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Adsorption Purification of Used Industrial Oil Using Natural Aluminosilicates

The results of adsorption purification of used industrial oil in the presence of natural aluminosilicates, bentonite and mordenite, are discussed. It was found that the maximum degree of purification was achieved in the presence of mordenite and reached 61.68 % at an oiladsorbent ratio of 2.3 at a temperature of 70 °C. The data of the structural-group analysis of the oil showed that the main share of the hydrocarbon components removed during purification is accounted for by highly condensed aromatic ones. The supposed reasons for the different adsorption activity of bentonite and mordenite samples were judged from the data of chemical, mineralogical, textural, and IR spectroscopic analysis. Based on the results of the IR spectra of mordenite samples, it was concluded that energetically active hydroxyl groups can be responsible for their increased adsorption activity. The used oil before purification is characterized by a high cyclicity of the hydrocarbons which included in the composition (aromatic hydrocarbons account for 38 % of the total), while the oil subjected to adsorption purification with mordenite (M-50) mainly becomes free of aromatic rings (the proportion of aromatic hydrocarbons decreases up to 19.6 %). This is a consequence of the high polarizability of aromatic hydrocarbons, in which, compared with other oil components, a dipole moment is easily induced under the influence of the electrostatic field of the adsorbent.

Keywords: adsorption purification, waste industrial oil, bentonite, mordenite, degree of purification, IR-spectrum, structural group composition.

Introduction

Adsorption purification methods are some of the most common purification techniques, with a wide range of applications in the chemical, oil refining, food industries, in medicine, radio engineering, printing, etc. The most common adsorbents are activated carbons, silica gels, aluminum gels, artificial and natural zeolites, etc. The practical application of adsorption technologies in the processes of cleaning the earth, air, water from oil pollution [1], the extraction of lead, copper [2], fluorine [3] ions and many others, is the subject of a number of interesting review papers. At the same time, both synthetic sorbents and natural mineral resources are successfully used. Indicators which affect adsorption activity are the size of the adsorption surface and its availability, polarity, chemical composition, and the nature of intermolecular interaction with adsorbate [4–7]. When specifying a specific choice of the type of adsorbent, all its characteristics are taken into account, since in the end their use is economically justified only if a high degree of purification and the possibility of reusable regeneration are ensured, and if they are available, cheap, non-toxic, etc.

The issues of cost are a matter of history if the indicators of the adsorption activity of the sorbent are directly related to its physicochemical properties. Along with the fact that synthetic sorbents produced by the industry are characterized by high cost, the use of effective natural adsorbents, in particular, aluminosilicates, can become one of the links in the “green” technology, since, on the one hand, this will help reduce the volume of consumed production resources, while on the other hand, it will reduce the negative effect on the environment due, for example, to the purification of used lubricating oils.

More than 30 types of natural zeolites are known, and the most common of them are chabazite, phillipsite, lomontite, bentonite, mordenite, clinoptilolite, analcime, stilbite and erionite. Of these minerals, clinoptilolite and mordenite are of the greatest practical importance. They in the form of powders and filter materials are also used to purify water from synthetic surfactants, aromatic and carcinogenic organic compounds, dyes of various classes.

On the territory of Azerbaijan there are large industrial deposits of clinoptilolite, mordenite, kaolinite and bentonite (Aydag, Chananab, Dash-Salakhli deposits, etc.). Systematic studies conducted at the M.F. Nagiyev Institute made it possible to study the influence of nature, the charge of exchange cations, as well as the pH of the medium, thermal stability, porosity on the physicochemical characteristics of natural aluminosilicates of Azerbaijan [5–10]. The data obtained by the authors made it enable to develop scientific

cally based recommendations on the use of clinoptilolite, mordenite, kaolinite and bentonite for wastewater treatment from organic pollutants of various origins [9, 13].

Natural aluminosilicates of Azerbaijan also attracted close attention of catalytic chemists. The fundamental researches carried out [11–13], made it available to develop new zeolite catalysts for the production of alicyclic dienes, acetylene, and oxygen-containing compounds. It is shown that by varying the structure and composition of the zeolite, it is possible to implement different directions of hydrocarbon conversion to obtain the target products.

The given data testifies to the undoubted prospects of use of Azerbaijan's natural zeolites in the field of chemical technology. However, along with the listed advantages, they also have certain disadvantages, for which it should be noted that natural zeolites are complex and variable in composition multicomponent systems, the physicochemical properties of natural sedimentary zeolites significantly depend on the content of zeolite phases in the rock, type of cation-exchange form and nature of impurities, etc. Thus, even with the same content of the zeolite phase, depending on the selected deposit, there may be a discrepancy in the adsorption properties of individual samples.

A comparative study of the efficiency indicators of adsorption purification of used industrial oil (OIM) using natural aluminosilicates based on bentonite and mordenite, establishing the nature of their molecular sieve action, is the purpose of this study.

Experimental

Industrial oil BP ENERGOL GR XP 320 was taken as used oil (duration of operation 4500 hours at a temperature of 30–40 °C). The causes of aging, the possibility of its acid and solvent regeneration, as well as the energy and environmental efficiency of its combustion were considered in [14–16].

Two samples of natural zeolites of Nakhchivan (the main mineral is mordenite, the samples differ in depth, 30 and 50 cm, **M-30** and **M-50**, respectively) and the Dash-Salakhli deposit (the main mineral is bentonite, **B**) of Azerbaijan were taken for the study. Samples of all studied samples of aluminosilicates were taken directly at the deposits. Air-dried pieces of minerals were freed from impurities and inclusions visible to the naked eye. Further, the purification of bentonite and mordenite minerals, which dominate in one or another clay deposit, was carried out by soaking. At the same time, an approximately 10 % aqueous suspension of clays was prepared, thoroughly mixed with a mechanical stirrer until the lumps disappeared, left alone for two hours, and the most highly dispersed fraction was decanted with a siphon.

Bulk, apparent, and true density, porosity, layer void ratio, absolute water content and water absorption of adsorbents, specific surface area and pore volume were determined by known methods...

The method of single-stage static sorption was used in the work. Sorption was carried out by adding a sample of aluminosilicate rocks crushed to grains of 0.5–2.0 mm in size to the studied UIO samples. Then the mass was stirred with a magnetic stirrer for 15 minutes and then centrifuged. After that, oil samples were taken and the degree of purification was determined.

The degree of purification β_{pur} was calculated based on the results of the optical density of oil samples according to the formula:

$$\beta_{pur} = 100 - \frac{n_{init} - n_{eq}}{n_{init}} \cdot 100 \%,$$

where n_{init} — is the optical density of initial UIO; n_{eq} — is the optical density of UIO in the equilibrium state.

Adsorbents mineralogical and chemical composition analysis was studied using the XRD “MiniFlex 600” and the “S8 TIGER Series 2 WDXRF” spectrometer.

The refractive index (n_D) of oil samples was determined on an IRF-54V refractometer with an accuracy of 0.0001. The structural group composition of oil samples was determined by the *n-d-M* method.

To check the reproducibility of the results, each single experiment was repeated 3 times. Statistical processing of experimental data showed their satisfactory reproducibility. The experimental error did not exceed 5 %.

Results and Discussion

Comparative characteristics of the chemical and mineralogical composition of the studied adsorbents are presented in Tables 1 and 2. As can be seen from the presented data, the qualitative chemical composition of both types of adsorbents is characteristic of these types of zeolites. The main distinction between their

chemical composition lies in the different mass ratio of $\text{SiO}_2:\text{Al}_2\text{O}_3$:it made up 4:1 for bentonite and 5.4:1 for mordenite samples, as well as the content of calcium oxide (for bentonite, it is almost 4 times higher).

The main mineralogical components of the sample B are montmorillonite (more than 70 %) and feldspars, while M-30 and M-50 are characterized by the presence of a significant amount of quartz, illite, calcite, and hematite.

Table 1

Chemical composition of the adsorbents

Adsorbent	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	K_2O	CaO	TiO_2	Fe_2O_3	HTC*
B	2.17	4.62	12.23	48.75	0.93	1.89	6.32	0.64	10.18	9.73
M-30	1.34	2.16	13.25	71.64	–	2.05	1.42	0.68	0.04	7.42
M-50	1.35	2.3	13.04	70.21	–	2.09	1.83	0.7	0.21	8.27

*HTC — is the amount of components evaporating at 950 °C.

Table 2

Mineralogical composition of the adsorbents

Adsorbent	SiO_2 (α -quartz)	Feldspar	Illite	CaCO_3 (calcite)	Montmo- rillonite	Fe_2O_3 (hematit)	Volcan. ash	Etc. impurities
B	2.3	12.5	0.4	3.1	72.2	0.6	7.1	1.5
M-30	10.2	19.1	10.6	11.8	32	8.3	5.8	2.1
M-50	10.4	19	10.5	12.6	31.1	8	5.7	2.6

During the research, it was found that mordenite samples have a significantly lower bulk density (9 times less) and, on the contrary, large specific surface values (Table 3), which is explained by differences in the porous structure (given that a specific adsorbent fraction was used in the course of the experiments, it is possible the effect of particle size was not considered). In accordance with the type of zeolite and the noted structural features, differences are also observed in the water absorption of the samples. Mordenite samples are characterized by lower water absorption (2 times less relative to bentonite). The observed differences are due to their crystal structure.

Table 3

Physical properties of the adsorbents

Adsorbent	S_{sa} , m^2/g	Density, g/cm^3			$V_{sp.pr.ar}$	α	ε	W	WA
		ρ_{bulk}	ρ_{app}	ρ_{tr}					
B	172	0.930	0.810	0.752	13.36	54.62	0.005	14.1	127.6
M-30	425	0.102	0.942	0.860	20.18	65.50	0.11	7.53	52.1
M-50	480	0.115	0.905	0.811	29.47	69.73	0.15	6.28	59.8

Note. α — porosity; ε — void ratio; W — absolute water content; WA — water absorption.

The analysis of the obtained IR spectra confirmed that the studied zeolite samples belong to their structural types (table 4): the spectra contain absorption bands specific to zeolites in 2 regions: vibrational regions inside tetrahedra (internal asymmetric valence bands $1250\text{--}950\text{ cm}^{-1}$, symmetrical valence stretch $720\text{--}650\text{ cm}^{-1}$ and deformations in the T-O tetrahedron $500\text{--}420\text{ cm}^{-1}$); vibrations by external bonds of zeolite tetrahedra (double ring vibrations $650\text{--}500\text{ cm}^{-1}$, pore opening vibrations $300\text{--}420\text{ cm}^{-1}$, symmetric valence stretch $750\text{--}820\text{ cm}^{-1}$ and asymmetrical stretch $1050\text{--}1150\text{ cm}^{-1}$). Separate characteristic fluctuations were also identified. Thus, absorption bands in the region of $401\text{--}440\text{ cm}^{-1}$, which correspond to the vibrations of cations in the zeolite (interionic vibrations), were found only in mordenite samples. In addition, their spectra contain a band at about 780 cm^{-1} , which is characteristic of the Al–O bond inside aluminum-oxygen tetrahedra. Moreover, it has a greater intensity in M-50. This indicates a relatively higher aluminum content in it. The band at 665 cm^{-1} noted for bentonite indicates vibrations of Al–O–Si in the mixed silicon-aluminum-oxygen framework.

Characteristic bandwidths (bw) in the IR-spectra of zeolites

Samples						Frequency of the assignment
B		M-30		M-50		
A.b., cm^{-1}	Int., %	A.b., cm^{-1}	Int., %	A.b., cm^{-1}	Int., %	
				401.44	7.001	δ (T-O ₄)
		409.53	0.512	407.53	5.305	δ (T-O ₄)
		418.37	0.419	414.11	2.490	δ (T-O ₄)
				423.15	2.276	δ (T-O ₄)
		433.63	0.682	434.10	4.256	δ (T-O ₄)
440.49	0.264	441.12	3.257	441.06	4.385	δ (T-O ₄)
		456.31	0.754	449.84	2.568	δ (T-O ₄)
				473.72	4.593	δ (T-O ₄)
				502.97	5.818	к.с.к.
		514.29	1.110	509.30	5.385	к.с.к.
				523.69	5.580	к.с.к.
665.81	10.634					к.с.к.
		713.32	2.255			ν_s
721.76	9.785	721.86	2.328	721.94	9.796	ν_s
		776.10	3.482	772.58	14.704	ν_{as} (Si-O)
794.61	10.995					ν_{as} (Al-O)
		872.22	1.117	873.05	9.831	ν_s
		972.56	0.745			ν_{as}
				1022.95	3.210	ν_{as}
1038.29	5.714					ν_{as}
1644.47	9.539	1633.29	5.535	1643.73	17.568	δ (H ₂ O)
		3390.06	2.310	3396.17	8.194	ν_{as} H ₂ O
3417.95	7.026					B.c.OH
3626.65	6.257	3626.57	3.178	3626.35	9.574	B.c.OH
		3742.21	18.990	3742.21	23.045	ν_{as} H ₂ O
		3748.01	19.284	3748.96	24.637	ν_{as} H ₂ O
		3756.20	19.411	3756.10	24.551	ν_{as} H ₂ O
		3793.96	19.432	3794.02	23.939	ν_{as} H ₂ O
		3813.59	19.266	3813.58	27.022	ν_{as} H ₂ O
		3835.19	19.220	3829.92	27.259	ν_{as} H ₂ O
3851.04	20.800	3850.73	18.932	3850.71	27.200	ν_{as} H ₂ O
3861.00	26.185	3867.94	18.841			ν_{as} H ₂ O
		3897.37	18.439			ν_{as} H ₂ O

*h.b. — hydrogen bond; v.d.r. — vibrations of double rings.

However, the main differences in the IR spectra of bentonite and mordenite samples were associated with the absorption bands of water molecules. In the absorption spectrum of bentonite, a band of deformation vibrations of water at 1644 cm^{-1} (typical for adsorbed water) and stretching symmetric and asymmetric vibrations of OH groups at 3417.95 and 3626.65 cm^{-1} , respectively, was noted. In contrast to bentonite, in the spectrum of mordenite samples, the bands of deformation vibrations and stretching vibrations of OH groups are shifted to the high-frequency region, and bands related to stretching asymmetric vibrations of hydroxyl groups in the range of $3742\text{--}3850 \text{ cm}^{-1}$ were also found.

It is known that absorption bands in the region of stretching vibrations of OH groups can be caused by both structural hydroxyl groups and physically adsorbed water. Taking into account the data obtained, it can be concluded that both cases take place: the presence of adsorbed water on the surface of aluminosilicate samples is indicated by bands at 1633 , 1644 and 2146 , 2329 and 3417 cm^{-1} ; structural hydroxyl groups in bentonite, but located only in large cavities — at 3626 cm^{-1} , while in mordenite — by bands both in large (3626 cm^{-1}) and small (medium-intensive bands at 3742 , 3748 , 3756 , 3796 , 3813 , 3835 cm^{-1}) cavities [17]. In this position, the structural hydroxyl groups of mordenite are bonded to the silicon atom. The latter is now the generally accepted view. Also, when comparing the IR spectra of mordenite samples, attention was drawn to the increase in the intensity of structural hydroxyl groups at 3626 cm^{-1} relative to bentonite, as well

as the average intensity of the bands at $3742\text{--}3835\text{ cm}^{-1}$. Since the surfaces of clay minerals can act as centers for adsorption of coordinatively unsaturated ions of silicon, aluminum, magnesium, oxygen, and uncharged, as well as energetically active hydroxyl groups, for the latter the noted distinctive features in the IR spectra of the studied samples may indicate with a greater degree of probability their different adsorption activity.

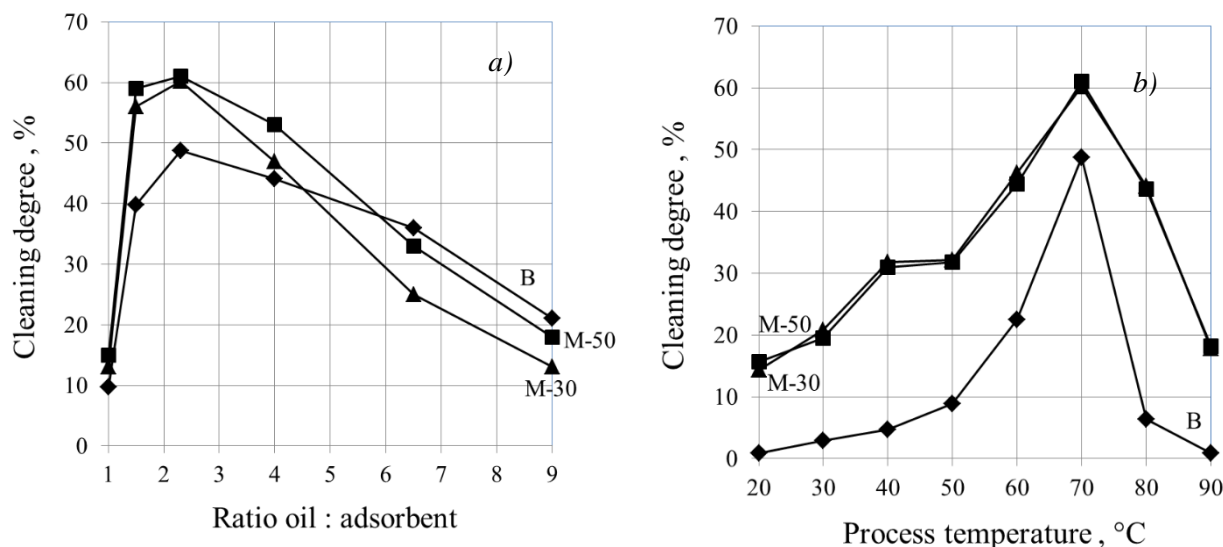


Figure. Dependence of the degree of oil purification on the ratio of oil: adsorbent (a) and process temperature (b)

The adsorption activity of zeolites was assessed by the degree of purification of UIO. The adsorption activity of zeolites was assessed by the degree of purification of UIO. The results obtained in the study of the effect of the oil to adsorbent ratio on the degree of oil purification made it possible to establish that mordenite samples had much greater sorption capacity with respect to aging products (Fig. a). The degree of oil purification in the presence of bentonite and mordenite differed by almost 13 % and amounted to 48.7 % and 61.86 % (for M-30), respectively. This is probably due to the manifestation by zeolites of the so-called “sieve effect” — selective throughput sorption of pores. According to the data available in the literature, the probable pore size of bentonite is 4 \AA versus 8 \AA for mordenite. The presence of this difference is apparently one of the reasons responsible for the differences in the sorption properties exhibited relative to the components of the used oil. And here a reservation should be made: the maximum values of this indicator for both adsorbents were noted at an oil: adsorbent ratio in the range of $1.5\text{--}2.3$. The similarity of this parameter for all three considered adsorbents indicates that the dimension of the inlet pores is of secondary importance, while the chemical structure of zeolites is of primary importance. It is understood as the presence of uncompensated surface force fields formed by complexes of silicon, aluminum and surface hydroxyl groups. Physical sorption on the surface of zeolites is carried out due to the excess negative charge of tetrahedrally forming metals, on the faces of crystals, as well as surface hydroxyl groups of an acidic and basic character.

According to now classical concepts, they are responsible for the orientational and inductive interaction of polar adsorbents with oil components. The low degree of purification at a low oil: adsorbent ratio is identical for both types of zeolites and, according to the literature data [15], is associated with the aggregation of adsorbent particles, which leads to a decrease in the total specific surface area and an increase in the diffusion path during adsorption.

The influence the temperature of adsorption purification is shown in fig. B. When comparing the effect of the process temperature on the degree of purification of UIO, it can be noted that the best results were obtained at $70\text{ }^{\circ}\text{C}$, which is in good agreement with the parameters recommended in the literature [19].

Used oil before purification is characterized by a high cyclicity of the constituent hydrocarbons (Table 5). Special attention should be paid to the distribution of the number of rings in the molecule of the original used oil — aromatic hydrocarbons account for 38 % of the total number, which indicates their high condensation and the corresponding carbon content (18.08 %). Whereas the oil subjected to adsorption purification with mordenite (M-50) gets rid mainly of aromatic rings. This is indicated by a decrease in the proportion of aromatic hydrocarbons to 19.6 % of the total, and an increase in the mass fraction of carbon in cycloalkane and alkyl substituents against the background of a 2-fold decrease in arene rings. This is a conse-

quence of the high polarizability of aromatic hydrocarbons, in which, compared with other oil components, a dipole moment is easily induced under the influence of the electrostatic field of the adsorbent [19, 20].

Table 5

Structural-group composition of oil samples according to the *n-d-M* method

Sample of oil	d_{20}^4	n_d^{20}	M	Carbon distribution, %				Average number of rings per molecule		
				C_{ap}	C_H	$C_{кор}$	C_{II}	K_{ap}	K_H	K_o
Initial	0.898	1.4996	311.82	18.08	29.54	47.61	52.38	0.67	1.10	1.77
after M-50 cleaning	0.878	1.4834	263.91	9.90	41.88	51.79	48.21	0.32	1.31	1.63

Conclusions

Thus, comparative studies of the sorption activity of natural aluminosilicates — bentonite and mordenite in the process of purification of used industrial oil made it possible to establish that the maximum degree of purification was achieved in the presence of mordenite and reached 61.68 % at an oil: adsorbent ratio of 2.3 at a temperature of 70 °C. The data of the structural-group composition of the purified oil indicated that the main components removed during adsorption purification are highly condensed aromatic hydrocarbons. The induction of a dipole moment in aromatic hydrocarbons is more likely due to the excess charge of surface hydroxyl groups, which, according to the results of IR-spectroscopic analysis, are localized in bentonite mainly in large cavities, while in mordenite, both in large and small ones. Thus, among the reasons for the different sorption activity of bentonite and mordenite, the dimension of the inlet pores is of secondary importance, while the chemical structure of zeolites is of primary importance.

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Табиғи алюмосиликаттар көмегімен өндірістік мұнай қалдықтарын адсорбциялық тазарту

Пайдаланылған өнеркәсіптік мұнайды табиғи алюмосиликаттар, бентонит және морденит қатысуымен адсорбциялық тазарту нәтижелері талқыланады. Тазартудың максималды дәрежесі мордениттің қатысуымен қол жеткізілді және 61,68 % мұнай: адсорбенттік қатынасы 2,3 70°C температурада жеткені анықталды. Бентонит пен морденит үлгілерінің әртүрлі адсорбциялық белсенділігінің болжамды себептері химиялық, минералогиялық, текстуралық және ИҚ-спектроскопиялық талдау деректері негізінде анықталды. Морденит үлгілерінің ИҚ-спектрлерінің нәтижелері бойынша олардың адсорбциялық белсенділігінің жоғарылауына энергетикалық белсенді гидроксил топтары жауапты болуы мүмкін деген қорытындыға келді. Мұнайдың құрылымдық-топтық талдауының мәліметтері тазарту кезінде жойылатын көмірсутекті компоненттердің негізгі үлесін жоғары конденсацияланған ароматтылар құрайтынын көрсетті. Тазартуға дейінгі мұнай қалдықтары көмірсутектердің жоғары циклілігімен сипатталады (ароматты көмірсутектер жалпы көлемнің 38 % құрайды), ал морденитпен (М-50) адсорбциялық тазартуға ұшыраған мұнай негізінен ароматты сақиналардан арылады (ароматты көмірсутектердің үлесі төмендейді). 19,6 %-ға дейін). Бұл басқа мұнай компоненттерімен салыстырғанда адсорбенттің электростатикалық өрісінің әсерінен дипольдік момент оңай индукцияланатын ароматты көмірсутектердің жоғары поляризациялануының салдары.

Кілт сөздер: адсорбциялық тазалау; өнеркәсіптік мұнай қалдықтары; бентонит; морденит; тазарту дәрежесі; ИҚ-спектрі; құрылымдық топ құрамы.

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Адсорбционная очистка отработанного индустриального масла с применением природных алюмосиликатов

Обсуждены результаты адсорбционной очистки отработанного индустриального масла в присутствии природных алюмосиликатов — бентонита и морденита. Установлено, что максимальная степень очистки достигалась в присутствии морденита и достигала 61,68 % при соотношении масло: адсорбент равном 2,3 при температуре 70 °С. О предполагаемых причинах проявляемой различной адсорбционной активности образцов бентонита и морденита судили по данным химического, минералогического, текстурного и ИК-спектроскопического анализа. На основе результатов ИК-спектров морденитных образцов сделан вывод о том, что за их повышенную адсорбционную активность могут быть ответственны энергетически активные гидроксильные группы. Данные структурно-группового анализа масла показали, что основная доля удаляемых в ходе очистки углеводородных компонентов приходится на высококонденсированные ароматические. Отработанное масло до очистки характеризуется высокой цикличностью входящих в состав углеводородов (на долю ароматических углеводородов приходится

38 % от общего числа), тогда как масло, подвергнутое адсорбционной очистке морденитом (М-50), избавляется в основном именно от ароматических колец (доли ароматических углеводородов уменьшается до 19,6 %). Это является следствием высокой поляризуемости ароматических углеводородов, в которых по сравнению с прочими компонентами масла под влиянием электростатического поля адсорбента легко индуцируется дипольный момент.

Ключевые слова: адсорбционная очистка; отработанное индустриальное масло; бентонит; морденит; степень очистки; ИК-спектр; структурно-групповой состав.

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