Composite sorbents based on waste from the crystalline silicon production and biochar

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Abstract The aim of this paper was to create a composite porous material based on waste from the crystalline silicon production and biochar from agricultural waste for sorption wastewater purification from copper. In the paper, we proposed a method for pelletizing fine crystalline silicon (gas treatment waste) and biochar from agricultural waste using liquid glass. The choice of liquid glass is due to the fact that this substance has high adhesive properties for the formation of durable composites, as well as an excess of alkali, which contributes to the exothermic reaction and the evolution of hydrogen gas upon the addition of finely divided silicon, as a result of which the composite material acquires a porous structure. Using the optical emission research method, we found that the samples of the prepared sorbents mainly consist of both macropores and meso- and micropores, the dimension of which depends on the ratio of components. In the course of research, we identified the optimal ratios and studied the mechanical and sorption properties of composite materials.

1. Introduction
The growth in the use of raw materials throughout the world is accompanied by an increase in the amount of waste generated, which represents potential losses for the economy of valuable material and energy resources. The involvement of primary natural resources in the consumption process leads to an increase in the negative impact on the environment. Therefore, it is reasonable for production to use secondary resources, rather than primary raw materials, to turn waste into revenues.

Currently, an active search is underway for materials capable of effectively extracting heavy metals from polluted waters and having a low cost. Nowadays, in the world, more than 200 different sorbents are produced and used, including both natural and artificial, created specifically for this purpose. Peat, sawdust, reed, aspen bark, buckwheat and oat husk, and many other agricultural waste products, as well as biochar obtained from them, are used as natural sorbents [1-4]. There are many reports of the synthesis of carbon materials using natural biomass as a precursor [5-7]. In particular, Subramanian et al. developed a technology for producing activated carbon from banana fibers [8]. Wang et al. generalized research in the production and use of biochar from waste [9]. Xiaolei Bao et al. [10] proposed a method for producing carbon nanocomposites to purify water from antibiotics. Clay materials in combination with organic carbon are often used as sorbents [11].

It was proposed to use aquatic plants, fungi [12, 13], composite systems from plants and mineral sorbents [14-16] as phytosorbents. Each of the proposed materials has its own advantages and disadvantages.
The most promising and cost-effective sorbents are those made of secondary raw materials. These materials allow us to solve two problems at once: water cleaning and waste disposal. Due to the availability and low cost, sorbents based on waste attract many Russian and foreign authors. In a joint Russian-Taiwanese project, the authors carry out research to create composite materials based on waste from the silicon production and biochar from agricultural waste.

The aim of this work is to develop a technology for producing a composite porous material based on biochar from agricultural waste and silicate waste from the crystalline silicon production and to study their properties.

2. Study Objects and Methods

It is known that the process of obtaining silicon is accompanied by the formation of a large amount of man-made waste in the form of quartz fines, charcoal, black coal and petroleum coke fines, fine fraction metal silicon screenings and refining slags. However, a significant part is accounted for by cyclone dust and sludge from wet gas cleaning (1 ton of silicon accounts for 280 - 900 kg of dust waste) going to sludge depostitories, which leads to a significant load on the environment near existing enterprises [17, 18]. Previously Nemchinova N.V. and Leonova M.S. studied the chemical composition of these wastes in detail and found that they contain 86-95.8% wt. silicon dioxide [19]. In this work, we used gas cleaning dust generated during the production of crystalline silicon; the chemical composition is presented in Table 1.

| Components | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | C₆ | Na₂O | SO₃ | P₂O₅ | K₂O | TiO₂ | SiC |
|------------|------|-------|-------|-----|-----|-----|------|-----|------|-----|------|-----|
| Content, % wt. | 86.3 | 0.37  | 0.30  | 1.4 | 1.20 | 5.8 | 0.07 | 0.14 | 0.12 | 0.28 | 0.02 | 4.15 |

Commercial samples of BAU-A birch coal according to GOST 6217-74 with a fraction of less than 1 mm were used as biochar.

A composite sorbent was prepared by pelletizing. To obtain a composite sorbent, we mixed gas cleaning dust and biochar in different weight ratios and added liquid glass. Then, we thoroughly mixed the samples, formed pellets and dried at a temperature of 50 °C in a Binder hot air oven, Germany (Figure 1).

The choice of liquid glass is due to the fact that this substance has high adhesive properties for the formation of durable composites, as well as an excess of alkali, which contributes to the exothermic reaction and the evolution of hydrogen gas upon the addition of finely divided Si according to reaction (1), as a result of which the composite material acquires a porous structure [19].
Si + 2NaOH + H₂O = Na₂O·SiO₂ + 2H₂↑++ 422.9 kJ/mol

(1)

The sorption characteristics of the composite samples were studied under static conditions by placing them in model solutions with a copper ion content of 10 to 1000 mg/l. 1 g of composite was added to each flask with a solution. The contents of the flasks were continuously stirred for a specified time, then the suspensions were sedimented and analyzed for the content of copper ions by the photocolorimetric method [20] or by atomic absorption spectroscopy using the Helios Omega device (USA). The experimental error did not exceed 10%.

To obtain kinetic curves of sorption, we placed weighed portions of the sorbent in model solutions of copper ions, kept for 6-48 hours, and recorded the current concentration of copper ions in the solution at fixed time intervals. The amount of sorbed metal was calculated by the formula

\[ A = \left( \frac{C_{\text{init}} - C_{\text{equil}}}{m \times 1000} \right) V, \]

(2)

where \( C_{\text{init}} \), \( C_{\text{equil}} \) are initial and equilibrium concentrations of copper ions in the solution, respectively, mg/l; \( m \) is the mass of the composite, g; \( V \) is the sample volume, ml.

3. Results and Discussion

Microscopic studies showed that the samples of prepared sorbents mainly consist of both macropores and meso- and micropores (Figure 2).

Figure 2. The porous structure of composites based on gas cleaning dust from the crystalline silicon production and biochar with the ratio of components in the composition of the pelletized material (Si:C), respectively: a – 1:1; b – 2:3; c – 4:1; d – 1:4.
As can be seen from the photographs, the samples of the composites contain a large number of micro-, meso- and macropores, where copper ions are easily adsorbed. The size and ratio of pores depends on the ratio of silicate waste and biochar. The optimal ratio with the formation of the maximum number of pores is gas cleaning dust: biochar 2:3.

Along with sorption properties, mechanical properties - mechanical abrasion resistance - are of great importance. In accordance with GOST 16188-70 and GOST 17219-71, we determined the mechanical abrasion resistance and the total volume of the obtained composites, and found that the highest mechanical resistance was observed in the sample at a Si:C ratio of 2:3, the lowest mechanical resistance - at a ratio of 1:4.

When assessing the degree of extraction of copper from an aqueous solution using the test samples, it was found that the maximum degree was observed in a composite with a Si:C ratio of 2:3, which is 30 mg/g.

Our study has shown that industrial waste (gas cleaning dust of the silicon production) and biochar (a product of the plant waste pyrolysis) can be disposed of by pelletizing to obtain a useful composite product with sorption properties towards metals, in particular copper.

4. Conclusion
It has been established that silicate waste from the metal silicon production and biochar from agricultural waste can serve as raw materials for the production of composite sorption material. The composite material is obtained by pelletizing using liquid glass as an additive.

The optimal condition for obtaining an effective sorbent is the ratio of components %, respectively: 19.09 – Si; 30 – C; 0.01 – liquid glass (p=1.47).

As a basis for the sorption material production, it is possible to use biochar from agricultural waste obtained using the electrochemical synthesis technology.

Composite material can be used in water purification from heavy metals, in particular copper.

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