Sorption of petroleum products by chemically modified agricultural waste

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Abstract. The work investigated the physical, mechanical and sorption properties of cellulose-containing wastes of agro-industrial production, formed as a result of manufacturing activities of one of the large agricultural enterprises in the Republic of Tatarstan. To improve the sorption properties, the wastes were chemically modified via treating them with sodium hydroxide solutions with 0.5, 1, and 3% concentrations at a temperature of (20 ± 2) ° C. Standard and operating diesel oils were used as sorbates. As a result of alkaline treatment, there is an increase in the maximum oil absorption of sorption materials in relation to engine oils, an increase in the sorption activity with respect to iodine, which characterizes the material porosity, as well as a decrease in the bulk density of the modified samples. The best physical, mechanical and sorption properties were found in cellulose-containing waste treated with a 3% sodium hydroxide solution.

1. Introduction

Purification of natural reservoirs and industrial wastewater from oil and oil products is an important and urgent environmental task due to the high level of oil production, transportation and processing; increasing volumes of commercial oil products use, which is due to the high motorization rate. After the entry of petroleum products into the aquatic environment, complex processes of migration, transformation, physical and chemical transformations of petroleum hydrocarbons begin. The nature and intensity of these transformations depend on the type of hydrocarbons, first of all; on the structure of their molecules and molecular weight; as well as on external factors, among which the most significant are the ambient temperature, air humidity, and solar radiation. For low-boiling oil fractions, which form the basis of automobile and aviation gasolines, the prevailing processes are evaporation and subsequent photochemical oxidation in the tropospheric layer with oxygen and free radicals the presence. The resulting products of oxidative transformations of alkanes and aromatic hydrocarbons in the troposphere are often even more toxic than the primary pollutants. Oil fractions with a heavy fractional composition due to their low volatility form thin films on water surfaces, impairing gas and heat exchange, and also settle to the bottom of reservoirs or in coastal areas.

Various methods are used to clean water bodies and industrial wastewater from oil and oil products, among which one of the most effective and promising is the sorption method based on the use of mineral, organic and composite materials. Waste from forestry, woodworking, food and other industries, as well as from agriculture have been proposed as an alternative to industrial sorbents [1-8]. Of particular interest is the use of cellulose-containing wastes for the sorption purification of aqueous media from various pollutants. One of the disadvantages of organic waste, which largely limits their wide practical use for sorption water purification, is the lower sorption capacity in comparison with industrial oil sorbents. To improve the sorption capacity of cellulose-containing wastes from the
woodworking industry and agriculture, various methods of their physical and chemical activation have been proposed: treatment with acid solutions [3, 9], surfactants [10], salts [11], ultrasonic action [12], and acylation [13-14].

A promising sorption material for the extraction of various pollutants from polluted waters is cereal straw, which is an inexpensive, large-tonnage, renewable resource generated as a waste at many agro-industrial enterprises. The straw sorption properties of various agricultural crops in relation to crude oil [15], dyes [16], heavy metal ions [17], and organic substances [18] have been studied. In order to hydrophobize the surface and increase the sorption efficiency of low-polar organic substances, straw was treated with polymer solutions [17], siloxanes [19], and acetic anhydride [20-21].

The study of the cellulose-containing wastes of agro-industrial production and their modification products use as sorption materials for water purification from oil products is an urgent task, the solution of which will ensure the waste recycling and reduce the anthropogenic impact on the environment.

2. Materials and methods

Fractionation of waste was carried out using a hand-held particle size analyzer applying sieves with a hole diameter of 0.5 mm to 5 mm.

To improve the sorption properties, the waste (wheat straw) was chemically modified with sodium hydroxide solutions with 0.5, 1, and 3% concentrations. For this purpose, 10 g of straw was placed in flat-bottomed flasks of 500 cm$^3$ each and 300 cm$^3$ of alkali solution was poured, then the contents of the flask were thoroughly mixed at a temperature of (20 ± 2) °C for 60 minutes. After the specified time, the modified waste was separated by filtration, washed with distilled water until a neutral pH of the filtrate was reached, and then dried to constant weight at 80–85 °C.

Finding the oil absorption value of the original and modified waste in relation to standard and operating engine oils was carried out by analogy with the determination of the oil capacity of sawdust according to the method described in [22].

The hygroscopic moisture content of the original and modified wastes, as well as the ash content of the wastes saturated with petroleum products after their use as sorption materials, were determined by the gravimetric method in accordance with the methodology proposed in [23] for sawdust.

Sorption activity for iodine, which characterizes the waste porosity, was determined by the iodometry method. A 1 g sample of the sorption material dried at a temperature of (110 ± 5) °C was placed into a 250 cm$^3$ conical flask, 100 cm$^3$ of a 0.2 M solution of iodine in potassium iodide was added and, closed with a stopper, was intensively stirred for 30 minutes in the laboratory shaker AVU-type apparatus. After settling the mixture and sedimentation of dispersed straw particles, a 10 cm$^3$ aliquot was pipetted from the clarified solution and placed in a 50 cm$^3$ flask. Then the sample was titrated with a solution of sodium thiosulfate with a molar concentration equivalent of 0.1 mol/dm$^3$ in the presence of a freshly prepared 0.5% starch solution until a stable blue color appeared. Simultaneously, a blank experiment was carried out to determine the initial iodine content in the solution.

The adsorption activity for iodine in percent by weight was calculated by the formula (1)

$$A = \frac{(V_1 - V_2) \cdot 12.7}{m}$$

where $V_1$ - volume of sodium thiosulfate titrant solution used for titration in blank experiment, cm$^3$; $V_2$ - volume of titrant solution spent on titration of the analyzed sample, cm$^3$; 12.7 - conversion factor, including the mass of iodine corresponding to 1 cm$^3$ of the titrant solution and the volume of iodine solution in potassium iodide taken for clarification with sorption material, g.

The arithmetic mean of the results of three parallel measurements was taken as the analysis outcome, the discrepancy between which did not exceed 5%.
3. Results and discussion

Physico-mechanical and sorption properties of cellulose-containing agricultural waste - wheat straw and the effect of alkaline treatment on these properties were studied. Waste was obtained at one of the large agricultural enterprises of the Republic of Tatarstan, where they are generated in large quantities every year.

Before testing, the waste was crushed, and then fine and coarse fractions were sifted out. For research, samples were taken with a particle size between 0.5 mm and 5 mm. After fractionation, the waste was washed with distilled water and dried to constant weight at a temperature of (110 ± 5) °C.

To increase the sorption capacity, the waste was subjected to chemical modification, including treatment with sodium hydroxide solutions. The physical and mechanical properties of the original and modified sorption materials were determined: hygroscopic moisture, bulk density, buoyancy. The results are shown in Table 1.

After modification of the starting material with weakly concentrated sodium hydroxide solutions, some change in sorbent properties is observed: a decrease in moisture content and bulk density, as well as an increase in buoyancy. A decrease in bulk density and humidity indicate an increase in the samples porosity, and, consequently, an increase in oil absorption, which is confirmed by the results of sorption capacity studies. Both the original and modified straw samples have high buoyancy, with the highest value equal to 98.9 ± 0.5% in 72 hours of testing was demonstrated by the sample treated with 3% alkali solution. The high value of the buoyancy index is an important factor in assessing the practical application potentiality of sorption materials, since when cleaning natural reservoirs it is necessary to remove oil products from the water surface.

Sorption properties of native and modified samples were studied in relation to oil products with a high boiling point and heavy fractional composition. Motor oils of two types were studied as sorbates: standard and KAMAZ engine oils. Under conditions of static sorption, the oil absorption of the original waste was determined, as well as their chemical modifications obtained by treatment with sodium hydroxide solutions with 0.5%, 1%, and 3% concentrations. Since water can also be sorbed together with the oil product when cleaning water bodies, for the original and modified samples of straw, along with the maximum oil absorption, the maximum water absorption was also determined. The results are shown in Table 2.

### Table 1. Physical and mechanical properties of the original and modified waste.

| Modifying agent | Hygroscopic humidity, % | Buoyancy, (72 hours) % | Bulk density, g/cm³ |
|-----------------|--------------------------|------------------------|---------------------|
| Sodium hydroxide 3% | 4.73±0.12 | 98.9±0.5 | 0.071±0.010 |
| Sodium hydroxide 1% | 4.26±0.10 | 98.7±0.6 | 0.075±0.011 |
| Sodium hydroxide 0.5% | 4.45±0.09 | 98.5±0.5 | 0.078±0.008 |
| Without treatment | 7.30±0.11 | 96.1±0.5 | 0.086±0.008 |

### Table 2. Sorption properties of the original and modified waste.

| Modifying agent | Oil absorption in relation to standard engine oil, g/g | Oil absorption in relation to operating engine oil, g/g | Water absorption, g/g |
|-----------------|--------------------------------------------------------|-------------------------------------------------------|-----------------------|
| Sodium hydroxide 3% | 2.36±0.08 | 2.68±0.10 | 0.65±0.04 |
| Sodium hydroxide 1% | 2.16±0.10 | 2.34±0.08 | 0.79±0.03 |
| Sodium hydroxide 0.5% | 2.07±0.08 | 2.23±0.08 | 0.88±0.05 |
| Without treatment | 1.95±0.9 | 2.13±0.10 | 1.18±0.05 |
With the alkali solution concentration increase, the maximum oil absorption of modified samples in relation to diesel oils increases. The highest rates of sorption capacity are observed in straw samples treated with a 3% sodium hydroxide solution: compared to native waste, their oil absorption increased by 21.1% with respect to standard engine oil, and by 25.8% with respect to operating oil. Under the influence of alkali solutions on cellulose, which is the basis of straw, structural and chemical changes occur; as well as physico-chemical processes, including cellulose swelling and its partial dissolution. As a result, low-molecular fractions soluble in sodium hydroxide are washed out of cellulose, which leads to an increase in the sorption capacity and buoyancy, as well as a decrease in the bulk density of the modified samples. A decrease in water absorption of modified samples may be due to the hydrophobization of the straw surface associated with these processes. It is known that when cellulose is treated with concentrated alkali solutions, chemical reactions occur, leading to a new compound formation - alkaline cellulose. For this reason, higher concentration alkali solutions were not used for chemical modification.

One of the conditions for the effective use of sorption materials is the presence of a highly developed surface, the area of which largely depends on the material porosity, the presence and number of micropores less than 1.5 nm in size, in particular. To assess the porosity, the sorption capacity for iodine for native and modified waste of wheat straw was investigated. The results are shown in Table 3.

Table 3. Sorption activity of waste by iodine.

| Modifying agent       | Sorption capacity by iodine, % |
|-----------------------|-------------------------------|
| Sodium hydroxide 3%   | 26.15±0.61                    |
| Sodium hydroxide 1%   | 24.43±0.49                    |
| Without treatment     | 21.71±0.64                    |

Sorption activity for iodine, which characterizes sorbents micro porosity, increases by 20.5% after chemical modification with a 3% sodium hydroxide solution.

For straw samples treated with a 3% alkali solution and showing the best sorption and physico-mechanical properties, the ash content after sorption was determined, for which the samples saturated with petroleum products were burned in a muffle furnace to constant weight. The amount of ash formed was 0.12% and 0.25% when using standard and operating engine oils, respectively. The increased ash content for the second sample is apparently explained by the presence of additives and engine parts wear products in the operating engine oil.

4. Conclusions

The physico-mechanical and sorption properties of cellulose-containing wastes of agro-industrial production have been investigated. Chemical modification of waste with alkaline solutions with 0.5–3% concentrations helps to reduce the bulk density, increase buoyancy, porosity and sorption capacity in relation to oil products with a heavy fractional composition.

Due to the high buoyancy exceeding 96% for all investigated samples low bulk density, which does not exceed 0.086 g / cm³, the presence of sorption properties, the studied waste can be recommended for using as a sorption load in barrier booms when cleaning the surface of water bodies from oil and petroleum products.

Utilization of waste sorption materials, saturated with petroleum products or oil after the completion of sorption, can be carried out via their burning. The resulting ash, amount of which is 0.12% and 0.25% when using standard and operating engine oils, respectively, can be further disposed of at industrial waste landfills.

The processing of straw and production of sorption materials on its basis for water bodies purification from oil and oil products will help to reduce the anthropogenic load on the environment and contribute to the rational use of natural resources.
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