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DETERMINATION OF THERMAL CAPACITY OF PROCESSED SORBENTS FROM RESIDUAL BIOMASS OF CHLORELLA SOROKINIANA AND DUCKWEED LEMNA MINOR

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Abstract: *Our article reviews the issues arising during the process of wastewater purification and utilization of spent adsorbents. We are offering different ways of utilization of spent sorbents produced from residual biomass of Chlorella Sorokiniana microalgae and Lemna Minor duckweed. We review the technology of adsorbent production from agricultural waste (carbonized millet husks), wastes of the thermally expanded graphite and chitosan biopolymer production, and residual biomass of Chlorella Sorokiniana microalgae and Lemna Minor duckweed, which is formed after all the valuable components have been extracted from the algae and duckweed. We have conducted a thermogravimetric analysis that demonstrated that the spent sorbents' decomposition when exposed to high temperatures results in a variety of exothermic effects in the 300 to 500 °C range. This fact allows us to recommend application of spent sorbents as a fuel for energy generation. For the first time we determine the specific heat of combustion of spent sorbents used in wastewater purification from oils (22857–25220 kJ/kg) and from heavy metal ions (19 079–21 117 kJ/kg). We demonstrate that the value of specific heat of combustion of spent sorbents produced from residual biomass is not less than that of classic fuels such as coals and brown coals. The specific heat value of combustion of spent sorbents used in wastewater purification from oils is higher than that of those used in wastewater purification from heavy metal ions because of the oil carbohydrates adsorbed on sorbents, which increases the material's calorific value.*

Keywords: *spent sorbents' utilization, fuel, residual biomass of Chlorella Sorokiniana microalgae and Lemna Minor duckweed, water purification.*

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Introduction

Purification of wastewaters and waste utilization are among the most important ecological problems. Few of the priority tasks of modern industry are closed-cycle water purification and waste-free production technologies. In order to reduce the toxicity level of wastewaters, we are using efficient sorption purification methods. Some prospective and profitable sorbents can be produced using secondary materials (lignin and cellulose-containing waste), which will allow solving two problems simultaneously: water purification and waste processing. The process of consumption of impurities (heavy metal ions from the wastewaters of the oil production industry) by the adsorbent cannot go on indefinitely as at some point the adsorbent reaches its saturation state and needs to be replaced. Thus, among the ecological problems of the sorption water purification are desorption (regeneration) and utilization of the sorbent. It is very important not only to purify the wastewaters of the industry, but also to achieve the minimal amount of the wastes for utilization, for them to be non-toxic and not harmful for the environment [1–4].

The employees of the Peter the Great St. Petersburg Polytechnic University have developed a technology for production of valuable components from the *Chlorella Sorokiniana* microalgae and *Lemna Minor* duckweed [5, 6]. After extraction of all the valuable components (lipids, carotenoids, pigments), a waste (remaining biomass) is formed, from which some sorption material were produced. In order to increase the sorption capacity of the sorbent, we have added some agricultural wastes (carbonized millet husk) [7-10], wastes from the thermally expanded graphite production [11–13], and a chitosan biopolymer was used as a binder [14–16].

We have obtained three types of sorbents:

1 – thermally expanded graphite plus chitosan plus remaining biomass;

2 – chitosan plus remaining biomass;

3 – chitosan plus remaining biomass plus carbonized millet husk.

Obtained sorption materials were used to purify wastewaters from heavy metal ions (HMI) and oil products (OP). The process of regeneration of used sorbents is ecologically unsafe and economically unsound. Thus, we have reviewed possible ways of utilization of spent sorbents while obtaining goods that are important for agriculture following the scheme at the figure 1:

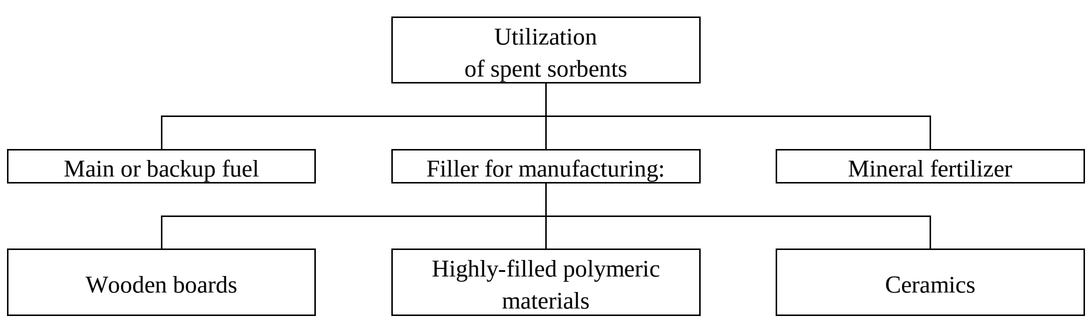

Figure 1. The scheme of utilization of spent sorption materials based on the wastes of agricultural complex

The goal of this work is researching the possibility of utilization of spent sorbents as main or secondary fuel for solid fuel boilers.

Devices and methods

Thermogravimetric research of spent sorbents was conducted using the “Derivatograph” device OD-103 produced by the Hungarian company “MOM”. A sample weight (0,2 g) was placed in fused alumina crucibles and heated in air to 1000° C at the rate of 10 degrees per minute. Calcined alumina was used as a reference; the temperature was recorded using a Pt-Pt/Rh thermocouple. Sample preparation of the analysis consisted of grinding the spent sorbents in an agate mortar until a powder state was reached.

Tests to determine the specific heat of combustion of spent sorbents were carried out in the laboratory of the Hamburg University of Technology (Germany) using an *IKA C* 5000 calorimeter. The device used is an adiabatic jacket calorimeter according to *DIN EN* 51900-3. Spent sorbents are pre-dried at 45 C until their mass becomes constant, then ground to sizes less than 0,25 mm.

According to *DIN EN* 51900-1, the calorific value $H_{o,v}$ can be determined as the ratio of the amount of heat released in the case of complete combustion and the mass of the sample under the following assumptions:

- burning occurs at a constant volume;
- the temperature of the fuel before combustion and the temperature of its products of combustion is 25 C;
- water present in the fuel before combustion, and water formed when hydrogen-containing compounds of combustible fuel are present in a liquid state after combustion;
- products of combustion of carbon and sulfur are present as carbon dioxide and sulfur dioxide in the gaseous state;
- nitrogen oxidation does not occur.

$H_{o,v}$ is determined using a calorimeter following the method described below. The calorimetric bomb is placed in a water-filled calorimetric vessel, which is located in an adiabatic insulating jacket. When the temperatures of calorimetric bomb and water in the calorimetric vessel equalize, the fuel sample is ignited. The rate of increase in temperature is recorded. From the temperature difference, the calorific value of the sample was calculated taking into account the heat capacity of the calorimeter:

$$H_{o,v} = \frac{C \cdot \Delta T - (\mathrm{Q_N} + \mathrm{Q_S} + Q_Z)}{m_p}, \qquad (1)$$

where $H_{o,v}$ is the calorific value of the sample, J/g; ΔT is the temperature change value, K; Q_{N} is the evolution of heat through the formation of nitric acid, J; $\mathrm{Q_S}$ – Heat generation Q_Z through the formation of SO_2, J; Q_Z is the amount of external heat, J; m_p is the sample mass, g;
C determines the heat capacity of the calorimetric system. J/K, according to the equation (2):

$$C = \frac{H_{o,v} \cdot m_{\mathrm{B}} + Q_{\mathrm{Z}}}{\Delta T}, \qquad (2)$$

where: $H_{o,v}$ is the heat of combustion of the reference substance in joules per gram; m_{B} is the mass of the reference substance in grams; Q_Z is the amount of external heat in joules; ΔT is the temperature rise determined in calibration in Kelvin.

The measurement is done in two stages. First, temperature compensation begins between the calorimetric bomb and calorimetric water. This compensation time is called a preliminary experiment. Subsequently, the main experiment begins with the ignition of the combustion sample and the determination of the increase in temperature.

From the given value of the heat of combustion and the element content, the calorific value can be calculated using equations (3) and (4):

$$H_{u,p} = H_{o,v} - [k \cdot \mathrm{H} + 0{,}8 \cdot (\mathrm{N} + \mathrm{O}) + k_1 \cdot w], \qquad (3)$$

$$\mathrm{N} + \mathrm{O} = 100 - (w + A + \mathrm{C} + \mathrm{H} + \mathrm{S}), \qquad (4)$$

where: k is the heat of evaporation, taking into account the volume work of water produced from hydrogen during combustion at 25 C = 23,727 J/%; k_1 is the specific heat of evaporation of water at constant pressure at 25 ° C, k_1 = 24,4 J/%; w is the analytical moisture content of the fuel,% by mass; A is the ash content of fuel, % by mass; C is the carbon content of fuel, % by mass; H is the hydrogen content of fuel, % by mass; S is the sulfur content of fuel, % by mass [17].

The measurement error does not exceed 2,5 %.

Results and discussion

Spent sorbents after purification of oil products were subjected to thermogravimetric analysis (measurement error did not exceed 2,5 %). The data of differential thermogravimetric analysis (DTA) of the spent sorbents of first composition, after purification of wastewater from OP, (Fig. 2) show that water removal occurs up to 120 C, weight loss lies in range from 0 to 7 %. The beginning of the decomposition of the components of the spent sorbents begins at 300 C, when the decomposition of hydrocarbons (OP) adsorbed from the wastewater occurs. Analysis of the DTA curve shows that decomposition of the spent adsorbent under the influence of temperature is accompanied by exothermic effects in the temperature range of 360–500 C. This confirms the possibility of using spent sorption materials as fuel for energy generation.

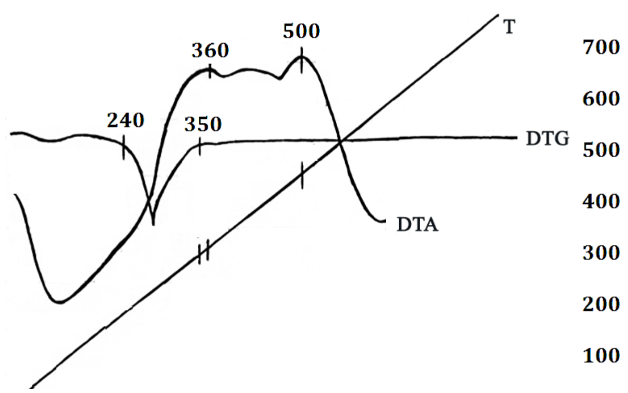

Figure 2. Thermogravimetric analysis of spent sorbents after wastewater purification from OP.

Using the *IKA C 5000* calorimeter and formulas 1 to 4 we have determined the specific heat of combustion of spent sorbents after purification of wastewater from HMI and OP (see Table 1).

Table 1

Comparative data of the specific heat of combustion of spent sorbents and classic fuel

№	Sorbent composition	Specific heat of combustion of spent sorbents after purification of wastewater from HMI, kJ/kg	Specific heat of combustion of spent sorbents after purification of wastewater from OP, kJ/kg
1	Thermally expanded graphite plus chitosan plus remaining biomass	21 117 ± 21	25 220 ± 15
2	Chitosan plus remaining biomass	20 674 ± 20	23 432 ± 23
3	Chitosan plus remaining biomass plus carbonized millet husk	19 079 ± 19	22 857 ± 22
For comparison			
	Fuel type	Specific heat of combustion, kJ/kg	

4	Charcoal	29 600
5	Coal	20 200
6	Brown coal, lignite	16 300

The table shows that the values of specific heat of combustion of spent sorbents made of residual biomass are not inferior to the classical types of fuel – coal and brown coal. The specific heat of combustion of spent sorbents after purification of wastewater from OP is higher (22 857–25 220 kJ/kg) than the specific heat of combustion of used sorbents after purification of wastewater from HMI. This fact is explained by the presence of petroleum hydrocarbons adsorbed on sorbents, which increase the caloric content of the substance. As a result of the analysis, it is possible to recommend the use of spent sorbents as fuel.

Conclusions

As a result of this work, we have reviewed the methods of utilization of spent sorbents made of residual biomass of *Chlorella Sorokiniana* microalgae and *Lemna minor* duckweed. Thermogravimetric analysis demonstrated that the exothermic effects in the temperature range of 360–500 C accompany decomposition of the spent sorbents under the influence of temperature. This allows us to recommend the use of spent adsorption materials as fuel for energy generation.

For the first time, the specific heat of combustion of the spent sorbents after purification of wastewater from OP was determined (22 857–25 220 kJ/kg) and from HMI (19 079–21 117 kJ/kg). We demonstrate that the values of specific heat of combustion of spent sorbents made of residual biomass are not inferior to the classical types of fuel – coal and brown coal. The specific heat of combustion of spent sorbents after purification of wastewater from OP is higher than the specific heat of combustion of used sorbents after purification of wastewater from HMI. This is due to the presence of petroleum hydrocarbons adsorbed on sorbents, which increase the caloric content of the substance.

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