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Activated Carbon for Wastewater Treatment from Phenol Compounds

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Abstract

Application of activated carbon (AC) obtained from cotton wastes (bolls, stems, and roots) for phenol adsorption from water, or wastewater dephenolization, is presented. The kinetics of phenol adsorption by carbon adsorbents were studied using UV/Vis spectrophotometer. The porosity of the formed ACs ranged from 1.952 to 2.339 cm^3/g, the volume of macropores was from 1.79 to 2.09 cm^3/g, while the commercial sample BAU-A showed 1.920 and 1.320 cm^3/g, respectively. The highest phenol adsorption rate, 32.49–52.80 mg/(g · min), was observed for contact time up to 5 min on carbon adsorbents obtained from cotton waste. The adsorption equilibrium was achieved within 5 min after the contact, which is shorter than the analogous commercial adsorbents (7–12 min). Sufficiently high phenol adsorption activity of AC from cotton stems, roots and bolls is revealed. Therefore, the use of AC from cotton wastes as adsorbents for the treatment of industrial wastewater to remove organic and other impurities can be recommended for environmental remediation applications.

Keywords: phenol adsorption activity, activated carbon, kinetics, cotton waste

INTRODUCTION

Currently, purification by means of adsorption with the help of conventional active carbon materials obtained from plant wastes has found wide application. Active carbon can be obtained from various carbon-containing raw materials. The world production of active coal has already reached about a million tons per year. To obtain active coal, different types of carbon-containing raw materials can be used: woodworking industry waste – lignin, bark, wood chips [1–3], bituminous and brown coals [4, 5], various types of agricultural wastes [6–8], as well as fruit seeds, husks, walnut shells [9, 10], carbon-containing industrial and domestic wastes [11, 12]. About 36 % of carbon sorbents are produced from wood, 28 % – from coal, 14 % – from brown coal, 10 % – from peat, and about 10 % – from coconut shells.

Activated carbon (AC) materials are used in the production of sugar for refining process and are a valuable tool in the technology of winemaking to eliminate unpleasant tastes, odours, to extract tannins in winemaking, as well as in many other branches of food and pharmaceutical industries. In choosing a sorption material, much attention is paid to its sorption characteristics, methods of regeneration and disposal of waste material, as well as the cost of manufacturing and the availability of a raw material base [13, 14].

Kyrgyzstan, as an agrarian country, has the richest resources of annually renewable plant raw materials, which have not yet found appropriate application in processing and use. The agriculture of the Republic alone can annually produce millions of tons of plant raw materials for chemical and energy processing – cotton and tobacco stalks, corn cobs and stalks, grain straw, sunflower husks and stalks, rice husks, fruit seeds and pomace, *etc*. Valuable products can be obtained by processing annually renewable weeds (wormwood – tarragon), the reserves of which are unlimited. However, the listed kinds of biomass are used as household fuel in rural areas, and some of them for feeding farm animals.

The application of these wastes to obtain sorbents will allow not only obtaining effective materials, but also at the same time linking their environmentally safe disposal with rational use. One of the leading places among them is the development of new sorption materials based on plant raw materials. The possibilities of sorption materials of plant origin are quite large, since they are capable of removing not only heavy metals and radionuclides but also organic substances from polluted waters.

Kyrgyzstan has huge resources of annually renewable plant materials like corn cobs, sunflower and rice husks, tobacco stems, cotton biomass, wild wormwood and other kinds of plant wastes. In this regard, it is relevant to study AC based on cotton wastes. Physicochemical characteristics of the feedstock show that the technological and chemical properties of cotton wastes fully satisfy the requirements for the quality of feedstock for producing activated carbon.

We have previously studied the chemical composition of cotton biomass (total mass, stems, bolls, and roots) to establish its suitability for the production of carbon adsorbents and chemical products. According to the chemical composition, cotton biomass fully meets the requirements for the production of carbon adsorbents since it is a low-ash, low-sulphur raw material with a high yield of volatile substances. When choosing adsorption materials, attention must be paid to such parameters as sorption value, cost, availability, non-toxicity, efficiency, the possibility of using secondary material resources, and the environmental safety of utilizing saturated adsorbents.

In this regard, we have previously investigated [15–17] the chemical and technological composition, the process of carbonization and activation of cotton biomass as an alternative source, since these plants are annually renewable, which makes it possible to harvest raw materials annually, without waiting for the attainment of a mature age, for example, like in trees of several decades.

In [15], the chemical and technical composition of cotton biomass (total mass, stems, capsules and roots) was studied to establish its suitability for obtaining carbon adsorbents and chemical products. It was found that the content of cellulose in the studied samples ranges from 37 to 48 %, lignin 21–31 %, hemicellulose 11–21 %. Wood of various species contains 40–50 % (wt.) cellulose, up to 15–30 % (wt.) hemicelluloses and 20–30 % lignin.

Thus, studies make it possible to replace relatively expensive wood pulp and cotton raw materials with non-wood plant waste in the production of cellulose and lignin. The technical composition of cotton biomass quite satisfies the requirements for the production of carbon adsorbents, since it is low-ash (3–5 %) and low-sulphur (0.02 %) raw material with a high yield of volatile substances (75–79 %).

Phenols are among the most common pollutants entering surface water with enterprise effluents [18–20]. Phenol is toxic, and it causes disfunctions of the nervous system. Dust, fumes, and phenol solution irritate the mucous membranes of the eyes, respiratory tract, and skin. The maximum permissible concentration (MPC) of phenol (Hygiene Standards 2.1.5.1315-03) is 0.001 mg/L for the sum of volatile phenols that give the water a chlorophenol odour during chlorination (trial chlorination method). This MPC applies to water bodies for domestic water use, provided that chlorine is used to disinfect water during its purification at waterworks. In other cases, the allowed content of the number of volatile phenols in water is 0.1 mg/L [21].

The present work is devoted to the study of the phenol adsorption activity of AC obtained from cotton wastes to determine its applicability for purifying water from organic pollutants, in particular, for dephenolization of wastewater.

EXPERIMENTAL

Activated carbon was used as a sorbent. The method of obtaining this material and its main properties were described previously [17]. In brief, 50 g of initial raw material of the size fraction of 3.0–5.0 mm was taken; the sample was placed in-

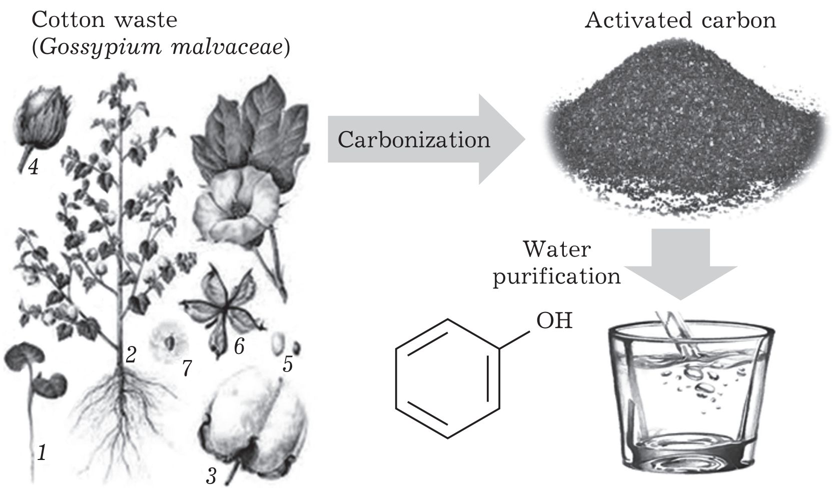

Fig. 1. Carbonization of cotton wastes to obtain activated carbon, and its application in water treatment. Names of numbered parts: *Gossypium malvaceae* sprout (*1*), root with stems (*2*), ripe cotton boll (*3*), green cotton boll (*4*), cottonseed (*5*, *7*), ripe bolls (*6*).

side a retort activator, then the retort-activator was closed, and the sample was heated for 8 min at 800−850 °C. Then the sample was quickly taken out of the vessel and poured out into hermetic ware. After it was cooled down to room temperature, the sample was taken for analysis. The whole process of production and application of AC is presented in Fig. 1, where AC is obtained from cotton wastes *via* carbonization and further applied for purification of water from phenol.

The adsorption of phenol from aqueous solutions by AC samples was carried out at room temperature (20±2 °C). For this purpose, 0.1 g of a dry AC sample was introduced into a phenol solution with the volume of 50 cm^3 and concentration C_0 (from 0.01 to 3 mg/cm^3). The solution was continuously stirred using a laboratory shaker, and the process lasted from 5 min to 3 h. After the experiment, the phenol solution was filtered into a volumetric flask with a capacity of 100 cm^3 (or separated by centrifugation). Solution pH was maintained using a buffer solution (12 % NH_4Cl in 6 % NH_4OH, pH 10). The residual concentration of phenol was determined with the help of a well-known spectrophotometric method by staining with 4-aminoantipyrine [22, 23].

The amount of phenol adsorption (A_{ph}, mg/g of coal) was calculated using the formula:

$$A_{ph} = ((C_0 - C_r) \cdot 50)/m$$

where C_0 is the concentration of the initial phenol solution, mg/cm^3; C_r is the concentration of phenol after adsorption, mg/cm^3; 50 is the volume of phenol solution, cm^3; m is the mass of AC, g.

RESULTS AND DISCUSSION

Adsorption methods of purification are used to remove soluble organic compounds from wastewater. Activated carbon materials are hydrophobic sorbents with a high degree of carbonization (90−98 %). They readily sorb hydrophobic compounds such as aliphatic and aromatic hydrocarbons, their halogen- and nitro-substituted derivatives and weakly hydrophilic compounds − lower alcohols, glycols, glycerol, acetone, lower carboxylic acids and some other substances. The adsorption of soluble organic impurities by AC occurs as a result of dispersion interactions between organic molecules and the adsorbent.

Earlier, we obtained AC materials and studied their adsorption capacity for methylene blue and iodine [17]. It is shown that these materials have a high adsorption activity for methylene blue: 210−220 mg/g (the requirement of the state standard is at least 210−225 mg/g), for iodine 70−81 %. Therefore, their use for clarification of industrial wastewater from various dyes and from inorganic and organic impurities is advisable.

The effectiveness of AC obtained from the cotton biomass carbonizates was evaluated by the following indicators: bulk density, elemental analysis, humidity, ash content, adsorption activity with respect to methylene blue and iodine, and the maximum sorption volume for benzene.

The composition and properties of AC obtained from the cotton waste including the total mass, stems, and roots were studied. The material was pyrolyzed at a temperature of 500 °C with subsequent activation with water vapor at 800–820 °C. Activation of carbonizates showed that, with the same process duration, the AC yields, degree of burning in the samples, the total mass and stems are almost the same, except for roots, which have a small degree of scalding, while the yield of AC is higher. In the process of carbonization and the subsequent activation of raw materials, the ash content of AC in comparison with the initial samples is 2–3 times higher.

Therefore, demineralization was carried out to remove water-soluble mineral impurities from AC. Here, the samples were subjected to treatment with water and hydrochloric acid (HCl) of different concentrations. When AC was treated with water at room temperature, its ash content changed insignificantly. Acid demineralization with a 5 % HCl solution under the same conditions reduces the ash content by 7–10 %, while with a 10 % HCl solution, the ash content decreases by 10–12 %.

Further increase in acid concentration does not affect the decrease in the ash content of ACs. Mineral impurities were removed much faster when boiled; in 0.5 h the ash content is reduced by a factor of 5–10. An increase in boiling time leads to a slight decrease in ash content. After demineralization, the ash content in AC from the total mass is 1.75 %, from stalks – 2.45 %, and from roots – 1.28 %. As a result of acid treatment, a decrease in ash content is observed, depending on specific parts of cotton plant: from 17.91 to 3.51 % for the total mass, from 20.54 to 3.64 % for stems, from 9.46 to 1.59 % for roots, and from 28.43 to 4.62 % for bolls. Very low-ash (1.59 %) AC was formed from cotton roots, and higher-ash ones from bolls (4.62 %).

To increase the adsorption capacity and the pore volume of carbonizates from cotton biomass at various pyrolysis temperatures, the materials were activated to various degrees of burning at a constant temperature of 800 °C for 8 min with steam [17]. During activation, the adsorbents undergo compaction and shrinkage. As a result, their characteristics can vary, as indicated by a decrease in bulk density: in stems at 500 °C, the bulk density is 0.303 g/cm^3, and at 800 °C – 0.282 cm^3/g. At the same time, the porosity of the resulting AC increases simultaneously, the total pore volume is from 1.952 to 2.415 cm^3/g, macroporosity (V_{ma}) is from 1.79 to 2.09 cm^3/g, and the volume of sorbing pores is from 0.162 to 0.244 cm^3/g.

The iodine adsorption activity after activation of the carbonizate obtained from stems at 500 °C reaches 56.93 %. With an increase of pyrolysis temperature to 800 °C, the activity increases to 70.91 % and is comparable to the BAU-A trademark, with adsorption capacity not less than 60 %. Such adsorbents can be used in a water treatment system, in the recovery of volatile organic solvents, and in the treatment of steam condensates.

Activated carbon from cotton bolls, which can be used for treatment of drinking water, wastewater, in the food industry, *etc.*, has a good iodine adsorption capacity (60.38–81.63 %). Activated carbon materials obtained from cotton waste, in terms of adsorption capacity of substances with different molecular sizes, are not inferior in some respects to the industrial AC models. Such ACs can be used in the food industry, for the treatment of drinking and wastewater. Samples also adsorb from 32 to 52 mg/g phenol; therefore, their use (they are cheaper than activated charcoal) is more preferable for dephenolization of wastewater.

The efficiency of the activation processes was assessed according to the following characteristics of AC from the carbonizates of cotton biomass: bulk density, the data of elemental analysis, moisture content, ash content, and phenol adsorption activity.

The studies of the physicochemical properties and the elemental composition of the obtained AC show that with the transition from the feedstock to carbonizate and further, changes occur in the adsorbent due to a decrease in the hydrogen content and the proportion of other elements, while carbon content increases in comparison with the initial carbonized feedstock and reaches 90 to 98.7 %.

Ash content sharply increases in the obtained carbonizate products. This was especially clearly observed in the carbonizate from the bolls up to 23 %, reaching 28.4 % after further activation. In the final product, *i. e.* in AC obtained from different parts of cotton, the ash content is higher than the permissible norm for industrial AC, which is an undesirable effect. Therefore, AC was demineralized by treating with distilled water and a 5 % HCl solution.

When AC is treated with distilled water, the ash content is reduced by 50 %, therefore, the water-soluble part is half of the residue, which is unacceptable for AC. When AC is treated with a

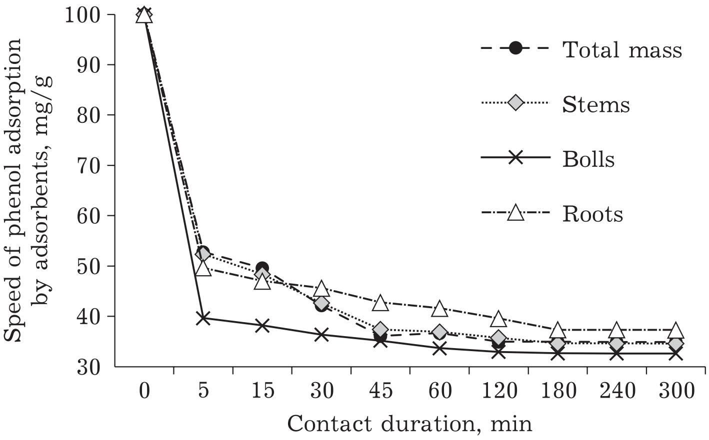

Fig. 2. Dependence of phenol adsorption rate on the time of contact with different parts of cotton plants.

5 % HCl solution, the ash content sharply decreases in all parts of cotton. Thus, the treatment with a 5 % HCl allows reducing the ash content by a factor of 3–6, compared to the feedstock.

To our knowledge, the primary porous structure of AC from plant biomass is formed at the stage of carbonization, while steam-gas activation is necessary to open the formed pores, which provides access to them for adsorptive molecules.

During activation, adsorbents undergo compaction and shrinkage, resulting in their size change, as indicated by a decrease in bulk density, for example, in stems at 500 °C, the bulk density is 0.303 cm^3/g, while at 800 °C the bulk density is 0.282 cm^3/g. At the same time, the porosity of the formed AC, the total pore volume ($V_\Sigma = V_{ma} + V_s$) increase from 1.952 to 2.339 cm^3/g, the volume of macropores (V_{ma}) increases from 1.79 to 2.09 cm^3/g, and the volume of sorbent pores (V_s – total volume of micropores and mesopores) increases from 0.162 to 0.244 cm^3/g simultaneously.

An increase in temperature from 700 to 800 °C led to a huge increase in pore volume. At a temperature of 500–600 °C, the development of porosity is limited (V_Σ = 1.95 cm^3/g). This is because at such temperatures the pores in coal are not completely free of volatile and resinous substances.

It can be seen that in terms of quality indicators (bulk density, porosity), AC meets the requirements for industrial ACs, adopted as analogs. Activated carbon materials from cotton biomass have a similar porous structure, however, in terms of the limiting volume of the sorption space, they are inferior to industrial samples of BAU and at the same time, they have higher volumes of macropores than their industrial counterparts.

As is known from the published sources, AC from wood absorbs phenol more quickly, for example, the adsorption equilibrium of the ACs "BAU" and "DOU" is achieved in 7 and 12 min, respectively [24]. On the other hand, for exemplary genesis, adsorption equilibrium is established after 1–10 days, for carbon on the zeolite – 3 days [25], for carbons from coals of medium degree of metamorphism – 10 days [26].

As noted in [2], brown coal adsorbents have a high dynamic capacity both in phenol (48–90 mg/g) and in oil products (123–256 mg/g) in a wide range of concentrations of these impurities in the initial aqueous solution: phenol 50–500 mg/L and petroleum products 89.5–1030 mg/L.

Figure 2 represents the results of kinetic studies of phenol adsorption from aqueous solutions on carbon adsorbents obtained from cotton biomass (stems, roots, bolls). As seen from the graph, the highest phenol adsorption rate – 32.49–52.80 mg/(g · min) – was observed with the contact duration of up to 5 min on carbon adsorbents obtained from cotton waste. After the contact duration of more than 180 min, there was only a slight increase in phenol adsorption: the change in the adsorption rate was 0.01–0.02 mg/(g · min).

CONCLUSION

The kinetics of phenol adsorption from water by carbon adsorbents obtained from cotton waste (bolls, stems, and roots) was studied. From the results of our studies, we can draw a practical conclusion that the obtained activated carbon materials based on cotton stems, roots and bolls have a sufficiently high phenol adsorption activity.

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