Pretreatment of Edible Oils for Physical Refining

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ABSTRACT

Physical refining of edible oils is briefly reviewed. Recent developments regarding the pretreatment of oils and fats are described in detail and methods are critically evaluated with special emphasis on their effectiveness in removing undesired minor components, their cost of operation and their effect on the environment.

This paper concerns the pretreatment of oils and fats for physical refining.

Physical refining was applied as early as the 1930s as a process for the preneutralization of products with a high initial free fatty acid (FFA) content (1). Direct caustic refining would have given high losses of neutral oil. The preneutralization was followed by caustic refining, bleaching and deodorization.

Later, it appeared possible to obtain edible products by physical refining of coconut oil, palm kernel oil and tallow, if proper pretreatment was applied before distillative neutralization.

The 1950s saw a breakthrough when physical refining could be used for another high FFA oil, viz, palm oil. The pretreatment consisted of a bleaching process modified by application of acids and calcium carbonate. For vegetable oils containing relatively low amounts of free fatty acid and higher amount of phosphatides, physical refining became possible only recently.

The classical oil refining procedure consisted of degumming, caustic neutralization, bleaching and deodorization. Caustic neutralization of vegetable oils with high phosphorus contents gives a soapstock which is difficult to split and involves high energy and effluent treatment costs. Omission of the caustic refining step is, therefore, economically very attractive, but this means that the degumming and/or pretreatment step must take over all the functions of the alkali refining process (except for FFA removal).

In refining vegetable oils, one has to deal with many minor components. After degumming, the following components have still to be removed and/or converted: carotenoids, chlorophylls and any brown pigments; phosphatides; metals, e.g., iron, copper, calcium, magnesium; free sugars and glycolipids; and oxidized lipids.

Chlorophylls, phosphatides, metals and sugars have to be removed in the pretreatment step to levels prescribed for the finished products. The stripping/deodorization step can only convert carotenoids and remove FFA, off-flavors and pesticides.

It is clear that the technical feasibility of physical refining very much depends on the optimal use of the properties of the bleaching earth applied during the pretreatment procedure.

The following properties of activated bleaching earth are important for the pretreatment (2).

Adsorption capacity. This depends on the surface area, pore size and pore volume of the earth. The presence of soap and phosphatides can markedly reduce the adsorption capacity in relation to, e.g., pigments. Absence of soap in physical refining is an advantage here.

Catalytic activity. This is dependent on the degree of acid treatment of the earth and on the bleaching temperature. The higher the temperature, the more rapid certain chemical reactions (e.g., decomposition of hydroperoxides) take place.

Ion-exchange properties. The bulk of natural bleaching earths consists of complex silicates with aluminum ions. These ions are partly leached by weathering and by the activation process and replaced with protons. These processes give the earth certain metal-binding properties.

There are some new developments concerning the removal of pigments by bleaching earth. Figure 1 exemplifies work done by Brimberg (3) on the kinetics of bleaching. It shows the concentration of chlorophyll in rapeseed oil (extinction at 660 μ) as a function of bleaching time. Apparently, at least two mechanisms play a role, because the slope of the curve is not constant.

Earth A is Tonsil Standard FF, which is an activated earth and gave the best results. Earth B is a natural earth and Earth C is the same natural earth but with a bigger particle size. Particle size therefore, also plays an important role in chlorophyll removal.

Figure 2 shows the influence of the water content on the rate of chlorophyll removal. The curves show the initial water contents; during the bleaching experiments, the water contents fell below 0.1% in all cases. In the experiments with the highest initial water content, the chlorophyll content did not decrease much during the first few minutes, but dropped very sharply after removal of the water.

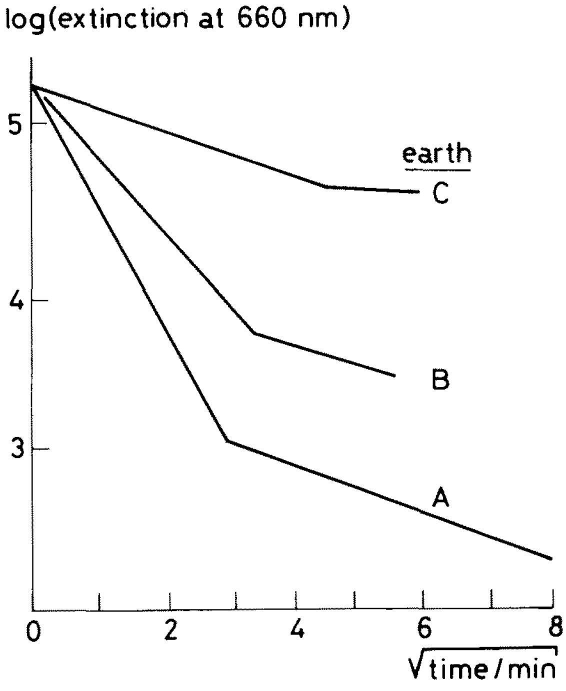

FIG. 1. Removal of chlorophyll from rape oil vs time variables and type of bleaching earth (1% earth; 80 C) (3).

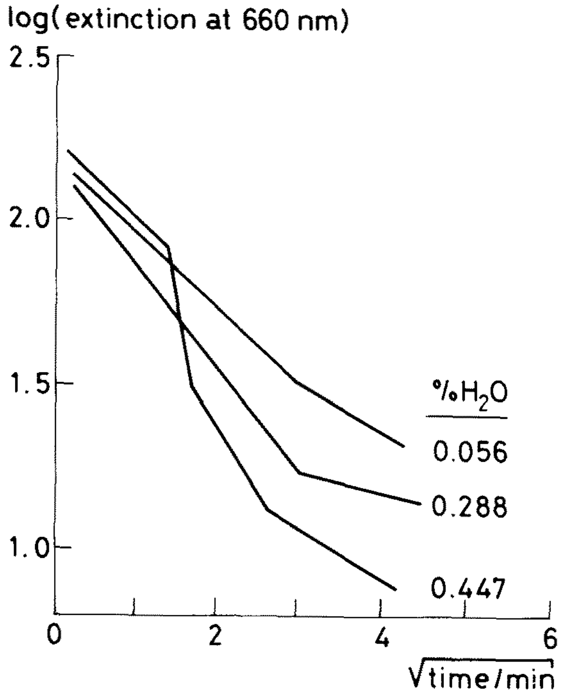

FIG. 2. Removal of chlorophyll from rape oil vs time variables, water content of oil plus earth (1% Earth; 80 C) (3).

These results are practically the same as those for the removal of carotenes and will no doubt provide more insight into the bleaching process and into a more economical use of bleaching earth.

A second group of important minor components are the phosphatides. Kock (4) and Zschau investigated the effects of the degree of activation and of the addition of water on removal of the last traces of phosphatides.

Table I shows that they varied the initial water content from 0 to 1.5% while using 1% of Optimum FF, Standard FF and ACCFF, respectively. Of these bleaching earths, Optimum FF has the highest activity, followed by Standard FF and ACCFF.

Optimum FF, which is the most acid earth, gave the lowest P content when 1% water and 1% earth were used. Also Standard FF reduced the P content to below the required 5 mg/kg. This work has already resulted in an improved bleaching technique for oils with P contents less than 30 mg/kg.

There is a batch pretreatment process for seed oils with low P contents. In step 1, the oil is heated to 65 C, followed by addition of bleaching earth and water. Then the oil is heated to 100-110 C in 15 min under vacuum to remove the water. Finally, the oil is bleached at 110 C for 30 min under vacuum, cooled and filtered. The process was successfully (and economically) applied to oils with low P contents from the so-called Alcon process. When starting from water-degummed oils, this wet bleaching technique does, however, not give the results desired. For these oils, another process has been developed by Mag and Grothues (5).

The batch version of this process follows. In step 1, the dry oil is stirred with 0.1% water for 15 min at 25 C to wet the oil and part of the gums. Then, 0.1-1.5 wt % H_3PO_4 is added and stirring is applied for 15-30 min. After that, 1-2.5% bleaching earth is added under vacuum and the oil heated to 170 C. Then the oil is quickly cooled and filtered. The oil normally contains less than 10 mg/kg phosphorus. The denatured gums become irreversibly fixed to the surface of the highly active earth. The use of H_3PO_4 requires use of closed filters with stainless steel blades. The filters tend to get clogged with the mixture of earth and phosphatides and have to be cleaned by means of caustic wash. Phosphatide contents of 0.3-0.4% require 1.5-2% of earth. The use of earth at temperatures of 170 C might, of course, form artifacts (like dimers and *trans* acids) and also increase the FFA content by 0.1-0.3%.

Recently, an alternative route was developed (6) in the form of a new low-temperature degumming technique for vegetable oils with P contents up to 1000 mg/kg. The new process, called superdegumming, mostly consists of 7 steps. In the first step, the oil is heated to 70 C; then a small amount of food-grade concentrated acid is added, followed by stirring 5-30 min and subsequent cooling to 25 C. Then, 1-5% water is added and stirring is continued for 2 hr to hydrate the phosphatides. By this treatment, use is made of the formation of liquid crystals, which can absorb the metals and sugar compounds. The sludge formed is centrifuged off – giving an oil with max 30 mg P/kg which is then further treated in a bleacher.

The advantage of this technique is that the oil is subjected to a mild treatment, which can be made in relatively simple equipment. In one step, the problems with phosphatides are eliminated and the oil can be bleached with relatively small amounts of earth.

Some attention should be given to the effects of wet bleaching and superdegumming on the removal of metals like iron (prooxidation) and Ca and Mg.

Table II (7) shows again that bleaching earth combined with acid or even with water only, can completely remove iron if a temperature of 120 C is used for bleaching. It is interesting to see that not only acids but also water with bleaching earth had the same effect, which demonstrates the ion-exchange properties of the earth.

Table III demonstrates the effect of superdegumming of factory-scale extracted bean oil (BO) on the P and metal contents of the oil (8). It is clear that such an oil is a very

TABLE I

Removal of Phosphatides from Bean Oil by Wet Bleaching (4)

Added amount of water (%)	Optimum FF	Standard FF	ACCFF
	P (mg/kg)	P (mg/kg)	P (mg/kg)
0	10.1	8.5	10.1
0.5	9.3	–	–
1.0	2.5	3.3	6.5
1.5	4.0	–	–

P content of crude oil: 15.5 mg/kg; 1% bleaching earth.

TABLE II

Removal of Iron from Palm Oil

	Iron content (mg/kg)
Crude oil	12.5
0.15% H_3PO_4 (85%)	9.0
0.15% H_3PO_4 (10%)	0.01
1.5% citric acid (10%)	0.01
1.5% H_3BO_3 (5%)	0.01
1.5% H_2O	0.01

Variable: acid or water addition before bleaching with 1% Optimum FF at 120 C (7).

TABLE III

Removal of Metals from Factory-Scale Extracted Bean Oil by Superdegumming (8)

	Nondegummed BO	Superdegummed BO
Phosphorus (mg/kg)	636	16
Calcium (mg/kg)	50	3.6
Magnesium (mg/kg)	62	3.1
Iron (mg/kg)	3.0	0.3^5

Mean of four runs.

good starting material for the next pretreatment step in the physical refining process.

The superdegumming technique is a good alternative in regard to the removal of sugar and glycolipids which, in the classical way, is carried out by a caustic treatment. For the removal and/or conversion of oxidized compounds, one very much relies on the catalytic properties of the bleaching earth. These properties ensure that the hydroperoxides are decomposed and that the decomposition products are mostly absorbed. How far bleaching can compensate for a certain degree of oxidation of the oil greatly depends on the bleaching conditions (amounts of earth, type of earth, temperature, etc.). In extreme cases, bleaching earth consumption will be high to obtain a stable finished product. However, it is already clear that, for normal-quality oils, their degree of oxidation can be reduced sufficiently by bleaching with 0.5-1.0% active earth.

The state of the art in regard to physical refining is now such that not only laurics, palm oil and edible tallows can be physically refined but also vegetable oils (containing less than 30 mg/kg P) can be treated successfully with a simple bleaching earth pretreatment. For heavily oxidized vegetable oil, cottonseed oil and fish oil, the classical caustic refining is still the most economical route and sometimes the only one feasible. Progress in physical refining will no doubt be extensive in the coming years against the background of improved degumming and bleaching techniques and increasing energy costs and environmental questions.

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