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OIL-CONTAMINATED WATER TREATMENT WITH MODIFIED ASH WOOD SAWDUST

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KEYWORDS

Oil Product

Woodworking Waste

Sorption Capacity

Ultrasonic Treatment

Ash Sawdust

ABSTRACT

In the current scenario treatment of oil hydrocarbons contaminated surface and water is one of the most critical environmental issues. Although various treatment methods are available, among these the most effective and environmentally friendly is the sorption method of treatment. The current study is an attempt to investigate the sorption capacity of native and ultrasonically modified ash sawdust sorbents to dissolved and emulsified oil hydrocarbons from wastewater and water bodies under dynamic conditions. Further, ash sawdust (*Fraxinus excelsior*) formed in woodworking enterprises of the Kama region, Republic of Tatarstan, was used as sorbents. To increase the sorption capacity, wood waste was exposed to ultrasound at a frequency of 35,000 Hz for 4 hours. Results of the study revealed that wood waste has sorption capacity and sorption oil hydrocarbons from wastewater were dependent on various factors. Further, the ultrasonic treatment of wood waste has been increased the sorption capacity of wood waste by 24 percent. Under dynamic conditions, the sorption capacity of ultrasound modified ash sawdust with relation to emulsified oil products was investigated, and reported that ash sawdust has 79% cleaning efficiency. The toxicity of ultrasound-modified ash sawdust was investigated by bio testing on *Daphnia magna straus* and reported that the ultrasound-modified ash sawdust has acute toxicity on experimental organisms.

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1 Introduction

Oil spills are a general problem and it usually occurred due to the escape of oil from crude oil confinement, extraction, transportation, and processing of oil. Various water bodies throughout the world are polluted with different hydrocarbon fractions. Under aquatic environment, petroleum hydrocarbons undergo various processes of migration and transformation, including dissolution of low molecular weight components, emulsification, evaporation of volatile fractions, photochemical oxidation, and finally biodegradation of oil spilled into the sea under the action of certain types of microorganisms. The cleanup of these oil spills is dependent on various recovery methods such as biological, mechanical, and physical methods. Mechanical and physical methods have various limitations and currently, the most promising method is the biological method. Among the various biological methods, the use of sorption is the most favored procedure for cleaning oil-spill because of its low cost. Uses of organic waste such as waste from agricultural, food and woodworking industries as sorption materials are not only cost-effective but also have high sorption capacity, and are environmentally friendly, and easily disposable. Further, various cellulose-containing wastes such as substandard grain, rice, buckwheat, barley, wheat husks, straw, cake, sawdust, walnut shells, coconut, almonds, onion husks, flax fire, leaf litter can be used as sorption materials (Ibrahim et al., 2010; Ofomaja et al., 2010; Fu & Chung, 2011; Wang, 2013; Wahi, 2013; Nagy et al., 2014; Stepanova, 2014; Kharlyamov et al., 2014; Yusupova, 2015; Zolgharnein, 2015; Balintova et al., 2016; Denisova et al., 2016; Denisova et al., 2017; Sippel & Akhmetgaleeva, 2019a). To improve the sorption characteristics of biopolymeric waste, various chemical methods and physical exposure have been proposed, among this, treatment with organic substances, solutions of alkalis, acids, hydrogen peroxide, thermal and ultrasonic exposure are the most common one. Further, modified cellulose-containing wastes can be effective sorbents concerning oil, oil products, heavy metal ions and other pollutants (Ofomaja et al., 2010; Ibrahim et al., 2010; Wang, 2013; Nagy et al., 2014; Stepanova, 2014; Kharlyamov et al., 2014; Denisova et al., 2016; Denisova et al., 2017; Sippel, 2019b).

In the current study, the sorption properties of ash sawdust (*Fraxinus excelsior*) concerning dissolved in water and emulsified oil hydrocarbons are studied. Ash wood is generally used for construction, decoration, furniture, stairs, crafts, toys, and carvings making. During the wood processing, a significant amount (5 to 50%) of waste is generated; this amount is depending on the type of wood use (Ofomaja et al., 2010). Unlike lump waste, which has a relatively wide range of uses (from the production of small sawn timber and glued blanks to wood-chemical products), soft waste (sawdust, shavings, bark) is of limited use and is buried at industrial waste landfills.

The use of ash sawdust as an adsorbent could be an excellent alternative to mitigate the contamination and remedy the places of

the spill for the sorption of oil. These bio adsorbents are a good source of cellulose and hemicellulose and lignin. In this regard, the use of ash sawdust as an effective, cheap, environmentally friendly sorption material seems to be promising. This study aims to evaluate the sorption properties of ash sawdust, to clean up oil spills while taking into consideration various factors.

2 Materials and Methods

Ultrasonic modification in wood waste was carried out according to the method described by Sippel & Akhmetgaleeva (2019a). Initially, this sorption material was sonicated in distilled water at a frequency of 35 kHz for predecided periods at a temperature of 25°C. After processing, the sawdust was thoroughly washed with distilled water to completely remove colored and water-soluble substances and drying it at 70°C to gain constant weight.

To determine the sawdust adsorption capacity with relation to dissolved oil products, a model solution was prepared by mixing oil and distilled water using a mechanical stirrer. Then the suspended oil was separated from the liquid and the solution was settled until the complete separation of the aqueous and organic phases. In the resulting model solution, the concentration of dissolved petroleum products was determined by IR spectroscopy using a KN-3 analyzer-concentration meter.

To determine the adsorption capacity of ash wood, 50 cm³ of the model solution containing dissolved petroleum products, and 1 g of sawdust were placed in 250 cm³ conical flasks. Then the contents of the flasks were vigorously stirred for various time periods (from 15 to 180 minutes). After a certain time, the ash sawdust was separated from the solution by filtration through a paper filter. The residual amount of petroleum products in the filtrate was determined by IR spectroscopy. The adsorption value of oil products A (mg/g) was calculated by the formula:

$$A = \frac{(C_{ucx} - C_{\kappa})}{m} \cdot V$$

C_{in} - initial concentration of oil product in the model solution (mg/dm³),

C_{fin} - final concentration of oil product in the solution (mg/dm³),

m - sample mass (g),

V - model solution volume (dm)³

To study oil absorption under dynamic conditions, a laboratory plant consisting of a supply and receiving container having a prepared solution and a filter column with the tested sorbent was assembled. The layout of the laboratory plant for this dynamic adsorption study is similar to that described by Yusupova (2015).

Initially, model solutions of various concentrations (50, 100, and 250 mg/dm³) were prepared in a separate container with emulsified oil products. For this purpose, the required amount of oil was mixed with distilled water in the presence of surfactants. The required water flow rate was set and passed through a glass column filled with the tested ash sawdust. The height of the sawdust layer was 0.1 and 0.2 m. Water samples from the column outlet were taken at regular intervals (15, 30, 60, 120, 180 minutes), and the residual content of oil products in the water was determined by IR spectroscopy.

The sawdust toxicity was determined by the bio-testing method following the method for measuring the amount of *Daphnia magna* Straus by direct counting (PNDFT 14.1:2:3:4.12-06, T 16.1:2:2.3:3.9-06, 2014). This technique is based on determining the mortality of daphnia when exposed to toxic substances present in the analyzed water when compared with a control sample, which does not contain harmful substances. The mortality of daphnia in the studied and control sample was taken into account at every 24 hours intervals; collected information suggested that not more than 50% of daphnia have died in all dilutions of the tested water.

To determine the toxicity of the analyzed aqueous extracts, the percentage of daphnia died in the tested water (A, %) was compared with the control sample:

$$A = \frac{X_K - X_T}{X_K} \cdot 100\%$$

where:

X_K is the number of daphnia that survived in the control sample;

X_T is the number of daphnia that survived in the tested aqueous extract.

At $A \leq 10\%$, the tested aqueous extract has no acute toxic effect.

This percentage of dead daphnia was used to calculate the harmless dilution ratio of the tested waters. At $A \geq 50\%$, the analyzed aqueous extract has an acute toxic effect. This value is used to determine the average lethal ratio of dilution of the test waters and to establish the hazard class of waste.

3 Results and Discussion

Ash sawdust (*Fraxinus excelsior*), formed as waste at one of the woodworking enterprises in Naberezhnye Chelny, Republic of Tatarstan, was used as a biosorption material in the current study. Sieve analysis of woodworking wastes showed a different fractional composition of sawdust, and the most massive fraction is particles with a size of 1-2 mm. The sorption capacity of native and ultrasound-modified ash sawdust was determined with dissolved and emulsified oil hydrocarbons. Further, adsorption of dissolved hydrocarbons from oil was carried out under static conditions using 4 hours of sonicated native ash sawdust. The kinetic relationships of the adsorption value of dissolved petroleum products by the original and modified samples are shown in Figure 1.

At the initial stage of adsorption, when the concentration of the adsorptive in the solution is maximum; the adsorption rate is highest and continues to increase until the adsorbent surface is completely saturated with adsorbate molecules. As the surface of the sorption material is saturated with adsorbate, the desorption rate was increased, and the adsorption equilibrium is gradually established. It was shown that the efficiency of purification from soluble oil hydrocarbons was 67.7% for native ash sawdust and 83.1% for sawdust subjected to ultrasonic modification for 4 hours.

In the case of model solutions, the possibility of purifying wastewater containing emulsified oil products was investigated.

Figure 1 Kinetic relationships of the adsorption value of dissolved petroleum products by the original (1) and modified (2) ash sawdust.

The experiment was carried out under dynamic conditions using ultrasonically modified ash sawdust as a column media. Figure 2 shows the relationship between the concentrations of oil at the outlet of the sorption column to the initial concentration of the model solution C/C_0 on the volume passed solution V . In case of a higher initial concentration of oil products in the model solution, the equilibrium state is reached faster.

Relationships in Figure 2 show that the post-treatment concentration of oil products quickly reaches the initial values, and the cleaning efficiency is 79%. The obtained result is natural because the dynamic activity of sorption materials is always lower than the static one. For activated carbon, the dynamic activity is 85-95% of the static one in industrial-type adsorbents; for silica gel, the dynamic activity is 60% lower than the static one.

One of the most important requirements for sorption materials to treat water bodies from various pollutants is their high ecological purity, including the safety of the sorbent itself and the avoidance of secondary pollution during its use. To assess the ecological safety of modified ash sawdust, their toxicity was studied by bio-testing for the lethality of the *Daphnia magna* Straus test object for a certain period. The results of the toxicity study are presented in Table 1. All dilutions after 48 hours show zero toxicity; an undiluted sample after 48 hours showed 10% mortality to daphnia, which indicates chronic toxicity.

The harmless multiplicity of dilution of aqueous extracts, which causes death not more than 10% of daphnia in 48 hours (BKR10-

48), for the ash sawdust understudy is:

$$\text{BKR}_{10-48} = 10^{\frac{(\lg 10 - \lg 1)(0,1 - 0,1)}{0,1} + \lg 1} = 10^0 = 1$$

According to the hazards materials classification criteria developed by the Ministry of Natural Resources and Environment, Russian Federation No. 536 dated 04th December 2014, the lethality of the ash sawdust belongs to class V of hazard materials. Modified ash woodworking wastes are practically non-hazardous, and their use as sorption materials will not cause secondary pollution of the hydrosphere. Waste sorbents saturated with oil or oil products can be utilized by incineration to obtain heat and electric energy or by pyrolysis to obtain carbon-containing products.

Ash sawdust is a readily available promising cost-effective organic material for oil-spill cleanup. Furthermore, it was observed that ultrasonic exposure modified sorbents and enhances the surface sorption. These results are in agreement with the findings of Onwuka et al. (2018) and Jmaa & Kallel (2019).

Conclusion

The sorption capacity of native and ultrasonically modified ash sawdust with respect to dissolved oil hydrocarbons under static conditions has been investigated. The ultrasonic treatment has been shown to increase the sorption capacity of wood waste by 24% in relation to dissolved oil hydrocarbons. The efficiency of

Figure 2 The relationship between the ratio of the concentration of oil at the outlet of the sorption column to the initial concentration of the model solution C/C_0 on the volume of the passed solution V (dm^3) when using modified ash sawdust as a sorption medium and the initial concentration of oil products (1 – 50 mg/dm^3 ; 2 – 100 mg/dm^3 ; 3 – 200 mg/dm^3).

Table 1 Mortality of *Daphnia magna* Straus in water extracts out of ash (*Fraxinus excelsior*) sawdust residues

Samples	Mortality of daphnia, %					Toxicity
	1 hour	2 hours	18 hours	24 hours	48 hours	
Ash tree	0	0	10	10	10	chronic
Ash tree 1:10	0	0	0	10	10	chronic
Ash tree 1:100	0	0	0	0	0	absent
Ash tree 1:1000	0	0	0	0	0	absent
Ash tree 1:10000	0	0	0	0	0	absent
Control sample	0	0	0	0	0	absent

ultrasound-modified ash sawdust sorption materials in the treatment of emulsified oil hydrocarbons was carried out under dynamic conditions by using a column medium and results of the study revealed 79% efficiency in emulsified oil products contaminated wastewater treatment. Further, the toxicity of the ultrasound-modified ash sawdust was determined by bio-testing and ash sawdust was classified as hazard class V waste, which suggested that the ash sawdust sorption will not lead to secondary pollution to the water bodies. These results suggested that ash sawdust can be used as an environmentally friendly, efficient, cheap and affordable sorption material for removing oil products from water environments. Further, ultrasonic exposure of ash sawdust enhances the efficiency of this sorption material and this is an environmentally safer method of increasing sorption capacity as compared to chemical modification.

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Conflict Of Interest

Authors would hereby like to declare that there is no conflict of interests that could possibly arise.

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