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## The Investigation of Wood Waste Ash and Linden as Sorbents of Petroleum Products

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### Abstract

Materials of vegetable origin, in particular, woodworking industry residues can be used as alternative sorption materials for extraction of different pollutants out of water media: heavy-metal ions, colorants, phenol, petroleum. Methods of sorption properties improvement of wood residues represent substantial interest. In this work sorption properties of wood residues: sawdust of ash tree (*Fraxinus excelsior*) and small-leaved linden (*Tilia cordata*) were investigated - with the aim of their further usage as sorbents at extraction of petroleum derivatives out of water media. Exhausted engine oil, having a considerable part of mineral component in its content, was investigated as the petroleum derivative. For the increase of oil absorption power processing of sawdust with ultrasound of frequency 35000 Hz with in different time intervals: from 30 up to 240 minutes was carried out. Values of maximum oil absorption power of native and processed samples in static conditions in relation to the exhausted engine oil were defined. Maximum oil absorption power of sawdust that underwent ultrasound processing amounted to 7.76 g/g for ash tree and 11.8 g/g for linden, what corresponds to the increase by 29.3% for ash tree and by 55.5% for linden in comparison with the initial sawdust. Sorption capacity of sawdust by methylene blue and iodine characterizing meso- and microporosity of sorption materials and its dependence on duration of ultrasound impact was defined. Toxicity of initial samples of linden and ash tree sawdust was defined by the method of biotesting, hazard class of residues was estimated.

### Keywords

Wood Residues, Sawdust, Petroleum Derivative, Oil Absorption Power, Sorption Capacity, Toxicity.

### Introduction

Cleaning of waste water and surface watercourses from petroleum and petroleum derivatives is an important and vital task due to the increase of extraction volume, transportation and processing of petroleum, usage of different petroleum derivatives: engine, transmission and industrial oils, automotive and aircraft fuels, which, getting into the environment, cause its pollution and degradation. Petroleum derivatives and petroleum are able to spread over water surface as a thin layer, covering vast surfaces with thin films, which sharply encumber ingress of oxygen out of atmosphere and decrease its content in water. Simultaneously with surface water pollution, content of ground water also changes and pollution of soil takes place. Getting into water objects petroleum hydrocarbons undergo different transformation and migration processes, including evaporation of light ends, partial solution of petroleum components, their photochemical oxidation under the influence of solar radiation, what leads to synthesis of secondary polluting substances, frequently more toxic than initial hydrocarbons. Heavy petroleum products, such as fuel oil and mineral oils, possessing low solubility and high boiling temperatures, represent special hazard.

Promising trend of water media cleaning from petroleum hydrocarbons and petroleum derivatives is usage of sorption processes with application of natural and synthetic sorbents, as well as residues of agricultural and other productions [1-5]. Usage of sawdust forming in large quantity at timber procurement and woodworking enterprises is of profound interest. To increase sorption capacity of wood residues different methods of their chemical modification are proposed: treatment with mineral and organic acids [1, 2, 4], alkalies [6-8], organic compounds [9].

Previously it was shown, that wood residues can be used as sorbents for removal of petroleum of devonian and carbonic deposits from the surface of water objects [1, 2, 6]. In this work we studied sorption properties of ash tree (*Fraxinus excelsior*) and linden (*Tilia cordata*) sawdust in relation to petroleum derivatives with high molecular weight and heavy fractional composition. Timbers of these species are widely used for manufacturing of furniture, ladders, as construction and finishing materials, for manufacturing of handcrafted items, toys, wood engraving etc. During processing of wood significant quantity of residues is produced, depending on the type of production amounting from 5 up to 50% of mass of the initial raw material, including less valuable soft residues due to limitation of their use: sawdust and chips.

In most cases, wood residues are accumulated on the territory of enterprises and waste deposits, representing one of the most significant problems of woodworking industry. In this connection, it becomes quite perspective to use woodworking residues as cheap, ecological and efficient sorption materials. Exhausted engine oil used in operation of KAMAZ truck was used as sorbate for research.

### Methods

Sawdust of linden and ash tree was investigated as sorbent that represented residues at woodworking enterprises of Prikamsky region. Preliminarily sawdust was subjected to fractionation, for research of sorption properties fractions with particle size of 1-2 mm were selected.

Modification of wood residues was carried out in an ultrasound device with frequency of 35000 Hz, for which purpose 10 g of sawdust was put into flat-bottomed flasks, poured over with 100 cm<sup>3</sup> of distilled water and placed into the ultrasound bath for 30-240 minutes at a temperature of 25 °C. Upon the expiration of a certain period of time sawdust was filtered out, multiply rinsed with distilled water before full removal of colored and water-soluble compounds and then dried at a temperature of 70-75 °C up to constant mass.

In the extract separated from sawdust, mass of the washed out part was defined by a gravimetric method.

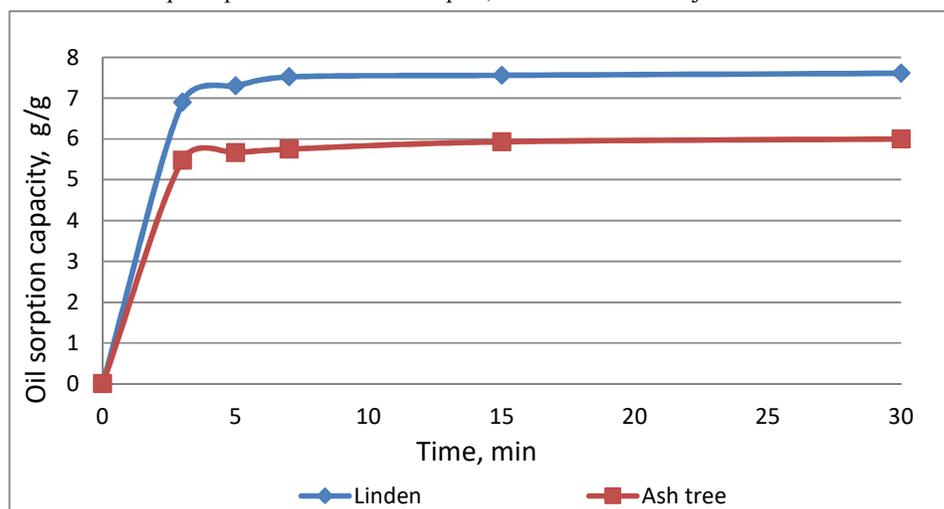
Volume of oil absorption power of wood sawdust was defined in a way similar to definition of oil capacity by the method, described in the work [10].

Sorption activity of samples by methylene blue was defined using photocalorimetric method by measuring optical density of clarified solution of the indicator. Sorption activity by iodine was defined by means of titration of clarified iodine solution with solution of sodium thiosulfate.

Definition of sawdust toxicity was carried out in accordance with “Methodology of measurement of *Daphnia magna* Straus quantity to define toxicity of drinking, fresh natural and wastewater, water extracts from ground, soils, sewage sludge, production and consumption waste by the method of counting forward” [11]. Methodology is based on mortality definition of daphnia at influence of toxic substances on them that are present in the test sample in comparison with the audit sample, i. e. water not containing toxic substances.

## Results and Discussion

Perspectives of usage of residues as sorbents of petroleum and petroleum derivatives are denied, first of all, by their physico-chemical properties, as well as big sorption capacity, supposing presence of highly developed porous structure with hydrophobic surface. Sorption capacity of investigated residues of linden and ash tree woodwork was defined in relation to exhausted engine oil in static conditions. It is shown (fig. 1) that main volume of the petroleum derivative is absorbed by sawdust within first five minutes of contacting, herewith further increase of sorption duration does not have significant influence on oil absorption power of sawdust samples, both native and subjected to ultrasound treatment.



**Figure 1: Dependence of Oil Absorption Power of Initial Linden and Ash Tree Sawdust on the Time of Contacting with the Petroleum Product.**

Major problem connected with the usage of natural materials as sorbents is insufficiently expressed sorption properties of these materials. With the aim of sorption properties improvement of investigated wood residues their processing with ultrasound was carried out with the frequency of 35000 Hz. Selection of modification way is determined by the fact that application of physical activity by means of ultrasound impact is ecologically more safe in comparison with chemical modification, including processing of wood residues with solutions of mineral acids, alkali and other aggressive substances. Data given in table 1 show that ultrasound modification of ash tree and linden sawdust promotes the increase of their sorption capacity in relation to the engine oil.

Time of sample processing, min	Maximum oil absorption power of sawdust after ultrasound processing, g/g	
	Ash tree	Linden
30	6.61±0.51	10.80±0.37
120	7.71±0.50	11.73±0.38
240	7.76±0.39	11.81±0.35
without processing	6.05±0.05	7.60±0.09

**Table 1: Values of Maximum Oil Absorption Power of Ash Tree and Linden Sawdust Depending on the Type of Sorption Material and Time of Ultrasound Processing.**

Increase of duration of ultrasound processing of the investigated samples from 30 up to 120 minutes leads to the increase of their maximum oil absorption power in relation to the exhausted engine oil, however, in case of further increase of ultrasound impact duration up to 240 minutes this indicator increases insignificantly, that is why long processing of samples is acknowledged to be inexpedient. Increase of oil absorption power of sawdust due to ultrasound impact amounted to 29.3% for ash tree and 55.5% for linden at processing duration 240 minutes.

Maximum oil absorption power of ash tree and linden sawdust subjected to ultrasound impact, noticeably supersedes maximum sorbent capacity of wood sawdust in relation to devonian and carbonic petroleum, mentioned in the work [10], which is apparently connected with differences in group and fractional composition of petroleum and mineral greasing materials. Exhausted oil of the diesel engine used in this work as sorbate, as distinct from petroleum, contains significant amount of hydrocarbon oxidation products with polar chemical bonds, what results in intensification of interrelation sorbate-sorbent and increase of absorption. Moreover, exhausted oil in comparison with petroleum possesses higher indicators of kinematic viscosity (10.65 mm<sup>2</sup>/s at 100 °C) and density (873 kg/m<sup>3</sup> at 20 °C), what leads to intensification of adhesive interaction, and, consequently, increase of oil absorption power.

Value of sorption to a large degree depends on the quantity and size of sorbent pores. We investigated sorption activity of ash tree and linden sawdust by methylene blue, that gives information about dimensions of pores with the diameter over 1.5 nm and by iodine, that witnesses presence of pores with the diameter over 1 nm. To define sorption activity by iodine and methyleneblue, samples of ash tree and linden sawdust were taken, not processed and processed with ultrasound within 30 minutes, 3 hours and 4 hours, with the aim to state the influence of processing time on sorption properties of materials.

Data given in table 2 show that sorption activity by iodine characterizing microporosity of sorbents, increases insignificantly after ultrasound processing. However, activity by methylene blue of modified samples increases 3 times in comparison with initial sawdust, what evidences considerable increase of volume of mesopores in sorbent structure.

Name of the sample	Duration of ultrasound processing, min	Sorption capacity by iodine, %	Sorption capacity by methylene blue, mg/g
Ash tree sawdust	without processing	15.91	8.75
Ash tree sawdust	30	18.39	22.12
Ash tree sawdust	180	18.40	25.05
Ash tree sawdust	240	18.41	26.64
Linden sawdust	without processing	21.90	30.60
Linden sawdust	30	22.94	87.65
Linden sawdust	180	26.01	88.04
Linden sawdust	240	27.03	90.01

**Table 2: Sorption Capacity by Iodine and Methylene Blue of Ash Tree and Linden Sawdust**

Increase of processing duration leads to the increase of sorption capacity of the investigated wood residues. So, after ultrasound processing within 240 minutes sorption activity by iodine increased by 16.01% for ash tree sawdust and by 18.81% for linden sawdust correspondingly and sorption activity by methylene blue – by 205.46 and 194.15% for ash tree and linden sawdust correspondingly. Higher values of sorption activity of linden sawdust in comparison with ash tree sawdust, in general, possibly is connected with presence of more developed surface of linden sawdust, what is confirmed by the values of pour density of materials that amount to 0.10 and 0.19 g/cm<sup>3</sup> for linden and ash tree sawdust, processed with ultrasound within 4 hours, correspondingly.

Increase of oil absorption power and sorption capacity of sawdust due to processing, apparently, is entailed by the change of wood structure. Ultrasound impact can lead to destruction of molecular chains, change of their conformation and disruption of intermolecular bonds of adjacent fibers [12]. Destruction of physical and chemical bonds encourages the increase of low-molecular components quantity, able to pass into the extract under the impact of ultrasound.

Gravimetric method was used to define mass loss of ash tree and linden sawdust at the result of ultrasound processing within 120 and 240 minutes; data are given in table 3.

Name of the sample	Duration of processing, min	Mass loss of the sample, g
Ash tree sawdust	120	0.497±0.01
Ash tree sawdust	180	0.506±0.01
Ash tree sawdust	240	0.515±0.01
Linden sawdust	120	0.712±0.01
Linden sawdust	180	0.738±0.01
Linden sawdust	240	0.765±0.01
Initial mass of samples – 10 g		

**Table 3: Mass Loss of Samples of Sorption Materials at Ultrasound Processing.**

The processing of ash tree and linden sawdust within 240 minutes leads to decrease of mass by 5.15 % and 7.65 % correspondingly. Mass loss of linden samples is somewhat bigger than that of ash tree, what is, evidently connected with differences in relevant wood species structure.

Due to extraction of water-soluble constituents out of wood structure, taking place under the influence of ultrasound, hydrophilic property of sorption materials decreases, and, as consequence, their oil absorption power increases.

Most basic requirement to petroleum sorbents largely defining the possibility of their further usage, besides sorption activity, cost, presence of raw materials base, is their safety for the natural environment. Toxicity and hazard class of the investigated residues of ash tree and linden were defined by the biotesting method based on mortality of *Daphnia magna* Straus for the definite time interval (table 4).

Samples	Mortality of daphnia, %				Toxicity
	1 hour	19 hours	24 hours	48 hours	
Initial linden	0	0	10	20	chronic
Linden 1:10	0	0	0	0	absent
Linden 1:100	0	0	0	0	absent
Linden 1:1000	0	0	0	0	absent
Linden 1:10000	0	0	0	0	absent
Ash tree 1:10	0	10	10	10	chronic
Ash tree 1:100	0	0	0	0	absent
Ash tree 1:1000	0	0	0	0	absent
Ash tree 1:10000	0	0	0	0	absent
Control sample	0	0	0	0	absent

**Table 4: Mortality of *Daphnia magna* Straus in Water Extracts out of Sawdust Residues.**

As a result of biotesting of water extract of woodwork residues it was shown that: at all dilutions after 48 hours toxicity is absent. In samples without dilution after 48 hours mortality of daphnia amounts to 10% for ash tree sawdust and 20% for linden sawdust, what evidences chronic toxicity. Harmless reciprocal dilution of ash tree and linden sawdust amounts to  $HRD_{10-48} = 10$ . In accordance with criteria of residues referral to hazard class by the degree of negative impact on the environment [13], investigated sawdust refers to V hazard class, i.e. represents non-dangerous residues that influences the environment in low degree, almost not disturbing its components. For this reason application of ash tree and linden woodwork residues as petroleum sorbents, will not lead to emission of harmful substances into water objects and will not entail secondary contamination of hydrosphere.

Exhausted sorption materials saturated with petroleum derivatives and petroleum is possible to use as fuel.

### Summary

Ash tree and linden sawdust, representing woodwork industry residues can be considered as efficient, low-cost, ecologically clean sorption materials for removal of petroleum derivatives out of water media.

Ultrasound modification of sawdust increases their oil absorption power by 29.3% for ash tree and 55.5% for linden at duration of impact 240 minutes.

Ultrasound processing of ash tree and linden sawdust also contributes to the increase of sorption activity of the investigated materials by iodine by 16.01% and 18.81% and by methylene blue by 205.46 and 194.15% correspondingly.

By the method of biotesting it was shown that ash tree and linden sawdust are referred to non-hazardous wastes and their application as petroleum sorbents excludes additional emission of contaminating substances into water objects.

### Conclusions

Application of ash tree and linden woodwork residues as sorbents of petroleum derivatives will contribute to the decrease of accumulated ecological damage, decrease of areas, designated for temporary and long-term storage of wastes, decrease of financial expenses on cleaning of waters contaminated with petroleum because of low cost of sorbents made of woodwork residues in comparison with synthetic sorbents, environmental improvement and preservation of human health at the expense of liquidation of wastes and cleaning of natural and waste waters contaminated with petroleum products.

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