On increasing the sorption capacity of semi-cokes with acid regenerates of water-desalting ion-exchange plants

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Abstract. In modern conditions, the problem of environmental protection has become one of the decisive factors determining the further development of mankind, along with technological and economic aspects. The approach is most effective when disposing the waste from one production provides an effective solution to the problem of environmental protection in other industries. The article investigates the possibility of using the acidic waste generated from the operation of ion exchange plants at power plants to increase the sorption capacity of carbon sorbents for phenol by changing the chemistry of the surface of coal. It has been established that an increase in the sorption capacity of active carbon ABG provides additional adsorption and increases the efficiency and cost-effectiveness of wastewater treatment from phenol.

1. Introduction

Currently, environmental protection is one of the significant factors influencing the further development of the whole mankind. In recent years, problems related to the pollution of the hydrosphere have worsened. The discharge of untreated or insufficiently treated wastewater containing toxic organic compounds, including phenols, into reservoirs leads to a decrease in biodiversity and even the disappearance of life in ecosystems. Development and introduction of low-waste and non-waste technological processes into practice is one of the ways to solve the problem of environmental protection and resource conservation. These technological processes ensure the utilization of wastewater from one production to increase the efficiency of another production.

Phenols are priority pollutants in the aquatic environment. They enter water bodies with wastewater from wood-chemical, aniline-dyeing, oil-refining, chemical industries (production of pesticides, organic dyes, varnishes, explosives, synthetic resins, plastics). The concentration of phenol in wastewater can reach 10 g/dm\textsuperscript{3}. In addition to phenols of technogenic origin, natural waters contain low molecular weight phenols, which are formed during the biochemical decomposition and transformation of organic substances (humic and fulvic acids). Phenol is a common protoplasmic poison and is toxic to all cells. Phenol leads to disruption of the gastrointestinal tract, liver and kidney diseases, it also is the cause of cancer \cite{1}.

Methods of phenol extraction from wastewater used in practice have a number of disadvantages: significant costs of chemicals, heat and electricity are required; the use of expensive equipment, high temperatures are often accompanied by the formation of secondary pollution. The solution to the problems of wastewater treatment is the development and widespread introduction into practice of new, reliable and highly economical technological processes.
For wastewater treatment of organic compounds, adsorption on activated carbons (AC) is often an effective method. Active carbons are quite effective and inexpensive materials. A huge variety of carbon materials exists, differing in raw materials and activation method. Today, a new class of cheap sorbents has appeared - semi-coke.

Earlier in our research [2], [3], we found that semi-coke has lower sorption capacity. Increasing the sorption capacity of the adsorbent with respect to the extracted component can be achieved by changing the structure and state of the surface of the adsorbent when using modifiers of various types [4]. Solutions of organic reagents, bases, mineral acids, for example, sulfuric acid, are used as modifiers.

Sulfuric acid is the main component of wastewater generated at power plants (SDPP, HPP) using ion exchange resins for cleaning large volumes of water and their repeated regeneration. The volume of acidic waste from the operation of ion-exchange units on cation exchanger is about 20-25% of the volume of desalted water. Basically, their composition includes sulfuric acid, the average concentration of which is 0.5 mol / dm$^3$ and Ca$^{2+}$ (average concentration of 0.016 mol / dm$^3$).

The purpose of the study is to identify the fundamental possibility of solving the problem of environmental pollution by reducing the amount of wastewater from ion-exchange plants used in power plants through the use of acidic wastewater, with the purpose of increasing the sorption capacity of AC in phenol.

2. Materials and Methods
As objects of study, the semi-coke of brand ABG is used in our research. The ABG is a coal-gas carbonized carbon sorbent, which is selected. It is obtained from coal raw materials (semi-coke) by the manufacturer CJSC “Karbonika-F”, Krasnoyarsk. This semi-coke is produced from the coal mined in the Kansko-Achinsky open pit. The unique technology of its receipt provides low costs.

The study of phenol adsorption from aqueous solutions in the concentration range from 0.001 to 1000 mg / dm$^3$ was carried out in static conditions using the AC ABG.

The ABG was additionally treated with acidic regenerants of ion-exchange units at a ratio of the mass of the sorbent in grams to the volume of the regenerate (in cm$^3$, 1:5, 1:10, 1:15) for 6-12 hours, followed by washing with 3 times the volume of demineralized water. The content of phenol in aqueous solutions after adsorption was determined by the method of molecular absorption spectroscopy.

3. Results
According to the obtained experimental data on the phenol adsorption from the AC ABG solution, the adsorption isotherms were built (Figure 1) and the values of phenol adsorption parameters from aqueous solutions were calculated: using the theories of monomolecular adsorption (Freundlich and Langmuir equations), the theory of volume filling of micropores (Dubinin-Radushkevich equation), and the generalized theory of the polymolecular adsorption developed by Brunauer, Emmett, and Teller (table 1) for industrial and modified sorbent wastewater from ion-exchange plants of thermal power plants.

It is established that the presence of Ca$^{2+}$ salts in the regenerate does not affect the efficiency of the treatment of AC and the subsequent adsorption of organic substances. The precipitate of CaSO$_4$ does not fall out with this content of components in the regenerate, since the value of the solubility product is not reached (PR(CaSO$_4$) = 2.25*10$^{-4}$).
Figure 1. Adsorption isotherms of the phenol AC ABG industrial (1), modified by acid regenerates of a thermal power station (2).

Table 1. Parameters of phenol adsorption from AC ABG aqueous solutions.

| Type of equation | ABG     | ABG (H₂SO₄) |
|------------------|---------|-------------|
| Freundlich       | 1/n     | 0.3536      | 0.344       |
|                  | b, mmol/g | 0.069      | 0.098       |
| Langmuir         | aₘ₀, mmol/g | 0.524      | 0.733       |
| BET              | aₘ₀, mmol/g | 0.524      | 0.714       |
|                  | -Q, kJ/mol | 14.734      | 13.987      |
| Dubinin-Radushkevich | aₘₐₓ, mmol/g | 1.064 | 1.330       |
|                  | E₀, kJ/mmol | 13.445      | 12.950      |
|                  | W, dm³/kg | 0.0935      | 0.1140      |

On the sorbent ABG treated as described, the adsorption of phenol was carried out from aqueous solutions under static conditions. The effect of the ratio (AC mass: a regenerate volume) on the sorption capacity of AC with respect to phenol is presented in Table 2.

Table 2. The effect of the ratio (AC mass: regenerate volume) on the AC sorption capacity.

| No. | The ratio of m (g): Vp (cm³) | Increasing the sorption capacity of AC, % |
|-----|-----------------------------|----------------------------------------|
| 1   | 1:5                         | 16                                     |
| 2   | 1:10                        | 33                                     |
| 3   | 1:15                        | 35                                     |

The effect of the duration of the process on the sorption capacity of the AC with respect to phenol is established: treatment of active carbon with an acid regenerate for 6 hours increases the sorption capacity by 33%, 8 hours by 48%, 10 hours by 54%, 12 hours by 55%.

4. Discussion

The presented adsorption parameters (Table 1) show that surface modification allows to obtain an adsorbent with satisfactory characteristics close to active coal (AG-3, AG-OV-1, SKD-515) widely used for wastewater treatment and at drinking water treatment stations.

The magnitude of the limiting adsorption volume W suggests that the adsorption of phenol obeys the bulk mechanism of filling the pores. The values of the characteristic energy indicate that the sorption of phenol is mainly in the micro- and mesopores of the adsorbent. The adsorption isotherm of phenol AC suggests the physical nature of adsorption (Table 1). The calculated value of the heat of adsorption confirms the conclusion about the physical nature of the interaction of phenol with the ABG surface.

The increase in the adsorption capacity for phenol is established. This is due to the appearance on the surface of the sorbent of new oxygen-containing functional groups (OFG), which are additional adsorption centers. Because of this, the amount of phenol interacting through a specific adsorption mechanism due to hydrogen bonds between OFG sorbents and the OH group of phenol increases. The degree of purification increases.

To determine the effect of modifier concentrations on the adsorption of organic substances, the adsorption of phenol from aqueous solutions was studied on the initial and acid-modified samples. It is
established that with an increase in the concentration of sulfuric acid of more than 2 mol / dm$^3$, the adsorption capacity of the modified samples with respect to phenol decreases. The combination of the obtained results allows us to conclude that the modification of carbon sorbents with acid allows one to increase the adsorption of phenol by 1.5 times. As a result of the research, the following conditions for the disposal of acid regenerates of water desalting plants were chosen: the treatment of industrial active carbons with acidic regenerate at a ratio of mass AC in grams to the volume of regenerate in cm$^3$ 1:10 for 10 hours, followed by washing the volume of water desalinated by ion exchange no less than 3 times.

The studied semi-coke has the following characteristics: the possibility of increasing the adsorption capacity, low production costs and transportation costs, minor costs for modification, and the possibility of effective utilization. (This semi-coke does not require regeneration due to the fact that the spent sorbent can be used to produce marketable products at the “Koks” OJSC, Kemerovo). We can conclude that in the Kuzbass region of Russia, the use of semi-coke to extract phenol from natural and waste waters is advisable.

5. Conclusion
Treatment of activated carbons with acid regenerate of water desalting plants allows utilization of acid regenerate of ion-exchange plants, reducing the volume of wastewater.

Treatment of sorbents with acid regenerates of water desalting plants leads to the formation of secondary adsorption centers on the surface of active carbons. They are able to interact with functional groups of organic substances due to a specific adsorption mechanism, providing them with additional adsorption, increasing the adsorption capacity of active carbons and the efficiency of wastewater treatment from phenol.

Thus, two tasks are simultaneously solved: an increase in the efficiency of purification of some industrial wastes (wastewater containing phenol) due to the utilization of another waste (acid regenerate of ion-exchange plants).

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