Acta Geodyn. Geomater., Vol.2, No.2 (138), 113-117, 2005

USE OF CLAY MINERALS FOR ADSORPTIVE CLEARING OF AQUEOUS-ALCOHOLIC SOLUTIONS

Valerij V. MANK and L. N. MELNYK

National University of Food Technologies, Vladimirskaya, 68, Kiev, Ukraine
Corresponding author's e-mail: emerald_era@hotmail.com, oloore@ua.fm

(*Received* September 2004*, accepted* May 2005)

ABSTRACT
Clay minerals palygorskite and hydromica effectively sorb impurities worsening ethanol quality. Using of combined sorbents for clearing aequeous-alcoholic solutions appears to be necessary. Natural minerals palygorskite and hydromica are ecologically safe adsorbents.

KEYWORDS: sorbents, mordenite, clinoptilolite, montmorillonite, saponite, glauconite, hydromica, palygorskite, Ukrainian deposits, "sortovka"

1. INTRODUCTION

A technological progress introduces in the production new kinds of engineering and technologies directed to the sparing of materials, energy and thermal resources with parallel preservation and improvement of product quality.

The production of food ethanol is one of those stabile and developing industries in Ukraine. To turn Ukraine economy oriented to the world market, one has to increase the productivity, apart from other things, by using progressive technologies in food-ethanol industry.

The demands for increasing quality of food alcohol have become more severe and tough making the problem of searching more effective methods for alcohol purification more actual and urgent. Impurities in food ethanol, aggravating their organoleptic properties, are the reason of disability to meet the demands of international standards.

Considerable quantity of refined ethanol is spent for the production of vodka items. A quality of vodka, so-called "sortovka", being received from 40 % aqueous-alcoholic solutions depends on the quality of the initial alcohol and water.

In the liqueuer-vodka production, "sortovkas" are subjected to the process of adsorptive clearing by active carbon, because they may contain rather high parts of aldehydes, ethers, higher alcohols, acids, negatively influencing the quality of vodka compared with standards.

Active carbon – is an effective sorbent, but expensive one. This fact has initiated a search of new cheaper and effective adsorbents, and this is the purpose of the given research.

Following minerals from Ukrainian deposits were used to find the effective sorbents: mordenite, clinoptilolite, montmorillonite, saponite, glauconite, hydromica and palygorskite.

2. METHODS

The research on "sortovka" cleaning was performed in laboratory conditions. After filtering both purified "sortovka" as well as initial one were analyzed to determine content of impurities and to compare each other. Analyses were carried out by gas chromatograph Colour-2000 with a pillar KP FFAP 50 m/0.32 mm*mkm.

3. RESULTS AND DISCUSSION

Obtained chromatogram of "sortovka" after adsorptive cleaning by palygorskite is shown in Fig. 1.

As a rule, each impurity of ethanol needs certain time to be escaped from a solution. At first, on a chromatogram there are lightly fugitive substances, such as acetaldehyde, methyl acetate and others. Peak of ethanol is very high because of its high concentration in "sortovka" compared to impurities therein. The chromatogram seems to be authentic, because all peaks have sharp image and a computer program demonstrates the concentration magnitude of each impurity. A similar chromatogram is referred to the manual on tool methods for the researches on analogous food articles (Nollet, ed., 1996).

For researching industrial "sortovka", designs with different component structure of impurities were taken.

The generalized experimental data obtained from researches on "sortovka", being adsorptively cleaned by natural dispersible minerals, are shown in Table 1.

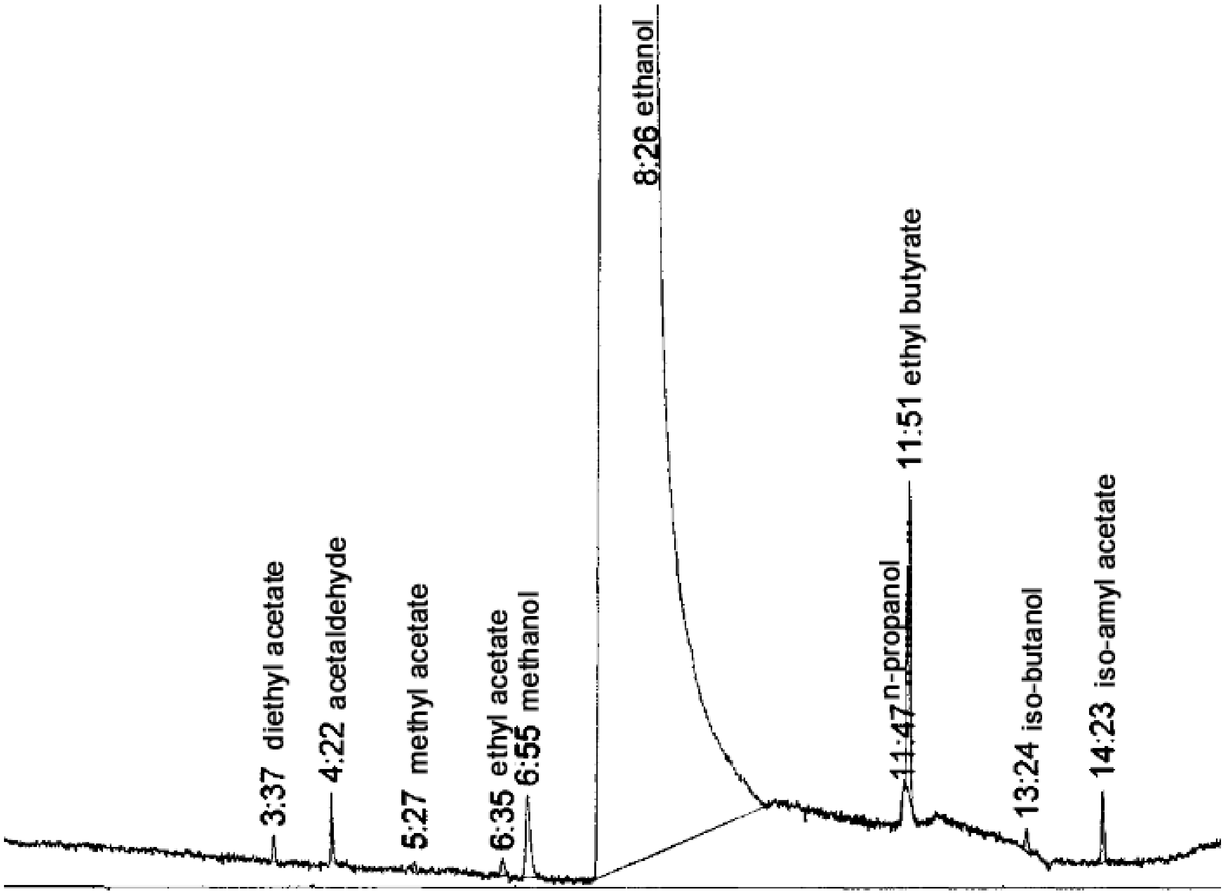

Fig. 1 Chromatogram of "sortovka" after adsorptive cleaning by palygorskite

Considering the outcomes of Table 1 all introduced minerals effectively adsorb higher alcohols. Palygorskite and hydromica also clean sortovka from aldehydes and ethers. Therefore, palygorskite and hydromica are apparently very effective sorbents to be used for "sortovka" adsorptive cleaning. Reserves of these minerals in Ukraine are rather large.

Interesting results were obtained when the initial "sortovka" was cleaned with different adsorbents, namely by palygorskite, hydromica and active carbon BFC (birch fissile coal) and CFC (core fissile coal). The results of this procedure are shown in Table 2.

As proved, "sortovka" cleaned by coal BFC has been accompanied by the accumulation of impurities, what demonstrates the presence of catalytic processes. Extension of purification time by BFC causes an increase of the content of undesirable impurities. Similar processes occur when "sortovka" is purified by CFC.

As seen from Table 2 the aldehyde content increases a little bit during several first minutes of contact between palygorskite and hydromica with "sortovka". Afterwards, the content of undesirable impurities decreases. Cleaning of "sortovka" from ethers by palygorskite is suggested to be more effective than that by hydromica. Both natural minerals also effectively clean higher alcohols reducing the initial contents 3-4 times.

Best results were obtained if "sortovka" was cleaned by the mixture of sorbents, as shown in Table 3.

The obtained results show the effective clearing of "sortovka" by combined sorbents consisting of palygorskite+hydromica in the ratio 1:7, palygorskite+BFC in the ratio 2:1, palygorskite+CFC in the ratio 2:1 . In this process the minor catalysis takes place and as the result n-butanol will be derived.

As we can see, using BFC as a sorbent in "sortovka", the impurity n-butanol, which one was not in the initial solution, will be found. N-butanol, tail impurity, is removed from a rectification column together with higher alcohols. The aforesaid impurity worsens the taste of "sortovka", adding an odour of higher alcohol and a rancid taste thereto. The amount of higher alcohols is increasing. CFC sorbs higher alcohols from "sortovka" better than BFC. The comparative analysis of adsorptive capacities of coals, palygorskite and hydromica shows, that the natural minerals are more effective in "sortovka" clearing and they can be offered for the industrial usage in vodka

Table 1 Contents of basic impurities in "sortovkas" purified by natural dispersible minerals

Sorbent	Contact time, sec.	Quantity of impurities, mg/dm^3		
		Aldehydes	Ethers	Higher alcohols
1	2	3	4	5
Initial "sortovka"	–	3.85…3.94	8.95… 9.64	12.6…13.54
Mordenite	600	4.65…5.04	8.52…9.6	3.28…4.33
	1200	4.38…5.17	8.44…9.35	2.43…4.14
	1800	4.3… 4.89	8.29…9.19	2.31…2.85
Palygorskite	600	2.14…2.75	7.54…8.22	2.81…3.57
	1200	2.63…2.7	7.94…9.14	3.19…3.90
	1800	3.02…3.16	9.55…9.67	2.50…3.39
Saponite	600	3.82…4.07	7.20…8.42	7.4…..7.9
	1200	3.65…4.29	6.70…7.00	5.07…7.8
	1800	3.52…4.00	6.41…6.77	4.9…..5.75
Glauconite	600	3.7….4.05	10.8…11.4	4.75…4.91
	1200	3.8….4.21	10.53..11.49	2.3…..3.2
	1800	3.9….4.33	10.3…11.02	2.04…2.75
Montmorillonite (Cherkassk)	600	3.6….4.2	9.14..10.63	7.05…8.21
	1200	3.62…4.66	9.6…..9.6	3.24…3.58
	1800	3.18…3.79	8.10…9.6	4.02…4.97
Clinoptilolite	600	4.15…4.25	8.67…9.02	5.12…5.33
	1200	4.37…4.45	11.0…11.06	4.30…4.75
	1800	3.69…3.82	10.1…10.19	4.02…4.17
Hydromica	600	4.22…4.75	7.64…8.45	3.45…3.81
	1200	3.02…3.75	8.38…9.65	3.92…4.17
	1800	3.12…3.45	8.45…9.81	4.10…4.26

Table 2 Contents of basic impurities in "sortovkas" purified by BFC, CFC, palygorskite and hydromica

Sorbent	Contact time, sec.	Quantity of impurities, mg/dm^3		
		Aldehydes	Ethers	Higher alcohols
Initial "sortovka"	–	8.75	15.733	3.2727
BFC	600	10.048	19.2309	6.0519
	1200	6.9237	14.5389	5.1209
	1800	13.935	17.843	6.062
CFC	600	12.428	16.662	6.1507
	1200	10.951	17.073	4.2564
	1800	6.5133	9.9114	2.5175
Palygorskite	600	10.055	15.23	0.50251
	1200	8.912	14.075	0.523
	1800	7.430	14.02	0.5122
Hydromica	600	9.120	15.320	0.920
	1200	8.07	15.270	0.850
	1800	8.000	15.030	0.630

Table 3 The contents of impurities in initial "sortovka" and in "sortovka" purified by palygorskite, hydromica and the combined sorbent (palygorskite+hydromica in the ratio 1:7) in mg/dm^3

Sorbent	Iso-butanol	N-butanol	Iso-aminol	N-aminol	Total quantity of higher alcohol impurities
Initail sortovka	3.1907	–	3.3155	3.7535	10.260
Palygorskite	0.78588	0.41394	1.2003	1.3089	3.709
Hydromica	1.8419	0.34584	0.87141	0.51582	3.575
Palygorskite+Hydromica in the ratio 1:7	1.0938	0.26922	0.69026	0.62727	2.681
Palygorskite+BFC in the ratio 2:1	0.21725	0.911	0.4820	0.5107	2.121
Palygorskite+CFC in the ratio 2:1	1.2978	0.3015	0.3975	0.82215	2.819

production instead of expensive coals or in a combination with them (Mank, Marinčenko, Melnik, 2004).

Using natural adsorbents for clearing of "sortovka" it is necessary to confirm their ecological safety. Thus patterns of initial palygorskite before and after adsorption were examined with the aim of finding harmful impurities in "sortovka" by the device MX 7304A. The obtained mass-spectra of the adsorbed sheet components, which were eliminated from the palygorskite surface due to temperature-programmed desorption in the temperature range 20 - 700 °C (Pokrovskiy, 1995), are introduced as temperature mass-spectrograms in Fig. 2.

We can see (Fig. 2A) five maximas of eliminated parts of destroyed molecules of water and groups OH (m = 18, 17), which are in an adsorption sheet: two - in the field of temperatures 50 - 150 °C, corresponding to physical connection of adsorbed molecules with the surface of an adsorbent, and three - in area 340 - 700 °C, corresponding to corruptings of chemical bonds.

There are also in the spectrogram peaks of parts of organic matters (m = 29, 44, 57) which belong to molecules of destroyed humic and fulvic acids present in soil waters.

After realization of impurities adsorption from aqueous-alcoholic mixtures, peaks of eliminated water and OH groups increased greatly (Fig. 2B).

New molecule fragments, which could appear during the adsorptive process and could worsen "sortovka" quality, have not been found. Thus natural palygorskite is ecologically safe adsorbent.

REFERENCES

Handbook of food Analysis vol/1 and 2, edited by L.M. Nollet: 1996, by Marsel Derkker, New York.

Mank, V., Marinčenko, V. and Melnik, L.: 2004, Kombinovanij sorbent. Charčova a pererebna promislovisť, Kiev, 26-27.

Pokrovskiy, V.A.: 1995, Temperature – programmed mass spectrometry of biomolecules in surface chemistry studies. Rapid Communications in Mass Spectrometry, Kiev, v. 9, 588-591.

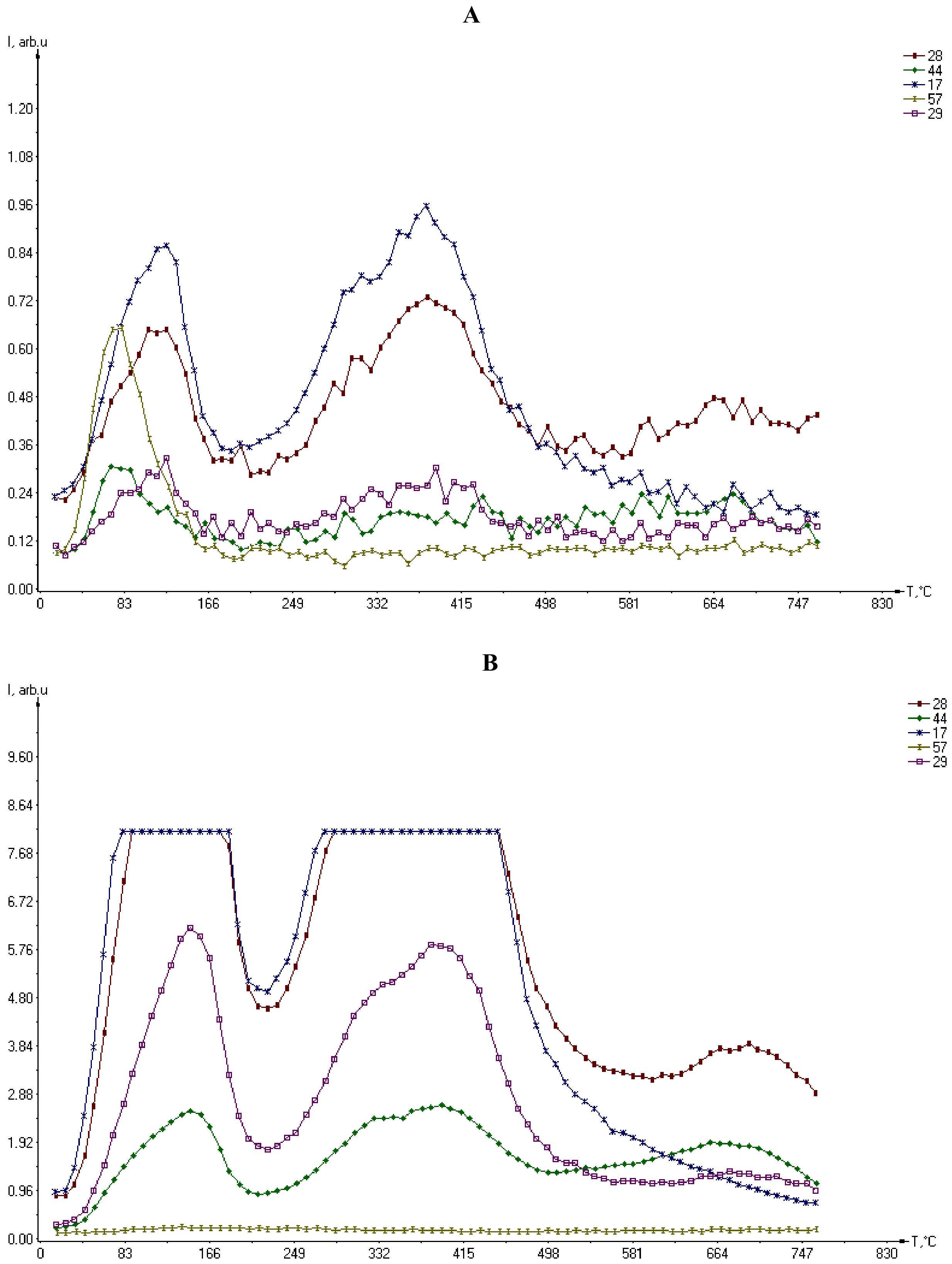

Fig. 2 Temperature mass-spektrograms of palygorskite
A – before adsorbtion,
B – after adsorbtion.