International Journal of Psychosocial Rehabilitation, Vol. 23, Issue 03, 2019
ISSN: 1475-7192

Removal of Petroleum Products from Water Surface by Chemically Modified Wood Waste

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Abstract--- *In this work, they studied the possibility of woodwork waste use to remove oil products from the water surface by the sorption method. We used sawdust of ash (Fráxinus excélsior) and linden (Tília cordáta) as sorption materials, formed at the woodworking enterprises of the Republic of Tatarstan, as sorbates - fresh and used diesel engine oils, characterized by high boiling points and heavy fractional composition. To increase the sorption capacity of wood waste, they were chemically modified with the solutions of sulfuric, nitric, hydrochloric, perchloric, phosphoric and acetic acids with the concentration of 0.5, 1 and 3%. They determined the values of the maximum oil absorption of the initial and modified samples of sorption materials in relation to fresh and used motor oils. It was established that ash and linden sawdust modified with a 3% solution of nitric acid have the highest sorption properties. Determination of the sorption capacity by iodine and methylene blue showed that modified sawdust, in comparison with the initial samples, has a more highly developed surface, combining different types of pores: both micro- and mesopores. Experiments on modeling engine oil spills on water surface showed that chemically modified sawdust are effective sorbents of oil products, the degree of water purification reaches 99%.*

Keywords--- *Acid Treatment, Oil Product, Oil Consumption, Wood Processing Waste, Sorption Capacity.*

I. INTRODUCTION

Purification of surface and wastewater from oil products is currently one of the most significant environmental problems. Oil products get into the environment during accidental spills in pumping and transportation systems, in oil depots, in oil product storages, at gas station facilities and stations, as well as with sewage from industrial enterprises, storm and melt water. When oil products get into hydrosphere objects, they undergo various transformation processes under the influence of external factors, including the evaporation of volatile fractions, dissolution, precipitation, and photochemical oxidation of hydrocarbons under the action of sunlight, which leads to secondary pollution. Heavy oil products are particularly dangerous: fuel oil and mineral oils have low solubility in water and high boiling points.

An effective and promising method for oil product extraction from aqueous media is the sorption processes using waste from agricultural, woodworking and other industries [1-10]. The use of vegetable raw material processing waste as sorption materials allows us to solve the dual problem in the field of environment protection: to ensure the use of waste accumulating in large volumes to obtain reagents for oil removal.

To improve the sorption properties of cellulose-containing waste, chemical and physical modification methods are used: treatment with solutions of alkalis, acids, hydrogen peroxide, organic solvents, and the exposure to

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Received: 10 Mar 2019 | Revised: 27 Mar 2019 | Accepted: 25 Apr 2019

ultrasound [1, 2, 4-6, 8]. They studied the effect of chemical modification on the sorption properties of ash and linden woodworking waste products and the removal of oil products from the water surface by modified wood waste. The petroleum products with a high molecular weight and heavy fractional composition were used as a sorbate: motor oil of viscosity grade SAE 10W-40 and waste oil from a diesel engine.

II. METHODS

Chemical modification of sawdust was carried out with the solutions of sulfuric, nitric, hydrochloric, perchloric, phosphoric and acetic acids at the concentration of 0.5, 1 and 3%. For this, 10 g of initial sawdust was placed in flat-bottomed flasks of 250 cm3 and 200 cm3 of acid solution was poured, after which the contents of the flask were thoroughly mixed for 40–60 minutes at the temperature of (20 ± 2) °C. Then, the modified sawdust was washed with distilled water to a neutral pH value and dried at 70–75 °C to constant weight.

The oil absorption of the initial and modified sawdust was determined similarly to the determination of oil absorption by the method described in [8].

The sorption activity of the samples was determined by the photocalorimetric method according to methylene blue via measuring the optical density of the clarified indicator solutions [11].

Iodine sorption activity was determined by titration of clarified iodine solutions with sodium thiosulfate solution [12].

The cellulose content in the sorption materials was determined by the nitrogen-alcohol method, for which a weighed portion of air-dried sawdust witht he weight of 1 g was placed in the flask of 250 cm3, 25 cm3 of nitric acid solution in ethanol was added and boiled for one hour with a reflux condenser. The treatment was repeated three times with new portions of the nitrogen-alcohol mixture. After the last treatment, the cellulose was filtered on a glass porous filter, washed with 10 cm3 of fresh nitrogen-alcohol mixture, and then with hot water until pH became neutral. Then the filter with cellulose was dried at the temperature of (103 ± 2) °C to constant weight and weighed.

To simulate pollution of the water surface with oil products, a pre-weighed round brass sieve was placed in a Petri dish, then 50 cm3 of distilled water and 3–9 cm3 of the studied oil product (engine oil) were poured, after which 1 g of sawdust was applied to the surface of the oil film. After 15 minutes, the sawdust was removed and weighed on an analytical balance, the amount of oil remaining in the Petri dish was extracted with carbon tetrachloride. The optical density of the solutions was determined by the photocalorimetric method. Based on the mass difference, the amount of absorbed oil was initially calculated, then the amount of sorbed water was calculated.

III. RESULTS AND DISCUSSION

Since the studied woodworking waste has a different fractional composition, the sieve analysis of the samples was carried out, according to the results of which it was found that the most massive fraction was sawdust with a particle size of 1-2 mm.

Under static conditions, the oil absorption of the initial sawdust of ash and linden was determined in relation to fresh and used motor oils. Figure 1 shows the graph of the initial sawdust of ash and linden oil intensity dependence on the contact time with respect to fresh semi-synthetic motor oil of SAE 10W-40 viscosity grade.

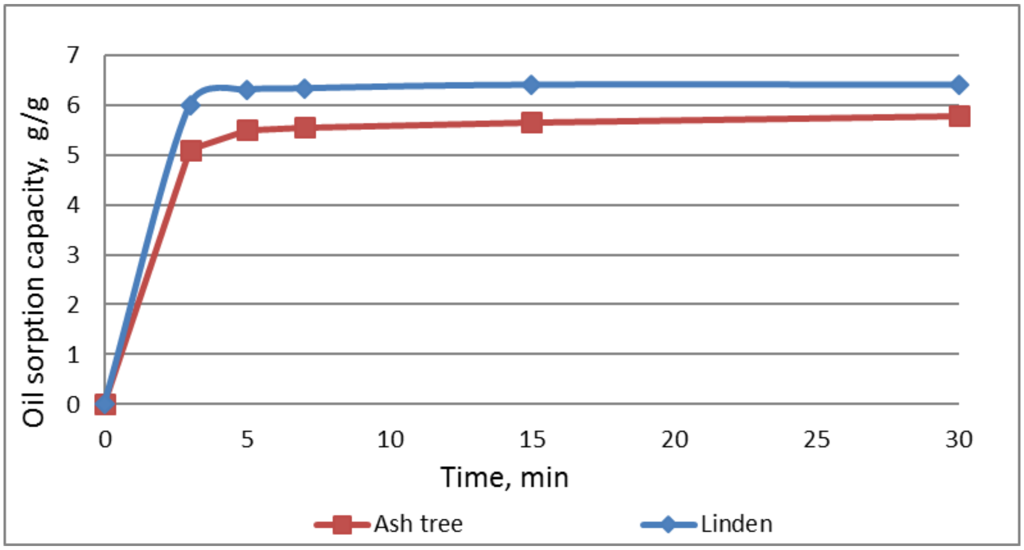

Fig. 1: The dependence of the oil intensity of the initial sawdust of linden and ash on the time of contact with the oil product

They showed that the main absorption of oil by sawdust occurs during the first 5 minutes of contacting. A further increase in exposure time does not contribute to a significant increase of the studied indicator. The maximum oil absorption for the initial sawdust of ash was 6.32 g/g for used oil and 5.88 g/g for fresh semi-synthetic oil, for the initial sawdust of linden - 7.40 g/g and 6.85 g/g, respectively.

In order to increase oil consumption, chemical modification of sawdust was carried out - the treatment with weakly concentrated solutions of sulfuric, nitric, hydrochloric, perchloric, phosphoric and acetic acids. The obtained values of maximum oil absorption depending on the type of oil product and acid concentration are presented in table 1 for sawdust ash and in table 2 for sawdust linden.

Table 1 - the Maximum oil absorption values of sawdust ash, depending on the type and concentration of acid

Modifying agent	*Maximum oil sorption capacity of sawdust ash when processing with acids concentration, g/g*		
	0,5 %	*1 %*	*3 %*
Sorbate - fresh engine oil			
Sulfuric acid	6,43±0,35	6,54±0,41	6,67±0,38
Nitric acid	6,63±0,39	6,79±0,33	6,92±0,45
Hydrochloric acid	6,39±0,44	6,49±0,49	6,57±0,35
Perchloric acid	6,41±0,36	6,51±0,39	6,58±0,44

Orthophosphoric acid	6,37±0,34	6,49±0,44	6,60±0,34
Acetic acid	6,31±0,45	6,40±0,41	6,49±0,39
Without treatment	5,88±0,18		
Sorbate - used diesel engine oil			
Sulfuric acid	7,37±0,38	7,57±0,33	7,66±0,45
Nitric acid	7,59±0,35	7,78±0,36	7,91±0,40
Hydrochloric acid	7,17±0,51	7,39±0,37	7,47±0,49
Perchloric acid	6,97±0,49	6,99±0,39	7,23±0,41
Orthophosphoric acid	7,11±0,46	7,22±0,45	7,44±0,52
Acetic acid	7,05±0,55	7,12±0,35	7,21±0,55
Without treatment	6,32±0,24		

They showed that acid modification contributes to oil absorption increase of sawdust relative to fresh and used motor oils. At the same time, ash sawdust treated with a 3% solution of nitric acid has the highest oil consumption, the increase makes 25.2% with respect to used diesel oil and 17.8% with respect to fresh engine oil as compared to unmodified waste samples.

Table 2: Maximum oil absorption values of linden sawdust depending on acid type and concentration

Modifying agent	*Maximum oil sorption capacity of linden sawdust when processing with acids concentration, g/g*		
	0,5 %	*1 %*	*3 %*
Sorbate - fresh engine oil			
Sulfuric acid	7,23±0,45	7,48±0,52	7,81±0,50
Nitric acid	7,99±0,49	8,14±0,35	8,28±0,35
Hydrochloric acid	7,26±0,35	7,41±0,53	7,58±0,32
Perchloric acid	7,36±0,45	7,55±0,50	7,67±0,36
Orthophosphoric acid	7,09±0,38	7,13±0,45	7,33±0,39
Acetic acid	6,83±0,33	7,18±0,39	7,23±0,35
Without treatment	6,85±0,19		
Sorbate - used diesel engine oil			
Sulfuric acid	8,28±0,31	8,49±0,41	8,92±0,38
Nitric acid	8,61±0,36	9,11±0,50	9,53±0,32

Hydrochloric acid	8,02±0,35	8,17±0,35	8,27±0,29
Perchloric acid	7,99±0,33	8,14±0,33	8,36±0,35
Orthophosphoric acid	7,42±0,45	7,54±0,37	7,78±0,41
Acetic acid	7,99±0,43	7,43±0,39	7,72±0,32
Without treatment	7,40±0,25		

For linden sawdust, the highest oil absorption value was also noted for the samples treated with the 3% solution of nitric acid: 8.28 g/g in relation to fresh motor oil (increase by 20.8%) and 9.53 g/g in relation to used diesel oil (increase by 28.9%).

Obviously, the interaction of the studied sorption materials with weak acid solutions leads to a slight increase of the maximum oil absorption. This fact is probably explained by the following: the acid treatment of wood waste contributes to the proportion of amorphous cellulose zone increase, which positively affects the increase of the specific surface and adsorption capacity of the material. The changes in the structure of wood biopolymer macromolecules under the action of acid solutions can contribute to the increase of the pore space and, accordingly, the oil absorption of wood sawdust.

For both the original and modified sawdust, the oil absorption in relation to the used oil is higher than in the case of fresh oil. The reason is that the used diesel engine oil, unlike fresh, contains hydrocarbon oxidation products with polar chemical bonds, which leads to increased sorbate-sorbent interaction and increased sorption. In addition, the used oil has a slightly higher density than fresh oil at 20 °C and kinematic viscosity at 40 °C, which leads to increased adhesion interaction and, as a consequence, to oil absorption increase.

One of the most important characteristics of sorption materials, which largely determines the possibilities of their practical application, is the sorption capacity, which is conditioned by the presence of a porous structure and a highly developed surface. To assess the effect of acid treatment on the sorption capacity of sawdust, iodine and methylene blue adsorption parameters were determined for the initial samples, as well as the samples subjected to treatment with 3% solutions of nitric and sulfuric acids. The data are presented in table 3. By the adsorption value of methylene blue, one can determine the presence of mesopores with the diameter of 1.5-200 nm in the sorption material, while the iodine sorption activity characterizes the microporosity of the sorbents and the presence of pores with the diameter of less than 1.5 nm.

Table 3: Sorption capacity for iodine and methylene blue sawdust of ash and linden

The name of the sample of the sorbation material	*Sorption capacity by methylene blue, mg/g*	*Sorption capacity by iodine, %*
Ash native sawdust	8,75	15,87
Ash sawdust modified H_2SO_4, 3%	21,19	17,11

Ash sawdust modified HNO_3, 3%	26,32	20,36
Linden native sawdust	30,60	21,80
Linden sawdust modified H_2SO_4, 3%	58,25	25,43
Linden sawdust modified HNO_3, 3%	87,42	27,08

It is obvious that modified sawdust have a more highly developed surface, combining different types of pores: both micro- and mesopores, in comparison with the initial samples. The increase of sorption activity for methylene blue (by 200% for ash and 185% for linden) indicates a noticeable increase of mesopores, and sorption activity increase for iodine (by 28% for ash and 24% for linden) characterizes micropore volume increase in the structure of the sorbent as the result of treatment with nitric acid solution.

They also studied the effect of acid treatment on the composition of sawdust, in particular, on the content of cellulose, which is the main organic component of wood. The nitrogen-alcohol method was used to determine the cellulose content in the initial and chemically modified linden sawdust. It was shown that the mass fraction of cellulose in the initial samples makes 51.06%, and in sawdust treated with the 3% solution of nitric acid, its value decreases to 46.22%. The decrease of the cellulose content in wood as the result of acid treatment can be explained by the hydrolysis of cellulose and hemicellulose with the formation of simple sugars (glucose, xylose, etc.), which increases the porosity and sorption capacity of sawdust.

A special problem when oil products enter the hydrosphere is their removal from the surface of water, since the sorption materials used in this case, in addition to oil products, also absorb water. We have studied the sorption capacity of modified sawdust during the removal of used engine oil from water surface. The results obtained for sawdust linden treated with the 3% solution of nitric acid are presented in table 4.

Table 4: The simulation results of oil film removal from water surface

Volume/ weight of oil product, ml/g	*Total oil and water-absorbing value, g/g*	*Oil absorption, g/g*	*Water absorption, g/g*	*The degree of removal of oil, %*
3/2.616	4.215	2.615	1.604	99.81
5/4.360	5.218	4.349	0.869	99.75
7/6.104	6.680	6.340	0.234	98.26
9/7.848	7.312	7.266	0.046	96.05

The simulation results show a high degree of water purification from oil product by modified linden sawdust. With a small amount of oil product spilled on water surface (3-5 cm3), the cleaning efficiency exceeds 99%, with a larger film thickness of the oil product, the degree of removal is slightly reduced.

IV. SUMMARY

Processing of ash and linden sawdust with weakly concentrated solutions of acids helps to increase their oil intensity in relation to fresh and used motor oils. In this case, the samples treated with a 3% solution of nitric acid have the highest sorption capacity in comparison with the initial waste.

They noted the increase of mesopore volume (by 200% for ash and linden) and micropore volume (by 28% for ash and 24% for linden) in the structure of sorbents as the result of treatment with nitric acid solution.

Modification of sawdust with weakly concentrated acid solutions helps to reduce the value of the mass fraction of cellulose in wood.

The results of experiments modeling engine oil spills on water surface showed that modified sawdust of linden and ash are effective oil sorbents. With a small amount of oil product, the water treatment efficiency is more than 99%.

V. CONCLUSIONS

Chemically modified sawdust of ash and linden can be considered as effective, inexpensive, affordable, environmentally friendly sorption materials for heavy oil product removal from water surface. The studied materials can be recommended as a sorption in floating booms and other floating adsorbing elements.

ACKNOWLEDGEMENTS

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

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