PURIFICATION OF CRUDE COTTONSEED OIL AND TECHNICAL GOSSYPOL ON A CHITIN SORBENT

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It has been shown that the use of chitin (technical), which is a production waste, as adsorbent permits the clarification of black cottonseed oil and the purification of technical gossypol.

Methods of purifying gossypol based on its conversion into acetates with subsequent hydrolysis and repeated recrystallization of the gossypol from its solutions in diethyl ether, chloroform, and benzene by the action of hexane or petroleum ether are known [1].

Adsorption methods are more promising. For the purification of cottonseed oil, methods involving the adsorption of gossypol on the passage of oil solutions (miscellas) through columns of alumina [2], magnesia [3], and anion-exchange resins [4] have been used; however, it is practically impossible to extract the gossypol in the native state from these sorbents. A. L. Markman and R. R. Avlyanova have shown the possibility of extracting and purifying gossypol by the principle of selective adsorption using polyamide resins as adsorbents [5].

The aim of the present work was to study the purification of technical gossypol and black cottonseed oil on a chitin sorbent not previously used for these purposes. Chitin is the most widespread aminopolysaccharide, being the main component of the external skeleton of invertebrates. In nature, chitin is present in the form of a complex with protein. In nature, chitin is present in the form of a complex with protein. In its structure, physicochemical properties, and biological role, chitin is analogous to the cellulose of plants. We used technical chitin from crab meal, GOST 2116–82, which is a waste from the manufacture of food products. This product as such did not possess satisfactory adsorption properties, in view of which it was treated with solutions of sodium hydroxide. For each experiment we used 10 g of chitin, and after its saponification with 50% NaOH in H_2O at 100°C we determined the amount of fat liberated and the yield of absorbent:

Reaction time, h	Fat, g	Adsorbent, g
2	0.28	1.9
4	0.27	2.0
6	0.25	2.0

After saponification with the aqueous alkali, only one fifth of the adsorbent, which retained its specific fishy odor, remained. After purification with alcoholic alkali an odorless adsorbent was obtained in high yield (Table 1).

The figures of Table 1 show that the optimum conditions are the saponification of chitin at 80°c with 5% alcoholic alkali for 4 h or with 10% alkali for 2 h. The adsorbent prepared in this way was used to clarify cottonseed oil and to purify technical gossypol. The experiments were performed under static conditions [6]. In view of the high oil capacity of the sorbent (31.6%) and its low density we used not the oil itself but a 10% miscella of it.

The sorption capacity of the chitin was studied as a function of the mixture of the solvents used for the preparation of the miscellas, the oil-chitin ratio, and the time of contact of the oil with the sorbent. As the solvents for the preparation of the miscellas

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TABLE 1. Treatment of Chitin (technical) with Alcoholic Alkali

Reaction time, h	Temperature, °C	5% NaOH		10% NaOH		20% NaOH	
		fat, g	adsorbent, g	fat, g	adsorbent, g	fat, g	adsorbent, g
2	40	0,23	5,20	0,45	4,90	0,40	3,20
	60	0,36	4,60	0.46	4,20	0.43	3,10
	80	0.38	3,60	0,50	5,00	0,36	3,90
4	40	0,28	4,80	0,45	3,00	0,40	3,30
	60	0,36	4,20	0,46	4,20	0.42	3,70
	80	0,45	4,20	0,48	4,30	0,42	3,90
6	40	0,38	4,40	0,40	4,80	0,43	4,30
	60	0,35	3,80	0,48	4,80	0,40	4,30
	80	0.48	3.60	0.46	3,90	0.40	2,90

we used carbon tetrachloride [6], chloroform, hexane, and extraction gasoline. The results of a study of the influence of the nature of the solvents on the clarification of cottonseed oil on 12-hour contact with the sorbent in an oil-sorbent ratio of 1:5 are given below. The degree of clarification was judged from the color index of the oils obtained in comparison with that of initial black oil.

Solvent	Color index of the clarified oil, red units at 35 yellow in a 13.5-cm layer
Initial oil	55 (in a 1-cm layer)
Carbon tetrachloride	25.0
Chloroform	12.0
Hexane	10.0
Gasoline	7.0

In all the solvents a considerable lightening of the color of the cottonseed oil from 55 red units (in a 1 cm layer) for the initial factory sample to 7.0 red units in a 13.5 cm layer was observed. Under otherwise identical conditions, the greatest lowering of the chromaticity index of the oil was achieved in gasoline, and this was followed by hexane and chloroform. In carbon tetrachloride the lightening of the color was somewhat worse (to 25 red units). It is important to note that the best results were obtained with a solution of the oil in gasoline, which is the main extractant used in the oils and fats industry.

To determine the minimum amount of sorbent at which an oil corresponding to the standard for an edible oil was obtained, we carried out experiments at different oil:sorbent ratios (from 1:1 to 1:6). It was found that the optimum was a ratio of 1:4, at which the color index of the oil amounted to 7.5 red units. A further increase in the amount of sorbent (1:5, 1:6) scarcely lowered the color index:

Amount of sorbent, g	Oil:sorbent ratio	Color index of the clarified oil, red units at 35 yellow in a 13.5-cm layer
1	1:1	20.0 (in a 1-cm layer)
2	1:2	53.0
3	1:3	25.0
4	1:4	7.5
5	1:5	7.0
6	1:6	8.0

An investigation of the influence of the time of contacting the oil with the sorbent at the optimum ratio on some indices of the clarified oil showed that a lightening of 7 red units in the color index was achieved after contacting for 12 h while after 2-6 h the oil was only slightly clarified. Simultaneously with the increase in the time of contact the acid No. of the oil fell (from 5.08 for the crude cottonseed oil to 0.25 mg of KOH for the clarified oil):

Time of contact, h	Color index, red units at 35 yellow in a 13.5 cm layer	Acid No., mg of KOH	Amount of free gossypol, %	Yield of clarified oil, %
Crude oil	55.0 (in a 1-cm layer)	5.08	0.12	
2	55.0	1.95	not detected	95.0
4	35.0	1.80	"	94.8
6	20.0	0.86	"	94.4
12	7.0	0.25	"	94.0

Free gossypol was absent from the clarified oil. the yield of clarified oil was 94.0%.

The fatty-acid composition of the oil after treatment with chitin was practically unchanged:

Acid	Amount by GLC, %	
	Crude Oil	Clarified Oil
$C_{14:0}$	0.5	0.6
$C_{16:0}$	24.2	25.7
$C_{16:1}$	Tr.	0.6
$C_{18:1}$	20.0	17.1
$C_{18:2}$	55.3	56.0

The indices obtained for the oil (low acid No. and color index, absence of free gossypol) give grounds for considering that when cottonseed oil is decolorized on chitins a refined edible oil corresponding to the requirements of GOST 1128–75 for the highest and first grades is obtained.

The regeneration of the used chitin was carried out either by washing with polar solvents (acetone, chloroform–ethanol (1:2)) or by hot saponification with 1% alcoholic NaOH. The composition of the fatty acids isolated from the fat after the regeneration of the chitin was: $C_{14:0}$ – 1.1; $C_{16:0}$ – 31.6; $C_{16:1}$ – 3.8; $C_{18:1}$ – 27.6; $C_{18:2}$ – 35.9%.

After regeneration the sorbent was used again for purifying a new portion of oil.

The number of working cycles on one and the same sample of chitin was determined in the following way. After each cycle the adsorbent was washed with acetone until the fat had been eliminated completely, and the color of the refined oil after the following cycle

TABLE 2. Influence of the Nature of the Solvents on the Purification of Gossypol on Chitin*

Solvent	Insoluble impurities, %	Purity of the soluble fraction, %	Amount of adsorbent, g	Yield of gosypol after purification		Purity of the gossypol, %
				г	%	
Chloroform	16,0	46,2	5 0	0,23	54,7	62,1
.	16,0	46,2	10,0	0,18	42,9	68,4
.	16,0	46,2	15,0	0,15	35,7	75,0
Benzene	18.0	47.3	5,0	0,32	78,0	51.9
.	18,0	47,3	10,0	0,19	46,3	76,9
.	18,0	47,3	15,0	0,15	36,6	78,9
Carbon tetrachloride	24,0	51,0	5,0	0,19	50.0	80,0
	24,0	51,0	10,0	0,19	50.0	85.4
.	24.0	51,0	15,0	0,15	39.5	85.7

*The amount of technical gossypol taken for purification was 0.5 g.

was compared with the color of the oil after the first cycle. After seven cycles the color index of the oil began to rise. Thus, one portion of chitin can purify seven volumes of a miscella of the crude oil without appreciable deterioration of the quality of the refined oil, provided that the sorbent is defatted with acetone at the end of each cycle.

The treated chitin was also used for the purification of technical gossypol.

To select a suitable solvent we used carbon tetrachloride, chloroform, and benzene. The experiments were conducted with the adsorbent under static conditions. The efficacy of purification was judged from the purity of the samples obtained. Table 2 gives the results of a study of the influence of the nature of the solvents on the purification of gossypol on chitin.

On comparing the behavior of different solvents under otherwise identical conditions (time and temperature of the process and amount of sorbent) (see Table 2), we see that the use of carbon tetrachloride gave gossypol with the highest purity (85.7%, as compared with 75-76% for benzene and chloroform).

Table 2 also shows that with an increase in the purity of the gossypol its yield fell. Satisfactory results were obtained at a gossypol:sorbent ratio of 1:20. An increase in the amount of sorbent led to a slight improvement in the purity of the gossypol. The time of contacting of the product to be purified with the sorbent is one of the most influential factors:

Time of contacting, h	Yield of purified gossypol		Purity of the gossypol, %
	g	%	
1	0.20	76.3	62.0
2	0.25	65.8	66.6
4	0.24	63.1	70.0
6	0.23	57.9	75.5
8	0.21	55.2	80.0
12	0.19	50.0	85.4
24	0.19	50.0	85.1

As can be seen from the results given above, with an increase in the time of contacting from one hour to 12 the purity of the gossypol obtained increased. Longer contact (24 h) did not improve its purity.

Thus, the optimum conditions for the purification of technical gossypol on chitin are: the use of carbon tetrachloride as solvent, a temperature of the process of 20-25°C, a gossypol:sorbent ratio of 1:20, and a time of contacting of 12 h.

EXPERIMENTAL

Defatting of the Sorbent. The adsorbent (10 g) was covered with 30 ml of sodium hydroxide solution. In the case of aqueous alkali, the reaction was conducted at the boil for 2-6 h. Saponification with alcoholic alkali was performed with 5-20% solutions at 40-80°c, likewise for 2-6 h. After the cooling of the solution, the excess of sodium hydroxide was neutralized with acetic acid, added in drops to neutrality. Then the sorbent was filtered off, washed with water, and dried at room temperature. No demineralization of the sorbent was carried out.

The oil content of the adsorbent was determined as described in [7].

Clarification of Black Cottonseed Oil. A 5 g sample of sorbent was covered with 10 ml of a 10% miscella of the crude oil, and the mixture was stirred for 10-15 min and was left overnight. Then the sorbent was filtered off and was washed with an appropriate solvent. The color index of the oils obtained was determined on a VNIIZh [All-Union Scientific-Research Institute of Fats] calorimeter [8].

Purification of Technical Gossypol under Static Conditions [6]. Technical gossypol (5 g) was dissolved in 800 ml of the appropriate solvent. The insoluble part was separated off and wash washed until a clear filtrate had been obtained, and the total volume of the solution was made up to 1000 ml. Then, for each experiment, a suitable amount of adsorbent was taken and was covered with 100 ml of the solution. The mixture was stirred for 10-15 min and was left overnight, after which the adsorbent was separated off by filtration, and the solvent was distilled off. The gossypol residue so isolated was washed with petroleum ether and dried, and the purity of the gossypol was determined by titration with Fehling's solution [9].

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LIPIDS OF THE SEEDS OF Cynoglossum officinale

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The compositions of the lipids and fatty acids of the seeds of Cynoglossum officinale, family Boraginaceae have been established. The bulk of the lipids consisted of neutral compounds (95.2%), while the amounts of glycolipids and phospholipids were 3.1 and 1.7%, respectively. Among the fatty acids, in addition to the usual components, acids characteristic for the Boraginaceae family have been found: 18:3 (6, 9, 12), 18:3 (9, 12, 15), 18:4 (6, 9, 12, 15), 20:1 (11), 22:1 (13), and 24:1 (15).

The family Boraginaceae includes about 100 genera and more than 2000 species of plants growing over the whole of the terrestrial globe. In the USSR 350 species have been found [1]. There is information in the literature on a study of the composition of the fatty acids (FAs) of the lipids of the seeds of about 40 species of plants of this family [2-5] but the class composition of the lipids of plants of the Boraginaceae family has not been investigated.

A feature of the FAs of representatives of the Boraginaceae family is the presence of the 18:4 (6, 9, 12, 15) acid, the amount of which in the seed lipids reaches 17%. In addition, in plants of this family the 18:3 (6, 9, 12) acid (γ-linolenic acid) and high-molecular-mass acids of the even series from 20:1 to 26:1 have been detected. In spite of the fact that the latter acids and γ-linolenic acid have been found separately in representatives of other families [6-8], the uniqueness of the Boraginaceae family consists in the simultaneous presence of all the above-mentioned acids in the seed lipids.

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