Thermo-oxidative Reactivation of Active Coal Used in Streptomycin Production

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Abstract. The spent active coal of streptomycin production contains on its surface the remains of inorganic acids, organic-originated alcohols and waste products, spores, mycelium of Streptomyces griseus, which after entering the environment with wastewater cause a significant harm to it. The recycling of that coal and its reuse betteres the economics of production and prevents harmful impurities from entering the environment together with that coal. Here it is demonstrated that thermal heating up to 300 °C allows to increase the adsorption activity according to methylene blue test and pH of aqueous extract of recycled sorbents close to the regulatory values, which raises the possibility of their re-use in the production of streptomycin. The raise of temperature more than 300 °C leads to decomposition of high-molecular organic substances on the surface of a coal with subsequent formation of a carbon film which covers the adsorbing pores and worsens the adsorption properties of active coal. After treatment with water vapor at a temperature of 800 °C the characteristics of the active coal meet the regulatory requirements of streptomycin production. Rational way to dispose an active coal which lost its recyclability is a burning at temperatures more than 800 °C. This completely neutralizes all the harmful impurities.

1. Introduction
In 1943-1944 the second largest at that time, streptomycin-aminoglycoside antibiotic produced by ray fungus Streptomyces globisporus streptomycini was discovered [1,2]. It was the first effective agent to cure widespread tuberculosis disease which had led in most cases to lethal outcome. [3]. For several decades, streptomycin-based medicines have also been used for treatment such diseases as plague, tularemia, brucellosis, venereal granuloma, etc. Since the advent of more effective with less side effects medicines the streptomycin itself and streptomycin-based medicines are increasingly frequently
are being used in livestock sector and crop production in many countries: USA, UK, India, Germany, Switzerland et al. In Russian Federation streptomycin is scheduled substance for "Essential Drugs List for medical treatment in 2019" as an antimicrobial medicinal product with systemic effect [4].

The process of streptomycin formulation after fermentation of Streptomyces griseus actinomycetes strains in a digest medium and removal of the mycelium by special methods of filtration from the culture liquid comprises steps of adsorption of the streptomycin with the powdered activated carbon brand of OU-A [5] at pH = 6-8, the filtering of activated carbon with adsorbed streptomycin out of inactive culture liquid, streptomycin desorption at pH = 2 from the sorbing agent with diluted aqueous - alcoholic solution of a mineral acid. An active charcoal is removed out from the obtained solution with filtration process. The solution is neutralized and concentrated by evaporation. Streptomycin is precipitated from concentrated solution with acetone, crystallized, sterilized, dried, pulverized and transferred for a packaging [6].

Due to the significant loss of adsorption capacity in the production process used powdered active coal in the production of streptomycin are usually being sent with sewage to the sewerage system. Once that coal get to the environment it causes significant harm. Thus, after the stage of streptomycin desorption an adsorption surface of active carbon in heavily polluted with such desorbing agents as acids (hydrochloric or sulfuric), alcohol (methyl, ethyl, isopropyl); non-desorbed residues of streptomycin, in other metabolites of Streptomyces griseus. While in ambient medium some impurities desorbed from a coal as a contaminant. Also, along with used coal the environment are received spores and particles of mycelium which got unfiltered while the stage preceding desorption of streptomycin. Those spores and particles of mycelium are able to produce Streptomyces griseus in the environment. The recycling may be the best way to use of such type coal.

Many enterprises in most developed countries such as USA, Belgium, Japan et al, operate plants for the regeneration and reactivation of used active coal. It allows to better the environmental friendliness and economic efficiency of existing production. Thus, 30-35% of the total volume of active coal produced by the US company "Calgon carbon Corporation" is a reactivated coal [7]. The cost of this process does not exceed 50-75% of the cost for a new batch of sorbent.

Currently there are several techniques to reactivate used activated carbons such as microbiological [8,9], microwave [10,11], thermal [12], thermo-oxidative [13,14], chemical [15,16], photocatalytic [17,18], electrochemical [19], with the aid of supercritical fluid [20], ultrasonic [21,22] and dielectric technique with a barrier discharge of plasma [23]. The presence in the used activated carbon residual parts of Streptomyces griseus spores and mycelium and streptomycin itself presuppose the use of techniques to reactivate adsorption properties alongside with sterilization.

Taking into account this fact, in the University’s laboratory of thermochemical treatment of plant raw materials there a research work was conducted. The topic of research was to revive the adsorption properties of active coals which had been used in the production of streptomycin of the Krasnoyarsk pharmaceutical manufacturing plant with thermal and thermo-oxidative techniques. The research work was carried out with the aid of an experimental laboratory unit equipped with electric heating, water vapor supply and a system of entrapment of heat-treated powdered active coal from waste gases. During this research study there was investigation within anoxic environment what is the effect the temperature delivers onto the adsorption properties and the pH of used activated carbon’s aqueous extract. The temperature parameters were, °C: 20,100,120, 200, 300, 400, 500, 600, 700, 800.
Figure 1. Dynamics of changes in pH of aqueous extract of active coal had been used in the production of streptomycin, depending on the reactivation temperature.

After the desorption of streptomycin with mineral acid and its filtration from the culture liquid, the value of pH of the aqueous extract of used active coal is 2 units. As the temperature rises the value of pH of the aqueous extract increased from 2 units to regulatory and technological values of 6-8 units in the temperature region of 600 to 800 °C. Increasing the pH of an aqueous extract is due to desorption of acid-type impurities from the surface of the coal.

Figure 2. Dynamics of changes in adsorption activity according to adsorption of methylene blue of active coal used in the production of streptomycin, depending on the reactivation temperature.

At the initial stage of heating, the adsorbing pores of an active coal are discharging from moisture, volatile impurities of organic and inorganic nature. It leads to an increase in the adsorption activity in terms of methylene blue. The value parameter of activity at 300 °C is 206 mg/g (figure.2) which is 94 % from the normative (220 mg/g, [5] ) and pH value of aqueous extract is 5 units (figure 1). Such a sorbent agent, considering increasing in its pH of aqueous extract for one unit up to the technological requirements (pH=6), may well be reused at the stage of adsorption of culture liquid in the streptomycin production. Subsequent cycles of reuse of such active coal depend on the degree of
filling its adsorption surface with accumulated impurities in each cycle which leading to reduction of its characteristics.

In the temperature range of 300 to 400 °C the activity in terms of methylene blue rapidly reduces as a result of decomposition processes and carbon condensation inside the pores of the active charcoal non-desorbed impurities of high-molecular organic substances, especially those containing cyclic carbon structures [24, 25]. To such substances belongs entirely streptomycin which has full title of its chemical formula: \( \text{O-2-Desoxy-2-(methylamino)-alpha-L-glucopyranosyl(1"2)-O-5-desoxy-3-S-formyl-alpha-L-lyxofuranosyl(1"4)-N,N'-bis(aminooiminomethyl)-D-streptamine.} \)

![Figure 3. Structural formula of streptomycin [6].](image)

Decomposition of streptomycin salts under normal conditions begins when the temperature is above 220 °C [26]. Under the influence of close to boiling temperatures viscous high-molecular substances inside the coal in mesopores under the pressure of the gases produced as a result of decomposition are transported through the pores to the outer surface of the coal. There those viscous high-molecular substances undergo their final decomposition process. After thermal detaching of the side radicals (\([-\text{HE}], [-\text{NH}], [-\text{NH2}], [-\text{CH3}], \text{etc.}\) from the basic molecule the remained unsaturated side carbon bonds of the molecules recombine against each other resulted with formation of new carbon cycles which adjoin to the basic molecule. Such processes lead to the formation of hexagonal carbon structures similar in structure to carbon crystallites of activated carbon. Formed from those hexagonal carbon structures pyrocarbon film on the surface of coal partially and sometimes completely covers the entrances to the pores of coal. As a result the adsorption capacity of coal in terms of methylene blue at reactivation temperature of 400 °C is sharply decreased to 127 mg/g which is 58% of the standard requirements. It confirms the presence on the adsorption surface of used coal a significant amount of high-molecular impurities subjected to destruction.

Further rise in temperature up to 800 °C causes shrinkage (reduction in surface) and partial destruction of the pyrocarbon film. This process unblocks a certain part of the pore entrances which leads to an increase in the adsorption activity in a term of methylene blue up to 175 mg/g. It is 80 % of regulatory requirements. This circumstance also attests to the fact of the absence at this temperature any organic substances decomposing on the surface of a coal and thus to its complete sterilization.

To bring the characteristics of used active coal to the requirements it was treated at a temperature of 800 °C in a laboratory unit with water vapor with a flow rate of 0.3 g / g of coal for 7 minutes. Combustion loss in terms of the non-volatile carbon is 6.3%, the adsorption activity in terms of methylene blue of obtained coal is 234 mg/g, value of pH of aqueous extract is 8 units which matches against standard indicators of active charcoal type OU-A (this type of coal used in the production of streptomycin) and it is the evidence of the complete removal pyrocarbon film from the surface of the coal.

After a critical loss of sorption capacity during the cycles adsorption–reactivation at a temperature of 300 °C and loss of the mass of coal during the cycles of adsorption–reactivation at 800 °C the used activated coal rationally to be disposed by incineration at temperatures over 800 °C. Due to this...
condition the spores and mycelium of Streptomyces griseus and other products of its metabolism are completely neutralized.

2. Summary
1. On the adsorption surface of used active coal while the production of streptomycin there is a significant amount of harmful impurities of organic and inorganic nature that can pollute the environment.

2. At thermal heating up to 300 °C adsorption activity of used coal in terms of methylene blue and pH of aqueous extract are restored to the close-to-regulatory values which allows to reuse them in production of streptomycin.

3. When the temperature rises above 300 °C the adsorption properties of reactivated active coals deteriorate significantly due to the formation of a pyrocarbon film consisted of organic impurities decomposed on the surface of the coal.

4. Thermo-oxidative reactivation by water vapor at 800 °C allows to completely restore the adsorption capacity of used coal for recycling in the production process as well as to carry out its sterilization.

5. For the complete disposal of used active coals after the production of streptomycin the most effective way is to incinerate at temperatures over 800 °C.

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