Use of modified carbon sorbents in extracting mercury from technogenic raw materials

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Abstract. Heavy metal pollution of the environment is an increasingly important issue because heavy metals of both natural and technogenic origin are highly toxic and non-degradable substances. Extracting heavy metals from industrial solutions using carbon sorbents is one of the promising and effective methods providing complete extraction of the pollutants. The paper describes the research on the potential use of the modified activated carbon obtained from brown coal as a sorbent for mercury extraction. The adsorption capacity of the modified ABG (activated brown granular) sorbent has been defined for a solution with the initial ion concentration of 5-15 mg/dm³ in static conditions. Isotherms have been plotted for the initial (ABG) and modified (АВГ-M) sorbents. The maximum adsorption capacity of ABG-M has been defined as 21.5 mg/g, which is 1.6 times that of ABG. The use of modified carbon sorbents in extracting heavy metals from waste waters and technogenic formations helps to achieve a high degree of purification without any additional chemical agents polluting the environment.

1. Introduction

Russia is one of the major countries having huge mineral-and-raw material resources, with up to a few billion cubic meters of the mining industrial wastes being down-stocked annually. Three quarters of the accumulated wastes on the territory of Russia (over 12 billion tons) come from the mining industries.

The territories where mining enterprises are concentrated have been conventionally considered environmental-risk zones. Therefore, processing of the mining industrial wastes is essential for the environmental safety of the country. The mining industrial wastes often contain a big proportion of useful components, which can make the waste processing economically sound. In particular, development of the technogenic raw material reserves can cover the industrial enterprises’ demand for metal ore.

There are two ways of extracting mercury from technogenic raw materials: reduction of the mercury to the elementary state with further extraction in a pure form; precipitation based on the mercury oxidation with further extraction of the bivalent mercury.

Extraction of heavy metals from technogenic formations and purification of the industrial waste water to MPC of 0.005 mg can be implemented with the use of a sorption technology that provides the withdrawal of the valuable components in the form of end products or salvage and allows a closed cycle in the treated water usage.

Promising sorbents include carbon sorbents with a high specific surface, developed porous structure and active functional groups. To obtain the carbon sorbents with the above properties, the following raw materials can be used: wood, turf, fossil charcoal, black oil fuel, as well as...
The paper considers the potential use of modified ABG carbon sorbents in extracting mercury ions from technogenic raw materials. The topic is of importance as sorption extraction of metal ions from solutions is one of the most economically practical methods of concentrating of valuable components.

The aim of the research has been to define the potential use of the modified carbon sorbents in extracting mercury from technogenic raw materials. The research tasks have been: to experimentally define the adsorption capacity of the modified ABG sorbent; to compare the obtained characteristics of the modified ABG and initial sorbents; and to draw conclusions based on the obtained results.

2. Materials and methods
The Azei and Mugun brown coal from the Tulun coal field, Irkutsk region, was used as a source raw material for obtaining the ABG sorbent. The ABG sorbent was obtained with a standard technology i.e. carbon carbonization and activation [1].

In order to increase the ABG sorbent’s sorption activity in relation to mercury ions, modification of the sorbent was done [5]. The modification procedure was the following: an activated carbonated coal sample (in this case, ABG) with the ratio of 1 gram: 2 ml was mixed with dichloroethane and was being stirred for 1 hour. Then the dichloroethane was filtered, and the ABG sorbent was being processed with oleum (1:7) in a retort with a reflux condenser at a temperature of 70℃ for 5 hours. After that, the obtained sorbent was washed with water to a neutral reaction and dried in a drying chamber at a temperature of 30℃. The comparative physical-mechanical characteristics and the porosity structure indices for the initial (ABG) and resulting (ABG-M) sorbents are represented in Table 1.

Table 1. Comparison of the physical-mechanical properties and the porosity structure indices of the sorbents.

| Sorbent | Bulk density, g/dm³ | Mechanical strength, % | Total porosity by water, cm³/g | Activity by iodine, % | Activity by MB, mg/g |
|---------|---------------------|------------------------|-------------------------------|----------------------|----------------------|
| ABG     | 420 [1]             | 68.0                   | 0.59                          | 55.0                 | 12.1                 |
| ABG-M   | 470 [5]             | 62.1                   | 0.65                          | 45.0                 | 12.8                 |

The analysis of Table 1 shows that the obtained sorbents have a porous structure consisting of micro-, mezzo- and macro-pores, which is confirmed with the total porosity on water adsorption and with the activity on iodine and methylene blue.

For the purpose of the study of the sorption activity of the ABG-M sorbent, standard test solutions of mercury nitrate were used (II) – Hg(NO₃)₂, with concentrations of 5-15 mg/dm³. The salt sample was solved in 50 ml of concentrated nitric acid HNO₃ (chemically pure), the solution was brought to the volume of 1 liter with distilled water, and with the help of the buffer solution the solution’s pH of 3.5-4.5 was obtained.

The sorption was done in static conditions. The modified coal sample was added to 100 ml of the target solution and was being shaken for 2 hours. The solution mercury concentration was defined with the atomic-emission spectrometer Vista ICP – AES.

3. Research results and analysis
Processing the ABG carbonated coal with oleum results in sulfonate groups catching both on the sorbent surface and inside the pores. The primary treatment of the activated carbonated coal with dichloroethane facilitates the penetration of the sulfonate agent (in this case, oleum) in the pore depth, thus enhancing oxidation and with this, the formation of the sulfonate groups. The presence of the
sulfonate groups in the pore depth increases the sorbent’s adsorption capacity in relation to mercury ions.

The paper presents the results of the research on mercury-ion sorption with the modified ABG sorbent in static conditions.

4. Discussion
Based on the obtained experimental data, comparative isotherms have been plotted for the initial- and resulting sorbents’ sorption (Figure 1).

![Figure 1. Mercury sorption isotherms for the ABG and ABG-M sorbents.](attachment:image.png)

The isotherms show that the mercury-sorption capacity of the ABG-M sorbent is higher than that of the initial ABG sorbent, which is explained by the formation of sulfonate groups on the surface of the modified sorbent and by the selectivity of the modified sorbent in relation to mercury ions. The maximum capacity of the ABG-M sorbent is 21.5 mg/g which is 1.6 times the one of the initial ABG sorbent.

5. Conclusion
The research has confirmed that the modified ABG sorbent can be effectively used for extracting mercury ions from technogenic raw materials. The use of the brown coal sorbents for the extraction of the valuable components from technogenic raw materials can to a certain extent solve the problem of mercury ion pollution of the environment.

References
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