Improvement of the quality and safety of alcohol solutions through their adsorptive refining by natural minerals

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Анотация: *Представени са резултатите от изследването на очистването на алкохолни разтвори от вредни примеси и тежки метали с палъгорскит и хидрослюда. Даден е механизмът на адсорбция на примесите с природните адсорбенти.*

Abstract: *This article presents the research results for adsorptive purification of alcoholic solutions from harmful impurities and heavy metals with paligorskite and hydromica. The authors have grounded the mechanism of adsorbing impurities by natural adsorbents.*

The quality of alcoholic drinks, specially, that of vodka, depends on physicochemical parameters of water and alcohol.

Composition of different impurities, which determine the taste of alcohol, aqueous-alcoholic solutions (sortovkas), and later of vodka can be reduced due to adsorptive refining of aqueous-alcoholic solutions by natural dispersible minerals, the deposits of which in Ukraine are very great.

Among the researched minerals of the Ukrainian deposits paligorskite and hydromica appeared to be the most effective adsorbents in refining aqueous-alcoholic solutions [1,2].

In order to define adsorptive capacity of paligorskite and hydromica as to the basic groups of impurities of ethanol which negatively influence the qualitative parameters of aqueous-alcoholic solutions, the authors of this article conducted the researches as to the selectivity of paligorskite and hydromica regarding ethers, aldehydes, higher alcohols.

During the experiments the authors used industrial samples of sortovka, paligorskite and hydromica of a fraction 3,0÷2,0 mms, termperature activated in advance at the temperature of 190 °C for 3 hours.

Sortovka passed through adsorbent bed, with the mass of 4gram and velocity of 0,001 m/s. The purified solutions were analyzed with the help of chromatograph "Цвет - 2000".

The histograms of paligorskite and hydromica were received with the help of the gas evaluator "Nova-2000". A composition of heavy metals in aqueous-alcoholic solutions before and after adsorptive refining by natural minerals was determined with the help of atom-adsorptive spectrometer "C - 115-M1". Restoration of adsorptive capacity of natural adsorbents was studied with the help of designed and produced laboratory-scale plant under specially drawn technique. The received resultes are represented in fig. 1-5.

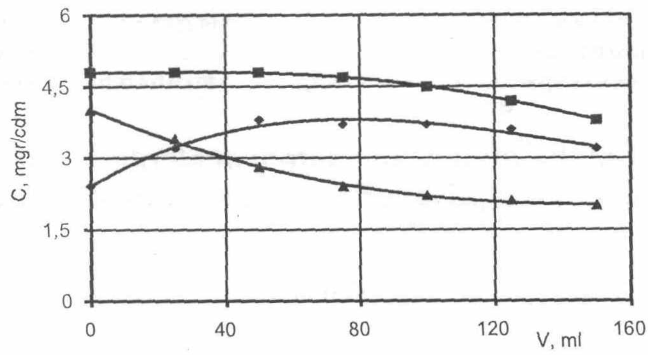
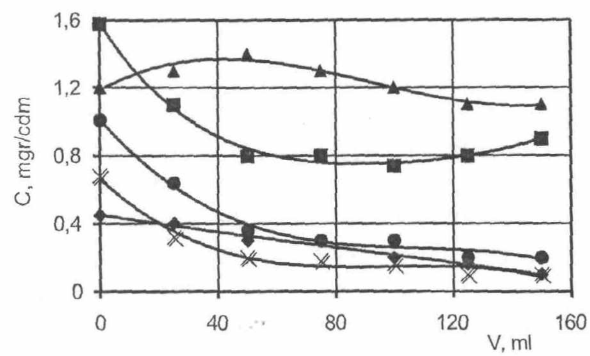


Fig. 1. Dependence of impurity concentrations in sortivka which passed through the bed of paligorskite (a), hydromica (b) of a fraction 3,0 ÷ 2,0 mm with velocity of sortovka 0,001 m/s.

♦ – aldehydes; ■ – ethers; ▲ – higher alcohols.

As it is clear from fig. 1 (a) paligorskite adsorbs aldehydes, ethers, higher alcohols, reducing their initial composition from 2,4 up to 1,5 mg/dm^3, from 4,8 up to 2,5 mg/dm^3, from 4 up to 2,8 mg/dm^3, accordingly. When refining aqueous-alcoholic solutions by hydromica, the composition of ethers decreases from 4,8 up to 3,8 mg/dm^3, higher alcohols from 3,8 up to 1,9 mg/dm^3, while the amount of aldehydes increases from 2,4 up to 3,1 mg/dm^3.

The resultes of research as to the selective adsorption of ethanol impurities by paligorskite and hydromica are represented in fig. 2 (a, b) and 3 (a, b).



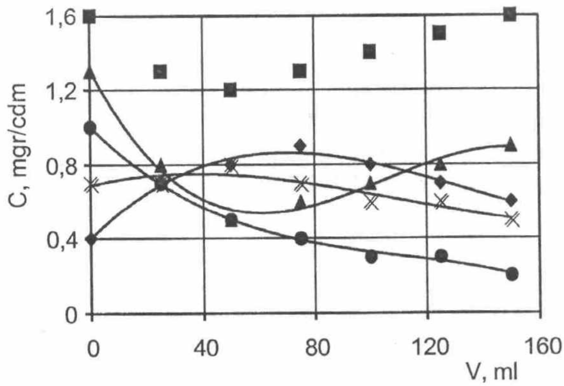
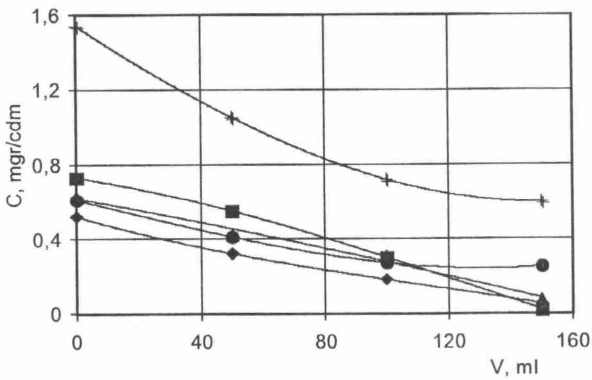


Fig. 2 Component-wise compositions of ethers the aqueous-alcoholic solution refined by paligorskite (a) and hydromica (b) of a fraction 2,0 ÷ 3,0 mm .
♦ – methyl acetate; ■ – ethyl acetate; ▲ – isobutil acetate; ● – isoamyl acetate;
x – ethylbutirat



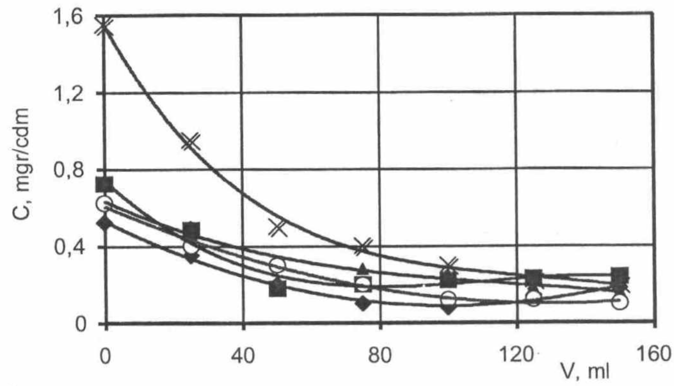


Fig. 3 Component-wise compositions of higher alcohols in aqueous-alcoholic solution refined by paligorskite (a) and hydromica (b) of a fraction 2,0 ÷ 3,0 mm.
♦ – n-propanol; ■ – isobutanol; ▲ – n-butanol; ● – isoamynol; **x** – n-amynol

From fig. 2 (a, b) and 3 (a, b) it is clear, that paligorskite better adsorbs ethyl acetate, methyl acetate, isoamyl acetate, ethylbutirat, n-propanol, n-butanol, isobutanol, while hydromica adsorbs more efficiently isobutyl acetate, n-amynol, isoamynol.

The adsorption of undesireable imurities from aqueous-alcoholic solutions is characterized by peculiarites of mineral porous structure, the magnitude of their pores size, introduced in fig. 4 (a, b) in the form of histograms.

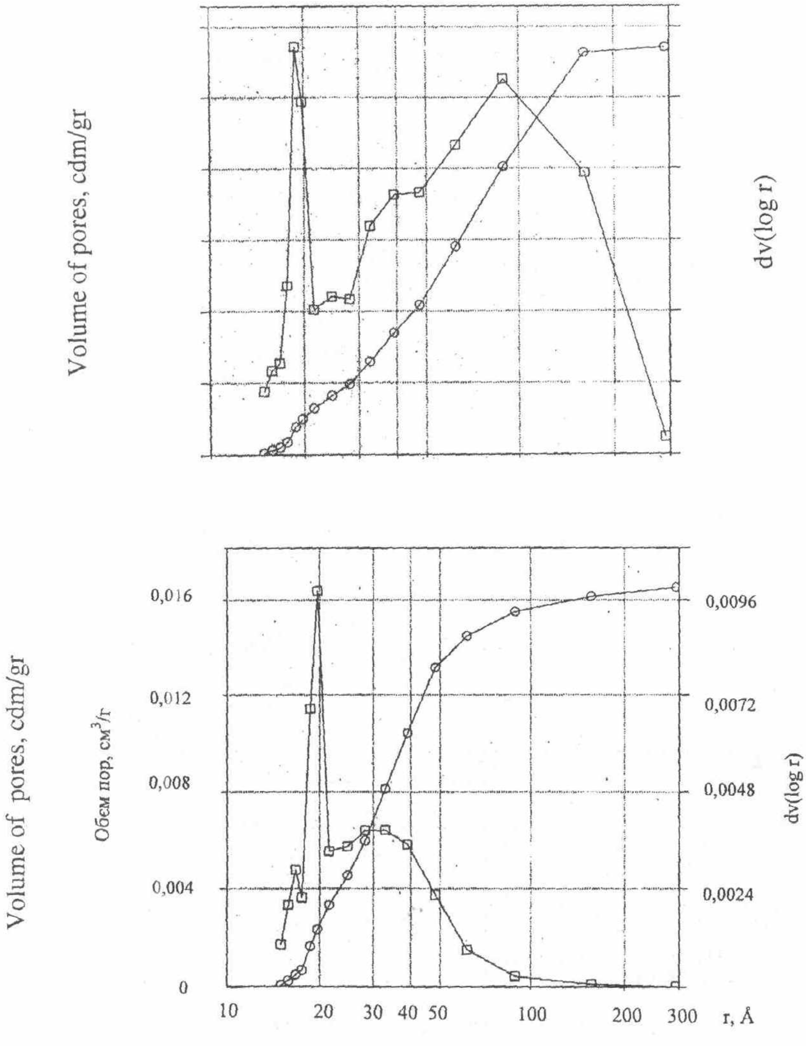


Fig. 4 Histograms of allocation of paligorskite (a) and hydromica (b) pores
○ – integral curve of allocation of pores size;
□ – differential curve of allocation of pores due to their sizes.

It is clear, that the histograms of paligorskite and hydromica differ essentially. The pores of paligorskite are distributed within limits of 1,5÷30,0 nm (fig. 4). The narrow allocation of pore widths around 2,0 nm (20 Å) is caused by the availability of micropores created in paligorskite during the formation of structure of silica-alumina beds. They are proportionate with the width of separate silicate bed (~1,0 nm).

The broad band of allocation mesopores, massed about 9,0 nm (90 Å) is explained by existence of slots between separate accumulations of silica-alumina beds. It is possible to consider that there are pores between separate dispersed particles of paligorskite.

The existence of such allocation of pores in a mineral causes adsorptive capacities, especially the selectivity of adsorption as to carbohydrates. In micropores ~2,0 nm proportionate organic molecules will be adsorbed. In other words, it is possible to suppose, that this mineral will adsorb selectively higher alcohols and aldehydes and will not practically adsorb the molecules of ethanol. On the histogram (fig. 4-a) there is allocation of pores not only due to linear dimensions, but also due to the size of pores: the size of micropores - 0,002 sm^3/g, mesopores - 0,021 sm^3/g, and the curve of allocation of pores size proves this. The received values can be used in calculations in order to define expenditure of paligorskite for adsorptive refining ofsortovka from impurities.

Capacity of hydromica to adsorb different impurities can be explained by the availability of pores which radiuses lie within limits 1,5÷9,0 nm (fig. 4-b). On the histogram it is shown, that hydromica has the greatest amount of pores with radius of 2,0 nm. The amount mesopores with radius from 2,2 up to 4,0 nm from 5,0 up to 9,0 nm - is lower. Fig.4 shows that the size of mesopores varies from 0,001 till 0,016 sm^3/g. Naturally, such holes are less accessible to molecules with large molecular weight.

In order to study ecological safety of the usage of paligorskite and hydromica, the aqueous-alcoholic solutions were refined from heavy metals. For comparision the authors of the article conducted the analysis as to the volume heavy metals after refining by natural minerals and birch active carbon (BAC-A).

The received data is represented in fig. 5.

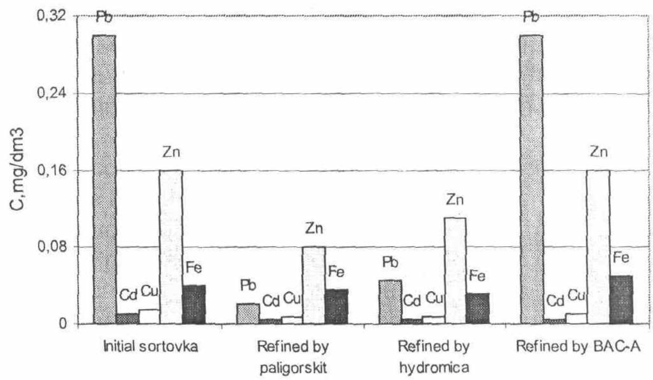


Fig. 5 Composition of heavy metals (mg/dm^3) in sortovka, refined be paligorskite, hydromica and BAC - A.

From fig. 5 it is clear, that the quantity of plumbum in aqueous-alcoholic solutions decreases in 5-10 times, cadmium, copper, zinc, iron - almost twice, and that proves the prospects of the usa of natural minerals, as sorbents of heavy metals from alcohol solutions. BAC-A does not adsorb heavy metals from aqueous-alcoholic solutions.

Comparing the results received, it is necessary to note, that paligorskite adsorbs more effectively plumbum and zinc from aqueous-alcoholic solutions, and hydromica is more effective when adsobing cadmium and iron.

Literature

1. *Mank V.V., Melnyk L.N.* Use of Clay minerals for adsorptive refining of aqueous-alcoholic solutions // Acta geodynamica et geomaterialia. - 2005. - V. 2. - №2 (138). - P. 113-117.

2. *Melnyk L.N., Mank V.V.* The usage of hydromica for adsorptive purification of aqueous-alcoholic solutions // Scientific works of NUFT. – 2005 - №16. – P.112-114

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