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EXPLORING THE POSSIBILITY OF PURIFICATION OF WATER-ALCOHOL SOLUTIONS OF DIFFERENT CONCENTRATIONS CONTAINING ALDEHYDES AND ESTERS BY MINERAL ADSORBENTS

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Проведено порівняльний аналіз адсорбційного очищення водно-спиртових розчинів різної концентрації клиноптилолітом та шунгітом на прикладі домішок етанолу ацетальдегіду та етилацетату. Експериментально встановлено оптимальні концентрації водно-спиртових розчинів та тривалості контакту водно-спиртових розчинів з адсорбентами для ефективної адсорбції альдегідів та естерів. Показано зв'язок концентрації водно-спиртових розчинів з коефіцієнтом ректифікації головних полярних домішок

Ключові слова: адсорбція, леткі домішки спирту, якість спирту етилового, цеоліти, клиноптилоліт, шунгіт

Проведен сравнительный анализ адсорбционной очистки водно-спиртовых растворов различной концентрации клиноптилолитом и шунгитом на примере примесей этанола ацетальдегида и этилацетата. Экспериментально установлены оптимальная концентрация водно-спиртовых растворов и продолжительность контакта водно-спиртовых растворов с адсорбентами для эффективной адсорбции альдегидов и эфиров. Показана связь концентрации водно-спиртовых растворов с коэффициентом ректификации головных полярных примесей

Ключевые слова: адсорбция, летучие примеси спирта, качество спирта этилового, цеолиты, клиноптилолит, шунгит

1. Introduction

The quality of alcoholic beverages is one of the major factors that determine their competitiveness and place in the consumer market. The most important requirement of alcoholic beverage producers to producers of ethanol as a raw material is the high quality of rectified alcohol. According to regulatory documentation, high requirements for the quality of alcohol, relating to physicochemical and organoleptic indicators are imposed. The determining factor in the formation of organoleptic indicators of alcohol and alcoholic beverages is the concentration of volatile impurities. This concerns, first of all, vodkas – traditional strong alcoholic beverages in Ukraine (unlike whiskey, brandy, rum, etc., whose quality is not related to the minimum content of impurities).

The majority of studies prove that the qualitative composition of impurities in alcohol is affected by the kind and defectiveness of raw materials, auxiliary types of raw materials, biochemical composition of wort, the level and composition of contamination of fermentation media, the type of yeast used, conditions for yeast cultivation, the thermo-enzymatic modes of processing of raw materials, as well as technologies for the separation of impurities in the process of alcohol rectification [1].

Currently, alcohol plants often recycle grain and grain products unsuitable for food and fodder purposes, which significantly influences the effectiveness of the technology, the yield of alcohol per unit of conventional starch and the quality of finished products.

The content of impurities that form organoleptic indicators of vodka can be reduced by purification. Vodka production involves the use of imported activated carbon, which has certain disadvantages. These are a high price, flammability, as well as the possibility of oxidation and esterification catalysis. So, the search for effective and cheap sorbents for the technology of alcoholic beverages is an urgent task. Natural disperse clay minerals, the deposits and variety of which in Ukraine are very large are promising for use as adsorbents for purification of alcohol and water-alcohol solutions. Therefore, the study of the possibility of using mineral adsorbents for this purpose is, above all, a research problem.

2. Literature review and problem statement

Zeolites are used as mineral adsorbents in many technological processes. Separation of carbon dioxide from flue gases [2], separation of gases (methane, carbon dioxide, hydrogen sulfide, water vapor) in the biogas technology [3], industrial drying of natural gas [4], purification and separation of complex mixtures [5], purification of wastewater containing heavy metals [6, 7] have been investigated.

Zeolites are also used in winemaking to reduce the metal content [8]. In crop production, mineral adsorbents can be used, for example, to keep moisture in the soil and to prevent the nitrification of organic nitrogen [9]. In poultry farming, there is evidence of an increase in feed efficiency, water consumption, nutrient utilization and manure improvement, as well as aflatoxicosis prevention [10]. In animal farming, rapid growth or decline in the incidence of diseases and deaths [11] or prevention of oxidative stress and correction of disorders of the antioxidant system of cows in the treatment of diseases of the reproductive system [12] are noted.

For medical purposes, zeolites are used as drug carriers, adjuvants in anticancer therapy, dietary supplements or antimicrobial agents [13].

Regarding the ethanol technology, zeolites are considered for ethanol extraction from dilute ethanol-water solutions [14] and bioethanol dehydration [15, 16].

With the help of zeolites, adsorption of tert-butyl ethanol in the production of methyl tert-butyl ester – additives to motor fuels that increase the octane number [17] has been investigated Theoretical substantiation of adsorption of primary alcohols C1-C4 has been given in [18]. The conclusion has been drawn that stability of adsorbed alcohols is governed by van der Waals dispersion interactions and steric zeolite constraints, which destabilize the local formation of hydrogen bonds. The decrease in the content of higher alcohols (isoamilol, isobutanol, n-butanol, isopropanol, n-propanol) in water-alcohol solutions by mineral adsorbents [19] has been investigated.

Crystal-chemical features of mineral adsorbents – zeolites – cause a unique combination of adsorption, ion exchange and catalytic properties, which promotes the effective use in agriculture, industry and medicine.

Zeolites have a complex tetrahedral structure in which an atom of silicon or aluminum is surrounded by four oxygen atoms. The tetrahedra are grouped in chains, in which adsorption cavities, having activated anionic centers on their surface are located. The excess negative charge of the anionic part of the alumosilicate zeolite skeleton is compensated by cations. If water is removed from zeolite, cavities may again be filled with water or other substance, which causes the use of zeolites for drying, purification and separation of complex mixtures. However, not all substances can penetrate into adsorption cavities and be held in them. This is due to the fact that adsorption cavities are interconnected by input channels-windows of a certain size, which depends on the crystal lattice structure of zeolite. Only those molecules can pass through the windows whose critical diameter is smaller than the diameter of input windows. The dimensions of input windows depend on the number of oxygen atoms in the tetrahedra rings and on the spatial orientation of these rings [20].

Clinoptilolite – the most common zeolite in soils and bottom sediments is one of the high-charged minerals with high ion-exchange capacity found in soils of the Central European countries. Natural clinoptilolite is a natural mineral of the zeolite group, the crystal-chemical formula of which is $(Na,K)_6[Al_6Si_{30}O_{72}]_{20}H_2O$ (unit cell) and $(Na,K)_{0,17}(H_2O)_{0,56}|[Al_{0,17}Si_{0,83}O_2]$ (rated to $[(Al,Si)O_2]$) [21]. Depending on geological conditions of ore deposits, sodium cations may be partially substituted by potassium, calcium or magnesium cations, but the inequality (Na+K)>(Ca+Mg) is always fulfilled in clinoptilolite. The Si/Al ratio in the structure of clinoptilolite from the Sokyrnytsya deposit is negligible – 3.84–4.13. The research of thermal stability of clinoptilolite of the Sokyrnytsya deposit (Ukraine) showed that no significant changes occur in its structure at a temperature below 850 °C. The unit cell parameters are within, nm: 1.77:1.80:0.74. Reduction of the Si/Al ratio in the structure of clinoptilolite causes distortion of its unit cell, that is, stretching in the direction *a* and compression in the direction *b*, which leads to a change in the configuration of structural channels that take the form of an ellipsoid. The size of input windows of crystal lattices is about 0.35 nm [22].

Shungite rocks are natural materials found in Karelia (Russian Federation) and Kazakhstan. The basic unit of the supramolecular structure of the carbon material of shungite rocks is a globule – fullerene-like formation with the size from 10 to 30 nm. Such globules differ in shape and size, which is due, in particular, to the number of carbon atoms (tens to hundreds). Globules consist of a closed shell or fragments of such a shell. The shell is smoothly curved packs of carbon layers that surround a nanosized population. The thickness of the spherical shell of the fullerene molecule with 60 carbon atoms is ~0.1 nm with a molecular radius of 0.357 nm. Layers of more ordered carbon have an interplanar spacing of 0.34 nm on the surface of microcrystals, and in the layers of complex structure, this spacing varies from 0.2 to 0.5 nm.

Mineral components are characterized by a fine distribution in the form of crystals, layered inclusions and nanocrystals. The basic components of the mineral part of shungite are magnesium silicates: $3MgO{\cdot}4SiO_2{\cdot}6H_2O$ (hydrated talc) and $3MgO{\cdot}2SiO_2{\cdot}6H_2O$ (hydrated serpentine). In addition, there are free α-SiO_2 (quartz), α-Fe_2O_3 (hematite), TiO_2 (rutile), $8MgO{\cdot}4SiO_2{\cdot}Mg(F,OH)$ (clinohumite), α-Al_2O_3 (corundum) and α-CrO_3 (eskolaite) [23, 24].

Consequently, the structure of the above-mentioned minerals has the properties that determine the suitability for adsorption of such simple substances as ethanol impurities.

The group of aldehydes contained in alcohol is represented by acetaldehyde, acetal, propionic and croton aldehydes. Free acetaldehyde gives bitterness to alcohol and bound – acetal – sometimes softness. As a rule, the content of free acetaldehyde (up to 90 % of the total amount of aldehydes) prevails in alcohol at the distiller output, and acetal is released after the onset of chemical equilibrium [25].

Esters – ethyl acetate and methyl acetate belong to compounds that, together with ethyl alcohol, create the smell of rectified ethyl alcohol. Ethyl butyrate, isobutyl acetate, isoamyl acetate are esters which should not be contained in ethyl alcohol. Such esters can be formed as a result of a violation of the alcohol production technology and give an unpleasant odor to alcohol: ethyl butyrate – the smell of rotten fruit, isobutyl acetate – fruity smell (pear essence). Esters of the above higher alcohols are not adsorbed by activated carbon, and are also difficult to remove during distillation [25]. In the total amount of esters, the content of which is standardized, the proportion of ethyl acetate also prevails.

Therefore, the research on the possibility of using the purification of water-alcohol solutions by selected natural mineral adsorbents instead of activated carbon in the alcoholic beverage industry is reasonable.

3. The aim and objectives of the study

The research was aimed at determining the feasibility of using mineral adsorbents such as clinoptilolite and shungite for adsorption of aldehydes and esters and studying the process characteristics of these adsorbents in water-alcohol solutions of different concentrations.

To achieve this aim, the following objectives were solved:

– to determine the influence of the concentration of water-alcohol solutions on the efficiency of adsorption of aldehydes and esters on the example of the representatives of the group: acetaldehyde and ethyl acetate with non-conventional mineral adsorbents such as clinoptilolite and shungite;

– to determine optimum durations of phase contact of rectified ethyl alcohol and water-alcohol solutions at concentrations of 40, 50, 80 % vol. with the investigated mineral adsorbents for the most effective purification of aldehydes and esters.

4. Materials and methods of the research on adsorption of aldehydes and esters

The research was conducted with underproof ethyl alcohol (non-compliance of concentrations of aldehydes and esters with DSTU).

Adsorption of aldehydes was investigated on the example of acetaldehyde, the content of which was 90 % and higher of the total amount of aldehydes in rectified ethyl alcohol. Adsorption of esters was determined on the example of ethyl acetate as the basic component of esters. The results are presented in mg/dm^3 of absolute alcohol.

In more detail, the methods of research on adsorption of aldehydes and esters are given in [26].

5. Results of the research on purification of rectified ethyl alcohol and water-alcohol solutions by mineral adsorbents

The dynamics of acetaldehyde adsorption from water-alcohol solutions of various concentrations by clinoptilolite during different phase contact times is shown in Fig. 1. The results are presented in mg/dm^3 of absolute alcohol.

The tendency of acetaldehyde sorption by clinoptilolite was similar for all investigated alcohol concentrations. With an increase in the phase contact to 5–20 minutes, the concentration of this impurity in the purified solution decreased, but later began to increase again. The arrangement of the curves is of interest – the best sorption results were observed with the concentration of 80 % vol.: the concentration of acetaldehyde decreased by almost 63 %.

So, the sorption process should be carried out rather quickly, since the increased duration of the alcohol-water mixture contact with a sorbent reduces the sorption efficiency. Another result is that it is not advisable to carry out sorption from both the water-alcohol solution at a concentration of 40 % vol. and rectified ethyl alcohol.

The dynamics of aldehyde adsorption by shungite on acetaldehyde, depending on the concentration of water-alcohol solutions and phase contact duration, is given in Fig. 2. The quality of the samples in the present research did not meet the standard requirements for the concentration of aldehydes.

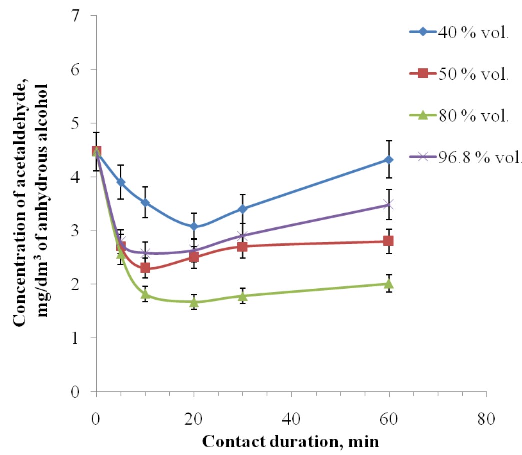

Fig. 1. The experimental curve of the concentration of acetaldehyde in water-alcohol solution after adsorption by clinoptilolite depending on the phase contact duration

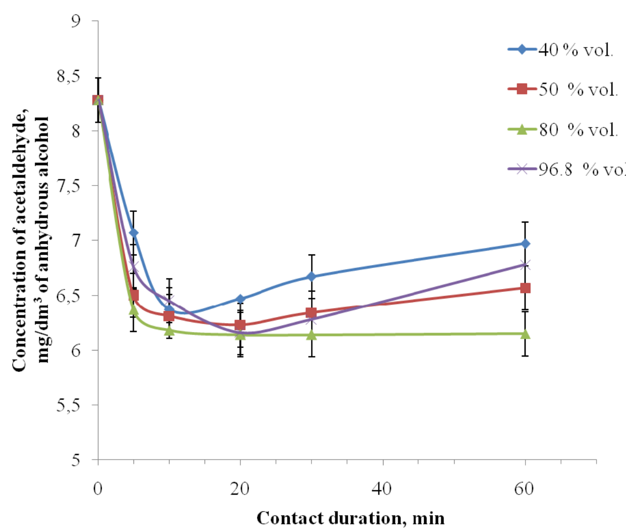

Fig. 2. The experimental curve of the concentration of acetaldehyde in water-alcohol solution after adsorption by shungite depending on the phase contact duration

Acetaldehyde adsorption by shungite occurred most intensively within 5–10 minutes. Moreover, acetaldehyde was most effectively adsorbed by shungite also from a water-alcohol solution at a concentration of 80 % vol. – the decrease was more than 25 %. The nature of the curves for other concentrations of water-alcohol solutions was generally similar, and the concentration of acetaldehyde in the water-alcohol solution increased again with the increasing duration of contact with the adsorbent.

Also, the sorption of ethyl acetate, the concentration of which is the greatest among esters in rectified ethyl alcohol and alcohol beverages, was investigated.

The concentrations of ethyl acetate after the processing of rectified ethyl alcohol and water-alcohol solutions with clinoptilolite are presented in Fig. 3, with shungite – in Fig. 4. The analysis of the results shows a fundamentally different distribution of indicators depending on the concentration of the water-alcohol solution. The adsorption of this impurity was the best at a concentration of 40 % vol., and with increasing ethanol concentration, the efficiency was reduced. From the graph (Fig. 3), it can also be assumed that the optimum phase contact duration may be even less than 5 minutes. But, unfortunately, technical provision for such conditions was not possible, as a decrease in the column height can radically change the research conditions.

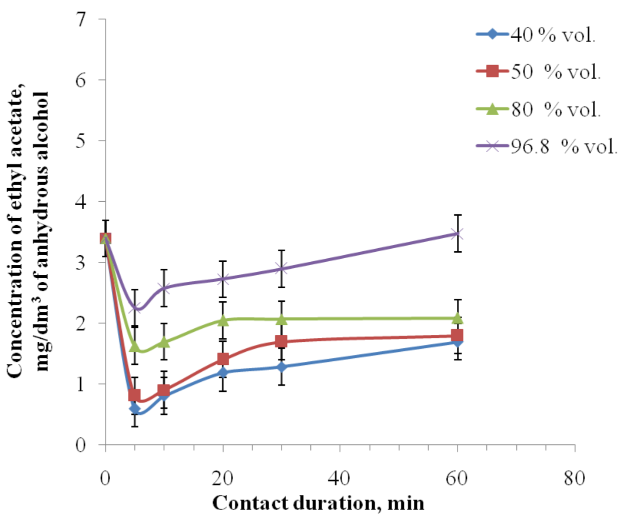

Fig. 3. The experimental curve of the concentration of ethyl acetate in water-alcohol solution after adsorption by clinoptilolite depending on the phase contact duration

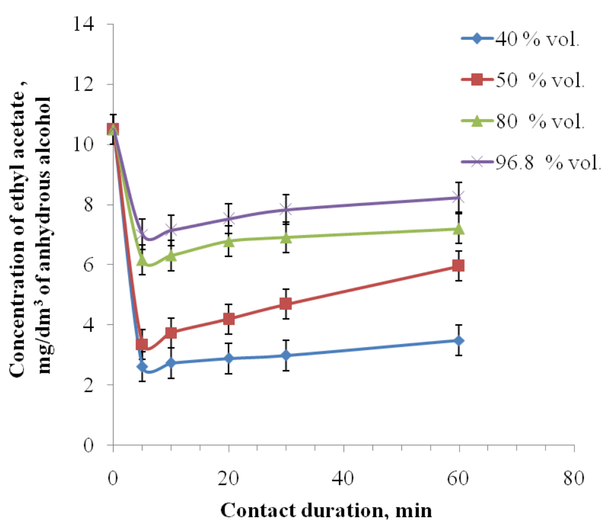

Fig. 4. The experimental curve of the concentration of ethyl acetate in water-alcohol solution after adsorption by shungite depending on the phase contact duration

Since this parameter of the starting alcohol corresponded to DSTU, the reduction of the content of this volatile impurity for rectified ethyl alcohol after adsorption by clinoptilolite was not so noticeable as for acetaldehyde. In contrast, with an increase in the contact duration up to 60 minutes, the concentration of ethyl acetate almost coincided with the concentration in the control sample.

The analysis of the results (Fig. 4) shows a greater difference in the indicators depending on the concentration of the water-alcohol solution, but the nature of the sequence of the curves in terms of the sorption efficiency for this impurity was similar to sorption by clinoptilolite. With increasing dilution, the difference became more noticeable: for the water-alcohol solution at a concentration of 40 % vol., the content of ethyl acetate after 5 minutes of the process reduced almost 5 times.

Note that adsorption of volatile impurities from the 40 % vol. alcohol-water mixture prepared from ethyl acetate non-standard rectified alcohol, can be brought into compliance with DSTU by this indicator.

6. Discussion of the results of research on adsorption of acetaldehyde and ethyl acetate by mineral adsorbents

The capacity of adsorption of ethanol impurities by mineral adsorbents depends, first of all, on the physicochemical characteristics of adsorbents, in particular, the size of the inlet openings in the cavity, conditions for the adsorption process. Also, sorption of substances of different nature, obviously, depends on the characteristics of the chemical structure of the impurity. Probably, the adsorption of the impurity from the water-alcohol solution depends on hydrogen bonds of not only the impurity with the mineral, but also the hydrogen bonds between water and ethanol. The magnitude of such bonds can be estimated by those properties that are already well-studied experimentally and published, for example, by the impurity rectification coefficient.

The impurity rectification coefficient is used to estimate the volatility of impurities compared with ethanol (Fig. 5). The volatility of ethanol and volatile impurities, including acetaldehyde and ethyl acetate, depends on the concentration of water-alcohol mixture. The volatility of individual components is characterized by the evaporation coefficient, which is characterized by the ratio of the concentration of this component in the vapor phase to its concentration in the liquid phase, provided that these phases are in equilibrium. The rectification coefficient is the ratio of the impurity evaporation coefficient to the ethanol evaporation coefficient. The rectification coefficient indicates how much the impurity content in vapor changes in relation to ethanol as compared to its content in the liquid. Both acetaldehyde and ethyl acetate are the head impurities (Fig. 5), for which the rectification coefficient is always greater than 1. That is, the volatility of these impurities at any ethanol concentration is greater than that of ethanol.

It is logical to assume that the impurity is more volatile if the magnitude of its hydrogen bonds with ethanol is lower. Consequently, the higher the rectification coefficient, the lower the magnitude of hydrogen bonds of this impurity with ethanol and the easier it is to be sorbed from ethanol by mineral adsorbents.

The magnitude of hydrogen bonds of impurities is not directly proportional to the concentration of water-alcohol mixtures. For example, for ethyl acetate, with an increase in this concentration, the rectification coefficient decreases hyperbolically. So, the magnitude of hydrogen bonds increases, therefore, the sorption of ethyl acetate from rectified ethyl alcohol is worse than that from the alcohol-water mixture with a concentration of about 40 % vol.

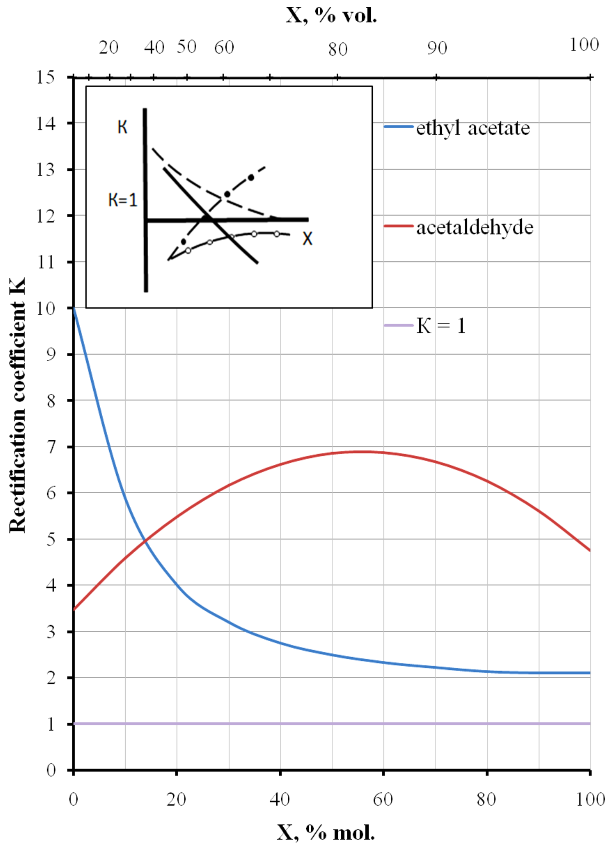

Fig. 5. Rectification coefficients of volatile impurities, concomitant to ethanol [29]

For acetaldehyde, the nature of the rectification coefficient has the form of a parabola, increasing to 80–85 % vol., and then falling again. Consequently, the magnitude of hydrogen bonds should be the lowest at the highest values of the rectification coefficient. Accordingly, the acetaldehyde sorption efficiency should be better at these concentrations. Some differences in the acetaldehyde concentration after adsorption for the concentrations of 40 % vol. and 96.8 % vol. are due to the higher content of water in the 40 % vol. solution. Probably, water competes with acetaldehyde both in the formation of hydrogen bonds, and in the size of the molecule.

7. Conclusions

As a result of the research, the expediency of adsorption of polar impurities of ethanol – aldehydes and esters – by mineral adsorbents such as clinoptilolite and shungite was proved:

1. It was determined that for acetaldehyde adsorption, the best concentration of the water-alcohol solution is 80–85 % vol., which is due to the lowest energy of hydrogen bonds with ethanol. The least appropriate concentrations of the solutions were 40 % vol. and 96.8 % vol. For effective ethyl acetate adsorption, the most suitable concentration was 40 % vol. With increasing concentration, the content of ethyl acetate in the solution after sorption increased.

2. The rational phase contact duration for the adsorption of acetaldehyde by clinoptilolite and shungite is 10 to 20 minutes. The concentration of acetaldehyde in these conditions decreased by 63 % for clinoptilolite and by 26 % for shungite. For the adsorption of ethyl acetate, the rational process duration was 5 minutes: the concentration decreased by 82 % for clinoptilolite and by 75 % for shungite.

Consequently, the use of clinoptilolite for the purification of water-alcohol solutions containing aldehydes, which worsen the taste of alcoholic beverages most of all, is more appropriate. The use of clinoptilolite in the production of vodkas of non-standard rectified alcohol will improve the taste of the final product.

References

1. Nahurna, N. A. Pryroda domishok etylovoho spyrtu ta zasoby rehuliuvannia khimichnykh i sensornykh kharakterystyk spyrtu [Text] / N. A. Nahurna, V. M. Holovchenko, V. H. Buriakov // Kharchova nauka i tekhnolohiya. – 2011. – Issue 3 (16). – P. 65–68.
2. Xiao, P. Capture of CO_2 from flue gas streams with zeolite 13X by vacuum-pressure swing adsorption [Text] / P. Xiao, J. Zhang, P. Webley, G. Li, R. Singh, R. Todd // Adsorption. – 2008. – Vol. 14, Issue 4-5. – P. 575–582. doi: 10.1007/s10450-008-9128-7
3. Liu, D. Adsorption Separation of CO_2/CH_4 Gas Mixture on Carbon Molecular Sieves Modified by Potassium Carbonate [Text] / D. Liu, H. Yi, X. Tang, S. Zhao, Z. Wang, F. Gao et. al. // Journal of Chemical & Engineering Data. – 2016. – Vol. 61, Issue 7. – P. 2197–2201. doi: 10.1021/acs.jced.5b00742
4. Farag, H. A. A. Natural gas dehydration by desiccant materials [Text] / H. A. A. Farag, M. M. Ezzat, H. Amer, A. W. Nashed // Alexandria Engineering Journal. – 2011. – Vol. 50, Issue 4. – P. 431–439. doi: 10.1016/j.aej.2011.01.020
5. Lively, R. P. Hollow Fiber Adsorbents for CO2Removal from Flue Gas [Text] / R. P. Lively, R. R. Chance, B. T. Kelley, H. W. Deckman, J. H. Drese, C. W. Jones, W. J. Koros // Industrial & Engineering Chemistry Research. – 2009. – Vol. 48, Issue 15. – P. 7314–7324. doi: 10.1021/ie9005244
6. Bezdieniezhnykh, L. Ya. Mozhlyvosti adsorbtsiynoho ochyshchennia stichnykh vod vid ioniv vazhkykh metaliv [Text] / L. Ya. Bezdieniezhnykh, T. M. Aleksieieva // Ekolohichna bezpeka. – 2009. – Issue 2 (6). – P. 54–57.
7. Nechytailo, L. Ya. Efektyvnist vykorystannia pryrodnoho sorbentu dlia ochyshchennia pytnoi vody vid nitrat-yoniv [Text] / L. Ya. Nechytailo, H. M. Ersteniuk // Nauk. zap. Ternop. nats. ped. un-tu. Ser.: khimiya. – 2015. – Issue 22. – P. 24–28.
8. Luchian, C. E. Innovative materials in winemaking [Text] / C. E. Luchian, C. Colibaba, M. Niculaua, M. Codreanu, V. V. Cotea // BIO Web of Conferences. – 2015. – Vol. 5. – P. 02023. doi: 10.1051/bioconf/20150502023
9. Ippolito, J. A. Zeolite Soil Application Method Affects Inorganic Nitrogen, Moisture, and Corn Growth [Text] / J. A. Ippolito, D. D. Tarkalson, G. A. Lehrsch // Soil Science. – 2011. – Vol. 176, Issue 3. – P. 136–142. doi: 10.1097/ss.0b013e31820e4063

10. Shariatmadari, F. The application of zeolite in poultry production [Text] / F. Shariatmadari // World's Poultry Science Journal. – 2008. – Vol. 64, Issue 01. – P. 76–84. doi: 10.1017/s0043933907001730
11. Colella, C. A critical reconsideration of biomedical and veterinary applications of natural zeolites [Text] / C. Colella // Clay Minerals. – 2011. – Vol. 46, Issue 2. – P. 295–309. doi: 10.1180/claymin.2011.046.2.295
12. Yarovan, N. I. Effect of zeolites on adaptation processes in cows [Text] / N. I. Yarovan // Russian Agricultural Sciences. – 2008. – Vol. 34, Issue 2. – P. 120–122. doi: 10.3103/s106836740802016x
13. Danilczuk, M. Molecular Sieves in Medicine [Text] / M. Danilczuk, K. Dlugopolska, T. Ruman, D. Pogocki // Mini-Reviews in Medicinal Chemistry. – 2008. – Vol. 8, Issue 13. – P. 1407–1417. doi: 10.2174/138955708786369537
14. Zhang, K. Adsorption of Water and Ethanol in MFI-Type Zeolites [Text] / K. Zhang, R. P. Lively, J. D. Noel, M. E. Dose, B. A. McCool, R. R. Chance, W. J. Koros // Langmuir. – 2012. – Vol. 28, Issue 23. – P. 8664–8673. doi: 10.1021/la301122h
15. Kontar, O. Ya. Sposib otrymannia spyrtu etylovoho znevodnenoho [Electronic resource] / O. Ya. Kontar, H. M. Valievakhin, E. R. Haleiev, O. I. Dokhov // Elektronnyi arkhiv Kharkivskoho natsionalnoho universytetu radioelektroniky. – 2014. – Available at: http://oai.org.ua/index.php/record/view/518945
16. Onuki, S. Ethanol production, purification, and analysis techniques: a review [Text] / S. Onuki, J. A. Koziel, J. (Hans) van Leeuwen, W. S. Jenks, D. Grewell, L. Cai // 2008 Providence, Rhode Island. – 2008. doi: 10.13031/2013.25186
17. Butland, T. D. Adsorption removal of tertiary butyl alcohol from wastewater by zeolite [Text] / T. D. Butland. – Worcester Polytechnic Institute, 2008.
18. Nguyen, C. M. Theoretical study of the adsorption of C1–C4 primary alcohols in H-ZSM-5 [Text] / C. M. Nguyen, M.-F. Reyniers, G. B. Marin // Physical Chemistry Chemical Physics. – 2010. – Vol. 12, Issue 32. – P. 9481. doi: 10.1039/c000503g
19. Marynchenko, V. O. Ochyshchennia vodno-spyrtovykh rozchyniv vid vyshchykh spyrtiv mineralnymy adsorbentamy [Text] / V. O. Marynchenko, L. V. Marynchenko, O. V. Fil // Naukovi pratsi Natsionalnoho universytetu kharchovykh tekhnolohyi. – 2014. – Vol. 20, Issue 5. – P. 214–219.
20. Pat. No. 51497A UA. Sposib dehidratatsyi etylovoho spyrtu. MPK 7 S07S7/13 [Text] / Melnyk L. M., Melnyk V. P., Mank V. V. et. al.; zaiavnyk ta patentovlasnyk: NUKhT. – No. 2002042978; declareted: 12.04.2002; published: 15.11.2002, Bul. No. 11.
21. Bakakin, V. V. Unifitsirovannye formul'nye i ob'emnye harakteristiki v sravnitel'noy kristallohimiy prirodnyh tseolitov [Text] / V. V. Bakakin, Yu. V. Seretkin // Zhurnal strukturnoy himyi. – 2009. – Vol. 50. – P. 123–130.
22. Grechanovskaya, E. E. Metrika elementarnoy yacheyki i otnoshenie Si/Al v tseolitah ryada geylandit-klinoptilolit Sokirnitskogo mestorozhdeniya (Zakarpat'e, Ukraina) [Text] / E. E. Grechanovskaya // Mineralohichnyi zhurnal. – 2010. – Vol. 32, Issue 4. – P. 12–22.
23. Mosin, O. V. The structure and composition of natural carbonaceous fullerene containing mineral shungite [Text] / O. V. Mosin, I. Ignatov // International Journal of Advanced Scientific and Technical Research. – 2013. – Vol. 6, Issue 11-12. – P. 9–21.
24. Ignatov, I. The structure and composition of carbonaceous fullerene containing mineral shungite and microporous crystalline aluminosilicate mineral zeolite. Mathematical model of interaction of shungite and zeolite with water molecules [Text] / I. Ignatov, O. V. Mosin // Advances in Physics Theories and Applications. – 2014. – Vol. 28. – P. 10–21.
25. Kravchuk, Z. Mikrodomishky etylovoho spyrtu. Yak vony vplyvaiut na yakist horilchanykh vyrobiv [Text] / Z. Kravchuk, T. Tatarynova, A. Kravchuk // Kharchova i pererobna promyslovist. – 2010. – Issue 4. – P. 50–52.
26. Marynchenko, L. Research of mineral adsorbents application for water-alcohol solutions purification in technology of alcoholic beverages [Text] / L. Marynchenko, V. Marynchenko, M. Hyvel // EUREKA: Physics and Engineering. – 2017. – Issue 4. – P. 3–10. doi: 10.21303/2461-4262.2017.00397