Research of innovative adsorbents in cottonseed oil refinement technology

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Abstract. Based on the results of a comprehensive research of the nature and colloid-chemical properties of selected local clays before and after their acid activation, it has been established that Shafrikan bentonite (Bukhara region) and Mayskiy clay (Tashkent region) are promising raw materials for obtaining effective adsorbents for the oil and fat industry. The new types of adsorbents in cottonseed oil bleaching technology have been studied. The main sorption properties of local clays as adsorbents have been determined. The dependence of the chromaticity of cottonseed oils on the sorption properties of innovative types of adsorbents has been established. The temperature limits of the first, second and third "effect" for selected samples of local clays has been established by the method of differential thermal analysis. A spectral method has been developed for quantitative evaluation of the selectivity of adsorbents in the bleaching of vegetable oils, in particular cottonseed oils. Mathematical models have been developed for obtaining activated adsorbents from local clays, and based on them the optimal modes of recommended processes have been selected. The intensifying role of vacuum in the production of activated adsorbents from local clays has been established.

1 Introduction

Various methods are used in purification and refinement of raw vegetable oils [1-5]. In the purification technology, the methods of bleaching of refined vegetable oils are the most important [6-8]. In the technology of adsorption purification of vegetable oils, many adsorbents and bleaches have been proposed, however, identifying the most effective and innovative adsorbents is of both scientific and practical interest. The purpose of the work was to study new innovative types of adsorbents in the technology of bleaching refined cottonseed oils and to establish the dependence of product quality on the adsorbing properties of local clays.

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2 Methods of research

Modern methods of physical and chemical research have been used in order to analyze and evaluate the quality of raw materials and bleached cottonseed oils, in particular, chromatography, NMR and other types of spectral analyses. Considering the prospect of industrial development of non-ore deposits, the following types of local clays have been studied in Uzbekistan: - Mayskaya clay, place of origin is Tashkent region; - secondary kaolin, place of origin is Angren deposit of the Tashkent region; - Dekhkanabad clay, place of origin is Kashkadarya region; - bentonite clay, place of origin is Shafrikan district, Bukhara region.

The well-known ascanite – bentonite of the Georgian origin have been used as a comparison reference sample.

Table 1 shows the results of the chemical analysis of used clays selected for the production of adsorbents.

As can be seen from Table 1. secondary Angren kaolin in its chemical composition differs from Mayskiy clay, and Dekhkanabad clay and Shafrikan bentonite are relatively distinguished by a high content of SiO2 and Al2O3.

It is known that aluminum oxide is an effective sorbent for free fatty acids, soap, etc.

Therefore, the presence of kaolin as an adsorbent has a positive effect on the selective adsorption of the above substances from the bleached oil.

In terms of argil content, secondary Angren kaolin belongs to semi-acid raw materials.

Table 1. Chemical composition of local clays selected for production of adsorbents.

Name of clay	Content of components, % per absolute dry matter						
	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	TiO_2	MgO
Ascanite-bentonite (control)	54.14	18.74	4.98	0.22	2.41	0.38	4.64
Mayskiy clay	50.9	9.45	3.80	0.71	12.3	-	9.25
Angren kaolin*	65.3	25.28	1.50	0.1	0.3	0.45	0.35
Dekhkanabad clay	50.8	9.35	3.55	0.5	13.5	0.3	3.48
Shafrikan bentonite	58.4	14.0	10.4	0.1	2.5	0.65	3.1

Table 2. Chemical composition of local clays selected for production of adsorbents (continuation).

Name of clay	Content of components, % per absolute dry matter					H_2O, %
	SO_3	Na_2O	K_2O	n.n.n.	Sum	
Ascanite-bentonite (control)	0.07	2.82	0.64	10.94	99.98	6.71
Mayskiy clay	-	1.84	1.34	10.20	99.82	8.15
Angren kaolin*	0.16	0.4	0.94	5.12	99.90	6.15
Dekhkanabad clay	3.9	3.06	1.25	10.10	99.85	8.56
Shafrikan bentonite	0.1	1.5	1.3	8.0	100.05	8.1

Note: * - data on secondary Angren kaolin.

Considering that during the acid activation of clays, along with the enrichment of the adsorbent with silica the removal of the cations (Ca2+, Mg2+, Na+, K+) from its crystal lattices is occurs, then it is clear that natural kaolin does not require such activation in its composition.

On the contrary, Mayskiy clay, Dekhkanabad clay, and Shafrikan bentonite are poor in SiO2 and require acid activation. Sedimentation analysis carried out according to the Sabonin-Robinson method [9] showed that, in terms of their granulometric composition, all the studied clay samples belong to finely dispersed raw materials, represented mainly by particles ranging in size from 1 to 10 microns.

Clay indicators carried out at a rate of 30°C/min. using Kurnakov pyrometer of FPK-55 brand [10] showed that for all the studied samples (except secondary Angren kaolin) three endothermic effects are observed.

Research results

Table shows the results of the studied used clays.

During heat treatment of these clays, it is necessary to adhere to the temperature limits indicated in Table. 2.

Table 3. Indicators of the studied local clays.

Name of the clay	Temperature of the "effect", °C		
	first	second	third
Ascanite-bentonite	200-250	500-700	850-900
Mayskiy clay	250-300	650-750	900-950
Angren kaolin*	500-700	900-1000*	1200-1250**
Dekhkanabad clay	250-320	700-800	900-950
Shafrikan bentonite	200-250	600-750	850-950

Note: * and ** – in these temperature ranges, exothermic effects are observed in kaolin.

It is known that during acid activation, part of the oxides dissolves and is removed from the surface layer of clays. At the same time, the adsorption and selectivity of clays in relation to oil-coloring pigments increases significantly.

All samples of local clays (except secondary Angren kaolin) were subjected to acid activation in the laboratory according to the traditional method.

In the adsorption processes of purification and clarification (bleaching) of food products, in particular vegetable oils, a significant role belongs to the transitional pores of adsorbents.

Bleaching of the oil has been carried out by the standard method for 30 minutes in laboratory conditions at a temperature of 90-95 °C and the introduction of the studied clays from 1.0 to 2.0% by weight of the oil.

Table 4 shows the results of research on the filterability, oil absorption and bleaching capacity of local adsorbents, where refined cottonseed oil with a chromaticity of 16 red units at 35 yellow units has been subjected to clarification.

Table 4. Results of oil absorption, filterability and bleaching capacity of the local adsorbents.

Name of the adsorbent	Bleaching capacity at 1% of adsorbent, %	Filterability at 1% of adsorbent, ml/5 sec	Oil absorption of the adsorbent, %
Ascanite-bentonite	31.5	15.5	50.9
Mayskiy clay	26.3	17.0	48.1
Angren kaolin*	25.0	18.5	46.3
Dekhkanabad clay	26.0	16.8	56.4
Shafrikan bentonite	30.8	14.9	42.7

Note: * - this sample of recyclable Angren kaolin was thermally activated at 350-500 °C for 3 hours.

From the data in Table 4, it can be seen that the highest value of bleaching capacity belongs to Shafrikan bentonite and Mayskiy clay. Thermally activated Angren kaolin also showed satisfactory results in bleaching capacity. In terms of filterability, not all local adsorbents are inferior to Ascanite – bentonite from Georgia (control variant).

Among the considered adsorbents, the highest oil absorption is observed in Dekhkanabad clay (56.4%), and the lowest in Shafrikan bentonite (42.7%), which puts it as the first in a series of irrational adsorbents. In order to intensify the process of acid activation of clays, the role of vacuum has been studied.

It has been established that increasing the vacuum to 2.3 kPa increases the bleaching capacity of both types of local adsorbents. At the same time, the best results are obtained on Shafrikian bentonite, whose bleaching capacity (32.8%) exceeds the well-known Ascanite - bentonite from Georgia (31.5%).

The internal pores of the clays are initially filled with air, which prevents the penetration of the solution and reduces the active surface of the clay due to the adsorption of gas molecules from the air. Vacuum promotes the removal of air from pores and capillaries and provides improved conditions for acid activation. With the change in the nature of the adsorbent and the methods of its activation, the nature of the oil bleaching process also changes. This is confirmed by the selective properties of the adsorbent of one or another component accompanying the oil. Moreover, the qualitative composition of the processed oil also plays an important role in adsorption purification, because its multicomponent composition depends on the type of seeds (medium fiber or fine fiber), and the conditions of its cultivation and processing as well.

We have established that the content of free fatty acids (FFA) and phosphatides in oils obtained from fine-fiber seeds is 0.25 mg KOH and 0.15% higher than in conventional oils, respectively. The content of linoleic acid (C18:2) in seeds of fine-fiber cotton is 6-10% higher and vice versa, oleic acid (C18:1) is 1-2% less than in medium-fiber cotton. The mass fraction of carotenoids, chlorophylls and gossypol in fine-fiber seeds is greater than in ordinary seeds. A similar trend of deterioration in the quality of the oil is observed when mixing (up to 50%) fine-fiber seeds into medium-fiber ones.

Table 5 shows the indicators of clarification of cottonseed oil according to the group of its accompanying components on local adsorbents.

Table 5. The degree of clarification of cottonseed oil according to the group of its accompanying components.

Name of the adsorbent	The degree of oil clarification	
	According to gossypol, carotenoids and their derivatives	According to chlorophyll, pheophytin and their derivatives
Ascanite-bentonite	1.612	1.032
Mayskiy clay	1.554	1.318
Angren kaolin*	1.785	1.097
Dekhkanabad clay	1.503	1.212
Shafrikan bentonite	1.678	1.431

Note: * - recyclable Angren kaolin is thermally activated at a temperature of 350-500 °C for 3 hours.

From Table 5 it can be seen that the highest degree of oil clarification according to the group of gossypol, carotenoid and their derivatives is observed in recyclable Angren kaolin (1.785), Shafrikian bentonite (1.678) and control Ascanite - bentonite of Georgia (1.612); according to the group of chlorophyll, pheophytin and their derivatives – in Shafrikan bentonite (1.431) and Mayskiy clay (1.318).

Consequently, a spectral research of the multicomponent adsorption of oil-coloring substances showed the promise of creating adsorbent compositions (CA) from local clays.

3 Discussion

Analysis of porosity and, in particular, transitional pores of the studied clays before and after their acid activation has been carried out by the standard method on a Model-200 mercury pore-meter manufactured by Carlo Erba Strumantazion company (Italy) [11-13].

In this case, the duration of the analysis was 30 minutes, the maximum pressure of the introduced mercury was 20×105 kPa, and the mass of the studied samples was 0.977 g, each.

It has been established that after acid activation, the total pore volume of ascanite-bentonite (control) increased from 0.12 to 0.25 cm3/g, i.e. in 2.22 times. Under similar conditions of acid activation, total pore volume in Shafrikan bentonite increased from 0.1 to 0.28 cm3/g, i.e. 2.8 times, and the volume of transitional pores increased from 0.08 to 0.21 cm3/g, i.e. 2.63 times. If in its natural form the total pore volume is greater for ascanite-bentonite (0.12 cm3/g) than for Shafrikan bentonite (0.1 cm3/g), then a different picture is observed in the acid-activated form. Ascanite-bentonite in activated form has 0.03 cm3/g less than the volume of total pores and 0.01 cm3/g of transitional pores.

Consequently, in terms of total porosity and the content of transitional pores, activated Shafrikian bentonite is not inferior, but even surpasses the well-known ascanite-bentonite of Georgia origin.

Clays and adsorbents derived from them have the ability of strongly absorbing certain components associated with the oil.

The spectral method allows estimating the degree of purification of cottonseed oil and the selectivity of the adsorbent for one or another accompanying oil substance.

The measurement of the spectral characteristics of oils was carried out on the Raduga-2 color meter [14, 15], in which the C31 light source reproduces daylight with a light temperature of 6500 K according to GOST 7771-76. The thickness of the cuvette used for measurements was 10 mm.

Figure 1 shows the results of measuring the coefficient of transmission (τ) depending on of the length (λ) of the light wave.

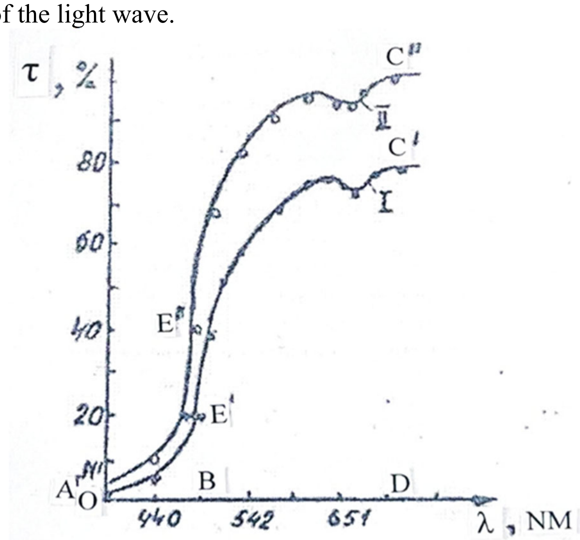

Fig. 1. Spectral characteristic of the cottonseed oil with a chromaticity of 14 red units at 35 yellow units (curve I) and 8 red units at 35 yellow units (curve II), bleached with a local adsorbent. Segment OB is the spectra of the carotenoid, gossypol and their derivatives area; BD is the spectra of the chlorophyll, pheophytin and their derivatives area.

4 Conclusions

Calculations have shown that the maximal degree of purification of cottonseed oil on Shafrikan bentonite corresponds to the group of gossypol, carotenoids and their derivatives. Further, on the group of chlorophyll, pheophytin and their derivatives.

In general, the degree of purification of the oil for all substances associated with triacylglycerines is 1.344 times.

Thereby, the proposed method can objectively characterize the degree of oil purification by adsorbents and their selective properties.

An efficient technology for obtaining activated adsorbents from local clays has been developed. The test of the proposed product in production conditions has given positive results.

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