Obtaining sorption material from sorghum for aqueous solutions purification from heavy metals

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Abstract. The paper presents the results of using straw (stalks) of sorghum as a sorbent for removing heavy metal ions of Cu (II) from aqueous solutions. The physical and chemical analysis of sorghum has been carried out. The modification of plant materials by exposure to a temperature of 130-150 ° C is proposed. Thermal activation allows obtaining a highly developed surface of the sorghum microstructure and increasing the total pore volume and their average diameter. The regularities of the effect of the concentration of the modified sorbent and the differences of its dispersed particles on the efficiency of water purification are investigated. The purification of an aqueous solution containing 50 mg/dm³ of Cu²⁺ ions was 95% under using a thermo-treated sorghum of 0.63–0.1 mm in an amount of 2.5 g per 100 ml of an aqueous solution. Thermal modification of sorghum allows you to get an effective sorbent and immediately solve two environmental problems, such as wastewater treatment and utilization of plant waste.

1. Introduction
At the present stage of the development of human civilization, technogenic pollution has affected almost all vital resources. Atmosphere, soil, surface and unprotected groundwater were especially polluted. Interest in water use is excessively high, as industry develops and megalopolises grow. The accumulation of excess heavy metal ions, one of which is copper, is of great concern due to toxicity. Heavy metals cause damage by accumulating in humans and animals. This can lead to serious illnesses such as mental confusion, allergies, memory loss, irritability, and balance in digestive problems. Effective removal of heavy metal ions from aqueous systems is very important for the protection of the environment and public health [1, 2].

Adsorption is an advantageous option for water and wastewater treatment due to its convenience, simplicity and ease of design. In addressing this issue, plant waste can be viewed as a sorbent obtained with minimal effort. The production of organic sorbents from renewable plant materials corresponds to current research trends [3]. Agricultural waste is varied in structure and properties, therefore, there are differences in sorption capacity, pore volume, efficiency of extraction of various substances from aquatic environments, therefore, research on the features and modification methods for their use in water purification does not lose its relevance [4-9]. The advantages of using plant waste for
wastewater treatment are as following: relatively simple processing technology, good adsorption potential, selectivity for heavy metal ions, low cost, availability, ease of regeneration [10].

Sorghum has a variety of forms and varietal crops, both annual and perennial. In general, sorghum belongs to the grass plants of the family of cereals. Sorghum grains are processed into cereals, flour and starch. Wickerwork, paper, brooms are made of straw. In addition, sorghum straw is the main source of natural fibers as an alternative raw material for bio composites. For example, it is considered as a biopolymer for the production of microfiber [11]. Sorghum straw is a source of getting cellulose production [12]. Sorghum straw is a renewable, cheap and widespread resource. These materials, due to their high porosity, are of interest as feedstock for the production of sorbents.

2. Materials and methods
Thermal Analysis (DTA) was carried out with the help of derivatograph of model 431Q - 1500 and device of synchronous thermal analysis STA 449 F1

The analysis of peculiarities of the chemical composition and structure of the CCP samples has been carried out by using the scanning electron microscope of high resolution «TESCAN MIRA 3 LMU».

To determine the bulk density the method GOST 19440-94 was used. The moisture of material, water absorption and ignition losses were determined using standard methods [13].

For roasting sorghum, a Liop LF-7/13-G2 muffle furnace was used.

To study the specific surface area and porosity of the sorbent at the micro level, we used the method of gas adsorption using the SoftSorb – II ver.1.0 device.

The purification efficiency of model solutions containing Cu$^{2+}$ ions was carried out in a static mode as follows: the sorghum sample was placed in 100 ml of an aqueous solution with a copper ion concentration of 50 mg/dm$^3$ and it was mixed for 20 minutes in a conical flask. Then the contents of the flask were filtered through a paper filter. The concentration of Cu$^{2+}$ ions in solutions before and after purification was determined by a colorimetric method according to the method GOST R 4388-72 with sodium diethyldithiocarbamate indicator at a wavelength of 440 nm.

After that the contents of the flask were left for sedimentation for 15 minutes. Clarified water was examined for the petroleum oil concentration, using concentration meter KH-3 (Russia)

The purification efficiency (E) was calculated according to the formula:

$$E=(C_1-C_2)/C_1 \times 100\%$$

where $C_1$ and $C_2$ - the concentrations of substances before and after of water purification, respectively.

The granulometric compositions of materials were determined using the method of sieve analysis. The principle of sieve analysis is to find the amount of material retained by a sieve with holes of a certain size. The sieves are arranged one above the other sequentially as the size of the holes in the grid decreases. 2.5-5.0; 2.0-2.5; 1.4-2.0; 1.4-1.25; 0.63-1.25; 0.63-1mm.

The grinding of sorghum samples was carried out in a porcelain mortar.

3. Results and discussion
The physical and chemical characteristics of sorghum were investigated in the work (Table 1). Sorghum water retention is 35%. Ignition losses are 98%, which indicates the predominant content of organic substances.

| Table 1. Physical and chemical properties of Sorghum. |
|-----------------------------------------------------|
| pH aqueous extract | 7,0 |
| Loss on ignition, % | 98 |
| Moisture content, % | 35 |
| Bulk density, kg / m$^3$ | 180 |
| Humidity, % | 8,5 |
A significant content of organic substances in the form of an amorphous phase is confirmed by the results of x-ray structural analysis (Fig. 1). The roentgenogram of the sample has a characteristic appearance. It is a broad line (gallo) with an angular width of $2\theta = 17 - 28^\circ$. The amorphous fraction in sorghum is represented by lignin and hemicellulose, which covers the semi-crystalline fraction of cellulose [14].

The thermal characteristics of sorghum has been studied using thermo gravimetric analysis (TGA), which was determined in the temperature range of 0 – 700 °C (Fig. 2).

Fig. 2 shows the variety of the fiber mass due to temperature. As the temperature rises, the weight of the fiber decreases. A significant jump in weight reduction is observed at temperature above 250 °C. This temperature was chosen as the maximum for further thermal modification of sorghum.

The modification was carried out as follows: stalks of sorghum of 5 mm length, dried for 3 days at a temperature of 20 – 23 °C, air humidity of about 30%, were burned in a muffle furnace at various temperatures for 20 minutes. It was experimentally confirmed that when conducting thermal activation with a temperature above 150 °C, the dried stalks are charred and burned. The optimal activation temperature was 130 – 150 °C.

Images of the sorghum particles surface were obtained by the scanning electron microscopy method.

Figure 1. Radiograph of stalks of sorghum.

Figure 2. Thermogravimetric analysis of sorghum (TGA).
Based on the microstructure, the crushed sorghum stalks are a smooth surface with pores (Fig. 3 a). During heat treatment, dirt and wax are removed from the surface of the sorghum stalk, thus creating a rough, highly developed surface (Fig. 3 b). According to the results obtained as a result of adsorption / desorption of nitrogen, it was found that the specific surface according to the BET method (SBET) of the initial sorghum was 0.9 m$^2$/g (Tab. 2). After heat treatment, the specific surface of the sorption material increased by 42%.

According to the analysis of the pores distribution at the micro level, an increase in the total porosity of the modified material is observed with an increase in the number of pores on the nanometric range from 1.7 to 300 nm (Tab. 2). The increase in total porosity and their specific surface is an important factor in adsorption processes.

The results of the study of the efficiency of purification of an aqueous solution containing Cu$^{2+}$ ions with sorbents with different particle diameters are shown in Figures 4 and 5.
Figure 4. Dependence of the purification efficiency of an aqueous solution containing 50 mg/dm$^3$ of Cu$^{2+}$ ions on the mass and dispersity of sorghum particles without modification.

From the presented illustrations, it is obvious that with an increase in the specific surface of sorghum particles due to its preliminary grinding, the degree of purification increases. Sorghum particles with a size of 5–10 mm have the lowest degree of water purification of 78%. The sorghum fraction with a particle range of 0.63–1 mm increases the degree of water purification from heavy metals to 89%.

Significant changes in water purification are observed when modified sorghum is used (Fig. 5).

Figure 5. Dependence of the purification efficiency of an aqueous solution containing 50 mg/dm$^3$ of Cu$^{2+}$ ions on the mass and dispersity of particles of thermal modified sorghum.

The use of modified sorghum increases the efficiency of water purification with all the differences in the dispersity of particles.

The highest rates of purification of an aqueous solution containing 50 mg/dm$^3$ of Cu$^{2+}$ ions were 95% using thermal-treated sorghum of 0.63–1 mm in the amount of 2.5 g per 100 ml of an aqueous solution.

4. Summary
As a result of the experiments, it was proved that it is possible to use sorghum plant waste to purify wastewater from heavy metal ions Cu$^{2+}$. Processing plant raw materials with a temperature of 130 – 150 °C for 20 minutes allows you to increase the activity of the sorbent by obtaining a highly developed surface, increasing the total porosity. The high purification efficiency of a 95 % solution containing Cu$^{2+}$ ions is possible due to the use of a modified sorghum of fraction 0.63–1 mm.
5. References

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