is 15,2 g/g for heavy crude petroleum. The effects of heating temperature, contact time and petroleum density on the petroleum sorption capacity of carbonized rice husks were investigated. The phase composition, microstructure and morphology of the *carbonized rice husks* were investigated by X-ray diffraction analysis, FTIR spectrometry and Scanning Election Microscope *(SEM)*.

Keywords: Rice husks, petroleum sorption, adsorption.

Introduction

Large-scale petroleum spills in aquatic environments commonly occur during the petroleum production, petroleum transportation, petroleum refining and petroleum storage. This can become a major environmental problem due to the toxicity of many compounds in petroleum to aquatic organisms, birds and humans [1-3]. Annually, the petroleum has been spilled on the surface of the ocean between 10,000,000-2,000,000 tons which a ton of them will be covered about 12 km^3 of the ocean surface [4]. Also, the toxic volatile constituents of petroleum spills are evaporated and as a consequence of this occur atmospheric pollution. Thus, clean-up of petroleum spills from water surface is very important. Different methods can be used for petroleum liquidation from water surface involving thermal, biological, mechanical and physicochemical (using coagulants and adsorbent materials). However, gathering of petroleum spills by adsorbent materials is the most safety and effective processes [5-7].

Different types of sorbents have been investigated necessary for cleanup petroleum spills from water including, raw cotton and sand [6], feather [8], wool and sepiolite [9, 13], peat [10], chrome shavings [5], exfoliated graphite [11], vermiculite [12], silica aerogels, zeolites and organoclays [7], and polypropylene [2]. However, among various reports, some petroleum adsorbents have high cost or poor buoyancy after petroleum sorption compared to agricultural waste materials.

In recent years, there has been a growing interest in the production of sorbents from agricultural wastes for petroleum spills clean-up such as banana trunk fibers [14], wheat straw [15], barley straw [3], kapok [16], garlic and onion peel [1], walnut shell [17], pith bagasse [18] rice straw [19] and rice husks [4, 20]. The adsorbents on base of rice husk are widely used in various processes including the purification and recovery of valuable substances from liquid

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and gaseous media. For example, treated and untreated rice husks as adsorbent materials have been investigated for removal of 4-dichlorophenol [21], formaldehyde and acetaldehyde [22], free fatty acid [23, 24], phenol [25], pyridine [26], metal ions [27], ammonium ions [28], methylene blue [29] and humic acids [30] in aqueous systems. On the other hand, rice husks are an irreplaceable source for obtaining of the valuable sorbent materials with high specific surface area and large pore volume by thermal treatment which necessary for petroleum liquidation from water surface.

Rice husks are an agricultural waste produced annually at 545 million tons [31]. Typically, rice husks consist of about 75% organic substances (cellulose, lignin, hemicelluloses), 15% amorphous SiO_2, 10% water and microelements [32]. Thus, converting rice husks into petroleum sorbents solves two environmental problems: utilization of an agricultural waste into a material for remediating petroleum contaminated aquatic environments. The advantages of petroleum sorbents obtained from rice husks are that they are ecologically safe, originate from a broad source of raw materials, have floatability after petroleum sorption, are high hydrophobic, have a low cost and have porous structure after thermally treatment that provides a high sorption capacity.

The unburned rice husks have been investigated by scientists [4, 20] for petroleum removal. However, the sorption capacity is lower because unburned rice husk is nonporous. The petroleum sorption capacity of rice husks increases after thermal treatment due to enhance its surface area and pore volume [33].

The aim of the present paper is the preparation of petroleum sorbent on the base of rice husks by thermal treatment under a CO_2 atmosphere. Also, investigation of its efficiency for removal of heavy crude petroleum and petroleum products from water surface and study of physicochemical characteristics of the obtained sorbents.

Materials and methods

Sample preparation

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

Methods

Physicochemical characteristics of the sorbents were investigated with infrared Fourier Transform spectroscopy, SEM scanning election microscope, SORBTOMETR-M, X-ray phase analysis).

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

IR spectra of the samples under investigation were recorded with IR spectrometers (“Nicolet-5700”) in the wave number range of 4000–400 cm^{-1} with Fourier transform, in tablets pressed with KBr.

The specific surface of samples was determined by the BET method was carried out on an analyzer to specific surface SORBTOMETR-M apparatus.

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

The sorption capacity of the samples were evaluated toward petroleum products possess 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 [34].

Results and discussion

Petroleum sorption of rice husks thermally treated at different temperatures

The effects of burning temperature on the petroleum sorption capacity of the sorbent materials were studied. Fig. 1 shows the relationship between burning 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 burning temperature from 300 to 700°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 occurred phase transformation of silica from amorphous to crystalline form and hence decreasing the sorption capacity of TRH [29]. One can see comparing the obtained experimental data that the highest sorption ability is exhibited by TRH, while the lowest is exhibited by virgin rice husk (RH), which is likely to be connected with high density of unburned rice husk. Also, the sorption capacity of adsorbent is in good agreement with pore volume and pore size. The thermally treated rice husks possess macro- and mesoporous structures (Fig. 9), which are preferable for the sorption of large molecules of petroleum. For further studies, thermally treated rice husk (TRH_{700}) was selected as petroleum sorbent. The experimental observations show that TRH float on the surface water after petroleum sorption because the TRH have low density than the virgin rice husk.

The effect of contact time on the sorption capacity of TRH_{700} was studied. One can see in Fig. 2 the sorption capacity of TRH_{700} increases with the contact time from the first 5 mins then sorption reached equilibrium. Also, this curve consists of two phases (rapid phase and slow phase). This effect can be explained; the heat-treated rice husk first absorbed of petroleum by macrospores then petroleum penetrated into the micropores until to reach equilibrium time. The equilibrium times for heavy crude petroleum on TRH_{700} and RH were 25 and 10 min, respectively. Summarizing the results, one can conclude that optimal conditions for TRH_{700} are: heating temperature 700 °C and sorption time 25 min in case of heavy crude petroleum sorption (Fig. 1, 2).

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 husk and virgin rice husk are shown on Fig. 3. The sorption capacity of samples increased with increasing of petroleum products density. One can see in Fig. 3. the sorption capacity increased three times for the TRH_{700} and for the RH the increase is four times. The sorption capacity of TRH_{700} increased more higher for petroleum products than RH. This effect may be due to less retention of petroleum products into the pores of RH. As a result, the gasoline (Ai-80) with the lowest density (ρ=0.734 g/cm^3) showed less sorption for sorbent materials, while the heavy crude petroleum (ρ=0.937 g/cm^3) indicated high sorption. Also, the influence of the density of the petroleum products on the sorption capacity of adsorbent materials has been investigated in similar studies [3, l5]. Our results show that petroleum sorption depends on the sorbent material and adsorbate type.

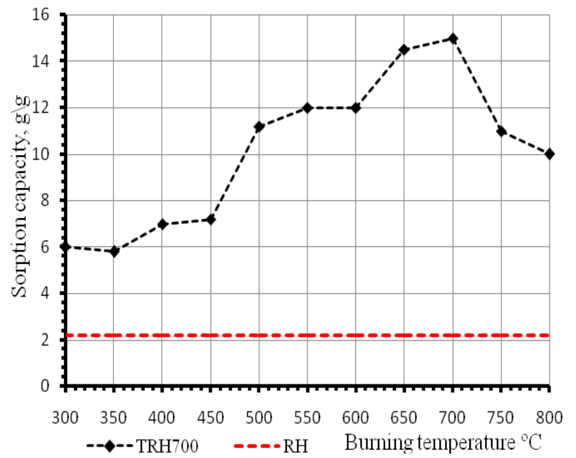

Figure 1 - Effect of burning temperature on petroleum sorption properties of TRH_{700} and RH.

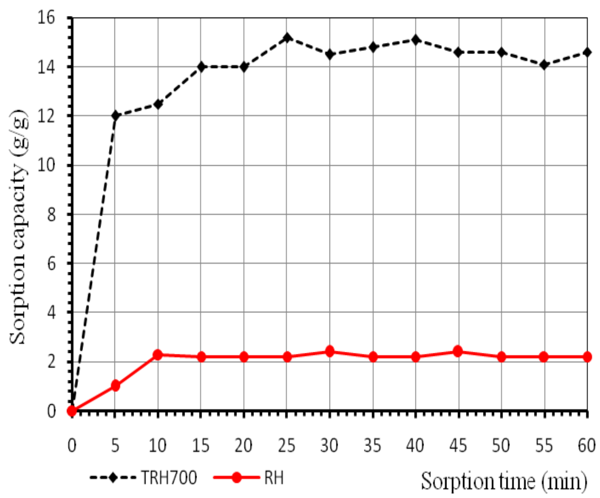

Figure 2 - Effect of contact time on sorption of heavy crude petroleum on TRH_{700} and RH.

The influence of petroleum products density on the sorption capacity of TRH_{700} and RH

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The influence of burning temperature on the specific surface area of TRH

The petroleum adsorption by adsorbent materials is related with their specific surface area. The result of the effect of burning temperature on surface area is shown in Figure 4. One can see in Fig. 4 that the specific surface area increase with increasing burning temperature to 700 °C however, further increase of burning temperature causes the decrease of the specific surface area. The increasing of specific surface area is explained by formation of new macro- and mesopores [36]. A decrease of specific surface area is connected with the increase of the density of rice husks because at higher temperature occur phase transformation of amorphous SiO_2 to cristobalite form and hence the specific surface area reduce. A similar result was found by Sathy Chandrasekhar *et al.* [37]. The highest surface area of TRH was obtained at 700ºC and hence this sorbent possess higher sorption capacity toward petroleum product.

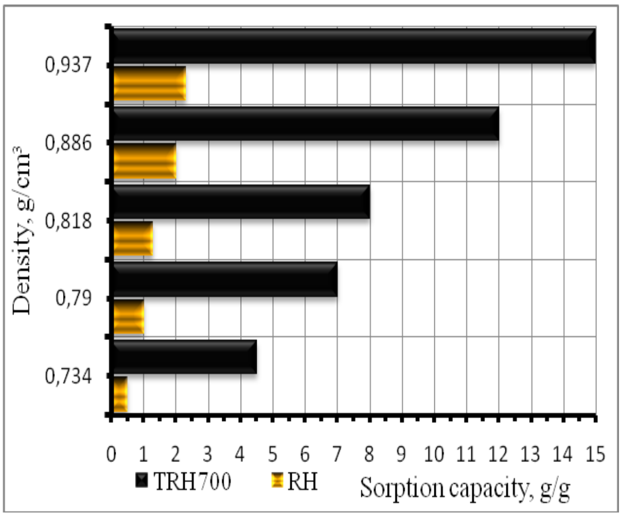

Figure 3 - Dependence between adsorbate density and sorption capacity for TRH_{700} and RH.

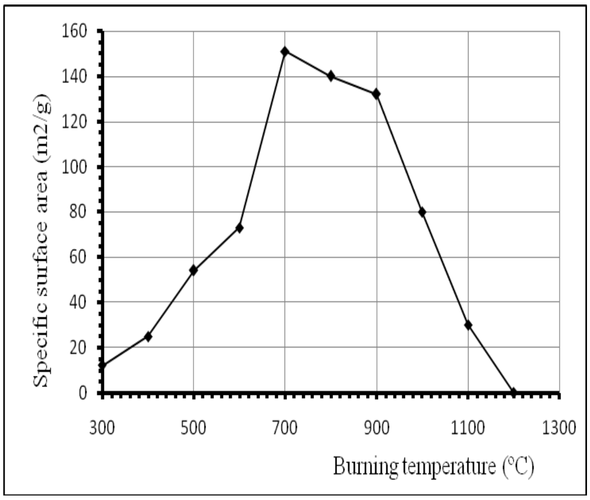

Figure 4 - Effect of burning temperature on surface area of TRH.

Element analysis of samples thermally treated at different temperature

The petroleum adsorption by thermally treated rice husks is correlated with their chemical composition. Figure 5 and 6 shows microanalysis using SEM/EDAX of TRH_{700}. Figures 5A and 5B shows the variation of weight percent of elements of the rice husks heated at different temperatures. One can see in Figs. 5A and 5B the weight percents of silicon and potassium increase with increasing burning temperature but by contrast decreasing of amount of aluminum and carbon. The weight percent of silicon in rice husk increases from 19.37% at 300ºC to 40.11% at 700ºC while the carbon content decreases with burning temperature, from 32.55% at 300ºC to 8.96% at 600ºC then increase again 12.3% at

800ºC. This can be explained by the fact that at higher temperature are occurred decomposition of organic substances in the rice husk and hence the silica content is increased [38]. The increasing of weight percent of SiO_2 influences on petroleum sorption capacity of rice husk because the silica is a good adsorbent. The existing of potassium in the rice husk causes to the formation of black particles during the combustion [39]. Figure 6 show that the main element of TRH_{700} is silicon and oxygen.

X-ray phase analysis of rice husk heat-treated at 400°C and 700°C

The rice husk heat-treated at 400°C and 700°C were investigated by X-ray diffraction. One can see, there is no difference between XRD patterns of TRH_{700} and TRH_{400}. As the result, the XRD pattern features two diffused peaks at 2Θ 22° and at 2Θ 44° which corresponds to the presence of amorphous silica and graphite structure, respectively [38]. As seen in Table 1 the full width at half maximum (FWHM 2-Theta) more on sample "400°C" that is indicate of smaller size crystallite carbon. At higher temperature the FWHM 2-Theta may be decreased due to destruction of cellulose structure in rice husk during its thermal treatment [40]. In this sample probability presence calcite - $CaCO_3$ in very small amount (less 1.0 %). The integral intensity of the amorphous phase (net Area - cps x 2-Theta) more for sample "700°C". It is obvious in XRD pattern that heat-treated rice husk mainly consist amorphous silica.

IR-analysis of rice husk heat-treated at 400˚C and 700˚C

Heat-treated rice husks were investigated by IR-spectroscopy for determination of surface functional groups of the samples. Figs. 8A, 8B and 8C show IR spectra of rice husks heat-treated at 400˚C and 700˚C and after petroleum sorption, respectively. The IR spectrum of TRH obtained at 400°C contains intensive absorption bands at 3384, 2922, 2852, 1599, 1453, 1383 and 1089 cm^{-1}. The broad peak about 3384 cm^{-1} corresponding to the –O–H stretching vibrations of water molecules. The intensity of characteristic absorption bands related to the –C–H stretching vibrations of methylene groups at 2852 cm^{-1} and 2922 cm^{-1}[41]. The peak at 1599 cm^{-1} can be attributed to the –C=O stretching vibrations of aldehyde and ketone gpoups.

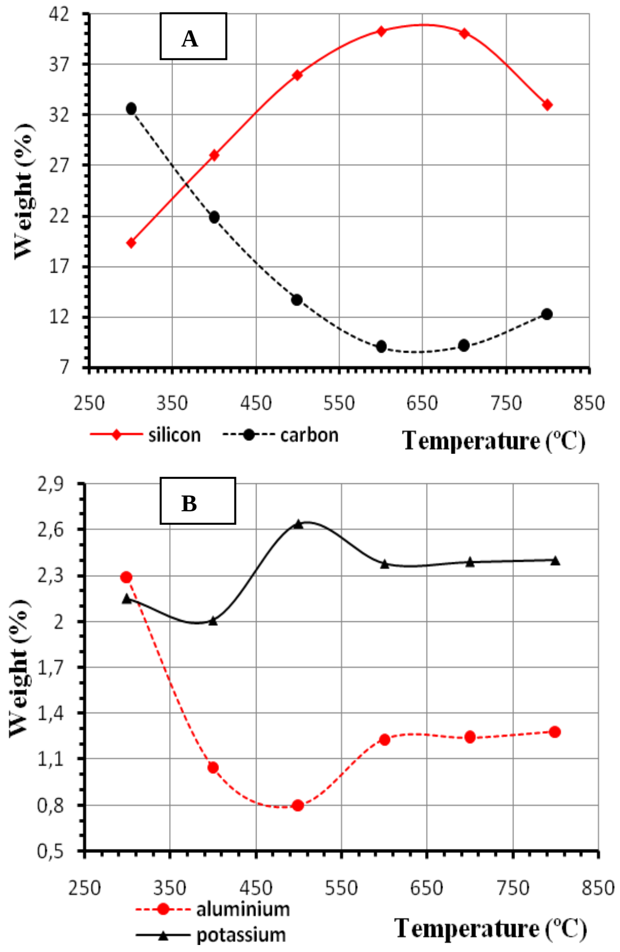

Figure 5 - Variation of weight percent of silicon, carbon (A) and potassium, aluminum (B) in TRH produced at different temperatures.

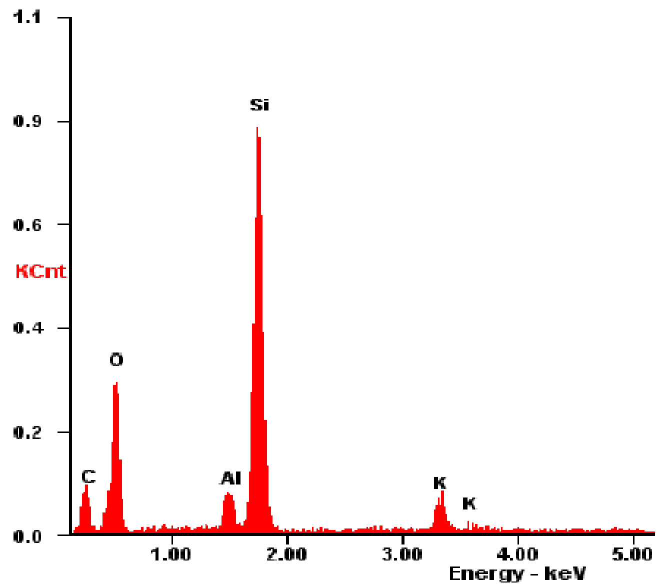

Figure 6 - Microanalysis using SEM/EDAX of TRH_{700}

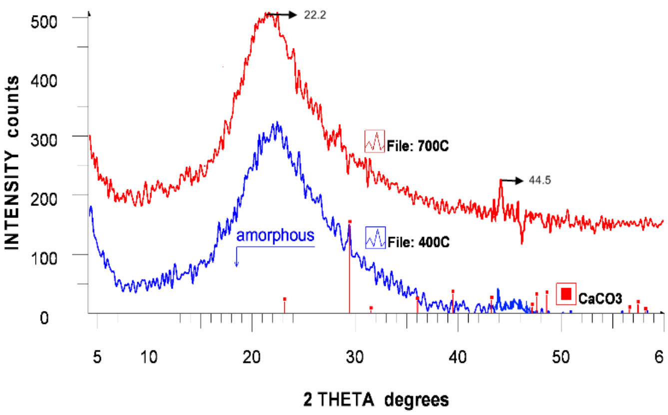

Figure 7 - XRD of the rice husk heat-treated at 400ºC and 700ºC.

The double peak about 1453 and 1383 cm^{-1} corresponding to the –C–O groups stretching from carboxylate groups. The strong peak at 1089 cm^{-1} at high intensity is attributed to the stretching vibrations of the siloxane groups [42]. Fig. 8B shows of IR spectra of TRH_{700}. The intensity of peaks at 2922 and 2852 cm^{-1} disappear when the burning temperature is increased from 400 to 700 °C [43]. This confirms that the evolution of CO_2 occurs at higher temperature region, *i. e.* residual methilene group decomposes [44]. Fig. 8C shows IR spectra of TRH_{700} after petroleum adsorption. One can see in Fig. 8C emerging of sharp peaks about 2923 and 2853 cm^{-1}. This result confirms that petroleum component combining with hydrophobic groups of TRH_{700} [35].

Table 1 - XRD analysis of heat-treated rice husks

Sample TRH	Obs. Max 2-Theta °	d (Obs. Max) Angstrom	FWHM 2-Theta °	Net Area Cps x 2-Theta °
400ºC	22.2 44.5	3,9658	8,999	2856,9
700ºC	22.2 44.5	3,9571	8,161	3195,6

SEM study of virgin and heat-treated samples

Figures 9 represent the microstructure of virgin and heat-treated materials. The SEM image of virgin rice husk (A) shows that the notable variform sphericity particles of silica on the organic matrix which consists of cellulose, hemi cellulose and lignin [45]. One can see on Fig. 9A that virgin rice husk is very solid and doesn't have any pores.

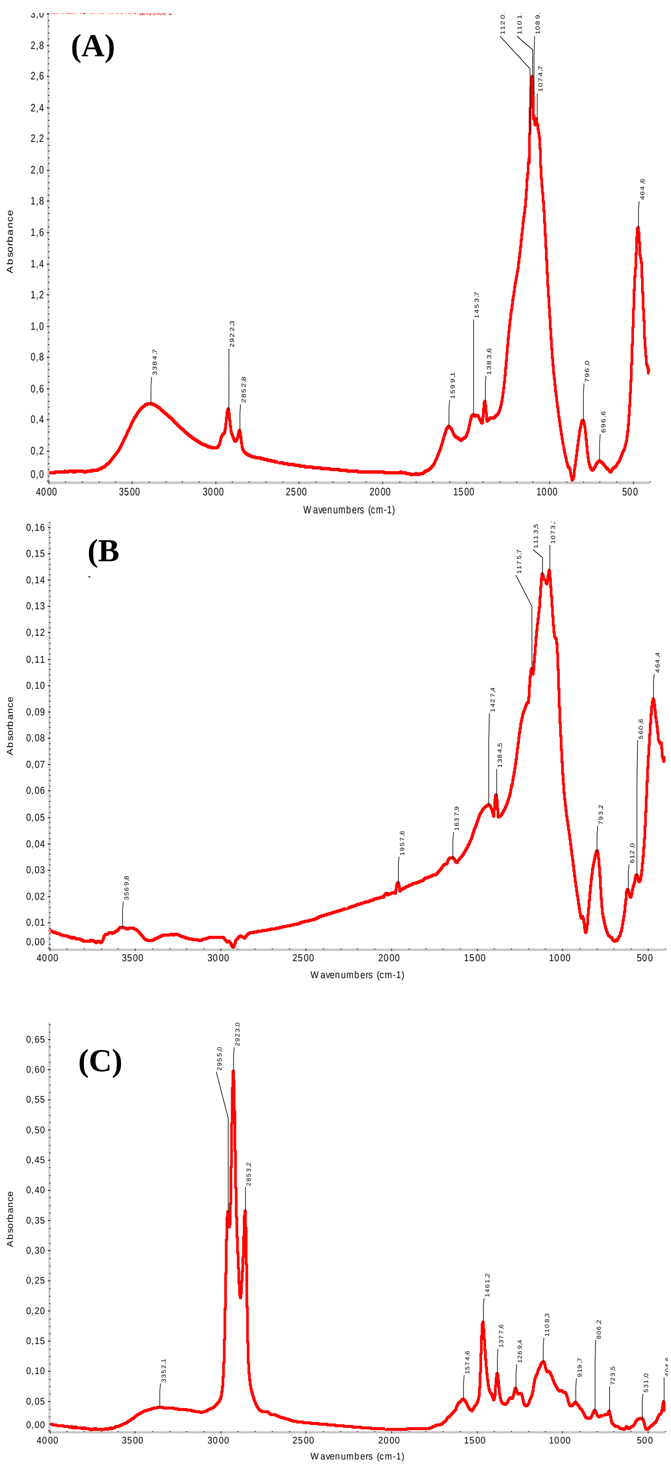

Figure 8 - FTIR spectrums of TRH: (A)-TRH_{400}; (B)-TRH_{700} and (C)- TRH_{700} after petroleum adsorption

The external wall of TRH_{400} shows (Fig. 9 B) the occurrence of a large number of button-like structures with small pores which doesn't have on the virgin rice husk particles. The emerging of pores and button-like structures due to fast removal of volatile organic components from the rice husk particle [45]. The cross-sections of

TRH_{400} are shown in Fig. 9 (C). The SEM image of TRH_{400} clearly shows the presence of pores and channels with diameter about 5–10 μm in the particles [31]. The emerging of channels during combustion of rice husk has been discussed by [31]. The interior structure of TRH_{400} shows (Fig. 9 D) the presence of formation of the backbone-like structures during combustion of rice husk [24]. Figure 9 (E) shows the cross-section of the TRH_{700}. One can see in fig. 9 (E) the distributions of mesopores and macropores in the rice husk particles obtained at 700°C. The particle of rice husks undergoes changes in the process of high burning temperature. Pores increase in number and size, new ones appear, two or more pores can merge into one, pores surface and volume change [46] (Fig. 9 E). The Fig. 9 (E) is similar to Fig. 9 (C), but the pore number of TRH_{700} is more than TRH_{400} as well as their size larger. The interior structure of TRH_{700} (F) shows the converting of backbone-like structures to reticulated structures of rice husk particles at higher temperature [46].

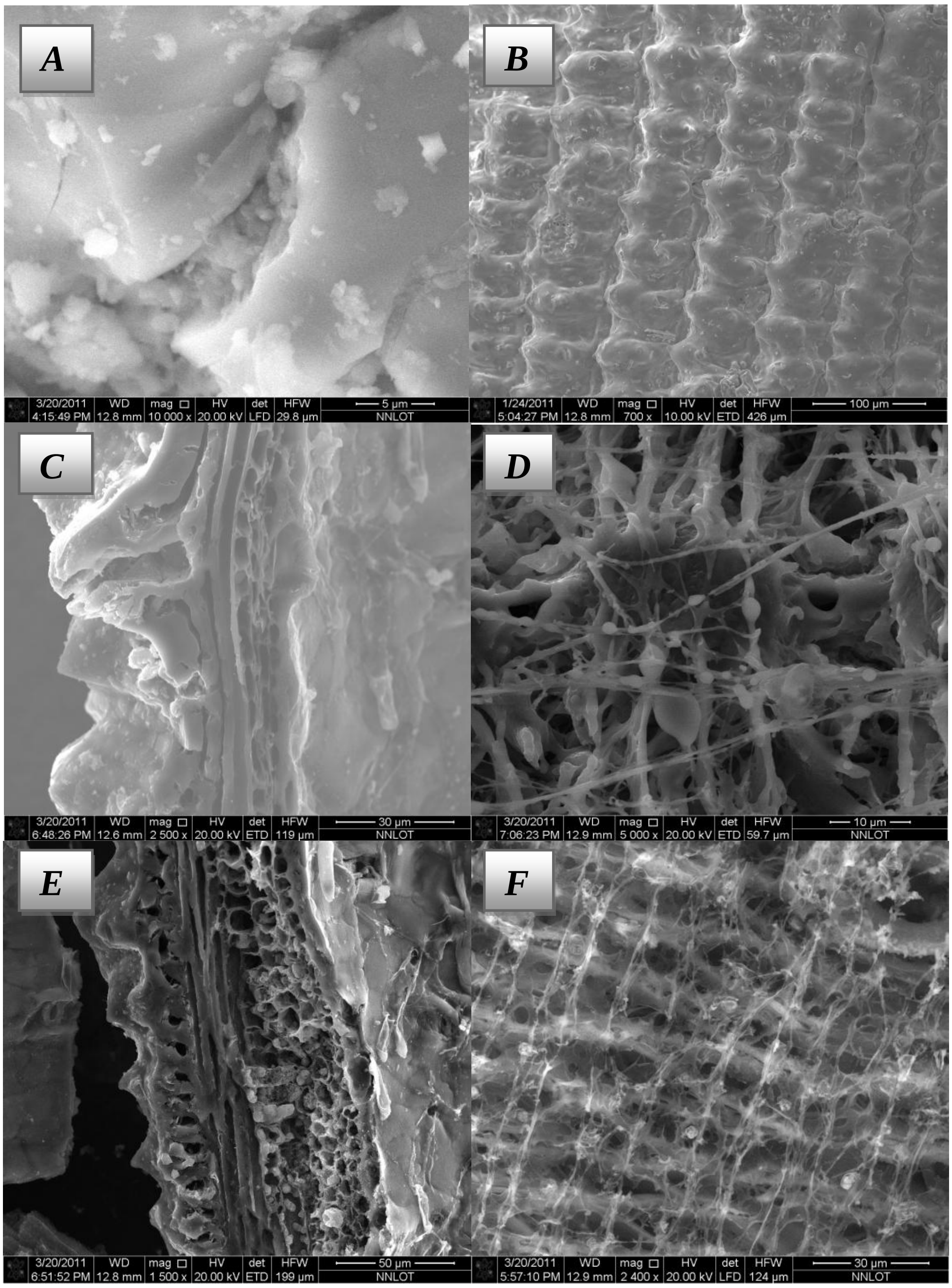

Figure 9 - SEM images of RH and TRH; RH (A), TRH_{400} (B, C, D) and TRH_{700} (E, F)

High petroleum sorption ability is determined by porous structure of sorbents, as well as by chemical interaction with the surface functional groups present in thermally treated samples [44].

One can see in SEM images that thermal treatment can allow one to obtain a developed structure with porosity than that of the virgin samples.

Conclusions

Thermally treated sorbents based on rice husks are an efficient absorber for heavy petroleum and petroleum products since it possess high porosity and have reactive surface groups including carboxyl, carbonyl and methylene. The results of SEM images show that thermal treatment can allow one to obtain a developed structure with porosity than that of the virgin samples. The XRD and SEM/EDAX microanalysis results show that heat-treated rice husk content mainly amorphous silica. The optimal conditions for heat treated rice husk are: heating temperature 700 °C and sorption time 25 min in case of heavy crude petroleum sorption while the sorption capacity of TRH_{700} is reached about 15g/g. The main advantages of using these TRH as petroleum sorbent are the following: low density, high buoyancy, porosity, non-toxicity of the materials, easy and efficient removal of saturated sorbents. Thus, these investigations confirm the possibility for obtaining efficient petroleum sorbents from rice husks which are currently considered to be an agricultural waste.

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