Application of modified ash-tree sawdust for oil removal from water surfaces

I Ya Sippel1,*, G A Akhmetgaleeva1 and K A Magdin1
1 Kazan Federal University, Kremlin street 18, Kazan 420008, Russia

*E-mail: irina.sippel@yandex.ru

Abstract. This paper shows the study on the possibility of using ash-tree (Fráxinus excélsior) wood-working waste for removing heavy-oil products from aqueous surfaces by sorption method. In order to improve sorption properties, ash-tree sawdust was exposed to ultrasound treatment at 35000 Hz for 5 hours in aqueous environment. Waste diesel engine oil was used as a sorbate. The physico-mechanical properties of modified sawdust are determined: bulk density, buoyancy, moisture content, ash content and physicochemical characteristics of sorbate. The simulation of motor oil spills on the water surface was carried out; oil and water absorption were determined. It was shown that ultrasound-modified ash-tree sawdust is an effective sorbent, the degree of water purification from oil hydrocarbons amounted to 98-99% under static adsorption conditions.

1. Introduction

Purification of natural reservoirs and industrial wastewater from hydrocarbons of oil and petroleum products is an important and urgent task due to the increasing volume of petroleum products’ production and application and increased production of oil-polluted waters. One of the most effective methods for removing petroleum products from aqueous media is the use of sorbents. Various inorganic, organic, organomineral natural and synthetic substances have been proposed as sorption materials. To effectively remove emergency spills of petroleum products and oil from water surfaces, sorbents must have high sorption capacity, buoyancy, hydrophobicity, low cost and be harmless to the environment.

In recent years, there is an active ongoing search for new low-cost sorption materials based on plant waste from agriculture, forestry and woodworking industries: straw, sawdust, wood bark, leaves [1-6]. This waste has a wide renewable raw material base, low cost compared to industrial commercial sorbents, is environmentally friendly and affordable.

The use of cellulose-containing waste in native form is limited due to their insufficient sorption capacity compared to industrial oil sorbents. In order to improve their sorption properties, various activation methods are proposed: treatment with aqueous solutions of salts [7], organic and mineral acids [8-10], alkalis [11], organic compounds of various types [1, 12, 13]. The physico-chemical modification of organic cellulose-containing wastes is of interest; such treatment is targeted on their efficiency increase, since the use of non-chemical treatment avoids formation of chemically contaminated wastewater in the sorption materials production.

In this paper, ultrasonic activation of ash-tree wood-working waste, as well as physico-mechanical and sorption properties of modified products were investigated. Ash-tree wood is used in the manufacture of furniture, stairs, as a building and finishing material, while a significant amount of
waste is formed, the volumes of which often exceed the volumes of finished products. Wood-working enterprises waste often has no further use and is placed on industrial waste landfills, which increases the anthropogenic impact on environment. In this regard, the search and development of new methods for modifying sorption materials based on wood-working waste is an important and urgent task.

2. Materials and Methods
Ultrasonic activation of ash-tree sawdust was performed at a frequency of 35000 Hz at room temperature in an aquatic environment. 10 g sawdust samples were placed in chemical flasks with 250 cm$^3$ volume, added with 100 cm$^3$ of distilled water and placed in the ultrasonic unit for 5 hours. After the specified time, sawdust was separated from extracts, washed with distilled water to remove soluble compounds and dried to a constant mass at a temperature of (70±2) °C [14].

The content of organic substances in aqueous extracts after sawdust ultrasonic treatment was determined by the Chemical Oxygen Demand (COD) indicator using the bichromatometric titration method in accordance with the methodology [15].

Fractional composition of sawdust was determined by the sieve method using laboratory sieves 5; 3; 2; 1; 0.5 mm.

Determination of sawdust bulk density was carried out after exposition until reaching an air-dry state at a temperature of (103±2) ° C. Sawdust was poured in portions of 20-25 cm$^3$ in a 100 cm$^3$cylinder, after which the cylinder bottom was tapped on the wooden disc for 0.5 minutes in an inclined position; then the cylinder was weighed to an accuracy of 50 mg.

Sawdust buoyancy was determined by the method proposed in the work [16] for oil sorbents. The 3 g test samples were placed in a 50 cm$^3$ chemical glass half filled with water and kept at room temperature for 72 hours. The sawdust left afloat was then extracted from the water and dried at a temperature of (105 ± 1) °C to a constant mass. According to the mass difference, buoyancy percentage was calculated.

The ash content and hygroscopic moisture of the modified sawdust were determined by the gravimetric method. To determine the moisture, sawdust was placed in the weighing bottle and weighed with an error of up to 0.001 g. Then the weighing bottles with sawdust were brought to a constant mass in the drying cabinet at a temperature (100±2) °C. The first weighing was carried out no earlier than 10 hours after the start of drying, repeated weighting - after 2 hours.

Moisture W was calculated as a percentage with a rounding of no more than 0.1% according to the formula:

$$W = \frac{m_1-m_2}{m_2-m_0} \cdot 100\%$$

(1)

Where $m_0$- weighting bottle weight, g; $m_1$- weight of weighting bottle with the sample before drying, g; $m_2$-weight of weighting bottle with the sample after drying, g.

To determine the ash content, a porcelain crucible brought to a constant mass was filled with 2 g of sawdust, after which the suspended crucible with the sample was tempered for 5 hours at a temperature of (600 ±10) °C until the organic part of the sample was fully burnt out.

Ash content of sawdust $A$ was calculated as a percentage by mass according to formula (2) considering the conversion factor by moisture:

$$A = \frac{m_3-m_1}{m_2-m_1} \cdot k \cdot 100\%$$

(2)

Where $m_1$-crucible mass, g; $m_2$-crucible mass with the sample, g; $m_3$-crucible mass with ash, g; $k$- moisture conversion factor.

To simulate engine oil spills on the water surface, a pre-suspended brass mesh was placed in Petri dishes, after which 50 cm$^3$ distilled water and 3 cm$^3$ of oil product were poured. Then an even 1 g layer of modified ash sawdust was applied on the surface of the formed oil film. After 15 minutes, sawdust
saturated with oil products was extracted and kept to drain excess amounts of absorbed oil and water for 1 minute, after which it was weighed at the analytical scales. Thus, total oil and water absorption was determined. To determine the residual mass of the oil product not absorbed by sorbent, its extraction by tetrachloromethane was carried out. The whole sample volume remaining in the Petri dish was quantitatively transferred to the dividing funnel, added with 20 cm³ of tetrachloromethane and thoroughly shaken. Extraction was repeated until a colorless solution was obtained in the dividing funnel. Spectrophotometric method determined the oil product content in the extract and remaining un-sorbed oil mass was calculated. The amount of absorbed oil was calculated by the mass difference, then sorbed water was calculated [17]. Similar experiments were carried out with 5, 7 and 9 cm³ of motor oil.

For waste engine diesel oil, the determined physico-chemical parameters were the ones that mostly affect the intensity of the sorption process: viscosity and density. Kinematic viscosity was measured by a capillary viscometer after prolonged (at least 1 hour) thermostatting of the oil product at 40 °C and 100 °C. The density was determined by the bottle method and was calculated as the ratio of the tested petroleum product's mass to the mass of water taken in the same volume.

3. Results and Discussion

As a sorption research material, ash-tree (Fráxinus excélsior) sawdust formed as a waste at the wood-working enterprise of the Republic of Tatarstan was taken. The original sawdust is polydispersed in structure. The sieve analysis has shown that they have different particle-size distribution with the most mass being a fraction with particle size between 1 and 2 mm.

To increase the sorption capacity, ash-tree sawdust was exposed to ultrasound for 5 hours, after which their most important physical and mechanical parameters were determined and sorption properties in relation to motor oil were investigated. The efficiency of sorption purification of aqueous media from various pollutants depends on such sorbents characteristics as buoyancy, bulk density, moisture content. The main physical and mechanical characteristics of ash-tree sawdust subjected to 5-hour ultrasound treatment are shown in table 1.

Table 1. Physical and chemical characteristics of ultrasound modified ash sawdust.

| Parameters            | Value            |
|-----------------------|------------------|
| Packed density, g/cm³ | 0.190±0.002      |
| Buoyancy, %           | 76.8±1.6         |
| Humidity, %           | 4.77±0.12        |
| Ash content, %        | 0.271±0.025      |

Modified sawdust has a high buoyancy value (76.8%), which is an important circumstance when they are used to remove petroleum products from the water surface. High buoyancy value and low bulk density (0.190%) indicate significant porosity and the presence of a highly developed sorbent surface. Due to high buoyancy, modified ash-tree sawdust can be used in oil booms in sorption cleaning of water surfaces from petroleum products.

The low ash content of samples (0.271%) indicates a low content of mineral components, which is an important condition for the waste sorption material disposal by incineration after water purification process completion.

The sorption capacity of modified sawdust was investigated in relation to the waste engine oil of the KAMAZ diesel vehicle. The sorption of petroleum products with high molecular weight and heavy fractional composition depends on the viscosity and density of the oil product, since adhesion occurs in line with adsorption processes. Some of the most important physico-chemical characteristics of the studied motor oil for the sorption process are presented in table 2.
Table 2. Physical and chemical characteristics of used motor oil.

| Parameters                              | Value |
|-----------------------------------------|-------|
| Kinematic viscosity at 100 °C, mm²/s    | 10.8  |
| Kinematic viscosity at 40 °C, mm²/s     | 95.9  |
| Viscosity index                         | 73.0  |
| Density at 20 °C, kg/m³                 | 887.0 |
| Density in degrees API                  | 27.7  |

Waste motor oil has high kinematic viscosity and density values due to the presence of high-molecular oxidative polymerization and condensation products in its composition; those are formed when operating a diesel engine under the influence of high temperatures, air oxygen, catalytic effects of metals.

In laboratory conditions, the simulation of water surface contamination by motor oil was carried out and the possibility of using modified ash-tree sawdust as sorption materials was investigated. The results of the experiments are presented in table 3.

Table 3. Results of modeling the removal of motor oil from the water surface with ultrasound modified ash sawdust.

| Volume/weight of motor oil, cm³/g | Total motor oil sorption capacity and water uptake, g/g | Water uptake, g/g | Motor oil sorption capacity, g/g | Motor oil removal efficiency, % |
|-----------------------------------|---------------------------------------------------------|-------------------|---------------------------------|--------------------------------|
| 3/2.661                           | 3.385                                                   | 0.735             | 2.650                           | 99.6                           |
| 5/4.435                           | 4.941                                                   | 0.542             | 4.399                           | 99.2                           |
| 7/6.209                           | 6.524                                                   | 0.384             | 6.140                           | 98.9                           |
| 9/7.983                           | 8.129                                                   | 0.266             | 7.863                           | 98.5                           |

In addition to hydrocarbons, in oil-polluted aquatic environments sorbents also absorb water, which reduces their oil capacity, so in experiments on modeling oil spills on the water surface water absorption of modified sorption materials samples was determined. Water absorption of ash-tree sawdust is due to the presence of organic groups with polar covalent bonds in the wood, such as OH, COOH. In addition to water absorption, the absorption of motor oil and the amount of total oil and water absorption were also determined.

The efficiency of water purification under the conditions of the experiment is 98.5-99.6% depending on the content of the oil product. With an increase in the volume of motor oil used to model the spill, the water absorption of the modified samples is noticeably reduced, apparently due to the hydrophobization of the sorbent surface as a result of ultrasound treatment.

In the process of ultrasonic sawdust treatment, the content of organic substances in the water phase was analyzed, for which the Chemical Oxygen Demand indicator was determined. The schedule of changes in organic matter content in aqueous extracts depending on the duration of ultrasonic sawdust treatment is presented in Figure 1. For comparison, a dependence graph of the Chemical Oxygen Demand indicator for extracts obtained without ultrasound exposure is given. It is shown that the main amount of organic substances is extracted from the sawdust matrix in the first 30 minutes of ultrasound treatment.
Figure 1. Dependence of chemical oxygen consumption of ash-tree sawdust extracts from processing time: 1 - extracts obtained as a result of ultrasound treatment; 2 — extracts obtained without ultrasound treatment

In the literature, it is noted that ultrasound treatment is used in various technological processes to accelerate extraction of water-soluble substances from wood: phenolic compounds, cyclic alcohols, monosaccharides, some polysaccharides [18-20]. Under the ultrasound influence, there are changes in the wood matrix, which contributes to the extraction of low-molecular components, increase in pore volume, increase of surface hydrophobicity.

The consequence of ultrasonic effects on wood waste is the formation of a highly developed porous sorbent structure, as well as high sorption activity in relation to non-polar sorbates.

4. Conclusions
Modified ash-tree sawdust are effective sorption materials in relation to heavy petroleum products with high molecular weight. Experiments to simulate motor oil spills on water surfaces showed high cleaning efficiency amounting to 98-99%.

Due to high buoyancy (76.8%), modified ash-tree sawdust can be used in oil booms in sorption cleaning of water surfaces from petroleum products. The low ash content value (0.271%) indicates a high content of organic matter, which is an important condition for waste sorbent disposal by incineration.

The use of ash-tree sawdust for the petroleum products removal from the surfaces of reservoirs will ensure their effective cleaning, obtain environmentally friendly, affordable, inexpensive wood waste-based sorption materials, which will lead to a decrease in the volume of waste generation and accumulation and reduce the negative impact on the environment.

Acknowledgements
The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.

References
[1] Shariff I, Shaobin W and Ha M A 2010 Biochemical Engineering J. 49 pp 78–83
[2] Rahman M S and Islam M R 2009 Chemical Engineering J. 149 pp 273–80
[3] Vázquez G, Alonso R, Freire S, González-Álvarez J and Antorrena G 2006 *J. Hazardous Materials* **133** pp 61–67

[4] Wan Ngah W S and Hanafiah M A 2008 *Bioresource Technology* **99**(10) pp 3935–48

[5] Balintova M, Demcak S and Pagacova В 2016 *International journal of energy and environment* **10** pp 189–94

[6] Ferrero F J 2007 *J. Hazardous Materials* **142** pp 142–52

[7] Janoš P, Coskun S, Pilařová V and Rejnek J 2009 *Bioresource Technology* **100** pp 1450–53

[8] Su P, Granholm K, Pranovich A, Harju L, Holmbom B and Ivaska A 2012 *Bioresources* **7** (2) pp 2141–55

[9] Huang L, Oua Z, Boving T B, Tyson J and Xing B 2009 *Chemosphere* **76** pp 1056–61

[10] Sippel I Ya and Akhmetgaleeva G A 2019 *J. Computational and Theoretical Nanoscience* **16** (12) pp 5261–64

[11] Lucaci D and Duta A 2009 Bulletin of the Transilvania University of Brasov **2**(51) pp 143–50

[12] Argun M E and Dursun S 2006 *J. Int. Environmental Application & Science* **1**(1-2) pp 27-40

[13] Argun M E, Dursun S and Karatas M 2009 *Desalination*, **249** pp 519–27

[14] Sippel I Ya and Akhmetgaleeva G A 2019 *Helix* **9**(4) pp 5170–74

[15] END F 14. 1:2 2014 100-97 Quantitative chemical analysis of water, Methods of measurements execution of chemical oxygen consumption in samples of natural and purified wastewater by titrimetric method (M.: FSI FCAM) 15

[16] Kamenshchikov F A and Bogomolny E I 2005 *Oil sorbents* M-Izhevsk (SIC Regular and chaotic dynamics) pp 78-80

[17] Denisova T R, Shaikhiev I G, Mavrim G V, Sippel I Yaand Kuznetsova N P 2016 *Research J. of Pharmaceutical, Biological and Chemical Sciences* **7**(5) pp 1742–50

[18] Antonova G F, Bazhenov AV, Varaksina T N, Konovalov N T, Konovalova N N and Stasova V V 2006 *Chemistry of plant raw materials* **3** pp 5-16

[19] Vostrikov S V and Novikova I V 2002 *Izvestiya vuzov. Food technology* **4** pp 26–28

[20] Yuan T-Q, Xu F, He J and Sun R-C 2010 *Biotechnology Advances* **28** pp 583–93