Preparation of porous rice husks by pyrolysis methods for the removal of emulsified oils from wastewater

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Abstract

This article provides experimentally study of the oil removal efficiency of pyrolyzed rice husks, which mainly comprised of amorphous silica and carbon. A case-study approach was chosen to gain a detailed understanding of an adsorbent for the removal of emulsified oils from wastewater. The research results have also shown that the oil removal efficiency increased to 94 % in the case of rice husk pyrolyzed at 600 ºC. The investigation of SEM and AFM has shown that pyrolysis under steam of rice husks drastically modifies the structure with high porosity. The evidence from this study suggests that formation of the spherical and needle-like silica nanoparticles with the diameters of about 100–150 nm that emerged after pyrolysis.

Keywords: Pyrolyzed rice husk; Oily wastewater; Adsorbent; Oil removal efficiency

Introduction

Oil and oil products are one of the most dangerous components of wastewater contamination. This can cause major environmental problems due to the toxicity of many compounds in oil to aquatic organisms and humans (Kim *et al*., 2013 and Gammoun *et al.*, 2007) The oil concentration of different industrial wastewater is frequently higher than 40,000 mg/l (Sokker *et al.*, 2011). Oil in wastewater may be found as free, dissolved and bound states. Free oil is usually removed by a sedimentation method. The methods of electrocoagulation and electroflotation are used for the removal of emulsified oil products. However, by these methods the oil concentration in water is reduced to only 20 mg/l. Mamedov (2013) reported that the deeper cleaning of emulsified oils to 0.5-1 mg/l is achieved by adsorption. Thus, the removal of emulsified oils from wastewater by adsorption is an important task.

Different types of adsorbents have been investigated in this context by Jamaly *et al.*, (2015), Yeom *et al.*, (2016), Mažeikienė *et al.*, (2014), Nikkhah *et al.*, (2015) and Ibrahim *et al.*, (2009).

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Adsorbents based on rice husk are widely used in various processes including the purification and recovery of valuable substances from liquid and gaseous media (Srinivasan *et al.*, 2008, Kumagai *et al.*, 2008, Kim *et al.*, 2008, Mahvi *et al.*, 2004, Abo-El-Eneina *et al.*, 2009, Chandrasekhar et al., 2006 and Imyim *et al.*, 2010). Rice husks are an agricultural waste that results in 545 million tons annually (Mansurov *et al.*, 2009).

Typically, rice husks consist of about 75% organic substances (cellulose, lignin, hemicelluloses), Watari *et al.* (2003) reported that 15% amorphous SiO_2, 10% water and microelements. Thus, converting rice husks into oil adsorbents by pyrolysis can solve two environmental problems: utilization of an agricultural waste and remediation of contaminated aquatic environments. Baiseitov *et al.* (2016) suggested that the advantages of oil adsorbents obtained from rice husks are their ecological safeness, origin from a broad source of raw materials yielding low cost, and porous structure after pyrolysis that provides a high sorption capacity.

The aim of this paper is investigating the sorbent efficiency of pyrolyzed rice husks for the removal of emulsified oils from wastewater and the physicochemical characteristics of the obtained adsorbents. For this, the oil adsorbent was prepared by pyrolysis with water-steam activation.

Materials and methods

Sample preparation

The samples were pyrolyzed according to the procedure developed at R.M. Mansurova Laboratory of Carbon Nanomaterial's at the Institute of Combustion Problems Kudaibergenov *et al.* (2012) introduced a pilot plant for pyrolysis of rice husks was built Fig.1. Typically, 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 rotator reactor and pyrolyzed in a muffle furnace under water steam flow (300 ml/min) at 300-800 °C for 1 hour and the resulting pyrolyzed rice husks (PRH) were designated as PRH_{300}, PRH_{400}, PRH_{500}, PRH_{600}, PRH_{700} and PRH_{800}, respectively. The size of pyrolyzed rice husk particles was 0.5-3 mm.

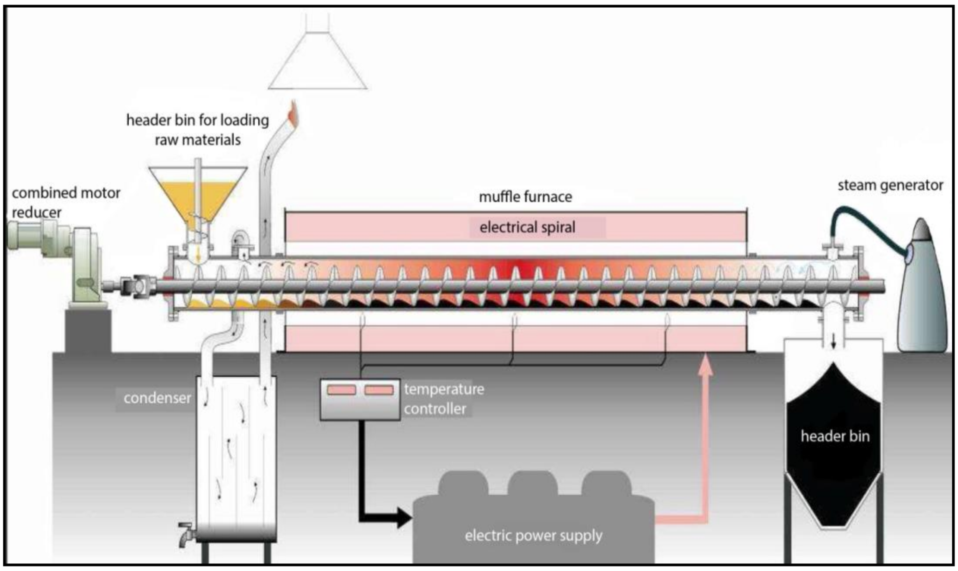


Fig.1: A schematic diagram of the pilot plant for rice husk pyrolysis

Characterization

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 area of the samples was determined by the BET method using a SORBTOMETR-M apparatus. Mansurova (2001) described that the porosity and density of samples was determined according to the procedure. The microstructures and microanalysis of adsorbents were investigated with an SEM (Quanta 3D 200i, USA) at an accelerated voltage of 20 kV (performed by National Nanotechnological Laboratory of Open Type of Kazakh National University). The surface appearance of pyrolyzed rice husk was also observed by Atomic Force Microscopy (Ntegra Therma). Oil sorption was investigated in the continuous tubular contractor (15 mm in diameter and column depth was 500 mm). Real oily wastewater sample were used, which was supplied by oil-field Karazhanbas of Kazakhstan (initial oil concentration is 35 mg/l). Sorption in continuous tubular contractor was carried out with 10 g of adsorbents. Jamaly *et al.* (2015) reported that flow rate of oily wastewater was 2.5 cm^3/min and effluent volume was 1000-2000 cm^3. The experiments were conducted at room temperature. Lanin (2009) described that the extract of oil from oily wastewater was carried out using the procedure. The total oil concentration of oily wastewater was determined by digital photoelectrocolorimeter AR-101 APEL (Japan) at a wavelength of 540 nm. The oil removal efficiency was calculated according to the equation:

Removal efficiency:

$$R_e = [(C_0 - C) / C_0] \bullet 100, (\%)$$

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

Results and discussion

Oil sorption of rice husks pyrolyzed at different temperatures

The effects of pyrolysis temperature on the oil removal efficiency were studied. Fig.2 shows that the oil concentration of wastewater decreased with increasing pyrolysis temperature of the rice husks from 300 to 600 °C. At higher pyrolysis temperatures the oil concentration increased. The reduction in oil removal can be explained by decreasing of specific surface area and porosity of PRH at higher temperature (Table 1). For further studies, pyrolyzed rice husk (PRH_{600}) was selected as oil adsorbent. The oil removal efficiency of PRH_{600} is 94 %.

The dependence of removal efficiency of PRH_{600} on the effluent volume is shown in Fig. 3. The removal efficiency of PRH_{600} decreased with the increase of effluent volume.

The removal efficiency decreased for 42% in case of PRH_{600}.

Table 1: Structural characteristics of rice husks pyrolyzed at different temperatures

300	49	0.75	1.46	18
400	90	1.12	1.25	22
500	150	1.82	0.92	28
600	215	1.89	0.60	33
700	213	1.80	0.42	45
800	202	1.72	0.39	48

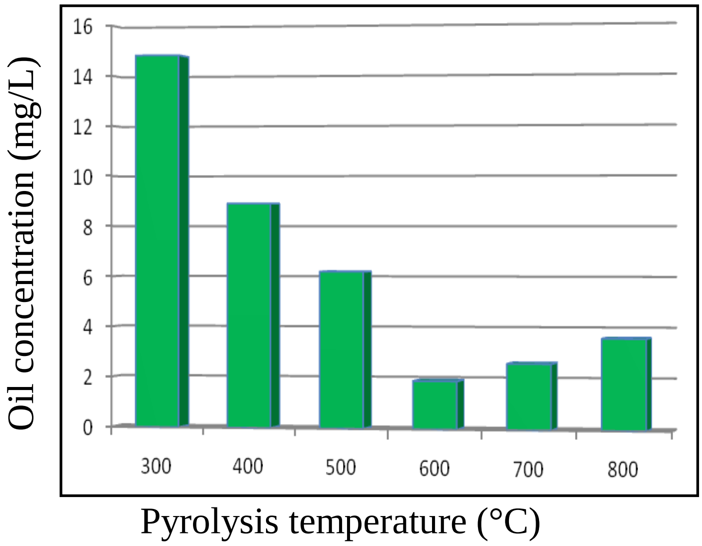


Fig.2: Effect of pyrolysis temperature on the oil concentration of wastewater (wastewater flow rate: 2,5 cm^3/min, effluent volume: 1000 cm^3, pH=2; initial oil concentration: 35 mg/l)

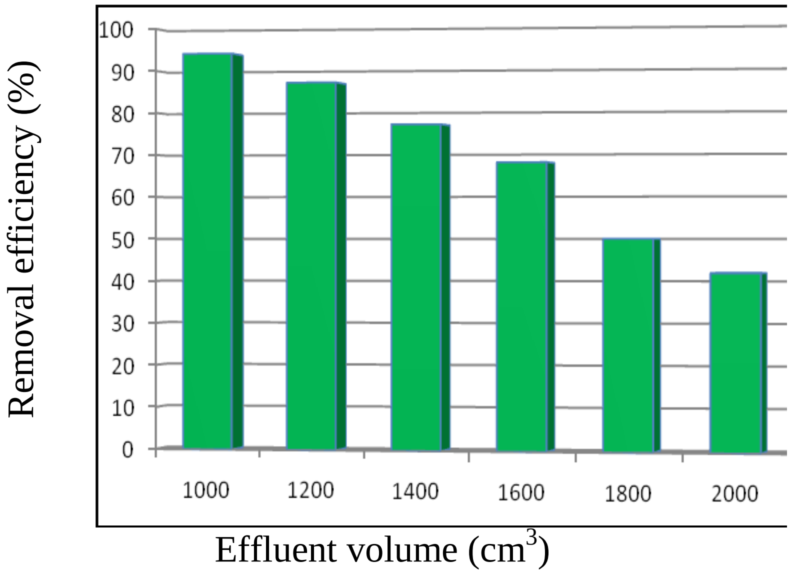


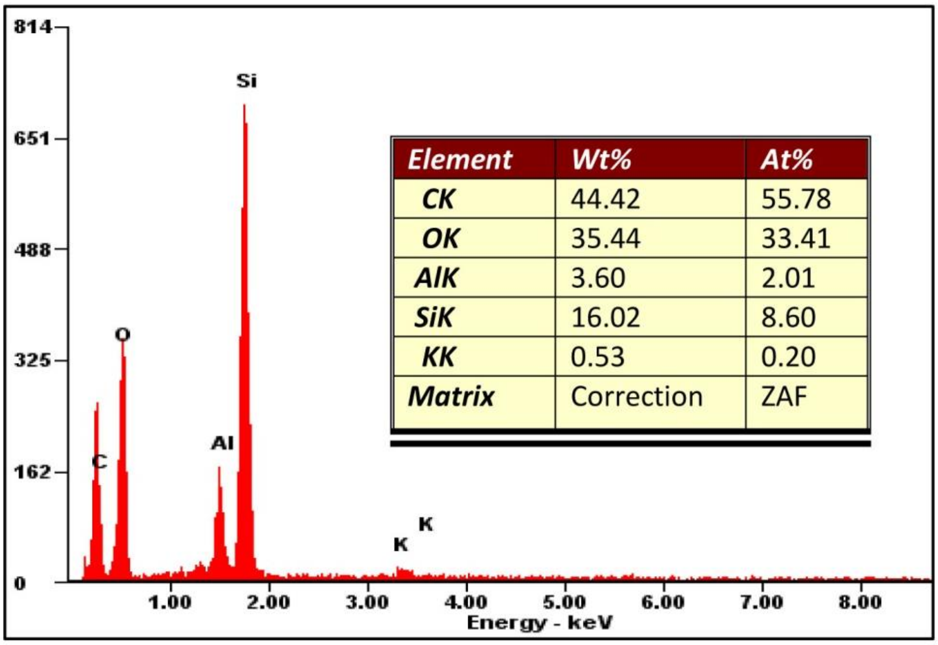
Fig 3. Effect of effluent volume on removal efficiency of PRH_{600}

The influence of pyrolysis temperature on the structural characteristics of rice husks

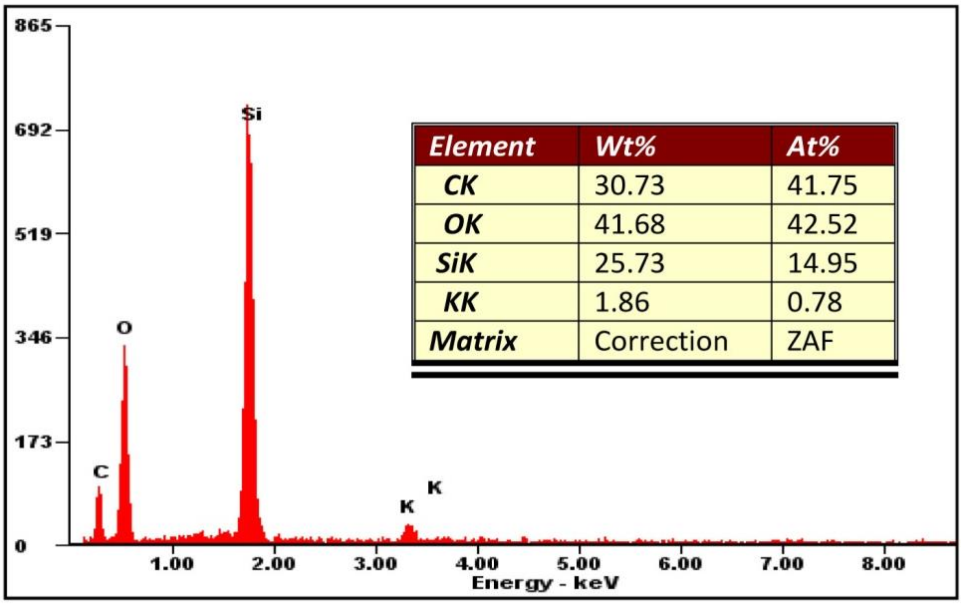
Oil sorption by adsorbent materials is dependent on the specific surface area and porosity of the materials. The effect of the pyrolysis temperature on the structural characteristics of rice husks is shown in Table 1. Kalderis *et al.*, 2008 reported that the specific surface area, porosity and weight loss increased with increasing pyrolysis temperature up to 600 °C, however, the further increase of temperature caused a decrease of the specific surface area and porosity. The increase of thespecific surface area and porosity can be explained by formation of new micro- and mesopores during pyrolysis. Chandrasekhar *et al.*, (2006), revealed that the decrease of specific surface area and porosity of rice husks at higher temperature may be connected with the phase transformation of silica. The largest surface area and porosity of PRH was obtained at 600 ºC, which correlated to the highest sorption capacity for oil products. During pyrolysis the major weight loss occurred within temperature range 300-600°C, where a large amount of volatile products were released. Table 1 also shows the bulk density of rice husks decreased with increasing pyrolysis temperature. It is can be explained that carbonaceous compounds in the rice husks are evolved at higher temperatures.

Microanalyses of virgin and pyrolyzed rice husks

Oil adsorption by pyrolyzed rice husks is seemingly dependent on their chemical composition. Fig. 4(A, B) shows the results of microanalyses of virgin rice husk and PRH_{600} using SEM/EDAX, respectively. In Fig. 4(A) and (B) the variation of weight percent of five elements (C, O, Al, Si, K) in the virgin and pyrolyzed rice husks is observed. While the weight percentage of oxygen, silicon and potassium increased with increasing pyrolysis temperature, the amount of carbon decreased. Furthermore, aluminum disappeared at high temperature. Thereby, the element silicon in the pyrolyzed rice husks most probably existing as silica. In detail, the weight percentage of silicon in rice husk increased from 16.02% to 25.73% and the carbon content decreased from 44.42% to 30.73% at 600 ºC. Chen *et al.*, (2011) reported that 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. Increasing the weight percent of silica positively influences the oil sorption ability of rice husk due to the good adsorbent properties of silica (SiO_2). Fig. 4(B) also shows that the



A



B

Fig.4: Microanalysis of virgin and pyrolyzed rice husks using SEM/EDAX

principal elements in PRH_{600} are silica and carbon. Besides that, the results of XRD analyses reveal that silica in the pyrolyzed rice husk is amorphous.

IR analysis of virgin and pyrolyzed rice husk

Virgin and pyrolyzed rice husks were also investigated by IR spectroscopy to determine the functional groups on the surface of the samples. Fig. 5(A) and (B) show IR spectra of virgin and pyrolyzed rice husks at 600 ºC respectively. The broad peak at about 3500 cm^{-1} corresponds to the –O–H-stretching vibrations of water molecules. Genieva *et al.*, (2008) introduced that the characteristic absorption bands at 2926 cm^{-1}, 2114 cm^{-1}, 1423 and 1383 cm^{-1} are related to the –C–H stretching vibrations of methylene groups. The peak at 1632 cm^{-1} can be attributed to the –C=O stretching vibrations of carbonyl groups in aldehydes and ketones. The peak at 1515 cm^{-1} corresponds to the –C–O groups stretching of carboxylates. Chen *et al.* (2011), described that the broad peaks at 1095, 898, 796, 662 and 471 cm^{-1} are attributed to the stretching vibrations of siloxane groups. Fig. 5(B) shows the modified IR spectrum of PRH_{600}. The peaks at 3500, 2926, 2114, 1632, 1515, 1383, 898 and 662 cm^{-1} disappeared after pyrolysis. This indicates the evolution of CO_2 and H_2O at higher temperature; *i. e.* residual methylene group may decompose

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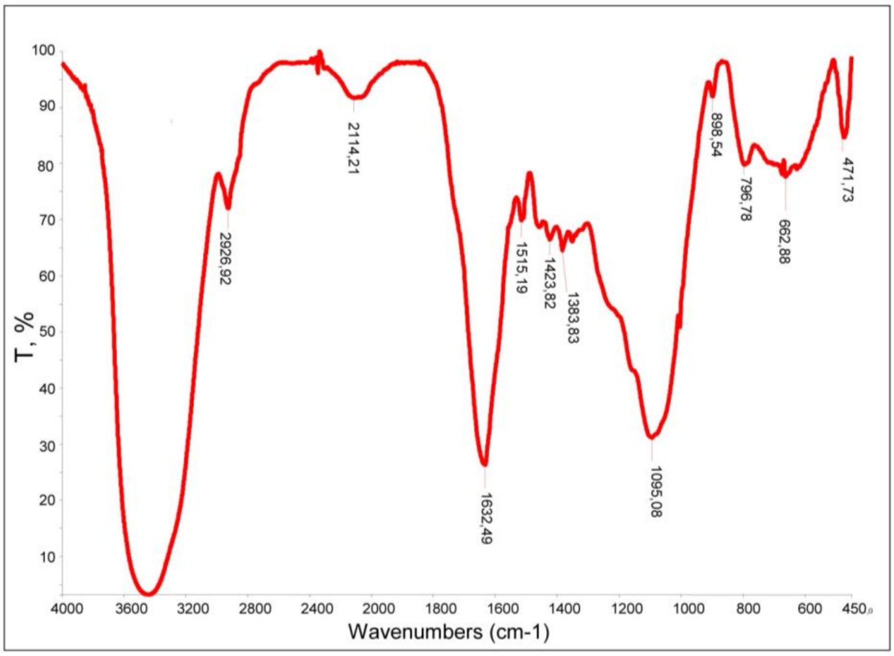
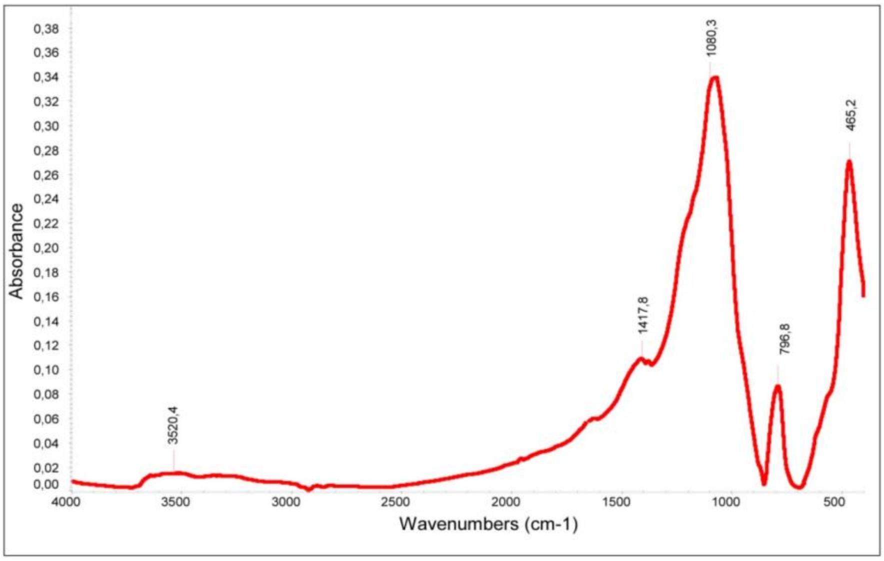


A



B

Fig.5: FTIR spectra of virgin and pyrolyzed rice husk; (a)-virgin rice husk, (b)-PRH_{600}

Surface morphology of the pyrolyzed rice husks

Fig. 6 depict SEM images of pyrolyzed rice husks. Kudaibergenov *et al.,* (2012) and Bharadwaj *et al.,* (2008) reported that the external wall of PRH_{300} and PRH_{600} shows the occurrence of a large number of button-like structures which were not found in the virgin rice husk particles (Fig. 6A,B). Fig. 6A, B shows that the amount of button-like structures of particles increased with increasing pyrolysis temperature. The increasing amount of button-like structures of particles positively influences the oil sorption capacity of rice husk due to the emergence of voids in the button of particles. The voids in the button of particles can be seen in cross-section of PRH_{600} (Fig. 6C, D) Furthermore, it is visible that PRH_{300} particles are much denser than PRH_{600}.

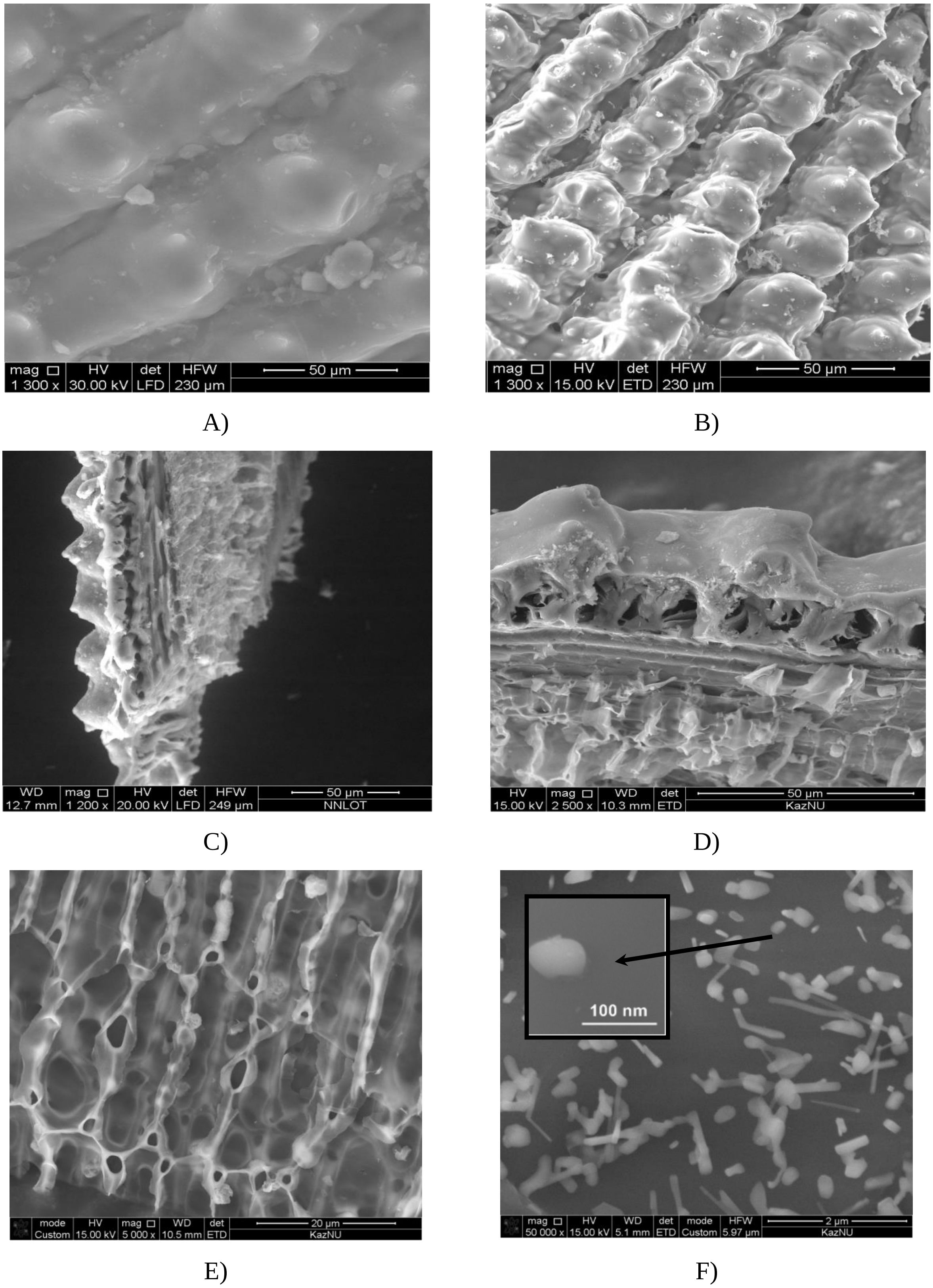
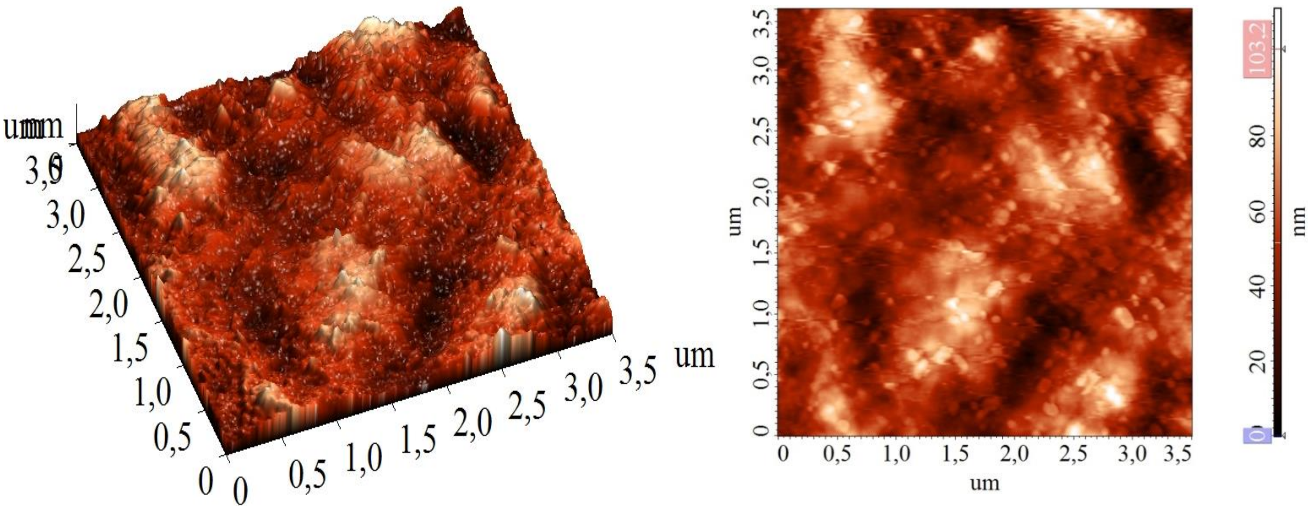


Fig. 6: SEM images of pyrolyzed rice husks; (A, B)-external walls of PRH_{300} and PRH_{600}, (C, D)- cross-section of PRH_{600}, (E, F)-interior structure of PRH_{600} with different magnifications

Fig. 6 (E, F) shows the interior structure of PRH_{600} with different magnification and indicated that particles underwent drastic changes in this process of high–temperature treatment.

The interior structure of PRH_{600} is shown in Fig. 6 (E) and illustrates the presence of pores in the particles with the diameters of about 3–5 µm. The emerging of pores and button-like structures may be caused by the fast removal of volatile organic components from the particle [28]. Fig. 6 (F), shows with high magnification interior structure of PRH_{600}. As can be seen, the formation of spherical and needle-like nanoparticles with the diameters of about 100–150 nm emerged after pyrolysis.

The morphology of the PRH_{600} was also investigated by atomic force microscopy. Fig. 7A, B depict the AFM image of PRH_{600}. AFM observation of PRH_{600} also shows the presence of spherical silica nanoparticles on the surface of rice husk without agglomeration. According to the AFM results, the particle size of silica is approximately 20-50 nm in diameter. The emergence of silica nanoparticles during pyrolysis of rice husk has been discussed earlier by Tzong-Horng *et al.*, (2004).



A B

Fig. 7: AFM images of PRH_{600}; (A) 2-dimension and (B) 3D image

The size and shape of particles that produced during the pyrolysis of rice husks are also positive influences on the oil sorption capacity of adsorbents due to the providing of unique properties. According to the results from our microscopic investigations, the pyrolyzed adsorbent has a highly porous structure with numerous voids and pores corresponding to these characteristics of oil adsorbents.

Conclusions

Pyrolyzed rice husk has very high oil removal efficiency, since they possess high porosity and reactive surface functionalities. Results showed that the oil removal efficiency increased to 94 % in case of rice husk pyrolyzed at 600 ºC. The results of SEM and AFM showed that pyrolysis under steam of rice husks allows drastic modification of the structure with high porosity. In conclusion, this study demonstrates the possibility to obtain effective oil adsorbents from rice husks, which are currently considered to be an agricultural waste. The results of this investigation show that the pyrolyzed rice husk has very high oil removal efficiency and may successfully be used as an effective adsorbent for purification of oil contamination in wastewater.

Acknowledgements

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