Adsorption of a pyridine-phenol mixture from aqueous solutions with preheated active carbons

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Abstract. The article investigates the fundamental possibility of using preheating of the activated carbon in air and in an inert atmosphere to increase its adsorption capacity during adsorption extraction from aqueous solutions of a mixture of phenol – pyridine. It is found that such a modification affects more adsorption of pyridine than of phenol. At the same time, heating in an inert atmosphere turned out to be more efficient.

1. Introduction

In large industrial regions, a high level of environmental pollution, including the hydrosphere, actualizes the task of developing and putting into practice technological processes with closed water-circulation cycles. In this case, the ingress of insufficiently treated wastewater into the population’s water supply sources can be excluded.

With wastewater from pharmaceutical, metallurgical and coke-chemical plants, toxic compounds such as pyridine and phenol can be released into water bodies. In addition, a low molecular weight of phenols can be formed during the biochemical decomposition of humic acids. Biochemical methods used in practice for wastewater treatment containing pyridine and phenol are not effective enough. The concentration of organic components in the effluent after the treatment plant may exceed permissible values in 1.5-2 times [1]. An effective method of purification and purification of wastewater with a low concentration of organic components is adsorption using carbon materials.

The capacity of industrial activated carbons (AC) in relation to highly soluble and water-miscible organic compounds (the latter includes pyridine) is low due to the low selectivity of adsorption. Since the energies of the interaction of the solute and solvent with the adsorbent are close [2]. To increase the adsorption selectivity, we need to either increase the adsorption of the organic component due to the specific interaction of the sorbate with the surface groups of the sorbent or reduce the adsorption of water. We can achieve a similar effect by modifying the AC with vapors and solutions of acids, bases, oxidizers, and reducing agents of various types.

Earlier we established [3] that the modification of AC with acid solutions, which increase the adsorption of phenols from aqueous media, drastically reduced the adsorption of pyridine. One of the ways to change the chemical state of the surface of an activated carbon is a heat treatment. At the same time, when heated in air, an increase in the surface oxygen compounds (SOC) of various types (acidic and basic) occurs, and during a heat treatment in an inert environment (for example, hydrogen or nitrogen), the decrease in SOC (predominantly acidic) occurs [4-5]. Previous studies also demonstrate that heating at temperatures above 120 C leads to a noticeable increase in the adsorption of pyridine.
from aqueous solutions, whereas the adsorption of phenol varies slightly, and heating AC in a nitrogen atmosphere at 1,000°C reduces water adsorption [5-7].

The purpose of this study was to clarify the possibility of using the preliminary thermal treatment of AC to increase the adsorption of the phenol-pyridine mixture from aqueous solutions.

2. Materials and Methods
The objects of our study are the granulated industrial active carbons of the grades AG-OV-1 (designation A-1) and SKD-515 (designation S-1) (manufactured by the Sorbent LLC., Perm, Russia). They were previously washed with distilled water from dust fractions and dried to air-dry condition. Then, one part of the AC prepared in this way was subjected to heat treatment in air at 250 ± 1.0°C for 5 hours (reference A-2 and S-2 for AG-OV-1 and SKD-515, respectively). And another part of the AC was subjected to heat treatment in air at 1000 ± 5.0°C for 2 hours under nitrogen atmosphere (designation A-3 and S-3 for AG-OV-1 and SKD-515, respectively). All modified samples were cooled in a desiccator and stored tightly sealed.

The adsorption of phenol and pyridine was carried out from aqueous solutions in the concentration range from 0.010 to 2.00 g/l with a ratio of organic components of 1:1. The equilibrium concentration of pyridine was determined by its own absorption at 256 nm; it was after reaction with 4-aminoantipyrine at 490 nm for phenol. In selected conditions, the components do not interfere with each other’s definition.

3. Results
Experimental adsorption isotherms are shown in Figure 1.

![Figure 1. Adsorption isotherms of phenol (a) and pyridine (b) from an aqueous solution with the joint presence (ratio 1:1) of active carbon samples.](image)

The obtained adsorption isotherms were analyzed using the models of polymolecular adsorption (BET equation) and volume filling of micropores (Dubinin-Radushkevich equation), modified for the case of adsorption from highly soluble and miscible substances from solutions. It was established that both models with high correlation (R^2 > 98%) describe the adsorption behavior of the studied organic components. Adsorption parameters calculated using the BET equation are presented in Table 1.
Table 1. Parameters of phenol and pyridine adsorption from an aqueous solution with the joint presence (ratio 1:1) of active carbon samples.

| Brand AC | q_{max}, mmol / g | -Q_L, kJ / mol | -Q_S, kJ / mol | R^2 |
|----------|------------------|----------------|----------------|-----|
| Phenol   |                  |                |                |     |
| A-1      | 0.89             | 16.93          | 8.88           | 99.29 |
| A-2      | 0.90             | 19.39          | 9.27           | 99.50 |
| A-3      | 0.97             | 20.70          | 8.62           | 99.67 |
| S-1      | 0.75             | 19.37          | 9.72           | 99.45 |
| S-2      | 0.98             | 20.66          | 9.48           | 99.19 |
| S-3      | 1.07             | 20.95          | 10.25          | 98.36 |
| Pyridine |                  |                |                |     |
| A-1      | 0.11             | 19.04          | 13.48          | 99.99 |
| A-2      | 0.27             | 20.34          | 10.96          | 99.74 |
| A-3      | 0.62             | 17.25          | 6.25           | 99.71 |
| S-1      | 0.21             | 20.15          | 11.24          | 99.99 |
| S-2      | 0.53             | 19.16          | 7.29           | 99.68 |
| S-3      | 0.51             | 18.10          | 4.61           | 99.87 |

The magnitude of the limiting adsorption volume (W_0), calculated by the Dubinin-Radushkevich equation, is shown in Figure 2.

Figure 2. The limiting adsorption volume occupied by phenol (a) and pyridine (b) when extracted from an aqueous solution with the joint presence (ratio 1:1) of active carbon samples.

4. Discussion

Studies have shown that heating the samples of industrial AUs in air at 250°C practically does not change the maximum monolayer adsorption (q_{max}) for phenol for A-2 (the change in q_{max} is 1%, which is comparable to the error in determining). While the growth of q_{max} for S-2 reaches 30%. The adsorption of pyridine from a mixture with phenol increases significantly: q_{max} increases by more than 2 times for both A-2 and S-2. The change in the value of the limiting adsorption volume (W_0) (Figure 2) for phenol is the opposite. For A-2, its growth is 12.5%, and 6.2% for S-2. In the case of pyridine, W_0 increases by 32% and 71% for A-2 and S-2, respectively. Probably, this behavior is associated with the competition of molecules of organic substances among themselves, and water for the primary adsorption centers of specific adsorption, the number of which increases with this method of processing AC [5]. In this case, all components of the solution can become secondary adsorption centers for each other. The calculated heat of adsorption (Q_L) indicates a high contribution of a specific interaction (hydrogen bond) in the formation of a monolayer of both phenol and pyridine on the surface of the AC data (Table 1). When a subsequent layer of organic components is formed, the specific interaction fraction decreases (Q_S does not exceed 11 kJ / mol) [8].

Preheating AC in a nitrogen atmosphere (samples A-3 and S-3) also leads to an increase in the adsorption of organic components from their mixture. The maximum adsorption of the monolayer for
phenol on A-3 and S-3 increases by 10% compared with A-2 and S-2. For pyridine, this parameter (q_{max}) is increased by 5.6 and 2.4 times if compared to the industrial AC for A-3 and S-3, respectively. The limiting adsorption volume of AC heated in this way is increased by ~ 24% for phenol and ~ 100% for pyridine (Figure 2). As in the case of A-2 and S-2, a monolayer of phenol and pyridine on A-3 and S-3 is formed due to the specific interaction of components with the surface of an AC (Table 1). Formation of the next component layer for pyridine occurs only due to dispersion interaction \[8\].

5. Conclusion
Studies have shown that the heating of AC can be used to increase the adsorption of a mixture of phenol-pyridine from aqueous solutions. Preliminary heat treatment both in air and in nitrogen atmosphere allows to increase the adsorption from the mixture worse than pyridine, a sorbed component. The nature of changes in the parameters of the adsorption of phenol and pyridine from aqueous solutions when co-present depends on the transformations of the chemical state of the surface of the AC during the heating. And also, the nature of changes in the parameters of the adsorption of phenol and pyridine from aqueous solutions when co-present depends on the redistribution of the ratio of micro- and mesopores and their availability.

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