ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

The Influence of Ash Tree Sawdust Acid Treatment On the Removal of Crude Oil from Water Surfaces.

Tatiana R. Denisova[1]*, Ildar G. Shaikhiev[2], Gennady V. Mavrin[1], Irina Ya. Sippel[1], and Nadezhda P. Kuznetsova[1]

[1]Kazan Federal University, Naberezhnye Chelny Institute, Russia, Naberezhnye Chelny, Mira Prospect, 68/19
[2]Kazan National Research Technological University, Russia, Kazan, Karla Marksa street, 68

ABSTRACT

Agricultural and timber industry wastes may constitute a significant source of promising oil sorption materials. In this study the potential application of *Fráxinus excélsior* ash tree sawdust as sorption material for crude oil removal was investigated. The effect of acid treatment on physicochemical and sorption properties of sawdust was studied in a batch system. Oil sorption capacity and water uptake of sorption materials in static system were evaluated. For the determination of raw and treated samples structure and surface changes X-ray diffraction analysis, atomic force microscopy, FTIR spectroscopy and contact angle evaluation were used. The highest oil sorption capacity was shown by 3% HNO_3 treated sawdust, 43.2% and 37.4% increase of oil sorption capacity for Devonian oil and Carbon oil, respectively, was observed in comparison with untreated sawdust. The exhibited reduction of modified sawdust water uptake indicated the increase of sorbent material hydrophobicity that was confirmed by the results of contact angle determination. Based on atomic force microscopy results, the surface roughness of treated sawdust was shown to be enhanced that could be a primary factor affecting on oil sorption capacity improvement. Thus, acid treated ash tree sawdust was shown to have improved oil sorption and physicochemical characteristics for crude oil removal.

Keywords: ash tree sawdust, acid treatment, oil sorption capacity, water uptake.

Corresponding author

INTRODUCTION

Oil pollution has steadily increased with the increased oil consumption. The risks of petroleum contamination are significant during oil and its derivatives transportation, transfer, storage and processing. Oil discharges result in severe negative consequences for organisms and environment [1]. Spilled oil in water media may cause a great hazard, 1 m^3 of spilled oil contaminates approximately 12 km^2 of water surface. Therefore there is a strong need to collect the spilled oil quickly and the sorption method can be optimum for the oil spill recovery. The sorption method application have numerous advantages such as high oil sorption rate and sorption capacity, high oil retention capacity during transfer, high recovery of the sorbed oil through simple method, good reusability, and excellent physical and chemical resistance against deformation, photo-degradation and chemical attacks [2].

Oil sorbent materials can be classified into organic, inorganic and synthetic organic products. Despite the best properties of synthetic materials as oil sorbent they are expensive, not renewable and biodegradable. From environmental engineering point of view, natural sorbent materials are more attractive because of their availability, the possibility of sorbent collection, complete oil removal from the spill site, easy disposal with the least environmental hazard, more economical than most synthetic sorbents [2]. Different agricultural wastes and nature materials can be used as oil sorbents such as kapok, sawdust, leaves residues, sisal, coir fiber, oat husk, wheat husk, barley husk and straw, bagasse etc. [1-11] However these materials still have some limitations primarily due to their poor hydrophobicity, resulting in low oil–water separation selectivity and efficiency [8]. The sorption properties of nature materials can be improved by their chemical treatment with different reagents [1, 4-8].

In this work *Fráxinus excélsior* ash tree sawdust, waste from the local timber industry was suggested to be the oil sorbent for the crude oil removal. Raw and acid treated sawdust samples primarily were investigated to determine oil sorption capacity and water uptake in static system and then to evaluate their performance for spilled oil treatment from water surface. The influence of several parameters such as acid type and concentration, acid treatment time, oil and sawdust contact time on oil sorption efficiency was studied. Also the impact of acid treatment on physicochemical characteristics of sawdust was evaluated by means of atomic force microscopy, sensile drop method, FTIR spectroscopy and X-ray diffraction analysis. The results obtained in the experiments and observed sawdust surface changes showed that acid treatment allowed improving sawdust sorption characteristics mainly due to surface roughness increase and enhanced hydrophobicity. Thus, the present study demonstrates the efficiency of acid treated sawdust usage as low-cost oil sorbent.

METHODS

Fráxinus excelsior sawdust obtained from local timber manufactory in Naberezhnye Chelny with the particle size from 1 to 2 mm was investigated as an oil sorption material. Devonian oil and Carbon oil produced by Leninogorskneft Oil and Gas Production Board, JSC TATNEFT were used as experimental oils for oil sorption capacity determination.

For raw ash tree sawdust treatment 0.5, 1 and 3% sulfur, nitric, phosphoric, hydrochloric, perchloric and acetic acid solutions were used. 10 g of ash tree sawdust were placed into the 250 cm^3 flat-bottom flask, and then 200 cm^3 of acid solution with needed concentration were poured. The flask content had been rigorously mixed during 15 - 60 minutes at 20°C. Then treated sawdust had been washed with distilled water until the neutrality was achieved and dried at 70°C to the constant weight.

For the determination of sawdust samples oil sorption capacity in static system previously weighted brass mesh was placed into a Petri dish, then 50 cm^3 of oil were poured and 1 g of sorption material was placed above to form a continuous layer. After specific time intervals (from 3 to 30 minutes) the mesh with the sorption material was lifted and left allowing the excess oil dripping from the test cell. Then the mesh was weighed and the oil sorption capacity was calculated by weights difference. The oil sorption capacity in static system was estimated as sorbed oil weight and sorption material weight ratio:

$$A = \frac{m_1}{m_2},$$

где m_1 – the sorbed oil weight, g; m_2 – the sorption material weight, g.

The sorption material water uptake was determined similarly the oil sorption capacity evaluation.

For oil spill simulation 50 cm^3 of distilled water and 3 cm^3 of oil were poured into the Petri dish. Then 1 g of sorption material was placed above the oil layer. After 15 minutes contact the sawdust samples were lifted and weighted, and the remaining in the Petri dish amount of oil was estimated by CCl_4 extraction. The amount of sorbed oil and, secondly, the amount of sorbed water were evaluated by the weights difference.

The infrared spectra of investigated samples were analyzed by the means of FTIR spectrometer Nicolet is 5 in frequency range from 400 to 4000 cm^{-1}.

Interactions between solid and liquid were characterized based on contact angle θ between droplet and solid surface. This parameter was evaluated by «Kruss DSA 20E» device with tangent method for raw and treated ash tree sawdust samples. Distilled water was used as a wetting liquid.

X-ray diffraction analysis was conducted on X-ray diffractometer Ultima IV RIGAKU with the use of copper cathode tube. The structural composition changes were evaluated by comparison of diffraction pattern ranges intensity.

An atomic force microscope (MultiMode V, USA) was used to reveal the morphology of the samples. The 250-350 kHz cantilevers (Veeco, USA) with silicone tips (tip curvature radius is of 10-13 nm) were used in all measurements. The microscopic images were obtained with 512 × 512 resolution. The scanning rate was 1 Hz. The antivibrational system (SG0508) was used to eliminate external distortions.

RESULTS

At the initial stage of the experiments the oil sorption capacity of raw and treated samples of sorption material was determined (Table 1).

Table 1: The maximum values of ash tree sawdust oil sorption capacity as the dependence of acid type and acid concentration used for the treatment

The modifying agent	Sawdust oil sorption capacity, g oil/g sorbent		
	0,5 %	1 %	3 %
For Devonian oil			
H_2SO_4	5,44	5,66	5,54
HNO_3	5,46	5,70	5,93
HCl	5,11	5,07	5,25
$HClO_4$	5,72	5,75	5,52
H_3PO_4	4,76	5,46	4,77
CH_3COOH	5,56	5,10	4,96
Untreated	4,14		
For Carbon oil			
H_2SO_4	5,79	5,92	5,82
HNO_3	6,13	6,52	6,6
HCl	5,71	5,37	5,68
$HClO_4$	6,36	5,81	5,91
H_3PO_4	5,26	5,70	5,97
CH_3COOH	5,92	5,91	5,36
Untreated	4,90		

The maximum oil sorption capacity values for sawdust samples treated by 3% HNO_3 as treatment time dependence are presented in Table 2.

The applicability of the sorption material for oil removal from water surfaces is significantly influenced by its water uptake capacity. Hence at the next stage of the experiments water uptake of raw and treated samples was determined (Table 3).

Table 4 presents the results of the experiments that simulated the removal of oil layer from water surface by raw and treated sorption materials.

Table 2: The maximum oil sorption capacity of 3% HNO_3 treated sawdust at different treatment time

Treatment time	The maximum oil sorption capacity, g oil/g sorbent	
	For Devonian oil	For Carbon oil
15 min.	5,94	6,54
30 min.	5,93	6,60
45 min.	5,70	6,65
60 min.	5,87	6,36
Untreated	4,14	4,90

Table 3: The ash tree sawdust maximum water uptake as the dependence of acid type and acid concentration used for the treatment

The modifying agent	The ash tree sawdust maximum water uptake, g water/g sorbent		
	0,5 %	1 %	3 %
H_2SO_4	4,24	5,04	4,33
HNO_3	4,88	4,66	4,68
HCl	4,96	4,29	4,98
$HClO_4$	6,04	6,22	5,69
H_3PO_4	4,58	4,66	4,52
CH_3COOH	5,96	6,44	7,12
Untreated	5,22		

Table 4: Oil sorption capacity and water uptake of raw and treated samples

The modifying agent	Total oil sorption capacity and water uptake, g/g sorbent	Oil sorption capacity, g oil/g sorbent	Water uptake, g water/g sorbent	Oil removal efficiency, %	Water uptake difference, %
For Devonian oil					
Untreated	3,111	2,546	0,564	97,66	-
3% H_2SO_4	2,913	2,603	0,310	99,85	-45,04
3% HNO_3	2,706	2,588	0,118	99,27	-79,08
3% H_3PO_4	3,021	2,606	0,415	99,96	-26,42
3% HCl	2,919	2,594	0,325	99,50	-42,38
3% $HClO_4$	3,221	2,606	0,615	99,96	+9,04
3% CH_3COOH	3,100	2,606	0,494	99,96	-12,41
For Carbon oil					
Untreated	3,377	2,594	0,783	98,03	-
3% H_2SO_4	3,129	2,642	0,487	99,85	-37,80
3% HNO_3	3,093	2,645	0,448	99,96	-42,78
3% H_3PO_4	3,140	2,619	0,521	98,98	-33,46
3% HCl	3,026	2,644	0,382	99,92	-51,21
3% $HClO_4$	3,363	2,645	0,718	99,96	-8,30
3% CH_3COOH	3,177	2,645	0,532	99,96	-32,06

For characterization of the samples infrared spectra, surface morphology and diffraction patterns of untreated and treated by 3% HNO_3 sawdust was analyzed (fig. 1 - 3). Contact angle between distilled water and sorption material was estimated by sensile drop method. The results showed 38.8 ± 3.27° for raw material and 57.3 ± 5.32° for treated sample.

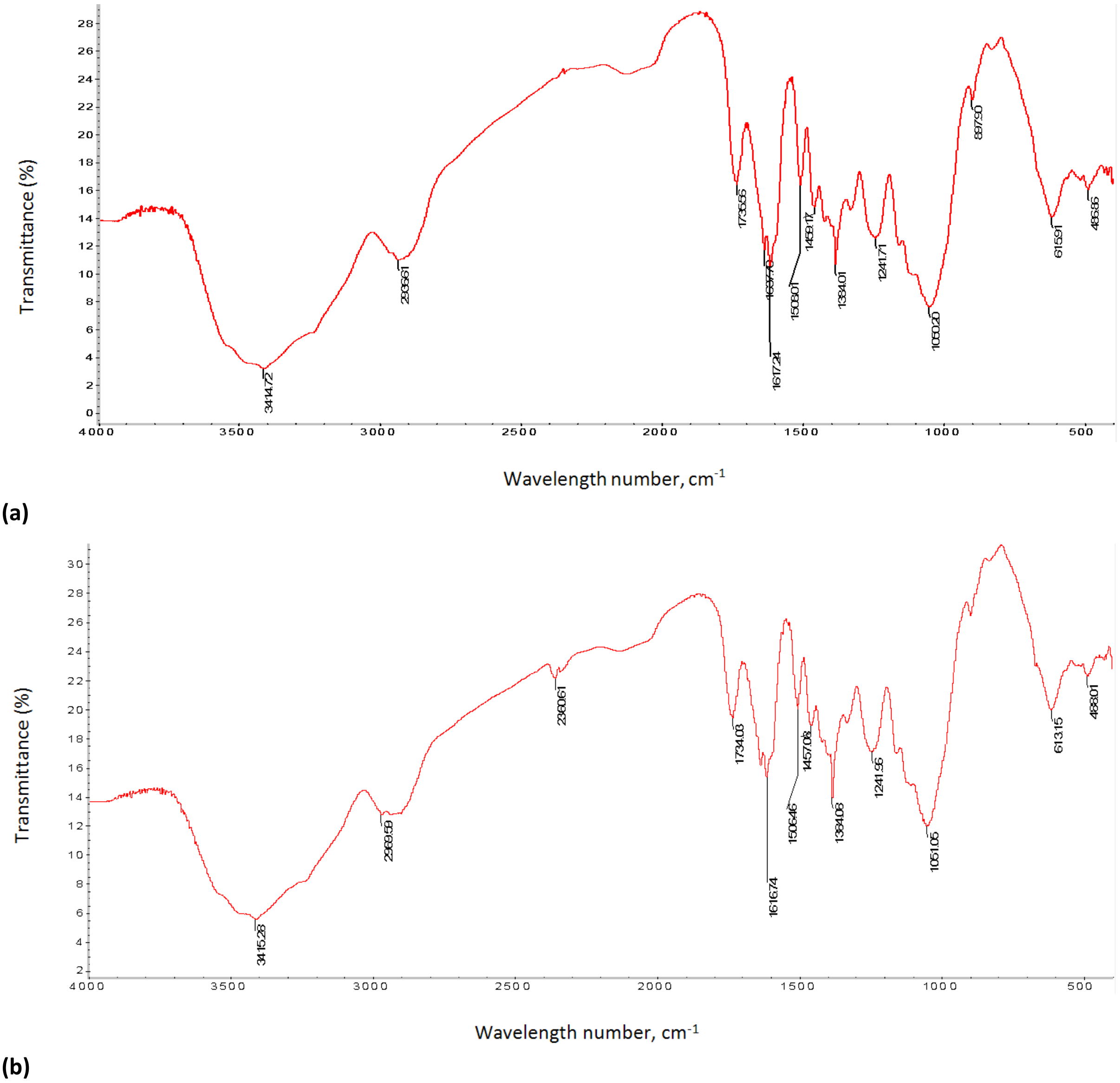
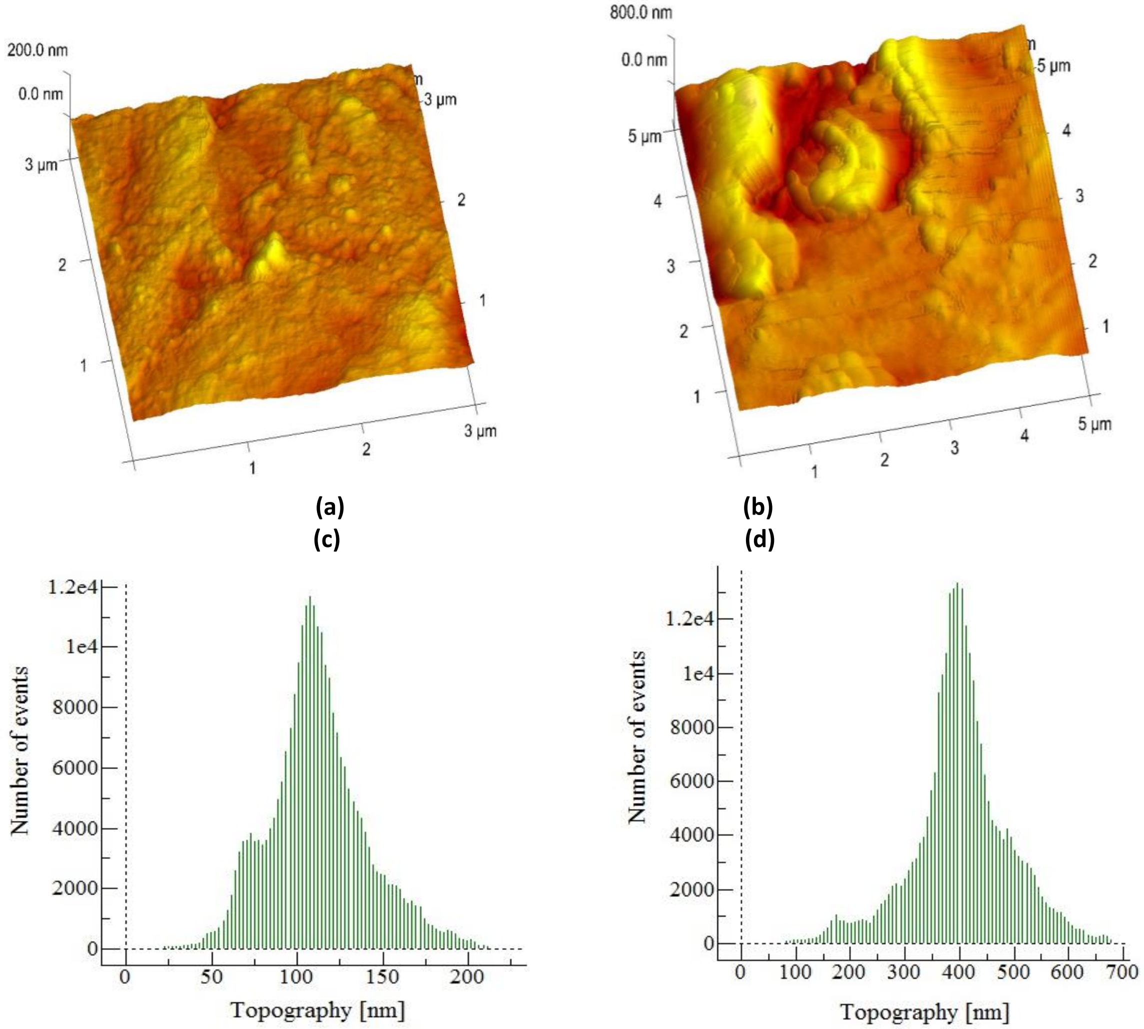
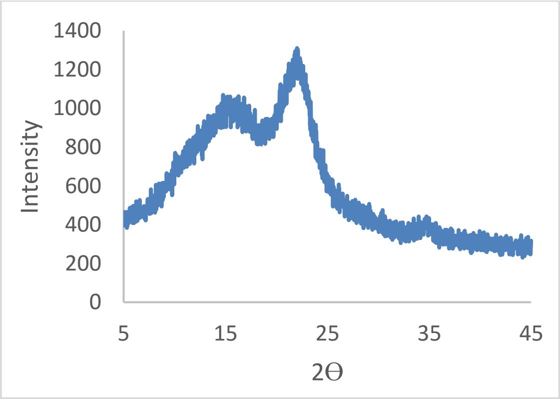


Figure 1: FTIR spectra of untreated (a) and treated by 3% HNO_3 (b) sawdust

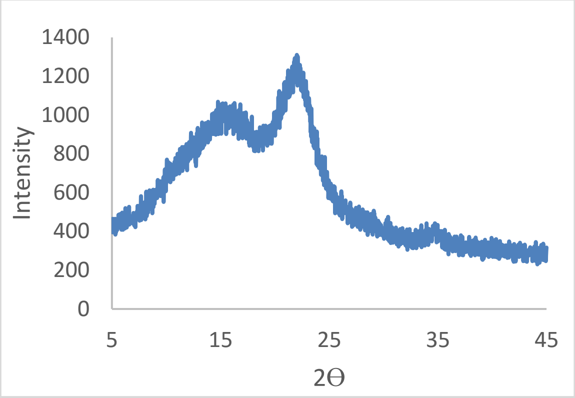


(a) **(b)**
(c) **(d)**

Figure 2: The microscopic images and morphology of untreated (a, c) and treated by 3% HNO_3 (b, d) sawdust



(a)



(b)

Figure 3: X-ray diffraction patterns of untreated (a) and treated by 3% HNO_3 (b) sawdust

DISCUSSION

According the initial investigations, oil sorption capacity of raw ash tree sawdust was 4.14 g oil/g and 4.90 g oil/g sorbent for Devonian oil and Carbon oil, respectively. Then influence of acid concentration on oil sorption capacity of sawdust was estimated (Table 1).

Table 1 shows that acid treatment by acid solutions with various concentrations leads to 15-43% and 7-25% increase of oil sorption capacity for Devonian oil and Carbon oil, respectively. The maximum enhance of this parameter was obtained for samples treated by 3% HNO_3. The increase in oil sorption capacity of acid treated cellulose sorption materials had been reported by others [4, 5, 7], namely, the oil sorption capacity increase from 4.52 g oil/g sorbent to 5.85 g oil/g sorbent for Devonian oil and from 5.38 g oil/g sorbent to 6.46 g oil/g sorbent for Carbon oil had been observed for oat husk treated by 3% H_2SO_4 [4].

Considering the highest oil sorption capacity of sawdust treated by 3% HNO_3, the impact of treatment time with the use of this acid solution on sawdust oil sorption capacity was determined further. Presented in Table 2 data suggest that variation of treatment duration from 15 to 60 minutes do not significantly influence on oil sorption capacity. The highest values of mentioned characteristic are observed at 15 minutes treatment of ash tree sawdust by 3% HNO_3 when using Devonian oil as the experimental oil and at 45 minutes treatment for Carbon oil. Acid treatment obviously promotes the increase of sawdust surface hydrophobicity. It is confirmed by the enhanced values of contact angle between treated sawdust and distilled water in comparison with untreated one. Contact angle had been changed from 38.8 ± 3.27° observed for raw material to 57.3 ± 5.32° obtained for the sample treated by 3% HNO_3.

The sawdust hydrophylicity decrease may be caused by the removal of some portion of hydrophilic low molecular weight compounds from sawdust biopolymers due to their hydrolysis and extraction into the solution. Therefore the hydrophobicity of the sorption material can be increased. This suggestion is confirmed by the results of FTIR spectroscopy of raw and acid treated sawdust (Fig. 1).

The infrared spectra shown in Fig. 1 are generally similar, however transmittance difference can be observed. These increments demonstrate partial compound changes in sawdust polymer structure. The indicated transmittance increase observed for some bands and the offset to the larger wavelength side at 600-1500cm^{-1} in treated sawdust spectrum affirm the assumption that hydrolysis of hemicelluloses, cellulose, lignin and other nature polymers occurs due to acid treatment.

The X-ray diffraction patterns (fig. 3) of raw and treated by 3% HNO_3 sawdust samples show that acid treatment do not result in any significant changes in sawdust structure. The sorption material crystallinity does not actually change, considering its values from 0.18 for raw material to 0.19 for modified sawdust the amorphous structure of sorbent is supposed.

The results of the experiments conducted to determine the influence of acid concentration on sawdust water uptake are presented in Table 3. The sawdust modification by $HClO_4$ and CH_3COOH solutions facilitates 9-36% increase of sorption material water uptake, and treatment by other acids promotes the reduction of this characteristic by 3-19%. The minimal water uptake was observed for sawdust treated by 0.5% H_2SO_4. This fact as reported earlier may be attributed to the removal of some hydrophilic low molecular weight compounds from sawdust biopolymers due to their extraction to the solution.

The enhanced hydrophobicity of treated sawdust is confirmed by the results of the experiments that simulated the removal of oil layer from water surface by the use of raw and modified sorption material samples (Table 4). As shown in Table 4, sawdust water uptake had been reduced while the entrapped oil percentage had slightly increased due to insignificant amount of oil.

Previous investigations of nature materials sorption characteristics [2, 8] demonstrated that high surface hydrophobicity significantly affects on the ability of sorption material to retain oil. Nevertheless, according other reports, the surface roughness and porosity may constitute the primary factor influencing on oil sorption capacity. Abdullah et al. [2] reported that even if nature waxy coating on the surface of some vegetable fibers which ensured excellent oleophilic properties had been removed, as long as the initial structure with high roughness and porosity remained intact, high oil entrapment and retention could be still achieved.

The surface images (fig. 2) obtained for raw and treated sawdust by means of atomic force microscope MultiMode V showed that the surface of sorption material had irregular structure with numerous protrusions. Histograms of surface sites altitude distribution is presented for each sample (fig. 2c, 2d). The surface roughness can be estimated based on histogram peak. For the raw material protrusions with 120 nm height prevail and generally protrusions height varies from 25 to 210 nm, while for the treated sawdust roughness increase can be observed. The surface protrusions with 400 nm height are the most common with general height variation from 80 to 680 nm. The enhanced roughness and, respectively, increased surface area allow improving oil sorption capacity of the material.

Thus, in this study physicochemical and sorption characteristics of ash tree sawdust were investigated and the results show that low concentration acid treatment of sawdust promotes the improvement of sorption properties. Particularly the enhanced surface roughness and hydrophobicity contribute to the increase of oil sorption capacity and selectivity of the material. The best performance had been shown by ash tree sawdust treated by 3% HNO_3. The sawdust as an ample and low-cost timber industry waste is effective and environmentally friendly oil sorbent and can be successfully used for the removal of spilled oil from water surfaces.

ACKNOWLEDGEMENTS

The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University. Microscopic investigations were carried out in the laboratory "Spectroscopy, microscopy and thermal analysis" of Kazan National Research Technological University.

REFERENCES

[1] S.S. Banerjee, M.V. Joshi, R.V. Jayaram. Treatment of oil spill by sorption technique using fatty acid grafted sawdust. Chemosphere. 2006, 64. P. 1026 – 1031.
[2] M.A. Abdullah, A.U. Rahmah, Z. Man. Physicochemical and sorption characteristics of Malaysian Ceiba pentandra (L.) Gaertn. as a natural oil sorbent. Journal of Hazardous Materials. 2010, 177. P. 683–691.
[3] T.R. Annunciado, T.H.D. Sydenstricker, S.C. Amico. Experimental investigation of various vegetable fibers as sorbent materials for oil spills. Marine Pollution Bulletin. 2005, 50 (11). P. 1340 – 1346.
[4] S.V. Stepanova, V.V. Domozhirov, I.G. Shaikhiev. The investigation of sulfuric acid treatment influence on oil and water sorption capacity of oat processing wastes. Herald of Technological University. 2014, 8. P. 228 – 231.
[5] I.G. Shaikhiev, O.A. Kondalenko, S.M. Trushkov. Agricultural prosessing wastes as a sorbent for collecting of petrol from water surfaces. Exposition Oil and Gas. 2010, 5 (11). P. 46 – 50.
[6] S. Ibrahim, S. Wang, H.M. Ang. Removal of emulsified oil from oily wastewater using agricultural waste barley straw. Biochemical Engineering Journal. 2010, 49. P. 78 – 83.

[7] S.V. Stepanova, A.Sh. Shaimardanova, I.G. Shaikhiev. Birch leaf litter and its chemically modificated patterns for oil removal. Herald of Technological University. 2013, 14. P. 215-217.

[8] J. Wang, Y. Zheng, A. Wang. Superhydrophobic kapok fiber oil-absorbent: Preparation and high oil absorbency. Chemical Engineering Journal. 2012, 213. P. 1–7.

[9] S.M. Sidik, A.A. Jalil, S. Triwahyono, S.H. Adam, M.A.H. Satar, B.H. Hameed. Modified oil palm leaves adsorbent with enhanced hydrophobicity for crude oil removal. Chemical Engineering Journal. 2012, 203. P. 9 – 18.

[10] X. Sun. Acetylation of sugarcane bagasse using NBS as a catalyst under mild reaction conditions for the production of oil sorption-active materials. Bioresource Technology. 2004, 95 (3). P. 343 – 350.

[11] L. Vlaev, P. Petkov, A. Dimitrov, S. Genieva. Cleanup of water polluted with crude oil or diesel fuel using rice husks ash. Journal of the Taiwan Institute of Chemical Engineers. 2011, 42. P. 957 – 964.