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Study of bentonites during processing of high color raw cotton oils

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Abstract. The paper investigates and recommends the multicomponent composition of cottonseed oil subjected to adsorption purification, divided into macro- and micro-impurities, and according to the qualitative composition: into substances that have an acidic, coloring and unsaponifiable nature. The authors come to the conclusion that it is necessary to develop a combined thermally differentiated capable of purification on local activated sorbents.

1 Introduction

The technology for the production of refined cottonseed oil provides for a number of processes that ensure maximum removal from it of substances harmful to human health (gossypol, chlorophyll and their derivatives, soap residues, chemical reagents, and others).

It is known that the study of the kinetic regularities of the adsorption purification of vegetable oils makes it possible to rationally organize this process and its instrumentation [1]. The rate of depletion of the adsorption capacity of the adsorbent in the case of a monomolecular mechanism of carotene adsorption is largely determined by internal diffusion. This is indicated by the directly proportional dependence of the rate constants. To their average speeds:

$$\frac{\Delta n_i^s}{\Delta \tau} = \frac{k}{2\sqrt{\tau}} \tag{1}$$

where: k is the constant of adsorption of carotene by sorbents from C0;

τ - phase contact time.

2 Research methods

The study of mass transfer during the adsorption of carotene from oil makes it possible to represent the porous structure of the adsorbent as a model of a uniformly porous solid and calculate the numerical values of the effective internal diffusion coefficients Di of carotene based on the solution of the following system of equations describing adsorption from the bulk [2]:

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$$\frac{\partial\left(n_i^s + C\right)}{\partial r} = D_i\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} * \frac{\partial C}{\partial r}\right); \tag{2}$$

$$n_i^s = f(C) \tag{3}$$

$$C(r,0)=0; \quad \frac{\partial C}{\partial r_{r=0}} = 0; \tag{4}$$

$$C(R,\tau)=C_\tau \qquad C_\tau(0)=C_0 \tag{5}$$

where: r- is the current radius of the sorbent particle, m;

R-radius of the sorbent particle, m;

Cτ-surface of a sorbent particle, m;

D_i -coefficient of internal diffusion, m2/s;

Here, equations (1-3) include the material balance, which takes into account the rate of substance transfer in a spherical grain of the adsorbent, the adsorption isotherm equation, initial and boundary conditions for linear isotherms, which are the initial section of the carotene adsorption isotherm.

When calculating Di, the following relation is used, which is valid for the theoretical kinetic curve j() and obtained by solving system (1-3)

$\theta = D_e * \tau / R^2 < 0,1$):

$$j(\theta) = \left[1 + \frac{V}{V_3(1 + K_{a\partial c} * n_{i\max}^s v)}\right]\left\{1 - \frac{1}{x-\beta}\left[\alpha * l^{\alpha^2\theta}(1 + lrf\alpha\sqrt{B} - \beta l^{\rho^2\theta})(1 + lrf\beta\sqrt{\theta})\right]\right\} \tag{6}$$

where: θ-dimensionless time;

V3-volume of grains, m3;

v-molar volume of carotene, cm3/mol;

α and β are the roots of the equation.

From here:

$$X^2 + \frac{3V_3\left(1 + K_{a\partial c} * n^s{}_{i\max} * \nu * \rho_k\right)}{V} * X\frac{3V_3\left(1 + K_{a\partial c} * n^s{}_{i\max} * \nu * \rho_k\right)}{V} = 0 \tag{7}$$

where:

ρk - is the apparent density of the adsorbent, g/cm3;

Based on the obtained values of Di in coordinates:

Lg De= $f\left(\frac{1}{T}\right)$ determine the numerical value of the activation energy of carotene (E2), which is (for activated carbon):

$$E_2 = 35.64 \text{ kJ/mol}.$$

A study of the adsorption kinetics of substances associated with oil shows that industrial processes are carried out in modes that are far from optimal.

The effectiveness of the process of adsorption purification and clarification of oil is evaluated not only by its discoloration, but also by the removal of other undesirable impurities (free fatty acids, soap, pesticides).

This also reduces the content of coloring pigments (gossypol, carotene, chlorophyll and their derivatives), phospholipids, products of primary (peroxide value) and secondary oxidation of moisture, and others [3].

In practice, the removal of pigments that give the oil a green or gray-green tint (chlorophyll and its derivatives) is a difficult task, because. not every adsorbent is able to absorb them. Metal impurities (Fe, Cu, etc.) are catalysts for undesirable oil oxidation and they have a detrimental effect even at very small amounts.

During storage of cotton seeds, gossypol is oxidized by atmospheric oxygen, and the content of bound gossypol and gossypurpurine increases. Increased humidity and temperature intensify the above processes, which contributes to the dark coloration of cottonseed oil.

Cottonseed oil contains from 0.6 to 2.8% by weight of the oil malvic and steroculinic cyclopropenoid acids, which have a harmful biological effect on the human body and are difficult to remove from the oil during refining.

It should be noted that aflatoxins in cottonseed oil are poorly removed during its alkaline refining and can be completely removed only during its adsorption purification (bleaching) with clays or coal.

The multicomponent composition of cottonseed oil subjected to adsorption purification is divided into macro- and micro-impurities, and according to the qualitative composition: into substances that have an acidic, coloring and unsaponifiable nature.

When refining difficultly refined cottonseed oil by the emulsion method, even using alkali, followed by adsorption purification with clays or coals, it is not always possible to obtain a standard oil with low color

Melanophosphatides increase the color intensity of unrefined oils, since they belong to non-hydratable groups of phospholipids, which adversely affect the refinability of cottonseed oils, especially the bleaching process. The same role is played by gossyphospholipids and phosphatins.

A comprehensive analysis of the refining processes of vegetable oils, in particular, cottonseed oils, showed that each type of processed raw material is a complex multicomponent mixture with different physical and chemical properties. This requires an individual approach in choosing the method and mode of their refining.

It is known that the main component of the process of adsorption purification of oils is an adsorbent that has a polymineral composition. The nature of the adsorbent surface, the value of its specific surface area and porosity determines the efficiency of polymolecular adsorption, i.e. purification and clarification of oils.

Moreover, colloid-chemical properties (dispersion, porosity, sign and magnitude of the particle charge (value of e-potential), swelling, hydrophilicity, heat of wetting, ion-exchange capacity, colloidality, etc.) characterize the main properties and parameters of adsorbents.

In the oil and fat industry, the following types of adsorbents are mainly used: bleaching earths, activated carbons, etc. Moreover, most of them are used in an activated form.

In practice, natural clays are one of the main sources of adsorbents. Moreover, not all clays exhibit high adsorption activity in their natural form.

The bleaching ability of bentonites during heat treatment increases slightly, which is probably due to the presence of a significant amount of sesquioxides in them.

3 Results and discussions

As impurities of natural clays, carbonates, sulfates, oxides, quartz, opals, calcites, substances of organic origin, etc. are accompanied. Moreover, for each type of mineral adsorbent, the methods and modes of activation must be determined experimentally, depending on the nature and composition of the adsorbent, as well as, his destination. So, for example, to obtain an active adsorbent from bentonite, it is necessary to extract about half of the original Al2O3 completely - iron, alkali and alkaline earth metals. Acid activation of bentonites contributes to a significant increase in the volume of transitional pores [4].

With severe acid activation of clays, due to the dissolution of sesquioxides, the crystal structure of montmorillonite is destroyed, mainly, and inactive silicon oxides are formed.

At the same time, micropores disappear, the number of hydrogen bonds on the surface of the adsorbent increases, which are significantly enriched with transitional pores (3–20 nm), which are necessary for cleaning and clarifying oil solutions containing macromolecular substances.

Acid activation of natural clays contributes to the production of highly bleaching adsorbents.

Today, special attention is paid to the study of natural bentonites, highly colloidal, plastically swelling clays in water. Bentonites are composed of clay minerals (montmorillonite, beidellite, nokfonite, hektronite and saponite) [5].

Montmorillonite minerals occur naturally as very small and imperfect crystals. They differ in structure from pyrophyllite only in the ability of the lattice to swell.

In Russia, bentonites and gumbrin are used for bleaching vegetable oils, in Georgia - bentonite - ascanite, in Armenia - Ijevan bentonite.

However, the lack of special equipment and technology for the production and use of ion exchangers in Uzbekistan did not allow them to be introduced into oil and fat production.

As can be seen, the quality of the adsorbent and the scope of its application are also determined by the porosity of its structure and the state of the surface of the particles. In this case, the molecular sieve properties of clay also play an important role

Experimental studies of adsorbents are carried out by physical (true, apparent specific gravity, pore volume, etc.), structural-sorption (monolayer capacity, size of effective pore radii, limiting sorption volumes, etc.), colloid-chemical (hydrophilicity, swelling, plasticity, structure formation, etc.), as well as granulometric, mineralogical and chemical methods, including the determination of salt composition, total absorption capacity and cationic composition [2-3].

A well-known set aimed at measuring the properties of sensors: physio-thermal treatment, hydrothermal treatment; chemical treatment with solutions of mineral acids, base salts, water-soluble, explosive compounds (surfactants), polyelectrolytes (G1E); combined acid-heat treatment, acid-base, alkaline-acid, alkali-surfactant, acid-PE, PE-thermal, radiation polymerization of dosed monomers.

Today's testing of synthetic dosers (silica gel, zeolite, etc.) does not allow them to be introduced into oil and fat production.

The removal of oxides of aluminum, alkali and alkaline earth metals and their replacement in the diffusion layer by hydrogen occurs during the acid activation of clays according to the following scheme: bentonite-(Na; Mg; La; Al)+H2SO4 $\rightarrow$ bentonite H+ + (N2SO4; MgSO4; CaSO4; Al2(SO3)3).

In activated clays, the typical structure of montmorillonite is preserved, but the nature of their surface and porosity changes significantly. Moreover, the adsorption of coloring oil pigments mainly occurs in the active centers of clay.

Highly hydrophilic adsorbents form hydrate shells on the surface, making the adsorbent particles inaccessible to hydrophobic molecules. The adsorption of water vapor and the heat of wetting can serve as an estimate of the degree of adsorbent hydrophilicity.

The value of surface tension at the adsorbent-adsorbate interface can serve as an indicator of adsorption.

For the adsorption of substances associated with oil, which have a high molecular weight and amphiphilic properties, acid activation adsorbents are required, which have hydrogen ions on the surface.

In practice, activated carbons (grades A, B, C) are sometimes used to clarify high-dark oils. However, this is accompanied by difficulties in separating the coal from the clarified oil.

Considering the complex multicomponent composition of bleached oils and fats, in some cases, mixtures of various adsorbents are resorted to.

The replacement of the well-known ascanite-bentonite imported from abroad (Georgia) with local clays contributes to significant savings in resources and improving the quality of edible oils [6].

4 Conclusions

We have studied the effectiveness of using a composition of adsorbents from local clays in the purification and bleaching of cottonseed oils.

Unfortunately, industrial testing of such compositions has shown the need to optimize the thermodynamic and hydrodynamic modes of cottonseed oil bleaching on the proposed adsorbent compositions

Therefore, in order to increase the efficiency of the process of adsorption purification of cottonseed oil, it is necessary to develop a combined thermally differentiated capable of purification on local activated sorbents.

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