Sorption Activity of “Taunit”-Series Carbon Nanomaterials

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Abstract. The work is dedicated to finding new modern adsorbents in order to intensify production technologies of vodka and improve the quality of finished products. In the present paper, the technology of carbon nanotubes (CNTs) synthesis is described; CNTs “Taunit”-series were obtained via chemical vapor decomposition at NanoTechCenter Ltd. (Tambov, Russia). The CNTs properties were determined by scanning electron microscopy, nitrite adsorption, laser diffraction, and thermogravimetry. The principle characteristics measured for the water-alcohol mixture were as follows: rigidity, alkalinity, oxidability, volume fraction of methyl alcohol, weight concentration of acetaldehyde, and 2-propanol and organoleptic parameters, found by using gas-chromatographic analysis. The studies performed demonstrate that the “Taunit”-series carbon nanostructured materials can be effectively used for filtering water-alcohol mixtures in the vodka production.

1. Introduction

Currently, a dynamic method for sorting handling is used in the production of vodka at most distilleries. This method consists in the fact the water-alcohol mixture is treated on coal-cleansing batteries including a sand pre-filter, a coal column and a sand filter (classical technology).

As a rule, activated carbon is used as a filter material in the coal column. BAU-A activated birch carbon made from wood charcoal through steam treatment at a temperature of above 800 ºC and pre- or post-fragmentation is most widely used for purifying water-alcohol solutions. However, studies have shown that over the past 10-15 years, wood chemical plants use not only birch, and, moreover, beech and oak, but also soft woods for producing raw charcoal. The charcoal made by them satisfies the requirements of chemical industries, but does not correspond to the requirements for production of vodka. Nevertheless, the mixed charcoal is used for manufacturing the BAU-A activated carbon. As a result, the activated carbon of low quality is obtained; it has low strength and underdeveloped microporous structure. This is due to the fact that “ballast porosity” is formed during activation of charcoal obtained from soft (loose) wood. It represents a large number of coal macro pores that appear to be “traffic arteries” but are not involved in adsorption processes, since it is known that activated carbon micropores play a determining role for cleansing water-alcohol solutions. In this regard, searching for new advanced adsorbents to intensify the vodka production technology and improve the quality of the finished product is highly urgent [1-5].

The authors suggest to use carbon nanomaterials, in particular, carbon nanotubes (CNTs) as alternative adsorbents for removing dangerous compounds in vodka production processes. The CNTs possess a large specific surface area (for single-walled CNTs - up to 3,000 m²/g), reactivity, well-developed porosity and tunable surface-containing functional groups. Therefore, adsorption
processes are one of the promising trends in their use. In particular, carbon nanotubes are widely used to eliminate organic and inorganic compounds from aqueous media [6–8].

Thus, the aim of the present paper is to develop new nanomaterials (nanotubes namely) to improve purification of water-alcohol liquids, as well as their physical, chemical and organoleptic properties.

The research novelty lies in application of new adsorbents, not previously used in the vodka production technology, for purifying water-alcohol liquids.

2. Methods and Procedures

“Taunit”-series carbon nanostructured materials “Taunit”, manufactured at NanoTechCenter Ltd. (Tambov, Russia) based on the Specifications No. 2166-001-77074291-2012 [9], were employed herein as adsorbents. Their properties were determined by the adsorption of iodine [10], methylene blue [11] and acetic acid [12].

Electron microscopy studies of the CNTs were conducted on a Neon 40 scanning electron microscope (Carl Zeiss, Germany) according to the appropriate procedures [13,14]. The device has the following characteristics: spatial resolution of 2.5 nm, accelerating voltage of 0.3...30 kV, maximum sample size - diameter of up to 200 mm, height of 80 mm, and cathode - LaB6.

Gas-chromatographic analysis of the water-alcohol liquid was performed according to the Russian National Standard No. 32039-2013 “Vodka and Ethyl Alcohol Proceeding from Food Raw Materials. A Gas-Chromatographic Method for Determining Authenticity”, which allows for identifying 29 impurities [15].

Alkalinity [16], oxidability [17], rigidity [18], contents of iron, sulfates, chlorides and silicates [19] were determined in the water-alcohol liquid, and a sensory analysis was carried out [20, 21].

The optical density of vodka was measured on as SF-26 spectrophotometer at wavelengths of 220, 240 and 260 nm in cuvettes with an absorbing layer length of 50 mm.

The hydrogen parameter (pH value) was measured with a “Microprocessor pH Meter HI 9321” ion meter.

3. Experimental

3.1. Synthesis of Carbon Nanostructured Materials (CNTs)

The “Taunit”, “Taunit-M” and “Taunit-MD” CNTs were obtained by catalytic pyrolysis of hydrocarbons in a batch reactor [22, 23]. A propane-butane gas mixture was used. The composition of the catalyst systems used in the CNT synthesis is presented in Table 1.

| CNT        | Taunit   | Taunit-M | Taunit MD        |
|------------|----------|----------|------------------|
| Catalyst   | Ni-MgO   | Co-Mo/MgO-Al2O3 | Co-Mo/ MgO-Al2O3-Fe2O3 |

The technology for catalyst preparation in the “Taunit” CNTs synthesis comprises the following steps:
1. stirring catalyst precursor substances with distilled water under heating;
2. thermal decomposition of the mixture at 600°C during 30 min.

The technology for catalyst preparation in the “Taunit-M” and “Taunit-MD” CNTs synthesis comprises the following steps:
1. preparing solutions of catalyst precursor substances and auxiliary organic components;
2. temperature treatment of the obtained mixtures under periodic stirring at 60°C until dissolution;
3. annealing the solutions at 500-550°C during 30 min;
4. calcinating the obtained xerogels at 600°C during 2 h;
5. grinding the xerogels to get the fraction of < 100-200 µm.
The characteristics of the obtained CNTs used in the present research are shown in Table 2.

Table 2. Characteristics of the “Taunit”-series CNTs [23].

| Parameter                              | "Taunit" | "Taunit-M" | "Taunit-MD" |
|----------------------------------------|----------|------------|-------------|
| Outer diameter, nm                     | 20-70    | 8-15       | 30-80       |
| Inner diameter, nm                     | 5-10     | 4-8        | 10-20       |
| Length, µm                             | 2 and more | 2 and more | 20 and more |
| Total amount of impurities, %, (after purification) | up to 5 | up to 5 | up to 5 |
| Bulk density, g/cm³                    | 0.4÷0.6  | 0.03÷0.05  | 0.03÷0.05  |
| Specific geometrical surface, m²/g     | 120      | 180-200    | 300 and more|
| Adsorption activity by methylene blue, mg/g* | 110.0  | 207.5      | 275.0       |
| Thermal stability (°C)                 | up to 600 | up to 600  | up to 600   |

The data presented in this table demonstrate that the adsorption activity is well correlated with the specific geometrical surface parameters, and the best values were obtained for the “Taunit MD” CNTs.

According to the conducted electron-microscopic researches, the studied “Taunit”-series CNTs represent one-dimensional, nanoscale, thread-like formations of polycrystalline cylindrical graphite, predominantly of cylindrical shape, with an internal channel – “multiwalled nanotubes” (MWCNTs) (Figs. 1-3). The “Taunit” CNTs synthesized from the propane-butane mixture over the Ni/MgO catalyst has a MWCNT diameter of 20-70 nm and a catalyst particle diameter of 30-50 nm (Fig. 1). In the “Taunit-M” CNTs synthesized from the propane-butane mixture over the (Co,Mo)/MgO-Al₂O₃ catalyst, the MWCNTs diameter is about 10-20 nm, and the catalyst particle diameter is about 10-15 nm. The bundles of the “Taunit-MD” thin CNTs synthesized over the Co-Mo/ MgO-Al₂O₃-Fe₂O₃ are characterized by a diameter of an individual MWCNTs of 4-8 nm; in this case, the bundle length is up to 100 or more µm. Their form represent black polydisperse powders with a grain size of 1-300 µm. They are hydrophobic and not prone to caking. As can be seen from the table, the adsorption activity parameters are well correlated with the specific geometrical surface of the studied CNTs. The “Taunit MD” CNTs presents the best parameters.

Figure 1. An SEM image of the “Taunit” CNTs synthesized from the propane-butane mixture over the Ni/MgO catalyst [23].
3.2. Processing Water-Alcohol Liquids with the “Taunit”-Series CNTs

The studies on processing the water-alcohol liquid with the “Taunit”-series CNTs were performed as follows: the liquid was stirred with the addition of the calculated amount of the CNTs (0.5, 1.0 and 2.0 kg per 10,000 L) during 1 h, then the mixture was left in contact for 1 h more and filtered.

Before and after the filtration, the gas-chromatographic analysis was carried out with the water-alcohol liquid samples: the rigidity, alkalinity oxidability, pH value, content trace elements and tasting parameters were determined.

The results of the analyses of the water-alcohol liquid before and after the processing are shown in Table 3 and Fig. 4.

The gas-chromatographic analysis showed that the initial and processed sorting contain the same amount of toxic microimpurities (the mass concentration of acetaldehyde, 2-propanol is 1 mg/dm³, and the volume fraction of methyl alcohol is 0.0058 % by weight of anhydrous alcohol).
| №   | Name sample            | Rigidity, F | Alkalinity (cm³ of 0.1 n HCl per 100 cm³) | Oxidability according to Lang, min | Tasting score, unit | pH | Mass concentration of, mg / dm³ |   |
|-----|------------------------|-------------|--------------------------------------|-----------------------------------|-----------------|----|---------------------------------|---|
|     | Maximum permissible value for sortings on the "Lux" alcohol |             |                                      |                                   |                 |    |                                 |   |
| 1   | Initial sorting        | 0.02        | 0.1                                  | 10.5                              | 9.30            | 6.2 | 0.004                           | 5.0 | 0.8 | 0.2 |
| 2   | Sorting after processing with the "Taunit" CNTs, kg / thousand. decalitres | 0.5         | 0.3                                  | 11.2                              | 9.44            | 6.5 | 0.005                           | 8.1 | 1.3 | 0.2 |
| 3   | 1.0                     | 0.3         | 0.3                                  | 12.3                              | 9.46            | 6.6 | 0.005                           | 8.1 | 1.2 | 0.25 |
| 4   | 2.0                     | 0.25        | 0.25                                 | 12.0                              | 9.45            | 6.6 | 0.005                           | 8.1 | 1.2 | 0.2 |
| 5   | Sorting after processing with the "Taunit-M" CNTs, kg / thousand. decalitres | 0.5         | 0.25                                 | 12.0                              | -               | 6.7 | 0.004                           | 5.5 | 0.9 | 0.25 |
| 6   | 1.0                     | 0.2      | 0.20                                 | 13.4                              | 9.48            | 6.78| 0.004                           | 5.5 | 0.9 | 0.25 |
| 7   | 2.0                     | 0.25        | 0.20                                 | 14.0                              | 9.47            | 6.80| 0.004                           | 5.5 | 0.9 | 0.25 |
| 8   | Sorting after processing with the "Taunit-MD" CNTs, kg / thousand. decalitres | 0.5         | 0.20                                 | 13.0                              | -               | 6.95| 0.0045                          | 6.0 | 1.0 | 0.28 |
| 9   | 1.0                     | 0.25        | 0.25                                 | 14.4                              | 9.50            | 7.11| 0.0045                          | 6.0 | 1.0 | 0.28 |
| 10  | 2.0                     | 0.25        | 0.25                                 | 16.0                              | 9.51            | 7.3 | 0.0045                          | 6.0 | 1.0 | 0.28 |
The initial sorting possessed a rigidity of 0.02, alkalinity of 0.1 cm³ of 0.1 n HCl solution per 100 cm³; oxidability (according to Lang) of 10.5 min, and pH value of 6.2. The content of iron, sulphates, chlorides and silicate was 0.004, 5.0, 0.8 and 0.2 mg/dm³, respectively.

After processing, the increases of the following parameters took place: alkalinity - from 0.1 to 0.2-0.3 cm³ of 0.1 n HCl solution per 100 cm³, and pH value - from 6.2 to 6.5-7.3, thereby indicating the "alkaline" properties of the CNTs. For the "Taunit" CNTs, the content of sulfates and chlorides also increased. The other parameters slightly changed.

**Figure 4.** Difference in the oxidability (min) after the processing with the CNTs.

The difference in the oxidability between the sorting after the processing increased by 0.7-5.5 min, the best one – by 5.5 min - was observed for the "Taunit-MD" CNTs at its dosage of 2 kg/10,000 L.

**Figure 5.** Difference in the tasting scores (min) after the processing with the CNTs.
The processing with the CNTs allowed improving the organoleptic characteristics of vodka, since the tasting scores increased by 0.14–0.21 units, the best difference, by 0.21 units, was observed for the "Taunit-MD" CNTs at its dosage of 2 kg/10,000 L.

Conclusion

The study was conducted to obtain new modern adsorbents in order to intensify production technologies of vodka and improve the quality of finished products. Studies have indicated that “Taunit”-series materials can be used effectively for product refining. It can be concluded that the “Taunit”-series CNTs adsorbents are promising for cleansing water-alcohol solutions, and the best results were achieved for the "Taunit-MD" CNTs.

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