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Water-alcohol adsorbing cleaning out of higher alcohols by shungite

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Abstract

Introduction. The aim of the research work is to increase the quality and safety of high spirits solutions at the expense of using natural adsorbent shungite.

Materials and methods. Water-alcohol solutions with 40% concentration and natural adsorbent shungite and being under research here. The solution was passed through the layer of shungite. The content of alcohol was determined by a calorimeter method. Components composition of alcohol was being established with the help of chromatograph “Agileut HP-6890” having a column HP FFAP 50m/032 mm-mkm.

Results and discussion. The duration of interaction of water-alcohol solutions with shungite for 20 minutes is optimal in cleaning process. Alcohol is adsorbed more effectively at 0-10°C temperature of the solution decreasing its content from 12.5 to 1.5 mg/dm^3. Increasing the temperature of water-alcohol solution from 10 to 25°C is followed by increasing the quantity of alcohol from 1.5 to 2 mg/dm^3. The cleaning process at 25^{0}C of water-alcohol solution is considered irrelevant. Shungite effectively adsorbs alcohol which is harmful for human’s health. Hence, the content of n-propanol decreases from 1.71 to 1.35 mg/dm^3. The content of methanol in water-alcohol solution also decreases from 0.0016 to 0.00035 mg/dm^3. It can be explained by the fact than shungite has got a developed spongy structure and high adsorbing properties. The existence of shungite deposits, its reasonable price and ecological security gives way to its using for cleaning water-alcohol solutions. The decreased concentration of alcohols in water-alcohol solutions improves orhanoleptic properties of alcoholic drinks and increases their drinking quality.

Conclusions. It is highly recommended to use the results of the research for the production of alcohol beverages. This will improve their quality and safety.

Introduction

High quality rectified ethyl alcohol produced out of food raw material is used to obtain competitive beverages in Ukrainian alcohol production. Rectified alcohol consists of ethanol, water and volatile impurities that significantly affect not only its organoleptic and physico-chemical properties, but also the products produced out of it.

About 200 different contaminants have been identified, but their content does not exceed 0.5-0.6% of the total ethanol [1, 3]. The largest share of them (0.35-0.45 %) are higher alcohols (fusel oil) that provide specific ethanol unpleasant smell and taste and therefore their content is regulated.

The main task of brahorektyfication is to get rectified alcohol with a minimum content of impurities that degrade its quality. However, unwanted impurities remain in ethanol and get into water-alcohol solutions out of which vodka is produced.

Nowadays , alcohol companies in Ukraine use sorption processes to clean water-alcohol out of higher alcohols and other unwanted impurities [4-6]. As sorbents the most commonly used are wood active carbon BAU-A. Active coal contributing to catalytic processes is combustible adsorbent and too expensive.

In recent years, the scientific literature reported about water-alcohol cleaning with natural clay minerals from Ukrainian fields by palygorskite, glauconite, saponins [7-12]. Natural adsorbents were effective absorbing contaminants of alcohol, but during the separation of water-alcohol_out of sorbent there is significant hydraulic resistance in the absorber created by a layer clay stuff. Such state of things has become a prerequisite for continuation searching cheap and effective materials that could technologically and economically meet the requirements for adsorbents of alcoholic beverage industry.

A number of researchers for cleaning fruit and vegetable juices and other products used natural carbon containing adsorbent shungit which has high adsorption properties, mechanical stability, and is an environmentally safe sorbent [13].

Materials and methods

The object of research – the process of cleaning water-alcohol solutions.

Materials: water-alcohol solutions, natural sorbent shungite, the quality of cleaning water-alcohol solutions.

Water-alcohol solution has concentration of 40 volumetric percent. The choice of such concentration is caused by the typical concentration alcohol beverages like horilkas.

Industrial samples of water-alcoholic solution were used in research work.

Shungite. Industrial sample of shungite was used for cleaning water-alcohol solutions. The size of shungite particles is 2 mm.

Experimental installation. The laboratory set up has been designed for this purpose and the diagram is shown in fig. 1.

The main element of the installation is the adsorption column 0.45 m high and 0.024 m in diameter. The bottom hole and the layer of the adsorbent column were covered with cloth filter to prevent ingress of powdered Shungite into purified water-alcohol solution. Pretermoactivated shungit was put in the adsorption column in an amount of 230 g. Water-alcohol with concentration of 40% was added to the pressure container 1. Delivery speed of water-alcohol into the column and the length of the contact were regulated by valve 2. Water-alcohol delivery was carried upwards: its first 150 cm^3 returned back to cleaning. Selected samples were analyzed according to the generally accepted physicochemical and chromatographic methods [6].

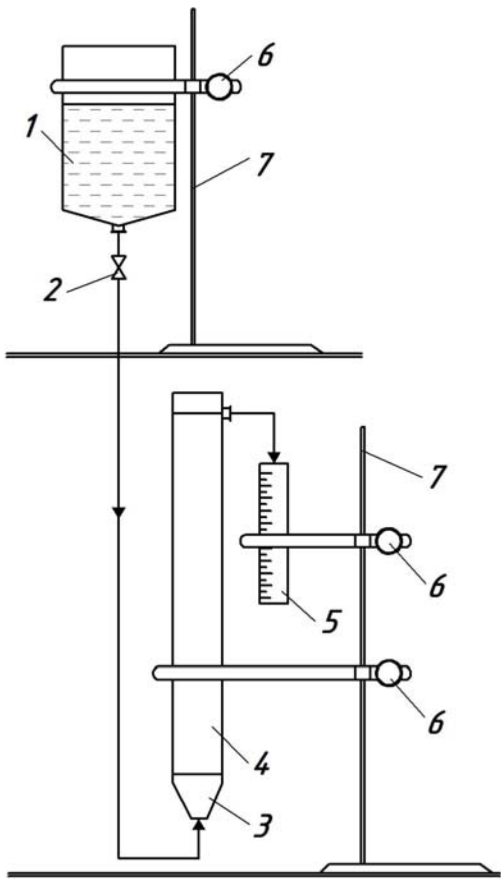

Fig. 1 - Laboratory installation for cleaning water-alcohol:
1 - lifting capacity 2 - control valve,
3 - adsorption column, 4 - adsorption material, 5 - measuring cylinder,
6 – clip, 7 - tripod

Preparation of research shungite samples.

Before using minerals were weighed on laboratory scales and dried in Electrical SESh-1 at a temperature of 140° C for 1.5 h. The dried adsorbent was cooled for 30 minutes in a desiccator and filled in the adsorption column.

Methods of conducting the experiment.

The strength of water-alcohol solutions was checked by areometrical method.

Mass concentration of higher alcohols (except propyl and isopropyl) in water-alcohol was determined by colorimetric method measuring the optical density of the colored solution obtained after interaction of higher alcohols with salicylic aldehyde and concentrated sulfuric acid. Sequence of determination of the mass concentration of higher alcohols with salicylic aldehyde was as follows: 10 cm^3 of concentrated sulfuric acid was slowly added into the tube: 5 cm^3 of researching water-alcohol were put into the first tube, 5 cm^3 of standard solutions containing fusel alcohols 1, 2, 3, 4, 5 mg/dm^3 of anhydrous alcohol were put in the others. 0.7 cm^3 of alcoholic solution of salicylic aldehyde was added into each tube. The tubes were closed with ground-crusts. The contents of the tubes were shaken and placed in a boiling water bath for 10 minutes. The tubes were cooled to a temperature of 20 ± 0,5 °C and the optical density of the formed yellow solution was measured immediately for photoelectric filter with a wavelength of light of 540 nm in a cuvette with a thickness of 20 mm facets compared with distilled water.

Chromatographic determination of the content of higher alcohols was performed on chromatograph «Agileut HP-6890", with a column HP FFAP 50 m/032mm-mkm.

Result processing.

According to the results the calibration curve was constructed by plotting on the horizontal axis the mass concentration of fusel oil, and corresponding values of absorbance of standard solutions were constructed on the vertical axis. Mass concentration of fusel oil in studying water-alcohol was determined by its optical density.

Results and discussion

The results are presented in fig. 2 and 3.

As it can be seen from fig. 2, the content of higher alcohols in water-alcohol in her contact with Shungite falls rapidly during the first 15 minutes, decreasing from 12.5 to 2.0 mg/dm^3. The following duration of their interaction reduced the number of fusel oil to 0.8 mg/dm^3.

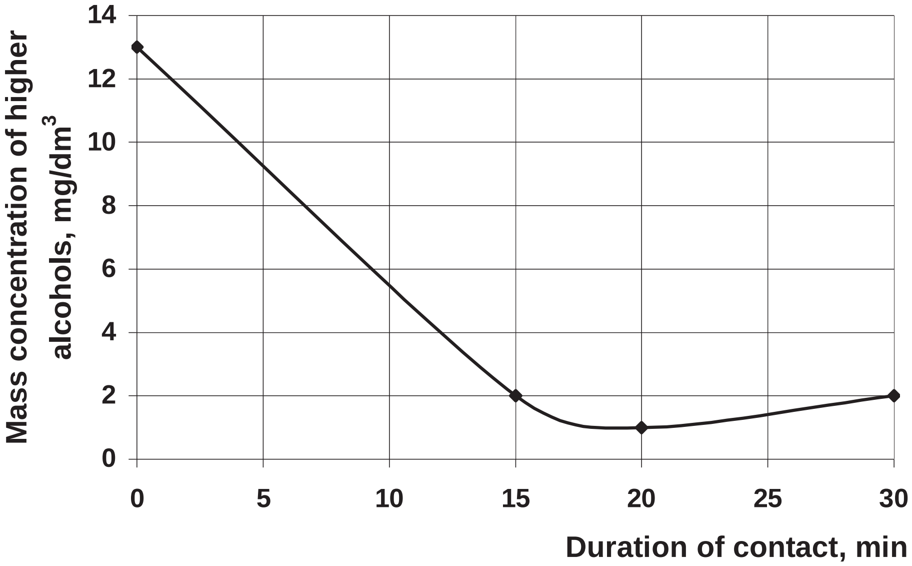

Fig. 2. Duration effect of processing water-alcohol on the content of higher alcohols

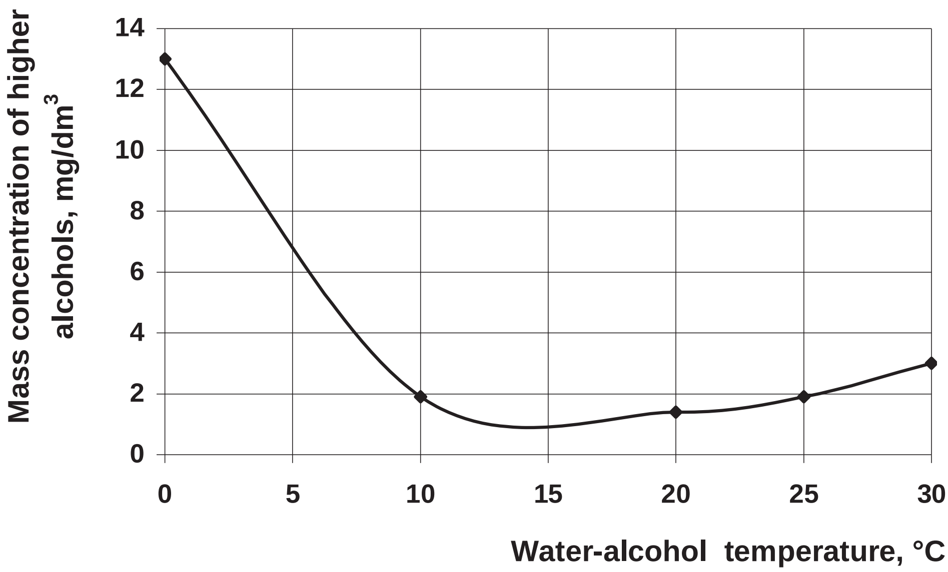

Fig. 3. Effect of water-alcohol temperature on the content of higher alcohols at the duration of its processing by Shungite for 30 min

But with duration increasing of interaction water-alcohol and Shungites to 30 minutes the content of higher alcohols increased to 1.6 mg/dm^3. This can be explained by the fact that the activity of Shungite during the first 15 minutes is the highest and its active centers were filled with molecules of higher alcohols. Then the presence of oxygen created conditions for passage of catalytic processes accompanied by an increase in the content of impurities. Therefore, it follows that the duration of cleaning water-alcohol by Shungite should not exceed 30 minutes.

From the analysis of the results presented in fig. 3, we see that higher alcohols were adsorbed efficiently at water-alcohol temperatures 0-10 °C. In this temperature range the concentration of higher alcohols in water-alcohol solution decreased from 12.5 to 1.5 mg/dm^3. When the temperature was risen to 20 °C, an increase in the number of higher alcohols to 2.0 mg/dm^3 was observed. A further increase in temperature during water-alcohol purification by Shungite helped to rise the number of fusel oil. This can be explained by the fact that the adsorption is an exothermic process accompanied by heat, so the lower temperature processing of water-alcohol by adsorbent, the better fusel oil is adsorbed.

Dynamics of adsorbtion n-propanol, i-propanol and methanol from water-alcohol by shungite at different duration of its interaction with the adsorbent presents scientific interest, as the presence of the above mentioned additives significantly impairs sensory parameters both water-alcohol and vodkas.

The results of chromatographic analysis of the original and refined water-alcohol by shungite are presented in the table.

Dynamics of n-propanol, i-propanol, methanol content

Name of additive	Content of impurities in the original water-alcohol mg/dm^3	The duration of contact of water-alcohol with Shungite, minutes					
		5	10	15	20	25	30
n-propanol	0.4074	0.2008	0.1853	0.1635	0.1466	0.1267	0.1407
i-propanol	1.7180	1.6624	1.6309	1.5949	1.5843	1.4115	1.3533
methanol	0.0016	0.0004	0.0004	0.0004	0.0004	0.0004	0.00035

It is seen that shungite effectively adsorbs n-propanol at 25 minutes interaction with water-alcohol and reduces its content more than three times. A longer contact with water-alcohol promotes a slight increase in the concentration of n-propanol, indicating the presence of catalytic processes.

Adsorption capacity of shungite for i-propanol appeared to be negligible. Probably, branching of molecule i-propanol makes absorption difficult.

Methanol is adsorbed by Shungit over interaction time of the adsorbent with water-alcohol. Already after 5 minutes the content of this harmful impurity is reduced four times, remaining at this level for 25 minutes. Thus, a reasonable duration of the sorption process of n-propanol and methanol should be regarded as 25 minutes.

Conclusions

1. Shungite is an effective sorbent for the removal of higher alcohols out of water-alcohol.
2. When using shungite with particles size 2.0 mm the duration of process should not exceed 25 minutes at water-alcohol temperature 10-25 °C.
3. Shungite effectively adsorbs higher alcohols harmful for people’s health. The content of n-propanol decreases from 0.41 to 0.14 mg/dm^3, i-propanol from 1.71 to 1.35 mg/dm^3 and methanol - four times.

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