

## Developing a Technology for the Regeneration of Active Coal after Pyridine Adsorption from Wastewater

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### Abstract

Results are presented for chemical and low-temperature thermal regeneration by air and nitrogen of commercial active coal of AG-OV-1 and SKD-515 trademark spent after pyridine adsorption from model solutions and real wastewaters. Inexpediency of chemical regeneration is demonstrated. Basing on the data of thermogravimetric analysis, an optimum temperature value has been chosen for the regeneration of the active coals by means of nitrogen and air flow. A comparative analysis has been performed concerning the efficiency of low-temperature thermal regeneration in inert and oxidizing media. The results obtained have allowed the low-temperature thermal regeneration by means of an inert gas (nitrogen) to be recommended for practical purposes.

**Key words:** regeneration, active coal, pyridine

### INTRODUCTION

Intensive development of the industry has resulted in the fact that in many regions there was an adverse environmental situation connected, in particular, with an overwhelming anthropogenous loading on water supply sources for population as well. The problem is aggravated with the imperfection of technological processes at many enterprises enforced to discharge imperfectly purified wastewater into natural water reservoirs as well as the absence of efficient purifying methods. Wastewaters from chemical enterprises containing a mixture of organic and mineral substances are the most difficult for processing.

One of prospective lines in the creation of efficient environmentally safe industrial technologies consists in employing adsorption technologies. The most universal adsorbents are presented by active coal (AC). It is known that the efficiency and profitability of sorption technologies depends on the possibility of carbon adsorbents reusing. In this connection the choice of the most

efficient and cheap way regenerate carbon adsorbents represents an urgent problem.

The methods of regeneration could be tentatively divided into three types: 1) chemical method (employing liquid or gaseous reagents at the temperature lower than 110 °C), 2) low-temperature thermal method (employing vapours or gases at 100–400 °C), and 3) thermal method (at the temperature range of 800–900 °C in an inert gas atmosphere or in superheated water vapour) [1]. The choice of the way of regeneration depends on the properties both of an adsorbent and an adsorbate.

Owing to scarce publications concerning the adsorption of pyridine by active coals, some contradictions in the literature data concerning the possibility of pyridine adsorption extraction from aqueous solutions [1–3], pyridine ability to form of hydrogen and ionic bonds [3, 4], as well as the absence of any information on restoring the adsorption properties of spent carbon adsorbents after pyridine extraction one cannot choose a method for the regeneration without carrying out experimental studies. In

this connection we have investigated the possibility of chemical regeneration, as well as of low-temperature thermal reactivation by means of air and nitrogen for the purpose of choosing the most efficient way to restore the adsorption properties of active coals after pyridine adsorption.

## EXPERIMENTAL

The subject of inquiry was presented by commercial AC of AG-OV-1 and SKD-515 trademark (SPC Sorbent Products, Perm, Russia), spent due to the adsorption of pyridine from model solutions and real wastewaters of the Koks JSC (Kemerovo, Russia) undergone biological purification.

The spending of adsorbents was carried out using laboratory-scale installations under dynamic conditions until a complete saturation of adsorbents ( $C/C_0 \approx 1$ ) in model solutions with the concentration of  $31.3 \text{ mg/dm}^3$  (the content of pyridine in real wastewaters after biological purification) and in real wastewater, the MPC value for pyridine being equal to  $0.2 \text{ mg/dm}^3$ .

The adsorption isotherms were registered under static conditions at the solution : adsorbent ratio equal to 100 : 1 for model solutions with the concentration of pyridine ranging within  $2 \cdot 10^{-3} - 5 \text{ g/dm}^3$ , and for 100.0 g of real wastewater with the weighed sample of an adsorbent ranging from 0.0200 to 1.000 g. The concentration of pyridine was determined from optical absorption of pyridine aqueous solutions at the wavelength  $\lambda = 256 \text{ nm}$  [5] using SF-46 spectrophotometer.

The excess Gibbs adsorption value was calculated according to the equation

$$\Gamma_i = \frac{(C_{0i} - C_i)m_0}{m} \quad (1)$$

Here  $m_0$  is the mass of the solution, g;  $m$  is the mass of an adsorbent, g;  $C_{0i}$ ,  $C_i$  are the initial and final (equilibrium) concentration of the  $i$ -th component, respectively, g/g [2].

The calculation of the adsorption capacity values for active carbons under investigation was performed with the use of the Dubinin-Radushkevich equation modified for the case of absolutely mixing liquids at a low concentration of one component ( $i$ ) [2]:

$$\Gamma_i = \Gamma_i^0 \exp \left[ - \left( \frac{RT \ln \left( \frac{1}{C_{\text{eq}} \gamma} \right)}{EV_M} \right)^2 \right] \quad (2)$$

Here  $C_{\text{eq}}$  is the equilibrium concentration of pyridine, g/g;  $E$  is the characteristic energy, J/cm<sup>3</sup>;  $\gamma$  is the activity coefficient;  $\Gamma_i^0$  is the maximum adsorption capacity of an adsorbent, g/g;  $V_M$  is the volume of an adsorbent, cm<sup>3</sup>/mol.

Differential mass loss curves were registered employing a NETZSCH STA 409 PG/PC derivatograph with a mass spectrometric unit in the following mode: the temperature ranging from 20 to 400 °C, the rate of temperature increase amounting to 2.5 °C/min, in the atmosphere of oxygen-helium mixture with the content of oxygen equal to 21 % (imitating air) as well as in the atmosphere of helium. The products of thermal desorption were trapped into an aqueous HCl solution with the concentration of  $0.1 \text{ mol/dm}^3$ .

The specific surface area ( $S$ ) as well as the volume of micropores and mesopores ( $V$ ) were determined from low-temperature nitrogen adsorption employing a Sorbtometr-M apparatus (Institute of Catalysis, SB RAS, Novosibirsk) according to the BET method.

## RESULTS AND DISCUSSION

The chemical regeneration was carried out using an aqueous HCl solution with the concentration of  $0.1 \text{ mol/dm}^3$ . The consumption of the solution amounted to  $150 \text{ cm}^3/\text{g}$  of active coal. The estimation of the adsorption-desorption balance has demonstrated that employing such a method, pyridine can be completely removed from AC surface. However, the re-adsorption of pyridine on spent adsorbent exhibits an abrupt change in the form of the adsorption isotherm (Fig. 1) as well as a decrease in the adsorption capacity of the adsorbent (Table 1), which could be connected, to all appearance, with partial acid adsorption onto the surface of active coals resulting under pyridine re-adsorption in the formation of pyridinium ions those are adsorbed in a more difficult manner [6].

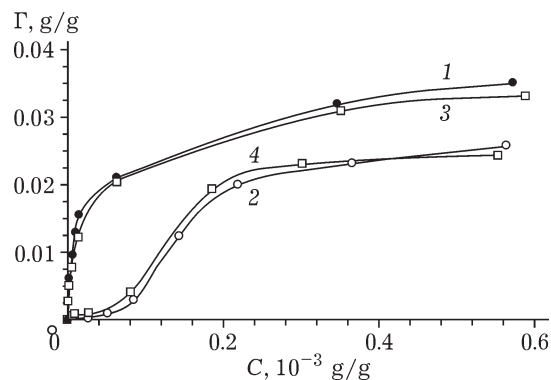


Fig. 1. Isotherms of pyridine adsorption from aqueous solution by commercial AC (1, 3) and by the AC after reactivation by HCl solution (2, 4): 1, 2 – AG-OV-1; 3, 4 – SKD-515.

Due to the reduction of the adsorption efficiency as well as a plenty of waste by-products it is inexpedient to use chemical regeneration, thus we have investigated the possibility of low-temperature thermal regeneration of adsorbents.

In order to choose an optimum temperature of thermal reactivation we carried out preliminary thermogravimetric studies. DTG curves were registered both for commercial AC and for samples after pyridine adsorption from an aqueous solution with the concentration equal to  $1.70 \text{ g/dm}^3$  in the atmosphere of helium or of oxygen-helium mixture with oxygen content of 21 %, as air imitation (Fig. 2).

As the result of the analysis performed we have established that for commercial samples under investigation in the inert environment (see

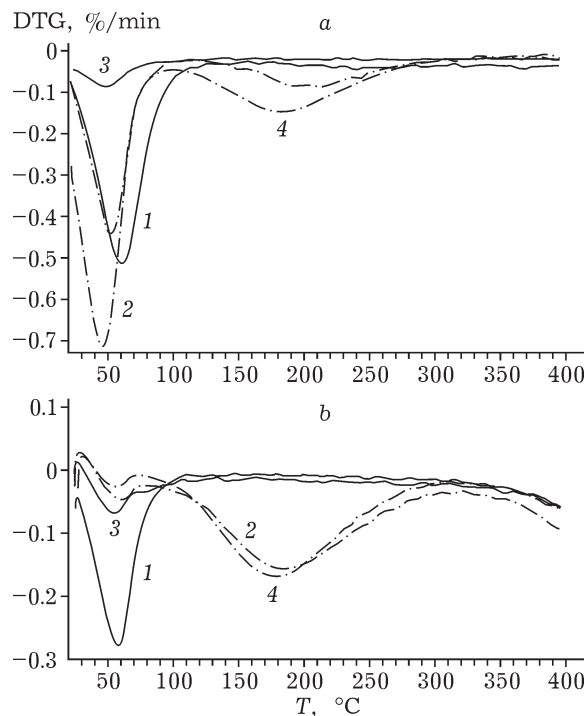


Fig. 2. Differential mass loss curves in helium atmosphere (a) and in oxygen-helium atmosphere (b): 1, 3 – commercial AC of AG-OV-1 and SKD-515 trademark, respectively; 2, 4 – AG-OV-1<sub>ads</sub> and SKD-515<sub>ads</sub> samples after pyridine adsorption from aqueous solution.

Fig. 2, a) a single mass-loss region is observed (22–113 and 25–88 °C for AG-OV-1 and SKD-515, respectively) connected with the removal of surface moisture.

For samples after pyridine adsorption we observed two mass loss regions: surface mois-

TABLE 1

Physicochemical characteristics of adsorbents

Samples	$\Gamma^0$ , g/g	$S_{\text{BET}}$ , $\text{m}^2/\text{g}$	$S_{\text{micro}}$ , $\text{m}^2/\text{g}$	$V^{\text{S}}$ , $\text{cm}^3/\text{g}$	$V_{\text{micro}}$ , $\text{cm}^3/\text{g}$	$V_{\text{meso}}$ , $\text{cm}^3/\text{g}$
AG-OV-1						
Initial	0.086	766	652	0.47	0.33	0.14
Regenerated by HCl	0.064	760	673	0.44	0.32	0.12
Regenerated by nitrogen	0.312	717	590	0.36	0.20	0.16
Regenerated by air	0.093	683	421	0.46	0.22	0.24
SKD-515						
Initial	0.065	791	404	0.56	0.36	0.20
Regenerated by HCl	0.050	786	409	0.52	0.37	0.15
Regenerated by nitrogen	0.161	769	415	0.54	0.31	0.23
Regenerated by air	0.141	732	398	0.50	0.26	

Note.  $S_{\text{BET}}$  – total specific surface,  $S_{\text{micro}}$  – specific surface for micropores,  $V^{\text{S}}$  – total volume of pores,  $V_{\text{micro}}$ ,  $V_{\text{meso}}$  – the volumes of micropores and mesopores, respectively.

ture is removed within the range of 25–100 °C, whereas water and pyridine are removed within the temperature range of 125–278 °C (AG-OV-1) and 108–297 °C (SKD-515).

The investigation of mass loss for commercial samples in oxygen-helium medium (see Fig. 2, b) has demonstrated that at the temperature lower than 40 °C there is a small increase in the mass observed (up to 0.02 %) which is absent in inert media. This fact could be connected with the absorption of oxygen by AC with the formation of surface complexes [7]. Within the temperature range of 40–110 °C we observed surface moisture removal. Oxidative destruction for both samples begins at 375 °C.

For AC after pyridine adsorption in the presence of oxygen at the temperature lower than 40 °C one can also observe an increase of the mass (0.01 and 0.03 % for AG-OV-1 and SKD-515, respectively) and a region of surface moisture removal (40–70 °C). In addition, there is a region of mass loss (70–310 °C) corresponding to the removal of adsorbed pyridine as well as water bound with pyridine. The temperature of beginning the oxidative destruction of adsorbents is shifted to 362 °C.

The comparison of data concerning thermal desorption in inert and oxidizing media demonstrates that the mechanism of water desorption out of AC surface after pyridine adsorption from aqueous solutions is different for these cases. In an inert environment at the temperature lower than 100 °C, one can observe the removal of 87 and 54 % of total adsorbed water for AG-OV-1 and SKD-515, respectively, whereas in the presence of oxygen within the same temperature range there is only 7 and 3 % of surface water removal is observed, and the most part of water is removed together with pyridine.

Basing on the set of data obtained, we have chosen the following conditions for the low-temperature desorption of pyridine: for an inert gas the temperature ranged within 350–400 °C, the processing time being up to 4 h; for air the temperature ranged within 320–350 °C, time is up to 4 h.

The low-temperature thermal reactivation of adsorbents was carried out using nitrogen or air at 350 °C during 4 h, the gas flow rate being equal to 100 cm<sup>3</sup>/min. The estimation of the adsorption-desorption balance has demonstrated that the low-temperature regenerations both

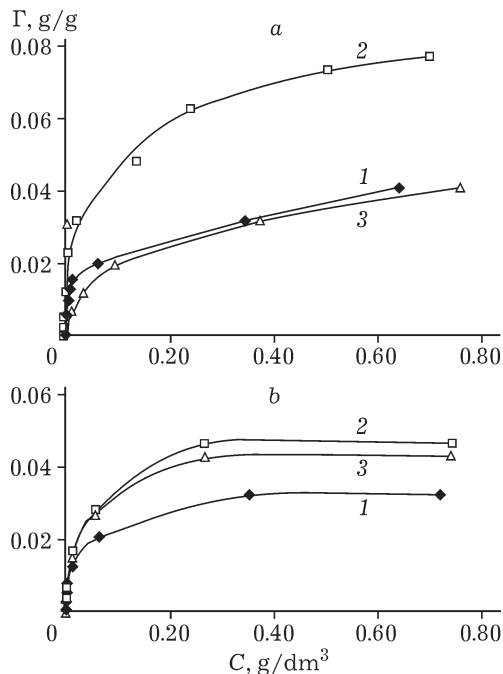


Fig. 3. Isotherms of pyridine adsorption from aqueous solutions by commercial AC such as AG-OV-1 (a) and SKD-515 (b): 1 – initial AC; 2, 3 – AC after low-temperature reactivation in the atmosphere of nitrogen and air, respectively.

by inert gas (nitrogen) and by air results in pyridine removal from AC surface in to the extent lower than 80 % for AG-OV-1 and 70 % for SKD-515.

The adsorption of pyridine from aqueous solutions onto spent adsorbents after regeneration by nitrogen (Fig. 3) results in a considerable increase in the adsorption capacity values for active coals under investigation (see Table 1). The regeneration by air results in the fact that the adsorption capacity value for AG-OV-1 almost does not change, whereas the adsorption capacity for SKD-515 grows.

The investigation of the specific surface, as well as the volume of micropores and mesopores for initial and spent adsorbents after reactivation has demonstrated that the porosity parameters of AC change insignificantly (see Table 1). The increase in the adsorption of pyridine on the adsorbents after the reactivation procedure could be connected, to all appearance, with its embedding into the structure of AC [8] and the formation thereof additional adsorption centres.

The comparative analysis of the results of adsorbents regeneration with the use of the methods proposed revealed, that, firstly, in the

case of reactivation by air the adsorption of pyridine proceeds somewhat worse and, moreover, the temperatures interval between the complete pyridine removal and the beginning of coal burning is rather narrow ( $\Delta T = 52\text{ }^{\circ}\text{C}$ ), thus it is inconvenient to use this method in practice.

For the regeneration of AC spent during wastewater treatment from pyridine we have revealed the same regularities as for model solutions.

#### CONCLUSION

The studies carried out have demonstrated that a low-temperature thermal reactivation by means of an inert gas (nitrogen) could be recommended to perform for practical purposes.

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