Technologies for producing traditional and non-traditional adsorbents for deep purification of aqueous-alcohol solutions based on Paulownia wood

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Abstract. This article presents the technology of obtaining activated carbon adsorbents from Pavlovnia tree waste in two different ways and in two stages. In the process of pyrolysis, the product is charred in an oxygen-free environment, and then activated in the presence of steam at temperatures from 300°C to 800°C. In the process of thermal activation of adsorbents, separation of tar resin and carbonaceous gases - CO, CO_2, CH_4 and other gases was observed between 250-400°C. When activated in the presence of water vapor, with the help of a steam generator with a temperature of 180°C-200°C, for 1.5 hours, under a pressure of 50-100 Pa, the loss of tarry resin substances was achieved. It is possible to obtain an adsorbent with high pores.

1. Introduction

Our Republic still does not have an enterprise for the production of activated carbons from wood. In this regard, organizing the production of carbon adsorbents from local wood raw materials in the republic remains an important task. Currently, to purify water and alcohol products from harmful substances, factories of the Republic of Uzbekistan traditionally use imported activated carbons, for example, BAU-A grades imported from Russia [1- 6].

To obtain activated carbon, wood chip waste from Paulownia trees was used, which was activated without oxygen at different temperatures and activation times [7- 10]. Previously, the initial wood raw material was subjected to thermal activation in the temperature range of 300–800°C for 30–90 minutes. Then the charred mass was treated with sharp water steam [11-12]. The raw materials for the production of coals and activated carbons are sawdust and shavings, stems, crowns and shells of fruits: coniferous trees - pine, larch, juniper, deciduous trees - oak, cedar, beech, birch. In addition, cotton stems and bolls, kenaf waste, food waste from cherry, cherry, peach, grape seed shells, etc. are used [13-15]. They contain lignin, lignocellulose and cellulose, which during heat treatment lose moisture, release carbon dioxide, and some even nitrogen and sulfur dioxide and turn into coal. It consists of carbons located at the sites of fused aromatic rings, tightly linked by single and double bonds. These rings can be broken or destroyed only when coal is burned [13]. It is known that activated carbons are obtained from various hydrocarbon sources, from various types of wood and other cellulose-containing plants [16], peat [17], from various grades of coal, i.e. brown and hard coal [18], liquid and gaseous hydrocarbon raw materials [19], synthetic polymers [20], plant waste and from mineral raw materials, etc.

When pruning trees and logging, up to 25% biomass is formed as waste. Wood waste has high humidity, so obtaining heat by burning it is unprofitable. It would be more efficient to produce coal by pyrolysis with its simultaneous activation with sulfuric or nitric acids. The sources of raw materials for the production of carbon adsorbents include: grain straw, corn stalks or trunks, cotton waste, rice or wheat hulls and wood, sunflower plates, etc. [21-22]. It is known that technical lignin, tree bark, shavings and sawdust are hydrocarbon raw materials for the production of adsorbents [20]. The adopted 1-stage wood activation technology is carried out in a pyrolysis installation in a

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fluidized bed without separation into parts: bark, sawdust, shavings, stems and crowns [23]. The standard indicators of AC obtained from these collections are not inferior to the adsorbents BAC-A and BAC-MF. A relationship has been discovered between preparing forests, giving them shape, trimming stems, crowns and even root waste, and pyrogenetic treatment [24-27].

2. Materials and Methods

It is known from the literature that 95% of the mass of the Pavlovna tree is made up of organic substances. The element content for all trees is the same and on average is: C - 48±2%, O - 44±2%, H - 6±1% and N - 0.1-0.3%. These elements form such organic substances as: cellulose, lignin, hemicellulose, tannins, pectin, resins, etc. The inorganic composition of wood consists of the elements calcium, potassium, sodium, magnesium, iron and other metals. Such metals in the form of oxides are formed in ashes in the form of ash. With an increase in the content of high molecular weight organic substances and some polyvalent metals and a decrease in ash, the strength increases. Paulownia has this ability. The salt composition of Pavlovna charcoal has the composition (in percentages) CaCO3-18.2; $CaSiO_3$-17.2; $CaSO_4$-16.6; K_3PO_4-15.3; Na_3PO_4-15.8; $MgCO_3$-4.4; $MgSiO_3$-4.4; $FeCO_3$-3.4; $FeSiO_3$-4.7. It is known that if the wood contains more organic substances and less ash, then the coal formed from this carbon material will be strong.

Consequently, those that are highly hydrophobic will have high adsorption capacity. Therefore, the production of activated carbon by steam-gas activation of local wood is currency- and resource-saving.

During the study using the traditional method, pyrolysis and activation of carbon adsorbent from Paulownia wood was carried out in two stages:

The first stage is to load raw materials from crushed wood of 3-5 mm in size into the pyrolysis installation, and tightly close its lid. Then turn on the electrical power from 60 to 65 volts and set the pyrolysis temperature. When the temperature has risen to the specified temperature, we note the time and hold it for 1.5-2 hours to obtain a thermally activated adsorbent.

In the second stage, after holding for 1.5-2 hours, we turn on the steam generator with a temperature from 120°C to 200°C. Then, when heating the steam generator, we drop water from the water tank using a water tap to produce water steam. The resulting steam in the steam generator is supplied to the pyrolysis installation using a steam tap and held for 1.5-2 hours to obtain an adsorbent with steam-gas activation. As a result of two-stage activation of charcoal, we obtain an adsorbent with high specific surface area and porosity.

In order to reduce imported adsorbents in the Republic, we have developed a laboratory pilot installation for the production and activation of charcoal based on the local Paulownia tree.

The production of activated carbon adsorbent from wood is carried out in the following order:

During the pyrolysis process, raw materials from crushed Paulownia wood in the form of chips measuring 50-100 mm are loaded into the pyrolysis installation. Then we close the lid hermetically so that the oxygen in the air of the pyrolysis installation does not penetrate inside. Then we turn on the electrical power with a voltage of 60-65 volts, and then set the estimated pyrolysis temperature from 300 to 800°C. Upon reaching the set temperature, we time it and maintain it for 1.5-2 hours to obtain a thermally activated adsorbent. During the thermal activation of adsorbents within the range of 250-400°C, resin and 4-carbon gases - CO, CO_2, CH_4, etc. are released.

3. Results and Discussion

We carried out the pyrolysis process in a laboratory installation at high temperatures in the range of 400-450°C without oxygen, and this process is the decomposition of wood. Pyrolysis begins at a temperature of 200°C with the release of carbon oxides; when the temperature rises to 300°C, smoke is released and then, when the temperature rises to 350°C, pore formation occurs. The pyrolysis process continues for one hour at a temperature of 400°C without oxygen. To obtain highly porous adsorbents based on plant waste, it is necessary to optimize pyrolysis conditions so as not to affect the destruction of the carbon structure. After thermal activation, the physicochemical characteristics of activated adsorbents were studied. During the analyses, we studied the humidity, ash content, porosity and adsorption activity of the resulting adsorbents. The adsorption isotherm of benzene by the resulting activated adsorbents was studied. When the activation temperature increases from 300°C to 500°C, the capacity of the adsorbent monolayer (a_m) (0.18÷0.63) and the specific surface area (S_{sp}) (43÷52 m^2/g) increase accordingly. When the temperature reaches 600-700°C, the monolayer capacity (a_m) (0.50÷0.41) and specific surface area (S_{sp}) (120÷90 m^2/g) decrease. In the process of pyrolysis, first, with increasing temperature, the organic substances of wood swell, and as a result, the specific surface area increases. When the temperature reaches a certain value of 600-700°C, the specific surface area decreases due to the fact that some resin-forming substances in the charcoal close the pores.

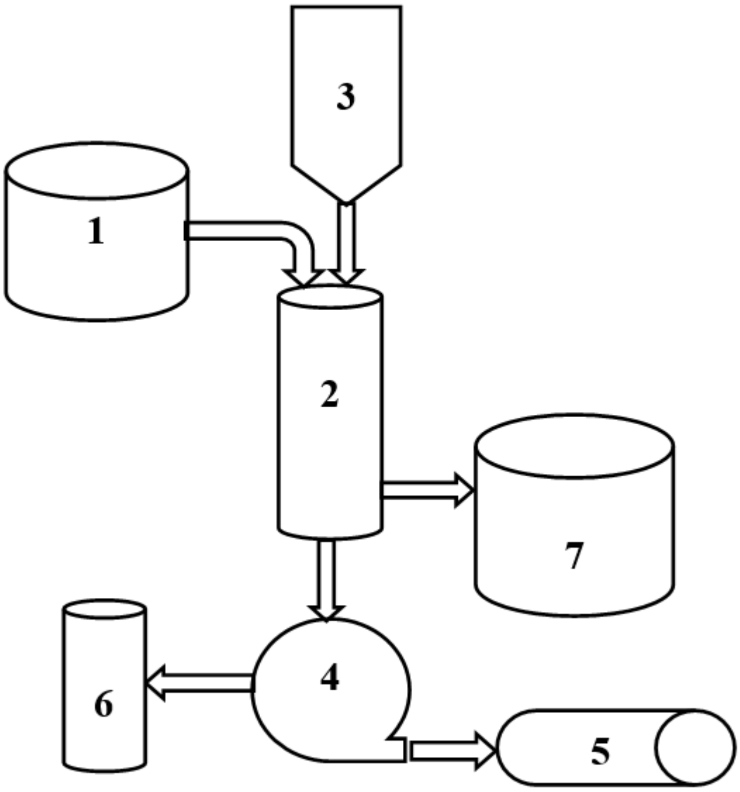

Fig. 1. Laboratory pilot plant for the production of steam-activated adsorbent based on Paulownia wood. 1- Raw materials (Wood); 2- Pyrolysis reactor; 3- Steam generator; 4- Sump; 5- Resin settling tank; 6- Container for releasing carbon gases (CO, etc.); 7 - Ready-made steam-activated adsorbent.

Then, with increasing temperature, melting and removal of the resin leads to an increase in the specific surface area S_{sp} = 217 m^2/g, creating additional pores. From the data presented, we can draw a conclusion about the structural adsorption parameters of benzene vapor adsorption.
The mesapore volume in relation to the adsorption capacity V_s is 25.7% for the adsorbent obtained at 300°C; 45% - for adsorbent 400°C; 44% - for adsorbent 500°C; 31% - for adsorbent 600°C; 23.9% - for an adsorbent of 700°C, and 50% for an adsorbent of 800°C. As a result of our research, we concluded that for the studied adsorbents thermally activated in the temperature range 300-800°C, the characteristic values of S_{sp}, W_0, W_{me}, V_s are, respectively: for 400°C - 3.5; 2.3; 1.0; 1.9; for 500°C -3.5; 2.3; 1.0; 2.0; for 600°C – 2.8; 2.6; 1.0; 2.2; for 700°C - 2.3; 2.7; 1.13; 2.3; for 800°C - 5.0; 3.0; 1.0; 2.4. In this case, the adsorbate forms a monolayer on the surface of the sorbent, the volume of which exceeds the volume of micro- and mesopores (Figure 1).
The results of the study, the physico-chemical properties of activated carbons when activated at 800°C were highly effective than at other temperatures. Based on this, activated carbon brand PPAC-A (Paulownia pargas-activated carbon adsorbent) is superior in all respects to the compared adsorbents PTA-A (Paulownia temperature-activated adsorbent), ChAC-A (Chinar activated carbon adsorbent) and BAC-A (Birch activated carbon adsorbent), i.e. bulk density by 8 g/dm3, strength by 0.5%, and acetone porosity by 1.6% and the fractional composition of large grains of activated carbon by 1.2% higher, humidity by 0.5% and ash content by 1.25-1.9% lower. A comparative analysis of the adsorbents given in Table 1 shows that the adsorbent brand PTA-A was the most optimal.

Table 1. Physic-chemical characteristics of activated wood-based adsorbents

№	Coal grades at temperature 800°C	Bulk density, g/dm^3	mechanical durability, %	Humidity, %	Ash content, %	Porosity, %	Factional composition, %	
							№36	№10
1	PTA-A	238	10.4	10.0	6.0	42.1	4.5	95.5
2	PPAC-A	246	10.9	9.5	4.7	44.3	3.3	96.7
3	ChAC-A	230	9.8	2.0	9.2	41.5	4.6	95.4
4	BAC-A	220	8.4	10.0	7.0	42.7	5.7	94.3

The purpose of the research is to select and study local raw materials, as well as to develop a technology for producing carbon adsorbents for purifying aqueous-alcohol solutions from impurities. Using microwave research, the ash content of coal can be reduced to obtain high-quality wood-based activated carbon adsorbent. Experiments have been carried out to determine and reduce the ash content of coal, i.e. to remove impurities, as well as to reduce the moisture content of coal. In connection with this, the development of technology for producing highly activated carbons with microwave radiation was studied. In Fig. 2 outlines the technology in which we propose to activate carbon adsorbents.

Activation of the adsorbent by microwave radiation was carried out as follows: the original crushed (1÷2 mm) coal and the thermally activated adsorbent were kept in water for 24 hours. The residual water was drained, and the coal mass was transferred to a plate. The activation time in the microwave lasted from 0.5 to 1.5 minutes. The essence of activation by microwave radiation is that during microwave radiation of wet coal, moisture is bombarded under the influence of magnetic radiation. In this case, the outer and inner surfaces of the wetted carbon surface are exposed to microwave radiation at high speed, which leads to the opening of the surface and internal pores of the coal. The opening of the pores occurs as a result of the release of energy generated by the collision of microwave rays with water located in the pores of the coal. The adsorbent becomes a microwave-active adsorbent as a result of the formation of additional pores in primary carbons at 300-500°C and thermally activated carbons at temperatures of 600-800°C. The ash content and moisture content of microwave-activated adsorbents and conventional (thermally activated) adsorbents, as well as their porosity with respect to acetone, were studied.

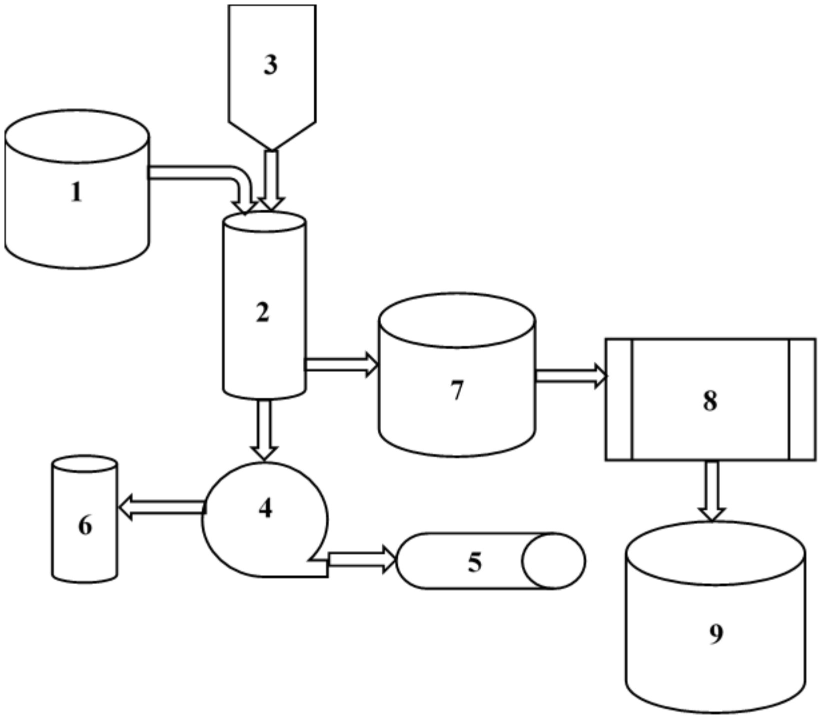

Fig. 2. Laboratory pilot plant for the production of adsorbent based on Paulownia wood with activation by microwave radiation. 11- Raw materials (wood waste); 2- Pyrolysis reactor; 3- Electric transformer; 4- Thermocouple; 5- Sump; 6- Carbon dioxide; 7- Resin container; 8- Ready pyrolysis adsorbent in a desiccator; 9- Adsorbent in swelling; 10- Filter; 11- Microwave oven; 12- carbon monoxide - CO. 13- Microwave activated adsorbent.

The dependences of the loss of moisture and ash content of coal on the activation time of the adsorbent using microwave radiation were determined. This method produced an adsorbent with a high specific surface area and saved a large amount of time for activation. In addition, dielectric heating of substances containing polar molecules occurs in a microwave oven. The electrical component of electromagnetic waves accelerates the movement of molecules with the help of a dipole moment, and intermolecular interactions lead to the absorption of electromagnetic radiation and a resonant increase in the internal temperature of substances. As a result, the pores of the adsorbent, saturated with a water molecule, open.

In the steam-gas method, steam is supplied from top to bottom and goes out, and in this method, steam comes out up and out. Also, the advantage of this method is that when activated in the traditional way, a lot of time was lost, that is, 1.5 hours. The proposed method of activating the adsorbent is less energy-intensive, reduces the process time by 13 times, and an increase in pores is observed due to the release of water vapor from the inner to the outer surface of the thermally activated adsorbent.

Based on the selected raw materials, the optimal modes for producing porous adsorbents (Tpyr. - 800±50°C, R-600±50 W, τ-7 min, ν-2450 MHz) with high adsorption efficiency were determined, by initially activating pyrolysis by the usual method, and then using water vapor at a temperature of 800°C±50°C, as well as by activating it using microwave radiation after pyrolysis using an unconventional method.

The chromatogram results show that after the adsorption of an aqueous-alcohol solution with the BAC-A adsorbent, the composition and content of carcinogenic substances in the solution was reduced to 1.5580 mg/l, acetaldehyde - 0.5580 mg/l, methanol - 0.0005 mg/l, isopropanol - 1.9374 mg/l in 1.5 times lower than the original amount, and also methanol decreased by 0.1 times, and isopropanols by 1.4 times.

Table 2. Results of a chromatogram, analysis of the composition and impurity content of an aqueous-alcohol solution before and after adsorption purification using the developed adsorbent MRPAC-A (Microwave Radiation Paulownia Activated Carbon Adsorbent) in comparison with BAC-A

№	Impurity name	Peak release time for gas chromatogram analysis, (min),	Concentration of impurities in aqueous-alcohol solution				MPC of aqueous-alcoholic solution after cleaning with carbon (OTR No. 71), mg
			before cleaning, mg/l	after cleaning with coal BAC-A, mg/l	after cleaning with coal РАУ-А, mg/l	after cleaning with coal MRPAC-A, mg/l	
1	Acetaldehyde	3.71	0.7973	0.2611	0.1308	0.1301	8,0
2	Methyl acetate	4.45	0.0920	0.0397	0.0323	0.0193	13,0
3	Ethyl acetate	5.04	0.0576	-	-	-	
4	Methanol	5.19	0.0006	0.0004	0.0002	0.0002	0,05
5	isopropanol	5.54	2.6250	1.3760	0.0226	0.0223	6,0

The results of the analysis of chromatograms show that after the adsorption of ethyl alcohol by the PPAC-A adsorbent, the content of impurities was: acetaldehyde - 0.1308 mg/l, methyl acetate - 0.0323 mg, methanol - 0.0002 mg/l, isopropanol - 0.0226 mg/l, i.e. the amount of acetaldehyde decreased by 6.0 times, compared to: with the original adsorbent, by 2.0 times, with the BAC-A adsorbent, the methanol content was 2.5 times, the amount of isopropanol decreased by almost 90 times. Also, after the adsorption of ethyl alcohol by the MRPAC-A adsorbent, the composition of the aqueous-alcohol solution is as follows: acetaldehyde - 0.1301 mg/l, ethyl acetate - 0.0193 mg, methanol - 0.0002 mg/l, isopropanol - 0.0223 mg/l, the amount of acetaldehyde decreased by 6.12 times compared to post-treatment with adsorbent, 2.1 times compared to adsorbent BAC-A, methanol - 2.5 times. Compared to imported adsorbent, the amount of isopropanol decreased by almost 90 times. A technology has been created for the production of adsorbents based on activated carbon under the influence of microwave radiation in an unconventional way, activated by water vapor under a pressure of 3 MPa and further used in the technology of deep purification from harmful compounds (acetaldehyde, methyl acetate, ethyl acetate and isopropanol) from aqueous-alcohol solutions using adsorbents with activated carbon.

4. Conclusions

The adsorbent is used as an import-substituting adsorbent for the adsorption of acetaldehyde, methyl acetate, ethyl acetate and isopropanol during deep purification from harmful impurities from aqueous-alcohol solutions using adsorbents obtained by traditional and non-traditional methods.

A basic technological scheme and technological line for the production of adsorbents PTA-A and PPAC-A using the traditional method and MRPAC-A using the non-traditional method have been developed. When purifying aqueous-alcohol solutions (acetaldehyde, methyl acetate, ethyl acetate, methanol and isopropanol) from harmful impurities with the participation of adsorbents activated MRPAC-A and the imported analog BAC-A, the adsorption of acetaldehyde was 6.12 times greater, methanol 2.6 times greater, as well as isopropanol 100 times. According to the results, the economic efficiency of purifying aqueous-alcohol solutions using the activated adsorbent MRPAC-A is estimated at 76.613 million soums per year. Savings of the activated adsorbent MRPAC-A obtained by an unconventional method in comparison with the adsorbent during activation with water vapor have been achieved by 13.0 times in time and 160.0 times in energy consumption.

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